ELEMENTARY PRINCIPLES OF CHEMICAL PROCESSES

THIRD EDITION

2005 Edition with Integrated Media and Study Tools

CD-ROM INCLUDED

RICHARD M. FELDER
RONALD W. ROUSSEAU

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Dedication

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

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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 the B.Ch.E. degree from the City College of New York and the Ph.D. in chemical engineering from Princeton University, and he worked for the Atomic Energy Research Establishment (Harwell, England) and Brookhaven National Laboratory before joining the North Carolina State faculty. He has authored or coauthored over 200 papers on chemical process engineering and engineering education and presented hundreds of seminars, workshops, and short courses in both categories to industrial and research institutions and universities throughout the United States and abroad. Since 1991 he has co-directed the National Effective Teaching Institute under the auspices of the American Society for Engineering Education. He is a member of the Publication Board of *Chemical Engineering Education* and since 1988 has written the "Random Thoughts" column for that journal. His honors include the R.J. Reynolds Award for Excellence in Teaching, Research, and Extension, the AT&T Foundation Award for Excellence in Engineering Education, the Chemical Manufacturers Association National Catalyst Award, the ASEE Chester F. Carlson Award for Innovation in Engineering Education, the ASEE Chemical Engineering Division Lifetime Achievement Award for Pedagogical Scholarship, and a number of national and regional awards for his publications on engineering education including the 1988, 1989, 1996, and 2003 ASEE William J. Wickenden Award for the outstanding paper in the *Journal of Engineering Education.* Many of his publications can be found at <*http://www.ncsu.edu/effective_teaching*>.

Ronald W. Rousseau holds the Cecil J. "Pete" Silas Endowed Chair and also chairs the School of Chemical & Biomolecular Engineering at the Georgia Institute of Technology. He is an executive editor of *Chemical Engineering Science*, a member of the Publication Board of *Chemical Engineering Education*, and a topic editor for *Crystal Growth and Design*; he has been a member of the advisory boards of the Wiley Series in Chemical Engineering and of *Separations Technology*, a consulting editor for the *AIChE Journal*, and an associate editor of the *Journal of Crystal Growth.* He was the editor of the *Handbook of Separation Process Technology* (Wiley, 1987). In addition to his commitment to undergraduate education, he has been an active researcher in the field of separation science and technology. Among the many topics his work has addressed, recent attention has focused on the fundamentals of crystal nucleation and growth and the applications of crystallization science and technology. His contributions to the field of chemical separations technology were recognized through the Clarence G. Gerhold Award of the Separations Division of the American Institute of Chemical Engineers (AIChE). He is a Fellow of both AIChE and the American Association for the Advancement of Science. He is a graduate of Louisiana State University and an elected member of the LSU Engineering Hall of Distinction. He has served as chair of the Council for Chemical Research, member of the Board of Directors of AIChE, and chair of the AIChE Publication Committee.

Drs. Felder and Rousseau were joint recipients of the 2002 Warren K. Lewis Award for Contributions to Chemical Engineering Education from the American Institute of Chemical Engineers.

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Preface to the Third Edition
2005 Edition
with Integrated Media and Study Tools

An introductory stoichiometry 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, unit operations and transport phenomena, kinetics and reactor design, and process dynamics and control. More fundamentally, it introduces the engineering approach to solving process-related problems: breaking a process down 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 the book to fulfill each of these functions. Moreover, recognizing that the stoichiometry 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, from traditional industrial chemistry and petroleum engineering to materials engineering, environmental science and technology, biomedical, biochemical, and genetic engineering, information technology, law, and medicine, and we describe the variety of research, design, and production problems engineers typically 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 structural and motivational framework for the presentation of all of the text material. When we bring in concepts from physical chemistry—for example, 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 computational techniques such as curve-fitting, root-finding methods, and numerical integration, we present them on the same need-to-know basis in the context of process analysis.

FEATURES

Industrial Process Case Studies

An important feature of the book is a set of industrial process case studies that demonstrate the role of single-unit calculations in the analysis of multiple-unit processes. We have designed the case studies to be worked on as term projects by individuals or (preferably) small teams of

students, beginning after the students have completed the introductory chapter on material balances (Chapter 4). In each study, the students are asked to produce a flowchart of a moderately complex process from a given description, to perform material and energy balance calculations on the process, and to answer questions that require consideration of how the overall process is structured and why it might be structured that way. Knowing the problems associated with the case study, the students tend to be on the lookout for course content that will help them obtain the required solutions. The case study thus provides both motivation for learning the text material and a feeling for the contextual significance of this material.

SI Units

SI units are used widely but not exclusively throughout the text, and extensive SI data tables, including steam tables, are contained in the appendices.

Interactive Chemical Process Principles CD

The *Interactive Chemical Processes Principles* CD in the book contains:

- instructional tutorials,
- a learning style assessment tool,
- physical property lookup tables with an embedded routine for calculating sensible heats,
- *Visual Encyclopedia of Chemical Engineering Equipment,*
- E-Z Solve.

(See pages xiv-xvi for a more detailed description.)

Computational Software (E-Z Solve)

E-Z Solve

Computer programming is not covered explicitly, but problems that lend themselves to computer-aided solution are given after each chapter. An exceptionally robust and user-friendly equation-solving program (E-Z Solve) included on the Interactive Chemical Process Principles CD makes it possible for students to analyze relatively large processes without having to spend excessive time on algebraic and numerical calculations.

Website

Updates to the text and additional resources to support its use may be found at
<http://www.ncsu.edu/felder-public/EPCP.html>

- **Errata listing**—any errors found in the text will be listed on the website.
- **Illustrative course Web site**—A home page from the material and energy balance course at N.C. State University containing links to the course syllabus, policies and procedures, class handouts, study guides for exams, and old exams.
- **Handouts for students**—Tips on maintaining confidence, taking tests, and identifying and taking advantage of learning resources on campus.
- **Index of Learning Styles**—A self-scoring instrument that allows students (and instructors) to determine their learning style preferences. After taking the test, users can obtain information about the strengths of their learning styles and suggestions for how to get more out of their courses. (Also on the CD inside the text)
- **"Stoichiometry Without Tears'**—An article from *Chemical Engineering Education* offering suggestions for teaching the stoichiometry course.

Resources on the publisher's website

Visit the website at <*http://www.wiley.com/college/felder*> to access various resources. Some resources are password-protected, and available only to instructors using this text in their course. Visit the Instructor Companion Site portion of this website to register for a password.

Notes to Instructors

Suggestions for chapter 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, possibly augmented with one case study. 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, to add Chapter 10 on computer-aided balances or Chapter 11 on transient balances, or to cover appended material on numerical analysis.

Teaching and promoting a systematic approach to process analysis

We have consistently found that the key to student success in the stoichiometry course is approaching the 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.

Homework problems and assignment schedules

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 Companion Site at <*http://www.wiley.com/college/felder*>, and there is enough duplication of problem types for the schedules to be varied considerably from one course offering to another.

Student Workbook *New!*

Student Workbook

A new feature of this updated edition is the availability of a supplementary workbook containing detailed outlines of solutions to selected chapter-end problems, with spaces for students to insert equations and numerical solutions. Working through these problems will help students become comfortable with the systematic approach sooner rather than later. We suggest that workbook problems be included in regular homework assignments, but at the very least, instructors should encourage their students to solve the problems on their own. **Problems in the Workbook are designated by an icon in the margin of this text.**

Developing creativity with open-ended problems

In addition to the basic material and energy problems at the end of the chapters, we have provided a variety of open-ended problems that focus on conceptual understanding and creative thinking, both imbedded within chapter-end problems and as separate "Creativity Exercises." We encourage instructors to assign these open-ended problems on a regular basis and perhaps to include similar problems on tests after ample practice has been provided in assignments. The problems can be introduced in a variety of ways: as focal points for in-class brainstorming sessions, as parts of regular or extra-credit homework assignments, or as individual or group projects with rewards (e.g., bonus points on subsequent tests) for the solutions exhibiting the greatest fluency (quantity of solutions). Far more than the algorithmic drills, these exercises convey a sense of the challenging and intellectually stimulating possibilities in a chemical engineering career. Conveying this sense may be the most valuable task that can be accomplished in the introductory chemical engineering course.

Using the case studies

We have discussed in the Preface the motivational aspects of the case studies and the way the studies complement the formal text material. An additional benefit occurs if the assignments are made to groups, an approach we regularly use in our classes. We invariably see the groups starting out in a state of semi-anarchy and then developing cohesiveness as the weeks go by. By the end of the term most students have learned how to divide the labor appropriately and to learn from one another, since they know they are liable to be tested on any part of the project and not just the part for which they were personally responsible. This is the part of the course the students usually say they enjoyed most. We have also found that periodic conferences between the groups and the instructor to discuss the case studies provide added educational benefits to all parties concerned.

Resources for instructors

The Instructor Companion Web Site contains resources for instructors, including illustrative assignment schedules, reproducible copies of figures in the text, and problem solutions. The password-protected site is accessible only to instructors who are using the text for their course. Go to <*http://www.wiley.com/college/felder*> and click on the link to "Instructor Companion Site" to register for a password.

RMF
RWR

Interactive Chemical Process Principles

(CD near front of text)

The CD that accompanies this edition of the text contains a variety of resources for students and instructors collected under the title *Interactive Chemical Process Principles* (ICPP). Some of the components of ICPP are instructional aids for the stoichiometry course, and others are computational and reference tools that should prove useful throughout the chemical engineering curriculum. One or more of the ICPP tools can be effectively applied to almost every example and problem in the book. Icons throughout the book remind students and instructors when the tools on the CD may be helpful.

In this section, we provide an overview of ICPP and some thoughts on how it might be used effectively as an adjunct to the text. We encourage you to read through this outline and then explore the tools for yourself. If you are a student, you will soon be able to recognize when you can use the tools for problem solving; if you are an instructor, you will see when suggestions for using the tools might be helpful in your lecture notes or assignments.

Index of Learning Styles

What is your Learning Style?

Students learn in a variety of ways. For example, some students are concrete and practical. These students appreciate many illustrations, examples, and applications of course material and are uncomfortable with abstract mathematical presentations. Other students are much more comfortable with abstraction and are easily bored by repetitive calculations and examples. Some learn visually, getting much more from pictures and diagrams than they do from words and formulas, while others benefit more from verbal explanations than from visual representations. The list of such differences is endless.

A student's *learning style* is a set of preferences for certain ways of taking in and processing information. The **Index of Learning Styles** (ILS) is an instrument that enables you to assess several of your learning style preferences. We sugggest that the first thing you do when you begin to explore ICPP is to complete the ILS, determine your learning style profile, and then read the accompanying material that suggests study strategies (if you are a student) or teaching strategies (if you are an instructor) that might work effectively for you in the stoichiometry course and in subsequent courses.

Instructional Tutorials

Interactive Tutorials

ICPP contains six interactive tutorials, designed for students to work through after they have progressed to certain points in the text. In each tutorial, process descriptions are given, questions are posed, and students enter answers and receive affirmation or corrective feedback, and then go on to additional questions. Process simulations are also included, so that students may predict how process systems will respond to changes in certain system variables, and then explore the effects of those changes experimentally. The active involvement and immediate feedback implicit in these exercises can significantly reinforce learning.

Once students can successfully work through a tutorial from beginning to end, they may be confident that they have mastered a significant portion of the material covered in that tutorial. If they have repeated trouble with a part of the tutorial, they will be able to identify gaps in their understanding of the course material and get help with them.

The tutorials and the points in the course when they may be completed are as follows:

1. Basic process calculations and process system variables (end of Chapter 3).
2. Material balances on nonreactive single-unit processes (end of Section 4.3).
3. Material balances on reactive multiple-unit processes (end of Chapter 4).
4. Material balances on multiphase systems (end of Chapter 6).
5. Material and energy balances on nonreactive processes (end of Chapter 8).
6. Material and energy balances on reactive processes (end of Chapter 9).

Physical Property Database

Physical Property Database

The physical property database of ICPP contains easily accessed values of molecular weights, specific gravities, phase transition points, critical constants, vapor pressures, heat capacities, and latent heats for many species that duplicate the values found in Appendix B of the text. The values retrieved from the database may be incorporated into process calculations performed using E-Z Solve.

The principal benefit to students is a built-in function for integrating tabulated heat capacities between specified temperature limits. Without this tool, polynomial formulas in Table B.2 of the text must be integrated term-by-term and the initial and final temperatures must be entered as the limits, with tedious calculations being required for the associated arithmetic. With the Physical Property Database tool, the desired species is selected from a pull-down menu, the initial and final temperatures are typed in, and a single click leads to the calculation of the integral. This feature will be most helpful in Chapters 8 and 9 of the text.

