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David M. Himmelblau / James B. Riggs

Basic Principles and Calculations in Chemical Engineering

Fifth Edition

Prentice Hall International Series
in the Physical and Chemical
Engineering Sciences

HEAT, ENERGY, OR WORK EQUIVALENTS

(ft)(lb$_f$)	kWh	hp-hr	Btu	calorie*	Joule
0.7376	2.773×10^{-7}	3.725×10^{-7}	9.484×10^{-4}	0.2390	1
7.233	2.724×10^{-6}	3.653×10^{-6}	9.296×10^{-3}	2.3438	9.80665
1	3.766×10^{-7}	5.0505×10^{-7}	1.285×10^{-3}	0.3241	1.356
2.655×10^{6}	1	1.341	3.4128×10^{3}	8.6057×10^{5}	3.6×10^{6}
1.98×10^{6}	0.7455	1	2.545×10^{3}	6.4162×10^{5}	2.6845×10^{6}
74.73	2.815×10^{-5}	3.774×10^{-5}	9.604×10^{-2}	24.218	1.0133×10^{2}
3.086×10^{3}	1.162×10^{-3}	1.558×10^{-3}	3.9657	1×10^{3}	4.184×10^{3}
7.7816×10^{2}	2.930×10^{-4}	3.930×10^{-4}	1	2.52×10^{2}	1.055×10^{3}
3.086	1.162×10^{-6}	1.558×10^{-6}	3.97×10^{-3}	1	4.184

*The thermochemical calorie = 4.184 J; the IT calorie = 4.1867 J (see Sec. 4.1).

PRESSURE EQUIVALENTS

mm Hg	in. Hg	bar	atm	kPa
1	3.937×10^{-2}	1.333×10^{-3}	1.316×10^{-3}	0.1333
25.40	1	3.387×10^{1}	3.342×10^{-2}	3.387
750.06	29.53	1	0.9869	100.0
760.0	29.92	1.013	1	101.3
7.502	0.2954	1.000×10^{-2}	9.872×10^{-3}	1

IDEAL GAS CONSTANT R

1.987 cal/(g mol)(K)
1.987 Btu/(lb mol)(°R)
10.73 (psia)(ft^3)/(lb mol)(°R)
8.314 (kPa)(m^3)/(kg mol)(K) = 8.314 J/(g mol)(K)
82.06 (cm^3)(atm)/(g mol)(K)
0.08206 L (atm)/(g mol)(K)
21.9 (in Hg)(ft^3)/(lb mol)(°R)
0.7302 (ft^3)(atm)/(lb mol)(°R)

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FIFTH EDITION

BASIC PRINCIPLES AND CALCULATIONS IN CHEMICAL ENGINEERING

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PTR Prentice Hall, Englewood Cliffs, New Jersey 07632

Library of Congress Cataloging-in-Publication Data

Himmelblau, David Mautner (date)
Basic principles and calculations in chemical
engineering

(Prentice-Hall international series in physical
and chemical engineering sciences)
Bibliography: p.
Includes index.
1. Chemical engineering—Tables. I. Title.
II. Series.
TP151.H5 1989 660.2 89-3728
ISBN 0-13-066572-X

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ISBN 0-13-066572-X

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Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*

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PREFACE

PURPOSE OF THE BOOK

This book is intended to serve as an introduction to the principles and techniques used in the field of chemical, petroleum, and environmental engineering. It lays a foundation of certain information and skills that can be repeatedly employed in subsequent courses as well as in professional life.

A good introductory book to chemical engineering principles and calclulations should (1) explain the fundamental concepts in not too stilted language together with generous use of appropriate equations and diagrams; (2) provide sufficient examples with detailed solutions to clearly illustrate (1); (3) present ideas in small packages that are easily identified as part of a larger framework; (4) include tests and answers that enable the reader to evaluate his or her accomplishments; and (5) provide the instructor with a wide selection of problems and questions to evaluate student competence. All of these features have been built into the fifth edition.

I kept in mind four major objectives for a reader in preparing this fifth edition:

1. to **develop systematic problem solving skills,** enhance confidence, and generate careful work habits;
2. to **learn what material balances are** and how to apply them;
3. to **learn what energy balances are** and how to apply them;
4. to learn how to **deal with the complexity of big problems.**

In addition to accomplishing these goals, a reader is exposed to background information on units and measurements of **physical properties,** basic laws about the **behavior of gas, liquids, and solids,** and some **basic mathematical tools.** Although communication and programming skills are essential for both students and professionals, assimilation of material in this book does not require mastery of either.

Other objectives that an instructor may want to include in a course, such as information about professional activities, developing a professional attitude, establishing personal goals, developing social awareness, and so on must be implemented by the instructor from other sources. Economic feasibility, a major factor in engineering decision making, costing, and optimization have been omitted because of lack of space. Nor has there been room for developing an appreciation of what processing equipment really looks like and how it works.

If this book is used as part of a scheduled course, the role of the teacher must be something more than just communicating the subject matter. The job of the teacher is to arouse emotional reactions of feeling good in connection with the content being conveyed. Creating positive feelings so that a student enjoys the subject makes a teacher effective.

SCOPE AND PARTS OF THE BOOK

The central themes of the book involve (1) learning how to formulate and solve (a) material balances, (b) energy balances, and (c) both simultaneously; (2) developing problem solving skills; and (3) becoming familiar with the use of units, physical properties, and the behavior of gases and liquids. At the front of each chapter is an information flow diagram that shows how the topics discussed in the chapter relate to the objective of being able to solve successfully problems involving material and energy balances. Figure P.1 shows the information flow among the chapters.

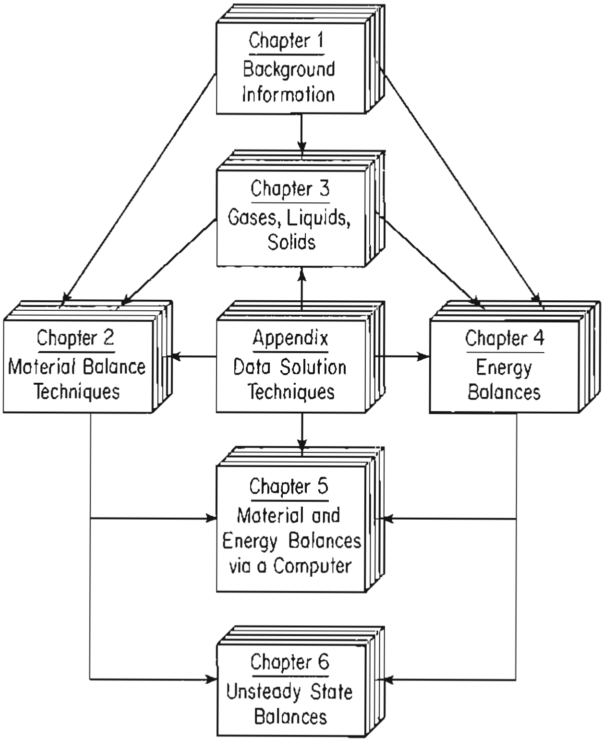

Figure P.1 The relationship of the chapters in this book.

GENERAL FEATURES OF THE BOOK

I have selected, arranged, and presented the material in this book with care based on past teaching experience. Some major features common to all the chapters are:

- The book is **self-contained** except for some homework problems that deliberately require outside information.
- The presentation is **detailed** enough so that reference to other books can be omitted.
- The **examples are simple** and concrete to make the book teachable and useful for self-instruction.
- The chapters are largely **independent** providing flexibility in teaching.
- The book has been reviewed for **readability.**
- The examples and homework problems support **good learning principles.**
- **Numerous illustrations** enhance learning.
- **Subheadings** clearly distinguish successive topics.
- **Thought problems** have been included for class discussion.
- A **table of contents** is listed **at the beginning of each chapter** to show the contents of the chapter.
- **Vital words and concepts** are in boldfaced type.
- What must be **memorized** is identified.
- At the end of each chapter **references** and numerous **supplementary references** are included.
- **Solutions** to about one-quarter of the **problems** in the problem sets are in the Appendix.
- **Data** for solving problems has been provided in tables and figures.

At the beginning of each section is a **list of objectives** to be achieved by the reader stated in such a way that attainment can be readily measured. Whether the objectives should go at the beginning or end of the section is a matter of controversy; that the text should have objectives is not. But we often present our objectives by such broad, fuzzy statements that neither the student nor the teacher can ascertain whether or not students have achieved them. (Unfortunately, this situation does not seem to inhibit the testing of students.) Each set of objectives is quite concrete and has a corresponding set of self-assessment questions and problems at the end of the respective section.

Piaget has argued that human intelligence proceeds in stages from the concrete to the abstract and that one of the big problems in teaching is that the teachers are formal reasoners (using abstraction) while many students are still concrete thinkers or at best in transition to formal operational thinking. I believe that this is true. Consequently, most topics are initiated with simple illustrations that illustrate the basic ideas. In this book the **topics are presented in order of easy assimilation** rather than in a strictly logical order. The organization is such that easy material is alternated with difficult material in order to give a "breather" after passing over each hump. For example, discussion of unsteady-state (lumped) balances has been deferred until the final chapter because experience has shown that most students lack the mathematical and engineering maturity to absorb these problems simultaneously with the steady-state balances.

A principle of educational psychology is to reinforce the learning experience by providing detailed guided practice following each new principle. We all have found from experience that there is a vast difference between having a student understand a principle and in establishing his or her ability to apply it. For example, can you learn how to play the piano from a series of lectures? By the use of numerous detailed **examples** following each brief section of text, it is hoped that straightforward, orderly methods of procedure can be instilled along with some insight into the principles involved. Furthermore, the wide variety of **problems** at the end of each chapter, about one-fourth of which are accompanied by **answers,** offer practice in the application of the principles explained in the chapter.

After all these years a perplexing problem still remains for an author in preparing a new edition, namely, the extent to which SI units should be used. It is evident that the transition to SI is well under way in a large number of chemical engineering departments in the United States, although some resistance to the system still exists. I believe that SI is an important system of measurement that chemical engineers must be able to deal with, but feel that chemical engineering students must be familiar with a variety of systems for some years to come. Consequently, it is premature to convert an undergraduate text entirely to the SI sytem of units even though most journals have done so. As a compromise, a little more than one-half of the text, examples, and problems and most of the tables employ SI units. For convenience, some of the crucial tables, such as the steam tables, are presented in both American engineering and SI units.

Self-assessment tests have been included to provide readers with questions and answers that assist in them in appraising and developing their knowledge about a particular topic. Self-assessment is intended to be an educational experience for a student. The availability of answers to the self-assessment questions together with supplementary reading citations for further study is an inherent characteristic of self-assessment. To help the reader think about the concepts and decide whether to study further is one reason for having appraisal questions.

How should you as a reader use the self-assessment problems? Some readers will start with the questions. Others will read the problems. Still others will refer to the answers first. These approaches and others are all acceptable if at the end of the procedure you can say: "Yes, this has been a worthwhile experience" or "I have learned something." The self-assessment materials are not a timed exercise so work at your pace. I suggest that you first go through the questions and problems, and write down the responses you think are most appropriate for the questions that are easy for you. Compare your responses with the answers in Appendix A. In those cases where you differ, read the section again, examine the examples, try some of the homework problems at the end of the chapter, or look up the references if necessary. In those cases in which you agree, but you felt uncomfortable with the subject matter, and the subject is significant to you, be sure to solve some of the problems at the end of the chapter for which answers are provided. After doing the easy problems, tackle the more difficult ones.

Let me now mention some of the new features of the fifth edition, features that were not present in earlier editions.

NEW FEATURES IN THE BOOK

For the fifth edition I have added a number of new features (and deleted some old ones) described below that make both teaching and self-study easier.

In this edition special attention has been devoted to presenting a **sound strategy for solving material balance and energy balance** problems, one that can be used again and again as a framework for solving word problems. All the examples showing how to solve material and energy balances have been reformulated according to this strategy (see Table 2.1). In teaching I ask students to memorize the strategy and apply it in all their homework problems and exams. I discourage the use of self-devised heuristic algorithms, or "cookbook" methods pointing out that they may be successful for one class of problems but fail quite dismally for others. By this means a student is guided into forming generalized patterns of attack in problem solving that can be used successfully in connection with unfamiliar types of problems. The text is designed to acquaint the student with a sufficient number of fundamental concepts so that he or she can (1) continue with his or her training, and (2) start finding solutions to new types of problems on his or her own. It offers practice in finding out what the problem is, defining it, collecting data, analyzing and breaking down information, assembling the basic ideas into patterns, and, in effect, doing everything but testing the solution experimentally.

A major problem in any book is to what extent and in what manner should problems involving the preparation of or use of computer codes be introduced into the text. If computer techniques are to be integrated into the classroom successfully, it is wise to start early in the game, but on the other hand the preparation (as opposed to use) of computer programs assumes that the student will have had some instruction and competence in programming prior to or concurrently with, the use of this book. The selection of appropriate problems and the illustration of good computer habits, pointing out instances in which computer solutions are not appropriate as well as instances when they are, are important. A compromise has been reached. At the end of each chapter you will find a few problems calling for the **preparation of a complete computer code.** Other **problems** that are more appropriately **solved with the aid of a computer program,** particularly a library code, than with a calculator, are designated by an asterisk (*) after the problem number. I have found that the use of prepared computer programs reduces the tedium of trial-and-error solution techniques and regenerates interest in the learning process.

Simple FORTRAN programs have been prepared for the reader's use that solve linear and nonlinear equations, retrieve the properties of water and steam, and of air-water mixtures, calculate the vapor pressure of pure substances, calculate enthalpy changes from heat capacity equations, and so on. A **disk containing these codes will be found in a pocket in the back of the book.** (Readers are encouraged to use library codes when available, codes that may be more accurate and robust than the simple codes provided.) As a result, the portions of the book formerly treating graphical integration, trial and error solutions, lever arm principles, and graphical solution methods has been drastically reduced.

Other new features are:

1. **Thought problems have been added** at the end of sections to challenge student problem solving skills and provide a basis for class discussion.
2. **Chapter 2 has been reorganized** to make it more understandable and teachable by separating the treatment of single subsystems and multiple subsystems, substantially reducing the emphasis on tie elements, and by employing a uniform strategy to solve all of the examples. Emphasis is now placed on **solving uncoupled vs. coupled material balance equations.**
3. Chapter 5 on the simultaneous solution of material and energy balance problems has been completely revised. It now focuses on **the use of flowsheeting codes to solve problems.** The problem set for Chapter 5 emphasizes the use of FLOWTRAN and PROCESS for complex problems, codes that have clear manuals and are available at most departments of chemical engineering.
4. In view of the interest in chemical engineering to expand the horizons of chemical engineering practice, a number of homework problems have been included in the areas of **biotechnology and solid state materials processing.**
5. A brief explanation of the **techniques for the solution of linear and nonlinear equations** has been added to the appendix.
6. An explanation of **least squares for data fitting** has been added to the appendix.
7. A discussion of the **accuracy and precision of data** has been added to Chapter 1.
8. How to use **spreadsheets and equation solving codes** for personal computers has been added to Chapter 2.
9. **Problem sets** have been changed and expanded.
10. The number of **worked-out examples** has been increased.

SUGGESTIONS FOR A COURSE

This book can be used in a variety of learning environments besides the traditional lectures, such as self-paced instruction, group study or discussion groups, and individual study. More topics have been included in the text than can be covered in one semester, so that an instructor has some choice as to pace of instruction and topics to include. In a lecture course for students with a background of having completed only freshman courses and no programming experience, Chapters 1, 2, 3, and 4 form the basis of an ample course. For more experienced students, if computer flowsheeting programs are available, perhaps Chapter 1 can be skimmed over and Chapter 5 included. Several case studies that are computer oriented are available to accompany Chapter 5 from various organizations and in publications such as the FLOWTRAN workbook. Chapter 6 will probably take at least one week (and probably two weeks) of time if you want to include it as well.

ACKNOWLEDGMENTS

I am indebted to many of my former teachers, colleagues and students who directly or indirectly helped me in preparing this book, in particular the present edition of it. Special thanks go to Kai Petersen and Keith Reinhardt for preparing a number of new homework problems. Professor Donald Woods was most helpful in providing information about sound techniques of problem solving. Far too many instructors using the text have contributed their corrections and suggestions for me to list them all by name. However, I do wish to express my appreciation for their kind assistance. Any further comments and suggestions for improvement of the book would be gratefully received.

David M. Himmelblau
Austin, Texas

INTRODUCTION TO ENGINEERING CALCULATIONS

1

The chemical engineering profession encompasses a wide variety of activities and is engaged in resolving problems that occur in industry, government, and academia. Problems encountered by chemical engineers are found in design, operation, control, troubleshooting, research, and even politics, the latter because of environmental and economic concerns. Chemical engineers work in numerous areas besides petroleum refining and the chemical and petrochemical industries because their background and experience are easily portable and found useful. You will find chemical engineers solving problems in industries such as

Drugs and pharmaceutics
Microelectronics
Biotechnology
Explosives and fireworks
Fats and oils
Fertilizer and agricultural chemicals
Foods and beverages
Leather tanning and finishing
Lime and cement
Man-make fibers
Metallurgical and metal products
Paints, varnishes, and pigments
Pesticides and herbicides
Plastic materials, synthetic resins

Rubber products
Soap and toiletries
Solid-state materials
Stone, clay, glass, and ceramics
Wood, pulp, paper, and board

Table 1.0 gives you some idea of the vast industrial capacity in the United States in which chemical engineers participate.

For you to learn how to appreciate and treat the problems that will arise in our modern technology, especially in the technology of the future, it is necessary to learn certain basic principles and practice their application. This text describes the principles of making material and energy balances and illustrates their application in a wide variety of ways.

We begin in this chapter with a review of certain background information. You have already encountered most of the concepts to be presented in basic chemistry and physics courses. Why, then, the need for a review? First, from experience we

TABLE 1.0 U.S. Production in 1986

Chemicals (in 10^9 lb)	
Sulfuric acid	73.64
Nitrogen	48.62
Oxygen	33.03
Ethylene	32.81
Lime	30.34
Ammonia	28.01
Sodium hydroxide	22.01
Chlorine	20.98
Phosphoric acid	18.41
Propylene	17.34
Sodium carbonate	17.20
Ethylene dichloride	14.53
Nitric acid	13.12
Urea	12.06
Ammonium nitrate	11.11
Benzene	10.23
Ethylbenzene	8.92
Carbon dioxide	8.50
Vinyl chloride	8.42
Styrene	7.84
Minerals (in 10^6 tons)	
Phosphate rock	1.2
Salt	36.8
Sulfur	12.2
Synthetic rubber (in metric tons)	4380
Fertilizers (in 10^6 tons)	
Nitrogen	10.4
Phosphate (P_2O_5)	8.6
Potash (K_2O)	1.0
Pesticides and herbicides (in 10^6lb)	
Herbicides	756
Insecticides	370
Fungicides	109
Plastics (in 10^6 lb)	
Thermosetting resins (phenols, urea, polyesters, epoxies)	5.8
Thermoplastic resins (polyetheyne, polystyrene, polypropylene, copolymers)	33.6
Synthetic fibers	
Cellulosics (rayon, acetate)	0.6
Polyester	3.3
Nylon	2.5
Olefinic and acrylic	3.0

have found it necessary to restate these familiar basic concepts in a somewhat more general and clearer fashion; second, you will need practice to develop your ability to analyze and work engineering problems. To read and understand the principles discussed in this chapter is relatively easy; to apply them to different unfamiliar situations is not. An engineer becomes competent in his or her profession by mastering the techniques developed by one's predecessors—thereafter comes the time to pioneer new ones.

The chapter begins with a discussion of units, dimensions, and conversion factors, and then goes on to review some terms you should already be acquainted with, such as:

- **(a)** Mole and mole fraction
- **(b)** Density and specific gravity
- **(c)** Measures of concentration
- **(d)** Temperature
- **(e)** Pressure

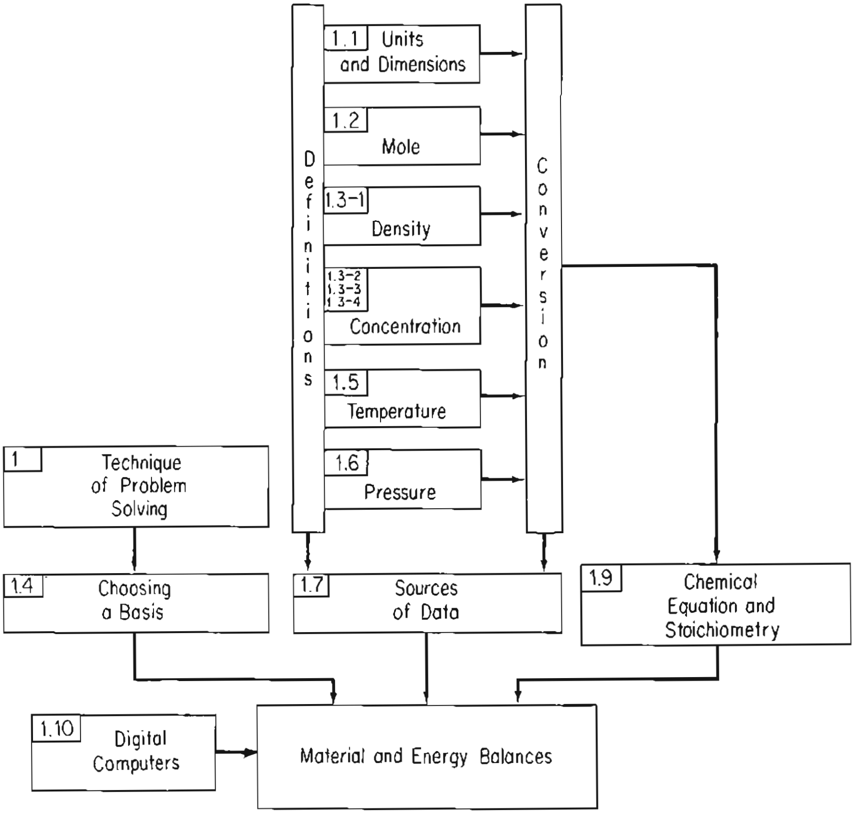

Figure 1.0 Hierarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

It then provides some clues on "how to solve problems," which should be of material aid in all the remaining portions of your career. Finally, the principles of stoichiometry are reviewed, and the technique of handling incomplete reactions is illustrated. Figure 1.0 shows the relation of the topics to be discussed to each other and to the ultimate goal of being able to solve problems involving both material and energy balances.

1.1 UNITS AND DIMENSIONS

Your objectives in studying this section are to be able to:

1. Add, subtract, multiply, and divide units associated with numbers.
2. Convert one set of units in a function or equation into another equivalent set for mass, length, area, volume, time, energy, and force.
3. Specify the basic and derived units in the SI and American engineering systems for mass, length, volume, density, and time, and their equivalences.
4. Explain the difference between weight and mass.
5. Define and know how to use the gravitational conversion factor g_c.
6. Apply the concepts of dimensional consistency to determine the units of any term in a function.

"Take care of your units and they will take care of you."

At some time in every student's life comes the exasperating sensation of frustration in problem solving. Somehow, the answers or the calculations do not come out as expected. Often this outcome arises because of inexperience in the handling of units. The use of units or dimensions along with the numbers in your calculations requires more attention than you probably have been giving to your computations in the past, but paying attention will help avoid such annoying experiences. The proper use of dimensions in problem solving is not only sound from a logical viewpoint—it will also be helpful in guiding you along an appropriate path of analysis from what is at hand through what has to be done to the final solution.

1.1-1 Units and Dimensions

Dimensions are our basic concepts of measurement such as *length, time, mass, temperature*, and so on; **units** are the means of expressing the dimensions, such as *feet* or *centimeters* for length, or *hours* or *seconds* for time. Units are associated with some quantities you may have previously considered to be dimensionless. A good example is *molecular weight*, which is really the mass of one substance per mole of that substance. This method of attaching units to all numbers which are not fundamentally dimensionless has the following very practical benefits:

(a) It diminishes the possibility of inadvertent inversion of any portion of the calculation.
(b) It reduces the calculation in many cases to simple ratios, which can be easily manipulated on a hand-held calculator.
(c) It reduces the intermediate calculations and eliminates considerable time in problem solving.
(d) It enables you to approach the problem logically rather than by remembering a formula and plugging numbers into the formula.
(e) It demonstrates the physical meaning of the numbers you use.

Every freshman knows that what you get from adding apples to oranges is fruit salad! The rule for handling units is essentially quite simple: **treat the units as you would algebraic symbols. You can add, subtract, or equate numerical quantities only if the units of the quantities are the same.** Thus the operation

5 kilograms + 3 joules

is meaningless because the dimensions of the two terms are different. The numerical operation

10 pounds + 5 grams

can be performed (because the dimensions are the same, mass) *only* after the units are transformed to be the same, either pounds, or grams, or ounces, and so on. **In multiplication and division, you can multiply or divide different units,** such as (10 centimeters ÷ 4 seconds) = 2.5 centimeters/second, **but you cannot cancel them out unless they are the same.** For example, 3 m^2/60 cm must first be converted to 3 m^2/0.6 m and then to 5 m. The units contain a significant amount of information content that cannot be ignored. They also serve as guides in efficient problem solving, as you will see shortly.

EXAMPLE 1.1 Dimensions and Units

Add the following:

(a) 1 foot + 3 seconds

(b) 1 horsepower + 300 watts

Solution

The operation indicated by

1 ft + 3 s

has no meaning since the dimensions of the two terms are not the same. One foot has the dimensions of length, whereas 3 seconds has the dimensions of time. In the case of

1 hp + 300 watts

the dimensions are the same (energy per unit time) but the units are different. You must transform the two quantities into like units, such as horsepower, watts, or something else, before the addition can be carried out. Since 1 hp = 746 watts,

$$746 \text{ watts} + 300 \text{ watts} = 1046 \text{ watts}$$

1.1-2 Conversion of Units and Conversion Factors

In this book, to help you follow the calculations, we will frequently make use of what is called the *dimensional equation*. It contains both units and numbers. One quantity is multiplied by a number of ratios termed **conversion factors** of equivalent values of combinations of time, distance, and so on, to arrive at the final desired answer. The ratios used are simple well-known values and thus the conversion itself should present no great problem. Examine Example 1.2.

EXAMPLE 1.2 Conversion of Units

If a plane travels at twice the speed of sound (assume that the speed of sound is 1100 ft/s), how fast is it going in miles per hour?

Solution

$$\begin{array}{c|c|c|c|c} 2 & 1100\text{ ft} & 1\text{ mi} & 60\text{ s} & 60\text{ min} \\ \hline & \text{s} & 5280\text{ ft} & 1\text{ min} & 1\text{ hr} \end{array} = 1500\,\frac{\text{mi}}{\text{hr}}$$

or

$$\begin{array}{c|c|c} 2 & 1100\text{ ft} & 60\,\dfrac{\text{mi}}{\text{hr}} \\ \hline & \text{s} & 88\,\dfrac{\text{ft}}{\text{s}} \end{array} = 1500\,\frac{\text{mi}}{\text{hr}}$$

Of course, it is possible to look up conversion ratios, which will enable the length of the calculation to be reduced; for instance, in Example 1.2 we could have used the conversion factor of 60 mi/hr equals 88 ft/s. However, it usually takes less time to use values you know than to look up shortcut conversion factors in a handbook. Common conversion ratios are listed on the inside front cover.

We have set up the dimensional equation with vertical lines to separate each ratio, and these lines retain the same meaning as an × or multiplication sign placed between each ratio. The dimensional equation will be retained in this form throughout most of this text to enable you to keep clearly in mind the significance of units in problem solving. It is recommended that you always write down the units next to the associated numerical value (unless the calculation is very simple) until you become quite familiar with the use of units and dimensions and can carry them in your head.

At any point in the dimensional equation you can determine the consolidated net units and see what conversions are still required. This may be carried out formally, as shown below by drawing slanted lines below the dimensional equation and writing the consolidated units on these lines, or it may be done by eye, mentally canceling and accumulating the units, or, you can strike out pairs of units as you proceed:

$$\begin{array}{c|c|c|c} 2 \times 1100\ \text{ft} & 1\ \text{mi} & 60\ \text{sec} & 60\ \text{min} \\ \hline \text{s} & 5280\ \text{ft} & 1\ \text{min} & 1\ \text{hr} \end{array}$$

$$\frac{\text{ft}}{\text{s}} \searrow \qquad \frac{\text{mi}}{\text{s}} \searrow \qquad \frac{\text{mi}}{\text{min}} \searrow$$

Consistent use of dimensional equations throughout your professional career will assist you in avoiding silly mistakes such as converting 10 centimeters to inches by multiplying by 2.54:

$$\begin{array}{c|c} 10\ \text{cm} & 2.54\ \text{cm} \\ \hline & \text{in.} \end{array} \neq 25.4\ \text{cm} \quad \text{but instead} \quad = 25.4\,\frac{\text{cm}^2}{\text{in.}}$$

Note how easily you discover that a blunder has occurred by including the units in the calculations.

Here is another example of the conversion of units.

EXAMPLE 1.3 Use of Units

Change 400 in.^{3}/day to cm^3/min.

Solution

$$\begin{array}{c|c|c|c} 400\ \text{in.}^3 & \left(\dfrac{2.54\ \text{cm}}{1\ \text{in.}}\right)^3 & 1\ \text{day} & 1\ \text{hr} \\ \hline \text{day} & & 24\ \text{hr} & 60\ \text{min} \end{array} = 4.56\,\frac{\text{cm}^3}{\text{min}}$$

In this example note that not only are the numbers raised to a power, but the units also are raised to the same power.

> There shall be one measure of wine throughout our kingdom, and one measure of ale, and one measure of grain . . . and one breadth of cloth. . . . And of weights it shall be as of measures.

So reads the standard measures clause of the *Magna Carta* (June 1215). The standards mentioned were not substantially revised until the nineteenth century. When the American colonies separated from England, they retained, among other things, the weights and measures then in use. It is probable that at that time these were the most firmly established and widely used weights and measures in the world.

No such uniformity of weights and measures existed on the European continent. Weights and measures differed not only from country to country but even from town to town and from one trade to another. This lack of uniformity led the National Assembly of France during the French Revolution to enact a decree (May 8, 1790) that called upon the French Academy of Sciences to act in concert with the Royal Society of London to "deduce an invariable standard for all of the measures and all weights." Having already an adequate system of weights and measures, the English did not participate in the French undertaking. The result of the French endeavor has evolved into what is known as the metric system.

Certainly in the American-British system there is ample room for confusion. The old question: "Which is heavier, a pound of feathers or a pound of gold?" indeed has a catch, one that is not obvious. The pound of feathers is heavier, because gold is measured in troy units in which 1 oz = 3.110×10^{-2} kg and the feathers are measured in avoirdupois units, in which 1 oz = 2.834×10^{-2} kg. But the troy pound comprises only 12 rather than 16 oz!

The metric system became preferred by scientists of the nineteenth century, partly because it was intended to be an international system of measurement, partly because the units of measurement were theoretically supposed to be independently reproducible, and partly because of the simplicity of its decimal nature. Problems in the specification of the units for electricity and magnetism led to numerous international conferences to rectify inconsistencies and culminated in 1960 in the eleventh General Conference on Weights and Measures adopting the SI (Système International) system[1] of units. As of this date the United States is the last large country not employing or engaged in transforming to some form of the SI units. Tables 1.1 and 1.2 show the most common systems of units used by engineers in the last few decades. Note that the SI, the cgs, the fps (English absolute), and the British engineering systems all have three basically defined units and that the fourth unit is derived from these three defined units.

Many of the derived units in the SI system are given special names (see Table 1.2) honoring physicists and have corresponding symbols. The unit of force, for example, has the symbols $\text{kg} \cdot \text{m} \cdot \text{s}^{-2}$; for convenience, this combination has been given the name *newton* and the symbol N. Similarly, the unit of energy is the newton · meter,

$$\text{N} \cdot \text{m} \Leftrightarrow \text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2}$$

with the short name *joule*, and symbol J. The unit of power is the *watt*, defined as one joule per second.

Only the American engineering system has four basically defined units. Consequently, in the American engineering system you have to use a conversion factor, g_c, a constant whose numerical value is not unity, to make the units come out properly. We can use Newton's law to see what the situation is with regard to conversion of units:

$$F = Cma \tag{1.1}$$

where[2] F = force
C = a constant whose numerical value and units depend on those selected for F, m, and a
m = mass
a = acceleration

---

[1] Note that the word "system" used in connection with SI units is redundant but commonly employed in English.

[2] A list of the nomenclature is included at the end of the book.

TABLE 1.1 Common Systems of Units

	Length	Time	Mass	Force	Energy*	Temperature	Remarks
Absolute (dynamic) systems							
Cgs	centimeter	second	gram	dyne*	erg, joule, or calorie	K, °C	Formerly common scientific
Fps (ft-lb-s or English absolute)	foot	second	pound	poundal*	ft poundal	°R, °F	
SI	meter	second	kilogram	newton*	joule	K, °C	Internationally adopted units for ordinary and scientific use
Gravitational systems							
British engineering	foot	second	slug*	pound weight	Btu(ft)(lb_f)	°R, °F	
American engineering	foot	second, hour	pound mass (lb_m)	pound force (lb_f)	Btu or (hp)(hr)	°R, °F	Used by chemical and petroleum engineers in the United States

*Unit derived from basic units; all energy units are derived.

TABLE 1.2 SI Units Encountered in this Book

Basic SI units

Physical quantity	Name of unit	Symbol for unit*
Length	metre, meter	m
Mass	kilogramme, kilogram	kg
Time	second	s
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol

Derived SI units

Physical quantity	Name of unit	Symbol for unit*	Definition of unit
Energy	joule	J	$kg \cdot m^2 \cdot s^{-2}$
Force	newton	N	$kg \cdot m \cdot s^{-2} \Bumpeq J \cdot m^{-1}$
Power	watt	W	$kg \cdot m^2 \cdot s^{-3} \Bumpeq J \cdot s^{-1}$
Frequency	hertz	Hz	cycle/s
Area	square meter		m^2
Volume	cubic meter		m^3
Density	kilogram per cubic meter		$kg \cdot m^{-3}$
Velocity	meter per second		$m \cdot s^{-1}$
Angular velocity	radian per second		$rad \cdot s^{-1}$
Acceleration	meter per second squared		$m \cdot s^{-2}$
Pressure	newton per square meter, pascal		$N \cdot m^{-2}$, Pa
Specific heat	joule per (kilogram · kelvin)		$J \cdot kg^{-1} \cdot K^{-1}$

Alternative units

Physical quantity	Allowable unit	Symbol for unit*
Time	minute	min
	hour	h
	day	d
	year	a
Temperature	degree Celsius	°C
Volume	litre, liter (dm^3)	L
Mass	tonne, ton (Mg)	t
	gram	g
Pressure	bar (10^5Pa)	bar

*Symbols for units do not take a plural form, but plural forms are used for the unabbreviated names.

In the cgs system the unit of force is defined as the dyne; hence if C is selected to be $C = 1\ \text{dyne}/(\text{g})(\text{cm})/\text{s}^2$, then when 1 g is accelerated at 1 cm/s^2

$$F = \begin{array}{c|c|c} \dfrac{1\ \text{dyne}}{\dfrac{(\text{g})(\text{cm})}{\text{s}^2}} & 1\ \text{g} & \dfrac{1\ \text{cm}}{\text{s}^2} \end{array} = 1\ \text{dyne}$$

Similarly, in the SI system in which the unit of force is defined to be the newton (N), if $C = 1\ \text{N}/(\text{kg})(\text{m})/\text{s}^2$, then when 1 kg is accelerated at 1 m/s^2,

$$F = \begin{array}{c|c|c} \dfrac{1\ \text{N}}{\dfrac{(\text{kg})(\text{m})}{\text{s}^2}} & 1\ \text{kg} & \dfrac{1\ \text{m}}{\text{s}^2} \end{array} = 1\ \text{N}$$

However, in the American engineering system we ask that the numerical value of the force and the mass be essentially the same at the earth's surface. Hence, if a mass of 1 lb_m is accelerated at g ft/s^2, where g is the acceleration of gravity (about 32.2 ft/s^2 depending on the location of the mass), we can make the force be 1 lb_f by choosing the proper numerical value and units for C:

$$F = (C)\begin{array}{c|c} 1\ \text{lb}_\text{m} & \dfrac{g\ \text{ft}}{\text{s}^2} \end{array} = 1\ \text{lb}_\text{f} \tag{1.2}$$

Observe that for Eq. (1.2) to hold, the units of C have to be

$$C \Bumpeq \frac{\text{lb}_\text{f}}{\text{lb}_\text{m}\left(\dfrac{\text{ft}}{\text{s}^2}\right)}$$

A numerical value of 1/32.174 has been chosen for the constant because 32.174 is the numerical value of the average acceleration of gravity (g) at sea level at 45° latitude when g is expressed in ft/s^2. The acceleration of gravity, you may recall, varies a few tenths of 1% from place to place on the surface of the earth and changes considerably as you rise up from the surface as in a rocket. With this selection of units and with the number 32.174 employed in the denominator of the conversion factor,

$$F = \left(\frac{1\ (\text{lb}_\text{f})(\text{s}^2)}{32.174(\text{lb}_\text{m})(\text{ft})}\right)\left(\begin{array}{c|c} 1\ \text{lb}_\text{m} & \dfrac{g\ \text{ft}}{\text{s}^2} \end{array}\right) = 1\ \text{lb}_\text{f}$$

The inverse of C is given the special symbol g_c:

$$g_c = 32.174\frac{(\text{ft})(\text{lb}_\text{m})}{(\text{s}^2)(\text{lb}_\text{f})} \tag{1.3}$$

Division by g_c achieves exactly the same result as multiplication by C in Newton's law. You can see, therefore, that in the American engineering system we have the convenience that the numerical value of a pound mass is also that of a pound force if the numerical value of the ratio g/g_c is equal to 1, as it is approximately in most cases. A nonstandard usage sometimes encountered analogous to lb_f and lb_m is kg_f

and kg_m; a conversion factor not equal to unity is involved in the transformation by an equation similar to Eq. (1.2).

Furthermore, a one pound mass is said to weigh one pound if the mass is in static equilibrium on the surface of earth. We can define **weight** as the opposed force required to support a mass. For the concept of weight for masses that are not stationary at earth's surface, or are affected by the earth's rotation (a factor of only 0.002 times the force exerted by gravity), or are located away from the earth's surface as in a rocket or satellite, consult your physics text.

To sum up, always keep in mind that the two quantities g and g_c are **not** the same. Also, **never forget that the pound (mass) and pound (force) are not the same units in the American engineering system** even though we speak of *pounds* to express force, weight, or mass. Nearly all teachers and writers in physics, engineering, and related fields in technical communications are careful to use the terms "mass," "force," and "weight" properly. On the other hand, in ordinary language most people, including scientists and engineers, omit the designation of "force" or "mass" associated with the pound or kilogram but pick up the meaning from the context of the statement. No one gets confused by the fact that a man is 6 feet tall but has only two feet. Similarly, you should interpret the statement that a bottle "weighs" 5 kg as meaning that the bottle has a mass of 5 kg and is attracted to the earth's surface with a force equal to

$$(5\ \text{kg})(9.80\ \text{m/s}^2) = 49(\text{kg})(\text{m})(\text{s}^{-2}) \qquad \text{if } g = 9.80\ \text{m/s}^2$$

Perhaps one of these days people will speak of "massing" instead of "weighing" and "mass-minding" instead of "weight-watching," but probably not soon. **In this book, we will not subscript the symbol lb with m (for mass) or f (for force)** unless it becomes essential to do so to avoid confusion. **We will always mean by the unit lb without a subscript the quantity pound mass.**

EXAMPLE 1.4 Use of g_c

One hundred pounds of water is flowing through a pipe at the rate of 10.0 ft/s. What is the kinetic energy of this water in $(\text{ft})(\text{lb}_f)$?

Solution

$$\text{kinetic energy} = K = \tfrac{1}{2}mv^2$$

Assume that the 100 lb of water means the mass of the water.

$$K = \frac{1}{2}\begin{array}{|c|c|c} 100\ \text{lb}_m & \left(\dfrac{10\ \text{ft}}{\text{s}}\right)^2 & \\ \hline & & 32.174\dfrac{(\text{ft})(\text{lb}_m)}{(\text{s}^2)(\text{lb}_f)} \end{array} = 155\ (\text{ft})(\text{lb}_f)$$

EXAMPLE 1.5 Use of g_c

What is the potential energy in $(\text{ft})(\text{lb}_f)$ of a 100-lb drum hanging 10 ft above the surface of the earth with reference to the surface of the earth?

Solution

$$\text{potential energy} = P = mgh$$

Assume that the 100 lb means 100 lb mass; g = acceleration of gravity = 32.2 ft/s^2.

$$P = \begin{array}{c|c|c|c} 100\ \text{lb}_m & 32.2\ \text{ft} & 10\ \text{ft} & \\ \hline & \text{s}^2 & & 32.174\dfrac{(\text{ft})(\text{lb}_m)}{(\text{s}^2)(\text{lb}_f)} \end{array} = 1001\ (\text{ft})(\text{lb}_f)$$

Notice that in the ratio of g/g_c, or 32.2 ft/s^2 divided by 32.174 (ft/s^2)(lb$_m$/lb$_f$), the numerical values are almost equal. A good many people would solve the problem by saying that 100 lb × 10 ft = 1000 (ft)(lb) without realizing that in effect they are canceling out the numbers in the g/g_c ratio.

EXAMPLE 1.6 Weight

What is the difference in the weight in newtons of a 100-kg rocket at height of 10 km above the surface of the earth, where $g = 9.76$ m/s^2, as opposed to its weight on the surface of the earth, where $g = 9.80$ m/s^2?

Solution

The weight in newtons can be computed in each case from Eq. (1.1) with $a = g$ if we ignore the tiny effect of centripetal acceleration resulting from the rotation of the earth (less than 0.3%):

$$\text{weight difference} = \begin{array}{c|c|c} 100\ \text{kg} & (9.80 - 9.76)\,\text{m} & 1\ \text{N} \\ \hline & \text{s}^2 & \dfrac{(\text{kg})(\text{m})}{\text{s}^2} \end{array} = 4.00\ \text{N}$$

Note that the concept of weight is not particularly useful in treating the dynamics of long-range ballistic missiles or of earth satellites because the earth is both round and rotating.

You should develop some facility in converting units from the SI system into the American engineering system, and vice versa, since these are the two sets of units in this text. Certainly you are familiar with the **common conversions** in both the American engineering and the SI systems. If you have forgotten, Table 1.3 lists a short selection of essential conversion factors. Memorize them. Common abbreviations and symbols also appear in this table.

The distinction between uppercase and lowercase letters should be followed, even if the symbol appears in applications where the other lettering is in uppercase style. Unit abbreviations have the same form for both singular and plural, and they are not followed by a period (except in the case of inches).

Other useful conversion factors are discussed in subsequent sections of this book.

One of the best features of the SI system is that (except for time) units and their multiples and submultiples are related by standard factors designated by the prefixes indicated in Table 1.4. Prefixes are not preferred for use in denominators (except for

TABLE 1.3 Basic Conversion Factors*

Dimension	American engineering	SI	Conversion: American engineering to SI
Length	12 in. = 1 ft 3 ft = 1 yd 5280 ft = 1 mi	10 mm† = 1 cm† 100 cm† = 1 m	1 in. = 2.54 cm 3.28 ft = 1 m
Volume	1ft^3 = 7.48 gal	1000 cm^{3†} = 1 L†	35.31 ft^3 = 1.00 m^3
Density	1 ft^3 H_2O = 62.4 lb$_m$	1 cm^{3†} H_2O = 1 g 1 m^3 H_2O = 1000 kg	—
Mass	1 ton$_m$ = 2000 lb$_m$‡	1000 g = 1 kg	1 lb = 0.454 kg
Time	1 min = 60 s 1 hr = 60 min	1 min† = 60 s 1 h† = 60 min†	—

*Some conversion factors in this table are approximate but have sufficient precision for engineering calculations.

†An acceptable but not preferred unit in the SI system.

‡2000 lb$_m$ is the "short ton"; 2240 lb$_m$ is the "long ton"; 1000 kg = 2204.6 lb$_m$ is the "metric ton."

TABLE 1.4 SI Prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{18}	exa	E	10^{-1}	deci*	d
10^{15}	penta	P	10^{-2}	centi*	c
10^{12}	tera	T	10^{-3}	milli	m
10^{9}	giga	G	10^{-6}	micro	μ
10^{6}	mega	M	10^{-9}	nano	n
10^{3}	kilo	k	10^{-12}	pico	p
10^{2}	hecto*	h	10^{-15}	femto	f
10^{1}	deka*	da	10^{-18}	atto	a

*Avoid except for areas and volumes.

kg). Do not use double prefixes; that is, use nanometer, not millimicrometer. The strict use of these prefixes leads to some amusing combinations of noneuphonious sounds, such as nanonewton, nembujoule, and so forth. Also, some confusion is certain to arise because the prefix M can be confused with m as well as with M = 1000 derived from the Roman numerical. When a compound unit is formed by multiplication of two or more other units, its symbol consists of the symbols for the separate units joined by a centered dot (e.g., N · m for newton meter). The dot may be omitted in the case of familiar units such as watthour (symbol Wh) if no confusion will result, or if the symbols are separated by exponents, as in $N \cdot m^2kg^{-2}$. Hyphens should not be used in symbols for compound units. Positive and negative exponents may be used with the symbols for units. If a compound unit is formed by division of one unit by another, its symbol consists of the symbols for the separate units either separated by a solidus or multiplied by using negative powers (e.g., m/s or $\mathrm{m \cdot s^{-1}}$ for meters per second). **We do not use the center dot for multiplication in this text.** A dot can easily get confused with a period or missed entirely in handwritten calculations. Instead, we will use parentheses or vertical rules, whichever is more convenient, for multiplication. Also, the SI convention of leaving a space between groups of numbers such as 12 650 instead of inserting a comma, as in 12,650, will be ignored to avoid confusion in handwritten numbers.

Note that in the SI system the symbols are *not* abbreviations. A symbol such as dm has to be taken as a whole. When prefixes are used with symbols raised to a power, the prefix is also raised to the same power. You should interpret $\mathrm{cm^3}$ as $(10^{-2}\cdot\mathrm{m})^3 = 10^{-6}(\mathrm{m^3})$, not as $10^{-2}(\mathrm{m^3})$.

Also watch out for ambiguities such as:

$$\mathrm{N\cdot m}\ \text{(newton × meter) vs. mN (millinewton)}$$

$$\mathrm{m\cdot s}\ \text{(meter × second) vs. ms (millisecond)}$$

and the use of symbols for units jointly with mathematical symbols leading to such unusual formulas as

$$N = 625\ \mathrm{N} \quad \text{(the first } N \text{ is the normal force)}$$

$$F = m\,(32\ \mathrm{m\cdot s^{-2}}) \quad \text{(the first } m \text{ stands for mass)}$$

1.1-3 Dimensional Consistency

Now that we have reviewed some background material concerning units and dimensions, we can immediately make use of this information in a very practical and important application. **A basic principle exists that equations must be dimensionally consistent.** What the principle requires is that each term in an equation must have the same net dimensions and units as every other term to which it is added or subtracted or equated. Consequently, dimensional considerations can be used to help identify the dimensions and units of terms or quantities in terms in an equation.

The concept of dimensional consistency can be illustrated by an equation that represents gas behavior and is known as the van der Waals equation, an equation to be discussed in more detail in Chap. 3:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

Inspection of the equation shows that the constant a must have the units of [(pressure)(volume)^2] in order for the expression in the first set of parentheses to be consistent throughout. If the units of pressure are atm and those of volume are $\mathrm{cm^3}$, a will have the units specifically of [(atm)(cm)^6]. Similarly, b must have the same units as V, or in this particular case the units of $\mathrm{cm^3}$. All equations must exhibit dimensional consistency.

EXAMPLE 1.7 Dimensional Consistency

Your handbook shows that microchip etching roughly follows the relation

$$d = 16.2 - 16.2e^{-0.021t} \qquad t < 200$$

where d is the depth of the etch in microns (micrometers; μm) and t is the time of the etch in seconds. What are the units associated with the numbers 16.2 and 0.021? Convert the relation so that d becomes expressed in inches and t can be used in minutes.

Solution

Both values of 16.2 must have the units of microns. The exponential must be dimensionless so that 0.021 must have the units of 1/seconds.

$$d_{\text{in.}} = \begin{array}{c|c|c} 16.2\ \mu\text{m} & 1\ \text{m} & 39.37\ \text{in.} \\ \hline & 10^6\ \mu\text{m} & 1\ \text{m} \end{array} \left(1 - e^{\begin{array}{c|c|c} 0.021 & 60\ \text{s} & t,\ \text{min} \\ \hline \text{s} & 1\ \text{min} & \end{array}}\right)$$

$$= 6.38 \times 10^{-4}(1 - e^{-1.26t_{\text{min}}})$$

Groups of symbols may be put together, either by theory or experiment, that have no net units. Such collections of variables or parameters are called **dimensionless** or **nondimensional groups.** One example is the Reynolds number (group) arising in fluid mechanics.

$$\text{Reynolds number} = \frac{Dv\rho}{\mu} = N_{\text{Re}}$$

where D is the pipe diameter, say in cm; v is the fluid velocity, say in cm/s; ρ is the fluid density, say in g/cm^3; and μ is the viscosity, say in centipoise, units that can be converted to g/(cm)(s). Introducing the consistent set of units for D, v, ρ, and μ into $Dv\rho/\mu$, we find, as expected, that all the units cancel out.

$$\begin{array}{c|c|c|c} \cancel{\text{cm}} & \cancel{\text{cm}} & \cancel{\text{g}} & (\cancel{\text{cm}})(\cancel{\text{s}}) \\ \hline & \cancel{\text{s}} & \cancel{\text{cm}^3} & \cancel{\text{g}} \end{array}$$

Before proceeding to the next section in this chapter, we need to mention briefly some aspects of significant figures, accuracy, and precision of numbers. Measurements collected by process instruments can be expected to exhibit some random error and may also be biased. Resolution of the proper values to use in making material and energy balances falls into the province of statistics, and is not treated here. Refer to Box et al.[3] for the appropriate techniques.

The significant figures in a number can be formally established by using scientific notation; that is, the rule that the first digit of all numbers is followed by a

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[3] G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters*, Wiley, New York, 1978.

decimal point and multiplied by a power of 10 (except for 10^0). Thus

$$4.61 \times 10^3$$

By this convention, the number of significant figures is one (for the first digit) plus the number of digits following the decimal point. Some examples are

Number	Number of significant digits
4.	1
4.0	2
4.0×10^2	2
4.000×10^2	4
3.14096×10^{-2}	6

We also need to mention something about the accuracy and precision of numbers as used in practice. *Accuracy* refers to how close a measured value is to its true value; *precision* refers to the degree of dispersion (or deviations) of measurements from their true values. In this book you will encounter integers such as 1, 2, 3 and so on, which are in some cases exact (2 reactors, 3 input streams) but in other cases are shortcut substitutes for presumed measurements in problem solving (3 moles, 10 kg). You can assume that 10 kg infers a reasonable number of significant figures in relation to the other values of parameters stated in an example or problem, such as 10 kg $\Bumpeq$ 10.00 kg. You will also occasionally encounter fractions such as $\frac{2}{3}$, which can also be treated as 0.6667 in relation to the accuracy of other values in a problem.

Feel free to round off parameters such as $\pi = 3.1416$, $\sqrt{2} = 1.414$, or Avogadro's number $N = 6.02 \times 10^{23}$. The conversion factors in Table 1.3 and other tables in this text have been rounded so that they can be memorized without too much difficulty. Also round-off your answers to problems even though in the intermediate calculations numbers are carried out to 10 or more digits in your computer, because the final answers can be no more accurate than the accuracy of the numbers introduced into the problem during its solution. For example, in this text for convenience we will use 273 K for the temperature equivalent to 0°C instead of 273.15 K, thus introducing a relative error of $0.15/273.15 = 0.00055$ into a temperature calculation (or an absolute error of 0.15). This is such a small error relative to the other known or presumed errors in your calculations that it can be neglected in almost all instances. Keep in mind, however, that in addition, subtraction, multiplication, and division, the errors you introduce propagate into the final answer. In addition and subtraction of several numbers, the maximum absolute error (M.A.E.) is equal to the sum of the M.A.E.'s of the individual values. In multiplication and division, the maximum relative error (M.R.E.) is the sum of the M.R.E.'s of the individual values. For powers and roots the M.R.E. of all the terms is the sum of the M.R.E.'s, each raised to the power of each term. Consequently, be cautious in truncating values of known accuracy too much. Carry along more digits than you need for your final result, and then round-off.

EXAMPLE 1.8 Propagation of Error

Given the maximum absolute errors in the pressures

$$p_1 = 2.0 \pm 0.3$$

$$p_2 = 8.0 \pm 0.5$$

$$p_3 = 4.0 \pm 0.1$$

what are the maximum absolute and relative errors in

$$p_4 = p_1 p_2 + p_3$$

and

$$p_5 = \frac{p_1 p_2}{p_3}$$

Solution

The fractional relative errors are:

$$p_1\text{:} \quad \frac{0.3}{2.0} = 0.15$$

$$p_2\text{:} \quad \frac{0.5}{8.0} = 0.063$$

$$p_3\text{:} \quad \frac{0.1}{4.0} = 0.025$$

For p_4:

$$\text{M.R.E. in } p_1 p_2 = 0.15 + 0.063 = 0.213$$

$$\text{M.A.E. in } p_1 p_2 = (0.213)(16) = 3.408$$

$$\text{M.A.E. in } p_4 = 3.408 + 0.1 = 3.508$$

$$\text{M.R.E. in } p_4 = \frac{3.508}{20} = 0.175$$

Because the errors are known to only one significant figure, we can truncate the relative error to 0.2. For p_5, the relative error is

$$0.15 + 0.063 + 0.025 = 0.24$$

and the absolute error is $[p_5 = (2.0)(8.0)/4.0 = 4.0]$

$$(4.0)(0.24) = 0.95 \quad (\text{or } 1)$$

By way of information, the error in $p_1^5 = 32$ is

$$\text{M.R.E.:} \quad (0.15)5 = 0.75$$

$$\text{M.A.E.:} \quad (0.75)32 = 24!$$

In the next section we review the concept of a mole of a material.

*Self-Assessment Test**

1. Convert 20 gal/hr to m^3/s; 50 $lb_f/in.^2$ to N/m^2.
2. On Phobos, the inner moon of Mars, the acceleration of gravity is 3.78 ft/sec^2. Suppose that an astronaut were walking around on Phobos, and this person plus space suit and equipment had an earth weight of 252 lb_f.
   (a) What is the mass in lb_m of the astronaut plus suit and equipment?
   (b) How much would the space-suited astronaut weigh in pounds on Phobos?
3. Prepare a table in which the rows are: length, area, volume, mass, and time. Make two columns, one for the SI and the other for the American engineering systems of units. Fill in each row with the name of the unit, and in a third column, show the numerical equivalency (i.e., 1 ft = 0.3048 m).
4. An orifice meter is used to measure flow rate in pipes. The flows rate is related to the pressure drop by an equation of the form

$$u = c\sqrt{\frac{\Delta p}{\rho}}$$

where u = fluid velocity
Δp = pressure drop
ρ = density of the flowing fluid
c = constant of proportionality

What are the units of c in the SI system of units?

5. What are the value and units of g_c?
6. In the SI system of units, the weight of a 180-lb man standing on the surface of the earth is approximately:
   (a) 801 N (b) 81.7 kg
   (c) Neither of these (d) Both of these
7. The thermal conductivity k of a liquid metal is predicted via the empirical equation $k = A \exp(B/T)$, where k is in J/(s)(m)(K) and A and B are constants. What are the units of A? Of B?
8. Fill in the following blanks:
   (a) __________ grams of prevention is worth __________ kilograms of cure.
   (b) A miss is as good as __________ kilometers.
   (c) Big sale on __________ liter hats!

Thought Problems

1. Comment as to what is wrong with the following two statements from a textbook:
   (a) Weight is the product of mass times the force of gravity.
   (b) A 67-kg person on Earth will weigh only 11 kg on the moon.
2. A state representative is proposing a bill in the legislature that declares: "No person shall discharge into the atmosphere any gaseous effluent containing radioactive materials." Would you be in favor of this bill? Is it feasible?

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*Answers to the self-assessment test problems are given in Appendix A.

1.2 THE MOLE UNIT

Your objectives in studying this section are to be able to:

1. Define a kilogram mole, pound mole, and gram mole.
2. Convert from moles to mass and the reverse for any chemical compound given the molecular weight.
3. Calculate molecular weights from the molecular formula.

What is a mole? The best answer is that a **mole** is a certain number of molecules, atoms, electrons, or other specified types of particles.[4] In particular, the 1969 International Committee on Weights and Measures approved the mole (symbol mol in the SI system) as being "the amount of a substance that contains as many elementary entities as there are atoms in 0.012 kg of carbon 12." Thus in the SI system the mole contains a different number of molecules than it does in the American engineering system. In the SI system a mole has about 6.023×10^{23} molecules; we shall call this a *gram mole* (symbol *g mol*) to avoid confusion even though in the SI system of units the official designation is simply mole (abbreviated mol). We can thereby hope to avoid the confusion that could occur with the American engineering system *pound mole* (abbreviated *lb mol*), which has $6.023 \times 10^{23} \times 453.6$ molecules. Thus a pound mole of a substance has more mass than does a gram mole of the substance.

Here is another way to look at the mole unit. To convert the number of moles to mass, we make use of the **molecular weight**—the mass per mole:

$$\text{the g mol} = \frac{\text{mass in g}}{\text{molecular weight}} \tag{1.4}$$

$$\text{the lb mol} = \frac{\text{mass in lb}}{\text{molecular weight}} \tag{1.5}$$

or

$$\text{mass in g} = (\text{mol. wt.})(\text{g mol}) \tag{1.6}$$

$$\text{mass in lb} = (\text{mol. wt.})(\text{lb mol}) \tag{1.7}$$

Furthermore, there is no reason why you cannot carry out computations in terms of ton moles, kilogram moles, or any corresponding units if they are defined analogously to Eqs. (1.4) and (1.5) even if they are not standard units. If you read

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[4] For a discussion of the mole concept, refer to the series of articles in *J. Chem. Educ.*, v. 38, pp. 549–556 (1961), and to M. L. McGlashan, *Phys. Educ.*, p. 276 (July 1977).

about a unit such as a kilomole (kmol) without an associated mass specification, or a kg mol, assume that it refers to the SI system and 10^3 g mol.

Values of the molecular weights (relative molar masses) are built up from the tables of atomic weights based on an arbitrary scale of the relative masses of the elements. **Atomic weight** of an element is the mass of an atom based on the scale that assigns a mass of exactly 12 to the carbon isotope ^{12}C, whose nucleus contains 6 protons and 6 neutrons. The terms atomic "weight" and molecular "weight" are universally used by chemists and engineers instead of the more accurate terms atomic "mass" or molecular "mass." Since weighing was the original method for determining the comparative atomic masses, as long as they were calculated in a common gravitational field, the relative values obtained for the atomic "weights" were identical with those of the atomic "masses."

Appendix B lists the atomic weights of the elements. On this scale of atomic weights, hydrogen is 1.008, carbon is 12.01, and so on. (In most of our calculations we shall round these off to 1 and 12, respectively, for convenience.)

A compound is composed of more than one atom, and the molecular weight of the compound is nothing more than the sum of the weights of the atoms of which it is composed. Thus H_2O consists of 2 hydrogen atoms and 1 oxygen atom, and the molecular weight of water is $(2)(1.008) + 16.000 = 18.02$. These weights are all relative to the ^{12}C atom as 12.0000, and you can attach any unit of mass you desire to these weights; for example, H_2 can be 2.016 g/g mol, 2.016 lb/lb mol, 2.016 ton/ton mol, and so on. Gold (Au) is 196.97 oz/oz mol!

You can compute average molecular weights for mixtures of constant composition even though they are not chemically bonded if their compositions are known accurately. Later (Example 1.13) we show how to calculate the average molecular weight of air. Of course, for a material such as fuel oil or coal whose composition may not be exactly known, you cannot determine an exact molecular weight, although you might estimate an approximate average molecular weight good enough for engineering calculations. Keep in mind that the symbol lb refers to lb_m unless otherwise stated.

EXAMPLE 1.9 Use of Molecular Weights

If a bucket holds 2.00 lb of NaOH (mol. wt. = 40.0), how many

(a) Pound moles of NaOH does it contain?
(b) Gram moles of NaOH does it contain?

Solution

Basis: 2.00 lb of NaOH

(a)
$$\frac{2.00 \text{ lb NaOH}}{} \left| \frac{1 \text{ lb mol NaOH}}{40.0 \text{ lb NaOH}} \right. = 0.050 \text{ lb mol NaOH}$$

(b₁)
$$\frac{2.00 \text{ lb NaOH}}{} \left| \frac{1 \text{ lb mol NaOH}}{40.0 \text{ lb NaOH}} \right| \frac{454 \text{ g mol}}{1 \text{ lb mol}} = 22.7 \text{ g mol}$$

or

(b$_2$)
$$\begin{array}{l|l|l} 2.00 \text{ lb NaOH} & 454 \text{ g} & 1 \text{ g mol NaOH} \\ \hline & 1 \text{ lb} & 40.0 \text{ g NaOH} \end{array} = 22.7 \text{ g mol}$$

EXAMPLE 1.10 Use of Molecular Weights

How many pounds of NaOH are in 7.50 g mol of NaOH?

Solution

Basis: 7.50 g mol of NaOH

$$\begin{array}{l|l|l} 7.50 \text{ g mol NaOH} & 1 \text{ lb mol} & 40.0 \text{ lb NaOH} \\ \hline & 454 \text{ g mol} & 1 \text{ lb mol NaOH} \end{array} = 0.661 \text{ lb NaOH}$$

Self-Assessment Test

1. What is the molecular weight of acetic acid (CH_3COOH)?
2. What is the difference between a kilogram mole and a pound mole?
3. Convert 39.8 kg of NaCl per 100 kg of water to kilogram moles of NaCl per kilogram mole of water.
4. How many pound moles of $NaNO_3$ are there in 100 lb?
5. One pound mole of CH_4 per minute is fed to a heat exchanger. How many kilograms is this per second?

Thought Problem

1. There is twice as much copper in 480 g of copper as there is in 240 g of copper, but is there twice as much copper in 480 g of copper as there is silver in 240 g of silver?

1.3 CONVENTIONS IN METHODS OF ANALYSIS AND MEASUREMENT

Your objectives in studying this section are to be able to:

1. Define density and specific gravity.
2. Calculate the density of a liquid or solid given its specific gravity and the reverse.
3. Look up the density or specific gravity of a liquid or solid in reference tables.
4. Interpret the meaning of specific gravity data taken from reference tables.
5. Specify the common reference material(s) used to determine the specific gravity of liquids and solids.

6. Convert the composition of a mixture from mole fraction (or percent) to mass (weight) fraction (or percent) and the reverse.
7. Transform a material from one measure of concentration to another, including mass/volume, moles/volume, ppm, and molarity.
8. Calculate the mass or number of moles of each component in a mixture given the percent (or fraction) composition, and the reverse, and compute the average molecular weight.
9. Convert a composition given in mass (weight) percent to mole percent, and the reverse.

There are certain definitions and conventions which we mention at this point since they will be used constantly throughout the book. If you memorize them now, you will immediately have a clearer perspective and save considerable trouble later.

1.3-1 Density

Density is the ratio of mass per unit volume, as, for example, kg/m^3 or lb/ft^3. It has both a numerical value and units. To determine the density of a substance, you must find both its volume and its mass. If the substance is a solid, a common method to determine its volume is to displace a measured quantity of inert liquid. For example, a known weight of a material can be placed into a container of liquid of known weight and volume, and the final weight and volume of the combination measured. The density (or specific gravity) of a liquid is commonly measured with a hydrometer (a known weight and volume is dropped into the liquid and the depth to which it penetrates into the liquid is noted) or a Westphal balance (the weight of a known slug is compared in the unknown liquid with that in water). Gas densities are quite difficult to measure; one device used is the Edwards balance, which compares the weight of a bulb filled with air to the same bulb when filled with the unknown gas.

In most of your work using liquids and solids, density will not change very much with pressure, but for precise measurements for common substances you can always look up in a handbook the variation of density with pressure. The change in density with temperature is illustrated in Fig. 1.1 for liquid water and liquid ammo-

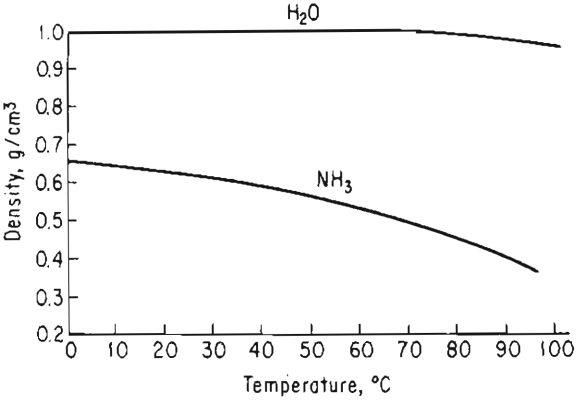

Figure 1.1 Densities of liquid H_2O and NH_3 as a function of temperature.

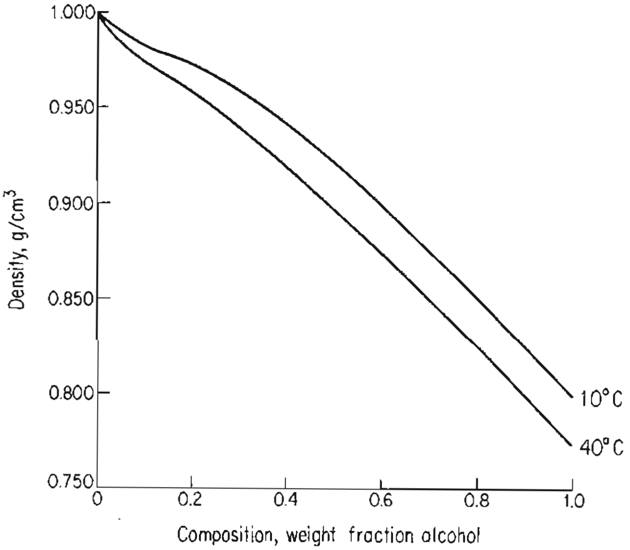

Figure 1.2 Density of a mixture of ethyl alcohol and water as a function of composition.

nia. Figure 1.2 illustrates how density also varies with composition. In the winter you may put antifreeze in your car radiator. The service station attendant checks the concentration of antifreeze by measuring the specific gravity and, in effect, the density of the radiator solution after it is mixed thoroughly. He has a little thermometer in his hydrometer kit in order to be able to read the density corrected for temperature.

1.3-2 Specific Gravity

Specific gravity is commonly thought of as a dimensionless ratio. Actually, it should be considered as the ratio of two densities—that of the substance of interest, *A*, to that of a reference substance. In symbols:

$$\text{sp gr} = \textbf{specific gravity} = \frac{(\text{lb/ft}^3)_A}{(\text{lb/ft}^3)_{\text{ref}}} = \frac{(\text{g/cm}^3)_A}{(\text{g/cm}^3)_{\text{ref}}} = \frac{(\text{kg/m}^3)_A}{(\text{kg/m}^3)_{\text{ref}}} \qquad (1.8)$$

The reference substance for liquids and solids is normally water. Thus the specific gravity is the ratio of the density of the substance in question to the density of water. The specific gravity of gases frequently is referred to air, but may be referred to other gases, as discussed in more detail in Chap. 3. Liquid density can be considered to be nearly independent of pressure for most common calculations, but, as indicated in Fig. 1.1 it varies somewhat with temperature; therefore, to be very precise when referring to specific gravity, state the temperature at which each density is chosen. Thus

$$\text{sp gr} = 0.73\frac{20^\circ}{4^\circ}$$

can be interpreted as follows: the specific gravity when the solution is at 20°C and the reference substance (water) is at 4°C is 0.73. Since the density of water at 4°C is very close to 1.0000 g/cm^3 in the SI system, the numerical values of the specific gravity and density in this system are essentially equal. Since densities in the American engineering system are expressed in lb/ft^3 and the density of water is about 62.4 lb/ft^3, it can be seen that the specific gravity and density values are not numerically equal in the American engineering system.

In the petroleum industry the specific gravity of petroleum products is usually reported in terms of a hydrometer scale called °API. The equation for the API scale is

$$°\text{API} = \frac{141.5}{\text{sp gr}\frac{60°}{60°}} - 131.5 \tag{1.9}$$

or

$$\text{sp gr}\frac{60°}{60°} = \frac{141.5}{°\text{API} + 131.5} \tag{1.10}$$

The volume and therefore the density of petroleum products vary with temperature, and the petroleum industry has established 60°F as the standard temperature for volume and API gravity. The °API is being phased out as SI units are accepted for densities.

There are many other systems of measuring density and specific gravity that are somewhat specialized; for example, the Baumé (°Be) and the Twaddell (°Tw) systems. Relationships among the various systems of density may be found in standard reference books.

1.3-3 Specific Volume $= \frac{1}{\rho}$

The specific volume of any compound is the inverse of the density, that is, the volume per unit mass or unit amount of material. Units of specific volume might be ft^3/lb$_m$, ft^3/lb mole, cm^3/g, bbl/lb$_m$, m^3/kg, or similar ratios.

1.3-4 Mole Fraction and Mass (Weight) Fraction

Mole fraction is simply the moles of a particular substance divided by the total number of moles present. This definition holds for gases, liquids, and solids. Similarly, the **mass (weight) fraction** is nothing more than the **mass (weight)** of the substance divided by the total mass (weight) of all substances present. Although the mass fraction is what is intended to be expressed, ordinary engineering usage employs the term **weight fraction.** Mathematically, these ideas can be expressed as

$$\text{mole fraction of } A = \frac{\text{moles of } A}{\text{total moles}} \tag{1.11}$$

$$\text{mass (weight) fraction of } A = \frac{\text{mass (weight) of } A}{\text{total mass (weight)}} \tag{1.12}$$

Mole percent and weight percent are the respective fractions times 100.

1.3-5 Analyses

The analyses of gases such as air, combustion products, and the like **are usually on a dry basis**—that is, water vapor is excluded from the analysis. Such an analysis, called an **Orsat analysis,** is explained in Sec. 2.3. If the gas acts as an ideal gas and its components are each measured by volume, you know (or will learn in Sec. 3.1) that volume percent under ordinary conditions is the same as mole percent. For example, consider the composition of air, which is approximately

21%	oxygen
79%	nitrogen
100%	total

This means that at room temperature and pressure, any sample of air will contain 21% oxygen by volume and also be 21 mole % oxygen.

> **In this book, the composition of gases will always be presumed to be given in mole percent or fraction unless otherwise stated.**

Analysis of liquids and solids are usually given by mass (weight) percent or fraction, but occasionally by mole percent.

> **In this text, the analysis of liquids and solids will always be assumed to be weight percent unless otherwise stated.**

EXAMPLE 1.11 Mole Fraction and Mass (Weight) Fraction

An industrial-strength drain cleaner contains 5.00 kg of water and 5.00 kg of NaOH. What are the mass (weight) fraction and mole fraction of each component in the bottle of water?

Solution

Basis: 10.0 kg of total solution

Component	kg	Weight fraction	Mol. wt.	kg mol	Mole fraction
H_2O	5.00	$\frac{5.00}{10.0} = 0.500$	18.0	0.278	$\frac{0.278}{0.403} = 0.690$
NaOH	5.00	$\frac{5.00}{10.0} = 0.500$	40.0	0.125	$\frac{0.125}{0.403} = 0.310$
Total	10.00	1.000		0.403	1.00

The kilogram moles are calculated as follows:

$$\frac{5.00 \text{ kg } H_2O}{} \left| \frac{1 \text{ kg mol } H_2O}{18.0 \text{ kg } H_2O} \right. = 0.278 \text{ kg mol } H_2O$$

$$\begin{array}{l|l} 5.00 \text{ kg NaOH} & 1 \text{ kg mol NaOH} \\ \hline & 40.0 \text{ kg NaOH} \end{array} = 0.125 \text{ kg mol NaOH}$$

Adding these quantities together gives the total kilogram moles.

EXAMPLE 1.12 Density and Specific Gravity

If dibromopentane (DBP) has a specific gravity of 1.57, what is its density in (a) g/cm^3? (b) lb$_m$/ft^3? and (c) kg/m^3?

Solution

No temperatures are cited for the dibromopentane or the reference compound (presumed to be water); hence we assume that the temperatures are the same and that water has a density of 1.00×10^3 kg/m^3 (1.00 g/cm^3).

(a)

$$\begin{array}{c|c} 1.57\,\dfrac{\text{g DBP}}{\text{cm}^3} & 1.00\,\dfrac{\text{g H}_2\text{O}}{\text{cm}^3} \\ \hline 1.00\,\dfrac{\text{g H}_2\text{O}}{\text{cm}^3} & \end{array} = 1.57\,\frac{\text{g DBP}}{\text{cm}^3}$$

(b)

$$\begin{array}{c|c} 1.57\,\dfrac{\text{lb}_m\,\text{DBP}}{\text{ft}^3} & 62.4\,\dfrac{\text{lb}_m\,\text{H}_2\text{O}}{\text{ft}^3} \\ \hline 1.00\,\dfrac{\text{lb}_m\,\text{H}_2\text{O}}{\text{ft}^3} & \end{array} = 97.97\,\frac{\text{lb}_m\,\text{DBP}}{\text{ft}^3}$$

(c)

$$\begin{array}{c|c|c} 1.57 \text{ g DBP} & \left(\dfrac{100 \text{ cm}}{1 \text{ m}}\right)^3 & 1 \text{ kg} \\ \hline \text{cm}^3 & & 1000 \text{ g} \end{array} = 1.57 \times 10^3\,\frac{\text{kg DBP}}{\text{m}^3}$$

or

$$\begin{array}{c|c} \dfrac{1.57 \text{ kg DBP}}{\text{m}^3} & \dfrac{1.00 \times 10^3 \text{ kg H}_2\text{O}}{\text{m}^3} \\ \hline \dfrac{1.00 \text{ kg H}_2\text{O}}{\text{m}^3} & \end{array} = 1.57 \times 10^3\,\frac{\text{kg DBP}}{\text{m}^3}$$

Note how the units of specific gravity as used here clarify the calculations.

EXAMPLE 1.13 Average Molecular Weight of Air

What is the average molecular weight of air and its composition by weight percent?

Solution

Basis: 100 lb mol of air

Component	Moles = percent	Mol. wt.	lb	weight %
O_2	21.0	32	672	23.17
N_2*	79.0	28.2	2228	76.83
Total	100		2900	100.00

*Includes Ar, CO_2, Kr, Ne, and Xe, and is called atmospheric nitrogen. The molecular weight is 28.2.

Table 1.5 lists the detailed composition of air.

The average molecular weight is 2900 lb/100 lb mol = 29.00.

TABLE 1.5 Composition of Clean, Dry Air near Sea Level

Component	Percent by volume = mole percent
Nitrogen	78.084
Oxygen	20.9476
Argon	0.934
Carbon dioxide	0.0314
Neon	0.001818
Helium	0.000524
Methane	0.0002
Krypton	0.000114
Nitrous oxide	0.00005
Hydrogen	0.00005
Xenon	0.0000087
Ozone	
Summer	0–0.000007
Winter	0–0.000002
Ammonia	0–trace
Carbon monoxide	0–trace
Iodine	0–0.000001
Nitrogen dioxide	0–0.000002
Sulfur dioxide	0–0.0001

Do **not** attempt to get an average specific gravity or average density for a mixture of solids or liquids by multiplying the individual component specific gravities or densities by the respective mole fractions of the components in the mixture and summing the products. The proper way to use specific gravity is demonstrated in the next example.

EXAMPLE 1.14 Application of Specific Gravity

In the production of a drug having a molecular weight of 192, the exit stream from the reactor flows at the rate of 10.3 L/min. The drug concentration is 41.2% (in water), and the specific gravity of the solution is 1.025. Calculate the concentration of the drug (in kg/L) in the exit stream, and the flow rate of the drug in kg mol/min.

Solution

For the first part of the problem, we want to transform the mass fraction of 0.412 into mass per liter of the drug. Take 1.000 kg of exit solution as a basis for convenience. See Fig. E1.14.

Basis: 1.000 kg solution

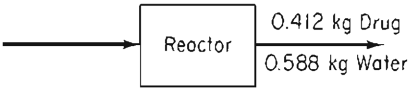

Figure E1.14

How do we get mass per volume (the density) from the given data which is in terms of mass per mass? Use the specific gravity of the solution.

$$\text{density of solution} = \frac{1.025\,\dfrac{\text{g soln}}{\text{cm}^3}}{1.000\,\dfrac{\text{g H}_2\text{O}}{\text{cm}^3}}\left|\,\frac{1.000\,\dfrac{\text{g H}_2\text{O}}{\text{cm}^3}}{}\right. = 1.025\,\frac{\text{g soln}}{\text{cm}^3}$$

Next

$$\frac{0.412\text{ kg drug}}{1.000\text{ kg soln}}\left|\frac{1.025\text{ g soln}}{1\text{ cm}^3}\right|\frac{1\text{ kg}}{10^3\text{ g}}\left|\frac{10^3\text{ cm}^3}{1\text{ L}}\right. = 0.422\text{ kg drug/L soln}$$

To get the flow rate, we take a different basis, 1 minute.

Basis: 1 min ≡ 10.3 L solution

$$\frac{10.3\text{ L soln}}{1\text{ min}}\left|\frac{0.422\text{ kg drug}}{\text{L soln}}\right|\frac{1\text{ kg mol drug}}{192\text{ kg drug}} = 0.0226\text{ kg mol/min}$$

1.3-6 Concentrations

Concentration means the quantity of some solute per fixed amount of solvent, or solution, in a mixture of two or more components; for example:

- **(a)** Mass per unit volume (lb_m of solute/ft^3, g of solute/L, lb_m of solute/bbl, kg of solute/m^3).
- **(b)** Moles per unit volume (lb mol of solute/ft^3, g mol of solute/liter, g mol of solute/cm^3).
- **(c)** Parts per million—a method of expressing the concentration of extremely dilute solutions. Ppm is equivalent to a weight fraction for solids and liquids because the total amount of material is of a much higher order of magnitude than the amount of solute; it is a mole fraction for gases. Why?
- **(d)** Other methods of expressing concentration with which you should be familiar are molarity (g mole/liter) and normality (equivalents/liter).

A typical example of the use of some of these concentration measures is the set of guidelines by which the Environmental Protection Agency defined the extreme levels at which the five most common air pollutants could harm people over stated periods of time.

- **(a)** *Sulfur dioxide:* 365 $\mu\text{g/m}^3$ averaged over a 24-hr period
- **(b)** *Particulate matter:* 260 $\mu\text{g/m}^3$ averaged over a 24-hr period

(c) *Carbon monoxide:* 10 mg/m^3 (9 ppm) when averaged over an 8-hr period; 40 mg/m^3 (35 ppm) when averaged over 1 hr

(d) *Nitrogen dioxide:* 100 μg/m^3 averaged over 1 year

It is important to remember that in an ideal solution, such as in gases or in a simple mixture of hydrocarbon liquids or compounds of like chemical nature, the volumes of the components may be added without great error to get the total volume of the mixture. For the so-called nonideal mixtures this rule does not hold, and the total volume of the mixture is bigger or smaller than the sum of the volumes of the pure components.

In Chap. 2 we will use **stream flows** and compositions in making material balances. To calculate the **mass flow rate,** $\dot{m}$, from a known **volumetric flow rate,** q, you multiply the volumetric flow rate by the mass concentration thus

$$\left.\frac{q\ \text{m}^3}{\text{s}}\right|\frac{\rho\ \text{kg}}{\text{m}^3} = \dot{m}\frac{\text{kg}}{\text{s}}$$

How would you calculate the volumetric flow rate from a known mass flow rate? From the volumetric flow rate you can calculate the **average velocity,** v, in a pipe if you know the area, A, of the pipe from the relation

$$q = Av$$

Self-Assessment Test

1. Answer the following questions true (T) or false (F).
   (a) The density and specific gravity of mercury are the same.
   (b) The inverse of density is the specific volume.
   (c) Parts per million expresses a mole ratio.
   (d) Concentration of a component in a mixture does not depend on the amount of the mixture.
2. A cubic centimeter of mercury has a mass of 13.6 g at the earth's surface. What is the density of the mercury?
3. What is the approximate density of water at room temperature?
4. For liquid HCN, a handbook gives: sp gr 10°C/4°C = 1.2675. What does this mean?
5. For ethanol, a handbook gives: sp gr 60°F/60°F = 0.79389. What is the density of ethanol at 60°F?
6. Commercial sufuric acid is 98% H_2SO_4 and 2% H_2O. What is the mole ratio of H_2SO_4 to H_2O?
7. A container holds 1.704 lb of HNO_3/lb of H_2O and has a specific gravity of 1.382 at 20°C. Compute the composition in the following ways:
   (a) Weight percent HNO_3
   (b) Pounds HNO_3 per cubic foot of solution at 20°C
   (c) Molarity at 20°C

8. The specific gravity of steel is 7.9. What is the volume in cubic feet of a steel ingot weighing 4000 lb?
9. A solution contains 25% salt by weight in water. The solution has a density of 1.2 g/cm^3. Express the composition as:
   (a) Kilograms salt per kilogram of H_2O
   (b) Pounds of salt per cubic foot of solution
10. A liquefied mixture of *n*-butane, *n*-pentane, and *n*-hexane has the following composition in percent:

n-C_4H_{10}	50
n-C_5H_{12}	30
n-C_6H_{14}	20

   For this mixture, calculate:
   (a) The weight fraction of each component
   (b) The mole fraction of each component
   (c) The mole percent of each component
   (d) The average molecular weight

Thought Problems

1. **"Drop in the Bucket.** Service Station Operator Balks At Paying for 'Shrinking' Gasoline" was a recent headline in the newspaper. The way the station operator sees it, when you pay for a gallon of gasoline, you should get a gallon of gasoline. He contends he's paying for thousands of gallons of gasoline each year he doesn't get. He's suing to try to settle the issue.

   The issue is "shrinking" gasoline. According to the American Petroleum Institute, gasoline shrinks at the rate of six gallons per 10,000 gallons for every one-degree-Fahrenheit drop in temperature and expands at the same rate when the temperature rises. On a typical 8,000-gallon shipment from a refinery at, say, 75 degrees, that means a loss of 72 gallons when the gasoline gets stored in the station operator's 60-degree underground tanks and thereafter is sold to customers.

   "It may seem like a small matter," he says, "but I'm a high-volume dealer, and I lose $3,000 to $4,000 a year to shrinkage." Major oil companies adjust their billing for temperature changes in big shipments to each other, but "We don't bill that way because changes in temperature in winter and summer balance each other out, so the dealer comes out pretty much even," an oil company spokesman says.

   "Dealers Don't Agree" was the next heading. "Dealers say that's nonsense." Why do you think the dealers believe the lack of temperature billing is not fair?
2. The National Museum is considering buying a Maya plaque from Honduras that the seller claims to be jade. Jade is either jadite (sp gr 3.2 to 3.4) or nephrite (sp gr 3.0). What liquid would you recommend using to test whether or not the mask is jade?
3. A refinery tank that had contained gasoline was used for storing pentane. The tank overflowed when the level indicator said that it was only 85% full. The level indicator was a DP cell that measured weight of fluid. Can you explain to the operator what went wrong?

1.4 BASIS

Your objectives in studying this section are to be able to:

1. State the three questions useful in selecting a basis.
2. Apply the three questions to problems and select a suitable basis or sequences of bases.

Have you noted in previous examples that the word **basis** has appeared at the top of the computations? This concept of basis is vitally important both to your understanding of how to solve a problem and also to your solving it in the most expeditious manner. The basis is the reference chosen by you for the calculations you plan to make in any particular problem, and a proper choice of basis frequently makes the problem much easier to solve. The basis may be a period of time—for example, hours, or a given mass of material—such as 5 kg of CO_2 or some other convenient quantity. In selecting a sound basis (which in many problems is predetermined for you but in some problems is not so clear), you should ask yourself the following questions:

(a) What do I have to start with?
(b) What do I want to find out?
(c) What is the most convenient basis to use?

These questions and their answers will suggest suitable bases. Sometimes, when a number of bases seem appropriate, you may find it is best to use a unit basis of 1 or 100 of something, as, for example, kilograms, hours, moles, cubic feet. For liquids and solids when a weight analysis is used, a convenient basis is often 1 or 100 lb or kg; similarly, 1 or 100 moles is often a good choice for a gas. The reason for these choices is that the fraction or percent automatically equals the number of pounds, kilograms, or moles, respectively, and one step in the calculations is saved.

EXAMPLE 1.15 Choosing a Basis

Aromatic hydrocarbons form 15 to 30% of the components of leaded fuels and as much as 40% of nonleaded gasoline. The carbon/hydrogen ratio helps to characterize the fuel components. If a fuel is 80% C and 20% H by weight, what is the C/H ratio in moles?

Solution

If a basis of 100 lb or kg of oil is selected, percent = pounds or kilograms.

Basis: 100 kg of oil (or 100 lb of oil)

Component	kg = percent or lb = percent	Mol. wt.	kg mol or lb mol
C	80	12.0	6.67
H	20	1.008	19.84
Total	100		

Consequently, the C/H ratio in moles is

$$C/H = \frac{6.67}{19.84} = 0.336$$

EXAMPLE 1.16 Choosing a Basis

Most processes for producing high-energy-content gas or gasoline from coal include some type of gasification step to make hydrogen or synthesis gas. Pressure gasification is preferred because of its greater yield of methane and higher rate of gasification.

Given that a 50.0-kg test run of gas averages 10.0% H_2, 40.0% CH_4, 30.0% CO, and 20.0% CO_2, what is the average molecular weight of the gas?

Solution

The obvious basis is 50.0 kg of gas ("what I have to start with"), but a little reflection will show that such a basis is of no use. You cannot multiply *mole percent* of this gas times kg and expect the answer to mean anything. Thus the next step is to choose a "convenient basis," which is 100 kg mol or lb mol of gas, and proceed as follows:

Basis: 100 kg mol or lb mol of gas

Component	percent = kg mol or lb mol	Mol. wt.	kg or lb
CO_2	20.0	44.0	880
CO	30.0	28.0	840
CH_4	40.0	16.04	642
H_2	10.0	2.02	20
Total	100.0		2382

$$\text{average molecular weight} = \frac{2382 \text{ kg}}{100 \text{ kg mol}} = 23.8 \text{ kg/kg mol}$$

It is important that your basis be indicated near the beginning of the problem so that you will keep clearly in mind the real nature of your calculations and so that anyone checking your problem will be able to understand on what basis they are performed. If you change bases in the middle of the problem, a new basis should be indicated at that time. Many of the problems that we shall encounter will be solved on one basis and then at the end will be shifted to another basis to give the desired answer. The significance of this type of manipulation will become considerably clearer as you accumulate more experience.

EXAMPLE 1.17 Changing Bases

A sample of medium-grade bituminous coal analysis is as follows:

Component	Percent
S	2
N	1
O	6
Ash	11
Water	3

The residuum is C and H in the mole ratio H/C = 9. Calculate the weight fraction composition of the coal with the ash and the moisture omitted.

Solution

Take as a basis 100 kg of coal, for then percent = kilograms.

Basis: 100 kg of coal

The sum of the S + N + O + ash + water is

$$2 + 1 + 6 + 11 + 3 = 23 \text{ kg}$$

Hence the C + H must be 100 − 23 = 77 kg.

To determine the kilograms of C and H, we have to select a new basis. Is 77 kg satisfactory? No. Why? Because the H/C ratio is in terms of moles, not weight (mass). Pick instead:

Basis: 100 kg mol of C + H

Component	Mole fraction	kg mol	Mol. wt.	kg
H	$\frac{9}{1+9} = 0.90$	90	1.008	90.7
C	$\frac{1}{1+9} = 0.10$	10	12	120
Total	1.00	100		210.7

Finally, to return to the original basis, we have

$$\text{H: } \frac{77\text{kg}}{} \left| \frac{90.7 \text{ kg H}}{210.7 \text{ kg total}} \right. = 33.15 \text{ kg H}$$

$$\text{C: } \frac{77 \text{ kg}}{} \left| \frac{120 \text{ kg C}}{210.7 \text{ kg total}} \right. = 43.85 \text{ kg C}$$

and we can prepare a table summarizing the results.

Component	kg	Wt. fraction
C	43.85	0.51
H	33.15	0.39
S	2	0.02
N	1	0.01
O	6	0.07
Total	86.0	1.00

The ability to choose the basis that requires the fewest steps in solving a problem can only come with practice. You can quickly accumulate the necessary experience if, as you look at each problem illustrated in this text, you determine first in your own mind what the basis should be and then compare your choice with the selected basis. By this procedure you will quickly obtain the knack of choosing a sound basis.

Self-Assessment Test

1. What are the three questions you should ask yourself in selecting a basis?
2. What would be good initial bases to select in solving Problems 1.13, 1.18, 1.30, and 1.47?

1.5 TEMPERATURE

Your objectives in studying this section are to be able to:

1. Define temperature.
2. Explain the difference between absolute temperature and relative temperature.
3. Convert a temperature in any of the four scales (°C, K, °F, °R) to any of the others.
4. Convert an expression involving units of temperature and temperature difference to other units of temperature and temperature difference.
5. Know the reference points for the four temperature scales.

Our concept of temperature no doubt originated with our physical sense of hot and cold. Temperature can be rigorously defined once you have an acquaintence with thermodynamics, but here we simply paraphrase Maxwell's definition:

> *The temperature of a body is a measure of its thermal state considered in reference to its power to transfer heat to other bodies.*

Measurement of the thermal state can be accomplished through a wide variety of instruments, including

(a) A thermometer containing a liquid such as mercury or alcohol.
(b) The voltage produced by a junction of two dissimilar conductors that changes with temperature and is used as a measure of temperature (the *thermocouple*).
(c) The property of changing electrical resistance with temperatures gives us a device known as the *thermistor*.
(d) Two thin strips of metal bonded together at one end expand at different rates with change of temperature. These strips assist in the control of the flow of water in the radiator of an automobile and in the operation of air conditioners and heating systems.
(e) High temperatures can be measured by devices called *pyrometers,* which note the radiant energy leaving a hot body.

Figure 1.3 illustrates the appropriate ranges for various temperature-measuring devices.

Temperature is normally measured in degrees **Fahrenheit** or **Celsius** (centigrade). The common scientific scale is the *Celsius* scale,[5] where 0° is the ice point of water and 100° is the normal boiling point of water. In the early 1700s, Gabriel D. Fahrenheit (1686–1736), a glassblower by trade, was able to build mercury thermometers that gave temperature measurements in reasonable agreement with each other. The *Fahrenheit* scale is the one commonly used in everyday life in the United States. Its reference points are of more mysterious origin, but it is reported that the fixed starting point, or 0° on Fahrenheit's scale, was that produced by surrounding the bulb of the thermometer with a mixture of snow or ice and sal ammoniac; the highest temperature was that at which mercury began to boil. The distance between these two points was divided into 600 parts or degrees. By trial Fahrenheit found that the mercury stood at 32 of these divisions when water just began to freeze, the temperature of human blood was at 96 divisions, and the mercury was at 212 divisions when the thermometer was immersed in boiling water. In the SI system, temperature is measured in kelvin, a unit named after the famous Lord Kelvin (1824–1907). Note that in the SI system the degree symbol is suppressed (e.g., the boiling point of water is 373 K).

The Fahrenheit and Celsius scales are *relative* scales; that is, their zero points were arbitrarily fixed by their inventors. Quite often it is necessary to use *absolute*

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[5] As originally devised by Anders Celsius a Swedish astronomer (1701–1744) in 1742, the freezing point was designated as 100°. Officially, °C now stands for *degrees Celsius*.

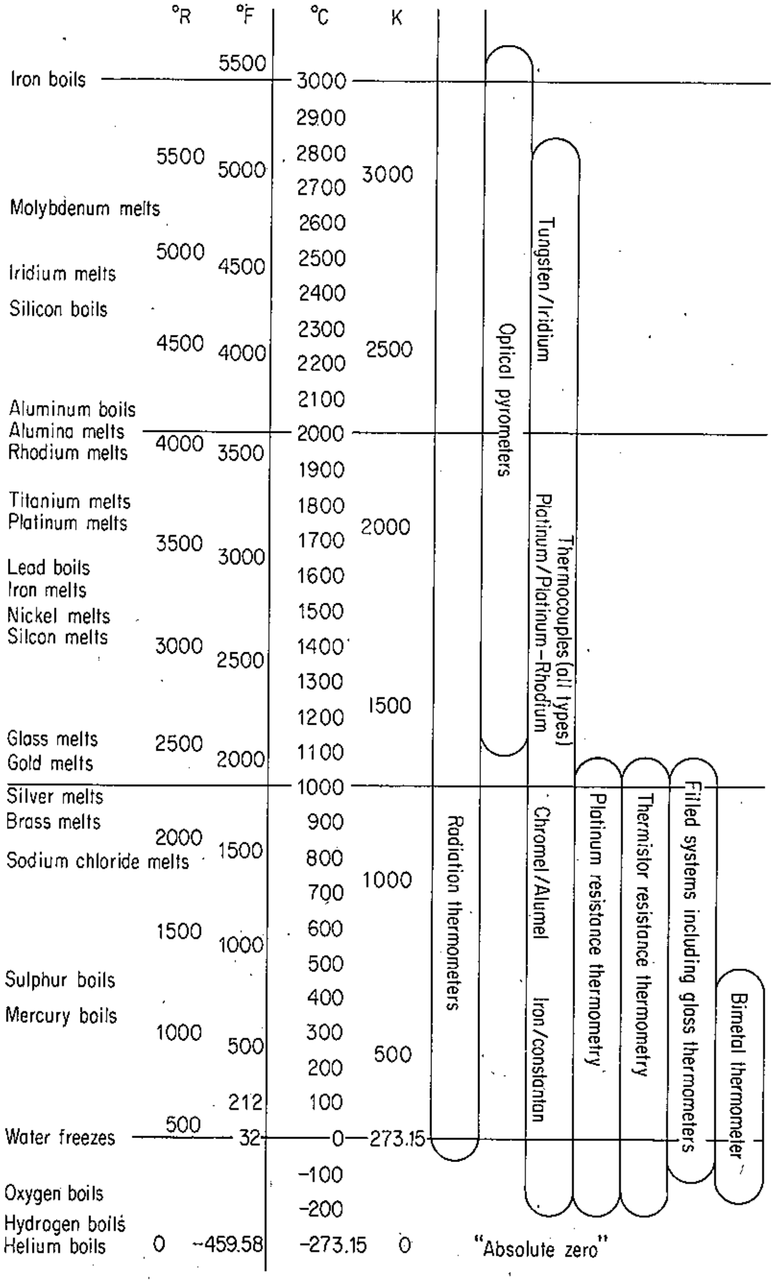


Figure 1.3 Temperature measuring instruments span the range from near absolute zero to beyond 3000 K. The chart indicates the preferred methods of thermal instrumentation for various temperature regions.

temperatures instead of relative temperatures. Absolute temperature scales have their zero point at the lowest possible temperature which we believe can exist. As you may know, this lowest temperature is related both to the ideal gas laws and to the laws of thermodynamics. The absolute scale which is based on degree units the size of those in the Celsius (centigrade) scale is called the *kelvin* scale; the absolute scale which corresponds to the Fahrenheit degree scale is called the *Rankine* scale in honor of W. J. M. Rankine (1820–1872), a Scottish engineer. The relations between relative temperature and absolute temperature are illustrated in Fig. 1.4. We shall round off absolute zero on the Rankine scale of −459.67° to −460°F; similarly, −273.15°C will be rounded off to −273°C. In Fig. 1.4 all the values of the temperatures have been rounded off, but more significant figures can be used. 0°C and its equivalents are known as *standard conditions of temperature.*

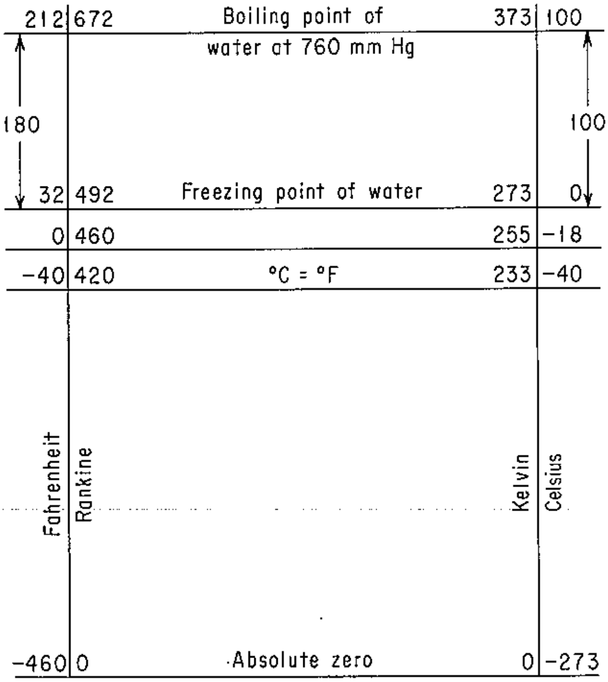


Figure 1.4 Temperature scales.

You should recognize that the unit degree (i.e., the unit temperature difference) on the kelvin–Celsius scale is not the same size as that on the Rankine-Fahrenheit scale. If we let Δ°F represent the unit temperature difference in the Fahrenheit scale, Δ°R be the unit temperature difference in the Rankine scale, and Δ°C and ΔK be the analogous units in the other two scales, you should be aware that

$$\Delta°\text{F} = \Delta°\text{R} \tag{1.13}$$

$$\Delta°\text{C} = \Delta\text{K} \tag{1.14}$$

Also, if you keep in mind that the Δ°C is larger than the Δ°F,

$$\frac{\Delta°\text{C}}{\Delta°\text{F}} = 1.8 \qquad \text{or} \qquad \Delta°\text{C} = 1.8\Delta°\text{F} \tag{1.15}$$

$$\frac{\Delta\text{K}}{\Delta°\text{R}} = 1.8 \qquad \text{or} \qquad \Delta\text{K} = 1.8\Delta°\text{R} \tag{1.16}$$

Unfortunately, the symbols Δ°C, Δ°F, ΔK, and Δ°R are not in standard usage because the Δ symbol becomes inconvenient, especially in typing. A few books try to maintain the difference between degrees of temperature (°C, °F, etc.) and the unit degree by assigning the unit degree the symbol C°, F°, and so on. But most journals and texts use the same symbol for the two different quantities. Consequently, **the proper meaning of the symbols °C, °F, K, and °R, as either the temperature or the unit temperature difference, must be interpreted from the context of the equation or sentence being examined.**

You should learn how to convert one temperature to another with ease. The relations between °R and °F and between K and °C are, respectively,

$$T_{°\text{R}} = T_{°\text{F}}\left(\frac{1\ \Delta°\text{R}}{1\ \Delta°\text{F}}\right) + 460 \tag{1.17}$$

$$T_{\text{K}} = T_{°\text{C}}\left(\frac{1\ \Delta\text{K}}{1\ \Delta°\text{C}}\right) + 273 \tag{1.18}$$

Because the relative temperature scales do not have a common zero at the same temperature, as can be seen from Fig. 1.4, the relation between °F and °C is

$$T_{°\text{F}} - 32 = T_{°\text{C}}\left(\frac{1.8\ \Delta°\text{F}}{1\ \Delta°\text{C}}\right) \tag{1.19}$$

After you have used Eqs. (1.17)–(1.19) a bit, they will become so familiar that temperature conversion will become an automatic reflex. During your "learning period," in case you forget them, just think of the appropriate scales side by side as in Fig. 1.4, and put down the values for the freezing and boiling points of water. Or, you can recover Eq. (1.19) by recognizing that the equation is linear (see Appendix M)

$$T_{°\text{F}} = b_0 + b_1 T_{°\text{C}} \tag{1.20}$$

Insert two known pairs of values of $T_{°\text{F}}$ and $T_{°\text{C}}$ in Eq. (1.20) and solve the resulting two equations together. For example, 0°C corresponds to 32°F, and 100°C corresponds to 212°F:

$$32 = b_0 + b_1(0) \tag{1.21a}$$

$$212 = b_0 + b_1(100) \tag{1.21b}$$

Solution of Eqs. (1.21a) and (1.21b) together yields

$$b_0 = 32.00 \qquad b_1 = 1.800$$

so that $T_{°\text{F}} = 32 + 1.8T_{°\text{C}}$.

EXAMPLE 1.18 Temperature Conversion

Convert 100°C to (a) K, (b) °F, and (c) °R.

Solution

(a)
$$(100 + 273)^\circ\text{C}\frac{1\ \Delta\text{K}}{1\ \Delta^\circ\text{C}} = 373\ \text{K}$$

or with suppression of the Δ symbol,

$$(100 + 273)^\circ\text{C}\frac{1\ \text{K}}{1^\circ\text{C}} = 373\ \text{K}$$

(b)
$$(100^\circ\text{C})\frac{1.8^\circ\text{F}}{1^\circ\text{C}} + 32^\circ\text{F} = 212^\circ\text{F}$$

(c)
$$(212 + 460)^\circ\text{F}\frac{1^\circ\text{R}}{1^\circ\text{F}} = 672^\circ\text{R}$$

or

$$(373\text{K})\frac{1.8^\circ\text{R}}{1\ \text{K}} = 672^\circ\text{R}$$

The suppression of the Δ symbol perhaps makes the temperature relations more familiar looking.

EXAMPLE 1.19 Temperature Conversion

The thermal conductivity of aluminum at 32°F is 117 Btu/(hr)(ft^2)(°F/ft). Find the equivalent value at 0°C in terms of Btu/(hr)(ft^2)(K/ft).

Solution

Since 32°F is identical to 0°C, the value is already at the proper temperature. The "°F" in the denominator of the thermal conductivity actually stands for Δ°F, so that the equivalent value is

$$\begin{array}{c|c|c} 117\ (\text{Btu})(\text{ft}) & 1.8\ \Delta^\circ\text{F} & 1\ \Delta^\circ\text{C} \\ \hline (\text{hr})(\text{ft}^2)(\Delta^\circ\text{F}) & 1\ \Delta^\circ\text{C} & 1\ \Delta\text{K} \end{array} = 211\ (\text{Btu})/(\text{hr})(\text{ft}^2)(\text{K}/\text{ft})$$

or with the Δ symbol suppressed,

$$\begin{array}{c|c|c} 117\ (\text{Btu})(\text{ft}) & 1.8^\circ\text{F} & 1^\circ\text{C} \\ \hline (\text{hr})(\text{ft}^2)(^\circ\text{F}) & 1^\circ\text{C} & 1\ \text{K} \end{array} = 211\ (\text{Btu})/(\text{hr})(\text{ft}^2)(\text{K}/\text{ft})$$

EXAMPLE 1.20 Temperature Conversion

The heat capacity of sulfuric acid in a handbook has the units cal/(g mol)(°C) and is given by the relation

$$\text{heat capacity} = 33.25 + 3.727 \times 10^{-2}T$$

where T is expressed in °C. Modify the formula so that the resulting expression gives units of Btu/(lb mol)(°R) and T is in °R.

Solution

The units of °C in the denominator of the heat capacity are Δ°C, whereas the units of T are °C. First, substitute the proper relation in the formula to convert T in °C to T in °R, and then convert the units in the resulting expression to those requested.

$$\text{heat capacity} = \left\{33.25 + 3.727 \times 10^{-2}\left[(T_{°\mathrm{R}} - 460 - 32)\frac{1}{1.8}\right]\right\}\frac{\text{cal}}{(\text{g mol})(°\text{C})}$$

$$\times \left.\frac{1\ \text{Btu}}{252\ \text{cal}}\right|\left.\frac{454\ \text{g mol}}{1\ \text{lb mol}}\right|\frac{1°\text{C}}{1.8°\text{R}} = 23.06 + 2.071 \times 10^{-2}\, T_{°\mathrm{R}}$$

Self-Assessment Test

1. What are the reference points of **(a)** the Celsius and **(b)** Fahrenheit scales?
2. How do you convert a *temperature difference*, Δ, from Fahrenheit to Celsius?
3. Is the unit temperature difference Δ°C a larger interval than Δ°F? Is 10°C higher than 10°F?
4. In Appendix E, the heat capacity of sulfur is $C_p = 15.2 + 2.68T$, where C_p is in J/(g mol)(K) and T is in K. Convert so that C_p is in cal/(g mol)(°F) with T in °F.
5. Complete the following table with the proper equivalent temperatures:

°C	°F	K	°R
−40.0			
	77.0		
		698	
			69.8

6. Suppose that you are given a tube partly filled with an unknown liquid and are asked to calibrate a scale on the tube in °C. How would you proceed?
7. Answer the following questions:
   (a) In relation to absolute zero, which is higher, 1°C, or 1°F?
   (b) In relation to 0°C, which is higher, 1°C, or 1°F?
   (c) Which is larger, 1Δ°C or 1Δ°F?

Thought Problem

1. In reading a report on the space shuttle you find the statement that "the maximum temperature on reentry is 1482.2°C. How many significant figures do you think are represented by this temperature?

1.6 PRESSURE

Your objectives in studying this section are to be able to:

1. Define pressure, atmospheric pressure, barometric pressure, standard pressure, and vacuum.
2. Explain the difference between absolute pressure and relative pressure (gauge pressure).
3. List four ways to measure pressure.
4. Convert from gauge pressure to absolute pressure and the reverse.
5. Convert a pressure measured in one set of units to another set, including kPa, mm Hg, in. H_2O, ft H_2O, atm, in. Hg, and psi using the standard atmosphere or density ratios of liquids.
6. Calculate the pressure from the density and height of a column of fluid.

$P = \frac{F}{A}$

Pressures, like temperatures, can be expressed by either absolute or relative scales. Pressure is defined as "normal force per unit area." Figure 1.5 shows a cylinder of water. Pressure is exerted on the top of the water by the atmosphere, and on the bottom of the cylinder by the water. If a hole were drilled in the side of the cylinder, you would have to exert a force against the water surface area by means of a plug to prevent the water from exiting the cylinder through the hole.

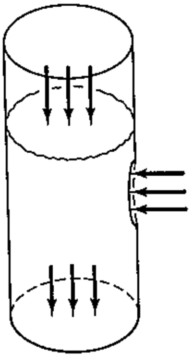


Figure 1.5 Pressure is the normal force per unit area. Arrows show the force exerted on the respective areas.

Figure 1.6 shows a column of mercury held in place by a sealing plate. Recall from physics that at the bottom of the column of mercury

$$p = \frac{F}{A} = \rho g h + p_0 \tag{1.22}$$

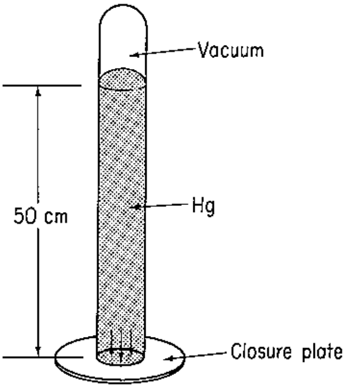


Figure 1.6 Pressure of a column of mercury.

where p = pressure at the bottom of the column of the fluid
F = force
A = area
ρ = density of the fluid
g = acceleration of gravity
h = height of the fluid column
p_0 = pressure at the top of the column of fluid

Suppose that the column of mercury has an area of 1 cm^2 and is 50 cm high. From Table D.1 we can find that the sp gr at 20°C and hence the density, essentially, of the Hg is 13.55 g/cm^3. Thus the force exerted on the 1-cm^2 section of that plate by the column of mercury is

$$F = \begin{array}{c|c|c|c|c|c|c} 13.55\ \text{g} & 980\ \text{cm} & 50\ \text{cm} & 1\ \text{cm}^2 & 1\ \text{kg} & 1\ \text{m} & 1\ \text{N} \\ \hline \text{cm}^3 & \text{s}^2 & & & 1000\ \text{g} & 100\ \text{cm} & \dfrac{1\ (\text{kg})(\text{m})}{\text{s}^2} \end{array}$$

$$= 6.64\ \text{N}$$

The pressure on the section of the plate covered by the mercury is

$$p = \frac{6.64\ \text{N}}{1\ \text{cm}^2} \left| \left(\frac{100\ \text{cm}}{1\ \text{m}}\right)^2 \right. = 6.64 \times 10^4 \frac{\text{N}}{\text{m}^2}$$

If we had started with units in the American engineering system, the pressure would be computed as

$$p = \begin{array}{c|c|c|c|c|c} 845.5\ \text{lb}_\text{m} & 32.2\ \text{ft} & 50\ \text{cm} & 1\ \text{in.} & 1\ \text{ft} & \\ \hline 1\ \text{ft}^3 & \text{s}^2 & & 2.54\ \text{cm} & 12\ \text{in.} & \dfrac{32.174(\text{ft})(\text{lb}_\text{m})}{(\text{s})^2(\text{lb}_\text{f})} \end{array}$$

$$= 1388 \frac{\text{lb}_\text{f}}{\text{ft}^2}$$

Sometimes in engineering practice, a liquid column is referred to as **head of liquid,** the head being the height of the column of liquid. **A pressure can be interpreted as**

the head, h, of a hypothetic column of liquid, so that the pressure at the base of a column of liquid would be calculated, say in inches of mercury, as

$$p \text{ (in inches of Hg)} = P_0 \text{ (in inches of Hg)} + h \text{ (in inches of Hg)} \qquad (1.23)$$

where p_0 is the gas pressure on the top of the column of mercury. Water, oil, or any other liquid could be substituted for Hg in Eq. (1.23). For example, suppose that you measure the pressure in a tank of water 2 ft down from the surface as 404.92 in. H_2O. What is the pressure 4 ft down from the surface? You can use Eq. (1.22) to calculate the pressure, but it is just as easy to use Eq. (1.23).

$$p = 404.92 \text{ in. } H_2O + 2 \text{ ft } (12 \text{ in./ft}) = 428.92 \text{ in. } H_2O \qquad (1.24)$$

Whether relative or absolute pressure is measured in a pressure-measuring device depends on the nature of the instrument used to make the measurements. For example, an open-end manometer (Fig. 1.7a) would measure a **relative pressure,** since the reference for the open end is the pressure of the atmosphere at the open end of the manometer. On the other hand, closing off the end of the manometer (Fig. 1.7b) and creating a vacuum in the end results in a measurement against a complete vacuum, or against "no pressure." This measurement is called **absolute pressure.** Since absolute pressure is based on a complete vacuum, a fixed reference point which is unchanged regardless of location or temperature or weather or other factors, absolute pressure then establishes a precise, invariable value which can be readily identified. Thus, the zero point for an absolute pressure scale corresponds to a perfect vacuum, whereas the zero point for a relative pressure scale usually corresponds to the pressure of the air which surrounds us at all times, and as you know, varies slightly.

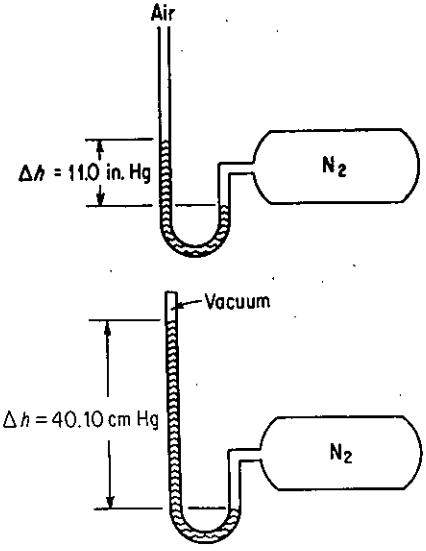


Figure 1.7 (a) Open-end manometer showing a pressure above atmospheric pressure. **(b)** Absolute pressure manometer.

If a mercury reading is set up as illustrated in Fig. 1.8, with the dish open to the atmosphere, the device is called a *barometer* and the reading of atmospheric pressure is termed **barometric pressure.**

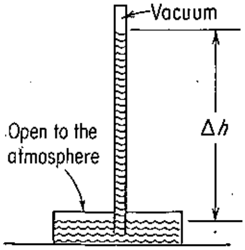


Figure 1.8 A barometer.

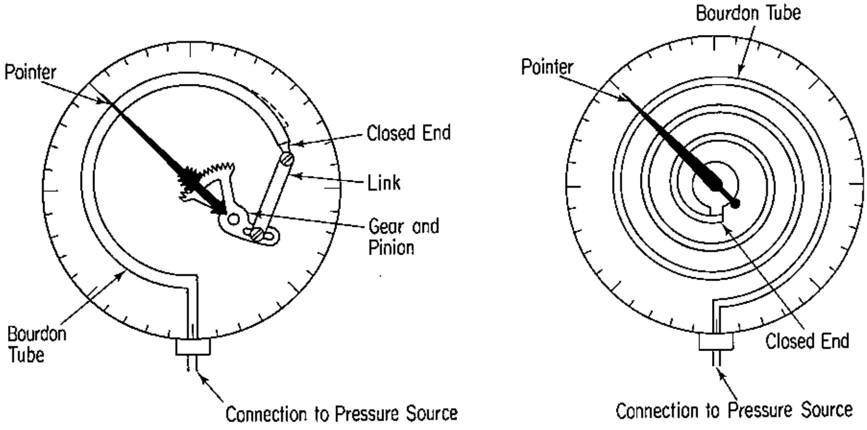
An understanding of the principle upon which a manometer operates will aid you in recognizing the nature of the pressure measurement taken from it. As shown in Fig. 1.7a for an open-end U-tube manometer, if the pressure measured for the N_2 is greater than atmospheric, the liquid is forced downward in the leg to which the pressure source is connected and upward in the open leg. Eventually, a point of hydrostatic balance is reached in which the manometer fluid stabilizes. The pressure exerted at the bottom of the U-tube in the part of the tube open to the atmosphere exactly balances the pressure exerted at the bottom of the U-tube in the part of the tube connected to the tank of N_2. Furthermore, the difference between the height of fluid in the leg open to the atmosphere and the height of fluid in the leg attached to the tank is exactly equal to the difference between the pressure in the tank and atmospheric pressure (expressed in units of fluid column length). If some degree of vacuum instead of a high pressure existed in a tank in an arrangement similar to that shown in Fig. 1.7a, the fluid column would rise on the vacuum side. Again, the difference in pressure between the pressure source in the tank and atmospheric pressure would be measured by the difference in the height of the two legs of fluid. Water and mercury are commonly used indicating fluids for manometers; the readings thus can be expressed in "inches or cm of water," "inches or cm of mercury," "mm of fluid flowing," and so on. (In ordinary engineering calculations we ignore the vapor pressure of mercury and minor changes in the density of mercury due to temperature changes in making pressure measurements.)

Another type of common measuring device is the visual *Bourdon gauge* (Fig. 1.9), which normally (but not always) reads zero pressure when open to the atmosphere. The pressure-sensing device in the Bourdon gauge is a thin metal tube with an elliptical cross section closed at one end which has been bent into an arc. As the pressure increases at the open end of the tube, it tries to straighten out, and the movement of the tube is converted into a dial movement by gears and levers. Figure 1.9 also illustrates a diaphragm capsule gauge. Figure 1.10 indicates the pressure ranges for the various pressure-measuring devices.

Pressure scales may be temporarily somewhat more confusing than temperature scales since **the reference point or zero point for the relative pressure scales is not constant,** whereas in the temperature scales the boiling point or the freezing point of water is always a fixed value. However, you will become accustomed to this feature with practice.

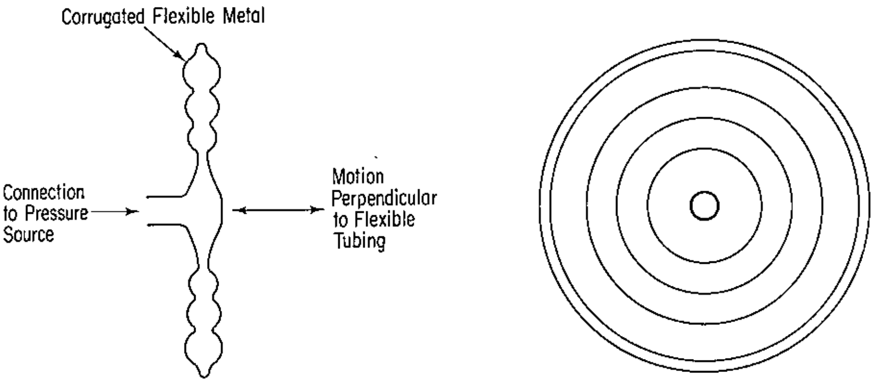
The relationship between relative and absolute pressure is illustrated in Figs. 1.11 and 1.12 and is given by the following expression:

$$\textbf{gauge pressure + barometer pressure = absolute pressure} \qquad (1.25)$$



(a) "C" Bourdon

(b) Spiral Bourdon



(c) Convex Diaphragm Capsule

Figure 1.9 Bourdon and diaphragm pressure-measuring devices.

Equation (1.25) can be used only with consistent units. Note that you must add the atmospheric pressure (i.e., the barometric pressure) to the gauge, or relative pressure (or manometer reading if open on one end), in order to get the absolute pressure.

Another term applied in measuring pressure which is illustrated in Figs. 1.11 and 1.12 is **vacuum.** In effect, when you measure pressure as "inches of mercury vacuum," you reverse the usual direction of measurement and measure from the barometric pressure down to zero absolute pressure, in which case a perfect vacuum would be the highest vacuum that you could achieve. The vacuum system of measurement of pressure is commonly used in apparatus which operate at pressures less than atmospheric—such as a vacuum evaporator or vacuum filter. A pressure that is only slightly below barometric pressure may sometimes be expressed as a "draft"

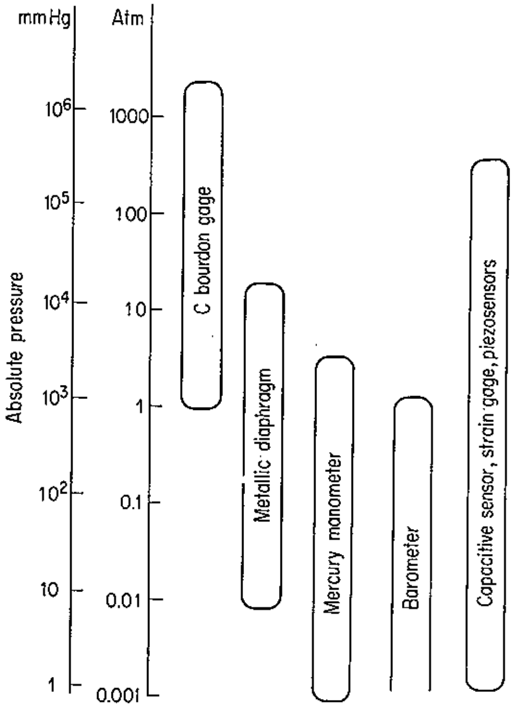


Figure 1.10 Ranges of application for pressure-measuring devices.

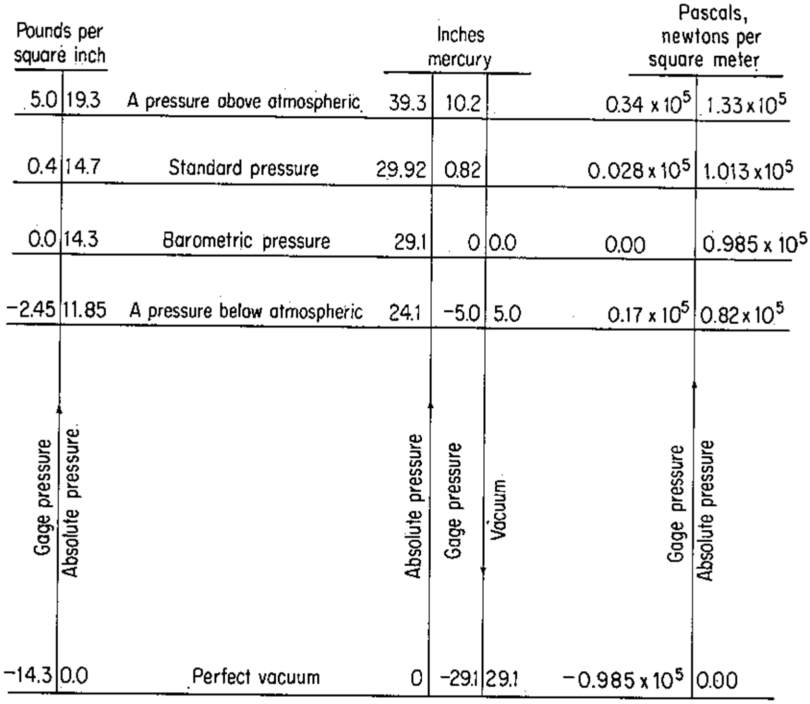


Figure 1.11 Pressure comparisons when barometer reading is 29.1 in Hg.

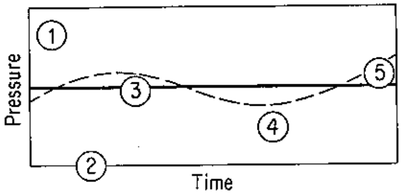


Figure 1.12 Pressure terminology. The standard atmosphere is shown by the heavy horizontal line. The dashed line illustrates the atmospheric (barometric) pressure, which changes from time to time. Point ① in the figure is a pressure of 19.3 psi referred to a complete vacuum or 5 psi referred to the barometric pressure: ② is the complete vacuum, ③ represents the standard atmosphere, and ④ illustrates a negative relative pressure or a pressure less than atmospheric. This type of measurement is described in the text as a vacuum type of measurement. Point ⑤ also indicates a vacuum measurement, but one that is equivalent to an absolute pressure above the standard atmosphere.

(which is identical to the vacuum system) in inches of water, as, for example, in the air supply to a furnace or a water cooling tower.

As to the units of pressure, Fig. 1.11 shows three common systems: pounds per square inch (psi), inches of mercury (in. Hg), and pascals. Pounds per square inch absolute is normally abbreviated "psia," and "psig" stands for "pounds per square inch gauge." For other units, be certain to carefully specify whether they are gauge or absolute; for example, state "300 kPa absolute" or "12 cm Hg gauge." Figure 1.11 compares the relative and absolute pressure scales in terms of the three systems of measurement when the barometric pressure is 29.1 in Hg (14.3 psia, 0.985×10^5 pascal). Other systems of expressing pressure exist; in fact, you will discover that there are as many different units of pressure as there are means of measuring pressure. Some of the other most frequently used systems are

- **(a)** Millimeters of mercury (mm Hg)
- **(b)** Feet of water (ft H_2O)
- **(c)** Atmospheres (atm)
- **(d)** Bars (bar): 100 kPa = 1 bar
- **(e)** Kilograms (force) per square centimeter (kg_f/cm^2)—a common but theoretically prohibited measure[6]

To sum up our discussion of pressure and its measurement, you should now be acquainted with:

- **(a)** *Atmospheric pressure*—the pressure of the air and the atmosphere surrounding us which changes from day to day

---

[6] Although the units of pressure in the SI system are pascal, you frequently find in common usage pressures denoted in the units of kg/cm^2 (i.e., kg_f/cm^2), units that have to be multiplied by

$$9.80 \times 10^4 \left(\frac{(kg_m)(m)}{(kg_f)(s^2)}\right)\left(\frac{cm^2}{m^2}\right) \quad \text{to get pascal.}$$

(b) *Barometric pressure*—the same as atmospheric pressure, called "barometric pressure" because a barometer is used to measure atmospheric pressure

(c) *Absolute pressure*—a measure of pressure referred to a complete vacuum, or zero pressure

(d) *Gauge pressure*—pressure expressed as a quantity measured upward from atmospheric pressure (or some other reference pressure)

(e) *Vacuum*—a method of expressing pressure measured downward from atmospheric pressure (or some other reference pressure)

You definitely must not confuse the standard atmosphere with atmospheric pressure. The *standard atmosphere* is defined as the pressure (in a standard gravitational field) equivalent to 1 atm or 760 mm Hg at 0°C or other equivalent value, whereas atmospheric pressure is a variable and must be obtained from a barometer each time you need it. The standard atmosphere may not equal the barametric pressure in any part of the world except perhaps at sea level on certain days, but it is extremely useful in converting from one system of pressure measurement to another (as well as being useful in several other ways to be considered later).

Expressed in various units, the *standard atmosphere* is equal to

1.000	atmospheres (atm)
33.91	feet of water (ft H_2O)
14.7	(14.696, more exactly) pounds per square inch absolute (psia)
29.92	(29.921, more exactly) inches of mercury (in. Hg)
760.0	millimeters of mercury (mm Hg)
1.013×10^5	pascal (Pa) or newtons per square meter (N/m^2); or 101.3 kPa

You can convert from one set of pressure measurements to another by using pairs of standard atmospheres as conversion factors, as shown in the examples below. If pressures are measured by a height of a column of one liquid A, and p_0 is the same for both columns, you can convert the pressure to the height of another column of liquid B by the use of Eq. (1.22).

$$p_0 + \rho_A g h_A = p_0 + \rho_B g h_B$$

or

$$\frac{h_A}{h_B} = \frac{\rho_B}{\rho_A}$$

How can you arrange to get the same p_0 for each column? Will leaving the upper end of each of the columns open to the atmosphere accomplish this objective?

EXAMPLE 1.21 Pressure Conversion

Convert 35 psia to inches of mercury.

Solution

Use the ratio of 14.7 psia to 29.92 in. Hg, an identity, to carry out the conversion.

Basis: 35 psia

$$\begin{array}{c|c} 35\ \text{psia} & 29.92\ \text{in. Hg} \\ \hline & \underbrace{14.7\ \text{psia}}_{\textbf{an identity}} \end{array} = 71.24\ \text{in. Hg}$$

EXAMPLE 1.22 Pressure Conversion

The density of the atmosphere decreases with increasing altitude. When the pressure is 340 mm Hg, how many inches of water is it? How many kilopascal?

Solution

Basis: 340 mm Hg

$$\begin{array}{c|c|c} 340\ \text{mm Hg} & 33.91\ \text{ft}\ H_2O & 12\ \text{in.} \\ \hline & 760\ \text{mm Hg} & 1\ \text{ft} \end{array} = 182\ \text{in.}\ H_2O$$

$$\begin{array}{c|c} 340\ \text{mm Hg} & 101.3\ \text{kPa} \\ \hline & 760.0\ \text{mm Hg} \end{array} = 45.3\ \text{kPa}$$

EXAMPLE 1.23 Pressure Conversion

The pressure gauge on a tank of CO_2 used to fill soda-water bottles reads 51.0 psi. At the same time the barometer reads 28.0 in. Hg. What is the absolute pressure in the tank in psia? See Fig. E1.23.

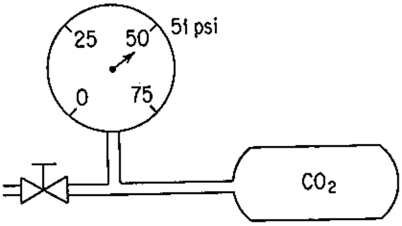


Figure E1.23

Solution

The pressure gauge is reading psig, not psia. From Eq. (1.25) the absolute pressure is the sum of the gauge pressure and the atmospheric (barometric) pressure expressed in the same units. We will change the atmospheric pressure to psia.

Basis: Barometric pressure = 28.0 in. Hg

$$\text{atmospheric pressure} = \begin{array}{c|c} 28.0\ \text{in. Hg} & 14.7\ \text{psia} \\ \hline & 29.92\ \text{in. Hg} \end{array} = 13.76\ \text{psia}$$

(*Note:* Atmospheric pressure does not equal 1 standard atm.) The absolute pressure in the tank is

$$51.0 + 13.76 = 64.8 \text{ psia}$$

In some instances the fluids in the legs of the manometer are not the same. Examine Fig. 1.13. When the columns of fluids are at equilibrium (it may take some time!) the relation between p_1, p_2 and the heights of the various columns of fluid is

$$p_1 + \rho_1 d_1 g = p_2 + \rho_2 g d_2 + \rho_3 g d_3 \qquad (1.26a)$$

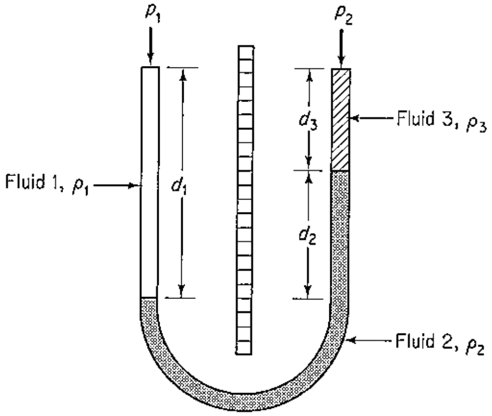


Figure 1.13 Manometer with three fluids.

Can you show for the case in which $\rho_1 = \rho_3 = \rho$ that the manometer expression reduces to

$$p_1 - p_2 = (\rho_2 - \rho)gd_2 \qquad (1.26b)$$

Finally, suppose that fluids 1 and 3 are gases. Can you ignore the gas density ρ relative to the manometer fluid density? For what types of fluids?

EXAMPLE 1.24 Pressure Conversion

Air is flowing through a duct under a draft of 4.0 cm H_2O. The barometer indicates that the atmospheric pressure is 730 mm Hg. What is the absolute pressure of the gas in inches of mercury? See Fig. E1.24.

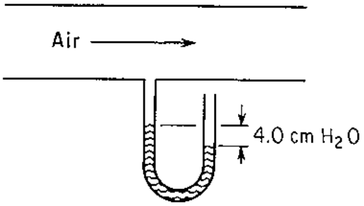


Figure E1.24

Solution

We can ignore the gas density above the manometer fluid. In the calculations we have to employ consistent units, and it appears in this case that the most convenient units are those of inches of mercury.

Basis: 730 mm Hg

$$\text{atmospheric pressure} = \begin{array}{c|c} 730 \text{ mm Hg} & 29.92 \text{ in. Hg} \\ \hline & 760 \text{ mm Hg} \end{array} = 28.7 \text{ in. Hg}$$

Basis: 4.0 cm H_2O draft (under atmospheric)

$$\begin{array}{c|c|c|c} 4.0 \text{ cm } H_2O & 1 \text{ in} & 1 \text{ ft} & 29.92 \text{ in. Hg} \\ \hline & 2.54 \text{ cm} & 12 \text{ in.} & 33.91 \text{ ft } H_2O \end{array} = 0.12 \text{ in. Hg}$$

What is another way to make the conversion?

Since the reading is 4.0 cm H_2O draft (under atmospheric), the absolute reading in uniform units is

$$28.7 - 0.12 = 28.6 \text{ in. Hg absolute}$$

EXAMPLE 1.25 Vacuum Pressure Reading

Small animals such as mice can live at reduced air pressures down to 20 kPa (although not comfortably). In a test a mercury manometer attached to a tank as shown in Fig. E1.25 reads 64.5 cm Hg and the barometer reads 100 kPa. Will the mice survive?

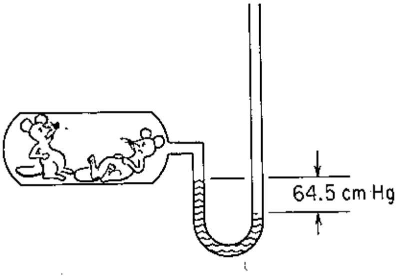


Figure E1.25

Solution

Basis: 64.5 cm Hg below atmospheric

We ignore any temperature corrections to convert the mercury density and also ignore the gas density above the manometer fluid. Then, since the vacuum reading on the tank is 64.5 cm Hg below atmospheric, the absolute pressure in the tank is

$$100 \text{ kPa} - \begin{array}{c|c} 64.5 \text{ cm Hg} & 101.3 \text{ kPa} \\ \hline & 76.0 \text{ cm Hg} \end{array} = 100 - 86 = 14 \text{ kPa absolute}$$

The mice probably will not survive.

EXAMPLE 1.26 Calculation of Pressure Difference

In measuring the flow of fluids in a pipeline, a differential manometer, as shown in Fig. E1.26, can be used to determine the pressure difference across an orifice plate. The flow rate can be calibrated with the observed pressure drop. Calculate the pressure drop $p_1 - p_2$ in pascal.

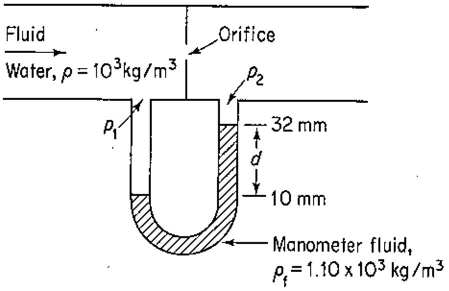


Figure E1.26

Solution

In this problem we cannot ignore the water density above the manometer fluid. Apply Eq. (1.26b), as the densities of the fluids above the manometer fluid are the same.

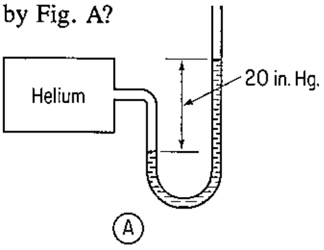
$$p_1 - p_2 = (\rho_f - \rho)gd$$

$$= \begin{array}{l|l|l|l|l} \frac{(1.10 - 1.00)10^3\ \text{kg}}{\text{m}^3} & \frac{9.807\ \text{m}}{\text{s}^2} & (22)(10^{-3})\text{m} & \frac{1\ (\text{N})(\text{s}^2)}{(\text{kg})(\text{m})} & \frac{1\ (\text{Pa})(\text{m}^2)}{1\ (\text{N})} \end{array}$$

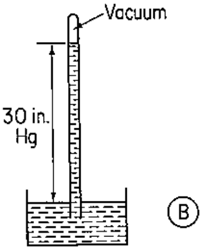
$$= 21.6\ \text{Pa}$$

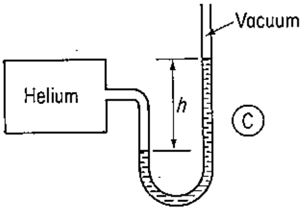
Self-Assessment Test

1. Write down the equation to convert gauge pressure to absolute pressure.
2. List the values and units of the standard atmosphere for six different methods of expressing pressure.
3. List the equation to convert vacuum pressure to absolute pressure.
4. Convert a pressure of 800 mm Hg to the following units:
   (a) psia (b) kPa
   (c) atm (d) ft H_2O
5. Your textbook lists five types of pressures: atmospheric pressure, barometric pressure, gauge pressure, absolute pressure, and vacuum pressure.
   (a) What kind of pressure is measured by Fig. A?



(b) What kind of pressure is measured by Fig. B?
(c) What would be the reading in Fig. C assuming that the pressure and temperature inside and outside the helium tank are the same as in parts (a) and (b)?





6. An evaporator shows a reading of 40 kPa vacuum. What is the absolute pressure in the evaporator in kilopascal?
7. Answer the following questions true (T) or false (F).
   (a) Air flows in a pipeline, and a manometer containing Hg that is set up as illustrated in Fig. E1.26 shows a differential pressure of 14.2 mm Hg. You can ignore the effect of the density of the air on the height of the columns of mercury.
   (b) Lowering the He pressure 10% in Fig. A of question 5 will not cause the length of the column of Hg to decrease by 10%.

Thought Problems

1. A magic trick is to fill a glass with water, place a piece of paper over the top of the glass to cover the glass completely, and hold the paper in place as the glass in inverted 180°. On the release of your support of the paper, no water runs out! Many books state that the glass should be completely filled with water with no air bubbles present. Then the outside air pressure is said to oppose the weight of the water in the inverted glass. However, the experiment works just as well with a half-filled glass. The trick does not work if a glass plate is substituted for the piece of paper. Can you explain why?
2. A large storage tank was half full of a flammable liquid quite soluble in water. The tank needed maintenance on the roof. Since welding was involved, the foreman attached to the vent pipe on the top of the tank (in which there was a flame arrestor) a flexible hose and inserted the end of the hose into the bottom of a drum of water sitting on the ground to pick up any exhaust vapors. When the tank was emptied, the water rose up in the hose, and the tank walls collapsed inward.

   What went wrong in this incident?

1.7 PHYSICAL AND CHEMICAL PROPERTIES OF COMPOUNDS AND MIXTURES

Your objectives in studying this section are to be able to:

1. Cite five sources of physical property data.
2. Go to the library and locate the five sources of data.

3. Retrieve data from the five sources to use in your calculations, employing the indexes and tables of contents.

Accurate values of physical properties are needed in almost all phases of chemical engineering design and analysis. Two ways to obtain data for the physical properties of components are: (a) by experimental measurement and/or (b) by estimation. As far as the cost of obtaining data is concerned, a substantial difference exists between the two approaches. To produce critically evaluated estimates, the time required is seldom more than a few hours, in comparison with several months needed for the experimental work. If the data you want are based on valid estimation and correlation techniques, you can bypass the expense and the waiting time required for experimental measurements.

Many of the materials we talk about and use every day are not pure compounds, but nevertheless you can obtain information about the properties of such materials. Data on materials such as coal, coke, petroleum products, and natural gas—which are the main sources of energy in this country—are available in reference books and handbooks. Some typical examples of analyses are shown in Tables 1.6 to 1.9. In the back of this book you will discover a number of appendices from which you can retrieve data necessary to solve most (but not all) of the problems at the end of the chapters. Scan through the appendices now. When you need to look

TABLE 1.6 Refinery Biological Treatment Unit Feed Characteristics

	Ranges reported*
Chlorides (mg/L)	200–960
COD (mg/L)	140–640
BOD_5 (mg/L)	97–280
Suspended solids (mg/L)	80–450
Alkalinity (mg/L as $CaCO_3$)	77–210
Temperature, (°F)	69–100
Ammonia, nitrogen (mg/L)	56–120
Oil (mg/L)	23–130
Phosphate (mg/L)	20–97
Phenolics (mg/L)	7.6–61
pH	7.1–9.5
Sulfides (mg/L)	1.3–38
Chromium (mg/L)	0.3–0.7

*Values are the averages of the minima and maxima reported by 12 refineries treating total effluent. Individual plants have reported data well outside many of these ranges.

SOURCE: *Manual on Disposal of Refinery Wastes,* American Petroleum Institute, New York, 1969, pp. 2–4.

TABLE 1.7 Typical Dry Gas Analyses

Type	Analysis (vol. %—excluding water vapor)									
	CO_2	O_2	N_2	CO	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}+
Natural gas	6.5					77.5	16.0			
Natural gas, dry*	0.2		0.6			99.2				
Natural gas, wet*	1.1					87.0	4.1	2.6	2.0	3.4
Natural gas, sour†	(H_2S 6.4)					58.7	16.5	9.9	5.0	3.5
Butane							2.0	3.5	75.4 *n*-butane 18.1 isobutane	
									Illuminants	
Reformed refinery oil	2.3	0.7	4.9	20.8	49.8	12.3	5.5	5.5	3.7	
Coal gas, by-product	2.1	0.4	4.4	13.5	51.9	24.3			3.4	
Producer gas	4.5	0.6	50.9	27.0	14.0	3.0				
Blast furnace gas	5.4	0.7	8.3	37.0	47.3	1.3				
Sewage gas	22.0		6.0		2.0	68.0				

*Dry gas contains much less propane (C_3H_8) and higher hydrocarbons than wet gas does.

†*Sour* implies that the gas contains significant amounts of hydrogen sulfide.

SOURCE: *Fuel Flue Gases*, American Gas Association, New York, 1941, p. 20.

TABLE 1.8 Ultimate Analysis of Petroleum Crude

			Weight %				
Type	Sp Gr	At °C	C	H	N	O	S
Pennsylvania	0.862	15	85.5	14.2			
Humbolt, Kan.	0.921		85.6	12.4			0.37
Beaumont, Tex.	0.91		85.7	11.0	2.61		0.70
Mexico	0.97	15	83.0	11.0	1.7		
Baku USSR	0.897		86.5	12.0		1.5	

SOURCE: Data from W.L. Nelson, *Petroleum Refinery Engineering*, 4th ed., McGraw-Hill, New York, 1958.

TABLE 1.9 Chemical Analyses of Various Wastes

Material	Raw paper	Charred paper	Tire rubber	Dry sewage sludge	Charred sewage sludge	Charred animal manure	Garbage composite *A*	Garbage composite *B*
Moisture	3.8	0.8	0.5	13.6	1.2	0.0	3.4	12.3
Hydrogen*	6.9	3.1	4.3	6.7	1.4	5.4	6.6	7.0
Carbon	45.8	84.9	86.5	28.7	48.6	41.2	57.3	44.4
Nitrogen	—	0.1	—	2.6	3.7	1.5	0.5	0.4
Oxygen*	46.8	8.5	4.6	26.5	—	26.0	22.1	42.1
Sulfur	0.1	0.1	1.2	0.6	—	0.4	0.4	0.2
Ash	0.4	2.5	3.4	34.9	45.7	25.5	10.2	5.9

* The hydrogen and oxygen values reflect that due to both the presence of water and that contained within the moisture-free material.

for additional data, consult some of the appropriate references listed in Tables 1.10 and 1.11.

In the next decade, we should expect two new modes of information retrieval to be implemented and available for an individual. With the widespread introduction of modems and communication software, potential users will be able to deal directly with data base vendors, both profit and nonprofit, at reasonable cost via local phone

TABLE 1.10 Sources of Physical Property Data

American Chemical Society, *Physical Properties of Chemical Compounds*, Vol. 22, ACS, Washington, D.C., 1959.

American Chemical Society, *Chemical Abstracts Service*, ACS, Washington, D.C. (Continuing printed, microform, and on-line electronic information service with over 12 million abstracts.)

American Gas Association, *Fuel Flue Gases*, AGA, New York, 1941.

American Petroleum Institute, *Technical Data Book—Petroleum Refining*, New York, 1970.

Aylward, G. H., and T. J. V. Findlay, *SI Chemical Data*, 2nd ed., Wiley, New York, 1976.

TABLE 1.10 *(continued)*

Chemsoft Inc., *Chemical Compounds Data Bank,* Gulf Publishing Company, Houston, 1987. (500 compounds on disc.)

Chen, C.-C. *Scientific and Technical Information Sources,* 2nd ed., MIT Press, Cambridge, Mass. 1987. (Reference book for publications.)

Daubert, T. E., and R. P. Danner, *Data Compilation—Tables of Properties of Pure Compounds,* Amercian Institute of Chemical Engineers, New York, 1985. (Properties and prediction equations for 1100 compounds; available as printed book and magnetic tape.)

Dechema, *Chemistry Data Series,* Deutsche Gesellschaft für Chemisches Apparatewesen e.v., Frankfurt, West Germany, (Continuing series on physical and thermodynamic properties.) Also an on-line data base; see National Technical Information Service document BMFT-FB-ID-80-006.

Engineering Sciences Data Unit Ltd., *International Data Series,* London. (Continuing series of data and equations.)

Gallant, R. W., *Physical Proerties of Hydrocarbons,* Gulf Publishing Company, Houston, 1968.

Handbook of Physics and Chemistry, CRC Press, Boca Raton, Fl., annual editions.

Hilsenrath, J., *Summary of On-Line or Interactive Physico-Chemical Numerical Data Systems,* National Bureau of Standards, Washington, D.C., 1980. (Description of 53 public-access data bases.)

Horvath, A. L., and E. Arnold, *Physical Properties of Inorganic Compounds—SI Units,* Crane, Russak, New York, 1975.

Institution of Chemical Engineers, *PPDS,* (Continuing data base of 32 properties of over 400 compounds.)

Jankowski, D. A., and T. B. Selover, *Chemical Engineering Data Sources,* American Institute of Chemical Engineers, New York, 1985.

Lange's Handbook of Chemistry and Physics, McGraw-Hill, New York; issued periodically.

Lin, C. T., et al., "Data Bank for Synthetic Fuels"; *Hydrocarbon Process.* p. 229 (May 1980).

Maizell, R., *How to Find Chemical Information,* 2nd ed., Wiley, New York, 1986.

Mann, D. B., D. E. Diller, and N. A. Olien, eds., *LNG Materials and Fluids,* National Bureau of Standards, Washington, D.C., 1977–80.

McCail, W. D., *Properties of Petroleum Fluids,* Petroleum Publishing Company, Tulsa, Okla., 1973.

Natural Gas Processors Suppliers Association, *Engineering Data Book,* Tulsa, Okla. (Continuing editions.)

Perry, R. H. and D. Green, *Chemical Engineers' Handbook,* 6th ed., McGraw-Hill, New York, 1980.

Reid, R. C., J. M. Prausnitz, and B. D. Poling, *The Properties of Gases and Liquids,* 4th ed., McGraw-Hill, New York, 1987.

U.S. Department of Energy, *Coal Conversion Technical Data Book,* Available from Superintendent of Documents, Washington, D.C., 1978.

Weast, R. C., *CRC Handbook of Chemistry and Physics* CRC Press, Boca Raton, Florida; issued annually.

Yaws, C. L. *Physical Properties, a Guide to the Physical, Thermodynamic and Transport Property Data of Industrially-Important Chemical Compounds,* McGraw-Hill, New York, 1987.

TABLE 1.11 Professional Journals

- Archival journals
  - AIChE Journal
  - Angewandte Chemie
  - Canadian Journal of Chemical Engineering
  - Chemical Engineering Communications
  - Chemical Engineering Fundamentals
  - Chemical Engineering Journal (Lausanne)
  - Chemical Engineering Research and Design
  - Chemical Engineering Science
  - Chemical Reviews
  - CODATA Bulletin
  - Journal of Chemical and Engineering Data
  - Journal of Chemical Engineering of Japan
  - Journal of Chemical Technology and Biotechnology
  - Journal of the American Chemical Society
  - Journal of the Chinese Institute of Chemical Engineers
- Other journals and magazines
  - Chemical Engineering
  - Chemical Engineering Progress
  - Chemical Engineer (London)
  - Chemical Processing
  - Chemical Technology
  - Chemical Technology Review
  - Chemie-Ingenieur-Technik
  - Chemistry and Industry (London)
  - German Chemical Engineering
  - International Chemical Engineering

calls. The other mode is information retrieval from compact read-only laser disks, which can store the order of 300,000 printed pages of material. Coupled with a microcomputer, a user will be able to search for and locate reliable information distributed by specialized professional organizations on a myriad of subjects, such as refrigerants, propellants, solvents, drugs, insecticides, and so on.

Self-Assessment Test

1. What are five sources of data on physical properties from reference books? What are two data banks that provide information on physical properties?
2. In what reference book might you find data on:
   - **(a)** Boiling point of inorganic liquids?
   - **(b)** Gas compositions for refinery gases?
   - **(c)** Vapor pressures of organic liquids?
   - **(d)** Chemical formula and properties of protocatechuic acid (3−, 4−)?
3. List the page numbers on which the items described in question 2 can be found in the reference you select.

Library Problem

1. Prepare a short description (about five lines) for numbers ____________ of the following terms. You may include some sketches if you want. List the name of the author, book, and publisher and also the call number of the books that you use to prepare your report.
   (1) Furnace
   (2) Boiler
   (3) Heat exchanger
   (4) Distillation column
   (5) Absorption tower
   (6) Adsorption
   (7) Liquid-liquid extraction
   (8) Leaching process
   (9) Evaporator
   (10) Chemical reactor

1.8 TECHNIQUES OF PROBLEM SOLVING

Your objectives in studying this section are to be able to:

1. Memorize the eight components of effective problem solving.
2. Apply the components to all types of problems.

Weiler's Law: Nothing is impossible for the person who doesn't have to do it.

Howe's Law: Every person has a scheme which will not work.

The 90/90 Law: The first 10% of the task takes 90% of the time. The remaining 90% takes the remaining 10%.

Gordon's Law: If a project is not worth doing, it's not worth doing well.

Slack's Law: The least you will settle for is the most you can expect to get.

O'Toole's Commentary: Murphy was an optimist.[7]

One of the main objectives of this book is to enhance your problem-solving skills. If you can form good habits of problem solving early in your career, you will save considerable time and avoid many frustrations in all aspects of your work, in and out of school. Being able to solve material and energy balances means that in addition to learning basic principles, formulas, laws, and so on, *you must be able to apply them.* Routine substitution of data into an appropriate equation will by no

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[7] Arthur Bloch, *Murphy's Law and Other Reasons Why Things Go Wrong!* Price/Stern/Sloan, New York, 1977.

means be adequate to solve any material and energy balances other than the most trivial ones.

Polya[8] recommends the use of four steps for solving problems and puzzles: define, plan, carry out the plan, and look back. The key features of this strategy are the interaction among the steps and the interplay between critical and creative thinking. A number of other helpful references are listed at the end of this chapter if you need assistance. Figure 1.14 sketches the general concept involved in problem solv-

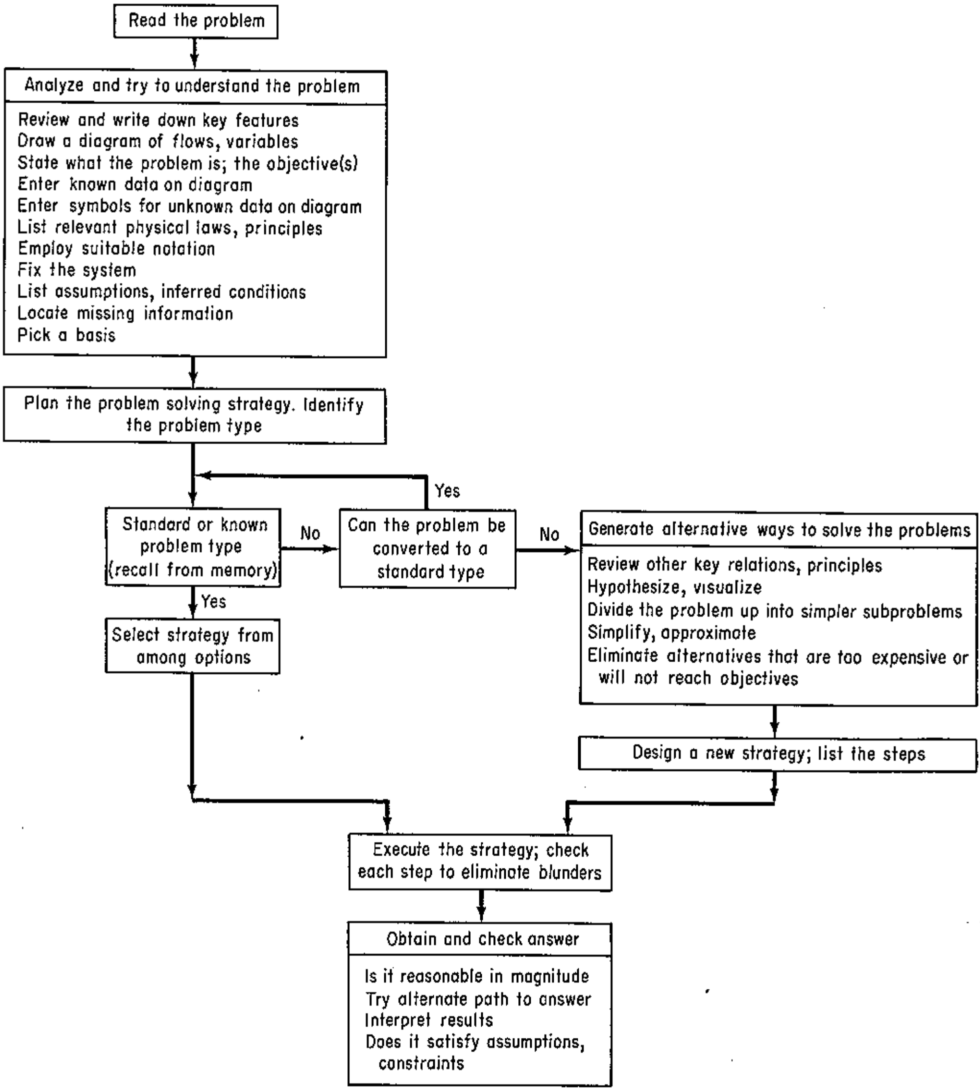

Figure 1.14 Program for problem solving.

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[8] G. Polya, *How to Solve It*, 2nd ed., Doubleday, New York, 1957.

ing. First, you must identify what result you are to achieve, that is, what the problem is. Then you must define the system, perhaps with the aid of a diagram. Various physical constraints will apply as well as the time available for you to work on the solution. In almost all cases you will have to look up data and make use of general laws. Finally, the results will have to be presented properly so that you can communicate them to someone else.

A more detailed checklist for solving material and energy balance problems is as follows:

(a) Read the available information through thoroughly and understand what is required for an answer. Sometimes, as in life, the major obstacle is to find out what the problem really is.
(b) Determine what additional data are needed, if any, and obtain this information.
(c) Draw a simplified picture of what is taking place and write down the available data. You may use boxes to indicate processes or equipment, and lines for the flow streams.
(d) Pick a basis on which to start the problem, as discussed in Sec. 1.4.
(e) If a chemical equation is involved, write it down and make sure that it is balanced.

By this time you should have firmly in mind what the problem is and a reasonably clear idea of what you are going to do about it; however, if you have not seen exactly how to proceed from what is available to what is wanted, then you should:

(f) Decide what formulas or principles are governing in this specific case and what types of calculations and intermediate answers you will need to get the final answer. If alternative procedures are available, try to decide which are the most expedient. If an unknown cannot be found directly, give it a letter symbol, and proceed as if you knew it.
(g) Make the necessary calculations in good form, being careful to check the arithmetic and units as you proceed.
(h) Determine whether the answer seems reasonable in view of your experience with these types of calculations.

You can work backward as well as forward in solving problems if the forward sequence of steps to take is not initially clear. Problems that are long and involved should be divided into parts and attacked systematically piece by piece. Additional suggestions with respect to problem solving appear in Tables 2.1, 2.2, and 2.3. Glance through these tables now.

If you can assimilate the procedure discussed above and make it a part of yourself—so that you do not have to think about it step by step—you will find that you will be able to materially improve your speed, performance, and accuracy in problem solving. Novice prospective engineers usually have the most difficulty with:

(a) Translating the physical problem into a mathematical description.
(b) Relating the physical problem to theory
(c) Simplifying a complex problem
(d) Learning how to ask the right questions

Look at Table 1.12 for the differences in technique between expert and novice engineers when solving problems.

Finally, we need to remark on the quality of data; the following quotation still holds true.

> The major difference between problems solved in the classroom and in the plant lies in the quality of the data available for the solution. Plant data may be of poor quality, in-

TABLE 1.12 A Comparison of the Problem-Solving Habits of a Novice and an Expert

A novice:	An expert:
Starts solving a problem before fully understanding what is wanted and/or what a good route for solution will be	Reviews the entire plan outlined in Fig. 1.14, mentally explores alternative strategies, and clearly understands what result is to be obtained
Focuses only on a known problem set that he or she has seen before and trys to match the problem with one in the set	Concentrates on similarities to and differences from known problems; uses generic principles rather than problem matching
Chooses one procedure without exploring alternatives	Examines several procedures serially or in parallel
Emphasizes speed of solution, unaware of blunders	Emphasizes care and accuracy in the solution
Does not follow an organized plan of attack such as outlined in Fig. 1.14, jumps about, and mixes problem-solving strategies	Goes through the problem-solving process step by step, checking, reevaluating, and recycling from dead ends to another valid path
Is unaware of missing data, concepts, laws	Knows what principles might be involved and where to get missing data
Exhibits bad judgment, makes unsound assumptions, poor approximations	Carefully evaluates the necessary assumptions and approximations
Gives up solving the problem because he or she does not know enough	Knows what the difficulty is and is willing to learn more that will provide the information needed
Gives up solving the problem because he or she does not have skills to branch away from a dead-end strategy	Aware that a dead end may exist for a strategy and has planned alternative strategies if a dead end is reached

conclusive, inadequate, or actually conflicting, depending on the accuracy of sampling, the type of analytical procedures employed, the skill of the technicians in the operation of analytical apparatus, and many other factors. The ability of an engineer to use the stoichiometric principles for the calculation of problems of material balance is only partly exercised in the solution of problems, even of great complexity, if solved from adequate and appropriate data. The remainder of the test lies in his ability to recognize poor data, to request and obtain usable data, and, if necessary, to make accurate estimates in lieu of incorrect or insufficient data.[9]

Self-Assessment Test

1. Prepare an information flow diagram showing the sequence (serial and parallel) of eight steps to be used in effective problem solving.
2. Take any example in Sec. 1.3, 1.5, or 1.6 and prepare an information flow diagram of your thought process in solving the example. Make a tree showing how the following classes of information are connected (put the solution as the last stage of the tree at the bottom):
   - **(a)** Information stated in the problem
   - **(b)** Information implied or inferred from the problem statement
   - **(c)** Information from your memory (internal data bank!)
   - **(d)** Information from an external data bank (reference source)
   - **(e)** Information determined by reasoning or calculations

   Label each class with a different-type box (circle, square, diamond, etc.) and let arrows connect the boxes to show the sequence of information flow for your procedure.
3. What should you do if you experience the following difficulties in solving problems?
   - **(a)** No interest in the material and no clear reason to remember
   - **(b)** Cannot understand after reading the material
   - **(c)** Read to learn "later"
   - **(d)** Rapidly forget what you have read
   - **(e)** Form of study is inappropriate

1.9 THE CHEMICAL EQUATION AND STOICHIOMETRY

Your objectives in studying this section are to be able to:

1. Write and balance chemical reaction equations.
2. Know the products of common reactions given the reactants.
3. Calculate the stoichiometric quantities of reactants and products given the chemical equation.
4. Define excess reactant, limiting reactant, conversion, degree of completion, and yield in a reaction.
5. Identify the limiting and excess reactants and calculate the percent excess reactant(s), the percent conversion, the percent completion, and

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[9] B. E. Lauer, *The Material Balance*, Work Book Edition, Department of Chemical Engineering, University of Colorado, Boulder, Colo., 1954, p. 89.

yield for a chemical reaction with the reactants being in nonstoichiometric proportions.

6. Calculate the amount of products for incomplete reactions.

As you already know, the chemical equation provides a variety of qualitative and quantitative information essential for the calculation of the combining weights (mass) of materials involved in a chemical process. Take, for example, the combustion of heptane as shown below. What can we learn from this equation?

$$C_7H_{16} + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O \tag{1.27}$$

It tells us about **stoichiometric ratios. First, make sure that the equation is balanced!** Then you can see that 1 mole (*not* lb_m or kg) of heptane will react with 11 moles of oxygen to give 7 moles of carbon dioxide plus 8 moles of water. These may be lb mol, g mol, kg mol, or any other type of mole, as shown in Fig. 1.15. One mole of CO_2 is formed from each $\frac{1}{7}$ mole of C_7H_{16}. Also, 1 mole of H_2O is formed

C_7H_{16}	+	$11O_2$	$\longrightarrow$	$7CO_2$	+	$8H_2O$
		Qualitative information				
heptane	reacts with	oxygen	to give	carbon dioxide	and	water
		Quantitative information				
1 molecule of heptane	reacts with	11 molecules of oxygen	to give	7 molecules of carbon dioxide	and	8 molecules of water
6.023×10^{23} molecules of C_7H_{16}	+	$11(6.023 \times 10^{23})$ molecules of O_2	$\longrightarrow$	$7(6.023 \times 10^{23})$ molecules of CO_2	+	$8(6.023 \times 10^{23})$ molecules of H_2O
1 g mole of C_7H_{16}	+	11 g moles of O_2	$\longrightarrow$	7 g moles of CO_2	+	8 g moles of H_2O
1 kg mole of C_7H_{16}	+	11 kg moles of O_2	$\longrightarrow$	7 kg moles of CO_2	+	8 kg moles of H_2O
1 lb mole of C_7H_{16}	+	11 lb moles of O_2	$\longrightarrow$	7 lb moles of CO_2	+	8 lb moles of H_2O
1 ton mole of C_7H_{16}	+	11 ton moles of O_2	$\longrightarrow$	7 ton moles of CO_2	+	8 ton moles of H_2O
1(100) g of C_7H_{16}	+	11(32) g of O_2	=	7(44) g of CO_2	+	8(18) g of H_2O
100 g		352 g		308 g		144 g
	452 g		=		452 g	
	452 kg		=		452 kg	
	452 ton		=		452 ton	
	452 lb		=		452 lb	

Figure 1.15 Application of the chemical equation.

with each $\frac{7}{8}$ mole of CO_2. Thus the equation tells us in terms of moles (*not* mass) the ratios among reactants and products. The coefficients of the compounds in the equation are known as **stoichiometric coefficients:** 1 for C_7H_{16}, 11 for O_2, and so on.

Stoichiometry (stoi-ki-om-e-tri)[10] deals with the combining weights of elements and compounds. The ratios obtained from the numerical coefficients in the chemical equation are the **stoichiometric ratios** that permit you to calculate the moles of one substance as related to the moles of another substance in the chemical equation. If the basis selected is to be mass (lb_m, kg) rather than moles, you should use the following method in solving problems involving the use of chemical equations: (1) Use the molecular weight to calculate the number of moles of the substance equivalent to the basis; (2) change this number of moles into the corresponding number of moles of the desired product or reactant by multiplying by the proper stoichiometric ratio, as determined by the chemical equation; and (3) then change the moles of product or reactant to a mass. These steps are indicated in Fig. 1.16 for the reaction in Eq. (1.27). You can combine these steps in a single dimensional equation, as shown in the examples below, for ease of calculations.

Basis : 10.0 kg C_7H_{16}

Component	*Mol. wt*
C_7H_{16}	100.1
O_2	32.0
CO_2	44.0
H_2O	18.0

$$\overset{\text{1 kg mole}}{C_7H_{16}} + 11O_2 \longrightarrow \overset{\text{7 kg mole}}{7CO_2} + 8H_2O$$

$$\frac{10.0\text{ kg }C_7H_{16}}{\dfrac{100.1\text{ kg }C_7H_{16}}{\text{kg mole }C_7H_{16}}} = 0.100\text{ kg mole }C_7H_{16} \longrightarrow \frac{0.700\text{ kg mole }CO_2}{\dfrac{1\text{ kg mole }CO_2}{44.0\ CO_2}} = 30.8\text{ kg }CO_2$$

10.0 kg C_7H_{16} yields 30.8 kg CO_2

Figure 1.16 Stoichiometry.

EXAMPLE 1.27 Use of the Chemical Equation

In the combustion of heptane, CO_2 is produced. Assume that you want to produce 500 kg of dry ice per hour and that 50% of the CO_2 can be converted into dry ice, as shown in Fig. E1.27. How many kilograms of heptane must be burned per hour?

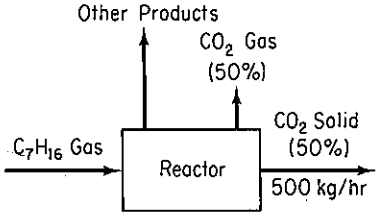

Figure E1.27

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[10] From the Greek *stoicheion*, basic constituent, and *metrein*, to measure.

Solution

Basis: 500 kg of dry ice (or 1 hr)

Mol. wt. heptane = 100.1. Chemical equation as in Fig. 1.15.

$$\begin{array}{l|c|c|c} 500\text{ kg dry ice} & 1\text{ kg CO}_2 & 1\text{ kg mol CO}_2 & 1\text{ kg mol C}_7\text{H}_{16} \\ \hline & 0.5\text{ kg dry ice} & 44\text{ kg CO}_2 & 7\text{ kg mol CO}_2 \end{array}$$

$$\left|\frac{100.1\text{ kg C}_7\text{H}_{16}}{1\text{ kg mol C}_7\text{H}_{16}}\right. = 325\text{ kg C}_7\text{H}_{16}$$

Since the basis of 500 kg of dry ice is identical to 1 hr, 325 kg of C_7H_{16} must be burned per hour. Note that kilograms are first converted to moles, then the chemical equation is applied, and finally moles are converted to kilograms again for the final answer.

EXAMPLE 1.28 Stoichiometry

Corrosion of pipes in boilers by oxygen can be alleviated through the use of sodium sulfite. Sodium sulfite removes oxygen from boiler feedwater by the following reaction:

$$2\text{Na}_2\text{SO}_3 + \text{O}_2 \longrightarrow 2\text{Na}_2\text{SO}_4$$

How many pounds of sodium sulfite are theoretically required (for complete reaction) to remove the oxygen from 8,330,000 lb of water (10^6 gal) containing 10.0 parts per million (ppm) of dissolved oxygen and at the same time maintain a 35% excess of sodium sulfite? See Fig. E1.28.

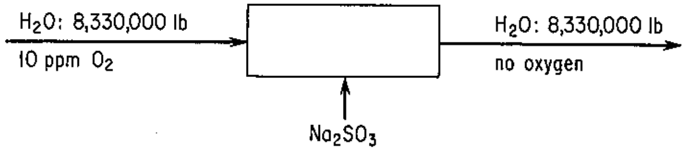

Figure E1.28

Solution

Additional data: mol. wt. of Na_2SO_3 is 126. Chemical equation: $2Na_2SO_4 + O_2 \rightarrow 2Na_2SO_4$.

Basis: 8,330,000 lb of H_2O with 10 ppm O_2 or 83.3 lb of O_2

$$\begin{array}{l|c} 8{,}330{,}000\text{ lb H}_2\text{O} & 10\text{ lb O}_2 \\ \hline & \underbrace{(1{,}000{,}000 - 10\text{ lb O}_2)\text{lb H}_2\text{O}}_{\textbf{effectively same as 1,000,000}} \end{array} = 83.3\text{ lb O}_2$$

$$\begin{array}{l|c|c|c} 8{,}330{,}000\text{ lb H}_2\text{O} & 10\text{ lb O}_2 & 1\text{ lb mol O}_2 & 2\text{ lb mol Na}_2\text{SO}_3 \\ \hline & 10^6\text{ lb H}_2\text{O} & 32\text{ lb O}_2 & 1\text{ lb mol O}_2 \end{array}$$

$$\begin{array}{|c|c} 126\text{ lb Na}_2\text{SO}_3 & 1.35 \\ \hline 1\text{ lb mol Na}_2\text{SO}_3 & 1 \end{array} = 886\text{ lb Na}_2\text{SO}_3$$

EXAMPLE 1.29 Stoichiometry

A limestone analyzes

$CaCO_3$	92.89%
$MgCO_3$	5.41%
Insoluble	1.70%

(a) How many pounds of calcium oxide can be made from 5 tons of this limestone?
(b) How many pounds of CO_2 can be recovered per pound of limestone?
(c) How many pounds of limestone are needed to make 1 ton of lime?

Solution

Read the problem carefully to fix in mind exactly what is required. Lime will include all the impurities present in the limestone which remain after the CO_2 has been driven off. Next, draw a picture of what is going on in this process. See Fig. E1.29.

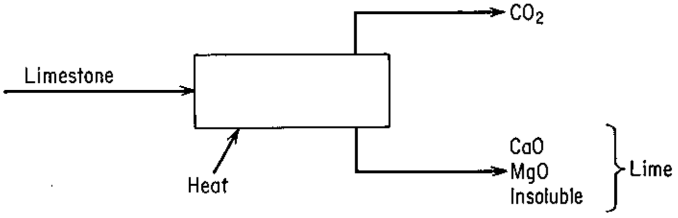

Figure E1.29

To complete the preliminary analysis you need the following chemical equations:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$MgCO_3 \longrightarrow MgO + CO_2$$

Additional data:

	$CaCO_3$	$MgCO_3$	CaO	MgO	CO_2
Mol. wt.:	100.1	84.32	56.08	40.32	44

Basis: 100 lb of limestone

This basis was selected because pounds = percent.

Component	lb = percent	lb mol	Lime	lb	CO_2(lb)
$CaCO_3$	92.89	0.9280	CaO	52.2	40.8
$MgCO_3$	5.41	0.0642	MgO	2.59	2.82
Insoluble	1.70		Insoluble	1.70	
Total	100.00	0.9920	Total	56.4	43.6

Note that the total pounds of products equal the 100 lb of entering limestone. Now to calculate the quantities originally asked for:

(a) $$\text{CaO produced} = \frac{52.2 \text{ lb CaO}}{100 \text{ lb stone}}\left|\frac{2000 \text{ lb}}{1 \text{ ton}}\right|\frac{5 \text{ ton}}{} = 5220 \text{ lb CaO}$$

(b) $$\text{CO}_2 \text{ recovered} = \frac{43.6 \text{ lb CO}_2}{100 \text{ lb stone}} = 0.436 \text{ lb}$$

or

(c) $$\text{Limestone required} = \frac{100 \text{ lb stone}}{56.4 \text{ lb lime}}\left|\frac{2000 \text{ lb}}{1 \text{ ton}}\right. = 3546 \text{ lb stone}$$

An assumption implicit in the calculations above is that the reaction takes place exactly as written in the equation and proceeds to 100% completion. When reactants, products, or degree of completion of the actual reaction differ from the assumptions of the equation, additional data must be made available to predict the outcome of reactions.

In industrial reactors you will rarely find exact stoichiometric amounts of materials used. To make a desired reaction take place or to use up a costly reactant, excess reactants are nearly always used. This excess material comes out together with, or perhaps separately from, the product—and sometimes can be used again. Even if stoichiometric quantities of reactants are used, but if the reaction is not complete or there are side reactions, the products will be accompanied by unused reactants as well as side products. In these circumstances some new definitions[11] must be understood:

(a) **Limiting reactant is the reactant that is present in the smallest stoichiometric amount.** In other words, if two or more reactants are mixed and if the reaction were to proceed according to the chemical equation to completion, **whether it does or not,** the reactant that would first disappear is termed the limiting reactant. For example, using Eq. (1.27), if 1 g mol of C_7H_{16} and 12 g mol of O_2 are mixed, C_7H_{16} would be the limiting reactant even if the reaction does not take place.

As a shortcut to determining the limiting reactant, all you have to do is to calculate the mole ratio(s) of the reactants and compare each ratio with the corresponding ratio of the coefficients of the reactants in the chemical equation thus:

	Ratio in feed		*Ratio in chemical equation*
$\frac{O_2}{C_7H_{16}}$:	$\frac{12}{1} = 12$	>	$\frac{11}{1} = 11$

If more than two reactants are present, you have to use one reactant as the reference substance, calculate the mole ratios of the other reactants in the feed relative to the reference, make pairwise comparisons versus the analogous ratios in the chemical

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[11] You need to be aware that other definitions of the terms exist in the literature.

equation, and rank each compound. For example, given the reaction

$$A + 3B + 2C \longrightarrow \text{products}$$

and that 1.1 moles of A, 3.2 moles of B, and 2.4 moles of C are fed as reactants into the reactor, we choose A as the reference substance and calculate

$$\begin{array}{llcl}
 & \underline{\textit{Ratio in feed}} & & \underline{\textit{Ratio in chemical equation}} \\
\frac{B}{A}: & \frac{3.2}{1.1} = 2.91 & < & \frac{3}{1} = 3 \\
\frac{C}{A}: & \frac{2.4}{1.1} = 2.18 & > & \frac{2}{1} = 2
\end{array}$$

We conclude that B is the limiting reactant relative to A, and that A is the limiting reactant relative to C, hence B is the limiting reactant among the set of three reactants. In symbols we have $B < A$, $C > A$ (i.e., $A < C$), so that $B < A < C$.

(b) **Excess reactant is a reactant present in excess of the limiting reactant.** The **percent excess** of a reactant is based on the amount of any excess reactant above the amount required to react with the limiting reactant according to the chemical equation, or

$$\text{excess} = \frac{\text{excess moles}}{\text{reacted moles}}.$$

$$\% \text{ excess} = \frac{\text{moles in excess}}{\text{moles required to react with limiting reactant}}(100)$$

where the moles in excess frequently can be calculated as the total available moles of a reactant less the moles required to react with the limiting reactant. A common term, **excess air,** is used in combustion reactions; it means the amount of air available to react that is in excess of the air theoretically required to *completely* burn the combustible material. The *required* amount of a reactant is established by the limiting reactant and is for all other reactants the corresponding stoichiometric amount. **Even if only part of the limiting reactant actually reacts, the required and excess quantities are based on the entire amount of the limiting reactant as if it had reacted completely.**

Air requirements for combustion vary with the need to ensure full utilization of the fuel's heating value but not generate excessive air pollutants. The excess air required in practice depends on the type of fuel, the furnace, and the burner. Fuel oil, for instance, requires 5 to 20% excess air depending on burner design. Excess air is recognized as a routine measure of heater performance.

Three other terms that are used in connection with chemical reactions have less clear-cut definitions: conversion, selectivity, and yield. No universally agreed upon definitions exist for these terms—in fact, quite the contrary. Rather than cite all the possible usages of these terms, many of which conflict, we shall define them as follows:

(c) **Conversion is the fraction of the feed or some material in the feed that is converted into products.** Thus, percent conversion is

$$100\frac{\text{moles of feed (or a compound in the feed) that react}}{\text{moles of feed (or a compound in the feed) introduced}}$$

What the basis in the feed is for the calculations and into what products the basis is being converted must be clearly specified or endless confusion results. Conversion is related to the **degree of completion** of a reaction, which is usually the percentage or fraction of the limiting reactant converted into products.

(d) **Selectivity is the ratio of the moles of a particular (usually the desired) product produced to the moles of another (usually undesired) product produced** in a set of reactions.

(e) **Yield,** for a single reactant and product, is the weight (mass) or moles of final product divided by the weight (mass) or moles of initial reactant (P lb of product A per R lb of reactant B) either fed or consumed. If more than one product and more than one reactant are involved, the reactant upon which the yield is to be based must be clearly stated. Suppose that we have a reaction sequence as follows:

$$\begin{tikzcd} A \arrow[r] \arrow[dr] & B \arrow[r] & C \\ & C & \end{tikzcd}$$

With B the desired product and C the undesired one. The yield of B is the moles (or mass) of B produced divided by the moles (or mass) of A fed or consumed. The selectivity of B is the moles of B divided by the moles of C produced.

The terms "yield" and "selectivity" are terms that measure the degree to which a desired reaction proceeds relative to competing alternative (undesirable) reactions. As a designer of equipment you want to maximize production of the desired product and minimize production of the unwanted products. Do you want high or low selectivity? Yield?

The employment of these concepts can best be illustrated by examples.

EXAMPLE 1.30 Limiting Reactant and Incomplete Reaction

Antimony is obtained by heating pulverized stibnite (Sb_2S_3) with scrap iron and drawing off the molten antimony from the bottom of the reaction vessel:

$$Sb_2S_3 + 3Fe \longrightarrow 2Sb + 3FeS$$

Suppose that 0.600 kg of stibnite and 0.250 kg of iron turnings are heated together to give 0.200 kg of Sb metal. Calculate:

(a) The limiting reactant
(b) The percentage of excess reactant
(c) The degree of completion (fraction)
(d) The percent conversion
(e) The yield

Solution

The molecular weights needed to solve the problem and the gram moles forming the basis are:

Component	kg	Mol. wt.	g mol
Sb_2S_3	0.600	339.7	1.77
Fe	0.250	55.85	4.48
Sb	0.200	121.8	1.64
FeS		87.91	

The process is illustrated in Fig. E1.30.

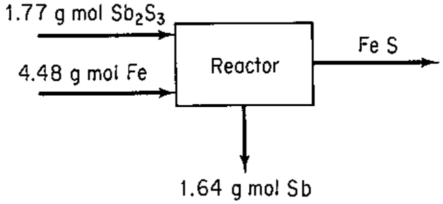

Figure E1.30

(a) To find the limiting reactant, we examine the chemical reaction equation and note that if 1.77 g mol of Sb_2S_3 reacts, it requires 3(1.77) = 5.31 g mol of Fe, whereas if 4.48 g mol of Fe reacts, it requires (4.48/3) = 1.49 g mol of Sb_2S_3 to be available. Thus Fe is present in the smallest stoichiometric amount and is the limiting reactant; Sb_2S_3 is the excess reactant.

(b) The percentage of excess reactant is

$$\%\ \text{excess} = \frac{1.77 - 1.49}{1.49}(100) = 18.8\%\ \text{excess}\ Sb_2S_3$$

(c) Although Fe is the limiting reactant, not all the limiting reactant reacts. We can compute from the 1.64 g mol of Sb how much Fe actually does react:

$$\frac{1.64\ \text{g mol Sb}}{} \left| \frac{3\ \text{g mol Fe}}{2\ \text{g mol Sb}} \right. = 2.46\ \text{g mol Fe}$$

If by the fractional degree of completion is meant the fraction conversion of Fe to FeS, then

$$\text{fractional degree of completion} = \frac{2.46}{4.48} = 0.55$$

(d) Let us assume that the percent conversion refers to the Sb_2S_3 since the reference compound is not specified in the question posed.

$$\frac{1.64\ \text{g mol Sb}}{} \left| \frac{1\ \text{g mol}\ Sb_2S_3}{2\ \text{g mol Sb}} \right. = 0.82\ \text{g mol}\ Sb_2S_3$$

$$\%\ \text{conversion of}\ Sb_2S_3\ \text{to Sb} = \frac{0.82}{1.77}(100) = 46.3\%$$

(e) The yield will be stated as kilograms of Sb formed per kilogram of Sb_2S_3 that was fed to the reaction:

$$\text{yield} = \frac{0.200\ \text{kg Sb}}{0.600\ \text{kg}\ Sb_2S_3} = \frac{1\ \ \text{kg Sb}}{3\,\text{kg}\ Sb_2S_3} = \frac{0.33\ \text{kg Sb}}{1\ \text{kg}\ Sb_2S_3}$$

EXAMPLE 1.31 Limiting Reactant and Incomplete Reactions

Aluminum sulfate can be made by reacting crushed bauxite ore with sulfuric acid, according to the following equation:

$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$$

The bauxite ore contains 55.4% by weight of aluminum oxide, the remainder being impurities. The sulfuric acid solution contains 77.7% H_2SO_4, the rest being water.

To produce crude aluminum sulfate containing 1798 lb of pure aluminum sulfate, 1080 lb of bauxite ore and 2510 lb of sulfuric acid solution are used.

(a) Identify the excess reactant.
(b) What percentage of the excess reactant was consumed?
(c) What was the degree of completion of the reaction?

Solution

We will omit the figure for this problem. You need to look up or calculate the molecular weights of the compounds involved. The pound moles of substances forming the basis of the problem can be computed as follows:

$$\begin{array}{c|c} 1798\ \text{lb}\ Al_2(SO_4)_3 & 1\ \text{lb mol}\ Al_2(SO_4)_3 \\ \hline & 342.2\ \text{lb}\ Al_2(SO_4)_3 \end{array} = 5.25\ \text{lb mol}$$

$$\begin{array}{c|c|c} 1080\ \text{lb bauxite} & 0.554\ \text{lb}\ Al_2O_3 & 1\ \text{lb mol}\ Al_2O_3 \\ \hline & 1\ \text{lb bauxite} & 101.96\ \text{lb}\ Al_2O_3 \end{array} = 5.87\ \text{lb mol}$$

$$\begin{array}{c|c|c} 2510\ \text{lb acid} & 0.777\ \text{lb}\ H_2SO_4 & 1\ \text{lb mol}\ H_2SO_4 \\ \hline & 1\ \text{lb acid} & 98.1\ \text{lb}\ H_2SO_4 \end{array} = 19.88\ \text{lb mol}$$

(a) The excess reactant can be determined as follows:

Ratio in feed	*Ratio in chemical equation*
$\dfrac{H_2SO_4}{Al_2O_3} : \dfrac{19.88}{5.87} = 3.39$	$\dfrac{3}{1} = 3$

Hence H_2SO_4 is the excess reactant.

(b) The $Al_2(SO_4)_3$ actually formed indicates that

$$\begin{array}{c|c} 5.25\ \text{lb mol}\ Al_2(SO_4)_3 & 3\ \text{lb mol}\ H_2SO_4 \\ \hline & 1\ \text{lb mol}\ Al_2(SO_4)_3 \end{array} = 15.75\ \text{lb mol}\ H_2SO_4\ \text{was consumed}$$

$$\frac{15.75}{19.88}(100) = 79.2\%$$

(c) The fractional degree of completion refers to the limiting reactant. For each mole of $Al_2(SO_4)_3$, 1 mole of Al_2O_3 was used:

$$\frac{5.25}{5.87} = 0.89$$

EXAMPLE 1.32 The Meaning of Selectivity and Yield

Two well-known reactions take place in the dehydrogenation of ethane:

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \quad \text{(a)}$$

$$C_2H_6 + H_2 \longrightarrow 2CH_4 \quad \text{(b)}$$

Given the following product distribution (in the gas-phase reaction of C_2H_6 in the presence of H_2) from the reaction of C_2H_6

Component	Percent
C_2H_6	35
C_2H_4	30
H_2	28
CH_4	7
Total	100

what is (a) the selectivity of C_2H_4 relative to CH_4 and (b) the yield of C_2H_4 in kilogram moles of C_2H_4 per kilogram mole of C_2H_6?

Solution

Basis: 100 kg mol of products

(a) The selectivity (as defined) is

$$\frac{30 \text{ kg mol } C_2H_4}{7 \text{ kg mol } CH_4} = 4.29 \frac{\text{mol } C_2H_4}{\text{mol } CH_4}$$

(b) The moles of C_2H_6 entering into the reaction can be determined from the C_2H_4 and the CH_4 formed.

$$\frac{30 \text{ kg mol } C_2H_4}{} \left| \frac{1 \text{ kg mol } C_2H_6}{1 \text{ kg mol } C_2H_4} \right. = 30 \text{ kg mol } C_2H_6$$

$$\frac{7 \text{ kg mol } CH_4}{} \left| \frac{1 \text{ kg mol } C_2H_6}{2 \text{ kg mol } CH_4} \right. = \underline{3.5 \text{ kg mol } C_2H_6}$$

$$33.5 \text{ kg mol } C_2H_6$$

Total $C_2H_6 = 33.5 + 35 = 68.5$ kg mol.

$$\frac{30 \text{ kg mol } C_2H_4}{68.5 \text{ kg mol } C_2H_6} = 0.44 \frac{\text{kg mol } C_2H_4}{\text{kg mol } C_2H_6}$$

You should remember that the chemical equation does not indicate the true mechanism of the reaction or how fast or to what extent the reaction will take place. For example, a lump of coal in air will sit unaffected at room temperature, but at higher temperatures it will readily burn. All the chemical equation indicates is the stoichiometric amounts required for the reaction and obtained from the reaction if it proceeds in the manner in which it is written. Also, remember to make sure that the chemical equation is balanced before using it.

Self-Assessment Test

1. Write balanced reaction equations for the following reactions:
   (a) C_9H_{18} and oxygen to form carbon dioxide and water
   (b) FeS_2 and oxygen to form Fe_2O_3 and sulfur dioxide
2. If 1 kg of benzene (C_6H_6) is oxidized with oxygen, how many kilograms of O_2 are needed to convert all the benzene to CO_2 and H_2O?
3. The electrolytic manufacture of chlorine gas from a sodium chloride solution is carried out by the following reaction:

$$2NaCl + 2H_2O \longrightarrow 2NaOH + H_2 + Cl_2$$

   How many kilograms of Cl_2 can one produce from 10 m^3 of a brine solution containing 5% by weight of sodium chloride? The specific gravity of the solution relative to water at 4°C is 1.07.
4. Calcium oxide (CaO) is formed by decomposing limestone (pure $CaCO_3$). In one kiln the reaction goes to 70% completion.
   (a) What is the composition of the solid product withdrawn from the kiln?
   (b) What is the yield in terms of pounds of CO_2 produced per pound of limestone charged?
5. In problem 3, suppose that 50.0 kg of NaCl reacts with 10.0 kg of H_2O.
   (a) What is the limiting reactant?
   (b) What is the excess reactant?
   (c) What components will the product solution contain if the reaction is 60% complete?

Thought Problems

1. An accident occurred in which one worker lost his life. A large steel evaporator in magnesium chloride service, containing internal heating tubes, was to be cleaned. It was shut down, drained, and washed. The next day two employees who were involved in the maintenance of the evaporator entered the vessel to repair the tubes. They were overcome, apparently from lack of oxygen. Subsequently, one employee recovered and escaped, but the other never regained consciousness, and died several days later.

   What in your opinion might have caused the accident (the lack of oxygen)?
2. A leaky pen will make itself known in Technicolor. Leaked information appears in the national news. But a leaking underground gasoline storage tank is extremely difficult to detect.

   Suggest some ways which can be used to detect leaky tanks. How effective are inventory control methods?
3. OSHA requires the use of breathing apparatus when working in or around tanks containing traces of solvents. While demolishing an old tank, a contractor purchased several cylinders of compressed air, painted gray. After two days he found that he needed more cylinders, and sent a truck for another cylinder. The driver returned with a black cylinder. None of the workers, including the man in charge of the breathing apparatus, noticed the change or, if they did, attached any importance to it. When the new cylinder was brought into use, a welder's facepiece caught fire. Fortunately, he pulled it off at once and was not injured.

   What would be the most likely cause of this incident?

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PROBLEMS

An asterisk designates problems appropriate for solution using a computer. Refer also to the problems that require writing computer programs at the end of the chapter.

Section 1.1

1.1. An engineer went to the liquor supermarket—which advertised the lowest prices in town—and bought what he thought was the usual $\frac{1}{2}$-gal jug for $7.77, but the jug turned out to be in reality a 1.75-L bottle. Was this a bargain in comparison with two "fifths" (of a gallon) at $7.99?

1.2. Convert the following quantities to the units shown in parentheses.
- **(a)** The speed of light in a vacuum is 2.998×10^8 m/s (mi/hr).
- **(b)** The speed of sound in air at standard temperature and pressure is 340.294 m/s (ft/s).
- **(c)** The speed of a car traveling 60 mi/hr (km/hr).
- **(d)** The standard football field is 100 yards long (m).

(e) A fifth (of a gallon) of rum is (cm^3).
(f) A passenger car gets 25 mi/gal (km/L).

1.3. The following test will measure your SIQ. List the correct answer.

(a) Which is the correct symbol?
 (1) nm (2) °K (3) sec (4) N/mm
(b) Which is the wrong symbol?
 (1) MN/m^2 (2) GHz/s (3) kJ/(s · m^3) (4) °C/M/s
(c) Atmospheric pressure is about:
 (1) 100 Pa (2) 100 kPa (3) 10 Mpa (4) 1 GPa
(d) The temperature 0°C is defined as:
 (1) 273.15°K (2) Absolute zero
 (3) 273.15 K (4) The freezing point of water
(e) Which height and mass are those of a petite woman?
 (1) 1.50 m, 45 kg (2) 2.00 m, 95 kg
 (3) 1.50 m, 75 kg (4) 1.80 m, 60 kg
(f) Which is a recommended room temperature in winter?
 (1) 15°C (2) 20°C (3) 28°C (4) 45°C
(g) The watt is:
 (1) One joule per second (2) Equal to 1 kg · m^2/s^3
 (3) The unit for all types of power (4) All of the above
(h) What force may be needed to lift a heavy suitcase?
 (1) 24 N (2) 250 N (3) 25 kN (4) 250 kN

1.4. Convert 9 × 10^8 (lb)/(ft^3)(hr) to g/(s)(cm^3).

1.5. In the United States a diet soft drink would be labeled "low cal" cola. In Australia, such drinks are sold as "low ____________" cola.

1.6. Your boss announced that the speed of the company Boeing 727 is to be cut from 525 mi/hr to 475 mi/hr to "conserve fuel," thus cutting consumption from 2200 gal/hr to 2000 gal/hr. How many gallons are saved in a 1000-mi trip?

1.7. It can be determined that the rate of energy loss from a person's body will normally vary by approximately 20 Btu/hr for each 1-°F change in skin temperature. Therefore, in going from a comfortably cool skin temperature of 90°F to a comfortably warm skin temperature of 93°F, the heat rejection rate is increased by only 60 Btu/hr. How much are the two rates, respectively, in watts?

1.8. Change the underlined quantities in the following popular phrases to the units given in parentheses.

(a) An ounce (g) of prevention is worth a pound (kg) of cure.
(b) Give her an inch (cm) and she'll take a mile (m).
(c) He demanded his pound (g) of flesh.
(d) First down and 10 yards (m) to go.
(e) A miss is as good as a mile (cm).
(f) More bounce to the ounce (kg).
(g) I love you a bushel (L) and a peck (cm^3).
(h) Walk a mile (ft) in his shoes.

1.9. Match the following quantities in list A with the most closely associated terms in list B.

LIST A

a. 1 million phones
b. 2000 mockingbirds
c. 10 millipedes
d. 1/1000 of a tent

e. 2×10^{18} mines
f. 10^{12} tories
g. two tenths of a fur
h. 10 cards
i. 10^{-6} scope
j. 10^{21} picolos
k. 0.000001 phone
l. 100 oars
m. $1/10^{6}$ graph

LIST B

1. 1 deckacards
2. 1 micrograph
3. 1 militant
4. 1 centipede
5. to decipher
6. 1 territory
7. 2 kilo-mockingbirds
8. to examine
9. 1 gigolo
10. 1 microphone
11. 1 microscope
12. 1 megaphone
13. 1 hector

1.10. A technical publication describes a new model 20-hp Stirling (air cycle) engine that drives a 68-kW generator. Is this possible?

1.11. A freeze-dried coffee is advertised as "97% caffeine-free." Is it possible for this coffee to contain only 0.14% caffeine? Explain.

1.12. The following is a synopsis of an article to appear in an engineering journal. Convert the quantities mentioned to the nearest whole unit shown in parentheses.

The ocean thermal energy conversion (OTEC) to electrical power utilizes the temperature difference between the warm surface water and the cold deep water. A proposed **(a)** 37,912 Btu/s (MW) OTEC power plant will require a **(b)** 9.15 m (ft)-diameter cold water supply pipe reaching a depth of **(c)** 900 m (ft). A test system was designed to measure the environmental loading and dynamic response of the barge and pipe. This system consisted of a **(d)** 2.4 m (ft) diameter fiberglass/foam pipe **(e)** 122 m (ft) long suspended vertically by a gimbal from a barge anchored **(f)** 3.7 km (mi) south of Honolulu, Hawaii, in **(g)** 374.9 m (ft) of water. The pipe wall was a composite of alternating **(h)** 9.7 mm (in.) fiberglass-reinforced plastic (FRP) and insulating foam of **(i)** 0.254 cm (in.), for an overall thickness of **(j)** 33 mm (in.).

Strain gauges and pressure transducers were attached at **(k)** 15.25 m (ft) intervals along the pipe and an accelerometer at **(l)** 29.3 m (ft) below the surface. The barge and pipe system, weighing a total of **(m)** 81,648 kg (ton) was anchored by **(n)** 22,680 kg (lb) concrete blocks on either side. A cable system held the barge in place.

The cable, rising from the bottom, consisted of a **(o)** 4.5 cm (in.) wire rope **(p)** 45.7 m (yd) long attached to a **(q)** 4,536 kg (ton) sinker followed by a second wire rope of **(r)** 579 m (ft). This was connected to a more flexible nylon rope **(s)** 365 m (ft) long and **(t)** 13 cm (in.) in diameter. The nylon ropes were attached to mooring buoys which were chained to the barge.

1.13. An elevator that weights 10,000 lb is pulled up 10 ft between the first and second floors of a building 100 ft high. The greatest velocity the elevator attains is 3 ft/s. How much kinetic energy does the elevator have in $(\text{ft})(\text{lb}_f)$ at this velocity?

1.14. Find the kinetic energy of a ton of water moving at 60 mi/hr expressed as
(a) $(\text{ft})(\text{lb}_f)$

(b) joules
(c) (hp)(s)
(d) (watt)(s)
(e) (liter)(atm)

1.15. Calculate the kinetic and potential energy of a missile moving at 12,000 mi/hr above the earth where the acceleration due to gravity is 30 ft/s^2.

1.16. Although gold is itself biologically inert, bacteria can degrade gold sulfide to open up the matrix of gold ore, making the gold more amenable to attack by cyanide. With this biotechnical step added in processing, yields may then be increased from, say, the original 60% up to as much as 90% recovery of gold in the ore, depending on the mineralogy.

Typically, this additional biological step is carried out in a pachuca, a cone-bottomed column familiar to the mining industry. Ground or milled ore, mixed with the aqueous bacterial solution, is introduced into the top of the column, and air is injected at the base. The injected air serves a number of functions: it maintains the solid in suspension, it mixes the solid with liquid—giving a three-phase gas/liquid/solid system—and it provides the oxygen and carbon dioxide required by the bacteria. The bacteria also require a feed of nitrogen and phosphorous, which can be added to the column if they are not indigenous to the ore.

The theory in simple; in practice it is a matter of economics as to whether the added steps in gold recovery are worthwhile. If a company sends in a sample containing on the average 2.5 g of gold per metric ton of ore, what could be the maximum additional capital and operating costs per ton of ore if the additional biological recovery step is to be employed?

1.17. Explain in detail whether or not the following equation for flow through a rectangular weir is dimensionally consistent. (This is the modified Francis formula.)

$$q = 0.415(L - 0.2h_0)h_0^{1.5}\sqrt{2g}$$

where q = volumetric flow rate, ft^3/s
L = crest height, ft
h_0 = weir head, ft
g = acceleration of gravity, 32.2 ft/(s)^2

1.18. Consider the following equation for the rate of heat transfer across a boundary layer:

$$Q = hA\,\Delta T$$

where Q = rate of heat transfer
h = heat transfer coefficient
A = area perpendicular to the transfer
ΔT = temperature difference

What are the SI units of the heat transfer coefficient?

1.19. Densities are sometimes expressed as a linear function of temperature, such as

$$\rho = \rho_0 + aT$$

where ρ is in g/cm^3 and T is in degrees K. What must the units of ρ_0 and a be?

1.20. An experimental investigation of the rate of mass transfer of SO$_2$ from an airstream into water indicated that the mass transfer coefficient could be correlated by an equation of the form

$$k_x = Ku^{0.487}$$

where k_x is the mass transfer coefficient in mol/(cm^2)(s) and u is the velocity in cm/s. Does the constant K have dimensions? What are they? If the velocity is to be expressed in ft/s, and we want to retain the same form of the relationship, what would the units of K' have to be if k_x is still mol/(cm^2)(s), where K' is the new coefficient in the formula.

1.21. The equation for the flow of water through a nozzle is as follows:

$$q = C\sqrt{\frac{2g}{1 - (d_1/d_2)^4}}\left(A\sqrt{\frac{\Delta p}{\rho}}\right)$$

where q = volume flowing per unit time
C = dimensionless constant
g = local gravitational acceleration
d_1 = smaller nozzle diameter
d_2 = larger nozzle diameter
A = area of nozzle outlet
Δp = pressure drop across nozzle
ρ = density of fluid flowing

State whether this equation is dimensionally consistent. Show how you arrived at your conclusion.

1.22. A useful dimensionless number called the *Reynolds number* is

$$\frac{DU\rho}{\mu}$$

where D = diameter or length
U = some characteristic velocity
ρ = fluid density
μ = fluid viscosity

Calculate the Reynolds number for the following cases:

	1	2	3	4
D	2 in.	20 ft	1 ft	2 mm
U	10 ft/s	10 mi/hr	1 m/s	3 cm/s
ρ	62.4 lb/ft^3	1 lb/ft^3	12.5 kg/m^3	25 lb/ft^3
μ	0.3 lb$_m$/(hr)(ft)	0.14×10^{-4} lb$_m$/(s)(ft)	2×10^{-6} centipoise (cP)	1×10^{-6} centipoise

1.23. Computers are used extensively in automatic plant process control systems. The computers must convert signals from devices monitoring the process, evaluate the data using the programmed engineering equations, and then feed back the appropriate control adjustments. The equations must be dimensionally consistent. Therefore, a conversion factor must be part of the equation to change the measured field variable into the proper units.

Crude oil pumped from a storage unit to a tanker is to be expressed in tons/hr, but the field variables of density and the volumetric flow rate are measured in lb/ft^3 and gal/min, respectively. Determine the units and the numerical value of the factor necessary to convert the field variables to the desired output.

1.24. The pressure drop for flow through a circular pipe may be calculated from the Darcy formula:

$$\Delta p = \frac{KfLpv^2}{D}$$

where Δp = $\text{lb}_f/\text{in.}^2$
K = a constant
f = friction factor, dimensionless
L = ft
p = lb_m/ft^3
v = ft/s
D = in.

What are the units of the constant, K?

1.25. The Francis weir formula is used in distillation column design to find the height of the liquid crest over the weir that controls liquid flow from the plate in the column

$$h = 0.48F\left(\frac{Q}{L}\right)^{0.67}$$

where h = liquid crest height, in.
F = dimensionless correction factor
Q = liquid flow rate, gal/min
L = weir length, in.

(a) What are the units associated with 0.48?
(b) Convert the equation above to the SI system so that Q can be introduced into the equation in the units of m^3/s and L and h in meters.

Section 1.2

1.26. Write the formula and calculate the molecular weight in grams of:
(a) Silver sulfate
(b) Anhydrous barium chloride
(c) Propyl benzoate
(d) Thyroxin (thyro-oxyindol)

1.27. Write the formula and calculate the molecular weight in pounds of **(a)** silver sulfate, **(b)** anhydrous barium chloride, **(c)** propyl benzoate, and **(d)** thyroxin (thyro-oxyindol).

1.28. How many pounds of compound are contained in each of the following?
(a) 64 g of $BaMnO_4$
(b) 40 lb mol of dimethyl amine
(c) 11 kg mol of nicotine

1.29. **(a)** How many g mol are represented by 100 g of CO_2?
(b) Calculate the weight in pounds of 3.5 g mol of nitrogen.

1.30. Convert the following:
(a) 105 g mol of potassium oxide to g
(b) 2 lb mol of aluminum acetate to lb
(c) 114 g mol of oxalic acid to lb
(d) 3 lb of quinine to g mol
(e) 40 g of trichlorobenzene to lb mol

1.31. How many pounds of compound are contained in each of the following?
- **(a)** 130 g mol of sodium hydroxide (anhydrous).
- **(b)** 300 g mol of sodium oleate.
- **(c)** 165 lb mol of sodium perchromate.
- **(d)** 62 lb mol of pure nitric acid.
- **(e)** 36 g mol of cupric tartrate.
- **(f)** 36 lb mol of cuprous phosphide (Cu_6P_2).
- **(g)** 72 lb mol of nickel bromide.
- **(h)** 12 g mol of nitrogen sulfide (N_4S_4).
- **(i)** 120 lb mol of potassium nitrate.
- **(j)** 11 g mol of stannic fluoride.

1.32. The structural formulas in Fig. P1.32 are for vitamins:
- **(a)** How many pounds of compound are contained in each of the following (do for each vitamin):
  - **(1)** 2.00 g mol
  - **(2)** 16 g
- **(b)** How many grams of compound are contained in each of the following (do for each vitamin):
  - **(1)** 1.00 lb mol
  - **(2)** 12 lb

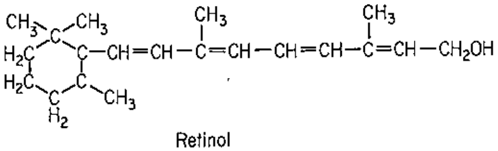
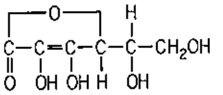
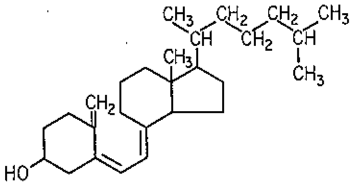
Vitamin	Structural formula	Dietary sources	Deficiency symptoms
Vitamin A	 Retinol	Fish liver oils, liver, eggs, fish, butter, cheese, milk; a precursor, β-carotene, is present in green vegetables, carrots, tomatoes, squash	Night blindness, eye inflammation
Ascorbic acid (vitamin C)		Citrus fruit, tomatoes, green peppers, strawberries, potatoes	Scurvy
Vitamin D	 Vitamin D_3	Fish liver oils, butter, vitamin-fortified milk, sardines, salmon; the body also obtains this compound when ultraviolet light converts 7-dehydrocholesterol in the skin to vitamin D	Rickets, osteomalacia, hypoparathyroidism

Figure P1.32

1.33. The recent correspondence from Dr. Morris and Professor Mullin concerning the mole seems to have left its dimensions unresolved. Morris asserts that the "mole has the dimensions of mass"; Mullin counters that "the mole is certainly related to mass, but this does not confer dimensions of mass on it."

State which authority is correct, Mullin or Morris, and explain in no more than two sentences why.

1.34. With the proper catalyst and temperature, ethane (C_2H_6) can be completely decomposed to acetylene (C_2H_2) and hydrogen (H_2). If the flow rate into the reactor is 100 lb/hr, what is the exit flow rate of H_2 in lb/hr?

Section 1.3

1.35. A proposed New Mexico coal gasification project is predicted to produce about 573,000 lb/hr of wet ash from one unit. It would form a pile 231 ft at the base, 100 ft high, and almost 7 mi long in 1 year! Based on these estimates, what was the density used for the ash in pounds per cubic foot?

1.36. The density of a certain solution is 8.80 lb/gal at 80°F. How many cubic feet will be occupied by 10,010 lb of this solution at 80°F?

1.37. The density of benzene at 60°F is 0.879 g/cm^3. What is the specific gravity of benzene at 60°F/60°F?

1.38. A solution of sulfuric acid at 60°F is found to have a specific gravity of 1.22. If this is equivalent to 30% H_2SO_4, what is the concentration of H_2SO_4 in lb mol/gal?

1.39. A liquid has a specific gravity of 0.90 at 25°C. What is its
(a) Density at 25°C in kg/m^3?
(b) Specific volume at 25°C in ft^3/lb$_m$?
(c) If the liquid is placed in a 1.5-L bottle that has a mass of 232 g, how much will the full bottle weigh?

1.40. Given a water solution that contains 1.704 kg of HNO_3/kgH_2O and has a specific gravity of 1.382 at 20°C, express the composition in the following ways:
(a) Weight percent HNO_3
(b) Pounds HNO_3 per cubic foot of solution at 20°C
(c) Molarity (gram moles of HNO_3 per liter of solution at 20°C)

1.41. Two immiscible liquids are allowed to separate in a vessel. One liquid has a specific gravity of 0.936; the second liquid weights 9.63 lb/gal. A block that is 9 in. by 9 in. by 9 in. and weights 25.8 lb is dropped into the vessel. Will the block float on the top, stop at the interface where the two liquids are separated, or sink? What fraction of the volume of the block is in one or both of the liquids?

1.42. Five thousand barrels of 28°API gas oil are blended with 20,000 bbl of 15°API fuel oil. What is the density of the mixture in lb/gal and lb/ft^3? Assume that the volumes are additive. 1 bbl = 42 gal.

$$\text{Specific gravity}\ \frac{60°F}{60°F} = \frac{141.5}{°\text{API} + 131.5}$$

Density of water at 60°F = 0.999 g/cm^3.

1.43. In a handbook you find that the conversion between °API and density is 0.800 density = 45.28°API. Is this a misprint?

1.44. One barrel each of gasoline (55°API), kerosene (40°API), gas oil (31°API), and isopentane (96°API) are mixed. What is the composition of the mixture expressed in weight percent and volume percent? What is the API gravity and the density of the mixture in g/cm^3 and lb/gal?

1.45. A tank for deep-sea diving consists of 60% He (atomic weight = 4.00), 20% N_2, and 20% O_2. The weight of the gas in the tank, excluding the tank weight, is 1.437 kg. What is the mass fraction of each of the components in the tank?

1.46. In the analysis of coal, a pseudo coal molecule can be postulated as represented by the following formula:

$$C_1H_{0.904}O_{0.187}S_{0.004}N_{0.021}$$

(a) What is the analysis of the coal by weight (mass) percent?
(b) What is the molecular weight of the pseudo molecule?

1.47. Solid fuel is used in many commerical areas from rocket boosters to rock concert light shows. Components of solid fuel fall into four main catagories: fuel, oxidizer, other special additives, and a binder. For example, various metal compounds and metal powders are used in fireworks to produce the brilliant colors that you see. An analysis shows that the powder from a gold cone fountain firework contained the following:

Percent by weight	Component	Purpose
2	C	Fuel
8	S	Fuel
53	KNO_3	Oxidizer
32	Fe	Color
4	Al	Color
1	Stearic acid—$CH_3(CH_2)_{16}CO_2H$	Organic binder
Total 100		

Calculate the mol % of each component.

1.48. Harbor sediments in the New Bedford, Massachusetts, area contain PCBs at levels up to 190,000 ppm according to a report prepared by Grant Weaver of the Massachusetts Coastal Zone Management Office (*Environ. Sci. Technol.*, v. 16, no. 9, p. 491A, 1982). What is the concentration in percent?

1.49. NIOSH sets standards for CCl_4 in air at 12.6 mg/m^3 of air (a time weighted average over 40 hr). The CCl_4 found in a sample is 4800 ppb (parts per billion; billion = 10^9). Does the sample exceed the NIOSH standard? Be careful!

1.50. The following table shows the annual inputs of phosphorus to Lake Erie.

	Short tons/yr
Source	
Lake Huron	2,240
Land drainage	6,740
Municipal waste	19,090
Industrial waste	2,030
	30,100
Outflow	4,500
Retained	25,600

SOURCE: *23rd Report to Committee on Government Operations*, U.S. Government Printing Office, Washington, D.C., 1970.

(a) Convert the retained phosphorus to concentration in micrograms per liter assuming that Lake Erie contains 1.2×10^{14} gal of water and that average phosphorus retention time is 2.60 yr.

(b) What percentage of the input comes from municipal water?

(c) What percentage of the input comes from detergents, assuming they represent 70% of the municipal waste?

(d) If 10 ppb of phosphorus triggers nuisance algal blooms, as has been reported in some documents, would removing 30% of the phosphorus in the municipal waste and all the phosphorus in the industrial waste be effective in reducing the eutrophication (i.e., the unwanted algal blooms) in Lake Erie?

(e) Would removing all the phosphate in detergents help?

1.51. A single piston reciprocating pump has a 15-cm-diameter piston with a 15-cm length of stroke. If the pump makes 16 strokes per minute, what is the pumping rate in **(a)** L/min? **(b)** gal/min?

1.52. A 15-in.-diameter sewer pipe is flowing full and carrying a flow of 2.7 million gallons per day. What is the average velocity of the water in the pipe?

1.53.* Solubility of formaldehyde in a solvent is measured by a spectrophotometer operating at 570 nm. The data collected are optical density versus concentration expressed in grams per liter.

Concentration, c	Optical density, d
100	0.086
300	0.269
500	0.445
600	0.538
700	0.626

Based on Beer's law, obtain the best estimates of the coefficients for a linear relation

$$c = b_0 + b_1 d$$

and plot the equation so obtained together with the data. Refer to Appendix M.

Section 1.4

1.54. Twenty-five pounds of gas consisting of 30% CO_2, 40% N_2, and 30% O_2 are placed in a cylinder 200 ft^3 in volume. What is the

(a) Average molecular weight of the gas?

(b) Density of the gas (in lb/ft^3)?

1.55. A mixture of gases contains 10.5% CO_2, 13.0% Cl_2, 12.7% N_2, and the balance hydrogen (all are mole percentages). The molecular weights are: $CO_2 = 44.01$, $Cl_2 = 70.90$, $N_2 = 28.01$, and $H_2 = 2.02$.

(a) What is the average molecular weight of the gas?

(b) Calculate the gas composition as weight fractions.

1.56. You are given 200 kg of a gas mixture containing

SO_2	20%
NO_2	20%
N_2	60%

What is
(a) The lb of N_2 in the gas?
(b) The average molecular weight of the gas?

1.57. You have 100 lb of gas of the following composition:

CH_4	30%
H_2	10%
N_2	60%

What is the average molecular weight of this gas?

1.58. A fuel gas is reported to analyze, on a mole basis, 20% methane, 5% ethane, and the remainder CO_2. Calculate the analysis of the fuel gas on a mass percentage basis.

1.59. Recent developments in ion chromatography are filling the analytical gap between the atomic adsorption spectroscopy and inductively coupled plasma metal spectroscopy. Ion chromatography can now not only determine what trace metals are present, but also their oxidation state, the degree of complexation, and the stability of the complex. For example, a nickel electroplating solution was analyzed by diluting it with a water eluant solution. The analysis revealed the following ion concentrations.

Metal cation	Concentration (mg/L)
Pb^{2+}	4
Cu^{2+}	0.5
Cd^{2+}	4
Co^{2+}	1
Zn^{2+}	2
Ni^{2+}	4

The other material in the solution was water.
(a) Calculate the concentration in mass % of each cation present.
(b) Calculate the composition in mol % of each cation present.

1.60. A gas mixture consists of three components: argon, *B*, and *C*. The following analysis of this mixture is given:

40.0 mol % argon

18.75 mass % *B*

20.0 mol % *C*

The molecular weight of argon is 40 and the molecular weight of *C* is 50. Find:
(a) The molecular weight of *B*
(b) The average molecular weight of the mixture

1.61. Two engineers are calculating the average molecular weight of a gas mixture containing oxygen and other gases. One of them uses the correct molecular weight of 32 for oxygen and determines the average molecular weight as 39.2. The other uses an incorrect value of 16 and determines the average molecular weight as 32.8. This is the only error in his calculations. What is the percentage of oxygen in the mixture expressed as mol %?

1.62. A liquid mixture of compounds A, B, and C containing 10 kg of A analyzes 25% B and contains 1.5 moles of C per mole of B. The respective molecular weights of A, B, and C are 56, 58, and 72; and the specific gravities are 0.58, 0.60, and 0.67. Calculate the analysis of the mixture in mole percent, the molecular weight of the mixture, the volume percent A on a B-free basis (ignore volume change on mixing), the density of the mixture, and the total number of moles of the mixture.

Section 1.5

1.63. In a report on the record low temperatures in Antarctica, *Chemical and Engineering News* said at one point that "the mercury dropped to −76°C." In what sense is that possible? Mercury freezes at −39°C.

1.64. Two engineers are arguing about the physical properties of a certain product. One claims that the melting point is −40°F, while the other claims that it is −40°C.
(a) Who is correct?
(b) The boiling point is 325 K. Determine the boiling point in °C, °R, and °F.
(c) Find $T_B - T_m$ (T_B = boiling point, T_m = melting point) for K, °C, °R, and °F.

1.65. "Further, the degree Celsius is exactly the same as a kelvin. The only difference is that zero degree Celsius is 273.15 kelvin. Use of Celsius temperature gives us one less digit in most cases" from [*Eng. Educ.*, p. 678 (April 1977)]. Comment on the quotation. Is it correct? If not, in what way or sense is it wrong?

1.66. (a) Convert 70°F to °C, K, °R.
(b) Convert 210 K to °C, °F, °R.

1.67. From what we know now, it is not going to be easy to make practical room-temperature superconductors. For one thing, scientists believe that getting a superconductor to carry more than a trickle of electrical current at room temperature would be very difficult. Even if we had room-temperature superconductivity, we would probably still work at the liquid nitrogen temperature, at which the current-carrying capacity of the superconductors is much greater.

Liquid nitrogen boils at 77 K and is required as a refrigerant for the highest-temperature superconductors proven to date. Its use represents a big improvement over the more costly and formerly required liquid helium, which boils at about −452°F. But it is far short of the room-temperature goal, which if attained, could lead rapidly to a revolution in cars, personal computers, and other yet-to-be-imagined consumer devices.

Convert the boiling point of liquid nitrogen to degrees Fahrenheit and degrees Rankine, and the boiling point of liquid helium to degrees Celsius and kelvin.

1.68. Given T_1 = 25°F, T_2 = 60°C, and $\Delta T = T_1 - T_2$, express T_1, T_2, and ΔT in all of the following units: °F, °C, °R, K.

1.69. Calculate all temperatures from the one value given:

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
°F	140				1000			
°R			500			1000		
K		298					1000	
°C				−40				1000

1.70. The emissive power of a blackbody depends on the fourth power of the temperature and is given by

$$W = AT^4$$

where W = emissive power, Btu/(ft^2)(hr)
A = Stefan-Boltzmann constant, 0.171×10^{-8} Btu/(ft^2)(hr)(°R)^4
T = temperature, °R

What is the value of A in the units J/(m^2)(s)(K^4)?

Section 1.6

1.71. The amplitude of sound at any given point is expressed as sound-pressure level (SPL). Its physical unit is the decibel, which is given as

$$\text{SPL} = 20 \ln (p/p_0) \qquad \text{in dB}$$

where p is the sound pressure being measured and p_0 is a reference pressure, usually 20 micronewtons per square meter (μN/m^2). The reference pressure of 20 μN/m^2 is approximately equal to the lowest pressure which a young person with normal hearing can barely detect at a frequency of 1000 Hz. Other measures of sound pressure may be encountered in the literature, such as dynes per square centimeter, microbars, and pounds per square inch.

Common examples of representative SPL (in dB) include:

Business office	50
Speech at 3 ft	65
Subway at 20 ft	95
Jet aircraft at 35 ft	130
On gantry during Saturn V launch	172

Convert the dB values of 0, 20, and those in the list above to:
(a) N/m^2
(b) μbar
(c) psi

1.72. Fill in the values in the blanks in the following:

(a) Consider a tank that is to take a pressure of 10 psi. This is the equivalent of (approximately) ____________ newtons/square meter (N/m^2), or ____________ kilonewtons/square meter (kN/m^2), or ____________ kilopascals (kPa).

(b) It may help to remember that 14.7 psi (____________ atm) = ____________ kN/m^2 or approximately ____________ MN/m^2.

(c) If your automobile tires take 24 psi of air, you will have to set the air-pump pressure to ____________ kN/m^2; if you need 26 psi, the pressure will be ____________ kN/m^2. If you are used to asking just for 30 lb of air in your car tires, you would in the future have to ask for ____________ kilograms.

(d) An absolute pressure of 10 micrometers of mercury is almost exactly equivalent to ____________ N/m^2, or ____________ Pa.

(e) If you are designing a corrosion-resistant tank of rolled (annealed) Hastelloy alloy C, the tensile strength needed for your calculations is 896 MN/m^2, which is the equivalent of ____________ psi. Perhaps it would be better to round it off to ____________ GN/m^2.

1.73. **"Holiday drivers stranded, Icicles blossom in Florida; 50 cities set record lows"** was the headline in the December 26 newspaper. After citing all of the cities with new low temperatures, the paper went on to say: "As the full force of the cold wave descended on the East it was 5 degrees Sunday morning in New York City. As one example of the strength of the cold air mass flowing from northwest Canada, the highest pressure ever recorded in the United States—31.42 inches of mercury—was measured on Christmas Eve in Miles City, Mont." Can this last statement be true?

1.74. The pressure gauge on a tank reads 50 psig on a day when the barometric pressure is 28.0 in. Hg. Find the absolute pressure in the tank in psia.

1.75. The growing use of ceramic fibers in the electronics, aerospace, and chemical process industries has prompted the development of a much faster manufacturing process, one several hundred times faster than current chemical vapor deposition (CVD) methods. The fibers are stronger and more flexible because they have a more uniform composition (i.e., no carbon core required). The reactor conditions may be varied from 1000 to 2500 K and the pressure from 100 to 700 kPa to accommodate a wide range of material processes. For example, silicon carbide fibers could be produced by mixing silicon chloride with methane and then heating the mix with an yttrium/aluminum laser, thus allowing strict control of the process temperature in the reactor. Convert the ranges for the reactor temperature and pressure to their corresponding American Engineering units (°R and psi).

1.76. Suppose that a submarine inadvertently sinks to the bottom of the ocean at a depth of 1000 m. It is proposed to lower a diving bell to the submarine and attempt to enter the conning tower. What must the minimum air pressure be in the diving bell at the level of the submarine to prevent water from entering into the bell when the opening valve at the bottom is cracked open slightly? Give your answer in absolute kilopascal. Assume that seawater has a constant density of 1.024 g/cm^3.

1.77. Air in a scuba diver's tank shows a pressure of 300 kPa absolute. What is the pressure in:

(a) psi **(b)** kPa **(c)** atm **(d)** bar
(e) in. Hg **(f)** ft H_2O **(g)** kg_f/cm^2

1.78. Flat-roof buildings are a popular architectural style in dry climates because of the economy of materials of construction. However, during the rainy season water may pool up on the roof decks so that structural considerations for the added weight must be taken into account. If 25 cm of water accumulates on a 10-m by 10-m area during a heavy rain storm, determine:

(a) The total added weight the building must support
(b) The force of the water on the roof in psi

1.79. A problem with wastewater treatment tanks set below ground was realized when the water table rose and an empty tank floated out of the ground. This buoyancy problem was overcome by installing a check valve in the wall of the tank so that if the water table rose high enough to float the tank, it would fill with water. If the density of concrete is 2080 kg/m^3, determine the maximum height at which the valve should be installed to prevent a buoyant force from raising a rectangular tank with inside dimensions of 30 m by 27 m and 5 m deep. The walls and floor have a uniform thickness of 200 mm.

1.80. A centrifugal pump is to be used to pump water from a lake to a storage tank that is

148 ft above the surface of the lake. The pumping rate is to be 25.0 gal/min, and the water temperature is 60°F. The pump on hand can develop a pressure of 50.0 psig when it is pumping at a rate of 25.0 gal/min. (Neglect pipe friction kinetic energy effects, or factors involving pump efficiency.)

(a) How high (in feet) can the pump raise the water at this flow rate and temperature?

(b) Is this pump suitable for the intended service?

1.81. You are asked to recommend a liquid for an open-top vertical manometer. As much accuracy as possible is needed, but the ceiling in the room restricts the column height to 3.35 m. Pressures will range up to 50 kPa gauge. Choose one of the substances from the following table, and explain the reasons for your choice. Give any calculations needed.

Substance	Density (g/cm^3)
Mercury	13.5939
Water	0.99823
Carbon tetrachloride	1.5940

1.82. A manometer uses kerosene, sp gr 0.82, as the fluid. A reading of 5 in. on the manometer is equivalent to how many millimeters of mercury?

1.83. The pressure gauge on the steam condenser for a turbine indicates 26.2 in. Hg of vacuum. The barometer reading is 30.4 in. Hg. What is the pressure in the condenser in psia?

1.84. A pressure gauge on a process tower indicates a vacuum of 3.53 in. Hg. The barometer reads 29.31 in. Hg. What is the absolute pressure in the tower in millimeters of mercury?

1.85. John Long says he calculated from a formula that the pressure at the top of Pikes Peak is 9.75 psia. John Green says that it is 504 mm Hg because he looked it up in a table. Which John is right?

1.86. The floor of a cylindrical water tank was distorted into 7-in. bulges due to the settling of improperly stablized soil under the tank floor. However, several consulting engineers restored the damaged tank to use by placing plastic skirts around the bottom of the tank wall and devising an air floatation system to move it to an adjacent location. The tank was 30.5 m in diameter and 13.1 m deep. The top, bottom, and sides of the tank were made of 9.35-mm-thick welded steel sheets. The density of the steel is 7.86 g/cm^3.

(a) What is the gauge pressure in kPa of the water at the bottom of the tank when it is completely full of water?

(b) What must the air pressure be in kPa beneath the empty tank in order to just raise it up for movement?

1.87. A pressure instrument has failed on a process line that requires constant monitoring. A bell-type gauge as shown in Fig. P1.87, is available which has oil (density of 0.800 g/cm^3) as a sealant liquid. Construction of the gauge limits the sealant liquid's travel to 12.7 cm before blowout of the oil occurs. What maximum pressures can this gauge measure in kPa?

1.88. One end of a mercury manometer at 70°F is attached to an evaporator at low pressure; the other is open to the atmosphere. The height of the mercury column is

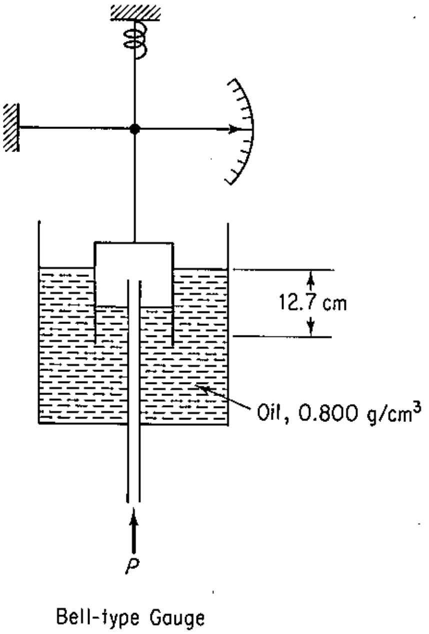


Figure P1.87

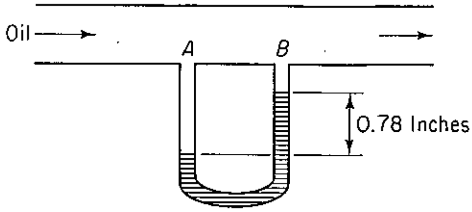


Figure P1.89

8.1 mm. How many kPa absolute is this? What is the equivalent reading in inches of Hg vacuum?

1.89. Examine Fig. P1.89. Oil (density = 0.91 g/cm^3) flows in a pipe, and the flow rate is measured via a mercury (density = 13.546 g/cm^3) manometer. If the difference in height of the two legs of the manometer is 0.78 in., what is the corresponding pressure difference between points A and B in mm Hg? At which point, A or B, is the pressure higher? The temperature is 60°F.

1.90. Water at 60°F is flowing through a pipeline, and the line contains an orifice plate for flow measurement. The pressure difference between the upstream and the downstream sides of the orifice plate is to be measured using an available U-tube manometer which is 48 in. high. If the maximum expected pressure drop across the orifice plate is 3.55 psi, what is the minimum specific gravity required of a manometer liquid that can be used to measure this differential pressure? Density of water at 60°F = 0.999 g/cm^3.

1.91. An inclined manometer is often used to measure small pressure differences. See Fig. P1.91.

(a) Find the equation for h in terms of L and θ.

(b) The process fluid is a gas at low pressure, the angle of inclination is 20°, $L = 10$ cm, and the manometer fluid is oil with a specific gravity of 0.8. What is the pressure differential (pascal) $p_1 - p_2$?

(c) If the process fluid is oil (sp gr = 0.8), the manometer fluid is water, and $L = 12$ in., what is the pressure drop in psi?

1.92. Pressure in a gas cell is measured with an inverted manometer, as shown in Fig. P1.92. The scale on the far right-hand side of the figure shows the distances in mm (not to scale) of the interfaces of the liquids in the manometer. What is the pressure

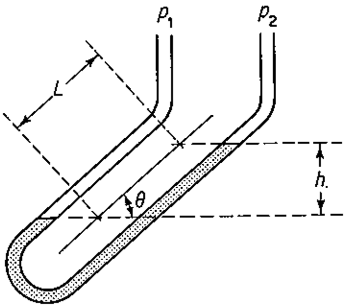


Figure P1.91

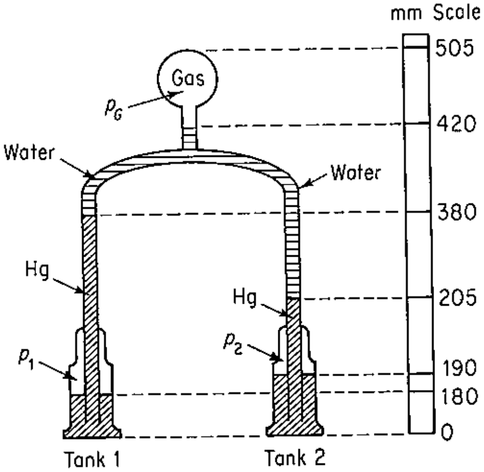


Figure P1.92

of the gas in psia if the pressures in the closed tanks are p_1 = 12.50 psia and p_2 = 9.17 psia? The density of Hg is 13.6 g/cm^3.

1.93. The pressure reading on the gauge shown in Fig. P1.93 is 2.4 psi. If the liquid level in the glass pipe connecting the two tanks is 16 ft below the bottom of the water tank, is the pressure gauge working properly? Show all calculations. What should the gauge read in psig?

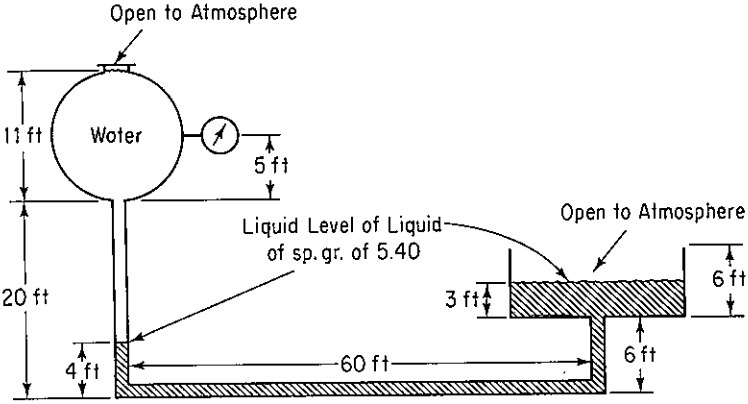


Figure P1.93

1.94. The indicating liquid in the manometer shown in Fig. P1.94 is water, and the other liquid is benzene. These two liquids are essentially insoluble in each other. If the manometer reading is ΔZ = 36.3 cm water, what is the pressure difference in kPa? The temperature is 25°C.

1.95. Examine Fig. P1.95. The barometric pressure is 720 mm Hg. The density of the oil is 0.80 g/cm^3. The Bourdon gauge reads 33.1 psig. What is the pressure in kPa of the gas?

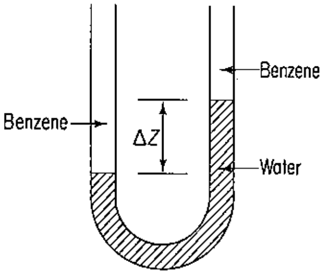
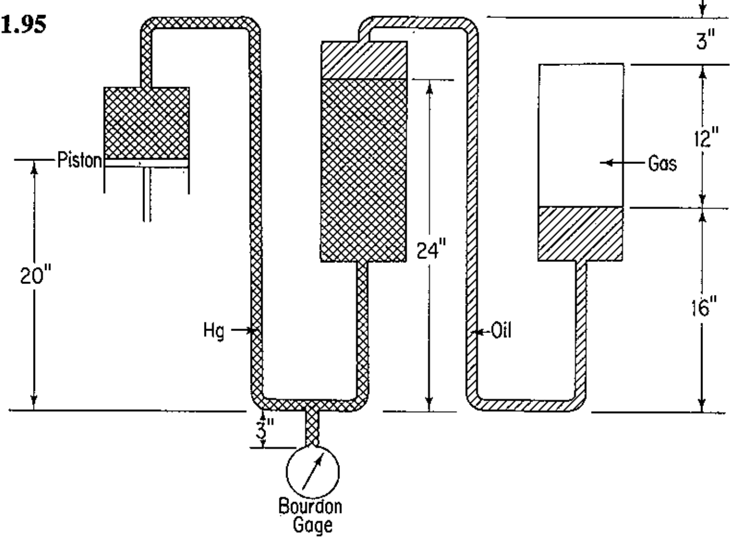


Figure P1.94

Figure P1.95



Section 1.7

1.96. Visit your library and carry out data searches for the following information. Report the values or equations found and their respective sources in complete detail: names of authors, article name, book or journal name, volume (if applicable), page number, and date of publication.

- **(a)** Density of lead thiocyanate [$Pb(CNS)_2$] at 20°C
- **(b)** Boiling point in °C of glyceryl tributyrate [$(C_2H_5CH_2CO_2)_3 \cdot C_3H_5$] at atmospheric pressure
- **(c)** Solubility of ammonium oxalate [$(NH_4)_2 \cdot C_2O_4$] at 40°C in water
- **(d)** Volume of methyl choride gas at 200°F and 6 psia

1.97. Does Perry's *Chemical Engineers' Handbook* contain information on densities of alcohol-water mixtures? osmotic pressure of sodium chloride solutions? corrosion properties of metals?

1.98. List four journals that publish physical property data and the libraries in which they are located.

Section 1.8

1.99. How would you estimate the rate at which a spherical water-filled capsule in outer space cools. List the types of information needed to solve such a problem, the assumptions that must be made, and what physical principles that you have studied in physics might be used to help solve the problem. Draw a picture of the process and indicate what the independent and dependent variables involved in the process might be.

1.100. Read the introductory portions of the book by Moshe F. Rubenstein, *Problem Solving* (Prentice-Hall, Englewood Cliffs, N.J., 1975), and compare the techniques outlined there with those listed in Sec. 1.8.

Section 1.9

1.101. $BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$

- **(a)** How many grams of barium chloride will be required to react with 5.00 g of sodium sulfate?
- **(b)** How many grams of barium chloride are required for the precipitation of 5.00 g of barium sulfate?
- **(c)** How many grams of barium chloride are needed to produce 5.00 g of sodium chloride?
- **(d)** How many grams of sodium sulfate are necessary for the precipitation of the barium of 5.00 g of barium chloride?
- **(e)** How many grams of sodium sulfate have been added to barium chloride if 5.00 g of barium sulfate is precipitated?
- **(f)** How many pounds of sodium sulfate are equivalent to 5.00 lb of sodium chloride?
- **(g)** How many pounds of barium sulfate are precipitated by 5.00 lb of barium chloride?
- **(h)** How many pounds of barium sulfate are precipitated by 5.00 lb of sodium sulfate?
- **(i)** How many pounds of barium sulfate are equivalent to 5.00 lb of sodium chloride?

1.102. $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

- **(a)** How many grams of silver nitrate will be required to react with 5.00 g of sodium chloride?
- **(b)** How many grams of silver nitrate are required for the precipitation of 5.00 g of silver chloride?
- **(c)** How many grams of silver nitrate are equivalent to 5.00 g of sodium nitrate?
- **(d)** How many grams of sodium chloride are necessary for the precipitation of the silver of 5.00 g of silver nitrate?
- **(e)** How many grams of sodium chloride have been added to silver nitrate if 5.00 g of silver chloride is precipitated?
- **(f)** How many pounds of sodium chloride are equivalent to 5.00 lb of sodium nitrate?
- **(g)** How many pounds of silver chloride are precipitated by 5.00 lb of silver nitrate?
- **(h)** How many pounds of silver chloride are precipitated by 5.00 lb of sodium chloride?
- **(i)** How many pounds of silver chloride are equivalent to 5.00 lb of silver nitrate?

1.103. The chemical composition of the material formed by an organism that grows in an incubator by degrading hexadecane ($C_{16}H_{34}$) can be written as $C_{4.4}H_{7.3}N_{0.86}O_{1.2}$. How many moles of oxygen are used to degrade 1 mole of hexadecane according to the following reaction?

$$C_{16}H_{34} + a_1O_2 + a_2NH_3 \longrightarrow C_{4.4}H_{7.3}N_{0.86}O_{1.2} + b_1CO_2 + b_2H_2O$$

where a_1, a_2, b_1, b_2 are constants to be determined.

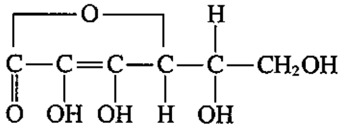
1.104. When benzene (C_6H_6) is burned with oxygen, how many pounds of oxygen are required to burn 10 lb of benzene to carbon dioxide and water vapor?

1.105. A plant makes liquid CO_2 by treating dolomitic limestone with commercial sulfuric acid. The dolomite analyzes 68.0% $CaCO_3$, 30.0% $MgCO_3$, and 2.0% SiO_2; the acid is 94% H_2SO_4 and 6% H_2O. Calculate:

(a) Pounds of CO_2 produced per ton dolomite treated

(b) Pounds of commercial acid required per ton of dolomite treated Mol. wt. data: $CaCO_3$, 100; $MgCO_3$, 84.3; SiO_2, 60; H_2SO_4, 98.

1.106. The formula for vitamin C is as follows:



How many pounds of this compound are contained in 2 g mol?

1.107. Removal of CO_2 from a manned spacecraft has been accomplished by absorption with lithium hydroxide according to the following reaction:

$$2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(l)$$

(a) If 1.00 kg of CO_2 is released per day per person, how many kilograms of LiOH are required per day per person?

(b) What is the penalty (i.e., the percentage increase) in weight if the cheaper NaOH is substituted for LiOH?

1.108. Some states and cities are placing a ban on laundry detergents containing more than 20% phosphates. In reading the detailed provisions of one law, it prohibits the sale of any detergent with a phosphorus pentoxide content of over 20% by weight. How much is this when expressed as weight percent sodium triphosphate, the compound found in the detergent?

1.109. Sulfuric acid can be manufactured by the contact process according to the following reactions:

(1) $S + O_2 \longrightarrow SO_2$

(2) $2SO_2 + O_2 \longrightarrow 2SO_3$

(3) $SO_3 + H_2O \longrightarrow H_2SO_4$

You are asked as part of the preliminary design of a sulfuric acid plant with a design capacity of 2000 tons/day of 66° Be (Baumé) (93.2% H_2SO_4 by weight) to calculate the following:

(a) How many tons of pure sulfur are required per day to run this plant?

(b) How many tons of oxygen are required per day?

(c) How many tons of water are required per day for reaction (3)?

1.110. Seawater contains 65 ppm of bromine in the form of bromides. In the Ethyl-Dow recovery process, 0.27 lb of 98% sulfuric acid is added per ton of water, together with the theoretical Cl_2 for oxidation; finally, ethylene (C_2H_4) is united with the bromine to form $C_2H_4Br_2$. Assuming complete recovery and using a basis of 1 lb of bromine, find the weights of acid, chlorine, seawater, and dibromide involved.

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$$

$$Br_2 + C_2H_4 \longrightarrow C_2H_4Br_2$$

1.111. The burning of limestone, $CaCO_3 \rightarrow CaO + CO_2$, goes only 70% to completion in a certain kiln.

(a) What is the composition (mass %) of the solid withdrawn from the kiln?
(b) How many kilograms of CO_2 are produced per kilogram of limestone fed? Assume that the limestone is pure $CaCO_3$.

1.112. In the semiconductor industry, integrated circuit (IC) production begins with the mechanical slicing of silicon rod into wafers. Once the wafers are sliced, the surfaces are lapped and polished to uniform flat surfaces. Contaminants and microscopic defects (work damage) are then removed chemically by etching. A traditional etching solution consists of a 4:1:3 volumetric ratio of 49% hydrofluoric, 70% nitric, and 100% acetic acids, respectively. Although work damage is usually only 10 μm deep, overetching to 20 μm per side is common. The reaction for dissolving the silicon surface is

$$3Si + 4HNO_3 + 18HF \longrightarrow 3H_2SiF_6 + 4NO + 8H_2O$$

Calculate the flow rate of the etching solution in kilograms per hour if 20 μm per side is to be etched for 6000 wafers per hour of 150 mm diameter. What is the limiting reagent?

Data	Mol. wt.
Si—2.33 g/cm^3	28.09
Sp gr 49% HF is 1.198	20.01
Sp gr 70% HNO_3 is 1.4134	63.01
Sp gr 100% CH_3CO_2H is 1.0492	60.05

1.113. One method of synthesizing the aspirin substitute, acetaminophen, involves a three-step procedure as outlined in Fig. P1.113. First, *p*-nitrophenol is catalytically hydrogenated in the presence of aqueous hydrochloric acid to the acid chloride salt of *p*-aminophenol with a 86.9% degree of completion. Next the salt is neutralized to obtain *p*-aminophenol with a 0.95 fractional conversion. Finally, the *p*-aminophenol is acetalated by reacting with acetic anhydryde, resulting in a yield of 3 kg mol of acetaminophen per 4 kg mol. What is the overall conversion fraction of *p*-nitrophenol to acetaminophen?

1.114. The most economic method of sewage wastewater treatment is bacterial digestion. As an intermediate step in the conversion of organic nitrogen to nitrates, it is reported that the *Nitrosomonas* bacteria cells metabolize ammonium compounds into cell tissue and expel nitrite as a by-product by the following overall reaction:

$$5CO_2 + 55NH_4^+ + 76O_2 \longrightarrow C_5H_7O_2N(\text{tissue}) + 54NO_2^- + 52H_2O + 109H^+$$

If 20,000 kg of wastewater containing 5% ammonium ions by weight flows

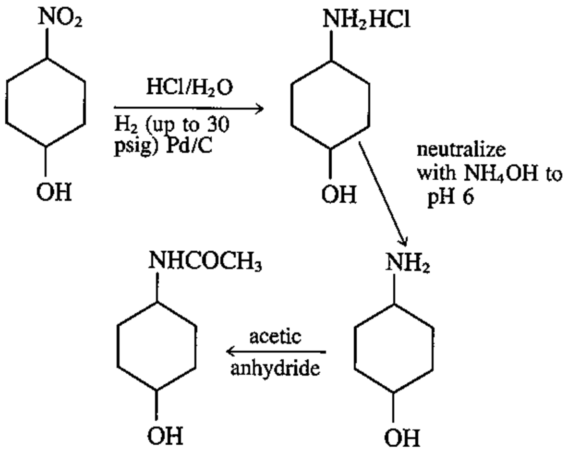


Figure P1.113

through a septic tank inoculated with the bacteria, how many kilograms of cell tissue are produced provided that 95% of the NH_4^+ is consumed?

1.115. One can view the blast furnace from a simple viewpoint as a process in which the principal reaction is

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

but some other undesired side reactions occur, mainly

$$Fe_2O_3 + C \longrightarrow 2FeO + CO$$

After mixing 600.0 lb of carbon (coke) with 1.00 ton of pure iron oxide, Fe_2O_3, the process produces 1200.0 lb of pure iron, 183 lb of FeO, and 85.0 lb of Fe_2O_3. Calculate the following items:

(a) The percentage of excess carbon furnished, based on the principal reaction
(b) The percentage conversion of Fe_2O_3 to Fe
(c) The pounds of carbon used up and the pounds of CO produced per ton of Fe_2O_3 charged
(d) What is the selectivity in this process?

1.116. Barite mineral ($BaSO_4$) is processed by heat fusion with soda ash (Na_2CO_3) followed by leaching with water to produce $BaCO_3$, which has several uses, including that of a rat poison. The overall reaction is

$$\begin{array}{lcccccc} & Na_2CO_3 & + & BaSO_4 & \longrightarrow & Na_2SO_4 & + & BaCO_3 \\ \text{Mol. wt.:} & 106 & & 233 & & 142 & & 197 \end{array}$$

The analysis shows the weight percents as: solid residue, 33.6% $BaSO_4$ and 66.4% $BaCO_3$; and soluble salts, 58.1% Na_2SO_4 and 41.9% Na_2CO_3. For the process, calculate:

(a) The composition of the mix before fusion
(b) The percent excess reactant
(c) The degree of completion

1.117. Diborane, B_2H_6, a possible rocket propellant, can be made by using lithium hydride (LiH):

$$6LiH + 2BCl_2 \longrightarrow B_2H_6 + 6LiCl$$

If you mix 200 lb of LiH with 1000 lb of BCl_3, you recover 45.0 lb of B_2H_6. Determine:

(a) The limiting reactant
(b) The excess reactant
(c) The percent excess reactant
(d) The percent conversion of LiH to B_2H_6
(e) The degree of completion of the reaction
(f) The yield of B_2H_6 based on the LiH charged (in lb/lb)
(g) The lb of LiCl produced

1.118. A common method used in manufacturing sodium hypochlorite bleach is by the reaction

$$Cl_2 + 2NaOH \longrightarrow NaCl + NaOCl + H_2O$$

Chlorine gas is bubbled through an aqueous solution of sodium hydroxide, after which the desired product is separated from the sodium chloride (a by-product of the reaction).

A water–NaOH solution that contains 1145 lb of pure NaOH is reacted with 851 lb of gaseous chlorine. The NaOCl formed weighs 618 lb.

(a) What is the limiting reactant?
(b) What was the percentage excess of the excess reactant used?
(c) What is the degree of completion of the reaction, expressed as the moles of NaOCl formed to the moles of NaOCl that would have formed if the reaction had gone to completion?
(d) What is the yield of NaOCl per amount of chlorine used (on a weight basis)?

1.119. An electric furnace produces phosphorus by the reaction

$$Ca_3(PO_4)_2(s) + 5C(s) + 3SiO_2(s) \longrightarrow 3CaSiO_3(s) + 5CO(g) + 2P(l)$$

The specific compounds in the slag *(solid product)* are $Ca_3(PO_4)_2$, $CaSiO_3$, and SiO_2. You analyze the slag from the reaction and find 2.0% P, 1% C, 36.0% CaO, and the rest silicon and oxygen compounds. Determine:

(a) The limiting reactant
(b) The excess reactants
(c) The kg of P actually produced per kg of $Ca_3(PO_4)_2$ charged to the process
(d) The kg mol of CO produced per kg of $Ca_3(PO_4)_2$ charged to the process
(e) The degree of completion of the reaction

1.120. An electric furnace produces iron (Fe, mol. wt. 55.85) from Fe_2O_3 by reaction with powdered coal (carbon). The reaction products are Fe, FeO, and CO. Twenty-five kilograms of Fe_2O_3 and 6 kg of C are charged to the furnace and after drawing off the Fe, the slag (FeO solid product remaining) is 3 kg. Determine:

(a) The limiting reactant
(b) The excess reactant
(c) The percent excess reactant
(d) The fractional degree of completion of the reaction

PROBLEMS THAT REQUIRE WRITING COMPUTER PROGRAMS

1.1. Write a program to convert °C into K, °F, and °R at 1°C intervals. Have the program arranged so that you can do the following:

(a) Read in a starting value of °C.

(b) Read in a stopping value of °C.

(c) Use a loop to convert °C to the other temperature scales at 1°C intervals between the starting and stopping values, inclusive.

(d) Print out the four temperatures for each conversion with appropriate column headings.

(e) Use comment lines where appropriate to indicate your procedure in conversion.

1.2. Write a computer program to convert millimeters of mercury into inches of mercury, feet of H_2O, and psia at 2 mm Hg (even-numbered) increments below 760 mm Hg. Have the computer arranged so that you can do the following:

(a) Read in a starting value for the millimeters of mercury.

(b) Stop at 760 mm Hg (the last value to be converted).

(c) Read in the necessary conversion factors, such as CPSIA in

$$\text{PSIA} = \text{CPSIA} * \text{HGMM}$$

(d) Use one-dimensional arrays to store values.

(e) Use a DO loop to compute all values. You must compute the number of iterations required with your program.

(f) Print out the results after all the conversions have been made.
  (1) Print your name at the top of the first page.
  (2) Print appropriate column headings at the top of each new page.
  (3) Print only 50 lines of conversion results per page.

1.3. Prepare a computer program to give the specific gravity of a fluid as a function of °Be (Baumé) and °API over the interval 0°–30° in 1° increments. Equation (1.10) gives the relation between specific gravity and °API (for liquids less dense than water), while the relationships for °Be are

liquids more dense than water

$$\text{sp gr} = \frac{145.0}{145.0 - {}^\circ\text{Be}}$$

liquids less dense than water

$$\text{sp gr} = \frac{140.0}{130.0 + {}^\circ\text{Be}}$$

Read the °API or °Be into the program as data.

MATERIAL BALANCES

2

Conservation laws occupy a special place in science and engineering. Common statements of these laws take the form of "mass (energy) is neither created nor destroyed," "the mass (energy) of the universe is constant," "the mass (energy) of any isolated system is constant," or equivalent statements. To refute a conservation law, it would be sufficient to find just one example of a violation.

But what degree of accuracy is needed to prove a violation? In an industrial environment, in spite of considerable effort, it is not possible to make a 99.9% closure of a mass balance. The results of errors in measurement in determining the amount of material in tanks, bins, drums, bags, and bottles; in obtaining representative samples; in analyzing the samples; and in determining the fate of raw materials fed into the system and products removed from it preclude such accuracy.

Our belief in the validity of the conservation laws rests on the experiences of Lavoisier and many of the scientists following in his path who studied chemical changes quantitatively and found invariably that the sum of the weights of the substances entering into a reaction equaled the sum of the weights of the products of the reaction. Thus our collective experience has been summed up and generalized as the law of the conservation of matter. Of course, we must exclude processes involving nuclear transformations, or else extend our law to include the conservation of both energy and matter.

Why study material balances as a separate topic? You will find that material balance calculations are almost invariably a prerequisite to all other calculations in the solution of both simple and complex chemical engineering problems. Furthermore, skills that you develop in analyzing material balances are easily transferred to other types of balances and other types of problems.

In this chapter we discuss the principle of the conservation of matter and how it can be applied to engineering calculations, making use of the background information discussed in Chap. 1. Figure 2.0 shows the relations between the topics discussed in this chapter and the general objective of making material and energy balances. In approaching the solution of material balance problems, we first consider how to analyze them in order to clarify the method and the procedure of solution. The aim will be to help you acquire a generalized approach to problem solving so that you may avoid looking upon each new problem, unit operation, or process as entirely new and unrelated to anything you have seen before. As you scrutinize the examples used to illustrate the principles involved in each section, explore the method of analysis, but avoid memorizing each example by rote, because, after all, they are only samples of the myriad of problems that exist or could be devised on the subject of material balances. Most of the principles we consider are of about the same degree of complexity as the law of compensation devised by some unknown, self-made philosopher who said: "Things are generally made even somewhere or some place. Rain always is followed by a dry spell, and dry weather follows rain. I have found it an invariable rule that when a man has one short leg, the other is always longer!"

In working these problems you will find it necessary to employ some engineering judgment. You think of mathematics as an exact science. For instance, suppose that it takes 1 man 10 days to build a brick wall; then 10 men can finish it in 1 day. Therefore, 240 men can finish the wall in 1 hr, 14,400 can do the job in 1 min. and with 864,000 men the wall will be up before a single brick is in place! Your password to success is the famous IBM motto: THINK.

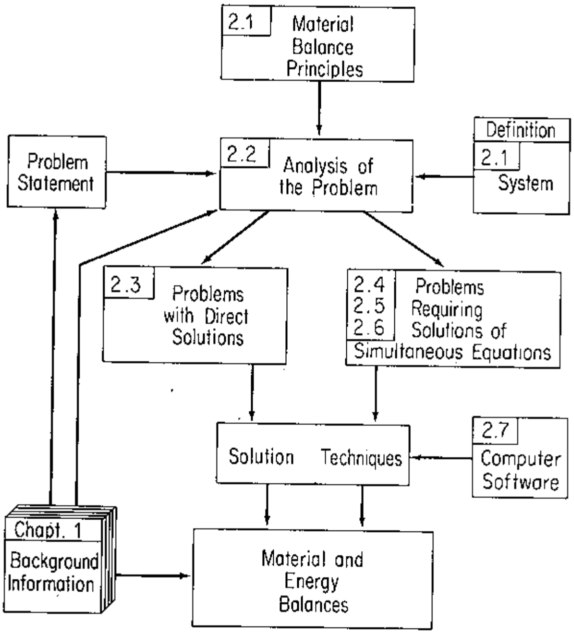


Figure 2.0 Hierarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

2.1 THE MATERIAL BALANCE

Your objectives in studying this section are to be able to:

1. Define the system and draw the system boundaries for which the material balance is to be made.
2. Explain the difference between an open and a closed system.
3. Write the general material balance in words including all terms. Be able to apply the balance to simple problems.
4. Cite examples of processes in which no accumulation takes place; no generation or consumption takes place; no mass flow in and out takes place.
5. Apply the material balance equation for the simplified case of input = output to the total mass of material and to an individual species.
6. Explain the circumstances in which the mass of a compound entering the system equals the mass of the compound leaving the system. Repeat for moles.

To make a material balance (or an energy balance as discussed in Chap. 4) for a process, you need to specify what the system is and outline its boundaries. According to the dictionary, a **process** is one or a series of actions or operations or treatments that result in an end [product]. Chemical engineering focuses on operations that cause physical and chemical change in materials. Innumerable textbooks[1] and reference books[2] give examples of processes such as

Chemical manufacture
Fluid transport
Handling of bulk solids
Size reduction and enlargement
Heat generation and transport
Distillation
Gas absorption
Bioreactions

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[1] McCabe, W. L., J. C. Smith, and P. Harriott, *Unit Operations of Chemical Engineering*, 4th ed., McGraw-Hill, NY, 1986.

[2] Perry, R. H. and D. W. Green, eds., *Chemical Engineers' Handbook*, 6th ed., McGraw-Hill, NY, 1984; Shreve, R. N. and J. A. Brink, *Chemical Process Industries*, 4th ed., McGraw-Hill, NY, 1977.

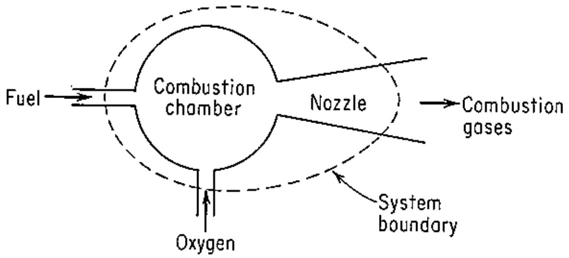

Figure 2.1 Flow (open) system defined for combustion.

and so on. The examples we use in this book often refer to abstractions of these processes, because we do not have the space here to describe the details of any of them. By **system** we mean any arbitrary portion or whole of a process set out specifically for analysis. Figure 2.1 shows a system in which flow and reaction take place; note particularly that the **system boundary** is formally circumscribed about the process itself to call attention to the importance of carefully delineating the system in each problem you work. An **open (or flow) system** is one in which material is transferred across the system boundary, that is, enters the system, leaves the system, or both. A **closed (or batch) system** is one in which there is no such transfer *during the time interval of interest*. Obviously, if you charge a reactor with reactants and take out the products, and the reactor is designated as the system, material is transferred across the system boundary. But you might ignore the transfer, and focus attention solely on the process of reaction that takes place only after charging is completed and before the products are withdrawn. Such a process would occur within a closed system.

A system boundary may be fixed with respect to the process equipment as in Fig. 2.1, or the boundary may be an imaginary surface that grows or shrinks as the process goes on. Think of a tube of toothpaste that is squeezed. A fixed boundary might be the tube itself, in which case mass crosses the boundary as you squeeze the tube. Or, you can imagine a flexible boundary surrounding the toothpaste itself that follows the extruded toothpaste, in which case no mass crosses the boundary.

A **material balance** is nothing more than an accounting for material flows and changes in inventory of material for a system. Examine Fig. 2.2. Equation (2.1) de-

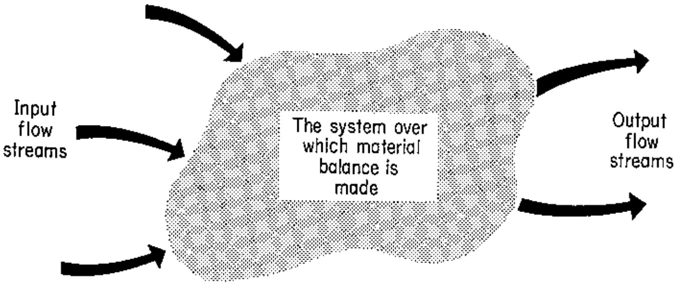

Figure 2.2 Any enclosed volume or system over which material balances are to be made. We are not concerned with the internal details, only with the passage of material across the volume boundaries and the change of material inside the system.

scribes in words the principle of the material balance applicable to processes both with and without chemical reaction:

$$\left\{\begin{matrix}\textbf{accumulation}\\ \textbf{within}\\ \textbf{the}\\ \textbf{system}\end{matrix}\right\} = \left\{\begin{matrix}\textbf{input}\\ \textbf{through}\\ \textbf{system}\\ \textbf{boundaries}\end{matrix}\right\} - \left\{\begin{matrix}\textbf{output}\\ \textbf{through}\\ \textbf{system}\\ \textbf{boundaries}\end{matrix}\right\} + \left\{\begin{matrix}\textbf{generation}\\ \textbf{within}\\ \textbf{the}\\ \textbf{system}\end{matrix}\right\} - \left\{\begin{matrix}\textbf{consumption}\\ \textbf{within}\\ \textbf{the}\\ \textbf{system}\end{matrix}\right\} \tag{2.1}$$

As a generic term, material balance can refer to a balance on a system for the

1. Total mass
2. Total moles
3. Mass of a chemical compound
4. Mass of an atomic species
5. Moles of a chemical compound
6. Moles of an atomic species
7. Volume (possibly)

With respect to a total mass balance, in this book the generation and consumption terms are zero whether a chemical reaction occurs in the system or not (we neglect the transfer between mass and energy in ordinary chemical processing)[3]; hence

$$\text{accumulation} = \text{input} - \text{output} \tag{2.2}$$

With respect to a balance on the total moles, if a chemical reaction does occur, you most likely will have to take into account the generation or consumption terms. In the absence of chemical reaction, the generation and consumption terms do not apply to a single chemical compound such as water or acetone; with a chemical reaction present in the system, the terms do apply.

From the viewpoint of both a mass balance or a mole balance for elements themselves, such as C, H, or O, the generation and consumption terms are not involved in a material balance. Finally, Eq. (2.1) should not be applied to a balance on a volume of material unless ideal mixing occurs (see Sec. 3.1) and the densities of the streams are the same. In this chapter, information about the generation and consumption terms for a chemical compound will be given *a priori* or can be inferred from the stoichiometric equations involved in the problem. Texts treating chemical reaction engineering describe how to calculate from basic principles gains and losses of chemical compounds.

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[3] For information concerning the conservation of mass and Einstein's principle in circumstances in which ordinary chemical reactions occur, read R. S. Treptow, *J. Chem. Educ.*, v. 63, pp. 103, 1052 (1986), or J. Maddox, *Nature*, v. 328, p. 755 (1987).

In Eq. (2.1) the accumulation term refers to a change in mass or moles (plus or minus) within the system with respect to time, whereas the transfers through the system boundaries refer to inputs to and outputs of the system. If Eq. (2.1) is written in symbols so that the variables are functions of time, the equation so formulated would be a differential equation. As an example, the differential equation for the O_2 material balance for the system illustrated in Fig. 2.1 might be written as

$$\frac{dn_{O_2 \text{ within system}}}{dt} = \dot{n}_{O_2 \text{ in}} - \dot{n}_{O_2 \text{ out}} - \dot{n}_{O_2 \text{ reacted}} \qquad (2.1a)$$

where $n_{O_2 \text{ within system}}$ denotes the moles of oxygen within the system boundary, and $\dot{n}_{O_2}$ denotes the rate at which oxygen enters, leaves or reacts, respectively, as indicated by the subscript. Each term in the differential equation represents a *rate* with the units of, say, moles per unit time. Problems formulated as differential equations with respect to time are called **unsteady-state** (or transient) problems and are discussed in Chap. 6. In contrast, in **steady-state** problems the values of the variables in the system do not change with time, hence the accumulation term in Eq. (2.1) is zero by definition.

In this Chapter for convenience in treatment we use an **integral balance** form of Eq. (2.1). What we do is to take as a basis a time period such as one hour or minute, and integrate Eq. (2.1a) with respect to time. The derivative (the left hand side) in the differential equation becomes

$$\int_{t_1}^{t_2} \frac{dn_{O_2 \text{ within system}}}{dt}\, dt = \int_{t_1}^{t_2} dn_{O_2 \text{ within system}} = n_{O_2}\big|_{t_2} - n_{O_2}\big|_{t_1} = \Delta n$$

where Δn is the difference in the n_{O_2} within the system at t_2 less that at t_1. A term on the right hand side of the differential equation becomes, as for example the first term,

$$\int_{t_1}^{t_2} \dot{n}_{O_2 \text{ in}}\, dt = n_{O_2 \text{ in}}$$

where $n_{O_2 \text{ in}}$ represents the entire net quantity of oxygen introduced into the system between t_1 and t_2. If the flow rate of O_2 into the system shown in Fig. 2.1 is constant at the rate of 1200 moles/hr, by choosing a basis of one hour

$$\int_0^1 \frac{1200 \text{ mol}}{\text{hr}} \left| \frac{dt \text{ hr}}{} \right. = 1200 \text{ mol } (1 - 0) = 1200 \text{ mol}$$

Most, but not all, of the problems discussed in this chapter are steady-state problems treated as integral balances for fixed time periods. If no accumulation occurs in a problem, and the generation and consumption terms can be omitted from consideration, the material balances reduce to the very simple relation

$$\left\{\begin{matrix}\text{mass/mole input}\\ \text{through the}\\ \text{system boundaries}\end{matrix}\right\} = \left\{\begin{matrix}\text{mass/mole output}\\ \text{through the}\\ \text{system boundaries}\end{matrix}\right\} \qquad (2.3)$$

or briefly: "What comes in must go out."

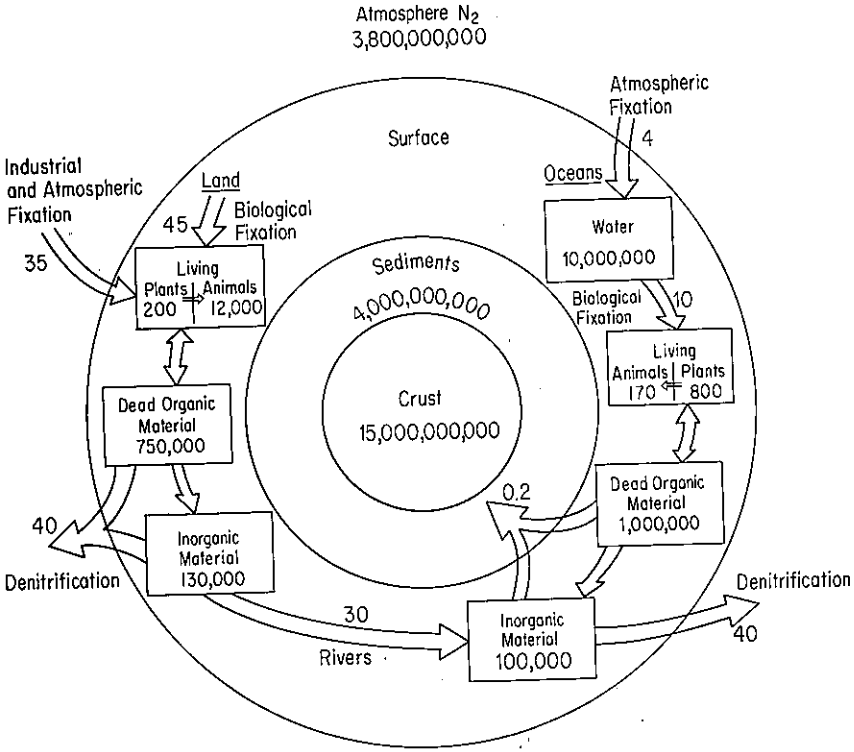


Figure 2.3 Distribution and annual rates of transfer of nitrogen in the biosphere (in millions of metric tons).

Material balances can be made for a wide variety of materials, at many scales of size for the system and in various degrees of complication. To obtain a perspective as to the scope of material balances, examine Figs. 2.3 and 2.4. Figure 2.3 illustrates a world-scale set of mass balances for nitrogen for different systems, while Fig. 2.4 shows a **flowsheet** for a chemical plant that includes both mass and energy flows.

In the process industries, material balances assist in the planning for process design, in the economic evaluation of proposed and existing processes, in process control, and in process optimization. For example, in the extraction of soybean oil from soybeans, you could calculate the amount of solvent required per ton of soybeans or the time needed to fill up the filter press, and use this information in the design of equipment or in the evaluation of the economics of the process. All sorts of raw materials can be used to produce the same end product, and quite a few different types of processing can achieve the same end result, so that case studies (simulations) of the processes can assist materially in the financial decisions that must be made.

Material balances are also used in the hourly and daily operating decisions of plant managers. If there are one or more points in a process where it is impossible or

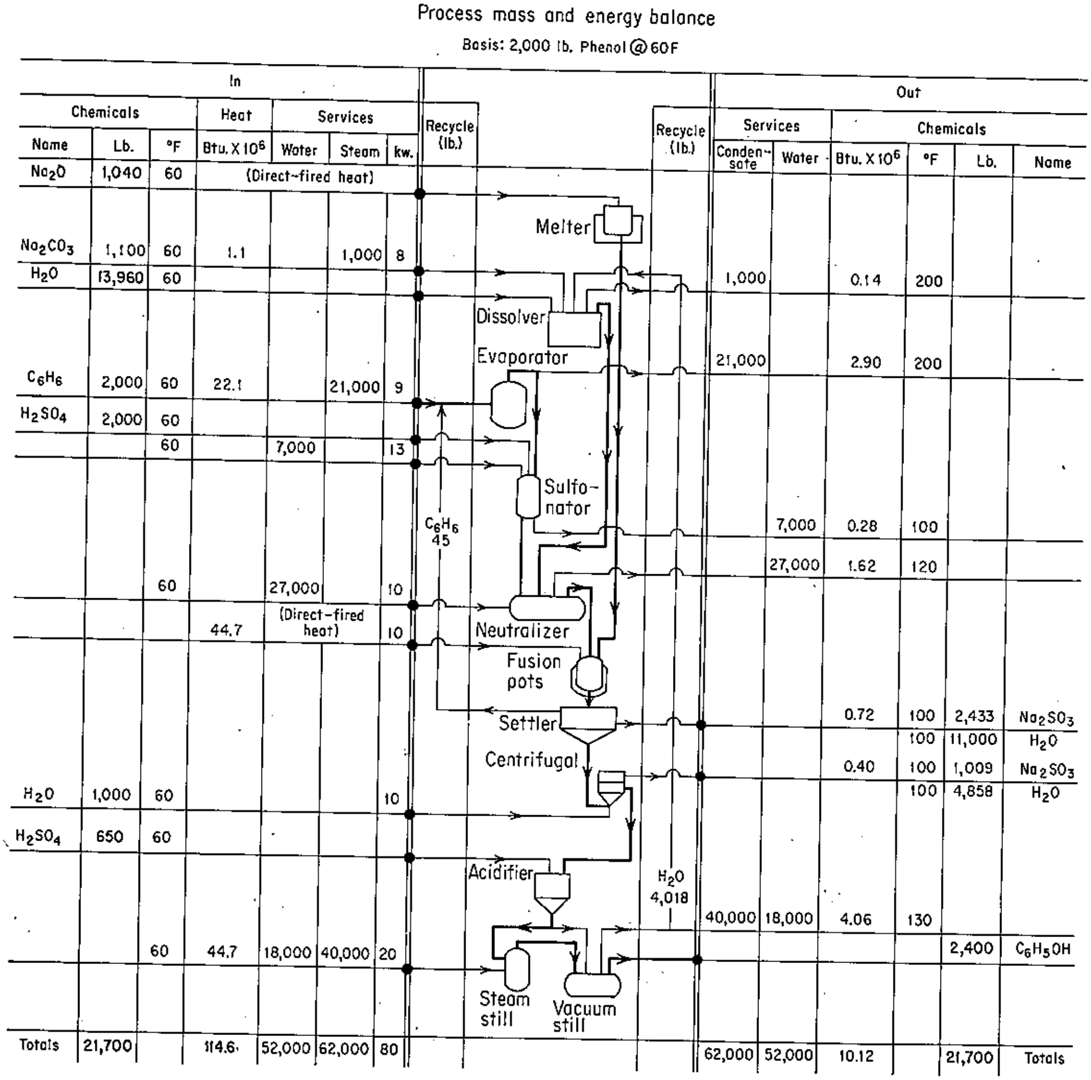


Figure 2.4 Material (and energy) balances in the manufacture of phenol presented in the form of a ledger sheet. [Taken from *Chem. Eng.*, p. 117 (April 1961) by permission.]

uneconomical to collect data, then if sufficient other data are available, by making a material balance on the process it is possible to get the information you need about the quantities and compositions at the inaccessible location. In most plants a mass of data is accumulated in data bases on the quantities and compositions of raw materials, intermediates, wastes, products, and by-products that is used by the production and accounting departments, and that can be integrated into a revealing picture of company operations.

We should also note in passing that balances using Eq. (2.1) can be made on many other quantities in addition to mass and moles. Balances on dollars are common (your bank statement, for example) as are balances on the number of entities, as in traffic counts, population balances, and social services.

We now look at some simple examples of the application of Eq. (2.1)

EXAMPLE 2.1 Total Mass Balance

A thickener in a waste disposal unit of a plant removes water from wet sewage sludge as shown in Fig. E2.1. How many kilograms of water leave the thickener per 100 kg of wet sludge that enter the thickener? The process is in the steady state.

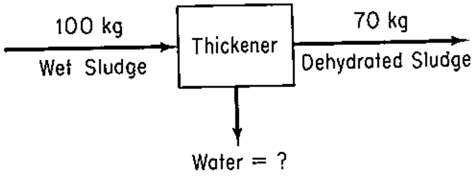


Figure E2.1

Solution

The system is the thickener (an open system). No accumulation, generation, or consumption occur. Use Eq. (2.3). The total mass balance is

In	=	*Out*
100 kg	=	70 kg + kg of water

Consequently, the water amounts to 30 kg.

EXAMPLE 2.2 Mass Balances for a Fluidized Bed

Hydrogenation of coal to give hydrocarbon gases is one method of obtaining gaseous fuels with sufficient energy content for the future. Figure E2.2 shows how a free-fall fluidized-bed reactor can be set up to give a product gas of high methane content.

Suppose, first, that the gasification unit is operated without steam at room temperature (25°C) to check the gas flow rate monitoring instruments.

(a) If 1200 kg of coal per hour (assume that the coal is 80% C, 10% H, and 10% inert material) is dropped through the top of the reactor without the air flowing, how many kg of coal leave the reactor per hour?

(b) If, in addition to the coal supplied, 15,000 kg of air per hour is blown into the reactor, at 25°C, how many kg of air per hour leave the reactor?

(c) Finally, suppose that the reactor operates at the temperatures shown in Fig. E2.2, and that 2000 kg of steam (H_2O vapor) per hour are blown into the reactor along with 15,000 kg/hr of air and the 1200 kg of coal. How many kg of gases exit the reactor per hour assuming complete combustion of the coal?

Solution

Basis: 1 hr

The system is the fluidized bed.

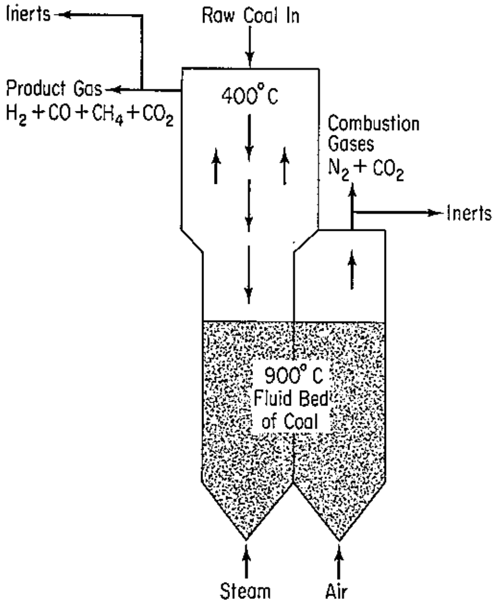


Figure E2.2

(a) If coal is dropped into the vessel without airflow or reaction, as would be the case at 25°C, 1200 kg of coal must remain in the reactor representing the accumulation:

$$\begin{array}{cccc} \underline{\textit{Accumulation}} & = \underline{\textit{Input}} & - & \underline{\textit{Output}} \\ 1200 & = 1200 & - & 0 \end{array}$$

Hence 0 kg of coal leave the reactor per hour.

(b) Because the accumulation is zero for air in the reactor, and no reaction occurs

$$\begin{array}{cccc} \underline{\textit{Output}} & = \underline{\textit{Input}} & - & \underline{\textit{Accumulation}} \\ 15{,}000 & = 15{,}000 & - & 0 \end{array}$$

The output is 15,000 kg/hr.

(c) All the material except the inert portion of the coal leaves as a gas. Consequently, we can add up the total mass of material entering the unit, subtract the inert material, and obtain the mass of combustion gases by difference:

$$\begin{array}{c|c} 1200\text{ kg coal} & 10\text{ kg inert} \\ \hline & 100\text{ kg coal} \end{array} = 120\text{ kg inert}$$

Entering material	*kg*
Coal	1,200
Air	15,000
Steam	2,000
Total	18,200 − 120 = 18,080 kg/hr of gases

EXAMPLE 2.3 Material Balances

(a) If 300 lb of air and 24.0 lb of carbon are fed to a reactor (see Fig. E2.3) at 600°F and after complete combustion no material remains in the reactor, how many pounds of carbon will have been removed? How many pounds of oxygen? How many pounds total?

(b) How many moles of carbon and oxygen enter? How many leave the reactor?

(c) How many total moles enter the reactor and how many leave the reactor?

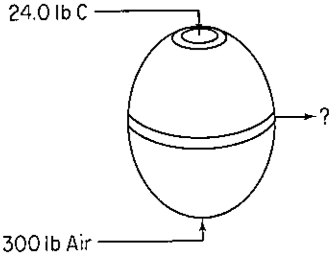


Figure E2.3

Solution

This is a problem without any accumulation. The system is the reactor and will be treated as an open system as shown in Fig. E2.3. We want to make a total mass balance and CO_2 and O_2 mole balances.

Basis: 300 lb air

First we calculate the lb mol of oxygen, nitrogen, and carbon entering:

$$\begin{array}{c|c|c} 300\text{ lb air} & 1\text{ lb mol air} & 21.0\text{ lb mol }O_2 \\ \hline & 29.0\text{ lb air} & 100\text{ lb mol air} \end{array} = 2.17\text{ lb mol }O_2$$

$$\begin{array}{c|c} 2.17\text{ lb mol }O_2 & 79.0\text{ lb mol }N_2 \\ \hline & 21.0\text{ lb mol }O_2 \end{array} = 8.17\text{ lb mol }N_2$$

$$\begin{array}{c|c} 24.0\text{ lb C} & 1\text{ lb mol C} \\ \hline & 12.0\text{ lb C} \end{array} = 2.00\text{ lb mol C}$$

The chemical reaction is

$$C + O_2 \longrightarrow CO_2$$

From the stoichiometry, 2.00 lb mol C requires 2.00 lb mol O_2 for complete combustion, so that a mole balance for O_2 leads to the conclusion that oxygen is the excess reactant, and that

$$\begin{array}{ccccccc} \underline{\textit{out}} & & \underline{\textit{in}} & & \underline{\textit{consumption}} & & \\ O_2\text{ out} & = & 2.17 & - & 2.00 & = & 0.17\text{ lb mol} \end{array}$$

The carbon as C that exits is zero because all the C as such is consumed; from the stoichiometry we conclude for the CO_2 that

$$\begin{array}{ccccccc} \underline{\textit{out}} & & \underline{\textit{in}} & & \underline{\textit{generation}} & & \\ CO_2 & = & 0 & + & 2.00 & = & 2.00\text{ lb mol} \end{array}$$

Summing up all the calculations in the form of a table, we have (mol. wt. atmospheric N_2 = 28.2)

	In		Out	
	lb	lb mol	lb	lb mol
C	24.0	2.00	0	0
O_2	69.5	2.17	5.5	0.17
N_2	230.5	8.17	230.5	8.17
CO_2	0	0	88.0	2.00
Total	324	12.34	324	10.34

We can now answer the questions posed in the problem.

(a) No carbon will be removed as the element C, but 88 lb of CO_2 will be removed, which contains 24 lb of C. Only 0.17 lb mol of O_2 will be removed as O_2; the remainder of the O_2 is in the CO_2. The total pounds removed will be that placed initially in the reactor, namely 324 lb.

(b) 2.00 lb mol C and 2.17 lb mol of O_2 enter the reactor, and 0 lb mol of C and 0.17 lb mol of O_2 as elemental species leave the reactor.

(c) 12.34 lb mol enters the reactor and 10.34 lb mol leaves the reactor.

Note that instead of making mole balances on CO_2 and O_2 as in Example 2.3, we could have made mole, or mass, balances on the elements C and O (or oxygen expressed as O_2) that would lead to the same final information. **You can avoid using the generation and consumption terms in Eq. (2.1) if you make element balances.**

Mole Balance

$$\begin{array}{rccccccccccc}
 & \multicolumn{5}{c}{\text{In}} & & \multicolumn{5}{c}{\text{Out}}\\
 & \underline{C} & & \underline{CO_2} & & \underline{O_2} & & \underline{C} & & \underline{CO_2} & & \underline{O_2}\\
\text{C:} & 2 & + & 0 & + & 0 & = & 0 & + & 2 & + & 0\\
\text{O:} & 0 & + & 0 & + & 2.17(2) & = & 0 & + & 2(2) & + & 0.17(2)\\
\text{or } O_2\text{:} & 0 & + & 0 & + & 2.17 & = & 0 & + & 2 & + & 0.17
\end{array}$$

Mass Balance

$$\begin{array}{rccccccccccc}
\text{C:} & 24 & + & 0 & + & 0 & = & 0 & + & 24 & + & 0\\
\text{O:} & 0 & + & 0 & + & 69.5 & = & 0 & + & 64 & + & 5.5\\
\text{or } O_2\text{:} & 0 & + & 0 & + & 69.5 & = & 0 & + & 64 & + & 5.5
\end{array}$$

Of course, the element balances make use of the same stoichiometric information, as do the component balances.

What can we conclude from Example 2.3? You can observe that although the total mass put into a process and the total mass recovered from a process have been shown to be equal, there is no such equality on the part of the *total* moles in and out, *if* a chemical reaction takes place. What is true is that the number of atoms of an element (such as C, O, or even oxygen expressed as O_2) put into a process must equal the atoms of the same element leaving the process. In Example 2.3 the total moles in and out are shown to be unequal, but the moles of O in (or moles expressed as O_2) equal the moles of O (or moles expressed as O_2) leaving.

Keeping in mind the remarks above for processes involving chemical reactions, we can summarize the circumstances under which the input equals the output for *steady-state processes* (no accumulation) as follows:

	Equality required for input and output of steady-state process	
Type of balance	Without chemical reaction	With chemical reaction
Total balances		
Total mass	Yes	Yes
Total moles	Yes	No
Component balances		
Mass of a pure compound	Yes	No
Moles of a pure compound	Yes	No
Mass of an atomic species	Yes	Yes
Moles of an atomic species	Yes	Yes

We now turn to more detailed consideration of material balance problems. Your basic task is to turn the problem, expressed in words, into a quantitative form, expressed in mathematical symbols and numbers, and then solve the resulting mathematical equations.

Self-Assessment Test

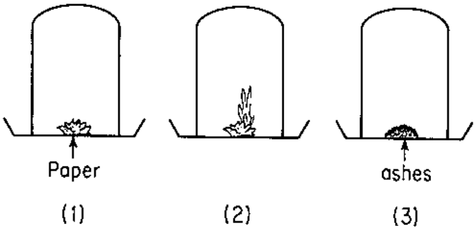
1. Draw a sketch of the following processes and place a dashed line around the system:
   (a) Tea kettle
   (b) Fireplace
   (c) Swimming pool
2. Show the materials entering and leaving the systems in problem 1. Designate the time interval of reference and classify the system as open or closed.
3. Write down the general material balance in words. Simplify it for each process in problem 1 above, stating the assumptions made in each simplification.
4. Classify the following processes as (1) batch, (2) flow, (3) neither, or (4) both on a time scale of one day:
   (a) Oil storage tank at a refinery
   (b) Flush tank on a toilet
   (c) Catalytic converter on an automobile
   (d) Gas furnace in a home

5. What is a steady-state process?
6. Do the inputs and outputs of the chemicals in Fig. 2.3 agree? Why not? Repeat for Fig. 2.4 for the chemicals.
7. Define a material balance. A mass balance.
8. Answer the following true (T) or false (F).
   (a) If a chemical reaction occurs, the total masses entering and leaving the system for a steady-state process are equal.
   (b) In combustion, all of the moles of C that enter a steady-state process exit from the process.
   (c) The number of moles of a chemical compound entering a steady-state process in which a reaction occurs with that compound can never equal the number of moles of that same compound leaving the process.
9. List the circumstances for a steady-state process in which the number of moles entering the system equals the number of moles leaving the system.

Thought Problem

1. Examine the Figure. A piece of paper is put into the bell in (1). In picture (2) we set fire to the paper. Ashes are left in (3). If everything has been weighed (the bell, the dish and the substances) in each case, we would observe that:
   (a) Case 1 would have the larger weight.
   (b) Case 2 would have the larger weight.
   (c) Case 3 would have the larger weight.
   (d) None of the above.

   Explain your answer.



2.2 PROGRAM OF ANALYSIS OF MATERIAL BALANCE PROBLEMS

Your objectives in studying this section are to be able to:

1. Define what the term "solution of a material balance problem" means.
2. Ascertain that a unique solution exists for a problem using the given data, and/or ascertain the number of degrees of freedom in a problem so that additional information can be obtained (and get it).
3. Decide which equations to use if you have redundant equations.

4. Solve a set of *n* independent equations containing *n* variables whose values are unknown.
5. Retain in memory and recall as needed the implicit constraints in a problem.
6. Prepare material flow diagrams from word problems.
7. Translate word problems and the associated diagrams into material balances with properly defined symbols for the unknown variables and consistent units for steady-state processes with and without chemical reaction.
8. State the maximum number of independent equations that can be generated in a specific problem.
9. Recite the 10 steps used to analyze material balance problems so that you have an organized strategy for solving material balance problems.

One of the main objectives you should have in studying this chapter is to develop a logical methodology of your own to solve material balance problems. Descartes summed up the matter more than three centuries ago, when he wrote in his "Discours de la Methode": "Ce n'est pas assez d'avoir l'esprit bon, mais le principal est de l'appiquer bien." In English: "It is not enough to have a good intelligence—the principal thing is to apply it well."

Much of the remaining portion of this chapter demonstrates the techniques of analyzing and solving problems involving material balances. Later portions of the text consider the case of combined material and energy balances. By **solving** we mean obtaining a **unique** solution. Refer to Appendix L for more information about the concept of a unique solution if the concept is not clear to you. Because material balance problems all involve the same principle, although the details of the applications of the principle may differ slightly, we shall examine in this section a generalized method of analyzing such problems which can be applied to the solution of any type of material balance problem.

We are going to discuss a strategy of analysis of material balance problems that will enable you to understand, first, how similar these problems are, and second, how to solve them in the most expeditious manner. For some types of problems the method of approach is relatively simple and for others it is more complicated, but the important point is to regard problems in distillation, crystallization, evaporation, combustion, mixing, gas absorption, or drying not as being different from each other but as being related from the viewpoint of how to proceed to solve them.

An orderly method of analyzing problems and presenting their solutions represents training in logical thinking that is of considerably greater value than mere knowledge of how to solve a particular type of problem. Understanding how to approach these problems from a logical viewpoint will help you to develop those fundamentals of thinking that will assist you in your work as an engineer long after you have read this material. But keep in mind the old Chinese proverb:

> None of the secrets of success will work unless you do.

First, let us examine how many material balances you can write in any given problem using Eq. (2.1). Whether a chemical reaction occurs or not, you can write for the defined system a balance on

(a) Total mass

(b) Mass (or moles) of each atomic species (H, C, O, etc.)

without using the generation or consumption terms in Eq. (2.1). If a chemical reaction does not occur, you can also write a mass (or mole) balance for each component present in the system without involving the generation and consumption terms. How many balances are required to solve a problem? **You have to have the same number of independent balances as the number of variables whose values are unknown** (and are to be calculated). Refer to Appendix L for instances in which too few or too many equations are evolved from a problem. Thus, there is no point in beginning to solve a set of material balances unless you can be certain that the equations have a unique solution.

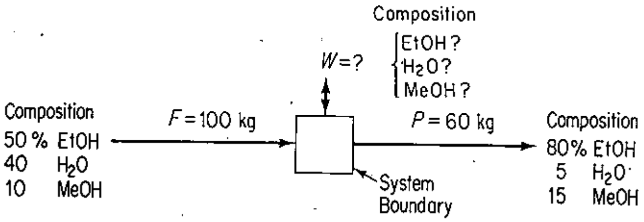


Figure 2.5 A process with three components without chemical reaction.

You can gain some experience by making mass balances on one unit for a simple problem comprised of just three components, as illustrated in Fig. 2.5. In Secs. 2.5 and 2.6 we will take up material balance problems involving more than one system. In Fig. 2.5 the system is the box, and we assume that the process is in the steady state without reaction, so that Eq. (2.3) applies. An independent mass balance equation based on Eq. (2.3) can be written for each compound involved in the process defined by the system boundary. We will use the symbol ω with an appropriate subscript to denote the mass fraction of a component in the streams F, W, and P, respectively. Each mass balance will have the form

$$\omega_{i,F}F = \omega_{i,P}P + \omega_{i,W}W \tag{2.4}$$

but we will, of course, insert the known values of the stream flow rates and mass fractions instead of the symbols where possible. Here are the three balances:

$$\begin{array}{llcll} & \underline{\textit{In}} & & \underline{\textit{Out}} & \\ \text{EtOH:} & (0.50)(100) & = & (0.80)(60) + \omega_{\text{EtOH},W}(W) & (2.4a) \\ \text{H}_2\text{O:} & (0.40)(100) & = & (0.05)(60) + \omega_{\text{H}_2\text{O},W}(W) & (2.4b) \\ \text{MeOH:} & (0.10)(100) & = & (0.15)(60) + \omega_{\text{MeOH},W}(W) & (2.4c) \end{array}$$

In addition, we can write a balance for the total material in and out:

$$\begin{array}{lcl} & \underline{\mathit{In}} & \underline{\mathit{Out}} \\ \text{Total:} & (1.00)\,100 = & (1.00)(60) + (\omega_{\mathrm{EtOH},W} \\ & & + \omega_{\mathrm{H_2O},W} + \omega_{\mathrm{MeOH},W})(W) \end{array} \tag{2.4d}$$

Remember that implicit constraints (equations) exist in the problem formulation because of the definition of mass fraction: namely, that the sum of the mass fractions in each stream must be unity:

$$\omega_{\mathrm{EtOH}} + \omega_{\mathrm{H_2O}} + \omega_{\mathrm{MeOH}} = 1 \tag{2.5}$$

We could substitute Eq. (2.5) into Eq. (2.4d) to simplify the latter equation, or retain it as a separate equation.

First, let us count the number of independent equations. You should recognize that not all of the four mass balances [Eqs. (2.4a)–(2.4d)], are independent equations. Do you see how the sum of the three component balances (2.4a), (2.4b), and (2.4c) equals the total mass balance? In any problem you can substitute the total material balance for any one of the component material balances if you plan to solve two or more equations simultaneously or if the substitution makes the solution procedure simpler.

Let us just consider Eq. (2.4a)–(2.4c) and (2.5). Are they a set of independent equations? If the answer (yes) is not obvious to you from the way in which the equations were formulated, you should review Appendix L to ascertain how to determine in a formal way whether the equations in a set of equations are independent. In general, **but not always,** in the absence of reactions, the number of independent equations equals the number of chemical compounds present, and with reactions occurring, the number of independent equations equals the number of atomic species present. But you may say the equations as posed are not linear because a mass fraction, an unknown, multiplies W, also unknown. However, Eq. (2.5) can be substituted into Eq. (2.4d), the latter solved directly for W, and W substituted into each of Eq. (2.4a)–(2.4c). The result is three linear equations. Can you show that they are independent?

In the first formulation of the problem, we had four independent equations to solve, Eqs. (2.4a)–(2.4c) plus Eq. (2.5). How many variables can have unknown values if a unique solution is to be obtained? Four! Let us count the number of variables whose values are unknown: W, $\omega_{\mathrm{EtOH},W}$, $\omega_{\mathrm{H_2O},W}$, and $\omega_{\mathrm{MeOH},W}$. The problem specifications worked out quite well—we have the same number of independent equations as unknown values of variables, and can solve the four equations to get a unique solution. To solve the equations as simply as possible, in this particular case you should note by inspection that the equations are not badly *coupled together* by the unknowns and can be reduced to three uncoupled independent linear equations by substituting Eq. (2.5) into Eq. (2.4), solving the latter for W, and substituting the value of W into Eq. (2.4a)–(2.4c). How many variables can have unknown values with three independent equations? Just three. You can solve each of the Eqs. (2.4a)–(2.4c) as simplified separately.

What should you do if the count of independent equations and unknown variables does not match up? The best procedure is to review your analysis of the problem to make sure that you have not ignored some equation(s) or variable(s), double counted, forgotten to look up some missing data, or made some error in your assumptions. For example, let us suppose that the value of P in Fig. 2.5 is not known. The mass balances and summation of mole fraction equations remain the same except that the symbol P representing a variable whose value is unknown is substituted for 60 kg. As a result, the problem contains four independent equations and five unknown variables, and thus has no unique solution unless one more independent equation or piece of information can be assembled. In some problems, no basis is cited, and the number of unknowns is one greater than the number of independent equations. In such a case, you can select an arbitrary basis of 1 or 100 kg, lb, mol, and so on, to provide the essential extra piece of information needed to obtain a unique solution.

Finally, examine Fig. 2.6. How many component mass balances can you make for the process in the figure? The answer is three!

$$50 = 0.80P + 0.05W$$

$$40 = 0.05P + 0.925W$$

$$10 = 0.15P + 0.025W$$

How many unknown variables are there? Two is the answer. Clearly, the problem is overspecified and does not have a unique solution as posed unless one of the equations is redundant. Can you show by the method described in Appendix L, or by substitution, that only two of the component balances (any two) are independent and the third is dependent (redundant)?

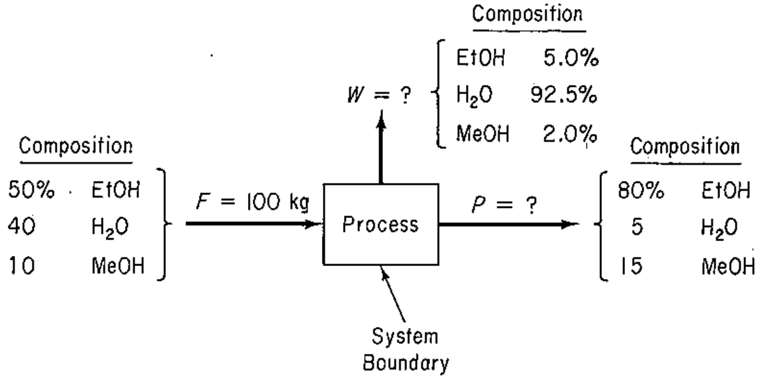


Figure 2.6 A steady state process with one input and two outputs.

If you use the Gauss–Jordan method outlined in Sec. L.1, you will find that the transformed augmented matrix for the set of equations above in the format of Eq. (L.4) will have only zeros in one row, indicating that one equation is not independent and hence redundant. (As explained in Appendix L, if the determinant of the augmented matrix were not equal to zero, the rank of the augmented matrix would be 3 and the rank of the coefficient matrix would be equal to 2, and consequently the equations would not have a unique solution.)

Could we have made mole balances instead of mass balances for the problem illustrated in Fig. 2.5? Certainly, because no chemical reaction occurs, but it would be inefficient to write such balances. However, if the concentrations had been given in mole percent (which they were not because the flows were of liquids) and *F* and *P* were stated in moles, mole balances would be more convenient to write than mass balances. In such cases, Eq. (2.6), the summation of mole fractions

$$x_{\text{EtOH}} + x_{\text{H}_2\text{O}} + x_{\text{MeOH}} = 1 \tag{2.6}$$

would be an implied independent equation analogous to Eq. (2.5).

Now let us look at material balances in which chemical reactions are involved. How does the procedure for analysis differ from the previous analysis for the case without chemical reaction? As mentioned in Sec. 2.1, because moles of a species and total moles are not conserved when a chemical reaction takes place, you will find it convenient to make the balances on the total mass and the mass or moles of each atomic species or multiple thereof (i.e., hydrogen expressed as H_2). For example, look at Fig. 2.7. Note that the flows in Fig. 2.7 are expressed as mass flows, but the compositions are in mole percent because the compounds are gases. We have no information about the extent of reaction or fraction conversion, but, you can write a total mass (not mole) balance, and a carbon, a hydrogen, a nitrogen, and an oxygen balance on the atomic species. Only four of the balances would be independent. The carbon balance might be in terms of C, and the hydrogen, nitrogen, and oxygen balances in terms of H_2, N_2, and O_2, respectively, or, if you prefer, in terms of H, N, and O. In making the balances on the atomic species, keep in mind that the units for each species balance can be either mass or moles. Do you understand why?

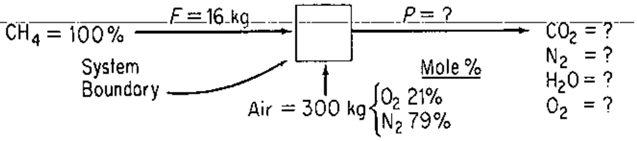


Figure 2.7 A steady state flow process with chemical reactions occuring and complete combustion.

Because you can make four independent balances for the process shown in Fig. 2.7, you can solve for four variables whose values are unknown in the process, such as n_{CO_2}, n_{N_2}, n_{O_2}, and $n_{\text{H}_2\text{O}}$, where *n* is the number of moles of each species in *P*; *P* would be the sum of the four *n*'s:

$$P = n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + n_{\text{O}_2} + n_{\text{N}_2} \tag{2.7a}$$

The element balances in moles (on the basis of 16 kg of $CH_4 \equiv 1$ kg mol CH_4) are

$$\begin{array}{c|c} 300 \text{ kg air} & 1 \text{ kg mol air} \\ \hline & 29 \text{ kg air} \end{array} = 10.35 \text{ kg mol air}$$

Balance	*CH_4 in*	*Air in*		*P out*	
C:	1		=	n_{CO_2}	(2.7b)
H_2:	2		=	n_{H_2O}	(2.7c)
O_2:		$10.35(.21) = 2.17$	=	$0.5n_{H_2O} + n_{O_2} + n_{CO_2}$	(2.7d)
N_2:		$10.35(.79) = 8.17$	=	n_{N_2}	(2.7e)

Use of the stoichiometric equation

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

and the concepts discussed in Sec. 1.9 (plus the assumption of complete combustion of CH_4) also leads to the conclusion that $n_{CO_2} = 1$ and $n_{H_2O} = 2$. The oxygen exiting would have to be calculated from the oxygen balance.

Instead of letting the unknown variables exiting the process in Fig. 2.7 be n, they could have been x_i, the mole fractions of each component. Then five variables whose values were unknown would exist: x_{CO_2}, x_{H_2O}, x_{O_2}, x_{N_2}, and P. Only four balances are independent. Have we made it impossible to solve this problem by just changing the variables? Of course not. *Hint:* Recall Eq. (2.6). Does an analogous independent equation apply if you make the unknowns mole fractions of the exiting components? The equations would be

$$\begin{aligned}
&C: && 1(1.0) && = P(x_{CO_2}) && (2.8a)\\
&H_2: && 1(2.0) && = P(x_{H_2O}) && (2.8b)\\
&O_2: && 2.17 && = P(0.5x_{H_2O} + x_{O_2} + x_{CO_2}) && (2.8c)\\
&N_2: && 8.17 && = P(x_{N_2}) && (2.8d)\\
&x_{CO_2} + x_{H_2O} + x_{O_2} + x_{N_2} = 1 && && && (2.8e)
\end{aligned}$$

You will find by experience that the second formulation of the problem is as straightforward as the first, but is a bit more complex to solve. Ask yourself the question: How would the formulation in Eq. (2.8e) compare with that in Eq. (2.7a) if you multiplied Eq. (2.8e) by P? Is $Px_i = n_i$? What are the units of the product of P and x?

EXAMPLE 2.4 Material Balances for a Distillation Column

A continuous still is to be used to separate acetic acid, water, and benzene from each other. On a trial run, the calculated data were as shown in Fig. E2.4. Data recording the benzene composition of the feed were not taken because of an instrument defect. The problem is to calculate the benzene flow in the feed per hour. How many independent material balance equations can be formulated for this problem? How many variables whose values are unknown exist in the problem?

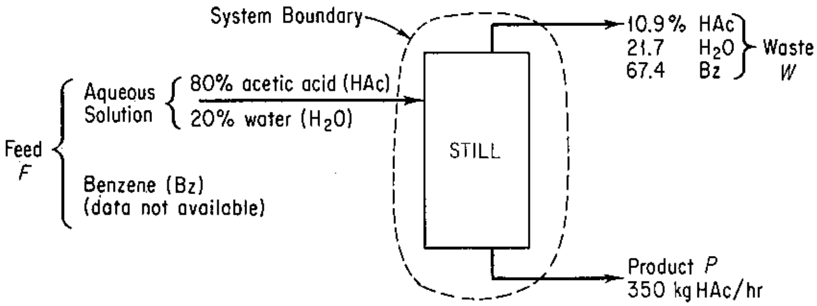


Figure E2.4

Solution

Examine Fig. E2.4. No reaction takes place, and the process is in the steady state. Values of two streams, W and F, are not known if 1 hr is taken as a basis, nor is the concentration of the benzene in F, $\omega_{Bz,F}$. (If you know the concentration of benzene in F, you know all the concentrations in the aqueous feed.) Three components exist in the problem, hence three mass balances can be written down (the units are kg):

Balance	*F in*	*W out*	*P out*	
HAc	$0.80(1 - \omega_{Bz,F})F$	$= 0.109W +$	350	(a)
H_2O	$0.20(1 - \omega_{Bz,F})F$	$= 0.217W +$	0	(b)
Benzene	$\omega_{Bz,F}F$	$= 0.674W +$	0	(c)

The total balance would be: $F = W + 350$ in kg. Are the three component balances independent? Because of the zero terms in the right-hand sides of Eqs. (b) and (c), no variation or combination of Eqs. (b) and (c) will lead to Eq. (a). Are Eqs. (b) and (c) redundant equations? No constant exists that when multiplied into Eq. (b) gives Eq. (c), hence the three mass balances are independent.

A more formal way of establishing independence is to form the coefficient matrix of the equations as explained in Sec. L.1:

$$\begin{array}{ccc} F & \omega_{Bz,F}F & W \\ \left[\begin{array}{c} 0.80 \\ 0.20 \\ 0 \end{array}\right. & \begin{array}{c} -0.80 \\ -0.20 \\ 1 \end{array} & \left.\begin{array}{c} -0.109 \\ -0.217 \\ -0.674 \end{array}\right] \end{array}$$

Can you show by elementary operations that the matrix is of full rank, hence the three component mass balances are independent?

EXAMPLE 2.5 Determination of the Number of Independent Balances

The organism *Lymomonos mobilis* is used to convert carbohydrates to ethanol. Glucose (formula $C_6H_{12}O_6$, mol. wt. 180 g/gmol) in a 100 g/L feed solution is converted to ethanol and carbon dioxide in a fermentation tank. The problem is to determine the final molar concentration of ethanol in the product stream and the number of liters of carbon dioxide gas produced at atmospheric pressure and temperature per liter of feed. Assume that carbon dioxide is insoluble in the liquid. Note that the water in the solution is not involved in the overall metabolism, and that for our purposes the mass flow rates of the materials out of and into the fermenter are constant.

How many independent material balances can be made for this problem, and how many values of the variables are unknown?

Solution

Figure E2.5 illustrates the steady-state process. All of the compositions are known. Three variables have values that are unknown if F is the basis: B, P, and G. Because the concentrations are in moles, we will make mole balances on the elements present. For convenience in presentation, we will take as a basis:

$$\frac{100\text{g}}{} \left| \frac{1 \text{ g mol}}{180 \text{ g}} \right. = 0.556 \text{ g mol of glucose that enters in } F$$

$$\begin{array}{lllll}
\underline{\textit{Balance}} & \underline{\textit{F in}} & \underline{\textit{B out}} & \underline{\textit{P out}} & \underline{\textit{G out}} \\
\text{C:} & 0.556(6) & = B(1) + & P(2) + & G(6) \\
\text{H:} & 0.556(12) & = B(0) + & P(6) + & G(12) \\
\text{O:} & 0.556(6) & = B(2) + & P(1) + & G(6)
\end{array}$$

The solvent water can be ignored.

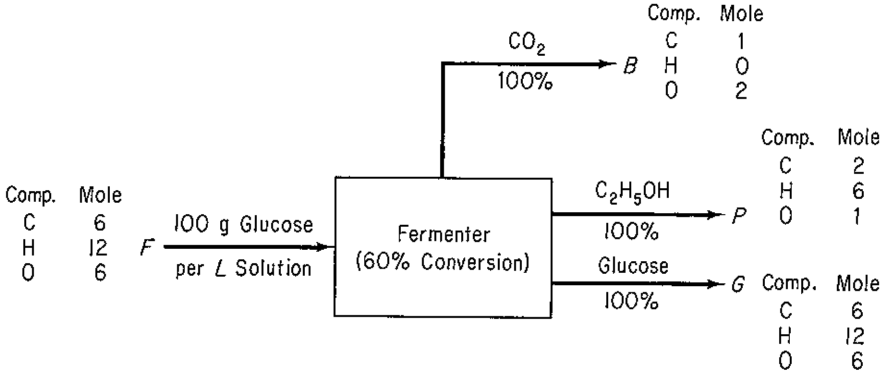


Figure E2.5

The question is: Are those equations independent? Perhaps you can tell by inspection. But, if not, form the coefficient matrix and determine its rank as described in Sec. L.1:

$$\begin{bmatrix} 1 & 2 & 6 \\ 0 & 6 & 12 \\ 2 & 1 & 6 \end{bmatrix} \longrightarrow \begin{bmatrix} 1 & 2 & 6 \\ 0 & 6 & 12 \\ 0 & -3 & -6 \end{bmatrix} \longrightarrow \begin{bmatrix} 1 & 2 & 6 \\ 0 & 6 & 12 \\ 0 & 6 & 12 \end{bmatrix} \longrightarrow \begin{bmatrix} 1 & 2 & 6 \\ 0 & 6 & 12 \\ 0 & 0 & 0 \end{bmatrix}$$

You can see that the three material balances are not independent: The rank of the coefficient matrix is only 2, hence we need one more piece of independent information to solve this problem.

For the extra piece of information needed, assume that 60% of the glucose reacts to form products in passing through the reactor.

$$\begin{array}{lccc} & \underline{\text{In}} & \underline{\text{Out}} & \underline{\text{Consumed}} \\ \text{Glucose balance:} & 0.556 = & G & + 0.556(0.6) \end{array}$$

Then the glucose exiting is the unreacted glucose, namely $G = 0.556(0.4) = 0.222$ gmol, and the material balances become:

$$\begin{array}{lccccc} \underline{\text{Balance}} & \underline{F \text{ in}} & & \underline{B \text{ out}} & \underline{P \text{ out}} & \underline{G \text{ out}} \\ \text{C:} & 0.556(6) & = & B(1) & + P(2) & + 0.222(6) \\ \text{H:} & 0.556(12) & = & B(0) & + P(6) & + 0.222(12) \\ \text{O:} & 0.556(6) & = & B(2) & + P(1) & + 0.222(6) \end{array}$$

Now we have two unknowns B and P, and seemingly three equations! But only two of the equations are independent; the rank of the coefficient matix

$$\begin{bmatrix} 1 & 2 \\ 0 & 6 \\ 2 & 1 \end{bmatrix}$$

can at most be two.

We can conclude from this example that **usually the number of independent material balances equals the number of atomic species in cases in which a reaction occurs, but not always.** If you assume that the balances are independent, but encounter difficulty in solving the equations you formulate, check to see if the equations are independent while checking for other errors.

To sum up the results of the discussion so far, associated with any stream entering or leaving a process are one or more of the so-called **stream variables** composed of the amounts of each of the n species in the stream. Keep in mind that the stream variables may be comprised of the total flow plus $(n-1)$ components or just the flows of the n species themselves. You want to formulate m independent material balances that can be solved for m variables whose values are unknown (not specified or chosen as a basis). (Additional stream variables such as pressure and temperature will be considered in subsequent chapters as well as other types of balances, such as energy balances.) If more variables whose values are unknown exist than independent equations, an infinite number of solutions exists for a material balance problem—not a satisfactory outcome. Such problems are deemed **underspecified.** Either values of additional variables must be found to make up the deficit or the problem must be posed as an optimization problem such as minimize some cost or revenue function subject to the constraints comprised of the material balances. On the other hand, if fewer values of the variables whose values are unknown exist than independent equations, the problem is **overspecified,** and no solution exists to the problem, as the equations are inconsistent. Again, the problem might be posed as an optimization problem, namely to minimize the sum of the squares of the deviations of the equations from zero (or their right-hand constants).

The difference between the number of variables whose values are unknown and the number of independent equations is known as the **number of degrees of**

freedom. If the degrees of freedom are positive, such as 2, you *must* seek out two additional independent equations or specifications of variables to get a unique solution to your material balance problem. If the degrees of freedom are negative, such as −1, you have too many equations or not enough variables in the problem. Perhaps you forgot to include one variable in setting up the information diagram for the problem. Perhaps some of the information you used was not correct. **Zero degrees of freedom means that the material balances problem is properly specified,** and you can then proceed to solve the equations for the variables whose values are unknown. (If the independent equations are nonlinear, possibly more than one solution exists, as, for example, in solving a quadratic equations $ax^2 + bx + c = 0$, the solutions for which are $x = (-b \pm \sqrt{b^2 - 4ac})/2a$; refer to Sec. L.2.)

EXAMPLE 2.6

Examine Fig. E2.6a, which represents a simple flow sheet for a single unit. Only the value of D is known. What is the minimum number of other measurements that must be made to determine all the other stream and composition values?

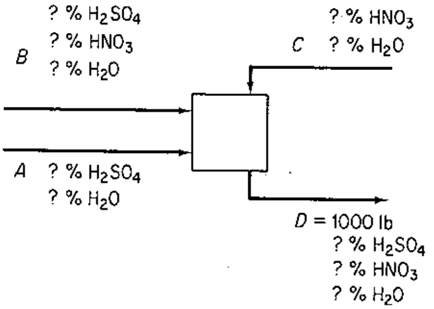


Figure E2.6a

Solution

What you are asked to find is the number of degrees of freedom for the problem in Fig. E2.6. Here is the count of the number of unknown values taking into account that in any stream, one of the composition values can be determined by difference from 100%. Do you remember why?

Stream	Net unknown variables
A	2
B	3
C	2
D	2
Total	9

As example of the count, in stream A specification of A plus one composition makes it possible to calculate the other composition and thus the mass flow of both the H_2SO_4 and the H_2O. In total only three independent material balance equations can be written (do you remember why?), leaving $9 - 3 = 6$ compositions and stream values that have to be specified, and three values to be solved for from the material balances.

Will any six values of the variables in Fig. E2.6a do? No. Only those values can be specified that will leave a number of independent material balances equal to the number of unknown variables. As an example of a satisfactory set of measurements, choose one composition in stream *A*, two in *B*, one in *C*, and two in *D* leaving the flows *A*, *B*, *C* as unknowns. What do you think of the selection of the following set of the measurements: *A*, *B*, *C*, two compositions in *D*, and one composition in *B*? Draw a diagram of the information, as in Fig. E2.6b (• = known quantity). Write down the three material balance equations. Are the three equations independent? You will find that they are not independent. Remember that the sum of the mass fractions is unity for each stream.

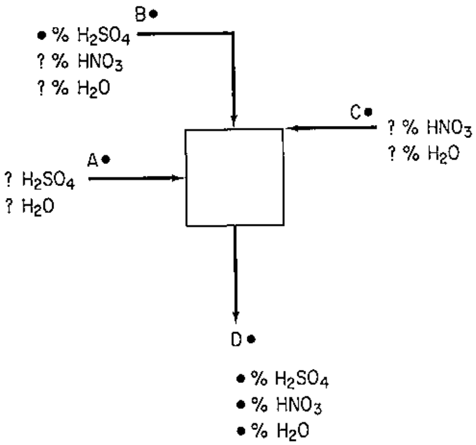


Figure E2.6b

So far we have focused attention on how to write down the material balances and the requirements that have to be met for the equations to have a solution. Now it is time to examine other important aspects of developing skills for successful problem solving. **Problem solving** is an interactive process involving a number of skills, some requiring more practice and experience than others. Figure 2.8 identifies many of the skills you need to develop to be successful in solving problems in this book, while Table 2.1 lists many of the common pitfalls you will encounter in problem solving. Table 2.2 offers some general suggestions to help you solve problems in addition to the obvious suggestion of avoiding the traps listed in Table 2.1. Table 2.3 is a checklist for self-assessment of your problem solving traits. How many of the items in the table pertain to your problem-solving techniques? Practice visual thinking, stress management, and awareness of the process whereby you solve problems. As formulated by Woods,[4] developing your awareness of your problem-solving skills is an important factor in improving them because

1. You can identify where you are when solving a problem.
2. You can develop a methodical approach.
3. You can, whenever you are stuck, identify the obstacle.

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[4] D. R. Woods, *Unit 1, Developing Awareness,* the McMaster Problem Solving Program, McMaster University, Hamilton, Ont., Canada, 1985.

4. You can describe to others what you have done and any difficulties that you are encountering.
5. You become aware of what skills need improvement.
6. You increase your level of confidence.
7. You develop traits of carefulness.

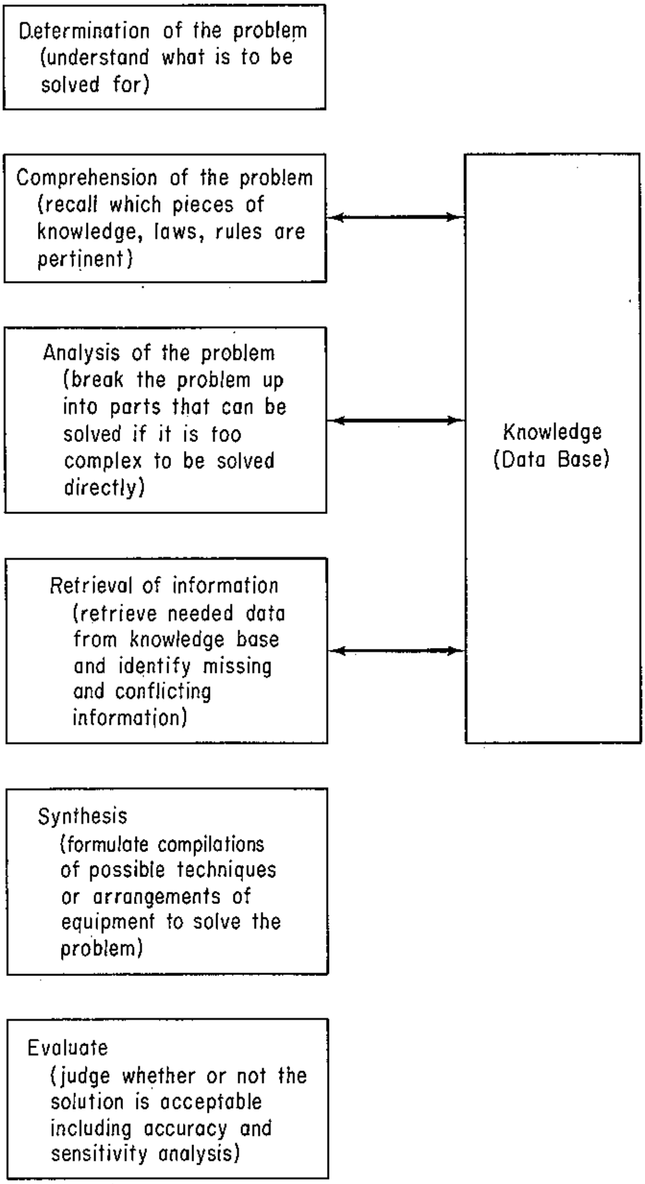


Figure 2.8 Skills needed to solve problems efficiently.

TABLE 2.1 Diagnosis of Reasons for Failing to Solve Problems
(*"Experience is the name everyone gives to their mistakes."* Oscar Wilde)

Failure to work on a problem in a systematic rather than a scatterbrained way
(start too soon; skip essential steps)

Failure to read/understand the problem thoroughly

Failure to draw a diagram and enter all data thereon and the symbols for the unknowns

Failure to ascertain the unknown

Fixing on the first, a poor, or an incorrect strategy of solution without considering alternative strategies

Selection of the wrong principle or equation to use
(total moles instead of total mass, ideal gas instead of real gas) and solution of the wrong problem

Working with false information

Picking the wrong entry from a data base, chart, or table
(wrong sign, wrong units, decimal misplaced, etc.)

Entering incorrect inputs/parameters into calculations
(transpose numbers, wrong units, etc.)

Failure to include units in each step of the calculations

Sloppy execution of calculations introduce errors
(add instead of subtract, invert coefficients, etc.)

Difficulty in distinguishing new features in a problem that superficially looks familiar

Incorrect algebraic manipulations

Use of unsatisfactory computer code for the problem
(too much error, premature termination)

Unable to locate needed data, coefficients by not reading the problem thoroughly or looking in the wrong data base

Unable to estimate what the answer should be to use in comparison with calculated answer

Knowledge (your data base) is inadequate
(you have forgotten, or never learned, some essential laws, equations, values of coefficients, conversion factors, etc.)

Only forward reasoning rather than both forward and backward reasoning is employed

Emotional stress
(fear of making a mistake, looking foolish or stupid)

Lack of motivation

Inability to relax

TABLE 2.2 Techniques Used by Experts to Overcome Barriers to Problem Solving

Read the problem over several times but at different times. Be sure to understand all facets of it. Emphasize different features each time.
Restate the problem in your own words. List assumptions.
Draw a comprehensive diagram of the process and enter *all* known information on the diagram. Enter symbols for unknown variables and parameters.
Formally write down what you are going to solve for: "I want to calculate . . . ".
Choose a basis.
Relate the problem to similar problems you have encountered before, but note any differences.
Plan a strategy for solution; write it down if necessary. Consider different strategies.
Write down all the equations and rules that might apply to the problem.
Formally write down everything you know about the problem and what you believe is needed to execute a solution.
Talk to yourself as you proceed to solve the problem.
Ask yourself questions as you go along concerning the data, procedures, equations involved, etc.
Talk to other people about the problem.
Break off problem solving for a few minutes and carry out some other activity.
Break up the solution of the problem into more manageable parts, and start at a familiar stage. Write down the objective for each subproblem (i.e., convert mole fraction to mass fraction, find the pressure in tank 2, etc.).
Repeat the calculations but in a different order.
Work both forward and backward in the solution scheme.
Consider if the results you obtained are reasonable. Check both units and order of magnitude of the calculations. Are the boundary conditions satisfied?
Use alternative paths to verify your solution.
Maintain a positive attitude—you know the problem can be solved—just how is the question.

TABLE 2.3 A Checklist of Personal Traits to Avoid In Problem Solving

1. When I fail to solve a problem, I do not examine how I went wrong.
2. When confronted with a complex problem, I do not develop a strategy of finding out exactly what the problem is.
3. When my first efforts to solve a problem fail, I become uneasy about my ability to solve the problem (or I panic!)
4. I am unable to think of effective alternatives to solve a problem.
5. When I become confused about a problem, I do not try to formalize vague ideas or feelings into concrete terms.
6. When confronted with a problem, I tend to do the first thing I can think of to solve it.
7. Often I do not stop and take time to deal with a problem, but just muddle ahead.
8. I do not try to predict the overall result of carrying out a particular course of action.
9. When I try to think of possible techniques of solving a problem, I do not come up with very many alternatives.
10. When faced with a novel problem, I do not have the confidence that I can resolve it.
11. When I work on a problem, I feel that I am grasping or wandering, and not getting a good lead on what to do.
12. I make snap judgments (and regret them later).
13. I do not think of ways to combine different ideas or rules into a whole.
14. Sometimes I get so charged up emotionally that I am unable to deal with my problem.
15. I jump into a problem so fast, I solve the wrong problem.
16. I depend entirely on the worked-out sample problems to serve as models for other problems.

SOURCE: Based on the ideas in a questionnaire in P.P. Heppner, *P.S.I.*, Department of Psychology, University of Missouri–Columbia, 1982.

If you are sure that the problem is one you have encountered before and solved successfully, you can simply follow your previous procedure. However, if the problem is or looks as if it is a new problem, you need to follow carefully the recommended checklist outlined in Table 2.4. An expert proceeds in problem solving by abbreviated steps; many are done only mentally. A beginner should go through each step explicitly until he or she becomes experienced. For guidance, perhaps you should turn to Sherlock Holmes (as cited in Arthur Conan Doyle's "The Naval Treaty"):

> *"Do you see any clue?"*
>
> *"You have furnished me with seven, but of course I must test them before I can pronounce upon their value."*

TABLE 2.4 Strategy For Analyzing Material Balance Problems ("A problem recognized is a problem half-solved." Ann Landers)

1. Draw a sketch of the process; define the system by a boundary.
2. Label the flow of each stream and the associated compositions with symbols.
3. Put all the known values of compositions and stream flows on the figure by each stream; calculate additional compositions from the given data as necessary. Or, at least initially identify the known parameters in some fashion.
4. Select a basis.
5. List by symbols each of the unknown values of the stream flows and compositions, or at least mark them distinctly in some fashion.
6. List the number of independent balances that can be written; ascertain that a unique solution is possible. If not, look for more information or check your assumptions.
7. Select an appropriate set of balances to solve; write the balances down with type of balance listed by each one. Do not forget the implicit balances for mass or mole fractions.
8. State whether the problem is to be solved by direct addition or subtraction or by the solution of simultaneous equations.
9. Solve the equations. Each calculation must be made on a consistent basis.
10. Check your answers by introducing them, or some of them, into the material balances. Are the equations satisfied? Are the answers reasonable?

"You must suspect someone?"

"I suspect myself."

"What?"

"Of coming to conclusions too rapidly."

If you use the steps in Table 2.4 as a mental checklist each time you start to work on a problem, you will have achieved the major objective of this chapter and substantially added to your professional skills. These steps do not have to be carried out in the order prescribed, and you may repeat steps as the issues in the problem become clearer. But they are all essential.

Past experience has indicated that the two major difficulties you will experience in solving material balance problems have nothing to do with the mechanics of solving the problem (once they are properly formulated!). Instead, you will find that the two main stumbling blocks are:

(a) After reading the problem you do not really understand what the process in the problem is all about. Help yourself achieve understanding by sketching the system—just a box with arrows as in Figs. 2.5 and 2.6 will do.

(b) After a first reading of the problem you are confused as to which values of compositions and flows are known and unknown. Help reduce the confusion by putting the known values down on your diagram as you discover them or calculate them, and by putting question marks or alphabetic symbols for the unknown quantities. Try to record the compositions as weight, or mole, fractions (or percents) as you proceed so as to assist in clarifying the choice of basis and the material balances that can be employed. Because you will have to set up and solve a material balance for each unknown you enter on the diagram, try to keep the number of unknown labels to as few as possible.

You should also be concerned with efficient problem solving. You will discover many correct ways to solve a given problem; all will give the same correct answer if properly applied. Not all, however, will require the same amount of time and effort. For example, you may want to solve a problem initially stated in units of pounds by converting the given units to grams or gram moles, solving for the required quantities in SI units and converting the answer back to American engineering units. Such a method is valid but can be quite inefficient—it consumes your time in unnecessary steps, and it introduces unnecessary opportunities for numerical errors to occur. You should, therefore, start developing the habit of looking for efficient ways to solve a problem, not just *a* way. A good example is to substitute the total mass balance for a component mass balance to reduce the number of unknown variables. Cadman publishes computer aided analysis codes that enable you to practice efficient problem solving; refer to the references at the end of this chapter.

We conclude the discussion in this section with a few remarks about solving the material balances you formulate in a problem. Appendix L describes how to solve sets of simultaneous equations, hence the details will not be repeated here. In many problems, you will find that the equations are sufficiently simple that selection of the obvious choice for the sequence of solution of the equations permits you to avoid having to solve two or more equations simultaneously. Typical examples of such problems will be found in the next section, Sec. 2.3, entitled "Solving Material Balance Problems Without Solving Simultaneous Equations." For example, problems in which the mass (weight) of one stream and the composition of one stream are unknown can be solved without difficulty by direct addition or direct subtraction. All you need is a simple hand calculator to compute the values of the unknown variables.

On the other hand, if you cannot avoid solving a set of simultaneous coupled equations because the set you are working with is tightly coupled in its initial structure and cannot be simplified even by successive substitution of one equation into another, you should read Sec. 2.7, in which computer-aided solutions are discussed. As explained in that section, you can use readily available software in computer center libraries or the computer codes in the pocket in the back of this book to solve sets of independent material balances.

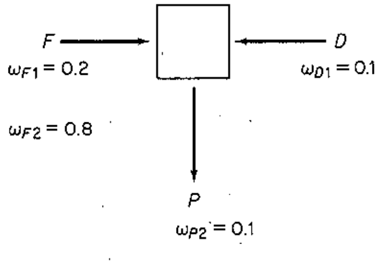
In the next section we examine examples of material balance problems that can be solved without solving simultaneous equations.

Self-Assessment Test

1. What does the concept "solution of a material balance problem" mean?
2. (a) How many values of unknown variables can you compute from one independent material balance?
   (b) From three?
   (c) From four material balances, three of which are independent?
3. A water solution containing 10% acetic acid is added to a water solution containing 30% acetic acid flowing at the rate of 20 kg/min. The product P of the combination leaves at the rate of 100 kg/min. What is the composition of P? For this process,
   (a) Determine how many independent material balances can be written.
   (b) List the names of the balances.
   (c) Determine how many unknown variables can be solved for.
   (d) List their names and symbols.
   (e) Determine the composition of P.
   In your solution set out the 10 steps specifically and label them.
4. Can you solve these three material balances for F, D, and P?

$$0.1F + 0.3D = 0.2P$$
$$0.9F + 0.7D = 0.8P$$
$$F + D = P$$

5. Cite two ways to solve a set of linear equations.
6. If you want to solve a set of independent equations that contain fewer unknown variables than equations (the overspecified problem), how should you proceed with the solution?
7. What is the major category of implicit constraints (equations) you encounter in material balance problems?
8. If you want to solve a set of independent equations that contain more unknown variables than equations, what must you do to proceed with the solution?
9. How many values of the concentrations and flow rates variables in the process shown in the figure are unknown? List them. The streams contain two components, 1 and 2.



10. How many material balances are needed to solve problem 9? Is the number the same as the number of unknown variables? Explain.
11. A synthesis gas analyzing CO_2: 6.4%, O_2: 0.2%, CO: 40.0%, and H_2: 50.8% (the balance is N_2) is burned with excess dry air. The problem is to determine the quantitative composition of the flue gas. How many degrees of freedom exist in this problem, that is, how may additional variables have to have their values specified?

2.3 SOLVING MATERIAL BALANCE PROBLEMS THAT DO NOT ENTAIL SOLVING SIMULTANEOUS EQUATIONS

Your objectives in studying this section are to be able to:

1. Define flue gas, stack gas, Orsat analysis, dry basis, wet basis, theoretical air (oxygen), required air (oxygen), and excess air (oxygen).
2. Given two of the three factors: entering air (oxygen), excess air (oxygen), and required air (oxygen), compute the third factor.
3. Apply the 10-step strategy to solve problems (with or without chemical reaction) having a direct solution (i.e., problems in which the equations are decoupled so that simultaneous equations do not have to be solved).

Problems in which the material balances are decoupled can be solved without the solution of sets of simultaneous equations. An example would be a problem in which one mass (weight) and one composition are unknown. Such a problem can be solved by direct addition or subtraction as shown in the examples below. You may find it necessary to make some brief preliminary calculations to decide whether or not all the information about the compositions and weights that you need to have is available. Of course, in a stream containing just one component, the composition is known, because that component is 100% of the stream. Once you find out that the number of degrees of freedom is zero, you can proceed to solve the equations in sequence one at a time. Before examining some examples, we need to emphasize some terms commonly used in combustion problems.

In dealing with problems involving combustion, you should become acquainted with a few special terms:

(a) **Flue or stack gas**—all the gases resulting from a combustion process including the water vapor, sometimes known as *wet basis*.

(b) **Orsat analysis or dry basis**—all the gases resulting from the combustion process not including the water vapor. (Orsat analysis refers to a type of gas analysis apparatus in which the volumes of the respective gases are measured over and in equilibrium with water; hence each component is saturated with water vapor. The net result of the analysis is to eliminate water as a component being measured.)

Pictorially, we can express this classification for a given gas as in Fig 2.9. To convert from one analysis to another, you have to adjust the percentages for the components as shown in Example 2.12.

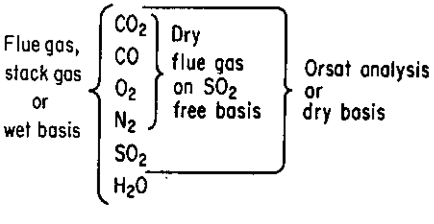


Figure 2.9 Comparison of gas analyses on different bases.

(c) **Theoretical air** (or **theoretical oxygen**)—the amount of air (or oxygen) required to be brought into the process **for complete combustion.** Sometimes this quantity is called the **required** air (or oxygen).

(d) **Excess air** (or **excess oxygen**)—in line with the definition of excess reactant given in Chap. 1, excess air (or oxygen) would be the amount of air (or oxygen) **in excess of that required for complete combustion** as computed in (c).

The calculated amount of excess air does not depend on how much material is actually burned but what can be burned. Even if only partial combustion takes places, as, for example, C burning to both CO and CO_2, **the excess air (or oxygen) is computed as if the process of combustion produced only CO_2.** The percent excess air is identical to the percent excess O_2 (a more convenient calculation):

$$\%\text{ excess air} = 100\frac{\text{excess air}}{\text{required air}} = 100\frac{\text{excess } O_2/0.21}{\text{required } O_2/0.21} \tag{2.9}$$

Note that the ratio 1/0.21 of air to O_2 cancels out in Eq. (2.9). Percent excess air may also be computed as

$$\%\text{ excess air} = 100\frac{O_2\text{ entering process} - O_2\text{ required}}{O_2\text{ required}} \tag{2.10}$$

or

$$\%\text{ excess air} = 100\frac{\text{excess } O_2}{O_2\text{ entering} - \text{excess } O_2}$$

since

$$O_2\text{ entering process} = O_2\text{ required for complete combustion} + \text{excess } O_2 \tag{2.11}$$

The precision of these different relations for calculating the percent excess air may not be the same. If the percent excess air and the chemical equation are given in a problem, you know how much air enters with the fuel, and hence the number of unknowns is reduced by one.

In the burning of coal, you may wonder how to treat the oxygen found in most coals in some combined form. Just assume that the oxygen is already combined with some of the hydrogen in the coal in the proper proportions to make water. Consequently, the O_2 does not enter into the combustion process, and the hydrogen equivalent to this oxygen does not enter the combustion reaction either. No corresponding oxygen is counted toward the required oxygen needed in the air. Only the remaining or "net" hydrogen requires oxygen from the air to form water vapor on burning.

Now let us look at some examples of solving material balance problems without having to solve simultaneous equations.

EXAMPLE 2.7 Excess Air

Fuels for motor vehicles other than gasoline are being eyed because they generate lower levels of pollutants than does gasoline. Compressed propane has been suggested as a source of economic power for vehicles. Suppose that in a test 20 lb of C_3H_8 is burned with 400 lb of air to produce 44 lb of CO_2 and 12 lb of CO. What was the percent excess air?

Solution

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Basis: 20 lb of C_3H_8

Since the percentage of excess air is based on the *complete combustion* of C_3H_8 to CO_2 and H_2O, the fact that combustion is not complete has no influence on the definition of "excess air." The required O_2 is

$$\frac{20 \text{ lb } C_3H_8}{} \left| \frac{1 \text{ lb mol } C_3H_8}{44 \text{ lb } C_3H_8} \right| \frac{5 \text{ lb mol } O_2}{1 \text{ lb mol } C_3H_8} = 2.27 \text{ lb mol } O_2$$

(The molecular weight of propane is actually 44.09, but we use the value of 44 for convenience.)

The entering O_2 is

$$\frac{400 \text{ lb air}}{} \left| \frac{1 \text{ lb mol air}}{29 \text{ lb air}} \right| \frac{21 \text{ lb mol } O_2}{100 \text{ lb mol air}} = 2.90 \text{ lb mol } O_2$$

The percent excess air is

$$100 \times \frac{\text{excess } O_2}{\text{required } O_2} = 100 \times \frac{\text{entering } O_2 - \text{required } O_2}{\text{required } O_2}$$

$$\%\text{ excess air} = \frac{2.90 \text{ lb mol } O_2 - 2.27 \text{ lb mol } O_2}{2.27 \text{ mol } O_2} \left| \frac{100}{} \right. = 28\%$$

In the following problems each step cited in Table 2.4 will be identified so that you can follow the strategy of the solution.

EXAMPLE 2.8 Material Balances with Combustion

A salesperson comes to the door selling a service designed to check "chimney rot." He explains that if the CO_2 content of the gases leaving the chimney rises above 15%, it is dangerous to your health, is against the city code, and causes your chimney to rot. On checking the flue gas from the furnace, he finds it is 30% CO_2. Suppose that you are burning natural gas which is about 100% CH_4 and that the air supply is adjusted to provide 130% excess air. Do you need his service?

Solution

Let us calculate the actual percentage of CO_2 in the gases from the furnace assuming that complete combustion takes place and the process is in the steady state. See Fig. E2.8a. The 130% excess air means 130% of the air required for complete combustion of CH_4. The chemical reaction is

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Step 1 The system is defined in Fig. E2.8a; note that a chemical reaction occurs.

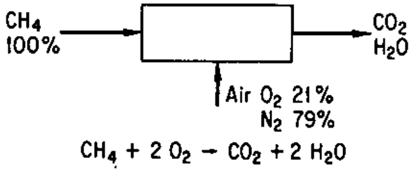


Figure E2.8a

Steps 2, 3, and 5 For clarity in labeling, Fig. E2.8a is repeated as Fig. E2.8b with all the species listed by each related stream, and the known (and easily calculated) compositions listed next to each elemental species.

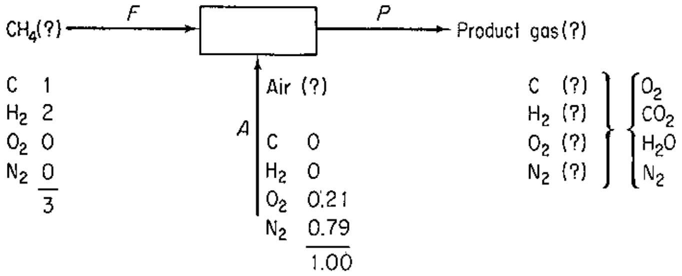


Figure E2.8b

Step 4 By picking a basis of 1 mole of CH_4, we can reduce the unknown quantities by one.

Basis: 1 mole of $CH_4 = F$

Step 6 We can only make four elemental material balances, C, H as H_2, O as O_2, and N as N_2, and one summation of moles in the product stream to equal P; hence one more piece of information is needed, as we have five unknowns: A, and the moles of C, H_2, O_2, and N_2 in P.

Step 3 (Repeated) The quantity of air can be ascertained because of the specification of the excess air, and is computed as follows: On the basis of 1 mole of CH_4, 2 moles of O_2 are required for complete combustion, or

$$\frac{2 \text{ mol } O_2 \;\Big|\; 1.00 \text{ mol air}}{\;\;\Big|\; 0.21 \text{ mol } O_2} = 9.52 \text{ mol air required}$$

composed of 2 moles of O_2 and 7.52 moles of N_2. The excess entering air is 9.52 (1.30) = 12.4 moles of air, composed of 2.60 moles of O_2 and 9.80 moles of N_2. Now we have left four quantities with unknown values. We can in principle make four independent material balances (C, H_2, O_2, N_2), and use one equation summing the moles in the product gas to calculate the product gas, so that the problem can be solved for the relative quantity of CO_2.

To sum up our calculations so far, we have entering the furnace together with 1 mole of C and 2 moles of H_2 the following moles:

	Air	O_2	N_2
Required portion	9.52	2.00	7.52
Excess portion	12.4	2.60	9.80
Total	21.92	4.60	17.32

Steps 7, 8, and 9 We could formally write down the balances if you wish:

Balance	*CH_4 in*	*Air in*	*P out*
C:	1		$= n_{CO_2}$
H_2:	2		$= n_{H_2O}$
O_2:		4.60	$= n_{O_2} + n_{CO_2} + \frac{1}{2}n_{H_2O}$
N_2:		17.32	$= n_{N_2}$

The n_{CO_2}, n_{H_2O}, and n_{N_2} can be calculated directly; the n_{O_2} can then be obtained from the oxygen balance. Or you might prefer to calculate the CO_2 and H_2O as follows using the combustion equation since all the entering C exits as CO_2 and all the H exits as H_2O:

$$\text{C balance:}\quad \frac{1 \text{ mol C in}}{1 \text{ mol } CH_4 \text{ in}}\left|\frac{1 \text{ mol } CO_2 \text{ out}}{1 \text{ mol C out}}\right. = 1 \text{ mol } CO_2 \text{ out}$$

$$H_2 \text{ balance:}\quad \frac{2 \text{ mole } H_2 \text{ in}}{1 \text{ mol } CH_4 \text{ in}}\left|\frac{1 \text{ mol } H_2O \text{ out}}{1 \text{ mol } H_2 \text{ out}}\right. = 2 \text{ mol } H_2O \text{ out}$$

and the nitrogen as follows:

$$N_2 \text{ balance:}\quad \frac{2 \text{ mol } O_2 \text{ in}}{1 \text{ mol } CH_4 \text{ in}}\left|\frac{0.79 \text{ mol } N_2}{0.21 \text{ mol } O_2}\right|\frac{(1.30 \text{ excess} + 1.00 \text{ req}) \text{ mol } O_2}{}$$

$$= 17.3 \text{ mol out}$$

In either case, $n_{O_2} = 4.60 - 1 - 1 = 2.60$.

Finally, we calculate the composition of the stack gas.

Component	Moles	Percent
CH_4	0	0
CO_2	1.00	4.4
H_2O	2.00	8.7
O_2	2.60	11.3
N_2	7.52 9.80	75.6
Total	22.9	100.0

The salesman's line seems to be rot all the way through.

Step 10 Check the answer.

EXAMPLE 2.9 Material Balance in Drying Pulp

A wet paper pulp is found to contain 71% water. After drying it is found that 60% of the original water has been removed. Calculate the following:

(a) The composition of the dried pulp
(b) The mass of water removed per kilogram of wet pulp

Solution

This is a steady steady-state process. No chemical reaction occurs.

Steps 1, 2, 3, and 5 The process is shown in Fig. E2.9.

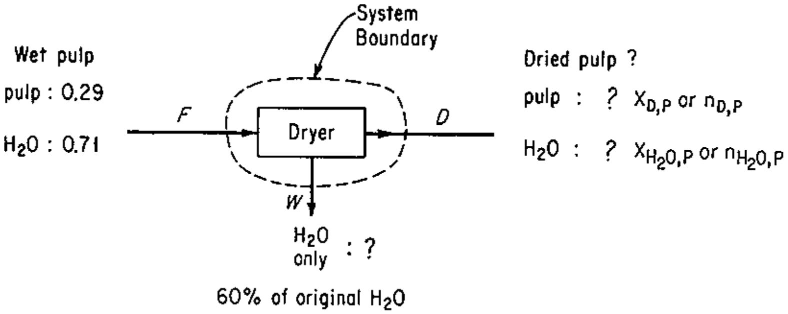


Figure E2.9

Step 4 Pick a convenient basis.

Basis: 1 kg of wet pulp

Step 3 (Repeated) From the statement about the mass of water removed, we can calculate that

$$H_2O \text{ removed} = 0.60(0.71) = 0.426 \text{ kg} = W$$

This is the answer to question (b).

Steps 5 and 6 Only two independent material balances (pulp and H_2O) and one sum of component masses or mass fractions (for the dried pulp) can be written. How many unknowns exist in this problem? Only two, either (a) D and $x_{D,P}$ or $x_{H_2O,P}$, or (b) D and $m_{D,P}$ or $m_{H_2O,P}$, or (c) $m_{D,P}$ and $m_{H_2O,P}$. Keep in mind that

$$\omega_{D,P} + \omega_{H_2O,P} = 1$$

or

$$m_{D,P} + m_{H_2O,P} = P$$

are implicit equations relating stream fluid variables. Consequently, a unique solution is possible.

Steps 7, 8, and 9 Formal statement of the component mass balances and the total balance is (in kg)

Balance	*F in*		*W out*		*D out*
Pulp	0.29	=	0	+	$m_{p,P}$
H_2O	0.71	=	0.426	+	$m_{H_2O,P}$
Total	1.00	=	0.426	+	P

By direct subtraction using the water balance, we can calculate $m_{H_2O,P}$:

$$m_{H_2O,P} = 0.71 - 0.426 = 0.284 \text{ kg}$$

or alternatively, we can use the fact that 40% of the original water exits with P:

$$(0.71)(0.40) = 0.284 \text{ kg } H_2O$$

Of course, all the pulp exits directly in P, so that

$$m_{p,P} = 0.29 \text{ kg}$$

The composition of the dried pulp is

Component	kg	Percent
Pulp (dry)	0.29	50.5
H_2O	0.284	49.5
Total	0.574	100.0

Step 10 We check to make sure that total kg in = total kg out

$$\frac{\textit{Wet pulp}}{1.00} = \frac{\textit{Water}}{0.426} + \frac{\textit{Dried pulp}}{0.574}$$

EXAMPLE 2.10 Crystallization

A tank holds 10,000 kg of a saturated solution of $NaHCO_3$ at 60°C. You want to crystallize 500 kg of $NaHCO_3$ without any accompanying water from this solution. To what temperature must the solution be cooled?

Solution

No reaction occurs in this problem. It is best viewed as an unsteady-state problem in which the material in the tank changes and some material is removed from the tank. (The problem could be forced to be a steady-state problem if material is placed into the tank and two types of material are removed, crystals and saturated solution at the unknown temperature.) The major difficulty posed in this problem is to get all the necessary information about the compositions of the solutions and solids.

Step 1 Figure E2.10a is a diagram of the process.

Steps 2 and 3 We do not have at this stage any of the compositions of the saturated solutions in the tank, hence we need to collect some additional data. It is not worth the trouble to label the unknown variables in Fig. 2.10a yet—there are too many of them. Both the initial and final solutions in the tank are saturated solutions; hence if we can find the final concentration of the $NaHCO_3$ in the tank, we can look up the corresponding temperature in a handbook containing solubility data.

Thus, additional data are needed on the solubility of $NaHCO_3$ as a function of temperature. From any handbook you can find

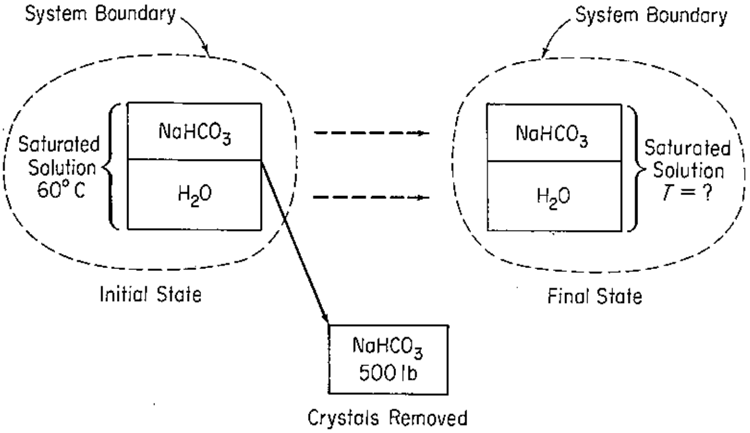


Figure E2.10a

Temp. (°C)	Solubility ($g\ NaHCO_3/100\ g\ H_2O$)
60	16.4
50	14.45
40	12.7
30	11.1
20	9.6
10	8.15

Because the initial solution is saturated at 60°C, we can calculate the composition of the initial solution at this stage:

$$\frac{16.4\ \text{g}\ NaHCO_3}{16.4\ \text{g}\ NaHCO_3 + 100\ \text{g}\ H_2O} = 0.141 \quad \text{or} \quad 14.1\%\ NaHCO_3$$

The remainder of the solution is water, or 85.9%

Step 4 Take a basis.

Basis: 10,000 kg of saturated solution at 60°C

Steps 2 and 3 (Repeated) We can now enter the known data concerning the compositions on the diagram as shown in Fig. E2.10b.

Steps 5 and 6 We are missing the mass of the final solution and its composition, but can make two independent mass balances and one summation of masses or mass fractions, so a unique solution is possible.

Steps 7, 8, and 9 A direct solution is possible by subtraction. The accumulation term in Eq. (2.1) is negative (depletion) and the generation and consumption terms are zero. Also, only transport out occurs; transport in is zero. The component and total balances in kilograms are (only two are independent)

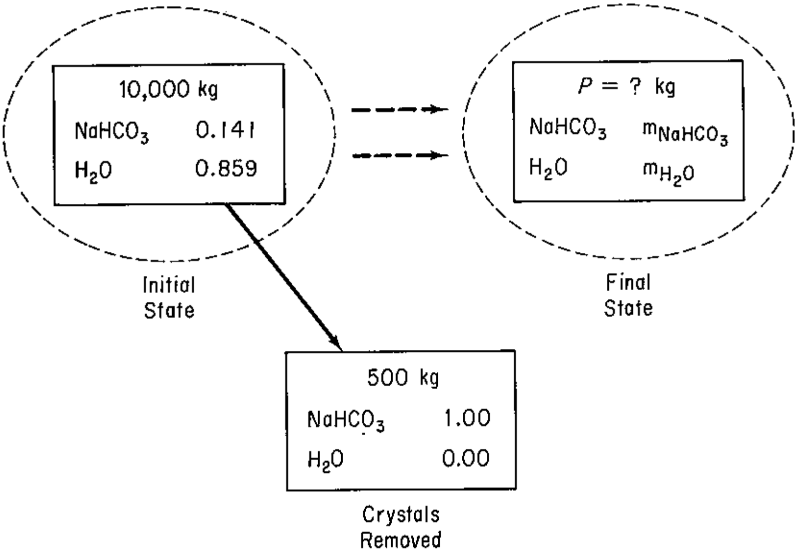


Figure E2.10b

Accumulation in Tank

	Final		*Initial*		*Transport out*
$NaHCO_3$	m_{NAHCO_3}	$-$	10,000 (0.141)	$=$	$-500(1.00)$
H_2O	m_{H_2O}	$-$	10,000 (0.859)	$=$	-0
Total	P	$-$	10,000	$=$	-500

The composition of the final solution is

Component	kg	Percent
m_{NaHCO_3}	910	9.6
m_{H_2O}	8590	90.4
Total	9500	100.0

Step 10 Check on total:

$$9500 + 500 = 10{,}000$$

To find the temperature of the final solution, calculate the composition of the final solution in terms of grams of $NaHCO_3$/100 gram of H_2O.

$$\frac{910 \text{ g } NaHCO_3}{8590 \text{ g } H_2O} = \frac{10.6 \text{ g } NaHCO_3}{100 \text{ g } H_2O}$$

Thus the temperature to which the solution must be cooled is (using linear interpolation)

$$30°\text{C} - \frac{11.1 - 10.6}{11.1 - 9.6}(10.0°\text{C}) = 27°\text{C}$$

EXAMPLE 2.11 Continuous Distillation

A novice manufacturer of alcohol for gasohol is having a bit of difficulty with a distillation column. The operation is shown in Fig. E2.11. Too much alcohol is lost in the bottoms (waste). Calculate the composition of the bottoms and the weight of alcohol lost in the bottoms.

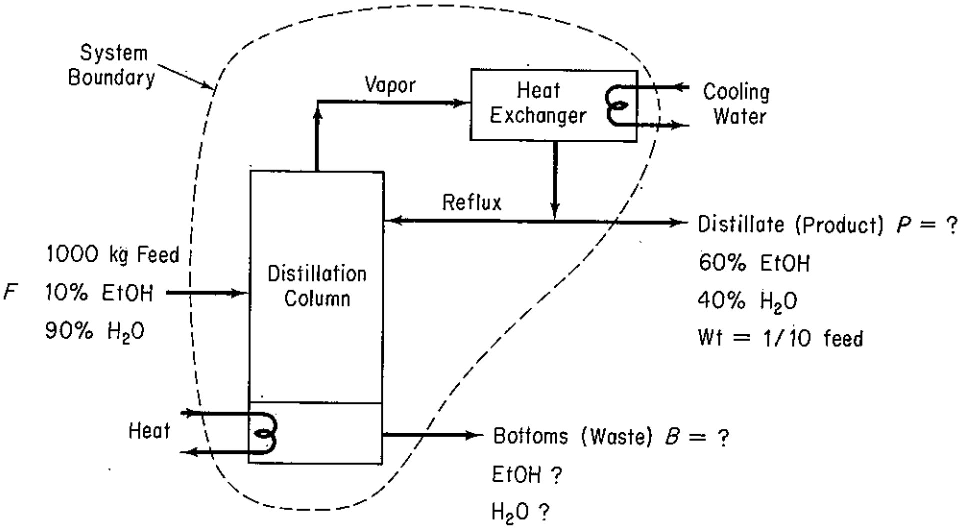


Figure E2.11

Solution

Steps 1, 2, and 3 See Fig. E2.11.

Step 4 Select as the basis the given feed

Basis: 1000 kg of feed

Step 3 (Continued) We are given that P is $\frac{1}{10}$ of F, so that

$$P = 0.1(1000) = 100 \text{ kg}$$

Steps 7, 8, and 9 Calculate B by direct subtraction using the total mass balance

$$B = 1000 - 100 = 900 \text{ kg}$$

Steps 5, 6, 7, 8, and 9 The unknown quantities are the bottoms compositions. We can make two component mass balances, or one sum of masses or mass fractions of the components in B plus one component mass balance, so that the problem has a unique solution.

The solution can be computed directly by subtraction.

	kg feed in	−	*kg distillate out*	=	*kg bottoms out*	*percent*
EtOH balance:	0.10(1000)	−	0.60(100)	=	40	4.4
H_2O balance:	0.90(1000)	−	0.40(100)	=	860	95.6
					900	100.0

If we use the total balance to calculate B, all we need to do is make one component balance because

$$\text{mass } H_2O \text{ in } B = 900 - 40 = 860 \text{ kg}$$

Step 10 *Check:* 900 kg B + 100 kg P = 1000 kg F.

EXAMPLE 2.12 Combustion

Ethane is initially mixed with oxygen to obtain a gas containing 80% C_2H_6 and 20% O_2 that is then burned in an engine with 200% excess air. Eighty percent of the ethane goes to CO_2, 10% goes to CO, and 10% remains unburned. Calculate the composition of the exhaust gas on a wet basis.

In this problem to save space we do not explicitly outline the steps in the analysis and solution of the problem. Use your mental checklist, nevertheless, to ascertain that each step is indeed taken into account.

Solution

We know the composition of the air and fuel gas; if a weight of fuel gas is chosen as the basis, the weight of air can easily be calculated. However, it is wasted effort to convert to a weight basis for this type of problem because all the compositions are expressed in moles or mole percent for gases. The total moles entering and leaving the boiler are not equal, but if we look at any one component and employ the stoichiometric principles discussed in Chap. 1, together with Eq. (2.1), we can easily obtain the composition of the stack gas. The net generation consumption terms in Eq. (2.1) can be evaluated from the stoichiometric equations listed below. The problem can be worked in the simplest fashion by choosing a basis of 100 moles of entering gas. See Fig. E2.12.

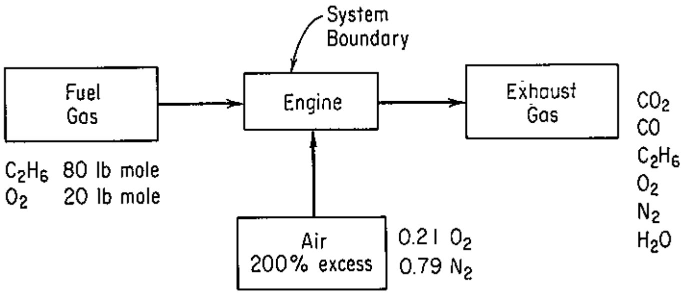


Figure E2.12

Basis: 100 lb mol of fuel

$$C_2H_6 + \tfrac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$C_2H_6 + \tfrac{5}{2}O_2 \longrightarrow 2CO + 3H_2O$$

The total O_2 entering is 3.00 times the required O_2 (100% required plus 200% excess). Let us calculate the required oxygen:

O_2 (for complete combustion):

$$\begin{array}{l|l} 80\text{ lb mol }C_2H_6 & 3.5\text{ lb mol }O_2 \\ \hline & 1\text{ lb mol }C_2H_6 \end{array} = 280\text{ lb mol }O_2$$

Required O_2:

$$280 - 20 = 260\text{ lb mol }O_2$$

(*Note:* The oxygen used to completely burn the fuel is reduced by the oxygen already present in the fuel to obtain the oxygen required in the entering air.)

Next we calculate the input of O_2 and N_2 to the system:

O_2 entering with air:

$$3(260\text{ lb mol }O_2) = 780\text{ lb mol }O_2$$

N_2 entering with air:

$$\begin{array}{l|l} 780\text{ mol}\cdot O_2 & 79\text{ lb mol }N_2 \\ \hline & 21\text{ lb mol }O_2 \end{array} = 2934\text{ lb mol }N_2$$

Now we apply our stoichiometric relations to find the components generated by the system:

$$\begin{array}{l|l|l} 80\text{ lb mol }C_2H_6 & 2\text{ lb mol }CO_2 & 0.8 \\ \hline & 1\text{ lb mol }C_2H_6 & \end{array} = 128\text{ lb mol }CO_2$$

$$\begin{array}{l|l|l} 80\text{ lb mol }C_2H_6 & 3\text{ lb mol }H_2O & 0.8 \\ \hline & 1\text{ lb mol }C_2H_6 & \end{array} = 192\text{ lb mol }H_2O$$

$$\begin{array}{l|l|l} 80\text{ lb mol }C_2H_6 & 2\text{ lb mol }CO & 0.1 \\ \hline & 1\text{ lb mol }C_2H_6 & \end{array} = 16\text{ lb mol }CO$$

$$\begin{array}{l|l|l} 80\text{ lb mol }C_2H_6 & 3\text{ lb mol }H_2O & 0.1 \\ \hline & 1\text{ lb mol }C_2H_6 & \end{array} = 24\text{ lb mol }H_2O$$

To determine the O_2 remaining in the exhaust gas, we have to find how much of the available (800 lb mol) O_2 combines with the C and H.

$$\begin{array}{l|l|l} 80\text{ lb mol }C_2H_6 & 3.5\text{ lb mol }O_2 & 0.8 \\ \hline & 1\text{ lb mol }C_2H_6 & \end{array} = 224\text{ lb mol }O_2\text{ to burn to }CO_2\text{ and }H_2O$$

$$\begin{array}{l|l|l} 80\text{ lb mol }C_2H_6 & 2.5\text{ lb mol }O_2 & 0.1 \\ \hline & 1\text{ lb mol }C_2H_6 & \end{array} = \underline{20\text{ lb}}\text{ mol }O_2\text{ to burn to }CO\text{ and }H_2O$$

244 lb mol O_2 total "used up" by reaction

By an oxygen (O_2) balance we get

$$O_2\text{ out} = 780\text{ lb mol} + 20\text{ lb mol} - 244\text{ lb mol} = 556\text{ lb mol }O_2$$

The water exiting is

$$H_2O \text{ out} = 192 \text{ lb mol} + 24 \text{ lb mol} = 216 \text{ lb mol } H_2O$$

The balances on the other compounds—C_2H_6, CO_2, CO, N_2—are too simple to be formally listed here.

Summarizing these calculations, we have:

Component	lb mol Fuel	 Air	 Exhaust gas	Percent in exhaust gas
C_2H_6	80	—	8	0.21
O_2	20	780	556	14.41
N_2	—	2934	2934	76.05
CO_2	—	—	128	3.32
CO	—	—	16	0.41
H_2O	—	—	216	5.60
Total	100	3714	3858	100.00

On a dry basis we would have (the water is omitted in the exhaust gas):

Component	lb mol	Percent
C_2H_6	8	0.22
O_2	556	15.27
N_2	2934	80.56
CO_2	128	3.51
CO	16	0.44
Total	3642	100.00

Do you know how to solve this problem using the element balances C, H, O, etc.?

Summary of Material Balances

Total mol in ≠ total mol out
Total lb in = total lb out:

Balances on atomic species
lb mol C in = lb mol C out: $2(80) = 128 + 16 + 2(8)$
lb mol H_2 in = lb mol H_2 out: $3(80) = 216 + 3(8)$
lb mol O_2 in = lb mol O_2 out: $20 + 780 = 128 + \frac{1}{2}(216) + \frac{1}{2}(16) + 556$
lb mol N_2 in = lb mol N_2 out: $2934 = 2934$

Balances on compounds
(Eq. 2.1)
lb mol C_2H_6 in = lb mol C_2H_6 out + lb mol C_2H_6 consumed: $80 = 8 + 72$
lb mol CO_2 in = lb mol CO_2 out − lb mol CO_2 generated: $0 = 128 - 128$
lb mol CO in = lb mol CO out − lb mol CO generated: $0 = 16 - 16$
lb mol H_2O in = lb mol H_2O out − lb mol H_2O generated: $0 = 216 - 216$
lb mol N_2 in = lb mol N_2 out + lb mol N_2 consumed: $2934 = 2934 + 0$
lb mol O_2 in = lb mol O_2 out + lb mol O_2 consumed: $800 = 556 + 244$

In the next section we discuss problems that require the simultaneous solution of coupled equations.

Self-Assessment Test

1. Explain the difference between flue gas analysis and Orsat analysis; wet basis and dry basis for a gas.
2. What does "SO_2 free basis" mean?
3. Write down the equations relating percent excess air to required air and entering air.
4. Will the percent excess air always be the same as the percent excess oxygen in combustion (by oxygen)?
5. In a combustion process in which a specified percentage of excess air is used, and in which CO is one of the products of combustion, will the analysis of the resulting exit gases contain more or less oxygen than if all the carbon had gone to CO_2?

In solving the following problems, be sure to employ the 10 steps listed in Table 2.4.

6. Pure carbon is burned in oxygen. The flue-gas analysis is:

CO_2	75 mol %
CO	14 mol %
O_2	11 mol %

What was the percent excess oxygen used?

7. Toluene, C_7H_8, is burned with 30% excess air. A bad burner causes 15% of the carbon to form soot (pure C) deposited on the walls of the furnace. What is the Orsat analysis of the gases leaving the furnace?
8. A cereal product containing 55% water is made at the rate of 500 kg/hr. You need to dry the product so that it contains only 30% water. How much water has to be evaporated per hour?
9. If 100 g of Na_2SO_4 is dissolved in 200 g of H_2O and the solution is cooled until 100 g of $Na_2SO_4 \cdot 10H_2O$ crystallizes out, find
   (a) The composition of the remaining solution *(mother liquor)*
   (b) The grams of crystals recovered per 100 g of initial solution
10. A synthesis gas analyzing CO_2: 6.4%, O_2: 0.2%, CO: 40.0%, and H_2: 50.8% (the balance is N_2) is burned with excess dry air. The problem is to determine composition of the flue gas. How many degrees of freedom exist in this problem, that is, how many additional variables have to have their values specified?

Thought Problems

1. In a small pharmaceutical plant, it had not been possible for a period of two months to get more than 80% of rated output from a boiler rated at 120,000 lb of steam per hour. The boiler had complete flow metering and combustion control equipment, but the steam flow could not be brought to more than 100,000 lb/hr.

   What would you recommend be done to find the cause(s) of the problem and alleviate it?
2. Although modern counterfeiters have mastered the duplication of the outside appearance of precious metals, some simple chemical/physical testing can determine their authenticity. Consult a reference book and determine the densities of gold, silver, copper, lead, iron, nickel, and zinc.

(a) Could the density of pure gold be duplicated by using any of these metals?
(b) Could the density of pure silver be duplicated by using any of these metals?
(c) Assume that the volumes are conserved on mixing of the metals. What is the weight percent composition of a lead/tin alloy that could be used to counterfeit silver? What physical property makes this alloy an unlikely candidate?

2.4 SOLVING MATERIAL BALANCE PROBLEMS INVOLVING SIMULTANEOUS EQUATIONS

Your objectives in studying this section are to be able to:

1. Write a set of independent material balance equations for a process.
2. Solve one or two simultaneous nonlinear equations.
3. Solve a set of linear equations.
4. Apply the 10-step strategy to solve steady-state problems (with or without chemical reaction) that require the solution of simultaneous equations.

In Sec. 2.3 you learned how to formulate uncoupled material balances that could be solved one equation at a time for the values of the unknown variables. All the equations were quite simple, and you did not have to solve two or more equations (called *irreducible equations* because of the nature of their coupling) simultaneously. You should have observed in Sec. 2.3 that the information provided with respect to the problems such as flows and concentrations was of a special structure that led to the resulting material balances being uncoupled.

Many of the problems that you will work with will lead to sets of equations that do have to be solved simultaneously. The purpose of this section is to show you that the formulation of such problems follows the same strategy as used in Sec. 2.3, the strategy outlined in Table 2.4. If only two or three coupled linear material balances are written for a problem, the unknown variables can be solved for by substitution of one equation into another. If the material balances consist of large sets of linear equations, you will find suggestions for solving them in Appendix L, and Fortran computer codes to solve them on the disk in the pocket in the back of this book. A single material balance that is a nonlinear equation of the form $f(x_1, \ldots, x_n) = 0$ can be plotted by hand or by using a computer routine, and the root(s), that is, the crossing(s) of the horizontal axis, located; examine Fig. 2.10. If two nonlinear material balances have to be solved, you can plot them and see where they intersect, as in Fig. 2.11. Or, you can use one of the computer codes on the disk accompanying this book to obtain a solution(s) (refer to Sec. L.2 for details). All of the discussion in Sec. 2.2 concerning writing independent equations applies in this section as well. By making a balance for each component or atomic species in the sys-

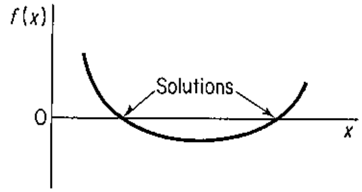


Figure 2.10 Solution(s) of a nonlinear equation by plotting.

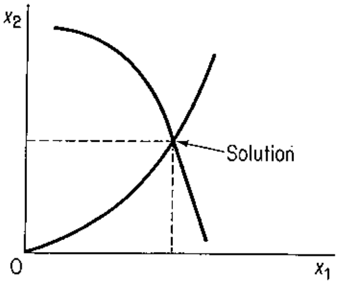


Figure 2.11 Solution of two simultaneous nonlinear equations by plotting.

tem defined, in most instances you can obtain a set of independent equations whether linear or nonlinear. A total mass balance may be substituted for one of the component mass balances. By following these rules of thumb, you should encounter no difficulty in generating sets of independent material balances for any process.

A special case of information structure occurs in some problems that leads to a particularly simple material balance, one that involves only two variables. For example, refer to Fig. 2.12. You note that no reaction takes place and the process presumably is in the steady state. Two components are present, hence you can write two independent mass balances:

$$\begin{aligned} &\text{EtOH:} \quad 0.50 = W(0) \quad + P(0.91) \\ &H_2O: \quad 0.50 = W(1.00) + P(0.09) \end{aligned}$$

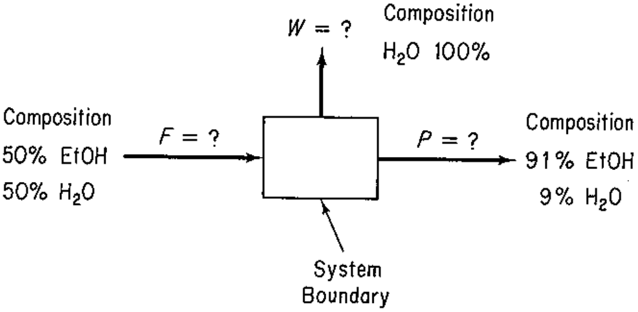


Figure 2.12 Ethanol is the tie component.

The ethanol (EtOH) balance directly relates F and P; W is not involved, as there is no ethanol in the W stream. A material or component that goes directly from one stream into another without changing in any respect or having like material added to it or lost from it is called a **tie component (element).** If a tie component exists in a problem, in effect you can write a material balance that involves *only two* streams. To detect a tie component, ask yourself the question: What component or element passes from one stream to another unchanged with constant mass? The answer is the tie component. Frequently, several components pass through a process with continuity so that more than one stream can be connected directly to its respective companion stream. Sometimes a minor constituent passes through with continuity, but if the percentage error for the analysis of this component is large, you should not use it as a tie component. A tie component can be useful even if you do not know all the compositions and weights in any given problem because the tie component enables you to put two streams on the same basis, thus effecting a *partial solution* even if the entire problem is not resolved.

Several examples follow in which two or more material balance equations have to be solved simultaneously.

EXAMPLE 2.13 Mixing

Dilute sulfuric acid has to be added to dry charged batteries at service stations to activate a battery. You are asked to prepare a batch of new acid as follows. A tank of old weak battery acid (H_2SO_4) solution contains 12.43% H_2SO_4 (the remainder is pure water). If 200 kg of 77.7% H_2SO_4 is added to the tank, and the final solution is 18.63% H_2SO_4, how many kilograms of battery acid have been made? See Fig. E2.13.

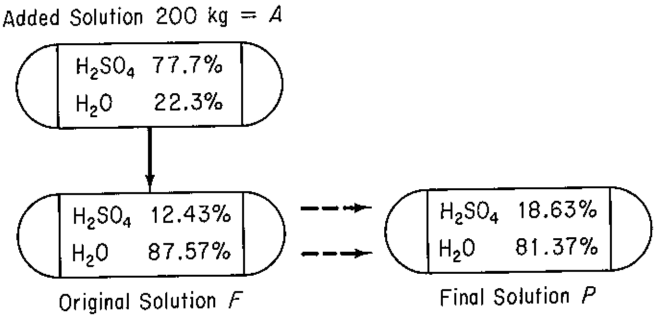


Figure E2.13

Solution

Steps 1, 2, and 3 All the data have been entered on Fig. E2.13. The unknown quantities are F and P.

Step 4 Take 200 kg of A as the basis.

Steps 5 and 6 Two components are present: H_2SO_4 and H_2O, hence you can write two independent mass balances. A unique solution exists.

Steps 7 and 8 The balances will be in kilograms.

Type of Balance	*Accumulation in Tank*				*A in*
	Final		*Initial*		
H_2SO_4	$P(0.1863)$	$-$	$F(0.1243)$	$=$	$200(0.777)$
H_2O	$P(0.8137)$	$-$	$F(0.8757)$	$=$	$200(0.223)$
Total	P	$-$	F	$=$	200

Note that any pair of the three equations are independent, but coupled, hence must be solved simultaneously to get F and P.

Step 9 Because the equations are linear and only two occur, you can take the total mass balance, solve it for F, and substitute for F in the H_2SO_4 balance to calculate P.

$$(P - 200)(0.1243) + 200(0.777) = P(0.1863)$$

$$P = 2110 \text{ kg acid}$$

$$F = 1910 \text{ kg acid}$$

Step 10 Check the answer using the H_2O balance.

EXAMPLE 2.14 Distillation

A typical distillation column is shown in Fig. E2.14 together with the known information for each stream. Calculate the kilograms of distillate per kilogram of feed and per kilogram of waste.

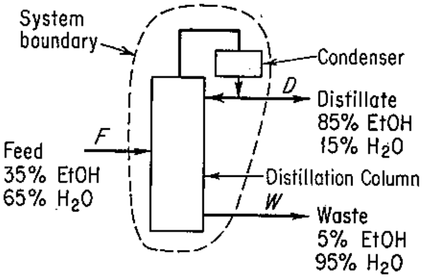


Figure E2.14

Solution

Superficially, the problem in this example looks to be similar to the problem in Example 2.11, but a different set of stream flow values are known and unknown in this example. Consequently, a set of coupled mass balances results. Compare Fig. E2.14 with Fig. E2.11.

Steps 1, 2, and 3 Figure E2.14 already has inscribed on it the preliminary information.

Step 4 Select a basis.

Basis: 1.00 kg of feed = F

Step 5 The unknown quantities are D and W.

Step 6 Two independent material balances can be written so that a unique solution is possible.

Step 7

Type of balance	*In*	=	*Out*
Total	1.00	=	$D + W$
EtOH	$1.00(0.35)$	=	$D(0.85) + W(0.05)$
H_2O	$1.00(0.65)$	=	$D(0.15) + W(0.95)$

Step 8 Two equations must be solved simultaneously.

Step 9 Solve for $W = (1.00 - D)$ using the total balance. Then

$$1.00(0.35) = D(0.85) + (1.00 - D)(0.05)$$

$$D = 0.375 \text{ kg/kg feed}$$

Since $W = 1 - 0.375 = 0.625$ lb,

$$\frac{D}{W} = \frac{0.375}{0.625} = \frac{0.60 \text{ kg}}{\text{kg}}$$

Step 10 Check your solution by using the H_2O balance.

EXAMPLE 2.15 Drying

Fish caught by human beings can be turned into fish meal, and the fish meal can be used as feed to produce meat for human beings or used directly as food. The direct use of fish meal significantly increases the efficiency of the food chain. However, fish-protein concentrate, primarily for aesthetic reasons, is used as a supplementary protein food. As such, it competes with soy and other oilseed proteins.

In the processing of the fish, after the oil is extracted, the fish cake is dried in rotary drum dryers, finely ground, and packed. The resulting product contains 65% protein. In a given batch of fish cake that contains 80% water (the remainder is dry cake), 100 kg of water is removed, and it is found that the fish cake is then 40% water. Calculate the weight of the fish cake originally put into the dryer.

Solution

Steps 1, 2, and 3 Figure E2.15 is a diagram of the process.

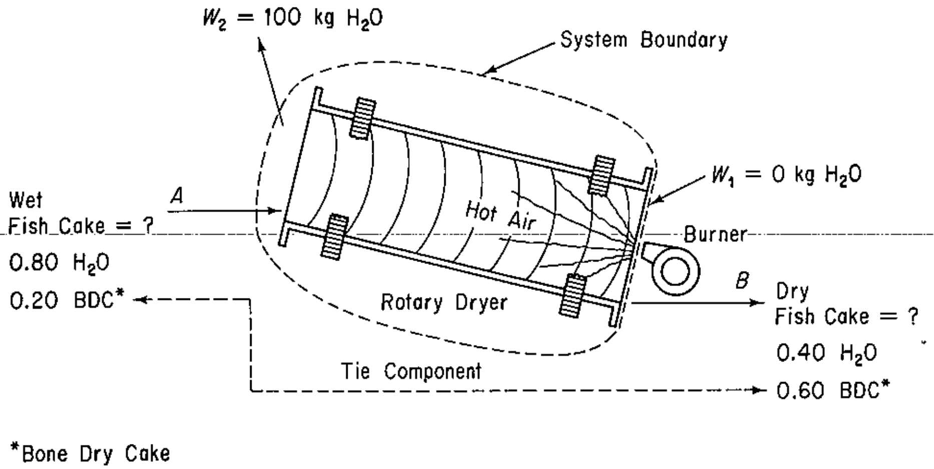


Figure E2.15

Step 4 Take a basis of what is given.

Basis: 100 kg of water evaporated = W

Step 5 The unknown stream flows are two: A and B. All the compositions are known.

Step 6 Two independent balances can be written so that a unique solution exists.

Steps 7 and 8 To solve the problem requires the use of two independent mass balance equations.

$$\begin{array}{lll} & \underline{\mathit{In}} \quad\quad \underline{\mathit{Out}} & \\ \text{Total balance:} & A = B + W = B + 100 & \left.\right\} \text{mass balances} \\ \text{BDC balance:} & 0.20A = 0.60B & \end{array}$$

Step 9 Notice that because the bone dry cake balance involves only two streams, you can set up a direct ratio of A to B, which is the essence of the tie component:

$$B = \frac{0.20\,A}{0.60} = \frac{1}{3}A$$

Introduction of this ratio into the total balance gives

$$A = \tfrac{1}{3}A + 100$$

$$\tfrac{2}{3}A = 100$$

$$A = 150 \text{ kg initial cake}$$

We did not use the water balance

$$0.80A = 0.40B + 100$$

because the BDC balance was slightly easier to use. The water balance can be used as a check on the calculations.

Step 10 Water balance:

$$0.80(150) \overset{?}{=} 0.40(150)(1/3) + 100$$

$$120 = 120$$

EXAMPLE 2.16 Crystallization

The solubility of barium nitrate at 100°C is 34 g/100 g of H_2O and at 0°C is 5.0 g/100 g of H_2O. If you start with 100 g of $Ba(NO_3)_2$ and make a saturated solution in water at 100°C, how much water is required? If the saturated solution is cooled to 0°C, how much $Ba(NO_3)_2$ is precipitated out of solution? The precipitated crystals carry along with them on their surface 4 g of H_2O per 100 g of crystals.

Solution

Steps 1, 2, and 3 The process can be viewed as an unsteady process without reaction in a tank as shown in Fig. E2.16. We first must calculate all the compositions for which data are given.

Step 4 Take as a basis 100 g of $Ba(NO_3)_2$.

Step 3 (Continued) The maximum solubility of $Ba(NO_3)_2$ in H_2O at 100°C is a saturated solution, 34 g/100 g of H_2O. Thus the amount of water required at 100°C is

$$\begin{array}{c|c} 100 \text{ g } H_2O & 100 \text{ g } Ba(NO_3)_2 \\ \hline 34 \text{ g } Ba(NO_3)_2 & \end{array} = 294.1 \text{ g } H_2O$$

If the 100°C solution is cooled to 0°C, the $Ba(NO_3)_2$ solution will still be saturated so that the

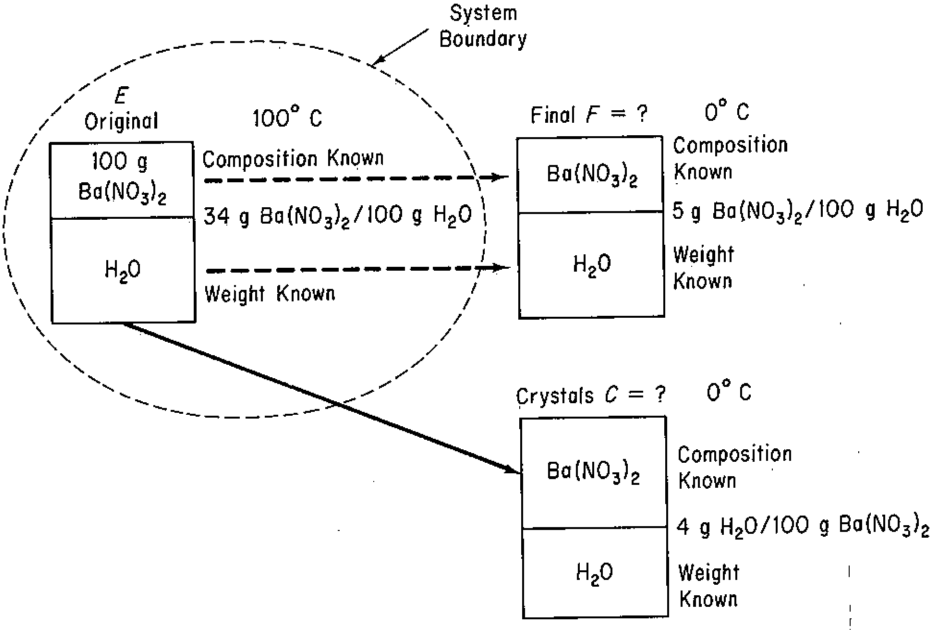


Figure E2.16

composition of the final solution is

$$Ba(NO_3)_2: \quad \frac{5}{100 + 5} = 0.0476$$

$$H_2O: \quad \frac{100}{100 + 5} = 0.9524$$

The composition of the crystals is

$$Ba(NO_3)_2: \quad \frac{100}{100 + 4} = 0.9615$$

$$H_2O: \quad \frac{4}{100 + 4} = 0.0385$$

Steps 5 and 6 We have two unknowns, F and C, and can make two independent mass balances so that the problem has a unique solution.

Steps 7, 8, and 9

Balance	*Final solution*		*Initial solution*		*Transport through boundary (out)*
$Ba(NO_3)_2$:	$F(0.0476)$	−	100	=	$-C(0.9615)$
H_2O:	$F(0.9524)$	−	294.1	=	$-C(0.0385)$
Total:	F	−	(100 + 294.1)	=	$-C$

Solve the $Ba(NO_3)_2$ and total balance to get

$$F = 305.2 \text{ g} \qquad C = 88.89 \text{ g}$$

Step 10 Check using the water balance

$$305.2(0.9524) - 294.1 \stackrel{?}{=} -88.89(0.0385)$$

$$-3.42 = -3.42$$

The $Ba(NO_3)_2$ that precipitates out on a dry basis is

$$\frac{88.89 \text{ g } C}{} \Bigg| \frac{0.9615 \text{ g } Ba(NO_3)_2}{1 \text{ g } C} = 85.5 \text{ g } Ba(NO_3)_2$$

EXAMPLE 2.17 Combustion

The main advantage of catalytic incineration of odorous gases or other obnoxious substances over direct combustion is the lower cost. Catalytic incinerators operate at lower temperatures—500 to 900°C compared with 1100 to 1500°C for thermal incinerators—and use substantially less fuel. Because of the lower operating temperatures, materials of construction do not need to be as heat resistant, reducing installation and construction costs.

In a test run, a liquid having the composition 88% C and 12% H_2 is vaporized and burned with dry air to a flue gas (fg) of the following composition on a dry basis:

CO_2	13.4%
O_2	3.6%
N_2	83.0%
	100.0%

To compute the volume of the continuous steady state combustion device, determine how many kilogram moles of dry fg are produced per 100 kg of liquid feed. What was the percentage of excess air used?

Solution

Steps 1, 2, and 3 The necessary data are placed in Fig. E2.17. Do not forget the water vapor! And that a reaction occurs!

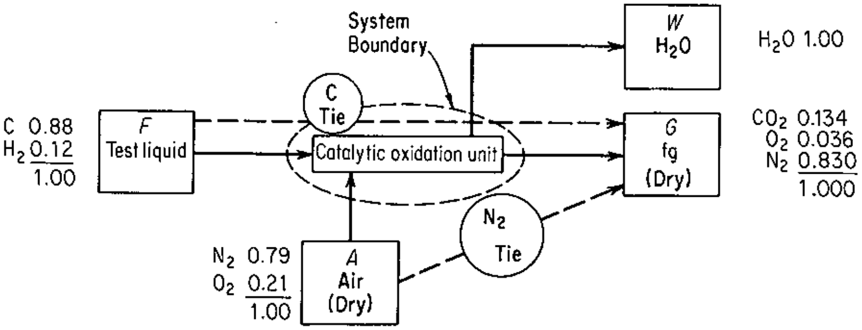


Figure E2.17

Step 4 Select 100 kg mol of dry fg as a convenient basis.

$$\text{Basis: } 100 \text{ kg mol dry fg} = G$$

Steps 5 and 6 F, A, and W are all unknown values; all the compositions are known. Four material balances on the elements can be made; hence the problem has a unique solution, and one equation will not be independent. Can you show that the rank of the matrix of the coefficients of F, A, and W is only 3?

Step 7 The atomic species balances (in moles) are (F is in kg; A, W, and G are in kg moles):

$$\begin{array}{lccccccc}
 & \underline{\quad F \quad} & & \underline{\quad A \quad} & & \underline{\quad W \quad} & & \underline{\qquad G \qquad} \\
\text{C:} & \dfrac{F(0.88)}{12} & + & 0 & = & 0 & + & 100(0.134) \\
\text{H}_2\text{:} & \dfrac{F(0.12)}{2.016} & + & 0 & = & W & + & 0 \\
\text{O}_2\text{:} & 0 & + & A(0.21) & = & W(\tfrac{1}{2}) & + & 100(0.134 + 0.036) \\
\text{N}_2\text{:} & 0 & + & A(0.79) & = & 0 & + & 100(0.830)
\end{array}$$

Steps 8 and 9 The equations can be solved sequentially starting with C, then N_2, and finally H_2 (to get W, although W is not asked for).

$$\text{From C:} \qquad F = \frac{13.4(12)}{0.88} = 182.73 \text{ kg}$$

$$\text{From N}_2\text{:} \qquad A = \frac{83.0}{0.79} = 105.06 \text{ kg mol}$$

$$\text{From H}_2\text{:} \qquad W = \frac{182.73(0.12)}{2.016} = 10.88 \text{ kg mol}$$

Step 10 Use the oxygen balance as a check.

$$105.06(0.21) \overset{?}{=} 10.88(\tfrac{1}{2}) + 17.00$$

$$22.06 \overset{?}{=} 22.44$$

An exact balance does not occur, but the answers agree reasonably well here. In many combustion problems, slight errors in the data will cause large differences in the calculated flows and percentage of excess air. Assuming that no mathematical mistakes have been made (it is wise to check), the better solution is the one involving the use of the most precise data.

We can now answer the requested questions.

$$\frac{G}{F} = \frac{100 \text{ kg mol}}{182.73 \text{ kg}} = \frac{54.73 \text{ kg mol } G}{100 \text{ kg } F}$$

The percent excess air can be calculated via two routes:

$$\% \text{ excess air} = 100 \times \frac{\text{excess O}_2}{\text{O}_2 \text{ entering} - \text{excess O}_2} \tag{a}$$

or

$$\%\text{ excess air} = 100 \times \frac{\text{excess } O_2}{\text{required } O_2} \qquad \text{(b)}$$

The excess O_2 is 3.6 mol; the O_2 entering is [13.4 + 3.6 + 10.88(0.5)] = 22.44 kg mol; and the required O_2 is

$$C + O_2 \longrightarrow CO_2: \quad \frac{182.73(0.88)}{12} \quad = 13.40 \text{ kg mol}$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O: \quad \frac{182.73(0.12)}{2.016}\left(\frac{1}{2}\right) = \frac{5.44 \text{ kg mol}}{18.84 \text{ kg mol}}$$

By Eq. (a),

$$\%\text{ excess air} = 100\frac{3.6}{22.44 - 3.6} = 19.1\%$$

By Eq. (b),

$$\%\text{ excess air} = 100\frac{3.6}{18.84} = 19.1\%$$

You can make use of the tie components as an alternative way to solve the problem in this example as follows.

Because we do not have to answer any questions about the water in the exit flue-gas stream, a tie element to relate the test fluid to the dry flue gas and one to relate the air to the dry flue gas would be sufficient to solve the problem. In examining the data to determine whether a tie element exists, we see that the carbon goes directly from the test fluid to the dry flue gas, and nowhere else, so carbon will serve as one tie component. The N_2 in the air all shows up in the dry flue gas, so N_2 can be used as another tie component.

Let us start to work the problem on a different basis.

Basis: 100 kg of test fluid

$$\frac{88 \text{ kg C}}{} \left| \frac{1 \text{ kg mol C}}{12 \text{ kg C}} \right. = 7.33 \text{ kg mol C}$$

$$\frac{12 \text{ kg } H_2}{} \left| \frac{1 \text{ kg mol } H_2}{2.016 \text{ kg } H_2} \right. = 5.95 \text{ kg mol } H_2$$

(a) By using kilogram moles of C as the tie component, we obtain

$$\frac{100 \text{ kg mol dry fg}}{13.4 \text{ kg mol C}} \left| \frac{7.33 \text{ kg mol C}}{100 \text{ kg test fluid}} \right. = \frac{54.7 \text{ kg mol dry fg}}{100 \text{ kg test fluid}}$$

(b) The N_2 serves as the tie component to tie the air to the dry flue gas, and since we know the excess O_2 in the dry flue gas, the percentage of excess air can be computed.

Basis: 100 kg mol of dry fg

$$\frac{83.0 \text{ kg mol } N_2}{} \left| \frac{1.00 \text{ kg mol air}}{0.79 \text{ kg mol } N_2} \right. = \frac{105.06 \text{ kg mol air}}{100 \text{ kg mol dry fg}}$$

$$(105.06)(0.21) = O_2 \text{ entering} = 22.06 \text{ kg mol } O_2$$

Or, saving one step,

$$\frac{83.0 \text{ kg mol N}_2 \;\Big|\; 0.21 \text{ kg mol O}_2 \text{ in air}}{\;\Big|\; 0.79 \text{ kg mol N}_2 \text{ in air}} = \frac{22.06 \text{ kg mol O}_2 \text{ entering}}{100 \text{ kg mol dry fg}}$$

$$\% \text{ excess air} = 100\frac{\text{excess O}_2}{\text{O}_2 \text{ entering} - \text{excess O}_2} = \frac{(100)3.6}{22.06 - 3.6} = 19.5\%$$

If a dry flue gas analysis shows some CO, as in the following hypothetical analysis:

CO_2	11.9%
CO	1.6%
O_2	4.1%
N_2	82.4%

then, on the basis of 100 moles of dry flue gas, we would calculate the percent excess air as follows:

O_2 entering with air:

$$\frac{82.4 \text{ kg mol N}_2 \;\Big|\; 0.21 \text{ kg mol O}_2}{\;\Big|\; 0.79 \text{ kg mol N}_2} = 21.9 \text{ kg mol O}_2$$

Excess O_2:

$$4.1 - \frac{1.6}{2} = 3.3 \text{ kg mol}$$

$$\% \text{ excess air} = 100\frac{3.3}{21.9 - 3.3} = 17.7\%$$

Note that to get the true excess oxygen, the apparent excess oxygen in dry flue gas, 4.1 kg moles, **has to be reduced by the amount of the theoretical oxygen not combining with the CO.** According to the reactions

$$C + O_2 \longrightarrow CO_2 \qquad C + \tfrac{1}{2}O_2 \longrightarrow CO$$

for each mole of CO in the dry flue gas, $\frac{1}{2}$ mole of O_2 which should have combined with the carbon to form CO_2 did not do so. This $\frac{1}{2}$ mole carried over into the flue gas and inflated the value of the true excess oxygen expected to be in the flue gas. For this analysis, 1.6 kg mol of CO are in the flue gas, so that (1.6/2) kg mol of theoretical oxygen are found in the flue gas in addition to the true excess oxygen. Always keep in mind that the definition of excess oxygen is based on complete combustion.

EXAMPLE 2.18 Combustion of Coal

A local utility burns coal having the following composition on a dry basis.

Component	Percent
C	83.05
H	4.45
O	3.36
N	1.08
S	0.70
Ash	7.36
Total	100.0

The average Orsat analysis of gas from the stack during a 24-hr test was

Component	Percent
$CO_2 + SO_2$	15.4
CO	0.0
O_2	4.0
N_2	80.6
Total	100.0

Moisture in the fuel was 3.90%, and the air on the average contained 0.0048 lb H_2O/lb dry air. The refuse showed 14.0% unburned coal, with the remainder being ash.

You are asked to check the consistency of the data before they are stored in a data base. Is the consistency satisfactory? What was the average percent excess air used?

Solution

This is a steady-state problem with reaction.

Steps 1, 2, and 3 The process is shown in Fig. E2.18. In making the diagram, do not forget the water in the stack!

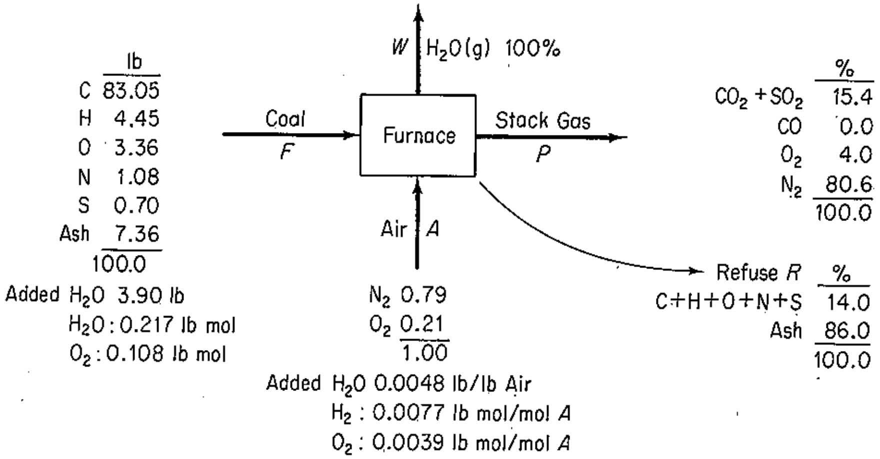


Figure E2.18

Step 4 Pick as a basis $F = 100$ lb.

Step 3, 7, and 8 We need first to get all the compositions possible and put them on the diagram. We calculate the H as H_2 and O as O_2 in the H_2O in both F and A, and the composition of R by use of an ash balance (ash is the tie component).

In coal:

$$\begin{array}{c|c|c} 3.90\ \text{lb H}_2\text{O} & 1\ \text{lb mol H}_2\text{O} & 1\ \text{lb mol H}_2 \\ \hline & 18\ \text{lb H}_2\text{O} & 1\ \text{lb mol H}_2\text{O} \end{array} = 0.217\ \text{lb mol H}_2$$

$$(0.108\ \text{lb mol O}_2)$$

In air:

$$\begin{array}{c|c|c} 0.0048\ \text{lb H}_2\text{O} & 29\ \text{lb air} & 1\ \text{lb mol H}_2\text{O} \\ \hline \text{lb air} & 1\ \text{lb mol air} & 18\ \text{lb H}_2\text{O} \end{array} = 0.0077 \frac{\text{lb mol H}_2\text{O}}{\text{lb mol air}}$$

$$(0.0077\ \text{lb mol H}_2/\text{lb mol A})$$

$$(0.0039\ \text{lb mol O}_2/\text{lb mol A})$$

We might neglect the C, H, O, N, and S in the refuse but will include the amounts to show what calculations are necessary if the amounts of the elements are significant. The ash balance is (ash is a tie component)

$$7.36 = R(0.86)$$

$$R = 8.56\ \text{lb}$$

The unburned coal in the refuse is

$$8.56(0.14) = 1.20\ \text{lb}$$

If we assume that the combustibles in the refuse occur in the same proportions as they do in the coal (which may not be true), the quantities of the combustibles in R on an ash-free basis are:

Component	wt %	lb	lb mol
C	89.65	1.076	0.0897
H	4.80	0.058	0.0537
O	3.63	0.0436	0.0027
N	1.17	0.014	0.0010
S	0.76	0.009	0.0003
	100.00	1.20	0.1474

Steps 5 and 6 We can make four additional balances (the C and S must be combined because of the stack gas analysis), and have only three unknown variables: A, W, and P; hence one balance can be used to check the data as it is redundant. The balances (all in lb mol) are:

	In			*Out*		
	in F	in A		in W	in P	in R
C + S:	$\frac{83.05}{12} + \frac{0.70}{32}$ +	0	=	0 +	$P(0.154)$	+ 0.0897 + 0.0003

	In			*Out*		
	in *F*	in *A*		in *W*	in *P*	in *R*
H_2:	$\frac{4.45}{2.016} + 0.217 +$	$0.0077A$	$=$	$W +$	0	$+ \quad \frac{0.0537}{2}$
O_2:	$\frac{3.36}{32} + 0.108 +$	$0.21A + 0.0039A$	$=$	$\frac{W}{2}$	$+ P(0.154 + 0.040) +$	$\frac{0.0027}{2}$
N_2:	$\frac{1.08}{28} +$	$0.79A$	$=$	$0 +$	$P(0.806)$	$+ \quad \frac{0.001}{2}$

Solve the C + S balance to get $P = 44.99$. Then solve the N_2 balance to get $A = 45.35$. Next, solve the H_2 balance to get $W = 2.747$. Finally, use the O_2 balance to serve as a check: $9.914 \overset{?}{=} 10.009$. The difference is about 1%. Inasmuch as the data provided are actual measurements, in view of the random and possibly biased errors in the data, the round-off error introduced in the calculations, and possible leaks in the furnace, the data seem to be quite satisfactory. Try calculating W, a small number, from both the H_2 and O_2 balances. What size error do you find?

To calculate the excess air, because of the oxygen in the coal and the existence of unburned combustibles, we will calculate the total oxygen in and the required oxygen:

$$\% \text{ excess air} = 100 \times \frac{O_2 \text{ entering} - O_2 \text{ required}}{O_2 \text{ required}}$$

Assume that no oxygen is required by the ash. The required O_2 is

Component	Reaction	lb		lb mol	Required O_2 (lb mol)
C	$C + O_2 \rightarrow CO_2$	83.05	C	6.921	6.921
H	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	4.45	H_2	2.207	1.104
O	—	3.36	O_2	0.105	(0.105)
N	—	—	—	—	—
S	$S + O_2 \rightarrow SO_2$	0.70	S	0.022	0.022
					7.942

and the oxygen in the air is (45.35)(0.21) = 9.524 lb mol.

$$\% \text{ excess air} = 100 \times \frac{9.524 - 7.942}{7.942} = 19.9\%$$

If you (incorrectly) calculated the % excess air from just the wet stack gas analysis, you would get

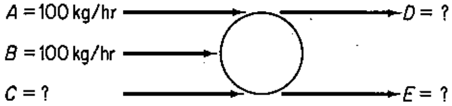
$$100 \times \frac{4.0}{15.4 + 2.747/2} = 23.8\%$$

In the next section we turn to the solution of material balance problems involving multiple units.

Self-Assessment Test

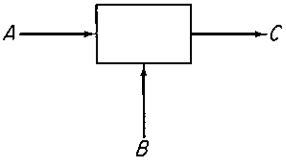
1. Write a set of independent material balance equations for the system shown. The liquid streams are A, B, C, D, and E. The components are 1, 2, and 3. The table lists the known mass fractions.

	A	B	C	D
1:	0.5	0.3	0.6	0.8
2:	0.3	0.2	0.4	0.2
3:	0.2	0.5		



2. In the figure the compositions are (no reaction occurs):

	A	B	C
$MgCO_3$:	0.10	0.05	0.0675
Na_2CO_3:	0.20	0.10	0.1350
H_2O:	0.70	0.85	0.7975



Write down the mass balances and solve for A and B given that $C = 100$ kg/hr.

3. Solve this equation for positive-real roots:

$$X^4 - X^3 - 10X^2 - X + 1 = 0$$

4. Solve these equations for a set of (x, y) that are real:

$$4.20x^2 + 8.80y^2 = 1.42$$
$$(x - 1.2)^2 + (y - 0.6)^2 = 1$$

In solving the following problems, be sure to employ the 10 steps listed in Table 2.4.

5. A coal analyzing 65.4% C, 5.3% H, 0.6% S, 1.1% N, 18.5% O, and 9.1% ash is burned so that all combustible is burnt out of the ash. The dry flue gas analyzes 13.00% CO_2, 0.76% CO, 6.17% O_2, 0.87% H_2, and 79.20% N_2. All the sulfur burns to SO_2, which is included in the CO_2 figure in the gas analysis (i.e., $CO_2 + SO_2 = 13.00\%$). Calculate:
   (a) Pounds of coal fired per 100 lb mol of dry flue gas as analyzed
   (b) Ratio of moles total combustion gases to moles of dry air supplied
   (c) Total moles of water vapor in the stack gas per 100 lb of coal if the air is dry
   (d) Percent excess air

6. A cellulose solution contains 5.2% cellulose by weight in water. How many kilograms of 1.2% solution are required to dilute 100 kg of 5.2% solution to 4.2%?
7. Hydrofluoric acid (HF) can be manufactured by treating calcium fluoride (CaF_2) with sulfuric acid (H_2SO_4). The other product of the reaction is calcium sulfate ($CaSO_4$). A sample of fluorospar (the raw material) contains 75% by weight CaF_2 and 25% inert (nonreacting) materials. The pure sulfuric acid used in the process is in 30% excess of that theoretically required. Most of the manufactured HF leaves the reaction chamber as a gas, but a solid cake is also removed from the reaction chamber that contains 5% of all the HF formed, plus $CaSO_4$, inerts, and unreacted sulfuric acid. How many kilograms of *cake* are produced per 100 kg of fluorospar charged to the process?
8. A solution contains 60% $Na_2S_2O_2$ and 1% soluble impurity in water. Upon cooling to 10°C, $Na_2S_2O_2 \cdot 5H_2O$ crystallizes out. The solubility of this hydrate is 1.4 lb $Na_2S_2O_2 \cdot 5H_2O$/lb free water. The crystals removed carry as adhering solution 0.06 lb solution/lb crystals. These are dried to remove the remaining water (but not the water of hydration). The final dry $Na_2S_2O_2 \cdot 5H_2O$ crystals must not contain more than 0.1% by weight of impurity. In order to meet this specification calculate:
   (a) The amount of water added before cooling
   (b) The percentage recovery of the $Na_2S_2O_2$ in the crystals.
9. Salt in crude oil must be removed before the oil undergoes processing in a refinery. The crude oil is fed to a washing unit where freshwater feed to the unit mixes with the oil and dissolves a portion of the salt contained in the oil. The oil (containing some salt but no water), being less dense than the water, can be removed at the top of the washer. The "spent" wash water (containing salt but no oil) is removed at the bottom of the washer. If the "spent" wash water contains 15% salt and the crude contains 5% salt, determine the concentration of salt in the "washed" oil product if the ratio of crude oil (with salt) to water used is 4:1.
10. A hydrocarbon fuel is burnt with excess air. The Orsat analysis of the flue gas shows 10.2% CO_2, 1.0% CO, 8.4% O_2, and 80.4% N_2. What is the atomic ratio of H to C in the fuel?

2.5 SOLVING MATERIAL BALANCE PROBLEMS INVOLVING MULTIPLE SUBSYSTEMS

Your objectives in studying this section are to be able to:

1. Write a set of independent material balances for a complex process involving more than one unit.
2. Solve problems involving several connected units by applying the 10-step strategy.

Chemical plants such as illustrated by the flowsheet in Fig. 2.4 are comprised of many interconnected units. However, you can easily apply the same techniques discussed so far to such complex processes. **All you have to do is divide the plant up into subsystems that you analyze one at a time.** If more than one piece of equipment or more than one junction point is involved in the problem to be solved, you can write material balances for each piece of equipment and a balance around the whole process. However, since the overall balance is nothing more than the sum of the balances about each piece of equipment, not all the balances you might write will be independent. Appendix L discusses how you can determine whether linear equations are independent or not.

Under some circumstances, particularly if you split a big problem into smaller parts to make the calculations easier, you may want to make a material balance about a **mixing point.** As illustrated in Fig. 2.13, a mixing point is nothing more than a junction of three or more streams and can be designated as a system in exactly the same fashion as any other piece of equipment. Examine Fig. 2.14. Which streams have the same composition? Is the composition of stream 5 the same as the composition inside the unit? It will be if the contents of the unit are **well mixed,** the assumption in this text. Streams 5, 6, and 7 must have the same composition, and presumably if no reaction takes place, the output composition is the properly weighted average of the input compositions 3 and 4.

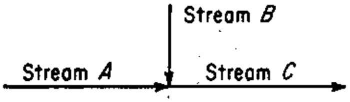


Figure 2.13 Mixing point.

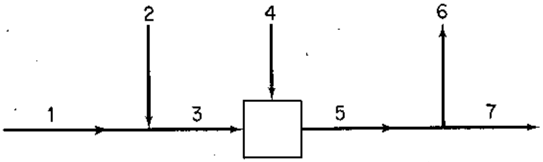


Figure 2.14 Multiple junction points.

Now let us turn to the analysis of simple combinations of units. Suppose that a system is comprised of three subsystems as indicated in Fig. 2.15. You can make material balances for the subsystems and overall system—just make sure that the balances selected for your solution are independent! How many values of the variables are unknown? There will be seven in all: W, P, A, B, C, $\omega_{KCl,A}$ and $\omega_{H_2O,A}$.

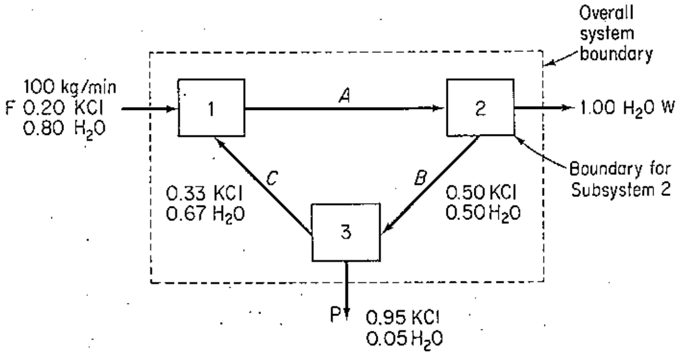


Figure 2.15 Flow diagram of a system comprised of three subsystems. No reaction takes place. The subsystem boundaries are the boxes.

How many independent equations must be written to obtain a unique solution? Seven. How many independent equations can you write? Two for each subsystem plus the sum of mass fractions for stream A. What are the names of such a set of equations? One set might be:

Unit 1, total: $100 + C = A$

Unit 1, KCl: $(0.20)(100) + (0.33)(C) = (\omega_{\text{KCl},A})(A)$

Unit 2, total: $A = W + B$

Unit 2, KCl: $(\omega_{\text{KCl},A})(A) = (0.50)B$

Overall, total: $100 = W + P$

Overall, KCl: $(0.20)100 = (0.95)P$

$\Sigma\,\omega_i = 1$: $\omega_{\text{KCl},A} + \omega_{\text{H}_2\text{O},A} = 1$

Other sets are possible. Write down a different set. Did you note that the set we have used has been chosen so as to include as few of the unknown variables as possible in a given equation; that is, we made component balances on KCl and not on H_2O. Keep in mind that the number of degrees of freedom summed for all the subsystems must be equal to zero to have a unique solution for the equations. In general, you can make the same number of independent balances as there are components or atomic species in each subsystem you define, **but not always.** Read the following example.

EXAMPLE 2.19 Independent Material Balances

Examine Fig. E2.19. The composition of each stream is as follows:

(1) Pure A
(2) Pure B
(3) A and B, concentrations known
(4) Pure C
(5) A, B, and C, concentrations known
(6) Pure D
(7) A and D, concentrations known
(8) B and C, concentrations known

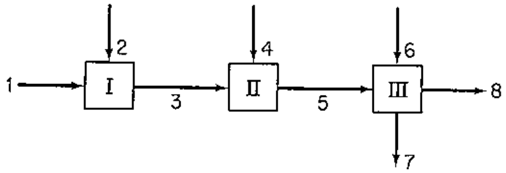


Figure E2.19

What is the maximum number of independent material balances that could be generated to solve this problem?

Solution

	Number of component balances
At unit I, two components are involved	2
At unit II, three components are involved	3
At unit III, four components are involved	4
Total	9

However, not all of the balances are independent. In the following list, all the concentrations are known values, and F represents the stream flow designated by the subscript.

Subsystem 1

$$\text{Balances}\begin{cases} A: & F_1(1.00) + F_2(0) = F_3(\omega_{F_3,A}) \\ B: & F_1(0) + F_2(1.00) = F_3(\omega_{F_3,B}) \end{cases}$$

Subsystem 2

$$\text{Balances}\begin{cases} A: & F_3(\omega_{F_3,A}) + F_4(0) = F_5(\omega_{F_5,A}) \\ B: & F_3(\omega_{F_3,B}) + F_4(0) = F_5(\omega_{F_5,\mathrm{B}}) \\ C: & F_3(0) + F_4(1.00) = F_5(\omega_{F_5,C}) \end{cases}$$

Subsystem 3:

$$\text{Balances}\begin{cases} A: & F_5(\omega_{F_5,A}) + F_6(0) = F_7(\omega_{F_7,A}) + F_8(0) \\ B: & F_5(\omega_{F_5,B}) + F_6(0) = F_7(0) + F_8(\omega_{F_8,B}) \\ C: & F_5(\omega_{F_5,C}) + F_6(0) = F_7(0) + F_8(\omega_{F_8,C}) \\ D: & F_5(0) + F_6(1.00) = F_7(\omega_{F_7,D}) + F_8(0) \end{cases}$$

If you take as a basis F_1, seven values of F_i are unknown, hence only seven independent equations need be written. The B balance in subsystem II and the C balance in subsystem III prove to be redundant (can you show why?), so that a unique solution can be obtained.

Can you show that one or more component balances around systems I and II, or II and III in Example 2.19, or the entire set of three units, will add *no* additional independent balances to the set of component material balances made on each individual unit? Can you show that a total balance on each unit, or on units I + II, or II + III, or around the entire system of three units, will add *no* additional independent balances? Can you substitute one of the indicated alternative material balances for an independent component balance? Yes (as long as the precision of the balance is about the same).

EXAMPLE 2.20 Multiple Units in Which No Reaction Occurs

Acetone is used in the manufacture of many chemicals and also as a solvent. In its latter role, many restrictions are placed on the release of acetone vapor to the environment. You are asked to design an acetone recovery system having the flowsheet illustrated in Fig. E2.20. As a starting point, make a material balance for the system shown in Fig. E2.20. All the concentrations shown in Fig. E2.20 of both gases and liquids are specified in *weight percent* to make the calculations simpler.

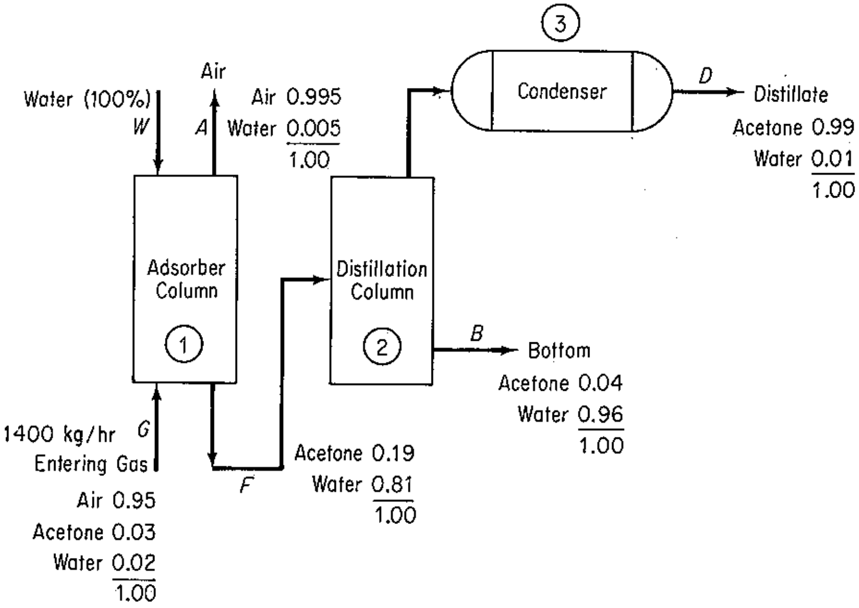


Figure E2.20

Solution

Steps 1, 2, and 3 All the stream compositions are given. No reaction occurs, and we assume that the process is in the steady state. All of the unknown stream flows are designated by symbols in the figure.

Step 4 Pick 1 hr as a basis so that $G = 1400$ kg.

Steps 5 and 6 We start the analysis with column 1. Three components exist in column 1, and three values of the streams are unknown: W, A, and F; hence a unique solution can be obtained for column 1.

Steps 7 and 8 The mass balances for column 1 are as follows.

	In	*Out*	
Air:	1400 (0.95)	$= A(0.995)$	(a)
Acetone:	1400 (0.03)	$= F(0.19)$	(b)
Water:	$1400\ (0.02) + W(1.00)$	$= F(0.81) + A(0.005)$	(c)

The air and acetone are tie components. (Check to make sure that the equations are independent.)

Step 9 Solve Eqs. (a), (b), and (c) to get

$$A = 1336.7 \text{ kg/hr}$$

$$F = 221.05 \text{ kg/hr}$$

$$W = 157.7 \text{ kg/hr}$$

Step 10 (Check) Use the total balance.

$$G + W = A + F$$

$$\begin{array}{rr} 1400 & 1336 \\ \underline{157.7} & \underline{221.05} \\ 1557.7 \cong & 1557.1 \end{array}$$

Steps 5 and 6 Applied to Units 2 and 3 Combined The subsystem boundary for analysis encompasses the distillation column and the condenser. Two components exist, and two values of the flow streams are unknown, D and B; hence a unique solution exists (if the mass balances are independent, as they are).

Steps 7 and 8 The mass balances are

Acetone: $221.05(0.19) = D(0.99) + B(0.04)$ (d)

Water: $221.05(0.81) = D(0.01) + B(0.96)$ (e)

Step 9 Solve Eqs. (d) and (e) to get

$$D = 34.91 \text{ kg/hr}$$

$$B = 186.1 \text{ kg/hr}$$

Step 10 (Check) Use the total balance

$$F = D + B \quad \text{or} \quad 221.05 \cong 34.91 + 186.1 = 221.01$$

As a matter of interest, what other mass balances could be written for the system and substituted for any one of the Eqs. (a)–(e)? Typical balances would be the overall balances.

	In		*Out*	
Air:	$G(0.95)$	=	$A(0.995)$	(f)
Acetone:	$G(0.03)$	=	$D(0.99) + B(0.04)$	(g)
Water:	$G(0.02)$	=	$A(0.005) + D(0.01) + B(0.96)$	(h)
Total:	$G + W$	=	$A + D + B$	(i)

Equations (f)–(i) do not add any extra information to the problem; the degrees of freedom are still zero. But any one of the equations can be substituted for one of Eqs. (a)–(e) as long as you make sure that the resulting set of equations is independent.

EXAMPLE 2.21 Multiple Units in Which a Reaction Occurs

In the face of higher fuel costs and the uncertainty of the supply of a particular fuel, many companies operate two furnaces, one with natural gas and the other with fuel oil. In the

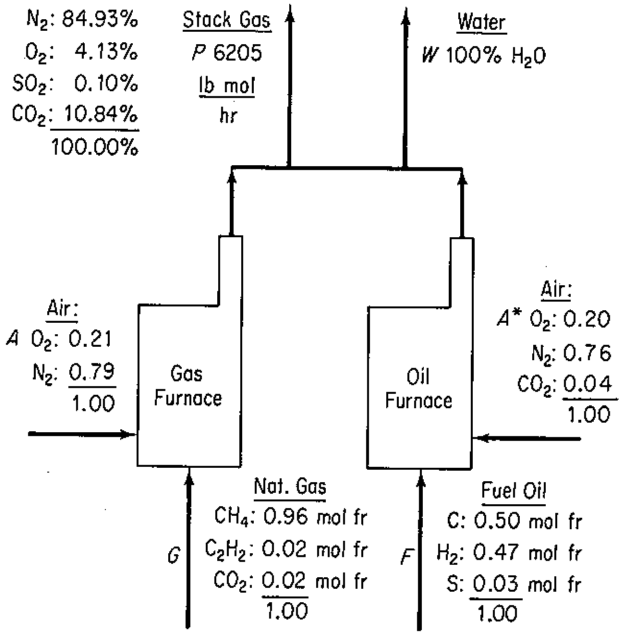


Figure E2.21

RAMAD Corp., each furnace had its own supply of oxygen; the gas furnace used air, and the fuel oil furnace used a gas stream that analyzed: O_2, 20%; N_2, 76%; and CO_2, 4%, but the stack gases went up a common stack. See Fig. E2.21.

During one blizzard, all transportation to the RAMAD Corp. was cut off, and officials were worried about the dwindling reserves of fuel oil because the natural gas supply was being used at its maximum rate possible. The reserve of fuel oil was only 1000 bbl. How many hours could the company operate before shutting down if no additional fuel oil was attainable? How many lb mol/hr of natural gas were being consumed? The minimum heating load for the company when translated into the stack gas output was 6205 lb mol/hr of dry stack gas. Analysis of the fuels and stack gas at this time were:

Natural gas		Fuel oil (API gravity = 24.0) (Mol %)		Stack gas (Orsat analysis)	
CH_4	96%	C	50	N_2	84.93%
C_2H_2	2%	H_2	47	O_2	4.13%
CO_2	2%	S	3	CO_2	10.84%
				SO_2	0.10%

Solution

We want to calculate F and G in lb mol/hr and then F in bbl/hr.

Steps 1, 2, and 3 The molecular weight of the fuel oil is 7.91 lb/lb mol, and the density is 7.578 lb/gal.

Step 4

Basis: 1 hr, so that $P = 6205$ lb mol

Steps 5 and 6 We have five atomic components in this problem and five streams whose values are unknown, A, G, F, A^*, and W; hence, if the elemental mole balances are independent, we can obtain a unique solution for the problem.

Step 7 The overall mole balances for the elements are

$$
\begin{array}{lll}
 & \underline{\qquad\qquad \textit{In} \qquad\qquad} & \underline{\qquad\qquad \textit{Out} \qquad\qquad} \\
H_2: & G(1.94) + F(0.47) & = W(1) \\
N_2: & A(0.79) + A^*(0.76) & = 6205(0.8493) \\
O_2: & A(0.21) + A^*(0.20 + 0.04) & = 6205(0.0413 + 0.001 + 0.1084) \\
 & \qquad + G(0.02) & \qquad + W(\tfrac{1}{2}) \\
S: & F(0.03) & = 6205(0.001) \\
C: & G(0.96 + (2)(0.02) + 0.02) & \\
 & \qquad + F(0.50) + 0.04A^* & = 6205(0.1084)
\end{array}
$$

Steps 8 and 9 Solve the S balance for F (inaccuracy in the SO_2 concentration will cause some error in F, unfortunately); the sulfur is a tie component. Then solve the other four balances simultaneously for G.

$$F = 207 \text{ lb mol/hr}$$

$$G = 498 \text{ lb mol/hr}$$

Finally, the fuel oil consumption is

$$\frac{207 \text{ mol}}{\text{hr}}\left|\frac{7.91 \text{ lb}}{\text{mol}}\right|\frac{\text{gal}}{7.578 \text{ lb}}\left|\frac{\text{bbl}}{42 \text{ gal}}\right. = 5.14 \text{ bbl/hr}$$

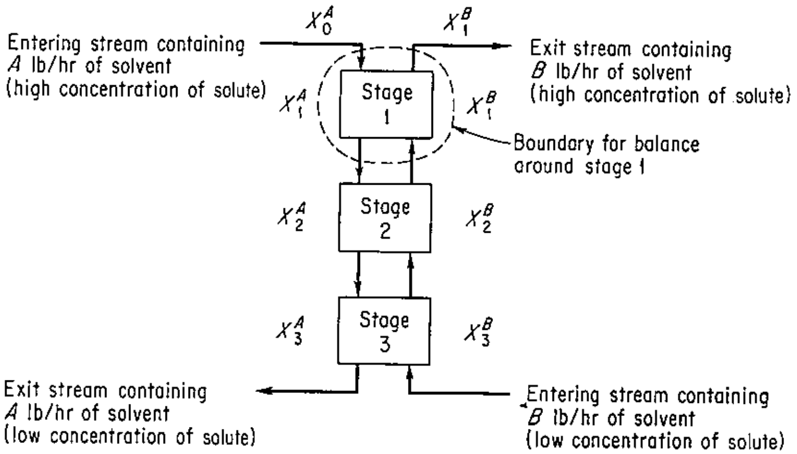
If fuel oil reserve was only 1000 bbl, this amount could last

$$\frac{1000 \text{ bbl}}{5.14 \dfrac{\text{bbl}}{\text{hr}}} = 195 \text{ hr}$$

EXAMPLE 2.22 Countercurrent Stagewise Mass Transfer

In many commercial processes such as distillation, extraction, absorption of gases in liquids, and the like, the entering and leaving streams represent two different phases that flow in opposite directions to each other, as shown in Fig. E2.22a. (The figure could just as well be laid on its side.)

This type of operation is known as *countercurrent* operation. If equilibrium is attained between each stream at each stage in the apparatus, calculations can be carried out to relate the flow rates and concentration of products to the size and other design features of the apparatus. We shall illustrate how a material balance can be made for such type of equipment. The letter X stands for the weight concentration of solute in pounds of solute per pound of stream, solute-free. The streams are assumed immiscible as in a liquid–liquid extraction process.