Visual Encyclopedia of Chemical Engineering Equipment

Equipment Encyclopedia

Most of the examples and problems in the text refer to items of equipment commonly found in chemical processes, such as reactors, heat exchangers, distillation columns, absorption towers, crystallizers, filters, and centrifuges. In some cases, brief explanations of these equipment items are given; in others, the terms are simply used. *The Visual Encyclopedia of Chemical Engineering Equipment*, created by Dr. Susan Montgomery of the University of Michigan, contains photographs, cutaway diagrams, movies, animations, and explanations of how the different equipment items work. It should be consulted to clarify references to process units in the text and to better understand how the processes described in the chapter-end problems work.

E-Z Solve

E-Z Solve

E-Z Solve is a powerful and user-friendly equation-solving program designed and written by Intellipro, the company that produced ICPP. It can be used to obtain numerical solutions of sets of linear and nonlinear algebraic equations of the types that occur in almost every chapter-end problem in Chapters 4 through 10 of the text, and it can also solve ordinary differential equations of the types that occur in Chapter 11. Examples of applications of E-Z Solve to representative stoichiometry problems are provided on the CD. E-Z Solve is convenient to use whenever a problem calls for solving three or more simultaneous linear algebraic equations or any number of nonlinear algebraic equations and ordinary differential equations.

We have found an interesting phenomenon associated with E-Z Solve, and that is that many students do not use it unless they are initially required to do so, probably because they are worried about the time it will take them to learn how. The result is that the students spend

hours slogging through manual solutions of equations that could be solved in minutes with E-Z Solve. Once they have used the tool two or three times, however, they turn to it constantly throughout the remainder of the chemical engineering curriculum.

E-Z Solve more than lives up to its name. Here, for example, are three equations in three unknowns (x_A, x_B, T_{dp}) that arise as part of a problem in Chapter 6.

$$(1)\ x_A = \frac{0.980(760)}{10^{6.84471 - \frac{1060.793}{T_{dp} + 231.541}}} \qquad (2)\ x_B = \frac{0.020(760)}{10^{6.88555 - \frac{1175.817}{T_{dp} + 224.867}}} \qquad (3)\ x_A + x_B = 1$$

Solving these equations manually requires trial and error. It would be a long and tedious task if done with a simple calculator, and not too difficult for a spreadsheet. To use E-Z Solve, the following three lines of code would be typed in:

```
xa = 0.980*760/10^(6.84471−1060.793/(Tdp+231.541))
xb = 0.020*760/10^(6.88555−1175.817/(Tdp+224.867))
xa + xb = 1
```

Once the equations are entered, a command to "Solve" would be entered followed by a click on "OK," and the solution for all three variables would immediately appear. The longer and more complex the text problem, the greater the time saving that results from using E-Z Solve to solve the material and energy balance equations and physical property estimation formulas that arise in the course of its solution.

Nomenclature

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

a, b, c, d	Either arbitrary constants 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.
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 ($\hat{H}$), all determined relative to a specified reference state.
m, M (kg), $\dot{m}$(kg/s)	Mass (m or M) or mass flow rate ($\dot{m}$) of a process stream or stream component.
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(N/m^2)	Partial pressure of species A in a mixture of gaseous species, $= y_A P$.
$p_A^*(T)$(N/m^2)	Vapor pressure of species A at temperature T.
P(N/m^2)	Total pressure of a system. Unless specifically told otherwise, assume that P is absolute pressure and not gauge pressure.
P_c(K)	Critical pressure. Values of this property are listed in Table B.1.
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_{mp}, T_{bp}, T_c(K)	Melting point temperature, boiling point temperature, and critical temperature, respectively. Values of these properties are listed in Table B.1.
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 ($\hat{U}$), all relative to a specified reference state.
V(m^3), $\dot{V}$, $\dot{v}$ (m^3/s), $\hat{V}$(m^3/mol)	Volume (V) of a fluid or process unit, volumetric flow rate ($\dot{V}$ or $\dot{v}$) 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 ($\dot{W}_s$). W is defined to be positive (in this text) if work is transferred from a system to 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 $X_{\text{final}} - X_{\text{initial}}$, where X is any system property. In continuous (open) systems, $\Delta \dot{X}$ denotes the difference $\dot{X}_{\text{output}} - \dot{X}_{\text{input}}$.
$\Delta \hat{H}_c, \Delta \hat{H}_f$(kJ/mol)	Heats of combustion and formation, respectively. Values of these properties at 25°C and 1 atmosphere are listed in Table B.1.
$\Delta \hat{H}_m, \Delta \hat{H}_v$(kJ/mol)	Heats of melting (fusion) and vaporization, respectively. Values of these properties at the

	normal melting and boiling points are listed in Table B.1.
ν_A	Stoichiometric coefficient of species A in a chemical reaction, defined to be positive for products, negative for reactants. For $N_2 + 3H_2 \rightarrow 2NH_3$, $\nu_{N_2} = -1$, $\nu_{H_2} = -3$, $\nu_{NH_3} = 2$.
ξ(mol)	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 is the stoichiometric coefficient of A in the reaction (see preceding definition). The value of ξ is the same regardless of which reactant or product is chosen as species A.
$\dot{\xi}$(mol/s)	Extent of reaction for a continuous process at steady state. If $\dot{n}_{A0}$(mol/s) of reactive species A enters the reactor and $\dot{n}_A$(mol/s) exits, then the extent of reaction is $\dot{\xi} = (\dot{n}_{A0} - \dot{n}_A)/\nu_A$, where ν_A is the stoichiometric coefficient of A in the reaction. The value of $\dot{\xi}$ is the same regardless of which reactant or product is chosen as species A.
ρ(kg/m^3)	Density.

Other Symbols

$\dot{}$ (e.g., $\dot{m}$)	Flow rate, such as mass flow rate.
$\hat{}$ (e.g., $\hat{U}$)	Specific property, such as 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. The intended use can usually be easily seen in context.

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Glossary of Chemical Process Terms

Equipment Encyclopedia

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.

Equipment Encyclopedia

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.

Equipment Encyclopedia

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.

Equipment Encyclopedia

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

Compressibility factor $z = PV/nRT$ 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.

Equipment Encyclopedia

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.

Equipment Encyclopedia

Crystallization   A process in which a liquid solution is cooled, or solvent is evaporated, to an extent that solid crystals of solute form. The crystals in the *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)   The temperature at which the first liquid droplet appears when the mixture is cooled at constant pressure.

Equipment Encyclopedia

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 liquid wetting the solid 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 a third 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 in a decanter.

Filtration A process in which a *slurry* of solid particles suspended in a liquid passes through a porous medium. Most of the liquid passes through the medium (e.g., a filter) to form the *filtrate,* and 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.

Heat exchanger A process unit through which two fluid streams at different temperatures flow on opposite sides of a metal barrier. 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 B.5–B.7 for water), the Antoine equation (Table B.4), or the Cox chart (Figure 6.1-4).

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.

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Part One

Engineering Problem Analysis

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Chapter 1

What Some Chemical Engineers Do for a Living

Last May, chemical engineering seniors at a large university 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. 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. 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 large chemical, petrochemical, pulp and paper, plastics and other materials, or textile manufacturing firms.
- Another 35% went to work for government agencies and design and consulting firms (many specializing in environmental regulation and pollution control) and for companies in fields such as microelectronics and biotechnology that have not traditionally been associated with chemical engineering.
- About 10% of the class went directly into graduate school in chemical engineering. The masters degree candidates will get advanced education in traditional chemical engineering areas (thermodynamics, chemical reactor analysis and design, fluid dynamics, mass and heat transfer, and chemical process design and control), and in about two years most of them will graduate and get jobs doing process or control systems design or product development. The doctoral degree candidates will get advanced education 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 a university faculty.
- The remaining 10% of the class went into graduate school in an area other than chemical engineering, such as medicine, law, or business.

- Several graduates went to work for companies manufacturing specialty chemicals—pharmaceuticals, paints and dyes, and cosmetics, among many other products. All of these companies used to hire only chemists to design and run their production processes, but in the past few decades they discovered that if they wanted to remain competitive they would have to pay attention to such things as mixing efficiency, heat transfer, automatic temperature and liquid level control, statistical quality control, and control of pollutant emissions. They also discovered that those are areas in which chemical engineers are educated and chemists are not, at which point these industries became an increasingly important job market for chemical engineers.

Equipment Encyclopedia
CVD reactors

- Some went to work for companies that manufacture integrated semiconductor circuits. A critical step in the production of (for example) computer chips involves coating small silicon wafers with extremely thin and uniform layers of silicon-containing semiconducting materials. The technique used for this process is *chemical vapor deposition,* in which the coating material is formed in a gas-phase reaction and then deposited on the surface of the wafer. The graduates working in this area may be called on to identify reactions that can be used to produce the desired films, determine the best conditions at which to run the reactions, design the reactors, and continue to improve their operation.
- Some took elective courses in biochemistry and microbiology and got jobs with small but rapidly growing biotechnology firms. One graduate works on the design of pharmaceutical production processes that involve *immobilized enzymes,* biological chemicals that can make specific reactions go orders of magnitude faster than they would in the absence of the enzymes. Several others work on processes that involve *genetic engineering,* in which recombinant DNA is synthesized and used to produce valuable proteins and other medicinal and agricultural chemicals that would be hard to obtain by any other means.

Equipment Encyclopedia
membranes

- Some joined companies that manufacture *polymers* (plastics). One is working on the development of membranes for desalination of seawater (fresh water passes through, salt is kept out) and for gas separations (hydrogen passes through and hydrocarbons are kept out, or vice versa); another is developing membranes to be used in hollow-tube artificial kidneys (blood flows from the patient's body through thin-walled tubes; metabolic wastes in the blood pass through the tube walls but proteins and other important body chemicals remain in the blood, and the purified blood is returned to the body).
- Four of the graduates went to medical school. (Chemical engineering graduates who take several electives in the biological sciences have a strong record of success in gaining medical school admission.) One went to law school. Three enrolled in Master of Business Administration programs and after graduation will probably move into management tracks in chemical-related industries.
- 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, 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 ten 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 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 chemical engineering students.

Even the chemical engineering graduates who go into a traditional chemical manufacturing process end up performing a wide variety of different tasks. Consider the following example, and see if any of the problems described seem to present the sort of challenge you can see yourself taking on and enjoying.

EXAMPLE 1

A chemist in your company's research and development division has discovered that if he mixes two reactants in a certain proportion at an elevated temperature, he obtains a product significantly more valuable than both reactants. The company contemplates manufacturing the product using a process based on this reaction. At this point the matter becomes an engineering problem or, more precisely, hundreds of engineering problems.

Equipment Encyclopedia
reactors

1. What type of reactor should be used? A long pipe? A large tank? Several smaller tanks? An extremely large test tube? How large? Made of what? Does it have to be heated? If so, how much and how? With an electrical heater inside or outside the reactor? By passing a hot fluid through a heating coil in the reactor? By heating the reactants before they get into the reactor? Does the reaction supply its own heat, so that heating is needed only for startup? If so, can the reactor "run away" and possibly explode? Should control measures be introduced to prevent this? What kind?
2. Where should the reactants be obtained? Buy them, or make them? In what proportions should they be fed to the reactor?

Equipment Encyclopedia
chemical separations

3. Should the reactor effluent, which contains the product and unconsumed reactants, be sold as is, or should the product be separated from the reactants and the latter be sent back to the reactor? If separation is desirable, how can it be accomplished? Heat the mixture and draw off and condense the vapor, which will be richer in the more volatile substances than the original mixture? Add another substance that extracts the product and is immiscible with the reactants, and then separate the two phases mechanically? If all of the process materials are gases at the reaction temperature, can the mixture be cooled to a temperature at which the product condenses but the reactants do not, or vice versa, or if they are liquids can the mixture be cooled to a temperature at which the product crystallizes? If one of these alternatives is chosen, what kind of equipment is needed? What size? What materials? What are the heating or cooling requirements? Are controls needed to keep the operation of the process within rigid limits? What kind of controls? Should they be manual or automatic?

Equipment Encyclopedia
materials transport and storage

4. How should the reactant and product streams be moved to and from the reactor and any heating, cooling, and separation equipment involved in the process? By gravity from a raised feed tank? With pumps, or blowers, or compressors, or conveyor belts? What kinds? How big? In pipes made of what?
5. Is enough known about the reaction system to be able to answer all of these questions, or should additional laboratory studies be carried out? What studies? Can the laboratory data be used directly to design the industrial plant, or should a smaller pilot plant be constructed first to test the design? How much smaller?
6. What can possibly go wrong with the process, and what can be done if and when it does?
7. Are waste products produced by the process? In what quantities? Are they potentially harmful if released untreated into the environment? If so, in what way? What should be done to reduce pollution hazards? Chemically treat the wastes? Dump liquid and solid wastes into containers, seal and cart them out to sea? Disperse gases in the atmosphere with a high stack? Precipitate solids electrostatically from gas exhausts?
8. How much of the process should be automated, and how should the automation be done?
9. How much will all of this cost? For how much can the product be sold, and to whom? How much money will the process net each year? Is it enough to make it worthwhile? If so, where should the plant be built?
10. Once the plant has been built, what procedure should be followed for startup?

11. Six months later when startup has been achieved, why is the product not coming out the way it did in the laboratory? Is it an equipment malfunction or a change in conditions somewhere between the laboratory and industrial process? How can we find out? What can be done to correct the problem? Is it necessary to shut down the operation for modifications?

12. Is it significant or just a coincidental series of bad breaks that there have been three explosions and four fires within six months in the reactor unit? In either case, how do we stop them from recurring?

13. All sorts of other things are going wrong with the process operation. Why weren't they on the list of things that could possibly go wrong? What can be done about them?

14. When the process finally starts working perfectly and the next day an order comes down to change the product specifications, how can it be done without redesigning the entire process? Why didn't they think of this before they built the plant?

The different careers and tasks described in this chapter are clearly too diverse to fall into a single category. They involve disciplines including physics, chemistry, biology, environmental science, medicine, applied mathematics, statistics, computer science, economics, management and information science, 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, a small amount of it is contained in this text, and most of it must be learned after graduation. There are, however, fundamental techniques that have been developed for setting up and attacking technical problems that are independent of the particular problem under consideration. 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, 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 systems mentioned in the chapter—chemical manufacturing processes, genetic engineering laboratories, pollution control facilities, and the others—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 of process design and analysis; in the same way, the techniques that we present in this chapter underlie all applications of the laws.

2.0 INSTRUCTIONAL 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 conversion factor tables. [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 American Engineering 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.
- 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 versus what 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 versus what 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. *The numerical values of two quantities may be added or subtracted only if the 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.*

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

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

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

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

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

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

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

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:

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

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

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

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

$$(36 \text{ mg}) \times \left(\frac{1 \text{ g}}{1000 \text{ mg}}\right) = 0.036 \text{ g} \qquad \textbf{(2.2-4)}$$

(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:

$$\frac{36 \text{ mg}}{} \left| \frac{1 \text{ g}}{1000 \text{ mg}} \right. = 0.036 \text{ g}$$

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

$$\frac{36 \text{ mg}}{} \left| \frac{1000 \text{ mg}}{1 \text{ g}} \right. = 36{,}000 \text{ mg}^2/\text{g}$$

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

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. 655)

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 $\equiv$ (1g·cm/s^2), 1 lb$_f$ $\equiv$ 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. 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 **American engineering 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.

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. 1-4 through 1-20 of *Perry's Chemical Engineers' Handbook.*[1]

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[1]R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook,* 7th Edition, McGraw-Hill, New York, 1997.

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	$1 \text{ N·m} = 1 \text{ kg·m}^2/\text{s}^2$
	erg (CGS)		$1 \text{ dyne·cm} = 1 \text{ g·cm}^2/\text{s}^2$
	gram-calorie	cal	$4.184 \text{ J} = 4.184 \text{ kg·m}^2/\text{s}^2$
Power	watt	W	$1 \text{ J/s} = 1 \text{ kg·m}^2/\text{s}^3$

TEST YOURSELF
(Answers, p. 655)

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 the American engineering system?

EXAMPLE 2.3-1   *Conversion Between Systems of Units*

Convert 23 $\text{lb}_{\text{m}} \cdot \text{ft/min}^2$ to its equivalent in kg·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

$$\frac{23\ \text{lb}_m \cdot \text{ft}}{\text{min}^2} \left| \frac{0.453593\ \text{kg}}{1\ \text{lb}_m} \right| \frac{100\ \text{cm}}{3.281\ \text{ft}} \left| \frac{1^2\ \text{min}^2}{(60)^2\ \text{s}^2} \right. \qquad \text{(Cancellation of units leaves kg·cm/s}^2\text{)}$$

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

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·m/s^2 (SI), g·cm/s^2 (CGS), and lb$_m$·ft/s^2 (American engineering). 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:

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

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

In the American engineering system, 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:

$$1\ \text{lb}_f \equiv 32.174\ \text{lb}_m \cdot \text{ft/s}^2 \qquad \textbf{(2.4-3)}$$

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

$$F = \frac{4.00\ \text{kg}}{} \left| \frac{9.00\ \text{m}}{\text{s}^2} \right| \frac{1\ \text{N}}{1\ \text{kg·m/s}^2} = 36.0\ \text{N}$$

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

$$F = \frac{4.00\ \text{lb}_m}{} \left| \frac{9.00\ \text{ft}}{\text{s}^2} \right| \frac{1\ \text{lb}_f}{32.174\ \text{lb}_m \cdot \text{ft/s}^2} = 1.12\ \text{lb}_f$$

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,

$$g_c = \frac{1\ \text{kg·m/s}^2}{1\ \text{N}} = \frac{32.174\ \text{lb}_m \cdot \text{ft/s}^2}{1\ \text{lb}_f}$$

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:

$$W = mg \qquad \textbf{(2.4-4)}$$

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:

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

(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. 655)

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

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

The weight of the water is

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

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:

$$
123,\!000,\!000 = 1.23 \times 10^8 \text{ (or } 0.123 \times 10^9)
$$

$$
0.000028 = 2.8 \times 10^{-5} \text{ (or } 0.28 \times 10^{-4})
$$

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:

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

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

(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 violent!

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 ($\downarrow$) denotes the last significant figure of each number.

$$
\begin{array}{r}
\downarrow \\
1530 \quad \downarrow \\
-\ 2.56 \\
\hline
1527.44 \implies 1530 \\
\uparrow
\end{array}
$$

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

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

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

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:

$$1.35 \implies 1.4$$
$$1.25 \implies 1.2$$

**TEST
YOURSELF
(Answers, p. 655)**

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.

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

2. Do the resulting arithmetic calculations 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.

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

The calculator solution is 0.239.

EXAMPLE 2.5-1   *Order-of-Magnitude Estimation*

The calculation of a process stream volumetric flow rate has led to the following formula:

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

Estimate $\dot{V}$ without using a calculator. (The exact solution is 0.00230.)

SOLUTION

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

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.

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.
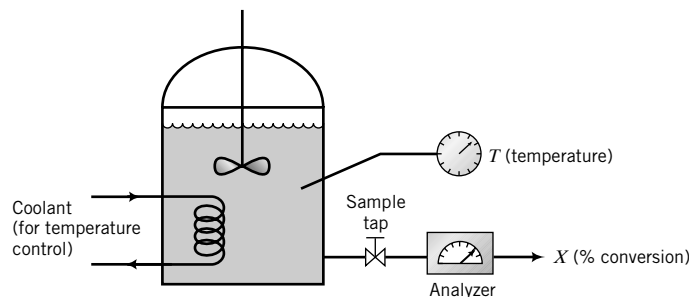
In theory X should have a unique value; however, in a real reactor X is a *random variable,* changing in an unpredictable manner from one run to another at the same experimental con-

ditions. 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 $45.0000\ldots$ 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 of 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.
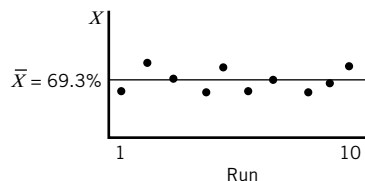
The more measurements of a random variable, the better the estimated value based on the sample mean. However, even with a huge number of measurements the sample mean is at best an approximation of the true value and could in fact be way off (e.g., if there is something wrong with the instruments or procedures used to measure X).

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 a random variable, X—for example, the percentage conversion 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 95%). 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:

$$\textbf{\textit{Range:}} \qquad\qquad\qquad R = X_{\max} - X_{\min} \qquad\qquad\qquad \textbf{(2.5-2)}$$

In the first plot of Figure 2.5-1 the range of X is 5% (73% − 68%) and in the second plot it is 43% (95% − 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

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

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

$$\textbf{\textit{Sample Standard Deviation:}} \qquad\qquad s_X = \sqrt{s_X^2} \qquad\qquad \textbf{(2.5-4)}$$

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) ($s_X^2 = 0.30, s_X = 0.55$) and large values are obtained for Set (b) ($s_X^2 = 50, s_X = 7.1$).

For typical random variables, roughly two-thirds of all measured values fall within one standard deviation of the mean; about 95% fall within two standard deviations; and about
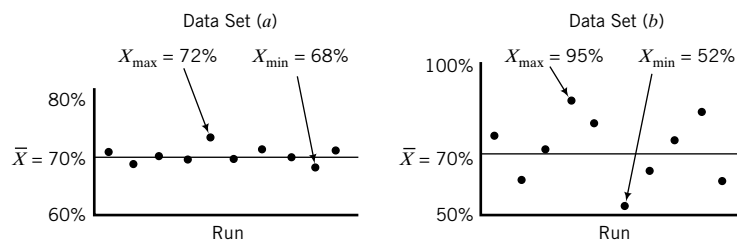
Figure 2.5-1   Scatter plots for two data sets with different levels of scatter.
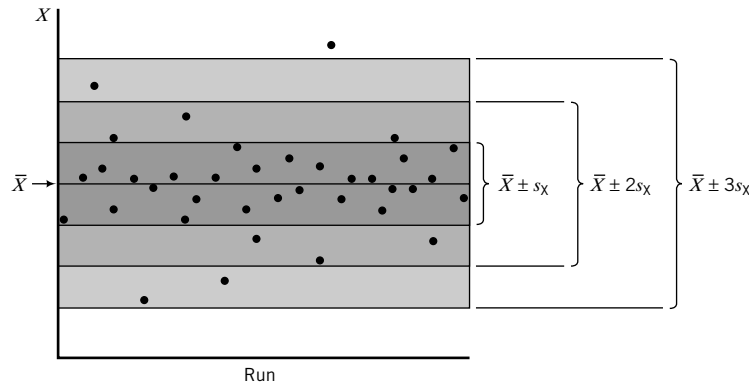
Figure 2.5-2 Data scatter about the mean.

99% fall within three standard deviations.[2] 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 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. 655)

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

Measurement	1	2	3	4	5
$\dot{V}(cm^3/s)$	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.

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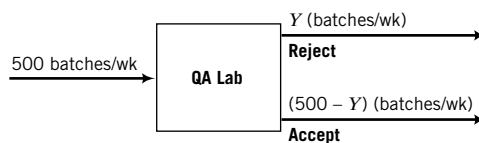
[2]The exact percentages depend on how the measured values are distributed about the mean—whether they follow a Gaussian distribution, for example—and how many points are in the data set used to calculate the mean and standard deviation.

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
$\bar{Y}$	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 $Y \leq \bar{Y} + 3s_Y$). 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

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

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

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

The maximum allowed value of Y is

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

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

2. $\bar{Y} + 2s_Y = 19.9 + (2)(2.8) = \boxed{25.5}$. 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

$$u(\text{m/s}) = u_0(\text{m/s}) + g(\text{m/s}^2)t(\text{s}) \tag{2.6-1}$$

This equation is dimensionally homogeneous, since each of the terms u, u_0, and gt has the same dimensions (length/time). On the other hand, the equation $u = u_0 + g$ is not dimensionally homogeneous (why not?) and therefore cannot possibly be valid.

Equation 2.6-1 is both dimensionally homogeneous *and* consistent in its units, in that each additive term has the units m/s. If values of u_0, g, and t with the indicated units are substituted into the equation, the addition may be carried out to determine the value of u. If an equation is dimensionally homogeneous but its additive terms have inconsistent units, the terms (and hence the equation) may be made consistent simply by applying the appropriate conversion factors.

For example, suppose that in the dimensionally homogeneous equation $u = u_0 + gt$ it is desired to express the time (t) in minutes and the other quantities in the units given above. The equation can be written as

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

Each additive term again has units of m/s (verify this), so the equation is consistent.

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

$$D(\text{ft}) = \frac{D'(\text{m})}{} \left| \frac{3.2808 \text{ ft}}{1 \text{ m}} \right. = 3.28D'$$

$$t(s) = \frac{t'(\text{min})}{} \left| \frac{60 \text{ s}}{1 \text{ min}} \right. = 60t'$$

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:

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

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 $\equiv e$, *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 $(20\ \text{s})$ or sin $(3\ \text{dynes})$.