A, B = lb of stream less solute in the stream
= lb of solvent

Figure E2.22a

Around stage 1 the solute material balance is (the superscript on X denotes the stream and the subscript the stage)

$$\overset{\textbf{in}}{\frac{A\text{ lb}}{\text{hr}}\bigg|\frac{X_0^A\text{ lb}}{\text{lb }A} + \frac{B\text{ lb}}{\text{hr}}\bigg|\frac{X_2^B\text{ lb}}{\text{lb }B}} = \overset{\textbf{out}}{\frac{A\text{ lb}}{\text{hr}}\bigg|\frac{X_1^A\text{ lb}}{\text{lb }A} + \frac{B\text{ lb}}{\text{hr}}\bigg|\frac{X_1^B\text{ lb}}{\text{lb }B}}\,.$$

or

$$A(X_0^A - X_1^A) = B(X_1^B - X_2^B) \tag{a}$$

Around stage 2 the solute material balance is

$$\overset{\textbf{in}}{\frac{A\text{ lb}}{\text{hr}}\bigg|\frac{X_1^A\text{ lb}}{\text{lb }A} + \frac{B\text{ lb}}{\text{hr}}\bigg|\frac{X_3^B\text{ lb}}{\text{lb }B}} = \overset{\textbf{out}}{\frac{A\text{ lb}}{\text{hr}}\bigg|\frac{X_2^A\text{ lb}}{\text{lb }A} + \frac{B\text{ lb}}{\text{hr}}\bigg|\frac{X_2^B\text{ lb}}{\text{lb }B}}$$

or

$$A(X_1^A - X_2^A) = B(X_2^B - X_3^B)$$

We could generalize that for any stage number n

$$A(X_{n-1}^A - X_n^A) = B(X_n^B - X_{n+1}^B) \tag{b}$$

Also, a solute material balance could be written about the sum of stage 1 and stage 2 as follows:

$$\overset{\textbf{in}}{A(X_0^A) + B(X_3^B)} = \overset{\textbf{out}}{A(X_2^A) + B(X_1^B)} \tag{c}$$

or to generalize for an overall solute material balance between the top end and the nth stage,

$$A(X_0^A - X_n^A) = B(X_1^B - X_{n+1}^B)$$

or for the $(n-1)$th stage,

$$A(X_0^A - X_{n-1}^A) = B(X_1^B - X_n^B)$$

Multiplying the equation by -1, we obtain

$$A(X_{n-1}^A - X_0^A) = B(X_n^B - X_1^B) \tag{d}$$

If we rearrange Eq. (d) assuming that A, B, X_0^A, and X_1^B are constants (i.e., steady-state operation) and X^A and X^B are the variables as we go from stage to stage, we can write

$$AX_{n-1}^A = \frac{B}{A}X_n^B + \left(X_0^A - \frac{B}{A}X_1^B\right) \tag{e}$$

Equations (a)–(e) represent an unusual type of equation, one that gives the relationship between discrete points rather than continuous variables; it is called a *difference* equation. In Eq. (e) the locus of these points will fall upon a line with the slope B/A and an intercept $[X_0^A - (B/A)X_1^B]$, as shown in Fig. E2.22b.

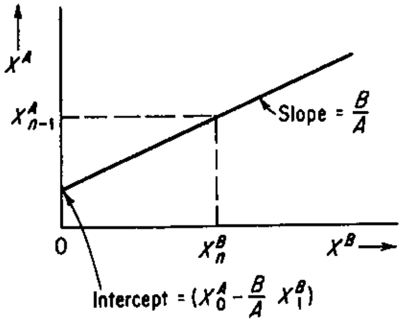
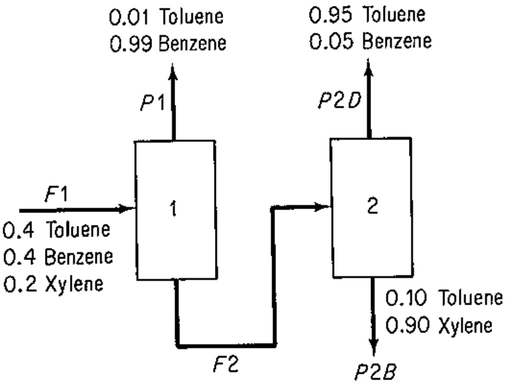


Figure E2.22b

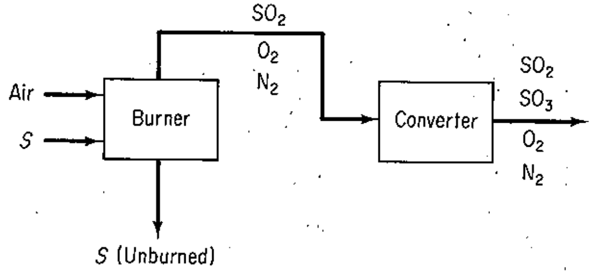
In the next section we look at material balances in which some material is recycled (fed back) from upstream in a process back to the start of the process.

Self-Assessment Test

1. A two-stage separations unit is shown in the figure. Given that the input stream F1 is 1000 lb/hr, calculate the value of F2 and the composition of F2.



2. A simplified process for the production of SO_3 to be used in the manufacture of sulfuric acid is illustrated in the figure. Sulfur is burned with 100% excess air in the burner, but for the reaction $S + O_2 \rightarrow SO_2$, only 90% conversion of the S to SO_2 is achieved. In the converter, the conversion of SO_2 to SO_3 is 95% complete. Calculate the lb of air required per 100 lb of sulfur burned, and the concentration in mole fraction or percent of the exit gas from the burner and from the converter.



2.6 RECYCLE, BYPASS, AND PURGE CALCULATIONS

Your objectives in studying this section are to be able to:

1. Draw a flow diagram for problems involving recycle, bypass, and purge.
2. Apply the 10-step strategy to solve steady-state problems (with and without chemical reaction) involving recycle, and/or bypass, and/or purge streams.
3. Solve problems in which a modest number of interconnected units are involved by making appropriate balances.
4. Use the overall conversion and single-pass (once-through) conversion concepts to solve recycle problems involving reactors.
5. Explain the purpose of a recycle stream, a bypass stream, and a purge stream.

Recycle stream is a term denoting a process stream that conducts material exiting or downstream from a unit back to the inlet or upstream of the same unit. For example, in a reactor, unreacted material is separated from the reactor products and *fed back* and joins with a stream of reactants that enter the reactor. Examine Figure 2.16. In Figure 2.4 you can observe the recycle of C_6H_6 from the settler back to the evaporator. As another example, in planning long space missions, all the food and water will have to be provided from stores on board the spacecraft. Figure 2.17 shows the recycle of O_2 and water.

Many industrial processes employ recycle streams. In some drying operations, the humidity in the air is controlled by recirculating part of the wet air that leaves

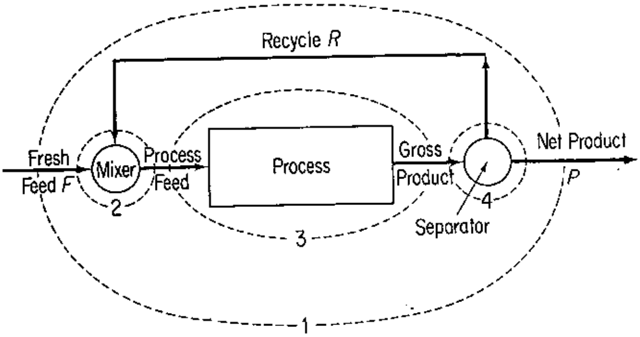


Figure 2.16 Process with recycle (the numbers designate possible system boundaries for the material balances—see the text).

the dryer. In chemical reactions, exit catalyst is returned to the reactor for reuse. Another example of the use of recycling is in fractionating columns where part of the distillate is refluxed through the column to maintain the quantity of liquid within the column.

Do not let recycle streams confuse you. The steps in the analysis and solution of material balance problems involving recycle are the same as described in Table 2.4. With a little practice in solving problems involving recycle, you should experience little difficulty in solving recycle problems in general. The essential point you should grasp with respect to recycle calculations in this chapter is that the processes such as shown in Fig. 2.4 or 2.16 are in the *steady state*.

> **No buildup or depletion of material takes place inside the process or in the recycle stream.**

The values of F, P, and R in Fig. 2.16 are *constant*. Unsteady-state processes such as startup and shutdown are discussed in Chapter 6.

2.6-1 Recycle in Processes without Chemical Reaction

The strategy listed in Table 2.4 is the strategy to be used in solving recycle problems. You can make component and total material balances for each subsystem as discussed in Sec. 2.5, as well as component and total balances for the overall process. Not all of the equations so formulated will be independent, of course. Depending on the information available concerning the amount and composition of each stream, you can determine the amount and composition of the unknowns. If tie components are available, they often simplify the calculations.

Examine Fig. 2.16. Material balances can be written for several different systems, four of which are shown by dashed lines in Fig. 2.16:

- **(a)** About the entire process including the recycle stream, as indicated by the dashed lines (marked 1 in Fig. 2.16)
- **(b)** About the junction point at which the fresh feed is combined with the recycle stream (marked 2 in Fig. 2.16)
- **(c)** About the process only (marked 3 in Fig. 2.16)
- **(d)** About the junction point at which the gross product is separated into recycle and net product (marked 4 in Fig. 2.16)

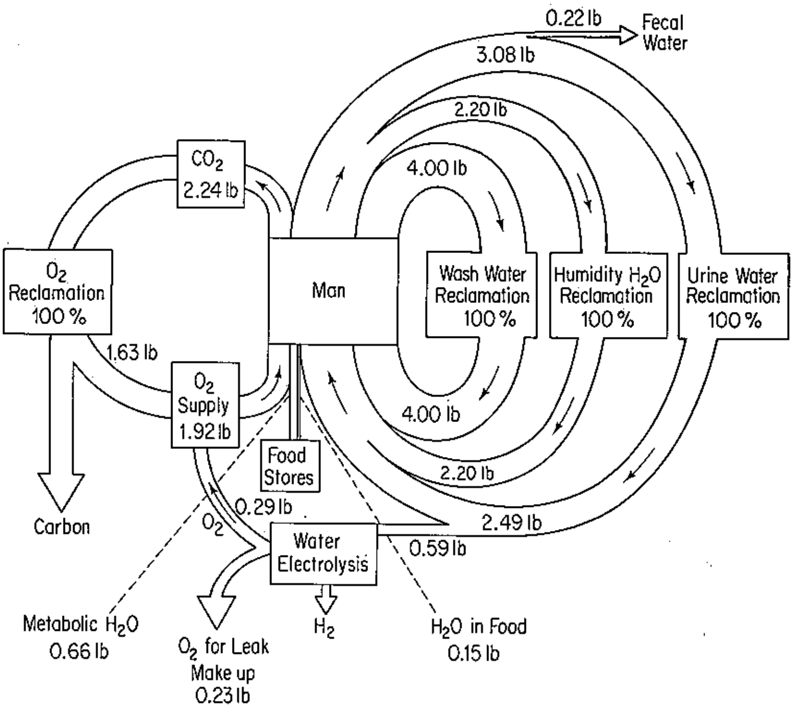


Figure 2.17 Water and oxygen recycle in a space vehicle.

In addition, balances can be made about combinations of subsystems, such as the process plus the separator (3 + 4). Only three of the four balances (a)–(d) are independent for one component. However, balance 1 will not include the recycle stream, so that the balance will not be directly useful in calculating a value for the recycle *R*. Balances 2 and 4 do include *R*. You could write a material balance for the combination of subsystems 2 and 3 or 3 and 4 and include the recycle stream.

EXAMPLE 2.23 Recycle

Examine the flow sheet in Fig. E2.23, a flowsheet that contains recycle streams. What is the maximum number of independent material balances that can be written for the system if each stream contains three components, ethanol, acetone, and methanol?

Solution

Three material balances (corresponding to three components) can be written each for units *A*, *B*, and *C*, for a total of 9. Any other material balance, such as one for the combined subsystem *A* and *B* or *A* and *C*, can be obtained by appropriate combination of the nine component material balances. However, all nine of the material balances may not be independent. How many would be independent would depend on the specific values of the flow streams and concentrations that are known and unknown.

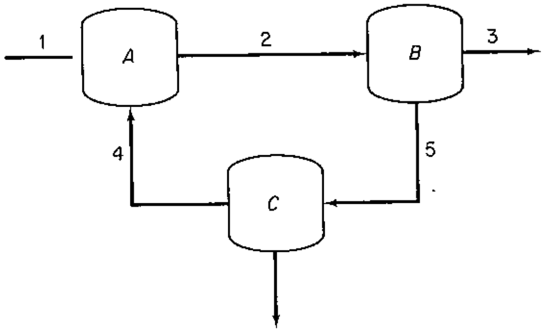


Figure E2.23

EXAMPLE 2.24 Recycle without Chemical Reaction

A distillation column separates 10,000 kg/hr of a 50% benzene–50% toluene mixture. The product *D* recovered from the condenser at the top of the column contains 95% benzene, and the bottoms *W* from the column contain 96% toluene. The vapor stream *V* entering the condenser from the top of the column is 8000 kg/hr. A portion of the product from the condenser is returned to the column as reflux, and the rest is withdrawn for use elsewhere. Assume that the compositions of the streams at the top of the column (*V*), the product withdrawn (*D*), and the reflux (*R*) are identical because the *V* stream is condensed completely. Find the ratio of the amount refluxed to the product withdrawn (*D*).

Solution

This is a steady-state problem without reaction occurring.

Steps 1, 2, and 3 See Fig. E2.24 for the known data, symbols, and other information.

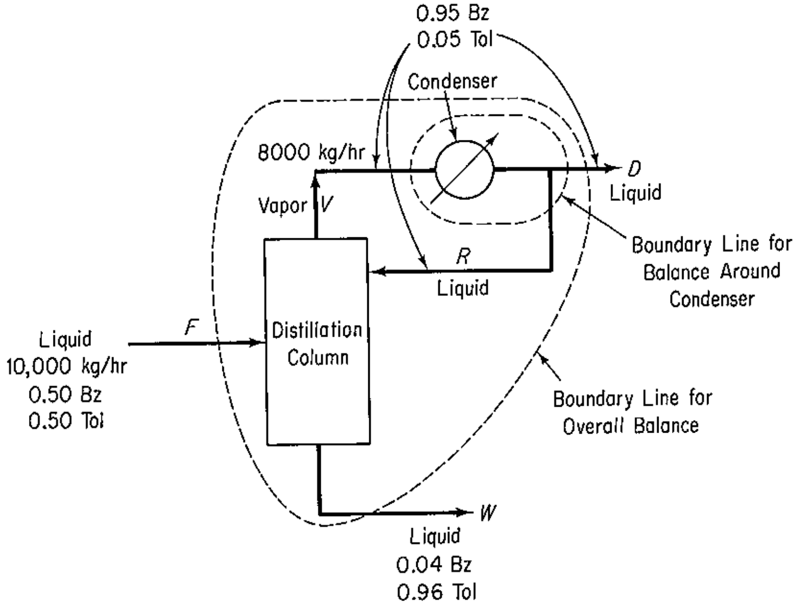


Figure E2.24

Step 4 Select a basis of 1 hr (equal to $F = 10{,}000$ kg).

Steps 5 and 6 All the compositions are known and three stream flows, D, W, and R, are unknown. No tie components are evident in this problem. Two component material balances can be made for the still and two for the condenser. Presumably three of these are independent; hence the problem has a unique solution. We can check as we proceed. A balance around either the distillation column or the condenser would involve the stream R. An overall balance would involve D and W but not R.

Steps 7, 8, and 9 What balances to select to solve for R is somewhat arbitrary. We will choose to use overall balances first to get D (and W), and then use a balance on the condenser to get R. Once D is obtained, R can be obtained by subtraction.

Overall Material balances:

Total material:

$$F = D + W$$

$$10{,}000 = D + W \tag{a}$$

Component (benzene):

$$F\omega_F = D\omega_D + W\omega_w$$

$$10{,}000(0.50) = D(0.95) + W(0.04) \tag{b}$$

Solving (a) and (b) together, we obtain

$$5000 = (0.95)(10{,}000 - W) + 0.04W$$

$$W = 4950 \text{ kg/hr}$$

$$D = 5050 \text{ kg/hr}$$

Balance around the condenser:

Total material:

$$V = R + D$$

$$8000 = R + 5050$$

$$R = 2950 \text{ kg/hr} \tag{c}$$

$$\frac{R}{D} = \frac{2950}{5050} = 0.58$$

Would the benzene or toluene balances on the condenser yield additional information to that obtained from the total balance, Eq. (c)? Write the balances down and check to see if they are redundant with Eq. (c).

EXAMPLE 2.25 Recycle without Chemical Reaction

The manufacture of such products as penicillin, tetracycline, vitamins, and other pharmaceuticals, as well as photographic chemicals, dyes, and other fine organic compounds, usually requires separating the suspended solids from their mother liquor by centrifuging, and then drying the wet cake. A closed-loop system (see Fig. E2.25a) for centrifuge unloading, drying, conveying, and solvent recovery is comprised of equipment especially designed for handling materials requiring sterile and contamination-free conditions.

Given the experimental measurements on the pilot plant equipment outlined in Fig. E2.25a, what is the lb/hr of the recycle stream R?

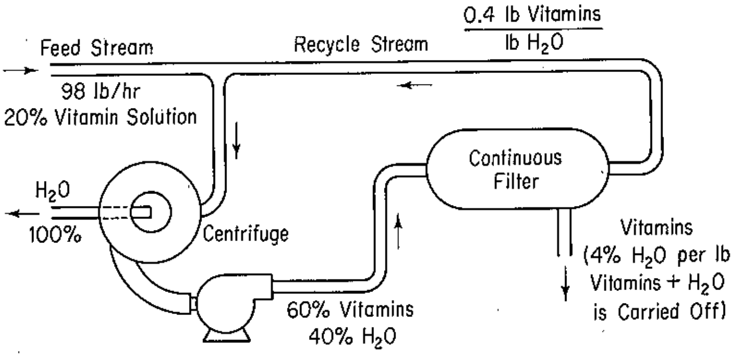


Figure E2.25a

Solution

Steps 1, 2, and 3 Figure E2.25a should be simplified with all the flows and compositions placed on it. Examine Fig. E2.25b. We computed the weight fraction of *V* in *R* from the data given in Fig. E2.25a. On the basis of 1 lb of water, the recycle stream contains (1.0 lb of H_2O + 0.4 lb of *V*) = 1.4 lb total. The recycle stream composition is

$$\frac{0.4 \text{ lb } V}{1 \text{ lb } H_2O}\left|\frac{1 \text{ lb } H_2O}{1.4 \text{ lb solution}}\right. = 0.286 \text{ lb } V/\text{lb solution}$$

so that there is 0.714 lb H_2O/lb solution.

Step 4 Pick as a basis 1 hr so that $F = 98$ lb.

Steps 5 and 6 We have four unknown values of variables, *W*, *C*, *P*, and *R*, and can make two component material balances on each of two units of equipment; hence the problem has a unique solution.

Steps 7, 8, and 9 Probably the most efficient procedure in solving this problem is to make overall mass balances to calculate *W* and *P*, and then write mass balances about one of the units to calculate *R*.

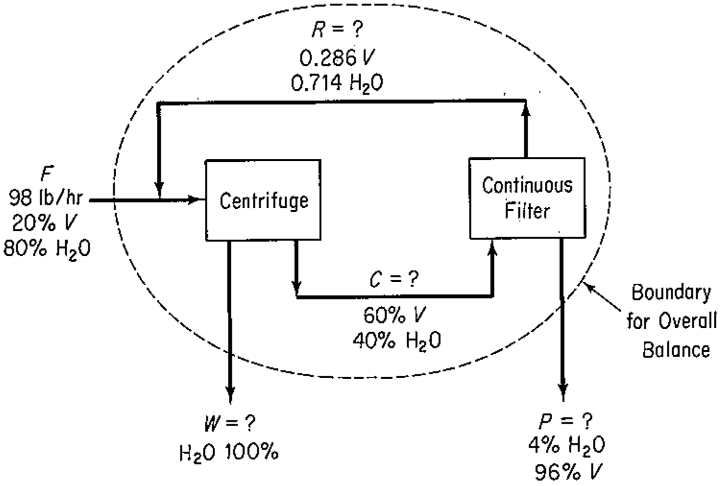


Figure E2.25b

Overall mass balances:

$$\begin{aligned}
&V: && 0.20(98) = 0 + 0.96P && \text{(a)}\\
&H_2O: && 0.80(98) = (1.0)W + 0.04P && \text{(b)}\\
&\text{Total:} && 98 = W + P && \text{(c)}
\end{aligned}$$

Observe that V is a tie component so that P can be calculated directly in Eq. (a): P = 20.4 lb, and W can be calculated from Eq. (c).

$$W = 98 - 20.4 = 77.6 \text{ lb}$$

Steps 7, 8, and 9 (Continued) To determine the recycle stream R, we need to make a balance that involves the stream R. Either (a) balances around the centrifuge or (b) balances around the filter will do. The latter are easier to formulate since the mixing of R and F does not have to be calculated.

Total balance on filter:

$$\begin{aligned}
C &= R + P\\
C &= R + 20.4
\end{aligned} \qquad \text{(d)}$$

Component V balance on filter:

$$\begin{aligned}
C\omega_C &= R\omega_R + P\omega_P\\
0.6C &= 0.286R + 0.96(20.4)
\end{aligned} \qquad \text{(e)}$$

Solving Eqs. (d) and (e), we obtain R = 23.4 lb/hr.

Step 10 Check the value of R using a material balance around the centrifuge.

2.6-2 Recycle in Processes with Chemical Reaction

Now let us turn to recycle problems in which a chemical reaction occurs. Recall from Sec. 1.9 that not all of the limiting reactant necessarily reacts in a process. Do you remember the concept of conversion as discussed in Sec. 1.9? Two bases for conversion are used in describing a process; examine Fig. 2.18.

(a) ***Overall fraction conversion:***

$$\frac{\text{mass (moles) of reactant in fresh feed—mass (moles) of reactant in output of the overall process}}{\text{mass (moles) of reactant in fresh feed}}$$

(b) ***Single-pass ("once-through") fraction conversion:***

$$\frac{\text{mass (moles) of reactant fed into the reactor—mass (moles) of reactant exiting the reactor}}{\text{mass (moles) of reactant fed into the reactor}}$$

When the fresh feed consists of more than one material, the conversion must be stated for a single component, usually the limiting reactant, the most expensive reactant, or some similar compound.

Note the distinction between *fresh feed* and *feed to the process*. The feed to the process itself is made up of two streams, the fresh feed and the recycled material.

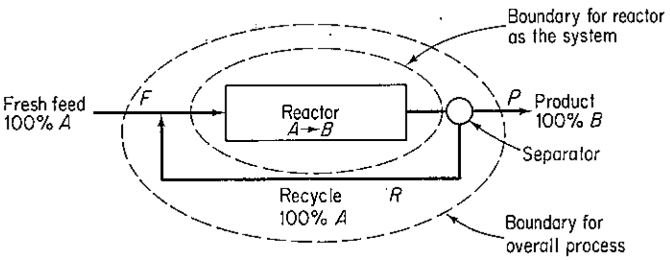


Figure 2.18 Recycle problem.

The gross product leaving the process is separated into two streams, the net product and the material to be recycled. In some cases the recycle stream may have the same composition as the gross product stream, while in other instances the composition may be entirely different depending on how the separation takes place and what happens in the process. Suppose that you are given the data that 30% of the *A* is converted to *B* on a single pass through the reactor, as illustrated in Fig. 2.18, and are asked to calculate the value of *R*, the recycle on the basis of 100 moles of fresh feed, *F*. We will make a balance for *A* with the reactor as the system.

Recall from Eq. (2.1) that for a specific chemical compound the steady-state material balance for a reactor is (the accumulation term in zero)

$$\left\{\begin{matrix}\textbf{input}\\\textbf{through}\\\textbf{system}\\\textbf{boundary}\end{matrix}\right\} - \left\{\begin{matrix}\textbf{output}\\\textbf{through}\\\textbf{system}\\\textbf{boundary}\end{matrix}\right\} + \left\{\begin{matrix}\textbf{generation}\\\textbf{within the}\\\textbf{system}\end{matrix}\right\} - \left\{\begin{matrix}\textbf{consumption}\\\textbf{within the}\\\textbf{system}\end{matrix}\right\} = 0 \qquad (2.12)$$

Reactants are consumed and products are generated. If a reaction takes place within the system, you must be given (or look up) information about the reaction stoichiometry and extent of reaction. Or, perhaps the question is to calculate the extent of conversion given some of the process data. In any case, the fraction of feed converted to products is always an essential additional piece of information that helps determine values of the terms in Eq. (2.12).

Let us examine how to apply Eq. (2.12) for a recycle reactor such as shown in Fig. 2.18, in which *A* is converted to *B*. How much *A* exits the reactor itself? The unconverted *A* is 70% of the *A* that enters the reactor. No *A* occurs in the *P* stream. The system is the reactor and the basis is 100 moles of fresh feed. The *A* balance is

$$\underbrace{[(1.0)(100) + (1.0)R]}_{\textit{Input of A}} - \underbrace{[(1.0)R + 0(P)]}_{\textit{Output of A}} - \underbrace{[0.30(100 + R)]}_{\textit{Consumption of A}} = 0$$

or

$$\underset{\textit{moles of A unconverted}}{0.70(100 + R)} = \underset{\textit{moles of A leaving the reactor}}{R}$$

$$R = 233 \text{ moles}$$

Note that in Fig. 2.18 all the *A* was recycled for simplicity of illustration of the principle, but such may not be the case in general. Nevertheless, Eq. (2.12) still applies.

The single-pass (mole) balance on A provides the crucial information to evaluate R. Will an A balance, or total balance, for the overall process enable you to solve for R? Try one and see why not. What is the overall fraction conversion of A for the entire process? Does that information help you solve for R?

EXAMPLE 2.26 Recycle with a Reaction Occurring

Immobilized glucose isomerase is used as a catalyst in producing fructose from glucose in a fixed-bed reactor (water is the solvent). For the system shown in Fig. E2.26a, what percent conversion of glucose results on one pass through the reactor when the exit stream/recycle ratio in moles is equal to 8.33? The reaction is

$$\underset{\text{d-glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{d-fructose}}{C_6H_{12}O_6}$$

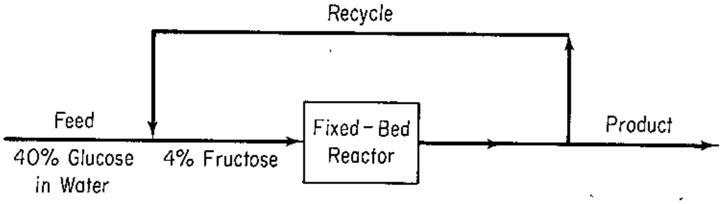


Figure E2.26a

Solution

We have a steady-state process with a reaction occurring.

Steps 1, 2, and 3 Figure E2.26b includes all the known and unknown values of the variables using appropriate notation (W stands for water, G for glucose, and F for fructose in the second position of the mass fraction subscripts). Note that the recycle stream and product stream have the same composition and consequently the same mass fraction symbols are used in the diagram for each stream.

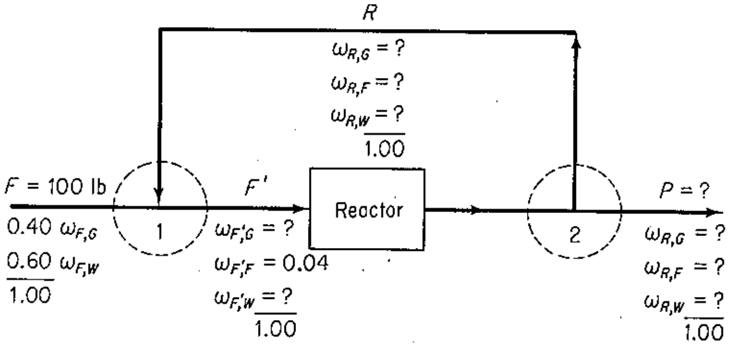


Figure E2.26b

Step 4 Pick as a basis F = 100 lb.

Steps 5 and 6 The sum of the mass fractions is one in each stream so that the unknown compositions can be picked to be $\omega_{F',G}$, $\omega_{R,G}$, $\omega_{R,W}$, and the unknown stream values are F' and P ($R = P/8.33$). Let f be the fraction conversion in the reactor. Three balances each can be make about the mixing point 1, the reactor, and the separation point 2. Not all the balances will be independent, but sufficient independent balances should exist to solve this problem. We can check as we proceed with the calculations rather than going through an extensive analysis at the beginning.

Steps 7, 8, and 9 We will start with overall balances, as they are the easiest to write.

Overall:

$$\textit{Total}:\quad 100 = P$$

Consequently,

$$R = \frac{100}{8.33} = 12.0 \text{ lb}$$

No water is generated or consumed, hence

$$\textit{Water}:\quad 100\,(0.60) = P\,(\omega_{R,W}) = 100\omega_{R,W}$$

$$\omega_{R,W} = 0.60$$

We now have left three unknown values of the variables plus f.

Mixing Point 1:

$$\textit{Total}:\quad 100 + 12 = F' = 112$$

$$\textit{Glucose}:\quad 100(0.40) + 12(\omega_{R,G}) = 112(\omega_{F',G})$$

$$\textit{Fructose}:\quad 0 + 12(\omega_{R,F}) = 112(0.04)$$

or

$$\omega_{R,F} = 0.373$$

Also, because $\omega_{R,F} + \omega_{R,G} + \omega_{R,W} = 1$,

$$\omega_{R,G} = 1 - 0.373 - 0.600 = 0.027$$

and then from the glucose balance,

$$\omega_{F',G} = 0.360$$

Reactor Plus Separator 2:

$$\textit{Total}:\quad F' = 12 + 100 = 112 \qquad \text{(redundant equation)}$$

Glucose:

$$\begin{array}{ccc} \underline{\textit{In}} & \underline{\textit{Out}} & \underline{\textit{Consumed}} \\ F'\omega_{F',G} & -\ (R+P)\omega_{R,G} & -\ fF'\omega_{F',G} = 0 \\ 112(0.360)\ - & 112(0.027) & -\ f(112)(0.360) = 0 \end{array}$$

$$f = 0.93$$

EXAMPLE 2.27 Recycle with a Reaction Occurring

Refined sugar (sucrose) can be converted to glucose and fructose by the inversion process.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{d\text{-Glucose}}{C_6H_{12}O_6} + \underset{d\text{-Fructose}}{C_6H_{12}O_6}$$

The combined quantity glucose/fructose is called inversion sugar. If 90% conversion of sucrose occurs on one pass through the reactor, what would be the recycle stream flow per 100 lb of sucrose solution entering the process shown in Fig. E2.27a? What is the concentration of inversion sugar (I) in the recycle stream and in the product stream? The concentrations of components in of the recycle stream and product stream are the same.

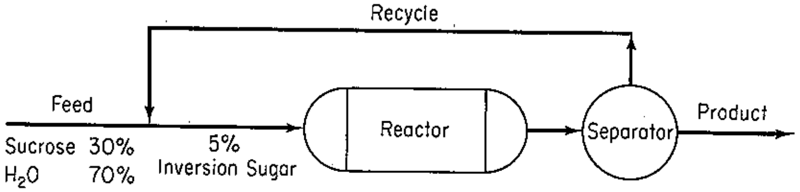


Figure E2.27a

Solution

Steps 1, 2, and 3 First we need to enter the concentrations and stream flows on the diagram. See Fig. E2.27b. (W stands for water, S for sucrose, and I for inversion sugar in the mass fraction subscripts.)

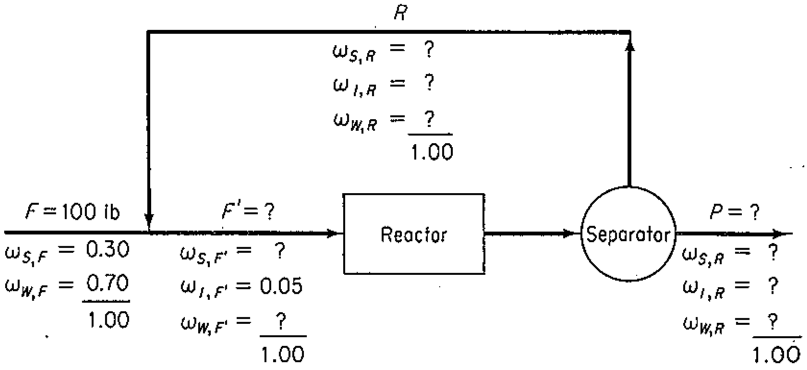


Figure E2.27b

Step 4

Basis: $F = 100$ lb

Steps 5 and 6 Keeping in mind that the sum of the mass fractions in each stream is unity, we have six unknown values of the variables, say $\omega_{S,F'}$, $\omega_{S,R}$, $\omega_{I,R}$, R, F', and P.

Steps 7, 8, and 9 Let us start with the necessary balances. Only the total balance in the overall balance is directly useful because the S and I balances involve the generation and consumption terms in Eq. (2.12).

Overall:

Total: $100 = P$

Mixing Point:

Total: $$100 + R = F' \quad \text{(a)}$$

Sucrose: $$100(0.30) + R\omega_{S,R} = F'\omega_{S,F'} \quad \text{(b)}$$

Inversion: $$0 + R\omega_{I,R} = F'(0.05) \quad \text{(c)}$$

Reactor plus Separator To avoid calculating the reactor output stream properties, we will make the system the reactor plus the separator. First we need to calculate the pounds of water consumed in the reaction per pound of sucrose consumed in the reaction.

1 mole sucrose uses 1 mole water

$$\frac{1 \text{ mol } W}{1 \text{ mol } S}\left|\frac{1 \text{ mol } S}{342.35 \text{ lb } S}\right|\frac{18 \text{ lb } W}{1 \text{ mol } W} = 0.0526\frac{\text{lb } W}{\text{lb } S}$$

Total: $F' = R + P = R + 100$ [redundant equation to (a)]

$$\text{Water:}\quad \underline{\textit{In}} \qquad \underline{\textit{Out}} \qquad \underline{\textit{Consumed}} \qquad \text{(d)}$$

$$F'(1 - 0.05 - \omega_{S,F'}) - (R + 100)(1 - \omega_{S,R} - \omega_{I,R}) - (F'\omega_{S,F'})(0.90)(0.0526) = 0$$

$$\text{Sucrose:}\quad \underline{\textit{In}} \qquad \underline{\textit{Out}} \qquad \underline{\textit{Consumed}} \qquad \text{(e)}$$

$$F'\omega_{S,F'} - (R + 100)\omega_{S,R} - (F'\omega_{S,F'})(0.90) = 0$$

We have five independent equations (a)–(e) that can be solved for the five unknown values of the variables listed in steps 5 and 6; the value of P is given by the overall total materials balance. Either by successive substitution of Eqs. (a)–(e) into each other or by use of a computer program (see Sec. 2.7), you can find

$$R = 20.9 \text{ lb}$$

$$\omega_{I,R} = \omega_{I,P} = 0.279$$

2.6-3 Bypass and Purge

Two additional commonly encountered types of process streams are shown in Fig. 2.19.

(a) A **bypass** stream—one that skips one or more stages of the process and goes directly to another stage

(b) A **purge** stream—a stream bled off to remove an accumulation of inerts or unwanted material that might otherwise build up in the recycle stream

A bypass stream is used to control the composition of a final exit stream from a unit by mixing the bypass stream and the unit exit stream in suitable proportions to obtain the desired final composition.

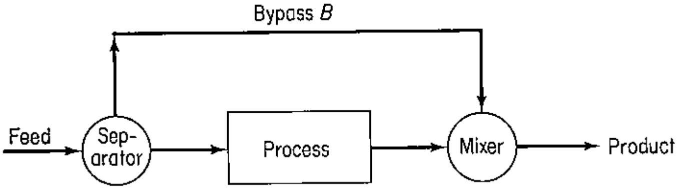


Figure 2.19a

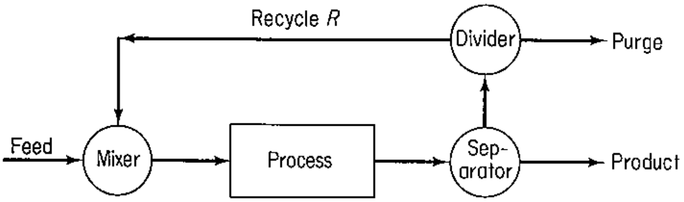


Figure 2.19b Recycle stream with purge.

As an example of the use of a purge stream, consider the production of NH_3. Steam reforming, with feedstock natural gas, LPG, or naphtha, is the most widely accepted process for ammonia manufacture. The route includes four major chemical steps:

$$\begin{array}{lccc} \text{Reforming:} & CH_4 + H_2O & \longrightarrow & CO + 3H_2 \\ \text{Shift:} & CO + H_2O & \longrightarrow & CO_2 + H_2 \\ \text{Methanation:} & CO + 3H_2 & \longrightarrow & H_2O + CH_4 \\ \text{Synthesis:} & 3H_2 + N_2 & \longrightarrow & 2NH_3 \end{array}$$

In the final stage, for the fourth reaction, the synthesis gas stream is approximately a 3:1 mixture of hydrogen to nitrogen, with the remainder about 0.9% methane and 0.3% argon.

Compressors step up the gas pressure from atmospheric to about 3000 psi—the high pressure that is needed to favor the synthesis equilibrium. Once pressurized and mixed with recycle gas, the stream enters the synthesis converter, where ammonia is catalytically formed at 400 to 500°C. The NH_3 is recovered as liquid via refrigeration, and the unreacted syngas is recycled.

In the synthesis step, however, some of the gas stream must be purged to prevent buildup of argon and methane. But purging causes a significant loss of hydrogen that could be used for additional ammonia manufacture, a loss that process designers seek to minimize.

Do you understand why the recycle process without a purge stream will cause an impurity to build up even though the recycle rate is constant? The purge rate is adjusted so that the amount of purged material remains below an acceptable specified economic level or so that the

$$\left\{\begin{matrix}\text{rate of}\\ \text{accumulation}\end{matrix}\right\} = 0 = \left\{\begin{matrix}\text{rate of entering material}\\ \text{and/or production}\end{matrix}\right\} - \left\{\begin{matrix}\text{rate of purge}\\ \text{and/or loss}\end{matrix}\right\}$$

Calculations for bypass and purge streams introduce no new principles or techniques beyond those presented so far. Two examples will make this clear.

EXAMPLE 2.28 Bypass Calculations

In the feedstock preparation section of a plant manufacturing natural gasoline, isopentane is removed from butane-free gasoline. Assume for purposes of simplification that the process and components are as shown in Fig. E2.28. What fraction of the butane-free gasoline is

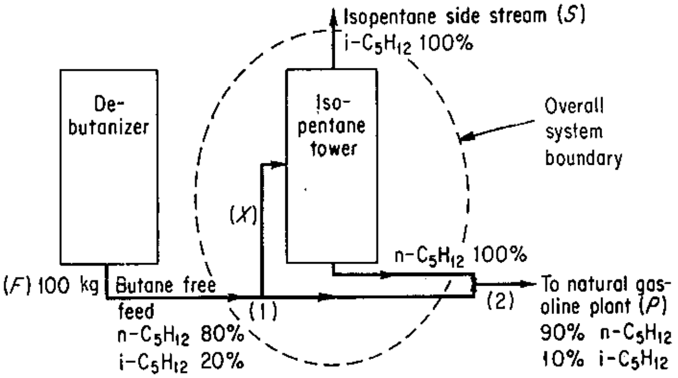


Figure E2.28

passed through the isopentane tower? Detailed steps will not be listed in the analysis and solution of this problem.

Solution

By examining the flow diagram you can see that part of the butane-free gasoline bypasses the isopentane tower and proceeds to the next stage in the natural gasoline plant. All the compositions are known. What kind of balances can we write for this process? We can write the following:

Basis: 100 kg feed

(a) *Overall balances* (each stream is designated by the letter F, S, or P):

Total material balance:

$$\begin{array}{cc} \underline{In} & \underline{Out} \\ 100 = & S + P \end{array} \qquad \text{(a)}$$

Component balance (n-C_5), *tie component:*

$$\begin{array}{cc} \underline{In} & \underline{Out} \\ 100(0.80) = & S(0) + P(0.90) \end{array} \qquad \text{(b)}$$

Consequently,

$$P = 100\left(\frac{0.80}{0.90}\right) = 88.9 \text{ kg}$$

$$S = 100 - 88.9 = 11.1 \text{ kg}$$

The overall balances will not tell us the fraction of the feed going to the isopentane tower; for this we need another balance.

(b) *Balance around isopentane tower:* Let x = lb of butane-free gas going to isopentane tower and y be the n–C_5H_{12} stream leaving the isopentane tower.

Total material balance:

$$\begin{array}{cc} \underline{In} & \underline{Out} \\ x = & 11.1 + y \end{array} \qquad \text{(c)}$$

Component (n-C_5), *a tie component:*

$$x(0.80) = y \tag{d}$$

Consequently, combining (c) and (d),

$$x = 11.1 + 0.8x$$

$$x = 55.5 \text{ kg or the desired fraction is } 0.555$$

Another approach to this problem is to make a balance at mixing points (1) or (2). Although there are no pieces of equipment at those points, you can see that streams enter and leave the junction.

(c) *Balance around mixing point* (2)*:*

material into junction = material out

Total material:

$$(100 - x) + y = 88.9 \tag{e}$$

Component (iso-C_5):

$$(100 - x)(0.20) + 0 = 88.9(0.10) \tag{f}$$

Equation (f) avoids the use of y. Solving yields

$$20 - 0.2x = 8.89$$

$$x = 55.5 \text{ kg as before}$$

EXAMPLE 2.29 Purge

Considerable interest exists in the conversion of coal into more convenient liquid products for subsequent combustion. Two of the main gases that can be generated under suitable conditions from insitu coal combustion in the presence of steam (as occurs naturally in the presence of groundwater) are H_2 and CO. After cleanup, these two gases can be combined to yield methanol according to the following equation

$$CO + 2H_2 \longrightarrow CH_3OH$$

Figure E2.29 illustrates the process.

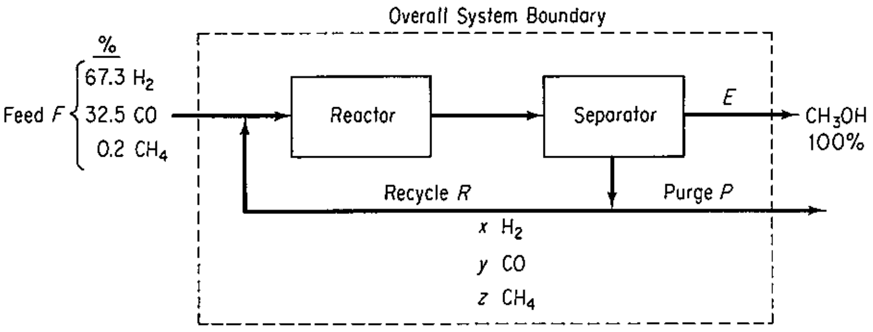


Figure E2.29

You will note in Fig. E2.29 that some CH_4 enters the process, but the CH_4 does not participate in the reaction. A purge stream is used to maintain the CH_4 concentration in the exit to the separator at no more than 3.2 mol%. The once-through conversion of the CO in the reactor is 18%.

Compute the moles of recycle, CH_3OH, and purge per mole of feed, and also compute the purge gas composition.

Solution

Steps 1, 2 and 3 Figure E2.29 is the sketch of the process. We will make balances about the whole process using the system designated by the dashed line, and also make a balance about the reactor plus separator to calculate the amount of recycle. Each of the stream flows has been labeled, and because the composition of the recycle and purge stream is not known, we have designated by x, y, and z, respectively, the mole fractions of H_2, CO, and CH_4. The ethanol stream is 100% CH_3OH; the purge and recycle streams have the same compositions.

Step 4 Take a basis of 100 moles of feed.

Step 5 The unknown stream flows and mole fractions of the components are R, E, P, x, y, and z.

Step 6 We can make three independent elemental material balances for the overall process: H_2, C, and O balances. A CO balance on the reactor plus separator will provide one additional balance. How can we obtain fifth and sixth balances so that the system of equations is determinate? One piece of information given in the problem statement that we have not used is the information about the upper limit on the CH_4 concentration in the purge stream. This limit can be expressed as $z \leqq 0.032$. Let us make

$$z = 0.032 \tag{a}$$

Another piece of information is the implicit balance,

$$x + y + z = 1 \tag{b}$$

Steps 7 and 8 The overall balances are (in moles):

$$H_2: \quad 67.3 + 0.2(2) = E(2) + P(x + 2z) \tag{c}$$

$$C: \quad 32.5 + 0.2 = E(1) + P(y + z) \tag{d}$$

$$O: \quad 32.5 = E(1) + P(y) \tag{e}$$

For a system composed of the reactor plus the separator (chosen to avoid calculating the unknown information about the reactor direct output), the CO balance is

$$\text{CO:} \quad \underbrace{32.5 + Ry}_{\textit{In}} - \underbrace{y(R + P)}_{\textit{Out}} = \underbrace{(32.5 + Ry)(0.18)}_{\textit{Consumed}} \tag{f}$$

Would a H_2 balance on the reactor plus separator yield any additional information not given in Eq. (f)? The balance would be

$$H_2: \quad 67.3 + Rx - x(R + P) = (67.3 + Rx)(0.18) \tag{g}$$

Experienced engineers would say that the hydrogen balance is redundant. You can verify this conclusion by looking at the coefficient matrix of Eqs. (f) and (g):

$$0.82(32.5 + Ry) = (R + P)y = Ry + Py$$

$$0.82(67.3 + Rx) = (R + P)x = Rx + Px$$

or

$$0.82(32.5) = (0.18y)R + (y)P$$
$$0.82(67.3) = (0.18x)R + (x)P$$

What is the rank of

$$M = \begin{bmatrix} 0.18y & y \\ 0.18x & x \end{bmatrix}$$

The det $[M] = 0.18yx - 0.18yx = 0$, hence the rank of M is one, and Eqs. (f) and (g) are not independent.

Step 9 Equation (a) can be substituted into Eqs. (b)–(f) and the resulting five equations solved by successive substitution or by using one of the computer programs on the disk in the pocket in the back of this book. The resulting values obtained are (in moles)

E	CH_3OH	31.25
P	purge	6.25
R	recycle	705
x	H_2	0.768
y	CO	0.200
z	CH_4	0.032

Step 10 Check to see that each of the balances (b)–(f) is satisfied.

Up to now we have discussed material balances of a rather simple order of complexity. If you try to visualize all the calculations that might be involved in even a moderate-sized plant, as illustrated in Fig. 2.4, the stepwise or simultaneous solution of material balances for each phase of the entire plant may seem to be a staggering task, but is a task that can be eased considerably by the use of computer codes as discussed in Sec. 2.7. Keep in mind that a plant can be described by a number of individual, interlocking material balances each of which, however tedious they are to set up and solve, can be set down according to the principles and techniques discussed in this chapter. In application there is always the problem of collecting suitable information and evaluating its accuracy, but this matter calls for detailed familiarity with any specific process and is not a suitable topic for discussion here. We can merely remark that some of the problems you will encounter have such conflicting data or so little useful data that the ability to perceive what kind of data are needed is the most important attribute you can bring to bear in their solution.

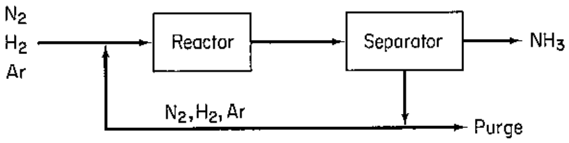
Self-Assessment Test

1. Explain what recycle and bypassing involve by means of words and also by a diagram.
2. Repeat for the term "purge."
3. If the components in the feed to a process appear in stoichiometric quantities and the subsequent separation process is complete so that all the unreacted reactants are recycled, what is the ratio of reactants in the recycle stream?

4. A material containing 75% water and 25% solid is fed to a granulator at a rate of 4000 kg/hr. The feed is premixed in the granulator with recycled product from a dryer which follows the granulator (to reduce the water concentration of the overall material in the granulator to 50% water, 50% solid). The product that leaves the dryer is 16.7% water. In the dryer, air is passed over the solid being dried. The air entering the dryer contains 3% water by weight (mass), and the air leaving the dryer contains 6% water by weight (mass).
   (a) What is the recycle rate to the granulator?
   (b) What is the rate of air flow to the dryer on a dry basis?
5. In the famous Haber process to manufacture ammonia, the reaction is carried out at pressures of 800 to 1000 atm and at 500 to 600°C using a suitable catalyst. Only a small fraction of the material entering the reactor reacts on one pass, so recycle is needed. Also, because the nitrogen is obtained from the air, it contains almost 1% rare gases (chiefly argon) that do not react. The rare gases would continue to build up in the recycle until their effect on the reaction equilibrium would become adverse so that a small purge stream is used.

   The fresh feed composed of 75.16% H_2, 24.57% N_2, and 0.27% Ar is mixed with the recycled gas and enters the reactor with a composition of 79.52% H_2. The gas leaving the ammonia separator contains 80.01% H_2 and no ammonia. The product ammonia contains no dissolved gases. Per 100 moles of fresh feed:
   (a) How many moles are recycled and purged?
   (b) What is the percent conversion of hydrogen per pass?

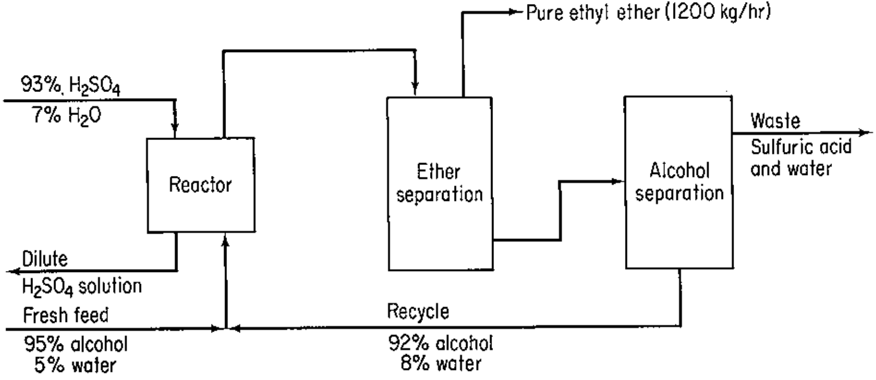
$$3H_2 + N_2 \longrightarrow 2NH_3$$



6. Ethyl ether is made by the dehydration of ethyl alcohol in the presence of sulfuric acid at 140°C:

$$2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O$$

   A simplified process diagram is shown below. If 87% conversion of the alcohol fed to the reactor occurs per pass in the reactor, calculate:
   (a) Kilograms per hour of fresh feed
   (b) Kilograms per hour of recycle



2.7 SOLVING MATERIAL BALANCE PROBLEMS WITH THE AID OF A COMPUTER

Your objectives in studying this section are to be able to:

1. Locate computer programs that will solve coupled sets of linear and/or nonlinear equations simultaneously.
2. Use such programs for which you have access.

The great potential of computers is their capacity to do anything that can be described mathematically as a series of operations and logical decisions—theoretically. From a practical viewpoint, we need to ask ourselves not merely whether it is feasible for a task to be performed on a computer, but whether it is sensible. Two criteria need to be applied to reach a decision: (1) can the task be performed (or the problem solved) at all without the use of a computer; and (2) is it better or cheaper or faster to use a computer to solve a problem than a hand-held calculator (or no machine at all)? To decide whether it is better or cheaper or faster to use a computer, you must consider, among other factors, the necessary investment of effort, time, and money. Is the problem to be solved just one time or many times? Is the accuracy of the solution enhanced through the use of the computer? Do you have a computer handy with the right program stored to solve the problem, or do you have to code an algorithm and debug it first? Answers to these and other questions will guide your choice of tools.

In this section we examine briefly how equation solvers, generic codes, spreadsheets, and flowsheeting codes can be used to solve material (and energy) balances.

2.7-1 Equation-Solving Programs

You can use inexpensive *equation-solving programs* available for microcomputers to solve linear and nonlinear material balances. Such codes may actually run faster than spreadsheet programs but not as fast as BASIC or Fortran programs. They are faster to program than BASIC or Fortran programs. A typical example of an equation-solving package is TK Solver Plus,[5] which contains the following sheets (modules):

1. The Variable Sheet, where you name and define variables to be used in your equations and models.
2. The Rule Sheet, where you define relationships among variables.
3. The Function Sheet, which contains a summary of all user-defined functions that are part of a model.
4. The Unit Sheet, where you enter rules (if needed) for the conversion of calculation and display units.

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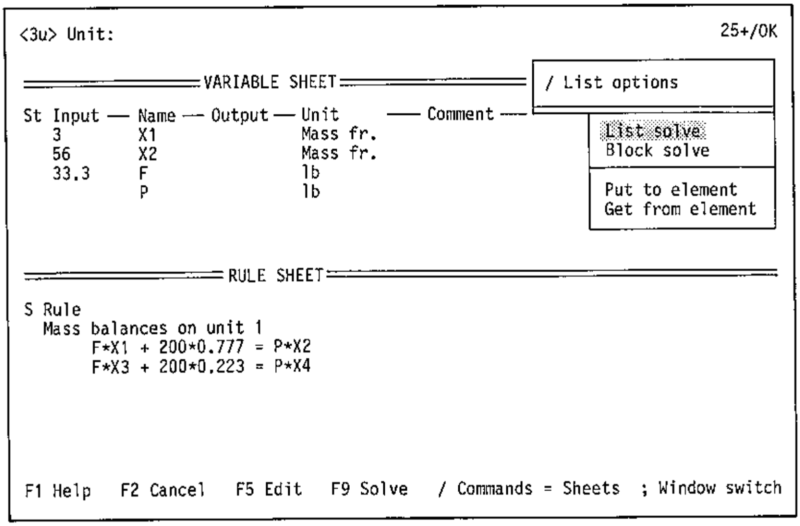
[5] A trademark of Universal Technical Systems, Inc., 1220 Rock St., Rockford, IL 61101.

5. The List Sheet, which summarizes all lists that have been created in the model.
6. The Plot Sheet, where you define the type and structure of plots of the model variables and relationships.
7. The Table Sheet, which summarizes all tables created in the model.
8. The Numeric Format Sheet, which lets you set numeric conventions such as number of decimal places, monetary format, etc.
9. The Global Sheet, which controls settings and defaults in effect throughout the model. Figure 2.20 illustrates two sheets.



```
<3u> Unit:                                                        25+/OK

===============VARIABLE SHEET======================
St Input — Name — Output — Unit        —— Comment ——
   3       X1              Mass fr.
   56      X2              Mass fr.
   33.3    F               lb
           P               lb

===============RULE SHEET==========================================
S Rule
  Mass balances on unit 1
       F*X1 + 200*0.777 = P*X2
       F*X3 + 200*0.223 = P*X4

F1 Help   F2 Cancel   F5 Edit   F9 Solve   / Commands = Sheets   ; Window switch
```

Figure 2.20 TK Solver Plus lets you view any two of its nine worksheets onscreen at once. Shown here are the Variable Sheet (top) and the Rule Sheet (bottom). After known values are entered into the Variable Sheet, the ! key is pressed to start the calculations. Once the solution is found, the values of the unknown variables appear in the output column spaces in the Variable Sheet.

Sheets generally have predefined row and column titles, guiding you as to what information should be placed in which cells.

All sheets but the Unit Sheet may have subsheets. The Plot Sheet, for example, may have a Line Chart, Bar Chart, or Pie Chart Subsheet, or all three at once. These subsheets in turn can be based on List Subsheets, on which the actual data values are entered. You can add text comments to any statement or expression by enclosing the comment in quotes.

Models (for our purposes material balances) are built on the Rules Sheet; everything else is support structure. A model's rules are just equations, which may be entered in any number and sequence. Equations are written in ordinary algebraic form, and the calculations can involve table lookup, user-defined functions, and so on.

TK Solver has two methods of solving equations. (1) The Direct Solver is just what it sounds like: values are substituted for variables, and both sides of an expression are calculated directly. (2) The Iterative Solver is used for nonlinear or simultaneous equations that cannot be evaluated directly. Iterative solving begins with a user-generated guess as to what a value might be. The software then uses this approximate value to generate a new guess that comes closer to the solution, and so on until a desired solution is reached. You do not have to choose the method of solution; the program makes the choice for you.

A number of iterative methods exist, as described in Appendix L. TK Solver uses a modified Newton–Raphson iterative procedure (see Sec. L.2), which is satisfactory for a wide variety of problems.

TK Solver Plus has 71 built-in functions, which can be used in rules, statements, and expressions. Built-in functions range from the mathematical constants π and e (natural log) through trigonometric, logarithmic, hyperbolic, mathematical, Boolean, and complex functions. Complex functions include such things as "Power," which returns real and imaginary values of a complex number raised to some power, and "Ptord," which returns the real and imaginary components of a complex number in rectangular form. The code does not let you use scientific notation such as the summation sign; instead, a command string has to be entered.

There are also several TK-specific functions, such as Element, which returns the value of a specified list element; Place, which puts a value into a specific place in a list; and Given, which returns one specific value if a particular variable is assigned an input value and another if the variable does not have an input value.

TK Solver Plus also provides a large set of library models (programs) that you can use as is or change for use in modified versions. Library models include: Roots of Equations, Differentiation and Integration, Differential Equations, Special Functions, Complex Variables, Optimization, Matrix Calculations, Arbitrary Length Integers, Interactive Tables, Graphics, Statistics and Curve Fitting, Engineering and Science (mostly chemistry), and Finance.

For example calculations, refer to Singh[6] or the manual that comes with the calculation program.

2.7-2 Generic Computer Codes to Solve Sets of Equations

After you have transformed a word problem into a formal set of linear or nonlinear equations, there remains the question of how to solve the equations. Appendix L discusses several techniques to accomplish this task using general computer programs. From a classical viewpoint, two major categories of solution techniques exist: (1) direct or (2) interactive. For linear equations, the direct methods come for the most part from the well-known Gaussian elimination algorithm explained in Sec. L1. Gaussian methods are far more rapid than iterative methods, but computer time is not the only factor to take into account. Direct methods need considerable memory (in order to store the entire matrix and the right-hand side, both of which are constantly modified in the course of the calculations). Furthermore, no approximate solution can be obtained before the end of the calculations when you arrive at the (theoretically) exact solution.

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[6] V. Singh, *Chem. Eng.*, p. 149 (February 17, 1986).

On the other hand, the situation is rather different in the case of iterative methods. If the system of equations is written in matrix form (see Sec. L.1) as $\mathbf{Ax} = \mathbf{b}$, the concept is to produce, starting with an initial guess x_0, a sequence of vectors x_k converging toward the desired solution reasonably rapidly. Substitution methods (outlined in Sec. L.2 for nonlinear equations) are one way to implement the concept.

In the pocket in the back of this book are four simple Fortran generic codes that can be used to solve sets of linear and nonlinear equations on microcomputers or mainframes. Because these programs are simple, and thus may on occasion fail to solve your problem, you may want to use more polished computer codes that are available in your computer center software library. Such codes are more robust, but of course it takes more of your time to understand how to use them proficiently.

If you formulate a material balance problem that results in nonlinear equations, you should review Sec. L.2. There you will find an outline of techniques to solve sets of nonlinear equations, and also recommendations as to computer codes that are state of the art. In the pocket in the back of the text is a simple Fortran code to solve sets of nonlinear equations based on Newton's method and another one based on an optimization technique. You can use them to solve one or more nonlinear equations, and they will be effective for most of the problems in this book.

2.7-3 Spreadsheet Programs

Within the last few years, spreadsheet programs[7,8] for microcomputers have achieved widespread acceptance. Spreadsheets were originally developed for business use as an electronic bookkeeping worksheet, hence they are a natural for solving material balance problems. They represent an easy-to-use, interactive visual program with user-friendly menus. A spreadsheet program can be applied to solving material balance problems without knowing a programming language. Furthermore, to enhance the capabilities of spreadsheet programs, numerous add-on products, such as word processors, three-dimensional graphics, general utilities, and communications links can be purchased.

A spreadsheet is nothing more than the storage and display on the monitor screen of a portion of a large two-dimensional matrix (array). It consists of numbered rows and columns identified by sequential letters. (Sometimes the rows have letters and the columns numbers.) Each cell or element in the array can be operated on by placing the cursor in it. The cursor can be moved from one cell to another by means of the arrow keys or a mouse. A cell can be used to store descriptive characters, a number (integer or real), or formulas containing standard mathematical functions and conditional relationships. The formulas may refer to data from any number of numeric or formula cells, and the results of calculations from applying such data to the data in the referenced cells appear in the formula cell. If the data in any cell are changed, the effect of the change is instantly propagated to the whole spreadsheet. This capability makes a spreadsheet well suited to study the effect of modifying one or more parameters in a material balance. Because process design is frequently broken down into problem definition, generation of alternative solutions,

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[7] D. F. Cobb and G. T. LeBlond, *Using 1-2-3*, 2nd ed., Que., Indianapolis, Ind., 1985.

[8] D. Ewing, *1-2-3 Macro Library*, Que., Indianapolis, Ind., 1985.

evaluation of alternatives, selection of the recommended solution, and implementation of the selected alternative, the "what if" capabilities of spreadsheets are a powerful aid to decision making.

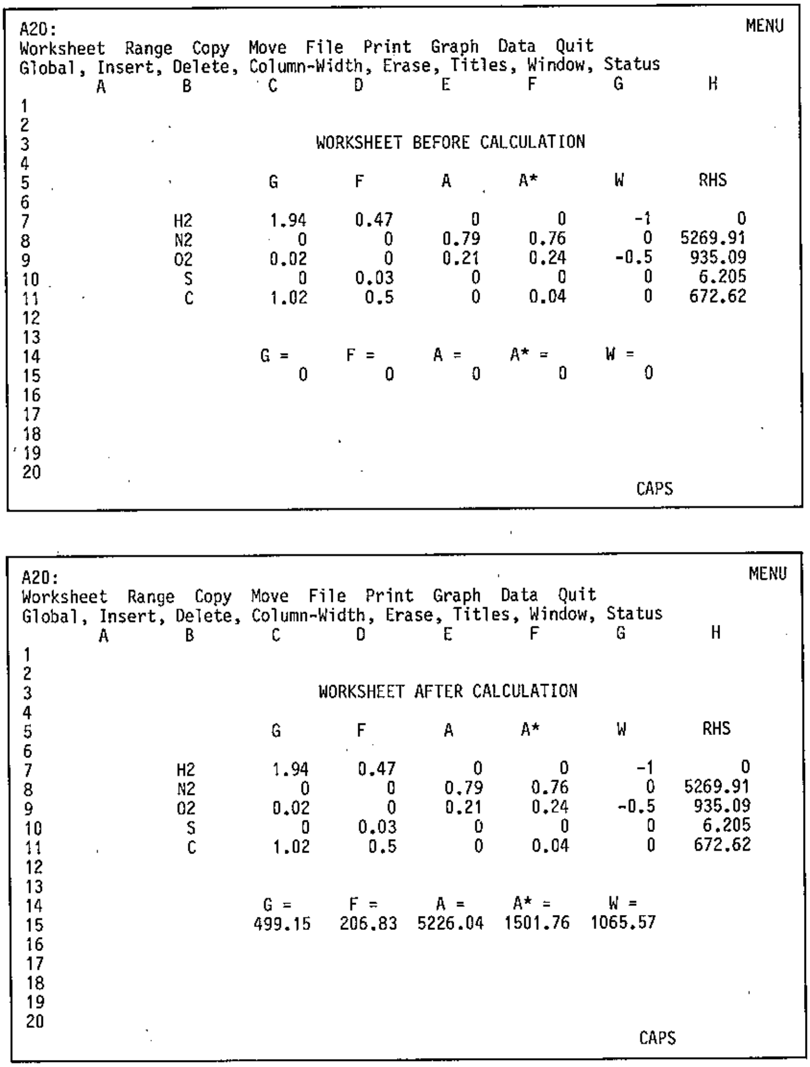
One advantage of spreadsheets is that the creation and execution of spreadsheets usually involves significantly less effort than writing and running a user-friendly program in BASIC or Fortran. Other advantages in engineering practice are low cost of execution, ease of execution, reasonable speed, and specific knowledge of the equations used in the calculations (in contrast to flowsheeting codes). Of course, the disadvantages are that spreadsheets cannot handle very complex material (and energy) balance problems more suitable for mainframe or minicomputers, and the speed is much less than Fortran programs executed on big computers. Furthermore, they are not particularly effective for the iterative solution of sets of simultaneous nonlinear equations or problems with many recycle streams.

Figure 2.21 illustrates a typical Lotus 1–2–3 template used to solve the problem in Example 2.21. Our purpose here is not to explain how to use your particular software package; refer to the documentation accompanying your disk. But to solve material balances without frustration, you need at the very least to be able to accomplish the following tasks:

Open, close, save, and delete spreadsheet files
Enter labels, data, and formulas that compute values for each cell
Introduce into a formula in one cell values of a variable(s) or formulas from another cell(s)
Copy the value of a variable or a formula in one cell into other cells
Execute an iterative calculation using the spreadsheet function

Other features of spreadsheet codes you can use include:

1. *Macros*. A simple command language can be used to create a series of predetermined steps that the program will execute whenever ALT and an appropriate label key are pressed. Such a grouping of commands is called a macro. A macro can be used to extract data from a data base, to perform a series of mathematical operations (such as finding the roots of a nonlinear equation), or to prompt you for desired data changes.
2. *Window*. The window feature allows the screen to be doubled horizontally or vertically and enables you to view two otherwise widely separated areas of the spreadsheet at the same time. One window may be used as a spreadsheet work area and the other for displaying instructions.
3. *Graph*. Results of a problem can be displayed graphically on the monitor screen. Using the "Graph" feature, you can create *XY* plots, bar charts, pie charts, and histograms.
4. *Translate*. You can transfer data from the spreadsheet program to other application programs, and vice versa. For instance, ASCII text files from BASIC programs can be transferred to and from the spreadsheet program through appropriate commands.



```
A20:                                                                     MENU
Worksheet  Range  Copy  Move  File  Print  Graph  Data  Quit
Global, Insert, Delete, Column-Width, Erase, Titles, Window, Status
        A         B         C         D         E         F         G          H
1
2
3                                   WORKSHEET BEFORE CALCULATION
4
5                           G         F         A         A*        W          RHS
6
7                 H2        1.94      0.47      0         0         -1         0
8                 N2        0         0         0.79      0.76      0    5269.91
9                 02        0.02      0         0.21      0.24      -0.5  935.09
10                S         0         0.03      0         0         0      6.205
11                C         1.02      0.5       0         0.04      0     672.62
12
13
14                          G =       F =       A =       A* =      W =
15                             0         0         0         0         0
16
17
18
19
20
                                                                  CAPS
```

```
A20:                                                                     MENU
Worksheet  Range  Copy  Move  File  Print  Graph  Data  Quit
Global, Insert, Delete, Column-Width, Erase, Titles, Window, Status
        A         B         C         D         E         F         G          H
1
2
3                                   WORKSHEET AFTER CALCULATION
4
5                           G         F         A         A*        W          RHS
6
7                 H2        1.94      0.47      0         0         -1         0
8                 N2        0         0         0.79      0.76      0    5269.91
9                 02        0.02      0         0.21      0.24      -0.5  935.09
10                S         0         0.03      0         0         0      6.205
11                C         1.02      0.5       0         0.04      0     672.62
12
13
14                          G =       F =       A =       A* =      W =
15                          499.15    206.83    5226.04   1501.76   1065.57
16
17
18
19
20
                                                                  CAPS
```

Figure 2.21 Lotus 1 2 3 solution for Example 2.21.

Spreadsheet codes commonly use a method called the Gauss–Seidel iterative method to solve a set of linear equations. The procedure is roughly as follows. Take an arbitrary value (often zero) and use it to initialize one or several of the unknowns in order to break all of the recycle of information in the system of equations. Then compute the rest of the unknowns via simple substitution. What results is only an approximation to a solution because at least one unknown has been given an arbitrary value. Because of the recycle of information in the equations, however, you can compute the values of the unknown variables again, and in so doing, you will get a better guess to use in a second round of calculations, and so on. During each iteration, the values of the unknown variables tend to change less and less. After a certain number of iterations, they do not change any more. The process has converged, and you have reached the solution. (Refer to Sec. L.2, under "Substitution," for the concept applied to nonlinear equations.)

To start out solving a material balance problem via a spreadsheet, you first must determine the size of the spreadsheet and its boundaries. Then you initialize all the points in that array (to zero, usually). Next, set aside a section of the spreadsheet with cells reserved for the known constants in the problem. You should label the constants across the page using the labeling features of your spreadsheet to avoid confusion. Then enter the constants.

You are now ready to enter the equations for the internal and boundary nodes. Some spreadsheets may start solving the equations as you enter them leading to all sorts of error messages. To avoid this outcome, define a constant in, say, cell A3 (first column, third row) to be zero, and multiply each equation by A3 as you enter it. Then, when you have completed entering all the equations, you need to solve the problem, change A3 from 0 to 1, and begin iteration. A formula is entered in a cell, but the formulas themselves are not displayed in the cell on the screen. What is displayed is the value given by the formula. For example, to show the product in cell D10 of the feed located in cell F24 and the concentration located in F25, you would enter into cell D10 the formula F24*F25. It is recommended that you set up the overall material balances about specific process units in addition to the equations entered on the main part of the spreadsheet. If you take this step, you can quickly check for errors in the setup of the balances. Also, as you enter equations and data, check interim calculations just as you would check out a computer code as it was written.

2.7-4 Flowsheeting Programs

In the 1960s, the chemical process industry initiated the use of large-scale programs for computer-aided process design. Such programs were frequently referred to as heat and material balancing programs, but now are generally called **flowsheeting programs**. Such programs accept information about a chemical process at the flowsheet level of detail, and make calculations that provide data about not only material and energy flows but also about costs, pipe layout, time effects, and other useful information for design and operation. Figure 2.22 illustrates the structure of a flowsheeting code. Such codes can simulate the steady-state (and unsteady-state in some cases) performance of large integrated chemical plants consisting of interconnected process units with recycle streams. Table 2.5 lists a number of flowsheeting codes and their sources.

Two extremes are encountered in flowsheeting software. At one extreme, the entire set of equations (and inequalities) representing the process is employed. This representation is known as the *equation-oriented* method of flowsheeting. The equations can be solved in a sequential fashion analogous to the modular representation described below or simultaneously by Newton's method, Broyden's method, or by employing sparse matrix techniques to reduce the extent of matrix manipulations. Refer to the review by Evans and Chapter 5.[9]

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[9] L. B. Evans, "Process Flowsheeting," in Proc. *Chem comp. 1982*, G. F. Froment, ed., KVI, Amsterdam, 1982.

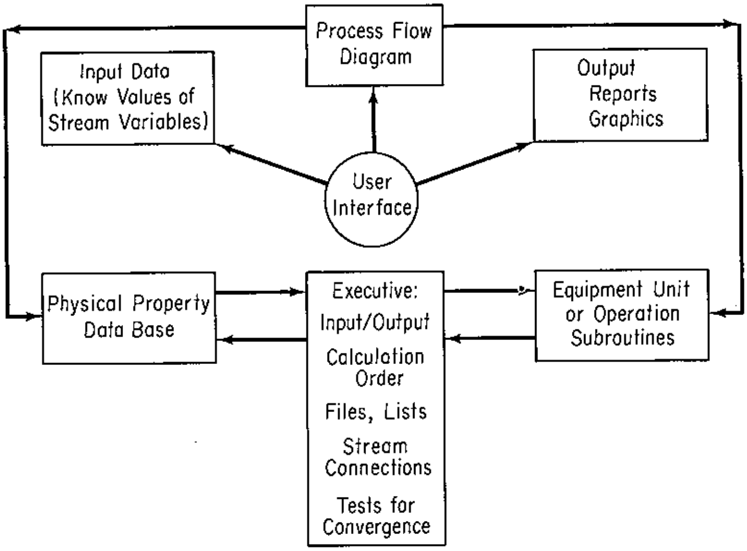

Figure 2.22 Structure of a Generic Flowsheeting Code.

At the other extreme, the process can be represented by a collection of modules (the *modular* method of flowsheeting) in which the equations (and other information) representing each subsystem or piece of equipment are collected together and coded so that the module may be used in isolation from the rest of the flowsheet and hence is portable from one flowsheet to another. Most of the flowsheeting codes of commercial importance are modular in character. Each module contains the equipment sizes, the material and energy balance relations, the rate equations, and allocated variables for component flow rates, and the temperatures, pressures, and phase conditions of each stream that enters and leaves the physical equipment represented by the module. Interconnections must be set up for the modules so that information can be transferred from module to module concerning the streams, compositions, flow rates, coefficients, and so on. In other words, the modules comprise a set of building blocks that can be arranged in general ways to represent any process. An executive routine calls the modules in the proper order, transmits information from a library of calculational subroutines, and picks out information on physical properties from an associated data base. Both sequential and simultaneous calculational sequences have been proposed for the modular approach as well as the equation-oriented approach (and intermediate mixtures of the two are possible as well). Either the program and/or the user must select the decision variables for recycle and provide estimates of certain stream values to make sure that convergence of the calculations occurs, especially in a process with many recycle streams.

Keep in mind that despite their portability, certain difficulties exist with modular codes relative to equation-based codes:

> The output of one module is the input to another. The input and output variables in a computer module are fixed so that you cannot arbitrarily introduce an output and generate an input.

TABLE 2.5 **Flowsheeting Codes**

Name	Author	Reference	Number of components in data bank	Availability
ASPENPLUS	Aspen Technology	[H]	Large	Aspen Technology Corp., Cambridge, Mass.; original Aspen from National Technical Information Service, Springfield, Va.
CAPES	Chiyoda Ltd.	[B]		Chiyoda Ltd., Yokohama, Japan
CHESS	R.L. Motard	[A]	98	Dept. Chem. Eng., Washington University, St. Louis, Mo.; microcomputer version from COADE, Houston, Tex.
CONCEPT	Computer Aided Design Center	[D]	105	Computer Aided Design Center, Cambridge, England.
DESIGN/2000	Chem Share	[I]		Chem Share, Houston, Tex.
FLOWTRAN	Various at Monsanto Co.	[C]	>200	Monsanto Co., St. Louis, Mo.
MPBII	Sood and Reklaitis	[J]		Dept. Chem Eng., Purdue University, West Lafayette, Ind.
PROCESS	Simulation Sciences	[E]	>600	Simulation Sciences, Fullerton, Calif.
SIMMOD	Chen and Stadtherr	[K]		Dept. Chem. Eng., University of Illinois at Urbana–Champaign, Urbana, Ill.
SPEEDUP	R. Sargent	[G]	100	British Technology Group, London
SYMBOL	Cambridge University	[F]	No 120	Computer Aided Design Center, Cambridge, England

TABLE 2.5 (*cont.*)

[A] Motard, R.A., Dept. Chem. Eng., Washington University, St. Louis, Mo.
[B] Chiyoda Ltd., Systems Eng., Section, *Outline of Capes,* Chiyoda Ltd., Yokohama, Japan, 1979.
[C] Rosen, E.M., and A.C. Pauls, "Computer Aided Chemical Process Design The FLOWTRAN System." *Comput. & Chem. Eng.*, v.1, p. 11 (1977).
[D] Thambynayagam, R.K.M., S.J. Banch, and P. Winter, "CONCEPT MK IV; A New Approach to Process Flowsheeting." *277th Event Eur. Fed. Chem. Eng.* (CHEMPLANT '80), Sept. 3–5, 1980, Heviz, Hungary.
[E] Brannock, N.F., V.S. Verneuil, and Y.L. Wang, "PROCESS Simulation Program—A Comprehensive Flowsheeting Tool for Chemical Engineers." *Comput. Chem. Eng.*, v.3, p. 329 (1979).
[F] Computer Aided Design Center, *SYMBOL*, Cambridge, England.
[G] Perkins, J.D., R.W.H. Sargent and S. Thomas in *Computer Aided Process Plant Design,* M.E. Leesley (Ed.), p. 566, Gulf Publishing Company, Houston (1982).
[H] Evans, L.B., et al., "ASPEN: An Advanced System for Process Engineering." *Comput. Chem. Eng.*, v.3, p. 319 (1979).
[I] Chem. Share Corp., *Guide to Solving Process Engineering Problems by Simulation* (Users Manual), Chem. Share Corp., Houston, 1979.
[J] Sood, M.K., and G.V. Reklaitis, "Material Balance Program—II," School of Chemical Engineering, Purdue University, West Lafayette, Ind., 1977.
[K] Chen, H.S., and M.A. Stadtherr, "A Simultaneous-Modular Approach to Process Flowsheeting and Optimization: I Theory and Implementation," *AIChE J.* v.32, p. 184 (1984).

2. The modules may require a fixed precedence order of solution (i.e., the output of one module must become the input of another); hence, convergence may be slower than in an equation-solving code, and the computational costs may be high.
3. To specify a parameter in a module as a design variable, you have to place a control block around the module and adjust the parameter such that design specifications are met. This arrangement creates a loop. If the values of many design variables are to be determined, you might end up with several nested loops of calculation.

Consequently, the concept of **tearing** has evolved in connection with modular flowsheeting codes to solve material (and energy) balances. Tearing involves decoupling the interconnections between the modules so that sequential information flow takes place. Tearing is required because of loops of information created by recycle streams. What you do in tearing is to provide guesses for values of some of the unknowns (the **tear variables**), usually the recycle streams, and then calculate the values of the tear variables from the modular subroutines. These calculated values form new guesses, and so on, until the differences between the guessed values and the calculated values are sufficiently small.

We cannot go into all of the details of flowsheeting program construction and application here. Refer to Chapter 5 and the to supplementary references at the end of this chapter for further information. However, let us look at an example of a very simple process with recycle to compare the simultaneous equation and modular solution techniques just to illustrate the concepts.

EXAMPLE 2.30 Comparison of Simultaneous Equation and Modular Techniques of Solving Material Balances

Figure E2.30 illustrates a two-stage process with one recycle stream. The objective is to use the total material balances for the process to calculate the amount of the recycle stream R as a function of α, the fraction of A recycled. Use $\alpha = \frac{1}{3}$ and $\alpha = 0.90$ for the comparison.

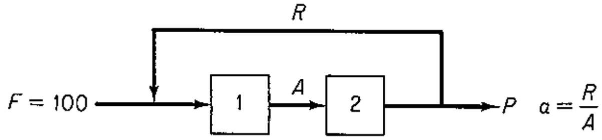

Figure E2.30

Solution

The material balances are

$$\text{Unit 1:} \quad 100 + R = A \qquad \text{(a)}$$

$$\text{Unit 2:} \quad A = R + P \qquad \text{(b)}$$

The fraction recycle is

$$A\alpha = R \qquad \text{(c)}$$

We have three independent equations to be solved containing three variables whose values are unknown. Any of the methods mentioned in Appendix L might be used to solve the equations. Gaussian elimination starts with the format

$$A - R \qquad = 100 \tag{a'}$$

$$A - R - P = 0 \tag{b'}$$

$$\alpha A - R \qquad = 0 \tag{c'}$$

$$\left[\begin{array}{ccc|c} 1 & -1 & 0 & 100 \\ 1 & -1 & -1 & 0 \\ \alpha & -1 & 0 & 0 \end{array}\right]$$

and successive elementary operations result in the matrix

$$\left[\begin{array}{ccc|l} 1 & 0 & 0 & 100\left(\dfrac{1}{1-\alpha}\right) \\ 0 & 1 & 0 & 100\left(\dfrac{\alpha}{1-\alpha}\right) \\ 0 & 0 & 1 & 100 \end{array}\right]$$

leading to the solution

$$A = 100\left(\frac{1}{1-\alpha}\right)$$

$$R = 100\left(\frac{\alpha}{1-\alpha}\right)$$

$$P = 100$$

For the two given values of α,

	$\alpha = \frac{1}{3}$	$\alpha = 0.9$
A	150	1000
R	50	900
P	100	100

Next, the modular approach to the solution of the problem would involve solving unit 1 for A first assuming a value for R, the tear variable. Then unit 2 would be solved, the value of R calculated, and the value calculated compared with the assumed value. If the error is not small enough, the new value of R from unit 2 would become the assumed value of R for unit 1, unit 1 solved again for A, and unit 2 solved again. The sequence of solutions would be repeated until the error in R became sufficiently small. Because R is initially not known, suppose that we start with $R = 0$ and $A = 100$ as the initial guesses. Thereafter

$$\text{Unit 1:} \qquad A_k = 100 + R_k \tag{d}$$

$$\text{Unit 2:} \qquad R_k = A_k \alpha \tag{e}$$

where k designates the stage in the iteration.

Successive calculations yield

	$\alpha = \frac{1}{3}$			$\alpha = 0.9$		
k	R	$A = 100 + R$	$R = A\alpha$	R	$A = 100 + R$	$R = A\alpha$
1	0	100	33.33	0	100	90
2	33.33	133.33	44.44	90	190	171
3	44.44	144.44	48.15	171	271	243.9
4	48.15	148.15	49.38	243.9	343.9	309.5
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.
∞	50.00	150.00	50.00	900	1000	900

Insofar as this book is concerned, if you are not familiar with a flowsheeting code, you will find it will be more trouble to solve a material balance problem using a flowsheeting code than it will be to use a standard equation-solving code such as one of those in the disk pocket in the back of the book.

Self-Assessment Test

1. Solve one or two of the examples in Sec. 2.6 and 2.7 using
   - (a) A personal computer-based equation-solving code
   - (b) A code from the disk in the pocket in the back of this book
   - (c) A code taken from your computer center library
   - (d) A spreadsheet program
   - (e) A flowsheeting code

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PROBLEMS

An asterisk designates problems appropriate for solution using a computer. Refer also to the problem that requires writing a computer program at the end of the chapter.

Section 2.1

2.1. By use of an overall steady-state material balance determine whether or not the petrochemical process indicated in Fig. P2.1 has been properly formulated. The block diagrams represent the steam cracking of naphtha into various products, and all flows are on an annual basis (i.e., per year).

2.2. Examine Fig. P2.2. Is the material balance satisfactory?

2.3. Does the plant shown in Fig. P2.3 yield a material balance that balances? Explain a possible reason for the outcome of your calculations.

2.4. Water balances on river basins for a season or for a year can be used to check predicted groundwater infiltration, evaporation, or precipitation in the basin. Prepare a water balance, in symbols, for a large river basin and its reservoir, including the physical processes indicated in Fig. P2.4 (all symbols are for 1 year and S = storage or inventory).

2.5. Examine the processes in Fig. P2.5. Each box represents a system. For each, state whether:

(a) The process is in the (1) steady state, (2) unsteady state, or (3) unknown condition

(b) The system is (1) closed, (2) open, (3) neither, or (4) both

The wavy line represents the initial fluid level when the flows begin. In case (c), the tank stays full.

Section 2.2

2.6. Make a set of all the independent material balances you can for the steady-state operation of the cooling tower in Fig. P2.6. Use F for the mass flow rate and ω for the

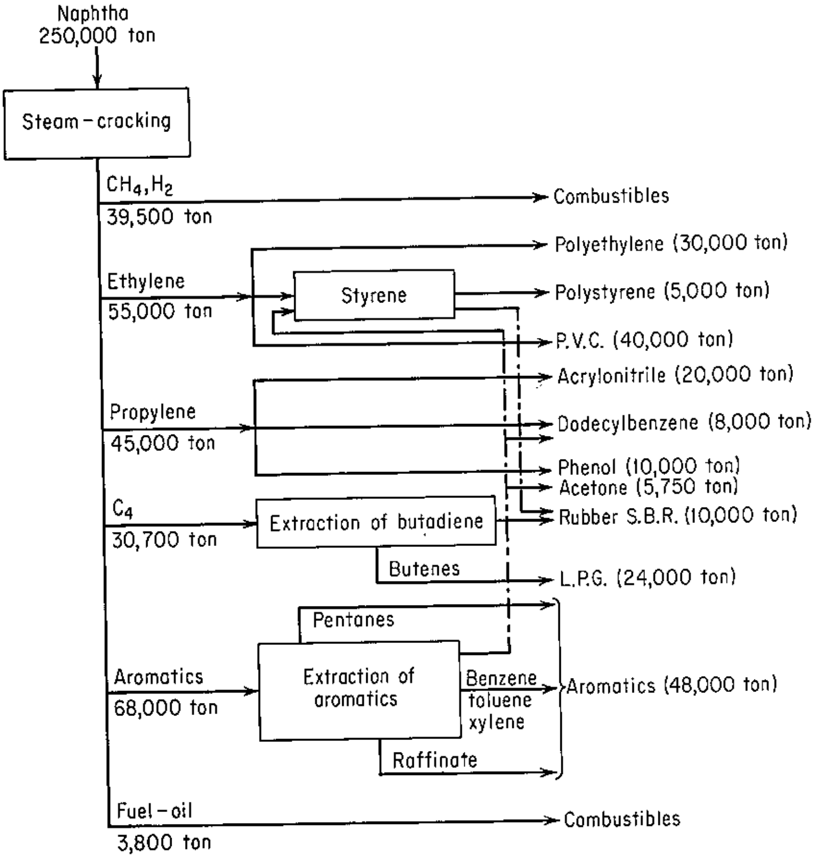


Figure P2.1

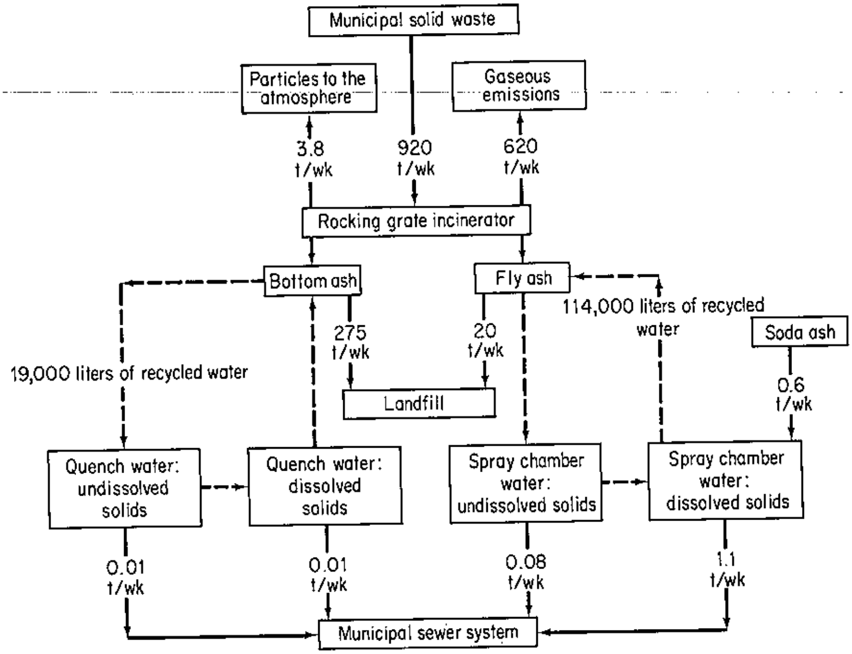


Figure P2.2

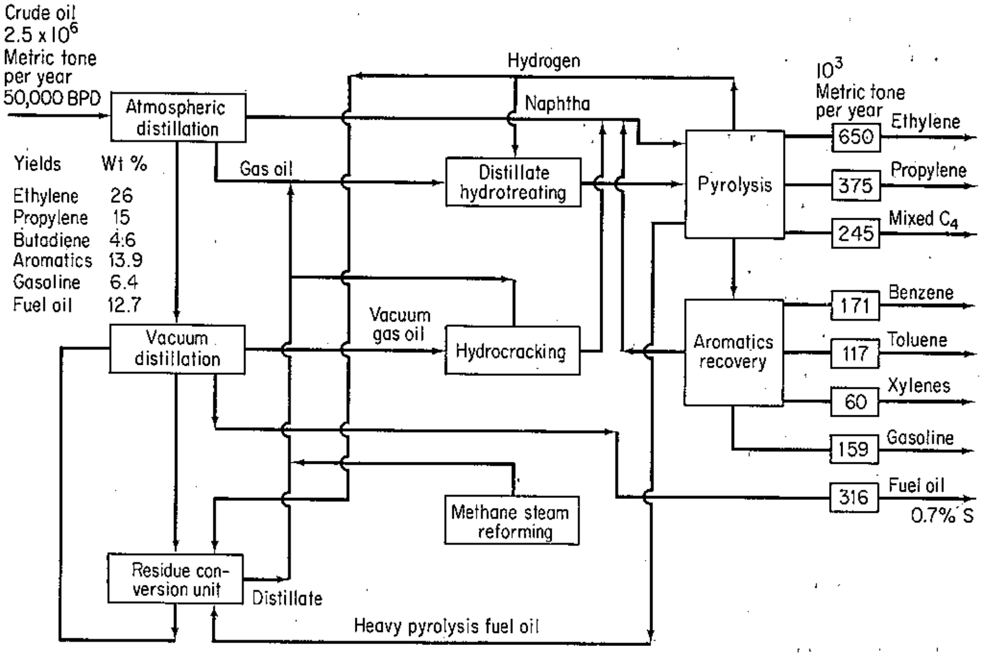


Figure P2.3

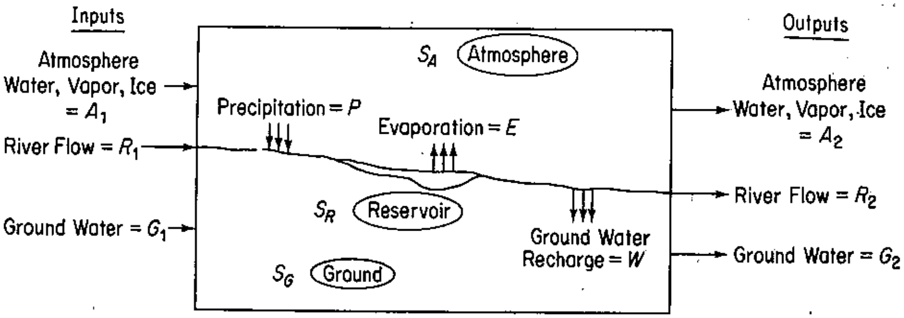


Figure P2.4

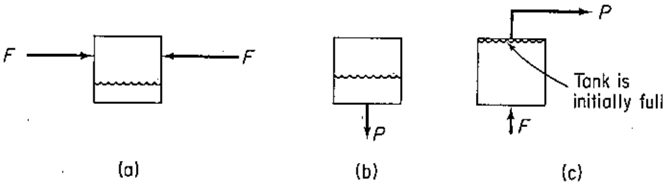


Figure P2.5

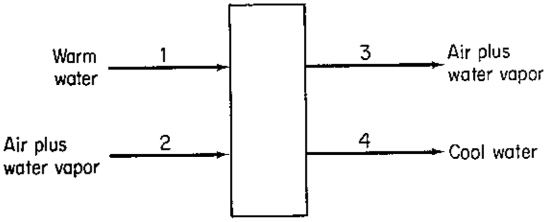
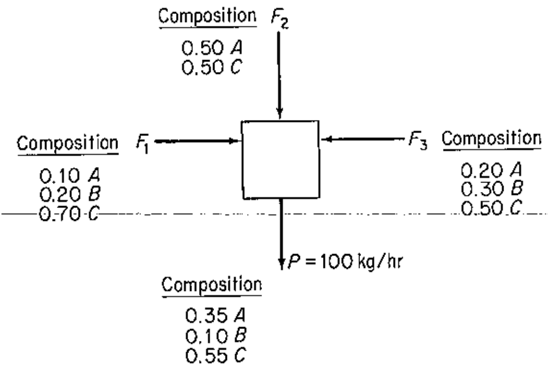


Figure P2.6

mass fraction, with the appropriate subscripts. Suppose that F was the molar flow rate. How would your equations change?

2.7. A cylinder containing CH_4, C_2H_6, and N_2 has to be prepared containing a mole ratio of CH_4 to C_2H_6 of 1.5 to 1. Available are (1) a cylinder of a N_2–CH_4 mixture (80% N_2, 20% CH_4), (2) a cylinder of 90% N_2 and 10% C_2H_6, and (3) a cylinder of pure N_2. List the total number and names (or symbols) of the unknown quantities and concentrations, and list by name the balances that you would use to solve this problem (do not make the balances). What is the residual number of degrees of freedom that have to be specified to make the problem completely determined (i.e., have a unique solution)?

2.8. For the process shown in Fig. P2.8, how many material balance equations can be written? Write them. How many independent material balance equations are there in the set?



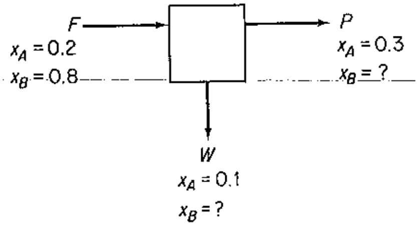


Figure P2.8

Figure P2.9

2.9. Examine the process in Fig. P2.9. No chemical reaction takes place, and x stands for mole fraction. How many stream values are unknown? How many concentrations? Can this problem be solved uniquely for the unknowns?

2.10. The separation of solids and liquids by washing is usually carried out in countercurrent staged apparatus. One such stage is shown in Fig. P2.10. For this stage with the analyses as shown in the figure, **(a)** state how many unknown variables exist, **(b)** list them by symbol, **(c)** state how many independent material balance equations can be written for the stage, and **(d)** write each one down. (ω = mass fraction; the subscripts designate components.)

2.11. Repeat Problem 2.9 for the process in Fig. P2.11.

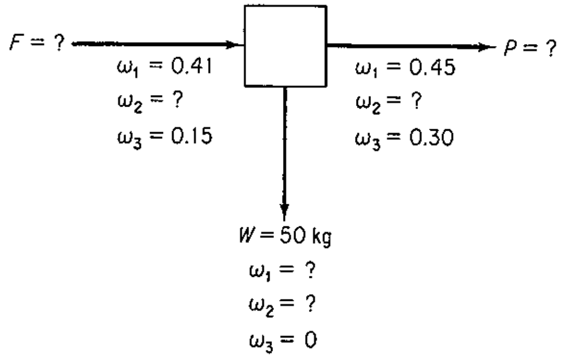


Figure P2.10

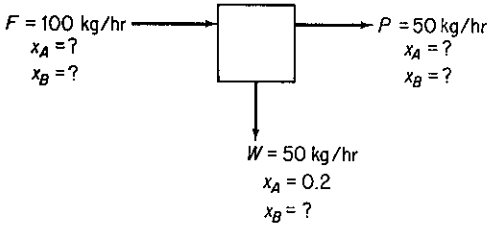


Figure P2.11

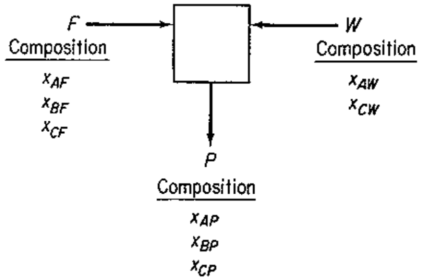


Figure P2.12

2.12. You have been asked to check out the process shown in Fig. P2.12. What will be the minimum number of measurements to make in order to compute the value of each of the stream flow rates and stream concentrations? Explain your answer. Can any arbitrary set of five be used; that is, can you measure just the three flow rates and two concentrations? Can you measure just three concentrations in stream F and two concentrations in stream W? No chemical reaction takes place and x is the mole fraction of component A, B, or C.

Section 2.3

2.13. A synthesis gas analyzing 6.4% CO_2, 0.2% O_2, 40.0% CO, and 50.8% H_2 (the balance is N_2) is burned with 40% dry excess air. What is the composition of the flue gas?

2.14. Hydrogen-free carbon in the form of coke is burned:
(a) With complete combustion using theoretical air
(b) With complete combustion using 50% excess air
(c) Using 50% excess air but with 10% of the carbon burning to CO only
In each case calculate the flue gas analysis and the Orsat analysis.

2.15. Thirty pounds of coal (analysis 80% C and 20% H ignoring the ash) are burned with 600 lb of air, yielding a gas having an Orsat analysis in which the ratio of CO_2 to CO is 3 to 2. What is the percent excess air?

2.16. An experimental solid rocket fuel consists of

H	5%
S	4%
C	65%
O	10%
Inert	16%
Total	100%

Assume on combustion that no C is left unburned and that the S is oxidized to SO_2. The inert does not go into the gas phase.

(a) If the fuel–air mixture calls for 20% excess air to oxidize the fuel, calculate the composition of the exit combustion gas.

(b) If the same fuel were oxidized in a laboratory furnace with 20% excess air and only 80% of the C was oxidized to CO_2, with 15% going to CO and 5% becoming soot (just C), what would the composition of the exit combustion gas be?

2.17. Pure methane is completely burned with air. The outlet gases from the burner, which contain no oxygen, are passed through a cooler, where some of the water is removed by condensation. The gases leaving the cooler have a nitrogen mole fraction of 0.8335. Calculate the following:

(a) The analysis of the gases leaving the cooler (mol % CO_2; H_2O, and N_2)

(b) The pounds of H_2O condensed per mole of CH_4 burned

(c) The average molecular weight of the gases leaving the cooler

2.18. The utilization of coal to produce gaseous fuels for heating and generating power as a supplement to the dwindling supplies of natural gas is a major research and development activity in the United States at the present time. Barriers to synthetic fuel production are more economic than technological, but there are still many technical problems to be resolved. In a test of pilot plant coal gasifier with a production rate of 25.8 m^3/hr, the output gas with a composition of 4.5% CO_2, 26% CO, 13% H_2, 0.5% CH_4, and 56% N_2 is burned with 10% excess air. Calculate the Orsat analysis of the combustion products.

2.19. In the anaerobic fermentation of grain, the yeast *Saccharomyces cerevisiae* digests glucose from plants to form the products ethanol and propenoic acid by the following overall reactions:

$$\text{Reaction 1:} \quad C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

$$\text{Reaction 2:} \quad C_6H_{12}O_6 \longrightarrow 2C_2H_3CO_2H + 2H_2O$$

In a batch process, a tank is charged with 4000 kg of a 12% glucose/water solution. After fermentation 120 kg of carbon dioxide are produced together with 90 kg of unreacted glucose. What are the weight percents of ethyl alcohol and propenoic acid remaining in the broth? Assume that none of the glucose is assimulated into the bacteria.

2.20. Semiconductor microchip processing often involves chemical vapor deposition (CVD) of thin layers. The material being deposited needs to have certain desirable properties. For instance, to overlay on aluminum or other bases, a phosphorus pentoxide–doped silicon dioxide coating is deposited as passivation (protective) coating, by the simultaneous reactions

$$\text{Reaction 1:} \quad SiH_4 + O_2 \longrightarrow SiO_2 + 2H_2$$

$$\text{Reaction 2:} \quad 4PH_3 + 5O_2 \longrightarrow 2P_2O_5 + 6H_2$$

Determine the relative masses of SiH_4 and PH_3 required to deposit a film of 5% by weight of phosphorus (P) in the protective coating.

2.21. In many fermentations, the maximum amount of cell mass must be obtained. However, the amount of mass that can be made is ultimately limited by the cell volume. Cells occupy a finite volume and have a rigid shape so that they cannot be packed beyond a certain limit. There will always be some water remaining in the interstices between the adjacent cells, which represents the void volume that at best can be as low as 40% of the fermenter volume. Calculate the maximum cell mass on a dry basis that can be obtained if the wet cell density is 1.1 g/cm^3. Assume the 40% void volume applies. Note that cells themselves consist of about 75% water and 25% solids, and cell mass is reported as dry weight in the fermentation industry.

2.22. Aviation gasoline is isooctane, C_8H_{18}. If it is burned with 20% excess air and 30% of the carbon forms carbon monoxide, what is the Orsat analysis?

2.23. Oxychlorination of hydrocarbons refers to a chemical reaction in which oxygen and hydrogen chloride react with a hydrocarbon in the vapor phase over a supported copper chloride catalyst to produce a chlorinated hydrocarbon and water. The oxychlorination of ethylene to produce 1, 2-dichloroethane (commonly, ethylene dichloride (EDC)) is of the greatest commercial importance. EDC is the precurser for vinyl chloride monomer, which when polymerized to polyvinyl chloride (PVC), becomes one of the most commonly used commercial plastics. The overall oxychlorination reaction of ethane is given by

$$2C_2H_4 + 4HCl + O_2 \longrightarrow 2C_2H_4Cl_2 + 2H_2O$$

Determine the mass, moles, and weight percent of the reactant and product streams if 200 kilogram moles of the limiting reactant, HCl, is fed with 10% excess air and 5% excess ethane. Ninety-five percent conversion of ethane occurs in the reactor.

2.24. Synthetic fibers are made in a wet spinning process by pumping a polymer solution (density ρ in g/cm^3, solids fraction ω_s) at a volumetric rate of Q (cm^3/min) through a spinnerette with n holes. See Fig. P2.24. The filaments emerge into a bath containing both solvent and nonsolvent. Part of the solvent is lost from the filaments and an equivalent weight of nonsolvent is picked up; this solidifies the filaments. Next, the filaments are washed free of solvent as they are stretched by a factor S between two sets of rolls. Finally, the filaments are dried in a hot roll rotating at V_f feet per

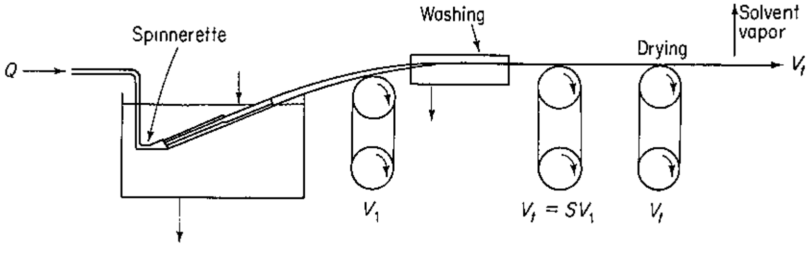


Figure P2.24

minute. Calculate the denier per filament (d.p.f.) (weight in grams of a filament 9000 m long) in terms of Q, n, ρ, ω_s, S (a constant), and V_t.

Section 2.4

2.25. To prepare a solution of 50.0% sulfuric acid, a dilute waste acid containing 28.0% H_2SO_4 is fortified with a purchased acid containing 96.0% H_2SO_4. How many kilograms of the purchased acid must be bought for each 100 kg of dilute acid?

2.26. A synthetic fuel oil known to contain only H and C gives on combustion an Orsat analysis of CO_2: 14.6%, CO: 2.0%, O_2: 2.8%, and N_2: 80.6%. Calculate the composition of the fuel oil.

2.27. A gas containing only CH_4 and N_2 is burned with air yielding a flue gas that has an Orsat analysis of CO_2: 8.7%, CO: 1.0%, O_2: 3.8%, and N_2: 86.5%. Calculate the percent excess air used in combustion and the composition of the CH_4–N_2 mixture.

2.28. A natural gas consisting entirely of methane (CH_4) is burned with an oxygen enriched air of composition 40% O_2 and 60% N_2. The Orsat analysis of the product gas as reported by the laboratory is CO_2: 20.2%, O_2: 4.1%, and N_2: 75.7%. Can the reported analysis be correct? Show all calculations.

2.29. When pure carbon is burned in air, some of it oxidizes to CO_2 and some to CO. If the molar ratio of N_2 to O_2 is 7.18, and the ratio of CO to CO_2 is 2.0 in the product gas, what is the percent excess air used? The exit gases contain only N_2, O_2, CO, and CO_2.

2.30. The products and by-products from coal combustion can create environmental problems if the combustion process is not carried out properly. A fuel analyzing 74% C, 14% H, and 12% ash is burned to yield a flue gas containing 12.4% CO_2, 1.2% CO, 5.7% O_2, and 80.7% N_2 on a dry basis. Your boss asks you to determine:

(a) The lb of coal fired per 100 lb mol of flue gas
(b) The percent excess air used
(c) The lb of air used per lb of coal

Can you accomplish the calculations? Explain.

2.31. A fuel composed of ethane (C_2H_6) and methane (CH_4) in unknown proportions is burned in a furnace with oxygen-enriched air (50.0 mole % O_2). Your Orsat analysis is: 25% CO_2, 60% N_2, and 15% O_2. Find:

(a) The composition of the fuel, that is, the mole percent methane in the methane–ethane mixture
(b) The moles of oxygen-enriched air used per mole of fuel

2.32. A power company operates one of its boilers on natural gas and another on oil (for peak period operation). The analysis of the fuels is as follows:

Natural Gas	Oil
96% CH_4 4% CO_2	$(CH_{1.8})_n$

When both boilers are on the line, the flue gas shows (Orsat analysis) 10.0% CO_2, 4.5% O_2, and the remainder N_2. What percentage of the total carbon burned comes from the oil? (*Hint:* Do not forget the H_2O in the stack gas.)

2.33. A fuel oil and a sludge are burned together in a furnace with dry air. Assume that the fuel oil contains only C and H.

	Sludge (%)		
Fuel oil (%)	Wet	Dry	Flue gas (%)
C = ?	Water = 50	S = 32	SO_2 = 1.52
	Solids = 50	C = 40	CO_2 = 10.14
H = ?		H_2 = 4	CO = 2.02
		O_2 = 24	O_2 = 4.65
			N_2 = 81.67

(a) Determine the weight percent composition of the fuel oil.
(b) Determine the ratio of kilograms of sludge to kilograms of fuel oil.

2.34. A power company operates one of its boilers on natural gas and another on oil. The analyses of the fuels show 96% CH_4, 2% C_2H_2, and 2% CO_2 for the natural gas and $C_nH_{1.8n}$ for the oil. The flue gases from both groups enter the same stack, and an Orsat analysis of this combined flue gas shows 10.0% CO_2, 0.63% CO, and 4.55% O_2. What percentage of the total carbon burned comes from the oil?

2.35. How much $CaCl_2 \cdot 6H_2O$ must be dissolved in 100 kg of water at 20°C to form a saturated solution? The solubility of $CaCl_2$ at 20°C is 6.70 g mol of anhydrous salt ($CaCl_2$) per kg of water.

2.36. One ton of a 30% (by weight) solution of Na_2CO_3 in water is cooled slowly to 20°C. During the cooling, 10% of the water originally present is evaporated. The carbonate precipitating out forms crystals of $Na_2CO_3 \cdot 10H_2O$. If the solubility of anhydrous Na_2CO_3 at 20°C is 2.15 lb/100 lb H_2O, what weight of $Na_2CO_3 \cdot 10H_2O$ crystallizes out?

2.37. Crystals of $Na_2CO_3 \cdot 10H_2O$ are dropped into a saturated solution of Na_2CO_3 in water at 100°C. What percent of the Na_2CO_3 in the $Na_2CO_3 \cdot 10H_2O$ is recovered in the precipitated solid? The precipitated solid is $Na_2CO_3 \cdot H_2O$. Data at 100°C: the saturated solution is 31.2% Na_2CO_3; the molecular weight of Na_2CO_3 is 106.

2.38. A water solution contains 60% $Na_2S_2O_2$ together with 1% soluble impurity. Upon cooling to 10°C, $Na_2S_2O_2 \cdot 5H_2O$ crystallizes out. The solubility of this hydrate is 1.4 lb $Na_2S_2O_2 \cdot 5H_2O$/lb free water. The crystals removed carry as adhering solution 0.06 lb solution/lb crystals. These are dried to remove the remaining water (but not the water of hydration). The final dry $Na_2S_2O_2 \cdot 5H_2O$ crystals must not contain more than 0.1% impurity. To meet this specification, the original solution, before cooling, is further diluted with water. On the basis of 100 lb of the original solution, calculate:
(a) The amount of water added before cooling
(b) The percentage recovery of the $Na_2S_2O_2$ in the dried hydrated crystals

2.39. A mixed acid containing 65% (by weight) H_2SO_4, 20% HNO_3, and 15% H_2O is to be made by blending the following liquids:
(1) A spent acid containing 10% HNO_3, 60% H_2SO_4 , and 30% H_2O
(2) A concentrated nitric acid containing 90% HNO_3 and 10% H_2O
(3) Concentrated sulfuric acid containing 98% H_2SO_4 and 2% H_2O

How many pounds of each of the three must be used to obtain 1000 lb of the mixed acid?

2.40. An aqueous etching solution containing 8.8% KI is to be prepared to etch gold in printed circuit boards. The desired solution is to be formed by combining a strong solution (12% KI and 3% I_2 in H_2O) with a weak solution (2.5% KI and 0.625% I_2).

(a) What should be the value of R, the ratio of the weights of the strong to the weak solution, to make up the desired etching solution? What will be the concentration of I_2 in the final solution?

(b) Note that you cannot independently vary the concentration of both KI and I_2 in the final mixture simply by varying the value of R. Derive a relationship between the weight fraction of KI and the weight fraction of I_2 in the mixture to illustrate this point.

2.41. The thermal destruction of hazardous wastes involves the controlled exposure of waste to high temperatures (usually 900°C or greater) in an oxidizing environment. Types of thermal destruction equipment include high-temperature boilers, cement kilns, and industrial furnaces in which hazardous waste is burned as fuel. In a properly designed system, primary fuel (100% combustible material) is mixed with waste to produce a feed for the boiler.

(a) Sand containing 30% by weight of 4,4′-dichlorobiphenyl [an example of a polychorinated biphenyl (PCB)] is to be cleaned by combustion with excess hexane to produce a feed that is 60% combustible by weight. To decontaminate 8 tons of such contaminated sand, how many pounds of hexane would be required?

(b) Write the two reactions that would take place under ideal conditions if the mixture of hexane and the contaminated sand were fed to the thermal oxidation process to produce the most environmentally satisfactory products. How would you suggest treating the exhaust from the burner? Explain.

(c) The incinerator is supplied with an oxygen-enriched airstream containing 40% O_2 and 60% N_2 to promote high-temperature operation. The exit gas is found to have a $x_{CO_2} = 0.1654$ and $x_{O_2} = 0.1220$. Use this information and the data about the feed composition above to find: (1) the complete exit gas concentrations and (2) the % excess O_2 used in the reaction.

2.42. A gas containing 20% N_2 and 80% CH_4 passes through a liquefication process. Thirty weight percent of the entering gas is recovered and the composition of the recovered gas which is a liquid is 60% N_2 by weight. Find the composition of the nonrecovered gas if 65 lb of entering gas is processed per minute. The temperature of the entering stream is 70°F; of the exit stream, 0°F. The pressures of all streams are about 1 atmosphere.

2.43. The organic fraction in the wastewater is measured in terms of the biological oxygen demand (BOD) material, namely the amount of dissolved oxygen required to biodegrade the organic contents. If the dissolved oxygen (DO) concentration in a body of water drops too low, the fish in the stream or lake may die. The Environmental Protection Agency has set the minimum summer levels for lakes at 5 mg/L DO.

(a) If a stream is flowing at 0.3 m^3/s and has an initial BOD of 5 mg/L before reaching the discharge point of a sewage treatment plant, and the plant discharges 3.785 ML/day of wastewater, with a concentration of 0.15 g/L BOD, what will be the BOD concentration immediately below the discharge point of the plant?

(b) The plant reports a discharge of 15.8 ML/day having a BOD of 72.09 mg/L. If the EPA measures the flow of the stream before the discharge point at 530 ML/day with 3 mg/L of BOD, and measures the downstream concentration of 5 mg/L BOD, is the report correct?

2.44. Printed circuit boards (PCBs) are used in the electronic industry to both connect and hold components in place. In production, 0.03 in. of copper foil is laminated to an insulating plastic board. A circuit pattern made of a chemically resistant polymer is then printed on the board. Next, the unwanted copper is chemically etched away by using selected reagents. If copper is treated with $Cu(NH_3)_4Cl_2$ (cupric ammonium chloride) and NH_4OH (ammonium hydroxide), the products are water and $Cu(NH_3)_4Cl$ (cuprous ammonium chloride). Once the copper is dissolved, the polymer is removed by solvents leaving the printed circuit ready for further processing. If a single-sided board 4 in. by 8 in. is to have 75% of the copper layer removed using the reagents above, how many grams of each reagent will be consumed?

Data: The density of copper is 8.96 g/cm^3.

2.45. A polymer blend is to be formed from the three compounds whose compositions and approximate formulas are listed in the table. Determine the percentages of each compound A, B, and C to be introduced into the mixture to achieve the desired composition.

	Compound (%)			
Composition	A	B	C	Desired mixture
$(CH_4)x$	25	35	55	30
$(C_2H_6)x$	35	20	40	30
$(C_3H_8)x$	40	45	5	40
Total	100	100	100	100

How would you decide to blend compounds A, B, C, and D [$(CH_4)_x = 10\%$, $(C_2H_6)_x = 30\%$, $(C_3H_8)_x = 60\%$] to achieve the desired mixture?

2.46.* In a gas-separation plant, the feed-to-butane splitter has the following constitutents:

Component	Mole %
C_3	1.9
i-C_4	51.6
n-C_4	46.0
C_5^+	0.6
Total	100.0

The flow rate is 5804 kg mol/day. If the overhead and bottoms streams from the butane splitter have the following compositions, what are the flow rates of the overhead and bottoms streams in kg mol/day?

	Mole %	
Component	Overhead	Bottoms
C_3	3.4	—
i-C_4	95.7	1.1
n-C_4	0.9	97.6
C_5^+	—	1.3
Total	100.0	100.0

2.47. A low-grade pyrites containing 32% S is mixed with 10 lb of pure sulfur per 100 lb of pyrites so the mixture will burn readily, forming a burner gas that analyzes (Orsat) 13.4% SO_2, 2.7% O_2, and 83.9% N_2. No sulfur is left in the cinder. Calculate the percentage of the sulfur fired that burned to SO_3. (The SO_3 is not detected by the Orsat analysis.)

2.48. Methane is flowing in a pipeline at the rate of 20.7 m^3/min at 30°C and 250 kPa. To check the flow rate, He is to be introduced at 25°C and 300 kPa. What is the minimum number of cm^3 per minute of He must be introduced if the minimum detectable downstream concentration of the He in the methane is 10 ppm?

2.49. In the manufacture of vinyl acetate, there is some unreacted acetic acid and other compounds that are discharged to the sewer. Your company has been cited as discharging more than the specified limit of several pollutants. It is not possible to measure the discharge directly because no flow measuring devices are in place, but you can take samples of liquid at different places in the sewer line, and measure the concentration of potassium chloride. At one manhole, the concentration is 0.105%. You introduce a solution of 400 g of KCl in 1L at a steady rate of 1 L per minute over $\frac{1}{2}$ hr at a manhole 500 ft downstream, and at 1200 ft downstream measure the average steady-state concentration of KCl as 0.281%. What is the flow rate of fluid in the sewer in kg/min?

2.50. Trace components can be used to measure flow rates in pipelines, process equipment, and rivers that might otherwise be quite difficult to measure. Suppose that the water analysis in a flowing creek shows 180 ppm Na_2SO_4. If 10 lb of Na_2SO_4 is added to the stream uniformly over a 1-hr period and the analysis downstream where mixing is complete indicates 330 ppm Na_2SO_4, how many gallons of water are flowing per hour? See Fig. P2.50. Assume that no Na_2SO_4 is lost in the streambed or in the vegetation in the stream.

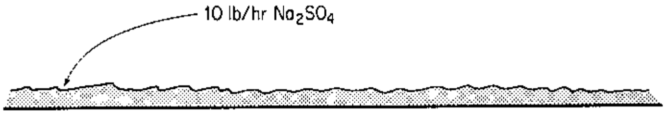


Figure P2.50

2.51. Your boss asks you to calculate the flow through a natural-gas pipeline. Since it is 26 in. in diameter, it is impossible to run the gas through any kind of meter or measuring device. You decide to add 100 lb of CO_2 per minute to the gas through a small $\frac{1}{2}$-in. piece of pipe, collect samples of the gas downstream, and analyze them for CO_2. Several consecutive samples after 1 hr are:

Time	Percent CO_2
1 hr, 0 min	2.0
10 min	2.2
20 min	1.9
30 min	2.1
40 min	2.0

(a) Calculate the flow of gas in pounds per minute at the point of injection.
(b) Unfortunately for you, the gas at the point of injection of CO_2 already contained 1.0% CO_2. How much was your original flow estimate in error (in percent)? [*Note:* In part (a) the natural gas is all methane, CH_4.]

2.52. The nose is an extremely sensitive detector of odors; it can be matched only by the most sensitive instrumental techniques. Many smells are identified by comparison with pure compounds diluted by odor-free air until they are near the odor threshold limit. However, with the introduction of flame photometric detectors it has been possible to measure the concentration of the sulfur compounds giving rise to odors in the ppb range with the aid of preconcentration (by a factor of 10^3 to 10^4).

The main offenders are known to be H_2S, mercaptans, and disulfides, which are present in crude-oil fractions. Because of their offensive smell and low olfactory levels, these compounds give rise to the majority of complaints. Typical detectable limits for the most important sulfur compounds are:

Compound	ppm
Hydrogen sulfide, H_2S	0.001–0.014
Methyl mercaptan, CH_3SH	0.001–0.0085
Ethyl mercaptan, C_2H_5SH	0.001–0.0026
Dimethyl sulfide, $(CH_3)_2S$	0.002–0.0052

If the concentration of methyl mercaptan is measured as 0.035 ppm in a waste stream flowing at 1.7 m^3/s (specific volume = 0.021 m^3/kg mol), how many kilograms of air have to be bled into the waste stream per second to reduce the concentration of methyl mercaptan in the stream to below detectable levels?

2.53. The Clean Air Act requires automobile manufacturers to warrant their control systems as satisfying the emission standards for 50,000 mi. It requires owners to have their engine control systems serviced exactly according to manufacturers' specifications and to always use the correct gasoline. In testing an engine exhaust having a known Orsat analysis of 16.2% CO_2, 4.8% O_2, and 79% N_2 at the outlet, you find to your surprise that at the end of the muffler the Orsat analysis is 13.1% CO_2. Can this discrepancy be caused by an air leak into the muffler? (Assume that the analyses are satisfactory.) If so, compute the moles of air leaking in per mole of exhaust gas leaving the engine.

2.54. A dairy produces casein which when wet contains 23.7% moisture. They sell this for \$8.00/100 lb. They also dry this casein to produce a product containing 10% moisture. Their drying costs are \$0.80/100 lb water removed. What should be the selling price of the dried casein to maintain the same margin of profit?

Section 2.5

2.55. See Fig. P2.55

$$F_1 + F_2 - F_3 = 0 \tag{1}$$

$$F_3 - F_4 - F_5 = 0 \tag{2}$$

$$F_1 + F_2 - F_4 - F_5 = 0 \tag{3}$$

For Fig. P2.55 how many independent equations are obtained from the overall balance around the entire system [Eq. (3)], plus the balances on units *A* [Eq. (1)], and *B* [Eq. (2)]?

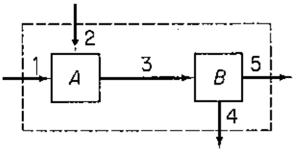


Figure P2.55

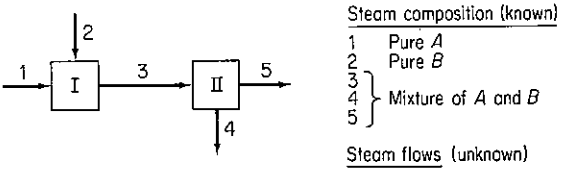


Figure P2.56

2.56. What is the maximum number of independent material balances that can be written for the process in Fig. P2.56?

2.57. What is the maximum number of independent material balances that can be written for the process in Fig. P2.57? The stream flows are unknown.

Suppose you find out that *A* and *B* are always combined in each of the streams in the same ratio. How many independent equations could you write?

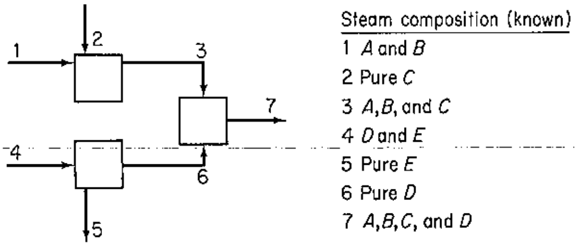


Figure P2.57

2.58. The diagram in Fig. P2.58 represents a typical but simplified distillation column. Streams 3 and 6 consist of steam and water, and do not come in contact with the fluids in the column which contains two components. Write the total and component material balances for the three sections of the column. How many independent equations would these balances represent?

2.59. A distillation process is shown in Fig. P2.59. You are asked to solve for all the values of the stream flows and compositions. How many unknowns are there in the system? How many independent material balance equations can you write? Explain each answer and show all details whereby you reached your decision. For each stream, the only components that occur are shown below the stream.

2.60. Metallurgical-grade silicon is purified to electronic grade for use in the semiconductor industry by chemically separating it from its impurities. Si metal reacts in varying degrees with hydrogen chloride gas at 300°C to form several polychlorinated

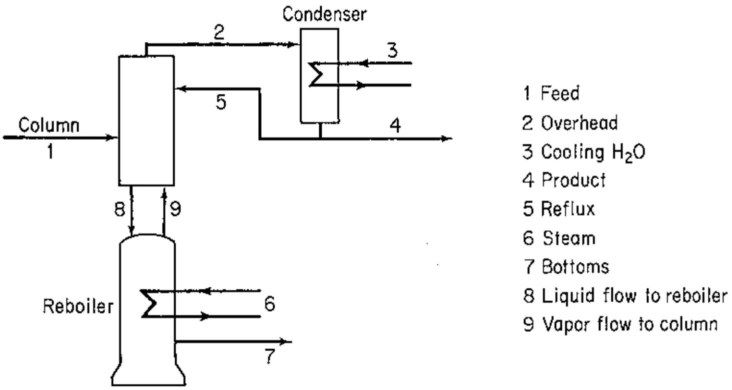


Figure P2.58

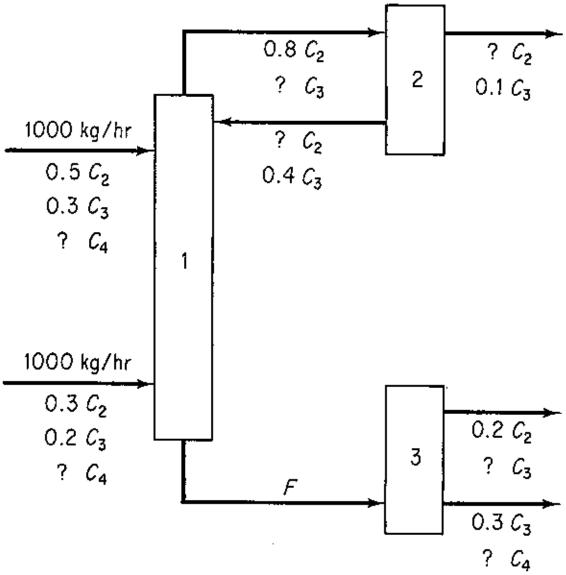


Figure P2.59

silanes. Trichlorosilane is liquid at room temperature and is easily separated by fractional distillation from the other gases. If 100 kg of silicon is reacted as shown in Fig. P2.60, how much trichlorosilane is produced?

2.61.* Two major types of "gasifiers" for solid fossil fuels are available commercially at the present time. The cocurrent or downdraft versions are used in small internal combustion engine applications for sawmills, remote communities, and to satisfy power needs for developing nations. A more recent advance is the fluidized-bed gasifier, which is appropriate for larger-scale conversion of biomass to "producer gas" or other products.

To take advantage of the most economical fuels, a company can burn producer gas (4.3% CO_2, 27% CO, 10% H_2, 1.0% CH_4, and the residual N_2) generated from a fluidized-bed gasifier using coal waste in one boiler or No. 6 fuel oil (87% C,

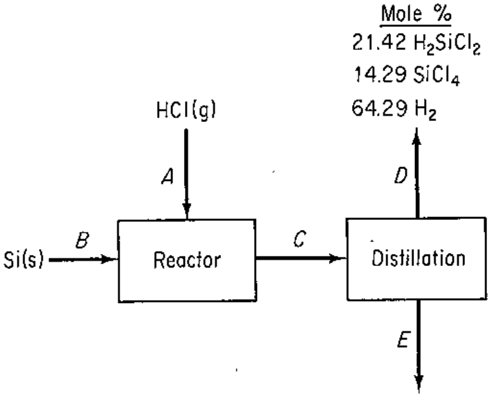


Figure P2.60

13% H_2) in a second boiler. One day both boilers are running and the Orsat analysis from the common stack is 8.2% CO_2, 0.4% CO, and 10% O_2 and the residual N_2.

(a) Calculate the fraction of the total carbon in the stack gas that comes from the fluidized-bed gasifier.

(b) How many moles of water would be produced in the gasifier per 100 moles of dry gas having the Orsat analysis above?

(c) How many total moles of air are fed to the process, and what is the overall effective percent excess air that was used?

2.62. In a distillation train a liquid hydrocarbon containing 20 mol % ethane, 40 mol % propane, and 40 mol % butane is to be fractionated into essentially pure components as shown in Fig. P2.62. On the basis of F = 100 moles, what is P (in moles) and the composition of stream A?

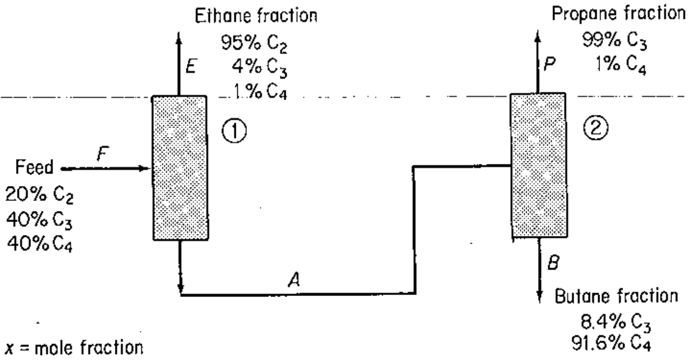


Figure P2.62

2.63.* A simplified flowsheet for the manufacture of sugar is shown in Fig. P2.63. Sugarcane is fed to a mill where a syrup is squeezed out, and the resulting "bagasse" contains 80% pulp. The syrup (E) containing finely divided pieces of pulp is fed to a screen which removes all the pulp and produces a clear syrup (H) containing 15% sugar and 85% water. The evaporator makes a "heavy" syrup and the crystallizer produces 1000 lb/hr of sugar crystals.

(a) Find the water removed in the evaporator, lb/hr

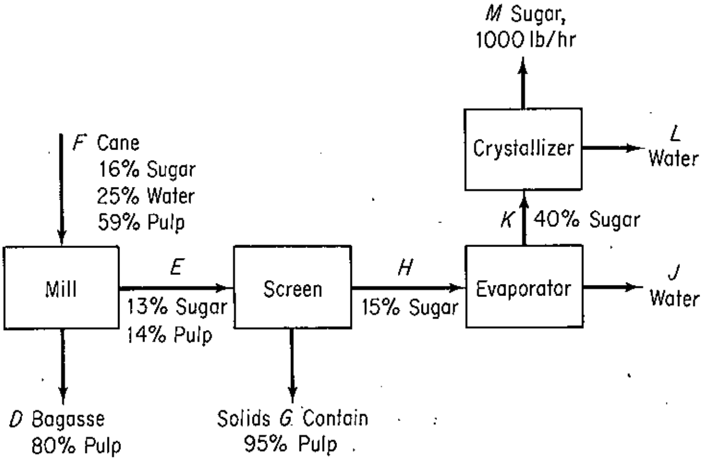


Figure P2.63

(b) Find the composition of the waste stream *G*

(c) Find the rate of feed of cane to the unit, lb/hr

(d) Of the sugar fed in the cane, what percentage is lost with the bagasse?

(e) Is this an efficient operation? Explain why or why not.

2.64.* Sodium hydroxide is usually produced from common salt by electrolysis. The essential elements of the system are shown in Fig. P2.64.

(a) What is the percent conversion of salt to sodium hydroxide?

(b) How much chlorine gas is produced per pound of product?

(c) Per pound of product, how much water must be evaporated in the evaporator?

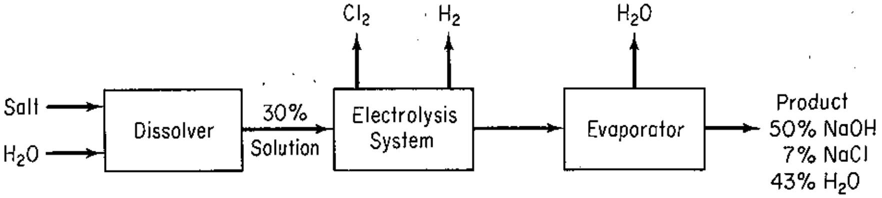


Figure P2.64

2.65.* The flowsheet shown in Fig. P2.65 represents the process for the production of titanium dioxide (TiO_2) used by Canadian Titanium Pigments at Varennis, Quebec. Sorel slag of the following analysis:

	Wt %
TiO_2	70
Fe	8
Inert silicates	22

is fed to a digester and reacted with H_2SO_4, which enters as a 67% by weight

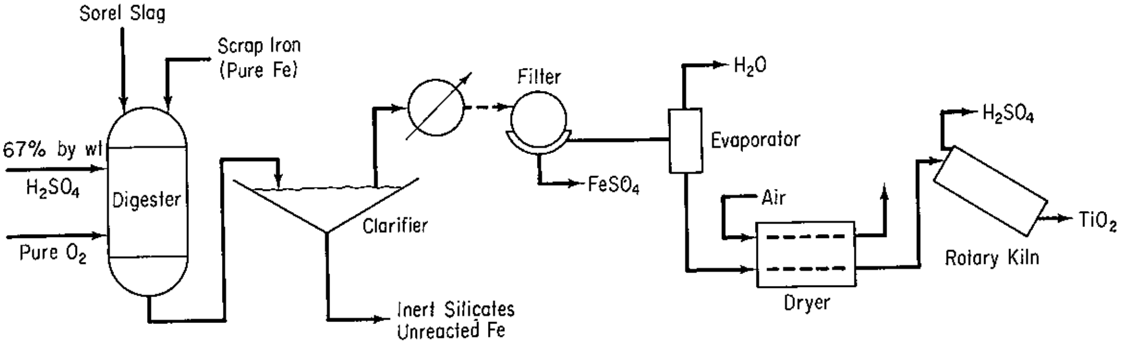


Figure P2.65

H_2SO_4 in a water solution. The reactions in the digester are as follows:

$$TiO_2 + H_2SO_4 \longrightarrow TiOSO_4 + H_2O \qquad (1)$$

$$Fe + \tfrac{1}{2}O_2 + H_2SO_4 \longrightarrow FeSO_4 + H_2O \qquad (2)$$

Both reactions are complete. The theoretically required amount of H_2SO_4 for the Sorel slag is fed. Pure oxygen is fed in the theoretical amount for all the Fe in the Sorel slag. Scrap iron (pure Fe) is added to the digester to reduce the formation of ferr*ic* sulfate to negligible amounts. Thirty-six pounds of scrap iron are added per pound of Sorel slag.

The products of the digester are sent to the clarifier, where all the inert silicates and unreacted Fe are removed. The solution of $TiOSO_4$ and $FeSO_4$ from the clarifier is cooled, crystallizing the $FeSO_4$, which is completely removed by a filter. The product $TiOSO_4$ solution from the filter is evaporated down to a slurry that is 82% by weight $TiOSO_4$.

The slurry is sent to a dryer from which a product of pure hydrate, $TiOSO_4 \cdot H_2O$, is obtained. The hydrate crystals are sent to a direct-fired rotary kiln, where the pure TiO_2 is produced according to the following reaction:

$$TiOSO_4 \cdot H_2O \longrightarrow TiO_2 + H_2SO_4 \qquad (3)$$

Reaction (3) is complete.

On the basis of 100 lb of Sorel slag feed, calculate:

(a) The pounds of water removed by the evaporator

(b) The exit lb of H_2O per lb dry air from the dryer if the air enters having 0.036 moles H_2O per mole dry air and the air rate is 18 lb mol of dry air per 100 lb of Sorel slag

(c) The pounds of product TiO_2 produced

2.66.* In the process for the production of pure acetylene, C_2H_2, (see Fig. P2.66), pure methane (CH_4) and pure oxygen are combined in the burner, where the following reactions occur:

$$CH_4 + 2O_2 \longrightarrow 2H_2O + CO_2 \qquad (1)$$

$$CH_4 + 1\tfrac{1}{2}O_2 \longrightarrow 2H_2O + CO \qquad (2)$$

$$2CH_4 \longrightarrow C_2H_2 + 3H_2 \qquad (3)$$

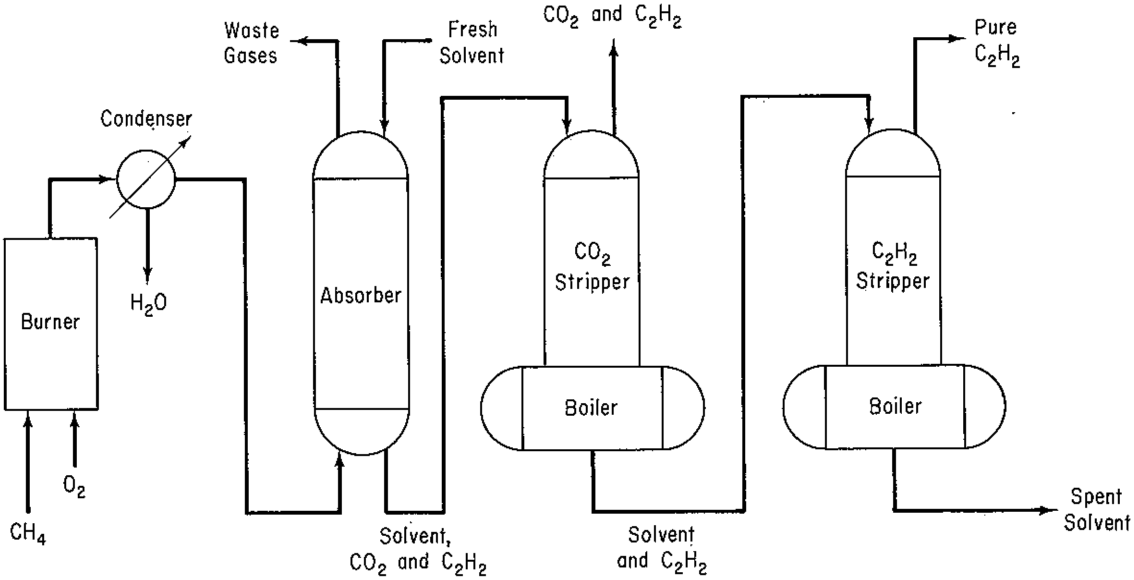


Figure P2.66

The gases from the burner are cooled in a condenser that removes all the water. The analysis of the gases leaving the condenser is as follows:

	Mol %
C_2H_2	8.5
H_2	25.5
CO	58.3
CO_2	3.7
CH_4	4.0
Total	100.0

These gases are sent to an absorber where 97% of the C_2H_2 and essentially all the CO_2 are removed with the solvent. The solvent from the absorber is sent to the CO_2 stripper, where all the CO_2 is removed. The analysis of the gas stream leaving the top of the CO_2 stripper is as follows:

	Mol %
C_2H_2	7.5
CO_2	92.5
Total	100.0

The solvent from the CO_2 stripper is pumped to the C_2H_2 stripper, which removes all the C_2H_2 as a pure product:

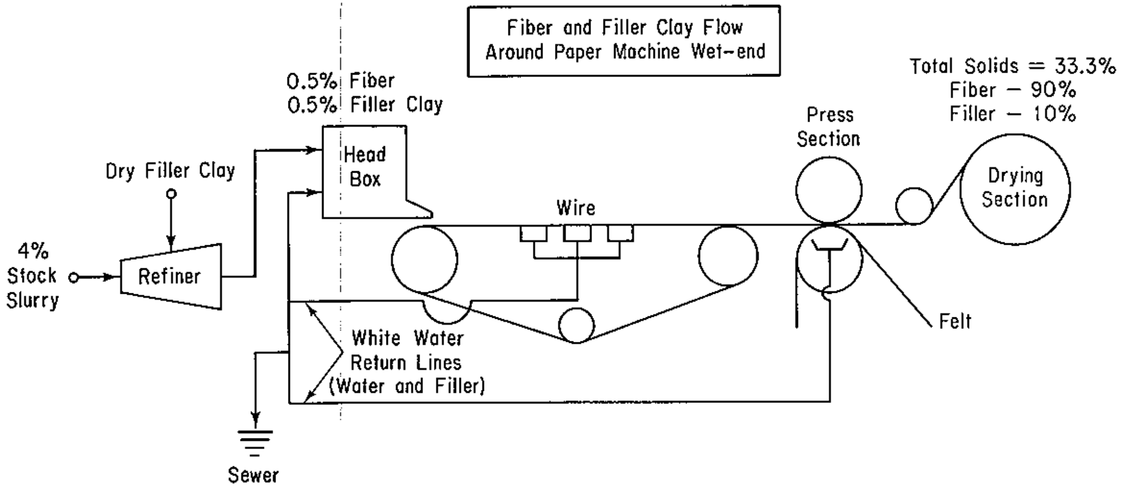

Fiber and Filler Clay Flow
Around Paper Machine Wet-end
0.5% Fiber
0.5% Filler Clay
Head Box
Dry Filler Clay
4% Stock Slurry
Refiner
Wire
Press Section
Total Solids = 33.3%
Fiber − 90%
Filler − 10%
Drying Section
Felt
White Water Return Lines (Water and Filler)
Sewer

Figure P2.67

(a) Calculate the ratio of the moles of O_2 to moles of CH_4 fed to the burner.
(b) On the basis of 100 lb mol of gases leaving the condenser, calculate how many pounds of water are removed by the condenser.
(c) What is the overall percentage yield of product (pure) C_2H_2, based on the carbon in the natural gas entering the burner?

2.67. In a paper machine system (see Fig. P2.67), a stock suspension of cellulose fibers in water enters the continuous refining system at 4% consistency (4 lb of fiber per 100 lb of mixture). A dry filler clay is added in the refining system, and this slurry then goes to the paper machine headbox. The headbox distributes the suspension of cellulose fibers and filler clay uniformily over a wire belt in the form of a thin sheet. This wet sheet becomes the desired paper after it is dried. In the headbox, the slurry is diluted with a recycle stream of white water that passed through the wire belt during the formation of the sheet, to a fiber consistency of 0.5%. Analysis shows that the filler consistency is also 0.5% at this point. The damp sheet leaving the press section and entering the drying section, where water is removed by the application of heat, contains 33.3% solids consisting of 90% fiber and 10% filler. Any excess white water from the machine, not needed for headbox dilution, is discarded.

Assuming no fiber loss through the wire and at the presses, calculate:
(a) The overall percent filler retention on the wet sheet
(b) The percent filler retention per pass (on the basis of the total filler that can be retained)

Section 2.6

2.68. Boron trichloride (BCl_3) gas can be fed into a gas stream and used for doping silicon. The simplest reaction (not the only one) is

$$4\,BCl_3 + 3Si \longrightarrow 3SiCl_4 + 4B$$

If all the BCl_3 not reacted is recycled (see Fig. P2.68), what is the mole ratio of recycle to $SiCl_4$ exiting the separator? The conversion on one pass through the reactor is 87% and 1 mole per hour of BCl_3 is fed to the reactor.

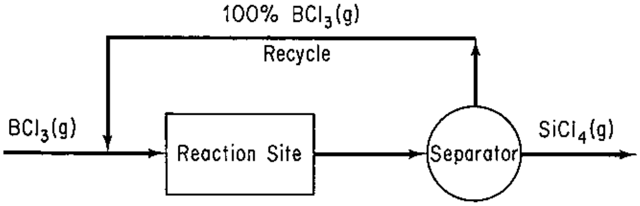


Figure P2.68

2.69. Examine Fig. P2.69. What is the quantity of the recycle stream in kg/hr?

2.70. The connections of computer components are often electroplated with relatively inert materials such as gold to to prevent short circuiting by oxide buildup. Gold cyanide solutions have traditionally been used in batch processing. A process for continuous plating and replenishing of the electrolyte bath as shown in Fig. P2.70 has been patented (U.S. patent 4,340,451). If the throughput of components requires 30 g/hr of gold plating, how many cubic centimeters of water are consumed per hour?

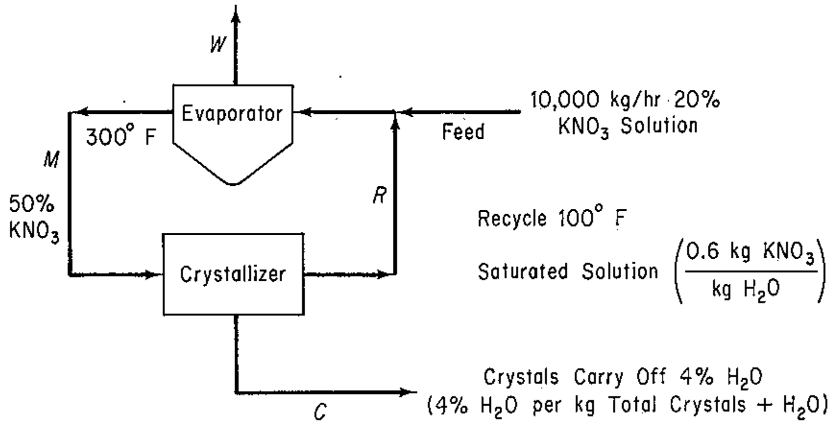


Figure P2.69

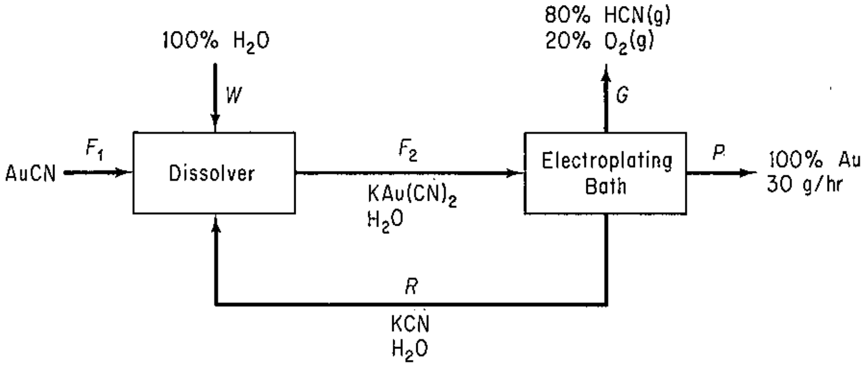


Figure P2.70

2.71.* The process shown in Fig. P2.71 is the catalytic dehydrogenation of propane to propylene. The composition and flow rate of the recycle stream are unknown. Certain data are known for the reactor, absorber, and distillation column as follows:

Reactor Effluent Composition Based on
100 kg mol of Propane Fed to Reactor

Component	Mol % in Product from reactor
Hydrogen	25.4
Methane	3.2
Ethylene	0.3
Ethane	5.3
Propylene	21.3
Propane	44.5
Total	100.0

Fractionator Performance

Component	Fraction of feed recovered in the overhead product
Methane	1.00
Ethane	1.00
Ethylene	1.00
Propylene	0.96
Propane	0.002

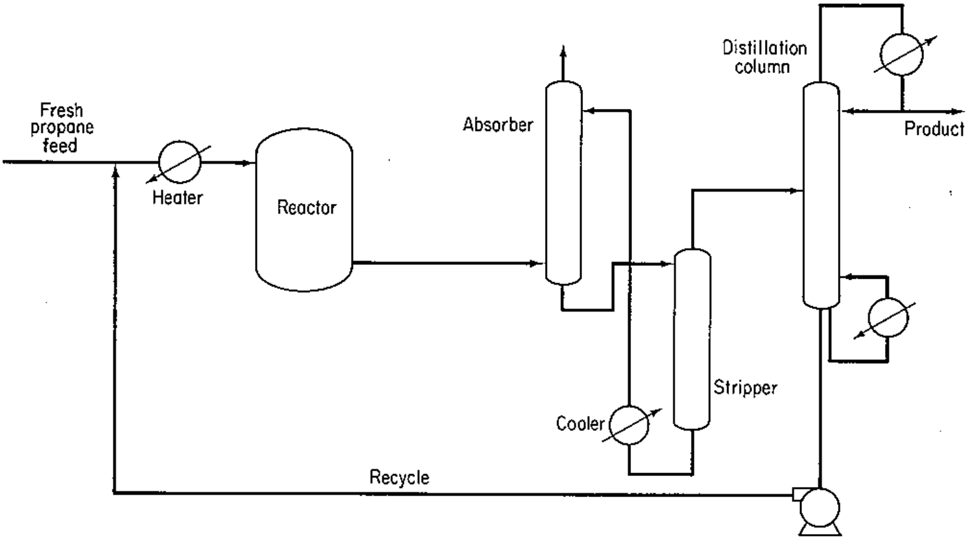


Figure P2.71

Absorber Performance Based on 100 kg mol of Absorber Feed

Component	kg mol of absorber feed	Fraction of absorber feed not absorbed
Hydrogen	25.4	1.00
Methane	3.2	0.95
Ethylene	0.3	0.70
Ethane	5.3	0.60
Propylene	21.3	0.01
Propane	44.5	0.003
Total	100.0	

Assume that the source of all the hydrogen in the product from the reactor is the propane feed, and that any loss of mass in the reactor is due to carbon formation. Also assume that none of the hydrogen in the reactor product is absorbed in the absorber.

Calculate the flow rates in the reactor feed (after the heater), the reactor product stream, the absorber bottoms stream, the distillation column bottoms, and the recycle stream in kilograms per 100 kg of propane fed to the process. Can you calculate the composition of the recycle stream as well?

2.72. The rate of production of ethanol by fermentation is slowed by the increasing concentrations of ethanol formed in the process. A method is being investigated in which the ethanol is to be separated continuously in situ with solvent. The solvent is then pumped off and the ethanol recovered. How many moles/hr of ethanol are recycled in the solvent for the system shown in Fig. P2.72?

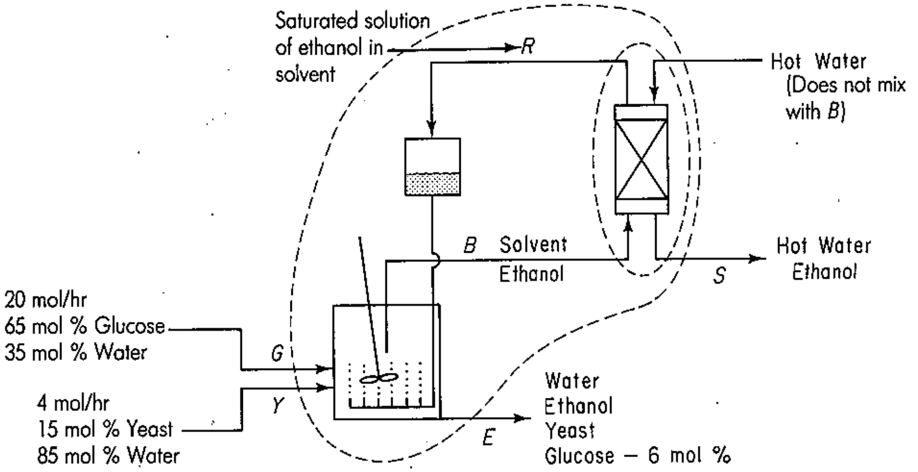


Figure P2.72

Data: glucose $\xrightarrow{\text{yeast}}$ 2 ethanol + $2CO_2$

92% conversion of glucose

saturated solvent: $0.24 \dfrac{\text{g EtOH}}{\text{g solvent}}$ in B

density of solvent: 0.84 g/cm^3

saturated solvent flow: 4.5 L/hr

Assume the participation of the yeast in the reaction is negligible.

2.73. A waste treatment plant operating under steady-state conditions processes a waste liquor containing 500 parts per million (ppm) of a noxious impurity. The impurity is removed with practically no loss of the carrier fluid. The treating process can remove the impurity down to a level of 10 ppm. By local ordinance, a maximum of 100 ppm is allowed in the discharge of the processed effluent to a nearby river. What fraction of the waste liquor must be sent through the waste treatment unit, and what fraction may be bypassed?

2.74. Seawater is to be desalinized by reverse osmosis using the scheme indicated in Fig. P2.74. Use the data given in the figure to determine:

(a) The rate of waste brine removal (B)

(b) The rate of desalinized water (called potable water) production (D)

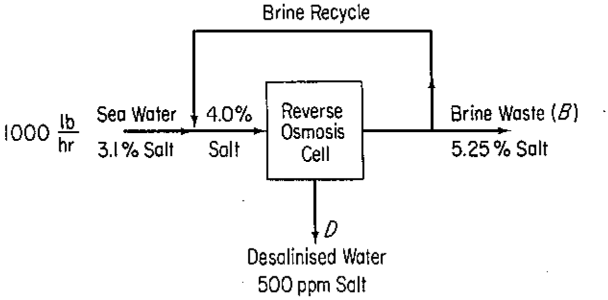


Figure P2.74

(c) The fraction of the brine leaving the osmosis cell (which acts in essence as a separator) that is recycled

(*Note:* ppm designates parts per million).

2.75. A solution containing 10% NaCl, 3% KCl, and 87% water is fed to the process shown in Fig. P2.75 at the rate of 18,400 kg/hr. The compositions of the streams are as follows in percent. Evaporator product, P: NaCl: 16.8, KCl: 21.6, H_2O: 61.6; Recycle, R: NaCl: 18.9 and the balance water. Calculate the kilograms per hour and complete compositions of every stream.

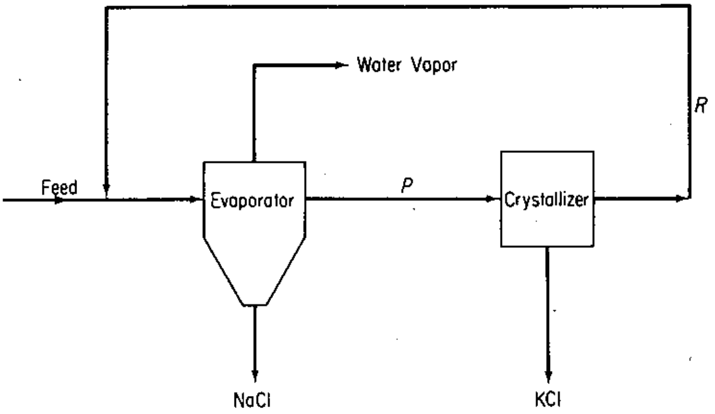


Figure P2.75

2.76. A 50% NaCl solution is to be concentrated in a triple-effect evaporator as shown in Fig. P2.76. (Each individual evaporator is termed an *effect*.) An equal amount of water is evaporated in each effect. Determine the composition of the outlet stream from effect 2 if the internal contents of effect 2 are uniformly mixed so that the outlet stream has the same composition as the internal contents of effect 2. The steam lines in each effect are completely separate from the evaporator contents so that no mixing of the steam with the contents occurs.

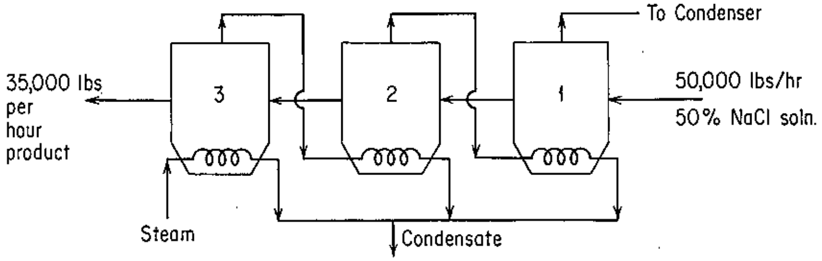


Figure P2.76

2.77.* A natural-gas plant at Short Junction, Oklahoma, produces gasoline by removing condensable vapors from the gas flowing out of gas wells. The gas from the well has the following composition:

Component	Mol %
CH_4	77.3
C_2H_6	14.9
C_3H_8	3.6
iso- and n-C_4H_{10}	1.6
C_5 and heavier	0.5
N_2	2.1
Total	100.0

This gas passes through an absorption column called a scrubber (see Fig. P2.77), where it is scrubbed with a heavy, nonvolatile oil. The gas leaving the scrubber has the following analysis:

Component	Mol %
CH_4	92.0
C_2H_6	5.5
N_2	2.5

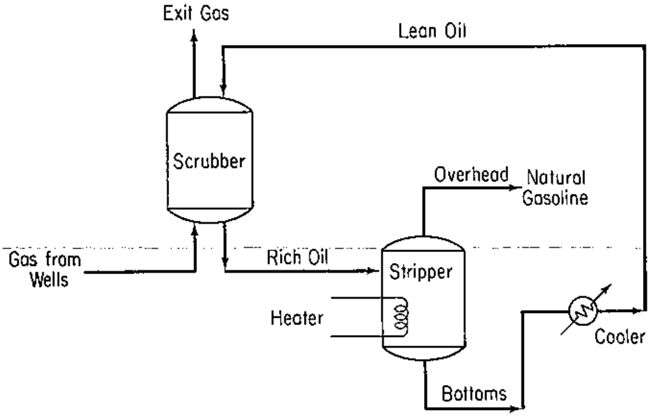


Figure P2.77

The scrubbing oil absorbs none of the CH_4 or N_2, much of the ethane, and all of the propane and higher hydrocarbons in the gas stream. The oil stream is then sent to a stripping column, which separates the oil from the absorbed hydrocarbons. The overhead from the stripper is termed *natural gasoline*, while the bottoms from the stripper is called *lean oil*. The lean-oil stream is cooled and returned to the absorption column. Assume that there are no leaks in the system. Gas from the wells is fed to the absorption column at the rate of 52,000 lb moles/day and the flow rate of the rich oil going to the stripper is 1230 lb/min (MW = 140). Calculate:

(a) The pounds of CH_4 passing through the absorber per day

(b) The pounds of C_2H_6 absorbed from the gas stream per day

(c) The weight percentage of propane in the rich oil stream leaving the scrubber

2.78. Given that the reaction for fresh feed A and B is

$$2A + 5B \longrightarrow 3C + 6D$$

in a reactor with recycle, find the desired recycle ratio (moles recycle/moles fresh feed) if in the fresh feed A is 20% in excess, the once-through conversion of B is 60%, and the overall conversion of B to products for the overall process is 90%. After the products exit from the reactor, a stream of pure B is separated from the products and forms the recycle.

2.79. Phthalic anhydride (PA) is produced by the oxidation of *o*-xylene (C_8H_{10}) in a fixed-bed reactor (Fig. P2.79) at 350°C according to the reaction

$$C_8H_{10} + 3O_2 \longrightarrow C_8H_4O_3 + 3H_2O$$

A condenser is used to remove all of the PA ($C_8H_4O_3$) as a mixture of solid and liquid. How many kilograms of *o*-xylene are recycled per hour if the purge gas is 78% N_2 and 60% conversion of *o*-xylene takes place on one pass through the reactor?

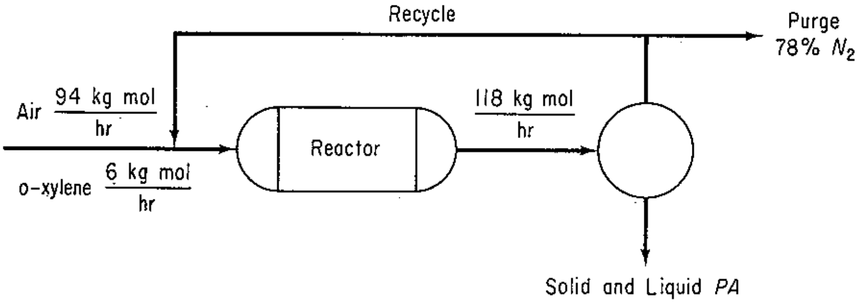


Figure P2.79

2.80. In the operation of a synthetic ammonia plant, an excess of hydrogen is burned with air so that the burner gas contains nitrogen and hydrogen in a 1 : 3 mole ratio and no oxygen. Argon is also present in the burner gas since it accounts for 0.94% of air. The burner gas is fed to a converter where a 25% conversion of the N_2–H_2 mixture to ammonia is produced. The ammonia formed is separated by condensation and the unconverted gases are recycled to the converter. To prevent accumulation of argon in the system, some of the unconverted gases are vented before being recycled to the converter. The upper limit of argon in the converter is to be 4.5% of the entering gases. What percentage of the original hydrogen is converted into ammonia?

2.81. Methanol (CH_3OH) can be converted into formaldehyde (HCHO) either by oxidation to form formaldehyde and water or by direct decomposition to formaldehyde and hydrogen. Suppose that in the fresh feed to the process the ratio of methanol to oxygen is 4 moles to 1, the conversion of methanol per pass in the reactor is 50%, and all of the oxygen reacts in the reactor—none leaves with the hydrogen. After the reaction a separation process removes first all the formaldehyde and water, and then all the hydrogen is removed from the recycled methanol. Determine the flow rates of each species and the total flow rates at each point in the process.

2.82. In a proposed process for the preparation of methyl iodide, 2000 kg/day of hydroiodic acid is added to an excess of methanol:

$$HI + CH_3OH \longrightarrow CH_3I + H_2O$$

If the product contains 81.6 wt % CH_3I along with the unreacted methanol, and the waste contains 82.6 wt % hydroiodic acid and 17.4% H_2O, calculate, assuming that the reaction is 40% complete in the process vessel:

(a) The weight of methanol added per day

(b) The amount of HI recycled

2.83. Acetic acid is to be generated by the addition of 10% excess sulfuric acid (of strength 100%) to calcium acetate. The reaction in the reactor

$$Ca(COOCH_3)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2CH_3COOH$$

goes to 90% completion. The unused calcium acetate and sulfuric acid are separated from the reaction products and are recycled back to the process. The acetic acid is separated from the reaction products and sold. The atomic weights are Ca = 40.08, S = 32.

(a) Draw a block diagram sketch for the process.

(b) Calculate the total amount of the recycle stream per hour based on 1000 lb of calcium acetate fed per hour.

(c) Calculate the pounds of acetic acid manufactured per hour.

2.84. Alkyl halides are used as an alkylating agent in various chemical transformations. The alkyl halide ethyl chloride can be prepared by the following chemical reaction:

$$2C_2H_6 + Cl_2 \longrightarrow 2C_2H_5Cl + H_2$$

In the reaction process shown in Fig. P2.84, fresh ethane and chlorine gas and recycled ethane are combined and fed into the reactor. A test shows that if 100% excess chlorine is mixed with ethane, a single-pass optimal conversion of 60% results, and of the ethane that reacts, all is converted to products and none goes into undesired products. Calculate:

(a) The fresh feed concentrations required for operation

(b) The moles of C_2H_5Cl produced in P per mole of C_2H_6 in the fresh feed F_1

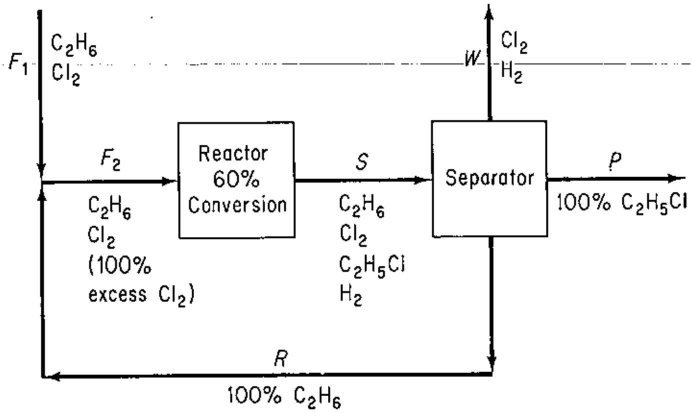


Figure P2.84

2.85.* A process for methanol synthesis is shown in Fig. P2.85. The pertinent chemical reactions involved are

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 \quad \text{(main reformer reaction)} \quad (a)$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad \text{(reformer side reaction)} \quad (b)$$

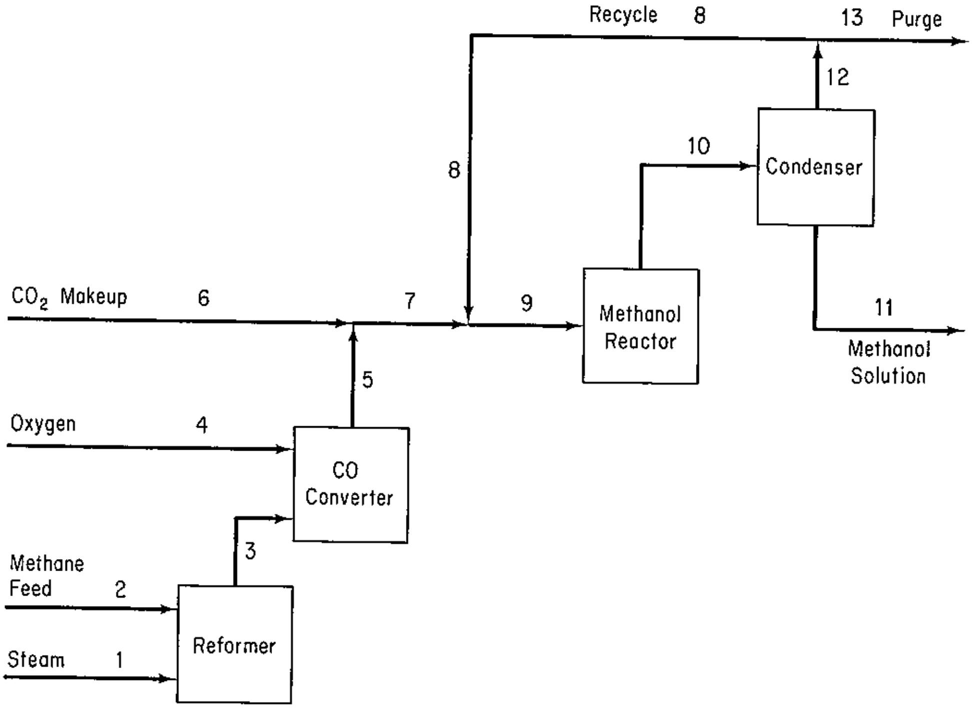


Figure P2.85

$$2CO + O_2 \longrightarrow 2CO_2 \qquad \text{(CO converter reaction)} \qquad (c)$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2 \qquad \text{(methanol reaction)} \qquad (d)$$

Ten percent excess steam, based on reaction (a), is fed to the reformer, and conversion of methane is 100%, with a 90% yield of CO_2. Conversion in the methanol reactor is 55% on one pass through the reactor.

A stoichiometric quantity of oxygen is fed to the CO converter, and the CO is completely converted to CO_2. Additional makeup CO_2 is then introduced to establish a 3-to-1 ratio of H_2 to CO_2 in the feed stream to the methanol reactor.

The methanol reactor effluent is cooled to condense all the methanol and water, with the noncondensible gases recycled to the methanol reactor feed. The H_2/CO_2 ratio in the recycle stream is also 3 to 1.

Because the methane feed contains 1% nitrogen as an impurity, a portion of the recycle stream must be purged as shown in the flow diagram to prevent the accumulation of nitrogen in the system. The purge stream analyzes 5% nitrogen.

On the basis of 100 mol of methane feed (including the N_2), calculate:

(a) How many moles of H_2 are lost in the purge
(b) How many moles of makeup CO_2 are required
(c) The recycle to purge ratio in mol/mol
(d) How much methanol solution (in kg) of what strength (weight percent) is produced

2.86.* An isomerizer is a catalytic reactor that simply tends to rearrange isomers. The number of moles entering an isomerizer is equal to the number of moles leaving. A

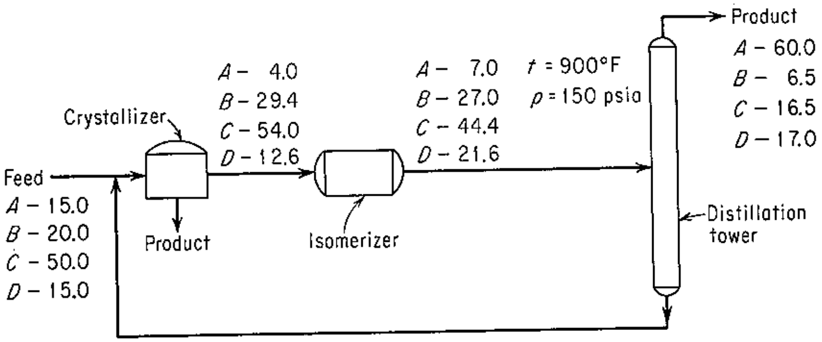


Figure P2.86

process, as shown in Fig. P2.86, has been designed to produce a *p*-xylene-rich product from an aromatic feed charge. All compositions on the flow sheet are in mole percent. The components are indicated as follows:

A	ethyl benzene
B	*o*-xylene
C	*m*-xylene
D	*p*-xylene

Eighty percent of the ethyl benzene entering the distillation tower is removed in the top stream from the tower. The ratio of the moles of fresh feed to the process as a whole to the moles of product from the crystallizer is 1.63. Find:

(a) The reflux ratio (ratio of moles of stream from the bottom of the distillation tower per mole of feed to the tower)

(b) The composition (in mole percent) of the product from the crystallizer

(c) The moles leaving the isomerizer per mole of feed

PROBLEM THAT REQUIRES WRITING A COMPUTER PROGRAM

2.1. A 15-stage extraction column similar to the one in Example 2.22 is set up to separate acetone and ethanol using two solvents, pure water and pure chloroform. The only added features to Fig. E2.22 in Example 2.22 are (1) that you must consider two solutes in each solvent instead of one solute in the two solvents and (2) the acetone-ethanol feed is introduced into stage 6. You know that the feed composition is 50 mol % ethanol and 50 mol % acetone and that the feed rate is 20 lb mol/hr. Assume that the water and chloroform are not soluble in each other. You want to have 1.50 mol % ethanol in the exit stream from the bottom of the column, and 2×10^{-5} mol % acetone in the exit stream from the top of the column. Determine the rates of flow of the two solvents. In each stage you are given a relationship between X_i^A and X_i^B ($i = 1, 2, 3$) in the two phases in terms of *mole fractions:*

$$\frac{x_i^B}{x_i^A} = \frac{\gamma_i^A}{\gamma_i^B} \tag{a}$$

Each of the γ's in phase A or phase B can be expressed in terms of some known constants and the mole fraction of the other two components. For component i,

$$\ln \gamma_i = 2x_i \sum_{j=1}^{3} x_j a_{ji} + \sum_{j=1}^{3} x_j^2 a_{ij} + \sum_{j=1}^{3} \sum_{\substack{k=1 \\ j \neq i \\ k \neq i \\ j<k}}^{3} x_j x_k a x^*_{ijk}$$

$$-2\sum_{i=1}^{3} x_i^2 \sum_{j=1}^{3} x_j a_{ij} - 2 \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} x_i x_j x_k a^*_{ijk} \tag{b}$$

where $a^*_{ijk} = a_{ij} + a_{ji} + a_{ik} + a_{ki} + a_{jk} + a_{kj}$. The values of the coefficients are

1: acetone 3: chloroform

2: ethanol 4: water

$a_{11} = 0.0$ $a_{12} = 0.5446$ $a_{13} = 0.9417$ $a_{14} = 1.872$

$a_{21} = 0.599$ $a_{22} = 0.0$ $a_{23} = 1.61$ $a_{24} = 1.46$

$a_{31} = 0.674$ $a_{32} = 0.501$ $a_{33} = 0.0$ $a_{34} = 5.91$

$a_{41} = 1.338$ $a_{42} = 0.877$ $a_{43} = 4.76$ $a_{44} = 0.0$

The γ's are obtained for each component, 1, 2, and 3, by permuting the subscripts cyclically $i \rightarrow j \rightarrow k \rightarrow i$. [*Hints:* Select some appropriate initial values for the flow rates of A and B. Divide the feed (stage 6) equally between both phases. The initial compositions can be provided by specifying both stage 1 and stage 15 and generating the remaining compositions by linear interpolation.] Be sure to include (1) one equation such as Eq. (a) for each component for each stage, (2) the correct number of component material balances for each stage (a total balance for the stage can be substituted for one component balance), and (3) $\Sigma\, x_i = 1$ for each stage for one phase (similar equations for the other phase are redundant).

GASES, VAPORS, LIQUIDS, AND SOLIDS

3

In planning and decision making for our modern technology, engineers and scientists must know with reasonable accuracy the properties of the fluids and solids with which they deal. By **property** we shall mean any measurable characteristic of a substance, such as pressure, volume, or temperature, or a characteristic that can be calculated or deduced, such as internal energy, to be discussed in Chap. 4. If you are engaged in the design of equipment, say calculating the volume required for a process vessel, you need to know the specific volume or density of the gas or liquid that will be in the vessel as a function of temperature and pressure. If you are interested in predicting the possibility or extent of rainfall, you have to know something about the relation between the vapor pressure of water and the temperature. Whatever your current or future job, you must be aware of the character and be able to locate sources of information concerning the physical properties of fluids and solids.

Clearly, it is not possible to have reliable, detailed experimental data at hand on all the useful pure compounds and mixtures that exist in the world. Consequently, in the absence of experimental information, we estimate (predict) properties based on modifications of well-established principles, such as the *ideal* gas law, or based on empirical correlations. Thus the foundation of the estimation methods ranges from quite theoretical to completely empirical, and their reliability ranges from excellent to terrible.

Before starting our examination of physical properties, we need to mention two concepts: **state** and **equilibrium.** A system will *possess a unique set of properties*, such as temperature, pressure, density, and so on, at a given time, *and thus is said to be in a particular state*. A change in the state of a system results in a change in at least one of its properties.

By *equilibrium we mean a state in which there is no tendency toward spontaneous change*. Another way to say the same thing is to say that equilibrium is a state in which all the rates of attaining and departing from the state are balanced. When a system is in equilibrium with another system, or the surroundings, it will not change its state unless the other system, or the surroundings, also changes.

What are solids, liquids, fluids, vapors, and gases? Rather than define the states of matter, a task that is not easy to accomplish with precision in the brief space we have here, let us instead characterize the states in terms of two quantities, flow and structure of the molecules:

State	Flow of collections of molecules	Structure of collections of molecules
Perfect gas	Extensive	None
Real gas	Extensive	Almost none
Liquid	Short distance	Related structure
Liquid crystal	Some	Some crystal structure
Amorphous solid	Little	Little
Real crystal	Almost none	Highly structured
Perfect crystal	None	Completely structured

At any temperature and pressure, a pure compound can exist as a gas, liquid, or solid, and at certain specific values of T and p, mixtures of phases exist, such as when water boils or freezes. Thus a compound (or a mixture of compounds) may consist of one or more phases. A **phase** is defined as a completely homogeneous and uniform state of matter. Liquid water would be a phase and ice would be another phase. Two immiscible liquids in the same container, such as mercury and water, would represent two different phases because the liquids have different properties.

In this chapter we first discuss ideal and real gas relationships, including some of the gas laws for pure components and mixtures of ideal gases. You will learn about methods of expressing the p–V–T properties of real gases by means of equations of state and, alternatively, by compressibility factors. Next we introduce the concepts of vaporization, condensation, and vapor pressure and illustrate how material balances are made for saturated and partially saturated gases. Finally, we examine the qualitative characteristics of gas-liquid-solid phases with the aid of diagrams. Figure 3.0 shows the interrelationships among the topics discussed in this chapter and how they relate to the making of material and energy balances.

3.1 IDEAL GAS LAWS

In 1787, Jacques Charles, a French chemist and physicist, published his conclusions about the relationship between the volume of gases and temperature. He demonstrated that the volume of a dry gas varies directly with temperature if the pressure remains constant. Charles, Boyle, Gay-Lussac, Dalton, and Amagat, the investigators who originally developed correlating relations among gas temperature, pressure, and volume, worked at temperatures and pressures such that the average distance be-

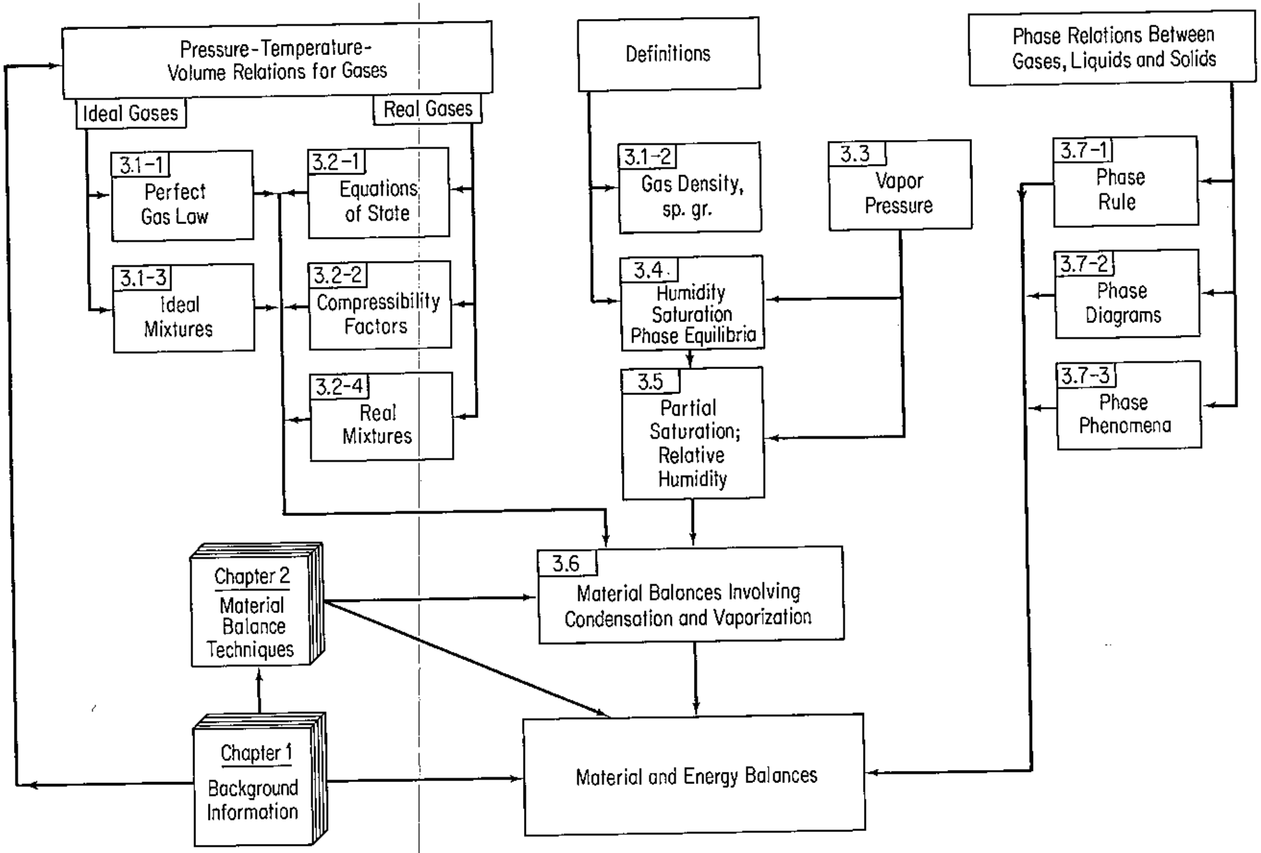


Figure 3.0 Hierarchy of topics to be studied in this chapter (section numbers are in the upper lefthand corner of the boxes).

tween the molecules was great enough to neglect the effect of the intermolecular forces and the volume of the molecules themselves. Under these conditions a gas came to be termed an **ideal gas.** More properly, an *ideal gas* is an imaginary gas which obeys exactly certain simple laws such as the laws of Boyle, Charles, Dalton, and Amagat. No real gas obeys these laws exactly over all ranges of temperature and pressure, although the "lighter" gases (hydrogen, oxygen, air, etc.) under ordinary circumstances obey the ideal gas laws with but negligible deviations. The properties of the "heavier" gases, such as sulfur dioxide and hydrocarbons, particularly at high pressures and low temperatures, deviate considerably from those predicted by the ideal gas laws. Vapors, under conditions near the boiling point, deviate markedly from the ideal gas laws. However, at low pressures and high temperatures, the behavior of a vapor approaches that of an ideal gas. Thus for many engineering purposes, the ideal gas laws, if properly applied, will give answers that are correct within a few percent or less. But for liquids and solids with the molecules compacted relatively close together, we do not have such general laws.

3.1-1 Calculations Using the Ideal Gas Law

Your objectives in studying this section are to be able to:

1. Write down the ideal gas law, and define all its variables and parameters and their associated dimensions.
2. Calculate the values and units of the ideal gas law constant in any set of units from the standard conditions.
3. Convert gas volumes to moles (and mass), and vice versa.
4. Use ratios of variables in the ideal gas law to calculate p, V, T, or n.

From the work of Boyle and Charles, scientists developed the relationship now called the **ideal gas law** (or sometimes the *perfect gas law*).

$$pV = nRT \tag{3.1}$$

where p = absolute pressure of the gas
V = total volume occupied by the gas
n = number of moles of the gas
R = ideal gas constant in appropriate units
T = absolute temperature of the gas

Sometimes the ideal gas law is written as

$$p\hat{V} = RT \tag{3.1a}$$

where $\hat{V}$ is the specific volume (volume per mole or mass) of the gas. Figure 3.1 illustrates the surface generated by Eq. (3.1a) in terms of the three properties p, $\hat{V}$, and T.

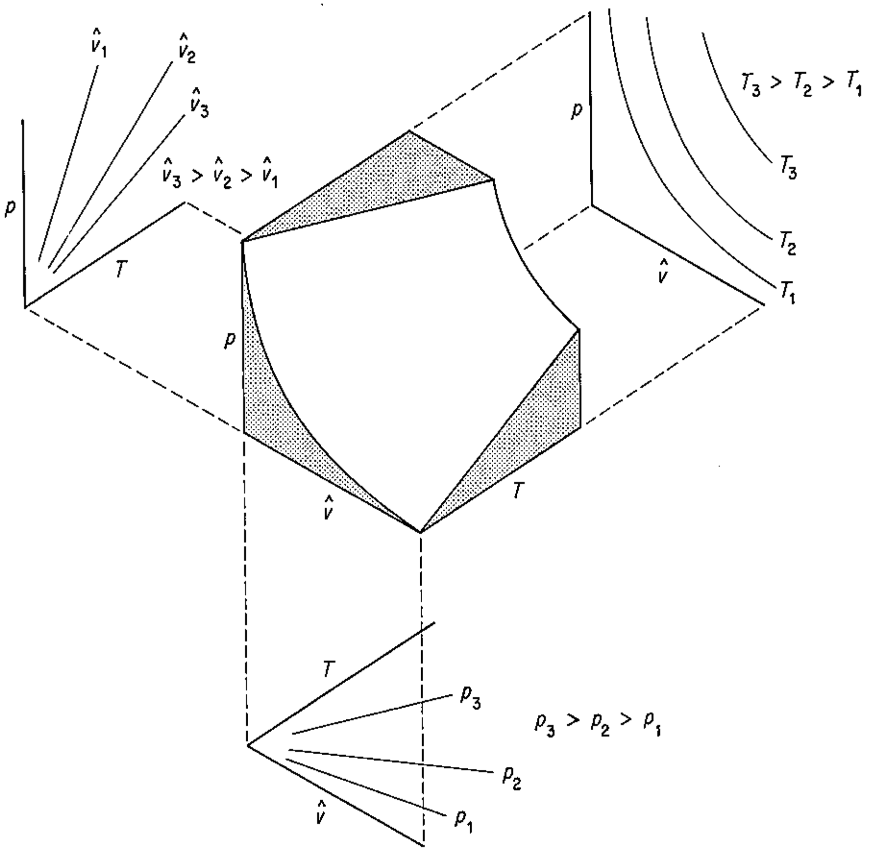


Figure 3.1 Representation of the ideal gas law in three dimensions as a surface.

Several arbitrarily specified standard states (usually known as *standard conditions*, or S.C.) of temperature and pressure have been selected by custom. See Table 3.1 for the most common ones. The fact that a substance cannot exist as a gas at 0°C and 1 atm is immaterial. Thus, as we see later, water vapor at 0°C cannot exist at a pressure greater than its saturation pressure of 0.61 kPa (0.18 in. Hg) without condensation occurring. However, the imaginary volume at standard conditions can be calculated and is just as useful a quantity in the calculation of volume-mole relation-

TABLE 3.1 Common Standard Conditions for the Ideal Gas

System	T	p	$\hat{V}$
SI	273.15K	101.325 kPa	22.415 m^3/kg mol
Universal scientific	0.0°C	760 mm Hg	22.415 liters/g mol
Natural gas industry	60.0°F (15.0°C)	14.696 psia (101.325 kPa)	379.4 ft^3/lb mol
American engineering	32°F	1 atm	359.05 ft^3/lb mol

ships as though it could exist. In the following, the symbol V will stand for total volume and the symbol $\hat{V}$ for volume per mole, or per unit mass.

Because the SI, universal scientific, and American engineering standard conditions are identical, you can use the values in Table 3.1 with their units to change from one system of units to another. Knowing the standard conditions also makes it easy for you to work with mixtures of units from different systems.

The next example illustrates how the standard conditions can be employed to convert mass or moles to volume. Do you see how to convert volume to moles or mass?

EXAMPLE 3.1 Use of Standard Conditions

Calculate the volume, in cubic meters, occupied by 40 kg of CO_2 at standard conditions.

Solution

Basis: 40 kg of CO_2

$$\frac{40\text{ kg }CO_2}{}\left|\frac{1\text{ kg mol }CO_2}{44\text{ kg }CO_2}\right|\frac{22.42\text{ m}^3\text{ }CO_2}{1\text{ kg mol }CO_2} = 20.4\text{ m}^3\text{ }CO_2\text{ at S.C.}$$

Notice in this problem how the information that 22.42 m^3 at S.C. = 1 kg mol is applied to transform a known number of moles into an equivalent number of cubic meters.

Incidentally, whenever you use cubic measure for volume, you must establish the conditions of temperature and pressure at which the cubic measure for volume exists, since the term "m^3" or "ft^3," standing alone, is really not any particular *quantity* of material.

You can apply the ideal gas law, Eq. (3.1), directly by introducing values for three of the four quantities, n, p, T, and V, and solving for the fourth. To do so, you need to look up or calculate R in the proper units. Inside the front cover you will find selected values of R for different combinations of units. Example 3.2 illustrates how to calculate the value of R in any set of units you want from the values of p, T, and $\hat{V}$ at standard conditions.

In many processes going from an initial state to a final state, you can use the ratio of ideal gas law in the respective states and eliminate R as follows (the subscript 1 designates the initial state, and the subscript 2 designates the final state)

$$\frac{p_1 V_1}{p_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2}$$

or

$$\left(\frac{p_1}{p_2}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right) \tag{3.2}$$

Note how Eq. (3.2) involves ratios of the same variable. This arrangement of the ideal gas law has the convenient feature that the pressures may be expressed in any system of units you choose, such as kPa, in. Hg, mm Hg, atm, and so on, as long as the same units are used for both conditions of pressure (do not forget that the pressure must be *absolute* pressure in both cases). Similarly, the grouping together of the *absolute* temperature and the volume terms gives ratios that are dimensionless. Notice how the ideal gas constant R is eliminated in taking the ratio of the initial to the final state.

Let us see how we can apply the perfect gas law both in the form of Eq. (3.2) and Eq. (3.1) to problems.

EXAMPLE 3.2 Calculation of *R*

Find the value for the universal gas constant R for the following combinations of units:

(a) For 1 lb mol of ideal gas when the pressure is expressed in psia, the volume is in ft³/lb mol, and the temperature is in °R.

(b) For 1 g mol of ideal gas when the pressure is in atm, the volume in cm³, and the temperature in K.

(c) For 1 kg mol of ideal gas when the pressure is in kPa, the volume is in m³/kg mol, and the temperature is in K.

Solution

(a) At standard conditions we will use the approximate values

$$p = 14.7 \text{ psia}$$
$$\hat{V} = 359 \text{ ft}^3/\text{lb mol}$$
$$T = 492^\circ\text{R}$$

Then

$$R = \frac{p\hat{V}}{T} = \frac{14.7 \text{ psia}}{492^\circ\text{R}} \left| \frac{359 \text{ ft}^3}{1 \text{ lb mol}} \right. = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(^\circ\text{R})(\text{lb mol})}$$

(b) Similarly, at standard conditions,

$$p = 1 \text{ atm}$$
$$\hat{V} = 22{,}415 \text{ cm}^3/\text{g mol}$$
$$T = 273.15 \text{ K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1 \text{ atm}}{273.15 \text{ K}} \left| \frac{22{,}415 \text{ cm}^3}{1 \text{ g mol}} \right. = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(\text{K})(\text{g mol})}$$

(c) In the SI system of units standard conditions are

$$p = 1.013 \times 10^5 \text{ Pa (or N/m}^2)$$
$$\hat{V} = 22.415 \text{ m}^3/\text{kg mol}$$
$$T = 273.15 \text{ K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1.013 \times 10^5 \text{ Pa}}{273.15 \text{ K}} \left| \frac{22.415 \text{ m}^3}{1 \text{ kg mol}} \right. = 8.313 \times 10^3 \frac{(\text{Pa})(\text{m}^3)}{(\text{K})(\text{kg mol})} = 8.313 \frac{\text{kJ}}{(\text{K})(\text{kg mol})}$$

To summarize, we want to emphasize that R does not have a universal value even though it is sometimes called the *universal gas constant*. The value of R depends on the units of p, $\hat{V}$, and T.

EXAMPLE 3.3 Application of the Ideal Gas Law

Calculate the volume occupied by 88 lb of CO_2 at a pressure of 32.2 ft of water and at 15°C.

Solution

See Fig. E3.3.

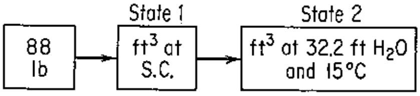


Figure E3.3

Solution 1 [Using Eq. (3.2)]:

At S.C. (state 1)	*At state 2*
$p = 33.91\ \text{ft H}_2\text{O}$	$p = 32.2\ \text{ft H}_2\text{O}$
$\hat{V} = 359\ \dfrac{\text{ft}^3}{\text{lb mol}}$	$\hat{V} = ?$
$T = 273\ \text{K}$	$T = 273 + 15 = 288\ \text{K}$

Basis: 88 lb of CO_2

Assume that the pressure is absolute pressure. First, we convert the mass of gas to moles and get the equivalent volume at standard conditions. Finally, we use Eq. (3.2), in which both R and (n_1/n_2) cancel out:

$$V_2 = V_1\left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)$$

You can say to yourself: The temperature goes up from 0°C at S.C. to 15°C at the final state, hence the volume must increase from S.C., hence the temperature ratio must be greater than unity. Similarly, you can say: The pressure goes down from S.C. to the final state, so that the volume must increase from S.C., hence the pressure ratio must be greater than unity. The calculations are

$$\begin{array}{l|c|c|c|c} 88\ \text{lb CO}_2 & & 359\ \text{ft}^3 & 288 & 33.91 \\ \hline & \dfrac{44\ \text{lb CO}_2}{1\ \text{lb mol CO}_2} & 1\ \text{lb mol} & 273 & 32.2 \end{array} = \begin{array}{l} 798\ \text{ft}^3\ \text{CO}_2 \\ \text{at } 32.2\ \text{ft H}_2\text{O and } 15^\circ\text{C} \end{array}$$

Solution 2 [using the gas constant R and the ideal gas law Eq. (3.1)].

First, the value of R must be obtained in the same units as the variables p, $\hat{V}$, and T. For 1 lb mol,

$$R = \frac{p\hat{V}}{T}$$

and at S.C.,

$$p = 33.91 \text{ ft } H_2O$$

$$\hat{V} = 359 \text{ ft}^3/\text{lb mol}$$

$$T = 273 \text{ K}$$

$$R = \frac{33.91 \,\big|\, 359}{\,\big|\, 273} = 44.59 \frac{(\text{ft } H_2O)(\text{ft}^3)}{(\text{lb mol})(\text{K})}$$

Now, using Eq. (3.1), insert the given values, and perform the necessary calculations.

Basis: 88 lb of CO_2

$$V = \frac{nRT}{p} = \frac{88 \text{ lb } CO_2}{\dfrac{44 \text{ lb } CO_2}{\text{lb mol } CO_2}} \left| \frac{44.59\ (\text{ft } H_2O)(\text{ft}^3)}{(\text{lb mol})(\text{K})} \right| \frac{288 \text{ K}}{32.2 \text{ ft } H_2O}$$

$$= 798 \text{ ft}^3\ CO_2 \text{ at } 32.2 \text{ ft } H_2O \text{ and } 15°\text{C}$$

If you will inspect both solutions closely, you will observe that in both cases the same numbers appear and that both are identical except that in the second solution using R two steps are used to obtain the solution.

EXAMPLE 3.4 Ideal Gas Law

An oxygen cylinder used as a standby source of oxygen contains O_2 at 70°F. To calibrate the gauge on the O_2 cylinder which has volume of 1.01 ft^3, all of the oxygen, initially at 70°F, is released into an evacuated tank of known volume (15.0 ft^3). At equilibrium, the gas pressure was measured as 4 in. H_2O gauge and the gas temperature in both cylinders was 75°F. See Fig. E3.4. The barometer read 29.99 in. Hg.

What did the pressure gauge on the oxygen tank read in psig if it was a Bourdon gauge?

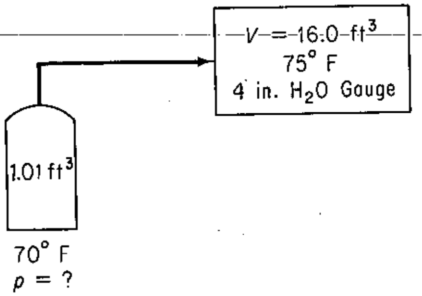


Figure E3.4

Solution

You must first convert the temperatures and pressures into absolute units:

$$460 + 70 = 530°\text{R}$$

$$460 + 75 = 535°\text{R}$$

atmospheric pressure = 29.99 in. Hg = 14.73 psia

$$\text{final pressure} = 29.99 \text{ in. Hg} + \begin{array}{c|c} 4 \text{ in. } H_2O & 29.92 \text{ in. Hg} \\ \hline \dfrac{12 \text{ in. } H_2O}{\text{ft } H_2O} & 33.91 \text{ ft } H_2O \end{array}$$

$$= 29.99 + 0.29 = 30.28 \text{ in. Hg absolute}$$

The simplest way to proceed, now that the data are in good order, is to apply the ideal gas law, Eq. (3.2). Take as a basis, 16.011 ft^3 (do not forget to include the volume of the O_2 tank in your system!) of O_2 at 75°F and 30.28 in. Hg. We want to determine the initial pressure in the O_2 tank alone.

$$p_1 = p_2\left(\frac{V_2}{V_1}\right)\left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right).$$

$$p_1 = 30.28 \text{ in. Hg}\left(\frac{16.01 \text{ ft}^3}{1 \text{ ft}^3}\right)\left(\frac{530°\text{R}}{535°\text{R}}\right) = 480 \text{ in. Hg absolute}$$

In gauge pressure,

$$p_1 = \begin{array}{c|c} (480 - 29.99) \text{ in. Hg} & 14.696 \text{ psia} \\ \hline & 29.92 \text{ in. Hg} \end{array} = 221 \text{ psig}$$

EXAMPLE 3.5 Application of the Ideal Gas Law

One important source of emissions from gasoline-powered automobile engines that causes smog is the nitrogen oxides NO and NO_2. They are formed whether combustion is complete or not as follows. At the high temperatures that occur in an internal combustion engine during the burning process, oxygen and nitrogen combine to form nitric oxide (NO). The higher the peak temperatures and the more oxygen available, the more NO is formed. There is insufficient time for the NO to decompose back to O_2 and N_2 because the burned gases cool too rapidly during the expansion and exhaust cycles in the engine. Although both NO and nitrogen dioxide (NO_2) are significant air pollutants (together termed NO_x), the NO_2 is formed in the atmosphere as NO is oxidized.

Suppose that you collect a sample of a NO-NO_2 mixture (after having removed the other combustion gas products by various separations procedures) in a 100-cm^3 standard cell at 30°C. Certainly some of the NO will have been oxidized to NO_2,

$$2NO + O_2 \longrightarrow 2NO_2$$

during the collection, storage, and processing of the combustion gases, so that measurement of NO alone will be misleading. If the standard cell contains 0.291 g of NO_2 plus NO and the pressure measured in the cell is 170 kPa, what percent of the NO + NO_2 is in the form of NO? See Fig. E3.5.

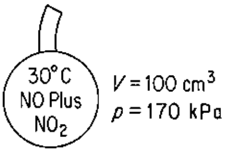


Figure E3.5

Solution

The gas in the cell is composed partly of NO and partly of NO_2. We can use the ideal gas law to calculate the total gram moles present in the cell.

Basis: 100 cm³ of gas at 170 kPa and 30°C

$$R = \frac{101.3\text{ kPa}}{273\text{ K}}\left|\frac{22.41\text{ L}}{1\text{ g mol}}\right|\frac{1000\text{ cm}^3}{1\text{ L}} = 8.316 \times 10^3\frac{(\text{kPa})(\text{cm}^3)}{(\text{K})(\text{g mol})}$$

$$n = \frac{pV}{RT} = \frac{170\text{ kPa}}{8.316 \times 10^3\frac{(\text{kPa})(\text{cm}^3)}{(\text{K})(\text{g mol})}}\left|\frac{100\text{ cm}^3}{303\text{ K}}\right. = 0.00675\text{ g mol}$$

If the mixture is composed of NO (MW = 30) and NO_2 (MW = 46), because we know the total mass in the cell we can compute the fraction of, say, NO. Let x = grams of NO; then $(0.291 - x)$ = g NO_2. In a table format the calculation is

Component	g	Mol. Wt.	g mol
NO	x	30	$\frac{x}{30}$
NO_2	$0.291 - x$	46	$\frac{0.291 - x}{46}$
Total	0.291		0.00675

or

$$\frac{x}{30} + \frac{0.291 - x}{46} = 0.00675$$

$$0.0333x + (0.291 - x)(0.0217) = 0.00675$$

$$x = 0.0366\text{ g}$$

The weight percent NO is

$$\frac{0.0366}{0.291}(100) = 12.5\%$$

and the mole percent NO is

$$\frac{0.0366\text{ g NO}}{0.00675\text{ g mol total}}\left|\frac{1\text{ g mol NO}}{30\text{ g NO}}\right.(100) = 18\%$$

Can you let x be the mole fraction NO and obtain the same result? (*Answer:* Yes.) Try the calculation.

Self-Assessment Test

1. Write down the ideal gas law.
2. What are the dimensions of T, p, V, n, and R?
3. List the standard conditions for a gas in the SI, universal scientific, and American engineering systems of units.

4. Calculate the volume in ft^3 of 10 lb mol of an ideal gas at 68°F and 30 psia.
5. A steel cylinder of volume 2 m^3 contains methane gas (CH_4) at 50°C and 250 kPa absolute. How many kilograms of methane are in the cylinder?
6. What is the value of the ideal gas constant R to use if the pressure is to be expressed in atm, the temperature in kelvin, the volume in cubic feet, and the quantity of material in pound moles?
7. Twenty-two kilograms per hour of CH_4 are flowing in a gas pipeline at 30°C and 920 mm Hg. What is the volumetric flow rate of the CH_4 in m^3 per hour?

Thought Problems

1. A candle is placed vertically in a soup plate, and the soup plate filled with water. Then the candle is lit. An inverted water glass is carefully placed over the candle. The candle soon goes out, and the water rises inside the glass. It is often said that this shows how much oxygen in the air has been used up. Is this conclusion correct?
2. A scientific supply house markets aerosol-type cans containing compressed helium for filling balloons, doing demonstrations, and the like. On the label there appears the notice: "Because the can contains helium, it quite naturally feels empty. It is actually lighter full than empty."

   Is this statement correct? If so, why? If not, why not?

3.1-2 Gas Density and Specific Gravity

Your objectives in studying this section are to be able to:

1. Define gas density and specific gravity.
2. Calculate the specific gravity of a gas even if the reference condition is not clearly specified.
3. Calculate the density of a gas given its specific gravity.

The **density of a gas** is defined as the mass per unit volume and can be expressed in kilograms per cubic meter, pounds per cubic foot, grams per liter, or other units. Inasmuch as the mass contained in a unit volume varies with the temperature and pressure, as we have previously mentioned, you should always be careful to specify these two conditions. If not otherwise specified, the densities are presumed to be at S.C. Density can be calculated by selecting a unit volume as the basis and calculating the mass of the contained gas.

EXAMPLE 3.6 Calculation of Gas Density

What is the density of N_2 at 27°C and 100 kPa expressed in:

(a) SI units?

(b) American engineering units?

Solution

(a)

Basis: 1 m^3 of N_2 at 27°C and 100 kPa

$$\begin{array}{c|c|c|c|c}
1\ \text{m}^3 & 273\ \text{K} & 100\ \text{kPa} & 1\ \text{kg mol} & 28\ \text{kg} \\
\hline
 & 300\ \text{K} & 101.3\ \text{kPa} & 22.4\ \text{m}^3 & 1\ \text{kg mol}
\end{array} = 1.123\ \text{kg}$$

density = 1.123 kg/m^3 of N_2 at 27°C (300 K) and 100 kPa

(b)

Basis: 1 ft^3 of N_2 at 27°C and 100 kPa

$$\begin{array}{c|c|c|c|c}
1\ \text{ft}^3 & 273\ \text{K} & 100\ \text{kPa} & 1\ \text{lb mol} & 28\ \text{lb} \\
\hline
 & 300\ \text{K} & 101.3\ \text{kPa} & 359\ \text{ft}^3 & 1\ \text{lb mol}
\end{array} = 0.0701\ \text{lb}$$

density = 0.0701 lb/ft^3 of N_2 at 27°C (80°F) and 100 kPa (14.5 psia)

The **specific gravity of a gas** is usually defined as the ratio of the density of the gas at a desired temperature and pressure to that of air (or any specified reference gas) at a certain temperature and pressure. The use of specific gravity occasionally may be confusing because of the manner in which the values of specific gravity are reported in the literature. You must be very careful in using literature values of specific gravity to ascertain that the conditions of temperature and pressure are known both for the gas in question and for the reference gas. Among the examples below, several represent inadequate methods of expressing specific gravity.

(a) *What is the specific gravity of methane?* Actually, this question may have the same answer as the question: How many grapes are in a bunch? Unfortunately, occasionally one may see this question and the best possible answer is

$$\text{sp gr} = \frac{\text{density of methane at S.C.}}{\text{density of air at S.C.}}$$

(b) *What is the specific gravity of methane* (H_2 = 1.00)? Again a poor question. The notation of (H_2 = 1.00) means that H_2 at S.C. is used as the reference gas, but the question does not tell what the conditions of temperature and pressure of the methane are. Therefore, the best interpretation is

$$\text{sp gr} = \frac{\text{density of methane at S.C.}}{\text{density of H}_2\text{ at S.C.}}$$

(c) *What is the specific gravity of ethane* (air = 1.00)? Same as question (b) except that in the petroleum industry the following is used:

$$\text{sp gr} = \frac{\text{density of ethane at 60°F and 760 mm Hg}}{\text{density of air at S.C. (60°F, 760 mm Hg)}}$$

(d) *What is the specific gravity of butane at* 50°C *and* 90 kPa? No reference gas nor state of reference gas is mentioned. However, when no reference gas is mentioned, it is taken for granted that air is the reference gas. In the case at hand the best thing to do is to assume that the reference gas and the desired gas are under the same conditions of temperature and pressure:

$$\text{sp gr} = \frac{\text{density of butane at 50°C and 90 kPa}}{\text{density of air at 50°C and 90 kPa}}$$

(e) *What is the specific gravity of* CO_2 *at* 60°F *and* 740 mm Hg (air = 1.00)?

$$\text{sp gr} = \frac{\text{density of } CO_2 \text{ at 60°F and 740 mm Hg}}{\text{density of air at S.C.}}$$

(f) *What is the specific gravity of* CO_2 *at* 60°F *and* 740 mm Hg (ref. air at S.C.)?

$$\text{sp gr} = \text{same as question (e)}$$

EXAMPLE 3.7 Specific Gravity of a Gas

What is the specific gravity of N_2 at 80°F and 745 mm Hg compared to

(a) Air at S.C. (32°F and 760 mm Hg)?

(b) Air at 80°F and 745 mm Hg?

Solution

First you must obtain the density of the N_2 and the air at their respective conditions of temperature and pressure, and then calculate the specific gravity by taking a ratio of their densities. Example 3.6 covers the calculation of the density of a gas, and therefore, to save space, no units will appear in the intermediate calculations:

(a)

Basis: 1 ft^3 of N_2 at 80°F and 745 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 745 & & 28 \\ \hline & 540 & 760 & 359 & \end{array} = 0.0697 \text{ lb } N_2/\text{ft}^3 \text{ at 80°F, 745 mm Hg}$$

Basis: 1 ft^3 of air at 32°F and 760 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 760 & & 29 \\ \hline & 492 & 760 & 359 & \end{array} = 0.0808 \text{ lb air/ft}^3 \text{ at 32°F, 760 mm Hg}$$

Therefore,

$$\text{sp.gr.} = \frac{0.0697}{0.0808} = 0.862 \frac{\text{lb } N_2/\text{ft}^3 \; N_2 \text{ at 80°F, 745 mm Hg}}{\text{lb air/ft}^3 \text{ air at S.C.}}$$

Note: Specific gravity is not a dimensionless number.

(b)

Basis: 1 ft^3 of air at 80°F and 745 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 745 & & 29 \\ \hline & 540 & 760 & 359 & \end{array} = 0.0721 \text{ lb/ft}^3 \text{ at 80°F and 745 mm Hg}$$

$$(\text{sp. gr.})_{N_2} = \frac{0.0697}{0.0721} = 0.967 \frac{\text{lb } N_2/\text{ft}^3 \; N_2 \text{ at 80°F, 745 mm Hg}}{\text{lb air/ft}^3 \text{ air at 80°F, 745 mm Hg}}$$

$$= 0.967 \text{ lb } N_2/\text{lb air}$$

Note that you can also obtain the specific gravity of a gas directly by taking the ratio of the ideal gas law densities of each gas. Thus (the gases are denoted by the respective subscripts A and B)

$$pV = \frac{mRT}{\text{mol. wt.}}$$

where m is the mass of gas. The gas density is

$$\rho = \frac{m}{V} = \frac{p(\text{mol. wt.})}{RT}$$

and the ratio of gas densities is

$$\text{sp gr} = \frac{\rho_A}{\rho_B} = \left(\frac{p_A}{p_B}\right)\left(\frac{\text{mol. wt.}_A}{\text{mol. wt.}_B}\right)\left(\frac{T_B}{T_A}\right) \tag{3.3}$$

For gases at the *same* temperature and pressure, the specific gravity is just the ratio of the respective molecular weights.

Self-Assessment Test

1. What is the density of a gas that has a molecular weight of 0.123 kg/kg mol at 300 K and 1000 kPa?
2. What is the specific gravity of CH_4 at 70°F and 2 atm compared to air at S.C.?

Thought Problem

1. Sea breezes provide welcome relief from the summer heat for residents who live close to the shore. No matter what part of the world—the coast of California, Australia where sea breezes can be very strong, even along the shores of the Great Lakes—the daily pattern in summertime is the same. The sea breeze, a wind blowing from sea to land, begins to develop three or four hours after sunrise and reaches its peak intensity by mid-afternoon. It may penetrate inland as much as 60 or 70 km. The sea breeze dies out in the evening and three or four hours after sunset may be replaced by a land breeze, blowing from land to sea. The land breeze, much weaker than the sea breeze, reaches its peak intensity just before sunrise.

   What causes these breezes?
2. A distillation column reboiler in a room, as shown in the figure, had been cleaned, but the

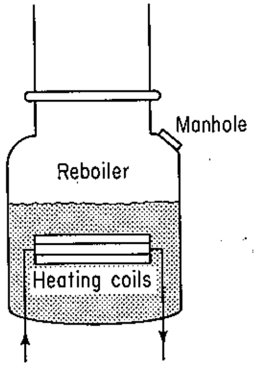


Figure TP3.2

manhole cover was not securely fastened on startup again. As a result benzene vapor escaped from the manhole and one operator died by asphyxiation. How could this occur?

3.1-3 Ideal Gas Mixtures

Your objectives in studying this section are to be able to:

1. Write down and apply Dalton's law and Amagat's law.
2. Define and use partial pressure in gas calculations.
3. Show that under certain assumptions the volume fraction equals the mole fraction in a gas.

Frequently, as an engineer, you will want to make calculations for mixtures of gases instead of individual gases. You can use the ideal gas law (under the proper assumptions of course) for a mixture of gases by interpreting p as the total pressure of the mixture, V as the volume occupied by the mixture, n as the total number of moles of all components in the mixture, and T as the temperature of the mixture. Is it possible to calculate a pressure or volume for the individual components? The answer is yes in a certain sense. Two classical definitions exist:

(a) The **partial pressure** of Dalton, p_i, namely the pressure that would be exerted by a single component in a gaseous mixture if it existed by itself in the *same volume* as occupied by the mixture and at the *same temperature* of the mixture

$$p_i V_{\text{total}} = n_i R T_{\text{total}} \tag{3.4}$$

where p_i is the partial pressure of component i. If you divide Eq. (3.4) by Eq. (3.1), you find that

$$\frac{p_i V_{\text{total}}}{p_{\text{total}} V_{\text{total}}} = \frac{n_i R T_{\text{total}}}{n_{\text{total}} R T_{\text{total}}}$$

or

$$p_i = p_t \frac{n_i}{n_t} = p_t y_i \tag{3.5}$$

where y_i is the mole fraction of component i. Can you show that Dalton's law of the summation of partial pressures is true?

$$p_1 + p_2 + \cdots + p_n = p_t \tag{3.6}$$

(b) The **partial volume** of Amagat, V_i, namely the volume that would be occupied by a single component of the mixture if the component were at the *same temperature and total pressure* as the mixture

$$p_{\text{total}} V_i = n_i R T_{\text{total}} \tag{3.7}$$

Division by Eq. (3.1) yields

$$\frac{p_t V_i}{p_t V_t} = \frac{n_i R T_t}{n_t R T_t}$$

or

$$V_i = V_t\left(\frac{n_i}{n_t}\right) = V_t y_i \tag{3.8}$$

Can you show that Amagat's law of the summation of partial volumes is true?

$$V_1 + V_2 + \cdots + V_n = V_t \tag{3.9}$$

To illustrate the significance of Eq. (3.4) and the meaning of partial pressure, suppose that you carried out the following experiment with ideal gases. Two tanks of 1.50 m^3 volume, one containing gas A at 300 mm Hg and the other gas B at 400 mm of Hg (both gases being at the same temperature of 20°C), are connected together. All the gas in B is forced into tank A isothermally. Now you have a 1.50-m^3 tank of $A + B$ at 700 mm of Hg. For this mixture (in the 1.50-m^3 tank at 20°C and a total pressure of 700 mm Hg) you could say that gas A exerts a partial pressure of 300 mm and gas B exerts a partial pressure of 400 mm. Of course you cannot put a pressure gauge on the tank and check this conclusion because the pressure gauge will read only the total pressure. These partial pressures are hypothetical pressures that the individual gases would exert and are equivalent to the pressures they actually would have if they were put into the same volume at the same temperature all by themselves. If the total pressure of the gaseous mixture is known as well as the mole fraction of a component, the partial pressure of the component can be calculated via Eq. (3.5):

$$p_A = 700\left(\frac{3}{7}\right) = 300 \text{ mm Hg}$$

An analogous explanation can be made for the partial volume of A in the mixture using Eq. (3.8):

$$V_A = 1.50\left(\frac{3}{7}\right) = 0.64 \text{ m}^3 \text{ at 700 mm Hg and 20°C}$$

Finally, Eq. (3.8) leads to the principle, stated earlier in Chap. 1, that

$$\text{volume fraction} = \text{mole fraction} = y_i \tag{3.10}$$

for an ideal gas.

EXAMPLE 3.8 Partial Pressures and Volumes

A gas-tight room has a volume of 1000 m^3. This room contains air (considered to be 21% O_2 and 79% N_2) at 20°C and a total pressure of 1 atm.

(a) What is the partial volume of O_2 in the room?

(b) What is the partial volume of N_2 in the room?

(c) What is the partial pressure of O_2 in the room?
(d) What is the partial pressure of N_2 in the room?
(e) If all of the O_2 were removed from the room by some method, what would be the subsequent total pressure in the room?

Solution

See Fig. E3.8

Basis: 1000 m^3 of air at 20°C and 1 atm

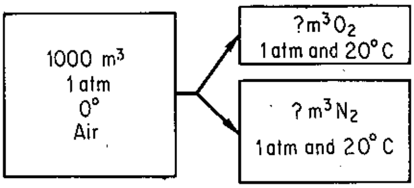


Figure E3.8

Partial volumes can be calculated by multiplying the total volume by the respective component mole fractions [Eq. (3.8)]:

$$
\begin{aligned}
&\textbf{(a)}\ V_{O_2} = (0.21)(1000) = && 210\ \text{m}^3\ O_2 \text{ at } 20^\circ\text{C, 1 atm} \\
&\textbf{(b)}\ V_{N_2} = (0.79)(1000) = && \underline{790\ \text{m}^3\ N_2 \text{ at } 20^\circ\text{C, 1 atm}} \\
&\qquad\qquad \text{total volume} = && 1000\ \text{m}^3 \text{ air at } 20^\circ\text{C, 1 atm}
\end{aligned}
$$

Note how the temperature and pressure have to be specified for the partial volumes to make them meaningful.

Partial pressures can be calculated by multiplying the total pressure by the respective component mole fractions [Eq. (3.5)]; the basis is still the same:

$$
\begin{aligned}
&\textbf{(c)}\ p_{O_2} = (0.21)(1\text{ atm}) = && 0.21 \text{ atm when } V = 1000\ \text{m}^3 \text{ at } 20^\circ\text{C} \\
&\textbf{(d)}\ p_{N_2} = (0.79)(1\text{ atm}) = && \underline{0.79 \text{ atm when } V = 1000\ \text{m}^3 \text{ at } 20^\circ\text{C}} \\
&\qquad\qquad \text{total pressure} = && 1.00 \text{ atm when } V = 1000\ \text{m}^3 \text{ at } 20^\circ\text{C}
\end{aligned}
$$

(e) If a tight room held dry air at 1 atm and all the oxygen were removed from the air by a chemical reaction, the pressure reading would fall to 0.79 atm.

For use in our subsequent calculations you should clearly understand now that the original room contained:

(1) 790 m^3 dry N_2 at 1 atm and 20°C
(2) $\underline{210}$ m^3 dry O_2 at 1 atm and 20°C
(3) 1000 m^3 dry air at 1 atm and 20°C (add 1 and 2)

or

(1) 1000 m^3 dry O_2 at 0.21 atm and 20°C
(2) 1000 m^3 dry N_2 at $\underline{0.79}$ atm and 20°C
(3) 1000 m^3 dry air at 1.00 atm and 20°C (add 1 and 2)

EXAMPLE 3.9 Calculation of Partial Pressures from Gas Analysis

A flue gas analyzes 14.0% CO_2, 6.0% O_2, and 80.0% N_2. It is at 400°F and 765.0 mm Hg pressure. Calculate the partial pressure of each component.

Solution

Use Eq. (3.5).

Basis: 1.00 kg (or lb) mol flue gas

Component	*kg (or lb) mol*	*p (mm Hg)*
CO_2	0.140	107.1
O_2	0.060	45.9
N_2	0.800	612.0
Total	1.000	765.0

On the basis of 1.00 mole of flue gas, the mole fraction y of each component, when multiplied by the total pressure, gives the partial pressure of that component.

Self-Assessment Test

1. Write down Dalton's law and Amagat's law.
2. A gas has the following composition at 120°F and 13.8 psia.

Component	Mol %
N_2	2
CH_4	79
C_2H_6	19

(a) What is the partial pressure of each component?
(b) What is the partial volume of each component if the total volume of the container is 2 ft^3?
(c) What is the volume fraction of each component?

3. (a) If the C_2H_6 were removed from the gas in problem 2, what would be the subsequent pressure in the vessel?
(b) What would be the subsequent partial pressure of the N_2?

3.1-4 Material Balances Involving Gases

Now that you have had a chance to practice applying the ideal gas law to simple transformations, we turn our attention back to material balances. The only difference between the subject matter of Chapter 2 and this section is that here the amount of material flow can be specified in terms of p, V, and T rather than solely mass or moles. For example, the basis for a problem, or the quantity to be solved for, might be a volume of gas at a given temperature and pressure rather than a mass of gas. The next two examples illustrate two of the same types of the problems you have encountered before.

EXAMPLE 3.10 Material Balance with Combustion

A synthesis gas analyzes 6.4% CO_2, 0.1% O_2, 39% CO, 51.8% H_2, 0.6% CH_4, and 2.1% N_2. It enters the combustion chamber at 90°F and a pressure of 35.0 Hg, and is burned with 40% excess air (dry) which is at 70°F and the atmospheric pressure of 29.4 in. Hg; 10% of the CO remains unburned. How many cubic feet of air are supplied per cubic foot of entering gas? How many cubic feet of product are produced per cubic foot of entering gas if the exit gas is at 29.4 in. Hg and 400°F?

Solution

This is a steady-state problem with reaction in which you can directly add and subtract quantities; you do not have to solve simultaneous equations.

Step 1, 2, and 3 Figure E3.10 illustrates the process and notation. With 40% excess air, certainly all the CO, H_2, and CH_4 should burn to CO_2 and H_2O; apparently, for some unknown reason, not all of the CO burns to CO_2. The product gases are shown in the figure.

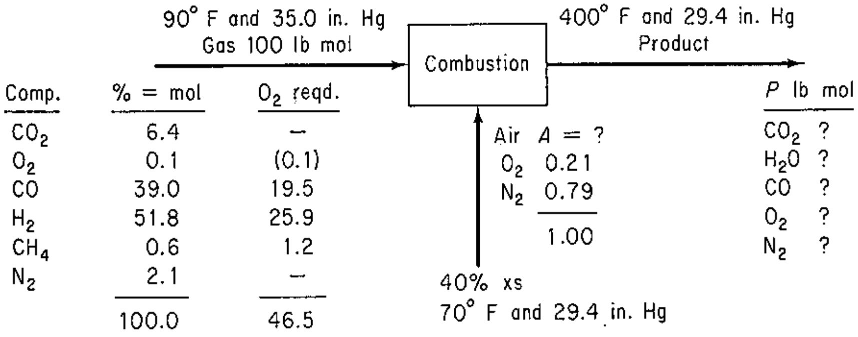


Figure E3.10

Step 4 You could take 1 ft^3 at 90°F and 35.0 in. Hg as the basis, but it is just as easy to take 1 lb mol because then % = lb mol. At the end of the problem you can convert lb mol to ft^3.

Basis: 100 lb mol synthesis gas

Step 3 (continued) The entering air can be calculated from the specified 40% excess air; the reactions for complete combustion are

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

the moles of oxygen required are listed in Fig. E3.10. The excess oxygen is

$$\text{Excess } O_2\text{:} \quad 0.4(46.5) = 18.6$$

$$\text{Total } O_2 = 46.5 + 18.6 = 65.10$$

$$N_2 \text{ in } 65.10\left(\frac{79}{21}\right) = 244.9$$

Total moles of air are 244.9 + 65.10 = 310 lb mol.

Steps 5 and 6 Five unknowns exist, the five products. You can make four element balances plus know the fraction of the entering CO that exits in P. Hence the problem has a unique solution.

Steps 7, 8, and 9 We can use the chemical equations plus elemental balances to directly calculate the products.

In with Fuel		*Out*	
N_2:	2.1	N_2:	$2.1 + 244.9 = 247.0$
H_2:	51.8	H_2O:	$51.8 + 0.6(2) = 53.0$
CO:	39.0	CO:	$39.0(0.10) = 3.9$
CO_2:	6.4	CO_2:	$6.4 + 39.0(0.9) + 0.6 = 42.1$

The oxygen (O_2) balance is

$$6.4 + 0.1 + \tfrac{1}{2}(39.0) + 65.1 = \tfrac{1}{2}(53.0) + \tfrac{1}{2}(3.9) + 42.1 + O_{2_{\text{out}}}$$

so that the exit O_2 is 20.55 lb mol. The total moles exiting sum up to be 366.55 lb mol.

Finally, we can convert the lb mol of air and product into the volumes requested:

$$T_{\text{gas}} = 90 + 460 = 550^\circ\text{R}$$

$$T_{\text{air}} = 70 + 460 = 530^\circ\text{R}$$

$$T_{\text{product}} = 400 + 460 = 860^\circ\text{R}$$

$$\text{ft}^3\text{ of gas: }\begin{array}{c|c|c|c} 100\text{ lb mol entering gas} & 359\text{ ft}^3\text{ at SC} & 550^\circ\text{R} & 29.92\text{ in. Hg} \\ \hline & 1\text{ lb mol} & 492^\circ\text{R} & 35.0\text{ in. Hg} \end{array} = 343 \times 10^2$$

$$\text{ft}^3\text{ of air: }\begin{array}{c|c|c|c} 310\text{ lb mol air} & 359\text{ ft}^3\text{ at SC} & 530^\circ\text{R} & 29.92\text{ in. Hg} \\ \hline & 1\text{ lb mol} & 492^\circ\text{R} & 29.4\text{ in. Hg} \end{array} = 1220 \times 10^2$$

$$\text{ft}^3\text{ of product: }\begin{array}{c|c|c|c} 366.55\text{ lb mol } P & 359\text{ ft}^3\text{ at SC} & 860^\circ\text{R} & 29.92\text{ in. Hg} \\ \hline & 1\text{ lb mol} & 492^\circ\text{R} & 29.4\text{ in. Hg} \end{array} = 2340.9 \times 10^2$$

The answers to the questions are

$$\frac{1220 \times 10^2}{343 \times 10^2} = 3.56\,\frac{\text{ft}^3\text{ air at }530^\circ\text{R and }29.4\text{ in. Hg}}{\text{ft}^3\text{ gas at }550^\circ\text{R and }35.0\text{ in. Hg}}$$

$$\frac{2340.9 \times 10^2}{343 \times 10^2} = 6.82\,\frac{\text{ft}^3\text{ product at }860^\circ\text{R and }29.4\text{ in. Hg}}{\text{ft}^3\text{ gas at }550^\circ\text{R and }35.1\text{ in. Hg}}$$

EXAMPLE 3.11 Material Balance without Reaction

Gas at 15°C and 105 kPa is flowing through an irregular duct. To determine the rate of flow of the gas, CO_2 from a tank was passed into the gas stream. The gas analyzed 1.2% CO_2 by volume before, and 3.4% CO_2 by volume after, addition. The CO_2 left the tank, was passed through a rotameter, and was found to flow at the rate of 0.0917 m^3/min at 7°C and 131 kPa. What was the rate of flow of the entering gas in the duct in cubic meters per minute?

Solution

This is a steady-state problem without reaction.

Steps 1, 2, and 3

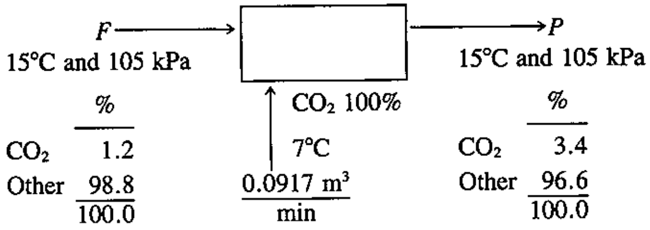


Figure E3.11

Assume that the entering and exit gases are at the same temperature and pressure.

Step 4 Take as a basis 1 min ≡ 0.0917 m^3 CO_2 at 7°C and 131 kPa. The gas analysis is in volume percent, which is the same as mole per cent. We could convert the 0.0917 m^3 to moles and solve the problem in terms of moles, but there is no need to do so because we can calculate the flow rate of F in m^3 at 7°C and 131 kPa, and then convert the calculated volume to 15°C and 105 kPa.

Steps 5 and 6 We do not know F and P, but can make two independent component balances, hence the problem has a unique solution.

Steps 7, 8, and 9

"Other" balance (m^3 at 7°C and 131 kPa): $F(0.988) = P(0.966)$ (a)

CO_2 balance (m^3 at 7°C and 131 kPa): $F(0.012) + 0.0917 = P(0.034)$ (b)

Total balance (m^3 at 7°C and 131 kPa): $F + 0.0917 = P$ (c)

Note that "other" is a tie component. Solution of Eqs. (a) and (c) gives

$$F + 0.0917 = F\left(\frac{0.988}{0.966}\right)$$

or $F = 4.0265$ m^3 at 7°C and 131 kPa. Finally, we convert to a volumetric flow rate at 15°C and 105 kPa:

$$\begin{array}{l|l|l}
4.0265\ \text{m}^3\ \text{at 7°C and 131 kPa} & 288\ \text{K} & 131\ \text{kPa} \\
\hline
 & 280\ \text{K} & 105\ \text{kPa}
\end{array} = 5.17\ \text{m}^3/\text{min at 15°C and 105 kPa}$$

Step 10 (Check)

$$\text{By Eq. (b):}\quad 4.026(0.012) + 0.0917 \stackrel{?}{=} 4.026\left(\frac{0.988}{0.966}\right)(0.034)$$

The equation checks out to a satisfactory degree of precision.

We have completed our review of the ideal gas law as applied to pure components and mixtures. In the next section we look at instances in which the ideal gas law does not apply.

Self-Assessment Test

1. A furnace is fired with 1000 ft^3 per hour at 60°F and 1 atm of a natural gas having the following volumetric analysis: CH_4: 80%, C_2H_6: 16%, O_2: 2%, CO_2: 1%, N_2: 1%. The exit

flue gas temperature is 800°F and the pressure is 760 mm Hg absolute; 15% excess air is used and combustion is complete. Calculate the:

(a) Volume of CO_2 produced per hour
(b) Volume of H_2O vapor produced per hour
(c) Volume of N_2 produced per hour
(d) Total volume of flue gas produced per hour

2. A flue gas contains 60% N_2 and is mixed with air. If the resulting mixture flows at a rate of 250,000 ft^3/hr and contains 70% N_2, what is the flow rate of the flue gas? State all your assumptions concerning the temperatures and pressures of the gas streams.

3.2 REAL GAS RELATIONSHIPS

We have said that at room temperature and pressure many gases can be assumed to act as ideal gases. However, for some gases under normal conditions, and for most gases under conditions of high pressure, values of the gas properties that you might obtain using the ideal gas law would be at wide variance with the experimental evidence. You might wonder exactly how the behavior of **real gases** compares with that calculated from the ideal gas laws. In Fig. 3.2 you can see how the $p\hat{V}$ product of

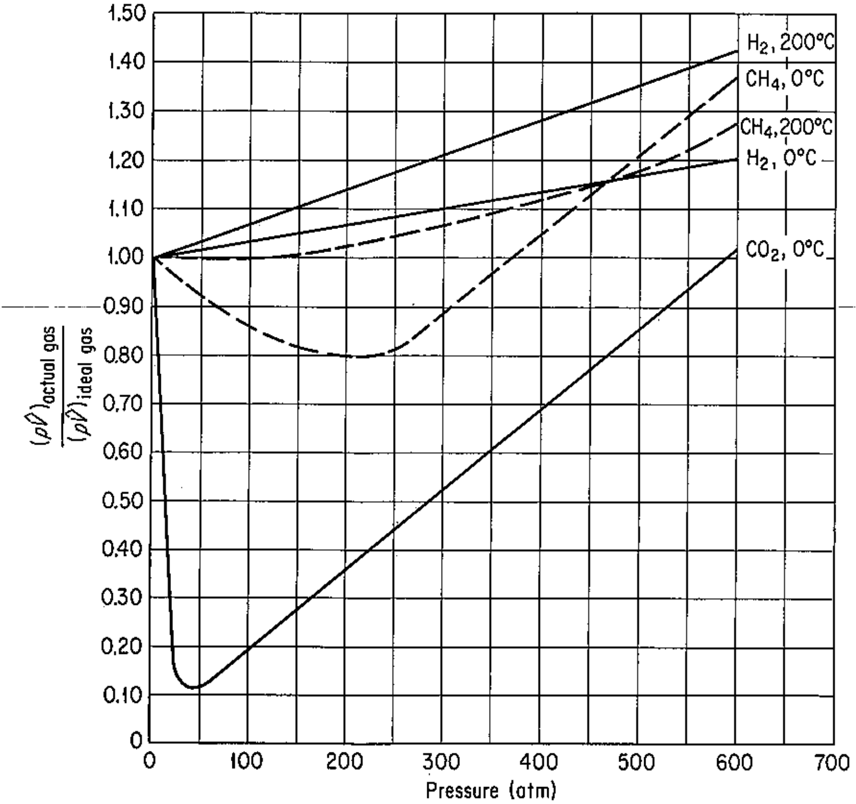


Figure 3.2 Deviation of real gases from the ideal gas law at high pressures.

several gases deviates from that predicted by the ideal gas laws as the pressure increases substantially. Thus it is clear that we need some way of computing the p–V–T properties of a gas that is not ideal, i.e. the real gas.

Essentially there are four methods of getting or predicting real gas properties:

(a) Equations of state
(b) Compressibility charts
(c) Estimated properties
(d) Actual experimental data

Even if experimental data are available, the other three techniques still may be quite useful for certain types of calculations. Of course, under conditions such that part of the gas liquefies, the gas laws apply only to the gas-phase portion of the system—you cannot extend these real gas laws into the liquid region any more than you can apply the ideal gas laws to a liquid.

Physical properties and/or the equations used to predict physical properties can be stored on spreadsheets. No programming experience is required, and simple calculations are easy to carry out using the spreadsheet software. Numerical data such as tables can be typed into cells, where they are easily seen. Equations can also be typed into cells and are introduced as needed. Labels and units as well as remarks can be added as needed.

3.2-1 Equations of State

Your objectives in studying this section are to be able to:

1. Cite two reasons for using equations of state to predict p, V, T properties of gases.
2. Write down the van der Waals equations.
3. Explain what the units are for the coefficients in van der Waals equation or other equations of state.
4. Solve the van der Waals equation or other equations of state for either p, V, n, or T given the values for the coefficients and the other variables.
5. Write down the names of five equations of state.

Equations of state relate the p–V–T properties of a pure substance (or mixtures) by theoretical or empirical relations. The simplest example of an equation of state is the ideal gas law itself. Table 3.2 lists a few of the commonly used equations of state (from among the hundreds that have been proposed) that involve two or more coefficients. In Secs. 1.7 and 4.3 and the supplementary references at the end of this chapter, you will find numerous sources of information about equations of state and

TABLE 3.2 Equations of State (for 1 Mole)*

Van der Waals:

$$\left(p + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT$$

$$a = \left(\frac{27}{64}\right)\frac{R^2T_c^2}{P_c}$$

$$b = \left(\frac{1}{8}\right)\frac{RT_c}{P_c}$$

Dieterici:

$$p = \frac{RT}{\hat{V} - b}e^{-a/\hat{V}RT}$$

Berthelot:

$$p = \frac{RT}{\hat{V} - b} - \frac{a}{T\hat{V}^2}$$

Redlich-Kwong:

$$\left[p + \frac{a}{T^{1/2}\hat{V}(\hat{V} + b)}\right](\hat{V} - b) = RT$$

$$a = 0.4278\frac{R^2T_c^{2.5}}{p_c}$$

$$b = 0.0867\frac{RT_c}{p_c}$$

Kammerlingh-Onnes:

$$p\hat{V} = RT\left(1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \cdots\right)$$

Holborn:

$$p\hat{V} = RT(1 + B'p + C'p^2 + \cdots)$$

Beattie-Bridgeman:

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\gamma}{\hat{V}^2} + \frac{\delta}{\hat{V}^3}$$

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0b + aA_0 - \frac{RB_0c}{T^2}$$

$$\delta = \frac{RB_0bc}{T^2}$$

Benedict-Webb-Rubin:

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\sigma}{\hat{V}^2} + \frac{\eta}{\hat{V}^4} + \frac{w}{\hat{V}^5}$$

$$\beta = RTB_0 - A_0 - \frac{C_0}{T^2}$$

$$\sigma = bRT - a + \frac{c}{T^2}\exp\left(-\frac{\gamma}{\hat{V}^2}\right)$$

$$\eta = cy\exp\left(-\frac{\gamma}{\hat{V}^2}\right)$$

$$w = a\alpha$$

Peng-Robinson:

$$p = \frac{RT}{\hat{V} - b} - \frac{a\alpha}{\hat{V}(\hat{V} + b) + b(\hat{V} - b)}$$

$$a = 0.45724\left(\frac{R^2T_c^2}{p_c}\right)$$

$$b = 0.07780\left(\frac{RT_c}{p_c}\right)$$

$$\alpha = [1 + \kappa(1 - T_r^{1/2})]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

ω = acentric factor (see p. 275)

---

*T_c and p_c are explained in Sec. 3.2-2; $\hat{V}$ is the specific volume.

TABLE 3.3 Overall Average Deviation Between Predicted and Experimental Values Based on 4010 Experimental Points

Equation	No. of coefficients	Absolute deviation %	Reference
Adachi-Lu-Sugie	4	1.05	*Fluid Phase Equilibria*, v. 11, p. 29 (1983)
Harmens-Knapp	3	1.36	*Ind. Eng. Chem. Fundam.*, v. 19, p. 291 (1980)
Schmidt-Wenzel	3	1.39	*Chemical Eng. Sci.*, v. 35, p. 1503 (1980)
Kumar-Starling	4	1.39	*Ind. Eng. Chem. Fundam.*, v. 21, p. 255 (1982)
Peng-Robinson	2	1.51	*Ind. Eng. Chem. Fundam.*, v. 15, p. 59 (1976)
Redlich-Kwong	2	1.64	*Chem. Rev.*, v. 44, p. 233 (1949)
Soave-Redlich-Kwong	2	1.72	*Chem. Eng. Sci.*, v. 27, p. 1197 (1972)
Ishikawa-Chung-Lu	2	2.71	*AIChE J.*, v. 26, p. 372 (1980)
Van der Waals	2	3.68	Ph.D. dissertation, Leiden, the Netherlands (1873)
Clausius	3	4.18	*Ann. Phys. Chem.*, v. 9, 337 (1881)
Wilson-Redlich-Kwong	2	4.42	*Adv. Cryog. Eng.*, v. 9, p. 168 (1964)

SOURCE: Y. Adachi, H. Sugie, and B. C.-Y. Lu, *J. Chem. Eng. Jpn.*, v. 17, p. 624 (1984)

values of their respective coefficients for various compounds (and sometimes for mixture). Computer data bases[1] are also good sources of the same information in a convenient form. An equation of state to be effective must represent experimental data for p–V–T properties in the gas region with reasonable precision.

In an evaluation of 11 cubic equations of state, Adachi, Sugie, and Lu reported the overall ratings listed in Table 3.3 based on 21 substances for which detailed experimental data were available in the literature. You can see that some of the two parameter equations of state listed in Table 3.2 do as good a job in predicting p–V–T properties, as do some of the equations of state with more coefficients.

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[1] P. Benedek and F. Olti, *Computer Aided Chemical Thermodynamics of Gases and Liquids: Theory, Models and Programs*, Wiley, New York, 1985.

Van der Waals equation. We will use the van der Waals equation as an example of an equation of state, not because it is the best in predicting p–V–T properties, but because it is not too bad, is simple, and can be used to explain the computation problems involving the use of equations of state. Figure 3.3 shows how well the van der Waals equation predicts the properties of CO_2 in comparison with experimental data. (Note how far the ideal gas law departs from the experimental data even at 52°C.) The van der Waals equation illustrates some of the typical theoretical development that has taken place as well as some of the computational problems involved in using equations of state. Keep in mind that some of the equations listed in Table 3.2 are completely empirical, whereas others, such as the van der Waals equation, are semiempirical; that is, although they were developed from theory, the constants in the equation or portions of the equation are determined by experiment for each gas.

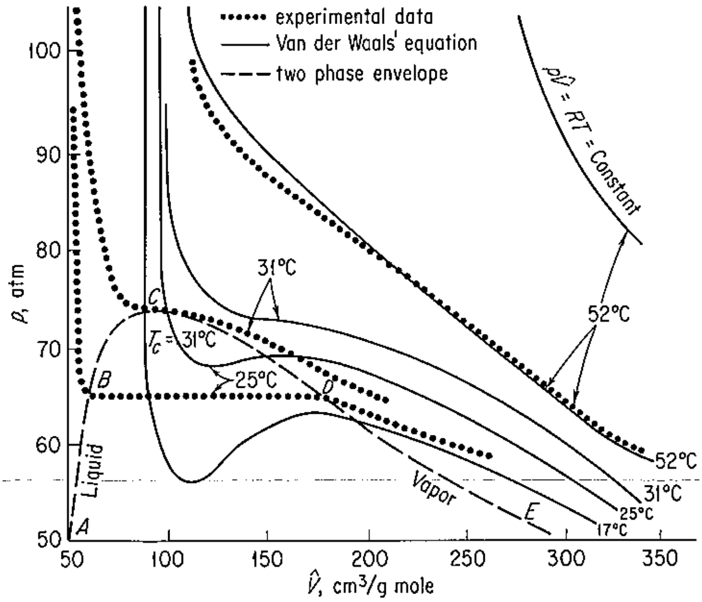

Figure 3.3 p–V–T properties of CO_2.

Van der Waals tried to include in the ideal gas law the effect of the attractive forces among the molecules by adding to the pressure term, in the ideal gas law, the term

$$\frac{n^2a}{V^2}$$

where n = number of moles
a = a constant, different for each gas
V = volume

He also tried to take into account the effect of the volume occupied by the molecules themselves by subtracting a term from the volume in the ideal gas law. These corrections led to the following equation:

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{3.11}$$

where a and b are constants determined by fitting the van der Waals equation to experimental p–V–T data, particularly the values at the critical point. Values of the van der Waals constants for a few gases are given in Table 3.4.

Let us look at some of the computational problems that may arise when using equations of state to compute p–V–T properties by using van der Waals equation as an illustration. Van der Waals equation can easily be explicitly solved for p as follows:

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \tag{3.12}$$

However, if you want to solve for V (or n), you can see that the equation becomes cubic in V (or n):

$$V^3 - \left(nb + \frac{nRT}{p}\right)V^2 + \frac{n^2 a}{p}V - \frac{n^3 ab}{p} = 0 \tag{3.13}$$

Most of the equations of state are expressed explicitly in terms of p and sometimes T. To solve for $\hat{V}$, given p and T, you must extract a real root. In the disk in the back of the book you will find two Fortran computer programs that can solve

TABLE 3.4 Constants for the Van der Waals and Redlich-Kwong Equations Calculated From the Listed Values of the Critical Constants

	van der Waals		Redlich-Kwong	
	a* $\left[\text{atm}\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2\right]$	b† $\left(\frac{\text{cm}^3}{\text{g mol}}\right)$	a‡ $\left[(\text{atm})(\text{K})^{1/2}\left(\frac{\text{cm}^3}{\text{g mol}}\right)\right]$	b† $\left(\frac{\text{cm}^3}{\text{g mol}}\right)$
Air	1.33×10^6	36.6	15.65×10^6	25.3
Ammonia	4.19×10^6	37.3	85.00×10^6	25.7
Carbon dioxide	3.60×10^6	42.8	63.81×10^6	29.7
Ethane	5.50×10^6	65.1	97.42×10^6	45.1
Ethylene	4.48×10^6	57.2	76.92×10^6	39.9
Hydrogen	0.246×10^6	26.6	1.439×10^6	18.5
Methane	2.25×10^6	42.8	31.59×10^6	29.6
Nitrogen	1.347×10^6	38.6	15.34×10^6	26.8
Oxygen	1.36×10^6	31.9	17.12×10^6	22.1
Propane	9.24×10^6	90.7	180.5×10^6	62.7
Water vapor	5.48×10^6	30.6	140.9×10^6	21.1

*To convert to psia (ft^3/lb mol)^2, multiply table value by 3.776×10^{-3}.

†To convert to ft^3/lb mol, multiply table value by 1.60×10^{-2}.

‡To convert to psia (°R)$^{1/2}$(ft^3/lb mol)^2, multiply table value by 2.807×10^{-3}.

nonlinear equations and can be used to solve for $\hat{V}$ if you have a *reasonable initial guess* for $\hat{V}$, say from the ideal gas law. One code uses Newton's method and the other a minimization method; refer to Appendix L for details of these methods. An alternative technique for finding the root of a function of a single variable is to plot the nonlinear function obtained by substituting p and T into the equation of state, collecting all the terms on the left-hand side of the equation, and finding at what value of $\hat{V}$ the left-hand function crosses the zero axis as $\hat{V}$ changes. Tao[2] gives a basic program for plotting and discusses some of the difficulties. Quite a bit of inexpensive software is available to execute such plots on any type of computer hardware.

EXAMPLE 3.12 Application of Van der Waals' Equation

A 5.0-ft^3 cylinder containing 50.0 lb of propane (C_3H_8) stands in the hot sun. A pressure gauge shows that the pressure is 665 psig. What is the temperature of the propane in the cylinder? Use van der Waals equation. See Fig. E3.12.

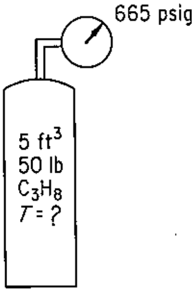

Figure E3.12

Solution

Basis: 50 lb of propane

The van der Waals constants obtained from any suitable handbook or Table 3.4 are

$$a = 3.49 \times 10^4 \text{ psia}\left(\frac{\text{ft}^3}{\text{lb mol}}\right)^2$$

$$b = 1.45 \frac{\text{ft}^3}{\text{lb mol}}$$

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

All the additional information you need is as follows:

$$p = 665 \text{ psig} + 14.7 = 679.7 \text{ psia}$$

$$R \text{ in proper units is } = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(°\text{R})}$$

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[2] B. Y. Tao, *Chem. Eng.*, p. 145 (August 17, 1987).

$$n = \frac{50 \text{ lb}}{44 \text{ lb/lb mol}} = 1.136 \text{ lb mol propane}$$

$$\left[679.7 + \frac{(1.136)^2(3.49 \times 10^4)}{(5)^2}\right][5 - 1.36(1.45)] = 1.136(10.73)T$$

$$T = 683°\text{R} = 223°\text{F}$$

Can you solve the Redlich-Kwong equation explicitly for T?

EXAMPLE 3.13 Solution of the Van der Waals Equation for V

We will work Example 3.12 backward and solve for V given p, T, and n:

$$p = 679.7 \text{ psia} \qquad a = 3.49 \times 10^4 \text{ psia}\left(\frac{\text{ft}^3}{\text{lb mol}}\right)^2$$

$$T = 683°\text{R} \qquad b = 1.45\frac{\text{ft}^3}{\text{lb mol}}$$

We use Eq. (3.13), a cubic equation in V:

$$f(V) = V^3 - \frac{pnb + nRT}{p}V^2 + \frac{n^2a}{p}V - \frac{n^3ab}{p} = 0 \tag{a}$$

Equation (a) might have one or three real roots, as indicated in Fig. E3.13, but we want a positive real root.

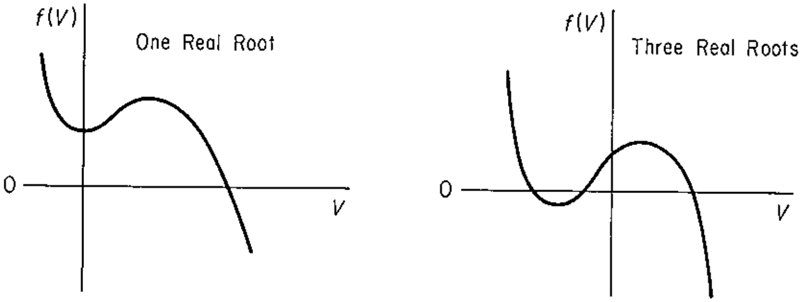

Figure E3.13

Solution

Let us apply Newton's method (refer to Appendix L) to obtain the desired root:

$$V_{k+1} = V_k - \frac{f(V_k)}{f'(V_k)} \tag{b}$$

where $f'(V_k)$ is the derivative of $f(V)$ with respect to V evaluated at V_k:

$$f'(V) = 3V^2 - \frac{2(pnb + nRT)}{p}V + \frac{n^2a}{p} \tag{c}$$

You can obtain a reasonably close approximation to V (or n) in many cases from the ideal gas law, useful at least for the first trial.

$$V_0 = \frac{nRT}{p}$$

$$= \frac{1.136\text{ lb mol}}{} \left| \frac{10.73\text{ (psia)(ft}^3)}{\text{(lb mol)(}^\circ\text{R)}} \right| \frac{683^\circ\text{R}}{} \left| \frac{}{679.7\text{ psia}} \right.$$

$$= 12.26\text{ ft}^3\text{ at }679.7\text{ psia and }683^\circ\text{R}$$

The second and subsequent estimates of V will be calculated using Eq. (b):

$$V_1 = V_0 - \frac{f(V_0)}{f'(V_0)}$$

$$f(V_0) = (12.26)^3 - \frac{(679.7)(1.137)(1.45) + (1.137)(10.73)(683)}{679.7}(12.26)^2$$

$$+ \frac{(1.137)^2(3.49 \times 10^4)}{679.7}(12.26) - \frac{(1.137)^3(3.49 \times 10^4)(1.45)}{679.7} = 738.3$$

$$f'(V_0) = 3(12.26)^2 - \frac{2[(679.7)(1.137)(1.45) + (1.137)(10.73)(683)]}{679.7}(12.26)$$

$$+ \frac{(1.137)^2(3.49 \times 10^4)}{679.7} = 216.7$$

$$V_1 = 12.26 - \frac{738.3}{216.7} = 8.85$$

On the next iteration

$$V_2 = V_1 - \frac{f(V_1)}{f'(V_1)}$$

and so on until the change in V_k from one iteration to the next is sufficiently small. The Newton code on the disk in back of the book will execute this technique for you. The final solution is 5.09 ft^3 at 679.7 psia and 683°R.

Other equations of state. Table 3.2 lists a few of the many equations of state in addition to van der Waals equation. The form of these equations is of interest inasmuch as they are attempts to fit the experimental data with as few constants in the equation as possible.

The two-constant, Peng-Robinson and Redlich-Kwong equations appear to be quite good according to Table 3.3. Figure 3.4 compares the van der Waals and the Redlich-Kwong equations of state with experimental data.

One form of the equation known as the *virial* form is illustrated by the equations of Kammerlingh-Onnes and Holborn. These are essentially power series in $1/\hat{V}$ or in p, and the quantities B, C, D, and so on, are known as *virial coefficients*. These equations reduce to $p\hat{V} = RT$ at low pressures.

In spite of their complications, equations of state are important for several reasons. They permit a concise summary of a large mass of experimental data and also permit accurate interpolation between experimental data points. They provide a con-

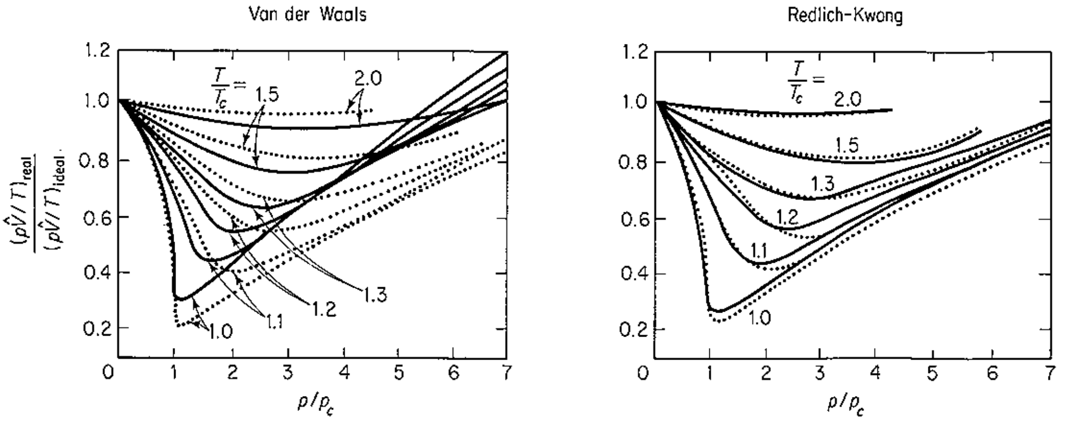

Figure 3.4 Comparison of experimental values (dots) with predicted values (solid lines) for two equations of state.

tinuous function to facilitate calculation of physical properties involving differentiation and integration. Finally, they provide a point of departure for the treatment of thermodynamic properties of mixtures. However, for instructional purposes, and for many engineering calculations, the techniques of predicting p–V–T values discussed in the next section are more convenient to use and usually have adequate accuracy.

Self-Assessment Test

1. Equations of state for gases are often used to predict p–V–T properties of gas. Cite two reasons.
2. The constants for an equation of state are usually evaluated in one of two ways.
   (a) What are these?
   (b) Which method would you expect to give an equation showing the least error?
3. What are some of the tests that you might apply to see how an equation of state fits p–V–T data?
4. What factors in a real gas cause the gas to behave in a nonideal manner? How are these factors taken into account in the van der Waals equation?
5. What are the units of a and b in the SI system for the Redlich-Kwong equation?
6. You measure that 0.00220 lb mol of a certain gas occupies a volume of 0.95 ft^3 at 1 atm and 32°F. If the equation of state for this gas is $pV = nRT(1 + bp)$, where b is a constant, find the volume at 2 atm and 71°F.
7. Calculate the temperature of 2 g mol of a gas using van der Waals equation with $a = 1.35 \times 10^{-6}\,(\text{m}^6)(\text{atm})(\text{g mol}^{-2})$, $b = 0.0322 \times 10^{-3}\,(\text{m}^3)(\text{g mol}^{-1})$ if the pressure is 100 kPa and the volume is 0.0515 m^3.
8. Calculate the pressure of 10 kg mol of ethane in a 4.86-dm^3 vessel at 300 K using two equations of state: (*a*) ideal gas and (*b*) Beattie–Bridgeman. For the latter, $A_0 = 5.880$, $a = 0.05861$, $B_0 = 0.09400$, $b = 0.01915$, and $c = 90.0 \times 10^4$. Compare with your answer the observed value of 34.0 atm.
9. The van der Waals constants for a gas are $a = 2.31 \times 10^6\,(\text{atm})(\text{cm}^3/\text{g mol})^2$ and $b = 44.9\,\text{cm}^3/\text{g mol}$. Find the volume per kilogram mole if the gas is at 90 atm and 373 K.

Thought Problems

1. Municipal sludge is being converted to sterile ash and readily biodegradable liquid effluent in a mile-deep well at Longmont, Colo. The nation's first deep well wet-air oxidation sludge destruction process reduces chemical oxygen demand (COD) by up to 68% and destroys all living organisms, according to Howard C. Delaney, superintendent of Longmont's wastewater treatment plant.
   The VerTech Treatment System is suspended in the conventionally drilled, concrete-encased well. Tubes of various diameters are concentrically fitted within the well to create annular spaces for the two-phase flow. Oxidation takes place at the bottom of the well.
   Why is it advantageous to oxidize the sludge at the bottom of a well rather than in a pond at ground level?
2. From the *Oil and Gas Journal,* p. 55, December 2, 1985.

   Gas trapped in a subsea blowout preventer (BOP) can be a serious problem in a deepwater drilling.

   Amoco used nitrogen to confirm a safe method to remove gas trapped in a subsea BOP. The gas can be recovered up the choke line by displacing the kill mud with water and then allowing the gas to expand against the lower hydrostatic gradient of the water.

   The test was conducted in the Gulf of Mexico from a semisubmersible working in 1,015 ft. of water.

   What is the difficulty with a gas bubble trapped in the BOP?

3.2-2 Critical State, Reduced Parameters, and Compressibility

Your objectives in studying this section are to be able to:

1. State the law of corresponding states.
2. Define the critical state.
3. Calculate the reduced temperature, reduced pressure, and reduced volume, and to use any two of these parameters to obtain the compressibility factor, z, from the Nelson and Obert charts.
4. Use compressibility factors and appropriate charts to predict the p–V–T behavior of a gas, or given the required data, find compressibility factors.
5. List Newton's corrections for H_2 and He to T_c and p_c.
6. Calculate the ideal critical volume and ideal reduced volume, and be able to use V_{r_i} as a parameter in the Nelson and Obert charts.

In the attempt to devise some truly universal gas law for high pressures, the idea of corresponding states was developed. Early experimenters found that at the critical point all substances are in approximately the same state of molecular dispersion. Consequently, it was felt that their thermodynamic and physical properties should be similar. The **law of corresponding states** expresses the idea that in the critical state all substances should behave alike.

Now that we have mentioned **critical state** several times, let us consider exactly what the term means. You can find many definitions, but the one most suitable for general use with pure component systems as well as with mixtures of gases is the following:

> **The critical state for the gas-liquid transition is the set of physical conditions at which the density and other properties of the liquid and vapor become identical.**

This point, for a pure component (only), is the highest temperature at which liquid and vapor can exist in equilibrium.

Refer to Fig. 3.5. The vertical lines between the curves are lines of constant temperature connecting the vapor and liquid phases, which are in equilibrium. As the temperature increases, the specific volumes of the vapor and liquid approach each other until finally at 374.14°C, the values are the same. At the critical state water undergoes a transition from liquid to vapor without the appearance of a distinct two-phase region. If you watch a liquid held at or above the critical temperature and expand its volume, you cannot tell when the liquid becomes a vapor, because no interface is formed between the phases—no liquid surface can be seen. This phenomenon occurs at such a high pressure and temperature for water that it is outside your everyday experience.

You can find experimental values of the critical temperature (T_c) and the critical pressure (p_c) for various compounds in Appendix D. If you cannot find a desired critical value in this text or in a handbook, you can always consult Reid, Prausnitz,

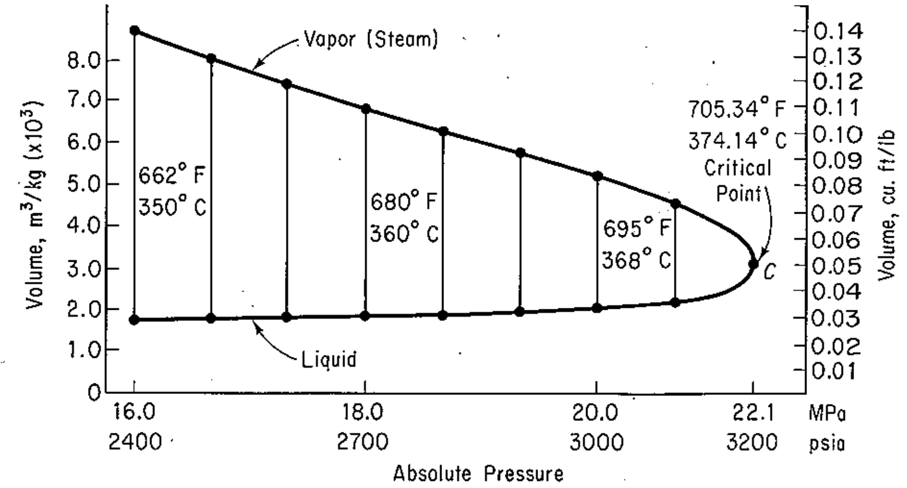

Figure 3.5 Critical point for a pure substance (water).

and Poling[3] or Hakata and Hirata,[4] which describe and evaluate methods of estimating critical constants for various compounds.

The gas–liquid transition described above is only one of several possible transitions exhibiting a critical point. Critical phenomena are observed in liquids and solids as well, as described in Sec. 3.7.

Another set of terms with which you should immediately become familiar are the **reduced conditions.** These are *corrected,* or *normalized,* conditions of temperature, pressure, and volume and are expressed mathematically as

$$T_r = \frac{T}{T_c} \tag{3.14}$$

$$p_r = \frac{p}{p_c} \tag{3.15}$$

$$V_r = \frac{V}{V_c} \tag{3.16}$$

The idea of using the reduced variables to correlate the p–V–T properties of gases, as suggested by van der Waals, is that all substances behave alike in their reduced (i.e., their corrected) states. In particular, any substance would have the same *reduced* volume at the same *reduced* temperature and pressure. If a relationship does exist involving the reduced variables that can be used to predict p_r, T_r, and V_r, what would the equation be? Certainly, the simplest form of such an equation would be to imitate the ideal gas law, or

$$p_r\hat{V}_r = \gamma RT_r \tag{3.17}$$

where γ is some universal constant. Although Eq. (3.17) works for many gases at high temperature and pressure, it fails to predict gas properties adequately in the region where the ideal gas law applies (at low pressure somewhat below $p_r = 1.0$).

A more convenient and accurate way that has been developed to tie together the concepts of the law of corresponding states and the ideal gas law is to revert to a correction of the ideal gas law, that is, a generalized equation of state expressed in the following manner:

$$pV = znRT \tag{3.18}$$

where the dimensionless quantity z is called the **compressibility factor** and is a function of the pressure and temperature:

$$z = \psi(p, T) \tag{3.19}$$

One way to look at z is to consider it to be a factor that makes Eq. (3.18) an equality. If the compressibility factor is plotted for a given temperature against the pressure for different gases, you obtain figures like Fig. 3.6(a). However, if the compressibility is plotted against the reduced pressure as a function of the reduced

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[3] R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids,* 4th ed., McGraw-Hill, New York, 1987.

[4] T. Hakata and M. Hirata, *J. Chem. Eng. Japan,* v. 3, p. 5(1970).

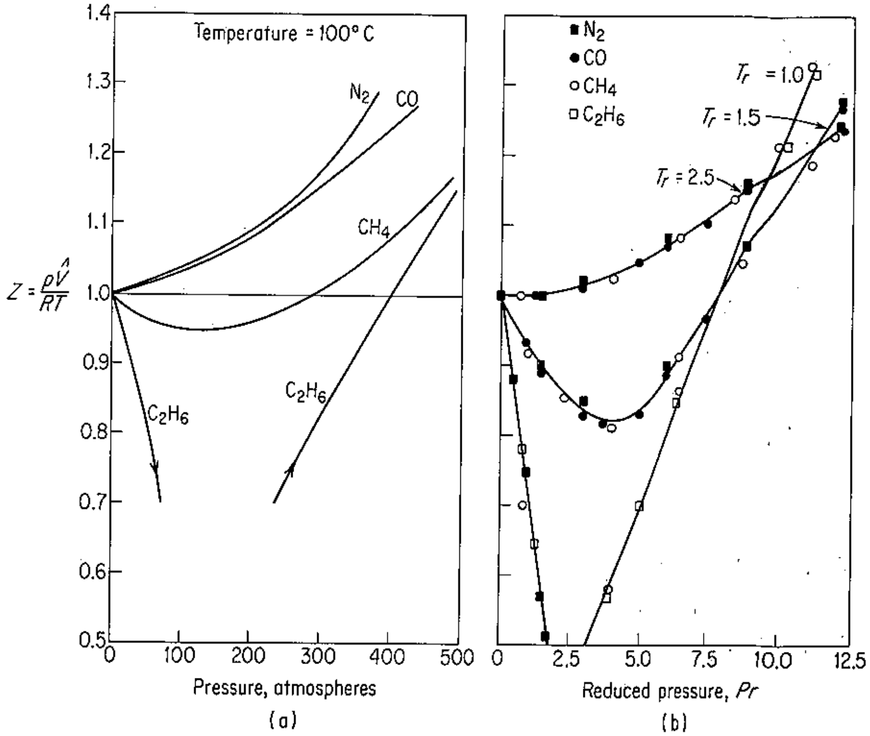

Figure 3.6 (a) Compressibility factor as a function of temperature and pressure; (b) compressibility as a function of reduced temperature and reduced pressure.

temperature,

$$z = \psi(p_r, T_r) \tag{3.20}$$

then for most gases the compressibility values at the same reduced temperature and reduced pressure fall at about the same point, as illustrated in Fig. 3.6(b).

This outcome permits the use of what is called a generalized compressibility factor, and Figs. 3.7 are the *generalized compressibility charts* or z-factor charts prepared by Nelson and Obert.[5] These charts are based on 30 gases. Figures 3.7(b) and (c) represent z for 26 gases (excluding H_2, He, NH_3, H_2O) with a maximum deviation of 1%, and H_2 and H_2O within a deviation of 1.5%. Figure 3.7(d) is for 26 gases and is accurate to 2.5%, while Fig. 3.7(e) is for nine gases and errors can be as high as 5%. For H_2 and He only, Newton's corrections to the actual critical constants are used to give pseudocritical constants

$$T_c' = T_c + 8 \text{ K}$$

$$p_c' = p_c + 8 \text{ atm}$$

which enable you to use Figs. 3.7(a-e) for these two gases as well with minimum er-

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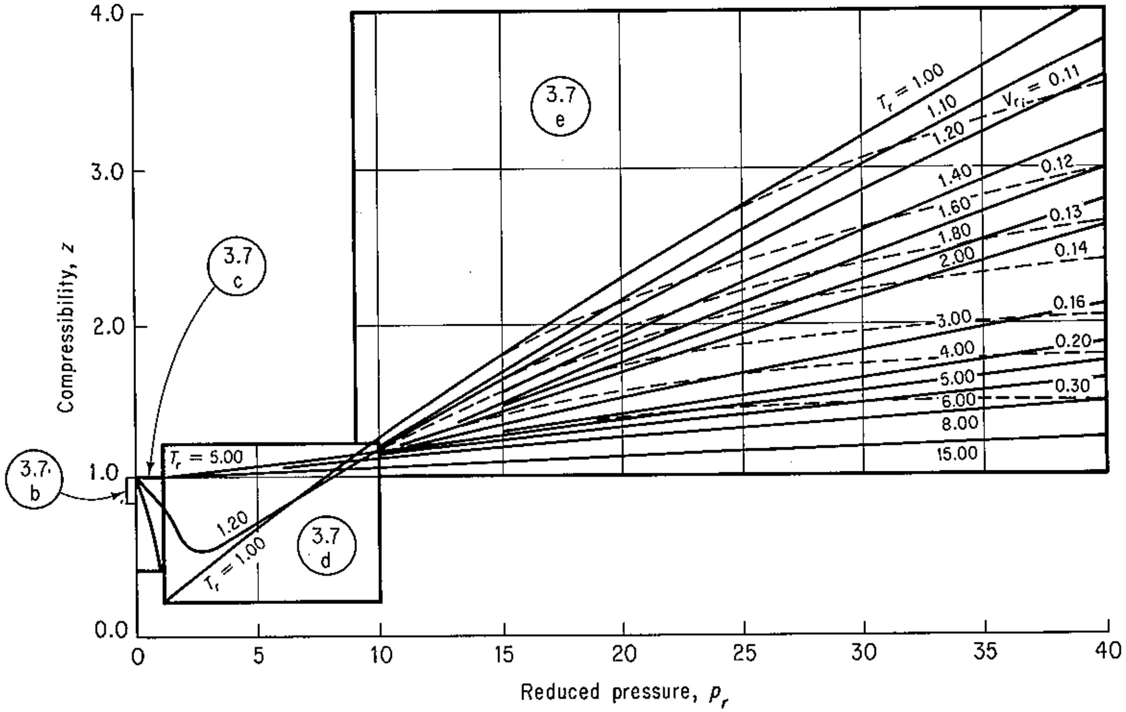
[5] L. C. Nelson and E. F. Obert, *Chem. Eng.*, v. 61, No. 7, pp. 203–208(1954). Figures 3.7b and c include data reported by P. E. Liley, *Chem. Eng.*, p. 123 (July 20, 1987).



(a)

Figure 3.7 (a) Generalized compressibility chart showing the respective expanded portions. (b) Generalized compressibility chart, very low reduced pressure. (c) Generalized compressibility chart, low pressure (d) Generalized compressibility chart, medium pressures (e) Generalized compressibility chart, high pressures. (f) Generalized compressibility chart, with special scales.

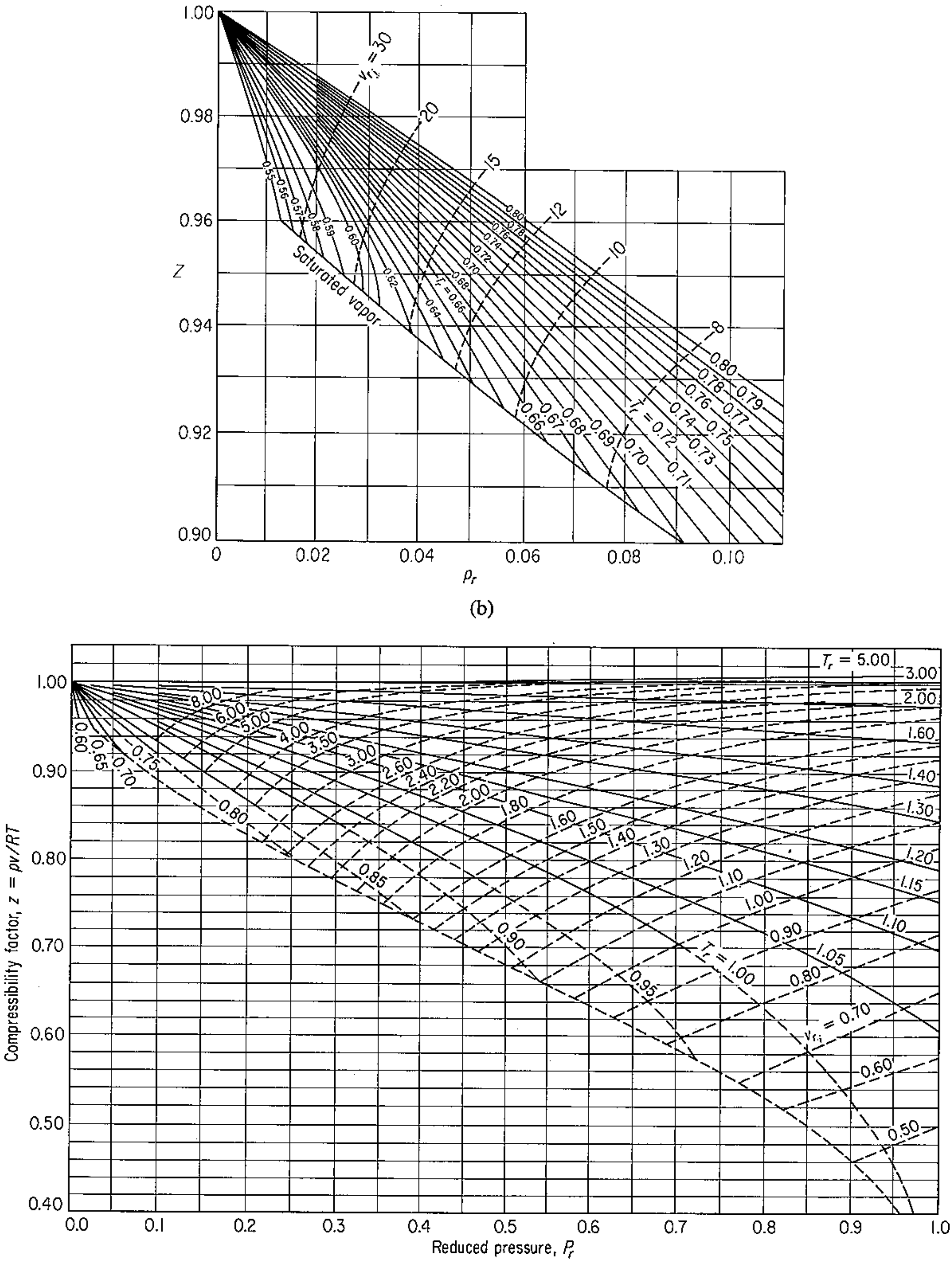
ror. Figure 3.7(f) is a unique chart which, by having several parameters plotted simultaneously on it, helps you avoid trial-and-error solutions or graphical solutions of real gas problems. One of these helpful parameters is the ideal reduced volume defined as

$$V_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}} \tag{3.21}$$

$\hat{V}_{c_i}$ is the ideal critical volume, or

$$\hat{V}_{c_i} = \frac{RT_c}{p_c} \tag{3.22}$$

Both V_{r_i} and $\hat{V}_{c_i}$ are easy to calculate since T_c and p_c are presumed known. The development of the generalized compressibility chart is of considerable practical as well as pedagogical value because it enables engineering calculations to be made with considerable ease and also permits the development of thermodynamic functions for gases for which no experimental data are available. All you need to know to use



(b)

(c)

Figure 3.7 *(cont.)*

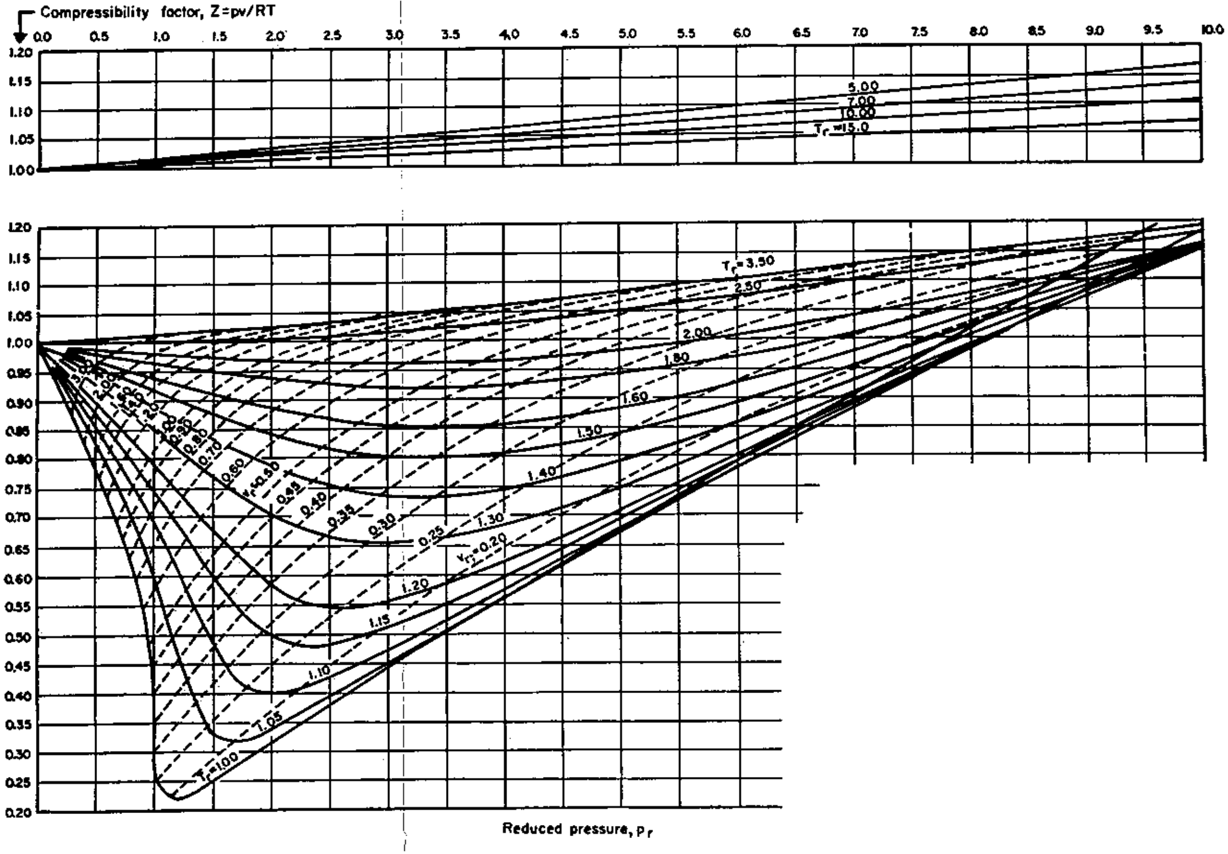


Figure 3.7 (*cont.*)

(d)

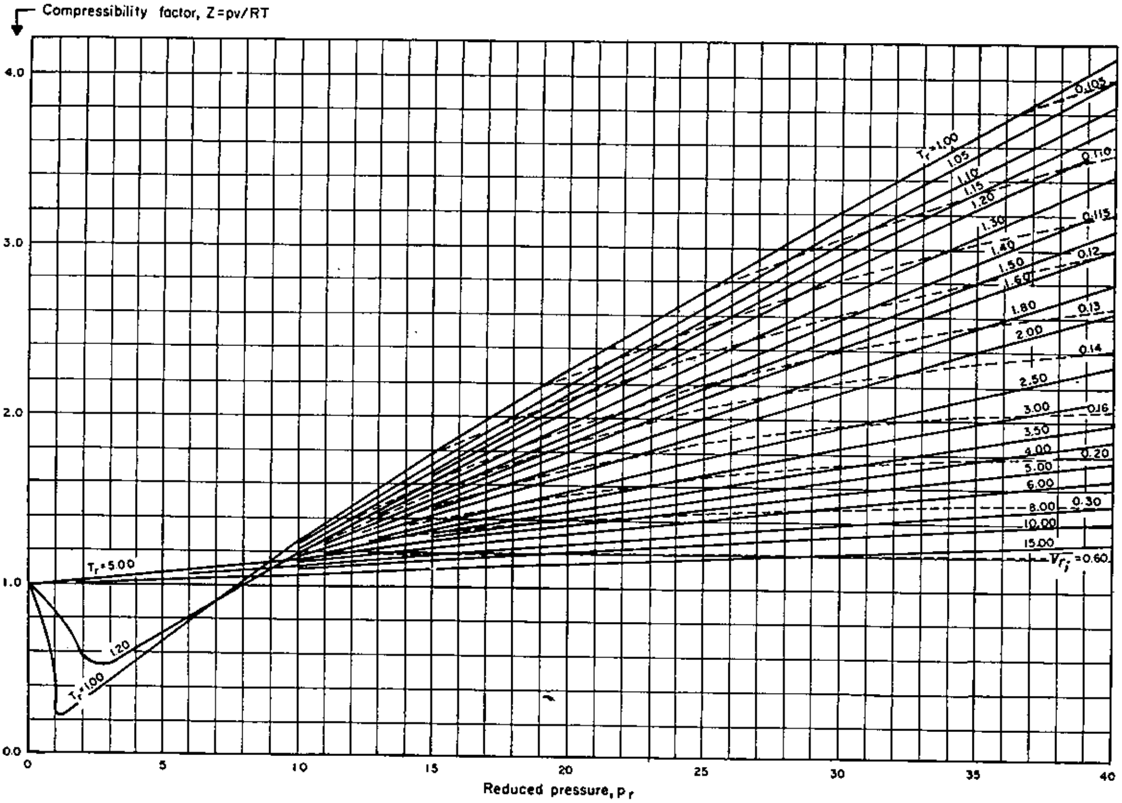


Figure 3.7 *(cont.)* (e)

these charts are the critical temperature and the critical pressure for a pure substance (or the pseudovalues for a mixture, as we shall see later). The value $z = 1$ represents ideality, and the value $z = 0.27$ is the compressibility factor at the critical point.

Quite a few authors have suggested that the generalized compressibility relation [Eq. (3.20)] could provide better accuracy if another parameter for the gas were included in the argument on the right-hand side (in addition to p_r and T_r). Clearly, if a third parameter is used, adding a third dimension to p_r and T_r, you have to employ a *set* of tables or charts rather than a single table or chart. Lydersen et al.[6] developed tables of z that included as the third parameter the critical compressibility factor, $z_c = p_c \hat{V}_c/RT_c$. Pitzer[7] used a different third parameter termed the *acentric* factor ω, defined as being equal to $-\ln p_{rs} - 1$, where p_{rs} is the value of the reduced vapor pressure at $T_r = 0.70$. Table 3.5 lists a few values of ω for common gases.

Viswanath and Su[8] compared the z factors from the Nelson and Obert charts, the Lydersen–Greenkorn–Hougen charts, and the two-parameter (T_r and p_r)

[6] A. L. Lydersen, R. A. Greenkorn, and O. A. Hougen, *Univ. Wis. Eng. Exp. St. Rep. No. 4*, Madison, Wis., 1955.

[7] K. S. Pitzer, *J. Am. Chem. Soc.*, v. 77, p. 3427 (1955).

[8] D. S. Viswanath and G. J. Su, *AIChE J.*, v. 11, p. 202 (1965).

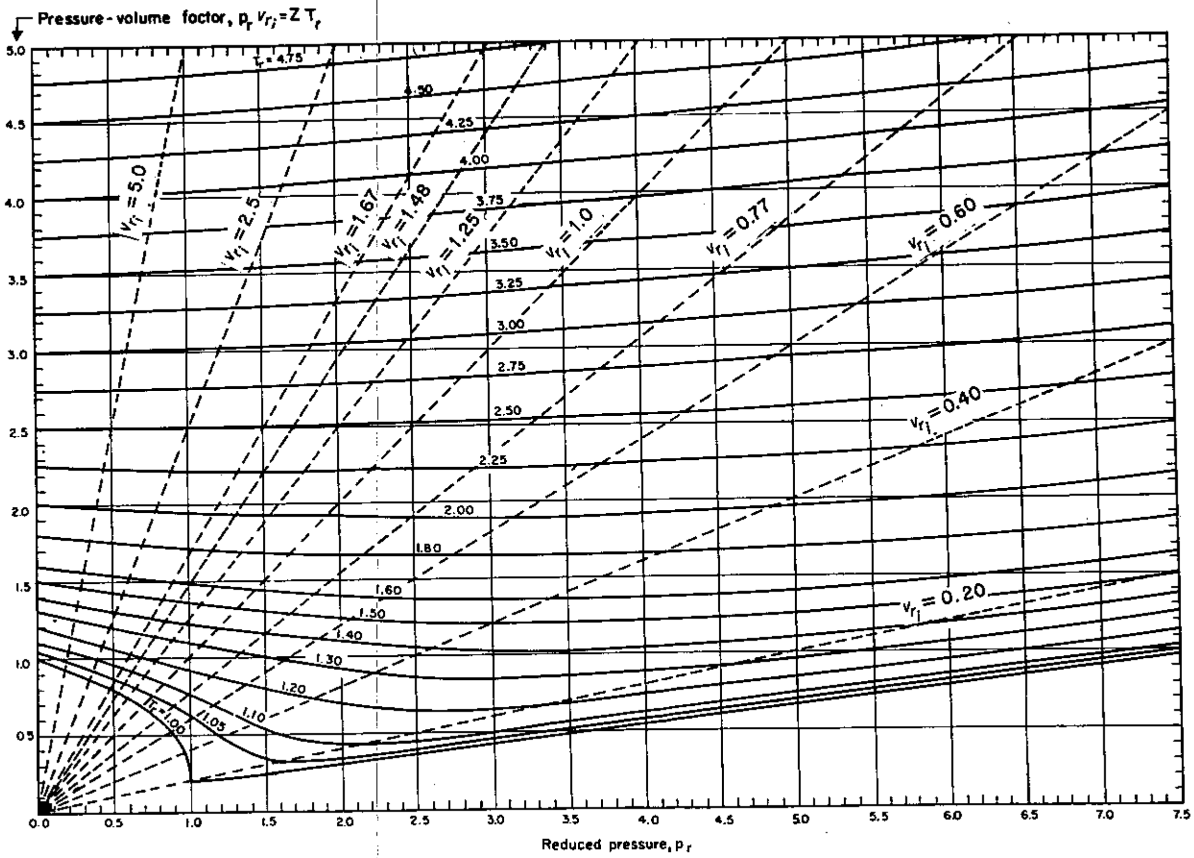


Figure 3.7 *(cont.)*

(f)

TABLE 3.5 Values Of The Pitzer Acentric Factor

Compound	Acentric factor
Ammonia	0.250
Argon	−0.002
Carbon dioxide	0.225
Carbon monoxide	0.049
Chlorine	0.073
Ethylene	0.085
Hydrogen	−0.220
Ethane	0.098
Hydrogen sulfide	0.100
Methane	0.008
Methanol	0.559
Nitrogen	0.040
Oxygen	0.021
Propane	0.152
Sulfur dioxide	0.251
Water vapor	0.344

Viswanath and Su chart with the experimental z's for T_r's of 1.00 to 15.00 and p_r's of 0 to 40 for 19 gases with the following results:

	Viswanath–Su	Nelson–Obert	Lydersen–Greenkorn–Hougen
Number of points	415	355	339
Average deviation (%) in z	0.61	0.83	1.26

It is seen that all these charts yield quite reasonable values for engineering purposes. Because the increased precision that may accompany the use of a third parameter in calculating z is not necessary for our purposes, and because the presentation of z values so as to include the third parameter is considerably more cumbersome, we shall not show the three-parameter tables here.

EXAMPLE 3.14 Use of the Compressibility Factor

In spreading liquid ammonia fertilizer, the charges for the amount of NH_3 are based on the time involved plus the pounds of NH_3 injected into the soil. After the liquid has been spread, there is still some ammonia left in the source tank (volume = 120 ft^3), but in the form of a gas. Suppose that your weight tally, which is obtained by difference, shows a net weight of 125 lb of NH_3 left in the tank as a gas at 292 psig. Because the tank is sitting in the sun, the temperature in the tank is 125°F.

Your boss complains that his calculations show that the specific volume of the gas is 1.20 ft^3/lb and hence that there are only 100 lb of NH_3 in the tank. Could he be correct? See Fig. E3.14.

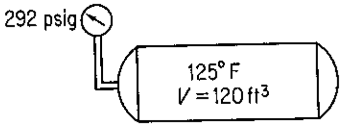


Figure E3.14

Solution

Basis: 1 lb of NH_3

Apparently, your boss used the ideal gas law in calculating his figure of 1.20 ft^3/lb of NH_3 gas:

$$R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(^\circ\text{R})}$$

$$T = 125^\circ\text{F} + 460 = 585^\circ\text{R}$$

$$p = 292 + 14.7 = 306.7 \text{ psia}$$

$$n = \frac{1 \text{ lb}}{17 \text{ lb/lb mol}}$$

$$\hat{V} = \frac{nRT}{p} = \frac{\frac{1}{17}(10.73)(585)}{306.7} = 1.20 \text{ ft}^3/\text{lb}$$

However, he should have used the compressibility factor because NH_3 does not behave as an ideal gas under the observed conditions of temperature and pressure. Let us again compute the mass of gas in the tank this time using

$$pV = znRT$$

What is known and unknown in the equation?

$$p = 306.7 \text{ psia}$$

$$V = 120 \text{ ft}^3$$

$$z = ?$$

$$n = \tfrac{1}{17} \text{ lb mol}$$

$$T = 585^\circ\text{R}$$

The additional information needed (taken from Appendix D) is

$$T_c = 405.5K = 729.9^\circ\text{R}$$

$$p_c = 111.3 \text{ atm} = 1636 \text{ psia}$$

Then, since z is a function of T_r and p_r,

$$T_r = \frac{T}{T_c} = \frac{585^\circ\text{R}}{729.9^\circ\text{R}} = 0.801$$

$$p_r = \frac{p}{p_c} = \frac{306.7 \text{ psia}}{1636 \text{ psia}} = 0.187$$

From the Nelson and Obert chart, Fig. 3.7(c), you can read $z = 0.855$. Now $\hat{V}$ can be calculated as

$$\hat{V} = \frac{znRT}{p} = \hat{V}_{\text{ideal}}\left(\frac{z}{z_{\text{ideal}}}\right)$$

or

$$\hat{V} = \frac{1.20 \text{ ft}^3 \text{ ideal}}{\text{lb}} \left| \frac{0.855}{1} \right. = 1.03 \text{ ft}^3/\text{lb NH}_3$$

$$\frac{1 \text{ lb NH}_3}{1.03 \text{ ft}^3} \left| \frac{120 \text{ ft}^3}{} \right. = 117 \text{ lb NH}_3$$

Certainly 117 lb is a more realistic figure than 100 lb, and it is easily possible to be in error by 8 lb if the residual weight of NH_3 in the tank is determined by difference. As a matter of interest you might look up the specific volume of NH_3 at the conditions in the tank in a handbook—you would find that $\hat{V} = 0.973$ ft³/lb, and hence the compressibility factor calculation yielded a volume with an error of only about 4%.

Example 3.15 Use of the Compressibility Factor

Suppose that 3.500 kg of liquid O_2 is vaporized into a tank of 0.0284-m³ volume at −25°C. What will the pressure in the tank be; will it exceed the safety limit of the tank (100 atm)?

Solution

See Fig. E3.15.

Basis: 3.500 kg O_2

We know from Appendix D that

$$T_c = 154.4 \text{ K}$$

$$p_c = 49.7 \text{ atm}$$

However, this problem cannot be worked exactly the same way as the preceding problem because we do not know the pressure of the O_2 in the tank. Thus we need to use the other parameter, V_{r_i}, that is available on the Nelson and Obert charts. We first calculate

$$\hat{V}\,(\textit{molal volume}) = \frac{0.0284 \text{ m}^3}{3.500 \text{ kg}} \left| \frac{32 \text{ kg}}{1 \text{ kg mol}} \right. = 0.2597 \text{ m}^3/\text{kg mol}$$

Note that the *molal volume must* be used in calculating V_{r_i} since $\hat{V}_{c_i}$ is a volume per mole. Next,

$$\hat{V}_{c_i} = \frac{RT_c}{p_c} = \frac{0.08206(\text{m}^3)(\text{atm})}{(\text{kg mol})(\text{K})} \left| \frac{154.4 \text{ K}}{49.7 \text{ atm}} \right. = 0.255\frac{\text{m}^3}{\text{kg mol}}$$

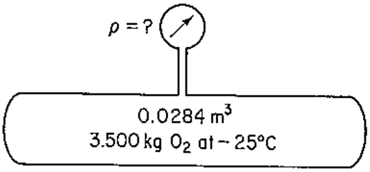


Figure E3.15

Then

$$V_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}} = \frac{0.260}{0.255} = 1.02$$

Now we know two parameters, V_{r_i} and,

$$T_r = \frac{T}{T_c} = \frac{248\text{ K}}{154.4\text{ K}} = 1.61$$

From the Nelson and Obert chart [Fig. 3.7],

$$p_r = 1.43$$

Then

$$\begin{aligned} p &= p_r p_c \\ &= 1.43(49.7) = 71.1\text{ atm} \end{aligned}$$

The pressure of 100 atm is not exceeded.

Self-Assessment Test

1. What is the ideal critical volume? What is the advantage of using V_{c_i}?
2. In a proposed low pollution vehicle burning H_2–O_2, the gases are to be stored in tanks at 2000 psia. The vehicle has to operate from −40 to 130°F.
   - (a) Is the ideal gas law a sufficiently good approximation for the design of these tanks?
   - (b) A practical operating range requires that 3 lb_m of hydrogen be stored. How large must the hydrogen tank be if the pressure is not to exceed 2000 psia?
   - (c) The H_2/O_2 ratio is 2 on a molar basis. How large must the oxygen tank be?
3. A carbon dioxide fire extinguisher has a volume of 40 L and is to be charged to a pressure of 20 atm at a storage temperature of 20°C. Determine the mass in kilograms of CO_2 within a charged extinguisher assuming it initially contains CO_2 at 1 atm.
4. Calculate the pressure of 4.00 g mol CO_2 contained in a 6.25×10^{-3} m^3 fire extinguisher at 25°C.

3.2-3 Calculation of *p–V–T* Properties via Generalized Group Contribution Methods

The group contribution method has been successful in estimating *p–V–T* properties of pure components (as well as other thermodynamic properties). As indicated by the name, the idea is that compounds can be constituted from combinations of functional groups, the contribution of each group to a property can be tabulated, and the group contributions can be correlated and/or summed to give the desired property of the compound. The assumption is that a group such as $—CH_3$, or —OH, behaves identically no matter what the molecule may be in which it appears. This assumption is not quite true, so that any group contribution method yields approximate properties. Probably the most widely used group contribution method is UNIFAC,[9,10] which forms a part of many data bases.

3.2-4 Gaseous Mixtures

Your objectives in studying this section are to be able to:

1. Use Dalton's law and an equation of state such as the van der Waals law to compute the total pressure of a gas mixture.
2. Use average constants given the desired weighting method in an equation of state.
3. Compute the mean compressibility factor.
4. Use Kay's method of pseudocritical values to calculate the pseudoreduced values and predict p, V, T, and n via the compressibility factor.

So far we have discussed only pure compounds and their p–V–T relations. Most practical problems involve gaseous mixtures and there is very little experimental data available for gaseous mixtures. Thus the question is: How can we predict p–V–T properties with reasonable accuracy for gaseous mixtures? We treated ideal gas mixtures in Sec. 3.1.3, and saw, as we shall see later (in Chap. 4 for the thermodynamic properties), that for ideal mixtures the properties of the individual components can be added together to give the desired property of the mixture. But this technique does not prove to be satisfactory for real gases. The most desirable technique would be to develop methods of calculating p–V–T properties for mixtures based solely on the properties of the pure components. Possible ways of doing this for real gases are discussed below.

Averaged constants for equations of state. One way to employ equations of state is to use average values for the coefficients in the equation. Take, for example, the van der Waals equation [Eq. (3.12)]. How should the coefficients for the individual components be averaged to give the least error on the whole? For the van der Waals equation, you could proceed as follows. For b (use a linear sum of the mole fraction weights):

$$b_{\text{mixture}} = b_A y_A + b_B y_B + \cdots \tag{3.23}$$

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[9] A. Fredenslund, J. Gmehling, and P. Rasmussen, *Vapor–Liquid Equilibria Using UNIFAC,* Elsevier, Amsterdam, 1977.

[10] D. Tiegs, J. Gmehling, P. Rasmussen, and A. Fredenslund, *Ind. Eng. Chem. Res.*, v. 26, p. 159 (1987).

For a (use a linear sum of the mole fraction weights of the square roots of a_i):

$$a^{1/2}_{\text{mixture}} = a_A^{1/2} y_A + a_B^{1/2} y_B + \cdots \tag{3.24}$$

If you are puzzled as to the reasoning behind the use of the square-root weighting for a, remember that the term in the van der Waals equation involving a is

$$\frac{n^2 a}{V^2}$$

in which the number of moles is squared. The method of average constants can be successfully applied to most of the other equations of state listed in Table 3.2. The average constants can also be calculated from the pseudoreduced constants listed in Table 3.2. For example, for the van der Waals equation,

$$a = \frac{27}{64}\frac{R^2T_c^2}{p_c} \qquad \text{and} \qquad b = \frac{RT_c}{8p_c}$$

you could average T_c and p_c and then compute a and b for the mixture.

Mixing rules used to estimate coefficients in gaseous mixtures via equations of state sometimes involve not only weighted sums of the coefficients of the pure components but interaction coefficients as well. Consequently, it is difficult to add new substances to a data base because of the large amount of data that has to be collected if the equation of state has more than two or three interaction coefficients.

Mean compressibility factor. Another approach toward the treatment of gaseous mixtures is to say that $pV = z_m nRT$, where z_m can be called the *mean compressibility factor*. With such a relationship the only problem is how to evaluate the mean compressibility factor satisfactorily. One obvious technique that might occur to you is to make z_m a mole average as follows:

$$z_m = z_A y_A + z_B y_B + \cdots \tag{3.25}$$

Since z is a function of both the reduced temperature and the reduced pressure, it is necessary to decide what pressure will be used to evaluate p_r.

(a) *Assume Dalton's law of partial pressures*. For each component z is evaluated at T_r and the reduced *partial pressure* for each gaseous component. The reduced partial pressure is defined as

$$p_{r_A} = \frac{p_A}{p_{c_A}} = \frac{(p_T)y_A}{p_{c_A}} \tag{3.26}$$

(b) *Assume Amagat's law of pure component volumes*. For each component z is evaluated at T_{r_i} and the reduced *total pressure* on the system.

Pseudocritical properties. Many weighting rules have been proposed to combine the critical properties of the components of a real gas mixture in order to get an effective set of critical properties (*pseudocritical*) that enable *pseudo-reduced* properties of the mixture to be computed.[11] The pseudoreduced properties in turn are used in exactly the same way as the reduced properties for a pure compound, and in effect the mixture can be treated as a pure compound. In instances where you know nothing about the gas mixture, this technique is preferable to any of those discussed previously.

In Kay's method, pseudocritical values for mixtures of gases are calculated on the assumption that each component in the mixture contributes to the pseudocritical value in the same proportion as the number of moles of that component. Thus the pseudocritical values are computed as follows:

$$p'_c = p_{c_A} y_A + p_{c_B} y_B + \cdots \tag{3.27}$$

$$T'_c = T_{c_A} y_A + T_{c_B} y_B + \cdots \tag{3.28}$$

where p'_c = pseudocritical pressure and T'_c = pseudocritical temperature. (It has also been found convenient in some problems to calculate similarly a weighted pseudo-ideal-critical volume V'_{ci}.) You can see that these are linearly weighted mole average pseudocritical properties. (In Sec. 3.7 we compare the true critical point of gaseous mixtures with the pseudocritical point.) Then the respective pseudo-reduced values are

$$p'_r = \frac{p}{p'_c} \tag{3.29}$$

$$T'_r = \frac{T}{T'_c} \tag{3.30}$$

If you are faced with a complicated mixture of gases whose composition is not well known, you still can estimate the pseudocritical constants from charts[12] such as shown in Fig. 3.8 (a) and (b) if you know the gas specific gravity. Figure 3.8 is good only for natural gases composed mainly of methane that contain less than 5% impurities (CO_2, N_2, H_2S, etc.).

Kay's method is known as a two-parameter rule since only p_c and T_c for each component are involved in the calculation of z. If a third parameter such as z_c, the Pitzer acentric factor, or $\hat{V}_{c_i}$ is included in the determination of the mean compressibility factor, then we would have a three-parameter rule. All the pseudocritical methods do not provide equal accuracy in predicting p–V–T properties, but most suffice for engineering work. Stewart et al.[13] reviewed 21 different methods of determining the pseudoreduced parameters by three-parameter rules (see Table 3.6). Although Kay's method was not the most accurate, it was easy to use and not consid-

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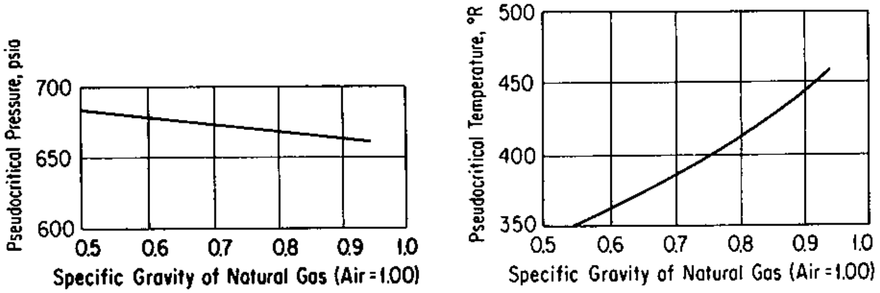
[11] You should still add Newton's corrections for H_2 and He.

[12] Natural Gasoline Supply Men's Association, *Engineering Data Book*, Tulsa, Okla., issued periodically.

[13] W. E. Stewart, S. F. Burkhart, and David Voo, paper given at the AIChE meeting in Kansas City, Mo., May 18, 1959. Also refer to A. Satter and J. M. Campbell, *Soc. Petrol. Engr. J.*, p. 333 (December 1963); and H. E. Barner and W. C. Quinlan, *I&EC Process Design and Development*, v. 8, p. 407 (1969).



(a) (b)

Figure 3.8 Estimation of critical properties of natural gases.

erably poorer than some of the more complex techniques of averaging critical properties.

In summary, we would have to state that no one method will consistently give the best results. Kay's pseudocritical method, on the average, will provide reasonable estimates, although other methods of greater accuracy (and of greater complexity) are available in the literature, as brought out in Table 3.6. All these methods begin to break down near the true critical point of the mixture and for highly polar compounds.

EXAMPLE 3.16 *p–V–T* Relations for Gas Mixture

A gaseous mixture has the following composition (in mole percent):

Methane, CH_4	20
Ethylene, C_2H_4	30
Nitrogen, N_2	50

at 90 atm pressure and 100°C. Compare the molal volume as computed by the methods of:

(a) the perfect gas law
(b) the van der Waals equation using averaged constants
(c) the mean compressibility factor and Dalton's law
(d) the mean compressibility factor and Amagat's law
(e) the pseudoreduced technique (Kay's method)

Solution

Basis: 1 g mol of gas mixture

Additional data needed are:

Component	$a(\text{atm})\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2$	$b\left(\frac{\text{cm}^3}{\text{g mol}}\right)$	T_c(K)	p_c(atm)
CH_4	2.25×10^6	42.8	191	45.8
C_2H_4	4.48×10^6	57.2	283	50.9
N_2	1.35×10^6	38.6	126	33.5

$$R = 82.06 \frac{(\text{cm}^3)(\text{atm})}{(\text{g mol})(\text{K})}$$

(a) Perfect gas law:

$$\hat{V} = \frac{nRT}{p} = \frac{1(82.06)(373)}{90} = 340 \text{ cm}^3 \text{ at 90 atm and 373 K}$$

TABLE 3.6 Prediction Of p–V–T Values Of Gas Density By Pseudocritical Methods

Method	Percent root-mean-square deviation of density, 35 systems	Percent root-mean-square deviation of density, CO_2 and H_2S free systems
(1) Three-parameter Kay's rule: $T'_c = \sum T_{c_i} y_i$ $p'_c = \sum p_{c_i} y_i$ $z'_c = \sum z_{c_i} y_i$	10.74	6.82
(2) Empirical: $T'_c = \sum T_{c_i} y_i$ $\frac{T'_c}{p'_c} = \sum \frac{T_{c_i} y_i}{p'_{c_i}}$ $\hat{V}'_c = \sum \hat{V}_{c_i} y_i$	6.06	5.85
(3) Virial approach (Joffe's method III): $\frac{\mathrm{T}'_c}{\mathrm{p}'_c} = \frac{1}{8} \sum_i \sum_j y_i y_j \left[\left(\frac{T_{c_i}}{p_{c_i}}\right)^{1/3} + \left(\frac{T_{c_j}}{p_{c_j}}\right)^{1/3} \right]$ $\frac{T'_c}{\sqrt{p'_c}} = \sum y_i \frac{T_{c_i}}{\sqrt{p_{c_i}}}$ $\hat{V}'_c = \sum \hat{V}_{c_i} y_i$	4.98	4.24
(4) *"Recommended" method* $\frac{T'_c}{p'_c} = \frac{1}{3} \sum y_i \frac{T_{c_i}}{p_{c_i}} + \frac{2}{3} \left[\sum y_i \left(\frac{T_{c_i}}{p_{c_i}}\right)^{1/2} \right]^2$ $\frac{T'_c}{\sqrt{p'_c}} = \sum y_i \frac{T_{c_i}}{\sqrt{p_{c_i}}}$ $z'_c = \sum z_{c_i} y_i$	4.32	3.26

(b) To use average constants in the van der Waals equation, write it in the following fashion:

$$V^3 - \left(\bar{b} + \frac{RT}{p}\right)nV^2 + \left(\frac{\bar{a}}{p}\right)n^2V - \frac{\bar{a}\bar{b}}{p}n^3 = 0$$

where $\bar{a}$ and $\bar{b}$ are the average constants.

$$(\bar{a})^{1/2} = 0.2a^{1/2}_{CH_4} + 0.3a^{1/2}_{C_2H_4} + 0.5a^{1/2}_{N_2}$$

$$\bar{a} = 2.30 \times 10^6 \text{ atm}\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2$$

$$\bar{b} = 0.2b_{CH_4} + 0.3b_{C_2H_4} + 0.5b_{N_2} = 45.0\frac{\text{cm}^3}{\text{g mol}}$$

$$n = 1 \text{ g mol (the basis)}$$

$$V^3 - \left[45.0 + \frac{(82.06)(373)}{90}\right]V^2 + \left[\frac{2.30 \times 10^6}{90}\right]V - \left[\frac{(2.30 \times 10^6)(45.0)}{90}\right] = 0$$

Let $V_0 = 340$ [based on (a) above]. You can solve the cubic equation by plotting it or by Newton's method (see the disk in the back of this book) to get $\hat{V} = 316$ cm³ at 90 atm and 373 K.

(c) The table below shows how Dalton's law can be used to estimate a mean compressibility factor.

Component	p_c(atm)	T_c(K)	y	$(90)y = p$	$p_r = \frac{p}{p_c}$	$T_r = \frac{373}{T_c}$
CH_4	45.8	191	0.2	18	0.393	1.95
C_2H_4	50.9	283	0.3	27	0.530	1.32
N_2	33.5	126	0.5	45	1.343	2.96

Component	z	$(z)(y)$
CH_4	0.99	0.198
C_2H_4	0.93	0.279
N_2	1.00	0.500
	z_{mean} =	0.977

Then

$$V = \frac{z_{mean}RT}{p} = \frac{0.977(82.06)(373)}{90}$$

$$= 332 \text{ cm}^3 \text{ at 90 atm and 373 K}$$

(d) Combining Amagat's law and the z factor,

Component	p_c(atm)	T_c(K)	y	$p_r = \frac{90}{p_c}$	$T_r = \frac{373}{T_c}$
CH_4	45.8	191	0.2	1.97	1.95
C_2H_4	50.5	283	0.3	1.78	1.32
N_2	33.5	126	0.5	2.69	2.96

Component	z	$(z)(y)$
CH_4	0.97	0.194
C_2H_4	0.75	0.225
N_2	1.01	0.505
	z_{mean} =	0.924

$$V = \frac{0.924(82.06)(373)}{90} = 314 \text{ cm}^3 \text{ at 90 atm and 373 K}$$

(e) According to Kay's method, we first calculate the pseudocritical values for the mixture by Eqs. (3.27) and (3.28).

$$\begin{aligned} & \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_4 \qquad\qquad C_2H_4 \qquad\qquad N_2 \\ p_c' &= p_{c_A}y_A + p_{c_B}y_B + p_{c_C}y_C = (45.8)(0.2) + (50.9)(0.3) + (33.5)(0.5) \\ &= 41.2 \text{ atm} \\ T_c' &= T_{c_A}y_A + T_{c_B}y_B + T_{c_C}y_C = (191)(0.2) + (283)(0.3) + (126)(0.5) \\ &= 186 \text{ K} \end{aligned}$$

Then we calculate the pseudo-reduced values for the mixture by Eqs. (3.29) and (3.30):

$$p_r' = \frac{p}{p_c'} = \frac{90}{41.2} = 2.18, \qquad T_r' = \frac{T}{T_c'} = \frac{373}{186} = 2.01$$

With the aid of these two parameters we can find from Fig. 3.7d that $z = 0.965$. Thus

$$V = \frac{zRT}{p} = \frac{0.965(82.06)(373)}{90} = 328 \text{ cm}^3 \text{ at 90 atm and 373 K}$$

EXAMPLE 3.17 Use of Pseudo-reduced Ideal Molal Volume

In instances where the temperature or pressure of a gas mixture is unknown, it is convenient, to avoid a trial-and-error solution using the generalized compressibility charts, to compute a pseudocritical ideal volume and a pseudoreduced ideal volume as illustrated below. Suppose we have given that the molal volume of the gas mixture in the preceding problem was 326 cm^3 at 90.0 atm. What was the temperature?

Solution

Basis: 326 cm^3 of gas at 90.0 atm and T K

Component	T_c (K)	p_c (atm)	y	yT_c	yp_c
CH_4	190.7	45.8	0.20	38.14	9.16
C_2H_4	283.1	50.5	0.30	84.93	15.15
N_2	126.2	33.5	0.50	63.10	16.75
Total				186.2	41.06

Note we have used mole fractions as weighting factors to find an average $T_c' = 186.2$ and $p_c' = 41.2$ as in Example 3.16. Next we compute $\hat{V}'_{c_i}$:

$$\hat{V}'_{c_i} = \frac{RT'_c}{p'_c} = \frac{82.06(186.2)}{41.06} = 372.1 \text{ cm}^3/\text{g mol}$$

$$V'_{r_i} = \frac{\hat{V}}{\hat{V}'_{c_i}} = \frac{326}{372.1} = 0.876$$

$$p'_r = \frac{p}{p'_c} = \frac{90.0}{41.06} = 2.19$$

From Fig. 3.7d or Fig. 3.8, $T'_r = 1.98$. Then

$$T = T'_c T'_r = 186.2(1.98) = 369 \text{ K}$$

Self-Assessment Test

1. One pound mole of a mixture containing 0.400 lb mol of N_2 and 0.600 lb mol C_2H_4 at 50°C occupies a volume of 1.44 ft^3. What is the pressure in the vessel? Compute your answer by:
   (a) Averaged constants for the van der Waals equation
   (b) The mean compressibility factor (assuming Dalton's law)
   (c) Kay's method

3.3 VAPOR PRESSURE AND LIQUIDS

Your objectives in studying this section are to be able to:

1. Define vapor pressure, triple point, equilibrium, dew point, bubble point, saturated, superheated, subcooled, and quality, and be able to locate the region or point in a p–T chart in which each term applies.
2. Calculate the vapor pressure of a substance from a vapor-pressure equation given values for the coefficients in the equation, and look up the vapor pressure in reference books.
3. Calculate the temperature of a substance from a vapor-pressure equation given the values for the coefficients in the equation, and the vapor pressure.

4. Calculate the properties of a wet mixture given the temperature, pressure, and volume of the mixture.
5. Prepare a Cox chart; calculate the scaling factors for each axis so that the chart can be used to predict the vapor pressure of a liquid.

The terms *vapor* and *gas* are used very loosely. A gas that exists below its critical temperature is usually called a vapor because it can condense. If you continually compress a pure gas at constant temperature, provided that the temperature is below the critical temperature, some pressure is eventually reached at which the gas starts to condense into a liquid. Further compression does not increase the pressure but merely increases the fraction of gas that condenses. A reversal of the procedure just described will cause the liquid to be transformed into the gaseous state again, (i.e., vaporize). From now on, the word **vapor** will be reserved to describe a gas below its critical point in a process in which the phase change is of primary interest, while the word **gas or noncondensable gas** will be used to describe a gas above the critical point or a gas in a process in which it cannot condense.

Vaporization and condensation at constant temperature and pressure are equilibrium processes, and the equilibrium pressure is called the vapor pressure. At a given temperature there is only one pressure at which the liquid and vapor phases of a pure substance may exist in equilibrium. Either phase alone may exist, of course, over a wide range of conditions.

You can understand vapor pressure, vaporization, and condensation more easily with the aid of Fig. 3.9. Figure 3.9 is an expanded *p–T* diagram for pure water. For each temperature you can read the corresponding pressure at which water vapor and water liquid exist in equilibrium. You have encountered this condition of equilibrium many times—for example, in boiling. Any substance has an infinite number of boiling points, but by custom we say the **"normal" boiling point** is the temperature at which boiling takes place under a pressure of 1 atm (101.3 kPa, 760 mm Hg). Unless another pressure is specified, 1 atm is assumed, and the term **boiling point** is taken to mean the "normal boiling point." A piston exerting a force of 101.3 kPa could just as well take the place of the atmosphere, as shown in Fig. 3.10. For example, you know that at 100°C water will boil (vaporize) and the pressure will be 101.3 kPa or 1 atm (point *B*). Suppose that you heat water starting at 77°C (point *A*) in a container as in Fig. 3.10—what happens? We assume that the water vapor is at all times in equilibrium with the liquid water. This is a constant-pressure process. As the temperature rises and the confining pressure stays constant, nothing particularly noticeable occurs until 100°C is reached, at which time the water begins to boil (i.e., evaporate). It pushes back the piston and will completely change from liquid into vapor. If you heated the water in an enclosed cylinder, and if after it had all evaporated at point *B* you continued heating the water vapor formed at constant pressure, you could apply the gas laws in the temperature region *B-C* (and at higher temperatures). A reversal of this process from the temperature *C* would cause the vapor to condense at *B* to form a liquid. The temperature at point *B* would in these circumstances represent the **dew point.**

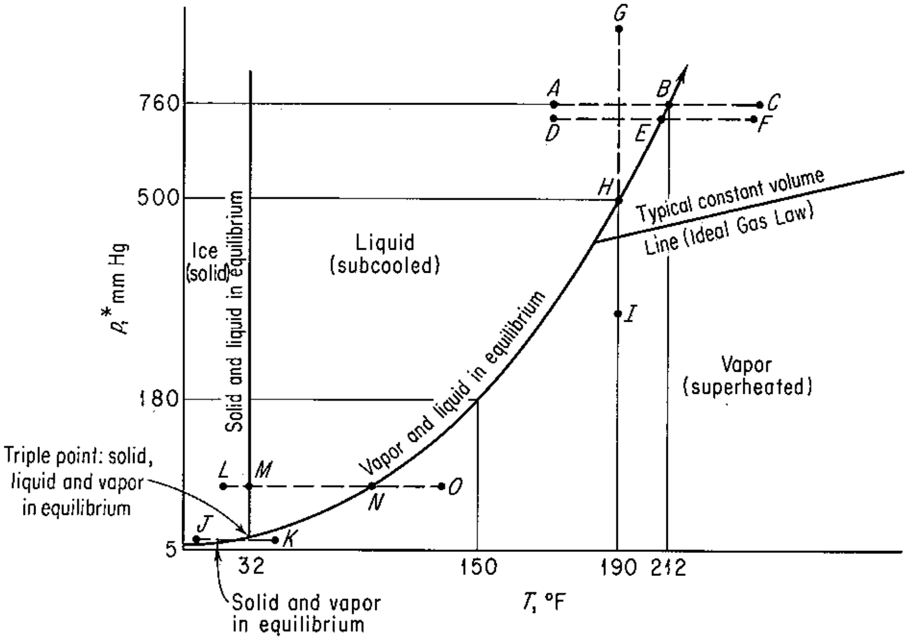


Figure 3.9 Vapor-pressure curve for water.

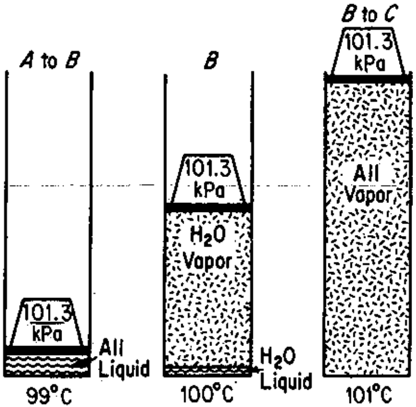


Figure 3.10 Transformation of liquid water into water vapor at constant pressure. The 101.3 kPa exerted by the piston includes the force of the atmosphere above the piston.

Suppose that you went to the top of Pikes Peak and repeated the experiment in the open air—what would happen then? Everything would be the same (points *D-E-F*) with the exception of the temperature at which the water would begin to boil, or condense. Since the pressure of the atmosphere at the top of Pikes Peak would presumably be lower than 101.3 kPa, the water would start to displace the air, or boil, at a lower temperature. You can see that (a) at any given temperature water exerts its vapor pressure (at equilibrium); (b) as the temperature goes up, the vapor pressure goes up; and (c) it makes no difference whether water vaporizes into air, into a cylinder closed by a piston, or into an evacuated cylinder—at any temperature it still exerts the same vapor pressure as long as the water is in equilibrium with its vapor.

A process of **vaporization or condensation at constant temperature** is illustrated by the lines *G–H–I* or *I–H–G*, respectively, in Fig. 3.9. Water would vaporize or condense at constant temperature as the pressure reached point *H* on the vapor-pressure curve (also look at Fig. 3.11.)

Figure 3.9 also shows the *p–T* conditions at which ice (in its common form) and water vapor are in equilibrium. When the solid passes directly into the vapor phase without first melting to become a liquid (line *J–K* as opposed to line *L–M–N–O*), it is said to **sublime.** Iodine crystals do this at room temperature; water sublimes only below 0°C, as when the frost disappears in the winter when the thermometer reads −6°C.

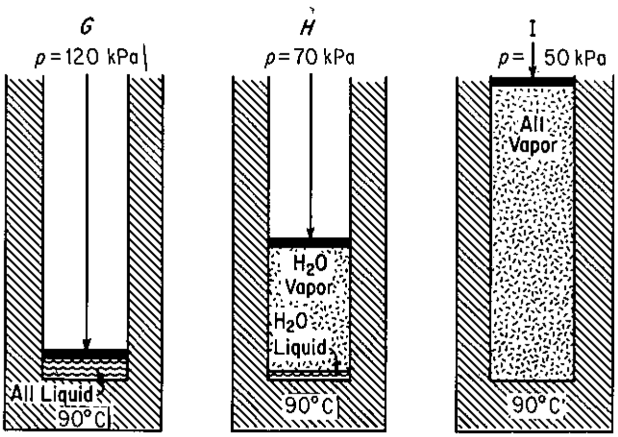


Figure 3.11 Transformation of liquid water into water vapor at constant temperature by changing the imposed pressure.

The vapor-pressure line extends well past the conditions shown in Fig. 3.9, all the way to the critical temperature and pressure (not shown). Why does it terminate at the critical temperature and pressure? Above the critical temperature, water can exist only as a gas.

A term commonly applied to the vapor–liquid portion of the vapor-pressure curve is the word **saturated, meaning the same thing as vapor and liquid in equilibrium** with each other. If a gas is just ready to start to condense its first drop of liquid, the gas is called a **saturated gas;** if a liquid is just about to vaporize, it is called a **saturated liquid.** These two conditions are also known as the **dew point** and **bubble point,** respectively.

The region to the right of the vapor-pressure curve in Fig. 3.9 is called the **superheated** region and the one to the left of the vapor-pressure curve is called the **sub-cooled** region. The temperatures in the superheated region, if measured as the difference (*O–N*) between the actual temperature of the superheated vapor and the saturation temperature for the same pressure, are called **degrees of superheat.** For example, steam at 500°F and 100 psia (the saturation temperature for 100 psia is 327.8°F) has (500 − 327.8) = 172.2°F of superheat. Another new term you will find used frequently is the word **quality.** A *wet* vapor consists of saturated vapor and saturated liquid in equilibrium. The mass fraction of vapor is known as the quality.

EXAMPLE 3.18 Vapor–Liquid Properties of Water

For each of the conditions of temperature and pressure listed below for water, state whether the water is a solid phase, liquid phase, vapor phase (superheated), or is a saturated mixture, and if the latter, calculate the quality. Use the steam tables (inside the back cover) to get your answers.

State	p (kPa)	T (K)	$\hat{V}$ (m^3/kg)
1	2000	475	—
2	1000	500	0.2206
3	101.3	200	—
4	245.6	400	0.505

Solution

State 1: liquid
State 2: vapor
State 3: solid
State 4: saturated vapor and liquid

The properties of a mixture of vapor and liquid in equilibrium (for a single component) can be computed from the individual properties of the saturated vapor and saturated liquid. At 400 K and 245.6 kPa with a specific volume of a wet steam mixture being 0.505 m^3/kg, what is the quality of the steam? From the steam tables the specific volumes of the saturated liquid and vapor are

$$\hat{V}_l = 0.001067 \text{ m}^3/\text{kg} \qquad \hat{V}_g = 0.7308 \text{ m}^3/\text{kg}$$

Basis: 1 kg of wet steam mixture

Let x = mass fraction vapor.

$$\frac{0.001067 \text{ m}^3}{1 \text{ kg liquid}}\left|\frac{(1-x)\text{kg liquid}}{}\right. + \frac{0.7308 \text{ m}^3}{1 \text{ kg vapor}}\left|\frac{x \text{ kg vapor}}{}\right. = 0.505 \text{ m}^3$$

$$0.001067 - 0.001067x + 0.7308x = 0.505$$

$$x = 0.69$$

Other properties of wet mixtures can be treated in the same manner.

3.3-1 Change of Vapor Pressure with Temperature

A large number of experiments on many substances have shown that a plot of the vapor pressure (p^*) of a compound against temperature does not yield a straight line but a curve, as you saw in Fig. 3.9. Many types of correlations have been proposed to transform this curve to a linear form ($y = mx + b$); a plot of ln (p^*) vs. ($1/T$), for moderate temperature intervals, is reasonably linear:

$$\underbrace{\ln (p^*)}_{y} \underset{=}{=} \underbrace{m\left(\frac{1}{T}\right) + b}_{mx + b} \tag{3.31}$$

Equation (3.31) is derived from the Clausius–Clapeyron equation (see Chap. 4). Empirical correlations of vapor pressure are frequently given in the form of the Antoine equation (refer to Appendix G for values of the constants):

$$\ln (p^*) = A - \frac{B}{T + C} \tag{3.32}$$

where A, B, C = constants different for each substance
T = temperature, K

Other more complex equations can be found in the sources cited in Tables 1.10 and 1.11 in Sec. 1.7 and the supplementary references at the end of this chapter.

As explained in Appendix M, you can estimate the values of the coefficients in Eq. (3.32) by the method of least squares. We look at another way, a graphical method. Over very wide temperature intervals experimental data will not prove to be exactly linear as indicated by Eq. (3.31), but have a slight tendency to curve. This curvature can be straightened out by using a special plot known as a Cox chart.[14] The ln or $\log_{10}$ of the vapor pressure of a compound is plotted against a special nonlinear temperature scale constructed from the vapor-pressure data for water (called a **reference substance**).

As illustrated in Fig. 3.12, the temperature scale is established as follows. First, you establish a logarithmic scale ($\log_{10}$ is easiest to use) as a horizontal axis to cover the desired range of vapor pressures. To get the special temperature scale with the desired labels for temperature in, say, common integers, such as 25, 50, 100, 200, and so on, you proceed as follows. For the first integer, say 100°F, you look up the vapor pressure of water at 100°F in the steam tables (Table C.1), namely 0.9487 psia. Locate this value on the vapor-pressure axis. Next, look up the vapor of water at, say, 200°F, namely 11.525 psia, and locate this value on the horizontal axis. You can compress or expand the temperature scale by adjusting the slope of the line you draw on the Cox chart for the vapor pressure of water. Draw a line with a slope so that it covers the desired range of temperatures. Proceed from 0.9487 psia on the horizontal axis vertically to the line you drew, and then proceed horizontally to the vertical (left-hand) axis. Make a tic mark labeled 100°F. Next, proceed from 11.525 psia on the vapor-pressure axis to the line you drew, and then go horizontally from the point so located to the vertical axis. Make a tic mark labeled 200°F. Continue as above to label the vertical axis with all the desired temperature labels. The vapor pressures of other substances plotted on this specially prepared set of coordinates will yield straight lines over extensive temperature ranges and thus facilitate the extrapolation and interpolation of vapor-pressure data. It has been found that lines so

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[14] E. R. Cox, *Ind. Eng. Chem.*, v. 15, p. 592 (1923).

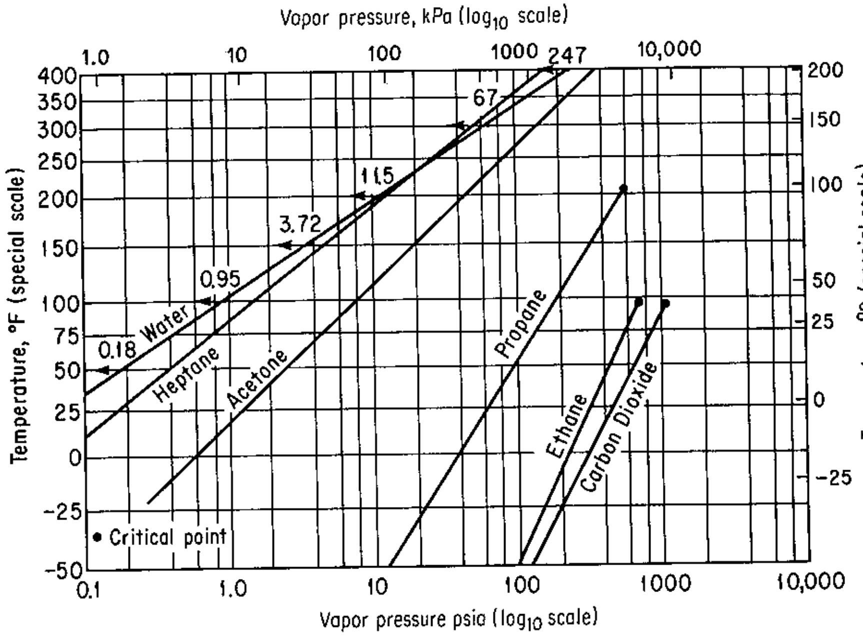

Figure 3.12 Cox chart.

constructed for closely related compounds, such as hydrocarbons, all meet at a common point. Since straight lines can be obtained on a Cox chart only two sets of vapor-pressure data are needed to provide complete information about the vapor pressure of a substance over a considerable temperature range. We discuss in Chap. 4 under the topic of the Clausius–Clapeyron equation other information that can be obtained from such vapor-pressure plots.

3.3-2 Change of Vapor Pressure with Pressure

The equation for the change of vapor pressure with total pressure at constant temperature in a system is

$$\left(\frac{\partial(p^*)}{\partial p_T}\right)_T = \frac{\hat{V}_l}{\hat{V}_g} \tag{3.33}$$

where $\hat{V}$ = molal volume of saturated liquid or gas
p_T = total pressure on the system

Under normal conditions the effect is negligible.

EXAMPLE 3.19 Extrapolation of Vapor-Pressure Data

The control of existing solvents is described in the *Federal Register*, v. 36, no. 158, August 14, 1971, under Title 42, Chapter 4, Appendix B, Section 4.0, Control of Organic Compound Emissions. Section 4.6 indicates that reductions of at least 85% can be accomplished by (a) incineration or (b) carbon adsorption.

Chlorinated solvents and many other solvents used in industrial finishing and processing, dry-cleaning plants, metal degreasing, printing operations, and so forth, can be recycled and reused by the introduction of carbon adsorption equipment. To predict the size of the adsorber, you first need to know the vapor pressure of the compound being adsorbed at the process conditions.

The vapor pressure of chlorobenzene is 400 mm Hg at 110.0°C and 5 atm at 205°C. Estimate the vapor pressure at 245°C and at the critical point (359°C).

Solution

The vapor pressures will be estimated by use of a Cox chart. See Fig. E3.19. The temperature scale is constructed by using the following data from the steam tables:

p^* H_2O(*psia*)	*t* (°F)
0.95	100
3.72	150
11.5	200
29.8	250
67.0	300
247	400
680	500
1543	600
3094	700

Vapor pressures from 3.72 to 3094 psia are marked on the horizontal logarithmic scale as shown in Fig. E3.19. We selected the vapor pressures to correspond to even values of the temperature in °F.

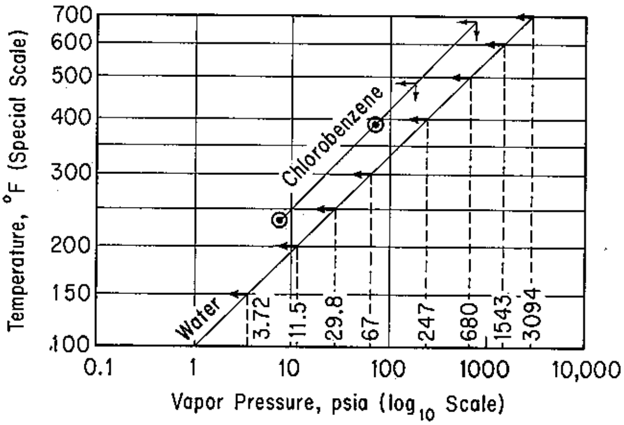

Figure E3.19

Next, we draw a line representing the vapor pressure of water at any suitable angle on the graph so as to stretch the desired temperature range from the bottom to the top of the vertical axis. For each vapor pressure, the temperature is marked and a horizontal line drawn to the ordinate. This establishes the temperature scale (which looks almost logarithmic in nature).

Next we convert the two vapor pressures of chlorobenzene into psia,

$$\begin{array}{l|l} 400\text{ mm Hg} & 14.7\text{ psia} \\ \hline & 760\text{ mm Hg} \end{array} = 7.74\text{ psia} \qquad 110^\circ\text{C} = 230^\circ\text{F}$$

$$\begin{array}{l|l} 5\text{ atm Hg} & 14.7\text{ psia} \\ \hline & 1\text{ atm Hg} \end{array} = 73.5\text{ psia} \qquad 205^\circ\text{C} = 401^\circ\text{F}$$

and plot these two points on the graph paper. Examine the encircled dots. Next we draw a straight line between the encircled points and extrapolate to 471°F (245°C) and 678°F (359°C). At these two temperatures read off the estimated vapor pressures:

	471°F(245°C)	678°F(359°C)
Estimated:	150 psia	700 psia
Experimental:	147 psia	666 psia

Experimental values are given for comparison.

An alternative way to extrapolate vapor pressure data would be to use the Othmer[15] plot as explained in Sec. 4.4, or to fit a vapor pressure equation, $p^* = f(T)$, from experimental data.

3.3-3 Liquid Properties

Considerable experimental data are available for liquid densities of pure compounds as a function of temperature and pressure. Refer to the sources listed in Tables 1.10 and 1.11 or the supplementary reference to this chapter for data and correlation formulas. Wooley[16] gives formulas (and a computer program) to estimate the liquid density given T_c, p, and ω, and/or any liquid density reference point.

As to liquid mixtures, it is even more difficult to predict the p–V–T properties of liquid mixtures than of real gas mixtures. Probably more experimental data (especially at low temperatures) are available than for gases, but less is known about the estimation of the p–V–T properties of liquid mixtures. For compounds with like molecular structures, such as hydrocarbons of similar molecular weight, called *ideal liquids*, the density of a liquid mixture can be approximated by assuming that the specific volumes are additive:

$$\hat{V}_{\text{average}} = \hat{V}_1 + \hat{V}_2 + \cdots + \hat{V}_n = \sum_{i=1}^{n} \hat{V}_i \qquad (3.34)$$

where n is the number of components in the mixture. For *nonideal liquids* or solids dissolved in liquids, experimental data or estimation techniques described in many of the references listed in Sec. 1.7 and 4.3 must be employed, as the specific volumes are not additive. Corresponding state methods are usually used, but with less assurance than for gas mixtures.[17,18]

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[15] D. F. Othmer and E. S. Yu, *Indus. Eng. Chem.*, v. 60, p. 20 (1968).

[16] R. J. Wooley, *Chem. Eng.*, p. 109 (March 31, 1986).

[17] N. Shah and C. L. Yaws, "Densities of Liquids," *Chem. Eng.*, p. 131 (October 25, 1976).

[18] V. K. Mathur and R. N. Maddox, "Liquid Density Correlations," *Indian Chem. Eng.*, v. 18, no. 2, p. 29 (1976).

Self-Assessment Test

1. Draw a *p–T* chart for water. Label the following clearly: vapor-pressure curve, dew-point curve, saturated region, superheated region, subcooled region, and triple point. Show where evaporation, condensation, and sublimation take place by arrows.
2. Describe the state and pressure conditions of water initially at 20°F as the temperature is increased to 250°F in a fixed volume.
3. Look in Appendix J at the diagram for CO_2 (Fig. J.2).
   (a) At what pressure is CO_2 solid in equilibrium with CO_2 liquid and vapor?
   (b) If the solid is placed in the atmosphere, what happens?
4. Use the Antoine equation to calculate the vapor pressure of ethanol at 50°C, and compare with the experimental value.
5. Determine the normal boiling point for benzene from the Antoine equation.
6. Prepare a Cox chart from which the vapor pressure of toluene can be predicted over the temperature range −20 to 140°C.

Thought Problems

1. In the startup of a process, Dowtherm, an organic liquid with a very low vapor pressure, was being heated from room temperature to 335°F. The operator suddenly noticed that the gauge pressure was not the expected 15 psig but instead was 125 psig. Fortunately, a relief valve in the exit line ruptured into a vent (expansion) tank so that a serious accident was avoided.

   Why was the pressure in the exit line so high?

2. A cylinder containing butadiene exploded in a research laboratory, killing one employee. The cylinder had been used to supply butadiene to a pilot plant. When butadiene gas was required, heat was supplied to the cylinder to raise the pressure of the butadiene in the tank. The maximum temperature that could be achieved in the tank on subsequent tests with a like tank was 160°C. At 152°C, the critical temperature for butadiene, the pressure is 628 $\text{lb}_f/\text{in.}^2$, less than one-half of the pressure required to rupture the tank by hydraulic test.

   Why did the tank explode?

3. **"Careless Campers Contaminate Mountain Water"** was a recent headline in the newspaper. The article went on:

> Beware! There are little monsters loose in those seemingly clean, pristine mountain streams. Their name: *Giardia,* and of specific interest to humans and pigs, *Giardia lamblia. Giardia* is a beet-shaped organism with no less than eight flagella. It is of concern to anyone who happens to slurp any down because it attaches itself by means of a sucking organism to the intestinal mucous membranes. The result is severe diarrhea, bordering on dysentery.
>
> The incidence of giardia in the wilderness areas of New Mexico and Colorado has vastly increased over the past five years. The disease it causes, giardiasis, is contracted by drinking water containing the organism. Unfortunately for all backpackers, horse packers, and day hikers, many of the lakes and streams are already tainted. No problem, you say—just drop in a chemical purification tablet and let it do the job? While chemical purification such as Halazone, iodine, or chlorine may kill many bacteria, the hale and hearty giardia goes unscathed.

What steps would you take to avoid the problem other than carrying a portable water supply with you? You need at least 210°F to kill the organisms by boiling water.

3.4 SATURATION AND EQUILIBRIA

Your objectives in studying this section are to be able to:

1. Define saturated gas.
2. Calculate the partial pressure of the components of a saturated ideal gas given combinations of the temperature, pressure, volume and/or number of moles present; or calculate the partial volume; or calculate the number of moles of vapor.
3. Determine the condensation temperature of the vapor in a saturated gas given the pressure, volume, and/or number of moles.
4. Use the relationship $K_i = y_i/x_i$ to calculate any one of the parameters given the other two.

In this section we discuss two categories of phase phenomena for:

1. An equilibrium mixture of pure vapor and a noncondensable gas
2. An equilibrium mixture of two (or more) components both of which can condense and vaporize

3.4-1 Vapor and a Noncondensable Gas at Equilibrium

How can you predict the properties of a mixture of a *pure vapor* (which can condense) *and a noncondensable gas* at equilibrium? A mixture containing a vapor behaves somewhat differently than does a pure component by itself. A typical example with which you are quite familiar is that of water vapor in air.

Water vapor is a gas, and like all gases its molecules are free to migrate in any direction. They will do so as long as they are not stopped by the walls of a container. Furthermore, the molecules will distribute themselves evenly throughout the entire volume of the container.

When any pure gas (or a gaseous mixture) comes in contact with a liquid, the gas will acquire vapor from the liquid. If contact is maintained for a considerable length of time, vaporization continues until equilibrium is attained, at which time the *partial pressure of the vapor in the gas will equal the vapor pressure* of the liquid at the temperature of the system. Regardless of the duration of contact between the liquid and gas, after equilibrium is reached no more net liquid will vaporize into the gas phase. The gas is then said to be **saturated** with the particular vapor at the given temperature. We can also say that the gas mixture is at its dew point. **Dew point for the mixture of pure vapor and noncondensable gas means the temperature at which the vapor just starts to condense when cooled at constant pressure.**

Now, what do these concepts mean with respect to the quantitative measurement of gas–vapor properties. Suppose that you inject liquid water at 65°C into a cylinder of air at the same temperature, and keep the system at a constant temperature of 65°C. The pressure at the top of the cylinder will be maintained at 101.3 kPa (1 atm). What happens to the volume of the cylinder as a function of time? Figure 3.13 shows that the volume of the air plus the water vapor increases until the air is saturated with water vapor, after which stage the volume remains constant. Figure 3.14(a) indicates how the partial pressure of the water vapor increases with time until it reaches its vapor pressure of 24.9 kPa (187 mm Hg). Why does the partial pressure of the air decrease?

Next, suppose that you carry out a similar experiment, but maintain the volume constant and let the total pressure vary in the cylinder. Will the pressure go up

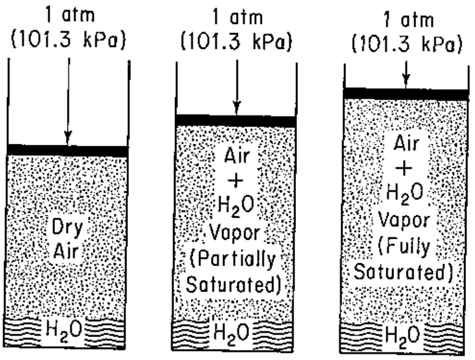
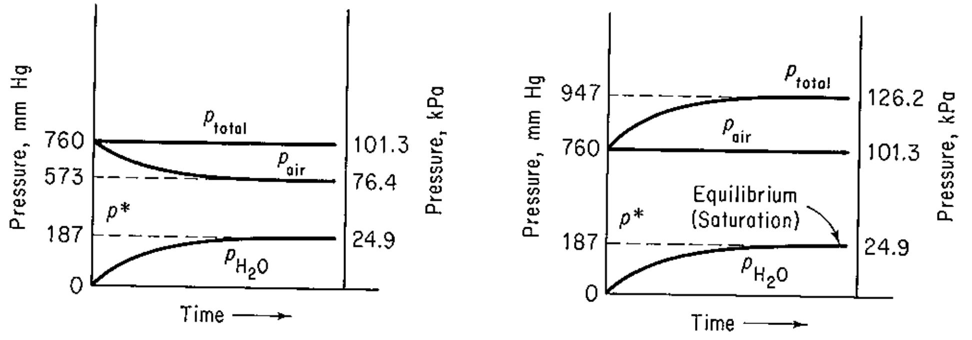


Figure 3.13 Evaporation of water at constant pressure and temperature of 65°C.



Constant Temperature
and Total Pressure
(Variable Volume)
(a)

Constant Temperature
and Volume
(Variable Pressure)
(b)

Figure 3.14 Change of partial and total pressures on vaporization of water into air at constant temperature: (a) constant temperature and pressure (variable volume); (b) constant temperature and volume (variable pressure).

or down with respect to time? What will be the asymptotic value of the partial pressure of the water vapor? The air? Look at Fig. 3.14(b) to see if your answers to these questions were correct.

Finally, is it possible to have the water evaporate into air and saturate the air, and yet maintain both a constant temperature, volume, and pressure in the cylinder? (*Hint:* What would happen if you let some of the gas-vapor mixture escape from the cylinder?)

Assuming that the ideal gas laws apply to both air and water vapor, as they do with excellent precision, we can say that the following relations hold *at saturation:*

$$\frac{p_{\text{air}}V}{p_{\text{H}_2\text{O}}V} = \frac{n_{\text{air}}RT}{n_{\text{H}_2\text{O}}RT}$$

or

$$\frac{p_{\text{air}}}{p_{\text{H}_2\text{O}}} = \frac{n_{\text{air}}}{n_{\text{H}_2\text{O}}} = \frac{p_{\text{air}}}{p_{\text{total}} - p_{\text{air}}} \tag{3.35}$$

in a volume V at temperature T.

EXAMPLE 3.20 Saturation

What is the minimum number of cubic meters of dry air at 20°C and 100 kPa that are necessary to evaporate 6 kg of ethyl alcohol if the total pressure remains constant at 100 kPa? Assume that the air is blown through the alcohol to evaporate it in such a way that the exit pressure of the air–alcohol mixture is at 100 kPa.

Solution

See Fig. E3.20. Assume that the process is isothermal. The additional data needed are

$$p^*_{\text{alcohol}} \text{ at } 20°\text{C} = 5.93 \text{ kPa}$$

$$\text{mol. wt. ethyl alcohol} = 46.07$$

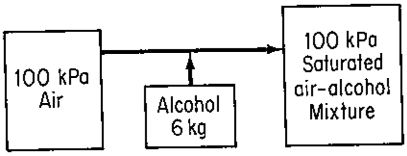


Figure E3.20

The minimum volume of air calls for a saturated mixture; any condition less than saturated would require more air.

Basis: 6 kg of alcohol

The ratio of moles of ethyl alcohol to moles of air in the final gaseous mixture is the same as the ratio of the partial pressures of these two substances. Since we know the moles of alcohol, we can find the number of moles of air:

$$\frac{p^*_{\text{alcohol}}}{p_{\text{air}}} = \frac{n_{\text{alcohol}}}{n_{\text{air}}}$$

From Dalton's law,

$$p_{\text{air}} = p_{\text{total}} - p^*_{\text{alcohol}}$$

$$p^*_{\text{alcohol}} = 5.93 \text{ kPa}$$

$$p_{\text{air}} = (100 - 5.93) \text{ kPa} = 94.07 \text{ kPa}$$

$$\begin{array}{l|l|l} 6 \text{ kg alcohol} & 1 \text{ kg mol alcohol} & 94.07 \text{ kg mol air} \\ \hline & 46.07 \text{ kg alcohol} & 5.93 \text{ kg mol alcohol} \end{array}$$

$$\begin{array}{|l|l|l} 22.4 \text{ m}^3 & 293 \text{ K} & 101.3 \text{ kPa} \\ \hline 1 \text{ kg mol} & 273 \text{ K} & 100 \text{ kPa} \end{array} = 50.3 \text{ m}^3 \text{ air at } 20°\text{C and } 100 \text{ kPa}$$

EXAMPLE 3.21 Saturation

A telescopic gas holder contains 10,000 ft^3 of gas saturated with water vapor at 80°F and a pressure of 6.0 in. H_2O above atmospheric. The barometer reads 28.46 in. Hg. Calculate the weight of water vapor in the gas.

Solution

The total pressure of the saturated gas must be calculated first, say, in inches of mercury. See Fig. E3.21.

$$\begin{array}{l|l|l} 6.0 \text{ in. } H_2O & 1 \text{ ft.} & 29.92 \text{ in. Hg} \\ \hline & 12 \text{ in.} & 33.91 \text{ ft } H_2O \end{array} = 0.44 \text{ in. Hg}$$

$$\text{barometer} = \underline{28.46} \text{ in. Hg}$$

$$p_{\text{total}} = 28.90 \text{ in. Hg}$$

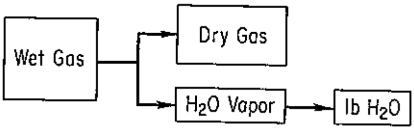


Figure E3.21

From the steam tables,

$$p^*_w = \text{vapor pressure of } H_2O \text{ at } 80°\text{F} = 1.032 \text{ in. Hg}$$

$$p_g = p_t - p^*_w$$

$$= 28.90 - 1.032 = 27.87$$

There exists

10,000 ft^3 wet gas at 28.90 in. Hg and 80°F
10,000 ft^3 dry gas at 27.87 in. Hg and 80°F
10,000 ft^3 water vapor at 1.032 in. Hg and 80°F

$$°\text{R} = 80 + 460 = 540°\text{R}$$

From the volume of water vapor present at known conditions, you can calculate the volume at S.C. and hence the pound moles and finally the pounds of water.

Basis: 10,000 ft^3 of water vapor at 1.032 in. Hg and 80°F

$$\frac{10{,}000\ \text{ft}^3\ \text{H}_2\text{O vapor}}{}\left|\frac{492°\text{R}}{540°\text{R}}\right|\frac{1.032\ \text{in. Hg}}{29.92\ \text{in. Hg}}\left|\frac{1\ \text{lb mol}}{359\ \text{ft}^3}\right|\frac{18\ \text{lb H}_2\text{O}}{1\ \text{lb mol H}_2\text{O}} = 15.8\ \text{lb H}_2\text{O}$$

EXAMPLE 3.22 Smokestack Emission and Pollution

A local pollution-solutions group has reported the Simtron Co. boiler plant as being an air polluter and has provided as proof photographs of heavy smokestack emissions on 20 different days in January and February. As the chief engineer for the Simtron Co., you know that your plant is not a source of pollution because you burn natural gas (essentially methane) and your boiler plant is operating correctly. Your boss believes the pollution-solutions group has made an error in identifying the stack—it must belong to the company next door that burns coal. Is he correct? Is the pollution-solutions group correct? See Fig. E3.22a.

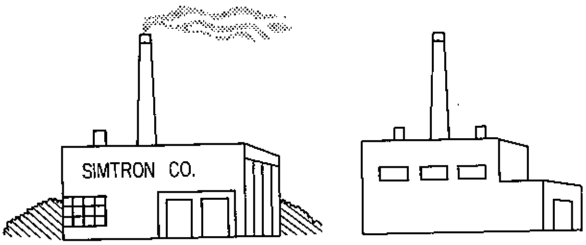


Figure E3.22a

Solution

Methane (CH_4) contains 2 kg mol of H_2 per kilogram mole of C, while coal (see references in Section 1.7) contains 71 kg of C per 5.6 kg of H_2 in 100 kg of coal. The coal analysis is equivalent to

$$\frac{71\ \text{kg C}}{}\left|\frac{1\ \text{kg mol C}}{12\ \text{kg C}}\right. = 5.92\ \text{kg mol C} \qquad \frac{5.6\ \text{kg H}_2}{}\left|\frac{\text{kg mol H}_2}{2.016\ \text{kg H}_2}\right. = 2.78\ \text{kg mol H}_2$$

or a ratio of 2.78/5.92 = 0.47 kg mol of H_2/kg mol of C. Suppose that each fuel burns with 40% excess air and that combustion is complete. We can compute the mole fraction of water vapor in each stack gas.

Steps 1, 2, and 3 The process is shown in Fig. E3.22b.

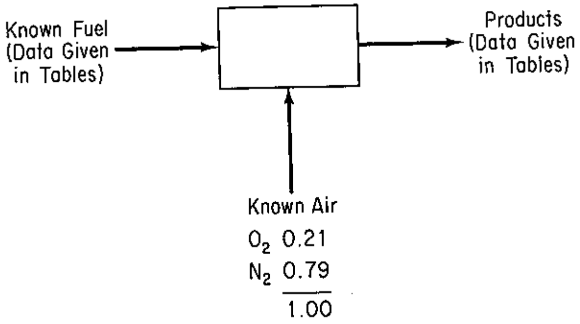


Figure E3.22b

Step 4

Basis: 1 kg mol C

Steps 5 and 6 The combustion problem is a standard type of problem having a unique solution in which both the fuel and air flows are given, and the product flows are calculated directly.

Steps 7, 8, and 9 Tables will make the analysis and calculations compact.

Natural Gas

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

		Composition of combustion gases (kg mol)			
Components	kg mol	CO_2	H_2O	Excess O_2	N_2
C	1.0	1.0			
H_2	2.0		2.0		
Air				0.80	10.5
Total		1.0	2.0	0.80	10.5

Required O_2: 2

Excess O_2: $2(0.40) = 0.80$

N_2: $(2.80)(79/21) = 10.5$

The total kilogram moles of gas produced are 14.3 and the mole fraction H_2O is

$$\frac{2.0}{14.3} = 0.14$$

Coal

$$C + O_2 \longrightarrow CO_2 \qquad H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

		Composition of gas produced (kg mol)			
Components	*kg mol*	CO_2	H_2O	Excess O_2	N_2
C	1	1			
H_2	0.47		0.47		
Air				0.49	6.5
Total		1	0.47	0.49	6.5

Required O_2: $1 + 0.47(1/2)$

$$\text{Excess } O_2: \quad \overset{C}{\overline{1(0.40) = 0.40}} \; \overset{H_2}{\overline{(0.47)(1/2)(0.40) = 0.094}}$$

N_2: $1.40(79/21)[1 + 0.47(1/2)] = 6.50$

The total kilogram moles of gas produced are 8.46 and the mole fraction H_2O is

$$\frac{0.47}{8.46} = 0.056$$

If the barometric pressure is, say, 100 kPa, the stack gas would become saturated and water vapor would start to condense at p^*:

	Natural gas	*Coal*
Pressure:	100(0.14) = 14 kPa	100(0.056) = 5.6 kPa
Equivalent temperature:	52.5°C	35°C

By mixing the stack gas with air, and by convective mixing above the stack, the mole fraction water vapor is reduced, and hence the condensation temperature is reduced. However, for equivalent dilution, the coal-burning plant will always have a lower condensation temperature. Thus, on cold winter days, the condensation of water vapor will occur more often and to a greater extent from power plants firing natural gas than from those using other fuels.

The public, unfortunately, sometimes concludes that all the emissions they perceive are pollution. Natural gas could appear to the public to be a greater pollutant than either oil or coal when, in fact, the emissions are just water vapor. The sulfur content of coal and oil can be released as sulfur dioxide to the atmosphere, and the polluting capacities of coal and oil are much greater than natural gas when all three are being burned properly. The sulfur contents as delivered to the consumers are as follows: natural gas, $4 \times 10^{-4}\%$ (as added mercaptans); number 6 fuel oil, up to 2.6%; and coal, from 0.5 to 5%. In addition, coal may release particulate matter into the stack plume.

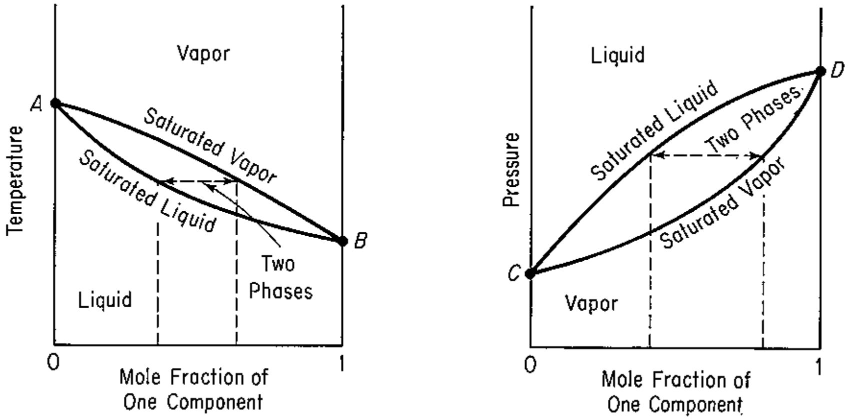
What additional steps would you take to resolve the questions that were originally posed?

3.4-2 Vapor-Liquid Equilibria for Multicomponent Systems

In a two-phase vapor–liquid mixture at equilibrium, if all the components can vaporize and condense, a component in one phase is in equilibrium with the same component in the other phase. The equilibrium relationship depends on the temperature and pressure, and perhaps composition, of the mixture. Figure 3.15 illustrates two cases, one at constant pressure and the other at constant temperature. At the pairs of points A and B, and C and D, the respective pure components exert their respective vapor pressures at the equilibrium temperature. In between the pairs of points, as the overall composition of the mixture changes, two phases exist, each having a different composition for the same component as indicated by the dashed lines. Two useful linear ("ideal") equations exist to relate the mole fraction of one component in the vapor phase to the mole fraction of the same component in the liquid phase.

Raoult's law. Used primarily for a component whose mole fraction approaches unity or for solutions of components quite similar in chemical nature, such as straightchain hydrocarbons. Let the subscript i denote component, p_i be the partial pressure of component i in the gas phases, y_i be the gas-phase mole fraction, and x_i be the liquid-phase mole fraction. Then:

$$p_i = p_i^* x_i \tag{3.36}$$



(a) Constant Pressure (b) Constant Temperature

Figure 3.15 Vapor-liquid equilibria for a binary mixture. The dashed lines show the equilibrium compositions (a) when the total pressure is constant and (b) when the temperature is constant over the composition range.

Note that in the limit where $x_i \equiv 1$, $p_i \equiv p_i^*$. Often an equilibrium constant K_i is defined from Eq. (3.36) as follows by assuming that Dalton's law applies to the gas phase ($p_i = p_t y_i$):

$$K_i = \frac{y_i}{x_i} = \frac{p_i^*}{p_t} \tag{3.37}$$

Henry's law. Used primarily for a component whose mole fraction approaches zero, such as a dilute gas dissolved in a liquid:

$$p_i = H_i x_i \tag{3.38}$$

where H_i is the *Henry's law constant*. Note that in the limit where $x_i \equiv 0$, $p_i \equiv 0$. What would be the equilibrium constant K_i based on Henry's law if Dalton's law applied to the gas phase? Values of H_i can be found in Perry and many other handbooks.

Equation (3.37) gives reasonable estimates of K_i values at low pressures for components well below their critical temperatures, but yields values too large for components above their critical temperatures, at high pressures, and/or for polar compounds. Nevertheless, Eq. (3.37) can be adapted to nonideal mixtures if K_i is made a function of temperature, pressure, and composition so that relations for K_i can be fit by experimental data and used directly, or in the form of charts, for design calculations. In the absence of experimental data, as with compressibility, three different techniques are used to estimate K_i values for nonideal vapor–liquid mixtures:

1. Equations of state
2. Activity coefficient methods
3. Group contribution methods

Refer to Prausnitz et al.[19] or the references in Sec. 1.7 for data to calculate K_i. If $T_{c,i}/T > 1.2$, Sandler[20] recommends the following empirical correlation:

$$K_i = \frac{p_{c,i}^{[7.224-7.534/T_{r,i}-2.598\ln T_{r,i}]}}{p_t} \tag{3.39}$$

Typical problems you may be asked to solve that involve the use of the equilibrium coefficient K_i are:

- **(a)** Calculate the bubble point temperature of a liquid mixture given the total pressure and liquid composition.
- **(b)** Calculate the dew point temperature of a vapor mixture given the total pressure and vapor composition.
- **(c)** Calculate the related equilibrium vapor–liquid compositions over the range of mole fractions from 0 to 1 as a function of temperature given the total pressure.

Analogous problems occur with respect to calculating the total pressure given a fixed temeprature. Also:

- **(d)** Calculate the composition of the vapor and liquid streams, and their respective quantities, when a liquid of given composition is partially vaporized (flashed) at a given temperature and pressure (the temperature must lie between the bubble and dewpoint temperatures of the feed).

To calculate the **bubble point temperature** (given the total pressure and liquid composition), you can write Eq. (3.37) as $y_i = K_i x_i$ and you know that $\Sigma\, y_i = 1$. Consequently, you want to solve the equation

$$1 = \sum_{i=1}^{n} K_i x_i \tag{3.40}$$

in which the K_i's are functions of solely the temperature. Because each of the K_i's increases with temperature, Eq. (3.40) has only one positive root. You can employ Newton's method to get the root (see Appendix L) if you can express each K_i as an explicit function of temperature. For an ideal solution, Eq. (3.40) becomes

$$p_t = \sum_{i=1}^{n} p_i^* x_i \tag{3.41}$$

and you might use Antoine's equation for p_i^*. Once the bubble point temperature is determined, the vapor composition can be calculated from

$$y_i = \frac{p_i^* x_i}{p_t}$$

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[19] J. M. Prausnitz, *Computer Calculations for Multicomponent Vapor–Liquid and Liquid-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, N.J., 1980.

[20] S. I. Sandler, in *Foundations of Computer Aided Design*, Vol. 2, R. H. S. Mah and W. D. Seider, eds., p. 83, American Institute of Chemical Engineers, New York, 1981.

To calculate the **dew point temperature** (given the total pressure and vapor composition), you can write Eq. (3.37) as $x_i = y_i/K_i$, and you know $\Sigma\, x_i = 1$. Consequently, you want to solve the equation

$$1 = \sum_{i=1}^{n} \frac{y_i}{K_i} \tag{3.42}$$

in which the K's are functions of temperature as explained for the bubble point temperature calculation. For an ideal solution,

$$1 = p_t \sum_{i=1}^{n} \frac{y_i}{p_i^*} \tag{3.43}$$

To calculate the amount of the respective vapor and liquid phases that evolve at equilibrium when a liquid of known composition flashes (**flash vaporization**) at a known temperature and pressure, you must use Eq. (3.37) together with a material balance. Figure 3.16 illustrates the steady-state process. A mole balance for component i gives

$$Fx_{F_i} = Lx_i + Vy_i \tag{3.44}$$

where F is the moles of liquid to be flashed, L is the moles of liquid at equilibrium, and V is the moles of vapor at equilibrium. Introduction of $y_i = K_i x_i$ into Eq. (3.44) gives

$$Fx_{F_i} = L\left(\frac{y_i}{K_i}\right) + Vy_i$$

so that

$$y_i = \frac{Fx_{F_i}}{\dfrac{L}{K_i} + (F - L)} = \frac{x_{F_i}}{1 - \dfrac{L}{F}\left(1 - \dfrac{1}{K_i}\right)} \tag{3.45}$$

where L/F is the fraction of liquid formed on vaporization. Consequently, after summing the y_i's you want to solve the following equation

$$1 = \sum_{i=1}^{n} \frac{x_{F_i}}{1 - \dfrac{L}{F}\left(1 - \dfrac{1}{K_i}\right)} \tag{3.46}$$

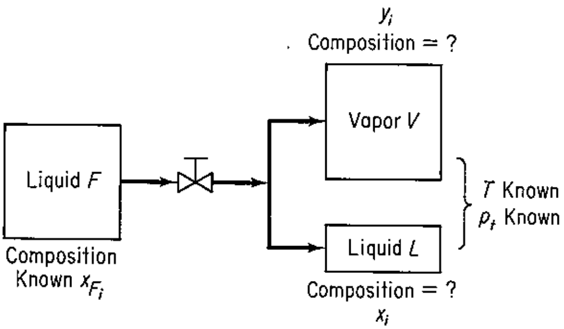

Figure 3.16 Flash vaporization with V and L in equilibrium.

for L/F (>0). Numerous computer programs have been reported in the literature to solve the flash vaporization problem.

Using the above equations, you can prepare figures such as Fig. 3.15 for binary mixtures.

The equations above are not the only formulations in which vapor–liquid calculations are conducted. For example, for the bubble point calculation, an equation equivalent to Eq. (3.40) would be

$$\ln \sum_{i=1}^{n} K_i x_i = 0$$

and an equation equivalent to Eq. (3.46) would be

$$\sum_{i=1}^{n} \frac{x_{F_i}(K_i - 1)}{(K_i - 1)(V/F) + 1} = 0$$

In selecting a particular form of the equation to be used for phase equilibria calculations, you must select a method of solving the equation that has desirable convergence characteristics. Convergence to the solution should

- **(a)** Lead to the desired root if the equation has multiple roots
- **(b)** Be stable, that is, approach the desired root asymptotically rather than by oscillating
- **(c)** Be rapid, and not become slower as the solution is approached

3.4-3 Liquid-Liquid and Liquid-Solid Equilibria for Multicomponent Systems

Liquid-liquid equilibria are treated essentially in the same way as nonideal vapor-liquid equilibria with activity-coefficient corrections in both phases. For liquid-solid equilibria, engineers rely almost entirely on recorded experimental data, as prediction of the liquid-phase composition is quite difficult. Refer to Prausnitz et al. for more information.

EXAMPLE 3.23 Vapor–Liquid Equilibrium Calculation

Suppose that a liquid mixture of 4.0% *n*-hexane and *n*-octane is vaporized. What is the composition of the vapor formed if the total pressure is 1 atm?

Solution

What the problem asks for is: What is the composition of the first vapor formed at equilibrium with $x_{C_6} = 0.040$ and a pressure of 1 atm? Examine Fig. 3.16a. The mixture can be treated as an ideal mixture because the components are quite similar. As an intermediate step, you must calculate the bubble point temperature by Eq. (3.41). You have to look up the coefficients of the Antoine equation to obtain the vapor pressures of the two components:

$$\ln(p^*) = A - \frac{B}{C + T}$$

where p^* is in mm Hg and T is in K:

	A	B	C
n-hexane (C_6):	15.8737	2697.55	−48.784
n-octane (C_8):	15.9798	3127.60	−63.633

Basis: 1 kg mol of liquid

We need to solve the following equation to get the bubble point temperature using one of the techniques described in Sec. L.2:

$$760 = \exp\left(15.8737 - \frac{2697.55}{-48.784 + T}\right)0.040 + \exp\left(15.9787 - \frac{3127.60}{-63.633 + T}\right)0.960$$

The solution is $T = 393.3$ K, where the vapor pressure of a hexane is 3114 mm Hg and the vapor pressure of octane is 661 mm Hg.

$$y_{C_6} = \frac{p^*_{C_6}}{p_t} x_{C_6} = \frac{3114}{760}(0.040) = 0.164$$

$$y_{C_8} = 1 - 0.164 = 0.836$$

EXAMPLE 3.24 Flash Calculation

Calculate the fraction of liquid that exists at equilibrium at 150°F and 50 psia when the liquid concentrations of the solution to be vaporized are as follows:

Component	Initial liquid mole fraction	K
C_2	0.0079	16.20
C_3	0.1321	5.2
i-C_4	0.0849	2.6
n-C_4	0.2690	1.98
i-C_5	0.0589	0.91
n-C_5	0.1321	0.72
C_6	0.3151	0.28
Total	1.0000	

The K values come from the *Engineering Data Book* of the Gas Processors Supply Association (1980).

Solution

We want to solve Eq. (3.46) for L/F. Start with an initial guess of $L/F = 1.0$. Successive stages of the iteration by Newton's method give

Stage	L/F	
1	1.0	
2	0.8565	
3	0.6567	
4	0.5102	
5	0.4573	
6	0.4511	which is sufficiently accurate

Self-Assessment Test

1. What does the term "saturated gas" mean?
2. If a container with a volumetric ratio of air to liquid water of 5 is heated to 60°C and equilibrium is reached, will there still be liquid water present? at 125°C?
3. A mixture of air and benzene contains 10 mole % benzene at 43°C and 105 kPa pressure. At what temperature does the first liquid form? What is the liquid?
4. The dew point of water in atmospheric air is 82°F. What is the mole fraction of water vapor in the air if the barometric pressure is 750 mm Hg?
5. Ten pounds of $KClO_3$ is completely decomposed and the oxygen evolved collected over water at 80°F. The barometer reads 29.7 in. Hg. What weight of saturated oxygen is obtained?
6. If a gas is saturated with water vapor, describe the state of the water vapor and the air if it is:
   - **(a)** Heated at constant pressure
   - **(b)** Cooled at constant pressure
   - **(c)** Expanded at constant temperature
   - **(d)** Compressed at constant temperature
7. Calculate **(a)** the dew point pressure for the following mixture at 100°F and **(b)** the liquid composition.

		K values at psia of		
Component	Mole fraction	190	200	210
C_2H_6	0.2180	3.22	3.07	2.92
C_3H_8	0.6650	1.005	0.973	0.920
i-C_4H_{10}	0.1073	0.45	0.43	0.41
n-C_4H_{10}	0.0097	0.315	0.305	0.295
Total	1.0000			

Thought Problems

1. Water was drained from the bottom of a gasoline tank into a sewer, and shortly thereafter a flash fire occurred in the sewer. The operator took special care to make sure that none of the gasoline entered the sewer.

   What caused the sewer fire?

2. The fluid in a large tank caught on fire 40 minutes after the start of a blending operation in which one grade of naphtha was being added to another. The fire was soon put out and the naphtha was moved to another tank. The next day blending was resumed in the second tank; 40 minutes later another fire started.

   Can you explain the reason for this sequence of events? What might be done to prevent such incidents?

3.5 PARTIAL SATURATION AND HUMIDITY

Your objectives in studying this section are to be able to:

1. Define relative saturation (humidity), molal saturation (humidity), absolute saturation (humidity), and humidity by formulas involving partial pressures of the gas components.
2. Given the partial saturation in one form, calculate the corresponding values in the other three forms as well as the dew point.

In Sec. 3.4 we dealt with mixtures of noncondensable gas and vapor in which the gas was saturated with the vapor. Often, the contact time required between the gas and liquid for equilibrium (or saturation) to be attained is too long, and the gas is not completely saturated with the vapor. Then the vapor is not in equilibrium with a liquid phase, and the partial pressure of the vapor is less than the vapor pressure of the liquid at the given temperature. This condition is called **partial saturation.** What we have is simply a mixture of two or more gases that obey the real gas laws. What distinguishes this case from the previous examples for gas mixtures is that under suitable conditions it is possible to condense part of one of the gaseous components. In Fig. 3.17 you can see how the partial pressure of the water vapor in a gaseous mixture at constant volume obeys the ideal gas laws as the temperature drops until saturation is reached, at which time the water vapor starts to condense. Until these conditions are achieved, you can confidently apply the gas laws to the mixture.

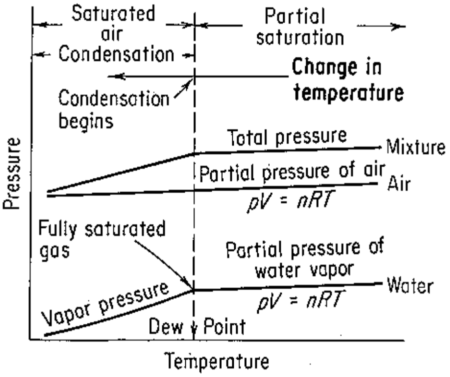

Figure 3.17 Transformation of a partially saturated water vapor-air mixture into a saturated mixture as the temperature is lowered (volume = constant).

Several ways exist to express the concentration of a vapor in a mixture with a noncondensable gas. You sometimes encounter mass or mole fraction (or percent), but more frequently one of the following:

(a) Relative saturation (relative humidity); Sec. 3.5.1
(b) Molal saturation (molal humidity); Sec. 3.5.2
(c) "Absolute" saturation ("absolute" humidity) or percent saturation (percent humidity); Secs. 3.5.3 and 4.9
(d) Humidity; Secs. 3.5.2 and 4.9

When the vapor is water vapor and the gas is air, the special term **humidity** applies. For other gases or vapors, the term **saturation** is used.

3.5-1 Relative Saturation

Relative saturation is defined as

$$\mathcal{RS} = \frac{p_{\text{vapor}}}{p_{\text{satd}}} = \text{relative saturation} \tag{3.47}$$

where p_{vapor} = partial pressure of the vapor in the gas mixture
p_{satd} = partial pressure of the vapor in the gas mixture *if* the gas were saturated at the given temperature of the mixture (i.e., the vapor pressure of the vapor component)

Then, for brevity, if the subscript 1 denotes vapor,

$$\mathcal{RS} = \frac{p_1}{p_1^*} = \frac{p_1/p_t}{p_1^*/p_t} = \frac{V_1/V_t}{V_{\text{satd}}/V_t} = \frac{n_1}{n_{\text{satd}}} = \frac{\text{mass}_1}{\text{mass}_{\text{satd}}} \tag{3.48}$$

You can see that relative saturation, in effect, represents the fractional approach to total saturation, as shown in Fig. 3.18. If you listen to the radio or TV and hear the announcer say that the temperature is 25°C(77°F) and the *relative humidity* is 60%, he or she implies that

$$\frac{p_{H_2O}}{p^*_{H_2O}}(100) = \%\,\mathcal{RH} = 60 \tag{3.49}$$

with both the p_{H_2O} and the $p^*_{H_2O}$ being measured at 25°C. Zero percent relative saturation means no vapor in the gas. What does 100% relative saturation mean? It

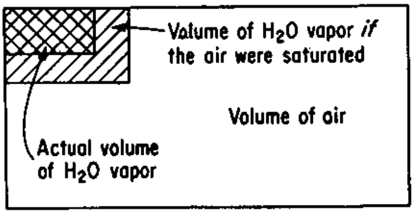

Figure 3.18 Partially saturated gas with the water and air separated conceptually.

means that the partial pressure of the vapor is the same as the vapor pressure of the substance that is the vapor.

EXAMPLE 3.25 Application of Relative Humidity

The weather reported on the radio this morning was that the temperature this afternoon would reach 94°F, the relative humidity would be 43%, the barometer 29.67 in. Hg, partly cloudy to clear, with the wind from SSE at 8 mi/hr. How many pounds of water vapor would be in 1 mi^3 of afternoon air? What would be the dew point of this air?

Solution

The vapor pressure of water at 94°F is 1.61 in. Hg. We can calculate the partial pressure of the water vapor in the air from the given percent relative humidity; from this point forward, the problem is the same as the examples in Section 3.4.

$$p_w = (1.61 \text{ in. Hg})(0.43) = 0.692 \text{ in. Hg}$$

$$(p_{\text{air}} = p_t - p_w = 29.67 - 0.692 = 28.98 \text{ in. Hg})$$

Basis: 1 mi^3 water vapor at 94°F and 0.692 in. Hg

$$\frac{1 \text{ mi}^3}{} \left| \left(\frac{5280 \text{ ft}}{1 \text{ mi}}\right)^3 \right| \frac{492°\text{R}}{554°\text{R}} \left| \frac{0.692 \text{ in. Hg}}{29.92 \text{ in. Hg}} \right| \frac{1 \text{ lb mol}}{359 \text{ ft}^3} \left| \frac{18 \text{ lb H}_2\text{O}}{1 \text{ lb mol}} \right. = 1.52 \times 10^8 \text{ lb H}_2\text{O}$$

Now the dew point is the temperature at which the water vapor in the air will first condense on cooling at *constant total pressure and composition*. As the gas is cooled you can see from Eq. (3.49) that the percent relative humidity increases since the partial pressure of the water vapor is constant while the vapor pressure of water decreases with temperature. When the percent relative humidity reaches 100%,

$$100\frac{p_{H_2O}}{p^*_{H_2O}} = 100\% \qquad \text{or} \qquad p_{H_2O} = p^*_{H_2O}$$

the water vapor will start to condense. This means that at the dew point the vapor pressure of water will be 0.692 in. Hg. From the steam tables you can see that this corresponds to a temperature of about 68–69°F.

3.5-2 Molal Saturation

Another way to express vapor concentration in a gas is to use the ratio of the moles of vapor to the moles of vapor-free gas:

$$\frac{n_{\text{vapor}}}{n_{\text{vapor-free gas}}} = \text{molal saturation} \tag{3.50}$$

If subscripts 1 and 2 represent the vapor and the dry gas, respectively, then for a binary system,

$$p_1 + p_2 = p_t$$

$$n_1 + n_2 = n_t$$

$$\frac{n_1}{n_2} = \frac{p_1}{p_2} = \frac{V_1}{V_2} = \frac{n_1}{n_t - n_1} = \frac{p_1}{p_t - p_1} = \frac{V_1}{V_t - V_1} \tag{3.51}$$

By multiplying by the appropriate molecular weights, you can find the mass of vapor per mass of dry gas:

$$\frac{(n_{\text{vapor}})(\text{mol. wt.}_{\text{vapor}})}{(n_{\text{dry gas}})(\text{mol. wt.}_{\text{dry gas}})} = \frac{\text{mass}_{\text{vapor}}}{\text{mass}_{\text{dry gas}}} \tag{3.52}$$

The special term **humidity** ($\mathscr{H}$) refers to the mass of water vapor per mass of bone-dry air and is used in connection with the humidity charts in Sec. 4.9.

3.5-3 "Absolute" Saturation (Humidity); Percentage Saturation (Humidity)

"Absolute" saturation is defined as the ratio of the moles of vapor per mole of *vapor-free* gas to the moles of vapor *that would be present* per mole of *vapor-free* gas *if the mixture were completely saturated* at the existing temperature and total pressure:

$$\mathscr{AS} = \text{"absolute saturation"} = \frac{\left(\dfrac{\text{moles vapor}}{\text{moles vapor-free gas}}\right)_{\text{actual}}}{\left(\dfrac{\text{moles vapor}}{\text{moles vapor-free gas}}\right)_{\text{saturated}}} \tag{3.53}$$

Using the subscripts 1 for vapor and 2 for vapor-free gas,

$$\text{percent absolute saturation} = \frac{\left(\dfrac{n_1}{n_2}\right)_{\text{actual}}}{\left(\dfrac{n_1}{n_2}\right)_{\text{saturated}}}(100) = \frac{\left(\dfrac{p_1}{p_2}\right)_{\text{actual}}}{\left(\dfrac{p_1}{p_2}\right)_{\text{saturated}}}(100) \tag{3.54}$$

Since p_1 saturated $= p_1^*$ and $p_t = p_1 + p_2$,

$$\text{percent absolute saturation} = 100\frac{\dfrac{p_1}{p_t - p_1}}{\dfrac{p_1^*}{p_t - p_1^*}} = \frac{p_1}{p_1^*}\left(\frac{p_t - p_1^*}{p_t - p_1}\right)100 \tag{3.55}$$

Now you will recall that p_1/p_1^* = relative saturation. Therefore,

$$\text{percent absolute saturation} = (\text{relative saturation})\left(\frac{p_t - p_1^*}{p_t - p_1}\right)100 \tag{3.56}$$

Percent absolute saturation is always less than relative saturation except at saturated conditions (or at zero percent saturation) when percent absolute saturation = percent relative saturation.

EXAMPLE 3.26 Partial Saturation

Helium contains 12% by volume of ethyl acetate. Calculate (a) the percent relative saturation and (b) the percent absolute saturation of the mixture at a temperature of 30°C and a pressure of 98 kPa.

Solution

The additional data needed are

$$p^*_{\text{EtAc}} \text{ at } 30^\circ\text{C} = 15.9 \text{ kPa} \qquad \text{(from any suitable handbook)}$$

Using Dalton's laws, we obtain

$$\begin{aligned} p_{\text{EtAc}} &= p_t y_{\text{EtAc}} = p_t\left(\frac{n_{\text{EtAc}}}{n_t}\right) = p_t\left(\frac{V_{\text{EtAc}}}{V_t}\right) \\ &= (98)(0.12) = 11.76 \text{ kPa} \\ p_{\text{He}} &= p_t - p_{\text{EtAc}} \\ &= 98 - 11.76 = 86.24 \text{ kPa} \end{aligned}$$

At 30°C:

(a) Percent relative saturation =

$$100\frac{p_{\text{EtAc}}}{p^*_{\text{EtAc}}} = 100\frac{11.76}{15.9} = 74.0\%$$

(b) Percent absolute saturation =

$$100\frac{\dfrac{p_{\text{EtAc}}}{p_t - p_{\text{EtAc}}}}{\dfrac{p^*_{\text{EtAc}}}{p_t - p^*_{\text{EtAc}}}} = \frac{\dfrac{11.76}{98 - 11.76}}{\dfrac{15.9}{98 - 15.9}}100 = \frac{\dfrac{11.76}{86.24}}{\dfrac{15.9}{82.1}}100$$

$$= 70.4\%$$

EXAMPLE 3.27 Partial Saturation

The percent absolute humidity of air at 86°F and a total pressure of 750 mm Hg is 20%. Calculate (a) the percent relative humidity and (b) the partial pressure of the water vapor in the air. (c) What is the dew point of the air?

Solution

Data from the steam tables are

$$p^*_{\text{H}_2\text{O}} \text{ at } 86^\circ\text{F} = 1.253 \text{ in. Hg} = 31.8 \text{ mm Hg}$$

To get the relative humidity, $p_{\text{H}_2\text{O}}/p^*_{\text{H}_2\text{O}}$, we need to find the partial pressure of the water vapor in the air. This may be obtained from

$$\mathcal{AH} = 20 = \frac{\dfrac{p_{\text{H}_2\text{O}}}{p_t - p_{\text{H}_2\text{O}}}}{\dfrac{p^*_{\text{H}_2\text{O}}}{p_t - p^*_{\text{H}_2\text{O}}}}100 = \frac{\dfrac{p_{\text{H}_2\text{O}}}{750 - p_{\text{H}_2\text{O}}}}{\dfrac{31.8}{750 - 31.8}}100$$

This equation can be solved for $p_{\text{H}_2\text{O}}$:

$$0.00886 = \frac{p_{\text{H}_2\text{O}}}{750 - p_{\text{H}_2\text{O}}}$$

(b)
$$p_{H_2O} = 6.58 \text{ mm Hg}$$

(a)
$$\% \mathcal{RH} = 100\frac{6.58}{31.8} = 20.7\%$$

(c) The dew point is the temperature at which the water vapor in the air would commence to condense, when cooled at constant total pressure. This would be at the vapor pressure of 6.58 mm Hg, or about 42°F.

Self-Assessment Test

1. A mixture of air and benzene is found to have a 50% relative saturation at 27°C and an absolute pressure of 110 kPa. What is the mole fraction of benzene in the air?
2. A TV announcer says that the dew point is 92°F. If you compress the air to 110°F and 2 psig, what is the percent absolute humidity?
3. Nine hundred forty-seven cubic feet of wet air at 70°F and 29.2 in. Hg are dehydrated. If the water removed contains 0.94 lb of H_2O, what was the relative humidity of the wet air?

Thought Problems

1. A stirred tank containing liquid CS_2 solvent had to be cleaned because of solid residue that had accumulated in the stirrer. To avoid a possible fire and explosion, the CS_2 was pumped out and the tank blanketed with nitrogen. Then the manhole cover was removed from the top of the tank, and a worker started to remove the solid from the stirrer rod with a scraper. At this point the maintenance worker left for lunch. When he returned to complete the job, a spark caused by the scraper striking the stirrer rod started a flash fire.

   How could the fire have occurred despite the preventive measure of using a N_2 blanket?

2. *From:* Marine Board of Investigation

   To: Commandant (MVI)

   Subj.: SS *V. A. FOGG*, O. N. 244971; sinking with loss of life in Gulf of Mexico on 1 February 1972

   Findings of Fact

   At 1240 on February 1, 1972, the tankship *V. A. FOGG* departed Freeport, Texas, en route to the Gulf of Mexico to clean cargo tanks that carried benzene residue. The vessel was due to arrive in Galveston, Texas, at 0200, on February 2. At approximately 1545, February 1, the *V. A. FOGG* suffered multiple explosions and sank. All 39 persons aboard died as a result of this casualty. Three bodies were recovered; two of the bodies were identified and one remained unidentified. The other persons were missing and presumed dead.

   You are asked your opinion of the most probable cause of the incident. What is your explanation?

3. On two different days the temperature and barometric pressure are the same. On day 1 the humidity is high, on day 2 the humidity is low. On which day is the air the most dense? Justify your answer with arguments using Dalton's law and the ideal gas law. Why does the air feel "heavier" on day 1 than on day 2?

3.6 MATERIAL BALANCES INVOLVING CONDENSATION AND VAPORIZATION

Your objective in studying this section is to be able to:

1. Solve material balance problems involving vaporization and condensation.

The solution of material balance problems involving partial saturation, condensation, and vaporization will now be illustrated. Remember the drying problems in Chap. 2? They included water and some bone-dry material, as shown at the top of Fig. 3.19. To complete the diagram, we add the air that is used to remove the water from the material being dried.

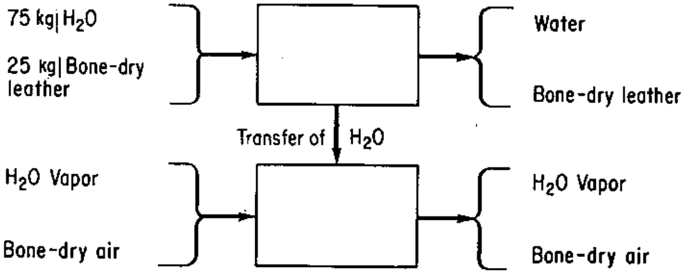

Figure 3.19 Complete drying schematic.

You can analyze material balance problems involving water vapor in air in exactly the same fashion as you analyzed the material balance problems for the drying of leather (or paper, etc.), depending on the information provided and sought. (Humidity and saturation problems that include the use of energy balances and humidity charts are discussed in Chap. 4.)

In connection with the examples that follow, we again stress that if you know the dew point of water in a gas, you automatically know the partial pressure of the water vapor in the gas. When a partially saturated gas is cooled at constant pressure, as in the cooling of air containing some water vapor at atmospheric pressure, the volume of the mixture may change slightly, but the mole fractions of the gas and water vapor remain constant until the dew point is reached. At this point water begins to condense; the gas remains saturated as the temperature is lowered. All that happens is that more water goes from the vapor into the liquid phase. **At the time the cooling is stopped, the gas is still saturated, and at its dew point.**

The material balance problems that follow are solved using the 10-step strategy presented in Table 2.4.

EXAMPLE 3.28 Material Balance with Condensation

If the atmosphere in the afternoon during a humid period is at 90°F and 80 $\mathcal{RH}$ (barometer reads 738 mm Hg) while at night it is at 68°F (barometer reads 745 mm Hg), what percent of the water in the afternoon air is deposited as dew at night?

Solution

Assume a closed system that reaches equilibrium.

Steps 1, 2, and 3: The data are shown in Fig. E3.28. The check marks indicate that the compositions of the streams can be calculated from the information given. Two pieces of information needed are:

$$\text{vapor pressure } H_2O \text{ at } 90°\text{F} = 36.1 \text{ mm Hg}$$

$$\text{vapor pressure } H_2O \text{ at } 68°\text{F} = 17.5 \text{ mm Hg}$$

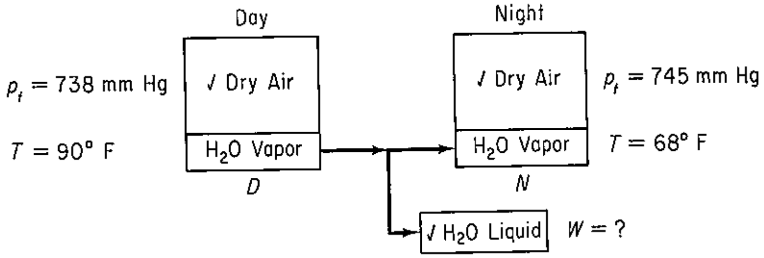

Figure E3.28

You can check to see if the dew point of the day air is below 68°F in which case no dew is deposited.

The partial pressure of the water pressure in the day air is

$$(36.1 \text{ mm Hg})(0.80) = 28.9 \text{ mm Hg} \Leftrightarrow 83°\text{F dew point}$$

Consequently, water does condense from the air as it cools. Now we need to get the compositions of the day and night air so we can carry out a material balance.

We calculate all the partial pressures in the *D* and *N* streams, the results of which in effect give us the compositions of the two streams.

$p_t = p_{\text{air}} + p_w$ so that

day: $p_{\text{air}} = 738 - 28.9 = 709.1$ mm Hg

night: $p_{\text{air}} = 745 - 17.5 = 727.5$ mm Hg

Steps 4, 5, and 6: If we take a basis, we have only two stream variables unknown; two component material balances can be made, hence the problem has a unique solution.

As a basis we could select 1 ft^3 of wet air, 1 lb mol wet (or dry) air, or many other suitable bases. The simplest basis to take is

Basis: 738 lb mol of moist day air

because then the moles = the partial pressures.

Steps 7, 8, 9: On the basis of 738 lb mol of moist day air, we have the following water in the saturated night air:

$$\begin{array}{c|c} 17.5 \text{ lb mol H}_2\text{O in night air} & 709.1 \text{ lb mol dry air} \\ \hline 727.5 \text{ lb mol dry air} & \end{array} = 17.06 \text{ lb mol H}_2\text{O}$$

Then

$$\text{Water balance:} \qquad 28.9 - 17.06 = 11.84 \text{ lb mol H}_2\text{O deposited as dew}$$

$$100\frac{11.84}{28.9} = 41\% \text{ of water in day air deposited as dew}$$

Step 10: Check your answer by selecting another basis on which to work the problem.

EXAMPLE 3.29 Dehydration

By absorption in silica gel you are able to remove all (0.93 kg) of the H_2O from moist air at 15°C and 98.6 kPa. The same air measures 1000 m^3 at 20°C and 108.0 kPa when dry. What was the relative humidity of the moist air?

Solution

Steps 1, 2, and 3: Figure E3.29 contains the known data. The check marks indicate that the moist air and other concentrations can be calculated from the data given.

Step 4: Either the *W* or the *A* stream can serve as the basis.

Basis: 1000 m^3 bone-dry air (BDA) at 20°C and 108.0 kPa

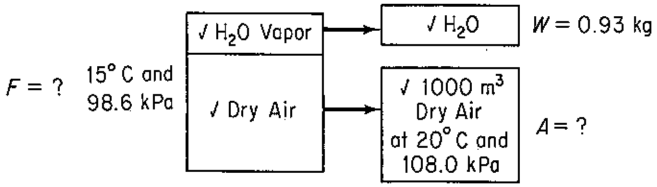

Figure E3.29

We first need to calculate the amounts (in kg mol) of water vapor and dry air in the original air. $W = 0.93$ kg or

$$\begin{array}{c|c} 0.93 \text{ kg H}_2\text{O} & 1 \text{ kg mol H}_2\text{O} \\ \hline & 18 \text{ kg H}_2\text{O} \end{array} = 0.0517 \text{ kg mol H}_2\text{O}$$

As for the dry air

$$\begin{array}{c|c|c|c} 1000 \text{ m}^3 \text{ BDA} & 273 \text{ K} & 108.0 \text{ kPa} & 1 \text{ kg mol} \\ \hline & 293 \text{ K} & 101.3 \text{ kPa} & 22.4 \text{ m}^3 \end{array} = 44.35 \text{ kg mol BDA}$$

Steps 5, 6, 7, 8 and 9: All of the water and all of the air were in the original moist air so that balances are trivial, and the problem has a unique solution. The partial pressure of the water vapor in the original air was

$$p_{H_2O} = p_t y_{H_2O} = 98.6\left(\frac{0.0517}{44.35 + 0.0517}\right) = 0.1147 \text{ kPa}$$

The vapor pressure at 15°C for water is 1.70 kPa, hence the fractional relative humidity of the original air was

$$\frac{0.1147}{1.70} = 0.067$$

EXAMPLE 3.30 Humidification

One thousand cubic meters of moist air at 101 kPa and 22°C and with a dew point of 11°C enters a process. The air leaves the process at 98 kPa with a dew point of 58°C. How many kilograms of water vapor are added to each kilogram of wet air entering the process?

Solution

Steps 1, 2, and 3 The known data appear in Fig. E3.30. The check marks indicate that the concentrations can be calculated from the given data. Additional data needed are

Dew point temp. (°C)	$p^*_{H_2O}$ (mm Hg)	$p^*_{H_2O}$ (kPa)
11	9.84	1.31[†]
58	136.1	18.14[†]

[†] These values give the partial pressures of the water vapor in the initial and final gas mixtures.

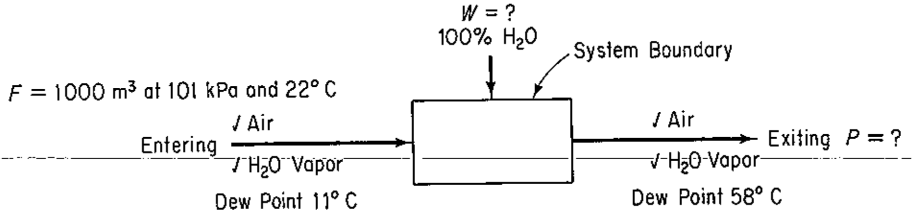

Figure E3.30

The partial pressures of the water vapor are the pressures at the dew point in each case, and the dry air has a partial pressure which is the difference between the total pressure and the partial pressure of the water vapor.

Let the subscript W stand for water vapor and DA stand for dry air:

$$\text{In:}\quad p_{DA} = p_t - p_W = 101 - 1.31 = 99.69\text{ kPa}$$

$$\text{Out:}\quad p_{DA} = 98 - 18.14 = 79.86\text{ kPa}$$

Step 4 Basis is 1000 m³ at 101 kPa and 22°C. Other bases could be selected such as 101 kg mol of moist entering air or 98 kg mol of moist exit air.

Steps 5 and 6 We have two unknowns, W and P, and can make both an air and water balance, so that the problem has a unique solution.

Steps 7, 8, and 9

$$\begin{array}{c|c|c|c} 1000\text{ m}^3 & 101\text{ kPa} & 273\text{ K} & 1\text{ kg mol} \\ \hline & 101.3\text{ kPa} & 295\text{ K} & 22.4\text{ m}^3 \end{array} = 41.19\text{ kg mol wet air}$$

Dry air is a tie component.

$$\text{DA balance:} \quad 41.19\left(\frac{99.69}{101}\right) = P\left(\frac{79.86}{98}\right)$$

$$P = 49.87 \text{ kg mol}$$

$$\text{Total balance:} \quad F + W = P$$

$$W = 49.87 - 41.19 = 8.68 \text{ kg mol } H_2O$$

Step 10 . Check using the water balance.

$$\text{Water balance:} \quad 41.19\left(\frac{1.31}{101}\right) + W = 49.87\left(\frac{18.1}{98}\right)$$

$$W = 8.68 \text{ kg mol } H_2O$$

Step 9 (Continued) To calculate the kg of wet air entering, we proceed as in Chap. 1.

Component	kg mol	Mol. wt.	kg
Dry air	$41.19\left(\frac{99.69}{101}\right)$	29	1179.0
H_2O	$41.19\left(\frac{1.31}{101}\right)$	18	9.6
Total	41.19		1188.6

$$\text{Water added} = \frac{(8.68)(18)}{1188.6} = 0.131 \frac{\text{kg water}}{\text{kg wet air in}}$$

EXAMPLE 3.31 Vaporization of the Products of Ammonia Synthesis

After ammonia is produced from N_2 and H_2, the products are cooled and separated in a partial condenser operated at −28°F and 2000 psia (the reaction pressure). Figure E3.31 illus-

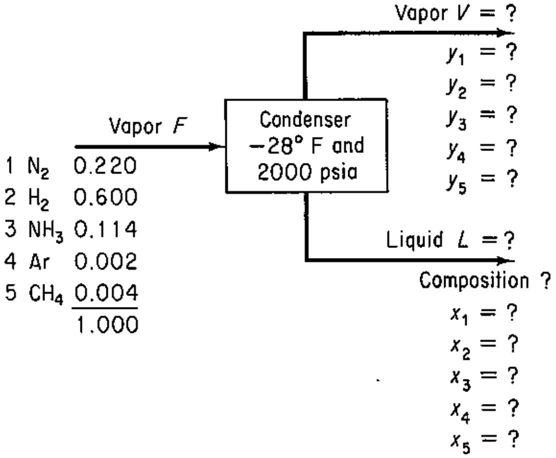

Figure E3.31

trates the separation process and gives the known data. Calculate the composition of the vapor and liquid streams. The equilibrium constants are

N_2:	66.67	Ar:	100
H_2:	50	CH_4:	33.33
NH_3:	0.015		

Solution

Steps 1, 2, and 3 Figure E3.31 contains the known data, and symbols for the unknown quantities.

Step 4

Basis: 100 lb mol = F

Steps 5 and 6 There are 12 variables whose values are unknown. You can make five component balances, invoke two sum of mole fraction relations for streams L and V, and write five equilibrium relations $y_i = K_i x_i$, hence the problem has a unique solution.

Step 7 Component material balances:

$$N_2: \quad 100(0.220) = Vy_1 + Lx_1 \tag{a}$$

$$H_2: \quad 100(0.660) = Vy_2 + Lx_2 \tag{b}$$

$$NH_3: \quad 100(0.114) = Vy_3 + Lx_3 \tag{c}$$

$$Ar: \quad 100(0.002) = Vy_4 + Lx_4 \tag{d}$$

$$CH_4: \quad 100(0.004) = Vy_5 + Lx_5 \tag{e}$$

Summation of mole fractions:

$$V: \quad y_1 + y_2 + y_3 + y_4 + y_5 = 1 \tag{f}$$

$$L: \quad x_1 + x_2 + x_3 + x_4 + x_5 = 1 \tag{g}$$

Equilibrium relations:

$$N_2: \quad y_1 = 66.67x_1 \tag{h}$$

$$H_2: \quad y_2 = 50x_2 \tag{i}$$

$$NH_3: \quad y_3 = 0.015x_3 \tag{j}$$

$$Ar: \quad y_4 = 100x_4 \tag{k}$$

$$CH_4: \quad y_5 = 33.33x_5 \tag{l}$$

Step 8 One method of solution is to solve all 12 equations simultaneously (the component material balances are nonlinear). By the following algebraic manipulations, the number of variables and equations can be reduced. Rearrange Eqs. (a)–(e). For example, for Eq. (a),

$$x_1 = \frac{100(0.220) - Vy_1}{L} \tag{m}$$

and

$$y_1 = \frac{100(0.220) - Lx_1}{V} \tag{n}$$

Substitute $y_i = K_i x_i$ into the set of equations corresponding to Eq. (m) and solve for x_i; for example,

$$x_1 = \frac{100}{V} \frac{0.220}{(L/V) + 66.67} \tag{o}$$

Introduce all the equations corresponding to Eq. (o) into Eq. (g) to get a single equation in which the unknowns are L and V.

$$\sum_{i=1}^{5} x_i(L, V) = 1 \tag{p}$$

A similar procedure applied with respect to Eqs. (n) and (f) gives another equation in which L and V are knowns; for example,

$$y_1 = \frac{100}{V} \frac{66.7(0.220)}{66.7 + (L/V)}$$

Insert all the y_i's into Eq. (f) to get

$$\sum_{i=1}^{5} y_i(L, V) = 1 \tag{q}$$

The overall material balance $100 = V + L$ can be combined with Eq. (p) and/or (q) to get a single equation in one unknown variable, V or L.

The solution is

		Concentration, mole fraction				
Stream	lb mol	N_2	H_2	NH_3	Ar	CH_4
V	89.73	0.2448	0.7339	0.0147	0.0022	0.0044
L	10.27	0.0037	0.0147	0.9815	0.0000	0.0001

You could use Eq. (3.46) to solve this problem without the detailed analysis above.

We have gone over a number of examples of condensation and vaporization, and you have seen how a given amount of air at atmospheric pressure can hold only a certain maximum amount of water vapor. This amount depends on the temperature of the air, and any decrease in the temperature will lower the water-bearing capacity of the air.

An increase in pressure also will accomplish the same effect. If a pound of saturated air at 75°F is isothermally compressed (with a reduction in volume, of course), liquid water will be deposited out of the air just like water being squeezed out of a wet sponge (Fig. 3.20). The vapor pressure of water is 0.43 psia at 75°F.

For example, if a pound of saturated air at 75°F and 1 atm is compressed isothermally to 4 atm (58.8 psia), almost three-fourths of the original content of water vapor now will be in the form of liquid, and the air still has a dew point of 75°F. Remove the liquid water, expand the air isothermally back to 1 atm, and you will find that the dew point has been lowered to about 36°F. Mathematically (1 = state at 1 atm, 4 = state at 4 atm) with $z = 1.00$ for both components:

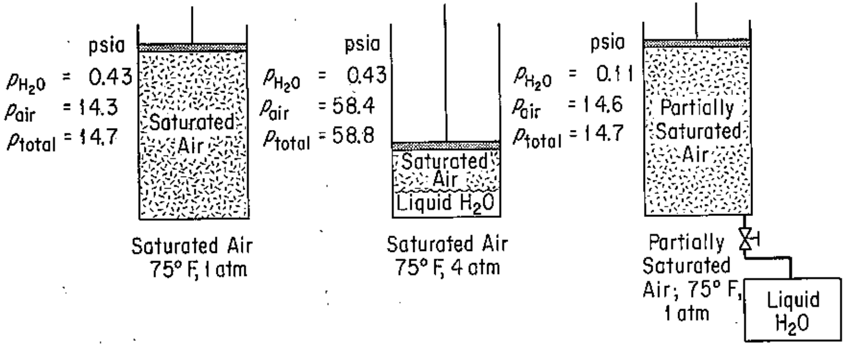

Figure 3.20 Effect of an increase of pressure on saturated air and a return to the initial pressure.

For saturated air at 75°F and 4 atm:

$$\left(\frac{n_{H_2O}}{n_{air}}\right)_4 = \left(\frac{p^*_{H_2O}}{p_{air}}\right)_4 = \frac{0.43}{58.4}$$

For the same air saturated at 75°F and 1 atm:

$$\left(\frac{n_{H_2O}}{n_{air}}\right)_1 = \left(\frac{p^*_{H_2O}}{p_{air}}\right)_1 = \frac{0.43}{14.3}$$

Since the air is the tie element in the process,

$$\left(\frac{n_4}{n_1}\right)_{H_2O} = \frac{\dfrac{0.43}{58.4}}{\dfrac{0.43}{14.3}} = \frac{14.3}{58.4} = 0.245$$

24.5% of the original water will remain as vapor after compression.

After the air-water vapor mixture is returned to a total pressure of 1 atm, the following two familiar equations now apply:

$$p_{H_2O} + p_{air} = 14.7$$

$$\frac{p_{H_2O}}{p_{air}} = \frac{n_{H_2O}}{n_{air}} = \frac{0.43}{58.4} = 0.00736$$

From these two relations you can find that

$$p_{H_2O} = 0.108 \text{ psia}$$

$$p_{air} = \underline{14.6}$$

$$p_{total} = 14.7 \text{ psia}$$

The pressure of the water vapor represents a dew point of about 36°F, and a relative humidity of

$$(100)\frac{p_{H_2O}}{p^*_{H_2O}} = \frac{0.108}{0.43}(100) = 25\%$$

Self-Assessment Test

1. Gas from a synthetic gas plant analyzes (on a dry basis) 4.8% CO_2, 0.2% O_2, 25.4% CO, 0.4% C_2H_4, 12.2% H_2, 3.6% CH_4, and 53.4% N_2. The coal used analyzes 70.0% C, 6.5% H, 16.0% O, and 7.5% ash. The entering air for combustion has a partial pressure of water equal to 2.67 kPa. The barometer reads 101 kPa. Records show that 465 kg of steam is supplied to the combustion vessel per metric ton of coal fired. Calculate the dew point of the exit gas.
2. A liquid solution of pharmaceutical material to be dried is sprayed into a stream of hot gas. The water evaporated from the solution leaves with the exit gases. The solid is recovered by means of cyclone separators. Operating data are:

Inlet air:	100,000 ft^3/hr, 600°F, 780 mm Hg, humidity of 0.00505 lb H_2O/lb dry air
Inlet Solution:	300 lb/hr, 15% solids, 70°F
Outlet air:	200°F, 760 mm Hg, dew point 100°F
Outlet solid:	130°F

Calculate the composition of the outlet solid—it is not entirely dry.

3. A gas leaves a solvent recovery system saturated with benzene at 50°C and 750 mm Hg. The gas analyzes, on a benzene-free basis, 15% CO, 4% O_2, and the remainder nitrogen. This mixture is compressed to 3 atm and is subsequently cooled to 20°C. Calculate the percent benzene condensed in the process. What is the relative saturation of the final gas?

Thought Problem

1. A large fermentation tank fitted with a 2-in. open vent was sterlized for 30 minutes by blowing in live steam at 35 psig. After the steam supply was shut off, a cold liquid substrate was quickly added to the tank at which point the tank collapsed inward.

   What happened to cause the tank to collapse?

3.7 PHASE PHENOMENA

Your objectives in studying this section are to be able to:

1. Write down the phase rule, define each parameter in the phase rule, and be able to apply the phase rule to determine the degrees of freedom, or the number of components, or the phases that exist in a system.
2. Sketch (roughly) the p–V–T surface and the two-dimensional projections thereof for water.
3. Predict the p–V–T behavior of a pure component or a mixture given the p–V–T diagram, and identify a specified state as residing in the solid, liquid, or vapor single-phase region or the solid plus liquid, solid plus vapor, or liquid plus vapor two-phase region.
4. Completely describe, from a phase diagram, all changes that occur on

cooling or heating a given composition of a two-component system; give all phases present at each temperature and approximate amounts of each phase; also, give the degrees of freedom at any point in the cooling or heating process.

5. Locate a reference containing the properties of a pure substance in your library.

We now consider briefly some of the qualitative characteristics of vapors, liquids, and solids. You need to know in any problem what materials are gases, liquids and solids so that you can apply the proper p–V–T relationships.

3.7-1 The Phase Rule

You will find the Gibb's phase rule a useful guide in establishing how many properties, such as pressure and temperature, have to be specified to definitely fix all the remaining properties and number of phases that can coexist for any physical system. **The rule can be applied only to systems in equilibrium.** It says that

$$F = C - \mathcal{P} + 2 \tag{3.57}$$

where F = number of degrees of freedom (i.e., the number of independent properties that have to be specified to determine all the intensive properties of each phase of the system of interest)

C = number of components in the system; for circumstances involving chemical reactions, C is *not* identical to the number of chemical compounds in the system but is equal to the number of chemical compounds less the number of independent-reaction and other equilibrium relationships among these compounds as discussed below.

$\mathcal{P}$ = number of phases that can exist in the system; a phase is a homogeneous quantity of material such as a gas, a pure liquid, a solution, or a homogeneous solid

Variables of the kind with which the phase rule is concerned are called *phase-rule variables,* and they are **intensive** properties of the system. **By this we mean properties that do not depend on the quantity of material present.** If you think about the properties we have employed so far in this book, you have the feeling that pressure and temperature are independent of the amount of material present. So is concentration, but what about volume? The total volume of a system is called an **extensive property because it does depend on how much material you have; the specific volume, on the other hand, the cubic meter per kilogram, for example, is an intensive property** because it is independent of the amount of material present. In Chap. 4 we take up additional intensive properties, such as internal energy and enthalpy. You should remember that the specific (per unit mass) values of these quantities are intensive properties; the total quantities are extensive properties.

An example will clarify the use of these terms in the phase rule. You will remember for a pure gas that we had to specify three of the four variables in the ideal gas equation $pV = nRT$ in order to be able to determine the remaining one unknown. You might conclude that $F = 3$. If we apply the phase rule, for a single phase $\mathcal{P} = 1$, and for a pure gas $C = 1$, so that

$$F = C - \mathcal{P} + 2 = 1 - 1 + 2 = 2 \qquad \text{variables to be specified}$$

How can we reconcile this apparent paradox with our previous statement? Since the phase rule is concerned with intensive properties only, the following are phase-rule variables in the ideal gas law:

$$\left.\begin{array}{l} p \\ \hat{V} \text{ (specific molar volume)} \\ T \end{array}\right\} \qquad \text{3 intensive properties}$$

Thus the ideal gas law would be written

$$p\hat{V} = RT$$

and once two of the intensive variables are fixed (F equals 2), the third is also automatically fixed.

The intensive property must be uniform throughout the phase. If a system at equilibrium consists of two nonreacting components such as NH_3 and H_2O, and two phases, liquid and vapor, intensive variables would be temperature (the same in both phases), pressure (the same in both phases), concentration in a phase (different in each phase), specific volume (different in each phase), and so on. The overall concentration (including both phases) for the system would not be an intensive property because it is not a value equal to the actual value of the concentration in either phase.

An **invariant** system is one in which no variation of conditions is possible without one phase disappearing. An example with which you may be familiar is the ice-water-water vapor system, which exists at only one temperature (0.01°C) and pressure (610 Pa):

$$F = C - \mathcal{P} + 2 = 1 - 3 + 2 = 0$$

With all three phases present, none of the physical conditions can be varied without the loss of one phase. As a corollary, if the three phases are present, the temperature, the specific volume, and so on, must always be fixed at the same values. This phenomenon is useful in calibrating thermometers and other instruments.

A complete discussion of the significance of the term C in the phase rule is beyond the scope of this book; however, a brief explanation will demonstrate the issues involved. The quantity C is calculated as

$$C = c^* - h$$

where c^* is the rank of the atom matrix and h is the number of stoichiometric constraints that exist in a reacting system. The atom matrix is just the matrix in which the rows represent the atomic species and the columns represent the chemical compounds in the system. Each element in the matrix is the number of atoms in the particular compound. Thus (for water)

	H_2O	H_2	O_2
H:	2	2	0
O:	1	0	2

for which the rank is two. Refer to Sec. L.1 to ascertain how the rank of the atom matrix can be evaluated. In any case C is not necessarily the number of compounds present in the system, n, and in fact the following inequality holds:

$$C \le c^* \le n$$

We do not have the space here to explain completely how h is calculated, but an example will make the idea clear. Suppose that a portion of 100g of $NH_4Cl(s)$ decomposes in an evacuated tank to $NH_3(g)$, $HCl(g)$, $N_2(g)$, $H_2(g)$, and $Cl_2(g)$. Thus $n = 5$, but the rank of the atomic matrix is $c^* = 3$. Because all the N, H, and Cl in the gas phase came from the $NH_4Cl(s)$, in the gas phase you know the following additional ratios must exist (called *stoichiometric constraints*) among all the compounds

$$\frac{\text{N}}{\text{H}} = \frac{1}{4} \qquad \frac{\text{Cl}}{\text{H}} = \frac{1}{4}$$

Consequently, $h = 2$, and the degrees of freedom for the system are

$$F = (3 - 2) - 2 + 2 = 1$$

in agreement with experimental observations. For more complicated reactions, consult Rao[21] (or one of the supplementary references at the end of this chapter) as to how to calculate h. Without a reaction, occurring, $h = 0$.

EXAMPLE 3.32 Application of the Phase Rule

Calculate the number of degrees of freedom (how many additional intensive variables must be specified to fix the system) from the phase rule for the following materials at equilibrium:

(a) Pure liquid benzene
(b) A mixture of ice and water only
(c) A mixture of liquid benzene, benzene vapor, and helium gas
(d) A mixture of salt and water designed to achieve a specific vapor pressure

What variables might be specified in each case?

Solution

$$F = C - \mathcal{P} + 2$$

(a) $C = 1$, $\mathcal{P} = 1$, hence $F = 1 - 1 + 2 = 2$. The temperature and pressure might be specified in the range in which benzene remains liquid.

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[21] Y. K. Rao, *Stoichiometry and Thermodynamics of Metallurgical Processes*, Cambridge University Press, New York, 1984.

(b) $C = 1$, $\mathcal{P} = 2$, hence $F = 1 - 2 + 2 = 1$. Once either the temperature or the pressure is specified, the other intensive variables are fixed.

(c) $C = 2$, $\mathcal{P} = 2$, hence $F = 2 - 2 + 2 = 2$. A pair from temperature, pressure, or mole fraction can be specified.

(d) $C = 2$, $\mathcal{P} = 2$, hence $F = 2 - 2 + 2 = 2$. Since a particular pressure is to be achieved, you would adjust the salt concentration and the temperature of the solution.

We are now going to consider how phase phenomena can be illustrated by means of diagrams.

3.7-2 Phase Phenomena of Pure Components

If we are to clearly understand phase phenomena, the properties of a substance should be shown in at least three dimensions, particularly if there can be more than one phase in the region for which the p–$\hat{V}$–T properties are to be presented. We previously overcame the handicap of using two dimensions to present three-dimensional data by showing, on the two-dimensionnal graph, lines of constant value for the other properties of the system (see Fig 3.3, which has p and $\hat{V}$ as axes, and lines of constant temperature as the third parameter). In this section we present a more elaborate picture of these p–$\hat{V}$–T properties. Figure 3.21 illustrates the relationships between the three-dimensional presentations of p–$\hat{V}$–T data for water and the conventional two-dimensional diagrams you usually encounter. Be certain that you view the central figure in Fig. 3.21 as a *surface* and not as solid figures; only the p–$\hat{V}$–T points on the surface exist, and no point exists above or below the surface.

You can see that the two-dimensional diagrams are really projections of the three-dimensional surfaces onto suitable axes. On the p–$\hat{V}$ diagram, you will observe lines of constant temperature called **isothermal lines,** and on the p–T diagram you will see lines of constant volume, called **isometric lines** or *isochores*. On the T–$\hat{V}$ diagram, we might have put lines of constant pressure known as **isobaric lines,** but these are not shown since they would obscure the more important features which are shown. The two-phase vapor-liquid region is represented by the heavy envelope in the p–$\hat{V}$ and the T–$\hat{V}$ diagrams. On the p–T diagram this two-phase region appears only as a single curve because you are looking at the three-dimensional diagram from the side. The p–T diagram shows what we have so far called the *vapor-pressure curve,* but examination of the associated diagrams show that the "curve" is really a surface on which two phases coexist, each having the properties found at the appropriate bounding line for the surface. A point on the surface shows merely the overall composition of one phase in equilibrium with another. For example, at point A we have liquid and at point B we have vapor, and in between them no single phase exists. If we added the liquid at A to the vapor at B, we would have a two-phase mixture with the gross properties shown by point M. You will notice that in the p–$\hat{V}$ diagram the lines of constant temperature and pressure become horizontal in the two-phase region, because if you apply the phase rule

$$F = C - \mathcal{P} + 2 = 1 - 2 + 2 = 1$$

only one variable can change—the specific volume. In the two-phase region, where

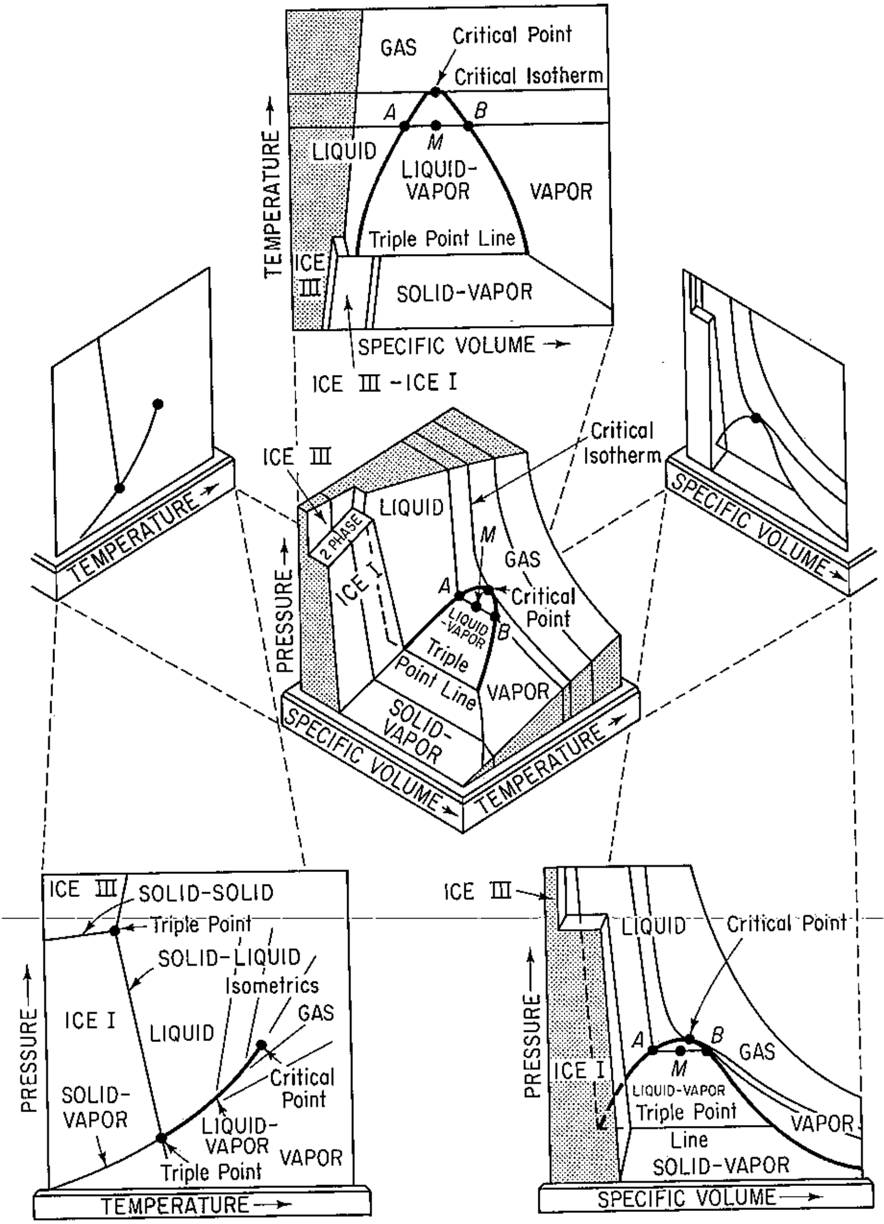

Figure 3.21 p–$\hat{V}$–T surface and projections for H_2O.

condensation or evaporation takes place, the pressure and temperature remain constant. Do you recall our discussion of boiling water?

Other features illustrated on the diagrams are the critical point, the **critical isotherm,** the **triple point** in the p–T diagram, which actually becomes a **triple-point line** in the p–$\hat{V}$ and T–$\hat{V}$ diagrams; and the existence of two solid phases and a liquid phase in equilibrium, such as solid ice I, solid ice III, and liquid. The temperature at the freezing point for water (i.e., the point where ice, water, air, and water vapor are in equilibrium) is not quite the same temperature as that at the triple point, which is the point where ice, water, and water vapor are in equilibrium. The presence of air at 1 atm lowers the freezing temperature by about 0.01°C, so that the triple point is at 0.00602 atm (0.610 Pa) and 0.01°C. Another triple point for the water system exists at 2200 atm and 20°C between ice III, ice I, and liquid water.

3.7-3 Phase Phenomena of Mixtures

Presentation of phase phenomena for mixtures that are completely miscible in the liquid state involves some rather complex reductions of three-, four-, and higher-dimensional diagrams into two dimensions. We shall restrict ourselves to two-component systems because, although the ideas discussed here are applicable to any number of components, the graphical presentation of more complex systems in an elementary text such as this is probably more confusing than helpful.

It would be convenient if the critical temperature of a mixture were the mole weighted average of the critical temperatures of its pure components, and the critical pressure of a mixture were simply a mole weighted average of the critical pressures of the pure components (the concept used in Kay's rule), but these maxims simply are not true, as shown in Fig. 3.22. The pseudocritical temperature falls on the dashed line between the critical temperatures of CO_2 and SO_2, whereas the actual critical point for the mixture lies somewhere else. The solid line in Fig. 3.22 illustrates how the locus of the actual critical points diverges from the locus of the pseudo critical points.

Figure 3.23 is a p–T diagram for a 25% methane/75% butane mixture. You can compare this figure with the one for a pure substance, water, as in Fig. 3.9; the p–T curve for pure butane or pure methane would look just like the diagram for water

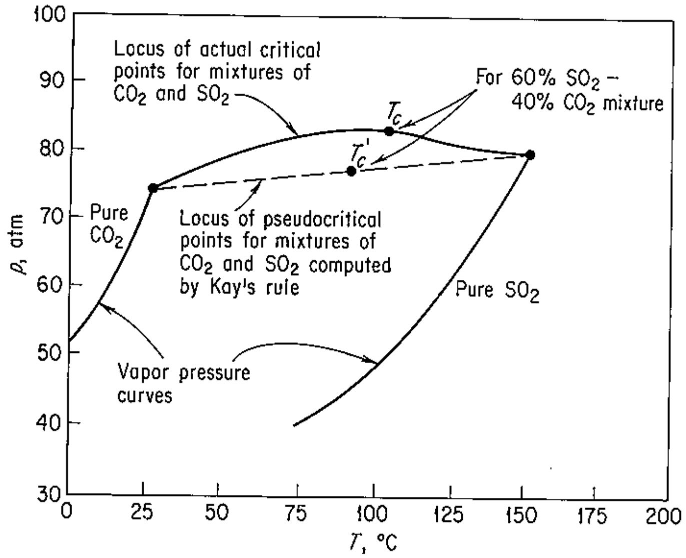

Figure 3.22 Critical and pseudocritical points for a mixture.

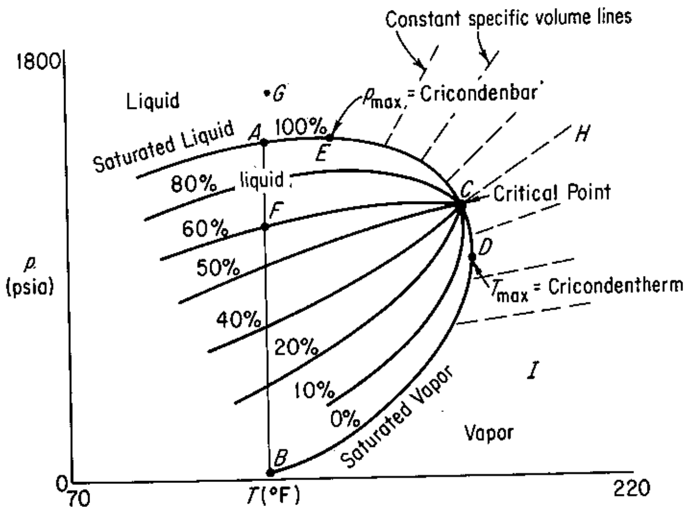

Figure 3.23 p–T diagram for binary system: 25% CH_4—75% C_4H_{10}.

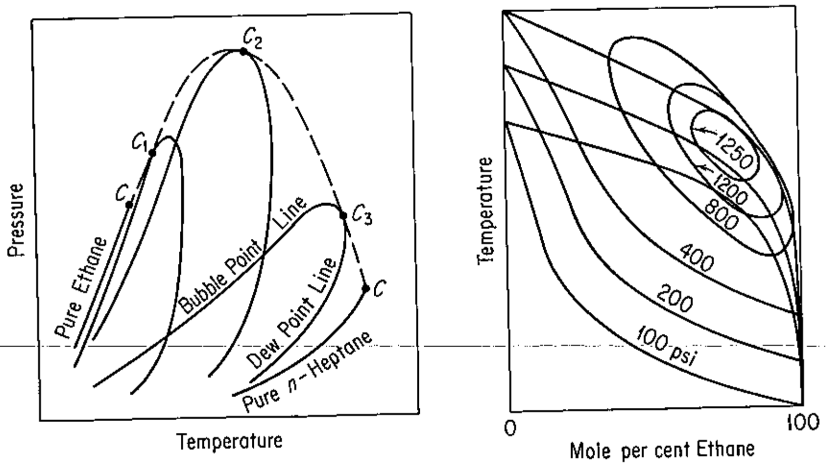

Figure 3.24 p–T and T–x diagrams for ethane-heptane mixtures of different compositions.

(excluding the solid phases). In Fig. 3.23, lines of constant specific volume are shown outside the envelope of the two-phase region. Inside the envelope are shown lines of constant fractions of liquid, starting at the high pressures, where 100% liquid exists (zero percent vapor), and ranging down to 0% liquid and 100% vapor at the low pressures. The 100% saturated liquid line is the bubble-point line and the 100% saturated vapor line is the dew-point line.

The critical point is shown as point C. You will note that this is not the point of maximum temperature at which vapor and liquid can exist in equilibrium; the latter is the **maximum cricondentherm,** point D. Neither is it the point of maximum pressure at which vapor and liquid can exist in equilibrium because that point is the

maximum cricondenbar (point E). The maximum temperature at which liquid and vapor can exist in equilibrium for this mixture is about 30° higher than the critical temperature, and the maximum pressure is 60 or 70 psia greater than the critical pressure. You can clearly see, therefore, that the best definition of the critical point was the one which stated that the density and other properties of the liquid and vapor become identical at the critical point. This definition holds for single components as well as mixtures.