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

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

The answers are thus

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

---

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 $r(\text{m})$, $s(\text{m/s}^2)$, and $t(\text{s})$ would constitute a dimensionless group?
4. If $z(\text{lb}_f) = a \sin(Q)$, 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 experiment in which a variable, y, is measured for several values of another variable, x:
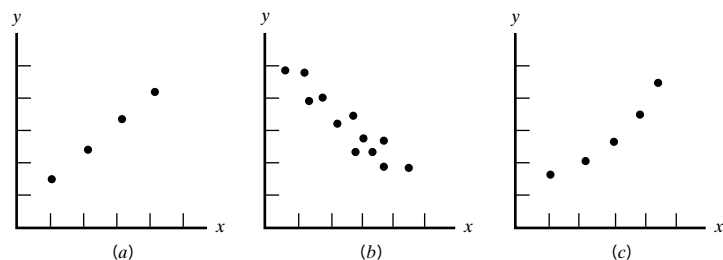
Figure 2.7-1 Representative plots of experimental data.

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 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

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

(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. 655)

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?

(a)   (b)   (c)
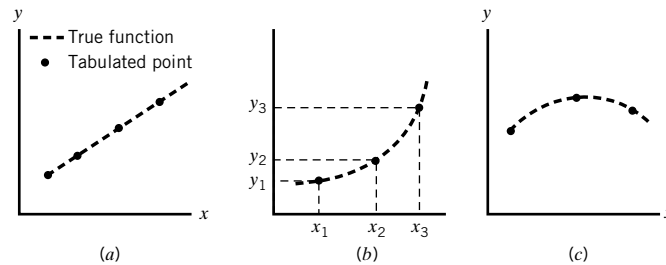
2.7b Fitting a Straight Line

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 program a computer 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 coordinate axes 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 2.71a, 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:
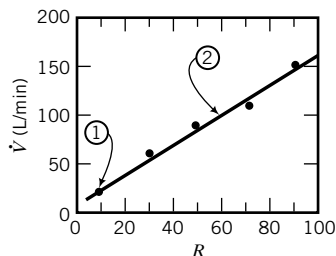
A line drawn through the data by visual inspection passes through the points ($R_1 = 10$, $\dot{V}_1 = 20$) and ($R_2 = 60, \dot{V}_2 = 101$). Therefore,

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

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

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

The result is, therefore,

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

Check: At point ②,

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

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

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

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

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.

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

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 formula and determine a and b.

SOLUTION

If the formula 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 $T^{1/2}$.
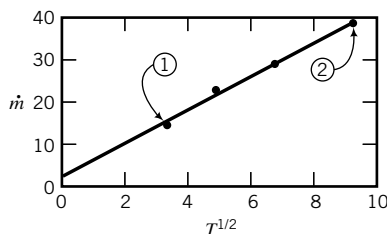
Since the plot is linear, the proposed formula is verified. A line drawn through the data points passes through the first and last points, so these points may be used to calculate the slope and intercept:

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

$$(T_1^{1/2} = 3.162, \dot{m}_1 = 14.76)$$

$$(T_2^{1/2} = 8.944, \dot{m}_2 = 38.47)$$

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

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

(verify the units), so that

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

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

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:

$$P = e^Q \iff \ln P = Q \qquad\qquad\qquad \textbf{(2.7-5)}$$

It follows that

$$\ln[e^Q] = Q \qquad \text{and} \qquad e^{\ln P} = P \qquad\qquad\qquad \textbf{(2.7-6)}$$

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

$$\ln x = 2.302585 \log_{10} x \qquad\qquad\qquad \textbf{(2.7-7)}$$

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:

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

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

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. 655)

1. The following plot is generated from experimental (x, y) data:
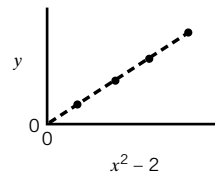
What equation would you use to relate x and y?

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 $(\sqrt{x_1}, y_1)$ and $(\sqrt{x_2}, y_2)$ be two points on the line; calculate $a = (y_2 - y_1)/(\sqrt{x_2} - \sqrt{x_1})$, $b = y_1 - a\sqrt{x_1}$

      (b) $1/y = a(x - 3)^2 + b$ **(e)** $y = ae^{bx}$

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

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

2.7d Logarithmic Coordinates

Suppose you wish to fit an exponential function $y = a \exp(bx)$ to measured (x, y) data. If there are many data points, calculating the logarithm of each y value (needed to plot $\ln y$ versus x) could take more time than the fitting procedure itself. However, suppose that an additional scale were drawn parallel to the $\ln y$ axis, on which values of y were shown adjacent to the corresponding values of $\ln y$ on the first scale. (See Figure 2.7-2.) Now, instead of having to calculate $\ln y$ for each tabulated y to locate the data points on the graph, you can find the y values on the second scale and locate the points directly. If the same type of scale (called a **logarithmic scale**) were drawn parallel to the other axis, you could also plot $\ln x$ values without having to calculate them from tabulated x values. A plot with logarithmic scales on both axes is called a **log plot,** and a plot with one logarithmic and one rectangular (equal interval) axis is called a **semilog plot.** *Log paper* is graph paper with logarithmic scales on both axes, and *semilog paper* has one logarithmic axis and one rectangular axis. Most computer plotting packages allow selection of log or semilog scales as alternatives to rectangular scales.

    When you plot values of a variable y on a logarithmic scale you are in effect plotting the logarithm of y on a rectangular scale. Suppose, for example, that y and x are related by the equation $y = a \exp(bx)$ ($\ln y = \ln a + bx$). 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.)
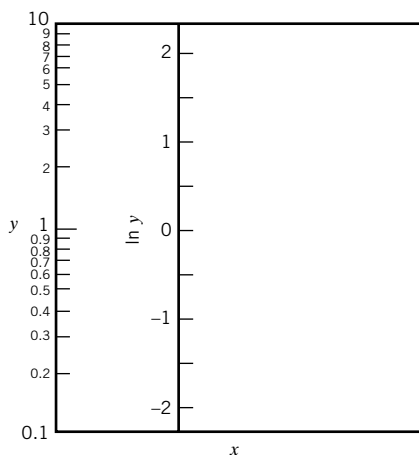
Figure 2.7-2 Construction of a logarithmic scale.

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**

$$\ln F = bt + \ln a \qquad \text{(since the plot appears linear)}$$

$$\Downarrow$$

$$F = ae^{bt}$$

$$b = \frac{\ln(F_2/F_1)}{t_2 - t_1} = \frac{\ln(0.0527/0.298)}{(30 - 15)} = -0.1155$$

$$\ln a = \ln F_1 - bt_1 = \ln(0.298) + (0.1155)(15) = 0.5218$$

$$\Downarrow$$

$$a = \exp(0.5218) = 1.685$$

or

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

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

2. **Log plot**

$$\ln F = b \ln t + \ln a \qquad \text{(since the plot appears linear)}$$

$$\Downarrow$$

$$F = at^b$$

$$b = \frac{\ln(F_2/F_1)}{\ln(t_2/t_1)} = \frac{\ln(0.0527/0.298)}{\ln(30/15)} = -2.50$$

$$\ln a = \ln F_1 - b \ln t_1 = \ln(0.298) + 2.5 \ln(15) = 5.559$$

$$\Downarrow$$

$$a = \exp(5.559) = 260$$

or

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

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

TEST YOURSELF
(Answers, p. 655)

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.)

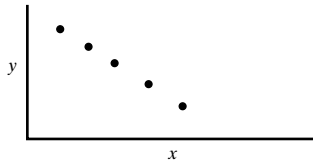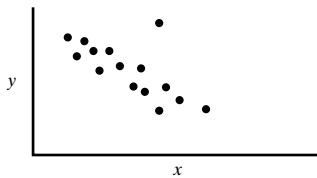**2.** What would you plot against what on what kind of axes to get a straight line for the following relationships (a and b are constants)?

      (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 as scattered as these, 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 2.39 through 2.42 at the end of this chapter.

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 kg·m/s^2 or $\text{lb}_m\text{·ft/s}^2$ 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) 3 wk to milliseconds.   **(c)** 554 m⁴/(day·kg) to cm⁴/(min·g).
  (b) 38.1 ft/s to miles/h.

2.2. Using the table of conversion factors on the inside front cover, convert
  (a) 760 miles/h to m/s.   **(c)** 5.37×10^3 kJ/min to hp.
  (b) 921 kg/m³ to lb_m/ft³.

2.3. Using a single dimensional equation, estimate the number of golf balls 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. 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.

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2.6. You are trying to decide which of two automobiles to buy. The first is American-made, costs $14,500, and has a rated gasoline mileage of 28 miles/gal. The second car is of European manufacture, costs

$21,700, and has a rated mileage of 19 km/L. If the cost of gasoline is $1.25/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?

2.7. A supersonic aircraft consumes 5320 imperial gallons of kerosene per hour of flight and flies an average of 14 hours per day. It takes roughly seven tons of crude oil to produce one ton of kerosene. The density of kerosene is 0.965 g/cm^3. How many planes would it take to consume the entire annual world production of 4.02×10^9 metric tons of crude oil?

2.8. 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 newtons.
  (c) the weight in dynes of a 10-ton object (not metric tons).

2.9. A waste treatment pond is 50 m long and 15 m wide, and has an average depth of 2 m. The density of the waste is 85.3 lb$_m$/ft^3. Calculate the weight of the pond contents in lb$_f$, using a single dimensional equation for your calculation.

2.10. 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 11.5 kg/m^3. Without using a calculator, estimate the required cylinder volume. Show your work.

2.11. 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 14.1 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 20.7 cm above the surface of the liquid. What is the liquid density?

2.12. 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.]

2.13. A horizontal cylindrical drum is 2.00 m in diameter and 4.00 m long. The drum is slowly filled with benzene (density = 0.879 g/cm^3). Derive a formula for W, the weight in newtons of the benzene in the tank, as a function of h, the depth of the liquid in centimeters.
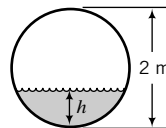
2.14. A **poundal** is the force required to accelerate a mass of 1 lb$_m$ at a rate of 1 ft/s^2, and a **slug** is the mass of an object that will accelerate at a rate of 1 ft/s^2 when subjected to a force of 1 lb$_f$.
  (a) Calculate the mass in slugs and the weight in poundals of a 175 lb$_m$ man (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 355 poundals is exerted on a 25.0-slug object. At what rate (m/s^2) does the object accelerate?

2.15. The **fern** is defined as the unit of force required to accelerate a unit of mass, called the **bung,** 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 ferns of a 3-bung object on the moon? What does the same object weigh in Lizard Lick, North Carolina?

2.16. 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) $(2.7)(8.632)$ **(c)** $2.365 + 125.2$
  (b) $(3.600 \times 10^{-4})/45$ **(d)** $(4.753 \times 10^4) - (9 \times 10^2)$

2.17. 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

2.18. 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?

2.19. 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.

*2.20. 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 2.19). 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.

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*Computer problem.

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?

2.21. A variable, Q, is reported to have a value of 2.360×10^{-4} kg·m²/h.

(a) Write a dimensional equation for Q', the equivalent variable value expressed in American engineering 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.

2.22. 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.

2.23. 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/cm³ 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.

2.24. 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:

$$d_p = 5.00 \text{ mm}$$

$$y = 0.100 \quad \text{(dimensionless)}$$

$$D = 0.100 \text{ cm}^2/\text{s}$$

$$\mu = 1.00 \times 10^{-5} \text{ N·s/m}^2$$

$$\rho = 1.00 \times 10^{-3} \text{ g/cm}^3$$

$$u = 10.0 \text{ m/s}$$

(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.

2.25. 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

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

(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 $r(\text{crystals/s})$ in terms of $D(\text{inches})$. (See Example 2.6-1.) Check the formula using the result of part (b).

2.26. 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 (lb_m/ft^3) and P is pressure ($\text{lb}_f/\text{in.}^2$).

(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).

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

$$V(\text{cm}^3) = e^t$$

where t is time is seconds.

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

(b) Both the exponential function and its argument must be dimensionless. The given equation seems to violate both of these rules, and yet the equation is valid. Explain this paradox. [*Hint:* Observe the result of part (a).]

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

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

(a) What are the 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).

*2.29. 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

*Computer problem.

(a) Use two-point linear interpolation to estimate the value of $p*$ at $T = 185°C$.