Figure 3.23 represents a two-component system with a fixed overall composition. You might wonder what a diagram would look like if we were to try to show systems of several compositions on one page. This has been done in Fig. 3.24. Here we have a composite p–T diagram, which is somewhat awkward to visualize, but represents the bubble-point and dew-point curves for various mixtures of ethane and heptane. These curves in essence are intersections of surfaces in the composition coordinate sliced out of a three-dimensional system and are stacked one in front of the other, although in two dimensions it appears that they intersect one another. The vapor-pressure curves for the two pure components are at the extreme sides of the diagrams as single curves (as you might expect). Each of the loops represents the two-phase area for a system of a specific composition. An infinite number of these surfaces are possible, of course. The dashed line indicates the envelope of the critical points for each possible composition. Although this line appears to be two-dimensional in Fig. 3.24, it actually is a three-dimensional line of which only the projection is shown in the figure.

Another way to illustrate the phase phenomena for the two-component systems we have been discussing is to use pressure-composition diagrams at constant temperature or, alternatively, to use temperature-composition diagrams at constant pressure. A temperature-composition diagram with pressure as the third parameter is illustrated in Fig. 3.24 for the ethane-heptane system.

More complicated phase diagrams for multicomponent systems (ternary and higher) can be found in the references at the end of the chapter.

Self-Assessment Test

1. Is the critical point a single phase? If not, what phases are present? Repeat for the triple point (for water).
2. What does a p–V–T value lying above the surface in Fig. 3.23 mean? Below the surface?
3. Can a liquid be changed to a vapor without passing through a distinct discontinuity in properties? Can a solid be transformed similarly to vapor?
4. Sketch the p–V, p–T, and T–V diagrams for water.
5. A vessel contains air: N_2(g), O_2(g), and Ar(g).
   (a) How many phases, components, and degrees of freedom are there according to the phase rule?
   (b) Repeat for a vessel one-third filled with liquid ethanol and two-thirds filled with N_2 plus ethanol vapor.
6. Can the following system exist at equilibrium: H_2O(s), H_2O(l), H_2O(g), decane(s), decane(l), decane(g)? (*Hint:* Decane is insoluble in water.)
7. How many independent properties are required to fix the equilibrium state of a pure compound?

8. Consider the system Mn(s), $AlCl_3$(g), $MnCl_2$(l), Al(l). What are C, $\mathcal{P}$, and F in the Gibb's phase rule? Al(l) is not miscible with $MnCl_2$(l).

Thought Problems

1. The advertisement reads "Solid dry ice blocks in 60 seconds right in your own lab! Now you can have dry ice available to you at any time, day or night, with this small, safe, efficient machine and readily available CO_2 cylinders. No batteries or electrical energy are required."

   How is it possible to make dry ice in 60 seconds without a compressor?
2. An inventor is trying to sell a machine that transforms water vapor into liquid water without ever condensing the water vapor. You are asked to explain if such a process is technically possible. What is your answer?

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PROBLEMS

An asterisk designates problems appropriate for solution using a computer. Refer also to the problems that require writing computer programs at the end of the chapter.

Section 3.1

3.1. One liter of a gas is under a pressure of 780 mm Hg. What will be its volume at standard pressure, the temperature remaining constant?

3.2. A gas occupying a volume of 1 m^3 under standard pressure is expanded to 1.200 m^3, the temperature remaining constant. What is the new pressure?

3.3. At standard conditions a gas that behaves as an ideal gas is placed in a 4.13-L container. By using a piston the pressure is increased to 31.2 psia, and the temperature is increased to 212°F. What is the final volume occupied by the gas?

3.4. An oxygen cylinder used an a standby source of oxygen contains 1.000 ft^3 of O_2 at 70°F and 200 psig. What will be the volume of this O_2 in a dry-gas holder at 90°F and 4.00 in. H_2O above atmospheric? The barometer reads 29.92 in. Hg.

3.5. Probably the most important constituent of the atmosphere that fluctuates is the water. Rainfall, evaporation, fog, and even lightning are associated with water as a vapor or a liquid in air. To obtain some feeling for how little water vapor there is at higher altitudes, calculate the mass of 1.00 m^3 of water vapor at 2.00 kPa and 23°C. Assume that water vapor is an ideal gas under these conditions.

3.6. You have 10 lb of CO_2 in a 20-ft^3 fire extinguisher tank at 30°C. Assuming that the ideal gas law holds, what will the pressure gauge on the tank read in a test to see if the extinguisher is full?

3.7. Divers work as far as 500 ft below the water surface. Assume that the water temperature is 45°F. What is the molar specific volume (ft^3/lb mol) for an ideal gas under these conditions?

3.8. A 25-L glass vessel is to contain 1.1 g moles of nitrogen. The vessel can withstand a pressure of only 20 kPa above atmospheric pressure (taking into account a suitable safety factor). What is the maximum temperature to which the N_2 can be raised in the vessel?

3.9. A gas in a storage container for plasma etching is at 90 mm Hg gauge pressure. What will be the **(a)** absolute pressure and **(b)** the gauge pressure if the volume of the container is doubled at the same temperature? The external atmospheric pressure is 14.7 psia.

3.10. *Columbia,* one of the Goodyear blimps, requires 5210 m^3 of helium to fill the balloon at 20°C and 101.3 kPa. Helium may be purchased in standard gas cylinders of 23 cm diameter and 132 cm height pressurized to 15,200 kPa. If Goodyear were to fill the blimp with these cylinders at $32 per cylinder, how much would it cost? Helium behaves ideally at these conditions.

3.11. Compressed air from a tank maintained at 125 psig is used to inflate to 30 psig a tire that has a volume of 0.50 ft^3, the temperature remaining constant. What volume of air is taken from the tank? What volume is this at standard pressure?

3.12. A recent newspaper report states: "Home meters for fuel gas measure the volume of gas usage based on a standard temperature, usually 60 degrees. But gas contracts when it's cold and expands when warm. East Ohio Gas Co. figures that in chilly Cleveland, the homeowner with an outdoor meter gets more gas than the meter says he does, so that's built into the company's gas rates. The guy who loses is the one with an indoor meter: If his home stays at 60 degrees or over, he'll pay for more gas than he gets. (Several companies make temperature-compensating meters, but they cost more and aren't widely used. Not surprisingly, they are sold mainly to utilities in the North.)"

Suppose that the outside temperature drops from 60°F to 10°F. What is the percentage increase in the mass of the gas passed by a noncompensated outdoor meter that operates at constant pressure? Assume that the gas is CH_4.

3.13. In Bhopal, India, a Union Carbide storage tank containing methyl isocyanate (CH_3NCO, a component used for the production of insecticide) leaked, resulting in injury and death to thousands of people. The American Occupational Saftey rules specify that workplace conditions are to be limited to concentrations less than 0.02 ppm of this compound. Assume ideal gas behavior. What is this concentration in mg/m^3 at 20°C and atmospheric pressure?

3.14. One of the experiments in the fuel-testing laboratory has been giving some trouble because a particular barometer gives erroneous readings owning to the presence of a small amount of air above the mercury column. At a pressure of 755 mm Hg the barometer reads 748 mm Hg, and at 740 the reading is 736. What will the barometer read when the actual pressure is 760 mm Hg?

3.15. From the known standard conditions, calculate the value of the gas law constant R in the following sets of units:

(a) cal/(g mol)(K)
(b) Btu/(lb mol)(°R)
(c) (psia)(ft^3)/(lb mol)(°R)
(d) J/(g mol)(K)
(e) (cm^3)(atm)/(g mol)(K)
(f) (ft^3)(atm)/(lb mol)(°R)

3.16. Two tanks are initially sealed off from one another by means of valve A. Tank I initially contains 1.00 ft^3 of air at 100 psia and 150°F. Tank II initially contains a nitrogen-oxygen mixture containing 95 mole % nitrogen at 200 psia and 200°F. Valve A is then opened allowing the contents of the two tanks to mix. After complete mixing had been effected, the gas was found to contain 85 mole % nitrogen. Calculate the volume of tank II. See Fig. P3.16.

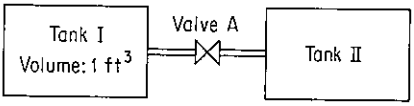


Figure P3.16

3.17. The majority of semiconductor chips used in the microelectronics industry are made of silicon doped with trace amounts of materials to enhance conductivity. The silicon initially must contain less than 20 parts per million (ppm) of impurities. Silicon rods are grown by the following chemical deposition reaction of trichlorosilane with hydrogen:

$$HSiCl_3 + H_2 \xrightarrow[1000°C]{} 3HCl + Si$$

Assuming that the ideal gas law applies, what volume of hydrogen at 1000°C and 1 atm must be reacted to increase the diameter of a rod 1 m long from 1 cm to 10 cm? The density of solid silicon is 2.33 g/cm^3.

3.18. The accident at the Three Mile Island nuclear plant began in March 1979 when a pressure relief valve of a water purifier stuck open. A series of operator errors and equipment failures stopped the flow of cooling water to the reactor core. As a result, the water began to boil and the core reached the temperature at which the steam reacted with the zirconium cladding of the fuel rods producing zirconium oxide (ZrO_2) and hydrogen gas (H_2). The hydrogen bubble that formed was estimated to be 28,000 L in volume and further impeded the flow of cooling water, which was at 250°C and 6900 kPa. From the measurements taken, determine the number of kilograms of zirconium reacted.

3.19. When a mixture of liquid hydrocarbons (C and H only) are burned in a test engine, the exhaust gas is found to contain 10.0% CO_2 on a dry basis. It is also found that the exhaust gas contains no oxygen or hydrogen (on the dry basis). Careful measurement indicates 173 ft^3 of air of 80°F and 740 mm Hg absolute enter the engine for every pound of fuel used.

Calculate the mass ratio of H to C in the fuel.

3.20. A medium-Btu gas analyzes 6.4% CO_2, 0.1% O_2, 39% CO, 51.8% H_2, 0.6% CH_4, and 2.1% N_2. It enters the combustion chamber at 90°F and a pressure of 35.0 in. Hg. It is burned with 40% excess air (dry) at 70°F and the atmospheric pressure of 29.4 in. Hg, but 10% of the CO remains unburned. How many cubic feet of air are supplied per cubic foot of entering gas?

3.21. How many lb of CS_2 must be burned with the stoichiometric quantity of O_2 ($CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$) to yield 200 ft^3 of gas at 300°C and 1 atm?

3.22. Pine wood has the following composition:

C	50.31%
H_2	6.20%
O_2	43.08%
Ash	0.41%

If you burn this wood in an approved stove using 60% excess air, what is

(a) The m^3 of air at 15°C and 98 kPa needed per kg of wood?
(b) The analysis of the flue gas?
(c) The m^3 of flue gas at 110°C and 98 kPa per m^3 air used (at 15°C and 98 kPa)?

3.23. Carbon dioxide dissociates at high temperatures according to the following equation:

$$2CO_2 \rightleftharpoons 2CO + O_2$$

At 3000°C and 1 atm CO_2 is 40% dissociated. If 5 L of CO_2 at 20°C and 1 atm is heated to 3000°C at constant pressure, what volume of the gas will result? State your assumptions.

3.24. An industrial fuel gas consists of 40% CO and 60% CH_4; 121 ft^3/min of the gas, measured at 500 psia and 90°F, is completely burned with 25% excess air that enters at 70°F and 770 mm Hg. The resultant gases leave the furnace at 570°F and 770 mm Hg. Compute the composition and number of cubic feet per minute of the hot gases leaving the furnace.

3.25. Turbojet aircraft operating under most conditions produce lower concentrations of pollutants than do motor vehicles. At idle, CO and unburned hydrocarbons are higher than in motor vehicles at idle, but in the operating mode the emission index (grams of pollutant per kilogram of fuel) is:

	CO	Hydrocarbons	NO_x
Turbojet	8.7	0.16	2.7
Automotive piston	300	55	27

Given that the Orsat analysis from a turbojet shows 12.2% CO_2, 0.4% CO, and 6.2% O_2, compute the net hydrogen/carbon ratio in the fuel (the fuel contains negligible sulfur and nitrogen). Also compute the cubic meters of air used at 27°C and 101.4 kPa/kg of fuel burned.

3.26. In the first stage of the manufacture of sulfuric acid by the contact process, iron pyrites (FeS_2) is burned in dry air, the iron being oxidized to Fe_2O_3. Sufficient air is supplied so that it is 40% in excess of that required if all the sulfur were oxidized to sulfur trioxide. Of the pyrites charges, 15% is lost by falling through the grate with the cinders and is not burned.

Calculate the cubic meters of air at 30°C and 150 kPa to be used per 100 kg of pyrites charged.

3.27. In a test on an oil-fired boiler, it is not possible to measure the amount of oil burned, but the air used is determined by inserting a venturi meter in the air line. It is found that 5000 ft^3/min of air at 80°F and 10 psig is used. The dry gas analyzes 10.7% CO_2, 0.55% CO, 4.75% O_2, and 84.0% N_2. If the oil is assumed to be all hydrocarbon, calculate the gallons per hour of oil burned. The specific gravity of the oil is 0.94.

3.28. Gas at 60°F and 42.1 in. Hg absolute is flowing through an irregular duct. To determine the rate of flow of the gas, He is passed into the gas stream. The gas analyzes 1.0% He by volume before, and 1.4% He after addition. The He tank is placed on a scale and is observed to lose 10 lb in 30 min. What is the rate of flow of the gas in the duct in cubic feet per minute?

3.29. A gas containing only C and H on complete combustion yields 0.302 kg mol of CO_2 and 0.309 kg mol of H_2O. What is the C/H ratio in the gas? The specific gravity of the gas at 20°C and 97.3 kPa compared to dry air at 80°C and 30.78 in. Hg is 1.631. Calculate the molecular formula of the gas.

3.30. A gaseous mixture consisting of 50 mol % hydrogen and 50 mol % acetaldehyde (C_2H_4O) is initially contained in a rigid vessel at a total pressure of 760 mm Hg abs. The formation of ethanol (C_2H_6O) occurs according to

$$C_2H_4O + H_2 \longrightarrow C_2H_6O$$

After a time it was noted that the total pressure in the rigid vessel had dropped to 700 mm Hg abs. Calculate the degree of completion of the reaction using the following assumptions: (1) all reactants and products are in the gaseous state; and (2) the vessel and its contents were at the same temperature when the two pressures were measured.

3.31. Pure ethylene (C_2H_4) and oxygen are fed to a process for the manufacture of ethylene oxide (C_2H_4O):

$$C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow C_2H_4O$$

Figure P3.31 is the flow diagram for the process. The catalytic reactor operates at 300°C and 1.2 atm. At these conditions, single-pass measurements on the reactor show that 50% of the ethylene entering the reactor is consumed per pass, and of this, 70% is converted to ethylene oxide. The remainder of the ethylene consumed decomposes to form CO_2 and water.

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

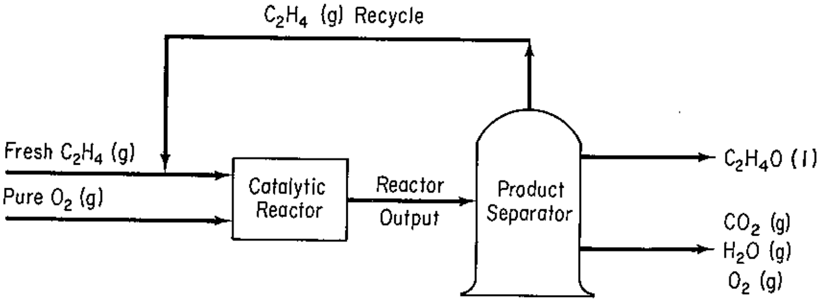


Figure P3.31

For a daily production of 10,000 kg of ethylene oxide:

(a) Calculate the m³/hr of total gas entering the reactor at SC if the ratio of the O_2 (g) fed to fresh C_2H_4 (g) is 3 to 2.

(b) Calculate the recycle ratio, m³ at 10°C and 100 kPa of C_2H_4 recycled, per m³ at SC of fresh C_2H_4 fed;

(c) Calculate the m³ of the mixture of O_2, CO_2 and H_2O leaving the separator per day at 80°C and 100 kPa.

3.32. What is the density of propane gas (C_3H_8) in kg per cubic meter at 200 kPa and 40°C? What is the specific gravity of propane?

3.33. What is the specific gravity of propane gas (C_3H_8) at 100°F and 800 mm Hg relative to air at 60°F and 760 mm Hg?

3.34. What is the mass of 1 m³ of H_2 at 5°C and 110 kPa? What is the specific gravity of this H_2 compared to air at 5°C and 110 kPa?

3.35. Gas from the Padna Field, Louisiana, is reported to have the following components and volume percent composition. What is:

(a) The mole percent of each component in the gas?
(b) The weight percent of each component in the gas?
(c) The apparent molecular weight of the gas?
(d) Its specific gravity?

Component	Percent	Component	Percent
Methane	87.09	Pentanes	0.46
Ethane	4.42	Hexanes	0.29
Propane	1.60	Heptanes	0.06
Isobutane	0.40	Nitrogen	4.76
Normal butane	0.5	Carbon dioxide	0.40
		Total	100.00

3.36. A gas used to extinguish fires is composed of 80% CO_2 and 20% N_2. It is stored in a 2-m^3 tank at 200 kPa and 25°C. What is the partial pressure of the CO_2 in the tank in kPa? What is the partial volume of the N_2 in the tank in m^3?

3.37. Methane is completely burned with 20% excess air, with 30% of the carbon going to CO. What is the partial pressure of the CO in the stack gas if the barometer reads 740 mm Hg, the temperature of the stack gas is 300°F, and the gas leaves the stack at 250 ft above the ground level?

3.38. A mixture of 15 lb N_2 and 20 lb H_2 is at a pressure of 50 psig and a temperature of 60°F. Determine the following (assuming ideality for the gas mixture):

(a) The partial pressure of each component
(b) The partial (or pure component) volumes
(c) The specific volume of the mixture
(d) The density of the mixture

3.39. The composition of mycelium from the production of antibiotics roughly resembles that of sewage sludge. In contrast to sewage sludge, however, the composition of mycelium remains largely constant. Therefore, mycelium is particularly suitable as model substrate for long-running experiments. In one experiment, 100 kg of product gas at 105 kPa and 460°C contains 60 kg of N_2, 15 kg of O_2, 20 kg of CO_2, and 5 kg of CH_4.

(a) Determine the following:
  (1) The mole fraction of each component
  (2) volume fraction of each component
  (3) partial pressure of each component
(b) Determine the volume occupied by the mixture in m^3.
(c) What is the density of the gas?
(d) What is the specific gravity of the gas?

3.40. Three thousand cubic meters per day of a gas mixture containing methane and *n*-butane at 21°C enters an absorber tower. The partial pressures at these conditions are 103 kPa for methane and 586 kPa for *n*-butane. In the absorber, 80% of the butane is removed and the remaining gas leaves the tower at 38°C and a total pressure of 550 kPa. What is the volumetric flow rate of gas at the exit? How many moles per day of butane are removed from the gas in this process? Assume ideal behavior.

3.41. Pure methane is completely burned with air. The outlet gases from the burner, which contain no oxygen, are passed through a cooler where some of the water is removed by condensation. The gases leaving the cooler have a nitrogen mole fraction of 0.8335. Calculate the following:

(a) The analysis of the gases leaving the cooler (mol % CO_2, H_2O, and N_2)
(b) The pounds of H_2O condensed per mole of CH_4 burned
(c) The average molecular weight of the gases leaving the cooler

If the exit gases from the cooler are at 130°F and 20 psia:

(d) What is the partial pressure of H_2O?
(e) What is the partial volume of H_2O per mole of CH_4?

Section 3.2

(*Note:* The use of a computer is recommended if equations of state are to be employed in solving a problem in this section.)

3.42.* Find the molar volume of methane at 350 K and 200 kPa abs (in cm^3/g mol). Use the van der Waals, Redlich–Kwong, and Benedict–Webb–Rubin equations. The nonlinear equation solving codes on the disk in the pocket at the back of this book will help you avoid trial-and-error solutions. The Benedict–Webb–Rubin constants are:

$A_0 = 182277.6$
$B_0 = 0.4546 \times 10^{-1}$ Use p in Pa
$C_0 = 0.3226 \times 10^{10}$ T in K
$a = 4409.7$ R in (Pa)(m^3)/(kg mol) (K)
$b = 0.252 \times 10^{-2}$ Then V will be in m^3/kg mol
$c = 0.3635 \times 10^{-9}$
$\alpha = 0.33 \times 10^{-3}$
$\gamma = 0.105 \times 10^{-1}$

3.43.* Find the molar volume (in cm^3/g mol) of propane at 375 K and 21 atm. Use the Redlich–Kwong and Peng-Robinson equations, and solve for the molar volume using the nonlinear equation solver NEWTON on the disk in the pocket at the back of this book. The acentric factor for propane to use in the Peng–Robinson equation is 0.1487.

3.44.* A 5-L tank of H_2 is left out overnight in Antarctica. You are asked to determine how many g moles of H_2 are in the tank. The pressure gauge reads 39 atm gauge and the temperature is −50°C. How many g moles of H_2 are in the tank? Use the van der Waals and Redlich–Kwong equations of state to solve this problem. (*Hint:* The nonlinear-equation-solving program on the disk in the pocket at the back of this book will make the execution of the calculations quite easy.)

3.45.* 4.00 g mol of CO_2 is contained in a 6250-cm^3 vessel at 298.15 K and 14.5 atm. Use the nonlinear equation solver NEWTON on the disk in the back of the book to solve the Redlich–Kwong equation for the molar volume. Compare the calculated molar volume of the CO_2 in the vessel with the known molar volume.

3.46.* Calculate the volume (in ft^3/lb) occupied by 1 g mol of CO_2 at 100 atm abs. and 50°C. Solve the Dieterici, van der Waals, Beattie–Bridgeman, and Redlich–Kwong equations of state using the nonlinear equation solver NEWTON on the disk in the back of the book. Which of the values from among the four equations would you use? Would the volume be more accurate if taken from the CO_2 chart (Fig. J.2)? Data for the coefficients are:

Dieterici

$a = 4.627 \times 10^6$ (atm)(cm^6)/g mol^2

$b = 46.3$ cm^3/g mol

Van der Waals

$a = 3.6 \times 10^6$ (atm)(cm^6)/g mol^2

$b = 42.8$ cm^3/g mol

Beattie–Bridgeman

$A_0 = 5.0065 \times 10^6$ $\quad b = 72.35$

$B_0 = 104.76$ $\quad c = 66 \times 10^7$

$a = 71.32$

Redlich–Kwong

Find p_c and T_c from Table D.1 in the Appendix.

3.47. Calculate the pressure of 176 g of CO_2 in a 6250-cm^3 tank at 298.15 K using the Redlich–Kwong equation of state.

3.48.* The fire department is inspecting the fire extinguishers in the chemical engineering building. A No. 2 gas cylinder, weighing 52.27 lb when completely evacuated, is placed on an accurate scale and filled with compressed carbon dioxide gas. When the gas in the cylinder has reached room temperature (54.5°F), the pressure in the cylinder is measured and found to be 338 psig. The capacity of the cylinder is 2.04 ft^3. Use the van der Waals equation of state to estimate what the *scale* will read in lb.

3.49. It is desired to market oxygen in small cylinders having volumes of 0.5 ft^3 and each containing 1.0 lb of oxygen. If the cylinders could be subjected to a maximum temperature of 120°F, calculate the minimum pressure for which they must be designed:

(a) Assuming the applicability of the perfect gas law

(b) Using the compressibility factor

(c) Using the van der Waals equation

3.50.* One of the biggest impediments to the realization of ambitious plans to build coal slurry pipelines has been lack of water in the right places. Much of the desirable low-sulfur coal in the United States comes from arid or semiarid regions in the West and in the northern Great Plains. Natives of these regions get upset and also litigious when coal companies talk of using thousands of acre-feet of scarce and valuable water every year just to carry powdered coal to the Midwest or East.

One way to get around the problem is to use liquid CO_2 instead of water as the transport medium. One advantage of liquid CO_2 is that it is less viscous than water. Friction in the pipeline would be lower, so less energy would be needed to transport a given amount of coal. Also there is little if any interaction between powdered coal and liquid carbon dioxide. Because of the lower viscosity and nonreactivity of liquid carbon dioxide (compared to water), slurries can carry more coal. That means additional energy savings and also means that a smaller pipelines could provide the same coal throughput.

About 8% of the coal shipped would be needed to produce the carbon dioxide if the CO_2 is discarded at the terminal. To have liquid CO_2 at, say 100°F, would not be possible because the critical temperature of CO_2 is 304.2 K (87.6°F) while the critical pressure is 72.9 atm. However, the fluid that exists at 100°F would serve satisfactorily as a transport medium.

Calculate by the following two ways the ft^3 of CO_2 at 120°F and 1200 psia that would be needed to transport 1 lb of coal (containing 74% carbon). Assume that 0.08 lb of (additional) coal per lb of transported coal is used to make the CO_2.

(a) Compressibility factor

(b) Van der Waals equation

3.51. A 100-ft^3 tank contains 95.1 lb moles of a nonideal gas at 1250 atm and 440°F. The critical pressure is known to be 50 atm. What is the critical temperature? Use a generalized compressibility chart to obtain your answer.

3.52. A gas is flowing at a rate of 100,000 scfh (std. cond. = 1 atm, 32°F). What is the actual volumetric gas flow rate if the pressure is 50 atm and the temperature is 600°R? The critical temperature is 40.0°F and the critical pressure is 14.3 atm.

3.53. Methyl chloride (mol. wt. = 50.49) is sold in small cylinders for medical purposes and as a refrigerant. A typical internal volume of a cylinder is 0.15 ft^3. If the weight of the CH_3Cl in the cylinder is 0.0997 lb, what is the pressure in the cylinder at 60°C?

3.54. Ethylene at 500 atm pressure and a temperature of 100°C is contained in a cylinder of internal volume of 1 ft^3. How many pounds of C_2H_4 are in the cylinder?

3.55. Vapor degreasing removes soluble contamination such as oils and grease from solid surfaces that are to be subjected to electrical, chemical, or electrochemical treatment. To store the solvent Freon-12 (CCl_2F_2) (T_c = 112°C, P_c = 39.6 atm), you have to design a cylinder to hold 750 kg of Freon-12 at a maximum temperature of 40°C and a pressure of 220 kPa absolute. What should the volume of the tank be?

3.56. Two identical cylinders contain different gases. One contains ethylene (C_2H_4) and the other contains nitrogen. Both have a molecular weight of 28, and both are at 25°C and 1000 psig pressure.

(a) Which cylinder contains the larger volume of gas measured at standard conditions? Verify your answer by giving the ratio of the volumes at standard conditions.

(b) Which cylinder weighs more? Verify your answer by giving the ratio of the weights of the gases in the two cylinders.

(*Note:* **On the next four problems check your calculations using the CO_2 chart in Appendix J, Fig. J.2.)**

3.57. One pound of carbon dioxide has a volume of 0.15 ft^3 at a pressure of 100 atm. What is the temperature of the gas?

3.58. A block of dry ice weighing 50 lb is dropped into an empty steel bomb, the volume of which is 5.0 ft^3. The bomb is closed and heated until the pressure gauge reads 1600 psig. What was the temperature of the gas in the bomb?

3.59. Calculate the specific volume of CO_2 at 600 atm and 40°C.

3.60. One-half of a cubic meter of CO_2 gas is held at a constant pressure of 3690kPa and is heated from 36°C to 77°C. Compare the volumes calculated for the gas after heating by considering it **(a)** as a nonideal gas and **(b)** as an ideal gas.

3.61. A steel cylinder contains ethylene (C_2H_4) at 200 psig. The cylinder and gas weigh 222 lb. The supplier refills the cylinder with ethylene until the pressure reaches 1000 psig, at which time the cylinder and gas weigh 250 lb. The temperature is constant at 25°C. Calculate the charge to be made for the ethylene if the ethylene is sold at $0.41 per pound, and what the weight of the cylinder is for use in billing the freight charges. Also find the volume of the empty cylinder in cubic feet.

3.62. A steel cylinder contains ethylene (C_2H_4) at 10^4 kPa gauge. The weight of the cylinder and gas is 70 kg. Ethylene is removed from the cylinder until the gauge pressure measured falls to one-third of the original reading. The cylinder and gas now weigh 52 kg. The temperature is contant at 25°C. Calculate:

(a) The fraction of the original gas (i.e., at 10^4 kPa) that remains in the cylinder at the lower pressure

(b) The volume of the cylinder in cubic meters

3.63. When a scuba diver goes to the dive shop to have his or her scuba tanks filled, the tank is connected to a compressor and filled to about 2100 psia while immersed in a tank of water. (Why immerse the tank in water? So that the compression of air into the tank will be approximately isothermal.)

Suppose that the tank is filled without inserting it into a water bath, and air at 27°C is compressed very rapidly from 1 atm absolute to the same final pressure. The final temperature would be about 700°C. Compute the fractional increase or decrease in the final quantity of air in the tank relative to the isothermal case:

(a) Assuming that the air behaves as an ideal gas

(b) Assuming that the air behaves as a real gas

Treat air as a single component with $p_c = 37.2$ atm and $T_c = 132.5$ K.

3.64. What is the density in g/L of a 50 mol % propane (C_3H_8)–50 mol % isobutane (i-C_4H_{10}) gaseous mixture at 23.4 atm and 195°C?

3.65. A gas has the following composition:

CO_2	10%
CH_4	40%
C_2H_4	50%

It is desired to distribute 33.6 lb of this gas per cylinder. Cylinders are to be designed so that the maximum pressure will not exceed 2400 psig when the temperature is 180°F. Calculate the volume of the cylinder required by Kay's method.

3.66. A gas composed of 20% ethanol and 80% carbon dioxide is at 500 K. What is its pressure if the volume per g mol is 180 cm³/g mol?

3.67. A sample of natural gas taken at 3500 kPa absolute and 120°C is separated by chromatography at standard conditions. It was found by calculation that the grams of each component in the gas were:

Component	g
Methane (CH_4)	100
Ethane (C_2H_6)	240
Propane (C_3H_8)	150
Nitrogen (N_2)	50
Total	540

What was the density of the original gas sample?

3.68.* A gaseous mixture has the following composition (in mol %):

C_2H_4	57
Ar	40
He	3

at 120 atm pressure and 25°C. Compare the experimental volume of 0.14 L/g mol with that computed by one or more of the equations of state.

3.69. You are in charge of a pilot plant using an inert atmosphere composed of 60% ethylene (C_2H_4) and 40% argon (Ar). How big a cylinder (or how many) must be purchased if you are to use 300 ft^3 of gas measured at the pilot-plant conditions of 100 atm and 300°F?

Cylinder type	Cost	Pressure (psig)	Gas (lb)
1A	$40.25	2000	62
2	32.60	1500	47
3	25.50	1500	35

State any additional assumptions. You can buy only one type of cylinder.

Section 3.3

3.70. Prepare a Cox chart for:

(a) Acetic acid vapor
(b) Heptane
(c) Ammonia
(d) Ethanol

from 0°C to the critical point (for each substance). Compare the estimated vapor pressure at the critical point with the critical pressure.

3.71. Use the Antoine equation (Appendix G) to estimate the vapor pressure of chloroform at 25°C and compare your calculated value with the experimental value obtained from a handbook. Do they agree? Then compute the temperature at which chloroform has a vapor pressure of 400 mm Hg absolute.

3.72. The vapor pressure of a highly volatile liquid (Q) was measured at 0°C and at 204°C. The results were 103 kPa and 998 kPa, respectively. If dry air in a container initially at 24°C and standard atmospheric pressure is saturated with Q at constant temperature and volume:

(a) What is the final pressure of the mixture?
(b) What is the composition of the final mixture?

3.73.* Estimate the vapor pressure of ethyl bromide at 125°C from vapor-pressure data taken from a handbook or a journal.

3.74.* From the following data, estimate the vapor pressure of sulfur dioxide at 100°C; the actual vapor pressure is about 29 atm.

t (°C)	−10	6.3	32.1	55.5
p^* (atm)	1	2	5	10

3.75. Use the Antoine equation to estimate the vapor pressure of sulfur dioxide at −10°C and compare with the experimental value (taken from a handbook).

Section 3.4

3.76. A large chamber contains dry N_2 at 27°C and 101.3 kPa. Water is injected into the chamber. After saturation of the N_2 with water vapor, the temperature in the chamber is 27°C.

(a) What is the pressure inside the chamber after saturation?

(b) How many moles of H_2O per mole of N_2 are present in the saturated mixture?

3.77. The vapor pressure of hexane (C_6H_{14}) at $-20°C$ is 14.1 mm Hg absolute. Dry air at this temperature is saturated with the vapor under a total pressure of 760 mm Hg. What is the percent excess air for combustion?

3.78. In a search for new fumigants, chloropicrin (CCl_3NO_2) has been proposed. To be effective, the concentration of chloropicrin vapor must be 2.0% in air. The easiest way to get this concentration is to saturate air with chloropicrin from a container of liquid. Assume that the pressure on the container is 100 kPa. What temperature should be used to achieve the 2.0% concentration? From a handbook, the vapor pressure data are (T, °C; vapor pressure, mm Hg): 0, 5.7; 10, 10.4; 15, 13.8; 20, 18.3; 25, 23.8; 30, 31.1.

At this temperature and pressure, how many kg of chloropicrin are needed to saturate 100 m^3 of air?

3.79. Fifty cubic feet of air saturated with water 90.0°F and 29.80 in. Hg are dehydrated. Compute the volume of the dry air and the pounds of moisture removed.

3.80. Suppose that a vessel of dry nitrogen at 70.0°F and 29.90 in. Hg is saturated thoroughly with water. What will be the pressure in the vessel after saturation if the temperature is still 70.0°F?

3.81. 100 lb mol per hour of hexane (C_6H_{14}) vapor are burned with 10% excess air in an efficient furnace. The barometric pressure is 760 mm Hg and the dew point of the ambient air is 80°F.

(a) What is the flow rate of the entering air (do not neglect the ambient H_2O), in standard cubic feet per minute? Assume the air is saturated at 80°F.

(b) What is the dew point of the exhaust gas if the exhaust pressure is 750 mm Hg?

(c) What is the flow rate of the exhaust gas in actual cubic feet per minute if the exhaust stack pressure is 750 mm Hg and the temperature is 350°F?

3.82. CH_4 is completely burned with air. The outlet gases from the burner, which contain no oxygen, are passed through an absorber where some of the water is removed by condensation. The gases leaving the absorber have a nitrogen mole fraction of 0.8335. If the exit gases from the absorber are at 130°F and 20 psia, calculate:

(a) To what temperature must this gas be cooled at constant pressure in order to start condensing more water?

(b) To what pressure must this gas be compressed at constant temperature before more condensation will occur?

3.83. A mixture of acetylene (C_2H_2) with an excess of oxygen measured 350 ft^3 at 25°C and 745 mm Hg pressure. After explosion, the volume of the dry gaseous product was 300 ft^3 at 60°C and the partial pressure of the dry product was 745 mm Hg. Calculate the partial volumes of acetylene and of oxygen in the original mixture. Assume that the final gas is saturated and that only enough water is formed to saturate the gas.

3.84. A mixture of air and benzene contains 10 mole % benzene at 38°C and 790 mm Hg pressure absolute. The vapor pressure of benzene is given as

$$\log_{10} p^* = 6.906 - \frac{1211}{220.8 + t}$$

where p^* is the vapor pressure in mm Hg and t is in °C. What is the dew point of the mixture?

3.85. It is desired to represent the vapor pressure of an organic substance by an equation of the form

$$p^* = p_0^* e^{m/T}$$

where p^* is the vapor pressure, T the absolute temperature, and m and p_0^* are unknown constants. If 100 m^3 of dry air (measured at standard conditions) is required to vaporize 0.5 kg mol of the organic material at a temperature of 290 K and a pressure of 1 atm and only 50 m^3 are required for the 0.5 kg mol at 340 K and 1 atm, calculate the constants p_0^* and m.

3.86. The vapor pressure of hexane (C_6H_{14}) at −20°C is 14.1 mm Hg. Dry air at this temperature is saturated with the vapor under a total pressure of 760 mm Hg.

(a) What is the percent excess air for combustion?

(b) What is the flue-gas analysis if complete combustion occurs?

3.87. Liquid hexane is insoluble in water; hence each substance exerts its vapor pressure independently of the other. Compute the partial pressure of **(a)** the hexane and **(b)** the water if the gas mixture, containing 150,000 kg of hexane (C_6H_{14}) and 4200 kg of water, is initially at 100°C and 200 kPa absolute. To what temperature must the mixture be lowered before the water starts to condense out, if the pressure remains constant? Has hexane started to condense at this temperature? Support your answers with the necessary data and calculations.

3.88. A solution containing 12 wt % of dissolved nonvolatile solid is fed to a flash distillation unit. The molecular weight of the solid is 123.0. The effective vapor pressure of the solution is equal to the mole fraction of water,

$$p = p^* x$$

where p = effective vapor pressure of the solution
p^* = vapor pressure of pure water
x = mole fraction of water

The pressure in the flash distillation unit is 1.121 psia and the temperature is 110°F. Calculate the pounds of pure water obtained in the vapor stream per 100 lb of feed solution and the weight percent of the dissolved nonvolatile solid leaving in the liquid stream.

3.89. A mixture of water (15%), dimethyl acetamide (70%), and some inert liquid that has negligible vapor pressure (15%) is to be flashed at 194°F and 1.94 psia. The K values are water: 5.26 and dimethylacetamide: 0.64. How many moles of vapor and liquid are formed at equilibrium, and what are the mole fractions of the vapor and liquid components?

3.90.* A mixture of hydrocarbons consisting of an equal number of moles each of propane, normal butane and normal pentane is to be fractionated in a well insulated column. The figure shows the compositions and the overall material balance. The overhead product is completely condensed to a saturated liquid at 100°F. What is the temperature in the top tray of the column where the liquid vaporizes at equilibrium to form the overhead? Hint: Assume that the pressure in the condenser is the same as that in the top tray.

3.91.* A mixture of 50% benzene and 50% toluene is contained in a cylinder at 19.34 in. Hg absolute. Calculate the temperature range in which a two phase system can exist.

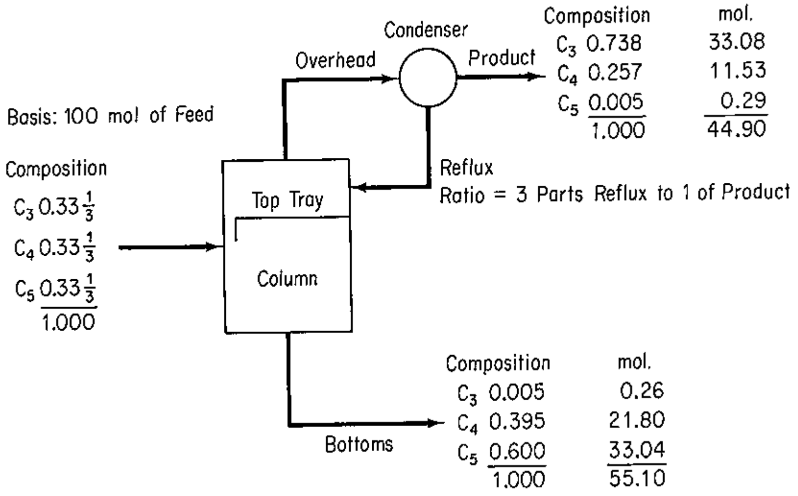


Figure P3.90

3.92. For an ideal binary system (of components designated by subscripts 1 and 2) with the vapor and liquid phases in equilibrium, show that if the temperature and pressure are specified

$$x_2 = \frac{K_1 - 1}{K_1 - K_2}$$

where x_i is the mole fraction of component i in the liquid phase, and K_i are the equilibrium constants $y_i = K_i x_i$.

3.93.* Calculate the liquid (L) and vapor (V) compositions and the temperature (in °F) for the flash vaporization of the following feed stream (F) at 300 psia for a value of V/F of **(a)** 0.3 and **(b)** 0.6.

Component	Mole fraction	b_i values		
		b_1	b_2	b_3
n-Hexane	0.05	0.2420	0.2713×10^{-2}	0.0876×10^{-4}
n-Pentane	0.20	0.5087	0.4625×10^{-2}	0.1051×10^{-4}
i-Pentane	0.20	0.5926	0.5159×10^{-2}	0.1094×10^{-4}
n-Butane	0.20	0.2126	0.7618×10^{-2}	0.1064×10^{-4}
i-Butane	0.35	0.2606	0.8650×10^{-2}	0.1017×10^{-4}

The equilibrium constants can be calculated from the relation

$$K_i = b_{1i} + b_{2i}(T - 250) + b_{3i}(T - 250)^2$$

where T is in °F.

3.94. For what temperature range can the following mixture be part liquid and part vapor at 100 psia?

	Mol %
Propane	10
i-Butane	10
n-Butane	40
i-Pentane	10
n-Pentane	30
Total	100

3.95. Assume that Raoult's law holds for the following mixture.

	Mol %
n-Butane	50
i-Pentane	30
n-Pentane	20
Total	100

(a) What is the dew point pressure of the mixture at 100°F?

(b) What is the dew point temperature at 50 psig? The barometer reads 775 mm Hg.
(c) What is the bubble point temperature at 70 psia?
(d) What is the bubble point pressure at 100°F?

3.96. Determine the moles of vapor and liquid that exist if 1128 moles of the following mixture is maintained at 325 psia and 100°F.

	Mole %	K value
Methane	13.7	8.8
Ethane	20.6	1.82
Propylene	15.9	0.78
Propane	33.2	0.71
Isobutane	7.2	0.35
n-Butane	9.4	0.27
Total	100.0	

3.97. A mixture of hydrocarbons has the following composition in mol %:

	Mol %
CH_4	1.0
C_2H_6	15.0
C_3H_8	25.0
i-C_4H_{10}	14.0
n-C_4H_{10}	25.0
n-C_5H_{12}	20.0
Total	100.0

The mixture exists at a pressure of 100 psia and is all in the vapor phase.

(a) What is the minimum temperature at which it could be a vapor?
(b) What mole % of the vapor is condensed if the mixture is cooled to 90°F?
(c) Calculate the liquid and vapor compositions in part (b).
(d) For the conditions in part (b), what percent of the total methane present is in the vapor phase? The pentane?
(e) What temperature is required to condense 40 mol % of the total (still at 100 psia)?
(f) What temperature is required to condense 100% of the vapor?
(g) If 100,000 ft^3 at S.C. of the original gas is introduced into a separator at 100 psia and 90°F, how many gallons per minute of liquid have to be handled by the pump removing liquid from this separator?

Assume that the liquid specific gravities are the same at 60°F and 90°F. Note the important effect of the 1% CH_4 on the bubble point and the insignificant effect of the pentane. Note also how the opposite is true for the dew point.

Section 3.5

3.98. The percent relative humidity of air at 90°F is 60% (where the vapor pressure of water is 0.698 psia). What is:

(a) The humidity of the air?
(b) The absolute humidity of the air?

3.99. Oxygen at 21°C and 1 atm with 80% relative humidity is supplied to a biotech reactor. Calculate:

(a) The molal humidity
(b) The humidity
(c) The percent saturation
(d) The relative humidity
(e) The dew point of the supplied gas.

3.100. If a gas at 140°F and 30 in. Hg abs. has a molal humidity of 0.03 mole of H_2O per mole of dry air, calculate:

(a) The percentage humidity
(b) The relative humidity (%)
(c) The dew point of the gas (°F)

3.101. The Weather Bureau reports a temperature of 90°F, a relative humidity of 85% and a barometric pressure of 14.696 psia.

(a) What is the molar humidity?
(b) What is the humidity (weight basis)?
(c) What is the percentage "absolute" humidity?
(d) What is the saturation temperature or the dew point?
(e) What is the number of degrees of superheat of the water vapor?
(f) Determine the molar humidity and dew point if the air is heated to 105°F, pressure remaining steady.
(g) Determine the molar humidity and dew point if the air is cooled to 60°F, pressure remaining steady.
(h) What fraction of the original water is condensed at 60°F?

3.102. On a warm day the barometric pressure is 29.92 in. Hg, the temperature is 90°F, and the relative humidity is 70%.

(a) What is the dew point of the air?

(b) At night the temperature drops to 60°F. What is the barometric pressure of the air? (State all assumptions but do not assume a constant pressure process.)

3.103. What is the mass of 3.00 m^3 of air at 27°C and a total pressure of 115 kPa absolute if the relative humidity of the air is 65%?

3.104. The Environmental Protection Agency has promulgated a national ambient air quality standard for hydrocarbons: 160 $\mu g/m^3$ is the maximum 3-hr concentration not to be exceeded more than once a year. It was arrived at by considering the role of hydrocarbons in the formation of photochemical smog. Suppose that in an exhaust gas benzene vapor is mixed with air at 25°C such that the partial pressure of the benzene vapor is 2.20 mm Hg. The total pressure is 800 mm Hg. Calculate:

(a) The moles of benzene vapor per mole of gas (total)

(b) The moles of benzene per mole of benzene free gas

(c) The weight of benzene per unit weight of benzene-free gas

(d) The relative saturation

(e) The percent saturation

(f) The micrograms of benzene per cubic meter

(g) The grams of benzene per cubic foot

Does the exhaust gas concentration exceed the national quality standard?

3.105. Sufficient oxygen at 21°C and 100 kPa absolute with 80% absolute saturation of water vapor is supplied to react with sewage to reduce the concentration of biological material to below the quality control limits. Calculate the following for the supplied gas:

(a) The molal saturation

(b) kg water/kg bone-dry oxygen

(c) The relative saturation

(d) The dew point

3.106. Thermal pollution is the introduction of waste heat into the environment in such a way as to adversely affect environmental quality. Most thermal pollution results from the discharge of cooling water into the surroundings. It has been suggested that power plants use cooling towers and recycle water rather than dump water into the streams and rivers. In a proposed cooling tower, air enters and passes through baffles over which warm water from the heat exchanger falls. The air enters at a temperature of 80°F and leaves at a temperature of 70°F. The partial pressure of the water vapor in the air entering is 5 mm Hg and the partial pressure of the water vapor in the air leaving the tower is 18 mm Hg. The total pressure is 740 mm Hg. Calculate:

(a) The relative humidity of the air-water vapor mixture entering and of the mixture leaving the tower

(b) The percentage composition by volume of the moist air entering and of that leaving

(c) The percentage composition by weight of the moist air entering and of that leaving

(d) The percent absolute humidity of the moist air entering and leaving

(e) The pounds of water vapor per 1000 ft^3 of mixture both entering and leaving

(f) The pounds of water vapor per 1000 ft^3 of vapor-free air both entering and leaving

(g) The weight of water evaporated if 800,000 ft^3 of air (at 740 mm and 80°F) enters the cooling tower per day

Section 3.6

3.107. A drier must evaporate 200 lb/hr of H_2O. Air at 70°F and 50% $\mathcal{RH}$ enters the drier, leaving at 140°F and 80% $\mathcal{RH}$. What volume of dry air is necessary per hour?

3.108. 1000 ft^3 of air, saturated with H_2O, at 30°C and 740 mm Hg, are cooled to a lower temperature and one-half of the H_2O is condensed out. Calculate:

(a) How many pounds of H_2O are condensed out

(b) The volume of dry air at 30°C and 740 mm Hg

3.109. Moist air at 25°C and 100 kPa with a dew point of 19.5°C is to be dehydrated so that during its passage through a large cold room used for food storage excess ice formation can be avoided on the chilling coils in the room. Two suggestions have been offered: (1) cool the moist air to below the saturation temperature at 100 kPa, or (2) compress the moist air above the saturation pressure at 25°C. Calculate the saturation temperature for (1) and the total pressure at saturation for (2).

(a) If 60% of the initial water in the entering moist air has to be removed before the air enters the cold room, to what temperature should the air in process (1) be cooled?

(b) What pressure should the moist air in process (2) reach?

(c) Which process appears to be the most satisfactory? Explain.

3.110. A mixture of air and water at a temperature of 30°C and a pressure of 750 mm Hg has a relative humidity of 75%. The wet gas is compressed to 40 psia and cooled to 20°C. How many cubic feet of original gas were compressed if 0.75 lb of condensate (water) was removed from a separator placed adjacent to the cooler?

3.111.* One hundred cubic meters of saturated gas at 25°C and 100 kPa (saturated with ethyl alcohol) are cooled so that one-half of the ethyl alcohol originally present condenses out. To what temperature was the gas cooled if the cooling occurs at constant pressure? List by number all the equations and other information you need to solve this problem. Include the known values of the variables and constants in the equations. List the unknowns by symbol. State in order the specific steps you would take to solve for the final temperature. Solve for it.

3.112. To ensure a slow rate of drying and thereby prevent checking of the dried product, the inlet relative humidity to a drier is specified as 70% at 75°F. The air leaving the drier has a relative humidity of 90% at 70°F. If the outside air has a dew point of 40°F, what fraction of the air leaving the drier must be mixed and recycled with the outside air to provide the desired moisture content in the air fed to the drier?

3.113. A dryer used to season wood evaporates 27 kg/hr of water from freshly cut greenwood. Air enters the dryer at 40% relative humidity and 47°C leaves the dryer at 80% relative humidity and 37°C. If the entire process operates at 100 kPa, how many m^3/hr of moist air enter the dryer?

3.114. A hydrocarbon fuel is burned with bone-dry air in a furnace. The stack gas is at 116 kPa and has a dew point of 47°C. The Orsat analysis of the gas shows 10 mol % carbon dioxide; the balance consists of oxygen and nitrogen. What is the ratio of hydrogen to carbon in the hydrocarbon fuel?

3.115. A low-energy gas from in situ combustion of shale oil has the following composition CO_2: 10.0%, CO: 20.0%, H_2: 20.0%, CH_4: 2.0%, and N_2: 48.0%. On combustion the Orsat analysis of the flue gas gives CO_2: 14.3%, CO: 1.0%, O_2: 4.3%, and N_2: 80.4%. Calculate the dew point of the flue gas if burned with air entering at 25°C and 30% relative humidity. The barometer reads 100 kPa.

3.116. Hot air that is used to dry pharmaceuticals is recycled in a closed loop to prevent the contamination of the moist material from atmospheric impurities. In the first conditioning step for the air, 5000 k mol/hr at 105 kPa and 42°C with a 90% relative humidity are fed to a condenser to remove some of the water picked up previously in the dryer. The air exists the condenser at 17°C and 100 kPa containing 91 k mol/hr of water vapor. Next, the air is heated in a heat exchanger to 90°C, and then goes to the dryer. By the time the air enters the dryer, the pressure of the stream has dropped to 95 kPa and the temperature is 82°C.

(a) How many moles of water per hour enter the condenser?
(b) What is the flow rate of the condensate water in kg/hr?
(c) What is the dew point of the air in the stream exiting the condenser?
(d) What is the dew point of the air in the stream entering the dryer?

3.117. Around airports jet aircraft can become major contributors to pollution, and as aircraft activity increases and public concern brings other sources under control, the relative contribution to aircraft to pollution could go up. Recently, federal-, state-, and local-government pressure has speeded the introduction of new combustors in aircraft. In a test for a supersonic aircraft fuel with the average composition $C_{1.20}H_{4.40}$, the fuel is completely burned with the exact stochiometric amount of air required. The air is supplied at 25°C and 101 kPa, with an absolute humidity of 80%. The combustion products leave at 480°C and 106 kPa pressure and are passed through a heat exchanger from which they emerge at 57°C and 100 kPa pressure.

(a) For the entering air, compute:
  (1) The dew point
  (2) The molal humidity
  (3) The relative humidity
(b) How much water is condensed in the heat exchanger per kilogram of gas burned, and hence must be removed as liquid water?

3.118.* A certain gas contains moisture, and you have to remove the moisture by compression and cooling so that the gas will finally contain not more than 1% moisture (by volume). You decide to cool the final gas down to 21°C.

(a) Determine the minimum final pressure needed.
(b) If the cost of the compression equipment is

$$\text{cost in \$} = (\text{pressure in psia})^{1.40}$$

and the cost of the cooling equipment is

$$\text{cost in \$} = (350 - \text{temp. K})^{1.9}$$

is 21°C the best temperature to use? Hint: Look at the list of computer programs on the disk in the back of this book.

3.119. Oxalic acid ($H_2C_2O_4$) is burned with 248% excess air, 65% of the carbon burning to CO. Calculate:

(a) The Orsat gas analysis
(b) The volume of air at 90°F and 785 mm Hg used per pound of oxalic acid burned
(c) The volume of stack gases at 725°F and 785 mm Hg per pound of oxalic acid burned
(d) The dew point of the stack gas

3.120. A synthesis gas is made by partial oxidation of butane (C_4H_{10}) in the presence of steam and air. The product synthesis gas has the percent composition 3.5% CO_2, 2.3% C_2H_4, 23.2% CO, 39.3% H_2, 11.6% CH_4, 1.7% C_2H_6, and 18.4% N_2. How many cubic meters of air (at 40% relative humidity, 30°C, 104 kPa) are used per cubic meter of butane (at 25°C, 120 kPa, dry)?

3.121. A flue gas from a furnace leaves at 315°C and has an Orsat analysis of 16.7% CO_2, 4.1% O_2, and 79.2% N_2. It is cooled in a spray cooler and passes under slight suction through a duct to an absorption system at 32.0°C to remove CO_2 for the manufacture of dry ice. The gas at the entrance to the absorber analyzes 14.6% CO_2, 6.2% O_2, and 79.2% N_2, due to air leaking into the system. Calculate the cubic meters of air leaked in per cubic meter of gas to the absorber, both measured at the same temperature and pressure.

3.122. Soybean flakes from an extraction process are reduced from 0.96 lb of C_2HCl_3 per pound of dry flakes to 0.05 lb of C_2HCl_3 per pound of dry flakes in a desolventizer by a stream of N_2 which vaporizes the C_2HCl_3. The entering N_2 contains C_2HCl_3 such that its dew point is 30°C. The N_2 leaves at 90°C with a relative saturation of 60%. The pressure in the desolventizer is 760 mmHg, and 1000 lb/hr of dry flakes pass through the drier.

(a) Compute the volume of N_2 plus C_2HCl_3 leaving the desolventizer at 90°C and 760 mm Hg in cubic feet per minute.

(b) The N_2 leaving the desolventizer is compressed and cooled to 40°C, thus condensing out the C_2HCl_3 picked up in the desolventizer. What must the pressure in the condenser be if the gas is to have a dew point of 30°C at the pressure of the desolventizer?

3.123. One thousand pounds of a slurry containing 10% by weight of $CaCO_3$ is to be filtered on a rotary vacuum filter. The filter cake from the filter contains 60% water. This cake is then placed into a drier and dried to a moisture content of 9.09 lb of H_2O/100 lb of $CaCO_3$. If the humidity of the air entering the drier is 0.005 lb of water per pound of dry air and the humidity of the air leaving the drier is 0.015 lb of water per pound of dry air, calculate:

(a) Pounds of water removed by the filter

(b) Pounds of dry air needed in the drier

3.124. Air is humidified in the spray chamber shown in Fig. P3.124. Calculate how much water must be added per hour to the tower to process 10,000 ft³/hr of air metered at the entrance conditions.

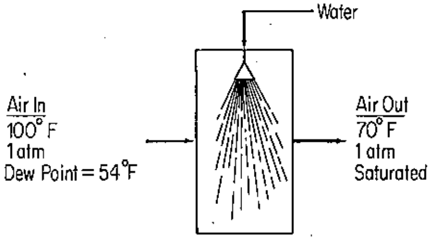


Figure P3.124

3.125. A wet sewage sludge contains 50% by weight of water. A centrifuging step removes water at a rate of 100 lb/hr. The sludge is dried further by air. Use the data in Fig. P3.125 to determine how much moist air (in cubic feet per hour) is required for the process shown.

3.126. Refer to the process flow diagram (Fig. P3.126) for a process that produces maleic anhydride by the partial oxidation of benzene. The moles of O_2 fed to the reactor

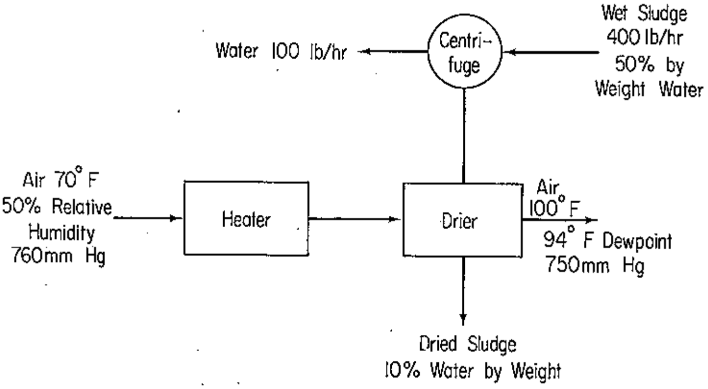


Figure P3.125

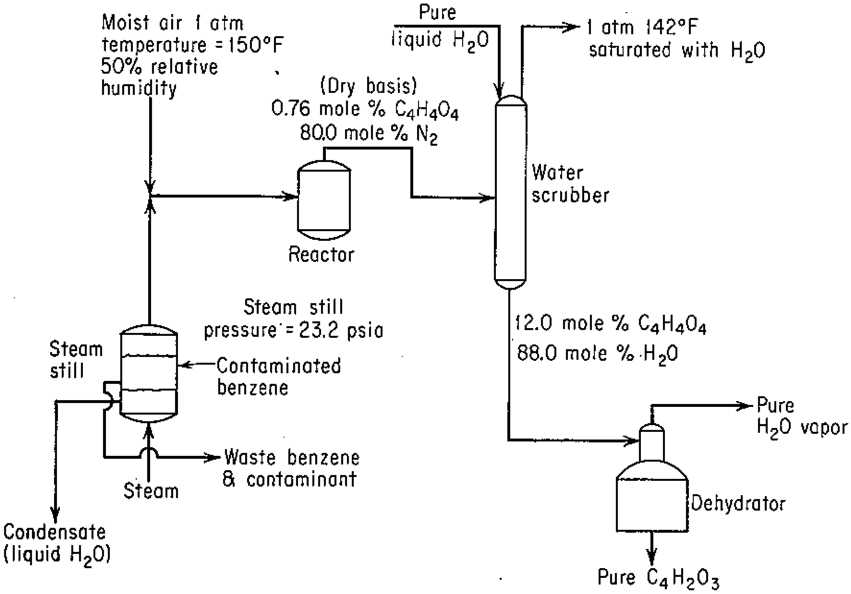
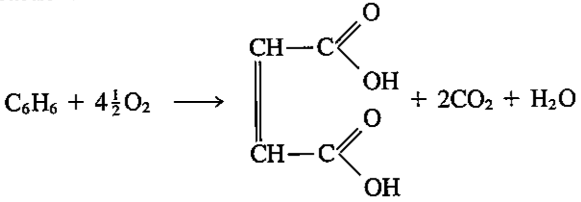


Figure P3.126

per mole of pure benzene fed to the reactor is 18.0. All the maleic acid produced in the reactor is removed with water in the bottom stream from the water scrubber. All the C_6H_6, O_2, CO_2, and N_2 leaving the reactor leave in the stream from the top of the water scrubber, saturated with H_2O. Originally, the benzene contains trace amounts of a nonvolatile contaminant that would inhibit the reaction. This contaminant is removed by steam distillation in the steam still. The steam still contains liquid phases of both benzene and water (benzene is completely insoluble in water). The benzene phase is 80% by weight, and the water phase is 20% by weight of the total of the two liquid phases in the still. Other process conditions are given in the flow sheet. Use the following vapor-pressure data:

Temperature (°F)	Benzene (psia)	Water (psia)
110	4.045	1.275
120	5.028	1.692
130	6.195	2.223
140	7.570	2.889
150	9.178	3.718
160	11.047	4.741
170	13.205	5.992
180	15.681	7.510
190	18.508	9.339
200	21.715	11.526

The reactions are



(1)

$$C_6H_6 + 7\tfrac{1}{2}O_2 \longrightarrow 6CO_2 + 3H_2O \qquad (2)$$

Calculate:

(a) The moles of benzene undergoing reaction (2) per mole of benzene feed to the reactor

(b) The pounds of H_2O removed in the top stream from the dehydrator per pound mole of benzene feed to the reactor

(c) The composition (mole percent, wet basis) of the gases leaving the top of the water scrubber

(d) The pounds of pure liquid H_2O added to the top of the water scrubber per pound mole of benzene feed to the reactor

Section 3.7

3.127. When production is taken from a gas reservoir, is it possible to decrease the pressure at the well and recover liquids as well as gas? Explain using the phase diagram in Fig. P3.127 showing the p–T properties of a two-component gas condensate.

3.128. At the critical point for Fig. P3.127, how many degrees of freedom exist according to the phase rule? How many degrees of freedom exist at each of the points in Fig. P3.127 marked A, B, C, D and E? Show your computations.

3.129. A vessel contains liquid ethanol, ethanol vapor, and N_2 gas. How many phases, components, and degrees of freedom are there according to the phase rule.

3.130. The triple point and the ice point for water differ by 0.0095°C. Why?

3.131. What is the number of degrees of freedom according to the phase rule for each of the following systems:

(a) Solid iodine in equilibrium with its vapor

(b) A mixture of liquid water and liquid octane (which is immiscible in water) both in equilibrium with their vapors

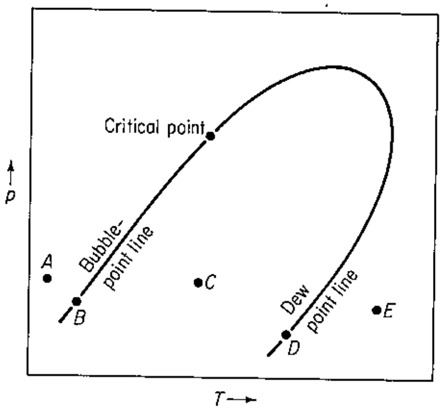


Figure P3.127

(c) CO, CO_2, H_2, H_2O, CH_3OH, and CH_4 in chemical equilibrium at high temperature

3.132. A mixture of zinc oxide (ZnO) and carbon reacts with the following reactions (the first listed reaction is the main reaction):

$$\begin{aligned} ZnO + C &\longrightarrow CO + Zn \\ ZnO + CO &\longrightarrow CO_2 + Zn \\ Zn + \tfrac{1}{2}O_2 &\longrightarrow ZnO \end{aligned}$$

Also, the carbon reacts as follows:

$$\begin{aligned} C + \tfrac{1}{2}O_2 &\longrightarrow CO \\ C + O_2 &\longrightarrow CO_2 \\ CO + \tfrac{1}{2}O_2 &\longrightarrow CO_2 \end{aligned}$$

If zinc produced by the reaction is in the liquid phase (and has a significant vapor pressure), at equilibrium how many degrees of freedom exist for the system?

3.133. In the decomposition of $CaCO_3$ in a sealed container from which the air was initially pumped out, you generate CO_2 and CaO. If not all of the $CaCO_3$ decomposes at equilibrium, how many degrees of freedom exist for the system according to the Gibbs phase rule?

3.134. Calculate C, $\mathcal{P}$, and F in the Gibbs phase rule for the following system in a closed vessel: AgCl(s), H_2O(s), H_2O(l), H_2O(g), H^+(aq), Cl^-(aq), HCl(g), CO_2(g), CO_2(aq), HCl(aq).

3.135. Water is pumped into a pipe at the rate of 250 kg/hr at 950 kPa and 175°C. Because of friction in the pipe, pressure losses due to pipe fittings and valves, the pressure at the exit of the pipe drops to 760 kPa. Is the entering water liquid, vapor, or a mixture of both? Determine the fraction of each. Is the exit water liquid, vapor, or both? Determine the fraction of each. From the steam tables or similar source, determine the density of the overall mixture in the pipe at both locations. How many degrees of freedom exist according to the phase rule at each location?

3.136. Examine the volume-pressure chart for toluene in Appendix J, Fig. J.1. If a cylinder contains toluene with a volume of 2.1 ft^3/lb mol at a pressure of 30 psia, is the toluene all liquid, all vapor, or a mixture of the two phases?

3.137. Is carbon dioxide at 31°C and 70 atm a two-phase or a single-phase system? Repeat for 25°C.

PROBLEMS THAT REQUIRE WRITING COMPUTER PROGRAMS

3.1. You need to fill a reactor with 8.00 lb of NH_3 gas to a pressure of 150 psia at a temperature of 250°F. Apply the van der Waals equation to find the volume of the reactor. Prepare a computer program to solve Eq. (3.13) for V. How do you select the initial estimate of V to start the calculations?

3.2. An experiment was designed to test the validity of Charles' law using the expansion of a fixed amount of air in a balloon in a flask of water. The data taken were as follows at 751 mm Hg constant pressure:

Temp. (°C)	Incremental vol. of balloon (cm^3)	Temp. (°C)	Incremental vol. of balloon (cm^3)
22	0.0	44	4.2
23	0.3	47	4.9
24	0.45	50	5.5
25	0.8	53	6.5
26	0.8	55	7.0
27	1.2	59	9.0
29	2.0	61	10.0
34	3.0	63	11.9
37	3.2	65	13.5
39	3.8	67	14.7
43	3.8		

Ascertain how well the ideal gas law (Charles' law) is obeyed. A least-squares computer code should be used to evaluate the experimental data. What was the initial volume of gas (at 22°C)? Assume that the pressure on the air in the balloon is constant.

3.3. Use the Benedict–Webb–Rubin (BWR) equation of state (see Table 3.2)

$$p = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{T^2}\right)\rho^2 + (bRT - a)\rho^3$$

$$+ a\alpha\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2)$$

where ρ is the density, to predict the density of a mixture of two nonideal gases. Let the pressure be in atmospheres and calculate the density in both gram moles per liter and pound moles per cubic foot for selected pairs of p and T. Use the following rule illustrated for A_0 to obtain the coefficients A_0, B_0, C_0, a, b, c, α, and γ for the mixture:

$$A_0 = \left(\sum_{i=1}^{n} x_i A_{0i}^{1/2}\right)^2$$

where n is the number of components in the mixture and x_i is the mole fraction. Values of the BWR constants for 38 pure components have been tabulated by H. W. Cooper and J. C. Goldfrank, *Hydrocarbon Processing*, v. 46, no. 12, p. 141 (1967). For reduced temperatures above 0.6 and reduced specific volumes less than 0.5, the BWR equation should be accurate to within 1%.

3.4. A cylinder containing 11 lb of CO_2 initially at 200°F and 1500 psia is heated to a final temperature of 400°F. Prepare a computer program to calculate the final pressure in psia using the van der Waals equation.

3.5. Write a complete program to convert mm Hg to psia for the range 100 to 760 mm Hg at each 10-mm increment. Print the results of each conversion.

ENERGY BALANCES

4

In this chapter we take up the second prominent topic in this book, energy balances. It is reported that the average power consumption in the United States per capita is equivalent to three dozen hard-working male slaves or nine horses running at full gallop! Clearly, conversion of inexpensive sources of energy has made the industrial revolution possible. Figure 4.1 indicates what these sources of energy are and how they are used.

To provide publicly acceptable, effective, and yet economical conversion of our resources into energy and to properly utilize the energy so generated, you must understand the basic principles underlying the generation, uses, and transformation of energy in its different forms. The answers to questions such as "Is thermal pollution inherently necessary"; "What is the most economic source of fuel"; "What can be done with waste heat"; "How much steam at what temperature and pressure are needed to heat a process" and related questions can only arise from an understanding of the treatment of energy transfer by natural processes or machines. As an example, examine Fig. 4.2 and try to answer the question: What can be done economically to reduce the loss of energy rejected as heat? Can you offer reasonable suggestions at this stage in your professional life?

In this chapter we discuss energy balances together with the accessory background information needed to understand and apply them correctly. Before taking up the energy balance itself, we discuss the types of energy that are of major interest to engineers and scientists and some of the methods that are used to measure and evaluate these forms of energy. Our main attention will be devoted to heat, work, enthalpy, and internal energy. Next, the energy balance will be described and applied to practical problems. Finally, we shall discuss the energy balance associated with reaction and how energy, evolving from reactions, fits into industrial process calculations. Figure 4.3 shows the relationships among the topics discussed in this chapter and in previous chapters.

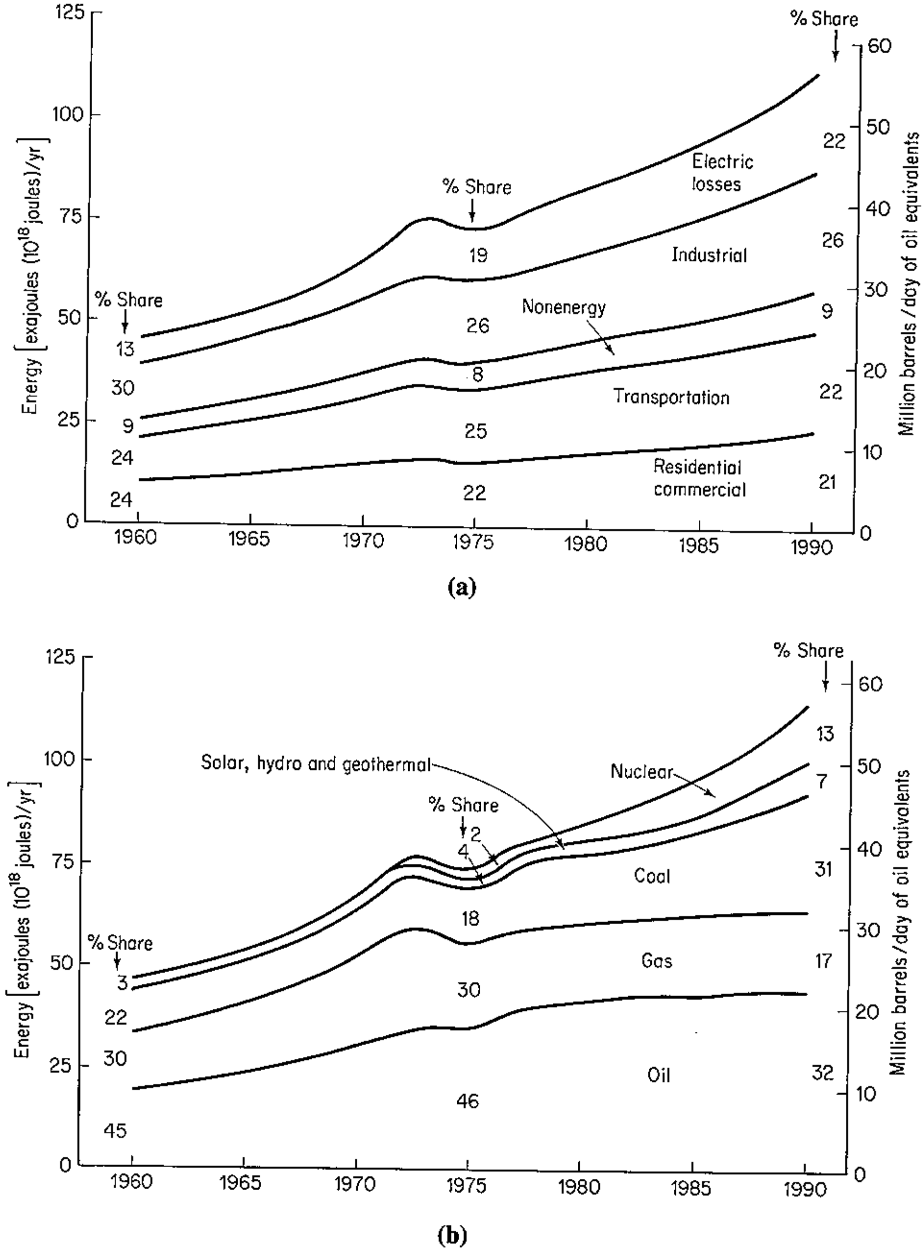


Figure 4.1 (a) United States energy demand by consuming sector; (b) United States energy supply by source.

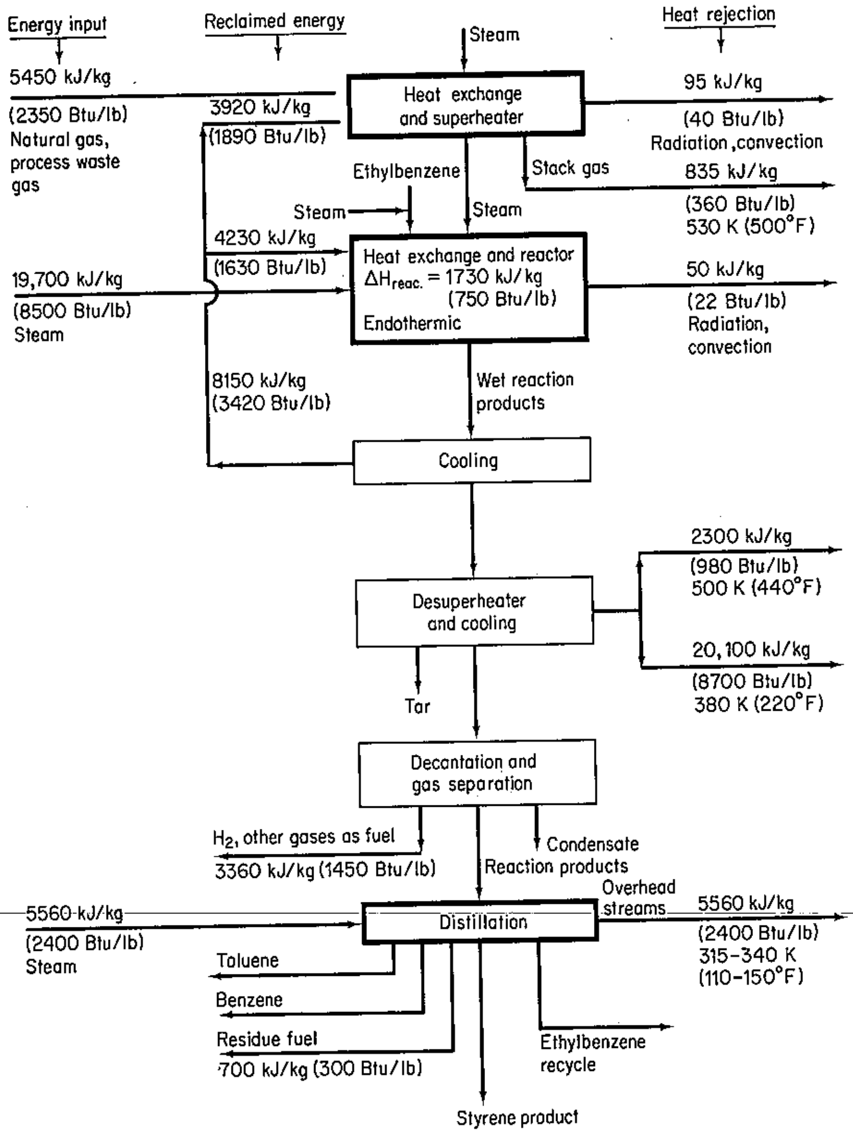


Figure 4.2 Energy balance in styrene production in the United States: 40% conversion of ethylbenzene to products, 90% selectivity to styrene. (From J. T. Reding and B. P. Shepherd, *Energy Consumption: The Chemical Industry*, Report EPA-650/2-75-032a, Environmental Protection Agency, Washington, D.C., April 1975.)

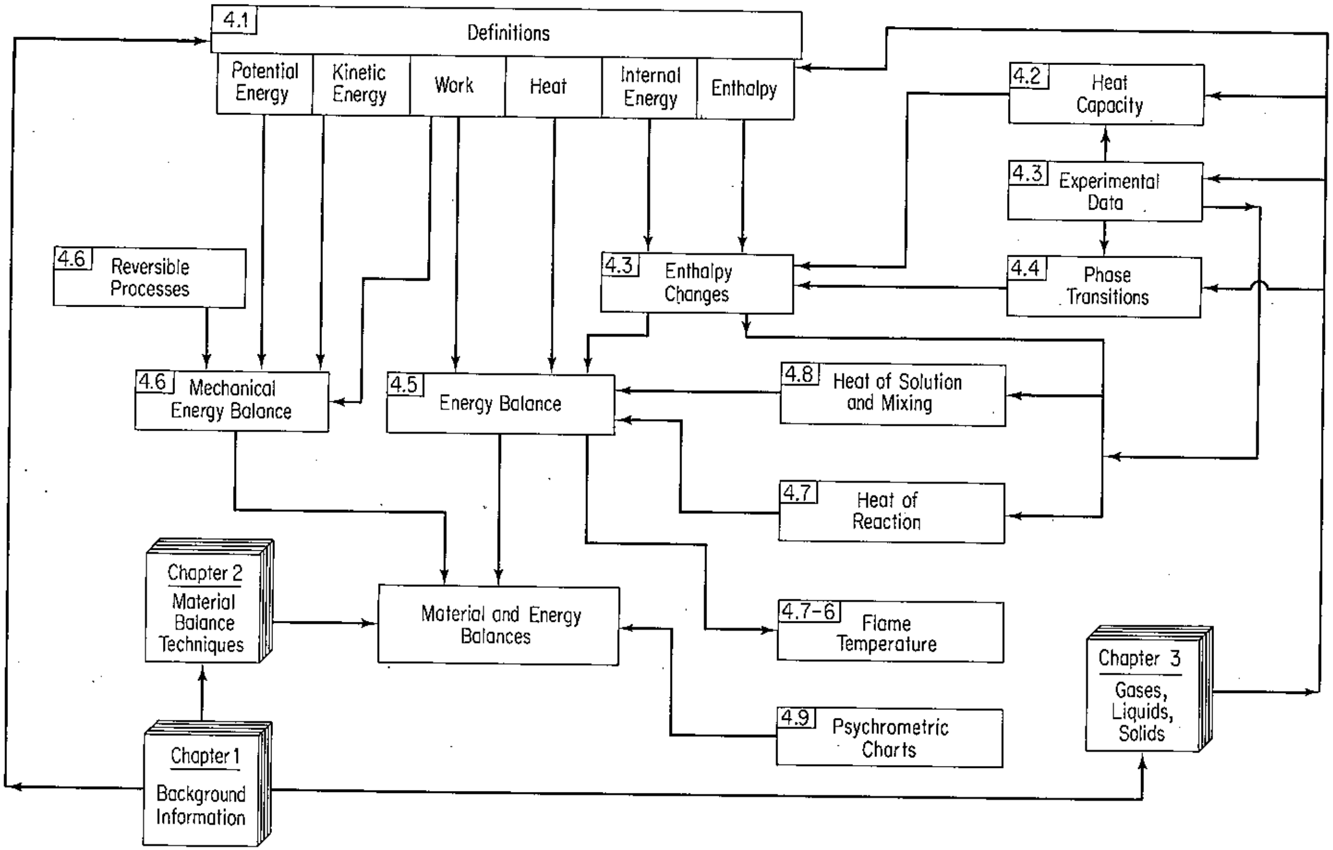


Figure 4.3 Hierarchy of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

4.1 CONCEPTS AND UNITS

Your objectives in studying this section are to be able to:

1. Define or explain the following terms: energy, system, closed system, nonflow system, open system, flow system, surroundings, property, extensive property, intensive property, state, heat, work, kinetic energy, potential energy, internal energy, enthalpy, initial state, final state, point (state) function, state variable, cyclical process, and path function.
2. Select and define a system suitable for problem solution, either closed or open, steady or unsteady state, and fix the system boundary.
3. Distinguish among potential, kinetic, and internal energy.
4. Convert energy in one set of units to another set.
5. List and apply the equations used to calculate kinetic energy, potential energy, and work.

As you already know, energy exists in many different forms. In Sec. 4.5 we assemble the various types of energy in the form of an energy balance. Before doing so, we need to clearly distinguish between the common types of energy, describe the units used to express energy, and learn how to calculate the values of various forms of energy.

What units are associated with energy? If you have forgotten, refer back to Table 1.1. No confusion exists with respect to the joule, but it is necessary to be careful in specifying what type of calorie or British thermal unit (Btu) is under consideration (there are four or five common kinds). For example, the type of calorie that is found in older tables of thermochemical properties of substances is the *thermochemical calorie* (equal to 4.184 J), whereas a second type of calorie is the *International Steam Table* (*I.T.*) *calorie* (equal to 4.1867 J). A kcal in nutrition is just called a "calorie"; that is, a hamburger containing 500 "calories" really contains 500 kcal.

In this section we characterize and define several common forms of energy. Unfortunately, many of the terms described below are used loosely in our ordinary conversation and writing, and thus have different connotations than those presented below. You may have the impression that you understand the terms from long acquaintance—be sure that you really do. For effective learning you must feel comfortable with them.

Certain terms that have been described in earlier chapters occur repeatedly in this chapter; these terms are summarized below with some elaboration in view of their importance.

System. Any arbitrarily specified mass of material or segment of apparatus to which we would like to devote our attention. A system must be defined by surrounding it with a system boundary. A system enclosed by a boundary that prohibits the transfer of mass across the boundary is termed a ***closed*** **system, or** ***nonflow*** **system,** in distinction to an ***open*** **system, or** ***flow*** **system,** in which the exchange of mass is permitted. All the mass or apparatus external to the defined system is termed the ***surroundings.*** Reexamine some of the example problems in Chap. 2 for illustrations of the location of system boundaries. You should always draw similar boundaries in the solution of your problems, since this step will fix clearly the system and surroundings.

Property. A characteristic of material that can be measured, such as pressure, volume, or temperature—or calculated, if not directly measured, such as certain types of energy. The properties of a system are dependent on its condition at any given time and not on what has happened to the system in the past.

An ***extensive property*** (variable, parameter) is one whose value is the sum of the values of each of the subsystems comprising the whole system. For example, a gaseous system can be divided into two subsystems which have volumes or masses different from the original system. Consequently, mass or volume is an extensive property.

An ***intensive property*** (variable, parameter) is one whose value is not additive and does not vary with the quantity of material in the subsystem. For example, temperature, pressure, density (mass per volume), and so on, do not change if the system is sliced in half or if the halves are put together.

Two properties are *independent* of each other if at least one variation of state for the system can be found in which one property varies while the other remains fixed. The number of independent intensive properties necessary and sufficient to fix the state of the system can be ascertained from the phase rule of Sec. 3.7-1.

State. The given set of properties of material at a given time. The state of a system does not depend on the shape or configuration of the system but only on its intensive properties.

Now that we have reviewed the concepts of system, property, and state, we can discuss the various types of energy with which we will be involved in this chapter. What forms can energy take? We shall consider here six quantities: work, heat, kinetic energy, potential energy, internal energy, and enthalpy. You probably have encountered many of these terms before.

Work. Work (W) is a term that has wide usage in everyday life (such as "I am going to work"), but has a specialized meaning in connection with energy balances. Work is a form of energy that represents a **transfer** between the system and surroundings. Work cannot be stored. For a mechanical force

$$W = \int_{\text{state 1}}^{\text{state 2}} \mathbf{F} \cdot ds \tag{4.1}$$

where **F** is an external force in the direction of s acting on the system (or a system force acting on the surroundings).

(a) The displacement may not be easy to define.
(b) Integration of $\mathbf{F} \cdot ds$ as shown in Eq. (4.1) does not always result in an equal amount of work being done by the system.
(c) Work can be exchanged without a mechanical force acting on the system boundaries (such as through magnetic or electric effects).

Note that unless the process (or path) under which work is carried out is specified from the initial to the final state of the system, you are not able to calculate the value of the work done. In other words, work done in going between the initial and final states can have *any* value, depending on the path taken. **Work is therefore called a *path function*,** and the value of W depends on the initial state, the path, and the final state of the system, as illustrated in the next example.

EXAMPLE 4.1 Calculation of Work by a Gas on a Piston

Suppose that an ideal gas at 300 K and 200 kPa is enclosed in a cylinder by a frictionless piston, and the gas slowly forces the piston up so that the volume of gas expands from 0.1 to 0.2 m³. Examine Fig. E4.1a. Calculate the work done by the gas on the piston if two different paths are used to go from the initial state to the final state:

Path *A*: expansion occurs at constant pressure (p = 200 kPa)
Path *B*: expansion occurs at constant temperature (T = 300 K)

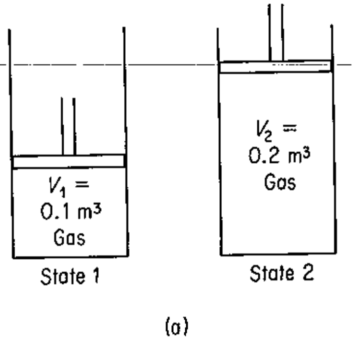


Figure E4.1a

Solution

The work is

$$W = \int_{\text{state 1}}^{\text{state 2}} \frac{\mathbf{F}}{A} \cdot A\, ds = \int_{V_1}^{V_2} p\, dV$$

because p is exerted normally on the piston face.

Path A

$$W = p\int_{V_1}^{V_2} dV = p(V_2 - V_1)$$

$$= \frac{200 \times 10^3\ \text{Pa}}{}\left|\frac{1\,\frac{\text{N}}{\text{m}^2}}{1\ \text{Pa}}\right|\frac{0.1\ \text{m}^3}{}\left|\frac{1\,\frac{\text{J}}{\text{m}}}{1\ \text{N}}\right.$$

$$= 20\ \text{kJ}$$

Path B

$$W = \int_{V_1}^{V_2} \frac{nRT}{V}\, dV = nRT \ln\left(\frac{V_2}{V_1}\right)$$

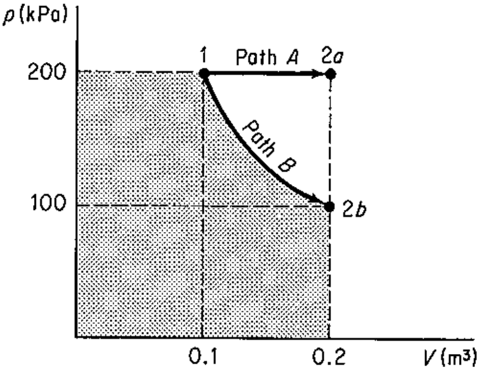
$$n = \frac{200\ \text{kPa}}{}\left|\frac{0.1\ \text{m}^3}{}\right|\frac{}{300\ \text{K}}\left|\frac{(\text{kg mol})(\text{K})}{8.314(\text{kPa})(\text{m}^3)}\right.$$

$$= 0.00802\ \text{kg mol}$$

$$W = \frac{0.00802\ \text{kg mol}}{}\left|\frac{8.314\ \text{kJ}}{(\text{kg mol})(\text{K})}\right|\frac{300\ \text{K}}{}\ \ln 2$$

$$= 20 \ln 2 = 13.86\ \text{kJ}$$

Figure E4.1b shows the two different quantities of work on a p–V plot.



(b) **Figure E4.1b**

Heat. In a discussion of *heat* we enter an area in which our everyday use of the term may cause confusion, since we are going to use heat in a very restricted sense when we apply the laws governing energy changes. Heat (Q) is commonly defined as that part of the total energy flow across a system boundary that is caused by a temperature difference between the system and the surroundings. Heat may be exchanged by conduction, convection, or radiation. Heat, as is work, is a path function. To evaluate heat transfer *quantitatively,* unless given a priori, you must apply the energy balance that is discussed in Sec. 4.5, evaluate all the terms except Q, and then solve for Q. Heat transfer can be *estimated* for engineering purposes by many empirical relations, which can be found in books treating heat transfer or transport processes. A typical relation to estimate the rate of heat transfer is that $\dot{Q}$ is proportional to the area for heat transfer and the temperature difference between the system at T_2 and its surroundings at T_1:

$$\dot{Q} = UA(T_2 - T_1)$$

where U is an empirical coefficient determined from experimental data.

Since heat and work are by definition mutually exclusive exchanges of energy between the system and the surroundings, we shall qualitatively classify work as energy that can be transferred to or from a mechanical state, or mode, of the system, while heat is the transfer of energy to atomic or molecular states, or modes, which are not macroscopically observable.

Kinetic energy. Kinetic energy (K) is the energy a system possesses because of its velocity relative to the surroundings at rest. Kinetic energy may be calculated from the relation

$$K = \tfrac{1}{2}mv^2 \tag{4.2a}$$

or

$$\hat{K} = \tfrac{1}{2}v^2 \tag{4.2b}$$

where the superscript caret (^) refers to the energy per unit mass (or sometimes per mole) and not the total kinetic energy as in Eq. (4.2a).

EXAMPLE 4.2 Calculation of Kinetic Energy

Water is pumped from a storage tank into a tube of 3.00 cm inner diameter at the rate of 0.001 m³/s. See Fig. E4.2. What is the specific kinetic energy of the water?

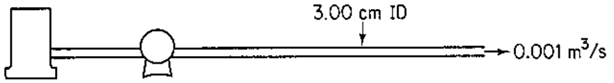


Figure E4.2

Solution

Assume that $\rho = \dfrac{1000\ \text{kg}}{\text{m}^3}$ $\qquad r = \tfrac{1}{2}(3.00) = 1.50\ \text{cm}$

$$v = \frac{0.001\ \text{m}^3}{\text{s}} \left| \frac{}{\pi(1.50)^2\ \text{cm}^2} \right| \left(\frac{100\ \text{cm}}{1\ \text{m}}\right)^2 = 1.415\ \text{m/s}$$

$$\hat{K} = \frac{1}{2} \left| \left(\frac{1.415\ \text{m}}{\text{s}}\right)^2 \right| \frac{1\ \text{N}}{1\ \dfrac{(\text{kg})(\text{m})}{\text{s}^2}} \left| \frac{1\ \text{J}}{1(\text{N})(\text{m})} \right. = 1.00\ \text{J/kg}$$

Potential energy. Potential energy (P) is energy the system possesses because of the body force exerted on its mass by a gravitational or electromagnetic field with respect to a reference surface. Potential energy for a gravitational field can be calculated from

$$P = mgh \tag{4.3a}$$

or

$$\hat{P} = gh \tag{4.3b}$$

where h is the distance from the reference surface and where the symbol $(\hat{\ })$ again means potential energy per unit mass (or sometimes per mole).

EXAMPLE 4.3 Calculation of Potential Energy

Water is pumped from one reservoir to another 300 ft away, as shown in Fig. E4.3. The water level in the second reservoir is 40 ft above the water level of the first reservoir. What is the increase in specific potential energy of the water in Btu/lb$_m$?

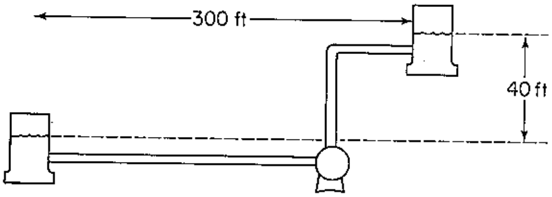


Figure E4.3

Solution

Let the water level in the first reservoir be the reference plane. Then h = 40 ft.

$$\hat{P} = \begin{array}{c|c|c|c} 32.2\ \text{ft} & 40\ \text{ft} & & 1\ \text{Btu} \\ \hline \text{s}^2 & & \dfrac{32.2(\text{lb}_m)(\text{ft})}{(\text{lb}_f)(\text{s}^2)} & 778.2(\text{ft})(\text{lb}_f) \end{array} = 0.0514\ \text{Btu/lb}_m$$

Internal energy. Internal energy (U) is a macroscopic measure of the molecular, atomic, and subatomic energies, all of which follow definite microscopic conservation rules for dynamic systems. Because no instruments exist with which to measure internal energy directly on a macroscopic scale, internal energy must be calculated from certain other variables that can be measured macroscopically, such as pressure, volume, temperature, and composition.

To calculate the internal energy per unit mass ($\hat{U}$) from the variables that can be measured, we make use of a special property of internal energy, namely, that it is an exact differential (because it is a *point* or *state* property, a matter to be described shortly) and, for a pure component, can be expressed in terms of just two intensive variables according to the phase rule for one phase:

$$F = C - \mathcal{P} + 2 = 1 - 1 + 2 = 2$$

Custom dictates the use of temperature and specific volume as the variables. If we say that $\hat{U}$ is a function of T and $\hat{V}$,

$$\hat{U} = \hat{U}(T, \hat{V})$$

by taking the total derivative, we find that

$$d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}} dT + \left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_T d\hat{V} \tag{4.4}$$

By definition $(\partial \hat{U}/\partial T)_{\hat{V}}$ is the heat capacity[1] at constant volume, given the special symbol C_v. For most practical purposes in this text the term $(\partial \hat{U}/\partial \hat{V})_T$ is so small that the second term on the right-hand side of Eq. (4.4) can be neglected. Consequently, *changes in the internal energy* can be computed by integrating Eq. (4.4) as follows:

$$\hat{U}_2 - \hat{U}_1 = \int_{T_1}^{T_2} C_v \, dT \tag{4.5}$$

Note that you can only calculate *differences* in internal energy, or calculate the internal energy relative to a reference state, *but not absolute values* of internal energy.

EXAMPLE 4.4 Internal Energy

An entrance examination for graduate school asked the following two multiple choice questions:

(a) The internal energy of a solid is equal to the
  (1) absolute temperature of the solid
  (2) total kinetic energy of its molecules
  (3) total potential energy of its molecules
  (4) sum of the kinetic and potential energy of its molecules
(b) The internal energy of an object depends on its
  (1) temperature, only
  (2) mass, only
  (3) phase, only
  (4) temperature, mass, and phase

Which answers would you chose?

Solution

Neither of these questions can be answered with the choices given. Internal energy itself cannot be evaluated—only its change can be. And such changes would include changes in potential energy of atoms, electron energy levels, vibrations inside the molecules, and so on.

In addition to using Eq. (4.4), internal energy changes can be calculated from enthalpy values, the next topic of discussion.

Enthalpy. In applying the energy balance you will encounter a variable which is given the symbol H and the name *enthalpy* (pronounced en´-thal-py). This

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[1] The term *heat capacity* has a long history of usage, but is not a scientifically proper connotation. Heat is, by definition, not "stored" in material.

variable is defined as the combination of two variables which will appear very often in the energy balance:

$$H = U + pV \tag{4.6}$$

where p is the pressure and V is the volume. (The term "enthalpy" has replaced the now obsolete terms "heat content" or "total heat," to eliminate any connection whatsoever with heat as defined earlier.)

To calculate the enthalpy per unit mass, we use the property that the enthalpy is also an exact differential. For a pure substance, the enthalpy for a single phase can be expressed in terms of the temperature and pressure (a more convenient variable than specific volume) alone. If we let

$$\hat{H} = \hat{H}(T, p)$$

by taking the total derivative of $\hat{H}$, we can form an expression corresponding to Eq. (4.4):

$$d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T}\right)_p dT + \left(\frac{\partial \hat{H}}{\partial p}\right)_T dp \tag{4.7}$$

By definition $(\partial\hat{H}/\partial T)_p$ is the heat capacity at constant pressure, given the special symbol C_p. For most practical purposes $(\partial\hat{H}/\partial p)_T$ is so small at modest pressures that the second term on the right-hand side of Eq. (4.7) can be neglected. Changes in enthalpy can then be calculated by integration of Eq. (4.7) as follows:

$$\hat{H}_2 - \hat{H}_1 = \int_{T_1}^{T_2} C_p\, dT \tag{4.8}$$

However, in high-pressure processes the second term on the right-hand side of Eq. (4.7) cannot necessarily be neglected, but must be evaluated from experimental data. Consult the references at the end of the chapter for details. One property of ideal gases that should be noted is that their enthalpies and internal energies are functions of temperature only and are not influenced by changes in pressure or specific volume.

As with internal energy, *enthalpy has no absolute value;* **only changes in enthalpy can be calculated.** Often you will use a reference set of conditions (perhaps implicitly) in computing enthalpy changes. For example, the reference conditions used in the steam tables are liquid water at 0°C (32°F) and its vapor pressure. This does not mean that the enthalpy is actually zero under these conditions but merely that the enthalpy has arbitarily been assigned a value of zero at these conditions. In computing enthalpy changes, the reference conditions cancel out as can be seen from the following:

initial state of system	*final state of system*
enthalpy $= \hat{H}_1 - \hat{H}_{\text{ref}}$	enthalpy $= \hat{H}_2 - \hat{H}_{\text{ref}}$

net enthalphy change $= (\hat{H}_2 - \hat{H}_{\text{ref}}) - (\hat{H}_1 - \hat{H}_{\text{ref}}) = \hat{H}_2 - \hat{H}_1$

Point, or state, functions. The variables specific enthalpy and specific internal energy (as well as temperature, pressure, and density) are called *point func-*

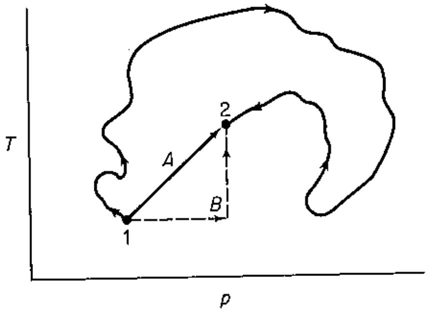


Figure 4.4 Point function.

tions, or *state variables,* meaning that their values depend *only* on the state of the material (temperature, pressure, phase, and composition) and *not* on how the material reached that state. Figure 4.4 illustrates the concept of a state variable. In proceeding from state 1 to state 2, the actual process conditions of temperature and pressure are shown by the wiggly line. However, you may calculate $\Delta\hat{H}$ by route A or B, or any other route, and still obtain the same net enthalpy change as for the route shown by the wiggly line. The change of enthalpy depends only on the initial and final states of the system. A process that proceeds first at constant pressure and then at constant temperature from 1 to 2 will yield exactly the same $\Delta\hat{H}$ as one that takes place first at constant temperature and then at constant pressure as long as the end point is the same. The concept of the point function is the same as that of an airplane passenger who plans to go straight to Chicago from New York but is detoured because of bad weather by way of Cincinnati. His trip costs him the same whatever way he flies, and he eventually arrives at his destination. The fuel consumption of the plane may vary considerably, and in analogous fashion heat (Q) or work (W), the two "path" functions with which we deal, may vary depending on the specific path chosen, while $\Delta\hat{H}$ is the same regardless of path. If the plane were turned back by mechanical problems and landed at New York, the passenger might be irate, but at least could get a refund. Thus $\Delta\hat{H} = 0$ if a cyclical process is involved which goes from state 1 to 2 and back to state 1 again, or

$$\oint d\hat{H} = 0$$

All the intensive properties we shall work with, such as $\hat{P}$, T, $\hat{U}$, p, $\hat{H}$, and so on, are state variables and depend only on the state of the substance of interest, so we can say, for example, that

$$\oint dT = 0$$

$$\oint d\hat{U} = 0$$

To sum up, always keep in mind that the values for a difference in a point function can be calculated by taking the value in the final state and subtracting the value in the initial state, regardless of the actual path.

In the next section we focus attention on the details of how to express the heat capacity as a function of temperature, and in Sec. 4.3 discuss how to use Eq. (4.8) to calculate enthalpy differences.

Self-Assessment Test

1. Contrast the following property classifications: extensive–intensive, measurable–unmeasurable, state–path.
2. Define heat and work.
3. Consider the hot-water heater in your house. Classify each case below as an open system, closed system, neither, or both.
   - **(a)** The tank is being filled with cold water.
   - **(b)** Hot water is being drawn from the tank.
   - **(c)** The tank leaks.
   - **(d)** The heater is turned on to heat the water.
   - **(e)** The tank is full and the heater is turned off.
4. The units of potential energy or kinetic energy are (select all the correct expressions):
   - **(a)** $(\text{ft})(\text{lb}_f)$
   - **(b)** $(\text{ft})(\text{lb}_m)$
   - **(c)** $(\text{ft})(\text{lb}_f)/(\text{lb}_m)$
   - **(d)** $(\text{ft})(\text{lb}_m)/(\text{lb}_f)$
   - **(e)** $(\text{ft})(\text{lb}_f)/(\text{hr})$
   - **(f)** $(\text{ft})(\text{lb}_m)/(\text{hr})$
5. Review the selection of a system and surroundings by reading two or three examples in Secs. 2.3 to 2.6, covering up the solution, and designating the system. Compare with the system shown in the example.
6. Will the kinetic energy per unit mass of an incompressible fluid flowing in a pipe increase, decrease, or remain the same if the pipe diameter is increased at some place in the line?
7. A 100-kg ball initially on the top of a 5-m ladder is dropped and hits the ground. With reference to the ground:
   - **(a)** What is the initial kinetic and potential enegy of the ball?
   - **(b)** What is the final kinetic and potential energy of the ball?
   - **(c)** What is the change in kinetic and potential energy for the process?
   - **(d)** If all the initial potential energy were somehow converted to heat, how many calories would this amount to? how many Btu? How many joules?
8. In expanding a balloon, two types of work are done by the air in the balloon (the system). One is stretching the balloon $dW = \sigma\, dA$, where σ is the surface tension of the balloon. The other is the work of pushing back the atmosphere. If the balloon is spherical and expands slowly from a diameter of 1 m to 1.5 m, what is the work done in pushing back the atmosphere? What assumptions must you make about T and p?

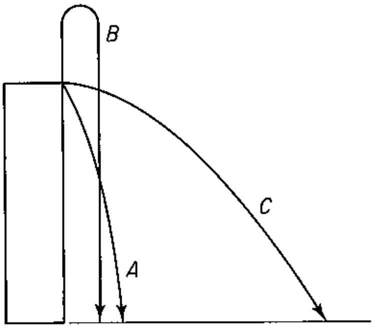
Thought Problems

1. A proposed goal is to replace 10% of the U.S. domestic gasoline production with ethanol grown from corn. What is your estimate of the fraction of the available U.S. cropland that would be required to support such a proposal? Assume 90.0 bu/acre and 2.6 gal ethanol/bu. Gasoline production is 1.2×10^{10} gal/year.
2. Another proposal is to supply 10% of the U. S. oil usage by coal liquefaction. What is

your estimate of the percentage of the coal now mined in the U.S. that would have to be added in order to fulfill this proposal? Assume 3.26 bbl of liquid per ton of coal.

3. Three baseballs are thrown from the top of a four-story building as shown in the figure. All have the same initial speed. Which of the following answers would you say best reflects the speed of the balls when they hit the ground?

   (1) *A* is greatest
   (2) *B* is greatest
   (3) *C* is greatest
   (4) *A* and *C* are the same and greatest
   (5) *A* and *B* are the same and greatest
   (6) All have the same speed



4.2 HEAT CAPACITY

Your objectives in studying this section are to be able to:

1. Define heat capacity.
2. Convert an expression for the heat capacity from one set of units to another.
3. Look up from a reference source an equation that expresses the heat capacity as a function of temperature, and compute the heat capacity at a given temperature.
4. Estimate the value of the heat capacity for solids and liquids.
5. Fit empirical heat capacity data with a suitable function of temperature by estimating the values of the coefficients in the function.

Before formulating the general energy balance, we shall discuss in some detail the calculation of enthalpy changes and provide some typical examples of such calculations. Our discussion will be initiated with consideration of the heat capacity C_p.

The two heat capacities have been defined as

$$\text{(a)} \qquad C_p = \left(\frac{\partial \hat{H}}{\partial T}\right)_p$$

(b) $$C_v = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}}$$

To give these two quantities some physical meaning, you can think of them as representing the amount of energy required to increase the temperature of a substance by 1 degree, energy that might be provided by heat transfer in certain specialized processes, but can be provided by other means as well. To determine from experiments values of C_p (or C_v), the enthalpy (or internal energy) change must first be calculated from an energy balance, and then the heat capacity evaluated. We will discuss C_p as C_v is not used very often.

Suppose that you want to calculate the heat capacity of steam at 10.0 kPa (45.8°C). You can determine the enthalpy change at essentially constant pressure from the steam tables (which list experimental values) as

$$H_{47.7^\circ\text{C}} - H_{43.8^\circ\text{C}} = (2588.1 - 2581.1)\ \text{kJ/kg} = 7.00\ \text{kJ/kg}$$

and if you assume C_p is essentially constant over the small temperature range indicated by the subscripts, then

$$C_p \cong \frac{\Delta H}{\Delta T} = \frac{7.00\ \text{kJ}}{\text{kg}}\left|\frac{}{3.9\Delta^\circ\text{C}}\right. = 1.79\frac{\text{kJ}}{(\text{kg})(\Delta^\circ\text{C})}$$

What are the units of the heat capacity? From the definitions of heat capacity you can see that the units are (energy)/(temperature difference) (mass or moles). The common units found in engineering practice are (we suppress the Δ symbol)

$$\frac{\text{J}}{(\text{kg mol})(\text{K})} \qquad \frac{\text{cal}}{(\text{g mol})(^\circ\text{C})} \qquad \frac{\text{Btu}}{(\text{lb mol})(^\circ\text{F})}$$

Because of the definition of the calorie or Btu, the heat capacity can be expressed in certain different systems of units and still have the same numerical value; for example, heat capacity may be expressed in the units of

$$\frac{\text{cal}}{(\text{g mol})(^\circ\text{C})} = \frac{\text{kcal}}{(\text{kg mol})(^\circ\text{C})} = \frac{\text{Btu}}{(\text{lb mol})(^\circ\text{F})}$$

and still have the same numerical value.

Alternatively, heat capacity may be in terms of

$$\frac{\text{cal}}{(\text{g})(^\circ\text{C})} = \frac{\text{Btu}}{(\text{lb})(^\circ\text{F})} \qquad \text{or} \qquad \frac{\text{J}}{(\text{kg})(\text{K})}$$

Note that

$$\frac{1\ \text{Btu}}{(\text{lb})(^\circ\text{F})} = \frac{4.184\ \text{J}}{(\text{g})(\text{K})}$$

and that the heat capacity of water in the SI system is 4184 J/(kg)(K) at 17°C. These relations are worth memorizing.

Figure 4.5 illustrates the behavior of the heat capacity of a pure substance over a wide range of absolute temperatures. Observe that at zero degrees absolute the heat

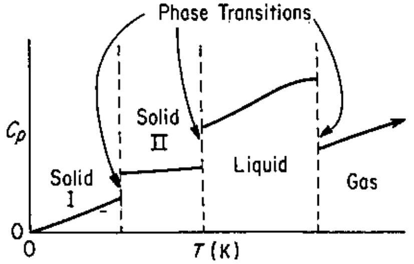


Figure 4.5 Heat capacity as a function of temperature for a pure substance.

capacity is zero. As the temperature rises, the heat capacity also increases until a certain temperature is reached at which a phase transition takes place. The phase transitions are shown also on a related p–T diagram in Fig. 4.6 for water. The phase transition may take place between two solid states, or between a solid and a liquid state, or between a solid and a gaseous state, or between a liquid and a gaseous state. Figure 4.5 shows first a transition between solid state I and solid state II, then the transition between solid state II and the liquid state, and finally the transition between the liquid and the gaseous state. Note that the heat capacity is a continuous function *only* in the region between the phase transitions; consequently, it is not possible to have a heat capacity equation for a substance that will go from absolute zero up to any desired temperature. What an engineer does is to determine experimentally the heat capacity between the temperatures at which the phase transitions occur, fit the data with an equation, and then determine a new heat capacity equation for the next range of temperatures between the succeeding phase transitions.

Experimental evidence indicates that the heat capacity of a substance is not constant with temperature, although at times we may assume that it is constant in order to get approximate results. For the ideal monoatomic gas, of course, the heat capacity at constant pressure is constant even though the temperature varies (see Table 4.1). For typical real gases, see Fig. 4.7; the heat capacities shown are for pure components.

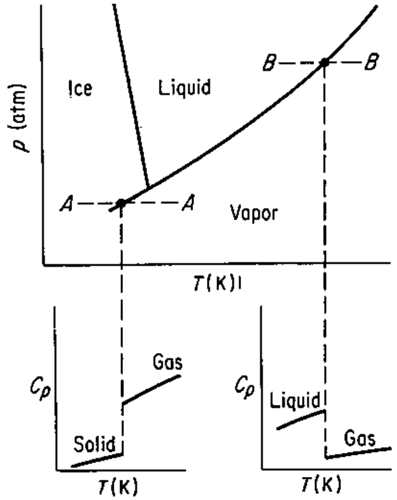


Figure 4.6 Heat capacity and phase transitions.

TABLE 4.1 Heat Capacities of Ideal Gases

Type of molecule	Approximate heat capacity*, C_p High temperature (translational, rotational, and vibrational degrees of freedom)	Approximate heat capacity*, C_p Room temperature (translational and rotational degrees of freedom only)
Monoatomic	$\frac{5}{2}R$	$\frac{5}{2}R$
Polyatomic, linear	$(3n - \frac{3}{2})R$	$\frac{7}{2}R$
Polyatomic, nonlinear	$(3n - 2)R$	$4R$

*n, number of atoms per molecule; R, gas constant defined in Sec. 3.1.

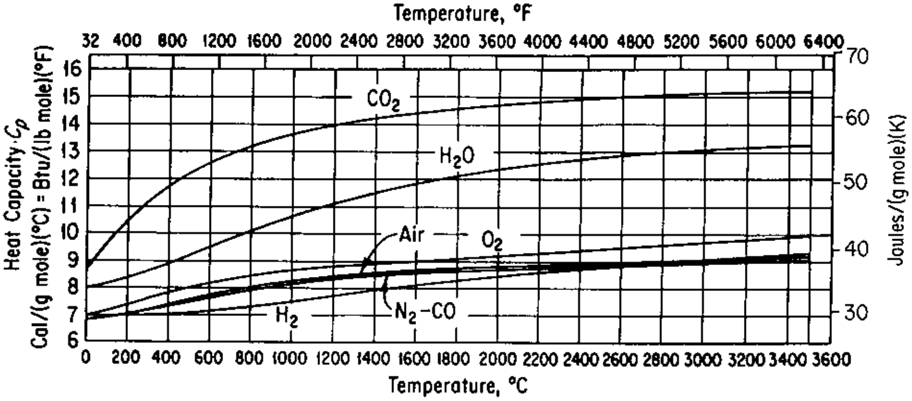


Figure 4.7 Heat capacity curves for the combustion gases.

For ideal gas mixtures, the heat capacity (per mole) of the mixture is the mole weighted average of the heat capacities of the components:

$$C_{p_{\text{avg}}} = \sum_{i=1}^{n} x_i C_{p_i} \tag{4.9}$$

For nonideal mixtures, particularly liquids, you should refer to experimental data or some of the estimation techniques listed in the literature (see the supplementary references at the end of chapter). Also, refer to Sec. 4.8 for details regarding mixtures.

Most of the equations for the heat capacities of solids, liquids, and gases are empirical. We usually express the heat capacity at constant pressure C_p as a function of temperature in a power series, with constants a, b, c, and so on; for example,

$$C_p = a + bT$$

or

$$C_p = a + bT + cT^2$$

where the temperature may be expressed in degrees Celsius, degrees Fahrenheit, degrees Rankine, or degrees kelvin. If C_p is expressed in the form of

$$C_p = a + bT + cT^{-1/2}$$

$$C_p \doteq a + bT - cT^{-2}$$

or a form such that you divide by T, then it is necessary to use kelvin or degrees Rankine in the heat capacity equations, because if degrees Celsius or Fahrenheit were to be used, you might divide at some point in the temperature range by zero. Since these heat capacity equations are valid only over moderate temperature ranges, it is possible to have equations of different types represent the experimental heat capacity data with almost equal accuracy. The task of fitting heat capacity equations to heat capacity data is greatly simplified by the use of digital computers, which can determine the constants of best fit by means of a standard prepared program and at the same time determine how precise the predicted heat capacities are. Heat capacity information can be found in Appendix E. The change of C_p with pressure at high pressures is beyond the scope of our work here. Sources of heat capacity data can be found in several of the references listed at the end of the chapter.

Specific heat is a term often considered synonymous with heat capacity, but this connotation has arisen from loose usage. In principle, specific heat is the ratio of the heat capacity of a substance to the heat capacity of a reference substance, such as

$$\frac{C_{p_A}}{C_{p_{H_2O}}} = \frac{\text{Btu}/(\text{lb}_A)(°\text{F})}{\text{Btu}/(\text{lb}_{H_2O})(°\text{F})}$$

The reference substance temperature must be specified. Because water has a heat capacity of 1.00 Btu/(lb)(°F) at about 17°C, numerical values of specific heats and heat capacities in the American engineering and thermochemical systems are about the same, although their units are not.

EXAMPLE 4.5 Heat Capacity Equation

The heat capacity equation for CO_2 gas is

$$C_p = 6.393 + 10.100T \times 10^{-3} - 3.405T^2 \times 10^{-6}$$

with C_p expressed in cal/(g mol)(ΔK) and T in K. Convert this equation into a form so that the heat capacity will be expressed over the entire temperature range in

(a) Cal/(g mol)(Δ°C) with T in °C

(b) Btu/(lb mol)(Δ°F) with T in °F

(c) J/(kg mol)(ΔK) with T in K

Solution

Changing a heat capacity equation from one set of units to another is merely a problem in the conversion of units. Each term in the heat capacity equation must have the same units as the left-hand side of the equation. To avoid confusion in the conversion, you must remember to distinguish between the temperature symbols that represent temperature and the temperature symbols that represent temperature difference even though the same symbol often is used for each concept. In the conversions below we shall distinguish between the temperature and the temperature difference for clarity.

(a) The heat capacity equation with T in °C and ΔT in Δ°C is

$$C_p \frac{\text{cal}}{(\text{g mol})(\Delta^\circ\text{C})} = 6.393 \begin{array}{c|c} \text{cal} & 1\ \Delta\text{K} \\ \hline (\text{g mol})(\Delta\text{K}) & 1\ \Delta^\circ\text{C} \end{array}$$

$$+\ 10.1000 \times 10^{-3} \begin{array}{c|c|c} \text{cal} & 1\ \Delta\text{K} & (T_{^\circ\text{C}} + 273)\ \text{K} \\ \hline (\text{g mol})(\Delta\text{K})(\text{K}) & 1\ \Delta^\circ\text{C} & \end{array}$$

$$-3.405 \times 10^{-6} \begin{array}{c|c|c} \text{cal} & 1\ \Delta\text{K} & (T_{^\circ\text{C}} + 273)^2\ \text{K}^2 \\ \hline (\text{g mol})(\Delta\text{K})(\text{K})^2 & 1\ \Delta^\circ\text{C} & \end{array}$$

$$= 6.393 + 10.100 \times 10^{-3} T_{^\circ\text{C}} + 2.757 - 3.405 \times 10^{-6} T^2_{^\circ\text{C}}$$

$$-1.860 \times 10^{-3} T_{^\circ\text{C}} - 0.254$$

$$= 8.896 + 8.240 \times 10^{-3} T_{^\circ\text{C}} - 3.405 \times 10^{-6} T^2_{^\circ\text{C}}$$

(b)

$$C_p \frac{\text{Btu}}{(\text{lb mol})(\Delta^\circ\text{F})} = 6.393 \begin{array}{c|c|c|c} \text{cal} & 454\ \text{g mol} & 1\ \text{Btu} & 1\ \Delta\text{K} \\ \hline (\text{g mol})(\Delta\text{K}) & 1\ \text{lb mol} & 252\ \text{cal} & 1.8\ \Delta^\circ\text{F} \end{array}$$

$$+\ 10.100 \times 10^{-3} \begin{array}{c|c|c|c|c} \text{cal} & 454\ \text{g mol} & 1\ \text{Btu} & 1\ \Delta\text{K} & \left(273 + \dfrac{T_{^\circ\text{F}} - 32}{1.8}\right)\text{K} \\ \hline (\text{g mol})(\Delta\text{K})(\text{K}) & 1\ \text{lb mol} & 252\ \text{cal} & 1.8\ \Delta^\circ\text{F} & \end{array}$$

$$-3.405 \times 10^{-6} \begin{array}{c|c|c|c|c} \text{cal} & 454\ \text{g mol} & 1\ \text{Btu} & 1\ \Delta\text{K} & \left(273 + \dfrac{T_{^\circ\text{F}} - 32}{1.8}\right)^2 \text{K}^2 \\ \hline (\text{g mol})(\Delta\text{K})(\text{K})^2 & 1\ \text{lb mol} & 252\ \text{cal} & 1.8\ \Delta^\circ\text{F} & \end{array}$$

$$= 6.393 + 10.100 \times 10^{-3}[273 + (T_{^\circ\text{F}} - 32)/1.8]$$

$$-3.405 \times 10^{-6}[273 + (T_{^\circ\text{F}} - 32)/1.8]^2$$

$$= 6.393 + 2.575 + 5.61 \times 10^{-3} T_{^\circ\text{F}} - 0.222$$

$$-0.964 \times 10^{-3} T_{^\circ\text{F}} - 1.05 \times 10^{-6} T^2_{^\circ\text{F}}$$

$$= 8.746 + 4.646 \times 10^{-3} T_{^\circ\text{F}} - 1.05 \times 10^{-6} T^2_{^\circ\text{F}}$$

Note: $T_\text{K} = 273 + \dfrac{T_{^\circ\text{F}} - 32}{1.8}$.

(c)

$$C_p \frac{\text{J}}{(\text{kg mol})(\Delta\text{K})} = 6.393 \begin{array}{c|c|c} \text{cal} & 4.184\ \text{J} & 1000\ \text{g} \\ \hline (\text{g mol})(\Delta\text{K}) & 1\ \text{cal} & 1\ \text{kg} \end{array}$$

$$+\ 10.1000 \times 10^{-3} \begin{array}{c|c|c|c} \text{cal} & 4.184\ \text{J} & 1000\ \text{g} & (T_\text{K})\text{K} \\ \hline (\text{g mol})(\Delta\text{K})(\text{K}) & 1\ \text{cal} & 1\ \text{kg} & \end{array}$$

$$-3.405 \times 10^{-6} \begin{array}{c|c|c|c} \text{cal} & 4.184\ \text{J} & 1000\ \text{g} & (T^2_\text{K})\text{K}^2 \\ \hline (\text{g mol})(\text{K})^2(\Delta\text{K}) & 1\ \text{cal} & 1\ \text{kg} & \end{array}$$

$$= 2.675 \times 10^4 + 42.27 T_\text{K} - 1.425 \times 10^{-2} T^2_\text{K}$$

EXAMPLE 4.6 Heat Capacity of the Ideal Gas

Show that $C_p = C_v + \hat{R}$ for the ideal monoatomic gas.

Solution

The heat capacity at constant volume is defined as

$$C_v = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}} \tag{a}$$

For any gas,

$$\begin{aligned} C_p &= \left(\frac{\partial \hat{H}}{\partial T}\right)_p = \left[\frac{\partial \hat{U} + \partial(p\hat{V})}{\partial T}\right]_p = \left[\frac{\partial \hat{U} + p\,\partial \hat{V}}{\partial T}\right]_p \\ &= \left(\frac{\partial \hat{U}}{\partial T}\right)_p + p\left(\frac{\partial \hat{V}}{\partial T}\right)_p \end{aligned} \tag{b}$$

For the *ideal gas*, since $\hat{U}$ is a function of temperature only,

$$\left(\frac{\partial \hat{U}}{\partial T}\right)_p = \left(\frac{\partial \hat{U}}{\partial T}\right)_{\hat{V}} = C_v \tag{c}$$

and from $p\hat{V} = \hat{R}T$ we can calculate

$$\left(\frac{\partial \hat{V}}{\partial T}\right)_p = \frac{\hat{R}}{p} \tag{d}$$

so that

$$C_p = C_v + \hat{R}$$

EXAMPLE 4.7 Calculation of C_p from an Equation for Enthalpy

Kelley, U.S. Bureau of Mines, gave an equation for the relative enthalpy of gaseous titanium tetrachloride as

$$H - H_{298} = 25.45T + 0.12 \times 10^{-3}T^2 + 2.36 \times 10^{-5}T^{-1} - 8390$$

where T is in K, H is cal/g mol, and H_{298} is a reference state for enthalpy. What is an equation for C_p in cal/(g mol)(K)?

Solution

$$C_p = \frac{dH}{dT} = 25.45 + 0.24 \times 10^{-3}T - 2.36 \times 10^{-5}T^{-2}$$

EXAMPLE 4.8 Fitting Heat Capacity Data

The heat capacity of carbon dioxide gas as a function of temperature has been found by a series of experiments to be as follows:

	1	2	3	4	5	6
T (K)	300	400	500	600	700	800
C_p [J/(g mol)(K)]	39.87 39.85 39.90	45.16 45.23 45.17	50.72 51.03 50.90	56.85 56.80 57.02	63.01 63.09 63.14	69.52 69.68 69.63

Find the values of the coefficients in the equation

$$C_p = a + bT + CT^2$$

that best fit the data.

Solution

Use a least-squares program (or directly minimize using the minimization code in the back of this book) to minimize the sum of the squares of the deviations between the predicted values of C_p and the experimental ones (refer to Appendix M):

$$\text{Minimize} \sum_{i=1}^{6} (C_{p_{\text{predicted},i}} - C_{p_{\text{experimental},i}})^2$$

The variables are a, b, and c.

The solution is

$$C_p = 25.47 + 4.367 \times 10^{-2}T - 1.44 \times 10^{-5}T^2$$

4.2-1 Estimation of Heat Capacities

We now mention a few ways by which to *estimate* heat capacities of solids, liquids, and gases. For the most accurate results, you should employ actual experimental heat capacity data or equations derived from such data in your calculations. However, if experimental data are not available, there are a number of equations and estimation techniques that you may use which give estimates of values for the heat capacities.

Solids. Only very rough approximations of solid heat capacities can be made. *Kopp's rule* (1864) should only be used as a last resort when experimental data cannot be located or new experiments carried out. Kopp's rule states that at room temperature the sum of the heat capacities of the individual elements is approximately equal to the heat capacity of a solid compound. For elements below potassium, numbers have been assigned from experimental data for the heat capacity for each element as shown in Table 4.2. For liquids Kopp's rule can be applied with a modified series of values for the various elements, as shown also in Table 4.2. For example, the heat capacity at room temperature of $Na_2SO_4 \cdot 10H_2O$ would be $2(6.2) + 1(5.4) + 14(4.0) + 20(2.3) = 119.8$ cal/(g mol)(°C). The heat capacity of coal can be estimated from equations in the *Coal Conversion Systems Technical Data Book* cited in the supplementary references. Consult Reid or Perry's *Handbook* for tables of heat capacity data for solids.

TABLE 4.2 Values for Modified Kopp's Rule: Atomic Heat Capacity at 20°C [cal/(g atom)(°C)]

Element	Solids	Liquids
C	1.8	2.8
H	2.3	4.3
B	2.7	4.7
Si	3.8	5.8
O	4.0	6.0
F	5.0	7.0
P or S	5.4	7.4
All others	6.2	8.0

Liquids

Aqueous solutions. For the special but very important case of aqueous solutions, a rough rule in the absence of experimental data is to use the heat capacity of the water only. For example, a 21.6% solution of NaCl is assumed to have a heat capacity of 0.784 cal/(g)(°C); the experimental value at 25°C is 0.806 cal/(g)(°C).

Hydrocarbons. An equation for the heat capacity of liquid hydrocarbons and petroleum products will be found in Appendix K.

Organic liquids. A simple and reasonably accurate relation between C_p in cal/(g)(°C) at 25°C and molecular weight is

$$C_p = kM^a$$

where M is the molecular weight and k and a are constants. Pachaiyappan et al.[2] give a number of values of the set (k, a). For example

Compounds	k	a
Alcohols	0.85	−0.1
Acids	0.91	−0.152
Ketones	0.587	−0.0135
Esters	0.60	−0.0573
Hydrocarbons, aliphatic	0.873	−0.113

Reid and San Jose[3] review a number of estimation methods for liquids and indicate their precision.

Gases and vapors

Petroleum vapors. The heat capacity of petroleum vapors can be estimated from[4]

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[2] V. Pachaiyappan, S. H. Ibrahim, and N. R. Kuloor, *Chem. Eng.*, p. 241 (October 9, 1967).

[3] R. C. Reid and J. L. San Jose, *Chem. Eng.*, pp. 67–71 (December 20, 1976).

[4] W. H. Bahlke and W. B. Kay, *Ind. Eng. Chem.*, v. 21, p. 942 (1929).

$$C_p = \frac{(4.0 - s)(T + 670)}{6450}$$

where C_p is in Btu/(lb)(°F), T is in °F, and s is the specific gravity at 60°F/60°F, with air as the reference gas.

Kothari–Doraiswamy equation. Kothari and Doraiswamy[5] recommend plotting

$$C_p = a + b \log_{10} T_r$$

Given two values of C_p at known temperatures, values of C_p can be predicted at other temperatures with good precision. The most accurate methods of estimating heat capacities of vapors are those of Dobratz[6] based on spectroscopic data and generalized correlations based on reduced properties.[7]

Additional methods of estimating solid and liquid heat capacities may be found in Reid et al.[8], who compare various techniques we do not have the space to discuss and make recommendations as to their use.

Self-Assessment Test

1. A problem indicates that the enthalpy of a compound can be predicted by an empirical equation $H\,(\text{J/g}) = -30.2 + 4.25T + 0.001T^2$, where T is in kelvin. What is the heat capacity at constant pressure for the compound?
2. What is the heat capacity at constant pressure at room temperature of O_2 if the O_2 is assumed to be an ideal gas?
3. A heat capacity equation in cal/(g mol)(K) for ammonia gas is

   $$C_p = 8.4017 + 0.70601 \times 10^{-2}T + 0.10567 \times 10^{-5}T^2 - 1.5981 \times 10^{-9}T^3$$

   where T is in °C. What are the units of each of the coefficients in the equation?
4. Calculate the heat capacity (C_p) of N_2 gas at 1 atm and 500 K.
5. Estimate the heat capacity (C_p) of acetic acid by (a) Kopp's rule and (b) Pachaiyappan's constants. Compare with the experimental value at room temperature.
6. Convert the following equation for the heat capacity of carbon monoxide gas, where C_p is in Btu/(lb mol)(°F) and T is in °F:

   $$C_p = 6.865 + 0.08024 \times 10^{-2}T - 0.007367 \times 10^{-5}T^2$$

   to yield C_p in J/(kg mol)(K) with T in kelvin.

Thought Problem

1. Textbooks often indicate that for solids and liquids the difference ($C_p - C_v$) is so small that you can say that $C_p = C_v$. Is this generally true?

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[5] M. S. Kothari and L. K. Doraiswamy, *Hydrocarbon Process. Pet. Refiner,* v. 43, no. 3, p. 133 (1964).

[6] C. J. Dobratz, *Ind. Eng. Chem.,* v. 33, p. 759 (1941).

[7] R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids,* 4th ed., McGraw-Hill, New York, 1987.

[8] Ibid.

4.3 CALCULATION OF ENTHALPY CHANGES (WITHOUT CHANGE OF PHASE)

Your objectives in studying this section are to be able to:

1. Calculate enthalpy (and internal energy) changes (excluding phase changes) from heat capacity equations, graphs and charts, tables, and computer data bases given the initial and final states of the material.
2. Become familiar with the steam tables and their use both in SI and American engineering units.
3. Ascertain the reference state for enthalpy values from the data source

Now that we have examined sources of heat capacity values, we turn to the details of the calculation of enthalpy and internal energy changes. We omit for the moment consideration of phase changes and examine solely the problem of how to calculate enthalpy (or internal energy) changes that take place in a single phase, that is, how to calculate the so-called **"sensible heat"** changes. Sensible heat is the enthaply difference (normally for a gas) between some reference temperature and the temperature of the material under consideration, excluding any enthalpy differences for phase changes that are termed latent heats and discussed in Sec. 4.4. We examine four procedures:

1. Use of heat capacity equations
2. Use of tables
3. Use of enthalpy charts
4. Use of computer data bases

4.3-1 How to Employ Heat Capacity Equations

Recall that if we use Eq.(4.8), $\Delta\hat{H}$ is the area under the curve in Fig. 4.8:

$$\int_{\hat{H}_1}^{\hat{H}_2} d\hat{H} = \Delta\hat{H} = \int_{T_1}^{T_2} C_p\,dT$$

If the heat capacity is expressed in the form $C_p = a + bT + cT^2$, then

$$\Delta\hat{H} = \int_{T_1}^{T_2} (a + bT + cT^2)\,dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) \tag{4.10}$$

If a different functional form of the heat capacity is available, the integration result

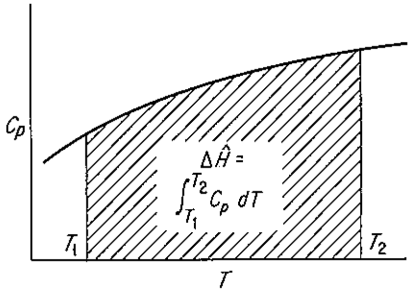

Figure 4.8 Calculation of enthalpy change.

will be different. Equation (4.10) can be stored in a data base and used to calculate enthalpy changes for a single phase as easily as the heat capacity equation can be stored. Can you develop an expression similar to Eq. (4.10) for $\Delta\hat{U}$ based on a polynomial expression for C_v as a function of temperature? Will the right-hand side look exactly the same as Eq. (4.10)?

EXAMPLE 4.9 Calculation of $\Delta\hat{H}$ for a Gas Mixture Using Heat Capacity Equations

The conversion of solid wastes to innocuous gases can be accomplished in incinerators in an environmentally acceptable fashion. However, the hot exhaust gases must be cooled or diluted with air. An economic feasibility study indicates that solid municipal waste can be burned to a gas of the following composition (on a dry basis):

CO_2	9.2%
CO	1.5%
O_2	7.3%
N_2	82.0%
	100.0%

What is the enthalpy difference for this gas per lb mol between the bottom and the top of the stack if the temperature at the bottom of the stack is 550°F and the temperature at the top is 200°F? Ignore the water vapor in the gas. Because these are ideal gases, you can neglect any energy effects resulting from the mixing of the gaseous components.

Solution

Heat capacity equations from Table E.2 [T in °F; C_p = Btu/(lb mol)(°F)] are

N_2: $C_p = 6.895 + 0.7624 \times 10^{-3}T - 0.7009 \times 10^{-7}T^2$

O_2: $C_p = 7.104 + 0.7851 \times 10^{-3}T - 0.5528 \times 10^{-7}T^2$

CO_2: $C_p = 8.448 + 5.757 \times 10^{-3}T - 21.59 \times 10^{-7}T^2 + 3.059 \times 10^{-10}T^3$

CO: $C_p = 6.865 + 0.8024 \times 10^{-3}T - 0.7367 \times 10^{-7}T^2$

Basis: 1.00 lb mol of gas

By multiplying these equations by the respective mole fraction of each component, and then adding them together, you can save time in the integration.

N_2: $0.82(6.895 + 0.7624 \times 10^{-3}T - 0.7009 \times 10^{-7}T^2)$

O_2: $0.073(7.104 + 0.7851 \times 10^{-3}T - 0.5528 \times 10^{-7}T^2)$

CO_2: $0.092(8.448 + 5.757 \times 10^{-3}T - 21.59 \times 10^{-7}T^2 + 3.059 \times 10^{-10}T^3)$

CO: $0.015(6.865 + 0.8024 \times 10^{-3}T - 0.7367 \times 10^{-7}T^2)$

$$C_{p_{\text{net}}} = 7.053 + 1.2242 \times 10^{-3}T - 2.6124 \times 10^{-7}T^2 + 0.2814 \times 10^{-10}T^3$$

$$\Delta\hat{H} = \int_{550}^{200} C_p\,dT = \int_{550}^{200} (7.053 + 1.2242 \times 10^{-3}T - 2.6124 \times 10^{-7}T^2 + 0.2814 \times 10^{-10}T^3)\,dT$$

$$= 7.053[(200) - (550)] + \frac{1.2242 \times 10^{-3}}{2}[(200)^2 - (550)^2] - \frac{2.6124 \times 10^{-7}}{3}[(200)^3 - (550)^3] + \frac{0.2814 \times 10^{-10}}{4}[(200)^4 - (550)^4]$$

$$= -2468.6 - 160.7 + 13.8 - 0.633$$

$$= -2616 \text{ Btu/lb mol gas}$$

4.3-2 Tabular Data

When the values of the physical properties used in your calculations must be accurate, you might well turn to tables. Tables can cover ranges of physical properties well beyond the range applicable for a single equation. Because the most commonly measured properties are temperature and pressure, tables for pure compounds usually are organized in columns and rows, with T and p being the independent variables. If the intervals between table entries are close enough, linear interpolation between entries is reasonably accurate.

Steam tables of all varieties are cited in several of the references in Table 4.5. Tables of the enthalpies for some important compounds at 1 atmosphere will be found in Appendix D.

If you remember that enthalpy values are all relative to some reference state, you can make enthalpy difference calculations merely by subtracting the initial enthalpy from the final enthalpy for any two sets of conditions as shown in the following examples.

EXAMPLE 4.10 Calculation of Enthalpy Change Using Tabulated Enthalpy Values

Calculate the enthalpy change for 1 kg mol of N_2 gas which is heated at a constant pressure of 100 kPa from 18°C to 1100°C.

Solution

We will use the data in Table 4.4 (the pressure is about 1 atm).

$$\text{at } 1100°\text{C} \Leftrightarrow 1373\text{K:} \quad \Delta\hat{H} = 34{,}715 \text{ kJ/kg mol (by interpolation)}$$

$$\text{at } 18°\text{C} \Leftrightarrow 291 \text{ K:} \quad \Delta\hat{H} = 524 \text{ kJ/kg mol}$$

Basis: 1 kg mol of N_2

$$\Delta\hat{H} = 34{,}715 - 524 = 34{,}191 \text{ kJ/kg mol}$$

Tables 4.3 and 4.4 list typical enthalpy data for the combustion gases. Some sources of enthalpy data are listed in Table 4.5. The most common source of enthalpy data for water is the steam tables which are reproduced in Appendix C1 and on a sheet that can be found inside the back cover.

To make use of the steam tables, you must first locate the region of the phase diagram in which the state lies. The tables are organized so that the saturation properties are given separately from the properties of superheated steam and subcooled liquid. Examine the large set of tables in the back of the book. In addition, the saturation properties are presented in two ways: (1) the saturation pressure is given at even intervals for easy interpolation, and (2) the saturation temperature given at even intervals for the same reason.

You can find the region in which a particular state lies by referring to one of the two tables for saturation properties. If, at the given T or P, the given specific intensive property lies outside the range of properties that can exist for saturated liquid, saturated vapor, or their mixtures, the state must be in either the superheated or the subcooled region. For example, look at a brief extract from the steam tables in SI units:

		Specific volume (m³/kg)			Enthalpy (kJ/kg)		
P_{sat}(kPa)	T_{sat}(°C)	v_l	v_{lg}	v_g	h_l	h_{lg}	h_g
101.325	100.0	0.001043	1.672	1.673	419.5	2256.0	2675.6
200.0	120.2	0.001061	0.8846	0.8857	504.7	2201.5	2706.2

For each saturation pressure, the corresponding saturation temperature (boiling point) is given along with the values of specific volume and enthalpy for both saturated liquid and saturated vapor. The volume and enthalpy value in the middle column designated by the subscript lg is the difference between the saturated vapor and saturated liquid states, and will be discussed in the next section.

TABLE 4.3 Enthalpies of Combustion Gases* (Btu/lb mol)

°R	N_2	O_2	Air	H_2	CO	CO_2	H_2O
492	0.0	0.0	0.0	0.0	0.0	0.0	0.0
500	55.67	55.93	55.57	57.74	55.68	68.95	64.02
520	194.9	195.9	194.6	191.9	194.9	243.1	224.2
537	313.2	315.1	312.7	308.9	313.3	392.2	360.5
600	751.9	758.8	751.2	744.4	752.4	963	867.5
700	1,450	1,471	1,450	1,433	1,451	1,914	1,679
800	2,150	2,194	2,153	2,122	2,154	2,915	2,501
900	2,852	2,931	2,861	2,825	2,863	3,961	3,336
1,000	3,565	3,680	3,579	3,511	3,580	5,046	4,184
1,100	4,285	4,443	4,306	4,210	4,304	6,167	5,047
1,200	5,005	5,219	5,035	4,917	5,038	7,320	5,925
1,300	5,741	6,007	5,780	5,630	5,783	8,502	6,819
1,400	6,495	6,804	6,540	6,369	6,536	9,710	7,730
1,500	7,231	7,612	7,289	7,069	7,299	10,942	8,657
1,600	8,004	8,427	8,068	7,789	8,072	12,200	9,602
1,700	8,774	9,251	8,847	8,499	8,853	13,470	10,562
1,800	9,539	10,081	9,623	9,219	9,643	14,760	11,540
1,900	10,335	10,918	10,425	9,942	10,440	16,070	12,530
2,000	11,127	11,760	11,224	10,689	11,243	17,390	13,550
2,100	11,927	12,610	12,030	11,615	12,050	18,730	14,570
2,200	12,730	13,460	12,840	12,160	12,870	20,070	15,610
2,300	13,540	14,320	13,660	12,890	13,690	21,430	16,660
2,400	14,350	15,180	14,480	13,650	14,520	22,800	17,730
2,500	15,170	16,040	15,300	14,400	15,350	24,180	18,810

*Pressure = 1 atm.

SOURCE: Page 30 Kobe, K.A., et al., *Thermochemistry of Petrochemicals,* Reprint No. 44 from the *Petroleum Refiner,* Gulf Publ. Co., Houston, TX (1958).

TABLE 4.4 **Enthalpies of Combustion Gases* (J/g Mol)†**

K	N_2	O_2	Air	H_2	CO	CO_2	H_2O
273	0	0	0	0	0	0	0
291	524	527	523	516	525	655	603
298	728	732	726	718	728	912	837
300	786	790	784	763	786	986	905
400	3,695	3,752	3,696	3,655	3,699	4,903	4,284
500	6,644	6,811	6,660	6,589	6,652	9,204	7,752
600	9,627	9,970	9,673	9,518	9,665	13,807	11,326
700	12,652	13,225	12,736	12,459	12,748	18,656	15,016
800	15,756	16,564	15,878	15,413	15,899	23,710	18,823
900	18,961	19,970	19,116	18,384	19,125	28,936	22,760
1,000	22,171	23,434	22,367	21,388	22,413	34,308	26,823
1,100	25,472	26,940	25,698	24,426	25,760	39,802	31,011
1,200	28,819	30,492	29,078	27,509	29,154	45,404	35,312
1,300	32,216	34,078	32,501	30,626	32,593	51,090	39,722
1,400	35,639	37,693	35,953	33,789	36,070	56,860	44,237
1,500	39,145	41,337	39,463	36,994	39,576	62,676	48,848
1,750	47,940	50,555	48,325	45,275	48,459	77,445	60,751
2,000	56,902	59,914	57,320	53,680	57,488	92,466	73,136
2,250	65,981	69,454	66,441	62,341	66,567	107,738	85,855
2,500	75,060	79,119	75,646	71,211	75,772	123,176	98,867
2,750	84,265	88,910	84,935	80,290	85,018	138,699	112,089
3,000	93,512	98,826	94,265	89,453	94,265	154,347	125,520
3,500	112,131	119,034	113,135	108,030	112,968	185,895	152,799
4,000	130,875	141,410	132,172	127,528	131,796	217,777	180,414

†To convert to cal/g mol multiply by 0.2390.

*Pressure = 1 atm.

SOURCE: Page 30 of Reference in Table 4.3.

TABLE 4.5 Sources of Enthalpy Data

1. American Petroleum Institute, Division of Refining, *Technical Data Book—Petroleum Refining,* 2nd ed., API, Washington, D.C., 1970.
2. American Petroleum Institute, Research Project 44, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds,* API, Washington, D.C., 1953. See also Reference 30.
3. American Society of Mechanical Engineers, *Thermodynamic Data for Waste Incineration,* Book No. H00141, New York, 1979.
4. Barner, H.E., and R.V. Scheuerman, *Handbook of Thermochemical Data for Compounds and Aqueous Species,* Wiley-Interscience, New York, 1978.
5. *Bulletin of Chemical Thermodynamics,* published by Department of Chemistry, Oklahoma State University, Stillwater, Okla., 74074. (Index, bibliography, reports.)
6. Chase, M.W., "JANAF Thermochemical Tables," *J. Phys. Chem. Ref. Data,* v. 11, p. 695 (1987).
7. Danner, R.P., and T.E. Daubert, eds., *Manual for Predicting Chemical Process Design Data,* American Institute of Chemical Engineers, New York (1984).
8. Engineering Sciences Data Unit Ltd., London. (Extensive series of property data.)
9. Fratzscher, W., et al., "The Acquisition, Collection, and Tabulation of Substance Data on Fluid Systems for Calculations in Chemical Engineering," *Int. Chem. Eng.,* v. 20, no. 1, pp. 19–28 (1980). (A list of references for data.)
10. Freeman, R.D., *Chemical Thermodynamics,* Bulletin No. 54 in CODATA Directory of Data Sources for Science and Technology, CODATA Secretariat, Paris, 1983.
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12. Haar, L., J.S.Gallagher, and G.S. Kell, *NBS/NRC Steam Tables,* Hemisphere, New York, 1984.
13. Hamblin, F.D., *Abridged Thermodynamic and Thermochemical Tables (S.I. Units),* Pergamon Press, Elmsford, N.Y. (paperback edition available), 1972.
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17. *Journal of Physical and Chemical Reference Data,* American Chemical Society, 1972 and following.
18. Keenan, J.H., et al., *Steam Tables,* Wiley, New York, 1978. (SI units.) Also J.H. Keenan and F.G. Keyes, *Thermodynamic Properties of Steam,* Wiley, New York, 1936.
19. Keenan, J.H., J. Chao, and J. Kaye, *Gas Tables (English Units),* 2nd ed., Wiley, New York, 1980.
20. Lin, C.T., et al., "Data Bank for Synthetic Fuels," *Hydrocarbon Process,* Parts 1, 2, 3 (August and November 1980).
21. Naumov, G.B., *Handbook of Thermodynamic Data* (translation into English of

TABLE 4.5 ***Continued***

Handbook of Thermodynamic Data, Atomizdat, Moscow, 1971). (Available as NTIS PB-226722/7.)

22. Perry, J.H., *Chemical Engineers' Handbook,* 6th ed., McGraw-Hill, New York, 1986.
23. Raznjevic, K., *Handbook of Thermodynamic Tables and Charts,* Hemisphere, New York, 1976.
24. Rossini, F.K., et al., "Tables of Selected Values of Chemical Thermodynamic Properties," *National Bureau of Standards, Circular* 500, 1952. (Revisions are being issued periodically under the Technical Note 270 series by other authors.)
25. Selover, T.B., National *Standard Reference Data Service of the USSR,* Hemisphere, New York (continuing series).
26. Selover, T.B., and E. Buck, "DIPPR in Its Seventh Year," *Chem. Eng. Prog.,* p. 18 (July 1987).
27. Stephenson, F.M. and S. Malanowski, *Handbook of the Thermodynamics of Organic Compounds,* Elsevier, New York (1987).
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33. Yaws, C.L., "Physical and Thermodynamic Properties" (Graphs), *Chem. Eng.,* Initiated with Part I in the June 10, 1974, issue. Subsequent issues: July 3, Aug. 19, Sept. 30, Oct. 28, Nov. 25, Dec. 23, 1974; Jan. 20, Feb. 17, Mar. 31, May 12, July 21, Sept. 1, Sept. 29, 1975. See "Physical Properties: A Guide. . .," published 1977, McGraw-Hill, New York; "Enthalpics of Formation for 700 Major Organic Compounds," *Chem. Eng.,* p. 81 (Sept. 26, 1988).

EXAMPLE 4.11 Use of the Steam Tables

Steam is cooled from 640°F and 92 psia to 480°F and 52 psia. What is $\Delta\hat{H}$ in Btu/lb?

Solution

Use the tables for the American engineering units in the pocket in the back of the book. You must employ double interpolation to get the specific enthalpies, $\Delta\hat{H}$, relative to the reference for the table:

	T (°F)					
p (psia)	600	700	p	600	640	700
90	1328.7	1378.1	92	1328.6		1378.0
95	1328.4	1377.8			1348.4	
	450	500	p	450	480	500
50	1258.7	1282.6	52	1258.4		1282.4
55	1258.2	1282.2			1272.8	

Note that the steam table values include the effect of pressure on $\Delta\hat{H}$ as well as temperature. An example of the interpolation needed at 600°F is

$$\tfrac{2}{5}(1328.7 - 1328.4) = 0.4(0.3) = 0.12$$

At $p = 92$ psia and $T = 600$, $\Delta\hat{H} = 1328.7 - 0.12 = 1328.6$.

The enthalpy change is

$$\Delta\hat{H} = 1272.8 - 1348.4 = -75.6 \text{ Btu/lb}$$

EXAMPLE 4.12 Calculation of the Change in Enthalpy for Water from the Steam Tables

Four kilograms of water at 27°C and 200 kPa are heated at constant pressure until the volume of the water becomes 1000 times the original value. What is the final temperature of the water?

Solution

The effect of pressure on the volume of liquid water can be neglected (refer to the table of the properties of liquid water), hence the initial specific volume is that of saturated liquid water at 300 K, or 0.001004 m³/kg. The final specific volume is

$$0.001004(1000) = 1.004 \text{ m}^3\text{/kg}$$

At 200 kPa, using interpolation, between 400 and 450 K we find T by solving

$$0.9024\frac{\text{m}^3}{\text{kg}} + \frac{(1.025 - 0.9024)\text{ m}^3\text{/kg}}{(450 - 400)\text{ K}}(T - 400)\text{ K} = 1.004\frac{\text{m}^3}{\text{kg}}$$

$$T = 400 + 41 = 441 \text{ K}$$

EXAMPLE 4.13 Enthalpy Change for Liquid Water

Water is heated from 400 K and 2000 kPa to 475 K and 5000 kPa. What are $\Delta\hat{H}$ and $\Delta\hat{U}$ in kJ/kg?

Solution

From the steam tables in SI units in the back of the book, the data are:

	$\Delta\hat{H}$	$\Delta\hat{U}$
400 K and 2000 kPa (kJ/kg)	533.76	531.63
475 K and 5000 kPa (kJ/kg)	861.96	856.18

$$\Delta\hat{H} = 861.96 - 533.76 = 328.20 \text{ kJ/kg}$$

$$\Delta\hat{U} = 856.18 - 531.63 = 324.55 \text{ kJ/kg}$$

4.3-3 Graphical Presentation of Enthalpy Data

You have often heard of saying: a picture is worth a 1000 words. Something similar might be said of two-dimensional charts, namely that you can get an excellent idea of the characteristics of the enthalpy of a substance in all regions of interest via a chart. Although the accuracy of the readings of values from a chart may be limited (depending on the scale of the chart), tracing out various processes on a chart enables you to rapidly visualize and analyze what is taking place. Primarily, charts are a simple and quick method of getting data to compute enthalpy changes. Figure 4.9 is an example chart. A number of the sources listed in the references in Table 4.6 and in the Appendices, as well as Perry's *Handbook,* include property charts. Reynolds[9] has an excellent collection of charts of 40 substances in his volume. Other sources of such charts are listed in Table 4.6. Appendix J contains charts for toluene and carbon dioxide.

Charts are drawn with various coordinates, such as

$$p \text{ versus } \hat{H}$$

$$p \text{ versus } \hat{V}$$

$$p \text{ versus } T$$

$$\hat{H} \text{ versus } \hat{S}^{10}$$

Since a chart has only two dimensions, the other parameters of interest have to be plotted as lines of constant value across the face of the chart. Recall, for example, that the p–$\hat{V}$ diagram for CO_2, Fig. 3.3, lines of constant temperature were shown as parameters. Similarly, on a chart with pressure and enthalpy as the axes, lines of constant volume and/or temperature might be drawn.

How many properties have to be specified for a single component gas to definitely fix the state of the gas? Because we know from our discussion in Sec. 3.7

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[9] W. C. Reynolds, *Thermodynamic Properties in SI,* Department of Mechanical Engineering, Stanford University, Stanford, Calif., 1979.

[10] S is *entropy*—this diagram is called a *Mollier* diagram.

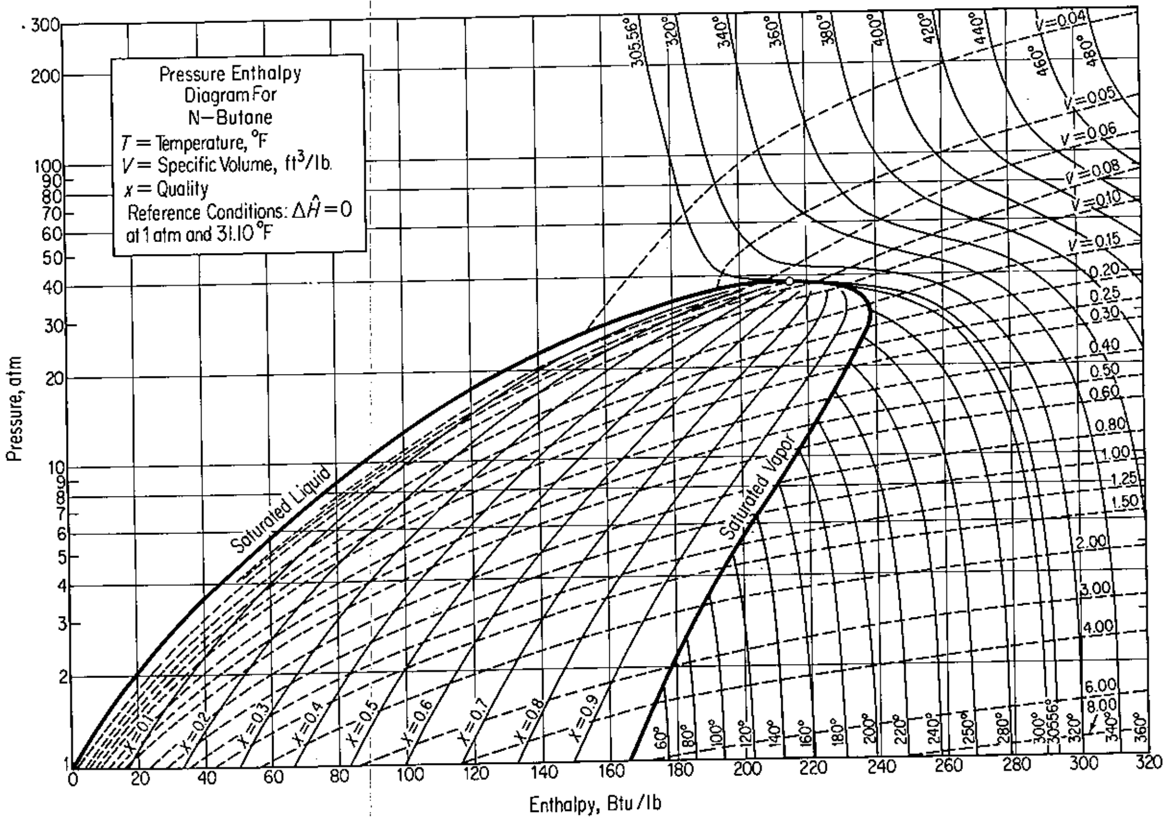

Figure 4.9 Pressure enthalpy diagram for *n*-butane.

TABLE 4.6 Thermodynamic Charts Showing Enthalpy Data for Pure Compounds*

Compound	Reference[†]
Acetone	2
Acetylene	1
Air	V.C. Williams, *AIChE Trans.*, v. 39, p. 93 (1943); *AIChE J.*, v. 1, p. 302 (1955).
Benzene	1
1,3-Butadiene	C.H. Meyers, *J. Res. Natl. Bur. Stand.*, v. A39, p. 507 (1947).
i-Butane	1, 3
n-Butane	1, 3, 4
n-Butanol	L.W. Shemilt, in *Proceedings of the Conference on Thermodynamic Transport Properties of Fluids*, London, 1957, Institute of Mechanical Engineers, London, 1958.
t-Butanol	F. Maslan, *AIChE J.*, v. 7, p. 172 (1961).
n-Butene	1
Chlorine	R.E. Hulme and A.B. Tilman, *Chem. Eng.* (January 1949).
Ethane	1, 3, 4
Ethanol	R.C. Reid and J.M. Smith, *Chem. Eng. Prog.*, v. 47, p. 415 (1951).
Ethyl ether	2
Ethylene	1, 3
Ethylene oxide	J.E. Mock and J.M. Smith, *Ind. Eng. Chem.*, v. 42, p. 2125 (1950).
Fatty acids	J.D. Chase, *Chem. Eng.*, p. 107 (March 24, 1980).
n-Heptane	E.B. Stuart et al., *Chem Eng. Prog.*, v. 46, p. 311 (1950).
n-Hexane	1
Hydrogen sulfide	J.R. West, *Chem. Eng. Prog.*, v. 44, p. 287 (1948).
Isopropyl ether	2
Mercury	General Electric Company Report GET-1879A, 1949.
Methane	1, 3, 4
Methanol	J.M. Smith, *Chem. Eng. Prog.*, v. 44, p. 52 (1948).
Methyl ethyl ketone	2
Monomethyl hydrazine	F. Bizjak and D.F. Stai, *AIAA J.*, v. 2, p. 954 (1964).
Neon	Cryogenic Data Center, National Bureau of Standards, Boulder, Colo.
Nitrogen	G.S. Lin, *Chem. Eng. Prog.*, v. 59, no. 11, p. 69 (1963).

*For mixtures, see V.F. Lesavage et al., *Ind. Eng. Chem.*, v. 59, no. 11, p. 35 (1967).

[†] 1. L.N. Cajar et al., *Thermodynamic Properties and Reduced Correlations for Gases*, Gulf Publishing Company, Houston, 1967. (Series of articles which appeared in the magazine *Hydrocarbon Processing* from 1962 to 1965.)

2. P.T. Eubank and J.M. Smith, *J. Chem. Eng. Data*, v. 7, p. 75 (1962).

3. W.C. Edmister, *Applied Hydrocarbon Thermodynamics*, Gulf Publishing Company, Houston, 1987.

4. K.E. Starling et al., *Hydrocarbon Processing*, 1971 and following. *Note:* Charts available separately from Gulf Publishing Company, Houston.

TABLE 4.6 *Continued*

Compound	Reference†
n-Pentane	1, 3, 4
Propane	1, 3, 4
n-Propanol	Shemilt (*see n*-Butanol).
Propylene	1, 3
Refrigerant 245	R.L. Shank, *J. Chem. Eng. Data,* v. 12, p. 474 (1967).
Sulfur dioxide	J.R. West and G.P. Giusti, *J. Phys.Colloid Chem.*, v. 54, p. 601 (1950).
Combustion gases	H.C. Hottel, G.C. Williams, and C.N. Satterfield, *Thermodynamic Charts for Combustion Processes* (I) Text, (II) Charts, Wiley, New York, 1949.
Hydrocarbons	3

that specifying two intensive properties for a pure gas will ensure that all the other intensive properties will have definite values, any two properties can be chosen at will. Since a particular state for a gas can be defined by any two independent properties, a two-dimensional thermodynamic chart can be seen to be a handy way to present many combinations of physical properties.

EXAMPLE 4.14 Use of Pressure–Enthalpy Chart for Butane

Calculate ΔH, ΔV, and ΔT changes for 1 lb of saturated vapor of *n*-butane going from 2 atm to 20 atm (saturated).

Solution

Obtain the necessary data from Fig. 4.9.

	$\hat{\Delta H}$ (Btu/lb)	$\hat{V}$ (ft^3/lb)	T (°F)
Saturated vapor at 2 atm:	179	3.00	72
Saturated vapor at 20 atm:	233	0.30	239

$$\Delta \hat{H} = 233 - 179 = 54 \text{ Btu/lb}$$

$$\Delta \hat{V} = 3.00 - 0.30 = 2.70 \text{ ft}^3/\text{lb}$$

$$\Delta T = 239 - 72 = 167°\text{F}$$

Enthalpies and other thermodynamic properties can be *estimated* by generalized methods based on the theory of corresponding states or additive bond contributions.[11]

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[11] R. R. Tarakad and R. P. Palmer, "A Comparison of Enthalpy Prediction methods," *AIChE J.*, v. 22, p. 409 (1976).

4.3-4 Retrieval of Data from Computer Data Bases

Values of the properties of hundreds of substances are available in the form of computer programs that can provide the values at any given state. Thus you avoid the need for interpolation and/or auxiliary computation, such as when only ΔH is given in a table and ΔU must be calculated from $\Delta U = \Delta H - \Delta pV$. One such program, that for the properties of water, is included on the disk in the back of this book. The program is abridged so that it does not have the accuracy nor cover the range of commercially available programs, but it is quite suitable for solving problems in this text.

Computer tapes can be purchased providing information on the physical properties of large numbers of compounds, and immediate access to computer-based information systems via the telephone can be obtained from computer service bureaus. Table 4.7 lists a number of such programs and data bases.

TABLE 4.7 Sources of Computer Based Property Data

American Institute of Chemical Engineers, *Data Compilation, Tables of Properties of Pure Compounds,* STN International (on-line access), Ohio.

Aslam, S., and M. Charmchi, *STEAM,* Mechanical Engineering Department, University of Lowell, Lowell, Mass., 1986.

Benedek, P., and F. Ogli, *Computer Aided Chemical Thermodynamics of Gases and Liquids,* Wiley-Interscience, New York, 1985.

CTS Engineering, *Steam Tables,* CTS Engineering, Monroe, La., 1986.

Ganapathy, U., *BASIC Programs for Steam Plant Engineers,* Marcel Dekker, New York, 1986.

GASPROPS, *A Computer Program for the Calculation of the Thermodynamic Properties of Ideal Gases and Combustion Products,* Wiley, New York, 1984.

Garvin, D., V.B. Parkin, and D.D. Wagman, "Thermodynamic Data Banks," *Chemtech,* p. 691 (November 1982).

Impulse Engineering, *IMP-STM 85/PC,* Impulse Engineering, San Francisco, 1985. (Steam and water-for PC.)

Irvine, T.F., and P.E. Liley, *Steam and Gas Tables with Computer Equations,* Academic Press, Orlando, Fla., 1984.

Moore, K.V., *4STEM: Thermodynamic Properties of Water and Steam,* DE86048580/GAR, tape, National Technical Information Service, Springfield, Va., 1986.

STEAMCALC, *A Computer Program for the Calculation of the Thermodynamic Properties of Steam,* Wiley, New York, 1984.

Thermodynamics Research Center, Texas A & M University, *Chemical Information System,* Computer Sciences Corp., Falls Church, Va. (on line).

Self-Assessment Test

1. Calculate the enthalpy change in 24 g of N_2 if heated from 300 K to 1500 K at constant pressure.

2. What is the enthalpy change when 2 lb of *n*-butane gas is cooled from 320°F and 2 atm to saturated vapor at 6 atm?
3. You are told that 4.3 kg of water at 200 kPa occupies (a) 4.3, (b) 43, (c) 430, (d) 4300, and (e) 43,000 liters. State for each case whether the water is in the solid, liquid, liquid-vapor, or vapor regions.
4. Two hundred pounds of a 35° API distillate is heated from 130°F to 275°F. Estimate the enthalpy change (in Btu). See Appendix K.
5. Water at 400 kPa and 500 K is cooled to 200 kPa and 400 K. What is the enthalpy change? Use the steam tables.

4.4 ENTHALPY CHANGES FOR PHASE TRANSITIONS

Your objectives in studying this section are to be able to:

1. Estimate the heat of fusion or heat of vaporization from empirical formulas, or look up the value in a reference table.
2. Estimate the heat of vaporization from the Clausius–Clapeyron equation or the Othmer plot.
3. Calculate an enthalpy change of a substance including the phase transitions.

In making enthalpy calculations, we noted in Fig. 4.5 that the heat capacity data are discontinuous at the points of a phase transition. The name usually given to the enthalpy changes for these phase transitions is *latent heat* changes, latent meaning "hidden" in the sense that the substance (e.g., water) can absorb a large amount of heat without any noticeable increase in temperature. Unfortunately, the word *heat* is still associated with these enthalpy changes for historical reasons, although they have nothing directly to do with heat as defined in Sec. 4.1. Ice at 0°C can absorb energy amounting to 334 J/g without undergoing a temperature rise or a pressure change, and similarly, liquid water at 1 atmosphere can absorb 2256.1 J/g before the temperature and pressure will change. Figure 4.10 shows, by the vertical lines at constant temperature, the enthalpies for the phase changes for water at 1 atmosphere pressure. The various enthalpy changes are termed:

Enthalpy change	Phase change
Heat of fusion	Solid to liquid
Heat of vaporization	Liquid to vapor
Heat of condensation	Vapor to liquid
Heat of sublimation	Solid to vapor

You can see from the chart for *n*-butane (Fig. 4.9) that the heats of vaporization (and

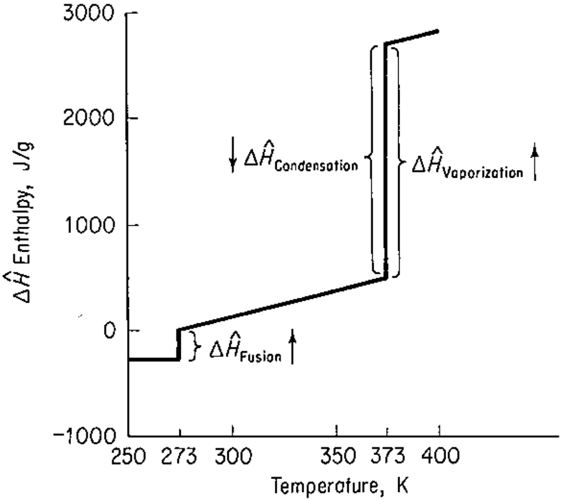

Figure 4.10 Enthalpy change for water at 1 atmosphere showing the phase transitions.

accordingly condensation) changes with temperature all the way up to the critical point, where it vanishes. Calculation of the *quality* of a liquid–vapor mixture was illustrated by Example 3.18.

You can find experimental values of latent heats in the references in Table 4.5, and a brief tabulation is listed in Appendix D. The symbols used for latent heat changes vary, but you usually find one or more of the following employed: $\Delta\hat{H}$, L, λ, Λ. Keep in mind that the enthalpy changes for vaporization given in the steam tables are for water under its vapor pressure at the indicated temperature.

In the absence of experimental values for the latent heats of transition, the following approximate methods will provide a rough *estimate of the molar latent heats*. Reid, Prausnitz and Poling, *The Properties of Gases and Liquids*, give many more methods.[12]

4.4-1 Heat of Fusion

No accurate, simple way to estimate ΔH_f exists. The heat of fusion for many elements and compounds can be roughly approximated by

$$\frac{\Delta\hat{H}_f}{T_f} = \text{constant} = \begin{cases} 2\text{–}3 & \text{for elements} \\ 5\text{–}7 & \text{for inorganic compounds} \\ 9\text{–}11 & \text{for organic compounds} \end{cases} \qquad (4.11)$$

where $\Delta\hat{H}_f$ = molar heat of fusion, cal/g mol
T_f = melting point, K

4.4-2 Heat of Vaporization

Because the heat of vaporization is so large, it is important to estimate ΔH_v accurately. Three techniques are discussed below.

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[12] See the supplementary references in Chap. 3.

Clausius–Clapeyron equation. The Clapeyron equation itself is an exact thermodynamic relationship between the slope of the vapor-pressure curve and the molar heat of vaporization and the other variables listed below:

$$\frac{dp^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_l)} \tag{4.12}$$

where p^* = vapor pressure
T = absolute temperature
$\Delta\hat{H}_v$ = molar heat of vaporization at T
$\hat{V}_i$ = molar volume of gas or liquid as indicated by the subscript g or l

Any consistent set of units may be used.

If experimental vapor-pressure data are available for a span of temperatures, or a correlation is available, dp^*/dT can be evaluated in the vicinity of T. Furthermore, $(\hat{V}_g - \hat{V}_l)$ can be estimated solely from $\hat{V}_g$ if we neglect V_l; hence for a nonideal gas

$$\frac{dp^*}{dT} = -\frac{\Delta\hat{H}_v}{z(RT^2/p^*)} \tag{4.13}$$

Eq. (4.13) can be solved for $\Delta\hat{H}_v$.

Another variation of Eq. (4.12) is as follows. Assume that:

- **(a)** $\hat{V}_l$ is negligible in comparison with $\hat{V}_g$.
- **(b)** The ideal gas law is applicable for the vapor:

$$\hat{V}_g = RT/p^*$$

Then

$$\frac{dp^*}{p^*} = \frac{\Delta\hat{H}_v\, dT}{RT^2} \tag{4.14}$$

Rearrange to

$$\frac{d\ln p^*}{d(1/T)} = 2.303\frac{d\log_{10} p^*}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R} \tag{4.15}$$

You can plot the $\log_{10} p^*$ vs. $1/T$ and obtain the slope $-(\Delta\hat{H}_v/2.303R)$.

If we further assume that $\Delta\hat{H}_v$ is constant over the temperature range of interest, integration of Eq. (4.15) yields an indefinite integral

$$\log_{10} p^* = -\frac{\Delta\hat{H}_v}{2.303RT} + B \tag{4.16}$$

The indefinite integral, Eq. (4.16), is known as the Clausius–Clapeyron equation. Unfortunately, a plot of $\ln p^*$ versus $1/T$ over a significant range of $1/T$ does not give a straight line. Consequently, Eq. (4.16) often is modified; one result is the Antoine equation discussed in Sec. 3.3. A definite integral of Eq. (4.15) is

$$\log_{10}\frac{p_1^*}{p_2^*} = \frac{\Delta\hat{H}_v}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.17}$$

Either of these equations can be used graphically or analytically to obtain $\Delta\hat{H}_v$ for a short temperature interval.

EXAMPLE 4.15 Heat of Vaporization from the Clausius–Clapeyron Equation

Estimate the heat of vaporization of isobutyric acid at 200°C.

Solution

The vapor-pressure data for isobutyric acid (from Perry's *Handbook*) are

Pressure (mm Hg)	Temp. (°C)	Pressure (atm)	Temp. (°C)
100	98.0	1	154.5
200	115.8	2	179.8
400	134.5	5	217.0
760	154.5	10	250.0

Basis: 1 g mol of isobutyric acid

Since $\Delta\hat{H}_v$ remains essentially constant for short temperature intervals, the heat of vaporization can be estimated from Eq. (4.17) and the vapor-pressure data at 179.8°C and 217.0°C.

$$179.8°\text{C} \Leftrightarrow 453.0\text{ K} \qquad 217°\text{C} \Leftrightarrow 490.2\text{K}$$

$$\log_{10}\frac{2}{5} = \frac{\Delta\hat{H}_v}{(2.303)(8.314)}\left(\frac{1}{490.2} - \frac{1}{453.0}\right)$$

$$\Delta\hat{H}_v = 45{,}483\text{ J/g mol at }200°\text{C}$$

The experimental value of $\Delta\hat{H}_v$ is not known at 200°C. At the normal boiling point (154.5°C), $\Delta\hat{H}_v = 41{,}300$ J/g mol, hence the value calculated is high. It should be lower than 41,300.

Reduced form of the Clapeyron equation. This is an equation in terms of the reduced pressure and temperature which gives good results:

$$d\ln p^* = -\frac{\Delta\hat{H}_v}{zRT_c}d\left(\frac{1}{T_r}\right)$$

or

$$\frac{\Delta\hat{H}_v}{zRT_c} = -\frac{d\ln p^*}{d(1/T_r)}$$

If we compute the right-hand side, say, from the Antoine equation (see Appendix G), we get

$$\frac{\Delta\hat{H}_v}{zRT_c} = \frac{B}{T_c}\left[\frac{T_r}{T_r + (C/T_c)}\right]^2 \tag{4.18}$$

Chen's equation. An equation that yields values of $\Delta\hat{H}_v$ (in kJ/g mol) to within 2% is *Chen's equation:*

$$\Delta\hat{H}_v = \frac{T_b[0.0331(T_b/T_c) + 0.0297 \log_{10} p_c - 0.0327]}{1.07 - T_b/T_c}$$

where T_b is the normal boiling point of the liquid in K, and p_c is the critical pressure in atmospheres.

Prediction using enthalpy of vaporization at the normal boiling point. As an example, Watson[13] found empirically that

$$\frac{\Delta\hat{H}_{v_2}}{\Delta\hat{H}_{v_1}} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}}\right)^{0.38}$$

where $\Delta\hat{H}_{v_2}$ = heat of vaporization of a pure liquid at T_2
$\Delta\hat{H}_{v_1}$ = heat of vaporization of the same liquid at T_1

Yaws[14] lists various other values of the exponent for various substances.

4.4-3 Reference Substance Plots

A number of graphical techniques have been proposed to estimate the molal heat of vaporization of a liquid at any temperature by comparing the $\Delta\hat{H}_v$ for the unknown liquid with that of a known liquid such as water. Two of these methods are described below.

Duhring plot. The temperature of the wanted compound A is plotted against the temperature of the known (reference) liquid at *equal vapor pressure*. For example, if the temperature of A (isobutyric acid) and the reference substance (water) are determined at 760, 400, and 200 mm Hg pressure, then a plot of the temperatures of A vs. the temperatures of the reference substance will be approximately a straight line over a wide temperature range, and have a slope of $(\Delta\hat{H}_{v_A}/\Delta\hat{H}_{v_{H_2O}})(T_{H_2O}/T_A)^2$.

Othmer plot. The Othmer plot[15] is based on the same concepts as the Duhring plot except that the *logarithms* of vapor pressures are plotted against each other at *equal temperatures*. As illustrated in Fig. 4.11, a plot of the $\log_{10}(p^*_A)$ against $\log_{10}(p^*_{\text{ref}})$ chosen at the same temperature yields a straight line over a very wide temperature range.

To indicate how to apply the Othmer plot to estimate the heat of vaporization of compound A, we apply the Clapeyron equation to each substance and take the

[13] K. M. Watson, *Ind. Eng. Chem.*, v. 23, p. 360 (1931); v. 35, p. 398 (1943).

[14] C. L. Yaws, *Physical Properties*, McGraw-Hill, New York, 1977.

[15] D. F. Othmer, *Ind. Eng. Chem.*, v. 32, p. 841 (1940). For a complete review of the technique and a comparative statistical analysis among various predictive methods, refer to D. F. Othmer and H. N. Huang, *Ind. Eng. Chem.*, v. 57, p. 40 (1965); D. F. Othmer and E. S. Yu, *Ind. Eng. Chem.*, v. 60, no. 1, p. 22 (1968); and D. F. Othmer and H. T. Chem, *Ind. Eng. Chem.*, v. 60, no. 4, p. 39 (1968).

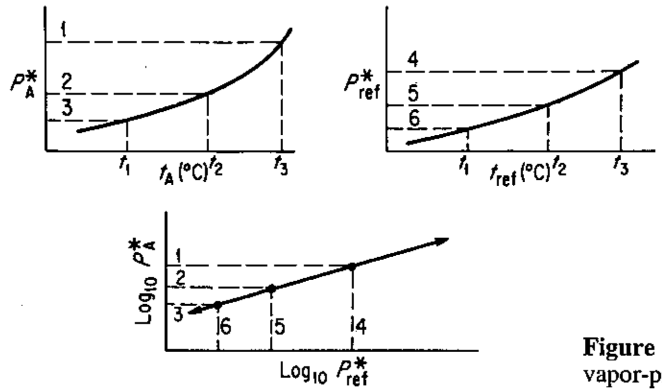

Figure 4.11 Othmer plot and vapor-pressure curves.

ratio:

$$\frac{d(\ln p_A^*)}{d(\ln p_{\text{ref}}^*)} = \frac{\dfrac{-\Delta\hat{H}_{v_A}}{R\,d(1/T_A)}}{\dfrac{-\Delta\hat{H}_{v_{\text{ref}}}}{R\,d(1/T_{\text{ref}})}} \tag{4.19}$$

By choosing values of vapor pressure at equal temperature ($T_A = T_{\text{ref}}$) in Eq. (4.19), we obtain

$$\frac{d \ln p_A^*}{d \ln p_{\text{ref}}^*} = \frac{\Delta\hat{H}_{v_A}}{\Delta\hat{H}_{v_{\text{ref}}}} = m = \text{slope of Othmer plot as in Fig. 4.11} \tag{4.20}$$

The Othmer plot works well because the errors inherent in the assumptions made in deriving Eq. (4.20) cancel out to a considerable extent. At very high pressures the Othmer plot is not too effective. Incidentally, this type of plot has been applied to estimate a wide variety of thermodynamic and transport relations, such as equilibrium constants, diffusion coefficients, solubility relations, ionization and dissociation constants, and so on, with considerable success.

Othmer recommended another type of relationship that can be used to estimate the heat of vaporization:

$$\ln p_{r_A}^* = \frac{\Delta\hat{H}_{v_A}}{\Delta H_{v_{\text{ref}}}}\left(\frac{T_{c_{\text{ref}}}}{T_{c_A}}\right) \ln p_{r_{\text{ref}}}^* \tag{4.21}$$

where p_r^* is the reduced vapor pressure. Equation (4.21) is effective and gives a straight line through the point $p_{c_A}^* = 1$ and $T_{c_A} = 1$. The Gordon method plots the log of the vapor pressure of A versus that of the reference substance at equal *reduced temperature*.

EXAMPLE 4.16 Use of an Othmer Plot

Repeat the calculation for the heat of vaporization of isobutyric acid at 200°C using an Othmer plot.

Solution

Data are as follows:

Temp. (°C)	p^*_{iso} (atm)	log p^*_{iso}	$p^*_{H_2O}$ (atm)	log $p^*_{H_2O}$
154.5	1	0	5.28	0.723
179.8	2	0.3010	9.87	0.994
217.0	5	0.698	21.6	1.334
250.0	10	1.00	39.1	1.592

Figure E4.16 is the Othmer plot.

$$\text{slope} = \frac{\Delta\hat{H}_{v_{iso}}}{\Delta\hat{H}_{v_{H_2O}}} = \frac{0.80 - 0.20}{1.42 - 0.90} = 1.15$$

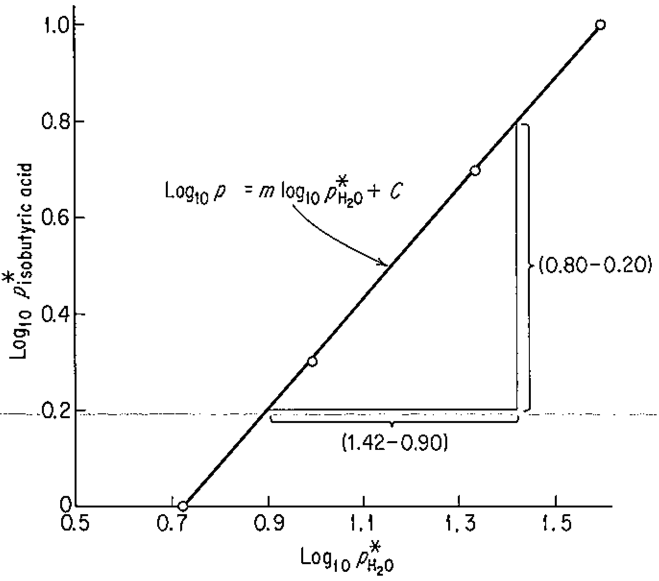

Figure E4.16

At 200°C(392°F), from the steam tables,

$$\Delta\hat{H}_{v_{H_2O}} = 34{,}895 \text{ kJ/kg mol} \qquad (1938.6 \text{ kJ/kg})$$

Then

$$\Delta\hat{H}_{v_{iso}} = (34{,}895)(1.15) = 40{,}130 \text{ kJ/kg mol}$$

The answer in this case is lower than that in Example 4.15. Without the experimental value, it is difficult to say what the proper answer is, but 40,130 is more reasonable than the value of 45,483 calculated in Example 4.15.

We are now equipped to include in the calculation of an enthalpy change the occurrence of a phase change. Because enthalpy is a state variable, any arbitary path from the initial to the final state will suffice for the actual computation. Simply choose the simplest possible path.

EXAMPLE 4.17 Calculation of Enthalpy Change Including Phase Transition

What is the enthalpy change in British thermal units when 1 gal of water is heated from 60°F to 1150°F and 240 psig?

Solution

We will use the steam tables for this problem.

Basis: 1 lb of H_2O at 60°F

From steam tables (ref. temp. = 32°F):

$$\hat{H} = 28.07 \text{ Btu/lb} \qquad \text{at } 60°\text{F}$$

$$\hat{H} = 1604.5 \text{ Btu/lb} \qquad \text{at } 1150°\text{F and 240 psig (254.7 psia)}$$

$$\Delta\hat{H} = (1604.5 - 28.07) = 1576.4 \text{ Btu/lb}$$

$$\Delta H = 1576(8.345) = 13{,}150 \text{ Btu/gal}$$

Note: The enthalpy value which has been used for liquid was taken from the steam tables for the saturated liquid under its own vapor pressure. Since the enthalpy of liquid water changes negligibly with pressure, no loss of accuracy is encountered for engineering purposes if the initial pressure on the water is not stated.

EXAMPLE 4.18 Calculation of Enthalpy Change Including a Phase Change

What is the enthalpy change of 1 kg of water from ice at 0°C to vapor at 120°C and 100 kPa?

Solution

In this problem we will use ΔH_f and ΔH_v in the calculations to illustrate how to calculate the overall enthalpy change when a table or chart is not available. Recall that enthalpy is a state function. Consequently, we can choose any convenient path between the initial and final state for the calculations. Figure E4.18 shows two different possible paths to be used to calculate ΔH. Which should be selected? The answer is the one with the best data. Usually, phase transitions are evaluated at the melting point (for a solid) and the normal boiling point of 1 atm (for a liquid) because you can easily find tabulated data at those temperatures, but any temperature would suffice. We will choose the path $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$ for which the data are

$$\Delta\hat{H}_f = 335 \text{ J/g at } 0°\text{C and } p^* \text{ or at } 101.3 \text{ kPa}$$

$$\Delta\hat{H}_v = 2256 \text{ J/g at } 100°\text{C } (101.3 \text{ kPa})$$

The heat capacity equations can be located in Table E.1 in the Appendix.

Liquid [J/(g mol)(K)]: $18.296 + 47.212 \times 10^{-2}T_K - 133.88 \times 10^{-5}T_K^2 + 1314.2 \times 10^{-9}T_K^3$

Vapor [J/(g mol)(K)]: $33.46 + 0.6880 \times 10^{-2}T_{°C} + 0.7604 \times 10^{-5}T_{°C}^2 - 3.593 \times 10^{-9}T_{°C}^3$

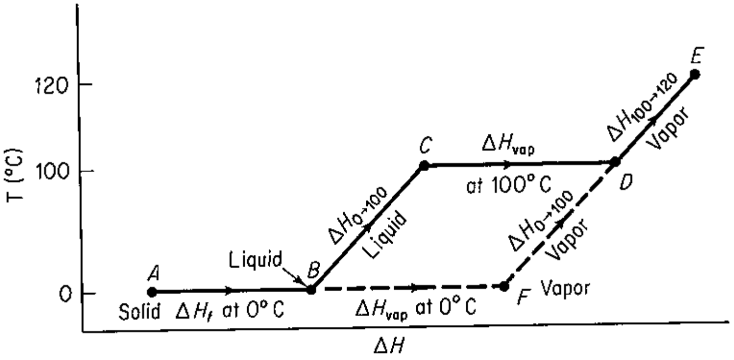

Figure E4.18 (not to scale)

$$\Delta\hat{H}_{\text{overall}} = \Delta\hat{H}_{\text{fusion at }0^\circ\text{C}} + \Delta\hat{H}_{\text{liquid at }0^\circ\text{C}\to 100^\circ\text{C}} + \Delta\hat{H}_{\text{vaporization at }100^\circ\text{C}} + \Delta\hat{H}_{\text{vapor }100\to 120^\circ\text{C}}$$

$$= 335 + \tfrac{1}{18}\int_{273}^{373} (18.296 + 47.212 \times 10^{-2}T - 133.88 \times 10^{-5}T^2$$

$$+ 1{,}314.2 \times 10^{-9}T^3)\,dT + 2256 + \tfrac{1}{18}\int_{100}^{120} (33.46 + 0.6880 \times 10^{-2}T$$

$$+ 0.7604 \times 10^{-5}T^2 - 3.593 \times 10^{-9}T^3)\,dT$$

$$= 335 + 418.6 + 2256 + 38.1 = 3048 \text{ J/g}$$

From the steam tables, the value of $\Delta\hat{H}$ is

$$\Delta\hat{H} = \overset{\Delta\hat{H}_f}{335} + \overset{\Delta\hat{H}_{0\to 120^\circ\text{C}}}{2716} = 3051 \text{ J/g}$$

Can you offer a reason for the small difference?

Now that we have finished describing ways to calculate the quantities that will appear in the energy balance, it is time to turn to consideration of the balance itself.

Self-Assessment Test

1. Calculate the enthalpy change in Btu/lb of benzene as it goes from a vapor at 300°F and 1 atm to a solid at 0°F and 1 atm.
2. What is the enthalpy change that occurs when 5 lb of water is heated from ice at 32°F to vapor at 250°F and 1 atm? Use the steam tables.
3. Estimate the heat of vaporization of water at 450 K from Watson's relation given that ΔH_v = 2256.1 kJ/kg at 373.14 K, and compare with experimental data.
4. Prepare an Othmer chart to predict the heat of vaporization of methyl alcohol at 90°C. Use water as the reference substance. Repeat using the Clausius–Clapeyron equation.
5. Air conditioners use Freon-12 as the working fluid. A charging when unit full holds 10 kg of saturated liquid at 20°C. If the unit contains 3 kg at 20°C, what is the quality? Use the following extract from the Freon-12 table in solving the problem.

Satn. pres., p^*(kPa)	Satn. temp., t_s(°C)	Volume (cm³/g) v_l	Volume (cm³/g) v_g	Enthalpy (J/g) h_l	Enthalpy (J/g) h_g
500	15.6	0.7438	34.82	50.66	194.0
600	22	0.7566	29.13	56.80	196.6

Thought Problems

1. Fire walkers with bare feet walk across beds of glowing coals without apparent harm. The rite is found in many parts of the world today and was practiced in classical Greece and ancient India and China, according to the *Encyclopaedia Britannica.*

   The temperature of glowing coals is about 1000°C. What are some of the possible reasons that fire walkers are not seriously burned?

2. A fire-induced BLEVE (boiling liquid expanding vapor explosion) in a storage tank can result in a catastrophy. The scenario is somewhat as follows: A pressure vessel (e.g., a pressurized storage tank), partially filled with liquid, is subjected to high heat flux from a fire. The temperature of the liquid starts to increase, causing an increase in pressure within the tank. When the vapor pressure reaches the safety relief valve pressure setting, the relief valve opens and starts to vent vapor (or liquid) to the outside. Concurrent with the previous step, the temperature of the portion of the tank shell not in contact with the liquid (i.e., the ullage space) increases dramatically.

   The heat weakens the tank shell around the ullage space. Thermally induced stresses are created in the tank shell near the vapor/liquid interface, and the heat-weakened tank plus the high internal pressure combine to cause a sudden, violent tank rupture. Fragments of the tank are propelled away from the tank at great force. Most of the remaining superheated liquid vaporizes rapidly due to the pressure release. The rest is mechanically atomized to small drops due to the force of the explosion. A fireball is created by the burning vapor and liquid.

   What steps would you recommend to prevent a BLEVE in the case of fire near a storage tank? [*Hint:* Two possible routes are: (1) prevent the fire from heating the tank; and (2) prevent the buildup of presure in the tank.]

4.5 THE GENERAL ENERGY BALANCE

Scientists did not begin to write energy balances for physical systems prior to the latter half of the nineteenth century. Before 1850 they were not sure what energy was or even if it was important. But in the 1850s the concepts of energy and the energy balance became clearly formulated. We do not have the space here to outline the historical development of the energy balance and of special cases of it, but it truly makes a most interesting story and can be found elsewhere.[16–19] Today we consider

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[16] E. J. Hoffman, *The Concept of Energy: An Inquiry into Origins and Applications,* Ann Arbor Science Publishers, Ann Arbor, Mich., 1977.

[17] V. V. Raman, "Where Credit Is Due—The Energy Conservation Principle," *Phys. Teacher,* p. 80(February 1965).

[18] T. M. Brown, *Am. J. Physics,* v. 33, no. 10, p. 1 (1965).

[19] L. K. Nash, *J. Chem. Educ.,* v. 42, p. 64 (1965) (a resource paper).

the energy balance to be so fundamental a physical principle that we invent new classes of energy to make sure that the equation indeed does balance. Equation (4.22) as written below is a generalization of the results of numerous experiments on relatively simple special cases. We universally believe the equation is valid because we cannot find exceptions to it in practice, taking into account the precision of the measurements.

It is necessary to keep in mind two important points as you read what follows. First, we examine only systems that are homogeneous, not charged, and without surface effects, in order to make the energy balance as simple as possible. Second, the energy balance is developed and applied from the macroscopic viewpoint (overall about the system) rather than from a microscopic viewpoint (i.e., an elemental volume within the system).

The concept of the macroscopic energy balance is similar to the concept of the macroscopic material balance, namely,

$$\left\{\begin{array}{l}\textbf{accumulation of}\\ \textbf{energy within the}\\ \textbf{system}\end{array}\right\} = \left\{\begin{array}{l}\textbf{transfer of energy}\\ \textbf{into system through}\\ \textbf{system boundary}\end{array}\right\} - \left\{\begin{array}{l}\textbf{transfer of energy out}\\ \textbf{of system through}\\ \textbf{system boundary}\end{array}\right\}$$

$$+ \left\{\begin{array}{l}\textbf{energy genera-}\\ \textbf{tion within}\\ \textbf{system}\end{array}\right\} - \left\{\begin{array}{l}\textbf{energy con-}\\ \textbf{sumption}\\ \textbf{within system}\end{array}\right\} \qquad (4.22)$$

Equation (4.22) can be applied to a single piece of equipment or to a complex plant such as that shown in Fig. 4.2.

While the formulation of the energy balance in words as outlined in Eq. (4.22) is easily understood and rigorous, you will discover in later courses that to express each term of Eq. (4.22) in mathematical notation may require certain simplifications to be introduced, a discussion of which is beyond our scope here, but they have a quite minor influence on our final balance.

In what follows we first treat systems in which no material flows in and out. Do you remember the name for such a system? Then we examine systems in which material does flow in and out. What is the name for such a system? Finally, in Sec. 4.7 we discuss energy balances for processes in which chemical reactions take place. Thus the energy generation and consumption terms will not play a role in this chapter unless sources such as radioactive decay or the slowing down of neutrons enter into the process.

4.5-1 Energy Balances for Closed Systems (without Chemical Reaction)

Your objectives in studying this section are to be able to:

1. Write down the general energy balance in words [Eq. (4.22)].
2. Write down the energy balance for a closed system in symbols [Eq. (4.23)], and apply it to solve energy balance problems.

3. Cite the signs for work and heat entering and leaving the system.
4. Calculate the total energy or any of its components (internal energy, kinetic energy, potential energy) associated with the mass of the system.

Figure 4.12 shows the various types of energy to be accounted for in Eq. (4.22). As to the notation, the subscripts t_1 and t_2 refer to the initial and final times for the period over which the accumulation is to be evaluated, with $t_2 > t_1$. The superscript caret (ˆ) means that the symbol stands for energy per unit mass; without the caret, the symbol means energy of the total mass present. Other notation is evident from Table 4.8 and is repeated in the notation list at the end of the book.

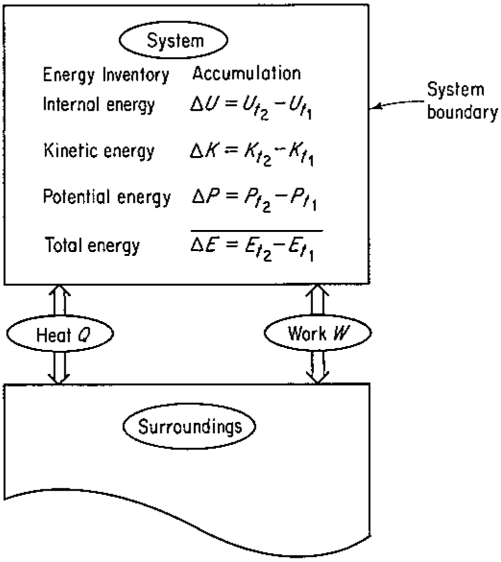

Figure 4.12 Terms in the energy balance for a closed system.

As is commonly done, we have split the total energy (E) associated with the mass in the system into three categories: internal energy (U), kinetic energy (K), and potential energy (P). Energy transported across the system boundary can be transferred by two modes: heat (Q) and work (W). (We discuss energy transferred with mass flow in Sec. 4.5-2.) Note that Q and W here are defined as the *net* transfer of heat and work, respectively, between the system and the surroundings, and respectively equal the integral of the net rate of flow of heat or work over the time interval t_1 to t_2:

$$Q = \int_{t_1}^{t_2} \dot{Q}\,dt \qquad W = \int_{t_1}^{t_2} \dot{W}\,dt$$

Other forms of energy can be split from Q, W, or ΔE, and included as separate terms in Eq. (4.23) if they are important enough to be distinguished. Keep in mind that the internal energies U_{t_1} and U_{t_2} in the system cannot be evaluated as absolute quantities—only $(U_{t_2} - U_{t_1}) = \Delta U$ can be calculated. The reference state cancels.

Equation (4.22) when translated into mathematical symbols becomes

$$\Delta E = E_{t_2} - E_{t_1} = Q - W \tag{4.23}$$

where Δ = **difference operator signifying *final* minus *initial* in time**

Q = **heat absorbed *by* the system *from* the surroundings** (by definition Q is ***positive for heat entering the system***)

W = **mechanical work done *by* the system *on* the surroundings** (by definition W is ***positive for work going from the system to the surroundings***)

[Equation (4.23) is known as the ***first law of thermodynamics*** for a closed system.]

Keep in mind that a system may do work, or have work done on it, without some obvious mechanical device such as a pump, shaft, and so on, being present. Often the nature of the work is implied rather than explicity stated. For example, a cylinder filled with gas enclosed by a movable piston implies that the surrounding atmosphere can do work on the piston or the reverse; a batch fuel cell does no mechanical work, unless it produces bubbles, but does deliver a current at a potential difference; electromagnetic radiation can impinge on or leave a system; and so forth.

Now for a word of warning: Be certain you use *consistent units* for all terms; in the American engineering system the use of foot-pound, for example, and Btu in different places in Eq. (4.23) is a common error for the beginner.

Let us look now at some examples of applications of the energy balance for closed systems. Remember to follow the checklist presented in Chap. 2 in analyzing the problem.

EXAMPLE 4.19 Application of the Energy Balance

Ten pounds of CO_2 at room temperature (80°F) are stored in a fire extinguisher having a volume of 4.0 ft^3. How much heat must be removed from the extinguisher so that 40% of the CO_2 becomes liquid?

Solution

This problem involves a closed system (Fig. E4.19) so that Eq. (4.23) applies. We can use the CO_2 chart in Appendix J to get the necessary property values.

Steps 1, 2, and 3 The specific volume of the CO_2 is $4.0/10 = 0.40$ ft^3/lb, hence CO_2 is a gas at the start of the process. The pressure is 300 psia and $\Delta\hat{H} = 160$ Btu/lb.

Step 4

Basis: 10 lb CO_2

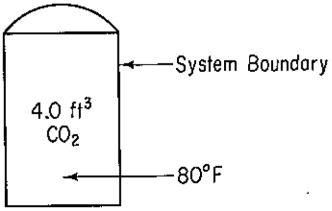

Figure E4.19

Steps 5 and 6 In the energy balance

$$\Delta E = Q - W$$

W is zero because the volume of the system is fixed, hence with $\Delta K = \Delta P = 0$,

$$Q = \Delta U = \Delta H - \Delta(pV)$$

We do not have values of $\Delta\hat{U}$, just values of $\Delta\hat{H}$, on the CO_2 chart. We can find $\Delta\hat{H}_{\text{final}}$ from the CO_2 chart by following the constant-volume line of 0.40 ft³/lb to the spot where the quality is 0.6. Hence the final state is fixed, and all the final properties can be identified, namely

$$\Delta\hat{H}_{\text{final}} = 81 \text{ Btu/lb}$$

$$p_{\text{final}} = 140 \text{ psia}$$

Steps 7, 8, and 9

$$Q = (81 - 160) - \left[\frac{(140)(144)(0.40)}{778.2} - \frac{(300)(144)(0.40)}{778.2}\right]$$

$$= -67.2 \text{ Btu} \quad \text{(heat is removed)}$$

EXAMPLE 4.20 Application of the Energy Balance

Argon gas in an insulated plasma deposition chamber with a volume of 2 L is to be heated by an electric resistance heater. Initially the gas, which can be treated as an ideal gas, is at 1.5 Pa and 300 K. The 1000-ohm heater draws current at 40 V for 5 minutes (i.e., 480 J of work is done by the surroundings). What is the final gas temperature and pressure at equilibrium? The mass of the heater is 12 g and its heat capacity is 0.35 J/(g)(K). Assume that the heat transfer to the chamber from the gas at this low pressure and in the short time period is negligible.

Solution

The system does not exchange mass with the surroundings, so Eq. (4.23) applies with $\Delta P = \Delta K = 0$:

$$\Delta E = Q - W = \Delta U$$

Steps 1, 2, and 3 The system is the gas plus the heater as shown in Fig. E4.20. Because of the assumption about the heat transfer, $Q = 0$. W is given as -480 J (work done on the system) in 5 minutes.

Step 4

$$\text{Basis} = 5 \text{ minutes}$$

Steps 5 and 6 For an ideal gas

$$pV = nRT$$

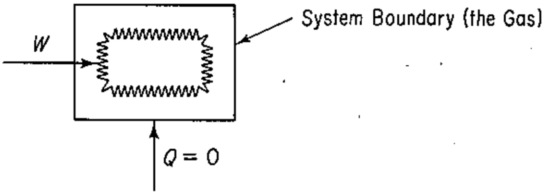

Figure E4.20

and initially we know p, V, and T, and thus can calculate the mass of the gas:

$$n = \frac{pV}{RT} = \begin{array}{c|c|c|c|c} 1.5\ \text{Pa} & 2\ \text{L} & 10^{-3}\ \text{m}^3 & 10^3(\text{g mol})(\text{K}) & \\ \hline & & 1\ \text{L} & 8.314 \times 10^3(\text{Pa})(\text{m}^3) & 300\ \text{K} \end{array}$$

$$= 1.203 \times 10^{-6}\ \text{g mol}$$

The heater mass and heat capacity are given, and the C_V of the gas is (see Sec. 4.2) $C_V = C_p - R$ since $C_p = \frac{5}{2}R$,

$$C_V = \tfrac{5}{2}R - R = \tfrac{3}{2}R$$

Assume that the heat capacity of the heater is C_V also. We know that

$$\Delta U = n \int_{300}^{T_p} C_V\, dT = nC_V(T - 300)$$

hence we can find T once we calculate ΔU from $-W = \Delta U$.

Steps 7, 8, and 9

$$\Delta U = -(-480\ \text{J}) = 480\ \text{J}$$

$$= \overbrace{(12)(0.35)(T - 300)}^{\textbf{heater}} + (1.203 \times 10^{-6})\overbrace{(\tfrac{3}{2})(8.314)(T - 300)}^{\textbf{gas}}$$

$$T = 414.3\ \text{K}$$

The final pressure is

$$\frac{p_2 V_2}{p_1 V_1} = \frac{n_2 RT_2}{n_1 RT_1}$$

or

$$p_2 = p_1\left(\frac{T_2}{T_1}\right) = 1.5\left(\frac{414.3}{300}\right) = 2.07\ \text{Pa}$$

EXAMPLE 4.21 Energy Balance

Ten pounds of water at 35°F, 4.00 lb of ice at 32°F, and 6.00 lb of steam at 250°F and 20 psia are mixed together in a container of fixed volume. What is the final temperature of the mixture? How much steam condenses? Assume that the volume of the vessel is constant with a value equal to the volume of the steam and that the vessel is insulated.

Solution

Steps 1, 2, and 3 We can assume that the overall batch process takes place with $Q = 0$ and $W = 0$ if we define the system as in Fig. E4.21. Let T_2 be the final temperature. The system consists of 20 lb of H_2O in one or two phases. ΔK and ΔP equal 0. The energy balance reduces to $\Delta U = 0$.

The initial properties can be obtained from the steam tables. Unfortunately, we can only retrieve $\Delta\hat{H}$ values, not the $\Delta\hat{U}$ values that we want (and could get from the SI steam tables) for the energy balance, hence we need also to collect values of p and $\hat{V}$.

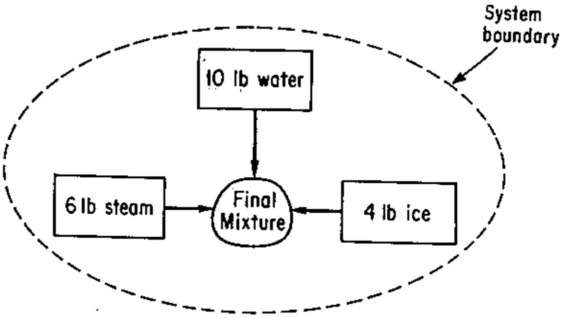

Figure E4.21

	$\Delta\hat{H}$ (Btu/lb)	$\hat{V}$ (ft^3/lb)	p (psia)	T (°F)
Ice	−143.6*	—	—	32
Water	3.02	0.0162		35
Steam	1168	20.81	20	250

*Heat of fusion (pressure and volume have no significant effect).

We know that $\Delta\hat{U} = \Delta\hat{H} - \Delta p\,\hat{V}$, so that the energy balance becomes

$$\Delta H - \Delta p\,V = 0 \tag{a}$$

The volume of the container is fixed at the initial volume of the steam, namely (6) (20.81) = 124.86 ft^3; we ignore the volumes of the ice and water in the calculations, as they are so small.

Step 4 The basis is 20 lb of water at the given conditions.

$$\text{Basis:}\begin{cases}\text{4 lb of ice at 32°F}\\ \text{10 lb of } H_2O \text{ at 35°F}\\ \text{6 lb of steam at 250°F and 20 psia}\end{cases}$$

Steps 5 and 6 If we assume that the final state of the water is liquid water in equilibrium with water vapor, an assumption to be checked out, we can calculate the final $\Delta\hat{H}$ of the 20 lb of water. We also know that the final water is saturated. The second condition to fix the state (quality, temperature, and pressure) of the system can evolve from the energy balance, hence the problem has a unique solution. However, the final state must be calculated indirectly if tables are to be used.

Steps 7, 8, and 9

$$\overbrace{20\,\Delta\hat{H}^{f}_{T_f}}^{\textbf{final } \Delta H} - \overbrace{(6\Delta\hat{H}^{s}_{T_s} + 10\Delta\hat{H}^{w}_{T_w} + 4\Delta\hat{H}^{i}_{T_i})}^{\textbf{initial } \Delta H}$$

$$= 20(p\hat{V})^{f}_{T_f} - 6(p\hat{V})^{s}_{T_s} - 10(p\hat{V})^{w}_{T_w} - 4(p\hat{V})^{i}_{T_i} \tag{b}$$

The last two terms on the right-hand side of Eq. (b) cannot be more than 1 Btu at the very most and can safely be neglected. Be sure to check this assumption! Thus the equation to be used is

$$20\Delta\hat{H}^{f}_{T_f} - 20(p\hat{V})^{f}_{T_f} = (6\Delta\hat{H}^{s}_{T_s} + 10\Delta\hat{H}^{w}_{T_w} + 4\Delta\hat{H}^{i}_{T_i}) - 6(p\hat{V})^{s}_{T_s} \tag{c}$$

Because of the phase changes that take place as well as the nonlinearity of the heat capacities as a function of temperature, it is not possible to replace the enthalpies in Eq. (c) with functions of temperature and get a linear algebraic equation that is easy to solve. Consequently, the strategy we will use is first to assume a final temperature and pressure, and next we will check the calculation via Eq. (c). We want to bracket the temperature if possible, and then can interpolate for the desired answer.

The pressure in the vessel drops as more steam condenses. Data for the specific volume of the steam as a function of temperature and pressure can be taken from the steam tables, at saturated conditions, and the mass of steam left at any assumed temperature (or pressure) can be calculated by dividing 124.86 ft³ by the specific volume of the steam.

The right-hand side of Eq. (c) is equal to

$$\frac{6\text{ lb}}{}\bigg|\frac{1168.0\text{ Btu}}{\text{lb}} + \frac{10\text{ lb}}{}\bigg|\frac{3.02\text{ Btu}}{\text{lb}} + \frac{4\text{ lb}}{}\bigg|\frac{-143.6\text{ Btu}}{\text{lb}}$$

$$-\frac{6\text{lb}_m}{}\bigg|\frac{20\text{ lb}_f}{\text{in}^2.}\bigg|\left(\frac{12\text{ in.}}{1\text{ ft}}\right)^2\bigg|\frac{20.81\text{ ft}^3}{\text{lb}_m}\bigg|\frac{1\text{ Btu}}{778(\text{ft})(\text{lb}_f)} = 6001.6\text{ Btu}$$

As an initial guess, suppose that one-half of the steam does not condense. Then the specific volume of the final steam is (124.86 ft³/3 lb) = 41.62 ft³/lb. The closest integer line in the steam tables in the saturated steam column for pressure is 10 psia (T = 193.21°F) with a specific volume of 38.462 ft³/lb and with $\Delta\hat{H}_{\text{steam}} = 1143.3$ Btu/lb and $\Delta\hat{H}_{\text{liquid}} = 161.17$ Btu/lb. Let us use these latter data as the initial assumption. We calculate

$$S = \frac{124.86\text{ ft}^3}{}\bigg|\frac{1\text{ lb steam}}{38.462\text{ ft}^3} = 3.246\text{ lb steam not condensed}$$

We check this assumption by seeing if Eq. (c′) balances:

$$S[\Delta\hat{H}_{T_f} - p\hat{V}]^f_{\text{vapor}} + (20 - S)[\Delta\hat{H}_{T_f} - p\hat{V}]^f_{\text{liquid}} \stackrel{?}{=} 6001.6 \qquad (c')$$

$$(p\hat{V})^f_{\text{vapor}} = \frac{(10)(12)^2(38.462)}{778} = 71.2\text{ Btu/lb}$$

$$(p\hat{V})^f_{\text{liquid}} \cong 0.0$$

$$3.246(1143.3 - 71.2) + (20 - 3.246)(161.17) \stackrel{?}{=} 6001.6$$

$$6180.28 \neq 6001.6$$

The initial guess for T_f and p was too low (we need a bigger specific volume for the steam, hence S is less). Next we assume that $T^* = 186$°F ($p^* = 8.566$ psia, $\hat{V}_{\text{vapor}} = 44.55$ ft³/lb, $\Delta\hat{H}_{\text{liquid}} = 153.93$ Btu/lb, and $\Delta\hat{H}_{\text{vapor}} = 1140.5$ Btu/lb).

$$S = \frac{124.86}{44.45} = 2.899\text{ lb not condensed}$$

Again we check Eq. (c′):

$$(p\hat{V})^f_{\text{vapor}} = \frac{(8.566)(12)^2(44.45)}{778} = 70.5\text{ Btu/lb}$$

$$(pV)^f_{\text{liquid}} \cong 0$$

$$2.899(1140.5 - 70.5) + (20 - 2.899)(153.93) \stackrel{?}{=} 6001.6$$

$$5734.29 \neq 6001.6$$

However, we have bracketed the solution. Linear interpolation for S gives

$$S = 2.899 + \left(\frac{6001.6 - 5734.29}{6180.28 - 5734.29}\right)(3.246 - 2.899)$$
$$= 3.11$$

Consequently, the steam condensed is $6 - 3.11 = 2.89$ lb, and the assumption in steps 5 and 6 proved correct.

Self-Assessment Test

1. Liquid oxygen is stored in a 14,000-L storage tank. When charged, the tank contains 13,000 L of liquid in equilibrium with its vapor at 1 atm pressure. What is the **(a)** temperature, **(b)** mass, and **(c)** quality of the oxygen in the vessel? The pressure relief valve of the storage tank is set at 2.5 atm. If heat leaks into the oxygen tank at the rate of 5.0×10^6 J/hr, **(d)** when will the pressure relief valve operate, and **(e)** what will be the temperature in the storage tank at that time?
   Data: at 1 atm, saturated, $\hat{V}_l = 0.0281$ L/g mol, $\hat{V}_g = 7.15$ L/g mol, $\Delta\hat{H} = -133.5$ J/g; at 2.5 atm, saturated, $\Delta\hat{H} = -116.6$ J/g.
2. Suppose that you fill an insulated Thermos to 95% of the volume with ice and water at equilibrium and securely seal the opening.
   - **(a)** Will the pressure in the Thermos go up, down, or remain the same after 2 hr?
   - **(b)** After 2 weeks?
   - **(c)** For the case in which after filling and sealing, the Thermos is shaken vigorously, what will happen to the pressure?
3. An 0.25-liter container initially filled with 0.225 kg of water at a pressure of 20 atm is cooled until the pressure inside the container is 100 kPa.
   - **(a)** What are the initial and final temperatures of the water?
   - **(b)** How much heat was transferred from the water to reach the final state?
4. Compute ΔE in Btu for 2 lb mol of an ideal monoatomic gas heated from 60°F to 160°F.
5. In a shock tube experiment, the gas (air) is held at room temperature at 15 atm in a volume of 0.350 ft^3 by a metal seal. When the seal is broken, the air rushes down the evacuated tube, which has a volume of 20 ft^3. The tube is insulated. In the experiment:
   - **(a)** What is the work done by the air?
   - **(b)** What is the heat transferred to the air?
   - **(c)** What is the internal energy change of the air?
   - **(d)** What is the final temperature of the air after 3 min?
   - **(e)** What is the final pressure of the air?

4.5-2 Energy Balances for Open Systems (without Chemical Reaction)

Your objectives in studying this section are to be able to:

1. Write down the energy balance for an open system [Eq. (4.24)] in words and symbols, explain each term, and apply the equation to

solve energy balance problems using the 10-step strategy plus two new steps.

2. Explain the "pV work" (flow work) concept.
3. Define isothermal, adiabatic, isobaric, and isometric processes.
4. Make the necessary assumptions and approximations to simplify and solve the energy balance for open systems.

We now apply Eq. (4.22) to systems in which mass as well as energy can pass through the system boundaries. Figure 4.13 illustrates the general case. All the notation is listed in Table 4.8. Keep in mind that the symbols m_1 or m_2 represent a *steady* flow of mass. We give an alternative formulation of the energy balance in terms of differentials in Chap. 6 [see Eqs. (6.8) and (6.9)], where emphasis is placed on the instantaneous rate of change of energy of a system rather than just the initial and final states of the system. The formulation in this chapter can be considered to be the result of integrating the differential balance [see Eq. (6.9)]. The **energy balance for the open system is**

$$\underbrace{m_{t_2}(\hat{U} + \hat{K} + \hat{P})_{t_2} - m_{t_1}(\hat{U} + \hat{K} + \hat{P})_{t_1}}_{\text{accumulation}} = \underbrace{(\hat{U}_1 + \hat{K}_1 + \hat{P}_1)m_1}_{\text{transfer in by mass flow}}$$

$$\underbrace{-(\hat{U}_2 + \hat{K}_2 + \hat{P}_2)m_2}_{\text{transfer out by mass flow}} + \underbrace{Q}_{\text{net transfer by heat}} \underbrace{- W + p_1\hat{V}_1 m_1 - p_2\hat{V}_2 m_2}_{\text{net transfer by work}} \tag{4.24}$$

The terms $p_1\hat{V}_1$ and $p_2\hat{V}_2$ in Eq. (4.24) and Table 4.8 represent the so-called "pV work," or "pressure energy" or "flow work," or "flow energy," that is, the work

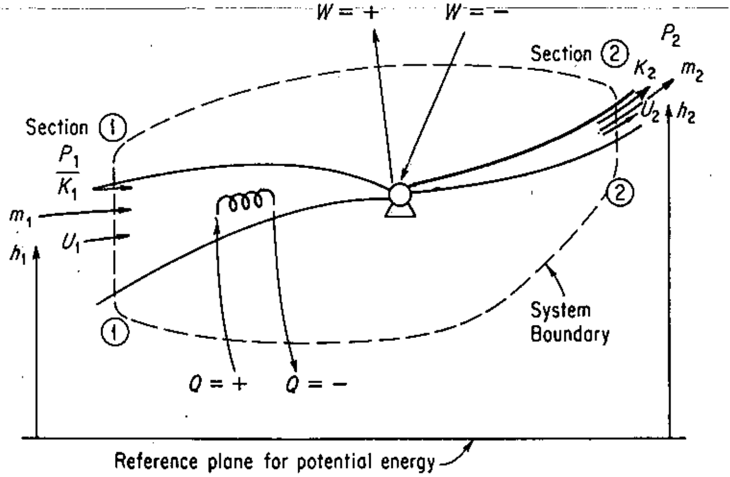

Figure 4.13 General process showing the system boundary and energy transport across the boundary.

TABLE 4.8 Summary of the Symbols to be Used in the General Energy Balance

Accumulation term				
Type of energy	*At time* t_1		*At time* t_2	
Internal	U_{t_1}		U_{t_2}	
Kinetic	K_{t_1}	E_{t_1}	K_{t_2}	E_{t_2}
Potential	P_{t}		P_{t_2}	
Mass	m_{t_1}		m_{t_2}	
Energy accompanying mass transport				
Type of energy	*Transport in*		*Transport out*	
Internal	U_1		U_2	
Kinetic	K_1		K_2	
Potential	P_1		P_2	
Mass	m_1		m_2	
Net heat input to system	Q			
Net work done by system on surroundings				
Mechanical work or work by moving parts	W			
Work to introduce material into system, less work recovered on removing material from system	$(p_2\hat{V}_2)m_2 - (p_1\hat{V}_1)m_1$			

done by the surroundings to put a unit mass of matter into the system at ① in Fig. 4.13 and the work done by the system on the surroundings as a unit mass leaves the system at ②. Because the pressures at the entrance and exit to the system are constant for differential displacements of mass, the work done by the surroundings on the system adds energy to the system at ①:

$$W_1 = \int_0^{\hat{V}_1} p_1\, d\hat{V} = p_1(\hat{V}_1 - 0) = p_1\hat{V}_1$$

where $\hat{V}$ is the volume per unit mass. Similarly, the work done by the fluid on the surroundings as the fluid leaves the system is $W_2 = p_2\hat{V}_2$, a term that has to be subtracted (why?) from the right-hand side of Eq. (4.24).

In practice we introduce the expression $\Delta\hat{U} + \Delta p\hat{V} = \Delta\hat{H}$ in Eq. (4.24) and thus retain the variable H. Then the energy balance reduces to a form easier to memorize:

$$\Delta E = E_{t_2} - E_{t_1} = -\Delta[(\hat{H} + \hat{K} + \hat{P})m] + Q - W \qquad (4.24a)$$

where $\Delta E = (\hat{U} + \hat{K} + \hat{P})_{t_2}m_{t_2} - (\hat{U} + \hat{K} + \hat{P})_{t_1}m_{t_1}$.

In Eq. (4.24a) the delta symbol (Δ) has two different meanings:

- **(a)** In ΔE, Δ means final minus initial in time.
- **(b)** In ΔH, and so on, Δ means out of the system minus into the system.

Such usage is perhaps initially confusing, but is very common; hence you might as well become accustomed to it. A more rigorous derivation of Eq. (4.24) from a microscopic energy balance may be found in Slattery.[20]

If there is more than one input and output stream to the system, Eq. (4.24a) would become

$$E_{t_2} - E_{t_1} = \sum_{\text{in}} m_i(\hat{H}_i + \hat{K}_i + \hat{P}_i) - \sum_{\text{out}} m_o(\hat{H}_o + \hat{K}_o + \hat{P}_o) + Q - W \qquad (4.25)$$

Here the subscript (o) designates an output stream and the subscript (i) designates an input stream.

In most problems you do not have to use all the terms of the general energy balance equation because certain terms may be zero or may be so small that they can be neglected in comparison with the other terms. Several special cases can be deduced from the general energy balance of considerable industrial importance by introducing certain simplifying assumptions:

(a) No mass transfer **(closed or batch system)** ($m_1 = m_2 = 0$):

$$\Delta E = Q - W \qquad (4.23)$$

(b) No accumulation ($\Delta E = 0$), no mass transfer ($m_1 = m_2 = 0$):

$$Q = W \qquad (4.26)$$

(c) No accumulation ($\Delta E = 0$), but with mass flow:

$$Q - W = \Delta[(\hat{H} + \hat{K} + \hat{P})m] \qquad (4.27)$$

(d) No accumulation, $Q = 0$, $W = 0$, $\hat{K} = 0$, $\hat{P} = 0$:

$$\Delta\hat{H} = 0 \qquad (4.28)$$

[Equation (4.28) is called the **"enthalpy balance."**]

Take, for example, the flow system shown in Fig. 4.14. Overall, between locations 1 and 5, we would find that $\Delta P = 0$. In fact, the only portion of the system where ΔP would be of concern would be between location 4 and some other location. Between 3 and 4, ΔP may be consequential, but between 2 and 4 it may be

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[20] J. C. Slattery, *Momentum, Energy, and Mass Transfer in Continua*, McGraw-Hill, New York, 1972.

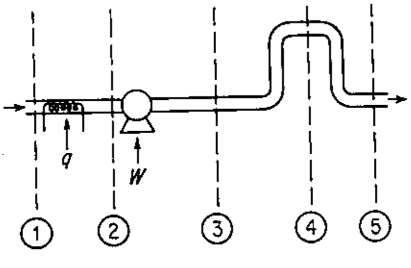


Figure 4.14 Flow system. The dashed lines delineate sub-systems.

negligible in comparison with the work introduced by the pump. Between location 3 and any further downstream point, both Q and W are zero. After reading the problem statements in the examples below but before continuing to read the solution, you should try to apply Eq. (4.24a) yourself to test your ability to simplify the energy balance for particular cases.

Some special process names associated with energy balance problems are worth remembering:

(a) *Isothermal* ($dT = 0$): constant-temperature process
(b) *Isobaric* ($dp = 0$): constant-pressure process
(c) *Isometric* or *isochoric* ($dV = 0$): constant-volume process
(d) *Adiabatic* ($Q = 0$): no heat interchange (i.e., an insulated system). If we inquire as to the circumstances under which a process can be called adiabatic, one of the following is most likely:
  (1) The system is insulated.
  (2) Q is very small in relation to the other terms in the energy equation and may be neglected.
  (3) The process takes place so fast that there is no time for heat to be transferred.

One further remark that we should make is that the energy balance we have presented has included only the most commonly used energy terms. If a change in surface energy, rotational energy, or some other form of energy is important, these more obscure energy terms can be incorporated in an appropriate energy expression by separating the energy of special interest from the term in which it presently is incorporated in Eq. (4.24a). As an example, kinetic energy might be split into linear kinetic energy (translation) and angular kinetic energy (rotation).

To assist you in solving problems involving energy balances, two additional steps should be added to your mental checklist for analyzing problems (see Table 2.4):

(a) *Step 3a:* Always write down the general energy balance, Eq. (4.24) or (4.24a), below your sketch. By this step you will be certain not to neglect any of the terms in your analysis.
(b) *Step 3b:* Examine each term in the general energy balance and eliminate all terms that are zero or can be neglected. Write down why you do so.

We now examine some applications of the general energy balance.

EXAMPLE 4.22 Application of the Energy Balance

Air is being compressed from 100 kPa and 255 K (where it has an enthalpy of 489 kJ/kg) to 1000 kPa and 278 K (where it has an enthalpy of 509 kJ/kg). The exit velocity of the air from the compressor is 60 m/s. What is the power required (in kW) for the compressor if the load is 100 kg/hr of air?

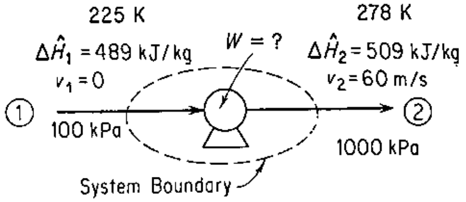


Figure E4.22

Solution

Steps 1, 2, and 3 Figure E4.22 shows the known quantities. The process is clearly a flow process or open system. Let us assume that the entering velocity of the air is zero.

Step 4

Basis: 100 kg of air = 1 hr

Steps 3a and 3b

$$\Delta E = -\Delta[(\hat{H} + \hat{K} + \hat{P})m] + Q - W$$

Let us simplify the energy balance:

(1) The process is in the steady state, hence $\Delta E = 0$.

(2) $m_1 = m_2$.

(3) $\Delta(\hat{P}m) = 0$.

(4) $Q = 0$ by assumption (Q would be small even if the system were not insulated).

(5) $v_1 = 0$ (value is not known but would be small).

The result is

$$W = -\Delta[(\hat{H} + \hat{K})m] = -\Delta H - \Delta K$$

Steps 5 and 6 We have one equation and one unknown, W (ΔK, in effect, and ΔH can be calculated), hence the problem has a unique solution.

Steps 7, 8, and 9

$$\Delta H = \frac{(509 - 489)\ \text{kJ}}{\text{kg}}\left|\frac{100\ \text{kg}}{}\right. = 2000\ \text{kJ}$$

$$\Delta K = \tfrac{1}{2}\text{m}(v_2^2 - v_1^2)$$

$$= \left(\frac{1}{2}\right)\frac{100\ \text{kg}}{}\left|\frac{(60\ \text{m})^2}{\text{s}^2}\right|\frac{1\ \text{kJ}}{\dfrac{1000(\text{kg})(\text{m}^2)}{(\text{s})^2}}\Bigg| = 180\ \text{kJ}$$

$$W = -(2000 + 180) = -2180\ \text{kJ}$$

(*Note:* The minus sign indicates work is done on the air.)

To convert to power (work/time),

$$\text{kW} = \frac{2180\ \text{kJ}}{1\ \text{hr}}\left|\frac{1\ \text{kW}}{\dfrac{1\ \text{kJ}}{\text{s}}}\right|\frac{1\ \text{hr}}{3600\ \text{s}} = 0.61\ \text{kW}$$

EXAMPLE 4.23 Application of the Energy Balance

Water is being pumped from the bottom of a well 15 ft deep at the rate of 200 gal/hr into a vented storage tank to maintain a level of water in a tank 165 ft above the ground. To prevent freezing in the winter a small heater puts 30,000 Btu/hr into the water during its transfer from the well to the storage tank. Heat is lost from the whole system at the constant rate of 25,000 Btu/hr. What is the temperature of the water as it enters the storage tank, assuming that the well water is at 35°F? A 2-hp pump is being used to pump the water. About 55% of the rated horsepower goes into the work of pumping and the rest is dissipated as heat to the atmosphere.

Solution

Steps 1, 2, and 3 Let the system consist of the well inlet, the piping, and the outlet at the storage tank. The process is a flow process since material continually enters and leaves the system. See Fig. E4.23.

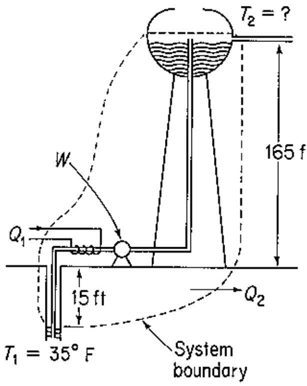


Figure E4.23

Steps 3a, 3b, and 7 The general energy balance is

$$\Delta E = -\Delta[(\hat{H} + \hat{K} + \hat{P})m] + Q - W$$

Step 4

Basis: 1 hr of operation

We will first simplify the energy balance:

(1) The process is in the steady state, so that $\Delta E = 0$.
(2) $m_1 = m_2$.
(3) $\Delta K \cong 0$ because we will assume that $v_1 = v_2 \cong 0$.

Then

$$0 = -\Delta[(\hat{H} + \hat{P})m] + Q - W$$

Steps 5 and 6 Only ΔH at the top of the tank is unknown, and can be calculated from the energy balance. The temperature can be retrieved from

$$\Delta H = m\,\Delta\hat{H} = m\int_{T_1=35^\circ\mathrm{F}}^{T_2} C_p\,dT = mC_p(T_2 - 35)$$

if C_p is an essential constant. Hence the problem has a unique solution.

Steps 7, 8, and 9 The total amount of water pumped is

$$\begin{array}{c|c} 200\text{ gal} & 8.33\text{ lb} \\ \hline \text{hr} & 1\text{ gal} \end{array} = 1666\text{ lb/hr}$$

The potential energy change is

$$\Delta P = m\Delta\hat{P} = mg\,\Delta h = \begin{array}{c|c|c|c} 1666\text{ lb}_m & 32.2\text{ ft} & 180\text{ ft} & \\ \hline & \text{s}^2 & & \dfrac{32.2\text{ (ft)(lb}_m)}{(\text{s}^2)(\text{lb}_f)} \end{array}$$

$$= 300{,}000\text{ (ft)(lb}_f)$$

or

$$\frac{300{,}000\text{ (ft)(lb}_f)}{778\text{ (ft)(lb}_f)/\text{Btu}} = 385.6\text{ Btu}$$

The heat lost by the system is 25,000 Btu while the heater puts 30,000 Btu into the system; hence the net heat exchange is

$$Q = 30{,}000 - 25{,}000 = 5000\text{ Btu}$$

The rate of work being done on the water by the pump is

$$W = -\begin{array}{c|c|c|c|c} 2\text{ hp} & 0.55 & 33{,}000\text{ (ft)(lb}_f) & 60\text{ min} & \text{Btu} \\ \hline & & (\text{min})(\text{hp}) & \text{hr} & 778\text{ (ft)(lb}_f) \end{array}$$

$$= -2800\text{ Btu/hr}$$

ΔH can be calculated from: $Q - W = \Delta H + \Delta P$:

$$5000 - (-2800) = \Delta H + 386$$

$$\Delta H = 7414\text{ Btu}$$

Because the temperature range considered is small, the heat capacity of liquid water may be assumed to be constant and equal to 1.0 Btu/(lb)(°F) for the problem. Thus

$$7414 = \Delta H = mC_p\,\Delta T = 1666(1.0)(\Delta T)$$

$\Delta T \simeq 4.5^\circ\text{F}$ temperature rise. Hence, $T = 39.5^\circ\text{F}$

EXAMPLE 4.24 Application of the Energy Balance

Steam (that is used to heat a biomass) enters the steam chest, which is segregated from the biomass, at 250°C saturated, and is completely condensed in the steam chest. The rate of the heat loss from the steam chest to the surroundings is 1.5 kJ/s. The reactants are placed in the vessel at 20°C and at the end of the heating the material is at 100°C. If the charge consists of 150 kg of material with an average heat capacity of C_p = 3.26 J/(g)(K), how many kilograms of steam are needed per kilogram of charge? The charge remains in the reaction vessel for 1 hr.

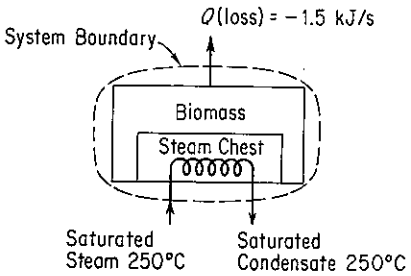


Figure E4.24a

Solution

Steps 1, 2, and 3 Figure E4.24a defines the system and lists the known conditions.
Steps 3a and 3b The energy balance is

$$\Delta E = -\Delta[(\hat{H} + \hat{K} + \hat{P})m] + Q - W \qquad \text{(a)}$$

Let us simplify the energy balance:

(1) The process is not in the steady state, so $\Delta E \neq 0$.
(2) We can assume that $\Delta K = 0$, and $\Delta P = 0$ in the system, and $W = 0$.
(3) The steam is the only material entering and leaving the system, and $m_1 = m_2$, and ΔK and ΔP of the entering and exit material are zero.

Consequently, Eq. (a) becomes

$$\Delta E = \Delta U = -\Delta[(\hat{H})m] + Q \qquad \text{(b)}$$

where ΔU refers only to the biomass and not the steam, and $\Delta H = \Delta(\hat{H}m)$ refers only to the steam and not the biomass.

Step 4

Basis: 1 hr of operation

Steps 5 and 6 We can calculate $\Delta H = m_{\text{steam}}\, \Delta\hat{H}_{\text{vaporization}}$ of the steam because we know Q, and can calculate for the biomass $\Delta U = \Delta H - \Delta(pV) = m_{\text{biomass}} C_{p,\,\text{biomass}}\, \Delta T$ [because we know that $\Delta(pV)$ for the liquid or solid charge will be negligible]. Thus we can calculate m_{steam} uniquely.

Steps 7, 8, and 9

(a) The heat loss is given as $Q = -1.50$ kJ/s or

$$\frac{-1.50\ \text{kJ}}{\text{s}}\left|\frac{3600\ \text{s}}{1\ \text{hr}}\right|\frac{1\ \text{hr}}{} = -5400\ \text{kJ}$$

(b) The specific enthalpy change for the steam can be determined from the steam tables. The $\Delta\hat{H}_{\text{vap}}$ of saturated steam at 250°C is 1701 kJ/kg, so that

$$\Delta\hat{H}_{\text{steam}} = -1701\ \text{kJ/kg}$$

(c) The enthalpy change of the biomass is

$$\Delta U = \Delta H_{\text{biomass}} = \frac{150\ \text{kg}}{}\left|\frac{3.26\ \text{kJ}}{(\text{kg})(\text{K})}\right|\frac{(373-293)\ \text{K}}{} = 39{,}120\ \text{kJ}$$

Introduction of all these values into Eq. (b) gives

$$39{,}120\text{ kJ} = -\left(-1701\frac{\text{kJ}}{\text{kg steam}}\right)(m_{\text{steam}}\text{ kg}) - 5400\text{ kJ} \qquad \text{(c)}$$

from which the kilograms of steam per hour, m_{steam}, can be calculated as

$$m_{\text{steam}} = \frac{44{,}520\text{ kJ}}{} \bigg| \frac{1\text{ kg steam}}{1701\text{ kJ}} = 26.17\text{ kg steam}$$

or

$$\frac{44{,}520\text{ kJ}}{} \bigg| \frac{1\text{ kg steam}}{1701\text{ kJ}} \bigg| \frac{1}{150\text{ kg charge}} = 0.17\frac{\text{kg steam}}{\text{kg charge}}$$

If the system had been chosen to be everything but the steam chest and lines, we would have a situation as shown in Fig. E4.24b. Under these circumstances heat would be transferred from the steam chest. From a balance on the steam chest (no accumulation),

$$Q_{\text{system II}} = \Delta H_{\text{steam}} \qquad \text{(d)}$$

As indicated in Fig. E4.24b, the value of $Q_{\text{system II}}$ is negative.

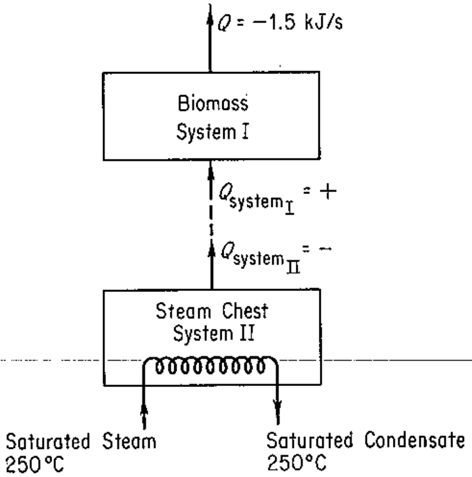


Figure E4.24b

The energy balance for system I with no mass flow in or out of system I is

$$\Delta E_{\text{system I}} = \Delta U_{\text{biomass}} = \Delta H_{\text{biomass}} = Q_{\text{I}} - 5400 \qquad \text{(e)}$$

Q_{II} and Q_{I} have opposite values because heat is removed from system II and added to system I. Because

$$Q_{\text{II}} = \Delta H_{\text{steam}} = (-1701)m$$

we know that $Q_{\text{I}} = +(1701)m$, and Eq. (e) becomes the same as Eq. (c).

Self-Assessment Test

1. In a refinery a condenser is to cool 1000 lb/hr of benzene that enters at 1 atm, 200°F, and leaves at 171°F. Assume negligible heat loss to the surroundings. How many pounds of

cooling water are required per hour if the cooling water enters at 80°F and leaves at 100°F?

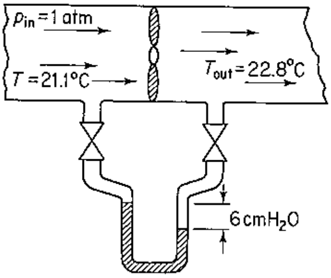
2. In a steady-state process, 10 g mol/s of O_2 at 100°C and 10 g mol/s of nitrogen at 150°C are mixed in a vessel which has a heat loss to the surroundings equal to $209(T - 25)$ J/s, where T is the temperature of the gas mixture in °C. Calculate the gas temperature of the exit stream in °C. Use the following heat capacity equations:

$$O_2: \quad C_p = 6.15 + 3.1 \times 10^{-3}T$$

$$N_2: \quad C_p = 6.5 + 1.25 \times 10^{-3}T$$

where T is in K and C_p is in cal/(g mol)(K).

3. An exhaust fan in a constant-area well-insulated duct delivers air at an exit velocity of 1.5 m/s at a pressure differential of 6 cm H_2O. Thermometers show the inlet and exit temperatures of the air to be 21.1°C and 22.8°C, respectively. The duct area is 0.60 m². Determine the actual power requirement for the fan.



4. A water system is fed from a very large tank, large enough so that the water level in the tank is essentially constant. A pump delivers 3000 gal/min in a 12-in.-ID pipe to users 40 ft below the tank level. The rate of work delivered to the water is 1.52 hp. If the exit velocity of the water is 1.5 ft/s and the water temperature in the reservoir is the same as in the exit water, estimate the heat loss per second from the pipeline by the water in transit.

Thought Problems

1. Do you save energy if you
   - **(a)** Let ice build up inside your freezer?
   - **(b)** Use extra laundry detergent?
   - **(c)** Light a fire in your conventional fireplace?
   - **(d)** Turn off your window air conditioner if you will be gone for a couple of hours?
   - **(e)** Turn off your furnace's pilot light during the spring and summer?
   - **(f)** Take baths rather than showers?
   - **(g)** Use long-life incandescent light bulbs?
   - **(h)** Use fluorescent rather than incandescent lights?
   - **(i)** Install your refrigerator beside your range?
   - **(j)** Drive 55 instead of 70 miles per hour?
   - **(k)** Choose a car with air conditioning, power steering, and an automatic transmission over one without these features?
2. Liquid was transferred by gravity from one tank to another tank of about the same height several hundred meters away. The second tank overflowed.

   What might cause such overflow?

4.6 REVERSIBLE PROCESSES AND THE MECHANICAL ENERGY BALANCE

Your objectives in studying this section are to be able to:

1. Define a quasi-static and a reversible process.
2. Identify a process as reversible or irreversible given a description of the process.
3. Define efficiency and apply the concept to calculate the work for an irreversible process.
4. Write down the steady-state mechanical energy balance for an open system and apply it to a problem.

In this section we examine some additional features of various types of energy changes with which you should become familiar.

4.6-1 Quasi-static and Reversible Processes

As explained in Sec. 3.3, a process at equilibrium will not undergo change—no work will be done and the system properties will not change. Suppose that a system at equilibrium is subjected to a differential external force (such as a higher temperature) so that a differential change occurs. The system will pass through nonequilibrium states, but with only very slight deviations from equilibrium if the driving force is infinitesimal. Such a process is said to be a **quasi-static process.** A quasi-static process is an idealization that can rarely be rigorously executed but can be approached with proper physical arrangements.

If there are no dissipative effects, that is, friction, viscosity, inelasticity, electrical resistance, and so on, during a quasi-static process, the process is termed **reversible.** Only an infinitesimal change is required to reverse the process, a concept that leads to the name "reversible." Most industrial processes exhibit heat transfer over finite temperature differences, mixing of dissimilar substances, sudden changes in phase, mass transport under finite concentration differences, free expansion, pipe friction, and other mechanical, chemical, and thermal nonidealities, and consequently are deemed **irreversible.** An irreversible process always involves a degradation of the potential of the process to do work, that is, will not produce the maximum amount of work that would be possible via a reversible process (if such a process could occur).

To illustrate the concept of reversibility, consider a gas confined in a cylinder by the piston shown in Fig. 4.15. During an expansion process the piston moves the distance x and the volume of gas confined in the piston increases from V_1 to V_2. Two forces act on the piston; one is the force exerted by the gas, equal to the pressure times the area of the piston, and the other is the force on the piston shaft and head

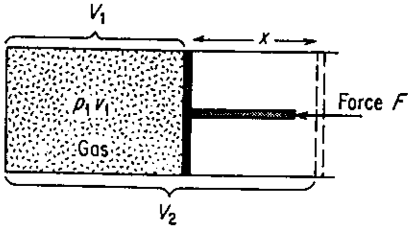


Figure 4.15 Gas expansion.

from outside. If the force exerted by the gas equals the force F, nothing happens. If F is greater than the force of the gas, the gas will be compressed, whereas if F is less than the force of the gas, the gas will expand.

In the latter case, the work done by the expanding gas and the piston will be $W = \int F\,dx$. The work of the gas would be $W = \int_{V_1}^{V_2} p\,dV$ if the process were reversible, that is, if the force F divided by the piston area were differentially less at all times than the pressure of the gas, and if the piston were frictionless; but in a real process some of the work done by the gas is dissipated by viscous effects, and the piston will not be frictionless, so that the work as measured by $\int F\,dx$ will be less than $\int p\,dV$. For these two integrals to be equal, none of the available energy of the system could be degraded to heat or internal energy. To achieve such a situation we have to ensure that the movement of the piston is frictionless and that the motion of the piston proceeds under only a differential imbalance of forces so that no shock or turbulence is present. Naturally, such a process would take a long time to complete.

EXAMPLE 4.25 Calculation of Work for a Batch Process

One kilogram mole of N_2 is in a horizontal cylinder at 1000 kPa and 20°C. A 6-cm^2 piston of 2-kg mass seals the cylinder and is fixed by a pin. The pin is released and the N_2 volume is doubled, at which time the piston is stopped again. What is the work done by the gas in this process?

Solution

Steps 1, 2, and 3 Draw a picture. See Fig. E4.25. From the ideal gas law we can compute the specific volume of the gas at the initial state

$$\hat{V}_1 = \frac{RT}{p} = \begin{array}{c|c} 8.31\ (\text{kPa})(\text{m}^3) & 293\ \text{K} \\ \hline (\text{K})(\text{kg mol}) & 1000\ \text{kPa} \end{array} = 2.43\ \text{m}^3/\text{kg mol}$$

Choose the gas to be the system.

Step 4 We can use as a basis 2.43 m^3 at 1000 kPa and 20°C.

Steps 5 and 6 We want to calculate the work done by the gas on the piston and the cylinder.

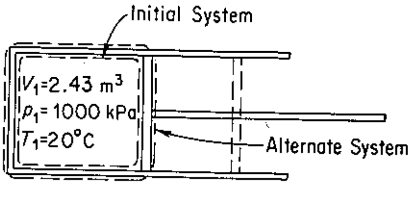


Figure E4.25

(a) Is the process a flow or a nonflow process? Since no material leaves or enters the cylinder, let us analyze the process as a nonflow system.

(b) This process is definitely irreversible because of friction between the piston and the walls of the cylinder, turbulence in the gas, the large pressure drops, and so on.

Consequently, we cannot calculate the work done on the piston by $\int p\,dV$.

Let us change our system to include the gas, the piston, and the cylinder. With this choice, the system expansion is still irreversible, but the pressure in the surroundings can be assumed to be atmospheric pressure and is constant. The work done in pushing back the atmosphere probably is done almost reversibly from the viewpoint of the surroundings and can be closely estimated by calculating the work done on the surroundings:

$$W = \int_{l_1}^{l_2} F\,dl = \int_{V_1}^{V_2} p\,dV = p\,\Delta V$$

ΔV of the gas is $2V_1 - V_1 = V_1 = 2.43\ \text{m}^3$, so that the volume change of surroundings is $-2.43\ \text{m}^3$. Then the work done on the surroundings is

Basis: 2.43 m³ at 101.3 kPa and 20°C (assumed)

$$W = \frac{101.3\ \text{kPa}}{} \left| \frac{-2.44\ \text{m}^3}{} \right| \frac{1(\text{N})(\text{m}^{-2})}{1\ \text{Pa}} \left| \frac{1\ \text{J}}{1\ (\text{N})(\text{m})} \right. = -247\ \text{kJ}$$

The minus sign indicates that work is done on the surroundings. From this we know that the work done by the alternative system is

$$W_{\text{system}} = -W_{\text{surroundings}} = -(-247) = 247\ \text{kJ}$$

This answer still does not answer the question of what work was done by the gas, because our system now includes both the piston and the cylinder as well as the gas. You may wonder what happens to the energy transferred from the gas to the piston itself. Some of it goes into work against the atmosphere, which we have just calculated; where does the rest of it go? Energy can go into raising the temperature of the piston or the cylinder or the gas. With time, part of it can be transferred to the surroundings to raise the temperature of the surroundings. From our macroscopic viewpoint we cannot say specifically what happens to this "lost" energy.

You should also note that if the surroundings were a vacuum instead of air, then *no work* would be done by the system, consisting of the piston plus the cylinder plus the gas, although the gas itself probably still would do some work on the piston.

EXAMPLE 4.26 Evaporation

How much work is done by 1 liter (1 dm³) of liquid water when it evaporates from an open vessel at 25°C?

Solution

Steps 1, 2, 3 and 4 Does the water do work in evaporating? Certainly! It does work against the atmosphere. Furthermore, the process, diagrammed in Fig. E4.26, is a reversible one because the evaporation takes place at constant temperature and pressure, and presumably the conditions in the atmosphere immediately above the open portion of the vessel are in equilibrium with the water surface. Assume that the atmospheric pressure is 100 kPa. The basis will be 1 L liquid water at 25°C.

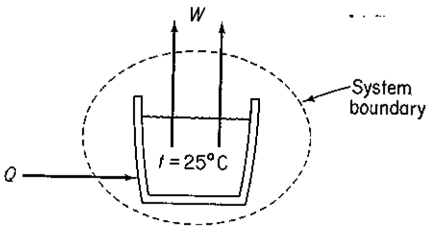


Figure E4.26

Steps 3a, 3b, 5, and 6 The general energy balance

$$\Delta E = -\Delta[(\hat{H} + \hat{K} + \hat{P})m] + Q - W$$

will not be useful in solving this problem because Q is unknown. However, imagine that an expansible bag is placed over the open face of the vessel so that the system now becomes a closed system. Because of the special conditions established for this problem, the work is

$$W = \int_{V_1}^{V_2} p\, dV = p\, \Delta V$$

Furthermore, the work is the reversible work done by the water in pushing back the atmosphere.

Steps 7, 8, and 9

$$W = \begin{array}{c|c|c|c|c} 100 \times 10^3\ \text{Pa} & 1\ \text{L} & 10^{-3}\ \text{m}^3 & 1(\text{N})(\text{m}^{-2}) & 1\ \text{J} \\ \hline & & 1\ \text{L} & 1\ \text{Pa} & 1(\text{N})(\text{m}) \end{array}$$

$$= 100\ \text{J}$$

Since practically all real processes are irreversible you may wonder why we bother paying attention to the theoretical reversible process. The reason is that it represents the best that can be done, the ideal case, and gives us a measure of our maximum accomplishment. In a real process we cannot do as well and so are less effective. A goal is provided by which to measure our effectiveness. And then, many processes are not too irreversible, so that there is not a big discrepancy between the practical and the ideal process.

Given the concept of an ideal (reversible process) and knowing the work in an actual process, two ways in which we can define mechanical efficiency are

$$\text{efficiency} = \eta_1 = \frac{\text{actual work output for the process}}{\text{work output for a reversible process}} \tag{4.29a}$$

and

$$\text{efficiency} = \eta_2 = \frac{\text{work input for a reversible process}}{\text{actual work input for the process}} \tag{4.29b}$$

depending on whether work is done by the system [Eq. (4.29a)] or work is being done on the system [Eq. (4.29b)].

Another type of efficiency is concerned just with the useful energy output divided by the total energy input:

$$\text{efficiency} = \eta_3 = \frac{\text{useful energy out}}{\text{energy in}} \tag{4.29c}$$

For example, assume that the conversion of fuel in a power plant yields 88 kJ in the steam product per 100 kJ of available energy from the coal being burned, the conversion of the energy in the steam to mechanical energy is 43% efficient, and the conversion of the mechanical to electrical energy is 97% efficient, all based on Eq. (4.29c). The overall efficiency is 1.00(0.88)(0.43)(0.97) = 0.37, meaning that two-thirds of the initial energy is dissipated as heat to the environment. These definitions provide a good way to compare process performance for energy conservation (but not the only way).

EXAMPLE 4.27 Use of Efficiency

Calculate the reversible work required to compress 5 ft³ of an ideal gas initially at 100°F from 1 to 10 atm in an adiabatic cylinder. Such a gas has an equation of state $pV^{1.40} = \text{constant}$. Then calculate the actual work required if the efficiency of the process is 80%.

Solution

Steps 1, 2, and 3 Figure 4.15 indicates the type of apparatus for the compression. Also,

$$V_2 = V_1\left(\frac{p_1}{p_2}\right)^{1/1.40} = 5\left(\frac{1}{10}\right)^{1/1.40} = 0.965\ \text{ft}^3$$

Step 4 The basis is 5 ft³ at 100°F and 1 atm.

Steps 5–9

$$W_{\text{rev}} = \int_{V_1=5}^{V_2=0.965} p\,dV = \int_{V_1}^{V_2} p_1\left(\frac{V_1}{V}\right)^{1.40} dV = p_1 V_1^{1.4}\int_{V_1}^{V_2} V^{-1.40}\,dV$$

$$= \frac{p_1 V_1^{1.40}}{1-1.40}\left(V_2^{-0.40} - V_1^{-0.40}\right) = \frac{p_2V_2 - p_1V_1}{1-1.40}$$

$$= \frac{[(10)(0.965) - (1)(5)](\text{ft}^3)(\text{atm})}{-0.40}\left|\frac{1.987\ \text{Btu}}{0.7302\ (\text{ft}^3)(\text{atm})}\right.$$

$$= -31.63\ \text{Btu}$$

The negative sign means that work is done on the system.

The actual work required is

$$\frac{31.63}{0.8} = 39.5\ \text{Btu}$$

So far we have looked at reversible work for closed systems. Next we examine reversible work in open systems.

4.6-2 Steady-State Mechanical Energy Balance

In some processes, such as distillation columns or reactors, heat transfer and enthalpy changes are *the* important energy components in the energy balance. Work, potential energy, and kinetic energy are zero or quite minor. However, in other processes, such as the compression of gases and pumping of liquids, work and the mechanical forms of energy are the important factors. For these processes, an energy balance treating solely the mechanical forms of energy becomes a useful tool.

The energy balance of Sec. 4.5 is concerned with various classes of energy without inquiring into how "useful" each form of energy is to human beings. Our experience with machines and thermal processes indicates that some types of energy cannot be transformed completely into other types, and that energy in one state cannot be transformed to another state without the addition of extra work or heat. For example, internal energy cannot be completely converted into mechanical work. To account for these limitations on energy utilization, the second law of thermodynamics was eventually developed as a general principle.

One of the consequences of the second law of thermodynamics is that two categories of energy of different "quality" can be envisioned:

(a) The so-called *mechanical* forms of energy, such as kinetic energy, potential energy, and work, which are *completely* convertible by an *ideal* (reversible) engine from one form to another within the class

(b) Other forms of energy, such as internal energy and heat, which are not so freely convertible

Of course, in any real process with friction, viscous effects, mixing of components, and other dissipative phenomena taking place which prevent the complete conversion of one form of mechanical energy to another, allowances will have to be made in making a balance on mechanical energy for these "losses" in quality.

A balance on mechanical energy can be written on a microscopic basis for an elemental volume by taking the scalar product of the local velocity and the equation of motion.[21] After integration over the entire volume of the system the ***steady-state mechanical energy balance*** **for a system with mass interchange with the surroundings** becomes, on a per unit mass basis,

$$\Delta(\hat{K} + \hat{P}) + \int_{p_1}^{p_2} \hat{V}\,dp + \hat{W} + \hat{E}_v = 0 \tag{4.30}$$

where $\hat{K}$ and $\hat{P}$ are associated with the mass in and out of the system, and E_v represents the loss of mechanical energy, that is, the irreversible conversion *by the flowing fluid* of mechanical energy to internal energy, a term which must in each individual process be evaluated by experiment (or, as occurs in practice, by use of already existing experimental results for a similar process). Equation (4.30) is sometimes called the **Bernoulli equation,** especially for the reversible process for which $\hat{E}_v = 0$. The mechanical energy balance is best applied in fluid-flow calculations when the kinetic and potential energy terms and the work are of importance, and the friction losses can be evaluated from handbooks with the aid of *friction factors* or *orifice coefficients.*

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[21] Slattery, *Momentum, Energy, and Mass Transfer* (see ref. 20)

EXAMPLE 4.28 Calculation of Reversible Work for a Flow Process

We will repeat the solution of the preceding example except that in this problem the process will be an open system.

Solution

Steps 1, 2, and 3 Figure E4.28 designates the system and data. The moles of gas are

$$\eta_1 = \frac{p_1 V_1}{RT_1} = \begin{array}{c|c|c|c} 1 \text{ atm} & 5 \text{ ft}^3 & & 1 \text{ (lb mol)(°R)} \\ \hline & & 560\text{°R} & 0.7302 \text{ (ft}^3\text{)(atm)} \end{array} = 0.0122 \text{ lb mol}$$

Figure E4.28

Step 4

Basis = 0.0122 lb mol

Steps 3a, 3b, and 7 The mechanical energy balance (per unit mass, or mole here)

$$\Delta(\hat{K} + \hat{P}) + \int_{p_1}^{p_2} \hat{V}\,dp + \hat{W} + \hat{E}_v = 0$$

can be simplified

$$\Delta\hat{K} = 0$$

$$\Delta\hat{P} = 0$$

$$\hat{E}_v = 0 \quad \text{(reversible)}$$

so that

$$\hat{W}_{\text{rev}} = -\int_{p_1}^{p_2} \hat{V}\,dp = -\int_{p_1}^{p_2} \hat{V}_1 \left(\frac{p_1}{p}\right)^{1/1.40} dp$$

$$= -\hat{V}_1 p_1^{0.714}[3.50(p_2^{0.286} - p_1^{0.286})]$$

$$W_{\text{rev}} = n_1 \hat{W}_{\text{rev}} = -n_1\left(\frac{V_1}{n_1}\right) p_1^{0.714}[3.50(p_2^{0.286} - p_1^{0.286})]$$

$$= -(5)(1)^{0.714}(3.50)[(10)^{0.286} - 1^{0.286}](\text{ft}^3)(\text{atm})\left(\frac{1.987 \text{ Btu}}{0.7302 \text{ (ft}^3\text{)(atm)}}\right)$$

$$= -44.3 \text{ Btu}$$

The actual work required to be done on the system is

$$\frac{44.3}{0.8} = 55.4 \text{ Btu}$$

EXAMPLE 4.29 Application of the Mechanical Energy Balance

Calculate the work per minute required to pump 1 lb of water per minute from 100 psia and 80°F to 1000 psia and 100°F. The exit stream is 10 ft above the entrance stream.

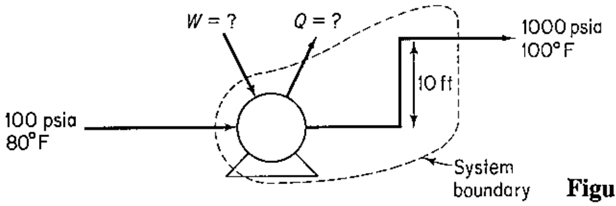


Figure E4.29

Solution

Steps 1, 2, and 3 The system is shown in Fig. E4.29.
Steps 3a, 3b, and 7 The general mechanical energy balance is

$$\Delta(\hat{K} + \hat{P}) + \int_{p_1}^{p_2} \hat{V}\, dp + \hat{W} + \hat{E}_v = 0 \qquad \text{(a)}$$

We will assume that $\Delta\hat{K}$ is insignificant, and also preliminarily assume that the process is reversible so that $E_v = 0$, and the pump is 100% efficient. (Subsequently, we will consider what to do if the process is not reversible.) Equation (a) reduces to

$$\hat{W} = -\int_{p_1}^{p_2} \hat{V}\, dp - \Delta\hat{P} \qquad \text{(b)}$$

Step 4

Basis: 1 min of operation = 1 lb H_2O

Steps 5 and 8 From the steam tables, the specific volume of liquid water is 0.01607 ft^3/lb_m at 80°F and 0.01613 ft^3/lb_m at 100°F. For all practical purposes the water is incompressible, and the specific volume can be taken to be 0.0161 ft^3/lb_m. We have only one unknown in Eq. (b): $\hat{W}$.

Step 9

$$\Delta\hat{P} = \begin{array}{c|c|c|c|c} 1\ \text{lb}_m & 10\ \text{ft} & 32.2\ \text{ft} & & 1\ \text{Btu} \\ \hline & & \text{sec}^2 & \dfrac{32.2(\text{ft})(\text{lb}_m)}{(\text{lb}_f)(\text{sec}^2)} & 778(\text{ft})(\text{lb}_f) \end{array} = 0.0129\ \text{Btu}$$

$$1\ \text{lb}_m \int_{100}^{1000} 0.0161\, dp = \begin{array}{c|c|c|c|c} 1\ \text{lb}_m & 0.0161\ \text{ft}^3 & (1000 - 100)\ \text{lb}_f & \left(\dfrac{12\ \text{in.}}{1\ \text{ft}}\right)^2 & 1\ \text{Btu} \\ \hline & \text{lb}_m & \text{in.}^2 & & 778(\text{ft})(\text{lb}_f) \end{array}$$

$$= 2.68\ \text{Btu}$$

$$\hat{W} = -2.68 - 0.0129 = -2.69 \frac{\text{Btu}}{\text{lb}_m}$$

About the same value can be calculated using Eq. (4.24) if $\hat{Q} = \hat{K} = 0$, because the enthalpy change for a reversible process for 1 lb of water going from 100 psia and 100°F to 1000 psia is 2.70 Btu. Make the computation yourself. However, usually the enthalpy data for liquids other than water are missing, or not of sufficient accuracy to be valid, which forces an engineer to turn to the mechanical energy balance.

We might now well inquire for the purpose of purchasing a pump-motor, say, as to what the work would be for a real process, instead of the fictitious reversible process assumed above. First, you would need to know the efficiency of the combined pump and motor so that the actual input from the surroundings (the electric connection) to the system would be known. Second, the friction losses in the pipe, valves, and fittings must be estimated so that the term $\hat{E}_v$ could be reintroduced into Eq. (4.30). Suppose, for the purposes of illustration, that $\hat{E}_v$ was estimated to be, from an appropriate handbook, 320 (ft)(lb$_f$)/lb$_m$ and the motor-pump efficiency was 60% (based on 100% efficiency for a reversible pump-motor). Then,

$$\hat{E}_v = \frac{320(\text{ft})(\text{lb}_f)}{1\ \text{lb}_m}\left|\frac{1\ \text{Btu}}{778\ (\text{ft})(\text{lb}_f)}\right. = 0.41\ \text{Btu/lb}_m$$

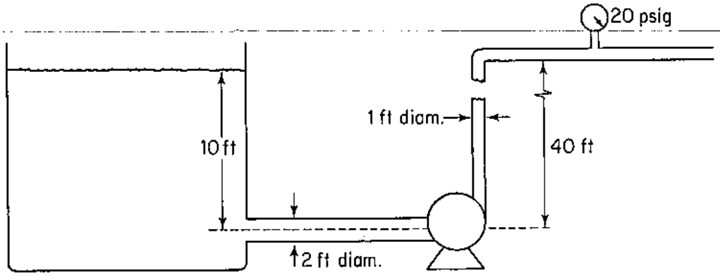
$$\hat{W} = -(2.68 + 0.013 + 0.41) = -3.10\ \text{Btu/lb}_m$$

Remember that the minus sign indicates that work is done on the system. The pump motor must have the capacity

$$\frac{3.10\ \text{Btu}}{1\ \text{min}}\left|\frac{1}{0.60}\right|\frac{1\ \text{min}}{60\ \text{sec}}\left|\frac{1.415\ \text{hp}}{1\ \text{Btu/sec}}\right. = 0.122\ \text{hp}$$

Self-Assessment Test

1. Which process will yield more work: (1) expansion of a gas confined by piston against constant pressure or (2) reversible expansion of a gas confined by a piston?
2. Differentiate between thermal and mechanical energy.
3. Define a reversible process.
4. Find Q, W, ΔE, and ΔH for the reversible compression of 3 moles of an ideal gas from a volume of 100 dm^3 to 2.4 dm^3 at a constant T of 300 K.
5. Water is pumped from a very large storage reservoir as shown in the figure at the rate of 2000 gal/min. Determine the minimum power (i.e., for a reversible process) required by the pump in horsepower.



Thought Problems

1. A news announcement in a professional journal described a 20-hp Stirling engine that was going to be connected to and drive a 68-kW generator. Would you buy one of these at $4500?
2. An author compared the effectiveness of gasoline-powered automobiles with electric-powered automobiles as in the following table, and concluded that electric-powered vehicles overall were more efficient. Is the comparison valid?

Efficiencies	Gasoline (bbl of oil)	Electric (bbl of oil)
KWh equivalent	1700	1700
Refinery efficiency	74% to gasoline	89% to heavy oil
Distribution efficiency	95%	
Power generation efficiency		40%
Power distribution efficiency		91%
Battery efficiency		70%
Motor, drive train efficiency	14.7%	80%
KWh available	175.7	308.8
Vehicle weight	2400 lb	2800 lb
Road load: 50 mph, level	8.4 kW	10 kW
Distance traveled	1045 miles	1545 miles

4.7 ENERGY BALANCES WITH CHEMICAL REACTION

So far we have not discussed how to treat energy balances in which chemical reactions occur. We do so in this section. For any given process, when a reaction takes place, the energy exchange with the surroundings will be different from the same process without a reaction. As you know, the observed heat transfer that occurs in a closed system (with zero work) as a result of a reaction represents the energy associated with the rearrangement of the bonds holding together the atoms of the reacting molecules. For an **exothermic reaction,** the energy required to hold the products of the reaction together is less than that required to hold the reactants together and the surplus energy is released. The reverse is true of an **endothermic reaction.** The energy change that appears directly as a result of a reaction is termed the *heat of reaction*, ΔH_{rxn}, a term that is a legacy of the days of the caloric theory. Note that "heat of reaction" is actually an *enthalpy change* and not heat transfer.

4.7-1 Standard Heat of Formation and Heat of Reaction

Your objectives in studying this section are to be able to:

1. Compute heats of formation from experimental data for the enthalpy change (including phase changes) of a process with a reaction taking place.
2. Look up heats of formation in reference tables for a given compound.
3. List the standard conventions and reference states used for reactions associated with the standard heat of formation.

4. Calculate the standard heat of reaction from tabulated standard heats of formation for a given reaction.

To take account of possible energy changes caused by a reaction, in the energy balance we incorporate in the enthalpy of each individual constituent an additional quantity termed the **standard heat** (really enthalpy) **of formation,**[22] $\Delta \hat{H}^\circ_f$, a quantity that is discussed in detail below. (The superscript ° denotes "standard state" and the subscript *f* denotes "formation.") Thus for the case of a single species *A* without any pressure effect on the enthalpy and omitting phase changes, the specific enthalpy change from the reference state is given by

$$\Delta \hat{H}_A = \Delta \hat{H}^\circ_{fA} + \int_{T_{\text{ref}}}^{T} C_{pA}\, dT \tag{4.31}$$

For several species, we would have in a stream

$$\Delta H_{\text{mixture}} = \sum_{i=1}^{s} n_i\, \Delta \hat{H}^\circ_{fi} + \sum_{i=1}^{s} \int_{T_{\text{ref}}}^{T} n_i C_{p_i}\, dT \tag{4.32}$$

where *i* designates each species, n_i is the number of moles of species *i*, and *s* is the total number of species. If phase changes take place, additional terms for the enthalpy of the phase changes have to be added to the right-hand side of Eq. (4.32) to give the **total enthalpy** of substance *A*:

$$\Delta \hat{H}_A = \Delta \hat{H}^\circ_{fA} + (\hat{H}_{T,p} - \hat{H}^\circ_{\text{ref}})$$

where $(\hat{H}_{T,p} - \hat{H}^\circ_{\text{ref}})$ includes both sensible heat and phase changes.

If a mixture enters and leaves a system without a reaction taking place, we would find that the same species entered and left so that the enthalpy change in Eq. (4.24a) would not be any different with the modification described above than what we have used before, because the terms that account for the heat of formation in the energy balance would cancel. For example, for the case of two species in a flow system, the output enthalpy would be

$$\Delta H_{\text{output}} = \underbrace{n_1\, \Delta \hat{H}^\circ_{f1} + n_2\, \Delta \hat{H}^\circ_{f2}}_{\text{"heat of formation"}} + \underbrace{\int_{T_{\text{ref}}}^{T_{\text{out}}} (n_1 C_{p1} + n_2 C_{p2})\, dT}_{\text{"sensible heat"}}$$

and the input enthalpy would be

$$\Delta H_{\text{input}} = \underbrace{n_1\, \Delta \hat{H}^\circ_{f1} + n_2\, \Delta \hat{H}^\circ_{f2}}_{\text{"heat of formation"}} + \underbrace{\int_{T_{\text{ref}}}^{T_{\text{in}}} (n_1 C_{p1} + n_2 C_{p2})\, dT}_{\text{"sensible heat"}}$$

Without reaction, observe that $\Delta H_{\text{output}} - \Delta H_{\text{input}}$ would only involve the sensible

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[22] Historically, the name arose because the changes in enthalpy associated with chemical reactions were generally determined in a device called a calorimeter, to which heat is added or removed from the reacting system so as to keep the temperature constant.

heat terms that we have described before; the heat-of-formation terms would be exactly the same in each enthalpy change and would cancel out.

However, if a reaction takes place, the quantities that enter and leave will differ, and the terms involving the heat of formation will not cancel. For example, suppose that species 1 and 2 enter the system, react, and species 3 and 4 leave. Then

$$\Delta H_{\text{out}} - \Delta H_{\text{in}} = (n_3\,\Delta\hat{H}^{\circ}_{f3} + n_4\,\Delta\hat{H}^{\circ}_{f4}) - (n_1\,\Delta\hat{H}^{\circ}_{f1} + n_2\,\Delta\hat{H}^{\circ}_{f2}) + \int_{T_{\text{ref}}}^{T_{\text{out}}} (n_3 C_{p3} + n_4 C_{p4})\,dT - \int_{T_{\text{ref}}}^{T_{\text{in}}} (n_1 C_{p1} + n_2 C_{p2})\,dT \tag{4.33}$$

You will be retrieving information on heats of formation from reference tables and data bases. The values in the tables have been reconciled from innumerable experiments. To determine the values of the standard heats (enthalpies) of formation, the experimenter usually selects either a simple flow process without kinetic energy, potential energy, or work effects (a flow calorimeter), or a simple batch process (a bomb calorimeter), in which to conduct the reaction. Consider an experiment in a flow process under standard state conditions in which the experimental arrangement is such that the summation of sensible heat terms on the right-hand side of Eq. (4.33) is zero and no work is done. The steady-state (no accumulation term) version of Eq. (4.24a) **for stoichiometric quantities of reactants and products** reduces to

$$Q = \Delta H$$

$$= \left(\sum_{\text{products}} n_i\,\Delta\hat{H}^{\circ}_{fi} - \sum_{\text{reactants}} n_i\,\Delta\hat{H}^{\circ}_{fi} \right) \equiv \Delta H^{\circ}_{\text{rxn}} \tag{4.34}$$

where $\Delta H^{\circ}_{\text{rxn}}$ is the symbol used for the **heat of reaction at the standard state.** Observe that the enthalpy change caused by the reaction in the prescribed type of experiment appears as heat transferred to or from the system, and the value of Q that is measured is the heat transferred from the reaction that occurs in the system and is equivalent to the standard heat of reaction at the standard state.

In general, a heat of reaction depends not only on the reaction stoichiometry but also on the number of moles that actually react, the temperature of the reaction, the phases of the products and reactants, and the pressure. The calculations that we shall make here will all be for low pressures, and, although the effect of pressure upon heats of reaction is relatively negligible under most conditions, if exceedingly high pressures are encountered, you should make the necessary corrections as explained in most texts on thermochemistry.

There are certain conventions and symbols which you should always keep in mind concerning thermochemical calculations if you are to avoid difficulty later on. These conventions can be summarized as follows:

(a) The reactants are shown on the left-hand side of the chemical equation, and the products are shown on the right: for example,

$$CH_4(g) + H_2O(l) \longrightarrow CO(g) + 3H_2(g)$$

(b) The conditions of phase, temperature, and pressure must be specified unless the last two are the standard conditions, as presumed in the equation above, when only the phase is required. This is particularly important for compounds such as H_2O, which can exist as more than one phase under common conditions. If the reaction takes place at other than standard conditions, you might write

$$CH_4(g,\ 1.5\ atm) + H_2O(l) \xrightarrow{50°C} CO(g,\ 3\ atm) + H_2(g,\ 3\ atm)$$

(c) Unless otherwise specified, all the constituents are at the standard state of 25°C (77°F) and 101.3 kPa (1 atm) total pressure. The heat of reaction under these conditions is called the ***standard heat of reaction,*** and is distinguished by the superscript ° symbol.

(d) Unless the amounts of material reacting are stated, it is assumed that the quantities reacting are the stoichiometric amounts shown in the chemical equation.

Data to compute the standard heat of reaction are reported and tabulated in two different but essentially equivalent forms:

(a) Standard heats of formation

(b) Standard heats of combustion

We first describe the standard heat of formation ($\Delta\hat{H}_f^\circ$) and then the standard heat of combustion ($\Delta\hat{H}_c^\circ$). The units of both quantities are usually tabulated as energy per mole, such as J/g mol, kJ/g mol, kcal/g mol, or Btu/lb mol. The "per mole" refers to the specified reference substance in the related stoichiometric equation.

The ***standard heat of formation*** is the special heat of reaction for the formation of 1 mole of a compound from its constituent elements, for example

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$$

in the standard state. The initial reactants and final products must be stable and at 25°C and 1 atm. The reaction does not necessarily represent a real reaction that would proceed at constant temperature but can be a fictitious process for the formation of a compound from the elements. By defining **the heat of formation as zero in the standard state for each *element,*** it is possible to design a system to express the heats of formation for all *compounds* at 25°C and 1 atm. If you use the conventions discussed above, then the thermochemical calculations will all be consistent, and you should not experience any confusion as to signs. Consequently, with the use of well-defined standard heats of formation, it is not necessary to record the experimental heats of reaction for every reaction that can take place. That would be an impossible task.

To sum up, a formation reaction is understood by convention to be a reaction that forms 1 mole of compound from the elements that make it up. Standard heats of reaction at 25°C and 1 atm for any reaction can be calculated from the tabulated (or experimental) standard heats of formation values by using Eq. (4.34), because the standard heat of formation is a state (point) function, as illustrated in the examples below.

EXAMPLE 4.30 Retrieval of Heats of Formation from Reference Data

What is the standard heat of formation of HCL(g)?

Solution

Look in Appendix F. The column heading is $-\Delta\hat{H}_f^\circ$.

$-\Delta\hat{H}_f^\circ$
92.311 kJ/g mol

which means that $\Delta\hat{H}_f^\circ = -92.312$ kJ/g mol.

In the reaction at 25°C and 1 atm,

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \longrightarrow HCl(g)$$

both $H_2(g)$ and $Cl_2(g)$ would be assigned $\Delta\hat{H}_f^\circ$ values of 0, and the value shown in Appendix F for HCl(g) of −92,312 J/g mol is the standard heat of formation for this compound as well as the standard heat of reaction for the reaction as written above:

$$\Delta H^\circ_{\text{rxn}} = \sum_{\text{products}} n_i\,\Delta\hat{H}^\circ_{fi} - \sum_{\text{reactants}} n_i\,\Delta\hat{H}^\circ_{fi}$$

$$= 1(-92.312) - [\tfrac{1}{2}(0) + \tfrac{1}{2}(0)] = -92.312 \text{ kJ/g mol HCl(g)}$$

The value tabulated in Appendix F might actually be determined by carrying out the reaction shown for HCl(g) and measuring the energy liberated in a calorimeter, or by some other more convenient method.

EXAMPLE 4.31 Determination of Heats of Formation from Experimental Data

Suppose that you want to find the standard heat of formation of CO from experimental data. Can you prepare pure CO from C and O_2 and measure the heat transfer? This would be far too difficult. It would be easier experimentally to find the heat of reaction for the two reactions shown below and subtract them as follows:

Basis: 1 g mol of CO

		$\Delta\hat{H}^\circ_{\text{rxn}}$(*experimental*)
A:	$C(\beta) + O_2(g) \longrightarrow CO_2(g)$	−393.51 kJ/g mol
B:	$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$	−282.99 kJ/g mol
A − *B*:	$C(\beta) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$	

$$\Delta\hat{H}^\circ_{\text{rxn}A-B} = (-393.51) - (-282.99) = \Delta\hat{H}_f^\circ = -110.52 \text{ kJ/g mol}$$

The energy change for the overall reaction scheme is the desired standard heat of formation per mole of CO(g). See Fig. E4.31.

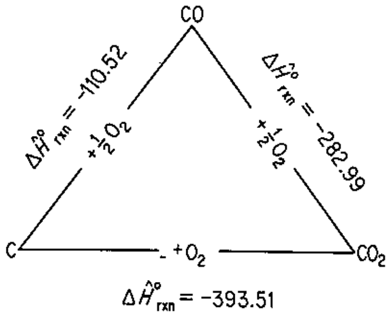

Figure E4.31

EXAMPLE 4.32 Calculation of the Heat of Reaction from Standard Heats of Formation

Calculate $\Delta\hat{H}^\circ_{\text{rxn}}$ for the following reaction of 4 g mol of NH_3:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

Solution

Basis: 4 g mol of NH_3

Tabulated data	*$NH_3(g)$*	*$O_2(g)$*	*$NO(g)$*	*$H_2O(g)$*
$\Delta\hat{H}^\circ_f$ per mole at 25°C and 1 atm (kcal/g mol)	−11.04	0	+21.60	−57.80

We shall use Eq. (4.34) to calculate $\Delta H^\circ_{\text{rxn}}$ for 4 g mol of NH_3:

$$\Delta H^\circ_{\text{rxn}} = [4(21.60) + 6(-57.80)] - [5(0) + 4(-11.04)]$$
$$= -216.24 \text{ kcal/4 g mol } NH_3.$$

EXAMPLE 4.33 Heat of Formation Including a Phase Change

If the standard heat of formation for $H_2O(l)$ is −285.838 kJ/g mol and the heat of evaporation is +44.012 kJ/g mol at 25°C and 1 atm, what is the standard heat of formation of $H_2O(g)$?

Solution

Basis: 1 g mol of H_2O

We shall proceed as in Example 4.31 to add the known chemical equations and the phase transitions to yield the desired chemical equation and carry out the same operations on the enthalpy changes. For reaction A, $\Delta\hat{H}^\circ_{\text{rxn}} = \Sigma\, \Delta\hat{H}^\circ_{f\,\text{products}} - \Sigma\, \hat{H}^\circ_{f\,\text{reactants}}$:

$$\begin{array}{llll}
A: & H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) & \Delta\hat{H}^\circ_{\text{rxn}} = -285.838 \text{ kJ/g mol} \\
B: & H_2O(l) \longrightarrow H_2O(g) & \Delta\hat{H}^\circ_{\text{vap}} = +44.012 \text{ kJ/g mol} \\
\hline
A + B: & H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) &
\end{array}$$

$$\Delta\hat{H}^\circ_{\text{rxn}\,A} + \Delta\hat{H}^\circ_{\text{vap}} = \Delta\hat{H}^\circ_{\text{rxn}\,H_2O(g)} = \Delta\hat{H}^\circ_{f\,H_2O(g)} = -241.826 \text{ kJ/g mol}$$

You can see that any number of chemical equations can be treated by algebraic methods, and the corresponding standard heats of reaction can be added or subtracted in the same fashion as are the equations. By carefully following these rules of procedure, you will avoid most of the common errors in thermochemical calculations.

To simplify matters, the value cited for $\Delta\hat{H}_{\text{vap}}$ of water in Example 4.33 was at 25°C and 1 atm. To calculate this value, if the final state for water is specified as $H_2O(g)$ at 25°C and 1 atm, the following enthalpy changes should be taken into account if you start with $H_2O(l)$ at 25°C and 1 atm:

$$\begin{array}{l} \Delta H_{\text{vap}} \text{ at } 25^\circ\text{C} \\ \text{and 1 atm} \end{array} \left\{ \begin{array}{l} H_2O(l)\ 25^\circ\text{C, 1 atm} \\ \quad \downarrow \ \Delta H_1 \\ H_2O(l)\ 25^\circ\text{C, vapor pressure at } 25^\circ\text{C} \\ \quad \downarrow \ \Delta H_2 = \Delta H_{\text{vap}} \text{ at the vapor pressure of water} \\ H_2O(g)\ 25^\circ\text{C, vapor pressure at } 25^\circ\text{C} \\ \quad \downarrow \ \Delta H_3 \\ H_2O(g)\ 25^\circ\text{C, 1 atm} \end{array} \right.$$

For practical purposes the value of ΔH_{vap} at 25°C and the vapor pressure of water, namely 43,911 J/g mol (10,495 cal/g mol), will be adequate for engineering calculations at one atmosphere.

There are many sources of tabulated values for the standard heats of formation listed in Table 4.5. A good source of extensive data is the *National Bureau of Standards Bulletin* 500, and its supplements by F. K. Rossini, or the serial publications of the Thermodynamics Research Center at Texas A & M University (API Research Project No. 44 and the TRC Data Project). A condensed set of values for the heats of formation may be found in Appendix F. If you cannot find a standard heat of formation for a particular compound in reference books or in the chemical literature, $\Delta\hat{H}_f^\circ$ may be estimated by the methods described in Verma and Doraiswamy[23] or by some of the authors listed as references in Table 4.5. Remember that the values for the standard heats of formation are negative for exothermic reactions.

Self-Assessment Test

1. Calculate the standard heat of formation of CH_4 given the following experimental results at 25°C and 1 atm:

$$\begin{array}{rcll} H_2(g) + \frac{1}{2}O_2(g) & \longrightarrow & H_2O(l) & \Delta H = -285.84 \text{ kJ/g mol } H_2 \\ \text{C(graphite)} + O_2(g) & \longrightarrow & CO_2(g) & \Delta H = -393.51 \text{ kJ/g mol C} \\ CH_4(g) + 2O_2(g) & \longrightarrow & CO_2(g) + 2H_2O(l) & \Delta H = -890.36 \text{ kJ/g mol } CH_4 \end{array}$$

   Compare your answer with that found in the table of heats of formation listed in Appendix F.

2. Calculate the standard heat of reaction for the following reaction from the heats of formation:

$$C_6H_6(g) \longrightarrow 3C_2H_2(g)$$

Thought Problems

1. Clipping from the *Wall Street Journal:*

Technical Disputes

Furnace efficiency is a comparison of the energy that goes into a furnace with the usable heat that comes out. Because oil furnaces use blowers to burn the fuel more efficiently and

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[23] K. K. Verma and L. K. Doraiswamy, *Ind. Eng. Chem. Fundam.*, v. 4, p. 389 (1965).

because oil produces less water vapor than gas, less heat is vented up the chimney, the Oil Jobbers Council says. The American Gas Association complains that such calculations ignore variations in oil quality that hurt efficiency. And it contends that oil furnaces are apt to "lose efficiency over time," while it says gas furnaces don't.

Which organization is correct, or is neither correct?

2. A review of additives to gasoline to give blends which improve its octane rating shows that oxygenated compounds necessarily contain lower energy (Btu per gallon). Methanol was the lowest, having a heat of reaction approximately one-half that of gasoline. Methanol costs 40 cents/gal, whereas unleaded premium gas costs 80 cents/gal, so that the result may seem like a standoff (i.e., half the energy at half the cost).

   Are the two fuels really equivalent in practical use?

4.7-2 Standard Heat of Combustion

Your objectives in studying this section are to be able to:

1. Look up heats of combustion in reference tables for a given compound.
2. List the standard conventions and reference states used for reactions associated with the standard heat of combustion.
3. Calculate the standard heat of reaction from tabulated standard heats of combustion for a given reaction.
4. Calculate the standard higher heating value from the lower heating value or the reverse.

Standard heats of combustion are the second method of recording thermochemical data. The standard heats of combustion do not have the same standard states as the standard heats of formation. The conventions used with the standard heats of combustion are

(a) The compound is oxidized with oxygen or some other substance to the products $CO_2(g)$, $H_2O(l)$, $HCl(aq)$,[24] and so on.

(b) The reference conditions are still 25°C and 1 atm.

(c) Zero values of $\Delta\hat{H}_c^\circ$ are assigned to certain of the oxidation products as, for example, $CO_2(g)$, $H_2O(l)$, and $HCl(aq)$, and to $O_2(g)$ itself.

(d) If other oxidizing substances are present, such as S or N_2, or if Cl_2 is present, it is necessary *to make sure that states of the products are carefully specified and are identical to (or can be transformed into) the final conditions which determine the standard state as shown in Appendix F.*

The standard heat of combustion of an unoxidized compound can never be

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[24] HCl(aq) represents an infinitely dilute solution of HCl (see Sec. 4.8).

positive but is always negative. A positive value would mean that the substance would not burn or oxidize. Standard heats of reaction can be calculated from standard heats of combustion by an equation analogous to Eq. (4.34):

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= -\left(\sum \Delta H^\circ_{c\,\text{products}} - \sum H^\circ_{c\,\text{reactants}}\right) \\ &= -\left(\sum_i n_{\text{prod}\,i}\,\Delta \hat{H}^\circ_{c\,\text{prod}\,i} - \sum_i n_{\text{react}\,i}\,\Delta \hat{H}^\circ_{c\,\text{react}\,i}\right)\end{aligned} \tag{4.35}$$

Note: The minus sign in front of the summation expression occurs because the choice of reference states is zero for the right-hand products of the standard reactions. Refer to Appendix F for values of $\Delta\hat{H}^\circ_c$.

For a fuel such as coal or oil, the negative of the standard heat of combustion is known as the **heating value** of the fuel. To determine the heating value, a weighed sample is burned in oxygen in a calorimeter bomb, and the energy given off is detected by measuring the temperature increase of the bomb and surrounding apparatus.

Because the water produced in the calorimeter is in the vicinity of room temperature, although the gas within the bomb is saturated with water vapor at this temperature, essentially all the water formed in the combustion process is condensed into liquid water. This is not like a combustion process in a furnace, where the water remains as a vapor and passes up the stack. Consequently, we have two heating values for fuels containing hydrogen: (1) the *gross,* or *higher, heating value,* in which all the water formed is condensed into the liquid state, and (2) the *net,* or *lower, heating value,* in which all the water formed remains in the vapor state. The value you determine in the calorimeter is the gross heating value; this is the one reported along with the fuel analysis and should be presumed unless the data state specifically that the net heating value is being reported.

You can estimate the heating value of a coal within about 3% from the Dulong formula[25]:

Higher heating value (HHV) in British thermal units per pound

$$= 14{,}544\text{C} + 62{,}028\left(\text{H} - \frac{\text{O}}{8}\right) + 4050\text{S}$$

where C = weight fraction carbon

$\text{H} - \frac{\text{O}}{8}$ = weight fraction net hydrogen

= total weight fraction hydrogen $-\frac{1}{8}$ weight fraction oxygen

S = weight fraction net sulfur

The values of C, H, S, and O can be taken from the fuel or flue-gas analysis. If the heating value of a fuel is known and the C and S are known, the approximate value of the net H can be determined from the Dulong formula. A general relation between the gross heating and net heating values is

$$\text{net Btu/lb coal} = \text{gross Btu/lb coal} - 91\ (\%\ \text{total H by weight})$$

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[25] H. H. Lowry, ed., *Chemistry of Coal Utilization,* Wiley, New York, 1945, Chap. 4.

Urban refuse or municipal solid waste is produced at a rate of about 11 kg (5 lb) per person per day, and contains both organic as well as nonorganic materials. Combustion of organic waste represents a supplemental source of supply of energy. Table 4.9 lists the HHV for typical wastes. If you "watch calories," Table 4.10 shows the calories in various foods. Table 4.11 indicates some heating values of typical coals.

TABLE 4.9 Higher Heating Value of Municipal Refuse (kJ/kg)

Refuse component	As delivered	Dry basis	Refuse component	As delivered	Dry basis
Lawn grass	4,780	19,320	Average	—	20,050
Meat scraps, cooked	32,260	32,260	Mail	14,150	14,820
Newspaper	18,530	19,710	Cardboard	16,370	17,260
Shrub cuttings	6,290	20,300	Ripe tree leaves	18,550	20,610
Vegetable food waste	4,170	19,220	Magazine	12,210	12,730

TABLE 4.10 Calorie Counts in Various Foods

Food	Portion	Kilocalories	Food	Portion	Kilocalories
Beer	12 oz	165	Orange juice	$\frac{1}{2}$ glass	56
Chicken, broiled	$\frac{1}{2}$	308	Soft drink	1 can	73
Coffee	1 cup	0	Toast	2 pieces	120
Martini	1 oz	168	Trout	1 lb	224

TABLE 4.11 Higher Heating Values of Typical Coals

Class	kJ/kg	Btu/lb
Meta-anthracite	26,680	11,480
Anthracite	33,110	14,250
Low-volatile bituminous	35,370	15,220
High-volatile bituminous	27,790	11,960
Subituminous	23,330	10,040
Lignite	17,290	7,440

EXAMPLE 4.34 Heating Value of Coal

Coal gasification consists of the chemical transformation of solid coal into gas. The heating values of coal differ, but the higher the heating value, the higher the value of the gas produced (which is essentially methane, carbon monoxide, hydrogen, etc.). The following coal has a reported heating value of 29,770 kJ/kg as received. Assuming that this is the gross heating value, calculate the net heating value.

Component	Percent
C	71.0
H_2	5.6
N_2	1.6
Net S	2.7
Ash	6.1
O_2	13.0
Total	100.0

Solution

The corrected ultimate analysis shows 5.6% hydrogen on the as-received basis.

Basis: 100 kg of coal as received

The water formed on combustion is

$$\begin{array}{c|c|c|c} 5.6\ \text{kg}\ H_2 & 1\ \text{kg mol}\ H_2 & 1\ \text{kg mol}\ H_2O & 18\ \text{kg}\ H_2O \\ \hline & 2.02\ \text{kg}\ H_2 & 1\ \text{kg mol}\ H_2 & 1\ \text{kg mol}\ H_2O \end{array} = 49.9\ \text{kg}\ H_2O$$

The energy required to evaporate the water is

$$\begin{array}{c|c} 49.9\ \text{kg}\ H_2O & 2370\ \text{kJ} \\ \hline 100\ \text{kg coal} & \text{kg}\ H_2O \end{array} = \frac{1183\ \text{kJ}}{\text{kg coal}}$$

The net heating value is

$$29{,}770 - 1183 = 28{,}587\ \text{kJ/kg}$$

The value 2370 kJ/kg is not the latent heat of vaporization of water at 25°C (2440 kJ/kg) but includes the effect of a change from a heating value at constant volume to one at constant pressure (−70 kJ/kg) as described in a later section of this chapter.

Use the Dulong formulate to calculate the HHV of this coal. Do you get 30,000 kJ/kg?

EXAMPLE 4.35 Calculation of Heat of Reaction from Heat of Combustion Data

Compute the heat of reaction of the following reaction from standard heat of combustion data:

$$\underset{\textbf{ethyl alcohol}}{C_2H_5OH(l)} + \underset{\textbf{acetic acid}}{CH_3COOH(l)} \longrightarrow \underset{\textbf{ethyl acetate}}{C_2H_5OOCCH_3(l)} + H_2O(l)$$

Solution

Basis: 1 g mol of C_2H_5OH

tabulated data	*C_2H_5OH (l)*	*CH_3COOH (l)*	*$C_2H_5OOCCH_3$(l)*	*H_2O (l)*
$\Delta\hat{H}_c^\circ$ per g mol at 25°C and 1 atm (kJ/g mol)	−1366.91	−871.69	−2274.48	0

We use Eq. (4.35):

$$\Delta H^{\circ}_{\text{rxn}} = -[(-2274.48) - (-1366.91 - 871.69)] = +35.9 \text{ kJ/g mol}$$

One of the common errors made in these thermochemical calculations is to forget that the standard state for heat of combustion calculations is liquid water, and that if gaseous water is present, a phase change (the heat of vaporization or heat of condensation) must be included in the calculations. Don't you forget!

With adequate data available you will find it simpler to use only the heats of combustion or only the heats of formation in the same algebraic calculation for a heat of reaction. Mixing these two sources of enthalpy change data, unless you take care, will only lead to error and confusion. Since the heat of combustion values are so large, calculations made by subtracting these large values from each other can be a source of error. To avoid other major errors, carefully check all signs and make sure all equations are not only balanced but are written according to the proper conventions.

Self-Assessment Test

1. Calculate the standard heat of reaction for the Sachse process (in which acetylene is made by partial combustion of LPG) from heat of combustion data:

$$C_3H_8(l) + 2O_2(g) \longrightarrow C_2H_2(g) + CO(g) + 3H_2O(l)$$

2. Can a standard heat of combustion ever be positive?
3. A synthetic gas analyzes 6.1% CO_2, 0.8% C_2H_4, 0.1% O_2, 26.4% CO, 30.2% H_2, 3.8% CH_4, and 32.6% N_2. What is the heating value of the gas measured at 60°F, saturated, when the barometer reads 30.0 in. Hg?

Thought Problem

1. The boiler efficiency and some data for a boiler are outlined in Problem 4.140. Degradation of performance and economic loss result from poor boiler performance. What are some of the steps you might take to improve boiler performance?

4.7-3 Heat of Reaction at Constant Pressure versus Constant Volume

Your objectives in studying this section are to be able to:

1. Calculate the heat transfer, Q, from a bomb calorimeter (constant volume) or a steady flow calorimeter (constant pressure), Q_p, from theory or experimental data.
2. Calculate the heat of reaction for either process.

Consider the heat of reaction of a substance obtained in a bomb calorimeter, such as in a bomb in which the volume is constant but not the pressure. For such a process (the system is the material in the bomb), the general energy balance, Eq. (4.2-4a), reduces to (with no work, mass flow, nor kinetic or potential energy effects)

$$\Delta U = U_{t_2} - U_{t_1} = Q_v \tag{4.36}$$

Here Q_v designates the heat transferred from the bomb. Next, let us assume that the heat of reaction is determined in steady-state flow calorimeter with 1 = entering fluid and 2 = exiting fluid, and with $W = 0$, $\Delta P = 0$, and $\Delta K = 0$. Then if the process takes place at constant pressure the general energy balance reduces to

$$\Delta H = Q_p$$

Here Q_p designates the heat transferred from the flow calorimeter.

If we subtract Q_v from Q_p and use $H = U + pV$, we find that

$$\begin{aligned} Q_p - Q_v &= \Delta H - \Delta U = \Delta H - [\Delta(H - pV)] \\ &= (H_2 - H_1) - [(H - pV)_{t_{12}} - (H - pV)_{t_1}] \end{aligned} \tag{4.37}$$

Suppose, furthermore, that the enthalpy change for the batch, constant-volume process is made identical to the enthalpy difference between the outlet and inlet in the flow process by a suitable adjustment of the temperature of the water baths surrounding the calorimeters. Then

$$H_{t_2} - H_{t_1} = H_2 - H_1$$

and

$$Q_p - Q_v = (pV)_{t_2} - (pV)_{t_1} \tag{4.38}$$

To evaluate the terms on the right-hand side of Eq. (4.38), we can assume for solids and liquids that the $\Delta(pV)$ change is negligible and can be ignored. Therefore, the only change which must be taken into account is for gases present as products and/or reactants. If, for simplicity, the gases are assumed to be ideal, then at constant temperature

$$pV = nRT$$

$$\Delta(pV) = \Delta n\, RT$$

and

$$Q_p - Q_v = \Delta n\,(RT) \tag{4.39}$$

Equation (4.39) gives the difference between the heat of reaction for the constant-pressure experiment and the constant-volume experiment.

EXAMPLE 4.36 Difference between Heat of Reaction at Constant Pressure and at Constant Volume

Find the difference between the heat of reaction at constant pressure and at constant volume for the following reaction at 25°C (assuming that it could take place):

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$$

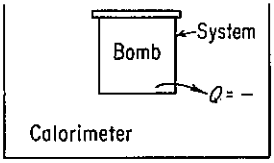


Figure E4.36

Solution

Basis: 1 mole of C(s)

Examine Fig. E4.36. The system is the bomb; $Q = +$ when heat is absorbed by the bomb. From Eq. (4.39), $Q_p - Q_v = \Delta n(RT)$.

$$\Delta n = 1 - \tfrac{1}{2} = +\tfrac{1}{2}$$

since C is a solid.

$$Q_p - Q_v = \tfrac{1}{2}RT = 0.5[8.314\ \text{J/(g mol)(K)}](298\ \text{K}) = 1239\ \text{J/g mol}$$

If the measured heat evolved from the bomb was 111,759 J,

$$Q_p = Q_v + 1239 = -111{,}759 + 1239 = -110{,}520\ \text{J}$$

The size of this correction is relatively insignificant compared to either the quantity Q_p or Q_v. In any case, the heat of reaction calculated from the bomb experiment is

$$\Delta\hat{H}_{\text{rxn}_v} = \frac{Q_v}{n} = \frac{-111{,}759\ \text{J}}{\text{g mol C(s)}}$$

Since reported heats of reaction are normally for constant-pressure processes, the value of −111,759 would not be reported, but instead you would report that

$$\Delta\hat{H}_{\text{rxn}_p} = \frac{Q_p}{n} = \frac{-110{,}521\ \text{J}}{\text{g mol C(s)}}$$

Self-Assessment Test

1. Is Q_p always bigger than Q_v? Explain.
2. The Claude ammonia synthesis gas reaction

$$CO(g) + 3H_2(g) \longrightarrow CH_4(g) + H_2O(l)$$

is carried out in a constant-volume bomb reactor. The molar ratio of H_2 to CO in the bomb at the start is 3 : 1. The reaction is complete. The initial and final temperature is 25°C. The initial pressure is 4 atm. The volume of the bomb is 1.50 L.
(a) Calculate the final pressure in the bomb reactor.
(b) Calculate the heat transfer to or from the reactor—state which.

Thought Problem

1. Does the vaporization of a given amount of liquid water at a given temperature require the same amount of heat transfer if the process is carried out in a closed system versus an open system?

4.7-4 Incomplete Reactions

Your objectives in studying this section are to be able to:

1. Calculate the heat of reaction at standard conditions for processes in which the reactants are not fed in stoichiometric quantities and the reaction may not go to completion.
2. Solve simple problems combining both material and energy balances.

If an **incomplete reaction occurs,** you should **calculate the standard heat of reaction only for the products which are actually formed from the reactants that actually react.** In other words, only the portion of the reactants that actually undergo some change and liberate or absorb some energy are to be considered in calculating the overall standard heat of the reaction. If some material passes through the reactor unchanged, it can contribute nothing to the *standard heat of reaction* calculations (however, when the reactants or products are at conditions *other* than 25°C and 1 atm, whether they react or not, you must include them in the enthalpy calculations as explained in Sec. 4.7-5). If several reactions occur simultaneously, your material balance must reflect what enters the reactor and is produced via the *independent* reactions.

EXAMPLE 4.37 Incomplete Reactions

An iron pyrite ore containing 85.0% FeS_2 and 15.0% gangue (inert dirt, rock, etc.) is roasted with an amount of air equal to 200% excess air according to the reaction

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

in order to produce SO_2. All the gangue plus the Fe_2O_3 end up in the solid waste product (cinder), which analyzes 4.0% FeS_2. Determine the standard heat of reaction per kilogram of ore.

Solution

The material balance for the problem must be worked out prior to determining the standard heat of reaction.

Steps 1, 2, and 3 The process is a steady-state open system (see Fig. E4.37). You calculate the excess air based on the stated reaction as if all the FeS_2 reacted to Fe_2O_3 even though some FeS_2 does not react. Six unknowns exist (including the N_2 in P) and five elemental balances can be written; the mass fraction of FeS_2 is given, hence the material balance problem has a unique solution. The molecular weights are Fe(55.85), Fe_2O_3(159.70), and FeS_2(120.0).

Step 4

Basis: 100 kg of pyrite ore

Steps 5 and 6 Rather than use the stoichiometry to determine generation and consumption of compounds, we will use five elemental balances, O_2, N_2, S, gangue, and Fe, plus

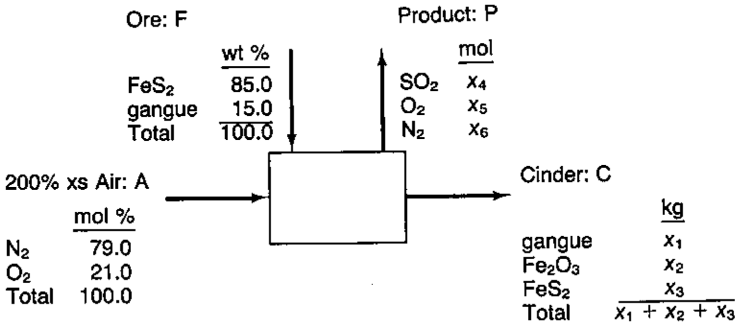


Figure E4.37

the information about the FeS_2 to calculate the moles of SO_2, O_2, and N_2 in the gaseous product, and the kg of gangue, Fe_2O_3, and FeS_2 in the cinder.

Step 3 (Continued) The excess air is

$$\text{Mol FeS}_2 = \frac{85.0}{120.0} = 0.7083 \text{ kg mol}$$

$$\begin{aligned}
\text{Required O}_2 &= 0.7083(11/4) = 1.9479 \text{ kg mol}\\
\text{Excess O}_2 &= 1.9479(2.00) = \underline{3.8958}\\
\text{Total O}_2 \text{ in} &= \qquad\qquad\qquad\; 5.8437 \text{ kg mol}\\
\text{Total N}_2 \text{ in} &= 5.8437(79/21) = 21.983 \text{ kg mol}
\end{aligned}$$

The element mass balances are

	In	*Out*
Gangue (kg):	15.0	$= x_1$
N_2 (kg mol):	21.983	$= x_6$
S (kg mol):	$2(85.0/120.0)$	$= x_4 + (x_3/120.0)(2)$
Fe (kg mol):	$1(85.0/120.0)$	$= (x_2/159.70)2 + (x_3/120.0)(1)$
O_2 (kg mol):	5.8437	$= x_4 + x_5 + (x_2/159.70)(1.5)$

Also,

$$\frac{x_3}{x_1 + x_2 + x_3} = 0.04$$

The solution of these equations is

In P	*In C*
$SO_2 = 1.368$ kg mol	Gangue = 15.0 kg
$O_2 = 3.938$	$Fe_2O_3 = 54.63 \Leftrightarrow 0.342$ kg mol
$N_2 = 21.983$	$FeS_2 = 2.90 \Leftrightarrow 0.0242$ kg mol

Next we calculate the standard heat of reaction. The moles of FeS_2 that react are $0.7083-0.0242 = 0.684$ kg mol. Oxygen and nitrogen have zero values for $\Delta\hat{H}_f^\circ$ and the gangue does not react. We will use the following tabulated heats of formation (in kJ/g mol) to calculate $\Delta H^\circ_{\text{rxn}}$:

Component:	FeS_2(c)	O_2(g)	Fe_2O_3(c)	SO_2(g)
$\Delta\hat{H}_f^\circ$	−177.9	0	−822.156	−296.90

Two equivalent ways exist to calculate the heat of reaction:

1. Use the material balance data directly.
2. Use the stoichiometric equation multiplied by (0.684/4).

$$\Delta H^\circ_{\text{rxn}} = \overset{Fe_2O_3}{\overline{342(-822.156)}} + \overset{FeS_2}{\overline{24.2(-177.9)}} + \overset{SO_2}{\overline{1{,}368(-296.90)}}$$

$$- \overset{FeS_2}{\overline{708.3(-177.90)}} = -5.656 \times 10^5 \text{ kJ}$$

or

$$\Delta H^\circ_{\text{rxn}} = \left[\left(\frac{2}{4}\right)(684)(-822.156) + \left(\frac{8}{4}\right)(684)(-296.90)\right]$$

$$- \left[(684)(-177.9) + \left(\frac{11}{4}\right)(684)(0)\right] = -5.657 \times 10^5 \text{ kJ}$$

Per kg of ore,

$$\Delta\hat{H}_{\text{rxn}} = -5.657 \times 10^5 \text{ kJ}/100 \text{ kg} = -5.657 \times 10^3 \text{ kJ/kg}$$

Note that only the moles reacting and produced are involved in computing the heat of reaction. The unoxidized FeS_2 is not included, nor is the N_2.

Self-Assessment Test

1. A dry low-Btu gas with the analysis of CO: 20%, H_2: 20% and N_2: 60% is burned with 200% excess dry air which enters at 25°C. If the exit gases leave at 25°C, calculate the standard heat of reaction per unit volume of entering gas measured at standard conditions (25°C and 1 atm).

Thought Problem

1. Thermal destruction systems have become recognized over the past decade as an increasingly desirable alternative to the more traditional methods of disposing of hazardous wastes in landfills and injection wells. What are some of the problems in the combustion of substances such as methylene chloride, chloroform, trichloroethylene, waste oil, phenol, aniline, and hexachloroethane?

4.7-5 Energy Balance When the Products and Reactants Are Not at 25°C

Your objectives in studying this section are to be able to:

1. Calculate heats of reaction at other than the standard temperature.
2. Calculate how much material must be introduced into a system to provide a prespecified quantity of heat transfer for the system.
3. Apply the general energy balance to processes involving reactions.
4. Determine the temperature of an incoming stream of material given the exit stream temperature (when a reaction occurs).

You no doubt realize that the standard state of 25°C for the heats of formation is only by accident the temperature at which the products enter and the reactants leave a process. In most instances the temperatures of the materials entering and leaving will be higher or lower than 25°C. However, since enthalpies (and hence heats of reaction) are point functions, you can use Eq. (4.24a) together with Eq. (4.33), (4.34), or (4.35), to answer questions about the process being analyzed. Typical questions might be:

(a) What is the heat of reaction at a temperature other than 25°C, but still at 1 atm?
(b) What is the temperature of an incoming or exit stream?
(c) What is the temperature of the reaction?
(d) How much material must be introduced to provide a specified amount of heat transfer for the system?

Consider the process illustrated in Fig. 4.16, for which the reaction is

$$\text{aA} + \text{bB} \longrightarrow \text{cC} + \text{dD}$$

Nonstoichiometric amounts of reactants and products, respectively, enter and leave the system.

In employing Eq. (4.24a) you should always **first choose a reference state** at which the heats of formation are known. This usually turns out to be 25°C and 1 atm. (If no reaction takes place, the reference state can be an inlet or outlet stream temperature.) Then the next step is to calculate the enthalpy changes for each stream

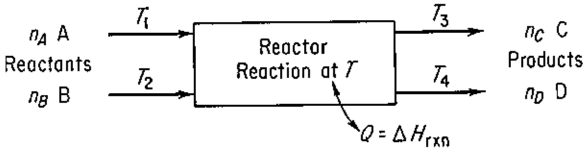


Figure 4.16 Process with reaction.

entering and leaving *relative to this reference state*. Usually, it proves convenient in calculating the enthalpy change to compute the sensible heat changes, the phase changes, and the heat of reaction separately, but this arrangement is not essential. **Any phase changes taking place among the reactants or products not accounted for in the heats of formation must be taken into account in applying the general energy balance.**

Because enthalpy is a state function, you can choose any path you want to execute the calculations for the overall enthalpy change in a process as long as you start and finish at the specified initial and final states, respectively. Figure 4.17 illustrates the idea. For example, suppose that the reference state is chosen to be 25°C and 1 atm, the state for which the $\Delta \hat{H}_f^\circ$'s are known. Figure 4.17 indicates that the path for the calculation for the reactants is from T_A (for A) and T_B (for B) to 25°C; next, the heats of formation are used to get ΔH_{rxn} at 25°C and 1 atm employing A, B, C, and D; and finally, the path for the products goes from 25°C to T_C and T_D. In Fig. 4.17, $T_C = T_D$. Pressure effects can be included along with temperature effects on the enthalpy, but we will omit consideration of the effect of pressure except for problems in which the enthalpy data are retrieved from tables (such as the steam tables) or data bases.

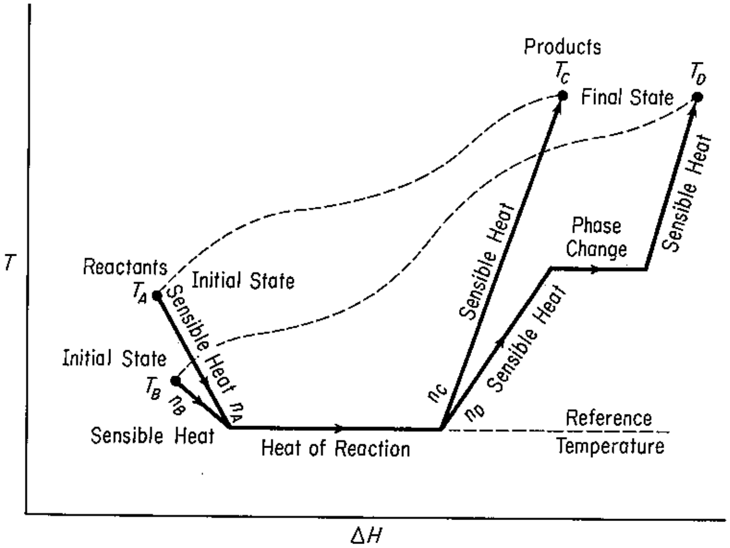


Figure 4.17 Calculation of enthalpy changes for a process in which a reaction takes place. The solid lines indicate an arbitrary selection of path whereas the dashed lines figuratively indicate the actual path taken by the materials—the actual path may not be known in practice.

We have discussed in earlier sections of this chapter methods that you can use to determine the sensible heat ΔH values for the individual streams:

(a) Obtain the enthalpy values from a set of published tables (e.g., the steam tables or tables such as in Appendix D).

(b) Analytically, graphically, or numerically, find

$$\Delta H = \int_{T_1}^{T_2} C_p \, dT$$

for each component individually, using the respective heat capacity equations.

(c) Retrieve values from a data base.

Let us first demonstrate how to calculate the **heat of reaction at a temperature other than 25°C.** By this we mean that stoichiometric quantities of the reactants enter and the products leave at the same temperature—a temperature different from the standard state of 25°C in stoichiometric quantities. Figure 4.18 illustrates the information flow for the calculations corresponding to those associated with Eq. (4.33) assuming a steady-state process ($\Delta E = 0$), no kinetic or potential energy changes, and $W = 0$. The general energy balance [Eq. (4.24)] reduces to

$$Q = \Delta H = [\Delta H_f^\circ + \Delta(H - H^\circ)]_{\text{products}} - [\Delta H_f^\circ + \Delta(H - H^\circ)]_{\text{reactant}}$$

or

$$Q = \overbrace{(\Delta H_{\text{P}} - \Delta H_{\text{R}})}^{\text{sensible}} + (\Delta H_{\text{rxn}_{T_{\text{ref}}}}) \tag{4.40}$$

in terms of the notation in Fig. 4.18. By definition, Q, as calculated by Eq. (4.40), is equal to the "heat of reaction at the temperature T," so that

$$\Delta H_{\text{rxn}_T} = \Delta H_{\text{rxn}_{T_{\text{ref}}}} + \Delta H_{\text{P}} - \Delta H_{\text{R}} \tag{4.41}$$

To indicate a simplified way to calculate $\Delta H_{\text{P}} - \Delta H_{\text{R}}$, particularly using a computer code, suppose that the heat capacity equations are expressed as

$$C_p = \alpha + \beta T + \gamma T^2 \tag{4.42}$$

Then, to obtain $\Delta H_{\text{P}} - \Delta H_{\text{R}}$, we add up the sensible heat enthalpy changes for the

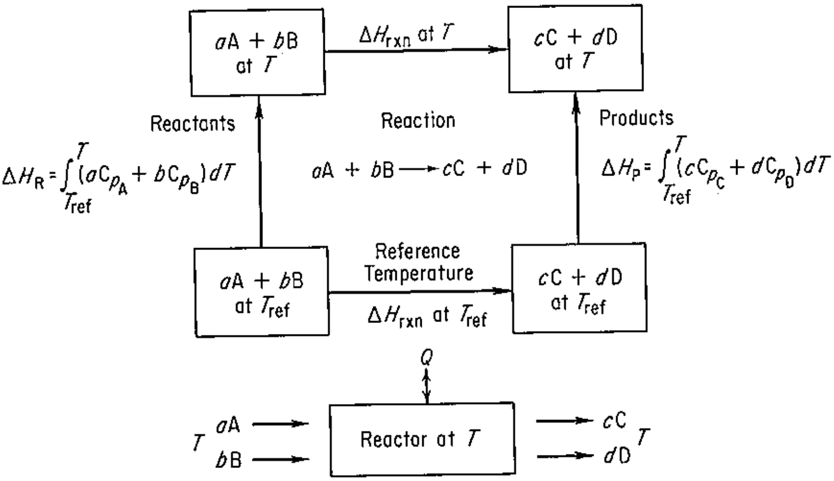


Figure 4.18 Heat of reaction at a temperature other than standard conditions.

products and subtract those for the reactants. Rather than integrate separately, let us consolidate like terms as follows. Each heat capacity equation is multiplied by the proper number of moles:

$$aC_{p_A} = a(\alpha_A + \beta_A T + \gamma_A T^2) \tag{4.43a}$$

$$bC_{p_B} = b(\alpha_B + \beta_B T + \gamma_B T^2) \tag{4.43b}$$

$$cC_{p_C} = c(\alpha_C + \beta_c T + \gamma_c T^2) \tag{4.43c}$$

$$dC_{p_D} = d(\alpha_D + \beta_D T + \gamma_D T^2) \tag{4.43d}$$

Then we define a new term ΔC_p which is equal to

$$\underset{\text{original expression}}{cC_{p_C} + dC_{p_D} - (aC_{p_A} + bC_{p_B})} = \underset{\text{equivalent new term}}{\Delta C_p}$$

and

$$\begin{aligned} [(c\alpha_C + d\alpha_D) - (a\alpha_A + b\alpha_B)] &= \Delta\alpha \\ T[(c\beta_C + d\beta_D) - (a\beta_A + b\beta_B)] &= T\,\Delta\beta \\ T^2[(c\gamma_C + d\gamma_D) - (a\gamma_A + b\gamma_B)] &= T^2\,\Delta\gamma \end{aligned} \tag{4.44}$$

Simplified, ΔC_P can be expressed as

$$\Delta C_p = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \tag{4.45}$$

Furthermore,

$$\begin{aligned} \Delta H_P - \Delta H_0 &= \int_{T_0}^{T} \Delta C_p\, dT = \int_{T_0}^{T} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2)\, dT \\ &= \Delta\alpha(T - T_0) + \frac{\Delta\beta}{2}(T^2 - T_0^2) + \frac{\Delta\gamma}{3}(T^3 - T_0^3) \end{aligned} \tag{4.46}$$

where we let $T_0 = T_{\text{ref}}$ for simplicity.

If the integration is carried out without definite limits,

$$\Delta H_P - \Delta H_R = \int (\Delta C_P)\, dT = \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 + C \tag{4.47}$$

where C is the integration constant.

Finally, ΔH_{rxn} at the new temperature T is

$$\Delta H_{\text{rxn}_T} = \Delta H_{\text{rxn}_{T_0}} + \Delta\alpha(T - T_0) + \frac{\Delta\beta}{2}(T^2 - T_0^2) + \frac{\Delta\gamma}{3}(T^3 - T_0^3) \tag{4.48a}$$

or

$$\Delta H_{\text{rxn}_T} = \Delta H_{\text{rxn}_{T_0}} + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 + C \tag{4.48b}$$

as the case may be. Using Eq. (4.48a) and knowing ΔH_{rxn} at the reference temperature T_0, you can easily calculate ΔH_{rxn} at any other temperature.

Equation (4.48b) can be consolidated into

$$\Delta H_{\text{rxn}_T} = \Delta H_0 + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 \tag{4.49}$$

where

$$\Delta H_0 = \Delta H_{\text{rxn}_{T_0}} + C$$

Now, if ΔH_{rxn} is known at any temperature T, you can calculate ΔH_0 as follows:

$$\Delta H_0 = \Delta H_{\text{rxn}_T} - \Delta\alpha(T) - \frac{\Delta\beta}{2}(T^2) - \frac{\Delta\gamma}{3}T^3 \tag{4.50}$$

Once you calculate the value of ΔH_0, you can use it to calculate ΔH_{rxn} at any other temperature.

Probably the easiest way to compute the necessary enthalpy changes is to use enthalpy data obtained directly from published tables or published formulas. Do not forget to take into account phase changes, if they take place, in the enthalpy calculations. If there is a phase change in one or more of the streams entering or leaving the process, you can conceptually think of the enthalpy changes that take place as shown in Fig. 4.17 if the phase difference is not included in $\Delta\hat{H}_f^\circ$. For example, if the product of combustion is water vapor, use $\Delta\hat{H}_f^\circ$ for water vapor, not for liquid water. Then the phase change from liquid water at 25°C to water vapor at 25°C automatically is taken into account. Otherwise, ΔH of the phase change must be accounted for separately by incorporating it into Eq. (4.46).

EXAMPLE 4.38 Calculation of Heat of Reaction at a Temperature Different from Standard Conditions

An inventor thinks he has developed a new catalyst that can make the gas-phase reaction

$$CO_2 + 4H_2 \longrightarrow 2H_2O + CH_4$$

proceed with 100% conversion. Estimate the heat that must be provided or removed if the gases enter and leave at 500°C.

Solution

Figure 4.18 applies. In effect we need to calculate heat of reaction at 500°C from Eq. (4.41) or Q in Eq. (4.40). For illustrative purposes we use the technique based on Eqs. (4.49) and (4.50). At standard conditions

Basis: 1 g mol of $CO_2(g)$

Tabulated data	*$CO_2(g)$*	*$H_2(g)$*	*$H_2O(g)$*	*$CH_4(g)$*
$-\Delta\hat{H}_f^\circ$(J/g mol)	393,513	0	241,826	74,848

$$\Delta\hat{H}_{\text{rxn}_{298\text{ K}}} = [-74{,}848 - 2(241{,}826)] - [4(0) - 393{,}513]$$
$$= -164{,}987 \text{ J/g mol } CO_2$$

First we shall calculate ΔC_p; units are $\dfrac{\text{J}}{(\text{g mol})(\text{K})}$

$$
\begin{aligned}
C_{p\,CO_2} &= 26.75 + 42.26 \times 10^{-3}T - 14.25 \times 10^{-6}T^2 &\quad T \text{ in K}\\
C_{p\,H_2} &= 26.88 + 4.35 \times 10^{-3}T - 0.33 \times 10^{-6}T^2 &\quad T \text{ in K}\\
C_{p\,H_2O} &= 29.16 + 14.49 \times 10^{-3}T - 2.02 \times 10^{-6}T^2 &\quad T \text{ in K}\\
C_{p\,CH_4} &= 13.41 + 77.03 \times 10^{-3}T - 18.74 \times 10^{-6}T^2 &\quad T \text{ in K}
\end{aligned}
$$

$$
\begin{aligned}
\Delta\alpha &= [1(13.41) + 2(29.16)] - [1(26.75) + 4(26.88)]\\
&= -62.54\\
\Delta\beta &= [1(77.03) + 2(14.49)](10^{-3}) - [1(42.26) + 4(4.35)](10^{-3})\\
&= 46.35 \times 10^{-3}\\
\Delta\gamma &= [1(-18.74) + 2(-2.02)](10^{-6}) - [1(-14.25) + 4(-0.33)](10^{-6})\\
&= -7.21 \times 10^{-6}
\end{aligned}
$$

$$\Delta C_p = -62.54 + 46.35 \times 10^{-3}T - 7.21 \times 10^{-6}T^2$$

Next we find ΔH_0, using as a reference temperature 298 K.

$$
\begin{aligned}
\Delta H_0 &= \Delta H_{\text{rxn}_{298}} - \Delta\alpha\, T - \frac{\Delta\beta}{2}T^2 - \frac{\Delta\gamma}{3}T^3\\
&= -164{,}987 - \left[(-62.54)(298) + \frac{46.35 \times 10^{-3}}{2}(298)^2\right.\\
&\quad \left. + \frac{-7.21 \times 10^{-6}}{3}(298)^3\right]\\
&= -164{,}987 + 18{,}637 - 2058 + 64 = -148{,}345 \text{ J/g mol } CO_2(g)
\end{aligned}
$$

Then, with ΔH_0 known, the ΔH_{rxn} at 773 K can be determined.

$$
\begin{aligned}
\Delta H_{\text{rxn}_{773\,\text{K}}} &= \Delta H_0 + \Delta\alpha\, T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3\\
&= -148{,}345 + \left[-62.54(773) + \frac{46.35 \times 10^{-3}}{2}(773)^2\right.\\
&\quad \left. + \frac{-7.21 \times 10^{-6}}{3}(773)^3\right]\\
&= -183{,}950 \text{ J} = Q
\end{aligned}
$$

Hence 183,950 J/g mol CO_2 must be removed.

EXAMPLE 4.39 Calculation of Heat of Reaction at a Temperature Different from Standard Conditions

Repeat the calculation of the preceding example using enthalpy values from Table 4.4 and Appendix D. Use linear interpolation in the tables.

Solution

The heat of reaction at 25°C and 1 atm from the preceding example is

$$\Delta\hat{H}_{\text{rxn}_{298\text{ K}}} = -164{,}987\frac{\text{J}}{\text{g mol}}$$

From Tables D.2 and 4.4b, $\Delta\hat{H}$ (J/g mol) values are [reference is 0°C (273 K)]:

Temp. (°C)	CO_2	H_2	H_2O	CH_4
25	912	718	837	879
500	22,345	14,615	17,795	24,014

From Eq. (4.41),

$$\begin{aligned}\Delta H_{\text{rxn}_{500°\text{C}}} &= \Delta H_{\text{rxn}_{25°\text{C}}} + \Delta H_{\text{products}} - \Delta H_{\text{reactants}}\\ &= -164{,}987 + [(1)(24{,}014 - 879) + (2)(17{,}795 - 837)]\\ &\quad -[(1)(22{,}345 - 912) + (4)(14{,}615) - 718)]\\ &= -184{,}957\frac{\text{kJ}}{\text{kg mol CO}_2}\end{aligned}$$

Note that the enthalpies of the products and of the reactants are both based on the reference temperature of 25°C. The answer is not quite the same as in Example 4.38 because the heat capacity data used there were not quite the same as those used in calculating the ΔH values in the tables, and because of the use of linear interpolation in the tables.

In most processes with reaction, the temperature of the entering materials and exit materials is not the same. Such cases can be represented by an information diagram such as Fig. 4.19. Equation (4.40) still applies. Phase changes must still be included, if applicable, as explained previously.

EXAMPLE 4.40 Application of the Energy Balance to a Process in which the Temperatures of the Entering and Exit Streams Differ

Carbon monoxide at 50°F is completely burned at 2 atm pressure with 50% excess air that is at 1000°F. The products of combustion leave the combustion chamber at 800°F. Calculate the heat evolved from the combustion chamber expressed as British thermal units per pound of CO entering.

Solution

Steps 1, 2, and 3 Refer to Fig. E4.40a. A material balance is needed before an energy balance can be made.

Step 4

Basis: 1 lb mol of CO (easier to use than 1 lb of CO)

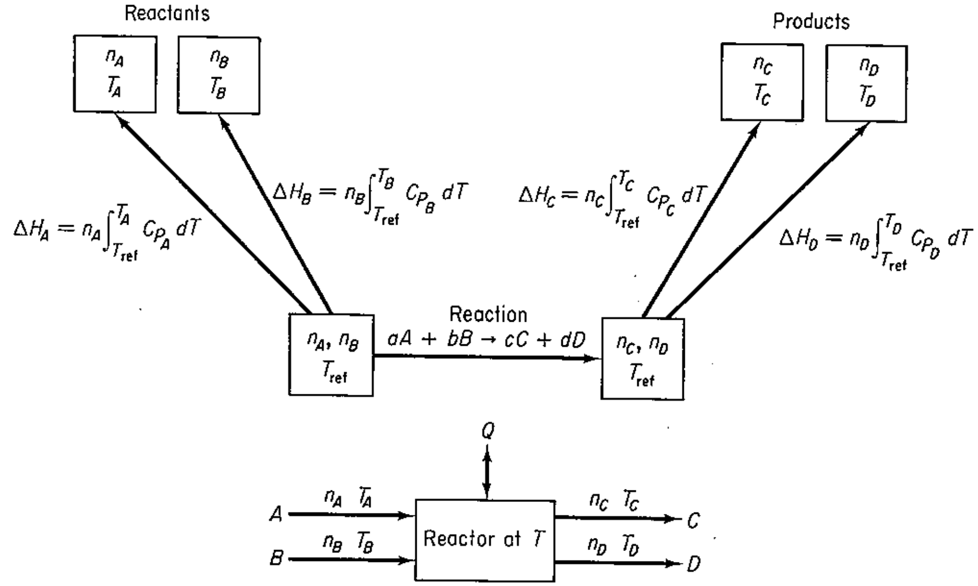


Figure 4.19 Information diagram for the case in which the reactants and products are not at the same temperature.

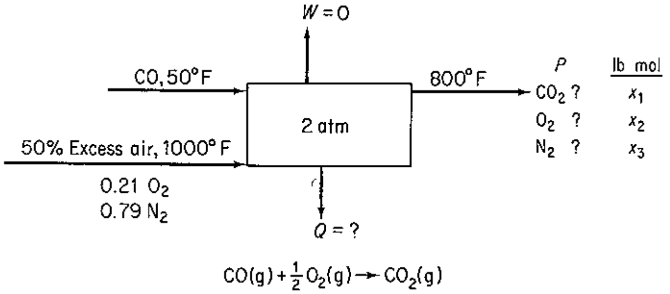


Figure E4.40a

Steps 5, 6, and 8 We have three elements, hence can make three independent balances. Because we have three unknown compositions, a unique solution exists, a solution that can be obtained by direct addition or subtraction.

Steps 2 and 3 (Continued) Amount of air entering:

$$\begin{array}{c|c|c|c}\text{1 lb mol CO} & \text{0.5 lb mol } O_2 & \text{1.5 lb mol } O_2 \text{ used} & \text{1 lb mol air} \\ \hline & \text{1 lb mol CO} & \text{1.0 lb } O_2 \text{ mol needed} & \text{0.21 lb mol } O_2\end{array} = 3.57 \text{ lb mol air}$$

composed of

$$3.57(0.79) = 2.82 \text{ lb mol } N_2$$

$$3.57(0.21) = 0.750 \text{ lb mol } O_2$$

Steps 7, 8, and 9 The element balances are

	In		*Out*		*In P* (lb mol)
C	1	=	x_1	CO_2	1
N_2	2.82	=	x_3	N_2	2.82
O_2	$1(0.5) + 0.750$	=	$x_1 + x_2 = 1 + x_2$	O_2	0.250

Steps 3a and 3b The general energy balance

$$\Delta E = -\Delta[(\hat{H} + \hat{P} + \hat{K})m] + Q - W$$

reduces to $Q = \Delta H$. Why? Only Q is unknown.

Steps 8 and 9 (Continued) Enthalpy data have been taken from Table 4.3. The heat of reaction at 25°C (77°F) and 1 atm from Example 4.31 after conversion of units is −121,672 Btu/lb mol of CO. We can assume that the slightly higher pressure than SC of 2 atm has no effect on the heat of reaction or the enthalpy values. Figure E4.40b shows the sensible heat (enthalpy) values for the entering and exiting materials.

$\Delta\hat{H}$ (Btu/lb mol; reference is 32°F)

Temp. (°F)	*CO*	*Air*	*O_2*	*N_2*	*CO_2*
50	125.2	—	—	—	—
77	313.3	312.7	315.1	313.2	392.2
800	—	—	5690	5443	8026
1000	—	6984	—	—	—

$$Q = \Delta H_{\text{rxn}_{77°\text{F}}} + \overbrace{\Delta H_{\text{products}} - \Delta H_{\text{reactants}}}^{\text{sensible}}$$

(a)
$$\Delta\hat{H}_{\text{rxn}_{77°\text{F}}} = -121{,}672 \text{ Btu/lb mol}$$

(b)
$$\begin{aligned}\Delta H_{\text{products}} &= \Delta H_{800°\text{F}} - \Delta H_{77°\text{F}}\\ &= \overbrace{(1)(8026 - 392.2)}^{\mathbf{CO_2}} + \overbrace{(2.82)(5443 - 313.2)}^{\mathbf{N_2}}\\ &\quad + \overbrace{(0.25)(5690 - 315.1)}^{\mathbf{O_2}}\\ &= 7634 + 14{,}466 + 1344\\ &= 23{,}444 \text{ Btu/lb mol}\end{aligned}$$

(c)
$$\begin{aligned}\Delta H_{\text{reactants}} &= \overbrace{\Delta H_{1000°\text{F}} - \Delta H_{77°\text{F}}}^{\textbf{air}} + \overbrace{\Delta H_{50°\text{F}} - \Delta H_{77°\text{F}}}^{\textbf{CO}}\\ &= (3.57)(6984 - 312.7) + (1)(125.2 - 313.3)\\ &= 23{,}817 - 188.1 = 23{,}628 \text{ Btu/lb mol}\end{aligned}$$

(d)
$$\begin{aligned}Q &= -121{,}672 + 23{,}444 - 23{,}628\\ &= -121{,}856 \text{ Btu/lb mol}\end{aligned}$$

$$\frac{-121{,}856 \text{ Btu}}{1 \text{ lb mol CO}} \left| \frac{1 \text{ lb mol CO}}{28 \text{ lb CO}} \right. = -4352 \text{ Btu/lb CO}$$

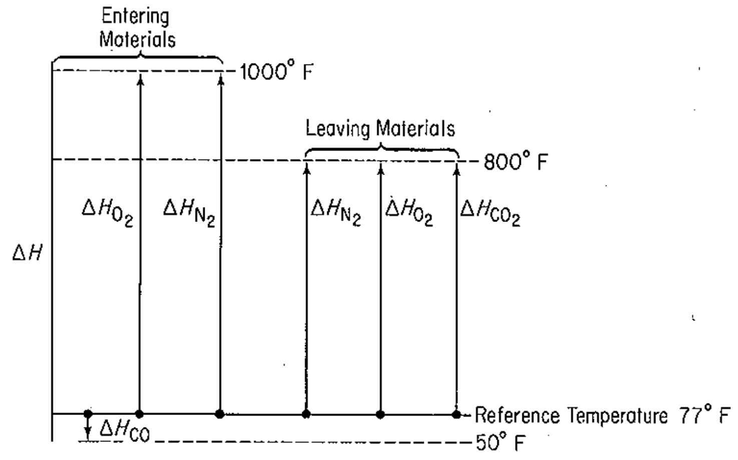


Figure E4.40b

Self-Assessment Test

1. Calculate the heat of reaction at 1000 K and 1 atm for the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$$

2. Methane is burned in a furnace with 100% excess dry air to generate steam in a boiler. Both the air and the methane enter the combustion chamber at 500°F and 1 atm, and the products leave the furnace at 2000°F and 1 atm. If the effluent gases contain only CO_2, H_2O, O_2, and N_2, calculate the amount of heat absorbed by the water to make steam per pound of methane burned.

3. A mixture of metallic aluminum and Fe_2O_3 can be used for high-temperature welding. Two pieces of steel are placed end to end and the powdered mixture is applied and ignited. If the temperature desired is 3000°F and the heat loss is 20% of $(\Delta H_{rxn_{25°C}} + \Delta H_{prod} - \Delta H_{react})$ by radiation, what weight in pounds of the mixture (used in the molecular proportions of $2Al + 1Fe_2O_3$) must be used to produce this temperature in 1 lb of steel to be welded? Assume that the starting temperature is 65°F.

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$$

Data	C_p, solid [Btu/(lb)(°F)]	Heat of fusion (Btu/lb)	Melting point (°F)	C_p, Liquid [Btu/(lb)(°F)]
Fe and steel	0.12	86.5	2800	0.25
Al_2O_3	0.20	—	—	—

Thought Problem

1. Many different opinions have been expressed as to whether gasohol is a feasible fuel for motor vehicles. An important economic question is: Does 10% grain-based-alcohol-in-gasoline gasohol produce positive net energy? Examine the details of the energy inputs

and outputs, including agriculture (transport, fertilizer, etc.), ethanol processing (fermentation, distilling, drying, etc.), petroleum processing and distribution, and the use of byproducts (corncobs, stalks, mash, etc.). Ignore taxes and tax credits, and assume that economical processing takes place.

4.7-6 Temperature of a Reaction

Your objectives in studying this section are to be able to:

1. Calculate the temperature of an entering or exiting steam of a process given all the other necessary information to obtain a unique solution.
2. Calculate the adiabatic reaction temperature.

We are now equipped to determine what is called the ***adiabatic reaction temperature.*** This is the temperature obtained inside the process when (1) the reaction is carried out under adiabatic conditions, that is, there is no heat interchange between the container in which the reaction is taking place and the surroundings; and (2) when there are no other effects present, such as electrical effects, work, ionization, free radical formation, and so on. In calculations of flame temperatures for combustion reactions, the adiabatic reaction temperature *assumes complete combustion*. Equilibrium considerations may dictate less than complete combustion for an actual case. For example, the adiabatic flame temperature for the combustion of CH_4 with theoretical air has been calculated to be 2010°C; allowing for incomplete combustion, it would be 1920°C. The actual temperature when measured is 1885°C.

The adiabatic reaction temperature tells us the temperature ceiling of a process. We can do no better, but of course the actual temperature may be less. The adiabatic reaction temperature helps us select the types of materials that must be specified for the container in which the reaction is taking place. Chemical combustion with air produces gases at a maximum temperature of 2500 K which can be increased to 3000 K with the use of oxygen and more exotic oxidants, and even this value can be exceeded although handling and safety problems are severe. Applications of such hot gases lie in the preparation of new materials, micromachining, welding using laser beams, and the direct generation of electricity using ionized gases as the driving fluid.

To calculate the adiabatic reaction temperature, you assume that all the energy liberated from the reaction at the reference temperature plus that brought in by the entering stream (relative to the same base temperature) is available to raise the temperature of the products. We assume that the products leave at the temperature of the reaction, and thus if you know the temperature of the products, you automatically know the temperature of the reaction. In effect, for this adiabatic process we can apply Eq. (4.40).

Since no heat escapes and the energy available is allowed only to increase the enthalpy of the products of the reaction, we have

$$\text{sensible } \Delta H_{\text{products}} = \underset{\text{"energy pool"}}{\boxed{\text{sensible } \Delta H_{\text{reactants}} - \Delta H_{\text{rxn}}}} \tag{4.51}$$

Any phase changes that take place and are not accounted for in the heats of formation must be incorporated into the "energy pool." Because of the character of the information available, the determination of the adiabatic reaction temperature or flame temperature may involve a trial-and-error solution; hence the iterative solution of adiabatic flame temperature problems is often carried out on a computer.

EXAMPLE 4.41 Adiabatic Flame Temperature

Calculate the theoretical flame temperature for CO gas burned at constant pressure with 100% excess air, when the reactants enter at 100°C.

Solution

The solution presentation will be abbreviated to save space. The system is shown in Fig. E4.41. We will use Table 4.4 for the data.

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

Basis: 1 g mol of CO(g); ref. temp. 25°C

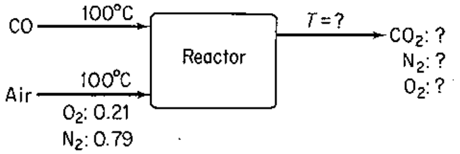


Figure E4.41

Material balance:

Entering reactants		Exit products	
Component	g mol	Component	g mol
CO(g)	1.00	$CO_2(g)$	1.00
O_2(req.)	0.50	$O_2(g)$	0.50
O_2(xs)	0.50	$N_2(g)$	3.76
O_2(total)	1.00		
N_2	3.76		
Air	4.76		

From Example 4.31, ΔH_{rxn} at 25°C = −282,990 J/g mol CO. Then, to fill in Eq. (4.51), $\Delta H_{\text{reactants}}$:

Component	Moles	Reactants (100°C, 373 K)	
		$\Delta\hat{H}$ (J/g mol)	ΔH (J)
CO(g)	1.00	2913 − 728	2,185
Air	4.76	2910 − 726	10,396
		$\Sigma\Delta H_R$ =	12,581

$$\Delta H_{\text{products}} = 12{,}581 + 282{,}990 = 295{,}571 \text{ J}$$

To find the temperature which yields a $\Delta H_{\text{products}}$ of 295,571 J, the simplest procedure is to assume various values of the exit temperature of the products until the $\Sigma\,\Delta H_P = 295{,}571$.

Assume that TFT (theoretical flame temperature) = 2000 K.

Component	Moles	$\Delta\hat{H}$ (J/g mol)	ΔH (J)
CO_2	1.00	(92,466 − 912)	91,554
O_2	0.50	(59,914 − 732)	29,591
N_2	3.76	(56,902 − 728)	211,214
		$\Sigma\Delta H_p$ =	332,359

Assume that TFT = 1750 K.

Component	Moles	$\Delta\hat{H}$ (J/g mol)	ΔH (J)
CO_2	1.00	(77,455 − 912)	76,543
O_2	0.50	(50,555 − 732)	24,912
N_2	3.76	(47,940 − 728)	177,517
		$\Sigma\Delta H_P$ =	278,972

Make a linear interpolation:

$$\text{TFT} = 1750 + \frac{295{,}571 - 278{,}972}{332{,}359 - 278{,}972}(250) = 1750 + 78$$

$$= 1828 \asymp 1555°\text{C}$$

If we use heat capacity equations to calculate the "sensible heats," we can obtain an analytic relation to be solved for the flame temperature as follows [C_p values are in J/(g mol)(K) and are good to ±1.5% up to 1500 K]; T is in K:

$$C_{pO_2} = 25.59 + 13.25 \times 10^{-3}T - 4.20 \times 10^{-6}T^2$$

$$C_{pN_2} = 27.02 + 5.81 \times 10^{-3}T - 0.29 \times 10^{-6}T^2$$

$$C_{pCO_2} = 26.75 + 42.26 \times 10^{-3}T - 14.25 \times 10^{-6}T^2$$

For the products

$$\Delta H_{\text{products}} = 1\int_{298}^{T}(26.75 + 42.26 \times 10^{-3}T - 14.25 \times 10^{-6}T^2)\,dT$$

$$+ 0.5 \int_{298}^{T} (25.59 + 13.25 \times 10^{-3}T - 4.20 \times 10^{-6}T^2)\, dT$$

$$+ 3.76 \int_{298}^{T} (27.02 + 5.81 \times 10^{-3}T - 0.29 \times 10^{-6}T^2)\, dT$$

$$295{,}571 = 141.14T + 35.37 \times 10^{-3}T^2 - 5.81 \times 10^{-6}T^3 - 45{,}047$$

the solution to which is (by Newton's method starting at $T = 2000$ K)

$$T = 1828 \text{ K}$$

Self-Assessment Test

1. Calculate the theoretical flame temperature when hydrogen burns with 400% excess dry air at 1 atm. The reactants enter at 100°C.

Thought Problems

1. Would burning a fuel with oxygen or with air yield a higher adiabatic flame temperature?
2. A recent news article said:

> Two workers were killed and 45 others hurt when a blast at the ____________ refinery shook a neighborhood and shot flames 500 feet into the air. Hydrogen from a "cracker unit" that separates crude oil into such products as gasoline and diesel fuel burned at temperatures from 4,000 to 5,000 degrees in the 9:50 A.M. accident at the refinery. The fire was put out about an hour later.

Is the temperature cited reasonable?

4.8 HEATS OF SOLUTION AND MIXING

4.8-1 Enthalpy Changes for Mixtures

Your objectives in studying this section are to be able to:

1. Distinguish between ideal solutions and real solutions.
2. Calculate the heat of mixing, or the heat of dissolution, at standard conditions given the moles of the materials forming the mixture.
3. Calculate the standard integral heat of solution.
4. Define the standard integral heat of solution at infinite dilution.
5. Apply the energy balance to problems in which the heat of mixing is significant.

So far in our energy calculations, we have been considering each substance to be a completely pure and separate material. The physical properties of an ideal solution or mixture may be computed from the sum of the properties in question for the individual components. For gases, mole fractions can be used as weighting values, or, alternatively, each component can be considered to be independent of the others. In most instances so far in this book we have used the latter procedure. Using the former technique, as we did in a few instances, we could write down, for the heat capacity of an ideal mixture,

$$C_{p\,\text{mixture}} = x_A C_{p_A} + x_B C_{p_B} + x_C C_{p_C} + \cdots \tag{4.52}$$

or, for the enthalpy,

$$\Delta\hat{H}_{\text{mixture}} = x_A \Delta\hat{H}_A + x_B \Delta\hat{H}_B + x_C \Delta\hat{H}_C + \cdots \tag{4.53}$$

These equations are applicable to ideal mixtures only.

When two or more pure substances are mixed to form a gas or liquid solution, we frequently find heat is absorbed or evolved from the system upon mixing. Such a solution would be called a "real" solution. Per mole of solute

$$\Delta\hat{H}^\circ_{\text{final solution}} - \Delta\hat{H}^\circ_{\text{initial components}} = \Delta\hat{H}^\circ_{\text{mixing}} \tag{4.54}$$

The **heat of mixing** ($\Delta\hat{H}^\circ_{\text{mixing}}$) (i.e, the enthaply change on mixing) has to be determined experimentally, but can be retrieved from tabulated experimental (smoothed) results, once such data are available. This type of energy change has been given the formal name ***heat of solution*** when one substance dissolves in another; and there is also the negative of the heat of solution, the ***heat of dissolution,*** for a substance that separates from a solution.

Tabulated data for heats of solution appear in Table 4.12 in terms of energy *per mole of solute* for consecutively added quantities of solvent to the solute; the gram mole refers to the gram mole of solute. Heats of solution are somewhat similar to heats of reaction in that an energy change takes place because of differences in the forces of attraction of the solvent and solute molecules. Of course, these energy changes are much smaller than those we find accompanying the breaking and combining of chemical bonds. Heats of solution are conveniently treated in exactly the same way as are the heats of reaction in the energy balance.

The solution process can be represented by an equation such as the following:

$$HCl(g) + 5H_2O \longrightarrow HCl\cdot 5H_2O$$

or

$$HCl(g) + 5H_2O \longrightarrow HCl(5H_2O)$$

$$\Delta H^\circ_{\text{soln}} = -64{,}047 \text{ J/g mol HCl(g)}$$

The expression $HCl(5H_2O)$ means that 1 mole of HCl has been dissolved in 5 moles of water, and the enthalpy change for the process is $-64{,}047$ J/g mol of HCl. Table 4.12 shows the heat of solution for various cumulative numbers of moles of water added to 1 mole of HCl.

The ***standard integral heat of solution*** is the cumulative $\Delta H^\circ_{\text{soln}}$ as shown in the next to last column for the indicated number of molecules of water. As succes-

TABLE 4.12 Heat of Solution of HCl* (at 25°C and 1 atm)

Composition	Total moles H_2O added to 1 mole HCl	$-\Delta\hat{H}^\circ$ for each incremental step (J/g mol HCl) $= -\Delta\hat{H}^\circ_{\text{dilution}}$	Integral heat of solution: cumulative $-\Delta\hat{H}^\circ$ (J/g mol HCl)	Heat of formation $-\Delta\hat{H}^\circ_f$ (J/g mol HCl)
$HCl(g)$	0			92,311
$HCl\cdot 1H_2O(aq)$	1	26,225	26,225	118,536
$HCl\cdot 2H_2O(aq)$	2	22,593	48,818	141,129
$HCl\cdot 3H_2O(aq)$	3	8,033	56,851	149,161
$HCl\cdot 4H_2O(aq)$	4	4,351	61,202	153,513
$HCl\cdot 5H_2O(aq)$	5	2,845	64,047	156,358
$HCl\cdot 8H_2O(aq)$	8	4,184	68,231	160,542
$HCl\cdot 10H_2O(aq)$	10	1,255	69,486	161,797
$HCl\cdot 15H_2O(aq)$	15	1,503	70,989	163,300
$HCl\cdot 25H_2O(aq)$	25	1,276	72,265	164,576
$HCl\cdot 50H_2O(aq)$	50	1,013	73,278	165,589
$HCl\cdot 100H_2O(aq)$	100	569	73,847	166,158
$HCl\cdot 200H_2O(aq)$	200	356	74,203	166,514
$HCl\cdot 500H_2O(aq)$	500	318	74,521	166,832
$HCl\cdot 1000H_2O(aq)$	1,000	163	74,684	166,995
$HCl\cdot 50{,}000H_2O(aq)$	50,000	146	75,077	167,388
$HCl\cdot\infty H_2O$		67	75,144	167,455

*To convert to cal/g mol multiply by 0.2390.

SOURCE: *National Bureau of Standards Circular 500,* U.S. Government Printing Office, Washington, D.C., 1952.

sive increments of water are added to the mole of HCl, the cumulative heat of solution (the integral heat of solution) increases, but the incremental enthalpy change decreases as shown in Table 4.12. Note that both the reactants and products have to be at standard conditions. The heat of dissolution would be just the negative of these values. The integral heat of the solution is plotted in Fig. 4.20, and you can see that an asymptotic value is approached as the solution becomes more and more dilute. At infinite dilution this value is called the ***standard integral heat of solution at infinite dilution*** and is −75,144 J/g mol of HCl. What can you conclude about the reference state for the heat of solution of pure HCl from Fig. 4.20? In Appendix H are other tables presenting standard integral heat of solution data and the heats of formation of

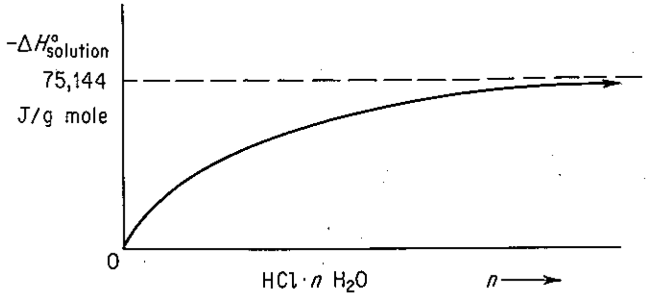


Figure 4.20 Integral heat of solution of HCl in water.

solutions. Since the energy changes for heats of solution are point functions, you can easily look up any two concentrations of HCl and find the energy change caused by adding or subtracting water. For example, if you mix 1 mole of $HCl\cdot 15\ H_2O$ and 1 mole of $HCl\cdot 5H_2O$, you obtain 2 moles of $HCl\cdot 10H_2O$, and the total enthalpy change at 25°C is

$$\begin{aligned}\Delta H^\circ &= [2(-69{,}486)] - [1(-70{,}989) + 1(-64{,}047)] \\ &= -3936\ \text{J}\end{aligned}$$

You would have to remove 3936 J to keep the temperature of the final mixture at 25°C.

To calculate the standard heat of formation of a solute in solution, you proceed as follows. What is the standard heat of formation of 1 g mol of HCl in 5 g mol of H_2O? We treat the solution process in an identical fashion to a chemical reaction:

$$\begin{array}{llll} & & & \qquad J/g\ mol \\ \hline \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) & = HCl(g) & A: & \Delta\hat{H}_f^\circ = -92{,}311 \\ \underline{HCl(g) + 5H_2O} & \underline{= HCl(5H_2O)} & \underline{B:} & \underline{\Delta\hat{H}^\circ_{soln} = -64{,}047} \\ \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) + 5H_2O & = HCl(5H_2O) & A + B: & \Delta\hat{H}_f^\circ = -156{,}358 \end{array}$$

It is important to remember that the heat of formation of H_2O itself does not enter into the calculation. The heat of formation of HCl in an infinitely dilute solution is

$$\Delta\hat{H}_f^\circ = -92{,}311 - 75{,}144 = -167{,}455\ \text{kJ/g mol}$$

Another type of heat of solution which is occasionally encountered is the partial molal heat of solution. Information about this thermodynamic property can be found in most standard thermodynamic texts or in books on thermochemistry, but we do not have the space to discuss it here.

One point of special importance concerns the formation of water in a chemical reaction. When water participates in a chemical reaction in solution as a reactant or product of the reaction, you must include the heat of formation of the water as well as the heat of solution in the energy balance. Thus, if 1 mole of HCl reacts with 1 mole of sodium hydroxide to form water and the reaction is carried out in only 2 moles of water to start with, it is apparent that you will have 3 moles of water at the end of the process. Not only do you have to take into account the heat of reaction when the water is formed, but there is also a heat of solution contribution. If gaseous HCl reacts with crystalline sodium hydroxide and the product is 1 mole of gaseous water vapor, you could employ the energy balance without worrying about the heat of solution effect.

EXAMPLE 4.42 Application of Heat of Solution Data

Hydrochloric acid is an important industrial chemical. To make aqueous solutions of it of commercial grade (known as *muriatic acid*), purified HCl(g) is absorbed in water in a tantalum absorber in a continuous process. How much heat must be removed from the absorber per 100 kg of product if hot HCl(g) at 120°C is fed into water in the absorber as shown in

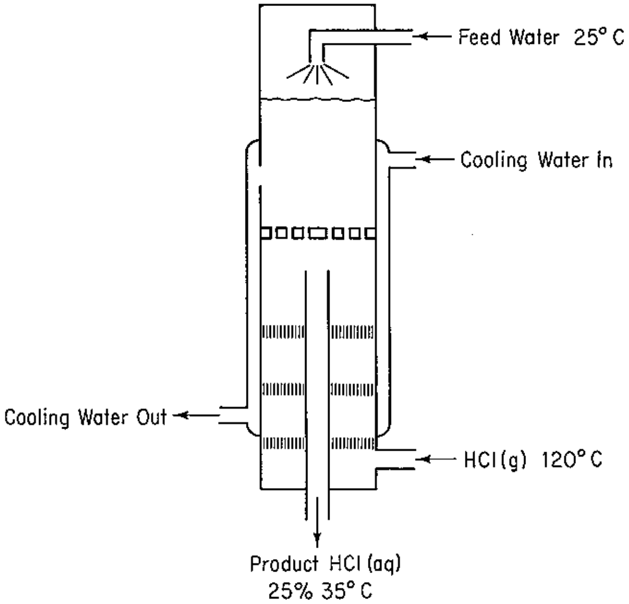


Figure E4.42

Fig. E4.42? The feed water can be assumed to be at 25°C, and the exit product HCl(aq) is 25% HCl (by weight) at 35°C.

Solution

Steps 1, 2, and 3 We need to add to the figure enthalpy data which are easiest to get per mole of HCl. Consequently, we will first convert the product into moles of HCl and moles of H_2O.

Component	kg	Mol. wt.	kg mol	Mole fraction
HCl	25	36.37	0.685	0.141
H_2O	75	18.02	4.163	0.859
Total	100		4.848	1.000

The mole ratio of H_2O to HCl is 4.163/0.685 = 6.077.

Step 4 The system will be the HCl and water (not including the cooling water).

Basis: 100 kg of product

Ref. temperature: 25°C

Steps 5 and 6 Equation (4.40) can be used to calculate $Q = \Delta H$, and both the initial and final enthalpies of all the streams are known or can be calculated directly, hence the problem has a unique solution. The kg and moles of HCl in and out, and the water in and out, have been calculated above.

Step 3 (Continued) The enthalpy values for the streams are [C_p for the HCl(g) is from Table E.1; C_p for the product is approximately 2.7 J/(g)(°C)]:

Stream	ΔH
Feed H_2O	0
$HCl(g)$	$685 \int_{25}^{120} C_p \, dT = 685(2747) = 1.883 \times 10^6$ J
$HCl(aq)$	$10^5 \int_{25}^{35} C_p \, dT = 2.7 \times 10^6$ J

By interpolation, the heat of solution data from Table 4.12 give

$$\Delta \hat{H}^\circ_{\text{solution}} = -65{,}442 \text{ J/g mol HCl}$$

$$\Delta H^\circ_{\text{solution}} = (-65{,}442)(685) = -4.4828 \times 10^7 \text{ J}$$

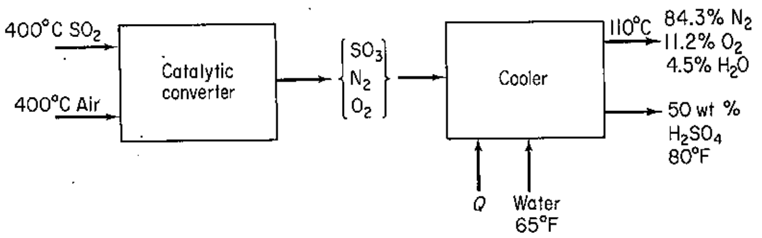
Steps 7, 8, and 9

$$Q = \Delta H = \Delta H_{\text{final products}} - \Delta H_{\text{entering feeds}} + \Delta H^\circ_{\text{solution}}$$
$$= 2.7 \times 10^6 - 1.883 \times 10^6 + (-4.4828 \times 10^7)$$
$$= -4.4 \times 10^7 \text{ J}$$

The negative value of Q means heat is removed from the system.

Self-Assessment Test

1. Is a gas mixture an ideal solution?
2. Give (a) two examples of exothermic mixing of two liquids and (b) two examples of endothermic mixing based on your experience.
3. (a) What is the reference state for H_2O in the table for the heat of solution of HCl?
   (b) What is the value of the enthalpy of H_2O in the reference state?
4. Use the heat of solution data in Appendix H to determine the heat transferred per mole of entering solution into or out of (state which) a process in which 2 g mol of a 50 *mole %* solution of sulfuric acid at 25°C is mixed with water at 25°C to produce a solution at 25°C containing a mole ratio of $10H_2O$ to $1H_2SO_4$.
5. Calculate the heat that must be added or removed per ton of 50 wt % H_2SO_4 produced by the process shown.



Thought Problems

1. A tanker truck of hydrochloric acid was inadvertently unloaded into a large storage tank used for sulfuric acid. After about one-half of the 3000-gal load had been discharged, a violent explosion occurred, breaking the inlet and outlet lines and buckling the tank.
   What might be the cause of the explosion?

2. A concentrated solution (73%) of sodium hydroxide was stored in a vessel. Under normal operations, solution was forced out by air pressure as needed. When application of air pressure did not work, apparently due to solidification of the caustic solution, water was poured through a manhole to dilute the caustic and free up the pressure line. An explosion took place and splashed caustic out of the manhole 15 ft into the air.

   What caused the incident?

4.8-2 Enthalpy–Concentration Charts

Your objectives in studying this section are to be able to:

1. Prepare an enthalpy–concentration chart for a binary mixture given the enthalpy or heat capacity data for the pure components, the heat capacity data for mixtures at various concentrations, and the necessary heats of mixing at various concentrations.
2. Use the enthalpy–concentration chart in solving material and energy balances.

A convenient way to represent enthalpy data for binary solutions is via an enthalpy–concentration diagram. Enthalpy–concentration diagrams (H–x) are plots of specific enthalpy versus concentration (usually weight or mole fraction) with temperature as a parameter. Figure 4.21 illustrates one such plot. If available,[26] such charts are useful in making combined material and energy balances calculations in distillation, crystallization, and all sorts of mixing and separation problems. You will find a few examples of enthalpy–concentration charts in Appendix I.

According to the phase rule $F = C - \mathcal{P} + 2$, hence in the single-phase region for a two-component system (with no reaction), $C = 2$, $\mathcal{P} = 1$, and $F = 2 - 1 + 2 = 3$. The enthalpy–concentration chart is for a fixed pressure; hence the state of the system is determined by specifying two of the following intensive variables: T, $\Delta\hat{H}$, or ω (or x or y).

At some time in your career you may find you have to make numerous repetitive material and energy balance calculations on a given binary system and would like to use an enthalpy-concentration chart for the system, but you cannot find one in the literature or in your files. How do you go about constructing such a chart?

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[26] For a literature survey as of 1957, see Robert Lemlich, Chad Gottschlich, and Ronald Hoke, *Chem. Eng. Data Ser.*, v. 2, p. 32 (1957). Additional references: for CCl_4, see M. M. Krishnaiah et al., *J. Chem. Eng. Data*, v. 10, p. 117 (1965); for EtOH–EtAc, see Robert Lemlich, Chad Gottschlich, and Ronald Hoke, *Br. Chem. Eng.*, v. 10, p. 703 (1965); for methanol–toluene, see C. A. Plank and D. E. Burke, *Hydrocarbon Process.*, v. 45, no. 8, p. 167 (1966); for acetone–isopropanol, see S. N. Balasubramanian, *Br. Chem. Eng.*, v. 11, p. 1540 (1966); for alcohol–aromatic systems, see C. C. Reddy and P. S. Murti, *Br. Chem. Eng.*, v. 12, p. 1231 (1967); for acetonitrile–water–ethanol, see Reddy and Murti, ibid., v. 13, p. 1443 (1968); for alcohol–aliphatics, see Reddy and Murti, ibid., v. 16, p. 1036 (1971); and for H_2SO_4, see D. D. Huxtable and D. R. Poole, *Proc. Int. Solar Energy Soc.*, Winnipeg, August 15, 1976, v. 8, p. 178 (1977).

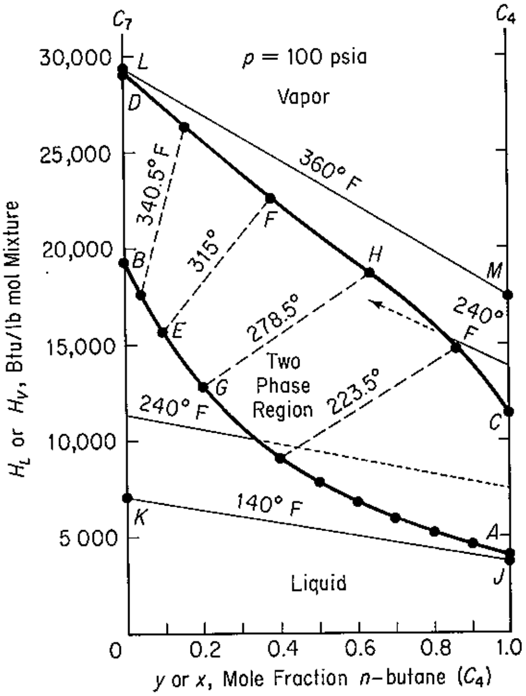


Figure 4.21 Enthalpy concentration chart for n-butane-n-heptane at 100 psia. Curve DFHC is the saturated vapor; curve BEGA is the saturated liquid. The dashed lines are equilibrium tie lines connecting y and x at the same temperature.

As usual, the first thing to do is choose a basis—some given amount of the mixture, usually 1 lb (or kg) or 1 lb mole (or kg mol). Then choose a reference temperature ($\Delta H_0 = 0$ at T_0) for the enthalpy calculations. Assuming that 1 lb is the basis, you then write an energy balance for solutions of various compositions at various temperatures:

$$\Delta\hat{H}_{\text{mixture}} = \omega_A \Delta\hat{H}_A + \omega_B \Delta\hat{H}_B + \Delta\hat{H}_{\text{mixing}} \tag{4.55}$$

where $\Delta\hat{H}_{\text{mixture}}$ = enthalpy of 1 lb of the mixture
$\Delta\hat{H}_A$, $\Delta\hat{H}_B$ = enthalpies of the pure components per pound relative to the reference temperature (the reference temperature does not have to be the same for A as for B)
$\Delta\hat{H}_{\text{mixing}}$ = heat of mixing (solution) per pound at the temperature of the given calculation
ω = mass fraction

In the common case where the $\Delta\hat{H}_{\text{mixing}}$ is known only at one temperature (usually 77°F), a modified procedure as discussed below would have to be followed to calculate the enthalpy of the mixture.

The choice of the reference temperatures for A and B locates the zero enthalpy datum on each side of the diagram (see Fig. 4.22). From enthalpy tables such as the steam tables, or by finding

$$(\Delta\hat{H}_A - \Delta\hat{H}_{A_0}) = \int_{T_0}^{T=77^\circ\text{F}} C_{p_A}\,dT$$

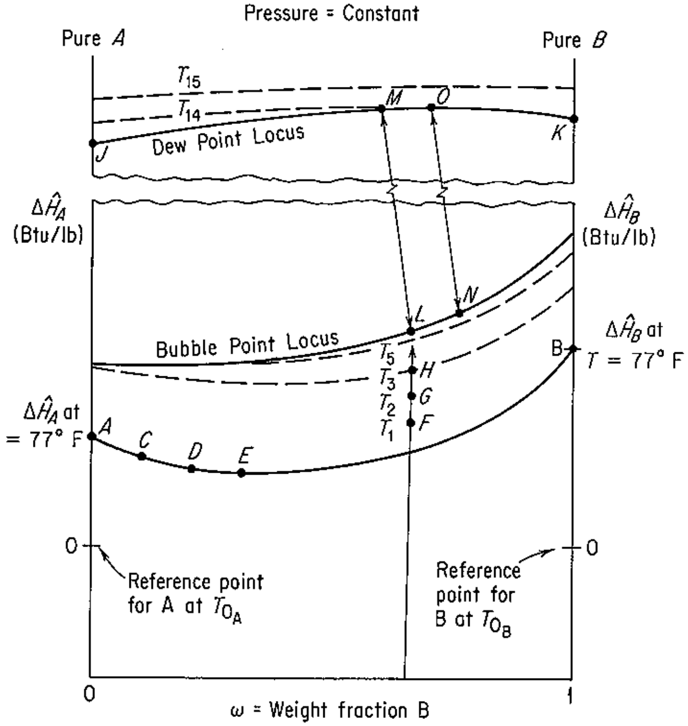


Figure 4.22 Enthalpy–concentration diagram.

you can find $\Delta\hat{H}_A$ at 77°F and similarly obtain $\Delta\hat{H}_B$ at 77°F for the pure substances. Now you have located points A and B. If one of the components is water, it is advisable to choose 32°F as T_0 because then you can use the steam tables as a source of data.

Now that you have $\Delta\hat{H}_A$ and $\Delta\hat{H}_B$ at 77°F (or any other temperature at which $\Delta\hat{H}_{\text{mixing}}$ is known), you can calculate $\Delta\hat{H}_{\text{mixture}}$ at 77°F by Eq. (4.55). For various mixtures such as 10% B_a and 90% A_b, 20% B_a and 80% A_b, and so on, plot the calculated $\Delta\hat{H}_{\text{mixture}}$ as shown by the points C, D, E, and so on, in Fig. 4.22, and connect these points with a continuous line.

You can calculate $\Delta\hat{H}_{\text{mixture}}$ at any other temperature T, once this 77°F isotherm has been constructed, by again calculating an enthalpy change as follows:

$$\Delta\hat{H}_{\text{mixture at any }T} = \Delta\hat{H}_{\text{mixture at 77°F}} + \int_{77°\text{F}}^{T} C_{p_\omega}\,dt \tag{4.56}$$

where C_{p_ω} is the heat capacity of the solution at concentration ω. These heat capacities must be determined experimentally, although in a pinch they might be estimated. Points F, G, H, and so on, can be determined in this way for a given composition, and then additional like calculations at other fixed concentrations will give you enough points so that all isotherms can be drawn up to the bubble-point line for the mixture at the pressure for which the chart is being constructed.

To include the vapor region on the enthalpy concentration chart, you need to know:

(a) The heat of vaporization of the pure components (to get points *J* and *K*)

(b) The composition of the vapor in equilibrium with a given composition of liquid (to get the tie lines *L–M*, *N–O*, etc.)

(c) The dew point temperatures of the vapor (to get the isotherms in the vapor region)

(d) The heats of mixing in the vapor region, usually negligible [to fix the points *M*, *O*, etc., by means of Eq. (4.55)] (Alternatively, the heat of vaporization of a given composition could be used to fix points *M*, *O*, etc.)

The use of enthalpy–concentration diagrams for combination material–energy balance problems will now be illustrated.

EXAMPLE 4.43 Application of the Enthalpy–Concentration Chart

One hundred pounds of a 73% NaOH solution at 350°F is to be diluted to give a 10% solution at 80°F. How many pounds of water at 80°F and ice at 32°F are required if there is no external source of cooling available? See Fig. E4.43. Use the steam tables and the NaOH–H_2O enthalpy–concentration chart in Appendix I as your source of data. (The reference conditions for the latter chart are $\Delta H = 0$ at 32°F for liquid water and $\Delta H = 0$ for an infinitely dilute solution of NaOH, with pure caustic having an enthalpy at 68°F of 455 Btu/lb above this datum.)

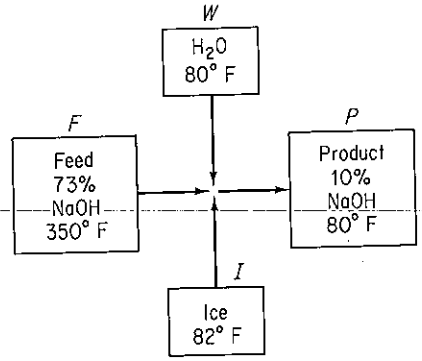


Figure E4.43

Solution

The data required to make a material and an energy balance are as follows:

From Appendix I			
NaOH conc.	Temp. (°F)	$\Delta\hat{H}$ (Btu/lb)	From the steam tables
73	350	468	$\Delta\hat{H}$ of liquid H_2O = 48 Btu/lb
10	80	42	$\Delta\hat{H}$ of ice = −143 Btu/lb (i.e., minus the heat of fusion)

We can make a material balance first. Assume a steady state adiabatic flow process occurs.

Basis: 100 lb of 73% NaOH at 350°F

NaOH balance: $100(0.73) = P(0.10)$ hence $P = 730$ lb

Total balance: $100 + W + I = P = 730$

Hence water plus ice added $= 730 - 100 = 630$ lb.

Next we make an energy balance; the process is steady state, so that

$$\Delta H_{\text{overall}} = 0 \qquad \text{or} \qquad \Delta H_{\text{in}} = \Delta H_{\text{out}}$$

To differentiate between the ice and the liquid water added, let us designate the ice as I lb, and then the H_2O becomes $(630 - I)$ lb:

In *Out*

$$\overbrace{\frac{100\ \text{lb}}{} \bigg| \frac{468\ \text{Btu}}{\text{lb}}}^{\textbf{73\% NaOH solution}} + \overbrace{\frac{(630 - I)\text{lb}}{} \bigg| \frac{48\ \text{Btu}}{\text{lb}}}^{\mathbf{H_2O}} + \overbrace{\frac{I\ \text{lb}}{} \bigg| \frac{-143\ \text{Btu}}{\text{lb}}}^{\textbf{ice}} = \overbrace{\frac{730\ \text{lb}}{} \bigg| \frac{42\ \text{Btu}}{\text{lb}}}^{\textbf{10\% NaOH solution}}$$

$$46{,}800 + 30{,}240 - 191I = 30{,}660$$

$$I = 243 \text{ lb ice at } 32°\text{F}$$

$$\text{liquid } H_2O \text{ at } 80°\text{F} = 387 \text{ lb}$$

EXAMPLE 4.44 Application of the Enthalpy–Concentration Chart

Six hundred pounds of 10% NaOH per hour at 200°F are added to 400 lb/hr of 50% NaOH at the boiling point. Calculate the following:

- **(a)** The final temperature of the exit solution
- **(b)** The final concentration of the exit solution
- **(c)** The pounds of water evaporated per hour during the process

Solution

Basis: 1000 lb of final solution ≡ 1 hr

Use the same NaOH–H_2O enthalpy–concentration chart as in Example 4.43 to obtain the enthalpy data. We can write the following material balance:

Component	*10% solution*	+	*50% solution*	=	*Final solution*	*wt %*
NaOH	60		200		260	26
H_2O	540		200		740	74
Total	600		400		1000	100

Next, the energy (enthalpy) balance (in Btu) is

Data:

	10% solution	*50% solution*
$\Delta\hat{H}$ (Btu/lb):	152	290

10% solution		*50% solution*		*Final solution*
600(152)	+	400(290)	=	ΔH
91,200	+	116,000	=	207,200

Note that the enthalpy of 50% solution at its boiling point is taken from the bubble-point curve at $\omega = 0.50$. The enthalpy per pound is

$$\frac{207{,}200 \text{ Btu}}{1000 \text{ lb}} = 207 \text{ Btu/lb}$$

On the enthalpy–concentration chart for NaOH–H_2O, for a 26% NaOH solution with an enthalpy of 207 Btu/lb, you would find that only a two-phase mixture of (1) saturated H_2O vapor and (2) NaOH–H_2O solution at the boiling point could exist. To get the fraction H_2O vapor, we have to make an additional energy (enthalpy) balance. By interpolation, draw the tie line through the point $x = 0.26$, $H = 207$ (make it parallel to the 220° and 250°F tie lines). The final temperature appears from Fig. E4.44 to be 232°F; the enthalpy of the liquid at the bubble point is about 175 Btu/lb. The enthalpy of the saturated water vapor (no NaOH is in the vapor phase) from the steam tables at 232°F is 1158 Btu/lb. Let x = lb of H_2O evaporated.

Basis: 1000 lb of final solution

$$x(1158) + (1000 - x)175 = 1000(207.2)$$

$$x = 32.6 \text{ lb of } H_2O \text{ evaporated/hr}$$

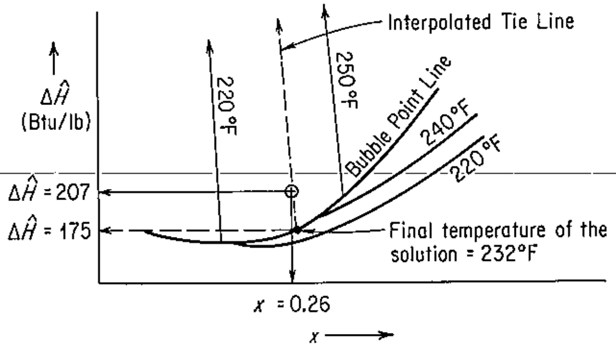


Figure E4.44

EXAMPLE 4.45 Nonadiabatic Equilibrium Vaporization

Enthalpy–concentration charts help make vaporization problems easy to solve. According to the phase rule $F = C - \mathcal{P} + 2$, and for a binary mixture of two phases without reaction, $C = 2$, $\mathcal{P} = 2$, and $F = 2$. If the pressure is fixed at some value, only one more intensive needs to be specified to fix completely the state and other properties of the system. In vaporization, suppose that you continuously feed a vapor–liquid mixture of known composition and temperature to a flash drum, and produce as product saturated liquid and vapor, the latter being of some preset composition. If the vapor is saturated and the mass fraction is given, the temperature of the vapor and liquid and all the other properties of the two products are fixed.

For example, suppose that 1000 lb/hr of a saturated liquid–vapor mixture of NH_3–H_2O at 200°F with an overall mass fraction for the combined phases of 30% NH_3 *by weight* is fed to a flash drum operating at 50 psia. If the exit saturated vapor is to be produced with a composition of 90% *by weight,* what is the composition of the saturated liquid product, the temperature of both phases, and the Btu/hr of heat added to or removed from the process if the products are at equilibrium? Use the ammonia–water chart in Appendix I for the data. See Fig. E4.45.

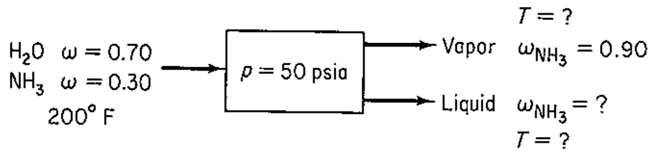


Figure E4.45

Solution

We will just sketch the details of the solution here, skipping the 10-step procedure to save space. At 50 psia, the following data can be retrieved from the ammonia–water chart (the values are not precise because the chart is so small):

	$\Delta\hat{H}$ (Btu/lb mixture)	ω_{NH_3}	T (°F)
Entering mixture	305	0.30	200
Exit vapor	800	0.90	160
Exit liquid	80	0.24	160

To get the data, you need to draw a 200°F tie line and a tie line line from $\omega = 0.90$ for the saturated vapor, both at 50 psia. We also must calculate the lb of liquid and vapor in the product in order to make an energy balance. Let the basis be 1 hr = 1000 lb material.

The material balances are

$$\text{Total:} \quad 1000 = V + L$$

$$NH_3\text{:} \quad 1000(0.30) = V(0.90) + L(0.24)$$

$$V = 91 \text{ lb} \qquad L = 909 \text{ lb}$$

The energy balance reduces to

$$Q = \Delta H = 909(80) + 91(800) - 1000(305) = -159{,}000 \text{ Btu/hr}$$

Heat must be removed.

Enthalpy changes can also be calculated using graphical techniques that are described in texts treating the unit operations of chemical engineering.

Self-Assessment Test

1. Use the NH_3–H_2O enthalpy–concentration chart in Appendix I to determine for 1 atm pressure what the mass fraction ammonia is at equilibrium in the gas and liquid phases for a liquid temperature of 130°F.
2. Estimate the heat of vaporization of an ethanol–water mixture at 1 atm and an ethanol mass fraction of 0.50 from the enthalpy–concentration chart in Appendix I.

3. Prepare an enthalpy–concentration chart for ethanol and water using the data in Table I.1 similar to the one in Appendix I for the acetic acid–water system.
4. For the sulfuric acid–water system, what are the phase(s), composition(s), and enthalpy(ies) existing at $\hat{H} = 120$ Btu/lb and $T = 260°\text{F}$?

4.9 HUMIDITY CHARTS AND THEIR USE

Your objectives in studying this section are to be able to:

1. Define humidity, humid heat, humid volume, dry-bulb temperature, wet-bulb temperature, humidity chart, moist volume, and adiabatic cooling line.
2. Explain and show by use of equations why the slope of the wet-bulb lines are the same as the adiabatic cooling lines for water–air mixtures.
3. Prepare a humidity chart given relations for the heat capacities of air and water.
4. Use the humidity chart to determine the properties of moist air, and to calculate enthalpy changes and solve heating and cooling problems involving moist air.

In Chap. 3 we discussed humidity, condensation, and vaporization. In this section we apply simultaneous material and energy balances to solve problems involving humidification, air conditioning, water cooling, and the like. Before proceeding, you should review briefly the sections in Chap. 3 dealing with vapor pressure and partial saturation.

Recall that the *humidity* $\mathcal{H}$ is the mass (lb or kg) of water vapor per mass (lb or kg) of bone-dry air (some texts use moles of water vapor per mole of dry air as the humidity)

$$\mathcal{H} = \frac{18 p_{H_2O}}{29(p_T - p_{H_2O})} = \frac{18 n_{H_2O}}{29(n_T - n_{H_2O})} \tag{4.57}$$

Table 4.13 lists some of the pertinent notation and data needed in preparing humidity charts.

You will also find it indispensable to learn the following definitions and relations.

(a) The ***humid heat*** is the heat capacity of an air–water vapor mixture expressed on the *basis of 1 lb or kg of bone-dry air*. Thus the humid heat C_S is

$$C_S = C_{p\,\text{air}} + (C_{p_{H_2O\,\text{vapor}}})(\mathcal{H}) \tag{4.58}$$

TABLE 4.13 Pertinent Data for Humidity Charts

Symbol	Meaning	SI value	American engineering value
$C_{p_{\text{air}}}$	Heat capacity of air	1.00 kJ/(kg)(K)	0.24 Btu/(lb)(°F)
$C_{p_{H_2O\ \text{vapor}}}$	Heat capacity of water vapor	1.88 kJ/(kg)(K)	0.45 Btu/(lb)(°F)
$\Delta\hat{H}_{\text{vap}}$	Specific heat of vaporization of water at 0°C (32°F)	4502 kJ/kg	1076 Btu/lb
$\Delta\hat{H}_{\text{air}}$	Specific enthalpy of air		
$\Delta\hat{H}_{H_2O\ \text{vapor}}$	Specific enthalpy of water vapor		

where the heat capacities are all per mass and not per mole. Assuming that the heat capacities of air and water vapor are constant under the narrow range of conditions experienced for air-conditioning and humidification calculations, we can write in American engineering units

$$C_S = 0.240 + 0.45(\mathcal{H}) \qquad \text{Btu/(°F)(lb dry air)} \tag{4.59}$$

or in SI units,

$$C_S' = 1.00 + 1.88(\mathcal{H}) \qquad \text{kJ/(K)(kg dry air)} \tag{4.59a}$$

(b) The ***humid volume*** is the volume of 1 lb or kg of dry air plus the water vapor in the air. In the American engineering system.

$$\begin{aligned}\hat{V} &= \begin{array}{c|c|c} 359\ \text{ft}^3 & 1\ \text{lb mol air} & T_{°F} + 460 \\ \hline 1\ \text{lb mol} & 29\ \text{lb air} & 32 + 460 \end{array} \\ &\quad + \begin{array}{c|c|c|c} 359\ \text{ft}^3 & 1\ \text{lb mol } H_2O & T_{°F} + 460 & \mathcal{H}\ \text{lb } H_2O \\ \hline 1\ \text{lb mol} & 18\ \text{lb } H_2O & 32 + 460 & \text{lb air} \end{array} \\ &= (0.730T_{°F} + 336)\left(\frac{1}{29} + \frac{\mathcal{H}}{18}\right)\end{aligned} \tag{4.60}$$

where $\hat{V}$ is in ft^3/lb dry air. In the SI system,

$$\begin{aligned}\hat{V} &= \begin{array}{c|c|c} 22.4\ \text{m}^3 & 1\ \text{kg mol air} & T_K \\ \hline 1\ \text{kg mol} & 29\ \text{kg air} & 273 \end{array} \\ &\quad + \begin{array}{c|c|c|c} 22.4\ \text{m}^3 & 1\ \text{kg mol } H_2O & T_K & \mathcal{H}\ \text{kg } H_2O \\ \hline 1\ \text{kg mol} & 18\ \text{kg } H_2O & 273 & \text{kg air} \end{array} \\ &= 2.83 \times 10^{-3}T_K + 4.56 \times 10^{-3}\mathcal{H}\end{aligned} \tag{4.60a}$$

where $\hat{V}$ is in m^3/kg dry air.

(c) The ***dry-bulb temperature*** (T_{DB}) is the ordinary temperature you always have been using for a gas in °F or °C (or °R or K).

(d) The ***wet-bulb temperature*** (T_{WB}) you may guess, even though you may never have heard of this term before, has something to do with water (or other liquid, if we are concerned not with humidity but with saturation) evaporating from around an ordinary mercury thermometer bulb. Suppose that you put a wick, or porous cotton cloth, on the mercury bulb of a thermometer and wet the wick. Next you either (1) whirl the thermometer in the air as in Fig. 4.23 (this apparatus is called a sling psychrometer when the wet-bulb and dry-bulb thermometers are mounted together), or (2) set up a fan to blow rapidly on the bulb at 1000 ft^3/min or more. What happens to the temperature recorded by the wet-bulb thermometer?

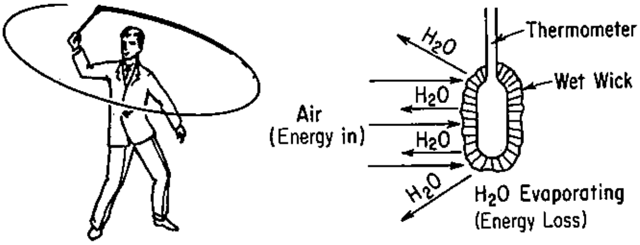


Figure 4.23 Wet-bulb temperature obtained with a sling psychrometer.

As the water from the wick evaporates, the wick cools down and continues to cool until the rate of energy transferred to the wick by the air blowing on it equals the rate of loss of energy caused by the water evaporating from the wick. We say that the temperature of the bulb with the wet wick at equilibrium is the wet-bulb temperature. (Of course, if water continues to evaporate, it eventually will all disappear, and the wick temperature will rise.) The equilibrium temperature for the process described above will lie on the 100% relative humidity curve (saturated-air curve).

Suppose that we prepare a graph on which the vertical axis is the humidity and the horizontal axis is the dry-bulb temperature. We want to plot the temperature of the thermometer as it changes to reach T_{WB}. This line is the so called **wet-bulb line.**

The equation for the wet-bulb lines is based on a number of assumptions, a detailed discussion of which is beyond the scope of this book. Nevertheless, the idea of the wet-bulb temperature is based on the equilibrium between the *rates* of energy transfer to the bulb and evaporation of water. Rates of processes are a topic that we have not discussed. The fundamental idea is that a large amount of air is brought into contact with a little bit of water and that presumably the evaporation of the water leaves the temperature and humidity of the air unchanged. Only the temperature of the water changes. The equation of the wet-bulb line is an energy balance

$$\underbrace{h_c(T - T_{WB})}_{\text{heat transfer to water}} = \underbrace{k'_g\,\Delta\hat{H}_{vap}(\mathcal{H}_{WB} - \mathcal{H})}_{\text{heat transfer from water}} \tag{4.61}$$

where h_c = heat transfer coefficient for convection to the bulb
T = temperature of moist air
k'_g = mass transfer coefficient
$\Delta\hat{H}_{vap}$ = latent heat of vaporization
$\mathcal{H}$ = humidity of moist air

Next, we can form the ratio

$$\frac{\mathcal{H}_{\mathrm{WB}} - \mathcal{H}}{T_{\mathrm{WB}} - T} = -\frac{h_c}{(k_g')\Delta\hat{H}_{\mathrm{vap}}} \tag{4.62}$$

to get the slope of the wet bulb line. For water only, it so happens that $h_c/k_g' \simeq C_S$ (i.e., the numerical value is about 0.25), which gives the wet-bulb lines the slope of

$$\frac{\mathcal{H}_{\mathrm{WB}} - \mathcal{H}}{T_{\mathrm{WB}} - T} = -\frac{C_S}{\Delta\hat{H}_{\mathrm{vap}}} \tag{4.63}$$

For other substances, the value of h_c/k_g' can be as much as twice the value of C_S for water.

Figure 4.24 shows the plot of the wet-bulb line as $T_{\mathrm{DB}} \rightarrow T_{\mathrm{WB}}$. The line is approximately straight and has a negative slope. Does this result agree with Eq. (4.63)?

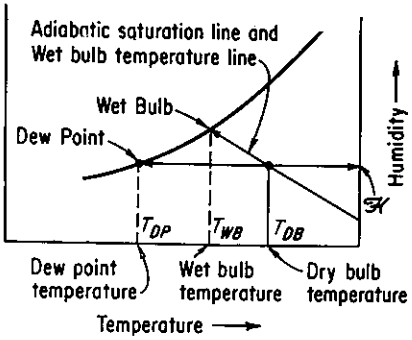


Figure 4.24 General layout of the humidity chart showing the location of the wet-bulb and dry-bulb temperatures, the dew point and dew-point temperature, and the adiabatic saturation line and wet-bulb line.

Another type of process of some importance occurs when adiabatic cooling or humidification takes place between air and water that is recycled as illustrated in Fig. 4.25. In this process the air is both cooled and humidified (its water content rises) while a little bit of the recirculated water is evaporated. At *equilibrium,* in the steady state, the temperature of the air is the same as the temperature of the water, and the exit air is saturated at this temperature. By making an overall energy balance around the process ($Q = 0$), we can obtain the equation for the adiabatic cooling of the air.

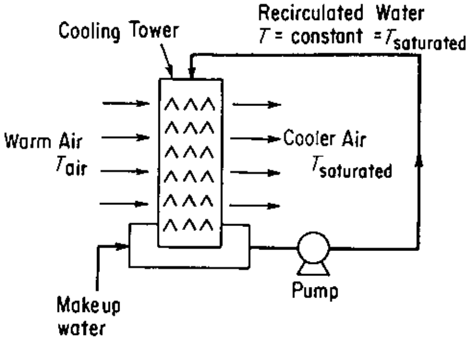


Figure 4.25 Adiabatic humidification with recycle of water.

The equation, when plotted on the humidity chart, yields what is known as an adiabatic cooling line. We take the equilibrium temperature of the water, T_S, as a reference temperature rather than 0°C or 32°F. Do you see why? We ignore the small amount of makeup water or assume that it enters at T_S. The energy balance is

$$\overbrace{C_{p\,\text{air}}(T_{\text{air}} - T_S)}^{\substack{\text{enthalpy of air}\\ \text{entering}}} + \overbrace{\mathcal{H}_{\text{air}}[\Delta\hat{H}_{\text{vap}\,\text{H}_2\text{O}\,\text{at}\,T_S} + C_{p\,\text{H}_2\text{O vapor}}(T_{\text{air}} - T_S)]}^{\substack{\text{enthalpy of water vapor}\\ \text{in air entering}}} \tag{4.64}$$

$$= \overbrace{C_{p\,\text{air}}(T_S - T_S)}^{\substack{\text{enthalpy of air}\\ \text{leaving}}} + \overbrace{\mathcal{H}_S[\Delta\hat{H}_{\text{vap}\,\text{H}_2\text{O}\,\text{at}\,T_S} + C_{p\,\text{H}_2\text{O vapor}}(T_S - T_S)]}^{\substack{\text{enthalpy of water vapor}\\ \text{in air leaving}}}$$

Equation (4.64) can be reduced to

$$T_{\text{air}} = \frac{\Delta\hat{H}_{\text{vap}\,\text{H}_2\text{O}\,\text{at}\,T_S}(\mathcal{H}_S - \mathcal{H}_{\text{air}})}{C_{p\,\text{air}} + C_{p\,\text{H}_2\text{O vapor}}\,\mathcal{H}_{\text{air}}} + T_S \tag{4.65}$$

which is the equation for adiabatic cooling.

Notice that this equation can be written as

$$\frac{\mathcal{H}_S - \mathcal{H}}{T_S - T_{\text{air}}} = -\frac{C_S}{\Delta\hat{H}_{\text{vap at}\,T_S}} \tag{4.66}$$

Compare Eq. (4.66) with Eq. (4.63). Can you conclude that the wet-bulb process equation, for water only, is essentially the same as the adiabatic cooling equation?

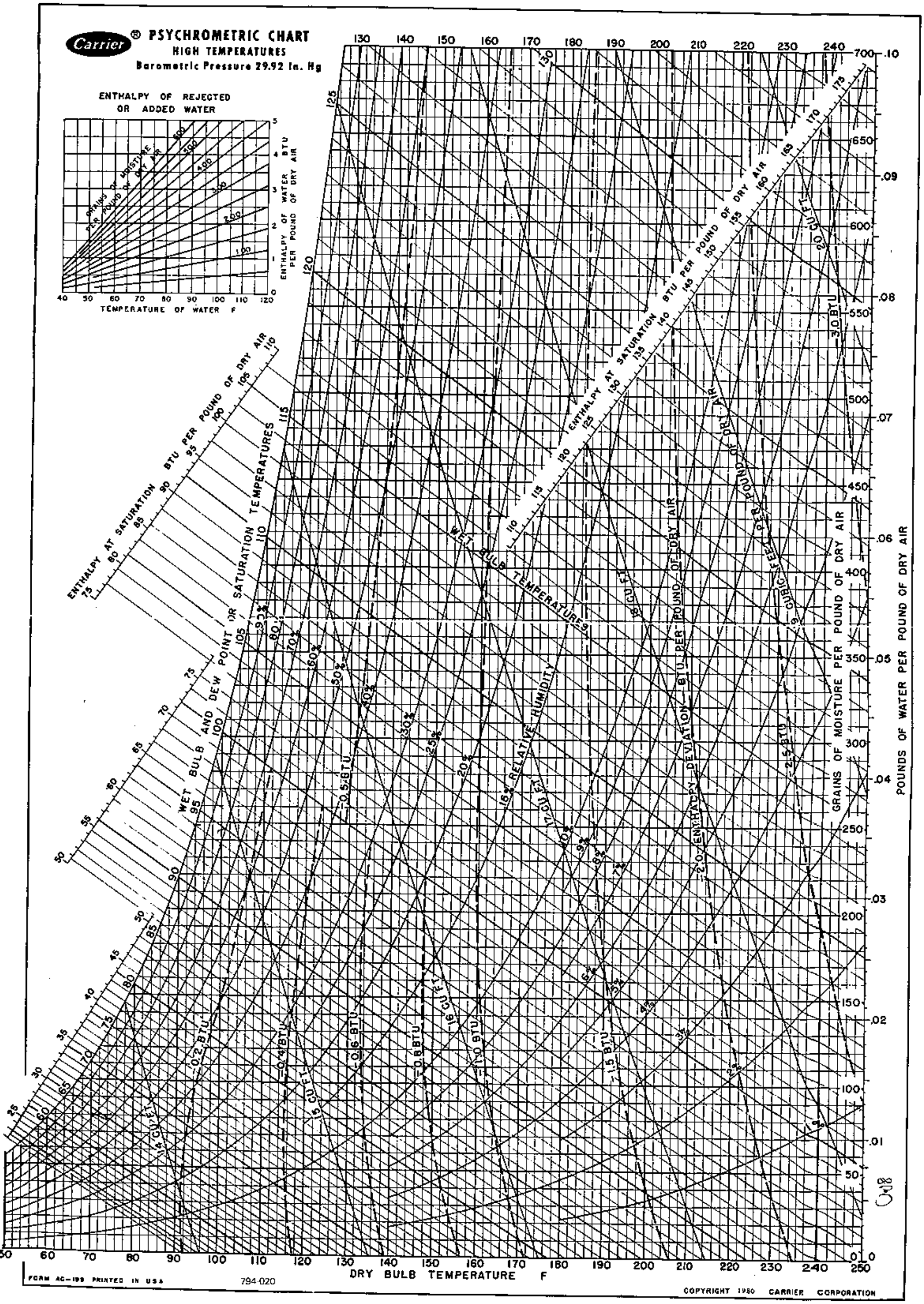
Of course! We have the nice feature that two processes can be represented by the same set of lines. For a detailed discussion of the uniqueness of this coincidence, consult any of the references at the end of the chapter. For most other substances besides water, the two equations will have different slopes.

Now that you have an idea of what the various features portrayed on the ***humidity chart*** (psychrometric chart) are, let us look at the chart itself (Fig. 4.26). It is nothing more than a graphical means to assist in the presentation of material and energy balances in water vapor–air mixtures and various associated parameters. Its skeleton consists of a humidity ($\mathcal{H}$)-temperature (T_{DB}) set of coordinates together with the additional parameters (lines) of

- **(a)** Constant relative humidity indicated in percent
- **(b)** Constant moist volume (humid volume)
- **(c)** Adiabatic cooling lines which are the same (for water vapor only) as the wet-bulb or psychrometeric lines
- **(d)** The 100% relative humidity (identical to the 100% absolute humidity) curve (i.e., saturated-air curve)

With any two values known, you can pinpoint the air-moisture condition on the chart and determine all the other associated values.

Off to the left of the 100% relative humidity line you will observe scales showing the enthalpy per mass of dry air of a saturated air–water vapor mixture. Enthalpy



0.357.

Figure 4.26a (Reprinted by permission of Carrier Corporation.)

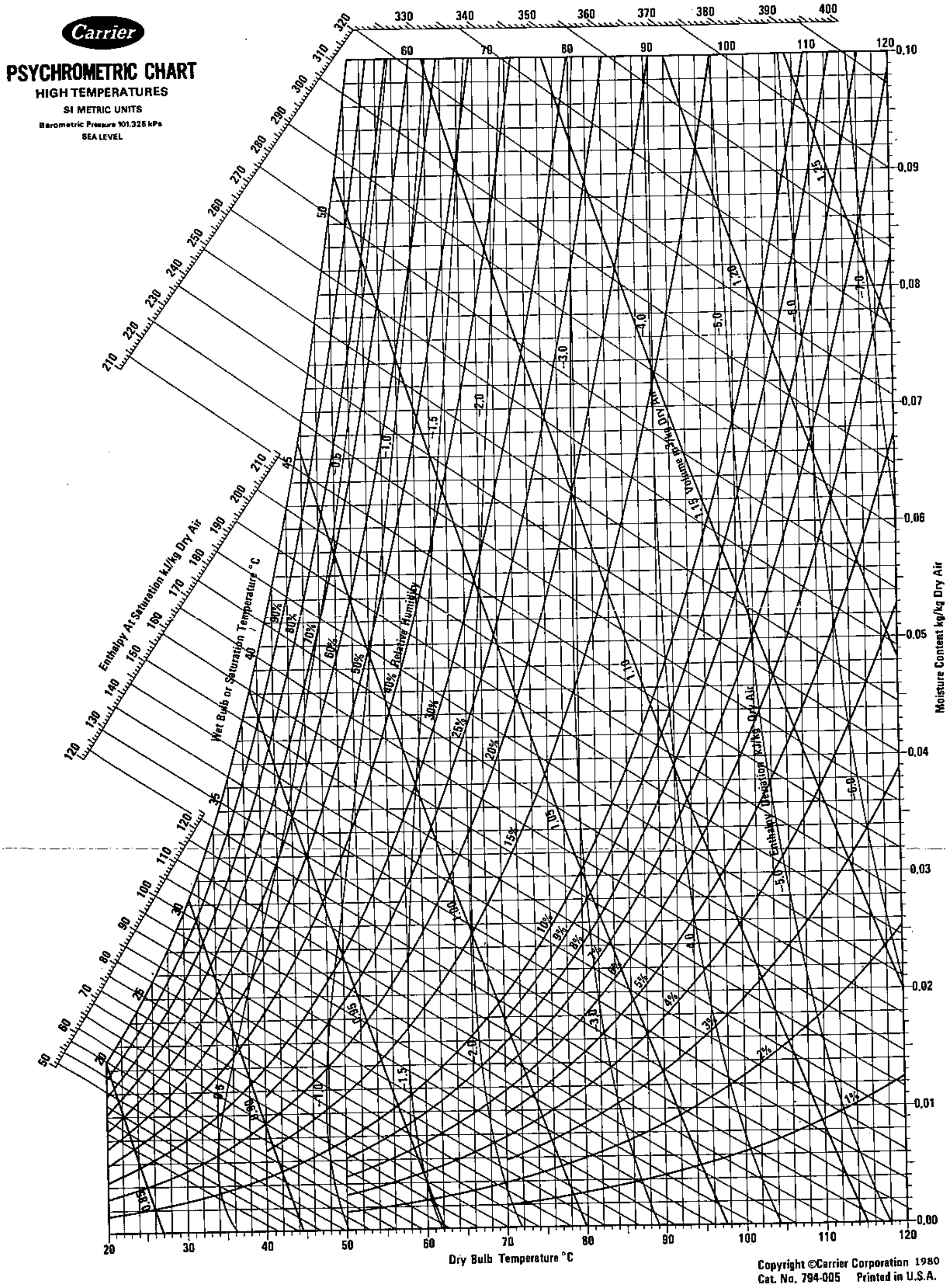


Figure 4.26b (Reprinted by permission of Carrier Corporation.)

adjustments for air less than saturated (identified by minus signs) are shown on the chart itself by a series of curves. The enthalpy of the wet air, in energy/mass of dry air, is

$$\Delta\hat{H} = \Delta\hat{H}_{\text{air}} + \Delta\hat{H}_{\text{H}_2\text{O vapor}}(\mathcal{H})$$

We should mention at this point that the reference conditions for the humidity chart are liquid water at 32°F (0°C) and 1 atm (not the vapor pressure of H_2O) for water, and 0°F and 1 atm for air. The chart is suitable for use only at normal atmospheric conditions and must be modified[27] if the pressure is significantly different than 1 atm. If you wanted to, you could calculate the enthalpy values shown on the chart directly from tables listing the enthalpies of air and water vapor or you could compute the enthalpies with reasonable accuracy from the following equation

$$\Delta\hat{H} = \underbrace{C_{p\text{air}}(T - T_{\text{ref}})_{\text{air}}}_{\text{enthalpy for air}} + \underbrace{\mathcal{H}[\overset{\substack{\text{heat of vaporation}\\ \text{of water at } T_{\text{ref}}}}{\Delta\hat{H}_{\text{vap}}} + C_{p\text{air}}(T - T_{\text{ref}})_{\text{water}}]}_{\text{enthalpy for water vapor}} \qquad (4.67)$$

In American engineering units, Eq. (4.67) is

$$\Delta\hat{H} = 0.240T_{°\text{F}} + \mathcal{H}(1061 + 0.45T_{°\text{F}}) \qquad (4.68)$$

because $C_S = 0.240 + 0.45\mathcal{H}$ and $T_{\text{WB}} = T_S$. Thus the wet-bulb process equation, for water only, is essentially the same as the adiabatic cooling equation. For other materials these two equations have different slopes.

Only two of the quantities in Eq. (4.67) are variables, if T_S is known, because $\mathcal{H}_S$ is the humidity of saturated air at T_S and $\Delta\hat{H}_{\text{vap H}_2\text{O at }T_S}$ is fixed by T_S. Thus, for any value of T_S, you can make a plot of Eqs. (4.65) and/or (4.68) on the humidity chart in the form of $\mathcal{H}$ vs. T_{air}. These curves, which are essentially linear, will intersect the 100% relative humidity curve at $\mathcal{H}_S$ and T_S, as described earlier.

The adiabatic cooling lines are lines of almost constant enthalpy for the entering air–water mixture, and you can use them as such without much error (1 or 2%). However, if you want to correct a saturated enthalpy value for the deviation which exists for a less-than-saturated air–water vapor mixture, you can employ the enthalpy deviation lines which appear on the chart and which can be used as illustrated in the examples below. Any process that is not a wet-bulb process or an adiabatic process with recirculated water can be treated by the usual material and energy balances, taking the basic data for the calculation from the humidity charts. If there is any increase or decrease in the moisture content of the air in a psychrometric process, the small enthalpy effect of the moisture added to the air or lost by the air may be included in the energy balance for the process to make it more exact as illustrated in Examples 4.47 and 4.49.

You can find further details regarding the construction of humidity charts in the references at the end of the chapter. Tables are also available listing all the ther-

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[27] See G. E. McElroy, *U.S. Bur. Mines Rep. Invest. No. 4615,* December 1947, or other Carrier charts. See *Educational Materials,* Carrier Corp., Syracuse, N.Y., 1980.

modynamic properties (p, $\hat{V}$, $\mathcal{H}$, and $\Delta\hat{H}$) in great detail.[28] Although we shall be discussing humidity charts exclusively, charts can be prepared for mixtures of any two substances in the vapor phase, such as CCl_4 and air or acetone and nitrogen, by use of Eqs. (4.57)–(4.67) if all the values of the physical constants for water and air are replaced by those of the desired gas and vapor. The equations themselves can be used for humidity problems if charts are too inaccurate or are not available. In the pocket in the back of this book is a Fortran computer program from which psychrometic data can be retrieved.

EXAMPLE 4.46 Properties of Moist Air from the Humidity Chart

List all the properties you can find on the humidity chart in American engineering units for moist air at a dry-bulb temperature of 90°F and a wet-bulb temperature of 70°F.

Solution

A diagram will help explain the various properties obtained from the humidity chart. See Fig. E4.46. You can find the location of point A for 90°F DB (dry bulb) and 70°F WB (wet bulb) by following a vertical line at T_{DB} = 90°F until it crosses the wet-bulb line for 70°F. This wetbulb line can be located by searching along the 100% humidity line until the saturation temperature of 70°F is reached, or, alternatively, by proceeding up a vertical line at 70°F until it intersects the 100% humidity line. From the wet-bulb temperature of 70°F, follow the adiabatic cooling line (which is the same as the wet-bulb temperature line on the humidity chart) to the right until it intersects the 90°F DB line. Now that point A has been fixed, you can read the other properties of the moist air from the chart.

(a) *Dew point*. When the air at A is cooled at constant pressure (and in effect at *constant humidity*), as described in Chap. 3, it eventually reaches a temperature at which the moisture begins to condense. This is represented by a horizontal line, a constant-humidity line, on the humidity chart, and the dew point is located at B, or about 60°F.

(b) *Relative humidity*. By interpolating between the 40% $\mathcal{RH}$ and 30% $\mathcal{RH}$ lines you can find that point A is at about 37% $\mathcal{RH}$.

(c) *Humidity* ($\mathcal{H}$). You can read the humidity from the right-hand ordinate as 0.0112 lb H_2O/lb dry air.

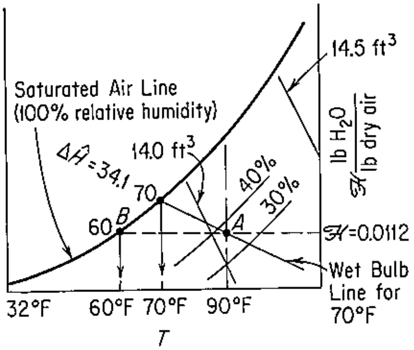

Figure E4.46

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[28] Byron Engelbach, *Microfilms of Psychrometric Tables*, University Microfilms, Ann Arbor, Mich., 1953.

(d) *Humid volume*. By interpolation again between the 14.0- and the 14.5-ft^3 lines, you can find the humid volume to be 14.097 ft^3/lb dry air.

(e) *Enthalpy*. The enthalpy value for saturated air with a wet-bulb temperature of 70°F is $\Delta\hat{H} = 34.1$ Btu/lb dry air (a more accurate value can be obtained from psychrometric tables if needed). The enthalpy deviation (not shown in Fig. E4.46—see Fig. 4.26) for less-than-saturated air is about -0.2 Btu/lb of dry air; consequently, the actual enthalpy of air at 37% $\mathcal{RH}$ is $34.1 - 0.2 = 33.9$ Btu/lb of dry air.

EXAMPLE 4.47 Heating at Constant Humidity

Moist air at 38°C and 48% $\mathcal{RH}$ is heated in your furnace to 86°C. How much heat has to be added per cubic meter of initial moist air, and what is the final dew point of the air?

Solution

As shown in Fig. E4.47, the process goes from point *A* to point *B* on a horizontal line of constant humidity. The initial conditions are fixed at $T_{DB} = 38°\text{C}$ and 48% $\mathcal{RH}$. Point *B* is fixed by the intersection of the horizontal line from *A* and the vertical line at 86°C. The dew point is unchanged in this process and is located at *C* at 24.8°C.

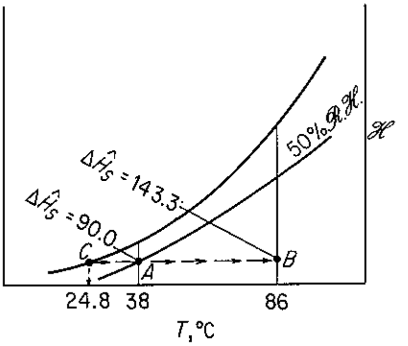

Figure E4.47

The enthalpy values are as follows (all in kJ/kg of dry air):

Point	$\Delta\hat{H}_{\text{satd}}$	δH	$\Delta\hat{H}_{\text{actual}}$
A	90.0	−0.5	89.5
B	143.3	−3.3	140.0

Also, at *A* the volume of the moist air is 0.91 m^3/kg of dry air. Consequently, the heat added is $(Q = \Delta\hat{H})140.0 - 89.5 = 50.5$ kJ/kg of dry air.

$$\frac{50.5\text{ kJ}}{\text{kg dry air}}\left|\frac{1\text{ kg dry air}}{0.91\text{ m}^3}\right. = 55.5\text{ kJ/m}^3\text{ initial moist air}$$

EXAMPLE 4.48 Cooling and Humidification

One way of adding moisture to air is by passing it through water sprays or air washers. See Fig. 4.48a. Normally, the water used is recirculated rather than wasted. Then, in the steady state, the water is at the adiabatic saturation temperature, which is the same as the wet-bulb

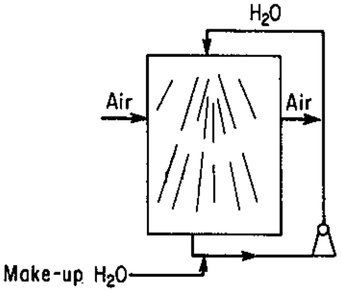

Figure E4.48a

temperature. The air passing through the washer is cooled, and if the contact time between the air and the water is long enough, the air will be at the wet-bulb temperature also. However, we shall assume that the washer is small enough so that the air does not reach the wet-bulb temperature; instead, the following conditions prevail:

	T_{DB}(°C)	T_{WB}(°C)
Entering air:	40	22
Exit air:	27	

Find the moisture added per kilogram of dry air.

Solution

The whole process is assumed to be *adiabatic*, and, as shown in Fig. E4.48b, takes place between points *A* and *B* along the adiabatic cooling line. The wet-bulb temperature remains constant at 22°C. Humidity values are

	$\mathcal{H}\left(\frac{\text{kg H}_2\text{O}}{\text{kg dry air}}\right)$	
B	0.0145	
A	0.0093	
Difference:	$0.0052 \frac{\text{kg H}_2\text{O}}{\text{kg dry air}}$	added

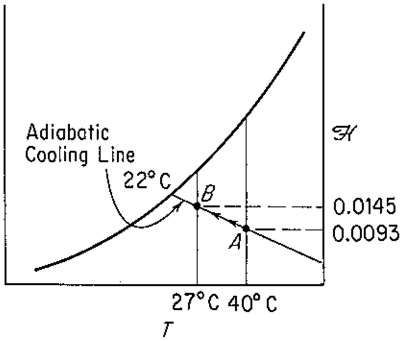

Figure E4.48b

EXAMPLE 4.49 Cooling and Dehumidification

A process that takes moisture out of the air by passing the air through water sprays sounds peculiar but is perfectly practical as long as the water temperature is below the dew point of the air. Equipment such as shown in Fig. E4.49a would do the trick. If the entering air has a dew point of 70°F and is at 40% $\mathcal{RH}$, how much heat has to be removed by the cooler, and how much water vapor is removed, if the exit air is at 56°F with a dew point of 54°F?

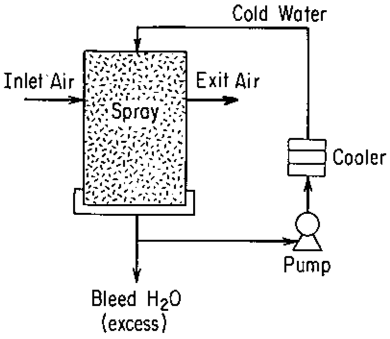

Figure E4.49a

Solution

From Fig. 4.26 in American engineering units the initial and final values of the enthalpies and humidities are

	A	B
$\mathcal{H}\left(\frac{\text{grains } H_2O}{\text{lb dry air}}\right)$	111	62
$\Delta\hat{H}\left(\frac{\text{Btu}}{\text{lb dry air}}\right)$	41.3 − 0.2 = 41.1	23.0 − 0 = 23.0

Look at Fig. E4.49b for the relative positions of *A* and *B*. The grains of H_2O removed are

$$111 - 62 = 49 \text{ grains/lb dry air}$$

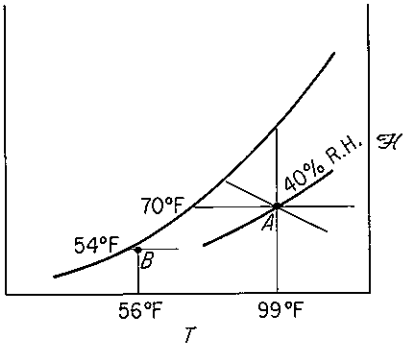

Figure E4.49b

The cooling duty is approximately

$$41.1 - 23.0 = 18.1 \text{ Btu/lb dry air}$$

In the upper left of the humidity chart is a little insert that gives the value of the small correction factor for the water condensed from the air which leaves the system. Assuming that the water leaves at the dew point of 54°F, read for 49 grains a correction of −0.15 Btu/lb of dry air. You could calculate the same value by taking the enthalpy of liquid water from the steam tables and saying,

$$\begin{array}{c|c|c} 22\text{ Btu} & 1\text{ lb H}_2\text{O} & 49\text{ grains rejected} \\ \hline \text{lb H}_2\text{O} & 7000\text{ grains} & 1\text{ lb dry air} \end{array} = 0.154\text{ Btu/lb dry air}$$

The energy (enthalpy) balance will then give us the cooling load:

$$\overbrace{41.1}^{\substack{\Delta H\\ \text{air in}}} - \overbrace{23.0}^{\substack{\Delta H\\ \text{air out}}} - \overbrace{0.15}^{\substack{\Delta H\\ \text{H}_2\text{O out}}} = 17.9\text{ Btu/lb dry air}$$

EXAMPLE 4.50 Combined Material and Energy Balances for a Cooling Tower

You have been requested to redesign a water-cooling tower that has a blower with a capacity of 8.30×10^6 ft³/hr of moist air (at 80°F and a wet-bulb temperature of 65°F). The exit air leaves at 95°F and 90°F wet bulb. How much water can be cooled in pounds per hour if the water to be cooled is not recycled, enters the tower at 120°F, and leaves the tower at 90°F?

Solution

Enthalpy, humidity, and humid volume data for the air taken from the humidity chart are as follows (see Fig. E4.50):

	A	*B*
$\mathcal{H}\left(\dfrac{\text{lb H}_2\text{O}}{\text{lb dry air}}\right)$	0.0098	0.0297
$\mathcal{H}\left(\dfrac{\text{grains H}_2\text{O}}{\text{lb dry air}}\right)$	69	208
$\Delta\hat{H}\left(\dfrac{\text{Btu}}{\text{lb dry air}}\right)$	$30.05 - 0.12 = 29.93$	$55.93 - 0.10 = 55.83$
$\hat{V}\left(\dfrac{\text{ft}^3}{\text{lb dry air}}\right)$	13.82	14.65

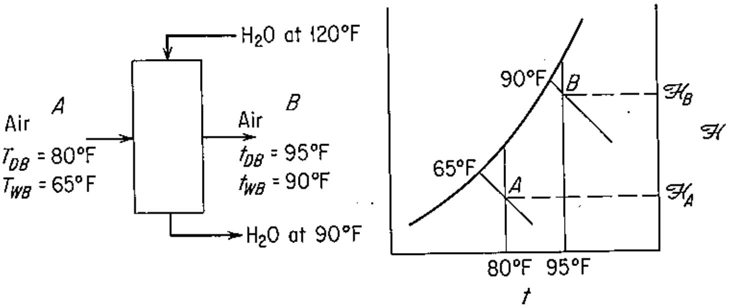

Figure E4.50

The cooling-water exit rate can be obtained from an energy balance around the process.

Basis: 8.30×10^6 ft^3/hr of moist air

$$\begin{array}{c|c} 8.30 \times 10^6\ \text{ft}^3 & \text{lb dry air} \\ \hline \text{hr} & 13.82\ \text{ft}^3 \end{array} = 6.00 \times 10^5\ \text{lb dry air/hr}$$

The relative enthalpy of the entering water stream is (reference temperature is 32°F and 1 atm)

$$\Delta\hat{H} = C_{p_{H_2O}}\,\Delta T = 1(120 - 32) = 88\ \text{Btu/lb}\ H_2O$$

and that of the exit stream is 58 Btu/lb H_2O. [The value from the steam tables at 120°F for liquid water of 87.92 Btu/lb H_2O is slightly different since it represents water at its vapor pressure (1.69 psia) based on reference conditions of 32°F and liquid water at its vapor pressure.] Any other datum could be used instead of 32°F for the liquid water. For example, if you chose 90°F, one water stream would not have to be taken into account because its relative enthalpy would be zero.

The loss of water to the air is

$$0.0297 - 0.0098 = 0.0199\ \text{lb}\ H_2O/\text{lb dry air}$$

(a) *Material balance for water stream:* Let W = lb H_2O entering the tower in the water stream per lb dry air. Then

$$W - 0.0199 = \text{lb}\ H_2O\ \text{leaving tower in the water stream per lb dry air}$$

(b) *Energy balance (enthalpy balance) around the entire process:*

air and water in air entering **water stream entering**

$$\begin{array}{c|c} 29.93\ \text{Btu} & 6.00 \times 10^5\ \text{lb dry air} \\ \hline \text{lb dry air} & \end{array} + \begin{array}{c|c|c} 88\ \text{Btu} & W\ \text{lb}\ H_2O & 6.00 \times 10^5\ \text{lb dry air} \\ \hline \text{lb}\ H_2O & \text{lb dry air} & \end{array}$$

air and water in air leaving

$$= \begin{array}{c|c} 55.83\ \text{Btu} & 6.00 \times 10^5\ \text{lb dry air} \\ \hline \text{lb dry air} & \end{array}$$

water stream leaving

$$+ \begin{array}{c|c|c} 58\ \text{Btu} & (W - 0.0199)\text{lb}\ H_2O & 6.00 \times 10^5\ \text{lb dry air} \\ \hline \text{lb}\ H_2O & \text{lb dry air} & \end{array}$$

$$29.93 + 88W = 55.83 + 58(W - 0.0199)$$

$$W = 0.825\ \text{lb}\ H_2O/\text{lb dry air}$$

$$W - 0.0199 = 0.805\ \text{lb}\ H_2O/\text{lb dry air}$$

The total water leaving the tower is

$$\begin{array}{c|c} 0.805\ \text{lb}\ H_2O & 6.00 \times 10^5\ \text{lb dry air} \\ \hline \text{lb dry air} & \text{hr} \end{array} = 4.83 \times 10^5\ \text{lb/hr}$$

Self-Assessment Test

1. What is the difference between the wet- and dry-bulb temperatures?
2. Can the wet-bulb temperature ever be higher than the dry-bulb temperature?
3. Explain why the slope of the wet-bulb lines are essentially the same as the slope of the adiabatic cooling lines for gaseous air and water mixtures.
4. Estimate for air at 70°C dry-bulb temperature, 1 atm, and 15% relative humidity the:
   (a) kg H_2O/kg of dry air
   (b) m^3/kg of dry air
   (c) Wet-bulb temperature (in °C)
   (d) Specific enthalpy
   (e) Dew point (in °C)
5. Calculate the following properties of moist air at 1 atm and compare with values read from the humidity chart.
   (a) The humidity of saturated air at 120°F
   (b) The enthalpy of air in part (a) per pound of dry air
   (c) The volume per pound of dry air of part (a)
   (d) The humidity of air at 160°F with a wet-bulb temperature of 120°F
6. Humid air at 1 atm and 200°F, and containing 0.0645 lb of H_2O/lb of dry air, enters a cooler at the rate of 1000 lb of dry air per hour (plus accompanying water vapor). The air leaves the cooler at 100°F, saturated with water vapor (0.0434 lb of H_2O/lb of dry air). Thus 0.0211 lb H_2O is condensed per pound of dry air. How much heat is transferred to the cooler?
7. A cooling tower that uses a cold-water spray provides a method of cooling and dehumidifying a school. During the day, the average number of students in the school is 100 and the average heat-generation rate per person is 800 Btu/hr. Suppose that the ambient conditions outside the school in the summer are expected to be 100°F and 95% $\mathcal{RH}$. You run this air through the cooler-dehumidifier and then mix the saturated exit air with recirculated air from the exhaust of the school building. You need to supply the mixed air to the building at 70°F and 60% $\mathcal{RH}$ and keep the recirculated air leaving the building at not more than 72°F. Leakage occurs from the building of the 72°F air also. Calculate:
   (a) The volumetric rate of air recirculation per hour in cubic feet at 70°F and 60% $\mathcal{RH}$
   (b) The volume of fresh air required at entering conditions
   (c) The heat transferred in the cooler-dehumidifier from the inlet air per hour

Thought Problems

1. The use of home humidifiers has recently been promoted in advertisements as a means of providing more comfort in houses with the thermostat turned down. "Humidification makes life more comfortable and prolongs the life of furniture." Many advertisers describe a humidifier as an energy-saving device because it allows lower temperatures (4 or 5°F lower) with comfort.

   Is this true?
2. In cold weather, water vapor exhausted from cooling towers condenses and fog is formed as a plume. What are one or two *economically practical* methods of preventing such cooling tower fog?

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PROBLEMS

An asterisk designates problems appropriate for solution using a computer. Refer also to the problems that require writing computer programs at the end of the chapter.

Section 4.1

4.1. Convert 45.0 Btu/lb_m to the following:

(a) cal/kg **(b)** J/kg

(c) kWh/kg **(d)** (ft)(lb_f)/lb_m

4.2. Convert the following physical properties of liquid water at 0°C and 1 atm from the given SI units to the equivalent values in the listed American engineering units.

(a) Heat capacity of 4.184 J/(g)(K)	Btu/(lb)(°F)
(b) Enthalpy of −41.6 J/kg	Btu/lb
(c) Thermal conductivity of 0.59 (kg)(m)/(s^3)(K)	Btu/(ft)(hr)(°F)

4.3. Convert the following quantities as specified.

(a) A rate of heat flow of 6000 Btu/(hr)(ft^2) to cal/(s)(cm^2).

(b) A heat capacity of 2.3 Btu/(lb)(°F) to cal/(g)(°C)

(c) A thermal conductivity of 200 Btu/(hr)(ft)(°F) to cal/(s)(cm)(°C).

(d) The gas constant, 10.73 (psia)(ft^3)/(lb mol)(°R) to cal/(g mol)(K).

4.4. A simplified equation for the heat transfer coefficient from a pipe to air is

$$h = \frac{0.026G^{0.6}}{D^{0.4}}$$

where h = heat transfer coefficient, Btu/(hr)(ft^2)(°F)
G = mass rate of flow, lb_m/(hr)(ft^2)
D = outside diameter of the pipe, (ft)

If h is to be expressed in J/(min)(cm^2)(°C), what should the new constant in the equation be in place of 0.026?

4.5. A problem for many people in the United States is excess body weight stored as fat. Many persons have tried to capitalize on this problem with fruitless weight-loss schemes. However, since energy is conserved, an energy balance reveals only two real ways to lose weight (other than water loss); (1) reduce the caloric intake, and/or (2) increase the caloric expenditure. In answering the following questions, assume that fat contains approximately 7700 kcal/kg (1 kcal is called a "dietic calorie" in nutrition, or commonly just "calorie").

(a) If a normal diet containing 2400 kcal/day is reduced by 500 kcal/day, how many days does it take to lose 1 lb of fat?

(b) How many miles would you have to run to lose 1 lb of fat if running at a moderate pace of 12 km/hr expends 400 kJ/km?

(c) Suppose that two joggers each run 10 km/day. One runs at a pace of 5 km/hr and the other at 10 km/hr. Which will lose more weight (ignoring water loss)?

4.6. The energy from the sun incident on the surface of the earth averages 2.0 cal/(min)(cm^2). It has been proposed to use space stations in synchronous orbits 36,000 km from earth to collect solar energy. How large a collection surface is needed (in m^2) to obtain 10^{11} watts of electricity? Assume that 10% of the collected energy is converted to electricity. Is this a reasonable size?

4.7. Explain specifically what the system is for each of the following processes; indicate if the energy transfer that takes place is by heat or work (use the symbols Q and W, respectively) or is zero.

(a) A liquid inside a metal can, well insulated on the outside of the can, is shaken very rapidly in a vibrating shaker.

(b) Hydrogen is exploded in a calometric bomb and the water layer outside the bomb rises in temperature by 1°C.

(c) A motor boat is driven by an outboard-motor propeller.

(d) Water flows through a pipe at 1.0 m/min, and the temperature of the water and the air surrounding the pipe are the same.

4.8. Draw a simple sketch of each of the following processes, and, in each, label the system boundary, the system, the surroundings, and the streams of material and energy that cross the system boundary.

(a) Water enters a boiler, is vaporized, and leaves as steam. The energy for vaporization is obtained by combustion of a fuel gas with air outside the boiler surface.

(b) Steam enters a rotary steam turbine and turns a shaft connected to an electric generator. The steam is exhausted at a low pressure from the turbine.

(c) A battery is charged by connecting it to a source of current.

4.9. Draw a simple sketch of the following processes; indicate the system boundary; and classify the system as open or closed.

(a) Automobile engine
(b) Water wheel
(c) Pressure cooker
(d) Human being
(e) River
(f) The earth and its atmosphere
(g) Air compressor
(h) Coffee pot

4.10. Are the following variables intensive or extensive variables? Explain for each.

(a) Pressure
(b) Volume
(c) Specific volume
(d) Refractive index
(e) Surface tension

4.11. Classify the following measurable physical characteristics of a gaseous mixture of two components as (1) an intensive property, (2) an extensive property, (3) both, or (4) neither:

(a) Temperature
(b) Composition
(c) Pressure
(d) Mass

4.12. Find the kinetic energy in $(\text{ft})(\text{lb}_f)/(\text{lb}_m)$ of water moving at the rate of 10 ft/s through a pipe 2 in. ID.

4.13. A windmill converts the kinetic energy of the moving air into electrical energy at an efficiency of about 30%, depending on the windmill design and speed of the wind. Estimate the power in kW for a wind flowing perpendicular to a windmill with blades 15 m in diameter when the wind is blowing at 20 mi/hr at 27°C and 1 atm.