(b) Write a computer subroutine to estimate the vapor pressure of 1-chlorotetradecane for any temperature between $98.5°C$ and $215.5°C$ using two-point linear interpolation. The subroutine must determine which two tabulated temperatures bracket the given temperature, and apply the interpolation to estimate $p*(T)$. Then write a main program to read and store the values of $p*$ and T given in the table and to generate a table of vapor pressures at temperatures $T = 100°C, 105°C, 110°C, \ldots, 215°C$, calling your subroutine to estimate $p*$ at each temperature. Check your program using the result of part (a).

2.30. 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 $\ln y = 0.693$).

$Solution:$ $\ln y = bx + \ln a \implies y = ae^{bx}$

$$b = (\ln y_2 - \ln y_1)/(x_2 - x_1) = (0 - 0.693)/(2.0 - 1.0) = -0.693$$

$$\ln a = \ln y_1 - bx_1 = 0.693 + 0.693 * 1.0 = 1.386 \implies a = e^{1.386} = 4.00$$

$$\Downarrow$$

$$y = 4.00e^{-0.693x}$$

(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).

2.31. 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) $1/\ln(y - 3) = (1 + a\sqrt{x})/b$

(d) $(y + 1)^2 = [a(x - 3)^3]^{-1}$

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

**(f)** $xy = 10^{[a(x^2 + y^2) + b]}$

(g) $y = [ax + b/x]^{-1}$

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


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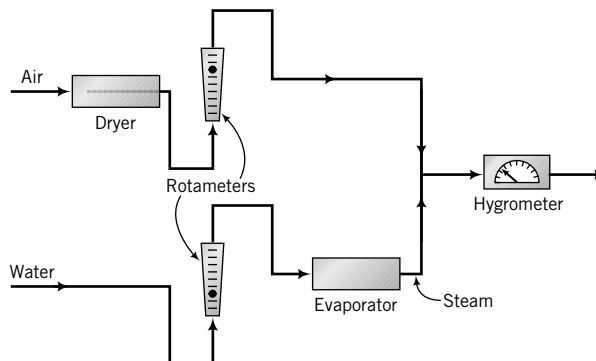
Steam and dry air are fed at known flow rates and mixed to form a gas stream with a known wa-
ter content, and the hygrometer reading is recorded; the flow rate of either the water or the air is
changed to produce a stream with a different water content and the new reading is recorded, and so
on. The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

2.33. The temperature in a process unit is controlled by passing cooling water at a measured rate through
a jacket that encloses the unit.
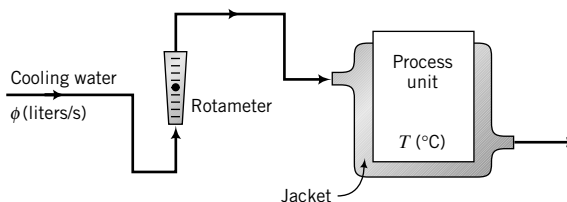
The exact relationship between the unit temperature $T(^\circ\text{C})$ and the cooling flow water flow rate
ϕ (L/s) is extremely complex, and it is desired to derive a simple empirical formula to approximate
this relationship over a limited range of flow rates and temperatures. Data are taken for T 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:
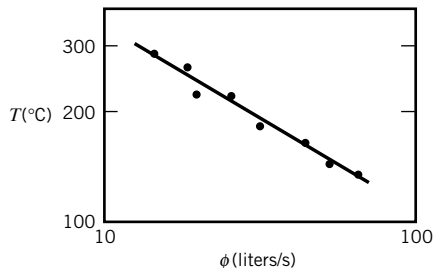
A line drawn through the data goes through the points ($\phi_1 = 25, T_1 = 210$) and ($\phi_2 = 40, T_2 =
120$).
(a) What is the empirical relationship between ϕ and T?
(b) Using your derived equation, estimate the cooling water flow rates needed to maintain the pro-
cess unit temperature at 85°C, 175°C, 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.

2.34. 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
	$\uparrow$					$\uparrow$
	C_{A0}					C_{Ae}
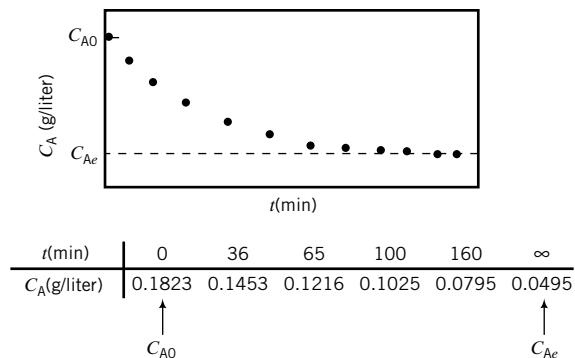
A proposed reaction mechanism predicts that C_A and t should be related by the expression

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

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

(a) Do the data support this prediction? If so, determine the value of k. (Use a semilog plot in your solution of this problem.)

(b) If the tank volume is 30.5 gallons and there is no B in the tank at $t = 0$, how much B(g) does the tank contain after two hours?

2.35. 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.

2.36. 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.)

2.37. 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_O 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.

2.38. 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.)

2.39. Fit (a) a line and (b) a line through the origin to the following data using the method of least squares (Appendix A.1):

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.

2.40. 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 into a river that passes by the plant.
 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). 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 other potential problems with the whole waste disposal procedure. Suggest several of them.

2.41. 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.

*2.42. 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

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

The *rate constant*, $k(s^{-1})$, 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).

2.43. Suppose you have n data points $(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)$ 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.

---

*Computer problem.

*2.44. Write a computer program to fit a straight line $y = ax + b$ to tabulated (x, y) data, assuming that no more than 100 data points will be taken in any one run. Your program should read in and store the data, evaluate the slope a and intercept b of the best line through the data using Equations A.1-3 through A.1-5 in Appendix A, then print out the measured values of x and y and calculated values of $y(= ax + b)$ for each tabulated value of x.

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

Equipment Encyclopedia
membrane

2.45. 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)

Diffusitivities 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	$\longleftarrow$ (so that $D = 1.34 \times 10^{-6} \text{cm}^2/\text{s}$)
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)** Write a computer program or spreadsheet to read in the (T, D) data and to calculate D_0 and E using the method of least squares (Appendix A.1). Then run the program and print out the results.

2.46. The Student Workbook contains a special exercise on linearization of equations.

Student Workbook

————

*Computer problem.

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**.

As a chemical engineer, you might be called upon to *design* or *operate* a process. **Design** includes formulation of a process flowsheet (layout) as well as specification of individual process units (such as reactors, separation equipment, heat exchangers) and associated operating variables, and **operation** involves the day-to-day running of the process. The process and all the equipment must produce product at a designated rate and with specified characteristics. Moreover, you may be responsible for maintaining the economic competitiveness of the process by identifying cost-cutting measures that reduce the use of raw materials or energy. At times the process may function poorly and you will embark on a *troubleshooting* exercise to find the problem. Market conditions may dictate a production rate greater than that which can be accommodated by the existing equipment at the current operating conditions and *debottlenecking* will be in order; sometimes the reverse happens and the production rate needs to be reduced and *turndown* becomes a concern.

The links among all of the activities and functions described in the preceding paragraph are the process streams connecting process units and forming the process flowsheet. 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 such information 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 INSTRUCTIONAL 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 temperature variation 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 2-91 through 2-120). Methods of estimating densities of gases and mixtures of liquids are given in Chapter 5 of this book.

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

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

and the volume of 6.20 lb_m of CCl_4 is

$$\frac{6.20 \text{ lb}_m \quad | \quad 454 \text{ g} \quad | \quad 1 \text{ cm}^3}{| \quad 1 \text{ lb}_m \quad | \quad 1.595 \text{ g}} = 1760 \text{ cm}^3$$

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*, 7th Edition, McGraw-Hill, New York, 1997.

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

$$
\begin{aligned}
\rho_{H_2O(l)}(4°C) &= 1.000 \text{ g/cm}^3 \\
&= 1000.\ \text{kg/m}^3 \\
&= 62.43 \text{ lb}_m/\text{ft}^3
\end{aligned}
\tag{3.1-2}
$$

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

$$
SG = 0.6\frac{20°}{4°}
$$

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.

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. 1-20 of *Perry's Chemical Engineers' Handbook.*

TEST YOURSELF
(Answers, p. 655)

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,

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

$$
V = \frac{215 \text{ kg}}{} \left| \frac{1 \text{ lb}_m}{0.454 \text{ kg}} \right| \frac{1 \text{ ft}^3}{845.7 \text{ lb}_m} = \boxed{0.560 \text{ ft}^3}
$$

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. 2-128 to 2-131 of *Perry's Chemical Engineers' Handbook*. For example, the *Handbook* gives the dependence of the volume of mercury on temperature as

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

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 ft³ 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

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

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

$$V(100°C) = \boxed{0.568\ \text{ft}^3}$$

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,

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

$$\Big\Downarrow D = (0.25/12)\ \text{ft}$$

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

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
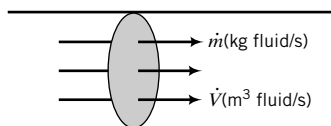
of flow. If the mass flow rate of the fluid is $\dot{m}(\text{kg/s})$[2], then every second m kilograms of the fluid pass through the cross section. If the volumetric flow rate of the fluid at the given cross section is $\dot{V}(\text{m}^3/\text{s})$, then every second V cubic meters of the fluid pass 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:

$$\rho = m/V = \dot{m}/\dot{V} \tag{3.2-1}$$

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. 655)

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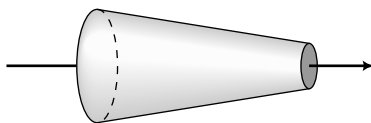
How do the mass flow rates of the gas at the inlet and outlet compare? (Remember the law of conservation of mass.) If the density of the gas is constant, how do the volumetric flow rates at these two points compare? What if the density decreases from inlet to outlet?

3.2b Flow Rate Measurement

Equipment Encyclopedia
process parameters—
flowrate measurement
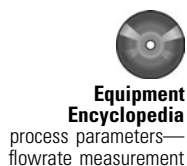
A **flowmeter** is a device mounted in a process line that provides a continuous reading of the flow rate in the line. Two commonly used flowmeters—the **rotameter** and the **orifice meter**—are shown schematically in Figure 3.2-1. *Perry's Chemical Engineers' Handbook,* pp. 5-7 through 5-17, describes many others.
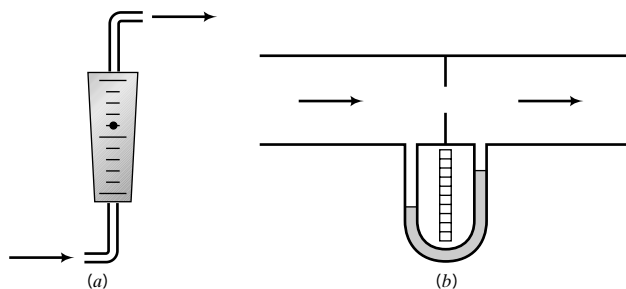

(a)   (b)

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

---

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

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 is an obstruction in the flow channel with a narrow opening through which the fluid passes. The fluid pressure drops (decreases) from the upstream side of the orifice to the downstream side; the pressure drop (which may be measured with a number of devices, including a differential manometer, which is discussed in the next section) varies with the flow rate—the greater the flow rate, the larger the pressure drop.

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

**TEST
YOURSELF
(Answers, p. 655)**

1. A steadily flowing steam 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 a real industrial situation, this "brainstorming" approach to creative problem solving is frequently used as the first step in solving the most difficult problems facing the company. 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 and/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 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.

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, l 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

$$\frac{34 \text{ kg } NH_3 \quad | \quad 1 \text{ kmol } NH_3}{| \quad 17 \text{ kg } NH_3} = 2.0 \text{ kmol } NH_3 \qquad \textbf{(3.3-1)}$$

and 4.0 lb-moles of ammonia is equivalent to

$$\frac{4.0 \text{ lb-moles } NH_3 \quad | \quad 17 \text{ lb}_m \text{ } NH_3}{| \quad 1 \text{ lb-mole } NH_3} = 68 \text{ lb}_m \text{ } NH_3 \qquad \textbf{(3.3-2)}$$

(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: there is 454 g/lb_m, for example, and therefore there is 454 mol/lb-mole, 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.**
$$\frac{100.0 \text{ g } CO_2 \quad | \quad 1 \text{ mol } CO_2}{| \quad 44.01 \text{ g } CO_2} = \boxed{2.273 \text{ mol } CO_2}$$

2.
$$\frac{2.273 \text{ mol } CO_2 \quad | \quad 1 \text{ lb-mol}}{| \quad 453.6 \text{ mol}} = \boxed{5.011 \times 10^{-3} \text{ lb-mole } CO_2}$$

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.
$$\frac{2.273 \text{ mol } CO_2 \quad | \quad 1 \text{ mol C}}{| \quad 1 \text{ mol } CO_2} = \boxed{2.273 \text{ mol C}}$$

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

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

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

$$\frac{100 \text{ kg CO}_2 \mid 1 \text{ kmol CO}_2}{h \mid 44.0 \text{ kg CO}_2} = 2.27 \frac{\text{kmol CO}_2}{h} \qquad \textbf{(3.3-3)}$$

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

$$\frac{850 \text{ lb-moles CO}_2 \mid 44.0 \text{ lb}_m \text{ CO}_2}{min \mid \text{lb-mole CO}_2} = 37,400 \frac{\text{lb}_m \text{CO}_2}{min} \qquad \textbf{(3.3-4)}$$

TEST YOURSELF
(Answers, p. 656)

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?

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, including a species A.

Mass fraction: $\quad x_A = \dfrac{\text{mass of A}}{\text{total mass}} \left(\dfrac{\text{kg A}}{\text{kg total}} \text{ or } \dfrac{\text{g A}}{\text{g total}} \text{ or } \dfrac{\text{lb}_m \text{ A}}{\text{lb}_m \text{ total}} \right) \qquad \textbf{(3.3-5)}$

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

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.

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

(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.

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

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

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

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.

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) $m_i = x_i m_{\text{total}}$	Molecular Weight M_i (g/mol)	Moles $n_i = m_i / M_i$	Mole Fraction $y_i = n_i / n_{\text{total}}$
O_2	0.16	16	32	0.500	0.150
CO	0.04	4	28	0.143	0.044
CO_2	0.17	17	44	0.386	0.120
N_2	0.63	63	28	2.250	0.690
Total	1.00	100		3.279	1.000

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 $y_{N_2} = 0.79$, $y_{O_2} = 0.21$,

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

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

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

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. 656)

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

$$\frac{5 \text{ L} \mid 0.02 \text{ mol NaOH}}{\text{L}} = 0.1 \text{ mol NaOH}$$

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

$$\frac{2 \text{ L} \mid 0.02 \text{ mol NaOH}}{\text{min} \mid \text{L}} = 0.04 \frac{\text{mol NaOH}}{\text{min}}$$

TEST YOURSELF
(Answers, p. 656)

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.**

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

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

2.

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

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.

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

$$\Downarrow$$

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

$$\Downarrow$$

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

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 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

$$ppm_i = y_i \times 10^6 \tag{3.3-9}$$

$$ppb_i = y_i \times 10^9 \tag{3.3-10}$$

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.

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[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}.

TEST
YOURSELF
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A liquid that is almost entirely water is reported to contain 125 ppb phenol (mass basis).

1. What is the mass fraction of phenol in the liquid?
2. How many milligrams of phenol are contained in one kilogram of the liquid?
3. What is the approximate concentration of phenol in the liquid 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.

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:

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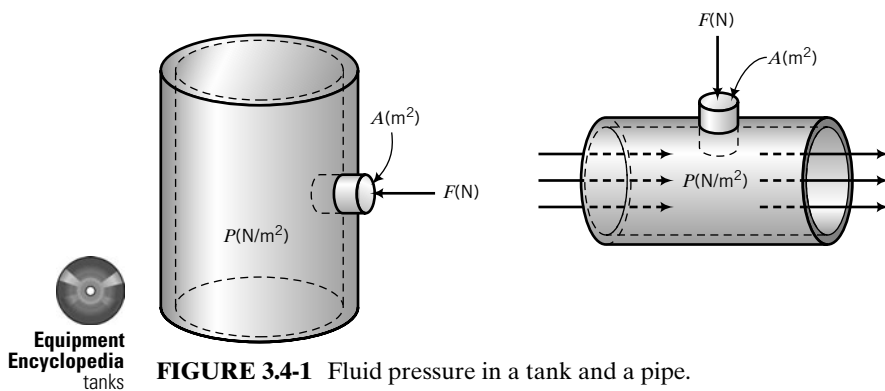

Equipment
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tanks

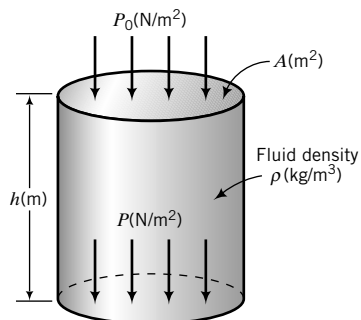**FIGURE 3.4-1** Fluid pressure in a tank and a pipe.

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

(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 $P_0 = 0$:*

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

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 $P_h(\text{mm Hg})$, 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.

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

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

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

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

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:

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

$$\Downarrow$$

$$P_h = \frac{10.4 \text{ m } H_2O}{} \left| \frac{1.013 \times 10^5 \text{ N/m}^2}{10.33 \text{ m } H_2O} \right. + \frac{1000.0 \text{ kg/m}^3}{} \left| \frac{9.807 \text{ m}}{\text{s}^2} \right| \frac{30.0 \text{ m}}{} \left| \frac{1 \text{ N}}{1 \text{ kg·m/s}^2} \right.$$

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

or

$$P_h = 396 \text{ kPa}$$

Next, the easy way, using Equation 3.4-3:

$$P_h = 10.4 \text{ m } H_2O + 30.0 \text{ m } H_2O = \boxed{40.4 \text{ m } H_2O}$$

(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. 656)**

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 $\text{lb}_f/\text{in.}^2$. 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. 656)**

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 in. Hg. What is the gauge pressure 4 in. below the surface? The absolute pressure? (Give the answers in in. Hg.)

3.4c Fluid Pressure Measurement

Perry's Chemical Engineers' Handbook (pp. 8-47 to 8-48) categorizes pressure-measurement devices as:

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process parameters—
pressure
measurement

- elastic-element methods—Bourdon tubes, bellows, or diaphragms
- liquid-column methods—manometers
- electrical methods—strain gauges, piezoresistive transducers, and piezoelectric transducers

We limit our discussion here to Bourdon gauges and manometers but recognize the importance of other methods in modern process sensors.

The most common mechanical device used for pressure measurement is a **Bourdon gauge**, which is 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 field 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 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**.
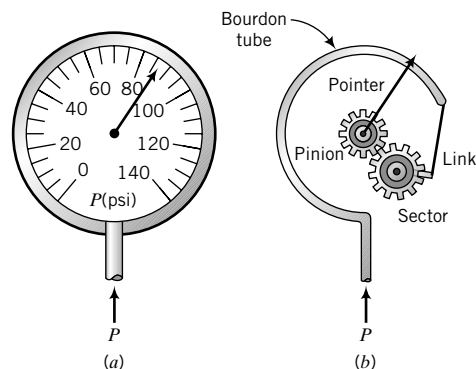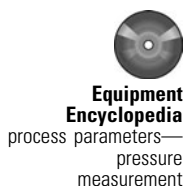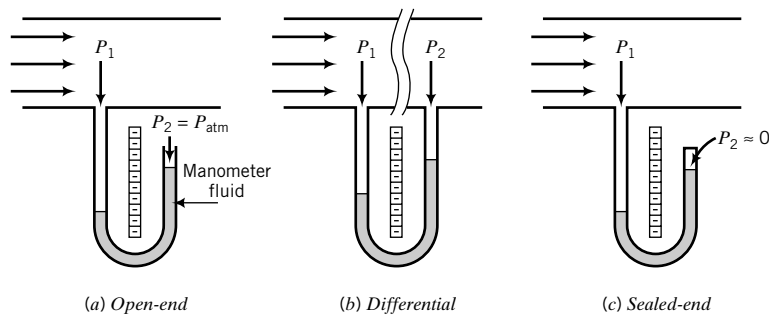

FIGURE 3.4-3 Bourdon gauge.

(a) Open-end   (b) Differential   (c) Sealed-end
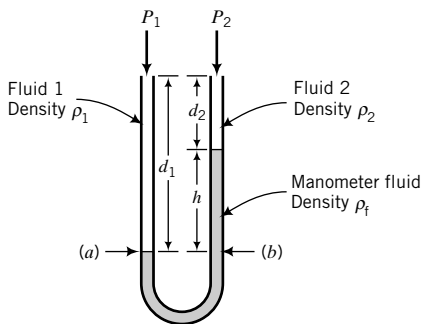
FIGURE 3.4-4 Manometers.

FIGURE 3.4-5 Manometer variables.

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: $\boxed{P_1 + \rho_1 g d_1 = P_2 + \rho_2 g d_2 + \rho_f g h}$ **(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: $\boxed{P_1 - P_2 = (\rho_f - \rho)g h}$ **(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: $\boxed{P_1 - P_2 = h}$ **(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/cm².
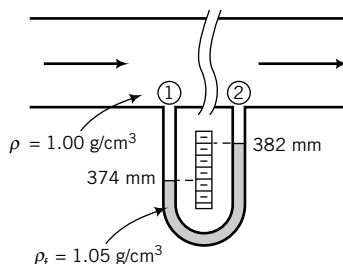
2. The pressure of gas being pulled though a line by a vacuum pump is measured with an open-end mercury manometer. A reading of −2 in. is obtained. What is the gas gauge pressure in inches of mercury? What is the absolute pressure if $P_{atm} = 30$ in. Hg?
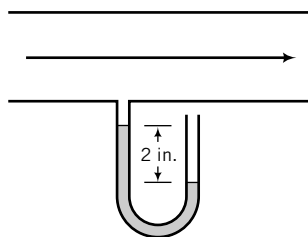
SOLUTION

1. $h = (382 - 374)$ mm $= 8$ mm. From Equation 3.4-6,

$$P_1 - P_2 = (\rho_f - \rho)gh$$

$$= \frac{(1.05 - 1.00) \text{ g}}{\text{cm}^3} \left| \frac{980.7 \text{ cm}}{\text{s}^2} \right| \frac{1 \text{ dyne}}{1 \text{ g·cm/s}^2} \left| \frac{8 \text{ mm}}{} \right| \frac{1 \text{ cm}}{10 \text{ mm}}$$

$$= \boxed{40 \frac{\text{dynes}}{\text{cm}^2}}$$

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. 656)

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
process parameters—
temperature
measurement

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 substance molecules. 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**), spectra 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:

$$T(\text{K}) = T(°\text{C}) + 273.15 \tag{3.5-1}$$

$$T(°\text{R}) = T(°\text{F}) + 459.67 \tag{3.5-2}$$

$$T(°\text{R}) = 1.8T(\text{K}) \tag{3.5-3}$$

$$T(°\text{F}) = 1.8T(°\text{C}) + 32 \tag{3.5-4}$$

Equations like these always have the form of the equation of a line ($y = ax + b$). If ($°A$) and ($°B$) stand for any two temperature units, to derive the equation for $T(°B)$ in terms of $T(°A)$ you must know equivalent values on each scale of two temperatures—say, T_1 and T_2. Then

1. Write $T(°B) = aT(°A) + b$
2. Substitute $T_1(°B)$ and $T_1(°A)$ in the equation—you then have one equation in two unknowns (a and b). Substitute $T_2(°B)$ and $T_2(°A)$ 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 $T(°\text{F})$ in terms of $T(°\text{C})$. Use $T_1 = 0°\text{C}$ (32°F) and $T_2 = 100°\text{C}$ (212°F).

SOLUTION

$$T(°\text{F}) = aT(°\text{C}) + b$$

Substitute T_1: $32 = (a)(0) + b \implies b = 32$

Substitute T_2: $212 = (a)(100) + 32 \implies a = 1.8$

$$\Downarrow$$

$$T(°\text{F}) = 1.8T(°\text{C}) + 32$$

A degree is 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 Kelvin. An interval of 1 Celsius degree or Kelvin therefore contains 1.8 Fahrenheit or Rankine degrees, leading to the conversion factors

$$\frac{1.8°\text{F}}{1°\text{C}}, \frac{1.8°\text{R}}{1\text{ K}}, \frac{1°\text{F}}{1°\text{R}}, \frac{1°\text{C}}{1\text{ K}} \tag{3.5-5}$$

$T(°\text{C}) \rightarrow$	0		1		2		3		4		5
$T(\text{K}) \rightarrow$	273		274		275		276		277		278

$T(°\text{F}) \rightarrow$	32	33	34	35	36	37	38	39	40	41
$T(°\text{R}) \rightarrow$	492	493	494	495	496	497	498	499	500	501
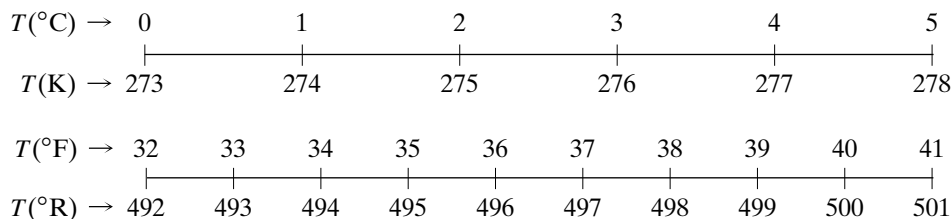
Note: These conversion factors refer to temperature intervals, not temperatures.[4] For example, to find the number of Celsius degrees between 32°F and 212°F you can say that

$$\Delta T(°C) = \frac{(212-32)°F}{} \left| \frac{1°C}{1.8°F} \right. = 100°C$$

but to find the Celsuis temperature corresponding to 32°F you must use Equation 3.5-4; you cannot say

$$T(°C) = \frac{32°F}{} \left| \frac{1°C}{1.8°F} \right.$$

A temperature   A temperature
                    interval

**TEST
YOURSELF
(Answers, p. 656)**

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?