4.14. Before it lands, a vehicle returning from space must convert its enormous kinetic energy to heat. To get some idea of what is involved, a vehicle returning from the moon at 25,000 mi/hr can, in converting its kinetic energy, increase the internal energy of the vehicle sufficiently to vaporize it. Obviously, a large part of the total kinetic energy must be transferred from the vehicle. How much kinetic energy does the vehicle have (in Btu)? How much energy must be transferred by heat if the vehicle is to heat up only 20°F/lb?

4.15. If benzene (sp gr = 0.879) flows at 4630 L/hr with a pressure differential of 3450 kPa, what is the power requirement in watts of the pump (if 100% efficient)?

4.16. If benzene (sp gr = 0.879) flows at 1220 gal/hr and a pressure differential of 500 psia, what is the power requirement of the pump in hp (if 100% efficient)?

4.17. You have a positive-displacement pump with a piston area of 1 m^2. The piston moves 4.63 m/hr to pump 4.63 m^3/hr of fluid. The required force will be 3450 kN. What is the power needed in kW?

4.18. Benzene (sp gr = 0.879) flows through an orifice that is 0.8 cm in diameter at the rate of 4.63 m^3/hr. What is the kinetic energy of the fluid in J/kg?

4.19. You pump benzene at the rate of 1220 gal/hr through an orifice that is 0.315 in.^{2} in diameter. What is the kinetic energy of the fluid in Btu/lb_m?

4.20. Constant advances in laser technology are aiding ongoing research in nuclear fusion at the Lawrence Livermore National Laboratory, California. Lasers are being used to heat deuterium–tritium fuel pellets, causing the surface to explode. The explosion heats and compresses the interior of the pellet, which causes fusion to take place. The laboratory has acquired a new laser system which combines the power of several lasers and has a maximum capability of delivering an energy pulse of 200 to 300 kJ (depending on the frequency of the light) in just one billionth of a second. What is the equivalent range of power expressed in watts?

4.21. The world's largest plant that obtains energy from tidal changes is at Saint Malo, France. The plant uses both the rising and falling cycle (one period in and out is 6 hr 10 min in duration). The tidal range from low to high is 14 m, and the tidal estuary (the LaRance River) is 21 km long with an area of 23 km^2. Assume that the efficiency of the plant in converting potential to electrical energy is 85%, and estimate the average power produced by the plant. (*Note:* Also assume that after high tide, the plant does not release water until the sea level drops 7 m, and after a low tide does not permit water to enter the basin until the level outside the basin rises 7 m, and the level differential is maintained during discharge and charge.)

4.22. Steam is used to cool a polymer reaction. The steam in the steam chest of the apparatus is found to be at 250.5°C and 4000 kPa absolute during a routine measurement at the beginning of the day. At the end of the day the measurement showed that the temperature was 650°C and the pressure 10,000 kPa absolute. What was the internal energy change of 1 kg of steam in the chest during the day? Obtain your data from the steam tables.

4.23. (a) Ten pound moles of an ideal gas are originally in a tank at 100 atm and 40°F. The gas is heated to 440°F. The specific molal enthalpy, $\Delta\hat{H}$, of the ideal gas is given by the equation

$$\Delta\hat{H} = 300 + 8.00T$$

where $\Delta\hat{H}$ is in Btu/lb mol and T is the temperature in °F.

(1) Compute the volume of the container (ft^3).

(2) Compute the final pressure of the gas (atm).

(3) Compute the enthalpy change of the gas.

(b) Use the equation above to develop an equation giving the molal internal energy, ΔU, in cal/g mol as a function of temperature, T, in °C.

4.24. You have calculated that specific enthalpy of 1 kg mol of an ideal gas at 300 kN/m^2 and 100°C is 6.05×10^5 J/kg mol (with reference to 0°C and 100 kN/m^2). What is the specific internal energy of the gas?

4.25. One hundred and fifty pounds of CO_2 has a specific enthalpy of 45,000 (ft)(lb_f)/lb_m with reference to 0°F and 1 psia. What is the enthalpy of this CO_2 in Btu/lb mol?

What is the total internal energy if the pressure is 6 atm and the temperature is 50°F?

4.26. One kilogram mole of steam at 150°C and 150 kPa is expanded to 210°C and 100 kPa. Thereafter it is condensed to water at 25°C and 100 kPa, and finally heated back to 150°C and 150 kPa. What is the overall **(a)** enthalpy change and **(b)** internal energy change per kilogram mole of steam for the process?

4.27. State which of the following variables are point, or state, variables, and which are not; explain your decision in one sentence for each one:

(a) Pressure
(b) Density
(c) Molecular weight
(d) Heat capacity
(e) Internal energy
(f) Ionization constant

Section 4.2

4.28.* Experimental values calculated for the heat capacity of ammonia from −40 to 1200°C are:

T (°C)	C_p° [cal/(g mol)(°C)]	T (°C)	C_p° [cal/(g mol)(°C)]
−40	8.180	500	12.045
−20	8.268	600	12.700
0	8.371	700	13.310
18	8.472	800	13.876
25	8.514	900	14.397
100	9.035	1000	14.874
200	9.824	1100	15.306
300	10.606	1200	15.694
400	11.347		

Fit the data by least squares for the following two functions:

$$\left.\begin{aligned} C_p^\circ &= a + bT + cT^2 \\ C_p^\circ &= a + bT + cT^2 + dT^3 \end{aligned}\right\} \quad \text{where } T \text{ is in °C}$$

4.29. Experimental values of the heat capacity C_p have been determined in the laboratory as follows; fit a second-order polynomial in temperature to the data ($C_p = a + bT + cT^2$):

T (°C)	C_p [J/(g mol)(°C)]
100	40.54
200	43.81
300	46.99
400	49.33
500	51.25
600	52.84
700	54.14

(The data are for carbon dioxide.)

4.30. A laboratory analysis from No. 46 well yields the following composition by volume for a product gas.

Component	Vol. %	Component	Vol. %
CH_4	90.05	N_2	5.518
C_2H_6	1.984	O_2	1.467
C_3H_8	0.202	H_2	0.31
C_4H_{10}	0.069	CO_2	0.662
C_5H_{12}	0.018		

What is the heat capacity (in Btu/(lb mol)(°F) of this gas at room temperature?

4.31. In a computer program you find that the relation for the specific enthalpy (J/g mol) of a gas is given by

$$\hat{H} = 32.97T + 6.694 \times 10^{-3}T^2 - 6.745 \times 10^{-7}T^3 + 5.481 \times 10^{-5}p$$

where T is in °C and p is in kPa, and the reference state is unspecified.

(a) Determine the value of the heat capacity C_p of the gas in J/(kg mol)(°C) at 100°C and 100 kPa.

(b) What is a function that expresses the specific internal energy (for the same reference state) assuming that the gas acts as an ideal gas.

(c) Determine the value of the heat capacity C_v of the gas in J/(kg mol)(°C) at 100°C and 100 kPa.

4.32. An equation for the heat capacity of acetone vapor is

$$C_p = 71.96 + 20.10 \times 10^{-2}T - 12.78 \times 10^{-5}T^2 + 34.76 \times 10^{-9}T^3$$

where C_p is in J/(g mol)(°C) and T is in °C. Convert the equation so that C_p is in Btu/(lb mol)(°F) and T is in °F.

4.33. Your assistant has developed the following equation to represent the heat capacity of air (with C_p in cal/(g mol) (K) and T in K):

$$C_p = 6.39 + 1.76 \times 10^{-3}T - 0.26 \times 10^{-6}T^2$$

(a) Derive an equation giving C_p but with the temperature expressed in °C.

(b) Derive an equation giving C_p in terms of Btu per pound per degree Fahrenheit with the temperature being expressed in degrees Fahrenheit.

4.34. To evaluate the suitability of Kopp's rule for the heat capacities of solids, compute the heat capacities of sodium sulfate (Na_2SO_4), dextrose ($C_6H_{12}O_6$), and copper ammonium sulfate [$CuSO_4(NH_4)_2 SO_4 \cdot 6H_2O$] and compare your values with the experimental ones at 25°C.

4.35. One hundred pounds of a 35°API distillate with an average boiling point of 250°F is cooled from 400°F to 300°F. Estimate the heat capacity of the distillate at each temperature using the equation in the text and the charts in Appendix K.

4.36. Estimate the heat capacity of gaseous isobutane at 1000 K and 200 mm Hg by using the Kothari–Doraiswamy relation

$$C_p = A + B \log_{10} T_r$$

from the following experimental data at 200 mm Hg:

C_p[cal/(K)(g mol)]	23.25	35.62
Temp. (K)	300	500

The experimental value is 54.40; what is the percentage error in the estimate?

Section 4.3

4.37. The heat capacity of carbon monoxide is given by the following equation:

$$C_p = 6.935 + 6.77 \times 10^{-4}T + 1.3 \times 10^{-7}T^2$$

where C_p = cal/(g mol)(°C)
T = °C

What is the enthalpy change associated with heating carbon monoxide from 500°C to 1000°C?

4.38. Two gram moles of nitrogen are heated from 50°C to 250°C in a cylinder. What is ΔH for the process? The heat capacity equation is

$$C_p = 27.32 + 0.6226 \times 10^{-2}T - 0.0950 \times 10^{-5}T^2$$

where T is in kelvin and C_p is in J/(g mol)(°C).

4.39. Calculate the enthalpy change (in J/kg mol) that takes place in raising the temperature of 1 kg mol of the following gas mixture from 50°C to 550°C.

Component	Mol %
CH_4	80
C_2H_6	20

4.40. Can you find the enthalpy change at constant pressure of substance such as CO_2 from the solid to the gaseous state by integrating $\int_{T_1}^{T_2} C_p\, dT$ from T_1 (the solid temperature) to T_2 (the gas temperature) for a constant-pressure path?

4.41.* Calculate the change in enthalpy for 5 kg mol of CO which is cooled from 927°C to 327°C using the program ENTH on the disk included with the book.

4.42.* Hydrogen sulfide is heated from 77°C to 227°C. What is the enthalpy change due to the heating? Use the program ENTH on the disk at the back of the book.

4.43.* What is the enthalpy change for acetylene when heated from 37.8°C to 93.3°C? Use the program ENTH on the disk in the back of the book.

4.44.* Use the steam tables to calculate the enthalpy change (in joules) of 2 kg mol of steam when heated from 400 K and 100 kPa to 900 K and 100 kPa. Repeat using the table in the text for the enthalpies of combustion gases. Repeat using the heat capacity for steam. Compare your answers. Which is most accurate?

4.45. A closed vessel contains steam at 1000.0 psia in a 4-to-1 vapor volume-to-liquid volume ratio. What is the steam quality?

4.46. Use the tables for the heat capacities of the combustion gases to compute the enthalpy change (in Btu) that takes place when a mixture of 6.00 lb mol of gaseous H_2O and 4.00 lb mol of CO_2 is heated from 60°F to 600°F.

4.47. Chemical vapor deposition (CVD) is an important technique in producing solid-state materials because of its potential application to a variety of materials with controlled properties. Although this method has advantages, the film formation rates are so low, usually 0.1 to 1.0 nm/s, that the application of this method has been limited to date to very expensive materials.

In one trial to test film growth the temperature was controlled by use of steam on the underside of the film surface in the reactor assembly. Titanium tetraisopropoxide [$Ti(OC_3H_7)_4$] was carried by a helium stream over the condensing surface, where it decomposed to TiO_2 plus gases.

The steam entered the reactor at 523 K and 130 kPa and exited at 540 K and 100 kPa. What was the internal energy change per kg of steam going through the reactor? Use the steam tables.

4.48. In a proposed molten-iron coal gasification process (*Chemical Engineering*, p. 17, July 1985), pulverized coal of up to 3 mm size is blown into a molten iron bath, and oxygen and steam are blown in from the bottom of the vessel. Materials such as lime for settling the slag, or steam for bath cooling and hydrogen generation, can be injected at the same time. The sulfur in the coal reacts with lime to form calcium sulfide, which dissolves into the slag. The process operates at atmospheric pressure and 1400 to 1500°C. Under these conditions, coal volatiles escape immediately and are cracked. The carbon conversion rate is said to be above 98%, and the gas is typically 65 to 70% CO, 25 to 35% H_2, and less than 2% CO_2. Sulfur content of the gas is less than 20 ppm.

Assume that the product gas is 68% CO, 30% H_2, and 2% CO_2, and calculate the enthalpy change that occurs on the cooling of 1000 m^3 of gaseous product from 1400°C to 25°C at 101 kPa. Use the table for the enthalpies of the combustion gases.

4.49. Use the CO_2 chart in the following calculations.

(a) Four pounds of CO_2 are heated from saturated liquid at 20°F to 600 psia and 180°F.

  (1) What is the specific volume of the CO_2 at the final state?

  (2) Is the CO_2 in the final state gas, liquid, solid, or a mixture of two or three phases?

(b) The 4 lb of CO_2 is then cooled at 600 psia until the specific volume is 0.07 ft^3/lb.

  (1) What is the temperature of the final state?

  (2) Is the CO_2 in the final state gas, liquid, solid, or a mixture of two or three phases?

4.50. The heat capacity of chlorine has been determined experimentally as follows:

T (°C)	C_p [cal/(g mol)(K)]
0	8.00
18	8.08
25	8.11
100	8.36
200	8.58
300	8.71
400	8.81
500	8.88
600	8.92
700	8.95

T (°C)	C_p [cal/(g mol)(K)]
800	8.98
900	9.01
1000	9.03
1100	9.05
1200	9.07

Calculate the enthalpy change required to raise 1 g mol of chlorine from 0°C to 1200°C.

Section 4.4

4.51. Water can exist in various states, depending on its temperature, pressure, and so on. From what you have learned in Sec. 3.7, what is the state (gaseous, liquid, solid, or combinations thereof) for water at the following conditions:
(a) 250°F and 1 atm
(b) −10°C and 720 mm Hg
(c) 32°F and 100 psia

4.52. Calculate the enthalpy change (in joules) that occurs when 1 kg of benzene vapor at 150°C and 100 kPa condenses to a solid at −20.0°C and 100 kPa.

4.53. The vapor pressure of zinc in the range 600 to 985°C is given by the equation

$$\log_{10} p = -\frac{6160}{T} + 8.10$$

where p = vapor pressure, mm Hg
T = temperature, K

Estimate the latent heat of vaporization of zinc at its normal boiling point of 907°C.

4.54. After graduation you accept a job as a chemical engineer at the Muleshoe Natural Gasoline Co. The laboratory technician brings you the following data for n-butane (C_4H_{10}) made at 30°C. Are these data internally consistent or not? Explain your answer in complete detail.

Data: Liquid specific gravity (water = 1.00 at 4°C) is 0.564
Vapor specific gravity (air = 1.00 at 0°C and 1 atm) is 6.50
Latent heat of vaporization is 85.2 cal/g
Vapor pressure relation (p is in atm and T is in K)

$$\log_{10} p = 1.767 - \frac{1337}{T} + 1.75 \log_{10} T - 0.004\, T$$

4.55. The vapor pressure of phenylhydrazine has been found to be (from 25° to 240°C)

$$\log_{10} p^* = 7.9046 - \frac{2366.4}{T + 230}$$

where p^* is in atm and T is in °C. What is the heat of vaporization of phenylhydrazine in Btu/lb at 200°F? Use the Clausius–Clapeyron equation.

4.56. Check the precision of the empirical relation proposed by Watson to calculate heats of vaporization. Take water as a test example. With boiling water at 100°C as the reference temperature, estimate the heat of vaporization of water at 300°C from Watson's relation. Compare your result with the actual value from the steam tables

4.57.* Make an Othmer plot for refrigerant 12, and calculate the latent heat of vaporization at 100°F; compare this value with the one calculated from the following experimental data:

T (°F)	p^* (psia)	$V_{(l)}$ (ft³/lb)	$V_{(g)}$ (ft³/lb)
86	108.04	0.01240	0.37657
90	114.49	0.01248	0.35529
100	131.86	0.01269	0.30794
120	172.35	0.01317	0.23326
140	221.32	0.01375	0.17799

The experimental value is 55.93 Btu/lb.

4.58. Make an Othmer plot to determine the heat of vaporization of ____________ at ____________ °C. Compare with an experimental value if one can be found in a handbook.

4.59. (a) Using the following data on the vapor pressure of Cl_2, plot $\log p^*$ against $1/T$, and calculate the latent heat of vaporization of Cl_2 as a function of temperature:

T (°F)	p^* (psia)
−22	17.8
32	53.5
86	126.4
140	258.5
194	463.5
248	771
284	1050

How satisfactory are these data?

(b) The vapor pressure of Cl_2 is given by Lange by the equation

$$\log p^* = A - \frac{B}{C + T}$$

where p^* is the vapor pressure in mm Hg, T is in °C, and for chlorine, $A = 6.86773$, $B = 821.107$, and $C = 240$. Calculate the latent heat of vaporization of chlorine at the normal boiling point (in Btu/lb). Compare with the experimental value.

4.60. Use of the steam tables:

(a) What is the enthalpy change needed to change 3 lb of liquid water at 32°F to steam at 1 atm and 300°F?

(b) What is the enthalpy change needed to heat 3 lb of water from 60 psia and 32°F to steam at 1 atm and 300°F?

(c) What is the enthalpy change needed to heat 1 lb of water at 60 psia and 40°F to steam at 300°F and 60 psia?

(d) What is the enthalpy change needed to change 1 lb of a water-steam mixture of 60% quality to one of 80% quality if the mixture is at 300°F?

(e) Calculate the ΔH value for an isobaric (constant pressure) change of steam from 120 psia and 500°F to saturated liquid.

(f) Repeat part (e) for an isothermal change to saturated liquid.

(g) Does an enthalpy change from saturated vapor at 450°F to 210°F and 7 psia represent an enthalpy increase or decrease? a volume increase or decrease?

(h) In what state is water at 40 psia and 267.24°F? At 70 psia and 302°F? At 70 psia and 304°F?

(i) A 2.5-ft^3 tank of water at 160 psia and 363.5°F has how many cubic feet of liquid water in it? Assume that you start with 1 lb of H_2O. Could it contain 5 lb of H_2O under these conditions?

(j) What is the volume change when 2 lb of H_2O at 1000 psia and 200°F expands to 245 psia and 460°F?

(k) Ten pounds of wet steam at 100 psia has an enthalpy of 9000 Btu. Find the quality of the wet steam.

Section 4.5

4.61. A cylinder contains 1 lb of steam at 600 psia and a temperature of 500°F. It is connected to another equal-sized cylinder which is evacuated. A valve between the cylinders is opened. If the steam expands into the empty cylinder, and the final temperature of the steam in both cylinders is 500°F, calculate Q, W, ΔU, and ΔH for the system comprised of both cylinders.

4.62. One pound of steam at 130 psia and 600°F is expanded isothermally to 75 psia in a closed system. Thereafter it is cooled at constant volume to 60 psia. Finally, it is compressed adiabatically to back to its original state. For each of the three steps of the process, compute ΔU and ΔH. For each of the three steps, where possible, also calculate Q and W.

4.63. Two 1-m^3 tanks submerged in a constant-temperature water bath of 77°C are connected by a globe valve. One tank contains steam at 40 kPa, while the second is completely evacuated. The valve is opened and the pressure in the two tanks equilibrates. Calculate:

(a) The work done in the expansion of the steam

(b) The heat transferred to the tanks from the water bath

(c) The change in internal energy of the combined steam system

4.64. You have 0.37 lb of CO_2 at 1 atm abs and 100°F contained in a cylinder closed by a piston. The CO_2 is compressed to 70°F and 1000 psia. During the process, 40.0 Btu of heat is removed. Compute the work required for the compression.

4.65. A system consists of 25 lb of water vapor at the dew point. The system is compressed isothermally at 400°F, and 988 Btu of work are done on the system by the surroundings. What volume of liquid was present in the system before and after compression?

4.66. Steam fills tank 1 at 1000 psia and 700°F. The volume of tank 1 equals the volume of tank 2. A vacuum exists in tank 2 initially. See Fig. P4.66. The valve connecting

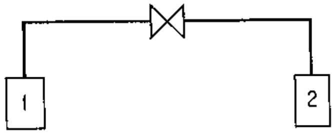


Figure P4.66

the two tanks is opened, and isothermal expansion of the steam occurs from tank 1 to tank 2. Find the enthalpy change per pound of steam for the entire process.

4.67. **(a)** A large piston does 12,500 (ft)(lb_f) of work in compressing 3 ft^3 of air to 25 psia. Five pounds of water circulates into and out of the water jacket around the piston and increases in temperature 2.3°F by the end of the process. What is the change of internal energy of the air?

(b) Suppose that the water does not circulate but is stationary and increases in temperature the same amount. What is the change now in the internal energy of the air?

(c) Suppose that the piston after compressing the gas returns to its original position, and all the 12,500 (ft)(lb_f) of work is recovered. What will the water temperature be in part (b)?

4.68. A household freezer is placed inside an insulated sealed room. If the freezer door is left open with the freezer operating, will the temperature of the room increase or decrease? Explain your answer.

4.69. One pound of water at 70°F is put into a closed tank of constant volume. If the temperature is brought to 80°F by heating, find Q, W, ΔU, and ΔH for the process (in Btu). If the same temperature change is accomplished by a stirrer that agitates the water, find Q, W, ΔE, and ΔH. What assumptions are needed?

4.70. On a winter day (38°F or 3°C outside average temperature) a "standard" house loses heat at the following rates:

(1) 2.1 kW is lost through partially insulated walls and roof by conductance,
(2) 0.3 kW is lost through the floor by conductance, and
(3) 1.9 kW is lost through the windows (no storm windows) by conductance.

Energy is also needed at the following rates:

(1) 2.3 kW to heat the air entering the house through cracks, flues, etc. (infiltration losses) and
(2) 1.1 kW to humidify the incoming air (because warm air must contain more water vapor than cold air for people to be comfortable).

On the same winter day, some energy is supplied to the house in the following amounts (on a day with average cloudiness):

(1) Sunlight through windows	0.5 kW
(2) People's heat transfer	0.2 kW
(3) Appliances' heat transfer	1.2 kW

If the house temperature is to be maintained at a constant value, what is the rate of energy that must be provided by the heating system in the house?

Suppose that the following design changes are made in the house:

(1) Added insultation of walls, roof, and floors cuts the losses incurred there by 60%.
(2) Tightly fitting double-glazed windows with selective coatings to reduce the passage of infrared light, or with special shutters, cut conductance losses by 70%.

(3) Elimination of cracks, closing of flues, and so on, cuts infiltration losses by 70%.

Now what is the total rate at which energy is lost from this house, all other factors remaining the same?

4.71. In the vapor-recompression evaporator shown in Fig. P4.71, the vapor produced on evaporation is compressed to a higher pressure and passed through the heating coil to provide the energy for evaporation. The steam entering the compressor is 98% vapor and 2% liquid, at 10 psia; the steam leaving the compressor is at 50 psia and 400°F; and 6 Btu of heat are lost from the compressor per pound of steam throughout. The condensate leaving the heating coil is at 50 psia, 200°F.

(a) Compute: The Btu of heat supplied for evaporation in the heating coil per Btu of work needed for compression by the compressor.

(b) If 1,000,000 Btu per hour of heat is to be transferred in the evaporator, what must be the intake capacity of the compressor in ft^3 of wet vapor per minute?

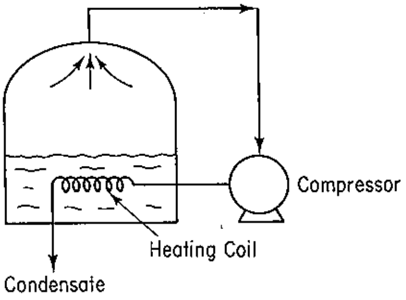


Figure P4.71

4.72. A 55-gal drum of fuel oil (15°API) is to be heated from 70°F to 180°F by means of an immersed steam coil. Steam is available at 220°F. How much steam is required if it leaves the coil as liquid water at 1 atm pressure?

4.73. Oil of average $C_p = 0.8$ Btu/(lb)(°F) flows at 2000 lb/min from an open reservoir standing on a hill 1000 ft high into another open reservoir at the bottom. To ensure rapid flow, heat is put into the pipe at the rate of 100,000 Btu/hr. What is the enthalpy change in the oil per pound? Suppose that a 1-hp pump (50% efficient) is added to the pipeline to assist in moving the oil. What is the enthalpy change per pound of the oil now?

4.74. Write the simplified energy balances for the following changes:

(a) A fluid flows steadily through a poorly designed coil in which it is heated from 70°F to 250°F. The pressure at the coil inlet is 120 psia, and at the coil outlet is 70 psia. The coil is of uniform cross section, and the fluid enters with a velocity of 2 ft/sec.

(b) A fluid is expanded through a well-designed adiabatic nozzle from a pressure of 200 psia and a temperature of 650°F to a pressure of 40 psia and a temperature of 350°F. The fluid enters the nozzle with a velocity of 25 ft/sec.

(c) A turbine directly connected to an electric generator operates adiabatically. The working fluid enters the turbine at 1400 kPa absolute and 340°C. It leaves the turbine at 275 kPa absolute and at a temperature of 180°C. Entrance and exit velocities are negligible.

(d) The fluid leaving the nozzle of part (b) is brought to rest by passing through the blades of an adiabatic turbine rotor and leaves the blades at 40 psia and at 400°F.

4.75. Your company produces small power plants that generate electricity by expanding waste process steam in a turbine. One way to ensure good efficiency in turbine operation is to operate adiabatically. For one turbine, measurements showed that for 1000 lb/hr steam at the inlet conditions of 500°F and 250 psia, the work output from the turbine was 86.5 hp and the exit steam leaving the turbine was at 14.7 psia with 15% wetness (i.e., with a quality of 85%).

Check whether the turbine is operating adiabatically by calculating the value of Q.

4.76. Feedwater heaters are used to increase the efficiency of steam power plants. A particular heater is used to preheat 10 kg/s of boiler feed water from 20°C to 188°C at a pressure of 1200 kPa by mixing it with saturated steam bled from a turbine at 1200 kPa, as shown in Fig. P4.76. Although insulated, the heater loses heat at the rate of 50 J per gram of exiting mixture. What fraction of the exit stream is steam?

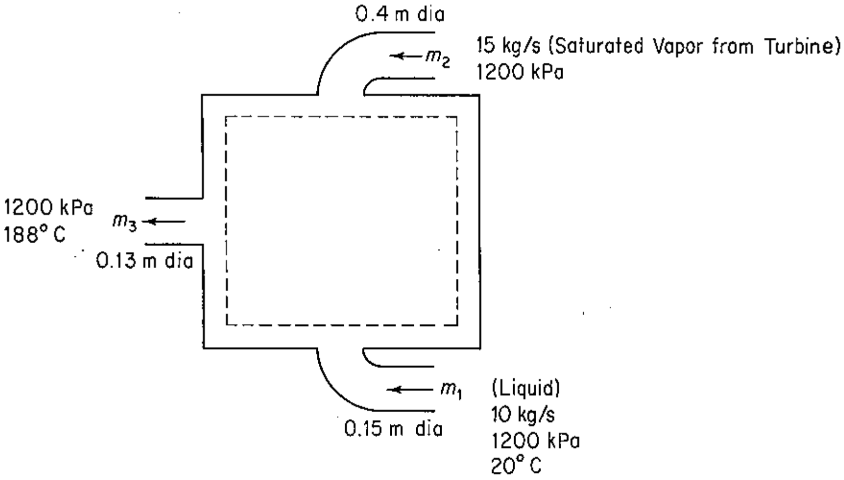


Figure P4.76

4.77. Hot reaction products (assume that the products have same properties as air) at 1000°C leave a reactor (see Fig. P4.77). To prevent further reaction, the process is designed to reduce the temperature of the products to 400°C by immediately spraying liquid water at 25°C into the gas stream.

(a) How many moles of water at 25°C are required per mole of products, and how many lb of water per 1000 ft³ of products (measured at 400°C and 0.41 in. Hg pressure gauge—the barometer is 29.75 in. Hg)?

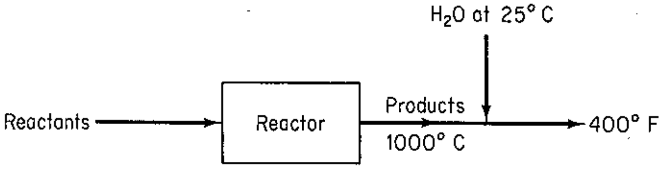


Figure P4.77

(b) Based on the data in part (a), explain in words and if possible with specific numbers how you would make the following adjustments or calculations.

1. What was the work done by or on the system if the system is the reactor?
2. What would be the increase or decrease in the lb of water required if the velocity of the 1000°C gas was assumed to be 20 ft/sec?
3. What would be the change in lb of water required if the reactor were not insulated and as a result lost 2000 Btu/lb mol of the 1000°C exit products?
4. What would be the change in lb of water required if the water temperature were 40°C instead of 25°C?
5. What would happen in your calculations if the hot gases contained a product that condensed at 500°C and 1 atm?

4.78. A plant is proposing to utilize waste gas, now being discarded at 750°F, to supply the heat for a waste heat boiler which is to produce saturated steam at 400°F from feed water at 70°F. The average molal heat capacity of the gas is 8.2. Under ideal conditions (i.e., no heat losses to the surroundings and very large heat exchange surfaces), what is the maximum possible production of steam, expressed as pounds of steam per pound mole of gas?

4.79. In a continuous reactor, the oxygen feed is compressed adiabatically from 100 to 200 kPa at a rate of 2 kg/min. The entering temperature of the oxygen is 20°C and the exit temperature is 100°C. If 7.675 kJ/hr of work are done on a system and the change in kinetic energy (ΔK) is a negative 10.0 kJ/kg, calculate the change in internal energy (ΔU) per 1.0 kg O_2 flowing through the compressor for the process. The change in potential energy (ΔP) is negligible. Oxygen behaves ideally at these conditions.

4.80. Cell growth liberates energy which must be removed; otherwise, the temperature will rise so much that the cells may be killed. In a continuous fermenter for the production of *Penicillium chrysogenum,* the cells generate 27.6 kJ/L per hour, and the volume of the well-insulated fermenter is 2 L. The feed temperature is 25°C and the exit temperature is equal to the temperature in the fermenter. *Penicillium chrysogenum* cannot grow above 42°C. Will the cells survive? Assume for simplicity that the inlet and outlet streams have a heat capacity of 4 J/(g)(°C) and the mass flow rates of 1025 g/hr are constant.

4.81. Three hundred kilograms per hour of air flow through a countercurrent heat exchanger as shown in Fig. P4.81. Two hundred thirty kilograms per hour of potassium carbonate solution are heated by the air. Assume that the heat exchanger has negligible heat losses. The terminal temperatures are given in Fig. P4.81. Calculate the temperature, in kelvin, of the exit potassium carbonate stream.

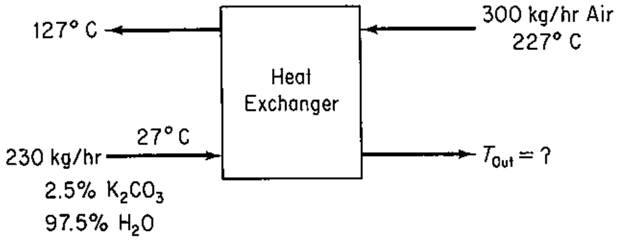


Figure P4.81

4.82. Boilers such as those used for generating steam must be purged periodically to prevent solids buildup. Solids in the boiler will lower both the efficiency and quality of the product steam. This process and the liquid removed are refered to as the blowdown. So that this energy is not wasted, the blowdown from a boiler operating at 1000 kPa is run into a flash chamber from which steam at 200 kPa is withdrawn. What fraction of the blowdown becomes available as steam at 200 kPa?

4.83. In a recycle fermenter, a cell separater is used to concentrate the cells and return them to the fermenter. The steady-state rate of cell production in the fermentation vessel is $Q = \mu XV$, where μ is a growth rate constant, X the (dry) cell concentration, and V the volume of the vessel. The volumetric flow rate into the fermenter and out of the separater is F. For the recycle fermenter shown in Fig. P4.83:

(a) Calculate the constant μ as a function of R, F, V, X_r, X_1.

(b) If $X_r/X_1 = 1.5$, calculate μ/D for $R/F = 0.5$, where D is the dilution rate (F_{in}/V).

(c) For $X_r/X_1 = 1.5$ and $R/F = 0.5$, calculate X_2/X_1.

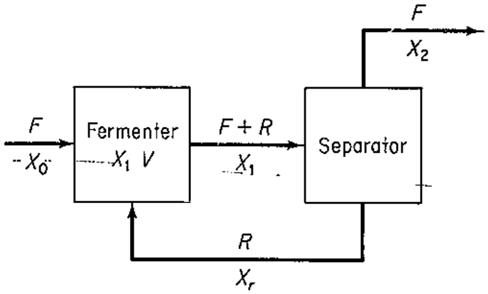


Figure P4.83

4.84. A chemical plant has just perfected a process for the manufacture of a new revolutionary drug. A large plant must be designed even before complete data are available. The research laboratory has obtained the following data for the drug.

boiling point at 101.3 kPa	250°C
vapor pressure at 230°C	55 kPa
specific gravity, 28/4	1.316
melting point	122.4°C
solubility in water at 76°C	2.2/100 parts water by weight
molecular weight	122
heat capacity of liquid	at 150°C is 2.09 kJ/(kg)(°C)
heat capacity of liquid	at 240°C is 2.13 kJ/(kg)(°C)

Calculate the heat duty for a vaporizer that will be required to vaporize 10,000 kg/hr of this chemical at atmospheric pressure (assume that no superheating of the vapor occurs). The entering temperature of the drug will be 130°C.

4.85. Water at 250 psia and 70°F enters a boiler, where it is converted to superheated steam at 250 psi absolute and 700°F. The superheated steam passes through an adiabatic turbine and emerges at a pressure of 15 psi gauge, 98% quality (i.e., 98% vapor). The exit wet steam is then condensed and subcooled to 100°F at a constant pressure of 15 psi gauge by heating air from 60°F to 200°F.

Per pound of steam, calculate Q, W, ΔH, and ΔU for (a) the boiler and (b) the turbine.

4.86. Saturated steam at 227°C is used in a heat exchanger to preheat a reactor feed stream.

(a) If the condensate is removed from the heat exchanger at 152°C and the flow rate is 1000 kg/hr, how many kJ are transferred to the feed stream in 1 hr?

(b) How much additional steam would be required if the condensate is removed at 227°C with the exit reactor feed stream temperature the same?

4.87. A process involving catalytic dehydrogenation in the presence of hydrogen is known as *hydroforming*. Toluene, benzene, and other aromatic materials can be economically produced from naphtha feed stocks in this way. After the toluene is separated from the other components, it is condensed and cooled in a process such as the one shown in Fig. P4.87. For every 100 kg of stock charged into the system, 27.5 kg of a toluene and water mixture (9.1% water) are produced as overhead vapor and condensed by the charge stream. Calculate:

(a) The temperature of the charge stream after it leaves the condenser

(b) The kilograms of cooling water required per hour

Additional data:

Stream	C_p [kJ/(kg)(°C)]	B.P. (°C)	ΔH_{vap} (kJ/kg)
$H_2O(l)$	4.2	100	2260
$H_2O(g)$	2.1	—	—
$C_7H_8(l)$	1.7	111	230
$C_7H_8(g)$	1.3	—	—
Stock (l)	2.1	—	—

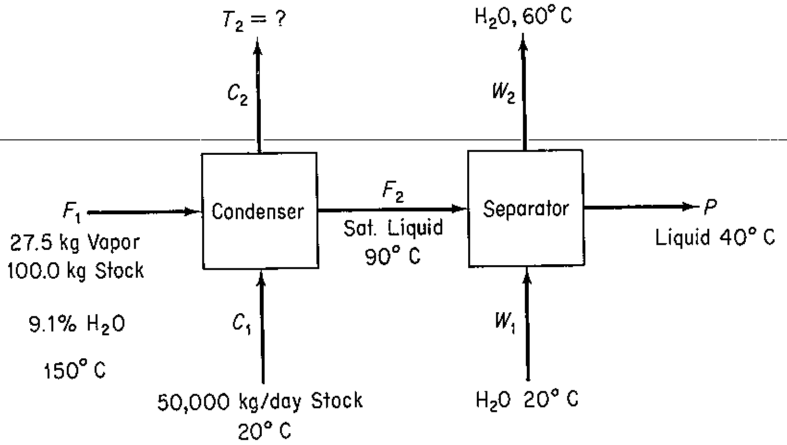


Figure P4.87

4.88. Simplify the general energy balance so as to represent the process in each of the following cases. Number each term in the general balance, Eq. (4.24a), and state why you retained or deleted it.

(a) A bomb calorimeter is used to measure the heating value of natural gas. A measured volume of gas is pumped into the bomb. Oxygen is then added to give a total pressure of 10 atm, and the gas mixture is exploded using a hot wire. The resulting heat transfer from the bomb to the surrounding water bath is measured. The final products in the bomb are CO_2 and water.

(b) Cogeneration (generation of steam both for power and heating) involves the use of gas turbines or engines as prime movers, with the exhausted steam going to the process to be used as a heat source. A typical installation is shown in Fig. P4.88.

(c) In a mechanical refrigerator the Freon liquid is expanded through a small insulated orifice so that part of it flashes into vapor. Both the liquid and vapor exit at a lower temperature than the temperature of the liquid entering.

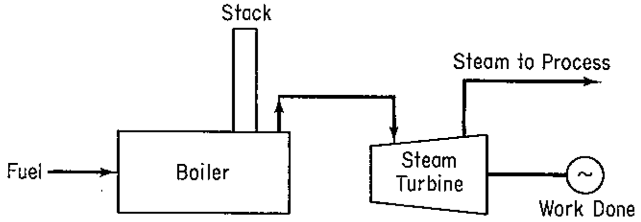


Figure P4.88

4.89. A desalted crude oil (40° API) is being heated in a parallel-flow heat exchanger from 70°F to 200°F with a straight-run gasoline vapor available at 280°F. If 400 gal/hr of gasoline is available (measured at 60°F, 63°API), how much crude can be heated per hour? Would countercurrent flow of the gasoline to the crude change your answer to this problem? Assume that $K = 11$ for the oil and 12.2 for the gasoline. C_p of the vapor is 0.95 Btu/(lb)(°F).

4.90. The process of throttling (i.e., expansion of a gas through a small orifice) is an important part of refrigeration. If wet steam (fraction vapor is 0.975) at 700 kPa absolute is throttled to 1 atm, find the following for the process:

(a) Heat transferred to or from steam
(b) Work done
(c) Enthalpy change
(d) Internal energy change
(e) Exit temperature

4.91. Solid CO_2 is being produced by adiabatically expanding high-pressure CO_2 at 70°F through a valve to a pressure of 20.0 psia.

(a) If 30% conversion of the initial CO_2 to the solid is desired, at what pressure must the CO_2 be before expansion?
(b) Is the high-pressure CO_2 gas, liquid, or a mixture of each?
(c) What is the approximate volume change per pound of CO_2 during the expansion?

4.92. Examine the simplified refinery power plant flow sheet in Fig. P4.92 and calculate the energy loss (in Btu/hr) for the plant. Also calculate the energy loss as a percentage of the energy input.

4.93. Start with the general energy balance, and simplify it for each of the processes listed below to obtain an energy balance that represents the process. Label each term in the general energy balance by number, and list by their numbers the terms retained or deleted followed by your explanation. (You do not have to calculate any quantities in this problem.)

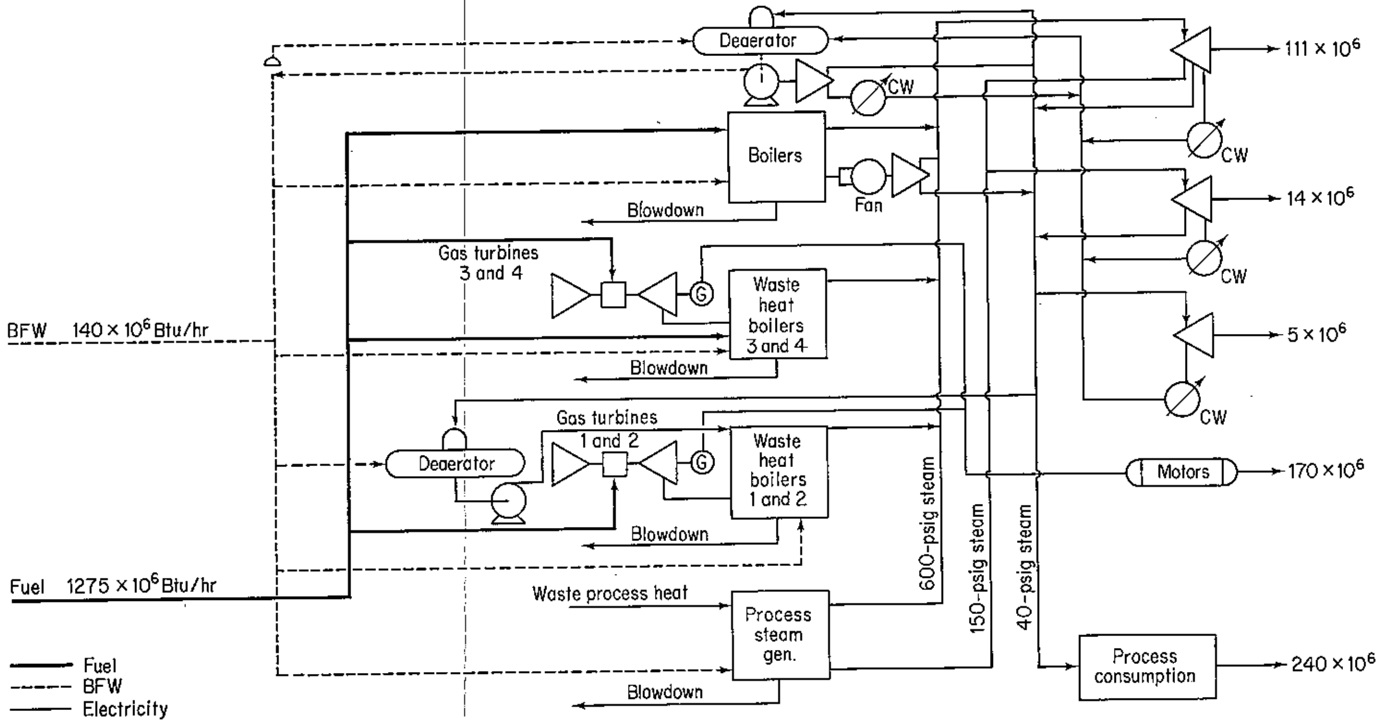

Deaerator
CW
Boilers
Fan
Blowdown
Gas turbines 3 and 4
G
Waste heat boilers 3 and 4
Blowdown
BFW 140 × 10^6 Btu/hr
Gas turbines 1 and 2
Deaerator
G
Waste heat boilers 1 and 2
Blowdown
Fuel 1275 × 10^6 Btu/hr
Waste process heat
Process steam gen.
Blowdown
600-psig steam
150-psig steam
40-psig steam
111 × 10^6
CW
14 × 10^6
CW
5 × 10^6
CW
Motors
170 × 10^6
Process consumption
240 × 10^6
Fuel
BFW
Electricity

Figure P4.92

(a) One hundred kilograms per second of water is cooled from 100°C to 50°C in a heat exchanger. The heat is used to heat up 250 kg/s of benzene entering at 20°C. Calculate the exit temperature of benzene.

(b) A feedwater pump in a power generation cycle pumps water at the rate of 500 kg/min from the turbine condensers to the steam generation plant, raising the pressure of the water from 6.5 kPa to 2800 kPa. If the pump operates adiabatically with an overall mechanical efficiency of 50% (including both pump and its drive motor), calculate the electric power requirement of the pump motor (in kW). The inlet and outlet lines to the pump are of the same diameter. Neglect any rise in temperature across the pump due to friction (i.e., the pump may be considered to operate isothermally).

(c) A caustic soda solution is placed in a mixer together with water to dilute it from 20% NaOH in water to 10%. What is the final temperature of the mixture if the materials initially are at 25°C and the process is adiabatic?

4.94. A distillation process has been set up to separate an ethylene-ethane mixture as shown in Fig. P4.94. The product stream will consist of 98% ethylene and it is desired to recover 97% of the ethylene in the feed. The feed, 1000 lb per hour of 35% ethylene, enters the preheater as a subcooled liquid (temperature = −100°F, pressure = 250 psia). The feed experiences a 20°F temperature rise before it enters the still. The heat capacity of liquid ethane may be considered to be constant and equal to 0.65 Btu/(lb)(°F) and the heat capacity of ethylene may be considered to be constant and equal to 0.55 Btu/(lb)(°F). Heat capacities and saturation temperatures of mixtures may be determined on a weight fraction basis. An optimum reflux ratio of 6.1 lb reflux/lb product has been previously determined and will be used. Operating pressure in the still will be 250 psia. Additional data are as follows:

Pressure = 250 psia

Component	Temp. sat. (°F)	Heat of vaporizatioin (Btu/lb)
C_2H_6	10°	140
C_2H_4	−30°	135

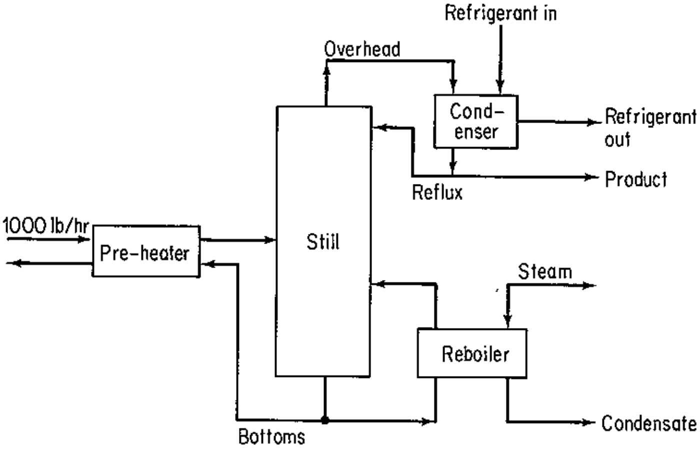


Figure P4.94

Determine:

(a) The pounds of 30 psig steam required in the reboiler per pound of feed.

(b) The gallons of refrigerant required in the condenser per hour assuming a 25°F rise in the temperature of the refrigerant. Heat capacity is approximately 1.0 Btu/(lb)(°F) and density = 50 lb/ft^3.

(c) The temperature of the bottoms as it leaves the preheater.

4.95. A dryer with a rating of 5.0×10^5 J/s is available to dry the products leaving the separator of a plant, as shown in Fig. P4.95. Is the heat input to the dryer large enough to do the job?

	C_p [J/(kg)(°C)]	H_{vap} (J/kg)
Urea	2500	
Solvent	2800	4.50×10^5

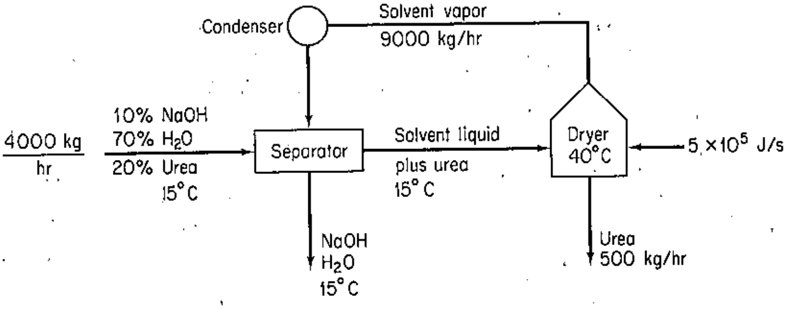


Figure P4.95

Section 4.6

4.96. A phase change (condensation, melting, etc.) of a pure component is an example of a reversible process because the temperature and pressure remain constant during the change. Use the definition of work to calculate the work done by butane when 1 kg of saturated liquid butane at 70 kPa vaporizes completely. Can you calculate the work done by the butane from the energy balance alone?

4.97. Calculate the work done when 1 lb mol of water in an open vessel evaporates completely at 212°F. Express your result in Btu.

4.98. One kilogram of steam goes through the following reversible process. In its initial state (state 1) it is at 2700 kPa and 540°C. It is then expanded isothermally to state 2, which is at 700 kPa. Then it is cooled at constant volume to 400 kPa (state 3). Next it is cooled at constant pressure to a volume of 0.4625 m^3/kg (state 4). Then it is compressed adiabatically to 2700 kPa, and 425°C (state 5), and finally it is heated at constant pressure back to the original state.

(a) Sketch the path of each step in a p–V diagram.

(b) Compute ΔU and ΔH for each step and for the entire process.

(c) Compute Q and W whenever possible for each step of the process.

4.99. Calculate the work done when 1 lb mol of water evaporates completely at 212°F in the following cases. Express your results in Btu/lb mol.

(a) A steady-state flow process: water flowing in a pipeline at 1 lb mol/min neglecting the potential and kinetic energy changes.

(b) A nonflow process: water contained in a constant-pressure, variable-volume tank.

4.100. A system consists of 25 lb of water vapor at the dew point. The system is compressed isothermally at 400°F, and 988 Btu of work is done on the system by the surroundings. What volume of liquid was present in the system before and after compression?

4.101. An inventor claims that his new device will compress steam isothermally from 14.7 psia and 500°F to 200 psia and 500°F with 100% efficiency. If so, what is the work in Btu per pound of steam calculated

(a) For a batch (closed) process?

(b) For a flow (open) process?

4.102. In the transport of pulverized coal by pipeline, water is the usual fluid to carry the coal. However, problems exist in obtaining water in arid western states so that liquid CO_2 (obtained from burning some of the coal) has been proposed as the transport fluid. To liquefy the pure CO_2 gas obtained after separation from N_2 and H_2O, the CO_2 is compressed isothermally and essentially reversibly from 15 psia and 60°F to saturated liquid. State assumptions about the states of the compounds.

(a) What is the specific volume of the saturated liquid?

(b) What is the final pressure on the saturated liquid?

(c) What is the work of compression per lb of CO_2?

(d) If the efficiency of the compressor is actually 90% (111% of the reversible work is the actual work required), and the cost of compression is \$0.034/kWh, how much does it cost to liquefy 1 lb of CO_2?

4.103. In a processing plant, milk flows from a storage tank maintained at 5°C through a valve to a pasteurizer via an insulated 10-cm-diameter pipe at the rate of 1000 L/min. The upstream pressure is 290 kPa and downstream pressure is 140 kPa. Determine the lost work (E_v) in J/min and the temperature change which occurs in the milk as a result of this throttling process. (Milk and water are sufficiently equivalent in properties for you to use those of water.)

4.104. A power plant is as shown in Fig. P4.104. If the pump moves 100 gal/min into the boiler with an overall efficiency of 40%, find the horsepower required for the pump. List all additional assumptions required.

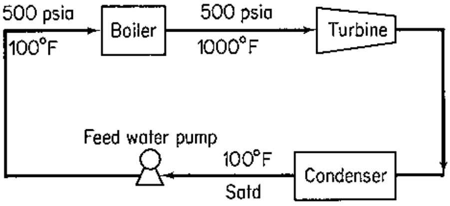


Figure P4.104

4.105. An office building requires water at two different floors. A large pipe brings the city water supply into the building in the basememt level, where a booster pump is located. The water leaving the pump is transported by smaller insulated pipes to the second and fourth floors, where the water is needed. Calculate the *minimum* amount of work per unit time (in horsepower) that the pump must do in order to deliver the necessary water, as indicated in Fig. P4.105. (*Minimum* refers to the fact that you should neglect the friction and pump energy losses in your calculations.) The water does not change temperature.

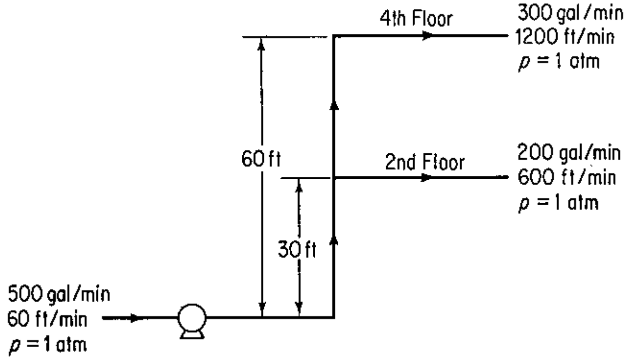


Figure P4.105

4.106. Water at 20°C is being pumped from a constant-head tank open to the atmosphere to an elevated tank kept at a constant pressure of 1150 kPa in an experiment as shown in Fig. P4.106. If water is flowing in the 5.0-cm line at a rate of 0.40 m^3/min, find

(a) The rating of the pump in joules per kilogram

(b) The rating of the pump in joules per minute

The pump and motor have an overall efficiency of 70% and the energy loss in the line can be determined to be 60.0 J/kg.

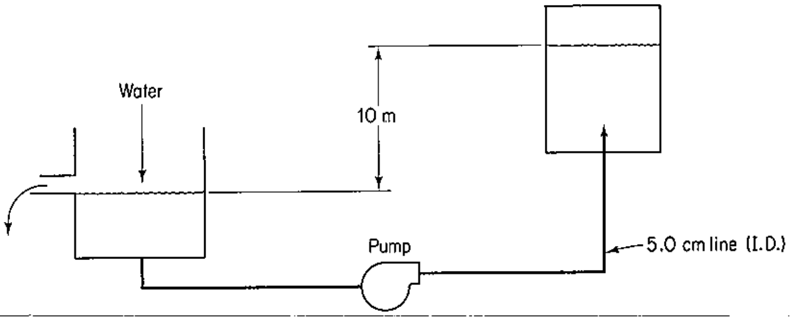


Figure P4.106

Section 4.7

4.107. Calculate the heat of reaction at 77°F and 1 atmosphere for the following reactions:

(a) $Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$

Data: ΔH_f° for Al_2O_3 = −399.09 kcal/g mol

(b) $4FeS_2(s) + 15O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_3(g)$

(c) $C_6H_5CHO(l) + 8O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l)$

4.108. Calculate the heat of reaction in the standard state for 1 mole of $C_3H_8(g)$ for the following reaction from the given data:

$$C_3H_8(l) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

Compound	$-\Delta\hat{H}_f^\circ$ (kcal/g mol)	Vaporization at 25°C kcal/g mol
$C_3H_8(g)$	24.820	3.823
$CO_2(g)$	94.052	1.263
$H_2O(g)$	57.798	10.519

4.109. At Texas City, Amoco operates a hydroformer in which cycloparaffin hydrocarbon vapors plus recycled hydrogen are passed at about 500°C and 20 atm pressure over a catalyst that produces an aromatic hydrocarbon. Cyclohexane produces benzene and hydrogen.

$$C_6H_{12}(g) \longrightarrow C_6H_6(g) + 3H_2(g)$$

The cyclohexane vapors are condensed, separated by distillation, and recycled in the process. Three volumes of hydrogen are recycled for every volume of feed stock, which consists of cyclohexane containing 5 mol % benzene. To initiate a design for the reactor, calculate standard heat of reaction per g mol of C_6H_{12}.

4.110. Hydrogen is used in many industrial processes, such as the production of ammonia for fertilizer. Hydrogen also has been considered to have a potential as an energy source because its combustion yields a clean product and it is easily stored as metal hydrides. Thermochemical cycles (a series of reactions resulting in a recycle of some of the reactants) can be used in the production of hydrogen from an abundant natural compound—water. One process involving a series of five steps is outlined below. State assumptions about the states of the compounds.

$$\begin{aligned}
3Fe_2O_3 + 18HCl &\xrightarrow{120^\circ C} 6FeCl_3 + 9H_2O && (1)\\
6FeCl_3 &\xrightarrow{420^\circ C} 6FeCl_2 + 3Cl_2 && (2)\\
6FeCl_2 + 8H_2O &\xrightarrow{650^\circ C} 2Fe_3O_4 + 12HCl + 2H_2 && (3)\\
2Fe_3O_4 + \tfrac{1}{2}O_2 &\xrightarrow{350^\circ C} 3Fe_2O_3 && (4)\\
3H_2O + 3Cl_2 &\xrightarrow{800^\circ C} 6HCl + \tfrac{3}{2}O_2 && (5)
\end{aligned}$$

(a) Calculate the standard heat of reaction for each step. State whether the reaction is endothermic or exothermic.

(b) What is the overall reaction? Is it exothermic or endothermic?

4.111. J. D. Park *et al.* [JACS *72*, 331–3 (1950)] determined the heat of hydrobromination of propene and cyctopropane. For hydrobromination (addition of HBr) of propene to 2-bromopropane (C_3H_7Br), they found that $\Delta H = -84{,}441$ J/g mol. The heat of hydrogenation of propene to propane is $\Delta H = -126{,}000$ J/g mol. N.B.S. Circ. 500 gives the heat of formation of HBr(g) as −36,233 J/g mol when the bromine is liquid and the heat of vaporization of bromine as 30,710 J/g mol. Calculate the heat of bromination of propane using gaseous bromine to form 2-bromopropane using the above data?

4.112. Compare prices of five fuels:

(1) Natural gas (all CH_4) at \$2.20 per 10^3 ft^3
(2) No. 2 fuel oil (33°API) at \$0.85 per gallon
(3) Dry yellow pine at \$95 per cord
(4) High-volatile A bituminous coal at \$55.00 per ton
(5) Electricity at \$0.032 per kilowatt

List the cost of each in descending order per 10^6 Btu. As far as energy consumption is concerned, would you be better off with a gas dryer or an electric dryer? Should you heat your house with wood, No. 2 fuel oil, or coal? (*Note:* A cord of wood is a pile 8 ft long, 4 ft high, and 4 ft wide.)

4.113. How would you determine the heat of formation of gaseous fluorine at 25°C and 1 atm?

4.114. Calculate the heat of reaction at the standard reference state for the following reactions:

(a) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(1)$
(b) $2CaO(s) + 2MgO(s) + 4H_2O(1) \longrightarrow 2Ca(OH)_2(s) + 2Mg(OH)_2(s)$
(c) $Na_2SO_4(s) + C(s) \longrightarrow Na_2SO_3(s) + CO(g)$
(d) $NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HCl(g)$
(e) $NaCl(s) + 2SO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 2Na_2SO_4(s) + 4HCl(g)$
(f) $SO_2(g) + \frac{1}{2}O_2(g) + H_2O(l) \longrightarrow H_2SO_4(l)$
(g) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
(h) $Na_2CO_3(s) + 2Na_2S(s) + 4SO_2(g) \longrightarrow 3Na_2S_2O_3(s) + CO_2(g)$
(i) $NaNO_3(s) + Pb(s) \longrightarrow NaNO_2(s) + PbO(s)$
(j) $Na_2CO_3(s) + 2NH_4Cl(s) \longrightarrow 2NaCl(s) + 2NH_3(g) + H_2O(l) + CO_2(g)$
(k) $Ca_3(PO_4)_2(s) + 3SiO_2(s) + 5C \longrightarrow 3CaSiO_3(s) + 2P(s) + 5CO(g)$
(l) $P_2O_5(s) + 3H_2O(l) \longrightarrow 2H_3PO_4(l)$
(m) $CaCN_2(s) + 2NaCl(s) + C(s) \longrightarrow CaCl_2(s) + 2NaCN(s)$
(n) $NH_3(g) + HNO_3(aq) \longrightarrow NH_4NO_3(aq)$
(o) $2NH_3(g) + CO_2(g) + H_2O(l) \longrightarrow (NH_4)_3CO_2(aq)$
(p) $(NH_4)_2CO_3(aq) + CaSO_4 \cdot 2H_2O(s) \longrightarrow CaCO_3(s) + 2H_2O(l)$
$+ (NH_4)_2SO_4(aq)$
(q) $CuSO_4(aq) + Zn(s) \longrightarrow ZnSO_4(aq) + Cu(s)$
(r) $C_6H_6(l) + Cl_2(g) \longrightarrow C_6H_5Cl(l) + HCl(g)$
benzene chlorobenzene
(s) $CS_2(l) + Cl_2(g) \longrightarrow S_2Cl_2(l) + CCl_4(l)$
(t) $C_2H_4(g) + HCl(g) \longrightarrow CH_3CH_2Cl(g)$
ethylene ethylchloride
(u) $CH_3OH(g) + \frac{1}{2}O_2(g) \longrightarrow H_2CO(g) + H_2O(g)$
methyl alcohol formaldehyde
(v) $C_2H_2(g) + H_2O(l) \longrightarrow CH_3CHO(l)$
acetylene acetaldehyde
(w) $n\text{-}C_4H_{10}(g) \longrightarrow C_2H_4(g) + C_2H_6(g)$
butane ethylene ethane
(x) $C_2H_4(g) + C_6H_6(l) \longrightarrow$ ethyl benzene(l)
ethylene benzene
(y) $2C_2H_4(g) \longrightarrow C_4H_8(l)$
ethylene 1-butane
(z) $C_3H_6(g) + C_6H_6(l) \longrightarrow$ cumene(l)
propene benzene isopropyl benzene

4.115. The process of converting SO_2 to sulfuric acid with the aid of nitrogen oxides can be expressed on an overall basis as follows:

$$SO_2(g) + NO_2(g) + H_2O(l) \longrightarrow H_2SO_4(l) + NO(g)$$

This process has been used by the chemical industry for over a century in what is known as the chamber process. With the high dilution of N_2 that accompanies the SO_2, the raw gases have to pass at low velocities through large lead chambers in order to react sufficiently. If 10,000 ft³/hr of NO (measured at S.C.) and 2750 lb/hr of H_2SO_4 are produced, what is the cooling required if the reaction is to proceed isothermally at 77°F?

4.116. Determine the heat of reaction at 25°C and 1 atm for the following reactions from heat of combustion data:

(a) $H_2S(g) + \frac{3}{2}O_2(g) \longrightarrow SO_2(g) + H_2O(g)$
(b) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
(c) $NO(g) + \frac{5}{2}H_2(g) \longrightarrow NH_3(g) + H_2O(g)$

4.117. A mixture of gaseous methane (CH_4) and hydrogen (H_2) was found to transfer heat in a reaction at 25°C of −150.0 kcal/g mol mixture; however, this value was determined under conditions such that the water produced left as a vapor rather than as a liquid as required for the standard values. Calculate the relative compositions of the mixture of CH_4 and H_2.

4.118. The following enthalpy changes are known for reactions at 25°C in the standard thermochemical state:

No.			$\Delta H°$(kJ)
1	$C_3H_6(g) + H_2(g)$	$\longrightarrow C_3H_8(g)$	−123.8
2	$C_3H_8(g) + 5O_2(g)$	$\longrightarrow 3CO_2(g) + 4H_2O(l)$	−2220.0
3	$H_2(g) + \frac{1}{2}O_2(g)$	$\longrightarrow H_2O(l)$	−285.8
4	$H_2O(1)$	$\longrightarrow H_2O(g)$	43.9
5	C(diamond) + $O_2(g)$	$\longrightarrow CO_2(g)$	−395.4
6	C(graphite) + $O_2(g)$	$\longrightarrow CO_2(g)$	−393.5

Calculate:
(a) The heat of formation of propylene
(b) The heat of combustion of propylene

4.119. When 2.00 g of MgO (mol. wt. = 40.32) are formed by burning Mg in air, the laboratory reports that 31,780 J were absorbed by the calorimeter. What is the heat of combustion of Mg per g mol?

4.120. About 30% of crude oil is processed eventually into automobile gasoline. As petroleum prices rise and resources dwindle, alternatives must be found. However, automobile engines can be tuned so that they will run on simple alcohols. Methanol and ethanol can be derived from coal or plant biomass, respectively. While the alcohols produce fewer pollutants than gasoline, they also reduce the travel radius of a tank of fuel. What percent increase in the size of fuel tank is needed to give an equivalent travel radius if gasoline is replaced by alcohol? Base your calculations on 40 kJ/g of gasoline having a sp gr of 0.84, and with the product water as a gas. Make the calculations for **(a)** methanol; **(b)** ethanol.

4.121. Calculate the heat of formation at 25°C of ethyl mercaptan (C_2H_5SH). The following thermal values at 25°C are available.

$$C_2H_5SH(g) + 4.5O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) + SO_2(g) \qquad \Delta H = -1{,}895{,}600 \text{ J/g mol}$$

$$H_2(g) + 0.5O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -241{,}826 \text{ J/g mol}$$

Latent heat of vaporization of water at 25°C is 44,012 J/g mol.

$$C(\beta) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393{,}510 \text{ J/g mol}$$

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -296{,}900 \text{ J/g/ mol}$$

If the first reaction were carried out in a constant-volume calorimeter, what would be the amount of heat liberated?

4.122. A consulting laboratory is called upon to determine the heating value of a natural gas in which the combustible is entirely methane. They do not have a Sargent flow calorimeter, but do have a Parr bomb calorimeter. They pump a measured volume of the natural gas into the Parr bomb, add oxygen to give a total pressure of 1000 kPa, and explode the gas–O_2 mixture with a hot wire. From the data they calculate that the gas has a heating value of 3.44×10^4 kJ/m^3. Should they report this value? Explain.

4.123. Calculate the heat of reaction at 25°C for the following reaction if it takes place at constant volume.

$$C_2H_4(g) + 2H_2(g) \longrightarrow 2CH_4(g)$$

4.124. If 1 lb mol of Cu and 1 lb mol of H_2SO_4(100%) react together completely in a bomb calorimeter, how many Btu is absorbed (or evolved)? Assume that the products are $H_2(g)$ and solid $CuSO_4$. The initial and final temperatures in the bomb are 25°C.

4.125. In the reaction

$$4FeS_2(s) + 11O_2(g) \longrightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

the conversion of $FeS_2(s)$ to $Fe_2O_3(s)$ is only 80% complete. If the standard heat of reaction for the reaction is calculated to be -197.7 kcal/g mol $FeS_2(s)$, what value of ΔH^0_{rxn} will you use in the energy balance per kg of FeS_2 fed?

4.126. Find the higher (gross) heating value of $H_2(g)$ at 0°C.

4.127. The chemist for a gas company finds a gas analyzes 9.2% CO_2, 0.4% C_2H_4, 20.9% CO, 15.6% H_2, 1.9% CH_4, and 52.0% N_2. What should the chemist report as the gross heating value of the gas?

4.128. What is the higher heating value of 1 m^3 of *n*-propylbenzene measured at 25°C and 1 atm and with a relative humidity of 40%?

4.129. An off-gas from a crude oil topping plant has the following composition:

Component	Vol. %
Methane	88
Ethane	6
Propane	4
Butane	2

(a) Calculate the higher heating value on the following bases: (1) Btu per pound, (2) Btu per mole, and (3) Btu per cubic foot of off-gas measured at 60°F and 760 mm Hg.

(b) Calculate the lower heating value on the same three bases indicated in part (a).

4.130. Calculate the lower heating value of methane at 100°C.

4.131. Compute the heat of reaction at 600 K for the following reaction:

$$S(\ell) + O_2(g) \longrightarrow SO_2(g)$$

4.132. Calculate the heat of reaction at 500°C for the decomposition of propane.

$$C_3H_8 \longrightarrow C_2H_2 + CH_4 + H_2$$

4.133. In a new process for the recovery of tin from low-grade ores, it is desired to oxidize stannous oxide, SnO, to stannic oxide, SnO_2, which is then soluble in caustic solution. What is the heat of reaction at 90°C and 1 atm for the reaction $SnO + \frac{1}{2}O_2 \longrightarrow SnO_2$? Data are:

	ΔH_f^0 (kJ/g mol)	C_p [J/(g mol)(K)], T in K
SnO	−283.3	$39.33 + 15.15 \times 10^{-3}T$
SnO_2	−577.8	$73.89 + 10.04 \times 10^{-3}T - \dfrac{2.16 \times 10^6}{T^2}$

4.134. Develop an equation to be used in a computer code from which the heat of the following reaction in kJ/g mol FeO can be calculated at any temperature T (in K).

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

	C_p [J/(g mol)(K)]
Fe	$14.1 + 29.71 \times 10^{-3}T + 1.80 \times 10^5T^{-2}$
FeO	$38.79 + 20.08 \times 10^{-3}T$
CO	$27.61 + 5.02 \times 10^{-3}T$
CO_2	$32.21 + 22.18 \times 10^{-3}T - 3.47 \times 10^{-6}T^2$

4.135. To take care of peak loads in the winter, the local gas company wishes to supplement its limited supply of natural gas (CH_4) by catalytically hydrogenating a heavy liquid petroleum oil that it can store in tanks. The supplier says that the oil has a U.O.P. Characterization Factor of 12.0 and an API gravity of 30°API. To minimize carbon deposition on the catalyst, twice the required amount of hydrogen is introduced with the oil. The reactants enter at 70°F and after heat exchange the products leave at 70°F. Calculate the following, per 1000 ft^3 of CH_4 at the standard conditions in the gas industry:

(a) The pounds of oil required
(b) The heat input or output to the catalytic reactor

4.136. Calculate the heat of reaction of the following reactions at the stated temperature:

(a) $MgO(s) + C(s) + Cl_2(g) \xrightarrow{850°C} MgCl_2(s) + CO(g)$

(b) $\underset{\text{methyl alcohol}}{CH_3OH(g)} + \frac{1}{2}O_2(g) \xrightarrow{200°C} \underset{\text{formaldehyde}}{H_2CO(g)} + H_2O(g)$

(c) $SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{300°C} SO_3(g)$

4.137. Sulfur can be recovered from the H_2S in natural gas by the following reaction:

$$3H_2S(g) + 1\tfrac{1}{2}O_2(g) \longrightarrow 3S(s) + 3H_2O(g)$$

For the stoichiometric ratio of materials, with H_2S and O_2 entering the process at 300°F and the products leaving the reactor at 100°F, calculate the heat of reaction in British thermal units per pound of sulfur formed. Assume that the reaction is complete. If it is only 75% complete, will this change your answer, and if so, how much?

4.138. Propane, butane, or liquefied petroleum gas (LPG) has seen practical service in passenger automobiles for 30 years or more. Because it is used in the vapor phase, it pollutes less than gasoline but more than natural gas. A number of cars in the Clean Air Car Race ran on LPG. The table below lists their results and those for natural gas. It must be kept in mind that these vehicles were generally equipped with platinum catalyst reactors and with exhaust-gas recycle. Therefore, the gains in emission control did not come entirely from the fuels.

	Natural gas, avg. 6 cars	LPG, avg. 13 cars	Fed std.
HC (g/mi)	1.3	0.49	0.22
CO (g/mi)	3.7	4.55	2.3
NO_x (g/mi)	0.55	1.26	0.6

Suppose that in a test butane gas at 100°F is burned completely with the stoichiometric amount of heated air which is at 400°F and a dew point of 77°F in an engine. To cool the engine, 12.5 lb of steam at 100 psia and 95% quality was generated from water at 77°F per pound of butane burned. It may be assumed that 7% of the gross heating value of the butane is lost as radiation from the engine. Will the exhaust gases leaving the engine exceed the temperature limit of the catalyst of 1500°F?

4.139. Liquid hydrazine (N_2H_4) is injected into a jet combustion chamber at 100°C, where it is ignited and burns in an airstream with 100% excess air preheated to 500°C. The hot gases issue directly from the end of the reactor. What is their temperature?

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(g) \qquad \begin{aligned} C_p\ N_2H_4(l) &= 33.2\ \text{cal/(g mol)(°C)} \\ \Delta H_v\ N_2H_4(l) &= 10.7\ \text{kcal/g mol at 25°C} \end{aligned}$$

4.140. The data for this problem have been taken from D. Dyer, G. Maples, and J. C. Maxwell, *Measuring and Improving the Efficiency of Boilers* (Cambridge, Mass.: MIT Press, 1982), Chapter 2. A boiler (see Fig. P4.140) burns the following fuel:

CH_4	90.05%	N_2	5.518%
C_2H_6	1.98%	O_2	1.467%
C_3H_8	0.202%	H_2	0.31%
C_4H_{10}	0.069%	CO_2	0.662%
C_5H_{12}	0.018%		

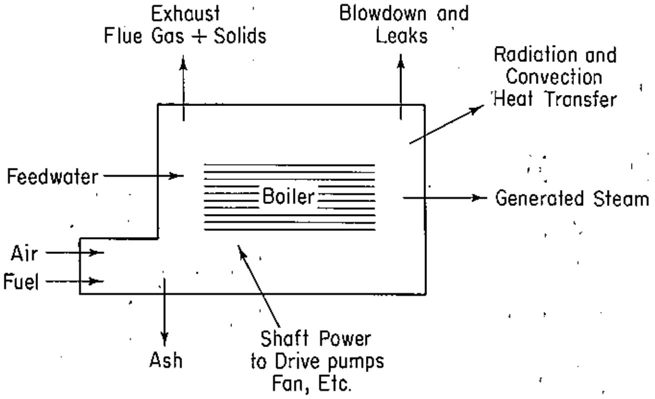


Figure P4.140

In a test for boiler efficiency, the following data were collected:

Variable	Value
Feedwater mass flow rate	50,603 lb/hr
Feedwater inlet temperature	228°F
Steam exit pressure	347.5 psig
Mass loss due to blowdown	0
Enthalpy of steam	1196.4 Btu/lb
Mass flow rate of fuel	2790.2 lb/hr
Inlet temperature of the fuel	55°F
Inlet pressure of the fuel	8.5 psig
Inlet temperature of the air	70°F
Inlet pressure of the air	14.7 psia
Relative humidity of the air	20%
Flue-gas temperature	345°F
Orsat analysis:	
CO_2 volume in flue gas	10.1%
CO volume in flue gas	0.1%
O_2 volume in flue gas	1.9%

Carry out material and energy balances, and calculate the boiler efficiency defined by

$$\text{efficiency} = \frac{(\text{mass of water evaporated/hr})(\Delta\hat{H}_{\text{steam}} - \Delta\hat{H}_{\text{feed water}})}{(\text{mass of fuel flow/hr})(\text{HHV}_{\text{fuel}})}$$

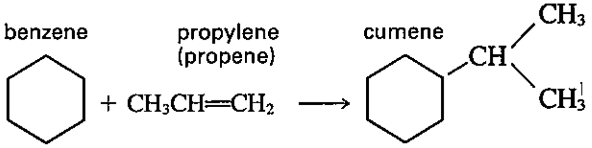
Also calculate the dew point of the exit flue gas and the air-to-fuel ratio in lb/lb.

4.141. Formaldehyde can be made by the partial oxidation of natural gas using pure oxygen made industrially from liquid air. The natural gas must be in large excess.

$$CH_4 + O_2 \longrightarrow CH_2O + H_2O$$

The CH_4 is heated to 400°C and the O_2 to 300°C and introduced into a reaction chamber. The products leave the cooled chamber at 600°C and show an Orsat analysis of CO_2 1.9, CH_2O 11.7, O_2 3.8, and CH_4 82.6%. How much heat is removed from the reaction chamber per 1000 kg of formaldehyde produced?

4.142. In a new process for making phenol, cumene (isopropylbenzene) is oxidized with air to form cumene hydroperoxide, which is then changed to phenol and acetone. The cumene is made by the direct alkylation of gaseous benzene, using a phosphoric acid–kieselguhr catalyst and operating conditions of 500 K.



Calculate the heat of reaction at 500 K.

Enthalpy data for benzene (C_6H_6) amd cumene (C_9H_{12}) are as follows:

	ΔH (J/g mol)	
T (K)	C_6H_6	C_9H_{12}
273	0	0
298	1,946	3,628
400	2,109	21,585
500	24,372	43,786

4.143. A catalytic converter for the production of SO_3 from SO_2 is operating as illustrated in Fig. P4.143. The material balance for 1 hr of operation is also shown in Fig. P4.143.

$$SO_2(g) + 0.5O_2(g) \longrightarrow SO_3 \qquad \Delta H^\circ_{25} = -98{,}280 \text{ J/g mol}$$

The unit is insulated and heat losses are negligible. It has been found that corrosion can be reduced considerably by keeping the discharge temperature at approximately 400°C.

Determine the heat duty of a cooler for the converter that will accomplish this purpose.

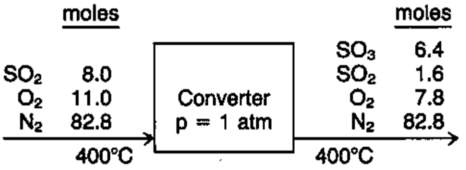


Figure P4.143

4.144. It is desired to volatilize the iron from a reaction mixture by treating it with chlorine gas and driving off the ferric chloride formed. The reaction is

$$Fe_2O_3(s) + 3C(s) + 3Cl_2(g) \longrightarrow 3CO(g) + 2FeCl_3(g)$$

The reaction mixture containing 10% Fe_2O_3 plus C is introduced into the reactor at 50°C. The Cl_2 gas is used in 10% excess and is preheated to 200°C by the products leaving. The reactor is kept at the vaporization point of $FeCl_3$ (300°C) at which the liquid $FeCl_3$ is vaporized and swept out by the gases formed.

Calculate the heat that must be added or removed from the reactor per gram of charge in order that the temperature will be maintained at 300°C. Use the following data if applicable.

$$\text{FeCl}_3\text{: } \Delta H_{\underset{280°\text{C}}{\text{fusion}°}} \quad c \longrightarrow l \qquad 43{,}095 \text{ J/g mol}$$

$$\Delta H^{\circ}_{\underset{300°\text{C}}{\text{vaporization}}} \quad l \longrightarrow g \qquad 26{,}108 \text{ J/g mol}$$

Approximate $C_p(s) = 121$ J/(g mol)(K)

Approximate $C_p(l) = 102.5$ J/(g mol)(K)

Approximate C_p of the charge = 1.26 J/(g)(K) mixt. of Fe_2O_3 + C

4.145. Three fuels are being considered as a heat source for a metallurgical process:

	Components	Percent
Gas	CH_4	96.0
	CO_2	3.0
	N_2	1.0
Oil (liquid)	$C_{16}H_{34}$	99.0
	S	1.0
Coke	C	95.0
	ash	5.0

Calculate the maximum flame temperature (i.e., combustion with the theoretically required amount of air) for each of the three fuels assuming that the fuels and air enter at 18°C, and the ash (C_p = 1.15 J/(g)(°C)) leaves the combustion chamber containing no carbon and at 527°C. Which fuel gives the highest temperature?

4.146.* Calculate the adiabatic flame temperature of $C_3H_6(g)$ at 1 atm when burned with 20% excess air, and the reactants enter at 25°C.

4.147.* A fuel oil (liquid) composed of C (86.0%), H (10.0%), and S (4.0%) is burned with 20% excess air. The oil enters the process at 200°F and the air at 300°F. The water vapor in the air is at a dew point of 101°F when the barometer reads 750 mm Hg. Compute the adiabatic flame temperature in the process. The mean heat capacity of the oil can be assumed to be 0.50 Btu/(lb)(°F) and the heat of reaction [to form $CO_2(g)$, $H_2O(g)$, and $SO_2(g)$] is 17,860 Btu/lb at 25°C and 1 atm.

4.148.* If CO at constant pressure is burned with excess air and the theoretical flame temperature is 1255 K, what was the percentage of excess air used? The reactants enter at 93°C.

4.149.* Which substance will give the higher theoretical flame temperature if the inlet percentage of excess air and temperature conditions are identical: (1) CH_4, (2) C_2H_6, or (3) C_4H_8?

Section 4.8

4.150. A mixture containing 65% H_2SO_4 (and 35% water) is at 320°F and 1 atm. Answer the following questions.

(a) How many phases are present in the mixture?

(b) What is the percent liquid and/or vapor in the mixture, and what is the mass fraction of each component?

(c) What is the enthalpy of the mixture?

(d) If 100 lb of this mixture is added to 50 lb of a 20% solution of H_2SO_4 at 220°F, what is the (1) mass, (2) composition, and (3) temperature and enthalpy of the final solution?

4.151. (a) In a petrochemical plant 1 ton/hr of 50% by weight H_2SO_4 is being produced at 250°F by concentrating 30% H_2SO_4 supplied at 100°F. From the data provided, find the heat that has to be supplied per hour.

Btu evolved at 100°F per lb mol H_2SO_4	Moles of H_2O per mol of H_2SO_4
18,000	2
21,000	3
23,000	4
24,300	5
27,800	10
31,200	22

C_p [Btu/(lb)(°F)]	30% H_2SO_4	50% H_2SO_4
100	0.80	0.70
250	0.75	0.60

The C_p of water vapor is about 0.50, and for water use, 1.0.

(b) Using the same data as in part (a), what is the temperature of a solution of 30% by weight H_2SO_4 if it is made from 50% H_2SO_4 at 100°F and pure water at 200°F if the process is adiabatic?

4.152.* (a) From the data plot the enthalpy of 1 *mole of solution* at 27°C as a function of the weight percent HNO_3. Use as reference states liquid water at 0°C and liquid HNO_3 at 0°C. You can assume that C_p for H_2O is 75 J/(g mol)(°C) and for HNO_3, 125 J/(g mol)(°C).

$-\Delta H_{\text{soln}}$ at 27°C (J/g mol HNO_3)	Moles H_2O added to 1 mole HNO
0	0.0
3,350	0.1
5,440	0.2
6,900	0.3
8,370	0.5
10,880	0.67
14,230	1.0
17,150	1.5
20,290	2.0
24,060	3.0

$-\Delta H_{\text{soln}}$ at 27°C (J/g mol HNO_3)	Moles H_2O added to 1 mole HNO
25,940	4.0
27,820	5.0
30,540	10.0
31,170	20.0

(b) Compute the energy absorbed or evolved at 27°C on making a solution of 4 moles of HNO_3, and 4 moles of water by mixing a solution of $33\frac{1}{3}$ mol % acid with one of 60 mol % acid.

4.153.* *National Bureau of Standards Circular 500* gives the following data for calcium chloride (mol. wt. 111) and water:

Formula	State	$-\Delta H_f$ at 25°C (kcal/g mol)
H_2O	Liquid	68.317
	Gas	57.798
$CaCl_2$	Crystal	190.0
	in 25 moles of H_2O	208.51
	50	208.86
	100	209.06
	200	209.20
	500	209.30
	1000	209.41
	5000	209.60
	∞	209.82
$CaCl_2 \cdot H_2O$	Crystal	265.1
$CaCl_2 \cdot 2H_2O$	Crystal	335.5
$CaCl_2 \cdot 4H_2O$	Crystal	480.2
$CaCl_2 \cdot 6H_2O$	Crystal	623.15

Calculate the following:

(a) The energy evolved when 1 lb mol of $CaCl_2$ is made into a 20% solution at 77°F

(b) The heat of hydration of the dihydrate to the hexahydrate

(c) The energy evolved when a 20% solution containing 1 lb mol of $CaCl_2$ is diluted with water to 5% at 77°F

4.154. A vessel contains 100 g of an $NH_4OH–H_2O$ liquid mixture at 25°C and 1 atm that is 15.0% by weight NH_4OH. Just enough aqueous H_2SO_4 is added to the vessel from an H_2SO_4 liquid mixture at 25°C and 1 atm (25.0 mole % H_2SO_4) so that the reaction to $(NH_4)_2SO_4$ is complete. After the reaction, the products are again at 25°C and 1 atm. How much heat (in J) is absorbed or evolved by this process? It may be assumed that the final volume of the products is equal to the sum of the volumes of the two initial mixtures.

4.155. An ammonium hydroxide solution is to be prepared at 77°F by dissolving gaseous NH_3 in water. Prepare charts showing:

(a) The amount of cooling needed (in Btu) to prepare a solution containing 1 lb mol of NH_3 at any concentration desired

(b) The amount of cooling needed (in Btu) to prepare 100 gal of a solution of any concentration up to 35% NH_3

(c) If a 10.5% NH_3 solution is made up without cooling, at what temperature will the solution be after mixing?

4.156. Prepare an enthalpy–concentration chart for the sulfuric acid–water system, and compare your chart with the one in Appendix I. You will have to look up the necessary data in reference books or the literature.

4.157. Draw the saturated-liquid line (1 atm isobar) on an enthalpy concentration chart for caustic soda solutions. Show the 200°F, 250°F, 300°F, 350°F, and 400°F isotherms in the liquid region, and draw tie lines for these temperatures to the vapor region. Using the data from *National Bureau of Standards Circular 500,* show where molten NaOH would be on this chart. Take the remaining data from the following table and the steam tables.

Temp. (°F)	x, Satd. liquid conc. wt fraction	$\Delta\hat{H}$, Enthalpy, satd. liquid (Btu/lb)
200	0	168
250	0.34	202
300	0.53	314
350	0.68	435
400	0.78	535

C_p for NaOH solutions [Btu/(lb)(°F)]

Wt % NaOH	Temperature (°F)				
	32	60	100	140	180
10	0.882	0.897	0.911	0.918	0.922
20	0.842	0.859	0.875	0.884	0.886
30		0.837	0.855	0.866	0.869
40		0.815	0.826	0.831	0.832
50			0.769	0.767	0.765

NOTE: All H_2O tie lines extend to pure water vapor.

SOURCE: J. W. Bertetti and W. L. McCabe, *Ind. Eng. Chem.*, v. 28, p. 375 (1936).

4.158. An evaporator at atmospheric pressure is designed to concentrate 10,000 lb/hr of a 10% NaOH solution at 70°F into a 40% solution. The steam pressure inside the steam chest is 40 psig. Determine the pounds of steam needed per hour if the exit strong caustic preheats the entering weak caustic in a heat exchanger, leaving the heat exchanger at 100°F.

4.159. A 50% by weight sulfuric acid solution is to be made by mixing the following:

(1) Ice at 32°F
(2) 80% H_2SO_4 at 100°F
(3) 20% H_2SO_4 at 100°F

How much of each must be added to make 1000 lb of the 50% solution with a final temperature of 100°F if the mixing is adiabatic?

4.160. Saturated steam at 300°F is blown continuously into a tank of 30% H_2SO_4 at 70°F. What is the highest concentration of liquid H_2SO_4 that can result from this process?

4.161. One thousand pounds of 10% NaOH solution at 100°F is to be fortified to 30% NaOH by adding 73% NaOH at 200°F. How much 73% solution must be used? How much cooling must be provided so that the final temperature will be 70°F?

4.162. A mixture of ammonia and water in the vapor phase, saturated at 250 psia and containing 80% by weight ammonia, is passed through a condenser at a rate of 10,000 lb/hr. Heat is removed from the mixture at the rate of 5,800,000 Btu/hr while the mixture passes through a cooler. The mixture is then expanded to a pressure of 100 psia and passes into a separator. A flow sheet of the process is given Fig. P4.162. If the heat loss from the equipment to the surroundings is neglected, determine the composition of the liquid leaving the separator by a material and energy balance set of equations.

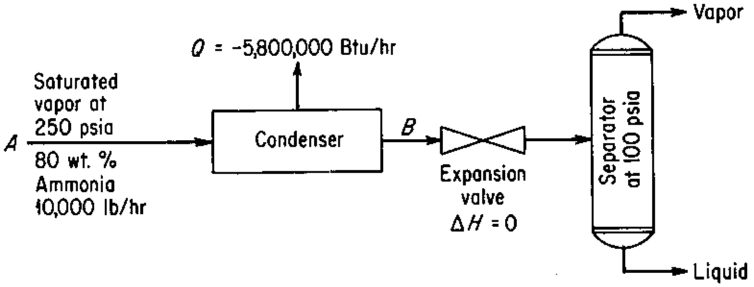


Figure P4.162

Section 4.9

4.163. Autumn air in the deserts of the southwestern United States during the day will typically be moderately hot and dry. If a dry-bulb temperature of 27°C and a wet-bulb temperature of 17°C is measured for the air at noon:
(a) What is the dew point?
(b) What is the percent relative humidity?
(c) What is the percent humidity?

4.164. The air supply for a dryer has a dry-bulb temperature of 32°C and a wet-bulb temperature of 25.5°C. It is heated to 90°C by coils and blown into the dryer. In the dryer, it cools along an adiabatic cooling line as it picks up moisture from the dehydrating material and leaves the dryer fully saturated.
(a) What is the dew point of the initial air?
(b) What is its humidity?
(c) What is its percent relative humidity?

(d) How much heat is needed to heat 100 m³ to 90°C?
(e) How much water will be evaporated per 100 m³ of air entering the dryer?
(f) At what temperature does the air leave the dryer?

4.165. Moist air at 100 kPa, a dry-bulb temperature of 90°C, and a wet-bulb temperature of 46°C is enclosed in a rigid container. The container and its contents are cooled to 43°C.
(a) What is the molar humidity of the cooled moist air?
(b) What is the final total pressure in atm in the container?
(c) What is the dew point in °C of the cooled moist air?

4.166. Calculate:
(a) The humidity of air saturated at 120°F
(b) The saturated volume at 120°F
(c) The adiabatic saturation temperature and wet-bulb temperature of air having a dry-bulb T = 120°F and a dew point = 60°F
(d) The percent saturation when the air in (3) is cooled to 82°F
(e) The pounds of water condensed/100 lb of moist air in (3) when the air is cooled to 40°F

4.167. A rotary dryer operating at atmospheric pressure dries 10 tons/day of wet grain at 70°F, from a moisture content of 10% to 1% moisture. The air flow is countercurrent to the flow of grain, enters at 225°F dry-bulb and 110°F wet-bulb temperature, and leaves at 125°F dry-bulb. See Fig. P4.167. Determine:
(a) The humidity of the entering and leaving air
(b) The water removal in pounds per hour
(c) The daily product output in pounds per day
(d) The heat input to the dryer
Assume that there is no heat loss from the dryer, that the grain is discharged at 110°F, and that its specific heat is 0.18.

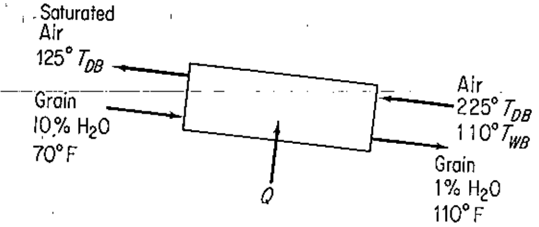


Figure P4.167

4.168. Temperatures (in °F) taken around a forced-draft cooling tower are as follows:

	In	Out
Air	85	90
Water	102	89

The wet-bulb temperature of the entering air is 77°F. Assuming the air leaving the tower to be saturated, calculate with the aid of the data given below:
(a) The humidity of the entering air
(b) The pounds of dry air through the tower per pound of water into the tower
(c) The percentage of water vaporized in passing through the tower

T (°F)	77	85	89	90	100	102
Saturated $\mathscr{H}$	0.0202	0.0264	0.030	0.031	0.0425	0.0455

C_p air = 0.24; C_p water vapor = 0.45; ΔH_v = 1040 Btu/lb at any of the temperatures encountered in this problem.

4.169. A dryer produces 180 kg/hr of a product containing 8% water from a feed stream that contains 1.25 g of water per gram of dry material. The air enters the dryer at 100°C dry-bulb and a wet bulb temperature of 38°C; the exit air leaves at 53°C dry-bulb and 60% relative humidity. Part of the exit air is mixed with the fresh air supplied at 21°C, 52% relative humidity, as shown in Fig. P4.169. Calculate the air and heat supplied to the heater, neglecting any heat lost by radiation, used in heating the conveyor trays, and so forth. The specific heat of the product is 0.18.

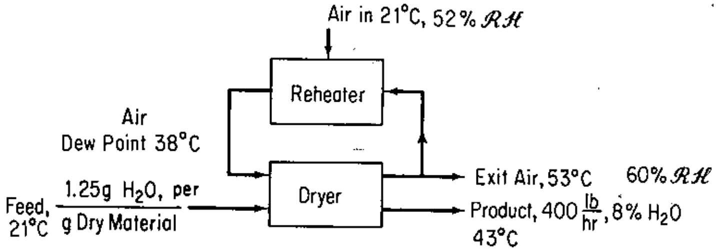


Figure P4.169

4.170. Air, dry bulb 38°C, wet bulb 27°C, is scrubbed with water to remove dust. The water is maintained at 24°C. Assume that the time of contact is sufficient to reach complete equilibrium between air and water. The air is then heated to 93°C by passing it over steam coils. It is then used in an adiabatic rotary drier from which it issues at 49°C. It may be assumed that the material to be dried enters and leaves at 46°C. The material loses 0.05 kg H_2O per kilogram of product. The total product is 1000 kg/hr.

(a) What is the humidity:

- **(1)** Of the initial air?
- **(2)** After the water sprays?
- **(3)** After reheating?
- **(4)** Leaving the drier?

(b) What is the percent humidity at each of the points in part (a)?

(c) What is the total weight of dry air used per hour?

(d) What is the total volume of air leaving the drier?

(e) What is the total amount of heat supplied to the cycle in joules per hour?

PROBLEMS THAT REQUIRE WRITING COMPUTER PROGRAMS

4.1. The enthalpy of a mixture of constant composition at any constant temperature T is

$$\Delta H_{\text{mixture}}(T, p) = \sum_{i=1}^{n} x_i \sum H_i^0(T, p) - \Delta H_{\text{mixture}}^{D}(T, p)$$

where the deviation, ΔH^D, is a correction because of high pressure. Use of the Benedict-Webb-Rubin (BWR) equation (see Table 3.2) gives the following for ΔH^D:

$$\Delta H^D = \left(B_0RT - 2A_0 - 4\frac{C_0}{T^2}\right)\rho + \frac{1}{2}(2bRT - 3a)\rho^2 + \frac{6}{5}(a\alpha\rho^5)$$

$$+ \frac{c\rho}{T^2}\left[\frac{3[1 - \exp(-\gamma\rho^2)]}{\gamma\rho^2} - \left(\frac{1}{2} - \gamma\rho^2\right)\exp(-\gamma\rho^2)\right]$$

Use the density values calculated in Computer Problem 3.3 for ρ, and prepare an additional subroutine to give $\Delta H^D_{\text{mixture}}(T, p)$ for selected T and p pairs. Refer to Computer Problem 3.3 for other pertinent information.

4.2. Prepare a computer program to find the adiabatic flame temperature of a gas such as in Problem 4.129. Assume that the principal reactant is completely burned.

4.3. Prepare a more general program than the one in Computer Problem 4.2 to compute the adiabatic flame temperature. Assume that several hydrocarbons of the form CH_n can be burned with various amounts of excess air. The percentage of excess air is to be read into the program as well as the type of fuel gas or solid. The only combustion products that need to be considered are carbon dioxide, carbon monoxide, water, hydrogen, oxygen, and nitrogen. Make provision for the following additional parameters:

(a) Pressure in the burner
(b) Humidity of the incoming air
(c) Number of moles of each hydrocarbon and of nitrogen in the fuel stream
(d) Standard heats of formation for all the hydrocarbon gases burned and the products (Assume that gaseous water is formed in the reaction.)
(e) Heat capacities of all components
(f) Inlet reactant temperature, which may be different for each reactant.

The gases can be treated as an ideal mixture.

4.4. Gonzales-Pozo listed the coefficients that can be used to predict the properties of saturated liquid water and steam based on the equation

$$Y = Ap + B/p + Cp^{1/2} + D\ln p + Ep^2 + Fp^3 + G$$

where p is the pressure in psia. Prepare a computer program to calculate the liquid and vapor specific volume, temperature, liquid enthalpy, heat of vaporization, vapor enthalpy, liquid internal energy, and vapor internal energy based on the set of coefficients in Table P4.4. Check your program calculations with the steam tables.

4.5. Prepare a graph in which the vertical axis shows the fraction of the gross energy input from the fuel in a combustion process that is available for transfer to the process as a fraction of the stack gas temperature in °F on the horizontal axis. Use as a third parameter lines of percent excess air that are used in the combustion. The graph you prepare can be used to answer such questions as:

(a) How much energy could be saved if the stack gas temperature were reduced 10% or the excess air reduced 10%?
(b) What conditions limit the extent to which the efficiency can be improved?

4.6. Prepare a Fortran program that will use the input number of atoms of C, H, and O in the fuel, the reactant moles and temperatures, and product composition and temperature, to make both material and energy balances for a combustion process. Assume that the process is adiabatic. Take the heat capacity equations and ΔH_f° data from Appendix K and Table D.1.

4.7. Prepare a Fortran program that uses either (a) the dry-bulb temperature plus the wet-bulb temperature, or (b) the dry-bulb temperature and the dew point, or (c) the dry-bulb temperature and the relative humidity of (1) the inlet air and (2) the outlet air, respectively, to calculate the amount of water condensed, the heat added or removed, and the dew point temperature of outlet air for a cooling unit given the input of wet air in m³/min.

TABLE P4.4

Property	*A*	*B*	*C*
Temperature (°F)	-0.17724	3.83986	11.48345
Liquid specific volume (ft³/lb)	-5.280126×10^{-7}	2.99461×10^{-5}	1.521874×10^{-4}
Vapor specific volume (ft³/lb)			
1–200 psia	-0.48799	304.717614	9.8299035
200–1,500 psia	2.662×10^{-3}	457.5802	-0.176959
Liquid enthalpy (Btu/lb)	-0.15115567	3.671404	11.622558
Vaporization enthalpy (Btu/lb)	0.008676153	-1.3049844	-8.2137368
Vapor enthalpy (Btu/lb)	-0.14129	2.258225	3.4014802
Liquid entropy [Btu/(lb)(°R)]	-1.67772×10^{-4}	4.272688×10^{-3}	0.01048048
Vaporization entropy [Btu/(lb)(°R)]	3.454439×10^{-5}	-2.75287×10^{-3}	-7.33044×10^{-3}
Vapor entropy [Btu/(lb)(°R)]	-1.476933×10^{-4}	1.2617946×10^{-3}	3.44201×10^{-3}
Liquid internal energy (Btu/lb)	-0.1549439	3.662121	11.632628
Vapor internal energy (Btu/lb)	-0.0993951	1.93961	2.428354

Property	*D*	*E*	*F*	*G*
Temperature (°F)	31.1311	8.762969×10^{-5}	-2.78794×10^{-8}	86.594
Liquid specific volume (ft³/lb)	6.62512×10^{-5}	8.408856×10^{-10}	1.86401×10^{-14}	0.01596
Vapor specific volume (ft³/lb)				
1–200 psia	-16.455274	9.474745×10^{-4}	-1.363366×10^{-6}	19.53953
200–1,500 p	0.82682	-4.601876×10^{-7}	6.3181×10^{-11}	-2.3928
Liquid enthalpy (Btu/lb)	30.832667	8.74117×10^{-5}	-2.62306×10^{-8}	54.55
Vaporization enthalpy (Btu/lb	-16.37649	-4.3043×10^{-5}	9.763×10^{-9}	$1{,}045.81$
Vapor enthalpy (Btu/lb)	14.438078	4.222624×10^{-5}	-1.569916×10^{-8}	$1{,}100.5$
Liquid entropy [Btu/(lb)(°R)]	0.05801509	9.101291×10^{-8}	-2.7592×10^{-11}	0.11801
Vaporization entropy [Btu/(lb)(°R)]	-0.14263733	-3.49366×10^{-8}	7.433711×10^{-12}	1.85565
Vapor entropy [Btu/(lb)(°R)]	-0.08494128	6.89138×10^{-8}	-2.4941×10^{-11}	1.97364
Liquid internal energy (Btu/lb	30.82137	8.76248×10^{-5}	-2.646533×10^{-8}	54.56
Vapor internal energy (Btu/lb)	10.9818864	2.737201×10^{-5}	-1.057475×10^{-8}	$1{,}040.03$

SOURCE: V. Gonzalez-Pozo, *Chem. Eng.*, p. 123 (May 12, 1986).

SOLVING MATERIAL AND ENERGY BALANCES VIA COMPUTER CODES

5

Now that you have accumulated some experience in making energy balances and in the principles of thermochemistry, it is time to apply this knowledge to more complex problems involving both material and energy balances. You have already encountered some simple examples of combined material and energy balances, as, for

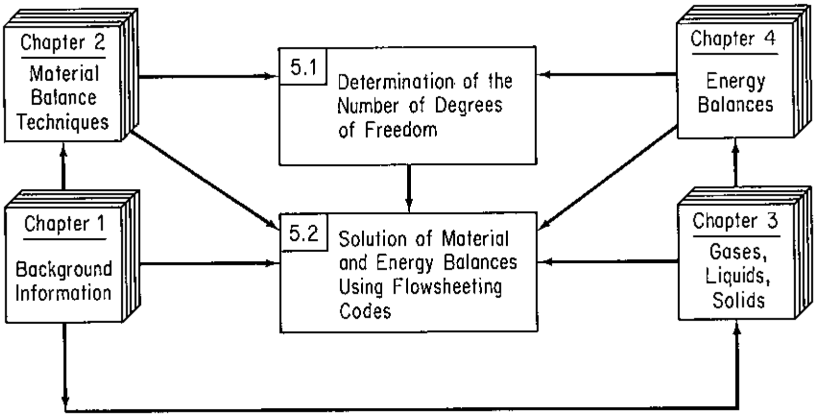


Figure 5.0 Hierarch of topics to be studied in this chapter (section numbers are in the upper left-hand corner of the boxes).

example, in the calculation of the adiabatic reaction temperature, where a material balance provides the groundwork for the writing of an energy balance. In fact, in all energy balance problems, however trifling they may seem, you must know the amount of material entering and leaving the process if you are to apply successfully the appropriate energy balance equation(s).

In this chapter we first examine how to make sure that a problem is properly and completely specified by extending our earlier treatment in Chap. 2 of the analysis of the degrees of freedom. Then we review how computer codes and, in particular, flowsheeting codes can be employed to solve complex problems. Figure 5.0 shows the relationships among two topics to be discussed in this chapter, and the relationships with topics in previous chapters.

5.1 ANALYSIS OF THE DEGREES OF FREEDOM

Your objectives in studying this section are to be able to:

1. Identify the names and numbers of variables in the streams entering and leaving a processing unit, and the variables associated with the unit itself.
2. Identify the types and numbers of all the equations (= 0) (and any inequality constraints (≤0)) that relate to the variables.
3. Determine the number of independent equations for each processing unit.
4. Calculate the number of degrees of freedom (decision variables) for single units and combination of units both without and with a reaction taking place.
5. Specify the values of variables equal to the number of degrees of freedom for a unit.
6. Accomplish numbers 1 through 5 for combinations of units, including bypass and recycle streams.

An important aspect of combined material and energy balance problems is how to ensure that the process equations or sets of modules are determinate, that is, have at least one solution, and hopefully no more than one solution. The question is: How many variables are unknown, and how many must have their values specified in any problem? The **number of degrees of freedom** is the number of variables in a set of *independent* equations to which values must be assigned to make the number of unknown variables plus the variables assigned values equal to the number of equations. We will first discuss the number of degrees of freedom associated with a process stream, next evaluate how many degrees of freedom exist for a unit module, and finally examine the degrees of freedom in a complete flowsheet.

Let N_d = number of degrees of freedom, N_v = number of variables, and N_r = number of equations (restrictions, constraints). Then for N_r independent equations in general

$$N_d = N_v - N_r \tag{5.1}$$

and we conclude that $N_v - N_r$ variables must be specified **as long as the N_r equations are still independent.** The latter is an important point because, as we showed in Chap. 2, it is not always easy to write the set of equations that exactly model a unit operation (ignoring problems with the theory underlying the equations). You can write too many equations, but not notice that one or more of them are not independent (i.e., can be derived by combining others). If you make a mistake in the count for N_d, you may formulate a set of equations that has an infinite number of solutions or a least-squares solution (for a set of indeterminate equations), and not understand why, or perhaps not even notice, that the results returned by executing a computer code are wrong.

How many variables are required to specify a process stream completely? To characterize a process stream we can select among temperature, pressure, total flow, overall mole fractions, phase fractions, mole fractions, total enthalpy, phase enthalpies, and so on. How many variables are needed to fix completely the state of the stream if we assume that phase and chemical equilibrium exist in the stream? A review of the phase rule shows that for a single phase, the degrees of freedom associated with a stream are equal to $C - 1 + 2 = C + 1$ intensive variables. A little thought will indicate that in the absence of reaction, you must in addition add the total flow rate of a stream to the count to specify the stream completely. The variables often associated with a stream are p, T, the total molar (mass) flow, and $C - 1$ overall mole (mass) fractions for the components. An equivalent set would be p, T, and the individual component molar flow rates. You cannot specify C compositions, and the molar flow rate as one composition is redundant.

Thus we can conclude that the number of variables needed to specify the condition of a stream completely is given by

$$N_v = N_{sp} + 2 \tag{5.2}$$

where N_{sp} is the number of chemical species in the stream. You should keep in mind that in a binary system, for example, in which one stream component is zero, for consistency you would count $N_{sp} = 2$ with the one component having a zero value treated as a restriction.

Next, let us look at how to ascertain the number of degrees of freedom for a complete process unit. We will see that each process unit has a different number of degrees of freedom associated with it. In particular we need to pay close attention as to how to count N_v and N_r in Eq. (5.1). The total number of variables for all streams entering or leaving the boundaries of a process unit would be

$$N_v = N_s(N_{sp} + 2) + N_Q + N_W + N_p \tag{5.3}$$

where N_s = total number of streams
N_Q = number of heat transfer variables
N_W = number of work variables
N_p = number of equipment parameters, such as kinetic rate constants, equilibrium constants, recycle ratio, and so on

What types of constraints do you have to include in the count for N_r for a process unit? Here is a list of the common restrictions:

- **(a)** Material balances
- **(b)** One energy balance
- **(c)** Equipment constraints involving the equipment parameters and equilibrium relations
- **(d)** Variables with prespecified values—one constraint for each specification (as long as the material and energy balances are still independent), or fixed ratios of components and so on. Note that if the energy balance is not involved in the process, the energy balance as a constraint will not be independent. It will be the same as an overall material balance.

We now take up five simple processes in Example 5.1, and evaluate the number of degrees of freedom for each.

EXAMPLE 5.1 Determining the Degrees of Freedom in a Process

We shall consider five typical processes, as depicted by the respective figures below, and for each ask the question: How many variables have to be specified [i.e., what are the degrees of freedom (N_d)] to make the problem of solving the combined material and energy balances determinate? All the processes will be steady-state ones, and the entering and exit streams single-phase streams.

(a) **Stream splitter** (Fig. E5.1a): We assume that $Q = W = 0$, and that the energy balance is not involved in the process. By implication of a splitter, the temperatures, pressures, and compositions of the inlet and outlet streams are identical, and $N_p = 0$. The count of the total number of variables, total number of constraints, and degrees of freedom is as follows.

Total number of variables		
$N_v = N_s(N_{sp} + 2) =$		$3(N_{sp} + 2)$
Number of independent equality constraints		
Material balances	1	
Compositions of Z, P_1, and P_2 are the same	$2(N_{sp} - 1)$	
$T_{P_1} = T_{P_2} = T_Z$	2	
$p_{P_1} = p_{P_2} = p_Z$	2	$2N_{sp} + 3$
Total no. d.f.		$N_{sp} + 3$

Did you note that we did not count N_{sp} material balances but only one? Why? Let us look at

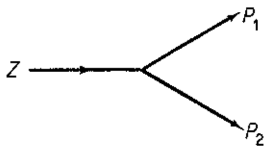


Figure E5.1a

some of the balances:

$$\text{Component 1: } Zx_{1Z} = P_1x_{1P_1} + P_2x_{1P_2}$$

$$\text{Component 2: } Zx_{2Z} = P_1x_{2P_1} + P_2x_{2P_2}$$

etc.

If $x_{1Z} = x_{1P_1} = x_{1P_2}$ and the same is true for x_2, and so on, only one independent material exists.

Do you understand the counts resulting from making the compositions equal in Z, P_1, and P_2? Write down the expressions for each component: $x_{iZ} = x_{iP_1} = x_{iP_2}$. Each set represents $2N_{sp}$ constraints. But you cannot specify every x_i in a stream, only $N_{sp} - 1$ of them. Do you remember why?

To make the problem determinate we might specify the values of the following decision variables:

Flow rate Z	1
Composition of Z	$N_{sp} - 1$
T_Z	1
p_Z	1
Ratio of split $\alpha = P_1/P_2$	1
Total no. d.f.	$N_{sp} + 3$

(b) Mixer (Fig. E5.1b): For this process we assume that $W = 0$, but Q is not.

Total number of variables (3 streams + Q)	$3(N_{sp} + 2) + 1$
Number of independent equality constraints	
Material balances	N_{sp}
Energy balance	1

Total no. d.f. $= 3(N_{sp} + 2) + 1 - (N_{sp} + 1) = 2N_{sp} + 6$

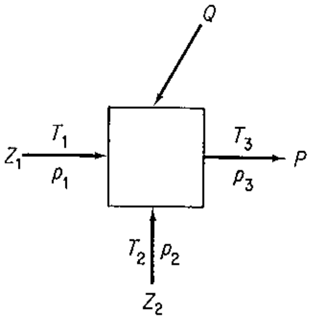


Figure E5.1b

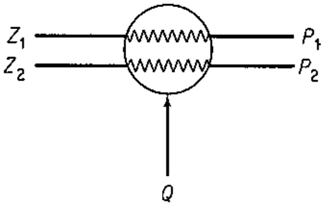


Figure E5.1c

(c) Heat exchanger (Fig. E5.1c): For this process we assume that $W = 0$ (but not Q) and $N_p = 0$.

Total number of variables		
$N_v = N_s(N_{sp} + 2) + 1 =$		$4N_{sp} + 9$
Number of independent equality constraints		
Material balances (streams 1 and 2)	2	
Energy balance	1	
Composition of inlet and outlet streams the same	$2(N_{sp} - 1)$	$2N_{sp} + 1$
Total no. d.f.		$2N_{sp} + 8$

One might specify four temperatures, four pressures, $2(N_{sp} - 1)$ compositions in Z_1 and Z_2, and Z_1 and Z_2 themselves to use up $2N_{sp} + 8$ degrees of freedom.

(d) Pump (Fig. E5.1d): Here $Q = 0$ but W is not; $N_p = 0$.

Total number of variables		
$N_v = N_s(N_{sp} + 2) + 1$		$2N_{sp} + 5$
Number of independent equality constraints		
Material balances	1	
Composition of inlet and outlet streams the same	$N_{sp} - 1$	
Energy balance	1	$N_{sp} + 1$
Total no. d.f.		$N_{sp} + 4$

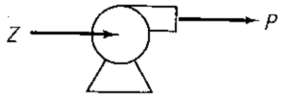


Figure E5.1d

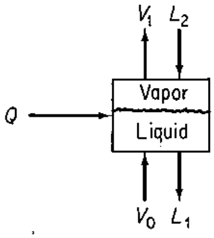


Figure E5.1e

(e) Two-phase well-mixed tank (stage) at equilibrium (Fig. E5.1e) (L, liquid phase; V, vapor phase): Here $W = 0$. Although two phases exist (V_1 and L_1) at equilibrium inside the system, the streams entering and leaving are single-phase streams. By equilibrium we mean that both phases are at the same temperature and pressure and that an equation is known that relates the composition in one phase to that in the other for each component.

Total number of variables (4 streams + Q)	$4(N_{sp} + 2) + 1$
Number of independent equality constraints	
Material balances	N_{sp}
Energy balance	1
Composition relations at equilibrium	N_{sp}
Temperatures of the streams V_1 and L_1 in the two phases equal	1
Pressures of the streams V_1 and L_1 in the two phases equal	1

Total no. d.f. $= 4(N_{sp} + 2) + 1 - 2N_{sp} - 3 = 2N_{sp} + 6$

In general you might specify the following variables to make the problem determinate:

Input stream L_2	$N_{sp} + 2$
Input stream V_0	$N_{sp} + 2$
Pressure	1
Q	1
Total	$2N_{sp} + 6$

Other choices are of course possible, but such choices must leave the equality constraints independent.

EXAMPLE 5.2 Proper Process Specification

Figure E5.2 shows an isothermal separations column. At present the column specifications call for the feed mass fractions to be $\omega_{C_4} = 0.15$, $\omega_{C_5} = 0.20$, $\omega_{iC_5} = 0.30$, and $\omega_{C_6} = 0.35$; the overhead mass fractions to be $\omega_{C_5} = 0.40$ and $\omega_{C_6} = 0$; and the residual product mass fraction to be $\omega_{C_4} = 0$. Unless specified as 0, the component exists in a stream.

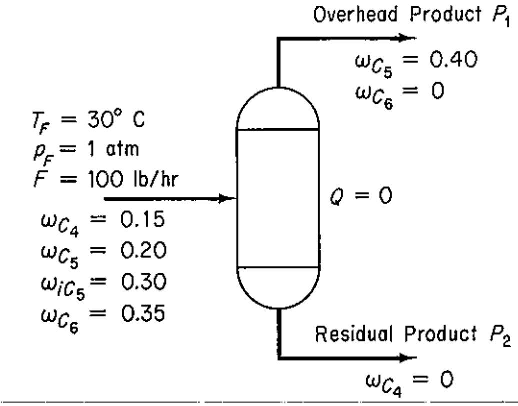


Figure E5.2

Given that $F = 100$ lb/hr, is the separator completely specified, that is, are the degrees of freedom $N_d = 0$? The streams P_1 and P_2 are not in equilibrium.

Solution

First we calculate N_v and then N_r. We will assume that all the stream temperatures and pressures are identical. Number of variables N_v:

$$N_v = (N_{sp} + 2)(3) = (4 + 2)(3) = \qquad 18$$

Number of restrictions and equations for N_r:

Component mass balances (no reaction) $= N_{sp}$	$= 4$
$T_F = T_{P_1} = T_{P_2}$	2
$p_F = p_{P_1} = p_{P_2}$	2

Initial column specifications:

(4 in F, 2 in P_1, and 1 in P_2 plus $T_F = 30°C$ and $p_F = 1$ atm)	9	
Total for N_r		17

Number of degress of freedom N_d: $18 - 17 =$ 1

Note that only four factors can be specified in stream F, namely the rate of F itself and three ω's; one of the ω's is redundant. One more variable must be specified for the process, but one that will not reduce the number of independent equations and restrictions already enumerated.

So far we have examined single units without a reaction occurring in the unit. How is the count for N_d affected by the presence of a reaction in the unit? The way N_v is calculated does not change. As to N_r, all restrictions and constraints are deducted from N_v that represent *independent* restrictions on the unit. Thus the number of material balances is not necessarily equal to the number of species (H_2O, O_2, CO_2, etc.) but instead is the number of independent material balances that exist determined in the same way as we did in Secs. 2.2 to 2.4, usually (but not always) equal to the number of elemental balances (H, O, C, etc.). Fixed ratios of materials such as the O_2/N_2 ratio in air or the CO/CO_2 ratio in a product gas would be a restriction, as would be a specified conversion fraction or a known molar flow rate of a material. If some degrees of freedom exist still to be specified, improper specification of a variable may disrupt the independence of equations and/or specifications previously enumerated in the unit of N_r, so be careful.

EXAMPLE 5.3 Degrees of Freedom with a Reaction Taking Place in the System

A classic reaction for producing H_2 is the so-called "water gas shift" reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Figure E5.3 shows the process data and the given information. How many degrees of freedom remain to be satisfied? For simplicity assume that the temperature and pressures of all entering and exit streams are the same and that all streams are gases. The amount of water which is in excess of that needed to convert all the CO completely to CO_2 is prespecified.

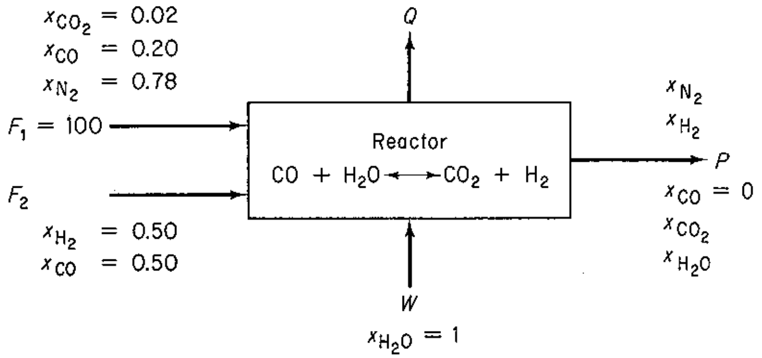


Figure E5.3

Solution

$N_v = N_s(N_{sp} + 2) + 1 = 4(5 + 2) + 1 =$ (+1 is for Q)			29
N_r: Independent material balances (C, O, N, H)	4		
Energy balance	1		
$T_{F_1} = T_{F_2} = T_W = T_P$	3		
$p_{F_1} = p_{F_2} = p_W = p_P$	3	11	
Compositions and flows specified:			
In F_1 ($x_{H_2O} = x_{H_2} = 0$)	5		
In F_2 ($x_{N_2} = x_{CO_2} = x_{H_2O} = 0$)	4		
In W (all but x_{H_2O} are 0)	4		
In P ($x_{CO} = 0$)	1	14	
Excess W given		1	
			26
$N_d = 29 - 26 =$			3

In the streams F_2 and W, only four compositions can be specified; a fifth specification is redundant. The total flows are not known. The given value of the excess water provides the information about the reaction products. Certainly, the temperature and pressure need to be specified, absorbing two degrees of freedom. The remaining degree of freedom might be the N_2/H_2 ratio in P, or the value of F_2, or the ratio of F_1/F_2, and so on.

EXAMPLE 5.4 Degrees of Freedom for the Case of Multiple Reactions

Methane burns in a furnace with 10% excess air, but not completely, so some CO exits the furnace, but no CH_4 exits. The reactions are:

$$CH_4 + 1.5O_2 \longrightarrow CO + 2H_2O$$
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
$$CO + 0.5O_2 \longrightarrow CO_2$$

Carry out a degree-of-freedom analysis for this combustion problem.

Solution

Figure E5.4 shows the process; all streams are assumed to be gases. Only two of the reactions are independent. Q is a variable here. For simplicity assume that the entering and exit streams are at the same temperatures and pressures.

$N_v = 3(6 + 2) + 1 =$ (+1 is for Q)		25
N_r:		
Material balances (C, H, O, N)	4	
Energy balance	1	
$T_A = T_F = T_P$	2	
$p_A = p_F = p_P$	2	
Compositions specified:		
In A ($N_{sp} - 1$)	5	
In F ($N_{sp} - 1$)	5	
In P	1	11
Percent excess air:		1
		21

$N_d = 25 - 21 = 4$

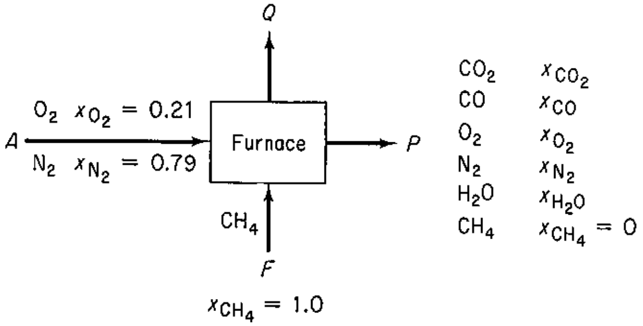


Figure E5.4

To have a well-defined problem you should specify (a) the temperature, (b) the pressure, (c) either the feed rate, or the air rate, or the product rate, and (d) either the CO/CO_2 ratio or the fraction of CH_4 converted to CO or alternatively to CO_2.

You can compute the degrees of freedom for combinations of like or different simple processes by proper combination of their individual degrees of freedom. In adding the degrees of freedom for units, you must eliminate any double counting either for variables or constraints and take proper account of interconnecting streams whose characteristics are often fixed only by implication.

Examine the mixer-separator in Fig. 5.1. For the mixer considered as a separate unit, from Example 5.1b, $N_d = 2N_{sp} + 6$. For the separator, an equilibirum unit:

$N_v = 3(N_{sp} + 2) + 1 =$		$3N_{sp} + 7$
N_r:		
Material balances	N_{sp}	
Equilibrium relations	N_{sp}	
Energy balance	1	
$T_Z = T_{P_1} = T_{P_2}$	2	
$p_Z = p_{P_1} = p_{P_2}$	2	$2N_{sp} + 5$
$N_d = (3N_{sp} + 7) - (2N_{sp} + 5) =$		$N_{sp} + 2$

The sum of the mixer and separator is $3N_{sp} + 8$.

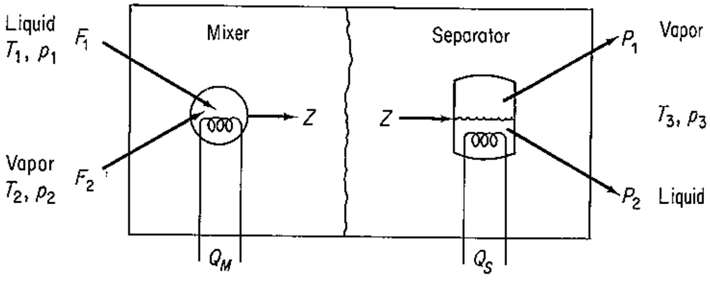


Figure 5.1 Degrees of freedom in combined units.

We must deduct redundant variables and add redundant restrictions as follows:

Redundant variables:	
Remove 1 Q	1
Remove Z	$N_{sp} + 2$
Redundent constraints:	
1 energy balance	1

Then $N_d = (3N_{sp} + 8) - (N_{sp} + 3) + 1 = 2N_{sp} + 6$, the same as in Example 5.1e.

EXAMPLE 5.5 Degrees of Freedom in a System Composed of Several Units

Ammonia is produced by reacting N_2 and H_2:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Figure E5.5a shows a simplified flowsheet. All the units except the separator and lines are adiabatic. The liquid ammonia product is essentially free of N_2, H_2, and A, and assume that the purge gas is free of NH_3. Treat the process as four separate units for a degree-of-freedom analysis, and then remove redundant variables and add redundant constraints to obtain the degrees of freedom for the overall process. The fraction conversion in the reactor is 25%.

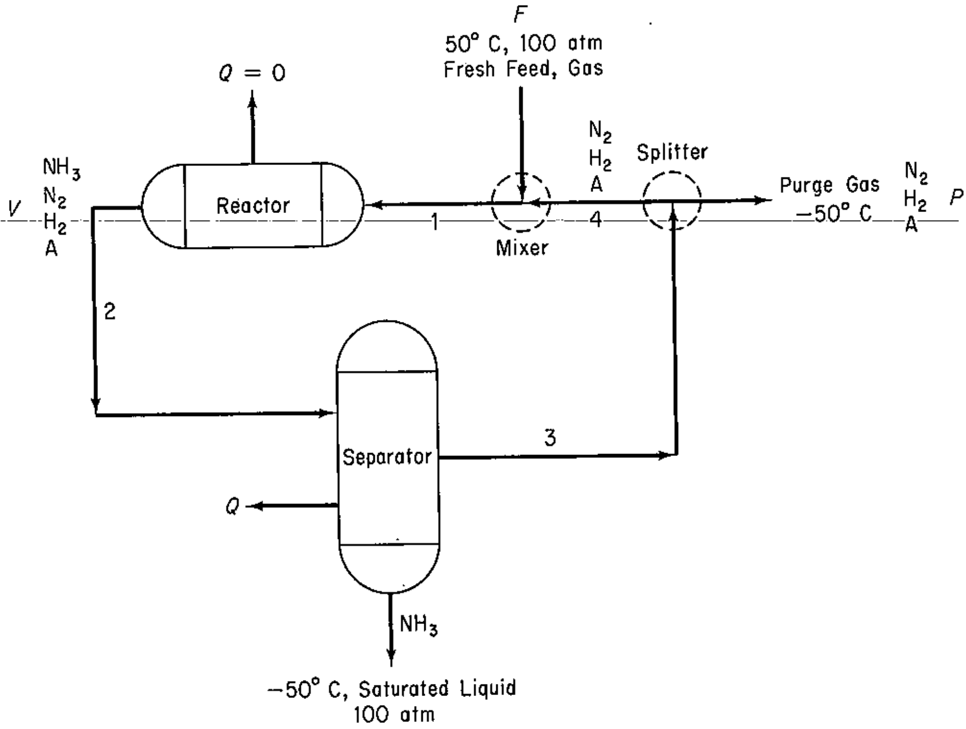


Figure E5.5a

Solution

Mixer:

$N_v = 3(N_{sp} + 2) + 1 = 3(6) + 1 =$		19
N_r:		
Material balances (H_2, N_2, A only)	3	
Energy balance	1	
Specifications:		
NH_3 concentration is zero	3	
$T_P = -50°C$	1	
$T_F = 50°C$	1	
Assume that $p_F = p_{\text{mix out}} = p_{\text{split}} = 100$	3	
$Q = 0$	1	13
N_d: $19 - 13 =$		6

Reactor:

$N_v = 2(N_{sp} + 2) + 1 = 2(6) + 1 =$		13
N_r:		
Material balances (H, N, A)	3	
Energy balances	1	
Specifications:		
NH_3 entering $= 0$	1	
$Q = 0$	1	
Fraction conversion	1	
$p_{\text{in}} = p_{\text{out}} = 100$ atm	2	
Energy balance	1	10
$N_d = 13 - 10$		3

Separator:

$N_v = 3(N_{sp} + 2) + 1 = 3(6) + 1 =$		19
N_r:		
Material balances	4	
Energy balance	1	
Specifications:		
$T_{\text{out}} = -50°C$	1	
$p_r = p_{\text{in}} = p_{NH_3} = 100$	3	
NH_3 concentration is 0 in recycle gas	1	
N_2, H_2, A are 0 in liquid NH_3	3	13
$N_d = 19 - 13$		6

Splitter:

$N_v = 3(N_{sp} + 2) = 3(6) =$		18
N_r:		
Material balances	1	
Specifications:		
NH_3 concentration $= 0$	1	
Compositions same $2(N_{sp} - 1)$	6	
Stream temperatures same $= -50°C$	3	
Stream pressures same $= 100$ atm	3	14
$N_d = 18 - 14$		4

The total number of degrees of freedom is 19 less the redundant information, which is as follows:

Redundant variables in interconnecting streams being eliminated:

Stream 1: (4 + 2) = 6
Stream 2: (4 + 2) = 6
Stream 3: (4 + 2) = 6
Stream 4: (4 + 2) = 6
24

Redundant constraints being eliminated:

Stream 1:	
NH_3 concentration = 0	1
p = 100 atm	1
Stream 2:	
p = 100 atm	1
Stream 3:	
NH_3 concentration = 0	1
p = 100 atm	1
T = −50°C	1
Stream 4:	
NH_3 concentration = 0	1
T = −50°C	1
p = 100 atm	1
	9

Overall the number of degrees of freedom should be

$$N_d = 19 - 24 + 9 = 4$$

We can check the count for N_d by making a degrees-of-freedom analysis about the entire process as follows:

Examine Fig. E5.5b.

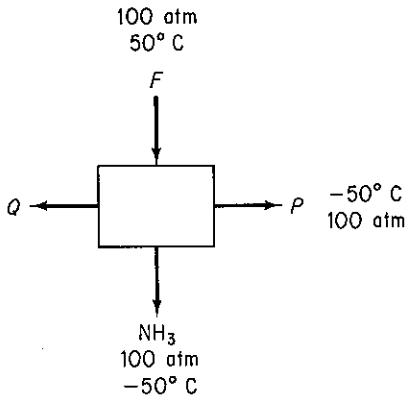


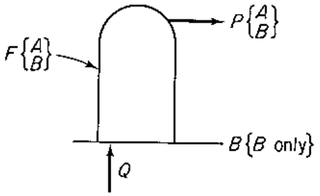
Figure E5.5b

$N_v = 3(4 + 2) + 1 =$		19
N_r:		
Material balances (H, N, A)	3	
Energy balance	1	
Specifications:		
Stream F (T = 50°C, p = 100 atm, NH_3 = 0)	3	
NH_3 stream (T = −50°C, p = 100 atm, three components have 0 concentration)	5	
Purge stream (T = −50°C, p = 100 atm, NH_3 = 0)	3	15
$N_d = 19 - 15 =$		4

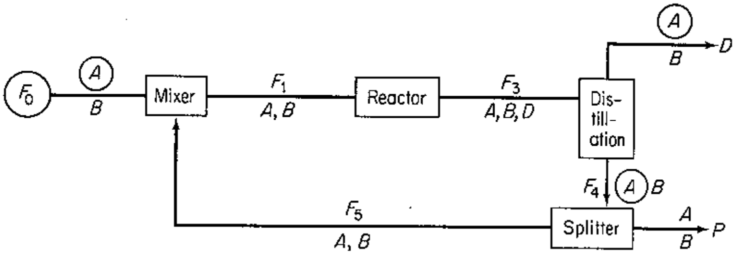
We do not have the space to illustrate additional combinations of simple units to form more complex units, but Kwauk[1] prepared several excellent tables summarizing the variables and degrees of freedom for distillation columns, absorbers, heat exchangers, and the like.

Self-Assessment Test

1. Is there any difference between the number of species present in a process and the number of components in the process?
2. Why are there N_{sp} + 2 variables associated with each stream?
3. Determine the number of degrees of freedom for a still.



4. Determine the number of degrees of freedom in the following process:



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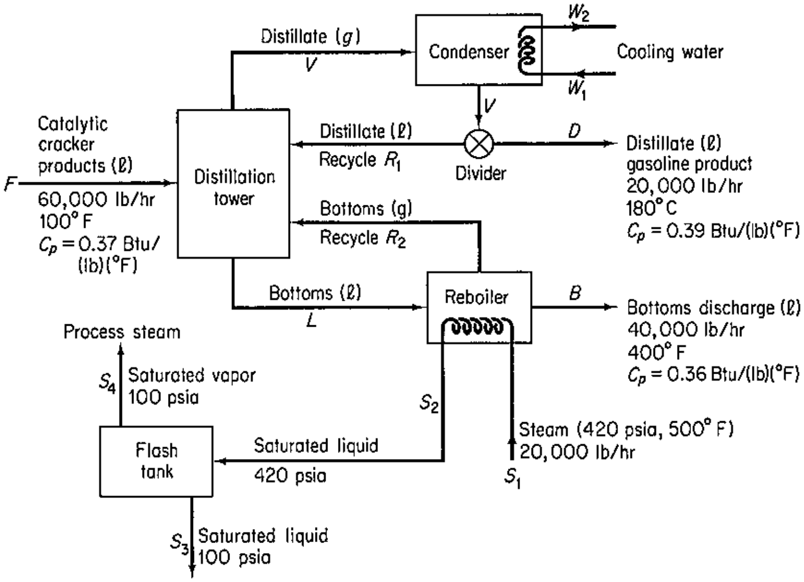
[1] M. Kwauk, *AIChE J.*, v. 2, p. 240 (1956).

The encircled variables have known values. The reaction parameters in the reactor are known as is the fraction split at the splitter between F_4 and F_5. Each stream is a single phase.

5. The accompanying figure represents the schematic flowsheet of a distillation tower used to recover gasoline from the products of catalytic cracker. Is the problem completely specified, that is, is the number of degrees of freedom equal to zero for the purpose of calculating the heat transfer to the cooling water in the condenser?



5.2 SOLVING MATERIAL AND ENERGY BALANCES USING FLOWSHEETING CODES

In Sec. 2.4 we discussed combining units from the viewpoint of making material balances. As more and more units are connected together in a plant, you can understand that the degree of complexity requires that the solution of material and energy balances be carried out via a computer code. Such a program can also, at the same time, determine the size of equipment and piping, evaluate costs, and optimize performance.

Once the process flowsheet is specified, the solution of the appropriate steady-state process material and energy balances is referred to as **flowsheeting,** and the computer code used in the solution is known as a **flowsheeting package.** The essential problem in flowsheeting without associated optimization is to solve (satisfy) a large set of linear and nonlinear equations to an acceptable degree of precision, normally by an iterative procedure. In flowsheeting without optimization, you must make sufficient specifications to take up *all* the degrees of freedom. Table 2.5 lists some typical codes used to execute flowsheeting. Individual process units that make up the process flowsheet are represented in the form of modules (building blocks) or as equation sets.

Figure 5.2 illustrates the main features of a flowsheeting program. We will examine some of the details concerning the material and energy balance phase. Fundamental to all flowsheeting codes is the calculation of mass and energy balances for the entire process. Inputs to the material and energy balances phase of the calculations for the flowsheet must be defined in sufficient detail to determine all the intermediate and product streams and the unit performance variables for all units.

Frequently, process plants contain recycle streams and control loops, and the solution for the stream properties requires iterative calculations. Thus efficient numerical methods for convergence must be used. In addition, appropriate physical properties and thermodynamic data have to be retrieved from a data base. Finally, a master program must exist that links all the building blocks, physical property data, thermodynamic calculations, subroutines, and numerical subroutines, and that also supervises the information flow. You will find that optimization and economic analysis are really the ultimate goal in the use of flowsheet codes.

Two extremes are encountered in flowsheeting software. At one extreme the entire set of equations (and inequalities) representing the process is written down, including the material and energy balances, the stream connections, and the rela-

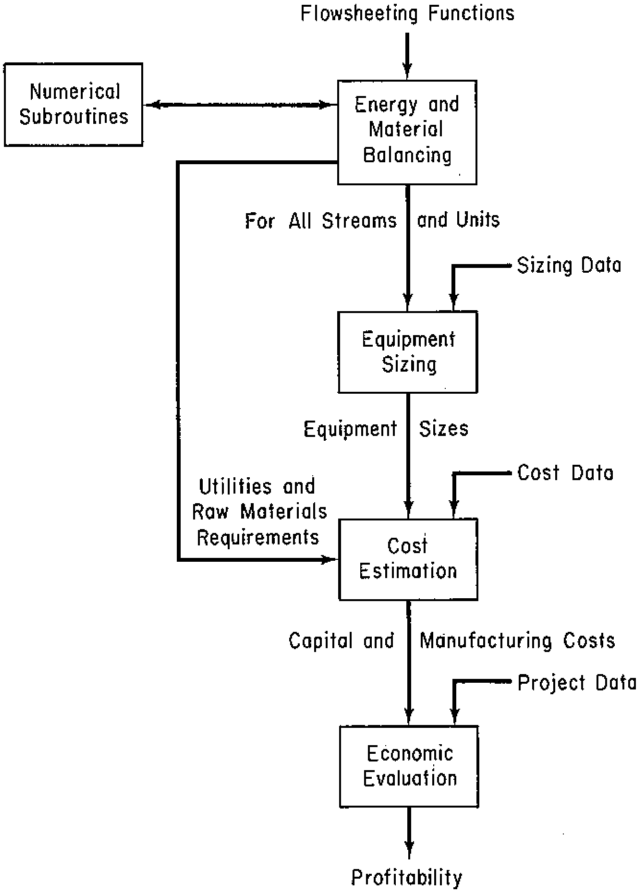


Figure 5.2 Information flow in a typical flowsheeting code.

tions representing the equipment functions. This representation is known as the **equation-oriented method** of flowsheeting. The equations can be solved in a sequential fashion analogous to the modular representation described below or simultaneously by Newton's method (or the equivalent), or by employing sparse matrix techniques to reduce the extent of matrix manipulations; references can be found at the end of this chapter.

At the other extreme, the process can be represented by a collection of modules (the **modular method**) in which the equations (and other information) representing each subsystem or piece of equipment are collected together and coded so that the module may be used in isolation from the rest of the flowsheet and hence is portable from one flowsheet to another. A module is a model of an individual element in a flowsheet (such as a reactor) that can be coded, analyzed, debugged, and interpreted by itself. Examine Fig. 5.3. Each module contains the equipment sizes, material and energy balance relations, the component flow rates, and the temperatures, pressures, and phase conditions of each stream that enters and leaves the physical equipment represented by the module. Values of certain of these parameters and variables determine the capital and operating costs for the units. Of course, the interconnections set up for the modules must be such that information can be transferred from module to module concerning the streams, compositions, flow rates, coefficients, and so on. In other words, the modules comprise a set of building blocks that can be arranged in general ways to represent any process.

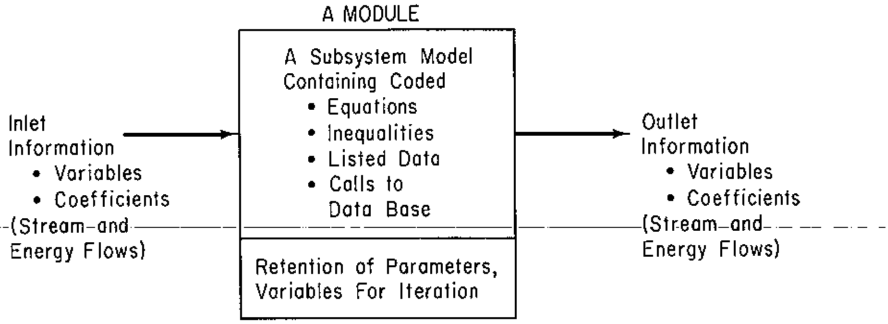


Figure 5.3 A typical process module showing the necessary interconnections of information.

Both sequential and simultaneous calculational sequences have been proposed for the modular approach as well as the equation-oriented approach. Either the program and/or the user must select the decision variables for recycle and provide estimates of certain stream values to make sure that covergence of the calculations occurs, especially in a process with many recycle streams. Reviews by Evans[2] and Rosen[3] point out many of the problems and practices pertaining to flowsheeting.

In addition to the two extremes, combinations of equations and modules can be

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[2] L. B. Evans, "Flowsheeting: A State of the Art Review," *Proc. Chemcomp. 1982,* G. F. Froment, ed., p. 1, KVI, Antwerp, Belgium (1982).

[3] E. Rosen, "Steady State Chemical Simulation-State of the Art Review," *Computer Applications to Chemical Engineering,* R. G. Squires and G. V. Reklaitis, eds., ACS Symposuim Series, no. 124, p. 3, 1980.

used. Equations can be lumped into modules, whereas modules can be represented by their basic equations or by polynomials that fit the input–output information.

In current practice, modularly organized simulators seems to prevail because (1) the modules are easier to construct and understand; (2) addition and deletion of modules for a flowsheet is easily accomplished without changing the solution strategy; (3) modules are easier to program and debug than sets of equations, and diagnostics for them easier to analyze; and (4) the modules already exist and work, whereas equation blocks for equipment are not prevalent. Difficulties encountered in equation-based codes usually stem from sets of equations associated with particular units. Embedding these equations as subproblems with special routines often alleviates the difficulties. By permitting the user to mix equations and subroutines, use can be made of "macros" in the general network representing a process. We will review equation-based flowsheeting first because it is much closer to the techniques used up to this point in this book, and then turn to consideration of modular-based flowsheeting.

5.2-1 Equation-Based Flowsheeting

Sets of linear and/or nonlinear equations can be solved simultaneously using an appropriate computer code (see Table L.1) by one of the methods described in Appendix L. Equation-based flowsheeting codes pertaining to chemical engineering can be used for the same purpose. The latter have some advantages in that the physical property data needed for the coefficients in the equations are transparently transmitted from a data base at the proper time in the sequence of calculations.

Whatever the code used to solve material and energy balance problems, you must provide certain input information to the code in an acceptable format. All flowsheeting codes require that you convert the information in the flowsheet (see Fig. 5.4) to an information flowsheet as illustrated in Fig. 5.5, or something equivalent. In the information flowsheet, you use the name of the mathematical model (subroutine for modular-based flowsheeting) that will be used for the calculations instead of the name of the process unit.

Once the information flowsheet is set up, the determination of the process topology is easy, that is, you can immediately write down the stream interconnections between the modules (or subroutines) that have to be included in the input data set. For Fig. 5.5 the matrix of stream connections (the **process matrix**) is (a negative sign designates an exit stream)

Unit	Associated streams				
1	1	−2			
2	2	−3			
3	3	8	−4	−13	
4	4	7	11	−9	−5
5	5	−6			
6	6	−8	−7		
7	10	−11	−12		
8	9	−10			

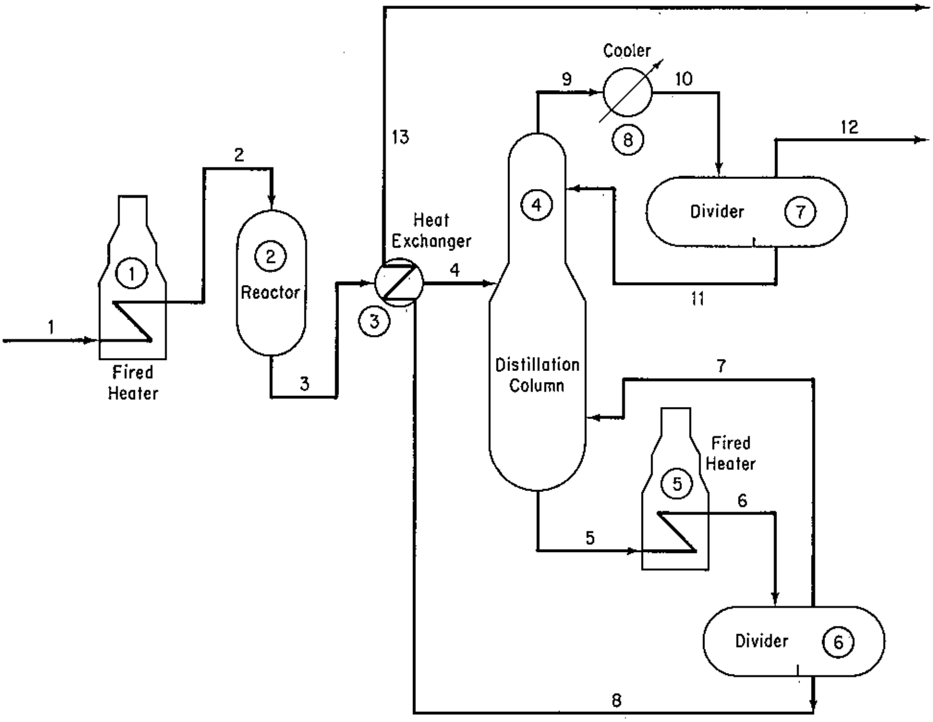


Figure 5.4 Hypothetical process flow sheet.

The interconnections between the unit modules may represent information flow as well as material and energy flow. In the mathematical representation of the plant, the interconnection equations are the material and energy balance flows between model subsystems. Equations for models such as mixing, reaction, heat exchange, and so on, must also be listed so that they can be entered into the computer code used to solve the equation. Table 5.1 lists the common type of equations that might be used for a single subsystem. In general, similar process units repeatedly occur in a plant and can be represented by the same set of equations, which differ only in the names of variables, the number of terms in the summations, and the values of any coefficients in the equations.

Equation-based codes can be formatted to include inequality constraints along with the equations. Such constraints might be of the form $a_1x_1 + a_2x_2 + \cdots \leqq b$, and might arise from such factors as

1. Conditions imposed in linearizing nonlinear equations
2. Process limits for temperature, pressure, concentration

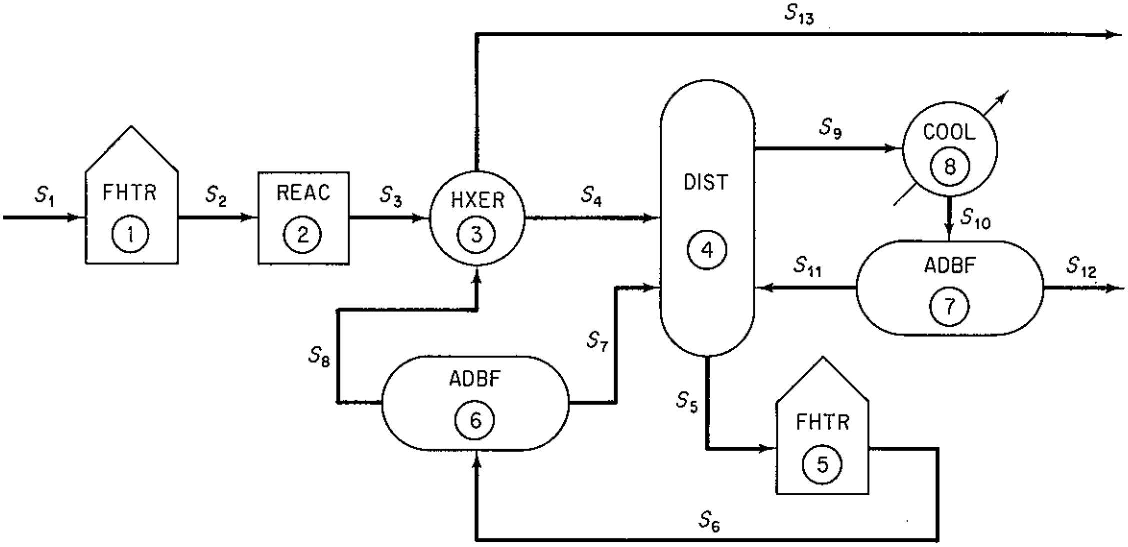
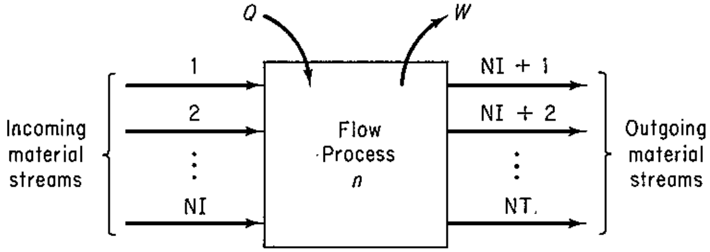


Figure 5.5 Information flow sheet for the hypothetical process (S stands for stream; module or computer code number is encircled).

TABLE 5.1 Generic Equations for a Steady-state Open System*

System diagram



Total mass balance (or mole balance without reaction)	Component mass or mole balances (without reaction)
$\sum_{i=1}^{\text{NI}} F_i = \sum_{i=\text{NI}+1}^{\text{NT}} F_i$	$\sum_{i=1}^{\text{NI}} F_i w_{i,j} = \sum_{i=\text{NI}+1}^{\text{NT}} F_i w_{i,j}$ for $j = 1, 2, \ldots, \text{NC}$
Energy balance	Summation of mole or mass fractions
$\sum_{i=1}^{\text{NI}} F_i H_i + Q_n - W_{s,n} = \sum_{i=\text{NI}+1}^{\text{NI}} F_i H_i$	$\sum_{j=1}^{\text{NC}} w_{i,j} = 1.0$ for $i = 1, 2, \ldots, \text{NI}$

TABLE 5.1 *(cont.)*

Vapor-liquid equilibrium distribution

$$y_j = K_j x_j \quad \text{for} \quad j = 1, 2, \ldots, \text{NC}$$

Equilibrium vaporization coefficients

$$K_j = K(T_i, P_i, \overline{W}_i) \quad j = 1, 2, \text{for} \ldots, \text{NC}$$

Physical property functions

$$\left.\begin{aligned} H_i &= H_{\text{VL}}(T_i, P_i, \overline{W}_i) \\ S_i &= S_{\text{VL}}(T_i, P_i, \overline{W}_i) \end{aligned}\right. \quad i = 1, 2, \ldots, \text{NI}$$

Total mole balance (with reaction)

$$\sum_{i=1}^{\text{NI}} F_i + \sum_{l=1}^{\text{NR}} R_l \left[\sum_{j=1}^{\text{NC}} V_{j,l} \right] = \sum_{i=\text{NI}+1}^{\text{NI}} F_i$$

Component mole balances (with reaction)

$$\sum_{i=1}^{\text{NI}} F_i w_{i,j} + \sum_{l=1}^{\text{NR}} V_{j,l} R_l = \sum_{i=\text{NI}+1}^{\text{NT}} F_i w_{i,j} \qquad \text{for } j = 1, 2, \ldots, \text{NC}$$

Molar atom balances

$$\sum_{i=1}^{\text{NI}} F_i \left[\sum_{j=1}^{\text{NC}} w_{i,j} a_{j,k} \right] = \sum_{i=\text{NI}+1}^{\text{NT}} F_i \left[\sum_{j=1}^{\text{NC}} w_{i,j} a_{j,k} \right] \qquad \text{for } k = 1, 2, \ldots, \text{NE}$$

Mechanical energy balance

$$\sum_{i=1}^{\text{NI}} (K_i + P_i) + \sum_{i=1}^{\text{NI}} \int_{P_{1,i}}^{P_{2,i}} V_i \, dp_l = \sum_{i=\text{NI}+1}^{\text{N}} (K_i + P_i) + \sum_{i=\text{NI}+1}^{\text{NT}} \int_{P_{1,i}}^{P_{2,i}} V_i \, dP_i + W_{s,n} + E_{v,n}$$

*Notation:

$a_{j,k}$	number of atoms of the *k*th chemical element in the *j*th component
F_i	total flow rate of the *i*th stream
H_i	relative enthalpy of the *i*th stream
K_j	vaporization coefficient of the *j*th component
NC	number of chemical components (compounds)
NE	number of chemical elements
NI	number of incoming material streams
NR	number of chemical reactions
NT	total number of material streams
p_i	pressure of the *i*th stream
Q_n	heat transfer for the *n*th process unit
R_l	reaction expression for the *l*th chemical reaction
T_i	temperature of the *i*th stream
$V_{j,l}$	stoichiometric coefficient of the *j*th component in the *l*th chemical reaction
$w_{i,j}$	fractional composition (mass of mole) of the *j*th component in the *i*th stream
$\overline{W}_i$	average composition in the *i*th stream
$W_{s,n}$	work for the *n*th process unit
x_j	mole fraction of component *j* in the liquid
y_j	mole fraction of component *j* in the vapor

3. Requirements that variables be in a certain order
4. Requirements that variables be positive or integer

A slack variable has to be included in such relations to make them into equations.

Four codes currently under development for equation-based flowsheeting are ASCEND,[4] Quasilin,[5] Speedup,[6] and TISFLO-II.[7] An equation-based code should include the following characteristics:

1. A method of easily entering the equations and inequality constraints in the code used to solve them. Slack variables can be used to transform the inequality constraints into equality constraints.
2. A possibility of using both continuous and discrete variables, the latter being particularly necessary to accommodate changes in phase or changes from one correlation to another.[8]
3. The option to use alternative forms of a function depending on the value of logical variables that outline the state of the process. A typical example is the calculation of p–V–T relations as the phase changes from gas to liquid. To fix on the appropriate form, the problem must be treated as an optimization problem in which feasibility is required on each cycle for each state with the logical variables treated as constraints for a state. Alternatively, the code can guess the state and if the logical constraints are violated, another guess can be made.
4. A method of solving submodels that defy normal equation-solving subroutines or are specially suited to ad hoc methods of solution.
5. The ability to build *macros*, that is, create complex models comprised of standard subelements. For example, distillation might be composed of trays, flash units, splitters, mixers, heat exchangers, and so on.
6. Provision for equivalence variables, that is, using the same name for two different variables if they are equal, such as the mass flow rate through a pump.
7. A method for solving individual models such as Newton or quasi-Newton methods combined with sparse matrix methods to convert the nonlinear alge-

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[4] M. H. Locke, and A. W. Westerberg "The Ascend-II System—A Flowsheeting Application of Successive Quadratic Programming Methodology," *Comput. Chem. Eng.*, v. 7, p. 615 (1983).

[5] H. P. Hutchinson, D. J. Jackson, and W. Morton, "Equation Oriented Flowsheet Simulation, Design and Optimization," *Proc. Europ. Fed. Chem. Eng. Conf. Comput. Appl. Chem. Eng.*, Paris, April 1983; "The Development of an Equation-Oriented Flowsheet Simulation and Optimization Package," *Comput. Chem. Eng.*, v. 10, p. 19 (1986).

[6] R. W. H. Sargent, J. D. Perkins, and S. Thomas, "Speedup: Simulation Program for Economic Evaluation and Design of Unified Processes," in *Computer-Aided Process Plant Design,* M. E. Leesley, ed., Gulf Publishing Company, Houston, 1982.

[7] J. A. de Leeuw den Bouter, A. G. Swenber, and M. G. G. Van Meulebrouk, "Simulation and Optimization with TISFLO—II," *Proc. Chemplant 80,* Heviz, Hungary, September 1980.

[8] J. D. Perkins, "Equation Oriented Flowsheeting," in *Foundations of Computer-Aided Design,"* A. W. Westerberg and J. J. Chien, eds., Cache Corp., Austin, Tex. 1983.

braic equations in the model to linearized approximates. Then the linearized equations can be solved iteratively taking advantage of their structure. The alternative is to use *tearing*. Tearing is discussed in detail in Sec. 5.2-2, treating modular-based flowsheeting, but briefly, by "tearing" we mean selecting certain output variables from a set of equations as known values so that the remaining variables can be solved by serial substitution. A residual set of equations equal to the number of tear variables will remain, and if these are not satisfied, new guesses are made for the values of the tear variables, and the sequence repeated. Examine Fig. 5.6c. Furthermore, the sensitivity of functions with respect to variables (the first partial derivatives) developed in Newton-like methods provides valuable information.

8. A method for *precedence ordering* so as to partition a model into a sequence of smaller models containing sets of irreducible equations (equations that have to be solved simultaneously as illustrated in Fig. 5.6).
9. A method to select initial guesses for the Newton-like solution procedure for the algebraic equations. Poor choices may lead to unsatisfactory results. You want the initial guesses to be as close to the correct answer as possible so that the procedure will converge. You can perhaps solve approximate models, and then pass to more complex ones.
10. Provision for *scaling* of the variables and equations. By scaling of variables we mean introducing transformations that make all the variables have ranges in the same order of magnitude. By scaling of equations we mean multiplying each equation by a factor that causes the value of the deviation of each equation from zero to be of the same order of magnitude.

An example of an equation-oriented flowsheeting code is ASCEND by Locke and Westerberg. Figure 5.7 shows the configuration of the various subroutines involved. Phasing of inputs, solving a problem, and generating outputs can be ordered by the user. Several independent programs operate on a file of the values of the variables and pointers that represent a flowsheet. A user supplies or makes use of existing subroutines containing equations that model a component in the flowsheet plus an input file that defines how these submodels should be assembled. ASCEND maintains a file that includes the user-supplied definition of the configuration plus definitions of variable packets (groups of associated variables), equation packets, types of variable and equation packets associated with an element in the flowsheet, a procedure to allow the user to create complex models (called "macros") from a simple set of inputs and default values so that the user has only to input the important parameters of interest or the exceptions to the default values.

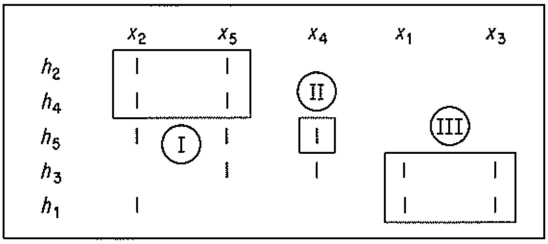
Internal representation and storage in ASCEND-II of a flowsheet which may contain hundreds or even thousands of variables is carried out by the GEV (Generator, Equation packet, Variable packet) method proposed by Berna, et al. (1980). Figure 5.8 shows (1) a flowsheet element, (2) the internal formulation of the element, and (3) the matrix representation of the element. A generator is a subroutine. It calculates the necessary partial derivatives and equation residuals for the Newton-Raphson portion of a solution. Equation packets are groups of equations grouped together because they represent the equations of the process matrix reserved for a sin-

h_1: $x_1^2 x_2 - 2x_3^{1.5} + 4 = 0$
h_2: $x_2 + 2x_5 - 8 = 0$
h_3: $x_1 x_4 x_5^2 - 2x_3 - 7 = 0$
h_4: $-2x_2 + x_5 + 5 = 0$
h_5: $x_2 x_4^2 x_5 + x_2 x_4 - 6 = 0$

(a) The n independent equations involving n variables ($n = 5$).

	x_1	x_2	x_3	x_4	x_5
h_1	1	1	1		
h_2		1			1
h_3	1		1	1	1
h_4		1			1
h_5		1		1	1

(b) The occurrence matrix (the l's represent the occurrence of a variable in an equation).



	x_2	x_5	x_4	x_1	x_3
h_2	1	1			
h_4	1	1			
h_5	1	1	1		
h_3		1	1	1	1
h_1	1			1	1

(c) The rearranged (partitioned) occurrence matrix with groups of equations (sets I, II, and III) that have to be solved simultaneously collected together in a precedence order for solution.

Figure 5.6 Partitioning and tearing. The equations are partitioned into blocks containing common variables, as in (*c*). Equations h_2 and h_4 (set I) are solved simultaneously for x_2 and x_5 first, then h_5 (set II) is solved for x_4, and lastly h_1 and h_3 are solved simultaneously. For example, assume a value for x_3; solve h_1 for x_1 then check to see if Equation h_3 is satisfied. If not, adjust x_3, solve h_1 for x_1, recheck h_3, and so on until both h_1 and h_3 are satisfied.

gle generator. In Fig. 5.8b, the corresponding equation packet would contain the equations for the material balance, equilibrium, and enthalpy balance for the flash unit. Variable packets are groups of associated variables grouped together for convenience. One example of a variable packet would be a stream variable packet containing the flowrate, temperature, pressure, enthalpy, and component mole fractions of

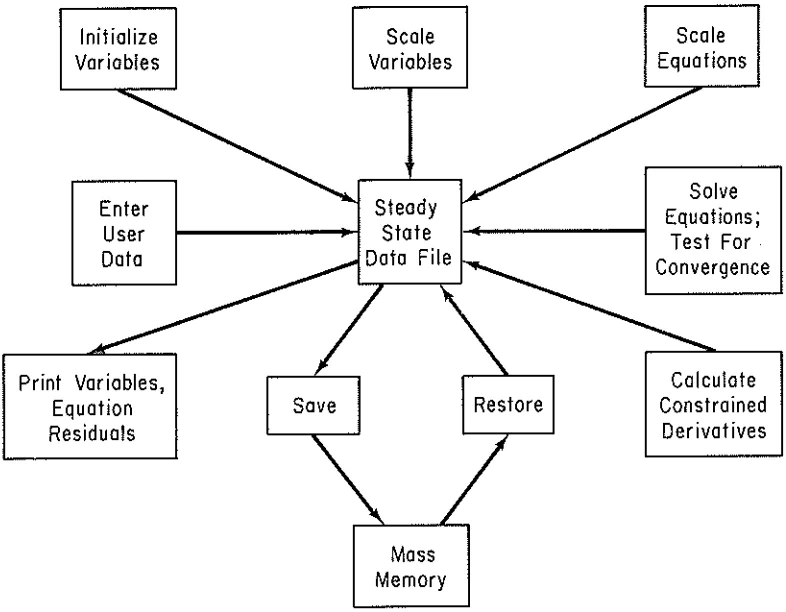
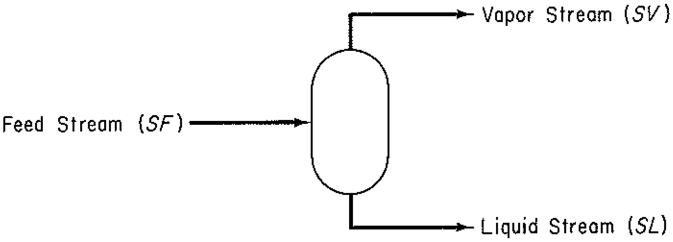
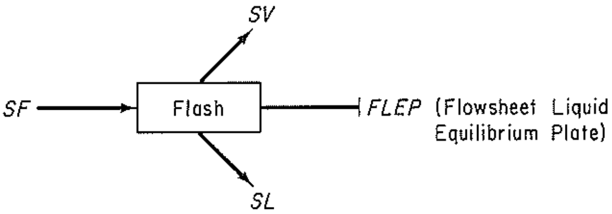


Figure 5.7 Information flow in ASCEND-II.

a stream. By specifying the elements in Fig. 5.8c, the user designates the generator to be used to calculate the partial derivatives and equation residuals for Newton or quasi-Newton methods of solution. Thus, an entire flowsheet can be characterized by a set of generators with associated variable packets and equation packets.



(a) The flowsheet element — a flash unit



(b) Internal representation of the flowsheet element via GEV

Figure 5.8 Three representations of an element in a flowsheet in ASCEND-II. (a) The flowsheet element—a flash unit. (b) Internal representation of the flowsheet element via GEV (c) Representation of the flowsheet element.

	SF	*SV*	*SL*
Material Balance	1	1	1
Equilibrium Relation	0	1	1
Enthalpy Balance	1	1	1

(c) Process matrix representation of the flowsheet element

Figure 5.8 (*cont.*)

EXAMPLE 5.6 Sequential Solution of Material Balances

Figure E5.6 shows 10 units that are part of a larger plant. The independent linear equations relating the flows of materials in and out of the units are listed in the figure. The incident matrix is shown below.

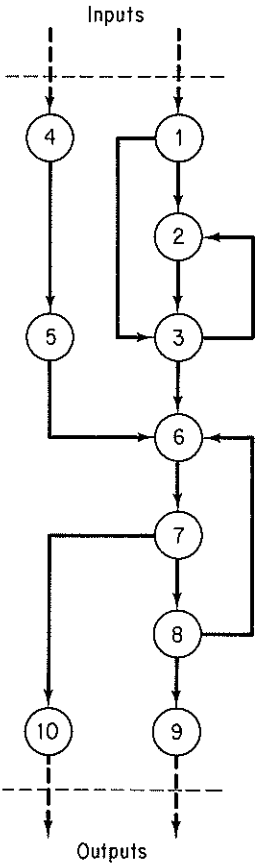
Equations	Variables												Interface variables			
	y_{12}	y_{13}	y_{23}	y_{32}	y_{36}	y_{45}	y_{56}	y_{67}	y_{86}	y_{78}	y_{710}	y_{89}	y_1	y_4	y_9	y_{10}
1	−1	−1	0	0	0	0	0	0	0	0	0	0	+1	0	0	0
2	+1	0	−1	+1	0	0	0	0	0	0	0	0	0	0	0	0
3	0	+1	+1	−1	−1	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	−1	0	0	0	0	0	0	0	+1	0	0
5	0	0	0	0	0	+1	−1	0	0	0	0	0	0	0	0	0
6	0	0	0	0	+1	0	+1	−1	+1	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0	+1	0	−1	−1	0	0	0	0	0
8	0	0	0	0	0	0	0	0	−1	+1	0	−1	0	0	0	0
9	0	0	0	0	0	0	0	0	0	0	0	+1	0	0	−1	0
10	0	0	0	0	0	0	0	0	0	0	+1	0	0	0	0	−1

Incidence matrix

Suppose that instead of a simultaneous solution of the equations, a sequential solution is wanted. In what order should the equations be solved? Partition the equations so that a sequential solution can be executed. Lump together blocks of equations that still have to be solved simultaneously.

Solution

From Fig. E5.6 you can see that it is not necessary to solve all 10 equations simultaneously. The system of equations can be broken up into lower-order subsystems, some of which can be comprised of individual equations or small groups of equations. These groups are associated with the so-called *irreducible* sets of equations. By inspection you can establish the following



Subsystem	Balance
1	$0 = y_1 - y_{12} - y_{13}$
2	$0 = y_{12} + y_{32} - y_{23}$
3	$0 = y_{23} - y_{32} - y_{36} + y_{13}$
4	$0 = y_4 - y_{45}$
5	$0 = y_{45} - y_{56}$
6	$0 = y_{36} + y_{56} + y_{86} - y_{67}$
7	$0 = y_{67} - y_{78} - y_{710}$
8	$0 = y_{78} - y_{86} - y_{89}$
9	$0 = y_{89} - y_9$
10	$0 = y_{710} - y_{10}$

Figure E5.6 An example system containing recycle and bypass streams.

precedence order:

Step	Subsystem equations(s)
1	1
2	4
3	5
4	2 and 3 simultaneously
5	6, 7, and 8 simultaneously
6	9
7	10

In the case of more complicated sets of equations that cannot easily be decomposed by inspection, refer to some of the supplementary references at the end of this chapter for suitable algorithms.

EXAMPLE 5.7 Simultaneous Material and Energy Balances

A distillation column separates 10,000 lb/hr of a 40% benzene–60% chlorobenzene liquid solution which is at 70°F. The liquid product from the top of the column is 99.5% benzene, while the bottoms (stream from the reboiler) contains 1% benezene. The total condenser uses water that enters at 60°F and leaves at 140°F, while the reboiler uses saturated steam at 280°F. The reflux ratio (the ratio of the liquid overhead returned to the column to the liquid overhead product removed) is 6 to 1. Assume that both the condenser and reboiler operate at 1 atm pressure, that the temperature calculated for the condenser is 178°F and for the reboiler 268°F, and that the calculated fraction benzene in the vapor from the reboiler is 3.9 wt% (5.5 mole %). Calculate the following:

- **(a)** The pounds of overhead product (distillate) and bottoms per hour
- **(b)** The pounds of reflux per hour
- **(c)** The pounds of liquid entering the reboiler and the reboiler vapor per hour
- **(d)** The pounds of steam and cooling water used per hour

Solution

Steps 1, 2, and 7 Figure E5.7a will help visualize the process and assist in pointing out what additional data have to be determined.

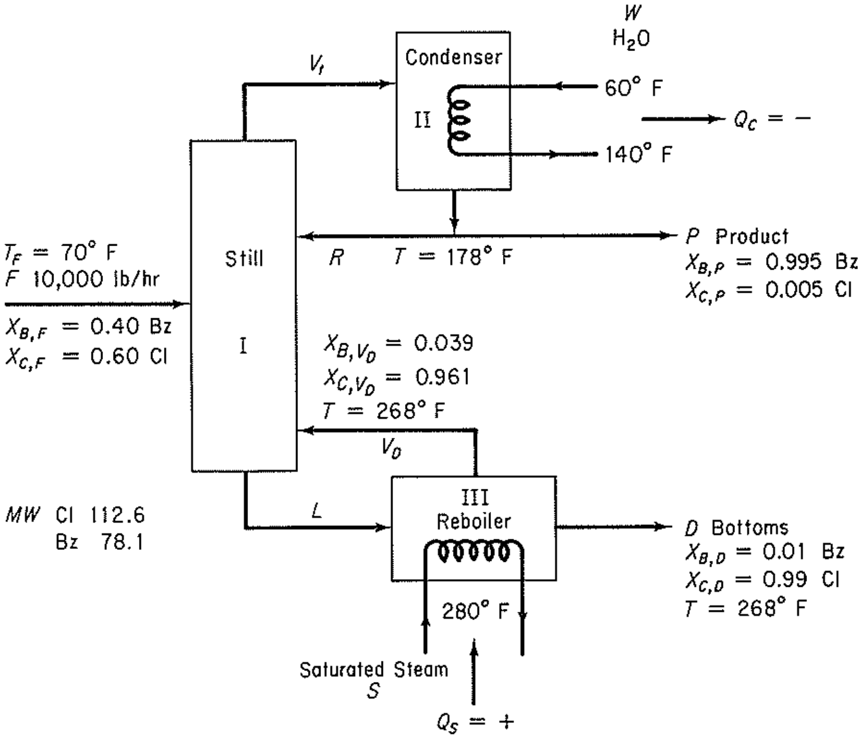


Figure E5.7a

Steps 5 and 6 An analysis of the degrees of freedom will reveal whether the process is properly specified or not. We assume that $\Delta\hat{H}_i$ is a function of temperature only so that $\Delta\hat{H}_i$ could be replaced as a variable by T_i. The water (W) and steam (S) can be calculated directly from Q_C and Q_S, respectively, hence will not be considered in the analysis of the degrees of freedom. Also, since the condenser is a total condenser, the liquid P and R have the same temperature and composition, and V_t must have the same composition as P. B is benzene and C is chlorobenzene.

Subsystem I (still)

7	unknown variables (R, V_D, V_t, L, $\omega_{B,L}$, T_{V_t}, T_L)
$\underline{-3}$	equations (components B and C, and energy)
4	net degrees of freedom

Subsystem II (condenser)

5	unknown variables (V_t, R, P, Q_c, T_{V_t})
$\underline{-2}$	equations (component B only independent, and energy)
3	net degrees of freedom

Subsystem III (reboiler)

6	unknown variables (L, D, V_D, Q_S, $\omega_{B,L}$, T_L)
$\underline{-3}$	equations (components B and C, and energy)
3	net degrees of freedom

Whole system

10	subsystem degrees of freedom (4 + 3 + 3)
−7	interconnections (V_t, T_{V_t}, R, L, $\omega_{B,L}$, T_L, V_D)
$\underline{-1}$	additional relations (reflex ratio specified: $R/P = 6$)
2	net degrees of freedom for the process

For the whole process, there are 7 + 5 + 6 = 18 minus 7 equals 11 variables whose values are unknown, and 9 equations plus extra relations.

Table E5.7 lists the possible equations for review to help decide on the two additional specifications needed. Not all of the equations are independent, of course, and some are nonlinear. Let us assume that V_t is saturated vapor at $T_{V_t} = 178°\text{F}$ and L is subcooled liquid at $T_L = 248°\text{F}$.

Consequently, the process has the correct number of specifications and can be solved. You must always check to make sure that the equations are independent because the data given might in some instances (as shown in Chap. 2) lead to dependence among two or more equations.

Rather than solve nine equations simultaneously for the nine values of the variables which are unknown, some of which will be nonlinear, we will carry out a sequential procedure that leads to the final solution via solving small sets of linear equations simultaneously.

Step 4

Basis: 1 hr

TABLE E5.7

Balance	In	Out
Overall process		
(a) Total mass (lb)	10,000	$= P + D$
(b) Benzene (lb)	10,000 (0.40)	$= P(0.995) + D(0.01)$
(c) Energy (Btu)	$Q_C + Q_S + 10{,}000\Delta\hat{H}_{F,70^\circ\mathrm{F}}$	$= P\,\Delta\hat{H}_{P,178^\circ\mathrm{F}} + D\,\Delta\hat{H}_{d,268^\circ\mathrm{F}}$
Process I (still)		
(d) Total mass (lb)	$10{,}000 + R + V_D$	$= V_t + L$
(e) Benzene (lb)	$10{,}000(0.40) + R(0.995) + V_D(0.039)$	$= V_t(0.995) + L_{B,L}$
(*f*) *Energy* (*Btu*)	$10{,}000(\Delta\hat{H}_{F,70^\circ\mathrm{F}}) + R\,\Delta\hat{H}_{R,178^\circ\mathrm{F}} + V_D\,\Delta\hat{H}_{V_D,268^\circ\mathrm{F}}$	$= V_t\,\Delta\hat{H}_{V_t,T_{V_t}} + L\,\Delta\hat{H}_{L,T_L}$
Process II (condenser)		
(g) Total mass (lb)	V_t	$= R + P$
(h) Benzene (lb)	$V_t(0.995)$	$= R(0.995) + P(0.995)$
(i) Energy (Btu)	$Q_C + V_t\,\Delta\hat{H}_{V_t,T_{V_t}}$	$= R\,\Delta\hat{H}_{R,178^\circ\mathrm{F}} + P\,\Delta\hat{H}_{P,178^\circ\mathrm{F}}$
(j) Reflex ratio given	R	$= 6P$
Process III (reboiler)		
(k) Total (lb)	L	$= V_D + D$
(l) Benzene (lb)	$L_{B,L}$	$= V_D(0.039) + D(0.01)$
(m) Energy (Btu)	$Q_S + L\,\Delta\hat{H}_{L,T_L}$	$= V_d\Delta\hat{H}_{V_D,268^\circ\mathrm{F}} + D\Delta\hat{H}_{D,268^\circ\mathrm{F}}$

Step 3 First we have to get some pertinent enthalpy or heat capacity data so that the energy balances can be used. If you used a computer program, the data would be retrieved from a data base. (The exit streams have the same composition as the solutions in the condenser or reboiler, respectively.) The heat capacity data for liquid benzene (Bz) and chlorobenzene (Cl) will be assumed to be as follows (no enthalpy tables are available):

	C_p [Btu/(lb)(°F)]		$\Delta\hat{H}_{\text{vaporization}}$(Btu/lb)	
Temp. (°F)	Cl	Bz	Cl	Bz
70	0.31	0.405		
90	0.32	0.415		
120	0.335	0.43		
150	0.345	0.45		
180	0.36	0.47	140	170
210	0.375	0.485	135	166
240	0.39	0.50	130	160
270	0.40	0.52	126	154

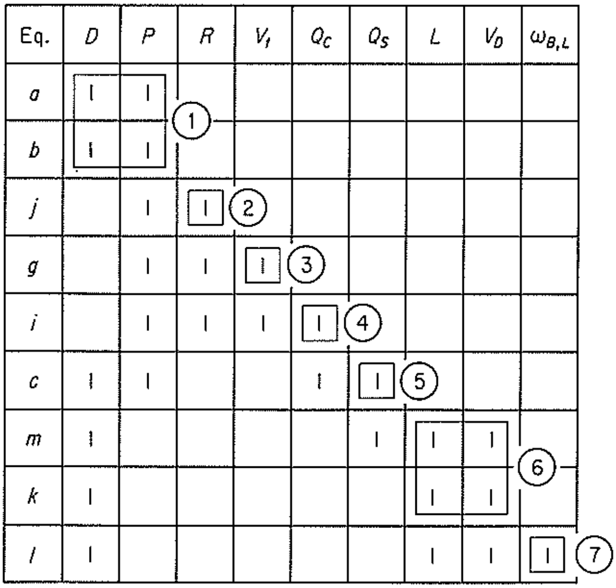
SOURCE: Data estimated from tabulations in D. Q. Kern, *Process Heat Transfer*, McGraw-Hill, New York, 1950, Appendix.

Assume that the solutions are ideal so that each component can be treated independently.

Steps 7 and 8 Next we determine the sequence of solution of the system equations. If you used a computer code, you might be asked to provide such a sequence, or possibly the code would select a sequence for you if you wished. As indicated by Fig. 5.6, we first prepare an occurrence matrix and then rearrange the matrix (here by inspection since it is a small matrix) to give the precedence order for solution. Figure E5.7b is the occurrence matrix, and Fig. E5.7c is the precedence matrix with the encircled numbers and associated

Eq.	R	V_D	V_f	L	P	D	$\omega_{B,L}$	Q_C	Q_S
a					1	1			
b					1	1			
c					1	1		1	1
g	1		1		1				
i	1		1		1			1	
j	1				1				
k		1		1		1			
l		1		1		1	1		
m		1		1		1			1

Figure E5.7b Occurence Matrix



Eq.	D	P	R	V_f	Q_C	Q_S	L	V_D	$\omega_{B,L}$
a	1	1							
b	1	1							
j		1	1						
g		1	1	1					
i		1	1	1	1				
c	1	1			1	1			
m	1					1	1	1	
k	1						1	1	
l	1						1	1	1

Figure E5.7c Precedence Ma

boxes indicating the equation to be solved, or set of equations to be solved, simultaneously. Note that we have substituted the overall balances for the process I (still) balances because common sense dictates making overall balances first.

Step 9

(1) Solution of Eqs. (a) and (b):

$$P = 3959 \text{ lb/hr} \quad \longleftarrow \quad \textcircled{a_1}$$

$$D = 6041 \text{ lb/hr} \quad \longleftarrow \quad \textcircled{a_2}$$

(The encircled letters indicate answers to the questions posed.)

(2) Solution of Eq. (j):

$$R = 6P = 6(3959) = 23{,}754 \text{ lb/hr} \quad \longleftarrow \quad \textcircled{b}$$

(3) Solution of Eq. (g):

$$V_t = R + P = 23{,}754 + 3959 = 27{,}713 \text{ lb/hr}$$

(4) Solution of Eq. (i):

$$Q_C = -27{,}713\Delta\hat{H}_{V_t,178°\text{F}} + 23{,}754\Delta\hat{H}_{R,178°\text{F}} + 3959\Delta\hat{H}_{P,178°\text{F}}$$

Use a reference temperature of 178°F so that the sensible heat changes are zero. In a computer code, all the calculations might use the same common reference temperature such as 77°F or 32°F; hence all the terms in Eq. (i) would be involved, but we do not know the heat capacity data with sufficient accuracy here to integrate over large temperature ranges.

$$\Delta\hat{H}_{V_t,178°\text{F}} = 0.995(170) + 0.005(140) \cong 170 \text{ Btu/lb} \qquad \text{(vapor)}$$

$$\Delta\hat{H}_{R,178°\text{F}} = 0 \qquad \text{(liquid)}$$

$$\Delta\hat{H}_{P,178°\text{F}} = 0 \qquad \text{(liquid)}$$

$$Q_C = -4.711 \times 10^6 \text{ Btu/hr} \qquad \text{(heat removed)}$$

To calculate W, assume that $C_{p_{H_2O}} = 1$ Btu/(lb)(°F)

$$Q_C = WC_{p_{H_2O}}(140 - 60) = W(80)$$

$$W = 5.89 \times 10^4 \text{ lb H}_2\text{O/hr} \quad \longleftarrow \quad \textcircled{d_1}$$

(5) Solution of Eq. (c):

$$-4.711 \times 10^6 + Q_S + 10{,}000\Delta H_{F,70°\text{F}} = 3959\Delta H_{P,178°\text{F}} + 6041\Delta H_{D,268°\text{F}}$$

Use as a reference temperature 70°F (all streams are liquid). To save space we make the assumption that the P stream is pure benzene and the B stream is pure chlorobenzene, and that average heat capacities are reasonable to use, quite satisfactory assumptions since the value of Q_C is one order of magnitude larger than the sensible heat terms.

$$\Delta\hat{H}_{F,70°\text{F}} = 0$$

$$\Delta\hat{H}_{P,178°\text{F}} = \int_{70}^{178} C_{p_P}\, dT = 0.435(178 - 70) = 47.0 \text{ Btu/lb}$$

$$\Delta\hat{H}_{D,268°\text{F}} = \int_{70}^{268} C_{p_D}\, dT = 0.355(268 - 70) = 70.3 \text{ Btu/lb}$$

$$Q_S = 5.32 \times 10^6 \text{ Btu/hr} \qquad \text{(heat introduced)}$$

To calculate S, assume that the saturated steam exits as saturated liquid at 280°F ($\Delta\hat{H}_{\text{vap}} = 923$ Btu/lb from the steam tables)

$$Q_S = \Delta\hat{H}_{\text{vap}\,H_2O}\, S = 923(S)$$

$$\text{at } 280°\text{F}$$

$$S = \frac{5.32 \times 10^6 \text{ Btu/hr}}{923 \text{ Btu/lb}} = 5760 \text{ lb/hr} \longleftarrow \textcircled{d_2}$$

(6) Solution of Eqs. (m) and (k):

$$L = V_D + 6041$$

$$5.32 \times 10^6 + \text{L}\, \Delta\hat{H}_{L,248°\text{F}} = V_D\, \Delta H_{V_D,268°\text{F}} + 6041 \Delta\hat{H}_{D,268°\text{F}}$$

Use a reference temperature of 248°F, as we do not know the composition of stream L.

$$\Delta\hat{H}_{L,248°\text{F}} = 0 \qquad \text{(liquid)}$$

$$\begin{aligned}\Delta\hat{H}_{V_D,248°\text{F}} &= \int_{248}^{268} C_{p_{V_D}}\, dT + \Delta\hat{H}_{V_D,268°\text{F}} \\ &= [0.039(0.515) + 0.961(0.395)](268 - 248) \\ &\quad + [0.039(154) + 0.961(126) = 127.1 \text{ Btu/lb} \qquad \text{(vapor)} \\ \Delta\hat{H}_{D,268°\text{F}} &= 70.3 \text{ Btu/lb} \qquad \text{(liquid)} \\ V_D &= 38{,}520 \text{ lb/hr} \longleftarrow \textcircled{c_2} \\ L &= 44{,}560 \text{ lb/hr} \longleftarrow \textcircled{c}\end{aligned}$$

(7) Solution of Eq. (1):

$$44{,}560\, \omega_{B,L} = 38{,}520(0.039) + 6041(0.01)$$

$$\omega_{B,L} = 0.035 \quad \text{(not required)}$$

5.2-2 Modular-Based Flowsheeting

The *sequential modular* method of flowsheeting, as mentioned previously, is the one most commonly encountered in computer packages. A module exists for each process unit in the information flowsheet. Given the values of each input stream composition, flow rate, temperature, pressure, enthalpy, and the equipment parameters, the module calculates the properties of its outlet streams. The output stream for a module can become the input stream for another module for which the calculations proceed until the material and energy balances are resolved for the entire process.

The underlying concept of modularity in flowsheeting packages for design and analysis is to represent equipment or unit operations by portable computer subroutines. By portable we mean that such a subroutine can be assembled as an element of a large group of subroutines and successfully represent a certain type of equipment in any process. Figure 5.9(a and b) shows typical standardized unit operations modules together with their flowsheet symbols. Internally, a very simple module might

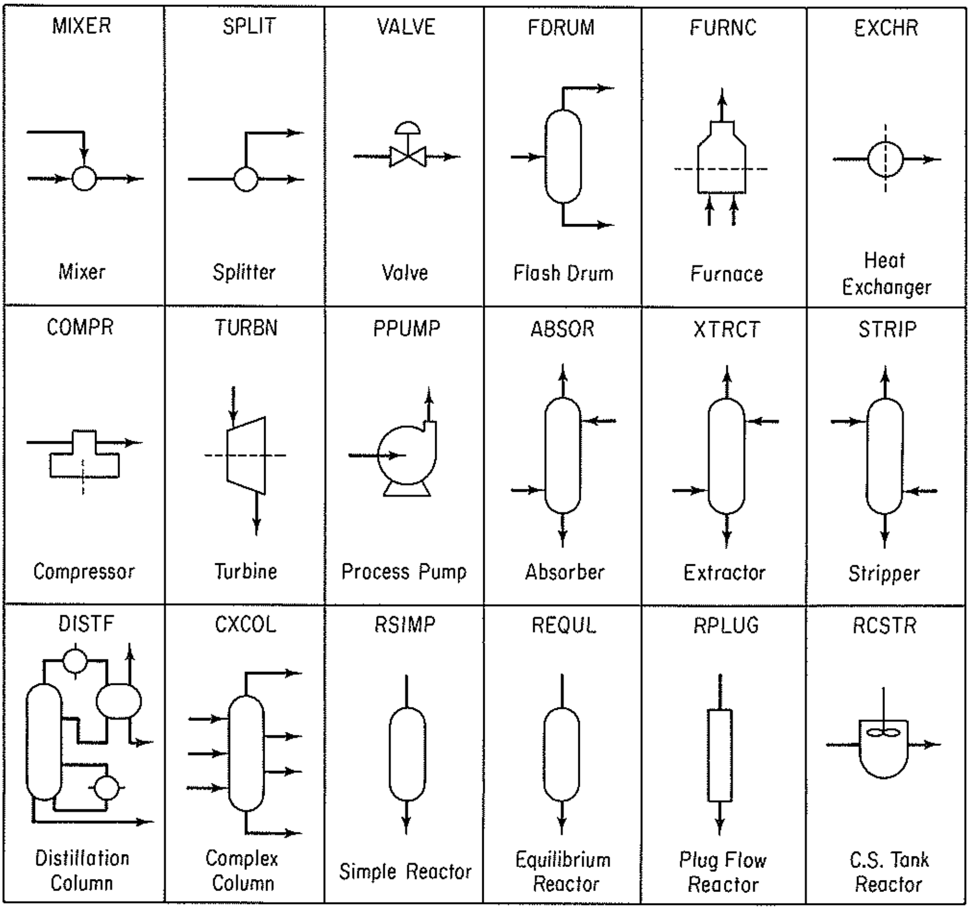


Figure 5.9a Typical process modules used in sequential modular-based flowsheeting codes with their subroutine names.

just be a table look-up program. However, most modules consist of Fortran subroutines that execute a sequence of calculations. Suroutines may consist of 100 to thousands of lines of code. Figure 5.10 illustrates the program used to execute a simple unit operation, the liquid pump subroutine PUMPX, in the FLOWTRAN package.

Other modules take care of equipment sizing and cost estimation, perform numerical calculations, handle recycle calculation (described in more detail below), optimize, and serve as controllers (executives) for the whole set of modules so that they function in the proper sequence. Figure 5.11 illustrates the information flow in a flowsheeting package composed of modules.

Modules representing equipment are written to be as general and as flexible as possible, so that they can be used for the analysis or design of a wide variety of plants. Then they can be applied to specific situations in the plant under consideration by introducing the parameters of the plant into the modules. Appropriate parameters are called upon as needed under the control of the executive program. These parameters may be physical dimensions (such as tube size in a heat ex-

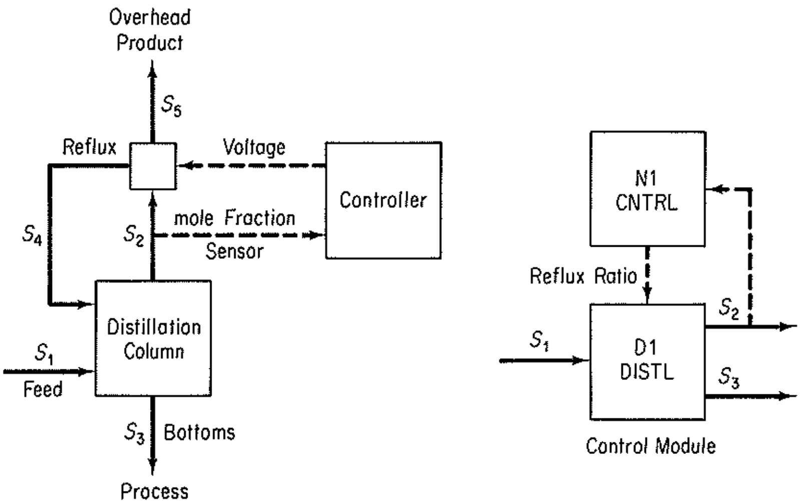


Figure 5.9b A feedback control module, N1: a graphical representation of a subroutine that adjusts equipment parameters to force a desired value of a stream variable. In the figure the feedback control block compares the stream variable value with the specification. When the convergence tolerance is satisfied, the next unit in the calculation order is computed. Otherwise, the control block adjusts the reflux ratio so as to achieve a specified distillate mole fraction.

```
     SUBROUTINE PUMPX (F, B, P, R)
C
C    Title        = Centrifugal pump size and power
C    Files        = FORTRAN 1, 6
C    Subprograms  = MOLVOL
C
C    B            Stream data for pump effluent
C    F            Stream data for pump feed
C    P(1)         Outlet pressure, psia
C    P(2)         Unit name
C    R(1)         Flowrate, gpm
C    R(2)         Pressure increase, psi
C    R(3)         Fluid horsepower, hp
C    R(4)         Pump efficiency
C    R(5)         Brake horsepower, hp
C    R(6)         Motor efficiency
C    R(7)         Electrical power, kilowatts
C
     IMPLICIT     DOUBLE PRECISION (A - H, O - Z)
     COMMON //    BHP, BHPL, DELP, EFFM, EFFP, EKW, FHP, GPM, GPML,
    1             VL, VV, X(20)
     COMMON /CONTRL/ NC, KOUT, KSKIP, KONV
     DIMENSION    B(*), F(*), P(2), R(7)
C
C                            Initialize
           UNAM   = P(2)
     IF    (KOUT .EQ. 2) GO TO 500
     DO 11 I      = 1, 7
   11      R(I)   = 0.
C                           Set outlet stream data from inlet stress
     DO 21 I      = 1, NC + 5
   21      B(I)   = F(I)
C                           Set outlet pressure
     IF    (P(1) .LE. 0.) GO TO 400
           B(NC + 3) = P(1)
C                           Check inlet flow and vapor fraction
     IF    (F(NC + 1) .LE. 0.) GO TO 402
     IF    (F(NC + 5) .GT. 0.) WRITE(1, 924) UNAM
```

```
C
C                             Compute pump flow and pressure increase
     DO 31 I      = 1, NC
   31      X(I)   = F(I)/F(NC + 1)
     IF    (MOLVOL(VL, VV, F(NC + 2), F(NC + 3), X, X, 2, 1) .EQ. 2)
    1             GO TO 406
           GPM    = F(NC + 1)*VL*.12468
           DELP   = B(NC + 3) - F(NC + 3)
C
C                             Compute fluid horsepower, pump efficiency,
C                             and brake horsepower
           FHP    = GPM*DELP*.5833E-3
           GPML   = LOG(MAX(20D0, MIN(GPM, 50000D0)))
           EFFP   = -.3161 + GPML*(.240123 - GPML*.0119889)
           BHP    = FHP/EFFP
C
C                             Compute motor efficiency and electrical
C                             power
           BHPL   = LOG(MAX(1D0, MIN(BHP, 5000D0)))
           EFFM   = .7982 + BHPL*(.033270 - BHPL*.0019334)
           EKW    = BHP/(1.34102*EFFM)
C
C                             Save results, print history report
           R(1)   = GPM
           R(2)   = DELP
           R(3)   = FHP
           R(4)   = EFFP
           R(5)   = BHP
           R(6)   = EFFM
           R(7)   = EKW
     WRITE (1, 902) UNAM, B(NC + 3), B(NC + 1)
     RETURN
C
C                             Print warning and error messages
 400 WRITE (1, 920) UNAM
     RETURN
 402 WRITE (1, 922) UNAM
     RETURN
 406 WRITE (1, 926) UNAM
     RETURN
C
C                             Print unit report
 500 WRITE (6, 950) UNAM, F(NC + 6), B(NC + 6)
     WRITE (6, 952) R(1), R(2), R(3), R(5), R(7), R(4), R(6)
     IF    (F(NC + 5) .GT. 0.) WRITE (6, 954)
     IF    (B(NC + 3) .LE. F(NC + 3)) WRITE (6, 956)
     RETURN
C
 902 FORMAT(1X, A6, 21H(PUMPX)  Outlet pres=, F7.1, 12H psia, Flow=,
    1      F10.1, 9H lbmol/hr)
C
 920 FORMAT(5H  ***, A6, '(PUMPX)  PARAM 1 is in error.  Feed',
    1                   ' pressure was used.')
 922 FORMAT(5H  ***, A6, '(PUMPX)  Feed flow is zero.')
 924 FORMAT(5H  ***, A6, '(PUMPX)  Feed is not all liquid.')
 926 FORMAT(5H  ***, A6, '(PUMPX)  Cannot compute fluid volume.')
C
 950 FORMAT(/ / 1X, A6, 17H(PUMPX)  Inlet = , A4, 12H , Outlet = , A4)
 952 FORMAT(5X, 11HFlow, gpm =, F9.2, 17H , Delta P, psi =, F8.2/
    1       5X, 11HFluid hp  =, F9.2, 17H , Brake hp     =, F8.2,
    2              12H , Elec kw =, F8.2/
    3       5X, 11HPump eff  =, F9.4, 17H , Driver eff   =, F8.4)
 954 FORMAT('    *Note: Inlet pressure is not less than outlet.')
 956 FORMAT('    *Note: Feed is not all liquid.  Outlet T AND FV ',
    1                   'may be wrong.')
     END
```

Figure 5.10 FLOWTRAN Subroutine for a Pump Block. The dummy arguments of the subroutine are: (1) F and B, the feed and effluent stream vectors containing stream flow information; (2) the equipment paramenter vector, R, which contains the outlet pressure; and (3) the retention vector, R, which contains the flowrate, pressure increase, fluid Hp, pump efficiency, brake Hp, motor efficiency, and electrical power in kilowatts, all of which are to be printed out. From Seader, I. D., W. D. Seider, and A. C. Pauls, *Flowtran Simulation—An Introduction* 3rd ed., CACHE, Austin, TX (1987).

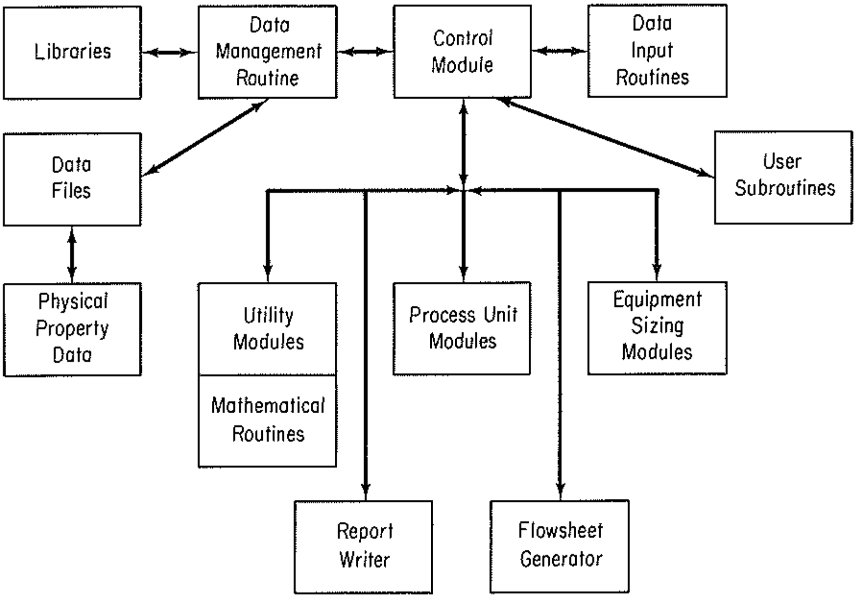


Figure 5.11 Information flow between modules in a typical sequential modular-based flowsheeting package.

changer), operating conditions (such as reflux ratio in a distillation column), reaction rate constants, convergence factors, and so one. Table 5.2 is a specification for a two-phase flash unit and Fig. 5.12 is the representation of a flash in FLOWTRAN.

Information flows between modules via the material streams. Associated with each stream is an ordered list of numbers that characterize the stream. Table 5.3 lists a typical set of parameters associated with a stream. As a user of a modular-based code, you have to provide

1. The process topology
2. Input stream information including physical properties, connections
3. Design parameters needed in the modules and equipment specifications
4. Convergence criteria

In addition, you may have to insert a preferred calculation order for the modules. When economic evaluation and optimization are being carried out, you must also provide cost data and optimization criteria.

Table 5.4 is a computer printout of the type of input data (for stream 11) needed for a process. The input data can be entered either in a batch mode or an interactive mode through a terminal, depending on the options available in the flowsheeting code, and its interactive flexibility. Most execute in a batch mode, but some allow preparation of input data in a conversational mode. In the initial processing of the input data, a main program is generated, compiled, loaded, and connected with the required modules and all the needed subprograms, and storage is allocated all prior to execution. Although you have to check the input data to make

TABLE 5.2 Specifications for a Two-phase Equilibrium Flash

Description

This flash capability solves the single-stage heat balance, material balance, and phase equilibrium relations for given inlet streams and user specifications. It applies to both the vapor–liquid and liquid–liquid cases. For liquid–liquid equilibria, replace "vapor" by "1st liquid" and "liquid" by "2nd liquid."

Inlet streams: Any number of vapor–liquid.

Outlet streams: One vapor and one liquid stream or one vapor–liquid stream.

Options for specifications

1. Temperature and pressure specified
2. Pressure and vapor fraction specified
3. Temperature and vapor fraction specified
4. Pressure and heat added specified
5. Temperature and heat added specified
6. Specified vapor flow rate

For all options, the vapor mole fraction and enthalpy, liquid mole fraction and enthalpy, and the unspecified values of temperature, pressure, or vapor fraction are calculated. In options 4 and 5, the inlet stream enthalpy must be known. In options 1, 2, and 3, the heat duty will be calculated if inlet stream enthalpy is known.

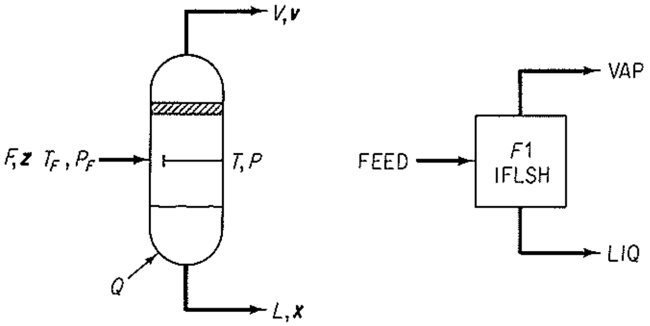
Under options 1, 4, and 5, it is possible for the result to be a subcooled liquid or a superheated vapor, in which case the vapor fraction is set equal to zero or 1 as appropriate, and the nonexistent phase composition has no meaning.

Additional results: Heat duty as discussed above

PPS requirements: K values and phase enthalpies

Outlet attributes: T, p, H, V

SOURCE: Adapted from *Functional Specifications for ASPEN,* Department of Chemical Engineering, Massachusetts Institute of Technology, December 1977.



```
TITLE C5-C6 FLASH
PROPS 2  1  1  1  1
RETR N-PENTANE NC6
BLOCK F1 IFLSH FEED LIQ VAP
PARAM F1  1  120  13.23
MOLES FEED 1  0.5  0.5
TEMP FEED 130
PRESS FEED 73.5
END CASE
END JOB
```

(a) Flash Vessel (b) Simulation Flowsheet (c) FLOWTRAN Program

Figure 5.12 Simulation of a Flash Unit in FLOWTRAN. From Sender, J. D., W. D. Seider, and A. C. Pauls, *Flowtran Simulation-An Introduction,* CACHE, Austin, TX (1987).

TABLE 5.3 Stream Parameters

1. Stream number*
2. Stream flag (designates type of stream)
3. Total flow, lb mol/hr
4. Temperature, °F
5. Pressure, psia
6. Flow of component 1, lb mol/hr
7. Flow of component 2, lb mol/hr
8. Flow of component 3, lb mol/hr
9. Molecular weight
10. Vapor fraction
11. Enthalpy
12. Sensitivity

*Corresponds to an arbitrary numbering scheme used on the information flowsheet.

certain that they are correct, most packages have extensive input data capabilities as part of the preprocessing phase that give diagnostic error and warning messages.

You can regard a module as an information modifier. It receives information about feed streams, streams coming from other modules, together with parameters, carries out computations with the information, and produces output information which is forwarded to other modules and/or is reported. Under some circumstances output information may be fed back as input to the module.

Often, modules are prepared at several levels of sophistication for the same type of equipment. Approximate models in modules are used in the initial stages of setting up a study of the whole plant to get a rough idea of whether a design is worth pursuing, and to investigate the suitability of various convergence techniques. Subsequently, the approximate models can be replaced by more comprehensive models. The more comprehensive and accurate the model is, the greater the cost of program development and program execution. Also, you may find complex programs more difficult to understand and use, and it is easier to make mistakes in using them.

Modular-based flowsheeting exhibits several advantages in design. The flowsheet architecture is easily understood because it closely follows the process flowsheet. Individual modules can easily be added and removed from the computer package. Furthermore, new modules may be added to or removed from the flowsheet without any difficulty or affecting other modules. Modules at two different levels of accuracy can be substituted for one another as mentioned above.

Modular-based flowsheeting also has certain drawbacks.

1. The output of one module is the input to another. The input and output variables in a computer module are fixed so that you cannot arbitrarily introduce an output and generate an input as can be done with an equation-based code.
2. The modules make it costly to generate reasonable accurate derivatives or their substitutes, especially if a module contains tables, functions with discrete variables, discontinuities, and so on. Perturbation of the input to a module is the

TABLE 5.4 Typical Input Data for a Process

COMPONENT NO.	MOL. WT.	LBS.	LB MOLES	DENSITY, LB/CU. FT.	SPEC. HEAT, BTU/(LB) (F)	HT. VAPOR.
1	2	0	0		3.5	
2	60	0	0			
3	78	4644.9	59.551	54.7		
4	84	0	0	44.3	0.43	154
APPROX. TOTAL		4644.9	59.551			

NO. STREAM	NO. COMPON.	FLOW RATE	CONNECTIONS	CALC. ORDER
11	4	59.551	12 −4	6

TEMP., °F	PRESS, PSIG	AVG. MOL. WT.	CONVG. FRACT.	EQUIPMENT
100.0	285.	78.0	0.02	2

primary way in which a finite-difference substitute for a derivative can be generated.

3. The modules may require a fixed precedence order of solution, that is, the output of one module must become the input of another; hence convergence may be slower than in an equation-solving method, and the computational costs may be high.
4. To specify a parameter in a module as a design variable, you have to place a control block around the module and adjust the parameter such that design specifications are met. This arrangement creates a loop. If the values of many design variables are to be determined, you might end up with several nested loops of calculation (which do, however, enhance stability). A similar arrangement must be used if you want to impose constraints.
5. Conditions imposed on a process (or a set of equations for that matter) may cause the unit physical states to move from a two-phase to a single-phase operation, or the reverse. As the code shifts from one module to another to represent the process properly, a severe discontinuity occurs and physical property values may jump about.

To obtain a solution for the material and energy balances in a flowsheet by the sequential modular method, you must partition the flowsheet, select tear streams, nest the computations, and thus determine the computation sequence.

Partitioning of the modules in a block information diagram into minimum-sized subsets of modules that have to be solved simultaneously can be executed by many methods. As with solving sets of equations, you want to obtain the smallest block of modules in which the individual modules are tied together by the information flow of outputs and inputs. Between blocks, the information flow occurs serially. A simple algorithm is to trace a path of the flow of information (material usually but could be energy or a signal) from one module to the next through the module output streams. The tracing continues until (a) a module in the path is encountered again, in which case all the modules in the path up to the repeated module form a group together which is collapsed and treated as a single module in subsequent tracing, or (b) a module or group with no output is encountered, in which case the module or group of modules is deleted from the block diagram. The block diagram in Fig. 5.13 can be partitioned by the following steps.

Start with an arbitrary unit, say 4, and any sequence.

Path 1:	Start:	$4 \rightarrow 5 \rightarrow 6 \rightarrow 4$	collapse as (456)
	Continue:	$(456) \rightarrow 2 \rightarrow 4$	collapse as (4562)
	Continue:	$(4562) \rightarrow 1 \rightarrow 2$	collapse as (45621)
	Continue:	$(45621) \rightarrow 7 \rightarrow 8 \rightarrow 7$	collapse (78)
	Continue:	$(45621) \rightarrow (78) \rightarrow 9$	terminate (no output)

Put number 9 on the precedence order list and delete module 9 from the information block diagram.

Continue: $(45621) \rightarrow (78) \rightarrow 9$ Terminate (put 78 on the list before 9)

Delete (78) from the block diagram.

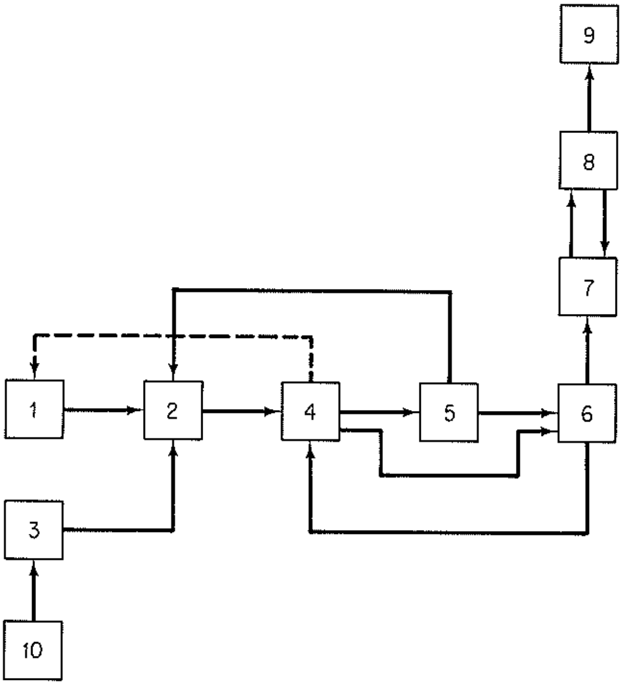


Figure 5.13 Block diagram to be partitioned.

Continue: (45621) Terminate (put 45621 before 78 in the list)

Delete (45621) from the block diagram

This completes the search in path 1, as no more modules exist.

Path 2: Start: 10 → 3 Terminate (put 3 in list before 45621)

Continue: 10 Terminate (put 10 in list before 3)

All of the modules have been deleted from the block diagram, and no more paths have to be searched. Computer techniques to partition complex sets of modules besides the one described above can be found in the supplementary references at the end of this chapter. Simple sets can be partitioned by inspection.

From a computational viewpoint, the presence of recycle streams is one of the major impedements in the sequential solution of a flowsheeting problem. Without recycle streams, the flow of information would proceed in a forward direction, and the calculational sequence for the modules could easily be determined from the precedence order analysis outlined above. With recycle streams present, large groups of modules have to be solved simultaneously, defeating the concept of a sequential solution module by module. For example, in Fig. 5.14, you cannot make a material balance on the reactor without knowing the information in stream S6, but you have to carry out the computations for the cooler module first to evaluate S6, which in turn depends on the separator module, which in turn depends on the reactor module. Partitioning will identify those collections of modules that have to be solved simultaneously (termed *maximal cyclical subsystems* or *irreducible nets*).

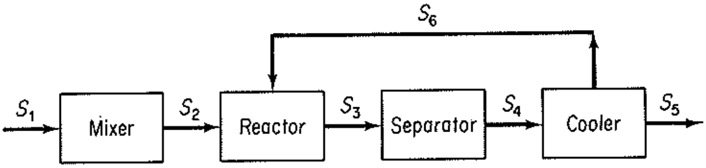


Figure 5.14 Modules in which recycle occurs; information (material) from the cooler module is fed back to the reactor.