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,

$$\Delta T(°C) = \frac{\Delta T(°F)}{} \left| \frac{1°C}{1.8°F} \right. = \frac{(80-20)°F}{} \left| \frac{1°C}{1.8°F} \right. = 33.3°C$$

---

[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 3.5-3 *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

$$C_p\left(\frac{\text{Btu}}{\text{lb}_\text{m}\cdot\text{°F}}\right) = 0.487 + 2.29 \times 10^{-4}T(\text{°F})$$

Determine the expression for C_p in J/(g · °C) in terms of $T(\text{°C})$.

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 $T(\text{°F})$ and simplify the resulting equation:

$$C_p\left(\frac{\text{Btu}}{\text{lb}_\text{m}\cdot\text{°F}}\right) = 0.487 + 2.29 \times 10^{-4}[1.8T(\text{°C}) + 32]$$

$$= 0.494 + 4.12 \times 10^{-4}T(\text{°C})$$

2. Convert to the desired temperature interval unit using Equation 3.5-5:

$$C_p\left(\frac{\text{J}}{\text{g}\cdot\text{°C}}\right) = [0.494 + 4.12 \times 10^{-4}T(\text{°C})]\frac{(\text{Btu})}{(\text{lb}_\text{m}\cdot\text{°F})}\left|\frac{1.8\text{°F}}{1.0\text{°C}}\right|\frac{1\text{ J}}{9.486 \times 10^{-4}\text{ Btu}}\left|\frac{1\text{ lb}_\text{m}}{454\text{ g}}\right.$$

$$\Downarrow$$

$$\boxed{C_p\left(\frac{\text{J}}{\text{g}\cdot\text{°C}}\right) = 2.06 + 1.72 \times 10^{-3}T(\text{°C})}$$

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 in a room 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$_\text{m}$/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. 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 American engineering system. The unit $lb_f/in.^2$ (psi) is also common in the American engineering system.

- The pressure at the base of a vertical column of fluid of density ρ and height h is given by the expression

$$P = P_o + \rho g h \qquad \text{(3.4-1)}$$

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.

Interactive Tutorial #1
Questions with Immediate Feedback

→ *Note*: This would be a good time to work through the first interactive tutorial.

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 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 (1 stone $= 14$ $lb_m \approx 6$ kg). 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) An oil pipeline across Alaska is 4.5 ft in diameter and 800 miles long. How many barrels of oil are required to fill the pipeline?
   (e) Estimate the volume of your body (cm³) 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/m³. 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.

3.3. The specific gravity of gasoline is approximately 0.70.
   (a) Determine 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 $V_{blend} = V_{gasoline} + V_{kerosene}$.

Student Workbook

3.4. Assume the price of gasoline in France is approximately 5 French francs per liter and the exchange rate is 5.22 francs per U.S. dollar. How much would you pay, in dollars, for 50.0 kg of gasoline in France, assuming gasoline has a specific gravity of 0.70. What would the same quantity of gasoline cost in the United States at a rate of $1.20 per gallon?

3.5. Liquid benzene and liquid *n*-hexane are blended to form a stream flowing at a rate of 700 lb_m/h. An on-line *densitometer* (an instrument used to determine density) indicates that the stream has a density of 0.850 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 American engineering units). State at least two assumptions required to obtain the estimate from the recommended data.

3.6. 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.

3.7. 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 cm³ 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.)

3.8. A rectangular block floats in pure water with 0.5 in. above the surface and 1.5 in. below the surface. When placed in an aqueous solution, the block of material floats with 1 in. 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.)

3.9. 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?

3.10. 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.

(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. 20-31 of *Perry's Chemical Engineers' Handbook*, 7th 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.

3.11. 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/kilograms of total body mass) is the fraction of the total body mass that is fat:

$$x_f = \frac{m_f}{m_b}$$

Prove that

$$x_f = \frac{\dfrac{1}{\rho_b} - \dfrac{1}{\rho_{nf}}}{\dfrac{1}{\rho_f} - \dfrac{1}{\rho_{nf}}}$$

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.[5]]

(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

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[5]If you can't work out the proof, take the given formula as valid and proceed to the next part.

lungs is roughly 1.2 liters. The mass of the gas is negligible. Use this information to improve your estimate of x_f.

3.12. 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 $50.0 \pm 0.05°C$ 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.

3.13. 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.
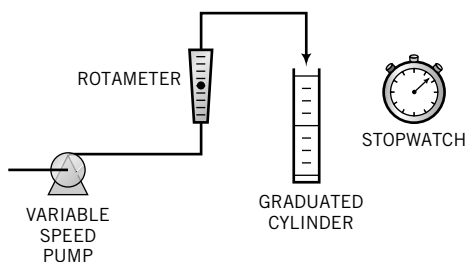
Rotameter Reading	Collection Time (min)	Volume Collected (cm^3)
2	1	297
2	1	301
4	1	454
4	1	448
6	0.5	300
6	0.5	298
8	0.5	371
8	0.5	377
10	0.5	440
10	0.5	453

(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 on p. 18 of Chapter 2:

$$s_x \approx \frac{\sqrt{\pi}}{2}\,\overline{D}_i = 0.8862\overline{D}_i$$

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 $(Y_{measured} - 1.74\overline{D}_i)$ and $(Y_{measured} + 1.74\overline{D}_i)$.[6] For a measured flow rate of 610 g/min, estimate the 95% confidence limits on the true flow rate.

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[6]W. Volk, *Applied Statistics for Engineers*, McGraw-Hill, New York, pp. 113–115, 1958.

3.14. How many of the following are found in 15.0 kmol of benzene (C_6H_6)? (a) kg C_6H_6; (b) mol C_6H_6; (c) lb-mole C_6H_6; (d) mol (g-atom) C; (e) mol H; (f) g C; (g) g H; (h) molecules of C_6H_6.

3.15. Liquid toluene is flowing through a pipe at a rate of 175 m³/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?

3.16. A mixture of methanol and methyl acetate contains 15.0 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 methyl acetate in the mixture is to be 100.0 lb-mole/h. What must the mixture flow rate be in lb_m/h?

3.17. 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.)

3.18. A suspension of calcium carbonate particles in water flows through a pipe. Your assignment is to determine both the flow rate and the composition of this slurry. You proceed to collect the stream in a graduated cylinder for 1.00 min; you then weigh the cylinder, evaporate the collected water, and reweigh the cylinder. The following results are obtained:

Mass of empty cylinder: 65.0 g
Mass of cylinder + collected slurry: 565 g
Volume collected: 455 mL
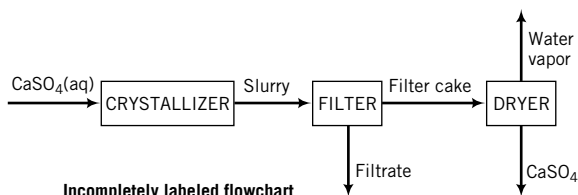Mass of cylinder after evaporation: 215 g

Calculate
    (a) the volumetric flow rate and mass flow rate of the suspension.
    (b) the density of the suspension.
    (c) the mass fraction of $CaCO_3$ in the suspension.

3.19. A mixture is 10.0 mole% ethyl alcohol, 75.0 mole% ethyl acetate ($C_4H_8O_2$), 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 ethyl acetate?

3.20. Certain solid substances, known as **hydrated** compounds, have well-defined molecular ratios of water to some other species, which often is a salt. 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.)

    Solid gypsum is formed in a crystallizer and leaves that unit as 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

Incompletely labeled flowchart

Student Workbook

Equipment Encyclopedia
crystallizer, filter, dryer

(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 $CaSO_4$.

3.21. 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.)

3.22. A mixture of ethanol (ethyl 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 ethanol?

(b) Repeat part (a) with the additional information that the specific gravity of the mixture at 20°C is 0.93518 (making it unnecessary to assume volume additivity). What percentage error results from the volume additivity assumption?

3.23. 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 700. 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.)

3.24. 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.

Determine which of the following two formulas should be used to estimate the density of the liquid mixture, $\bar{\rho}$, if the volume of the mixture equals the sum of the pure-component volumes.[7]

$$\bar{\rho} = \sum_{i=1}^{N} x_i \rho_i \quad \text{(A)} \qquad \frac{1}{\bar{\rho}} = \sum_{i=1}^{N} \frac{x_i}{\rho_i} \quad \text{(B)}$$

Determine whether (A) or (B) is the correct formula (show your proof), and then use the correct formula to estimate the density (g/cm³) of a liquid mixture containing 60.0 wt% acetone, 25.0 wt% acetic acid, and 15.0 wt% carbon tetrachloride.

3.25. A gaseous mixture of CO, CO_2, CH_4, and N_2 is analyzed with a gas chromatograph (see Problem 3.26). The output appears on a strip-chart recorder, as shown here.

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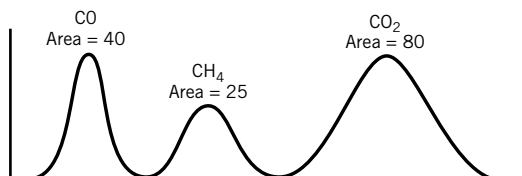
[7]This is an approximation for most liquids, unlike the exact statement that the mass of the mixture is the sum of the component masses.

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?

*3.26. A **gas chromatograph** (GC) is a device used to separate the components of a sample of a gas or liquid mixture and to provide a measure of the amount of each component in the sample. The output from a chromatographic analysis typically takes the form of a series of peaks on a strip-chart recorder. (See the preceding problem.) 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.

(a) 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, the dashes (—) would be replaced by 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

(b) Write a computer program (not a spreadsheet) to perform the same task—that is, calculate mole and mass fractions from measured chromatographic peak areas. The program should perform the following steps:

  i. read in N, the number of species to be analyzed;

  ii. read in $M_1, M_2, M_3, \ldots, M_N$, the molecular weights of the species;

  iii. read in $k_1, k_2, k_3, \ldots, k_N$, the calibration constants for the species;

  iv. read in N_d, the number of chromatographic analyses performed;

  v. for the first analysis, read in the measured peak areas $A_1, A_2, A_3, \ldots, A_N$;

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*Computer problem.

    vi. calculate and print out the sample number, the mole fractions of each species in the sample, and the mass fractions of each species in the sample;

    vii. Repeat steps v and vi for each of the remaining analyses. Test your program on the five-sample data set given in part (a).

3.27. *Biomass combustion*—burning of forests, grasslands, agricultural wastes, and other biological matter—is recognized as a serious threat to the environment.[8] The table below shows the distribution of carbon-containing compounds released to the atmosphere worldwide from all combustion sources as well as the portion coming from biomass burning.

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 compound; 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?

3.28. 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 87 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.

3.29. 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.
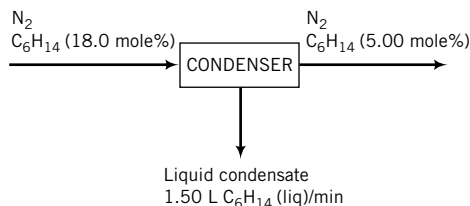
(a) What is the flow rate of the gas stream leaving the condenser in mol/min? (*Hint:* First calculate the molar flow rate of the condensate and note that the rates at which C_6H_{14} and N_2 enter the unit must equal the total rates at which they leave in the two exit streams.)

(b) What percentage of the hexane entering the condenser is recovered as a liquid?

3.30. The little-known rare earth element nauseum (atomic weight = 172) has the interesting property of being completely insoluble in everything but 12-year-old bourbon. This curious fact was discovered in the laboratory of Professor Ludwig von Schlimazel, the eminent German chemist whose

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[8]*Chemical & Engineering News*, **68**, 4(March 26, 1990).

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 Old Aardvark Bottled-in-Bond 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 Aardvark 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:

<p style="text-align:center">"Ed Settera. Add nauseum!"</p>

How many grams of nauseum did he weigh out? (Neglect the change in liquid volume resulting from the nauseum addition.)

3.31. 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:

$$C_A = C_{AO} \exp(-kt)$$

where C_{AO} is the initial concentration of A in the reactor and k is a constant.
(a) If C_A and C_{AO} 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_{AO} 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 $t = 200$ s.

3.32. 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$_2$O 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) 35.0 psi to cm of carbon tetrachloride

3.33. 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.)

3.34. A rectangular block of height L and horizontal cross-sectional area A floats at the interface between two immiscible liquids, as shown below.

Fluid 1
$\rho_1 (g/cm^3)$

h_0

h_1

h_2

L

Fluid 2
$\rho_2 (g/cm^3)$
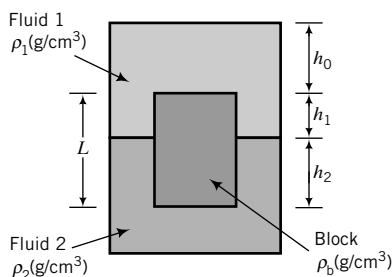
Block
$\rho_b (g/cm^3)$

(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.

3.35. The viewing window in a diving suit has an area of roughly 65 cm^2. 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.

3.36. 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.

Equipment
Encyclopedia
reactors

3.37. The chemical reactor shown below has a cover (called a *head*) that is held in place by a series of bolts. The head is made of stainless steel (SG = 8.0), is 3 in. thick, has a diameter of 24 in., and covers and seals an opening 20 in. in diameter. During *turnaround*, when the reactor is taken out of service for cleaning and repair, the head 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.

BOLTS

HEAD

REACTOR

24 in.

3 in.

20 in.

BOURDON
GAUGE
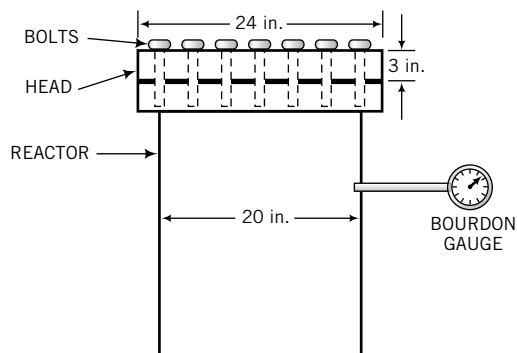
(a) What force (lb_f) were the bolts exerting on the head before they were removed? (*Hint:* Don't forget that a pressure is exerted on the top of the head by the atmosphere.) What happened

when the last bolt was removed by the operator? Justify your prediction by estimating the initial acceleration of the head upon removal of the last bolt.

(b) Propose an alteration in the turnaround procedure to prevent recurrence of an incident of this kind.

3.38. 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 prepares to put his plan into action.

(a) Prove that if the door is completely under water and h is the distance from the top of the door to the surface of the water, then the net force exerted on the door satisfies the inequality

$$F > \rho_{H_2O}ghA_{door}$$

(Don't forget that a pressure is also exerted on the door by the outside air.)

(b) Assume that water enters the room at about five times the rate at which it enters an average bathtub and that the door can withstand a maximum force of 4500 newtons (about 1000 lb$_f$). 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.

3.39. 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 came and 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?

Equipment Encyclopedia
manometer

3.40. 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.

Equipment Encyclopedia
manometer

3.41. Three different liquids are used in the manometer shown here.
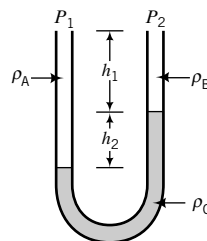
(a) Derive an expression for $P_1 - P_2$ in terms of ρ_A, ρ_B, ρ_C, h_1, and h_2.

(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).

Student Workbook

3.42. 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.
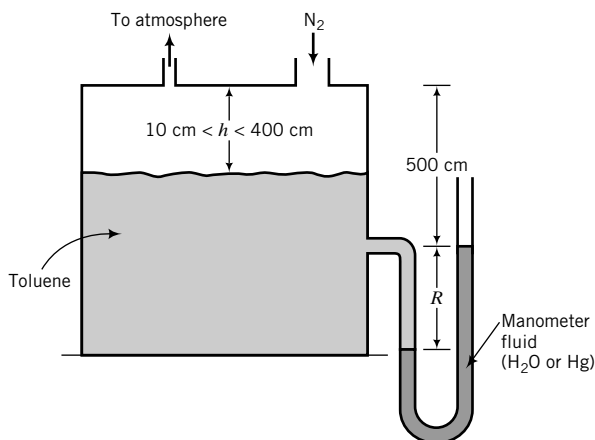
(a) When the toluene level in the tank is 150 cm below the top ($h = 150$ cm), the manometer fluid level in the open arm is at the height of the point where the manometer connects to the tank. What manometer reading, R (cm), would be observed if the manometer fluid is (i) mercury, (ii) water? Which manometer 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?

Equipment Encyclopedia manometer

3.43. 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.
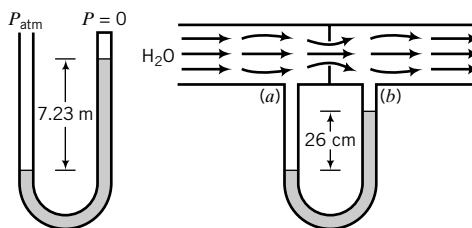
What is the pressure drop (mm Hg) from point (a) to point (b)?

Equipment Encyclopedia manometer

3.44. 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.
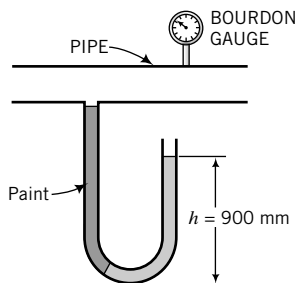
    (a) When the gas is not flowing, the pressure is the same everywhere in the pipe. How high above the bottom of the manometer would the mercury be in the arm connected to the pipe?

    (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?

3.45. An **inclined manometer** is a useful device for measuring small pressure differences.
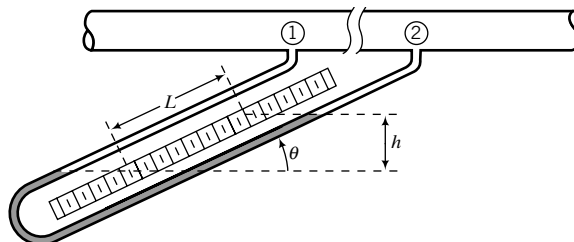
The formula given in Section 3.4 for the pressure difference in terms of the liquid-level difference h remains valid, but while h would be small and difficult to read for a small pressure drop if the manometer were vertical, L can be made quite large for the same pressure drop by making the angle of 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?

3.46. 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?
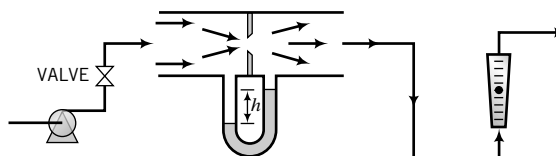
3.47. An orifice meter (see Figure 3.2-1) is to be calibrated for the measurement of the flow rate of a stream of liquid acetone. The differential manometer fluid has a specific gravity of 1.10.

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.

3.48. 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

3.49. 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?

Equipment Encyclopedia
thermocouple

3.50. A **thermocouple** is a temperature-measurement device that consists of two dissimilar metal wires joined at one end. An oversimplified diagram follows.
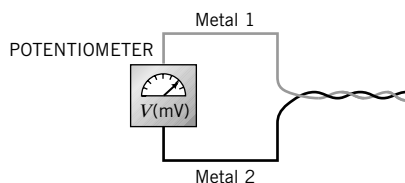
A voltage generated at the metal junction is read on a potentiometer or millivoltmeter. When certain metals are used, the voltage varies linearly with the temperature at the junction of the two metals:

$$V(mV) = aT(°C) + b$$

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?

Student Workbook

3.51. 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.

3.52. 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 $P(psig)$, $V(ft^3)$, $n(lb\text{-}mole)$, 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.)

3.53. 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.

Measurement point 1

CH₄

Measurement point 3

PREHEATER

Air

Measurement point 2
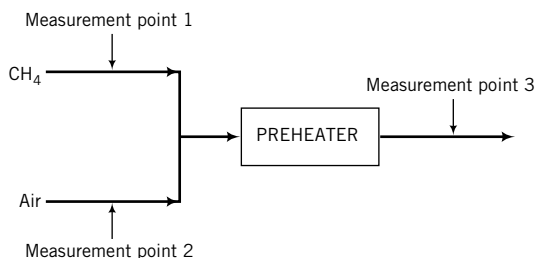
Data:
Flowmeter 1: $V_1 = 947 \text{ m}^3/\text{h}$
Flowmeter 2: $V_2 = 195 \text{ m}^3/\text{min}$
Manometer 1: $h_1 = 232$ mm
Manometer 2: $h_2 = 156$ mm
Manometer 3: $h_3 = 74$ mm
Resistance thermometer 1: $r_1 = 26.159$ ohms
Resistance thermometer 2: $r_2 = 26.157$ ohms
Resistance thermometer 3: $r_3 = 44.789$ ohms
Atmospheric pressure: A sealed-end mercury manometer reads $h = 29.76$ in.

The resistance thermometers were calibrated by measuring their resistances at the freezing and boiling points of water, with the following results:

$$T = 0°C: \qquad r = 23.624 \text{ ohms}$$
$$T = 100°C: \quad r = 33.028 \text{ ohms}$$

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:

$$\dot{n}\left(\frac{\text{kmol}}{s}\right) = \frac{12.186P(\text{atm})\dot{V}(\text{m}^3/\text{s})}{T(\text{K})}$$

where P is the *absolute* pressure of the gas.

(a) Derive the resistance thermometer calibration formula for T (°C) in terms of r (ohm).
(b) Convert the given gas law expressions to an expression for $\dot{n}$(kmol/min) in terms of P (mm Hg), T (°C), and $\dot{V}$(m³/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 m³/min.
(f) Calculate the total mass flow rate and the mass fraction of the methane at point 3.

*3.54. You are performing an experiment in which the concentration, C_A, of a reactive species is measured as a function of time, t, at several temperatures, T. At a fixed temperature, C_A varies with t according to the relation

$$1/C_A = 1/C_{A0} + kt \tag{1}$$

where C_A(mol/liter) is the concentration of A at time t(min), C_{A0}(mol/liter) is the inital concentration of A, and k [L/(mol·min)] is the reaction **rate constant**. The rate constant in turn depends on temperature, according to the formula

$$k = k_0 \exp[-E/(8.314T)] \tag{2}$$

where k_0 is a contant, T (K) is the reactor temperature, and E (J/mol) is the reaction *activation energy*.

Write a computer program that will carry out the following tasks:
(a) Read in M_A, the molecular weight of A, and N_T, the number of temperatures at which measurements were made.
(b) For the first temperature, read in the value of T in °C, the number of data points, N; and the concentrations and times $(t_1, C_{A1}), (t_2, C_{A2}), \ldots, (t_n, C_{An})$, where the times are in minutes and the concentrations are in grams of A/liter.
(c) Convert the temperature to kelvin and the concentrations to mol A/L.
(d) Use the method of least squares (Appendix A.1) in conjunction with Equation 1 to find the value of k that best fits the data. (*Hint:* First cast the equation in the form $y = kx + b$.) Store the values of k and T in arrays.
(e) Print out in a neat format the values of T (K), the converted concentrations (mol/L) and times, and k.
(f) Repeat steps (b) through (d) for the other temperatures.

[*For extra credit:* Use the method of least squares again in conjunction with Equation 2 to determine the value of E that best fits the calculated (T, k) values. Again, start by casting Equation 2 in the form $y = ax + b$.] It will be convenient to perform the least-squares slope calculation in a subroutine, since it must be done repeatedly. Test your program on the following data:

$$M_A = 65.0 \text{ g/mol}$$

t(min)	$T = 94°C$ C_A(g/L)	$T = 110°C$ C_A(g/L)	$T = 127°C$ C_A(g/L)	$T = 142°C$ C_A(g/L)
10	8.1	3.5	1.5	0.72
20	4.3	1.8	0.76	0.36
30	3.0	1.2	0.50	0.24
40	2.2	0.92	0.38	0.18
50	1.8	0.73	0.30	0.15
60	1.5	0.61	0.25	0.12

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*Computer problem.

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