To execute a sequential solution for a set of modules, you have to tear certain streams. *Tearing* in connection with modular flowsheeting involves decoupling the interconnections between the modules so that sequential information flow can take place. Tearing is required because of the loops of information created by recycle streams. What you do in tearing is to provide initial guesses for values of some of the unknowns (the tear variables), usually but not necessarily the recycle streams, and then calculate the values of the tear variables from the modules. These calculated values form new guesses, and so on, until the differences between the estimated and calculated values are sufficiently small. *Nesting* of the computations determines which tear streams are to be converged simultaneously and in which order collections of tear streams are to be converged.

Physical insight and experience in numerical analysis are important in selecting which variables to tear. For example, Fig. 5.15 illustrates an equilibrium vapor–liquid separator for which the combined material and equilibrium equations give the relation

$$\sum_{j=1}^{C} \frac{z_j(1 - K_j)}{1 - (V/F) + VK_j/F} = 0 \tag{5.4}$$

where z_j is the mole fraction of species j out of C components in the feed stream, $K_j = y_j/x_j$ is the vapor–liquid equilibrium coefficient, a function of temperature, and the stream flow rates are noted in the figure. For narrow-boiling systems, you can guess V/F, y_j, and x_j, and use Eq. (5.4) to calculate K_j and hence the temperature. This scheme works well because T lies within a narrow range. For wide-boiling ma-

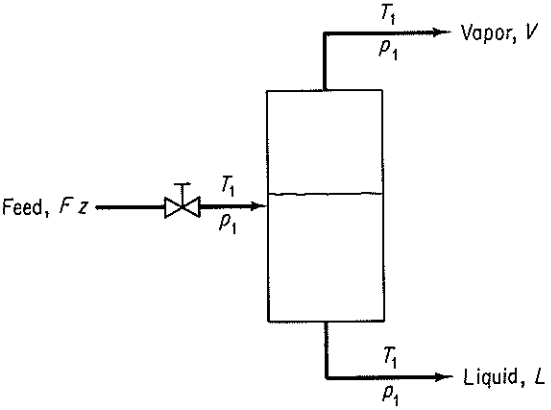


Figure 5.15 Vapor–liquid separato

terials, the scheme does not converge well. It is better to solve Eq. (5.4) for V/F by guessing T, y, and x, because V/F lies within a narrow range even for large changes in T. Usually, the convergence routines for the code comprise a separate module whose variables are connected to the other modules via the tear variables. Examine Fig. 5.16.

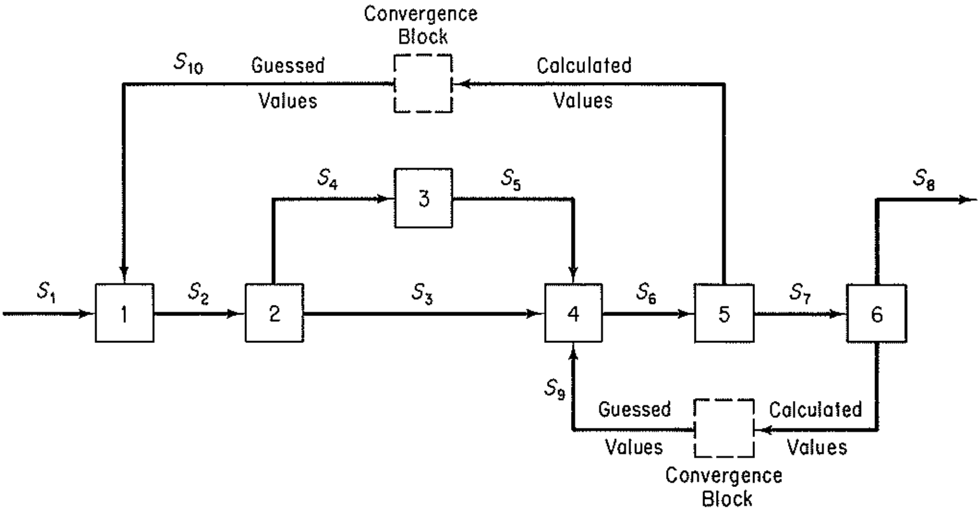


Figure 5.16 A computational sequence modular flowsheeting. Initial values of both recycles are guessed, then the modules are solved in the order 1, 2, 3, 4, 5, and 6. Calculated values for recycle streams S9 and S10 are compared to guessed values in a convergence block, and unless the difference is less than some prescribed tolerance, another iteration takes place with the calculated values, or estimates based on them, forming the new initial guessed values of the recycle streams.

An engineer can usually carry out the partitioning, tearing, nesting, and determine the computational sequence for a flowsheet by inspection if the flowsheet is not too complicated. In codes such as FLOWTRAN, the user supplies the computational sequence as input. Other codes determine the sequence automatically. In ASPEN, for example, the code is capable of determining the entire computational sequence, but the user can supply as many specifications as desired, up to and including the complete sequence. Consult one of the supplementary references at the end of this chapter for detailed information on optimal techniques of partitioning and tearing, techniques beyond our scope in this text.

Once the tear streams are identified and the sequence of calculations specified, everything is in order for the solution of material and energy balances. All that has to be done is to calculate the correct values for the stream flow rates and their properties. To execute the calculations, many computer codes use the method of successive substitution, which is described in Appendix L. The output(s) of each module on interation k is expressed as an explicit function of the input(s) calculated from the previous iteration, $k - 1$. For example, in Fig. 5.16 for module 1,

$$S2^{(k)} = f(S1^{(k-1)}, S10^{(k-1)}, \text{coefficients})$$

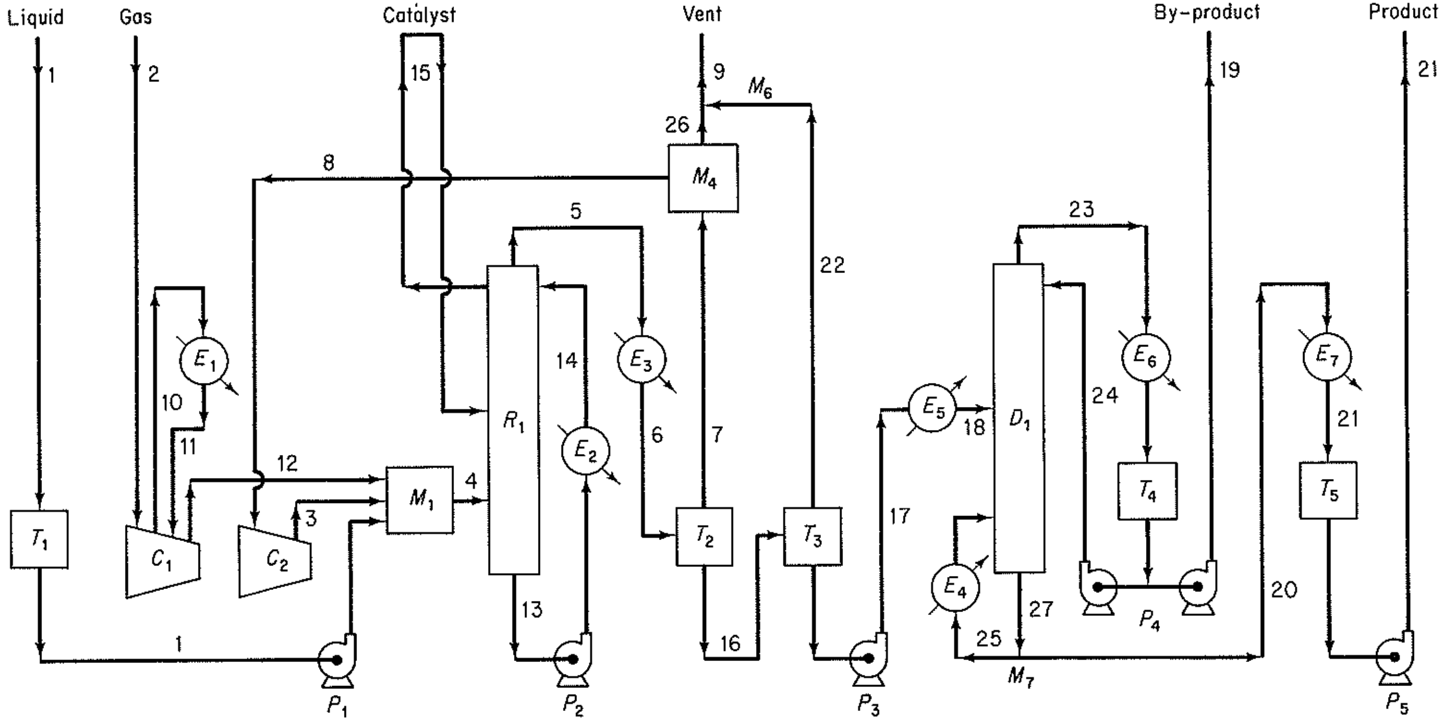


Figure E5.8 C = COMPRESSOR, D = DISTILLATION UNIT, E = HEAT EXCHANGER, P = PUMP, R = REACTOR, T = TANK, M = MIXER OR SPLITTER. Streams are identified by Arabic numbers.

To accelerate recycle stream convergence, the Wegstein method (refer to Appendix L) has been the mainstay of sequential modular flowsheeting for almost 25 years. Although this method neglects possible interaction between variables in tear streams, for most systems it works very well. A number of heuristics have been developed to improve convergence by delaying application of the Wegstein acceleration step until a specified number of direct substitution steps have been made and by setting bounds on the maximum acceleration allowed. With the use of Wegstein's method or direct substitution, it is necessary to control the convergence of recycle streams separately from the convergence of module specifications. Newton or quasi-Newton methods can also be used to solve for recycle streams.

EXAMPLE 5.8 Solution of Material and Energy Balances Using a Sequential Modular-Based Flowsheeting Code

Figure E5.8 is a hypothetical process used for demonstration by Diamond Shamrock Co. of their flowsheeting code PROVES. Makeup gas is compressed, combined with recycle gas, and fed, together with liquid raw material, into a three-phase, suspended bed catalytic reactor. The reactor is cooled by recirculating liquid through a heat reclamation steam generator. Reaction products are condensed and the pressure of the exit stream reduced in two stages. The gas from the first-stage separator is recirculated, whereas the liquid from the second-stage separator is fed into a distillation column. Pure product is withdrawn from the bottom of the column. The distillate is a by-product that is pumped to another plant.

Table E5.8a lists the input data for the flowsheeting code needed to solve the material and energy balances. Table E5.8b is a computer printout of the flow rates, temperatures, and pressures of the 21 major streams.

SUPPLEMENTARY REFERENCES

Flowsheeting Codes

BROYDEN, C. G., "A Class of Methods for Solving Nonlinear Simultaneous Equations," *Math Comput.*, v. 19, p. 577 (1965).

CHEN, H. S., and M. A. STADTHERR, "A Simultaneous-Modular Approach to Process Flowsheeting and Optimization: I. Theory and Implementation," *AIChE J.*, v. 30 (1984).

HANYAK, M. E., "Textual Expansion of Chemical Process Flowsheets into Algebraic Equation Sets," *Comput. Chem. Eng.*, v. 4, p. 223 (1980).

HILLESTAD, M., and T. HERTZBERG, "Dynamic Simulation of Chemical Engineering Systems by the Sequential Modular Approach," *Comput. Chem. Eng.*, v. 10, p. 377 (1986).

JOULIA, X., and B. KOEHRET, "Simultaneous Modular Approach to Process Flowsheeting," EFCE Pub. Ser. 1983, 27, Cong. Int. "Inf. Genie Chem," Vol. 2, C70/1-C70/7(1983).

MONTAGNA, J. M., and O. A. IRIBARREN, "Optimal Computation Sequence in the Simulation of Chemical Plants," *Comput. Chem. Eng.*, v. 12, p. 71 (1988).

NISHIDA, N., G. STEPHANOPOULOS, and A. W. WESTERBERG, "A Review of Process Synthesis," *AIChE J.*, v. 27, p. 321 (1981).

TABLE E5.8a Input Data

Number of streams	21	(first 21 only)
Number of components	4	
Number of operations	9	

Component [name, mol. wt., no., density (lb/ft^3), C_p (Btu/(lb) (F)), ΔH_{vap}]

Gas	2.	1	0	3.5	0
Catalyst	60.	2	0	0	0
Liquid A	78.	3	54.7	0.43	169.
Liquid B	84.	4	44.3	0.48	154.

Stream Data

No.	Flow Rate	Units*	Temp (°F)	Press (psig)
1	59.551	0	100.	0
2	183.	0	100.	0
3	0	0	140.	285.
4	0	0	100.	285.
5	0	0	400.	275.
6	0	0	120.	270.
7	0	0	120.	265.
8	0	0	120.	265.
9	0	0	120.	265.
10	183.	0	250.	95.
11	183.	0	120.	95.
12	183.	0	250.	285.
13	9000.	1	400.	285.
14	9000.	1	295.	285.
15	0.8	1	100.	0
16	0	0	120.	0
17	0	0	120.	0
18	0	0	200.	15.
19	0	0	200.	0
20	0	0	230.	5.
21	0	0	120.	0

Component Data

Stream No.	Gas	Catalyst	Liquid A	Liquid B
1	0	0	59.551	0
2	183.	0	0	0
3	0	0	0	0
4	0	0	0	0
5	0	0	0	0
6	0	0	0	0
7	0	0	0	0
8	0	0	0	0
9	9	9	9	9
10	183.	0	0	0
11	183.	0	0	0
12	183.	0	0	0

TABLE E5.8a (*Continued*)

```
   13          0          760.          81.          89159.
   14          0          760.          81.          89159.
   15          0            0.8          0               0
   16          0          0             0                0
   17          0          0             0                0
   18          0          0             0                0
   19          0          0             0                0
   20          0          0             0                0
   21          0          0             0                0

Stream Connections
   Module           Streams (-1 = out)
     T1              1      - 1
     C1              2       11       - 10       - 12
     E1             10      - 11
     C2              8        3
     M1             12        3          1       -  4
     R1              4       15         14       - 15       - 13       - 5
     E2             13      - 14
     E3              5      -  6
     T2              6      -  7       - 16
     M4              7      -  8       - 26
     M6             26       22       -  9
     T3             16      - 22       - 17
     E4             25      - 25
     E5             17      - 18
     D1             18       25         24       - 23       - 27
     E6             23      - 23
     T4             23      - 23
     M7             27      - 20       - 25
     E7             20      - 21
     T5             21      - 21
     P1              1      -  1
     P2             13      - 13
     P3             17      - 17
     P4A            24      - 24
     P4B            19      - 19
     P5             21      - 21


Suggested Calculation Order (1 = serial, 2 = in loop, 3 = end of loop)
     M1     R1     T2     M4     E3     C2     E5     D1     E7
     2      2      2      2      2      3      1      1      1


Convergence Tolerances
     Total flow        0.05
     Component flow    0.02    0.02    0.02    0.02
```

TABLE E5.8a *(Continued)*

Designation of Operations (type, no. inlet streams, fractional split)

M1	MIXR	3	0
M4	MIXR	1	0.07479
E3	EXCH	1	0
C2	COMP	2	0
E5	EXCH	1	0
E7	EXCH	1	0

Separation

(type, fraction of inlet component that goes into first outlet stream)

T2	SEPN	1	0	0	0

Distillation

[mole fraction in outlet stream (+ = 1st stream; − = 2nd stream)]

D1	DIST	0	0	−0.01099	0.01958

Reactor

(type, fraction conversion of key component, key component number, stoichiometric coefficient of components 1, 2, . . .)

R1	0.9	3.0	3.01423	0	1	−1.00032

Cooling Water Temperatures [F (inlet, temperature difference)]

87	28

Generated Steam Pressure [psig, temperature, ΔH_{vap} (Btu/lb)]

40	287	920

Compressor

[stream suction, stream discharge, key component, C_p/C_v, efficiency, interstage temperature of cooling gas (°F)]

C1	2	12	1	1.41	0.72	120
C2	8	3	1	1.41	0.72	

Heat Exchanger (1 = liq., 2 = gas, 4 = liq. + solid, 6 = boiling liq.,
7 = condensing vapor, 8 = noncondensable gas + condensing vapor)

TABLE E5.8a (*Continued*)

	Stream No. at Cool End	Phase at Cool End	Stream No. at Warm End	Phase at Warm End	Heat Duty (Btu/hr)
E1	11	2	10	2	
E2	14	4	13	4	1.7×10^6
E3	6	8	5	8	
E4	25	1	25	1	
E5	17	1	18	6	
E6	23	7	23	1	
E7	21	1	20	1	

Pump

[stream no., key component no., equipment type, dynamic head (ft), efficiency]

P1	1	3	1	600.	0.45
P2	13	4	1	80.	0.45
P3	17	4	1	50.	0.45
P4	23	4	1	50.	0.45
P5	21	4	1	20.	0.45

Reactor–Fluidized Bed [inlet stream no., outlet stream no., key component of product, reaction temp. (F), avg. press (psig), productivity (lb/hr) (ft³), reactor/bed volume]

R1	4	5	4	395.	285.	16.	1.5

Tank	Stream No. Inlet	Stream No. Outlet	Final Pressure (psig)	Phase†	Key Comp.	Retention Time (hr)
T1	1	– 1	0.	1	3	24.
T2	6	– 7 – 16	265.	1	4	0.1
T3	16	– 17 – 22		1	4	0.1
T4	23	– 19 – 24		1	4	0.1
T5	21	– 21		1	4	12.

*0, lbmol/hr; 1, lb/hr.

† liquid and/or solid; 2, gas; 3, gas + liquid (and solid).

TABLE E5.8b

```
      C O M P O N E N T               S T R E A M    N O .
                                      1                         2
  NO.      NAME     MOL. WT.    LBS      LBMOLES         LBS     LBMOLES

   1     GAS           2.0       0.0      0.000         366.0   183.000
   2     CATALYST     60.0       0.0      0.000           0.0     0.000
   3     LIQUID A     78.0    4644.9     59.551           0.0     0.000
   4     LIQUID B     84.0       0.0      0.000           0.0     0.000

           APPROX. TOTAL      4644.9     59.551         366.0   183.000

           TEMPERATURE, F.         100.0                    100.0
           PRESSURE, PSIG.           0.0                      0.0
           AVG.MOL.WEIGHT           78.0                      2.0


                                      6                         7
  NO.      NAME     MOL. WT.    LBS      LBMOLES         LBS     LBMOLES

   1     GAS           2.0     477.6    238.813         477.6   238.813
   2     CATALYST     60.0       0.0      0.000           0.0     0.000
   3     LIQUID A     78.0     464.4      5.955           0.0     0.000
   4     LIQUID B     84.0    4503.4     53.613           0.0     0.000

           APPROX. TOTAL      5445.6    298.381         477.6   238.813

           TEMPERATURE, F.         120.0                    120.0
           PRESSURE, PSIG.         270.0                    265.0
           AVG.MOL.WEIGHT           18.2                      2.0


                                      11                        12
  NO.      NAME     MOL. WT.    LBS      LBMOLES         LBS     LBMOLES

   1     GAS           2.0     366.0    183.000         366.0   183.000
   2     CATALYST     60.0       0.0      0.000           0.0     0.000
   3     LIQUID A     78.0       0.0      0.000           0.0     0.000
   4     LIQUID B     84.0       0.0      0.000           0.0     0.000

           APPROX. TOTAL       366.0    183.000         366.0   183.000

           TEMPERATURE, F.         120.0                    250.0
           PRESSURE, PSIG.          95.0                    285.0
           AVG.MOL.WEIGHT            2.0                      2.0
```

```
                              S T R E A M    N O .
            3                           4                          5
     LBS        LBMOLES          LBS        LBMOLES         LBS        LBMOLES

    434.7      217.363          800.7      400.363         477.6      238.813
      0.0        0.000            0.0        0.000           0.0        0.000
      0.0        0.000         4644.9       59.551         464.4        5.955
      0.0        0.000            0.0        0.000        4503.4       53.613

    434.7      217.363         5445.7      459.914        5445.6      293.381

         140.0                      100.0                      400.0
         285.0                      285.0                      275.0
           2.0                       11.8                       18.2


            8                           9                          10
     LBS        LBMOLES          LBS        LBMOLES         LBS        LBMOLES

    441.9      220.952          35.7       17.860         366.0      183.000
      0.0        0.000           0.0        0.000           0.0        0.000
      0.0        0.000           0.0        0.000           0.0        0.000
      0.0        0.000           0.0        0.000           0.0        0.000

    441.9      220.952          35.7       17.860         366.0      183.000

         120.0                      120.0                      250.0
         265.0                      265.0                       95.0
           2.0                        2.0                        2.0


            13                          14                         15
     LBS        LBMOLES          LBS        LBMOLES         LBS        LBMOLES

      0.0        0.000            0.0        0.000         0.0        0.000
    760.0       12.666          760.0       12.666         0.8        0.013
     81.0        1.038           81.0        1.038         0.0        0.000
  89159.0     1061.416        89159.0     1061.416         0.0        0.000

  90000.0     1075.122        90000.0     1075.122         0.8        0.013

         400.0                      295.0                      100.0
         285.0                      285.0                        0.0
          83.7                       83.7                       60.0
```

TABLE E5.8b *(Continued)*

```
         C O M P O N E N T                         S T R E A M    N O .
                                                  16                     17
    NO.        NAME        MOL. WT.         LBS       LBMOLES       LBS       LBMOLES

     1      GAS               2.0            0.0       0.000         0.0       0.000
     2      CATALYST         60.0            0.0       0.000         0.0       0.000
     3      LIQUID A         78.0          464.4       5.955       464.4       5.955
     4      LIQUID B         84.0         4503.4      53.613      4503.4      53.613

              APPROX. TOTAL               4967.9      59.568      4967.9      59.568

              TEMPERATURE, F.
              PRESSURE, PSIG.                  120.0                   120.0
              AVG. MOL. WEIGHT                   0.0                     0.0
                                                83.4                    83.4

        EQUIPMENT SPECIFICATION

ITEM           NAME               EQUI.          TYPE               REQUIRED
 NO.                               NO.                                 NO.

  1         COMPRESSOR              1       2-ST. DUPL. REC.            1
  2         COMPRESSOR              2       1-STAGE RECIPR.             1
  3         HEAT EXCHANGER          1       FIXED TUBE SHEET            1
  4         HEAT EXCHANGER          2       FLOATING HEAD               1
  5         HEAT EXCHANGER          3       FLOATING HEAD               1
  6         PUMP                    1       CENTRIFUGAL                 1
  7         PUMP                    2       CENTRIFUGAL                 1
  8         REACTOR                 1       FLUIDIZED BED               1
  9         TANK                    1       CYLINDRICAL                 1
 10         TANK                    2       CYLINDRICAL                 1
 11         TANK                    3       CYLINDRICAL                 1

 12         DISTILN. COLUMN         1       BUBBLE PLATE                1
 13           BOILER                1       FIXED TUBES                 1
 14           CONDENSER             1       FLOATING HEAD               1
 15           REFLUX PUMP           1       CENTRIFIGUAL                1
 16           REFLUX TANK           1       CYLINDRICAL                 1
 17         HEAT EXCHANGER          1       FLOATING HEAD               3
 18         HEAT EXCHANGER          2       FLOATING HEAD               1
 19         PUMP                    1       CENTRIFUGAL                 2
 20         PUMP                    2       CENTRIFUGAL                 1
 21         PUMP                    3       CENTRIFUGAL                 1
 22         TANK                    1       CYLINDRICAL                 2
```

```
                              S T R E A M   N O .
       18                     19                      20                        21
LBS       LBMOLES    LBS      LBMOLES       LBS      LBMOLES           LBS      LBMOLES

   0.0      0.000      0.0      0.000        0.0      0.000             0.0       0.000
   0.0      0.000      0.0      0.000        0.0      0.000             0.0       0.000
 464.4      5.955    418.1      5.360       46.3      0.594            46.3       0.594
4503.4     53.613      8.9      0.107     4494.5     53.505          4494.5      53.505

4967.9     59.568    427.1      5.467     4540.8     54.100          4540.8      54.100


      200.0               200.0                  230.0                    120.0
      285.0                 0.0                    5.0                      0.0
       83.4                78.1                   83.9                     83.9



 TEMP.       PRES.          PARAMETER 1         PARAMETER 2    MATERIAL
   F         PSIG

  250.        285.       1094.  SCFPM          285.  PSI.DIF.
  140.        285.       1322.  SCFPM           20.  PSI.DIF.
  250.         95.        237.  SQ.FT.         166.  M BTU/HR   STEEL
  400.        285.        571.  SQ.FT.        1700.  M BTU/HR   STEEL
  400.        275.        212.  SQ.FT.        1862.  M BTU/HR   STEEL
  100.          0.         10.  GPM            600.  FT.        CAST IRON
  400.        285.        253.  GPM             80.  FT.        CAST IRON
  395.        285.        422.  CU.FT.           0.             STEEL
  100.          0.      19820.  GAL.             0.             STEEL
  120.        265.        109.  GAL.             0.             STEEL
  120.          0.        109.  GAL.             0.             STEEL

  230.         10.         39.  PLATES          22.  IN.DIA.    STEEL
  338.        100.         59.  SQ.FT.         701.  M BTU/HR   STEEL
  200.         40.         47.  SQ.FT.         792.  M BTU/HR   STEEL
  200.         10.          9.  GPM             70.  FT.        CAST IRON
  200.         10.         78.  GAL.             0.             STEEL
  338.        100.         13.  SQ.FT.         339.  M BTU/HR   STEEL
  230.         40.         24.  SQ.FT.         239.  M BTU/HR   STEEL
  120.          0.         13.  GPM             50.  FT.        CAST IRON
  120.          0.         13.  GPM             50.  FT.        CAST IRON
  120.          0.        699.  GPM             20.  FT.        CAST IRON
  120.          0.       5981.  GAL.             0.             STEEL
```

TABLE E5.8b *(Continued)*

```
        UTILITIES REQUIREMENTS


                        EL. POWER    STEAM     WATER    G. STEAM*   BOILER
                          500 V    100 PSIG   COOLING    50 PSIG    FEEDWAT.

IT.     EQUIP-
NO.     MENT            KW          LBS/HR      GPM      LBS/HR       GPM

 1      COMP 1          184.1        0.0        0.0        0.0        0.0
 2      COMP 2            3.7        0.0        0.0        0.0        0.0
 3      EXCH 1            0.0        0.0       13.0        0.0        0.0
 4      EXCH 2            0.0        0.0        0.0     1663.0        3.6
 5      EXCH 3            0.0        0.0      146.3        0.0        0.0
 6      PUMP 1            2.3        0.0        0.0        0.0        0.0
 7      PUMP 2            6.0        0.0        0.0        0.0        0.0

TOTAL                   196.2        0.0      159.4     1663.0        3.6

*G. STEAM = GENERATED STEAM
```

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PROBLEMS

An asterisk designates problems appropriate for solution using a computer. Refer also to the problems that require writing computer programs at the end of the chapter.

```
                     EL. POWER     STEAM      WATER     G. STEAM*    BOILER
                       500 V      100 PSIG   COOLING     50 PSIG    FEEDWAT.

  IT.      EQUIP-
  NO.      MENT         KW         LBS/HR      GPM       LBS/HR       GPM

   1       DIST 1       0.2        857.0      62.0        0.0         0.0
   2       EXCH 5       0.0        415.3       0.0        0.0         0.0
   3       EXCH 7       0.0          0.0      18.8        0.0         0.0
   4       PUMP 3       0.1          0.0       0.0        0.0         0.0
   5       PUMP 4       0.1          0.0       0.0        0.0         0.0
   6       PUMP 5       0.0          0.0       0.0        0.0         0.0


  TOTAL                 0.6       1272.3      18.1        0.0         0.0
```

Section 5.1

5.1. Determine the number of degrees of freedom for the condenser shown in Fig. P5.1.

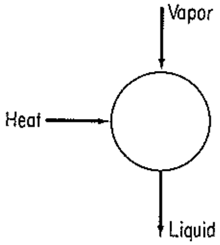


Figure P5.1

5.2. Determine the number of degrees of freedom for the reboiler shown in Fig. P5.2. What variables should be specified to make the solution of the material and energy balances determinate?

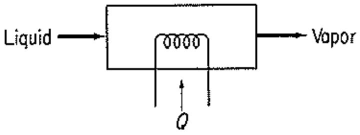


Figure P5.2

5.3. If to the equilibrium stage shown in Example 5.1 you add a feed stream, determine the number of degrees of freedom. See Fig. P5.3.

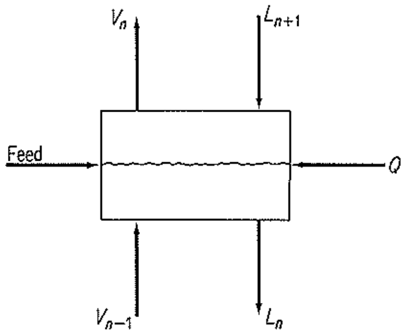


Figure P5.3

5.4. How many variables must be specified for the furnace shown in Fig. P5.4 to absorb all the degrees of freedom?

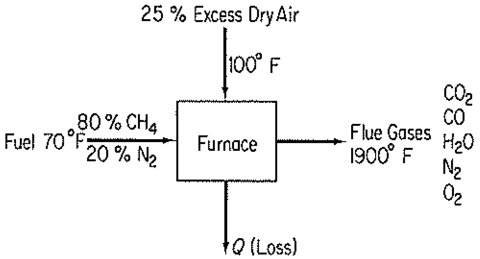


Figure P5.4

5.5. Figure P5.5 shows a simple absorber or extraction unit. S is the absorber oil (or fresh solvent), and F is the feed from which material is to be recovered. Each stage has a Q (not shown); the total number of equilibrium stages is N. What is the number of degrees of freedom for the column? What variables should be specified?

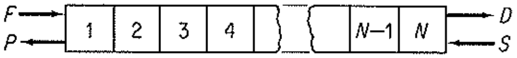


Figure P5.5

5.6. In a reactor model, rather than assume that the components exit from the reactor at equilibrium, an engineer will specify the r independent reactions that occur in the reactor, and the extent of each reaction, ξ_i. The reactor model must also provide for heating or cooling. How many degrees of freedom are associated with such a reactor model?

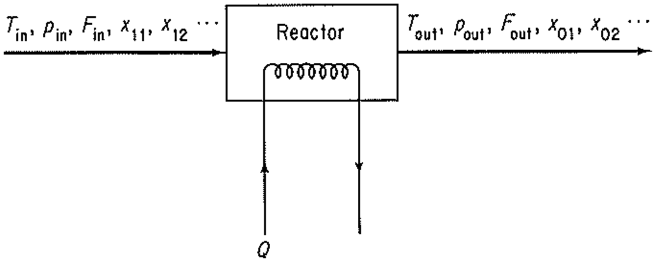


Figure P5.6

5.7. Set up decomposition schemes for the processes shown in Figure P5.7. What additional variables must be specified to make the system determinate if **(a)** the feed conditions are known; or **(b)** the product conditions are specified?

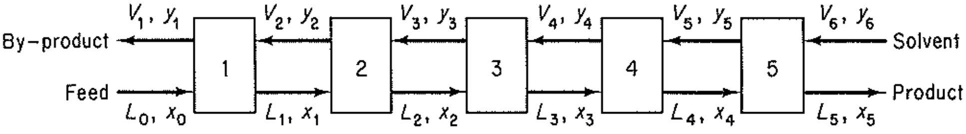


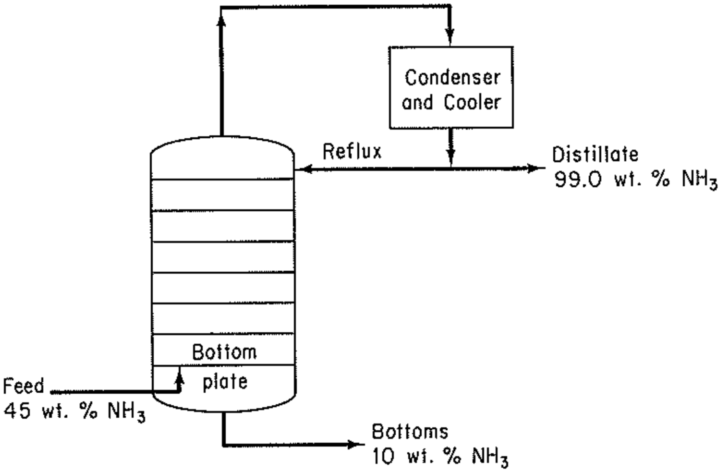
Figure P5.7

5.8. Determine whether or not the following problems are determinate in the sense that all the values of the material flows can be calculated.

(a) A vapor mixture containing 45 weight percent ammonia, balance water, and having an enthalpy of 1125 Btu per pound, is to be fractionated in a bubble-cap column operating at a pressure of 250 psia. The column is to be equipped with a total condenser. The distillate product is to contain 99.0 weight percent ammonia and the bottom product is to contain 10.0 weight percent ammonia. The distillate and the reflux leaving the condenser will have an enthalpy of 18 Btu/lb (Figure P5.8a).

(b) An engineer designed an extraction unit (Fig. P5.8b) to recover oil from a pulp using alcohol as a solvent. The inerts refer to oil-free and solvent-free pulp. Several of the streams in the plant were also used for oil recovery. These streams are shown as F_0 and F_1. Notice that the extracts from the first two stages were not clear but contained some inerts. (Both V_1 and V_2 contain all three components: oil, solvent, and inerts.) Equal amounts of S_1 and L_1 were added to stage 2. There are 2 lb of L_2 for each lb of V_2 leaving the second stage.

The raffinate from stage 1, L_1, contains 32.5 percent alcohol and also in this same stream the weight ratio of inerts to solution is 60 lb inert/100 lb solution. The remaining raffinate streams, L_2, L_3, and L_4, contain 60 lb inert/100 lb alcohol. The L_2 stream contains 15 percent oil.



(a)

Figure P5.8a

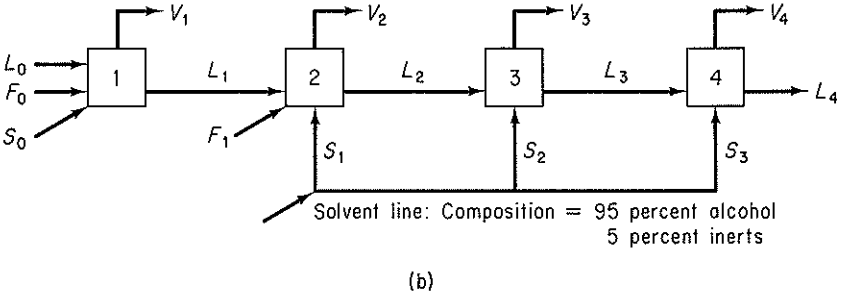
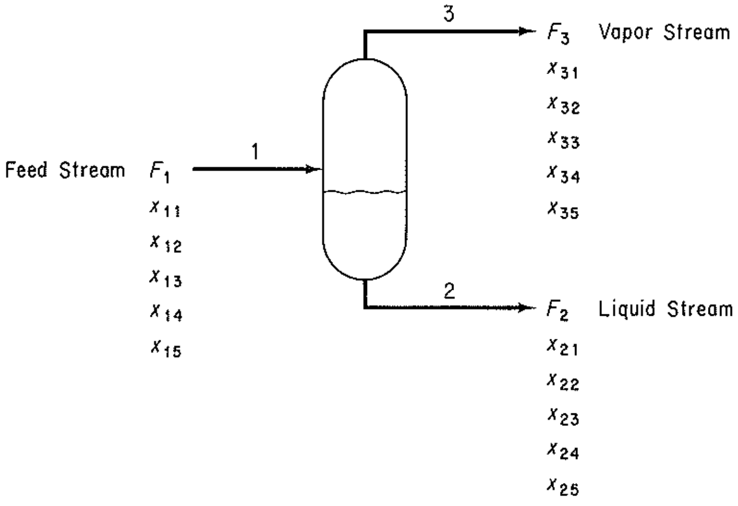


Figure P5.8b

5.9. Examine Fig. P5.9. Values of F_1, x_{11}, x_{12}, x_{13}, x_{14}, and x_{15} are known. Streams F_2 and F_3 are in equilibrium, and the three streams all have the same (known) temperatures and pressures. Is the problem completely specified, underspecified, or overspecified? Assume that the values of K in the equilibrium relations can be calculated from the given temperatures and pressures.



Description of the variables:

F_i — Molar flow for i^{th} stream
x_{ij} — Mole fraction of j^{th} component in i^{th} stream
K_j — Phase-equilibrium coefficient for the j^{th} component

The design variables are:

The Feed Stream, F_1, x_{11}, x_{12}, x_{13}, x_{14}
The Phase-Equilibrium coefficients, K_1, K_2, K_3, K_4, K_5

Figure P5.9

5.10. Book[9] describes a mixer-heat exchanger section of a monoethylamine plant that is illustrated in Fig. P5.10 along with the notation. Trimethylamine recycle enters in stream 4, is cooled in the heat exchanger, and is mixed with water from stream 1 in mixer 1. The trimethylamine–water mixture is used as the cold-side fluid in the heat exchanger and is then mixed with the ammonia–methanol stream from the gas absorber in mixer 3. The mixture leaving mixer 3 is the reaction mixture which feeds into the preheater of the existing plant.

Table P5.10 lists the 31 equations that represent the process in Fig. P5.10. C_i

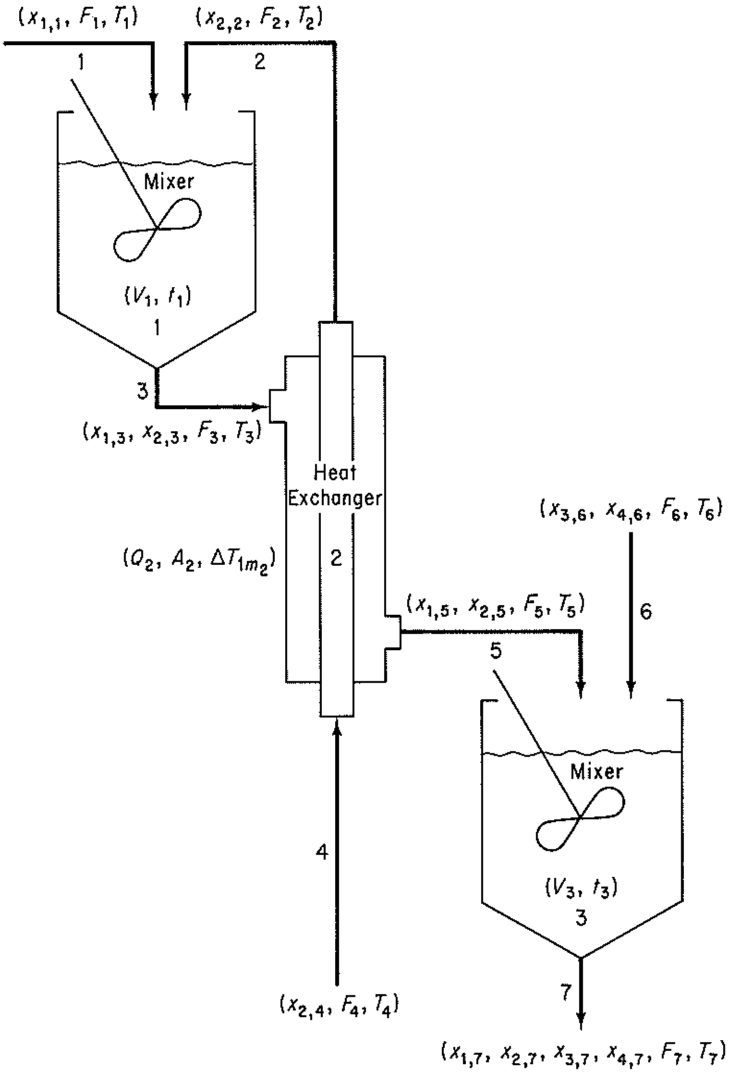


Figure P5.10

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[9] N. L. Book, Structural Analysis and Solution of Systems of Algebraic Design Equations, Ph. D. dissertation, University of Colorado, 1976.

TABLE P5.10 List of Equations to Model the Process

Material Balance Equations

Mole fraction equations

1. $x_{1,1} - 1 = 0$
2. $x_{2,2} - 1 = 0$
3. $x_{1,3} + x_{2,3} - 1 = 0$
4. $x_{2,4} - 1 = 0$
5. $x_{1,5} + x_{2,5} - 1 = 0$
6. $x_{3,6} + x_{4,6} - 1 = 0$
7. $x_{1,7} + x_{2,7} + x_{3,7} + x_{4,7} - 1 = 0$

Flow balance equations

8. $F_1 + F_2 - F_3 = 0$
9. $F_2 - F_4 = 0$
10. $F_3 - F_5 = 0$
11. $F_5 + F_6 - F_7 = 0$

Component balance equations

12. $x_{1,1}F_1 - y_1 = 0$
13. $x_{1,3}F_3 - y_1 = 0$
14. $x_{1,5}F_5 - y_1 = 0$
15. $x_{1,7}F_7 - y_1 = 0$
16. $x_{2,2}F_2 - y_2 = 0$
17. $x_{2,3}F_3 - y_2 = 0$
18. $x_{2,4}F_4 - y_2 = 0$
19. $x_{2,5}F_5 - y_2 = 0$
20. $x_{2,7}F_7 - y_2 = 0$
21. $x_{3,6}F_6 - y_3 = 0$
22. $x_{3,7}F_7 - y_3 = 0$
23. $x_{4,6}F_6 - y_4 = 0$
24. $x_{4,7}F_7 - y_4 = 0$

Energy Balance Equations

25. $C_1F_1T_1 + C_2F_2T_2 - C_3F_3T_3 = 0$
26. $C_4F_4T_4 - Q_2 - C_2F_2T_2 = 0$
27. $C_3F_3T_3 + Q_2 - C_5F_5T_5 = 0$
28. $C_5F_5T_5 + C_6F_6T_6 - C_7F_7T_7 = 0$

Equipment Specification Equations

29. $V_1 - (F_3)\left(\dfrac{V_1}{F_1}\right)/\rho_3 = 0$
30. $Q_2 - U_2A_2\,\Delta T_{lm_2} = 0$
31. $V_3 - (F_7)\left(\dfrac{V_3}{F_3}\right)/\rho_7 = 0$

---

is a heat capacity (a constant), F_i a flow rate, A area (a constant), ΔT_{lm} a log mean temperature difference

$$\frac{(T_4 - T_5) - (T_2 - T_3)}{\ln [(T_4 - T_5)/(T_2 - T_3)]}$$

U is a heat transfer coefficient (a constant), V_i a volume, y_i the molar flow rate of component i, x_i the mole fraction of component i, Q the heat transfer rate, and ρ_i the molar density (a constant). The question is: How many degrees of freedom exist for the process?

5.11. Cavett proposed the following problem as a test problem for computer-aided design. Four flash drums are connected as shown in Fig. P5.11. The temperature in each flash drum is specified, and equilibrium is assumed to be independent of composition so that vapor-liquid equilibrium constants are truly constant. Is the problem properly specified, or do additional variables have to be given? If the latter, what should they be? The feed is as follows

Component	Feed
1. Nitrogen and helium	358.2
2. Carbon dioxide	4,965.6
3. Hydrogen sulfide	339.4
4. Methane	2,995.5
5. Ethane	2,395.5
6. Propane	2,291.0
7. Isobutane	604.1
8. *n*-Butane	1,539.9
9. Isopentane	790.4
10. *n*-Pentane	1,129.9
11. Hexane	1,764.7
12. Heptane	2,606.7
13. Octane	1,844.5
14. Nonane	1,669.0
15. Decane	831.7
16. Undecane plus	1,214.5
Total	27,340.6

5.12. The flowsheet (Fig. P5.12) has a high-pressure feed stream of gaseous component A contaminated with a small amount of B. It mixes first with a recycle stream consisting mostly of A and passes into a reactor, where an exothermic reaction to form C from A takes place. The stream is cooled to condense out component C and passed through a valve into a flash unit. Here most of the unreacted A and the contaminant B flash off, leaving a fairly pure C to be withdrawn as the liquid stream. Part of the recycle is bled off to keep the concentration of B from building up in the system. The rest is repressurized in a compressor and mixed, as stated earlier, with the feed stream. The number of parameters/variables for each unit are designated by the number within the symbol for the unit.

How many degrees of freedom exist for this process?

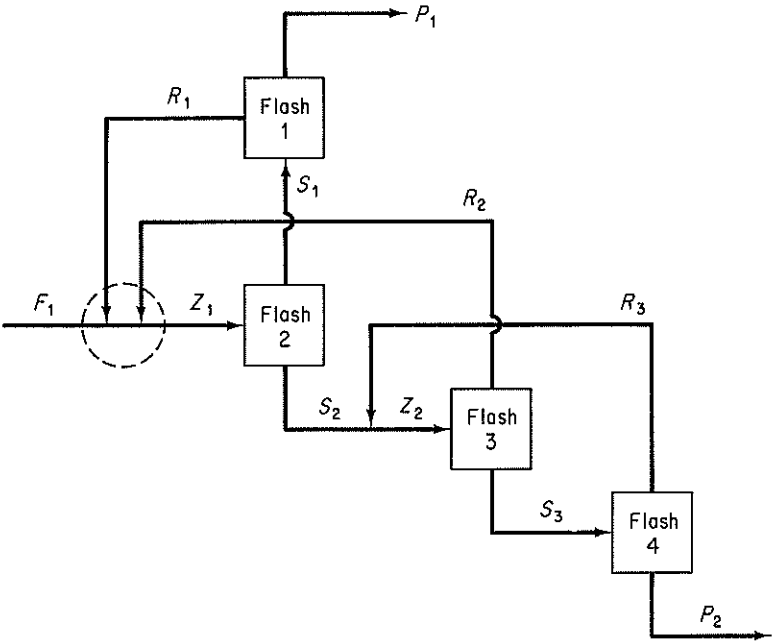


Figure P5.11

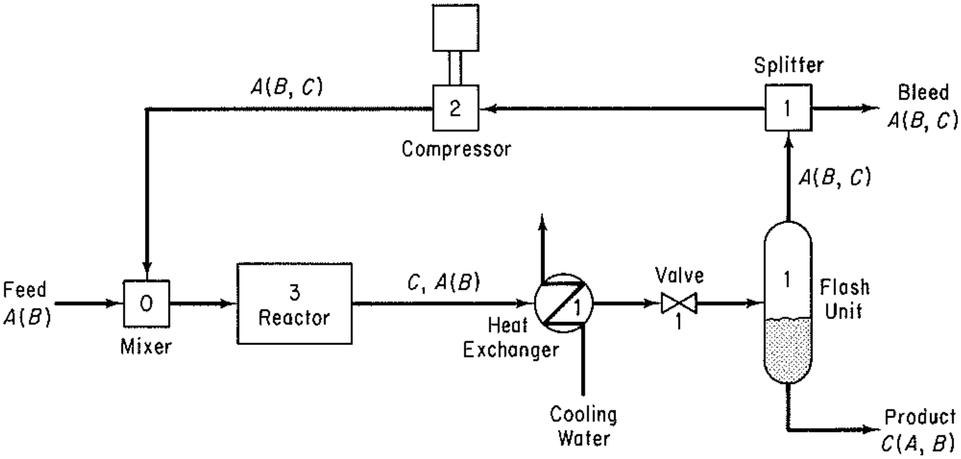


Figure P5.12

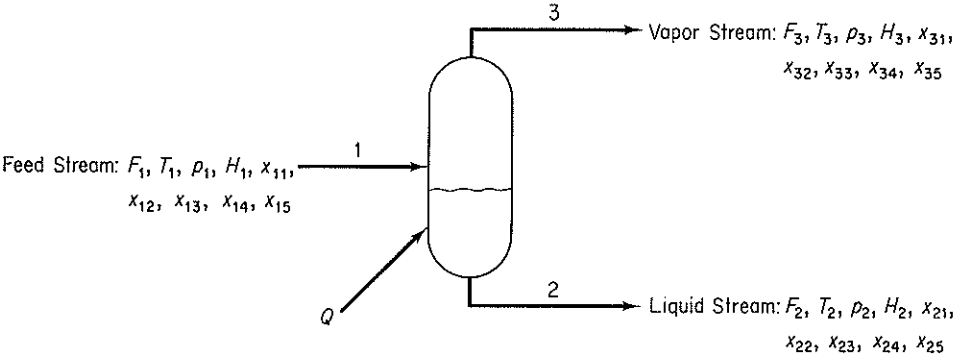
5.13. Determine a precedence order for solution of the set of seven equations and seven variables given by the following occurrence matrix:

$$\begin{array}{c|ccccccc}
 & & & & \text{Variable} & & & \\
 & & & & \rightarrow & & & \\
\text{Equation} \downarrow & x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 \\
\hline
1 & 1 & 0 & 1 & 0 & 1 & 0 & 0 \\
2 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \\
3 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \\
4 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
5 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\
6 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \\
7 & 0 & 0 & 1 & 0 & 1 & 0 & 1
\end{array}$$

5.14. Suggest a solution order for the set of equations in Table P5.14 representing the flash separator in Fig. P5.14. The selection of the first seven of the eight design variables to be calculated (feed stream variables and the equilibrium pressure) is standard for flash separations. The last design variable is usually selected as either

TABLE P5.14 Equations for the Flash Separator in Figure P5.14.

Equation No.	Equation
	The overall material balance equation:
1	$F_2 + F_3 - F_1 = 0$
	The individual component balance equations:
2–5	$F_2x_{2j} + F_3x_{3j} - F_1x_{1j} = 0 \qquad j = 1, 2, 3, 4$
	The stream composition equations:
6	$x_{15} + \sum_{j=1}^{4} x_{1j} = 1$
7	$\sum_{j=1}^{5} x_{2j} = 1$
8	$\sum_{j=1}^{5} x_{3j} = 1$
	The phase equilibrium equations:
9–13	$K_j = K_j(T_2, p_2) \qquad j = 1, 2, 3, 4, 5$
14–18	$x_{3j} - K_jx_{2j} = 0 \qquad j = 1, 2, 3, 4, 5$
19	$T_3 - T_2 = 0$
20	$p_3 - p_2 = 0$
	The enthalpies and energy balance equations:
21	$H_1 = H_1(T_1, p_1, x_{11}, x_{12}, x_{13}, x_{14}, x_{15})$
22	$H_2 = H_2(T_2, p_2, x_{21}, x_{22}, x_{23}, x_{24}, x_{25})$
23	$H_3 = H_3(T_3, p_3, x_{31}, x_{32}, x_{33}, x_{34}, x_{35})$
24	$F_1H_1 - F_2H_2 - F_3H_3 + Q = 0$



Variables:

F_i — Molar flow rate for the i^{th} stream
T_i — Temperature of the i^{th} stream, in degrees Rankine
p_i — Pressure of the i^{th} stream, in atmospheres
H_i — Enthalpy of the i^{th} stream, in Btu/mole
x_{ij} — Mole fraction of the j^{th} component in the i^{th} stream
K_j — Phase equilibrium coefficient of the j^{th} component
Q — Heat transfer to the unit Btu/hour

The Design Variables are:

Feed Stream: $F_1, T_1, p_1, x_{11}, x_{12}, x_{13}, x_{14}$
Equilibrium pressure: p_2
Heat load to the unit: Q

Figure P5.14

the equilibrium temperature, T_2, or Q. The choice of T_2 uncouples the material and energy balances, hence here Q has been selected, requiring a more challenging solution.

5.15. For the units shown in Fig. P5.15, indicate which recycle streams should be cut first.

5.16. Prepare a block diagram for the material flows in a methane evaporation plant. The following blocks can be used in addition to those shown in Fig. 5.9a: evaporator, tank, boiler.

5.17. Prepare a diagram of the modules for sequential solution of the phenosolvan plant in Fig. P5.17. Use Fig. 5.9a for the modules.

5.18. Prepare a block diagram of the modules involved in solving the material and energy balances for the extraction process used in a refinery for the production of normal paraffins shown in Fig. P5.18. Which additional modules not in Fig. 5.9a would you need? Also indicate what streams might be cut for a sequential modular solution of the material and energy balances.

5.19. In petroleum refining, lubricating oil is treated with sulfuric acid to remove unsaturated compounds, and after settling, the oil and acid layers are separated. The acid layer is added to water and heated to separate the sulfuric acid from the sludge contained in it. The dilute sulfuric acid, now 20% H_2SO_4 at 82°C, is fed to a

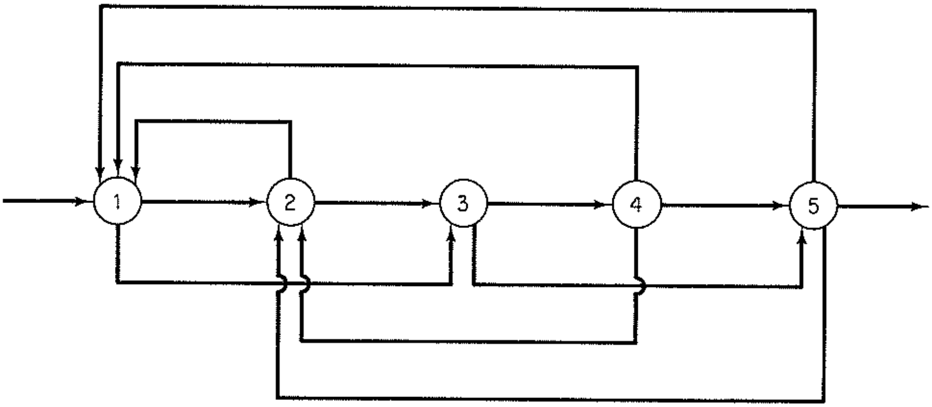


Figure P5.15

Simonson–Mantius evaporator, which is supplied with saturated steam at 400 kPa gauge to lead coils submerged in the acid, and the condensate leaves at the saturation temperature. A vacuum is maintained at 4.0 kPa by means of a barometric leg. The acid is concentrated to 80% H_2SO_4; the boiling point at 4.0 kPa is 121°C. How many kilograms of acid can be concentrated per 1000 kg of steam condensed?

5.20.* You are asked to perform a feasibility study on a continuous stirred tank reactor shown in Fig. P5.20 (which is presently idle) to determine if it can be used for the second-order reaction

$$2A \longrightarrow B + C$$

Since the reaction is exothermic, a cooling jacket will be used to control the reactor temperature. The total amount of heat transfer may be calculated from an overall heat transfer coefficient (U) by the equation

$$Q = UA\ \Delta T$$

where Q = total rate of heat transfer from the reactants to the water jacket in the steady state
U = empirical coefficient
A = area of transfer
ΔT = temperature difference (here $T_4 - T_2$)

Some of the energy released by the reaction will appear as sensible heat in stream $F2$, and some concern exists as to whether the fixed flow rates will be sufficient to keep the fluids from boiling while still obtaining good conversion. Feed data is as follows.

Component	Feed rate (lb mol/hr)	C_p [Btu/(lb mol)(°F)]	MW
A	214.58	41.4	46
B	23.0	68.4	76
C	0.0	4.4	6

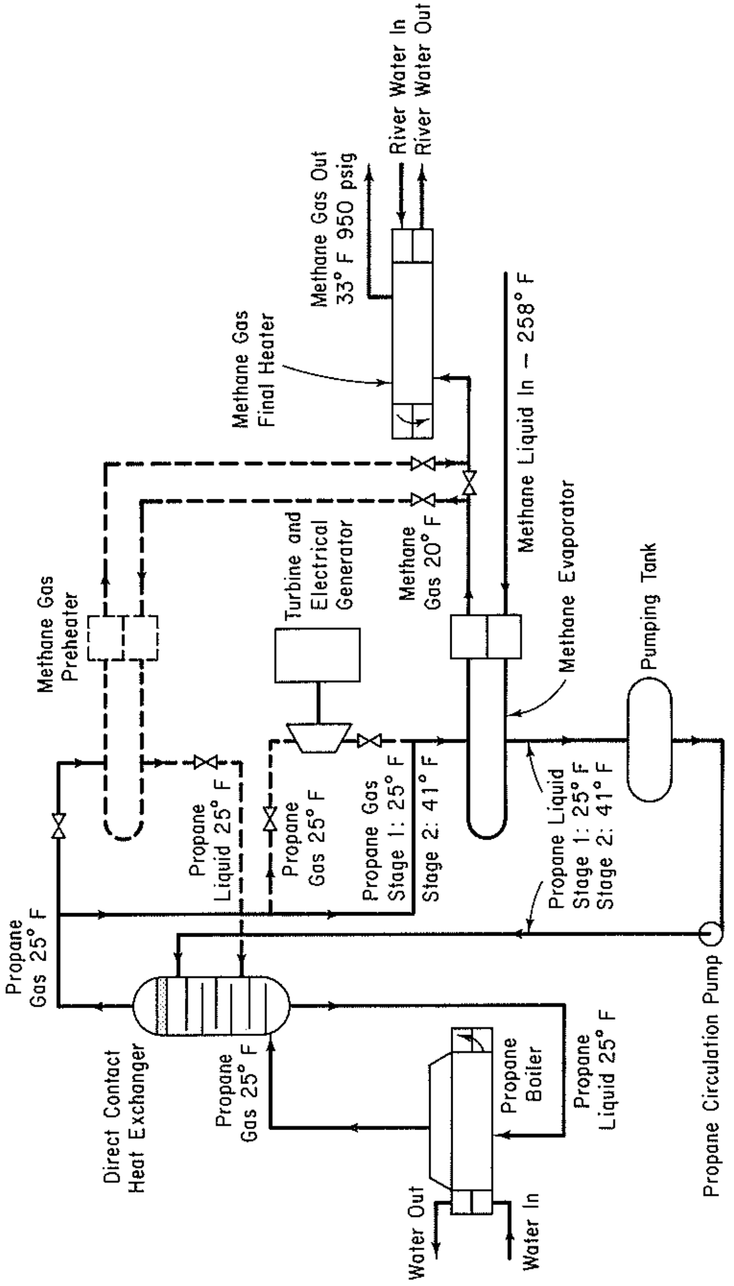

Methane Gas Out
33° F 950 psig
River Water In
River Water Out
Methane Gas
Final Heater
Methane Liquid In − 258° F
Methane Gas
Preheater
Turbine and
Electrical
Generator
Methane
Gas 20° F
Methane Evaporator
Pumping Tank
Propane
Gas 25° F
Propane
Liquid 25° F
Propane
Gas 25° F
Propane Gas
Stage 1: 25° F
Stage 2: 41° F
Propane Liquid
Stage 1: 25° F
Stage 2: 41° F
Direct Contact
Heat Exchanger
Propane
Gas 25° F
Propane
Boiler
Propane
Liquid 25° F
Water Out
Water In
Propane Circulation Pump

Figure P5.16

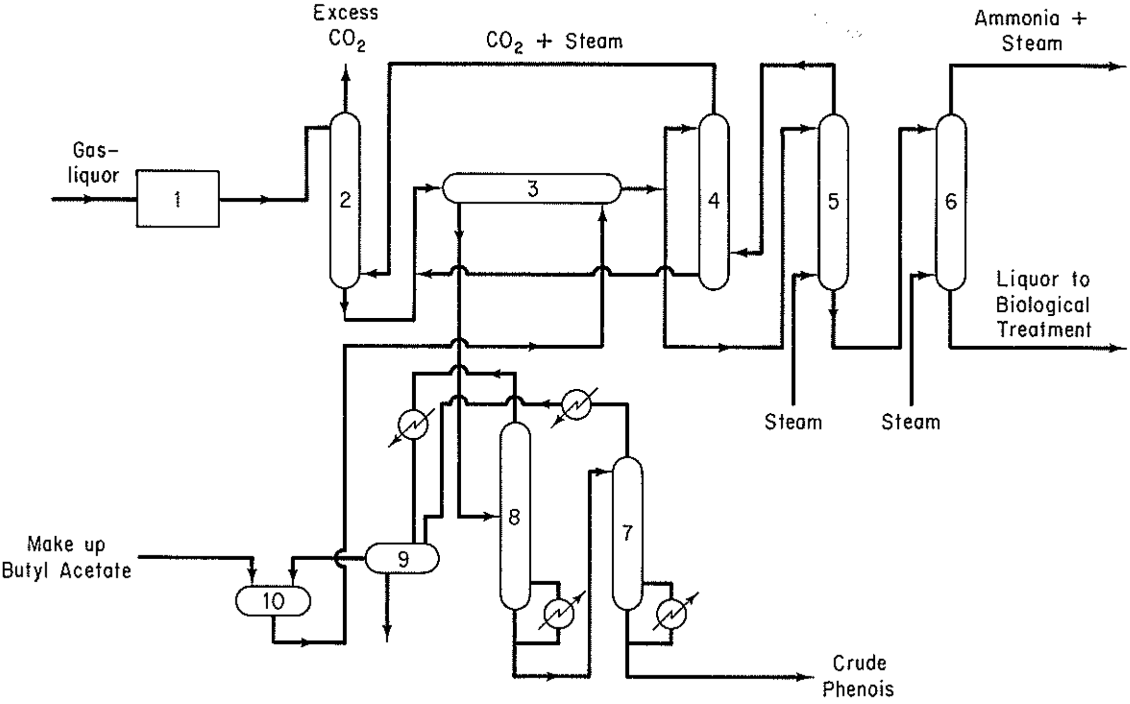


Figure P5.17 Phenosolvan plant—only one stream shown. Key: 1. Tar-oil separation (gravity); 2. Saturation tower; 3. Phenol extractor; 4. Butyl-acetate recovery tower; 5. Butyl-acetate stripping tower; 6. Ammonia stripping tower; 7. Atmospheric distillation tower; 8. Vacuum distillation tower; 9. Separator drum; 10. Butyl-acetate circulating drum.

The consumption rate of A may be expressed as

$$-2k(C_A)^2V_R$$

where

$$C_A = \frac{(F_{1,A})(\rho)}{\sum (F_{1,i})(MW_i)} = \text{concentration of } A\text{, lb mol/ft}^3$$

$$k = k_0 \exp\left(\frac{-E}{RT}\right)$$

k_0, E, R are constants and T is absolute temperature.

Write a computer program to solve for the temperatures of the exit streams and the product composition of the steady-state reactor using the following data:

Fixed parameters

$$\text{reactor volume} = V_R = 13.3 \text{ ft}^3$$

$$\text{heat transfer area} = A = 29.9 \text{ ft}^2$$

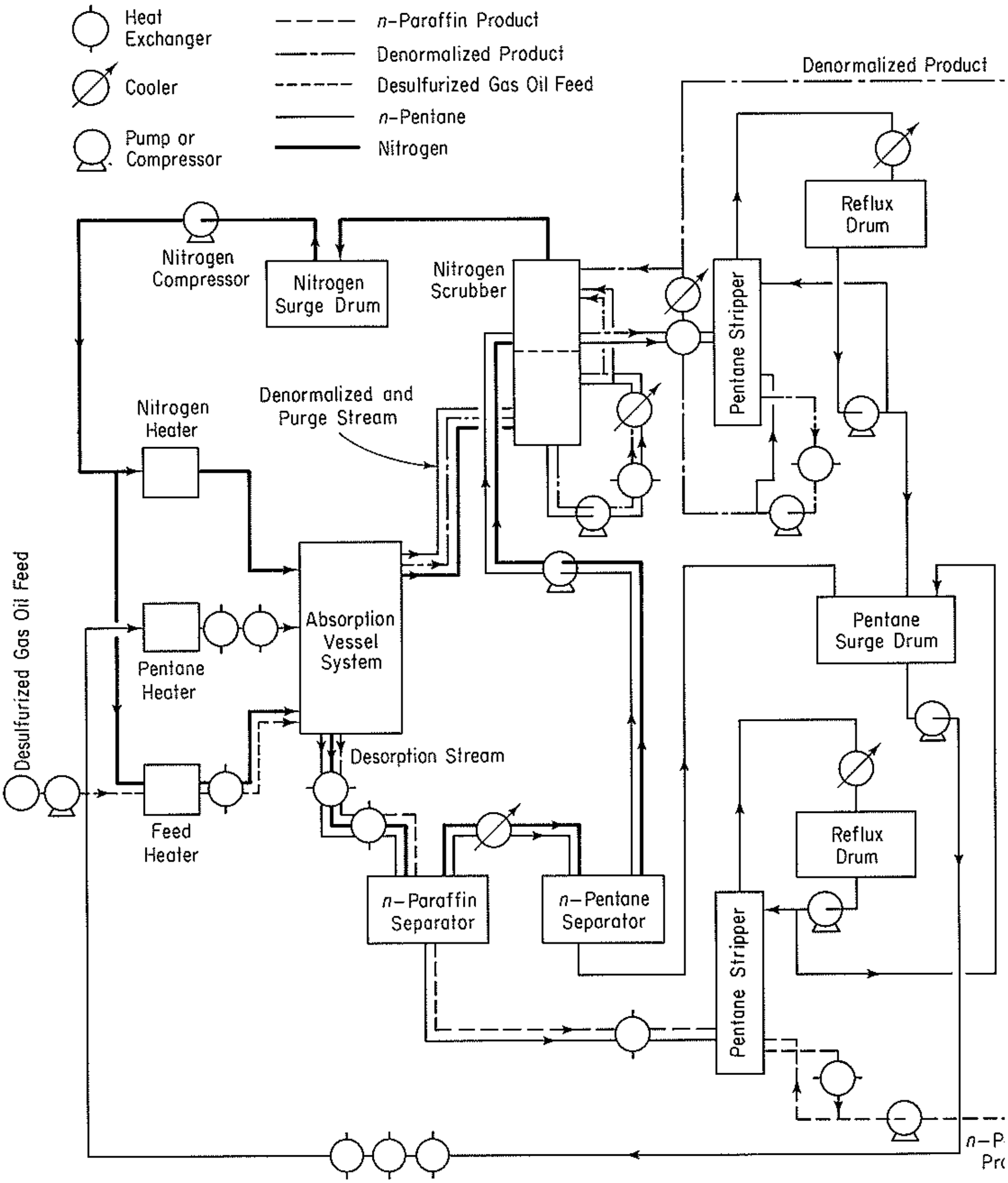


Figure P5.18 Flow chart for problem.

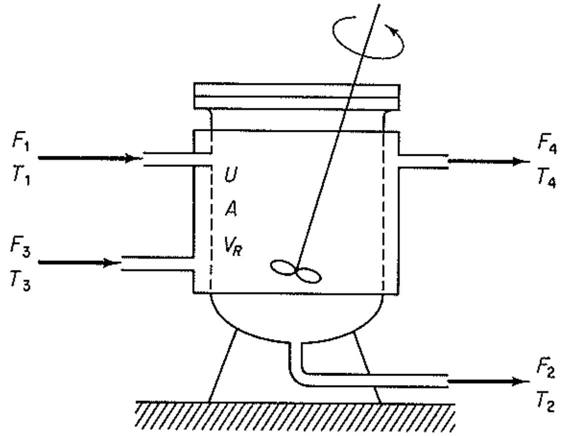


Figure P5.20

heat transfer coefficient = U = 74.5 Btu/(hr)(ft^2)(°F)

Variable input

reactant feed rate = F_i (see table above)

reactant feed temperature = T_1 = 80°F

water feed rate = F_3 = 247.7 lb mol/hr water

water feed temperature = T_3 = 75°F

Physical and thermodynamic data

reaction rate constant = k_0 = 34 lb mol B/(hr)(ft^2)

activation energy/gas constant = E/R = 1000°R

heat of reaction = ΔH = −5000 Btu/lb mol A

heat capacity of water = C_{p_w} = 18 Btu/(lb mol)(°F)

product component density = ρ = 55 lb/ft^3

The densities of each of the product components are essentially the same. Assume that the reactor contents are perfectly mixed as well as the water in the jacket, and that the respective exit stream temperatures are the same as reactor contents or jacket contents.

5.21. The steam flows for a plant are shown in Fig. P5.21. Write the material and energy balances for the system and calculate the unknown quantities in the diagram (A to F). There are two main levels of steam flow: 600 psig and 50 psig. Use the steam tables for the enthalpies.

5.22. Figure P5.22 shows a calciner and the process data. The fuel is natural gas. How can the energy efficiency of this process be improved by process modification? Suggest at least two ways based on the assumption that the supply conditions of the air and fuel remain fixed (but these streams can be possibly passed through heat exchangers). Show all calculations.

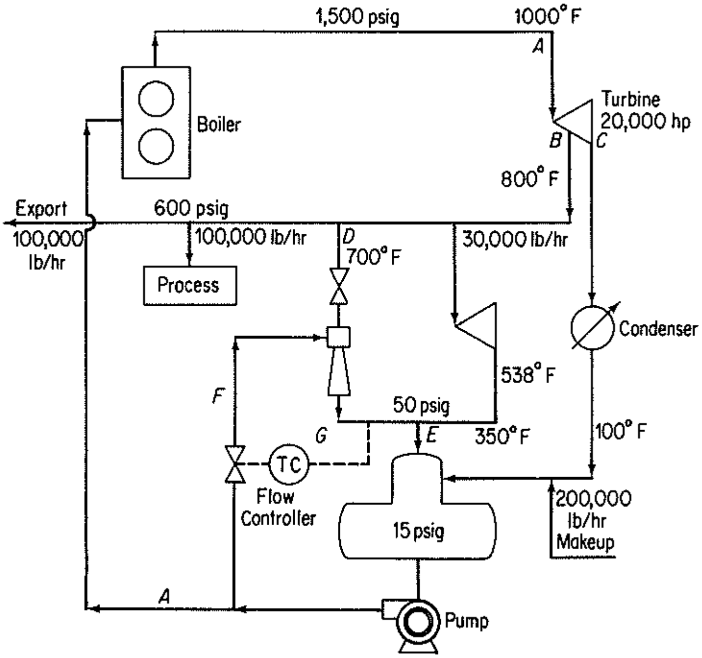


Figure P5.21

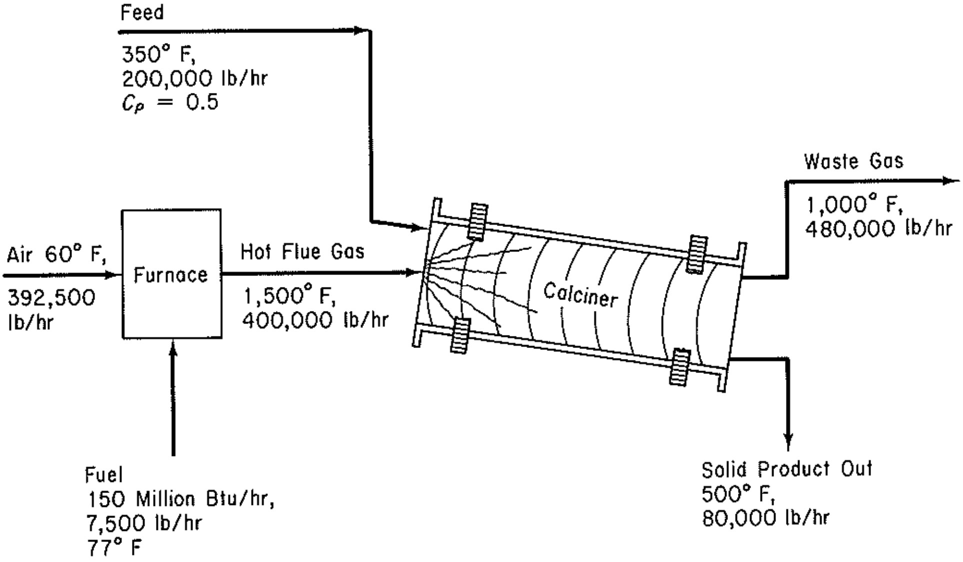


Figure P5.22

5.23. Limestone ($CaCO_3$) is converted into CaO in a continuous vertical kiln (see Fig. P5.23). Heat is supplied by combustion of natural gas (CH_4) in direct contact with the limestone using 50% excess air. Determine the kilograms of $CaCO_3$ that can be processed per kilograms of natural gas. Assume that the following average heat capacities apply:

$$C_p \text{ of } CaCO_3 = 234 \text{ J/(g mol)(°C)}$$

$$C_p \text{ of CaO} = 111 \text{ J/(g mol)(°C)}$$

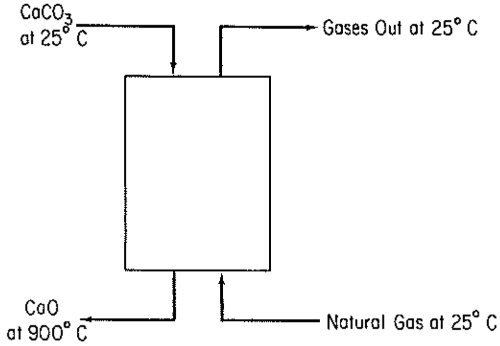


Figure P5.23

5.24. A feed stream of 16,000 lb/hr of 7% by weight NaCl solution is concentrated to a 40% by weight solution in an evaporator. The feed enters the evaporator, where it is heated to 180°F. The water vapor from the solution and the concentrated solution leave at 180°F. Steam at the rate of 15,000 lb/hr enters at 230°F and leaves as condensate at 230°F. See Fig. P5.24.

(a) What is the temperature of the feed as it enters the evaporator?

(b) What weight of 40% NaCl is produced per hour?

Assume that the following data apply:

Average C_p 7% NaCl soln:	0.92 Btu/(lb)(°F)
Average C_p 40% NaCl soln:	0.85 Btu/(lb)(°F)

$$\Delta\hat{H}_{\text{vap}}\ H_2O \text{ at } 180°F = 990 \text{ Btu/lb}$$

$$\Delta\hat{H}_{\text{vap}}\ H_2O \text{ at } 230°F = 959 \text{ Btu/lb}$$

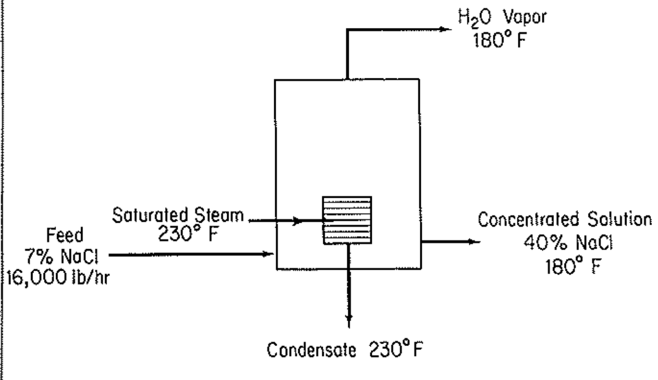


Figure P5.24

5.25. The Blue Ribbon Sour Mash Company plans to make commercial alcohol by a process shown in Fig. P5.25. Grain mash is fed through a heat exchanger where it is heated to 170°F. The alcohol is removed as 60% by weight alcohol from the first fractionating column; the bottoms contain no alcohol. The 60% alcohol is further fractionated to 95% alcohol and essentially pure water in the second column. Both stills operate at a 3 : 1 reflux ratio and heat is supplied to the bottom of the columns by steam. Condenser water is obtainable at 80°F. The operating data and physical properties of the streams have been accumulated and are listed for convenience:

Stream	State	Boiling point (°F)	C_p[Btu/(lb)(°F)] Liquid	Vapor	Heat of vaporization (Btu/lb)
Feed	Liquid	170	0.96	—	950
60% alcohol	Liquid or vapor	176	0.85	0.56	675
Bottoms I	Liquid	212	1.00	0.50	970
95% alcohol	Liquid or vapor	172	0.72	0.48	650
Bottoms II	Liquid	212	1.00	0.50	970

Prepare the material balances for the process, calculate the precedence order for solution, and

(a) Determine the weight of the following streams per hour:
  (1) Overhead product, column I
  (2) Reflux, column I
  (3) Bottoms, column I
  (4) Overhead product, column II
  (5) Reflux, column II
  (6) Bottoms, column II
(b) Calculate the temperature of the bottoms leaving heat exchanger III.
(c) Determine the total heat input to the system in Btu/hr.

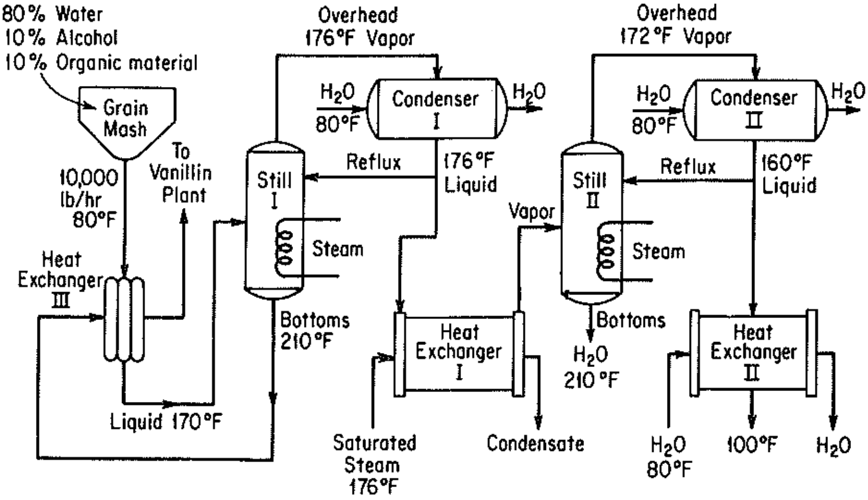
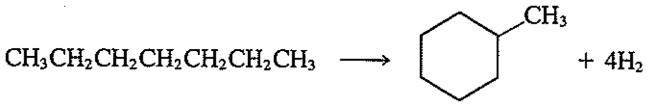


Figure P5.25

(d) Calculate the water requirements for each condenser and heat exchanger II in gal/hr if the maximum exit temperature of water from this equipment is 130°F.

5.26. Toluene, manufactured by the conversion of *n*-heptane with a Cr_2O_3-on-Al_2O_3 catalyst



by the method of hydroforming is recovered by use of a solvent. See Fig. P5.26 for the process and conditions.

The yield of toluene is 15 mole % based on the *n*-heptane charged to the reactor. Assume that 10 kg of solvent are used per kilogram of toluene in the extractors.

(a) Calculate how much heat has to be added or removed from the catalytic reactor to make it isothermal at 425°C.

(b) Find the temperature of the *n*-heptane and solvent stream leaving the mixer-settlers if both streams are at the same temperature.

(c) Find the temperature of the solvent stream after it leaves the heat exchanger.

(d) Calculate the heat duty of the fractionating column in kJ/kg of *n*-heptane feed to the process.

	$-\Delta H_f^\circ$*	C_p[J/(g)(°C)]		$\Delta H_{\text{vaporization}}$	Boiling point
	(kJ/g mol)	Liquid	Vapor	(kJ/kg)	(K)
Toulene†	12.00	2.22	2.30	364	383.8
n-Heptane	−224.4	2.13	1.88	318	371.6
Solvent	—	1.67	2.51	—	434

*As liquids.

† The heat of solution of toluene in the solvent is −23 J/g toluene.

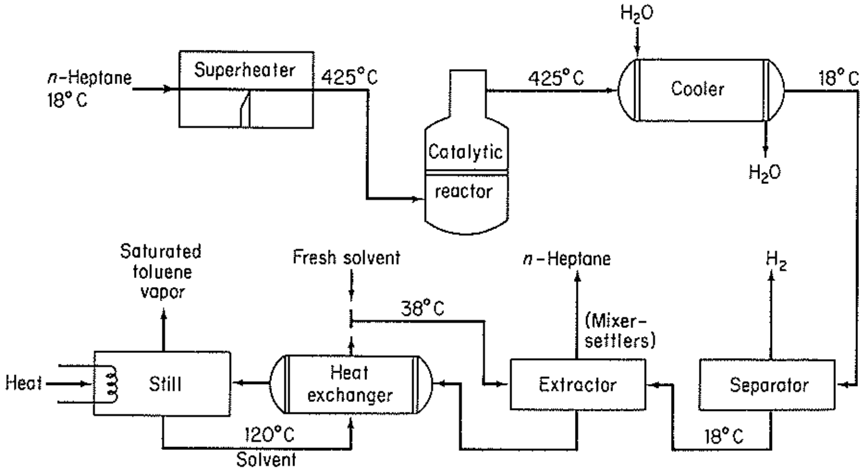


Figure P5.26

5.27. One hundred thousand pounds of a mixture of 50% benzene, 40% toluene, and 10% *o*-xylene is separated every day in a distillation-fractionation plant as shown on the flowsheet for Fig. P5.27.

	Boiling point (°C)	C_p Liquid [cal/(g)(°C)]	Latent heat of vap. (cal/g)	C_p vapor [cal/(g)(°C)]
Benzene	80	0.44	94.2	0.28
Toluene	109	0.48	86.5	0.30
o-Xylene	143	0.48	81.0	0.32
Charge	90	0.46	88.0	0.29
Overhead T_I	80	0.45	93.2	0.285
Residue T_I	120	0.48	83.0	0.31
Residue T_{II}	143	0.48	81.5	0.32

The reflux ratio for tower I is 6 : 1; the reflux ratio for tower II is 4 : 1; the charge to tower I is liquid; the charge to tower II is liquid. Compute:

(a) The temperature of the mixture at the outlet of the heat exchanger (marked as T^*)
(b) The Btu supplied by the steam reboiler in each column
(c) The quantity of cooling water required in gallons per day for the whole plant
(d) The energy balance around tower I

5.28. Sulfur dioxide emission from coal-burning power plants causes serious atmospheric pollution in the eastern and midwestern portions of the United States. Unfortunately, the supply of low-sulfur coal is insufficient to meet the demand. Processes presently under consideration to alleviate the situation include coal gasification followed by desulfurization and stack-gas cleaning. One of the more promising stack-gas-cleaning processes involves reacting SO_2 and O_2 in the stack gas with a solid metal oxide sorbent to give the metal sulfate and then thermally regenerating the sorbent and absorbing the resulting SO_3 to produce sulfuric acid. Recent laboratory experiments indicate that sorption and regeneration can be carried out with several metal oxides, but no pilot or full-scale processes have yet been put into operation.

You are asked to provide a preliminary design for a process that will remove 95% of the SO_2 from the stack gas of a 1000-MW power plant. Some data are given below and in the flow diagram of the process (Fig. P5.28). The sorbent consists of fine particles of a dispersion of 30% by weight CuO in a matrix of inert porous Al_2O_3. This solid reacts in the fluidized-bed sorber at 315°C. Exit solid is sent to the regenerator, where SO_3 is evolved at 700°C, converting all the $CuSO_4$ present back to CuO. The fractional conversion of CuO to $CuSO_4$ that occurs in the sorber is called α and is an important design variable. You are asked to carry out your calculations for $\alpha = 0.2$, 0.5, and 0.8. The SO_3 produced in the regenerator is swept out by recirculating air. The SO_3-laden air is sent to the acid tower, where the SO_3 is absorbed in recirculating sulfuric acid and oleum, part of which is withdrawn as salable by-products. You will notice that the sorber, regenerator, and perhaps the acid tower are adiabatic; their temperatures are adjusted by heat exchange with incoming streams. Some of the heat exchangers (nos. 1 and 3) recover heat by countercurrent exchange between the feed and exit streams. Additional heat is provided

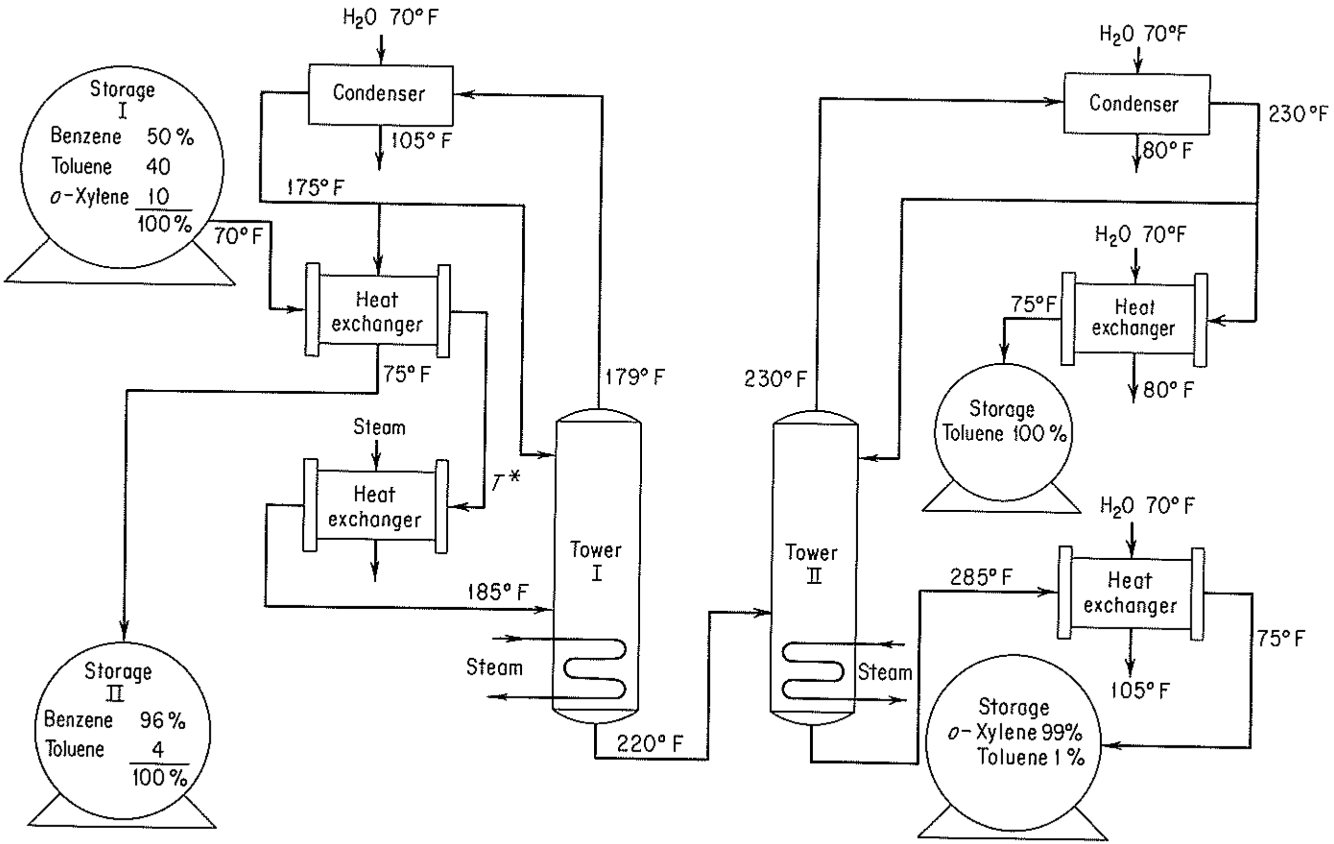

Storage I
Benzene 50 %
Toluene 40
o-Xylene 10
100 %
70° F
H_2O 70° F
Condenser
105° F
175° F
Heat exchanger
75° F
Steam
Heat exchanger
T*
179° F
185° F
Tower I
Steam
220° F
Storage II
Benzene 96 %
Toluene 4
100 %
230° F
Tower II
Steam
H_2O 70°F
Condenser
230 °F
80° F
H_2O 70°F
Heat exchanger
75°F
80° F
Storage Toluene 100 %
H_2O 70° F
285° F
Heat exchanger
75° F
105° F
Storage o-Xylene 99% Toluene 1 %

Figure P5.27

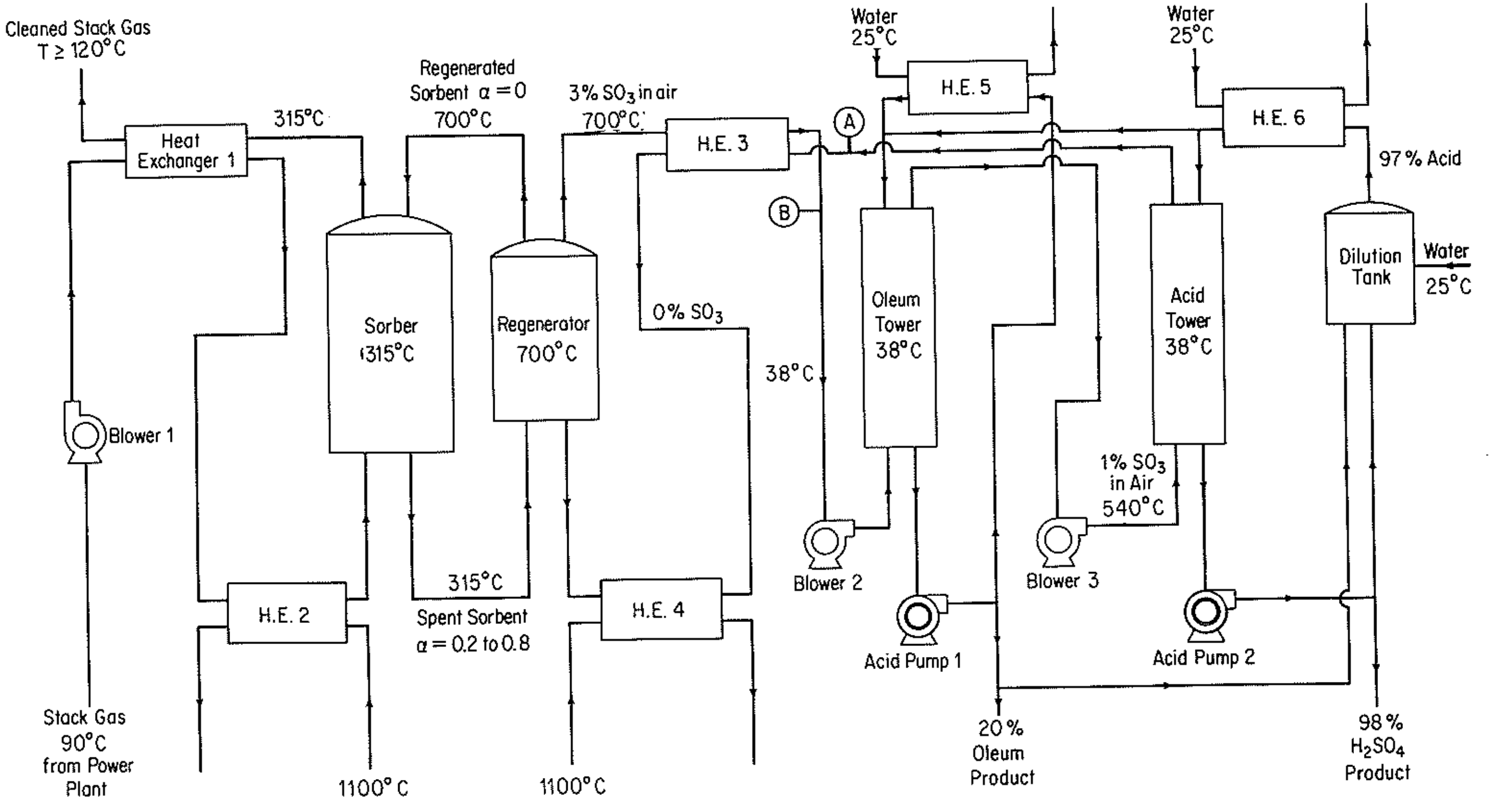

Cleaned Stack Gas
T ≥ 120°C
Heat Exchanger 1
315°C
Regenerated Sorbent α = 0
700°C
3% SO3 in air
700°C
H.E. 3
A
B
Water 25°C
H.E. 5
Water 25°C
H.E. 6
97% Acid
Sorber
315°C
Regenerator
700°C
0% SO3
38°C
Oleum Tower
38°C
Acid Tower
38°C
Dilution Tank
Water
25°C
Blower 1
1% SO3 in Air
540°C
Blower 2
Blower 3
315°C
H.E. 2
Spent Sorbent
α = 0.2 to 0.8
H.E. 4
Acid Pump 1
Acid Pump 2
Stack Gas
90°C
from Power Plant
1100°C
1100°C
20% Oleum Product
98% H2SO4 Product

Figure P5.28

by withdrawing flue gas from the power plant at any desired high temperature up to 1100°C and then returning it at a lower temperature. Cooling is provided by water at 25°C. As a general rule, the temperature difference across heat-exchanger walls separating the two streams should average about 28°C. The nominal operating pressure of the whole process is 100 kPa. The three blowers provide 6 kPa additional head for the pressure losses in the equipment, and the acid pumps have a discharge pressure of 90 kPa gauge. You are asked to write the material and energy balances and some equipment specifications as follows:

(a) Sorber, regenerator, and acid tower. Determine the flow rate, composition, and temperature of all streams entering and leaving.

(b) Heat exchangers. Determine the heat load, and flow rate, temperature, and enthalpy of all streams.

(c) Blowers. Determine the flow rate and theoretical horsepower.

(d) Acid pump. Determine the flow rate and theoretical horsepower.

Use SI units. Also, use a basis of 100 kg of coal burned for all your calculations; then convert to the operating basis at the end of the calculations.

Power plant operation. The power plant burns 340 metric tons/hr of coal having the analysis given below. The coal is burned with 18% excess air, based on complete combustion to CO_2, H_2O, and SO_2. In the combustion only the ash and nitrogen is left unburned; all the ash has been removed from the stack gas.

Element	Wt. %
C	76.6
H	5.2
O	6.2
S	2.3
N	1.6
Ash	8.1

Data on Solids*

	Al_2O_3		CuO		$CuSO_4$	
T (K)	C_p	$H_T - H_{298}$	C_p	$H_T - H_{298}$	C_p	$H_T - H_{298}$
298	79.04	0.00	42.13	0.00	98.9	0.00
400	96.19	9.00	47.03	4.56	114.9	10.92
500	106.10	19.16	50.04	9.41	127.2	23.05
600	112.5	30.08	52.30	14.56	136.3	36.23
700	117.0	41.59	54.31	19.87	142.9	50.25
800	120.3	53.47	56.19	25.40	147.7	64.77
900	122.8	65.65	58.03	31.13	151.0	79.71
1000	124.7	77.99	59.87	37.03	153.8	94.98

* Units of C_p are J/(g mol)(K); units of H are kJ/g mol.

5.29. When coal is distilled by heating without contact with air, a wide variety of solid, liquid, and gaseous products of commercial importance is produced, as well as some significant air pollutants. The nature and amounts of the products produced depend on the temperature used in the decomposition and the type of coal. At low temperatures (400 to 750°C) the yield of synthetic gas is small relative to the yield of liquid products, whereas at high temperatures (above 900°C) the reverse is true. For the typical process flow sheet, shown in Fig. P5.29:

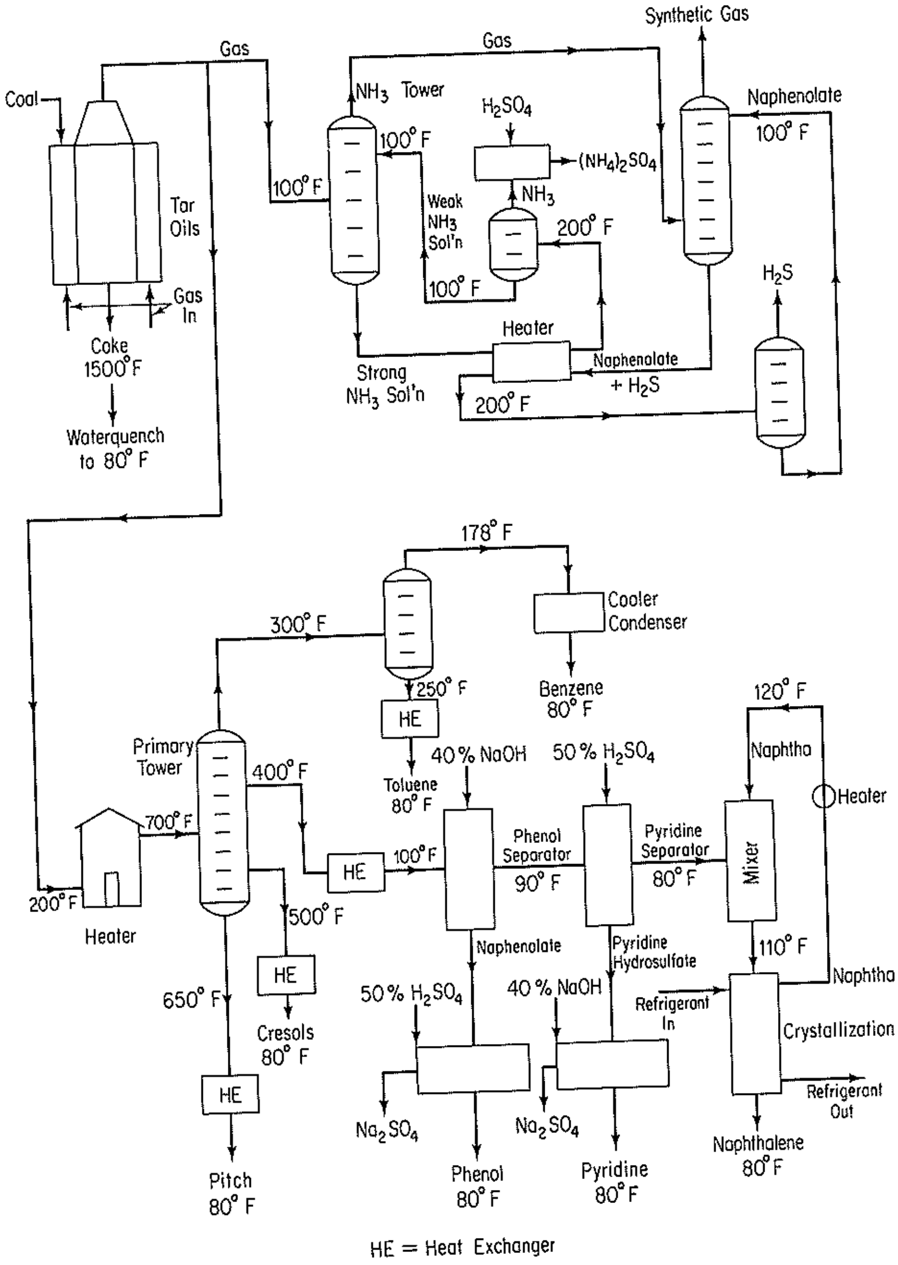


Figure P5.29

(a) How many tons of the various products are being produced?
(b) Make an energy balance around the primary distillation tower and benzol tower.
(c) How much (in pounds) of 40% NaOH solution is used per day for the purification of the phenol?
(d) How much 50% H_2SO_4 is used per day in the pyridine purification?
(e) What weight of Na_2SO_4 is produced per day by the plant?
(f) How many cubic feet of gas per day is produced? What percent of the gas (volume) is needed for the ovens?

Products produced per ton of coal charged	Mean C_p liquid (cal/g)	Mean C_p vapor (cal/g)	Mean C_p solid (cal/g)	Melting point (°C)	Boiling point (°C)
Synthetic gas—10,000 ft^3 (555 Btu/ft^3)					
$(NH_4)_2SO_4$, 22 lb					
Benzol, 15 lb	0.50	0.30	—	—	60
Toluol, 5 lb	0.53	0.35	—	—	109.6
Pyridine, 3 lb	0.41	0.28	—	—	114.1
Phenol, 5 lb	0.56	0.45	—	—	182.2
Naphthalene, 7 lb	0.40	0.35	$0.281 + 0.00111T_{°F}$	80.2	218
Cresols, 20 lb	0.55	0.50	—	—	202
Pitch, 40 lb	0.65	0.60	—	—	400
Coke, 1500 lb	—	—	0.35		—

	ΔH_{vap} (cal/g)	ΔH_{fusion} (cal/g)
Benzol	97.5	—
Toluol	86.53	—
Pyridine	107.36	—
Phenol	90.0	—
Naphthalene	75.5	35.6
Cresols	100.6	—
Pitch	120	—

5.30.* A gas consisting of 95 mol % hydrogen and 5 mol % methane at 100°F and 30 psia is to be compressed to 569 psia at a rate of 440 lb mol/hr. A two-stage compresser system has been proposed with intermediate cooling of the gas to 100°F via a heat exchanger. See Fig. P5.30. The pressure drop in the heat exchanger from the inlet stream (S1) to the exit stream (S2) is 2.0 psia. Using a process simulator program, analyze all of the steam parameters subject to the following constraints; the exit stream from the first stage is 100 psia; both compressers are positive-displacement type and have a mechanical efficency of 0.8, a polytropic efficiency of 1.2, and a clearance fraction of 0.05. Flowtran is organized to solve this problem with minimual effort, but other flowsheeting packages can be used.

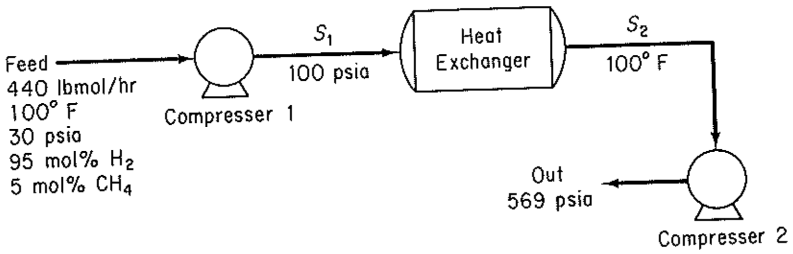
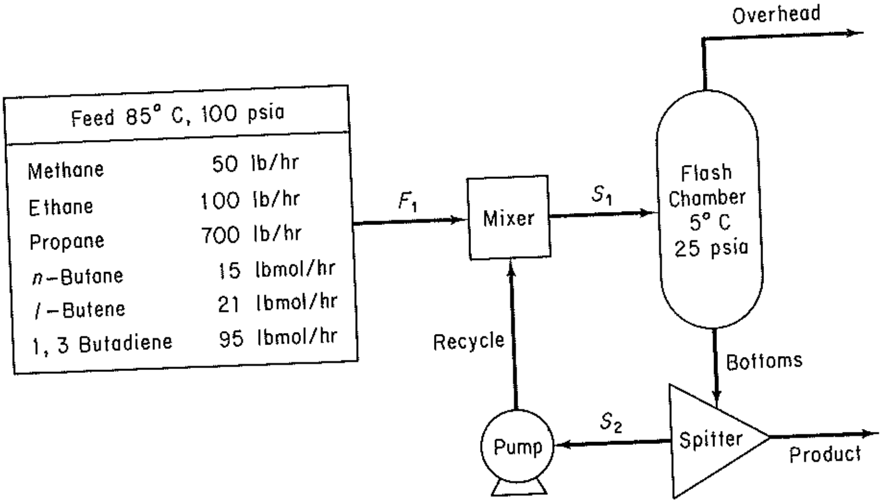


Figure P5.30

5.31. A gas feed mixture at 85°C and 100 psia having the composition shown in Fig. P5.31 is flashed to separate the majority of the light components from the heavy. The flash chamber operates at 5°C and 25 psia. To improve the separation process, it has been suggested to introduce a recycle as shown in Fig. P5.31. Will a significant improvement be made by adding a 25% recycle of the bottoms? 50%? With the aid of a computer process simulator, determine the molar flow rates of the streams for each of the three cases. This problem may readily be solved using Flowtran; however, other flowsheeting packages can be used.



Feed 85° C, 100 psia	
Methane	50 lb/hr
Ethane	100 lb/hr
Propane	700 lb/hr
n-Butane	15 lbmol/hr
l-Butene	21 lbmol/hr
1, 3 Butadiene	95 lbmol/hr

Figure P5.31

5.32. Conventional refrigeration cycles require vapor compression to high pressures. This requires a substantial amount of work, and typically it is the most expensive step of the process. However, a thermal compressor allows the mixture of a high-pressure vapor to be mixed with a low-pressure vapor to form an intermediate-pressure vapor. Using this device, it is possible to create a refrigeration cycle in which only va por is pumped to a higher pressure, thus allowing substantial savings in energy cost Solve the material and energy balances for the process shown in Fig. P5.32 subjec to the following specifications: 100 lb mol/hr of isopropyl alcohol refrigerant flow through the condenser, and there is a high/low pressure recycle ratio of 9 to 1 at th

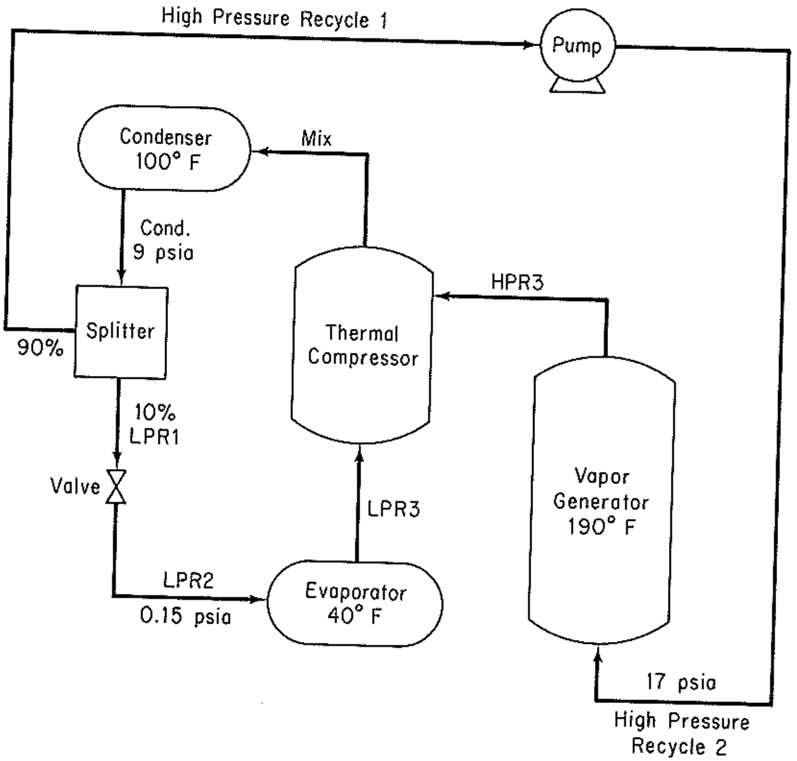


Figure P5.32

stream split. Calculate the energy exchange of each process unit. This problem may be readily solved using Flowtran; however, other flowsheeting packages can be used.

5.33. A mixture of three petroleum fractions containing lightweight hydrocarbons is to be purified and recycled back to a process. Each of the fractions is denoted by its normal boiling point: BP135, BP260, and BP500. The gases separated from this feed are to be compressed as shown in Fig. P5.33. The inlet feed stream (1) is at 45°C and 450 kPa, and has the composition shown. The exit gas (10) is compressed to 6200 kPa by a three-stage compressor process with intercooling of the vapor streams to 60°C by passing through a heat exchanger. The exit pressure for compressor 1 is 1100 kPa and 2600 kPa for compressor 2. The efficiencies for compressors 1, 2, and 3, with reference to an adiabatic compression, are 78, 75, and 72%, respectively. Any liquid fraction drawn off from a separator is recycled to the previous stage. Estimate the heat duty (in kJ/hr) of the heat exchangers and the various stream compositions (in kg mol/hr) for the system. Note that the separators may be considered as an adiabatic flash tanks in which the pressure decrease is zero. This problem has been formulated from *Application Briefs of Process,* the user manual for the computer simulation software package of Simulation Science, Inc., but other flowsheeting packages can be used to solve it.

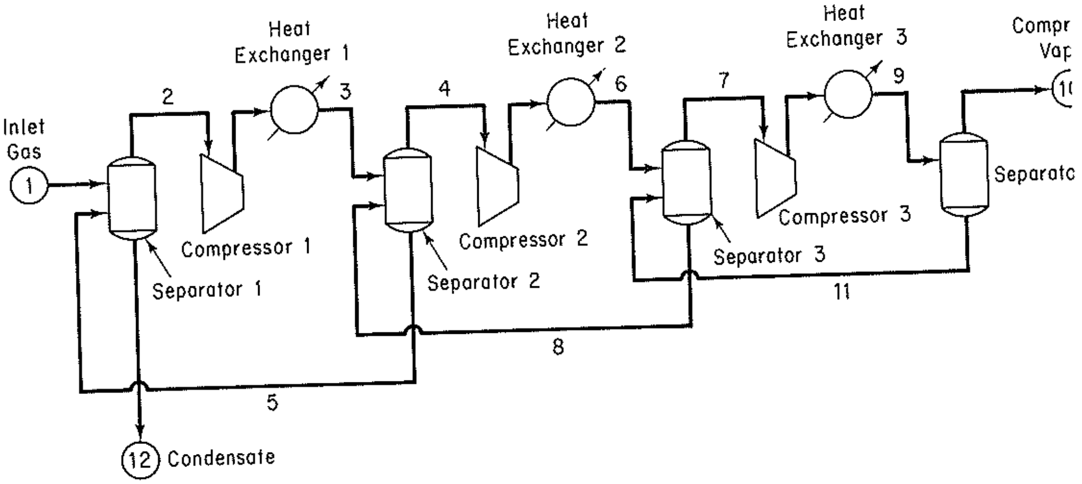


Figure P5.33

Component	kg mol/hr	M.W.	sp gr	Normal boiling point (°C)
Nitrogen	181			
Carbon dioxide	1,920			
Methane	14,515			
Ethane	9,072			
Propane	7,260			
Isobutane	770			
n-Butane	2,810			
Isopentane	953			
n-Pentane	1,633			
Hexane	1,542			
BP135	11,975	120	0.757	135
BP260	9,072	200	0.836	260
BP500	9,072	500	0.950	500

5.34. A demethanizer tower is used in a refinery to separate natural gas from a light hydrocarbon gas mixture stream (1) having the composition listed below. However, initial calculations show that there is a considerable energy wastage in the process. A proposed improved system is outlined in Fig. P5.34. Calculate the temperature (°F), pressure (psig), and composition (lb mol/hr) of all the process streams in the proposed system.

Inlet gas at 120°F and 588 psig stream (1) is cooled in the tube side of a gas–gas heat exchanger by passing the tower overhead stream (8) through the shell side. The temperature difference between the exit streams (2) and (10) of the heat exchanger is to be 10°F. Note that the pressure drop through the tube side is 10 psia and 5 psia on the shell side. The feed stream (2) is then passed through a chiller in which the temperature drops to -84°F and a pressure loss of 5 psi results. An adiabatic flash separater is used to separate the partially condensed vapor from the remaining gas. The vapor then passes through an expander turbine and is fed to the first tray of the tower at 125 psig. The liquid stream (5) is passed through a valve

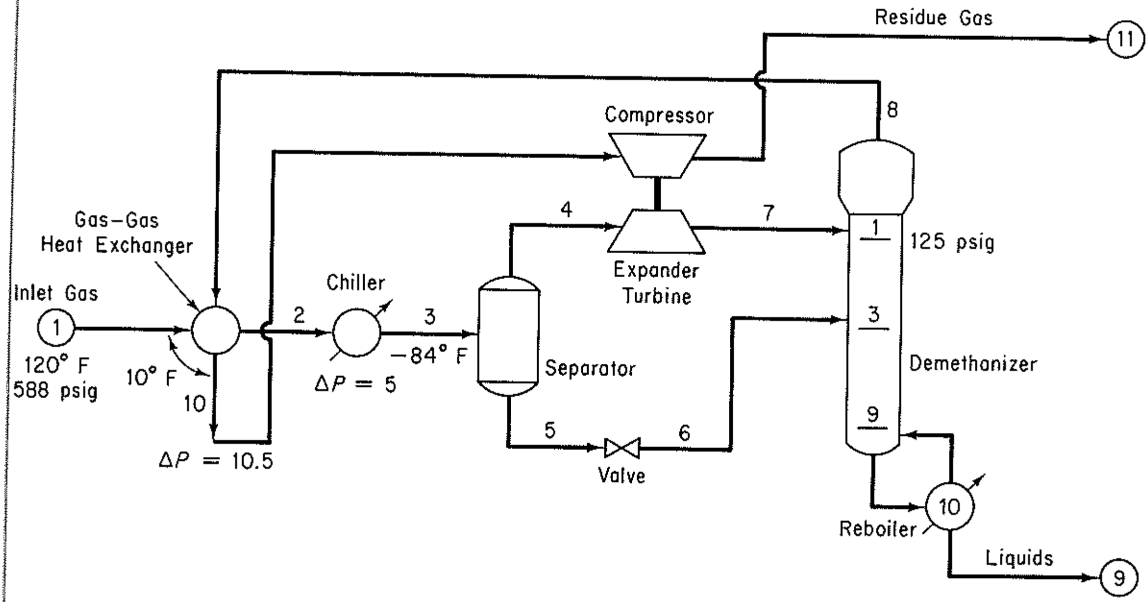


Figure P5.34

reducing the pressure to that of the third tray on the tower. The expander transfers 90% of its energy output to the compressor. The efficiency with respect to an adiabatic compression is 80% for the expander and 75% for the compressor. The process requirements are such that the methane-to-ethane ratio in the demethanizer liquids in stream 9 is to be 0.015 by volume; the heat duty on the reboiler is variable to achieve this ratio. A process rate of 23.06 × 10^6 standard cubic feet per day of feed stream 1 is required.

Component	Mol %
nitrogen	7.91
methane	73.05
ethane	7.68
propane	5.69
isopropane	0.99
n-butane	2.44
isopentane	0.69
n-pentane	0.82
C_6	0.42
C_7	0.31
Total	100.00

The tower has 10 trays, including the reboiler. *Note:* To reduce the number of trials, the composition of stream 3 may be referenced to stream 1 and if the exit stream of the chiller is given a dummy symbol, the calculations sequence can begin at the separator, thus eliminating the recycle loop.

Carry out the solution of the material and energy balances for the flowsheet in P5.34, determine the component and total mole flows, and determine the enthalpy flows for each stream. Also find the heat duty of each heat exchanger.

This problem has been formulated from *Application Briefs of Process*, the user manual for the computer simulation software package of Simulation Sciences, Inc., and is conveniently solved using Process, but other flowsheeting packages can be used.

5.35. A crude oil stream (1) at 1000 psia and 150°F having the composition shown in Table P5.35a is to be processed for shipping. The objectives are to (1) separate the hydrocarbons from the water and (2) reduce the pressure of the separated oil to atmospheric. Figure A in Fig. P5.35 illustrates a simplified version of a three-stage letdown process to carry out the objectives. The exit pressure of stream 3 from the first flash chamber, flash 1, is to be determined such that the product oil, stream 5, has a vapor pressure close to 14.7 psia. This specification is made directly on the process controller, and the exit pressure of the flash chamber 2 is the controlled parameter. To save computation time, each of the two compressor–heat exchanger–separator series shown in Figure B in Fig. P5.35 may first be modeled as isothermal flash units 4 and 5 inside the recycle loop. However, once the recycle is solved, the series should be substituted for these isothermal flash units in figure A in Fig. P5.35 and a rigorous calculation performed. Finally, a bubble point flash at 100°F should be performed on stream 5 as a check on the vapor pressure.

Other restrictions that are made on the system by the available equipment and the process are as follows. The water stream (W1) separated from flash 1 is split and 40% of the mass is delivered to the flash unit 2. All other water streams are discarded. The heat exchangers use utility water at 65°F and expel it at 75°F to cool the

TABLE P5.35a Feed Composition

	lb mol/hr
Water	3000.0
Carbon dioxide	35.0
Nitrogen	30.0
Methane	890.0
Ethane	300.0
Propane	520.0
Isobutane	105.0
n-Butane	283.0
Isopentane	100.0
n-Pentane	133.0
Cut 1	165.0
Cut 2	303.0
Cut 3	560.0
Cut 4	930.0
Cut 5	300.0
Cut 6	300.0
Cut 7	300.0
Cut 8	280.0
Cut 9	260.0
Cut 10	0.0
Total	8794.0

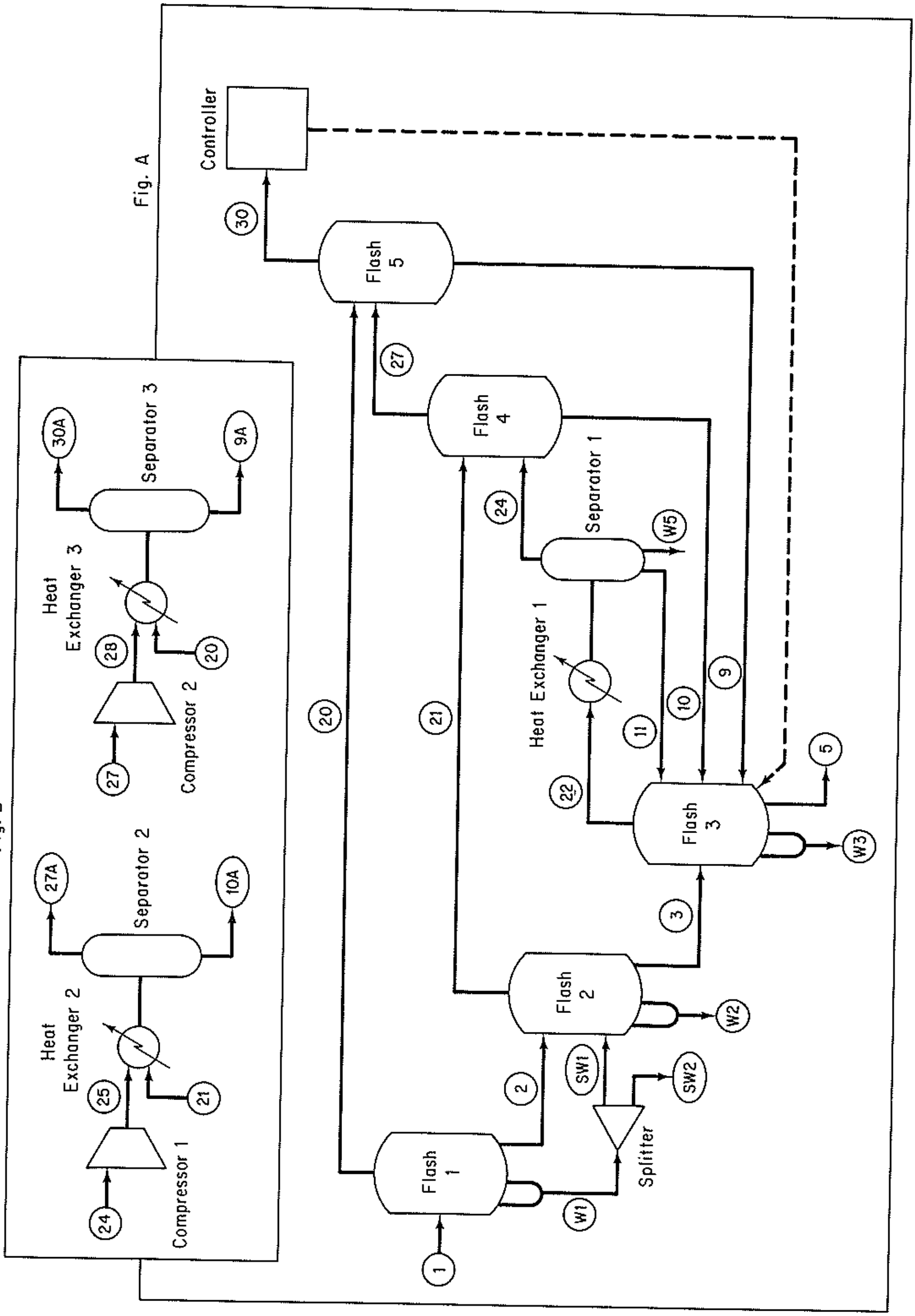


Fig. A
Fig. B
Controller
Flash 1
Flash 2
Flash 3
Flash 4
Flash 5
Separator 1
Separator 2
Separator 3
Heat Exchanger 1
Heat Exchanger 2
Heat Exchanger 3
Compressor 1
Compressor 2
Splitter
1
2
3
5
9
10
11
20
21
22
24
27
30
W1
W2
W3
W5
SW1
SW2
25
28
27A
10A
30A
9A

Figure P5.35

inlet streams to an exit temperature of 120°F. The pass through each exchanger results in a pressure drop of 3 psia in the hydrocarbon stream. Each compressor is 70% efficient with respect to an adiabatic compression and the outlet of pressure for compressors 1 and 2 are 100 psia and 300 psia, respectively. The operating conditions of the flash units are given in Table P5.35b. Additional data on the petroleum cuts are given in Table P5.35c.

Find the temperature, pressure, and liquid fraction of the exit product, and heat duty (if any) of each of the units in P5.35A.

This problem has been formulated from *Application Briefs of Process*, the user manual for the computer simulation software package of Simulation Sciences, Inc., but other flowsheeting packages can be used.

TABLE P5.35b

Flash unit	T (°F)	P (psia)	Operating condition
1	200	300	Isothermal
2	—	100	Adiabatic
3	—	14.7	Adiabatic
4	120	97	Isothermal
5	120	297	Isothermal

TABLE P5.35c Petroleum Cut Data

	MW	API Gravity	NBP °F
Cut 1	91	64	180
Cut 2	100	61	210
Cut 3	120	55	280
Cut 4	150	48	370
Cut 5	200	40	495
Cut 6	245	35	590
Cut 7	300	30	687
Cut 8	360	26	770
Cut 9	430	22	865
Cut 10	500	19	940

PROBLEMS THAT REQUIRE WRITING COMPUTER PROGRAMS

5.1. Determine the values of the unknown quantities in Fig. CP5.1 by solving the following set of linear material and energy balances that represent the steam balance:

(a) $181.60 - x_3 - 132.57 - x_4 - x_5 = -y_1 - y_2 + y_5 + y_4 = 5.1$
(b) $1.17x_3 - x_6 = 0$
(c) $132.57 - 0.745x_7 = 61.2$
(d) $x_5 + x_7 - x_8 - x_9 - x_{10} + x_{15} = y_7 + y_8 - y_3 = 99.1$
(e) $x_8 + x_9 + x_{10} + x_{11} - x_{12} - x_{13} = -y_7 = -8.4$

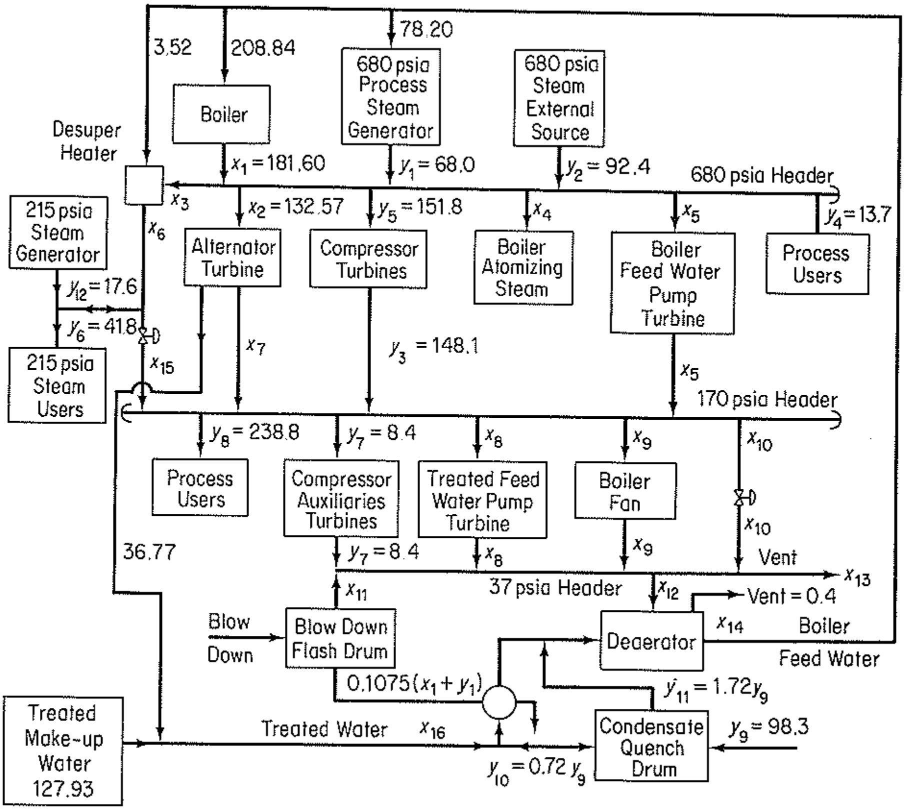


Figure CP5.1

(f) $x_6 - x_{15} = y_{12} - y_5 = 24.2$
(g) $-1.15(181.60) + x_3 - x_6 + x_{12} + x_{16} = 1.15y_1 - y_9 + 0.4 = -19.7$
(h) $181.60 - 4.594x_{12} - 0.11x_{16} = -y_1 + 1.0235y_9 + 2.45 = 35.05$
(i) $-0.0423(181.60) + x_{11} = 0.0423y_1 = 2.88$
(j) $-0.016(181.60) + x_4 = 0$
(k) $x_8 - 0.0147x_{16} = 0$
(l) $x_5 - 0.07x_{14} = 0$
(m) $-0.0805(181.60) + x_9 = 0$
(n) $x_{12} - x_{14} + x_{16} = 0.4 - y_9 = -97.9$

There are four levels of steam: 680, 215, 170, and 37 psia. The 14 x_i, $i = 3, \ldots, 16$, are the unknowns and the y_i are given parameters for the system. Both x_i and y_i have the units of 10^3 lb/hr.

5.2. Wilson and Belkin (D. B. Wilson and H. M. Belkin, in *Stoichiometry*, E. Henley, ed., Cache Corp., Austin, Tex., 1972, p. 180) described a simplified refinery shown in Fig. CP5.2a that used three different crude oils and could produce eight products. Figure CP5.2b shows the boiling-point elevation curves that characterize each type of crude. Table CP5.2a lists the respective products and uses. Table CP5.2b lists the desired production rates.

You are asked to specify the proper operating temperatures (10 of them) indi-

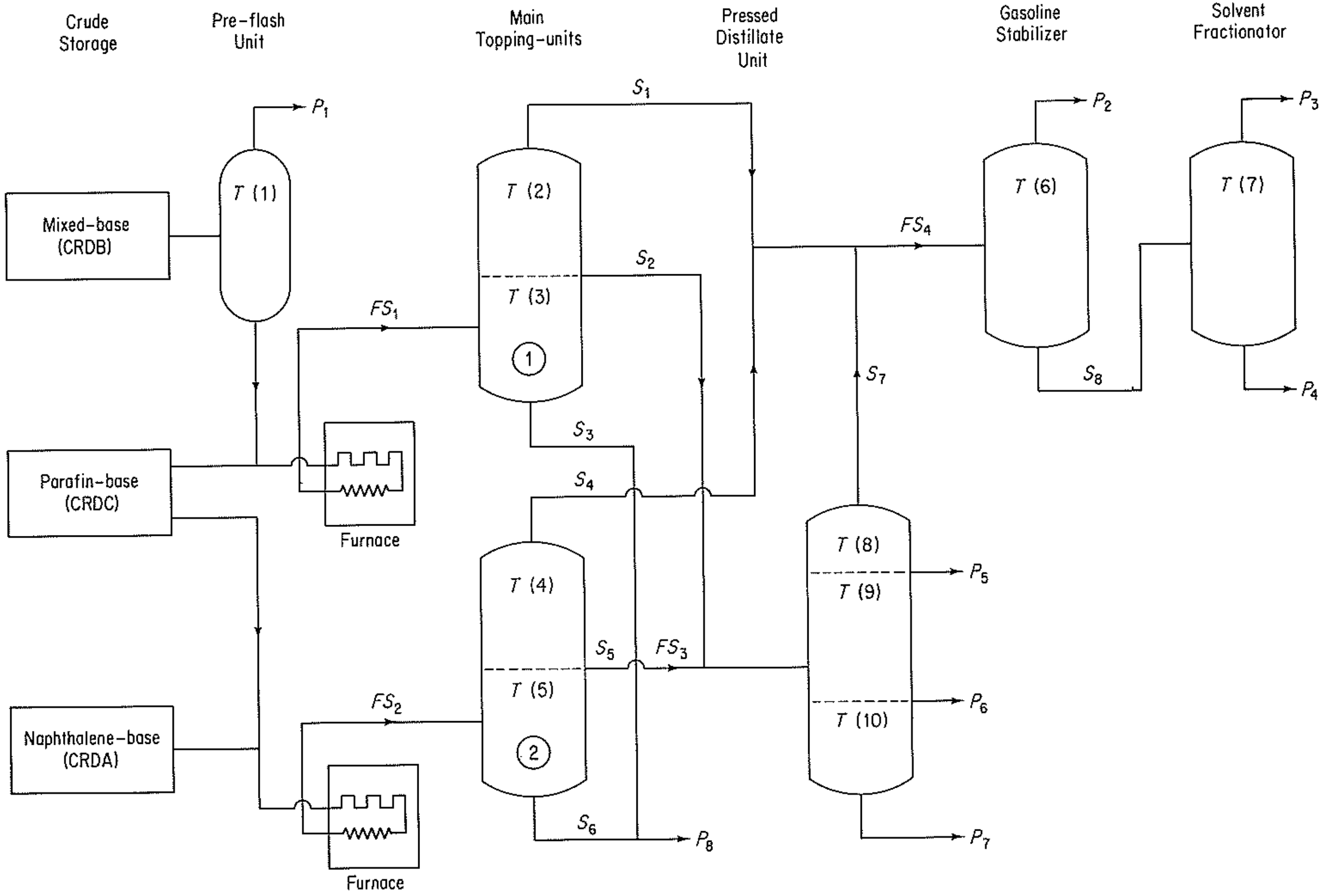


Figure CP5.2a

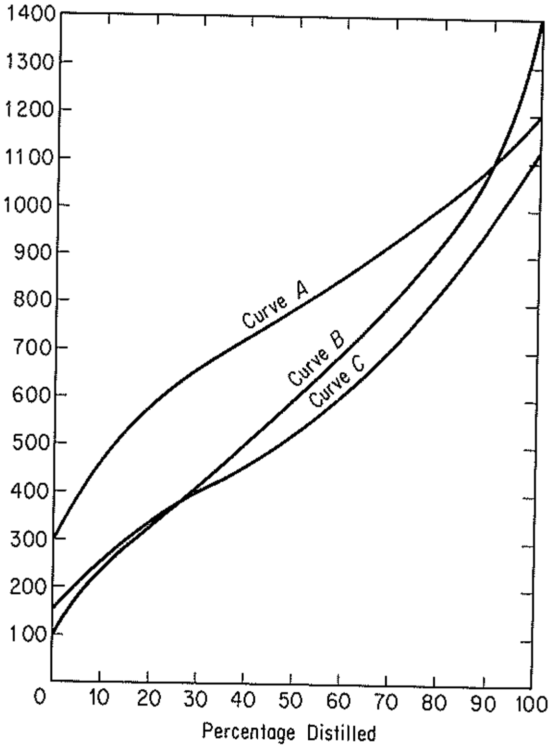


Figure CP5.2b

cated in Fig. CP5.2a by T(1) to T(10), given that the refinery will be supplied with 30,000 lb/hr of mixed-base crude and 43,000 lb/hr of paraffin-based crude.

Show that the process has 17 streams and 51 variables plus the fraction split between the two main topping units to give 52 variables in total and 34 degrees of freedom. Also show that if 10 values of the temperature are specified for three crude streams, 30 degrees of freedom are used. The other 4 degrees of freedom are taken up by specifying values for the three crude stream flows and the split between the topping units.

Table CP5.2c lists some of the restrictions placed on the temperatures selected and the possible range of values for each temperature. Functional relations for the boiling-point curves in terms of weight % distilled (FA, FB, and FC) versus temperature (°F) are

$$FA(T) = (27.50241 - 0.2061958T + 0.4441638 * 10^{-3}T^2 - 0.1853541 * 10^{-6}T^3)/100$$

$$FB(T) = (-0.2065866 + 0.7854635 * 10^{-1}T + 0.6124981 * 10^{-4}T^2 - 0.4395732 * 10^{-7}T^3)/100$$

$$FC(T) = (0.2424332 - 0.1151307T + 0.7828064 * 10^{-3}T^2 - 0.9227250 * 10^{-6}T^3 + 0.3437206 * 10^{-9}T^4)/100$$

Prepare a computer program in Fortran that determines the 10 temperatures in the refinery given the crude flow rates cited above and the fraction of crude C that is sent to topping unit 1. To adjust the temperatures, use any iterative technique that you wish.

TABLE CP5.2a Hydroskimming Refinery Products

Symbol	Name	True boiling-point range (°F)	Description of uses
P1	Fuel gas	150	Volatile products used by refinery for fuel
P2	Gasoline	125–425	Fuel for internal combustion engines
P3	Naphtha	355–510	Cleaner's solvents, paint thinners, chemical solvents, and stocks for blending of motor fuels
P4	Kerosene	422–555	Tractor fuel oil, stove oil, jet fuel
P5	Gas oil	440–700	Diesel engine fuel, fuels for industrial and household furnaces
P6	Cylinder stock	615–830	Unfinished heavy-oil stocks used directly as lubricants for steam engine cylinders; usually filtered but not dewaxed
P7	Fuel oil	750–1000	Industrial fuel
P8	Tar and asphalt	950–1400	Asphalt, road oil, roofing materials, and protective coating

TABLE CP5.2b

Product	Desired production rates (lb/hr)
Gasoline	As much as possible
Naphtha	Any amount
Kerosene	7400
Gas oil	Any amount
Cylinder stock	13,400
Fuel oil	11,000
Tar and asphalt	21,000
Fuel gas (to run equipment)	380

TABLE CP5.2c Temperature Ranges

Temperature point	Range of Values (°F)	Restrictions
T(1)	100–150	T(1) < T(2)
T(2)	225–375	T(2) < T(3)
T(3)	300–1000	
T(4)	225–375	T(4) < T(5)
T(5)	300–1050	
T(6)	125–350	T(6) < T(7)
T(7)	325–500	
T(8)	350–650	T(8) < T(9) and T(8) < T(10)
T(9)	440–700	T(9) < T(10)
T(10)	610–950	

UNSTEADY-STATE MATERIAL AND ENERGY BALANCES

6

In previous chapters all the material and all the energy balances you have encountered, except for the batch system balances, were *steady-state* balances, that is, balances for processes in which the accumulation term was zero. Now it is time for us to focus our attention briefly on **unsteady-state** processes. These are processes in which quantities or operating conditions within the system *change with time*. Sometimes you will hear the word *transient state* applied to such processes. The unsteady state is somewhat more complicated than the steady state and in general problems involving unsteady-state processes are somewhat more difficult to formulate and solve than those involving steady-state processes. However, a wide variety of important industrial problems fall into this category, such as the startup of equipment, batch heating or reactions, the change from one set of operating conditions to another, and the perturbations that develop as process conditions fluctuate. In this chapter we consider only one category of unsteady-state processes, but it is the one that is the most widely used, the lumped or macroscopic balances.

6.1 UNSTEADY-STATE MATERIAL AND ENERGY BALANCES

Your objectives in studying this section are to be able to:

1. Write down the macroscopic unsteady-state material and energy balances in words and in symbols.
2. Solve single linear ordinary differential material or energy balance equations given the initial conditions.
3. Take a word problem and translate it into a differential equation(s).

The basic expression in words, for either the material or the energy balance should by now be well known to you and is repeated below as Eq. (6.1). However, you should also realize that this equation can be applied at various levels, or strata, of description. In other words, an engineer can portray the operation of a real process by writing balances on a number of physical scales. A typical illustration of this concept might be in meterology, where the following different degrees of detail can be used on a descending scale of magnitude in the real world:

Global weather pattern
Local weather pattern
Individual clouds
Convective flow in clouds
Molecular transport
The molecules themselves

Similarly, in chemical engineering we write material and energy balances from the viewpoint of various scales of information:

- **(a)** Molecular and atomic balances
- **(b)** Microscopic balances
- **(c)** Dispersion balances
- **(d)** Plug flow balances
- **(e)** Macroscopic balances (overall balances, lumped balances)

in decreasing order of degree of detail about a process.[1] In this chapter, the type of balance to be described and applied is the simplest one, the macroscopic balance [(e) in the list above].

The macroscopic balance ignores all the detail within a system and consequently results in a balance about the entire system. Only time remains as an independent variable in the balance. The dependent variables, such as concentration and temperature, are not functions of position but represent overall averages throughout the entire volume of the system. In effect, the system is assumed to be sufficiently well mixed so that the output concentrations and temperatures are equivalent to the concentrations and temperatures inside the system.

To assist in the translation of Eq. (6.1)

$$\left\{\begin{matrix}\text{accumulation}\\ \text{or depletion}\\ \text{within the}\\ \text{system}\end{matrix}\right\} = \left\{\begin{matrix}\text{transport into}\\ \text{system through}\\ \text{system}\\ \text{boundary}\end{matrix}\right\} - \left\{\begin{matrix}\text{transport out}\\ \text{of system}\\ \text{through system}\\ \text{boundary}\end{matrix}\right\} + \left\{\begin{matrix}\text{generation}\\ \text{within}\\ \text{system}\end{matrix}\right\} - \left\{\begin{matrix}\text{consumption}\\ \text{within}\\ \text{system}\end{matrix}\right\} \quad (6.1)$$

---

[1] Additional information together with applications concerning these various types of balances can be found in D. M. Himmelblau and K. B. Bischoff, *Process Analysis and Simulation*, Swift Publishing Co., Austin, Tex., 1980.

into mathematical symbols, you should refer to Fig. 6.1. Equation (6.1) can be applied to the mass of a single species or to the total amount of material or energy in the system. Let us write each of the terms in Eq. (6.1) in mathematical symbols for a very small time interval Δt. Let the accumulation be positive in the direction in which time is positive, that is, as time increases from t to $t + \Delta t$. Then, using the component mass balance as an example, the accumulation will be the mass of A in the system at time $t + \Delta t$ minus the mass of A in the system at time t,

$$\text{accumulation} = \rho_A V\big|_{t+\Delta t} - \rho_A V\big|_t$$

where[2] ρ_A = mass of component A per unit volume
V = volume of the system

Note that the net dimensions of the accumulation term are the mass of A.

We shall split the mass transport across the system boundary into two parts, transport through defined surfaces S_1 and S_2, whose areas are known, and transport across the system boundary through other (undefined) surfaces. The net transport of A into (through S_1) and out of (through S_2) the system through defined surfaces can be written as

$$\text{net flow across boundary via } S_1 \text{ and } S_2 = \rho_A v S\,\Delta t\big|_{S_1} - \rho_A v S\,\Delta t\big|_{S_2}$$

where v = fluid velocity in a duct of cross section S
S = defined cross-sectional area perpendicular to material flow

Again note that the net dimensions of the transport term are the mass of A. Other types of transport across the system boundary can be represented by

$$\text{net residual flow across boundary} = \dot{w}_A\,\Delta t$$

where $\dot{w}_A$ is the rate of mass flow of component A through the system boundaries other than the defined surfaces S_1 and S_2.

Finally, the net generation-consumption term will be assumed to be due to a chemical reaction r_A:

$$\text{net generation-consumption} = \dot{r}_A\,\Delta t$$

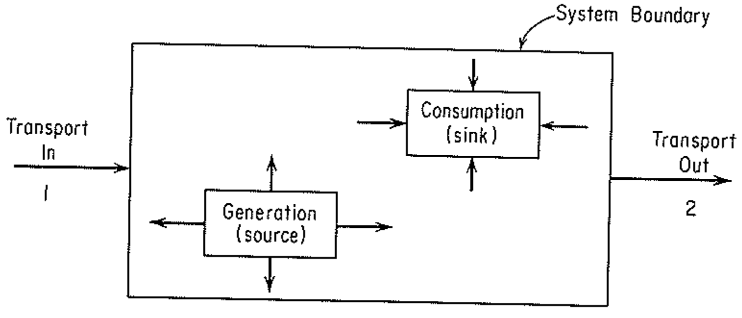


Figure 6.1 General unsteady-state process with transport in and out and internal generation and consumption.

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[2] The symbol $|_t$ means that the quantities preceding the vertical line are evaluated at time t, or time $t + \Delta t$, or at surface S_1, or at surface S_2, as the case may be as denoted by the subscript.

where $\dot{r}_A$ is the net rate of generation-consumption of component A by chemical reaction.

Introduction of all these terms into Eq. (6.1) gives Eq. (6.2). Equations (6.3) and (6.4) can be developed from exactly the same type of analysis. Try to formulate Eqs. (6.3) and (6.4) yourself.

Species material balances:

$$\underset{\text{accumulation}}{\rho_A V\big|_{t+\Delta t} - \rho_A V\big|_t} = \underset{\text{transport through defined boundaries}}{\rho_A vS\,\Delta t\,\big|_{S_1} - \rho_A vS\,\Delta t\,\big|_{S_2}} + \underset{\substack{\text{transport}\\ \text{through}\\ \text{other}\\ \text{boundaries}}}{\dot{w}_A\,\Delta t} + \underset{\substack{\text{genera-}\\ \text{tion or}\\ \text{consump-}\\ \text{tion}}}{\dot{r}_A\,\Delta t} \tag{6.2}$$

Total material balance:

$$\underset{\text{accumulation}}{\rho V\big|_{t+\Delta t} - \rho V\big|_t} = \underset{\text{transport through defined boundaries}}{\rho vS\,\Delta t\big|_{S_1} + \rho vS\,\Delta t\,\big|_{S_2}} + \underset{\substack{\text{transport}\\ \text{through}\\ \text{other}\\ \text{boundaries}}}{\dot{w}\,\Delta t} \tag{6.3}$$

Energy balance:

$$\underset{\text{accumulation}}{E\big|_{t+\Delta t} - E\big|_t} = \underset{\text{transport through defined boundaries}}{\left|\left(\hat{H} + \frac{v^2}{2} + gh\right)\dot{m}\,\Delta t\right|_{S_1} - \left|\left(\hat{H} + \frac{v^2}{2} + gh\right)\dot{m}\,\Delta t\right|_{S_2}}$$

$$+ \underset{\text{heat}}{\dot{Q}\,\Delta t} - \underset{\text{work}}{\dot{W}\,\Delta t} + \underset{\substack{\text{transport}\\ \text{through}\\ \text{other}\\ \text{boundaries}}}{\dot{B}\,\Delta t} \tag{6.4}$$

where $\dot{B}$ = rate of energy transfer accompanying $\dot{w}$
$\dot{m}$ = rate of mass transfer through defined surfaces
$\dot{Q}$ = rate of heat transfer to system
$\dot{W}$ = rate of work done by the system
$\dot{w}$ = rate of total mass flow through the system boundaries other than through the defined surfaces S_1 and S_2
ρ = total mass per unit volume

The other notation for the material and energy balances is identical to that of Chaps. 2 and 4; note that the work, heat, generation, and mass transport are now all expressed as rate terms (mass or energy per unit time).

If each side of Eq. (6.2) is divided by Δt, we obtain

$$\frac{\rho_A V\big|_{t+\Delta t} - \rho_A V\big|_t}{\Delta t} = \rho_A vS\big|_{S_1} - \rho_A vS\big|_{S_2} + \dot{w}_A + \dot{r}_A \tag{6.5}$$

Similar relations can be obtained from Eqs. (6.3) and (6.4). Next, if we take the limit of each side of Eq. (6.5) as $\Delta t \to 0$, we get

$$\frac{d(\rho_A V)}{dt} = -\Delta(\rho_A vS) + \dot{w}_A + \dot{r}_A \tag{6.6}$$

Similar treatment of the total mass balance and the energy balance yields the following two equations:

$$\frac{d(\rho V)}{dt} = -\Delta(\rho v S) + \dot{w} \tag{6.7}$$

$$\frac{d(E)}{dt} = -\Delta\left[\left(\hat{H} + \frac{v^2}{2} + gh\right)\dot{m}\right] + \dot{Q} - \dot{W} + \dot{B} \tag{6.8}$$

Can you get Eqs. (6.7) and (6.8) from (6.3) and (6.4), respectively? Try it.

The relation between the energy balance given by Eq. (6.8), which has the units of energy per unit time, and the energy balance given by Eq. (4.24), which has the units of energy, should now be fairly clear. Equation (4.24) represents the integration of Eq. (6.8) with respect to time, expressed formally as follows:

$$E_{t_2} - E_{t_1} = \int_{t_1}^{t_2} \{-\Delta[(\hat{H} + \hat{K} + \hat{P})\dot{m}] + \dot{Q} + \dot{B} - \dot{W}\}dt \tag{6.9}$$

The quantities designated in Eqs. (4.24) or (4.24a) without the superscript dot are the respective integrated values from Eq. (6.9).

To solve one or a combination of the very general equations (6.6), (6.7), or (6.8) analytically may be quite difficult, and in the following examples we shall have to restrict our analyses to simple cases. If we make enough (reasonable) assumptions and work with simple problems, we can consolidate or eliminate enough terms of the equations to be able to integrate them and develop some analytical answers. Numerical solutions are also possible for nonlinear equations.

In the solution of unsteady-state problems you have to apply the usual procedures of problem solving discussed in Chaps. 1, 2, and 4. Two major tasks exist:

(a) To set up the unsteady-state equation(s)
(b) To solve it (them) once the equation(s) is (are) established

After you draw a diagram of the system and set down all the information available, you should try to recognize the important variables and represent them by letters. Next, decide which variable is the independent one, and label it. The independent variable is the one you select to have one or a series of values, and then the other variables are all dependent ones—they are determined by the first variable(s) and the initial state of the process you selected. Which is chosen as an independent and which as a dependent variable is usually fixed by the problem but may be arbitrary. Although there are no general rules applicable to all cases, the quantities that appear prominently in the statement of the problem are usually the best choices. You will need as many independent equations as you have dependent variables.

As mentioned before, in the macroscopic balance the independent variable is time. In mathematics, when the quantity x varies with time, we consider dx to be the change in x that occurs during time dt if the process continues through the interval beginning at time t. Let us say that t is the independent variable and x is the dependent one. In solving problems you can use one or a combination of Eqs. (6.6)–(6.8) directly, or alternatively you can proceed, as shown in some of the examples, to set up the differential equations from scratch exactly in the same fashion as Eqs. (6.2)–(6.4) were formulated. For either approach the objective is to translate the problem statement in words into one or more simultaneous differential equations having the form

$$\frac{dx}{dt} = f(x, t) \tag{6.10}$$

Then, assuming this differential equation can be solved, x can be found as a function of t. Of course, we have to know some initial condition(s) or at one (or more) given time(s) know the value(s) of x.

If dt and dx are always considered positive when increasing, you can use Eq. (6.1) without having any difficulties with signs. However, if you for some reason transfer an output to the left-hand side of the equation, or the equation is written in some other form, you should take great care in the use of signs (see Example 6.2 below). We are now going to examine some very simple unsteady-state problems which are susceptible to reasonably elementary mathematical analysis. You can (and will) find more complicated examples in texts dealing with all phases of mass transfer, heat transfer, and fluid dynamics.

EXAMPLE 6.1 Unsteady-State Material Balance without Generation

A tank holds 100 gal of a water-salt solution in which 4.0 lb of salt is dissolved. Water runs into the tank at the rate of 5 gal/min and salt solution overflows at the same rate. If the mixing in the tank is adequate to keep the concentration of salt in the tank uniform at all times, how much salt is in the tank at the end of 50 min? Assume that the density of the salt solution is essentially the same as that of water.

Solution

We shall set up from scratch the differential equations that describe the process.

Step 1 Draw a picture, and put down the known data. See Fig. E6.1.

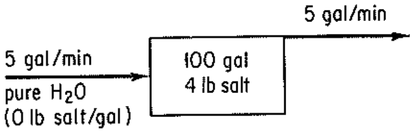


Figure E6.1

Step 2 Choose the independent and dependent variables. Time, of course, is the independent variable, and either the salt quantity or concentration in the tank can be the dependent variable. Suppose that we make the mass (quantity) of salt the dependent variable. Let x = lb of salt in the tank at time t.

Step 3 Write the known value of x at a given value of t. This is the initial condition:

$$\text{at } t = 0 \qquad x = 4.0 \text{ lb}$$

Step 4 It is easiest to make a total material balance and a component material balance on the salt. (No energy balance is needed because the system can be assumed to be isothermal.)

Total balance:

$$\textbf{accumulation} \quad = \quad \textbf{in}$$

$$[m_{\text{tot}}\ \text{lb}]_{t+\Delta t} - [m_{\text{tot}}\ \text{lb}]_t = \begin{array}{c|c|c|c} 5\ \text{gal} & 1\ \text{ft}^3 & \rho_{H_2O}\ \text{lb} & \Delta t\ \text{min} \\ \hline \text{min} & 7.48\ \text{gal} & \text{ft}^3 & \end{array}$$

$$\textbf{out}$$

$$- \begin{array}{c|c|c|c} 5\ \text{gal} & 1\ \text{ft}^3 & \rho_{\text{soln}}\ \text{lb} & \Delta t\ \text{min} \\ \hline \text{min} & 7.48\ \text{gal} & \text{ft}^3 & \end{array} = 0$$

This equation tells us that the flow of water into the tank equals the flow of solution out of the tank if $\rho_{H_2O} = \rho_{\text{soln}}$ as assumed. Otherwise, there is an accumulation term.

Salt balance:

$$\textbf{accumulation} \quad = \textbf{in} - \textbf{out}$$

$$[x\ \text{lb}]_{t+\Delta t} - [x\ \text{lb}]_t = 0 - \begin{array}{c|c|c} 5\ \text{gal} & x\ \text{lb} & \Delta t\ \text{min} \\ \hline \text{min} & 100\ \text{gal} & \end{array}$$

Dividing by Δt and taking the limit as Δt approaches zero,

$$\lim_{\Delta t \to 0} \frac{[x]_{t+\Delta t} - [x]_t}{\Delta t} = -0.05x$$

or

$$\frac{dx}{dt} = -0.05x \qquad \text{(a)}$$

Notice how we have kept track of the units in the normal fashion in setting up these equations. Because of our assumption of uniform concentration of salt in the tank, the concentration of salt leaving the tank is the same as that in the tank, or x lb/100 gal of solution.

Step 5 Solve the unsteady-state material balance on the salt. By separating the independent and dependent variables, we get

$$\frac{dx}{x} = -0.05\ dt$$

This equation is easily integrated between the definite limits of

$t = 0 \qquad x = 4.0$

$t = 50 \qquad X =$ the unknown value of x lb

$$\int_{4.0}^{X} \frac{dx}{x} = -0.05 \int_0^{50} dt$$

$$\ln \frac{X}{4.0} = -2.5 \qquad \ln \frac{4.0}{X} = 2.5$$

$$\frac{4.0}{X} = 12.2 \qquad X = \frac{4.0}{12.2} = 0.328\ \text{lb salt}$$

An equivalent differential equation to Eq. (a) can be obtained directly from the component mass balance in the form of Eq. (6.6) if we let ρ_A = concentration of salt in the tank at any time t in terms of lb/gal:

$$\frac{d(\rho_A V)}{dt} = -\left(\begin{array}{c|c} 5\ \text{gal} & \rho_A\ \text{lb} \\ \hline \text{min} & \text{gal} \end{array}\right) - 0$$

If the tank holds 100 gal of solution at all times, V is a constant and equal to 100, so that

$$\frac{d\rho_A}{dt} = -\frac{5\rho_A}{100} \tag{b}$$

The initial conditions are

$$\text{at } t = 0 \qquad \rho_A = 0.04$$

The solution of Eq. (b) would be carried out exactly as the solution of Eq. (a).

EXAMPLE 6.2 Unsteady-State Material Balance without Generation

A square tank 4 m on a side and 10 m high is filled to the brim with water. Find the time required for it to empty through a hole in the bottom 5 cm² in area.

Solution

Step 1 Draw a diagram of the process, and put down the data. See Fig. E6.2a.

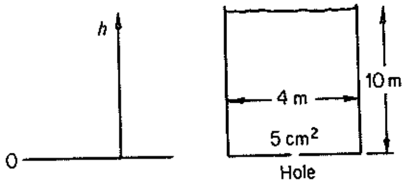


Figure E6.2a

Step 2 Select the independent and dependent variables. Again, time will be the independent variable. We could select the quantity of water in the tank as the dependent variable, but since the cross section of the tank is constant, let us choose h, the height of the water in the tank, as the dependent variable.

Step 3 Write the known value of h at a given value of t:

$$\text{at } t = 0 \qquad h = 10 \text{ m}$$

Step 4 Develop the unsteady-state balance(s) for the process. In an elemental time Δt, the height of the water in the tank drops Δh. The mass of water leaving the tank is in the form of a cylinder 5 cm² in area, and we can calculate the quantity as

$$\frac{5\text{ cm}^2}{}\left|\left(\frac{1\text{ m}}{100\text{ cm}}\right)^2\right|\frac{v^*\text{m}}{\text{s}}\left|\frac{\rho\text{ kg}}{\text{m}^3}\right|\frac{\Delta t\text{ s}}{} = 5\times 10^{-4}v^*\rho\,\Delta t \qquad \text{kg}$$

where ρ = density of water
v^* = average velocity of the water leaving the tank

The depletion of water inside the tank in terms of the variable h, expressed in pounds, is

$$\left.\frac{16\text{ m}^2}{}\left|\frac{\rho\text{ kg}}{\text{m}^3}\right|\frac{h\text{ m}}{}\right|_{t+\Delta t} - \left.\frac{16\text{ m}^2}{}\left|\frac{\rho\text{ kg}}{\text{m}^3}\right|\frac{h\text{ m}}{}\right|_{t} = 16\rho\Delta h \qquad \text{kg}$$

An overall material balance indicates that

$$\textbf{accumulation} = \textbf{in} - \textbf{out}$$

$$16\rho\Delta h = 0 - 5\times 10^{-4}\rho v^*\,\Delta t \tag{a}$$

Although Δh is a negative value, our equation takes account of this automatically. The accumulation is positive if the right-hand side is positive, and the accumulation is negative if the right-hand side is negative. Here the accumulation is really a depletion. You can see that the term ρ, the density of water, cancels out, and we could just as well have made our material balance on a volume of water.

Equation (a) becomes

$$\frac{\Delta h}{\Delta t} = -\frac{5 \times 10^{-4} v^*}{16}$$

Taking the limit as Δh and Δt approach zero, we get

$$\frac{dh}{dt} = -\frac{5 \times 10^{-4} v^*}{16} \tag{b}$$

Step 5 Unfortunately, this is an equation with one independent variable, t, and two dependent variables, h and v^*. We must find another equation to eliminate either h or v^* if we want to obtain a solution. Since we want our final equation to be expressed in terms of h, the next step is to find some function that relates v^* to h and t, and then we can substitute for v^* in the unsteady-state equation.

We shall employ the steady-state mechanical energy balance for an incompressible fluid, discussed in Chap. 4, to relate v^* and h. See Fig. E6.2b. Recall from Eq. (4.30) with $W = 0$ and $E_v = 0$ that

$$\Delta\left(\frac{v^2}{2} + gh\right) = 0 \tag{c}$$

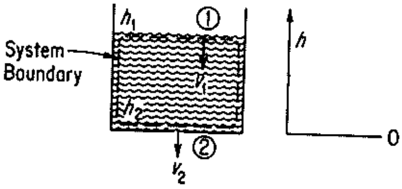


Figure E6.2b

We assume that the pressures are the same at section ①—the water surface—and section ②—the hole—for the system consisting of the water in the tank. Equation (c) reduces to

$$\frac{v_2^2 - v_1^2}{2} + g(h_2 - h_1) = 0 \tag{d}$$

where v_2 = exit velocity through the 5 cm² hole at boundary ②
v_1 = velocity of the water in the tank at boundary ①

If $v_1 \simeq 0$, a reasonable assumption for the water in the large tank at any time, at least compared to v_2, we have

$$\begin{aligned} v_2^2 &= -2g(0 - h_1) = 2gh \\ v_2 &= \sqrt{2gh} \end{aligned} \tag{e}$$

Because the exit-stream flow is not frictionless and because of turbulence and orifice effects in the exit hole, we must correct the value of v given by Eq. (e) for frictionless flow by an empirical adjustment factor as follows:

$$v_2 = c\sqrt{2gh} = v^* \tag{f}$$

where c is an orifice correction which we could find (from a text discussing fluid dynamics) has a value of 0.62 for this case. Thus

$$v^* = 0.62\sqrt{2(9.80)h} = 2.74\sqrt{h} \qquad \text{m/s}$$

Let us substitute this relation into Eq. (b) in place of v^*. Then we obtain

$$\frac{dh}{dt} = \frac{(5.4 \times 10^{-4})(2.74)(h)^{1/2}}{16}$$

or

$$-1.08 \times 10^4 \frac{dh}{h^{1/2}} = dt \tag{g}$$

Equation (g) can be integrated between

$$h = 10 \text{ m} \qquad \text{at } t = 0$$

and

$$h = 0 \text{ m} \qquad \text{at } t = \theta, \quad \text{the unknown time}$$

$$-1.08 \times 10^4 \int_{10}^{0} \frac{dh}{h^{1/2}} = \int_0^{\theta} dt$$

to yield θ,

$$\theta = 1.08 \times 10^4 \int_0^{10} \frac{dh}{h^{1/2}} = 1.08 \times 10^4 [2\sqrt{h}]_0^{10} = 6.83 \times 10^4 \text{ s}$$

EXAMPLE 6.3 Material Balance in Batch Distillation

A small still is separating propane and butane at 135°C and initially contains 10 kg moles of a mixture whose composition is $x = 0.30$ (x = mole fraction butane). Additional mixture ($x_F = 0.30$) is fed at the rate of 5 kg mol/hr. If the total volume of the liquid in the still is constant, and the concentration of the vapor from the still (x_D) is related to x_S as follows:

$$x_D = \frac{x_S}{1 + x_S}$$

how long will it take for the value of x_S to change from 0.30 to 0.40? What is the steady-state ("equilibrium") value of x_S in the still (i.e., when x_S becomes constant)? See Fig. E6.3.

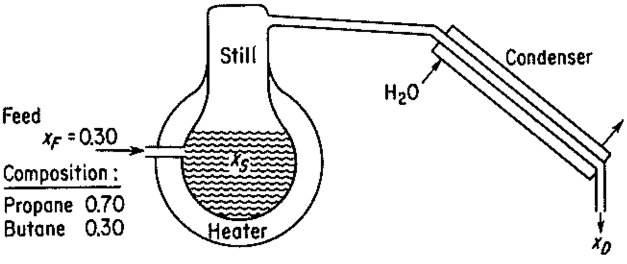


Figure E6.3

Solution

Since butane and propane form ideal solutions, we do not have to worry about volume changes on mixing or separation. Only the material balance is needed to answer the questions posed. If t is the independent variable and x_S the dependent variable, we can say that

Butane Balance (C_4): The input to the still is

$$\begin{array}{c|c|c} 5 \text{ mol feed} & 0.30 \text{ mol } C_4 & \Delta t \text{ hr} \\ \hline \text{hr} & \text{mol feed} & \end{array}$$

The output from the still is equal to the amount condensed,

$$\begin{array}{c|c|c} 5 \text{ mol cond.} & x_D \text{ mol } C_4 & \Delta t \text{ hr} \\ \hline \text{hr} & \text{mol cond.} & \end{array}$$

The accumulation is

$$\left.\begin{array}{c|c} 10 \text{ mol in still} & x_S \text{ mol } C_4 \\ \hline & \text{mol in still} \end{array}\right|_{t+\Delta t} - \left.\begin{array}{c|c} 10 \text{ mol in still} & x_S \text{ mol } CH_4 \\ \hline & \text{mol in still} \end{array}\right|_{t} = 10\Delta x_S$$

Our unsteady-state material balance is then

$$\textbf{accumulation} = \textbf{in} \qquad - \textbf{out}$$

$$10\,\Delta x_S = 1.5\,\Delta t - 5x_D\,\Delta t$$

or, dividing by Δt and taking the limit as Δt approaches zero,

$$\frac{dx_S}{dt} = 0.15 - 0.5x_D$$

As in Example 6.2, it is necessary to reduce the equation to one dependent variable by substituting for x_D:

$$x_D = \frac{x_S}{1 + x_S}$$

Then

$$\frac{dx_S}{dt} = 0.15 - \frac{x_S}{1 + x_S}(0.5)$$

$$\frac{dx_S}{0.15 - \dfrac{0.5x_S}{1 + x_S}} = dt$$

The integration limits are

$$\text{at } t = 0 \qquad x_S = 0.30$$

$$t = \theta \qquad x_S = 0.40$$

$$\int_{0.30}^{0.40} \frac{dx_S}{0.15 - [0.5x_S/(1 + x_S)]} = \int_0^{\theta} dt = \theta$$

$$\int_{0.30}^{0.04} \frac{(1 + x_S)\,dx_S}{0.15 - 0.35x_S} = \theta = \left[-\frac{x_S}{0.35} - \frac{1}{(0.35)^2}\ln(0.15 - 0.35x_S)\right]_{0.30}^{0.40}$$

$$\theta = 5.85 \text{ hr}$$

If you did not know how to integrate the equation analytically, or if you only had experimental data for x_D as a function of x_S instead of the given equation, you could always integrate the equation numerically on a digital computer.

The steady-state value of x_S is established at infinite time or, alternatively, when the accumulation is zero. At that time,

$$0.15 = \frac{0.5x_S}{1 + x_S} \qquad \text{or} \qquad x_S = 0.428$$

The value of x_S could never be greater than 0.428 for the given conditions.

EXAMPLE 6.4 Unsteady-State Chemical Reaction

A compound dissolves in water at a rate proportional to the product of the amount undissolved and the difference between the concentration in a saturated solution and the concentration in the actual solution at any time. A saturated solution of compound contains 40 g/100 g H_2O. In a test run starting with 20 kg of undissolved compound in 100 kg of pure compound is found that 5 kg is dissolved in 3 hr. If the test continues, how many kilograms of compound will remain undissolved after 7 hr? Assume that the system is isothermal.

Solution

Step 1 See Fig. E6.4.

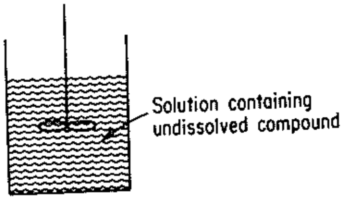


Figure E6.4

Step 2 Let the dependent variable x = the kilograms of *undissolved* compound a time t (the independent variable).

Step 3 At any time t the concentration of dissolved compound is

$$\frac{20 - x}{100}\left(\frac{\text{kg compound}}{\text{lb H}_2\text{O}}\right)$$

The rate of dissolution of compound according to the problem statement is

$$\text{rate}\,\frac{\text{kg}}{\text{hr}} = k(x\ \text{kg})\left[\frac{40\ \text{kg compound}}{100\ \text{kg H}_2\text{O}} - \frac{(20 - x)\ \text{kg compound}}{100\ \text{kg H}_2\text{O}}\right]$$

where k is the proportionality constant. We could have utilized a concentration measured on volume basis rather than one measured on a weight basis, but this would just change the valu and units of the constant k.

Next we make an unsteady-state balance for the compound in the solution (the system

$$\textbf{accumulation} = \textbf{in} - \textbf{out} + \textbf{generation}$$

$$\frac{dx}{dt} = 0 - 0 + kx\left(\frac{40}{100} - \frac{20 - x}{100}\right)$$

or

$$\frac{dx}{dt} = \frac{kx}{100}(20 + x)$$

Step 4 Solution of the unsteady-state equation:

$$\frac{dx}{x(20 + x)} = \frac{k}{100}\,dt$$

This equation can be split into two parts and integrated,

$$\frac{dx}{x} - \frac{dx}{x + 20} = \frac{k}{5}\,dt$$

or integrated directly for the conditions

$$\begin{array}{ll} t_0 = 0 & x_0 = 20 \\ t_1 = 3 & x_1 = 15 \\ t_2 = 7 & x_2 = ? \end{array}$$

Since k is an unknown, the first pair of conditions is given in order to evaluate k.

To find k, we integrate between the limits stated in the test run:

$$\int_{20}^{15} \frac{dx}{x} - \int_{20}^{15} \frac{dx}{x + 20} = \frac{k}{5}\int_{0}^{3} dt$$

$$\left[\ln \frac{x}{x + 20}\right]_{20}^{15} = \frac{k}{5}(3 - 0)$$

$$k = -0.257$$

(Note that the negative value of k corresponds to the actual physical situation in which undissolved material is consumed.) To find the unknown amount of undissolved compound at the end of 7 hr, we have to integrate again:

$$\int_{20}^{x_2} \frac{dx}{x} - \int_{20}^{x_2} \frac{dx}{x + 20} = \frac{-0.257}{5}\int_{0}^{7} dt$$

$$\left[\ln \frac{x}{x + 20}\right]_{20}^{x_2} = \frac{-0.0257}{5}(7 - 0)$$

$$x_2 = 10.7 \text{ kg}$$

EXAMPLE 6.5 Overall Unsteady-State Process

A 15% Na_2SO_4 solution is fed at the rate of 12 lb/min into a mixer that initially holds 100 lb of a 50-50 mixture of Na_2SO_4 and water. The exit solution leaves at the rate of 10 lb/min. Assuming uniform mixing, what is the concentration of Na_2SO_4 in the mixer at the end of 10 min? Ignore any volume changes on mixing.

Solution

In contrast to Example 6.1, both the water and the salt concentrations, and the total material in the vessel, change with time in this problem.

Step 1 See Fig. E6.5.

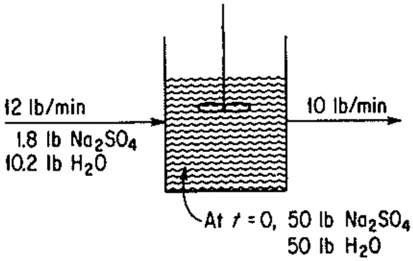


Figure E6.5

Step 2

$$\textit{Let } x = \text{fraction } Na_2SO_4 \text{ in the tank at time } t, \left(\frac{\text{lb } Na_2SO_4}{\text{lb total}}\right)$$

$$y = \text{total pounds of material in the tank at time } t$$

Step 3 At time $t = 0$, $x = 0.50$, $y = 100$.
Step 4 Material balances between time t and $t + \Delta t$:
(a) Total balance:

$$\begin{array}{ccccc} \textbf{accumulation} & = & \textbf{in} & - & \textbf{out} \end{array}$$

$$[y]_{t+\Delta t} - [y]_t = \Delta y = \left.\frac{12 \text{ lb}}{\text{min}}\right|\Delta t \text{ min} - \left.\frac{10 \text{ lb}}{\text{min}}\right|\Delta t \text{ min}$$

or

$$\frac{dy}{dt} = 2 \tag{a}$$

(b) Na_2SO_4 balance:

$$\textbf{accumulation}$$

$$\left[\left.\frac{x \text{ lb } Na_2SO_4}{\text{lb total}}\right| y \text{ lb total}\right]_{t+\Delta t} - \left[\left.\frac{x \text{ lb } Na_2SO_4}{\text{lb total}}\right| y \text{ lb total}\right]_t$$

$$= \quad \textbf{in} \quad - \quad \textbf{out}$$

$$= \left.\frac{1.8 \text{ lb } Na_2SO_4}{\text{min}}\right|\Delta t \text{ min} - \left.\frac{10 \text{ lb total}}{\text{min}}\right|\left.\frac{x \text{ lb } Na_2SO_4}{\text{lb total}}\right|\Delta t \text{ min}$$

or

$$\frac{d(xy)}{dt} = 1.8 - 10x \tag{b}$$

Step 5 There are a number of ways to handle the solution of these two differential equations with two unknowns. Perhaps the easiest is to differentiate the xy product in Eq. (b) and substitute Eq. (a) into the appropriate term containing dy/dt:

$$\frac{d(xy)}{dt} = x\frac{dy}{dt} + y\frac{dx}{dt}$$

To get y, we have to integrate Eq. (a):

$$\int_{100}^{y} dy' = \int_{0}^{t} 2\,dt'$$

$$y - 100 = 2t$$

$$y = 100 + 2t$$

Then

$$\frac{d(xy)}{dt} = x(2) + (100 + 2t)\frac{dx}{dt} = 1.8 - 10x$$

$$\frac{dx}{dt}(100 + 2t) = 1.8 - 12x$$

$$\int_{0.50}^{x} \frac{dx'}{1.8 - 12x} = \int_{0}^{10} \frac{dt'}{100 + 2t}$$

$$-\frac{1}{12}\ln\frac{1.8 - 12x}{1.8 - 6.0} = \frac{1}{2}\ln\frac{100 + 20}{100}$$

$$x = 0.267\,\frac{\text{lb Na}_2\text{SO}_4}{\text{lb total solution}}$$

An alternative method of setting up the dependent variable would have been to let x = lb of Na_2SO_4 in the tank at the time t. Then the Na_2SO_4 balance would be

$$\frac{dx}{dt}\,\frac{\text{lb Na}_2\text{SO}_4}{\text{min}} = \frac{1.8\text{ lb Na}_2\text{SO}_4}{\text{min}} - \frac{10\text{ lb total}}{\text{min}}\left|\frac{x\text{ lb Na}_2\text{SO}_4}{y\text{ lb total}}\right.$$

$$\frac{dx}{dt} = 1.8 - \frac{10x}{100 + 2t}$$

or

$$\frac{dx}{dt} + \frac{10}{100 + 2t}x = 1.8$$

The solution to this linear differential equation gives the pounds of Na_2SO_4 after 10 min; the concentration then can be calculated as x/y. To integrate the linear differential equation, we introduce the integrating factor $e^{\int (dt/10+0.2t)}$:

$$xe^{\int (dt/10+0.2t)} = \int (e^{\int (dt/10+0.2t)})(1.8)\,dt + C$$

$$x(10 + 0.2t)^5 = 1.8\int (10 + 0.2t)^5\,dt + C$$

at $x = 50$, $t = 0$, and $C = 35 + 10^5$;

$$x = 1.5(10 + 0.2t) + \frac{35 \times 10^5}{(10 + 0.2t)^5}$$

at $t = 10$ min;

$$x = 1.5(12) + \frac{35 \times 10^5}{(12)^5} = 32.1$$

The concentration is

$$\frac{x}{y} = \frac{32.1}{100 + 20} = 0.267 \frac{\text{lb Na}_2\text{SO}_4}{\text{lb total solution}}$$

EXAMPLE 6.6 Unsteady-State Energy Balance

Five thousand pounds of oil initially at 60°F is being heated in a stirred (perfectly mixed) tank by saturated steam which is condensing in the steam coils at 40 psia. If the rate of heat transfer is given by Newton's heating law,

$$\dot{Q} = \frac{dQ}{dt} = h(T_{\text{steam}} - T_{\text{oil}})$$

where Q is the heat transferred in Btu and h is the heat transfer coefficient in the proper units, how long does it take for the discharge from the tank to rise from 60°F to 90°F? What is the maximum temperature that can be achieved in the tank?

Additional Data:

$$\text{motor horsepower} = 1 \text{ hp; efficiency is } 0.75$$

$$\text{entering oil flow rate} = 1018 \text{ lb/hr at a temperature of } 60°\text{F}$$

$$\text{discharge oil flow rate} = 1018 \text{ lb/hr at a temperature of } T$$

$$h = 291 \text{ Btu/(hr)(°F)}$$

$$C_{P_{\text{oil}}} = 0.5 \text{ Btu/(lb)(°F)}$$

Solution

The process is shown in Fig. E6.6. The independent variable will be t, the time; the dependent variable will be the temperature of the oil in the tank, which is the same as the temperature of the oil discharged. The material balance is not needed because the process, insofar as the quantity of oil is concerned, is assumed to be in the steady state.

Our next step is to set up the unsteady-state energy balance for the interval Δt. Let T_S = the steam temperature and T = the oil temperature:

$$\text{accumulation} = \text{input} - \text{output}$$

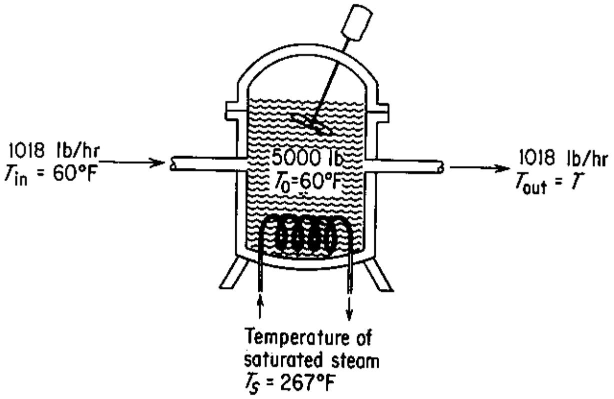


Figure E6.6

A good choice for a reference temperature for the enthalpies is 60°F because this choice makes the input enthalpy zero.

enthalpy of the input steam

$$\begin{array}{c|c|c|c} 1018\ \text{lb} & 0.5\ \text{Btu} & \overbrace{(T_{\text{in}} - T_{\text{ref}})}^{60°\text{F} - 60°\text{F}} & \Delta t\ \text{hr} \\ \hline \text{hr} & (\text{lb})(°\text{F}) & & \end{array} = 0$$

heat transfer

$$h(T_S - T) = \begin{array}{c|c|c} 291\ \text{Btu} & (267 - T)°\text{F} & \Delta t\ \text{hr} \\ \hline (\text{hr})(°\text{F}) & & \end{array}$$

input (Btu)

enthalpy of the output stream

$$\begin{array}{c|c|c|c} 1018\ \text{lb} & 0.5\ \text{Btu} & (T - 60)\text{F} & \Delta t\ \text{hr} \\ \hline \text{hr} & (\text{lb})(°\text{F}) & & \end{array}$$

output (Btu)

enthalpy change inside tank

$$\left[\begin{array}{c|c|c} 5000\ \text{lb} & 0.5\ \text{Btu} & (T - 60)°\text{F} \\ \hline & (\text{lb})(°\text{F}) & \end{array}\right]_{t+\Delta t} - \left[\begin{array}{c|c|c} 5000\ \text{lb} & 0.5\ \text{Btu} & (T - 60)°\text{F} \\ \hline & (\text{lb})(°\text{F}) & \end{array}\right]_{t}$$

accumulation (Btu)

The rate of change of energy inside the tank is nothing more than the rate of change of internal energy, which, in turn, is essentially the same as the rate of change of enthalpy (i.e., $dE/dt = dU/dt = dH/dt$) because $d(pV)/dt \simeq 0$.

We use Eq. (6.8) with $\dot{B} = 0$. The energy introduced by the motor enters the tank as $\dot{W}$ and is:

$$\dot{W} = \begin{array}{c|c|c} 3\ \text{hp} & 0.7608\ \text{Btu} & 3600\ \text{sec} \\ \hline 4 & (\text{sec})(\text{hp}) & 1\ \text{hr} \end{array} = \frac{1910\ \text{Btu}}{\text{hr}}$$

Then

$$2500\frac{dT}{dt} = 291(267 - T) - 509(T - 60) + 1910$$

$$\frac{dT}{dt} = 44.1 - 0.32T$$

$$\int_{60}^{90} \frac{dT}{44.1 - 0.32T} = \int_0^{\theta} dt = \theta$$

$\theta = 1.52$ hr.

A numerical solution using an appropriate computer program can be carried out for those differential equations for which analytical solutions are not possible.

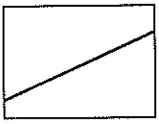
Self-Assessment Test

1. In a batch type of chemical reactor, do we have to have the starting conditions to predict the yield?
2. Is time the independent or dependent variable in macroscopic unsteady-state equations?

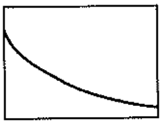
3. How can you obtain the steady-state balances from Eqs. (6.6)–(6.8)?

(a)

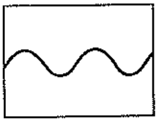
(b)



(c)



(d)



4. Which of the following plots of the response vs. time are not transient state processes?
5. Group the following words in sets of synonyms: (1) response, (2) input variable, (3) parameter, (4) state variable, (5) system parameter, (6) initial condition, (7) output, (8) independent variable, (9) dependent variable, (10) coefficient, (11) output variable, (12) constant.
6. A chemical inhibitor must be added to the water in a boiler to avoid corrosion and scale. The inhibitor concentration must be maintained between 4 and 30 ppm. The boiler system always contains 100,000 kg of water and the blowdown (purge) rate is 15,000 kg/hr. The makeup water contains no inhibitor. An initial 2.8 kg of inhibitor is added to the water and thereafter 2.1 kg is added periodically. What is the maximum time interval until the first addition of inhibitor?
7. In a reactor a small amount of undesirable by-product is continuously formed at the rate of 0.5 lb/hr when the reactor contains a steady inventory of 10,000 lb of material. The reactor inlet stream contains traces of the by-product (40 ppm), and the effluent stream is 1400 lb/hr. If on startup, the reactor contains 5000 pm of the by-product, what will be the concentration in ppm in 10 hr?

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Sherwood, T. K., and C. E. Reid, *Applied Mathematics in Chemical Engineering,* 2nd ed., McGraw-Hill, New York, 1957.

PROBLEMS

6.1. A tank containing 100 kg of a 60% brine (60% salt) is filled with a 10% salt solution at the rate of 10 kg/min. Solution is removed from the tank at the rate of 15 kg/min. Assuming complete mixing, find the kilograms of salt in the tank after 10 min.

6.2. A defective tank of 1500 ft^3 volume containing 100% propane gas (at 1 atm) is to be flushed with air (at 1 atm) until the propane concentration reduced to less than 1%. At that concentration of propane the defect can be repaired by welding. If the flow rate of air into the tank is 30 ft^3/min, for how many minutes must the tank be flushed out? Assume that the flushing operation is conducted so that the gas in the tank is well mixed.

6.3. A 2% uranium oxide slurry (2 lb UO_2/100 lb H_2O) flows into a 100-gal tank at the rate of 2 gal/min. The tank initially contains 500 lb of H_2O and no UO_2. The slurry is well mixed and flows out at the same rate at which it enters. Find the concentration of slurry in the tank at the end of 1 hr.

6.4. The catalyst in a fluidized-bed reactor of 200-m^3 volume is to be regenerated by contact with a hydrogen stream. Before the hydrogen can be introduced into the reactor, the O_2 content of the air in the reactor must be reduced to 0.1%. If pure N_2 can be fed into the reactor at the rate of 20 m^3/min, for how long should the reactor be purged with N_2? Assume that the catalyst solids occupy 6% of the reactor volume and that the gases are well mixed.

6.5. An advertising firm wants to get a spherical inflated sign out of a warehouse. The sign is 20 ft in diameter and is filled with H_2 at 15 psig. Unfortunately, the door to the warehouse is only 19 ft high by 20 ft wide. The maximum rate of H_2 that can be safely vented from the balloon is 5 ft^3/min (measured at room conditions). How long will it take to get the sign small enough to just pass through the door?

(a) First assume that the pressure inside the balloon is constant so that the flow rate is constant.

(b) Then assume the amount of H_2 escaping is proportional to the volume of the balloon, and initially is 5 ft^3/min.

(c) Could a solution to this problem be obtained if the amount of escaping H_2 were proportional to the pressure difference inside and outside the balloon?

6.6. A plant at Canso, Nova Scotia, makes fish-protein concentrate (FPC). It takes 6.6 kg of whole fish to make 1 kg of FPC, and therein is the problem—to make money, the plant must operate most of the year. One of the operating problems is the drying of the FPC. It dries in the fluidized dryer at a rate approximately proportional to its moisture content. If a given batch of FPV loses one-half of its initial moisture in the first 15 min, how long will it take to remove 90% of the water in the batch of FPC?

6.7. Water flows from a conical tank at the rate of $0.020(2 + h^2)$ m^3/min, as shown in Fig. P6.7. If the tank is initially full, how long will it take for 75% of the water to flow out of the tank? What is the flow rate at that time?

6.8. A sewage disposal plant has a big concrete holding tank of 100,000 gal capacity. It is three-fourths full of liquid to start with and contains 60,000 lb of organic material in suspension. Water runs into the holding tank at the rate of 20,000 gal/hr and the

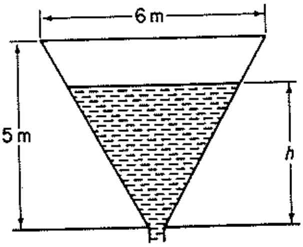

Figure P6.7

solution leaves at the rate of 15,000 gal/hr. How much organic material is in the tank at the end of 3 hr?

6.9. Suppose that in Problem 6.8 the bottom of the tank is covered with sludge (precipitated organic material) and that the stirring of the tank causes the sludge to go into suspension at a rate proportional to the difference between the concentration of sludge in the tank at any time and 10 lb of sludge/gal. If no organic material were present, the sludge would go into suspension at the rate of 0.05 lb/(min) (gal solution) when 75,000 gal of solution are in the tank. How much organic material is in the tank at the end of 3 hr?

6.10. In a chemical reaction the products X and Y are formed according to the equation

$$C \longrightarrow X + Y$$

The rate at which each of these products is being formed is proportional to the amount of C present. Initially: $C = 1, X = 0, Y = 0$. Find the time for the amount of X to equal the amount of C.

6.11. A tank is filled with water. At a given instant two orifices in the side of the tank are opened to discharge the water. The water at the start is 3 m deep and one orifice is 2 m below the top while the other one is 2.5 m below the top. The coefficient of discharge of each orifice is known to be 0.61. The tank is a vertical right circular cylinder 2 m in diameter. The upper and lower orifices are 5 and 10 cm in diameter, respectively. How long will be required for the tank to be drained so that the water level is at a depth of 1.5 m?

6.12. Suppose that you have two tanks in series, as diagrammed in Fig. P6.12. The volume of liquid in each tank remains constant because of the design of the overflow lines. Assume that each tank is filled with a solution containing 10 lb of A, and that the tanks contain 100 gal of aqueous solution each. If fresh water enters at the rate of 10 gal/hr, what is the concentration of A in each tank at the end of 3 hr? Assume complete mixing in each tank and ignore any change of volume with concentration.

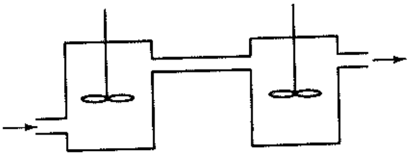

Figure P6.12

6.13. A well-mixed tank has a maximum capacity of 100 gal and it is initially half full. The discharge pipe at the bottom is very long and thus it offers resistance to the flow of water through it. The force that causes the water to flow is the height of the water in the tank, and in fact that flow is just proportional to this height. Since the height is proportional to the total volume of water in the tank, the volumetric flow rate of water out, q_o, is

$$q_o = kV$$

The flow rate of water into the tank, q_i, is constant. Use the information given in Fig. P6.13 to decide whether the amount of water in the tank increases, decreases, or remains the same. If it changes, how much time is required to completely empty or fill the tank, as the case may be?

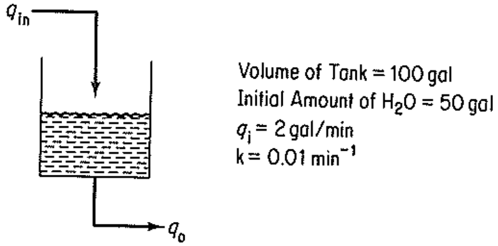

Figure P6.13

6.14. A stream containing a radioactive fission product with a decay constant of 0.01 hr^{-1} (i.e., $dn/dt = 0.01\ n$), is run into a holding tank at the rate of 100 gal/hr for 24 hr. Then the stream is shut off for 24 hr. If the initial concentration of the fission product was 10 mg/liter and the tank volume is constant at 10,000 gal of solution (owing to an overflow line), what is the concentration of fission product:

(a) At the end of the first 24-hr period?

(b) At the end of the second 24-hr period?

What is the maximum concentration of fission product? Assume complete mixing in the tank.

6.15. A radioactive waste that contains 1500 ppm of ^{92}Sr is pumped into a holding tank that contains 0.40 m^3 at the rate of 1.5×10^{-3} m^3/min. ^{92}Sr decays as follows:

$$^{92}\text{Sr} \longrightarrow {}^{92}\text{Y} \longrightarrow {}^{92}\text{Zr}$$

half-life: 2.7 hr 3.5 hr

If the tank contains clear water initially and the solution runs out at the rate of 1.5×10^{-3} m^3/min, assuming perfect mixing:

(a) What is the concentration of Sr, Y, and Zr after 1 day?

(b) What is the equilibrium concentration of Sr and Y in the tank?

The rate of decay of such isotopes is $dN/dt = -\lambda N$, where $\lambda = 0.693/t_{1/2}$ and the half-life is $t_{1/2}$. N = moles.

6.16. A cylinder contains 3 m^3 of pure oxygen at atmospheric pressure. Air is slowly pumped into the tank and mixes uniformly with the contents, an equal volume of which is forced out of the tank. What is the concentration of oxygen in the tank after 9 m^3 of air has been admitted?

6.17. Suppose that an organic compound decomposes as follows:

$$C_6H_{12} \longrightarrow C_4H_8 + C_2H_4$$

If 1 mole of C_6H_{12} exists at $t = 0$ but no C_4H_8 and C_2H_4, set up equations showing the moles of C_4H_8 and C_2H_4 as a function of time. The rates of formation of C_4H_8 and C_2H_4 are each proportional to the number of moles of C_6H_{12} present.

6.18. A large tank is connected to a smaller tank by means of a valve. The large tank contains N_2 at 690 kPa while the small tank is evacuated. If the valve leaks between the two tanks and the rate of leakage of gas is proportional to the pressure difference between the two tanks ($p_1 - p_2$), how long does it take for the pressure in the small tank to be one-half its final value? The instantaneous initial flow rate with the small tank evacuated is 0.091 kg mol/hr.

	Tank 1	Tank 2
Initial pressure (kPa)	700	0
Volume (m^3)	30	15

Assume that the temperature in both tanks is constant and is 20°C.

6.19. The following chain reactions take place in a constant-volume batch tank:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Each reaction is first order and irreversible. If the initial concentration of A is C_{A_0} and if only A is present initially, find an expression for C_B as a function of time. Under what conditions will the concentration of B be dependent primarily on the rate of reaction of A?

6.20. Consider the following chemical reaction in a constant-volume batch tank:

$$\begin{tikzcd} A \arrow[r, shift left, "k_1"] \arrow[d, "k_3"'] & B \arrow[l, shift left, "k_2"] \\ C & \end{tikzcd}$$

All the indicated reactions are first order. The initial concentration of A is C_{A_0}, and nothing else is present at that time. Determine the concentrations of A, B, and C as functions of time.

6.21. Tanks A, B, and C are each filled with 1000 gal of water. See Fig. P6.21. Workers have instructions to dissolve 2000 lb of salt in each tank. By mistake, 3000 lb is dissolved in each of tanks A and C and none in B. You wish to bring all the compositions to within 5% of the specified 2 lb/gal. If the units are connected A–B–C–A by three 50-gpm pumps,

(a) Express the concentrations C_A, C_B, and C_C in terms of t (time).

(b) Find the shortest time at which all concentrations are within the specified range. Assume the tanks are all well mixed.

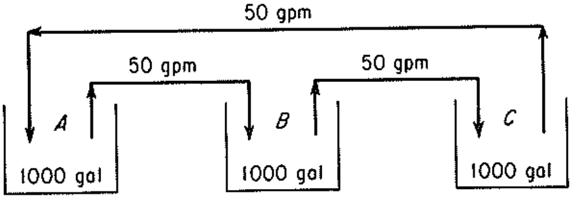

Figure P6.21

6.22. Determine the time required to heat a 10,000-lb batch of liquid from 60°F to 120°F using an external, counterflow heat exchanger having an area of 300 ft^2. Water a

180°F is used as the heating medium and flows at a rate of 6000 lb/hr. An overall heat transfer coefficient of 40 Btu/(hr)(ft^2)(°F) may be assumed; use Newton's law of heating. The liquid is circulated at a rate of 6000 lb/hr, and the specific heat of the liquid is the same as that of water (1.0). Assume that the residence time of the liquid in the external heat exchanger is very small and that there is essentially no holdup of liquid in this circuit.

6.23. A ground material is to be suspended in water and heated in preparation for a chemical reaction. It is desired to carry out the mixing and heating simultaneously in a tank equipped with an agitator and a steam coil. The cold liquid and solid are to be added continuously and the heated suspension will be withdrawn at the same rate. One method of operation for starting up is to (1) fill the tank initially with water and solid in the proper proportions, (2) start the agitator, (3) introduce fresh water and solid in the proper proportions and simultaneously begin to withdraw the suspension for reaction, and (4) turn on the steam. An estimate is needed of the time required, after the steam is turned on, for the temperature of the effluent suspension to reach a certain elevated temperature.

(a) Using the nomenclature given below, formulate a differential equation for this process. Integrate the equation to obtain n as a function of B and ϕ (see nomenclature).

(b) Calculate the time required for the effluent temperature to reach 180°F if the initial contents of the tank and the inflow are both at 120°F and the steam temperature is 220°F. The surface area for heat transfer is 23.9 ft^2, and the heat transfer coefficient is 100 Btu/(hr)(ft^2)(°F). The tank contains 6000 lb, and the rate of flow of both streams is 1200 lb/hr. In the proportions used, the specific heat of the suspension may be assumed to be 1.00.

If the area available heat transfer is doubled, how will the time required be affected? Why is the time with the larger area less than half that obtained previously? The heat transferred is $Q = UA(T_{\text{tank}} - T_{\text{steam}})$.

Nomenclature

W = weight of tank contents, lb

G = rate of flow of suspension, lb/hr

T_s = temperature of steam, °F

T = temperature in tank at any instant, perfect mixing assumed, °F

T_0 = temperature of suspension introduced into tank; also initial temperature of tank contents, °F

U = heat-transfer coefficient, Btu/(hr)(ft^2)(°F)

A = area of heat-transfer surface, ft^2

C_p = specific heat of suspension, Btu/(lb)(°F)

t = time elapsed from the instant the steam is turned on, hr

n = dimensionless time, Gt/W

B = dimensionless ratio, UA/GC_p

ϕ = dimensionless temperature (relative approach to the steam temperature) $(T - T_0)/(T_s - T_0)$

6.24. Consider a well-agitated cylindrical tank in which the heat transfer surface is in the form of a coil that is distributed uniformly from the bottom of the tank to the top of the tank. The tank itself is completely insulated. Liquid is introduced into the tank at a uniform rate, starting with no liquid in the tank, and the steam is turned on at the instant that liquid flows into the tank.

(a) Using the nomenclature of Problem 6.23, formulate a differential equation for this process. Integrate this expression to obtain an equation for ϕ as a function of B and f, where f = fraction filled = W/W_{filled}.

(b) If the heat transfer surface consists of a coil of 10 turns of 1-in.-OD tubing 4 ft in diameter, the feed rate is 1200 lb/hr, the heat capacity of the liquid is 1.0 Btu/(lb)(°F), the heat transfer coefficient is 100 Btu/(hr)(°F)(ft^2) of covered area, the steam temperature is 200°F, and the temperature of the liquid introduced into the tank is 70°F, what is the temperature in the tank when it is completely full? What is the temperature when the tank is half full? The heat transfer is given by $Q = UA(T_{\text{tank}} - T_{\text{steam}})$.

6.25. A cylindrical tank 5 ft in diameter and 5 ft high is full of water at 70°F. The water is to be heated by means of a steam jacket around the sides only. The steam temperature is 230°F, and the overall coefficient of heat transfer is constant at 40 Btu/(hr)(ft^2)(°F). Use Newton's law of cooling (heating) to estimate the heat transfer. Neglecting the heat losses from the top and the bottom, calculate the time necessary to raise the temperature of the tank contents to 170°F. Repeat, taking the heat losses from the top and the bottom into account. The air temperature around the tank is 70°F, and the overall coefficient of heat transfer for both the top and the bottom is constant at 10 Btu/(hr)(ft^2)(°F).

PROBLEM THAT REQUIRES WRITING A COMPUTER PROGRAM

6.1. Write a Fortran computer program for batch distillation. Calculate the mass fraction composition in the pot and the mass retrieved from the condenser given the initial mass and composition in the pot, and the final mass in the pot. Use Example 6.3 for the vapor–liquid equilibrium data and the general setup.

Appendix A

ANSWERS TO SELF-ASSESSMENT TESTS

Section 1.1

1. 2.10×10^{-5} m^3/s
2. **(a)** 252 lb$_m$; **(b)** 29.6 lb$_f$
3. Examine the conversion factors inside the cover.
4. c is dimensionless.
5. 32.174 (ft)(lb$_m$)/(s^2)(lb$_f$)
6. (a)
7. A has the same units as k; B has the units of T.
8. **(a)** 28.349, 0.454; **(b)** 1.609; **(c)** 37.85

Section 1.2

1. 60.05
2. A kilogram mole contains 6.02×10^{26} molecules, whereas a pound mole contains $(6.02 \times 10^{26})(0.454)$ molecules.
3. 0.123 kg mol NaCl/kg mol H_2O
4. 1.177 lb mol
5. 0.121 kg/s

Section 1.3

1. **(a)** F; **(b)** T; **(c)** F; **(d)** T
2. 13.6 g/cm^3
3. 62.4 lb$_m$/ft^3 (10^3 kg/m^3)
4. This means that the density at 10°C of liquid HCN is 1.2675 times the density of water at 4°C.
5. 0.79314 g/cm^3 (Note that you need the density of water at 60°F.)
6. 9
7. **(a)** 63%; **(b)** 54.3; **(c)** 13.8

8. 8.11 ft^3
9. (a) 0.33; (b) 18.7
10. (a) C_4 – 0.50, C_5 – 0.30, C_6 – 0.20; (b) C_4 – 0.57, C_5 – 0.28, C_6 – 0.15; (c) C_4 – 57, C_5 – 28, C_6 – 15; (d) 62.2 kg/kg mol

Section 1.4

1. See p. 32.
2. (a) 100 kg or 100 lb
   (b) 1 ton of water
   (c) The stated mass for each case
   (d) 100 cm^3 mixture

Section 1.5

1. (a) 0°C and 100°C; (b) 32°F and 212°F
2. $\Delta°F(1.8) = \Delta°C$.
3. Yes. Yes.
4. $92.76 + 0.198T_{°F}$.
5.

°C	°F	K	°R
−40.0	−40.0	233	420
25.0	77.0	298	537
425	796	698	1256
−234	−390	38.8	69.8

6. Immerse in ice-water bath and mark 0°C. Immerse in boiling water at 1 atm pressure and mark 100°C. Interpolate between 0°C and 100°C in desired intervals.
7. (a) 1°C; (b) 1°C; (c) 1 Δ°C

Section 1.6

1. Gauge pressure + barometric pressure = absolute pressure.
2. See p. 49.
3. Barometric pressure − vacuum pressure = absolute pressure.
4. (a) 15.5; (b) 106.6 kPa; (c) 1.052; (d) 35.6
5. (a) Gauge pressure; (b) barometric pressure, absolute pressure; (c) 50 in. Hg
6. In the absence of the barometric pressure, assume 101.3 kPa; then absolute pressure is 61.3 kPa.
7. (a) T; (b) T

Section 1.7

1. See p. 57.
2. (a) *Chemical Engineers' Handbook* and/or *Properties of Gases and Liquids*
   (b) *Technical Data Book—Petroleum Refining*
   (c) *Handbook of Physics and Chemistry* and others
   (d) *Chemical Engineers' Handbook*

Section 1.8

1. A serial sequence is adequate; some steps can be in parallel. Feedback may be inserted at various stages.
3. **(a)** Find a reason to remember; talk to others who are interested to ascertain what motivated them. Write down the reason for periodic pep talks with yourself.
   (b) Get a "bird's-eye view" of the whole section. Use the figure numbered 0 to see the relation to other sections. Look at a similar textbook. Ask for help; do not wait.
   (c) After scanning the serious reading count.
   (d) Take a few minutes as you read to mentally test yourself on what you have just read to reinforce learning. Continue to test at periodic intervals.
   (e) Practice using the information for an assumed quiz; predict quiz questions; use text examples or problems as samples.

Section 1.9

1. **(a)** $C_9H_{18} + \frac{27}{2}O_2 \longrightarrow 9CO_2 + 9H_2O$
   (b) $FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$
2. 3.08
3. 323
4. **(a)** $CaCO_3$ – 43.4%; CaO – 56.6%; **(b)** 0.308
5. **(a)** H_2O; **(b)** NaCl; **(c)** NaCl, H_2O, NaOH (assuming that the gas escapes)

Section 2.1

1, 2. The systems are somewhat arbitrary, as are the time intervals selected, but (a) and (c) can be closed systems (ignoring evaporation) and (b) open.
3. See Eqs. (2.1), (2.2), (2.3), and (2.3a).
4. **(a)** batch; **(b)** flow; **(c)** flow; **(d)** flow.
5. Accumulation is zero.
6. Figure 2.3—No, because many streams have no values and some streams, such as gases, are not included in the diagram. Figure 2.4—Yes.
7. Equation (2.1) or simplifications thereof.
8. **(a)** T; **(b)** T if *C* is regarded as an element; F if the exit compound is CO_2 and the entering reactant is *C*; **(c)** F
9. No chemical reaction takes place, or with reaction, the moles of reactants may equal the moles of product by accident.

Section 2.2

1. A set of unique values for the variables in the equations representing the problem.
2. **(a)** one; **(b)** three; **(c)** three
3. **(a)** two; **(b)** two of these three: acetic acid, water, total; **(c)** two; **(d)** feed of the 10% solution and mass fraction ω of the acetic acid in *P*; **(e)** 14% acetic acid, 86% water
4. Not for a unique solution. Only two are independent.
5. Substitution; Gauss–Jordan elimination; use of determinants.
6. Select the most accurate equations that will provide a unique solution. (Or use least squares if all must be used.)

7. The sum of the mass or mole fractions in one stream is unity.
8. Collect additional data so as to specify or evaluate the values of the excess unknown variables.
9. $F, D, P, \omega_{D2}, \omega_{P1}$.
10. Only two independent material balances can be written. The sum of the mass fractions for streams D and P yields two additional independent equations. One value of F, D, or P must be specified to obtain a solution. Note that specifying W_{D2} or W_{P1} will not help.
11. One

Section 2.3

1. Orsat (dry basis) does not include the water vapor in the analysis.
2. SO_2 is not included in the gas analysis.
3. See Eqs. (2.9)-(2.11).
4. Yes. See Eq. (2.9).
5. More
6. 4.5%
7. moles: 5.95 CO_2, 3.747 O_2, 44.0 N_2
8. 178 kg/hr
9. **(a)** 28% Na_2SO_4; **(b)** 33.3

Section 2.4

1. Three components = three independent equations. Any three of the four (1, 2, 3, total) will do.
2. $A = 35$ kg/hr; $B = 65$ kg/hr
3. 3.7321, 0.2680
4. $x = 0.2268$; $y = 0.3696$
5. **(a)** 252; **(b)** 1.063; **(c)** 2.31; **(d)** 33.8%
6. 33.3 kg
7. 186 kg
8. **(a)** 23.34; **(b)** 66.5%
9. 0.994
10. 0.81

Section 2.5

1.

	lb	fr.
tol	396	0.644
bz	19.68	0.032
xyl	200.00	0.325

2. 863 lb air/lb S

	Converter	Burner
SO_2	0.5%	9.5%
SO_3	9.4	—
O_2	7.4	11.5
N_2	82.7	79.0

Section 2.6

1. Recycle is feedback from downstream to upstream in the materials flow bypassing one or more units. Bypassing is feedforward bypassing one or more units.
2. Purge is a side stream usually small in quantity relative to main stream that is bled from the main stream to remove impurities from the system.
3. The stoichiometric ratio
4. **(a)** $R = 3000$ kg/hr; **(b)** air = 85,100 kg/hr
5. **(a)** 908 recycled and 3.2 purged ; **(b)** 9.05% conversion
6. **(a)** 1200.6 kg/hr; **(b)** 194.9 kg/hr

Section 3.1-1

1. $pV = nRT$
2. T: absolute temperature in degrees; p: absolute pressure in mass/(length)(time)^2; V: (length)^3/mole; n: mole; R: (mass)(length)^2/(time)^2(mole)(degree)
3. See p. 240.
4. 1883 ft^3
5. 2.98 kg
6. 1.32
7. 28.3 m^3/hr

Section 3.1-2

1. 0.0493 kg/m^3
2. 1.02 (lb CH_4/ft^3 CH_4 at 70°F and 2 atm)/(lb air/ft^3 at S.C.)

Section 3.1-3

1. See Eqs. (3.3) and (3.6).
2. (a) N_2, 0.28 psia; CH_4, 10.9 psia; C_2H_6, 2.62 psia
   (b) N_2, 0.04 ft^3; CH_4, 1.58 ft^3; C_2H_6, 0.38 ft^3
   (c) Same as the mole fractions
3. (a) 11.18 psia at 2 ft^3 and 120°F; (b) 0.28 psia at 2 ft^3 and 120°F

Section 3.1-4

1. (a) 2,735 ft^3/hr; (b) 5,034 ft^3/hr, (c) 22,429 ft^3/hr, (d) 30,975 ft^3/hr
2. 118,400 ft^3/hr

Section 3.2-1

1. See the last paragraph in Sec. 3.2-1. Also, they can be used for interpolation and extrapolation.
2. (a) Least squares and theory; (b) least squares would give the least error.
3. Comparison with experimental data; reduction in limit of ideal gas to $pV = nRT$; go through the critical point; holding one variable constant, the residual expression should be correct; derivatives give proper functions.
4. The volume occupied by the moles of the gas—by using $(V - nb)$, and the attractive forces existing between the molecules of the gas—by adding $[p + (n^2a/V^2)]$.
5. b is m^3; a is (K)$^{1/2}$(m)^6(kPa).
6. $V = 0.60$ ft^3
7. 314 K
8. (a) 50.7 atm; (b) 34.0 atm
9. 0.316 m^3/kg mol

Section 3.2-2

1. $\hat{V}_{c_i} = RT_c/P_c$. It can be used to calculate $\hat{V}_{ri}$, which is a parameter on the Nelson and Obert charts.

2. **(a)** No; **(b)** 5.08 ft^3; **(c)** 1.35 ft^3
3. 1.65 kg
4. 14.9 atm

Section 3.2-4

1. **(a)** 289 atm
   (b) 300 atm
   (c) 262 atm

Section 3.3

1. See Fig. 3.9.
2. Ice at its vapor pressure changes to liquid water at 32°F (at 0.0886 psia) and the pressure increases as shown in Fig. 3.12 with vapor and liquid in equilibrium. At 250°F, the pressure is 29.82 psia.
3. **(a)** 75 psia (5.112 atm); **(b)** it sublimes.
4. Experimental $p^* = 219.9$ mm Hg; predicted 220.9 mm Hg
5. 80.1°C

Section 3.4

1. The partial pressure of the vapor equals the vapor pressure of the gas. Liquid and vapor are in equilibrium.
2. Yes; yes
3. 21°C; benzene
4. 0.0373
5. 4.00 lb
6. **(a)** Both gas; **(b)** some liquid water, residual is gas; **(c)** both gas; **(d)** some liquid water, residual is gas.
7. 190 psia; $C_2H_6 = 0.0677$, $C_3H_8 = 0.660$, i-$C_4H_{10} = 0.2415$, n-$C_4H_{10} = 0.0308$

Section 3.5

1. 0.063 **2.** 57.3% **3.** 86% $\mathcal{RH}$

Section 3.6

1. 53°C (126°F) **2.** 71.2% H_2O **3.** 94.0%; 100%

Section 3.7

1. No, gas and liquid in equilibrium. The triple point in the p–T projection is actually a line on the pVT surface. The pressure and temperature are fixed but the volume is not fixed.
2. Nothing. The points are not realizable equilibrium values.
3. Yes for a liquid–vapor if the process goes above the critical point. Probably not for a solid–vapor unless a solid–liquid region can be formed with a smooth property transition.

4. See Fig. 3.23.
5. **(a)** $C = 3, \mathcal{P} = 1, F = 4$; **(b)** $C = 2, \mathcal{P} = 2, F = 2$
6. No. $C = 2, \mathcal{P} = 6$, F is negative, which is not possible.
7. Two
8. One

Section 4.1

1. Intensive—independent of quantity of material; extensive—dependent of quantity of material. Measurable—temperature, pressure; unmeasurable—internal energy, enthalpy. State variable—difference in value between two states depends only on the states; path variable—difference in two states depends on trajectory reaching in the final state.
2. Heat: energy transfer across a system boundary due to a temperature difference. Work: energy transfer across a system boundary by means of a vector force acting through a vector deplacement on the boundary.
3. **(a)** Open; **(b)** open; **(c)** open; **(d)** closed; **(e)** closed
4. (a)
6. Decrease
7. **(a)** $K_0 = 0$, $P_0 = 4900$ J; **(b)** $K_f = 0$; $P_f = 0$; **(c)** $\Delta K = 0$, $\Delta P = -4900$ J (a decrease); **(d)** 1171 cal, 4.64 Btu
8. Assume $P_{\text{atm}} = 1$ atm is constant; 1.26×10^5 J

Section 4.2

1. $C_p = 4.25 + 0.002T$
2. $\frac{7}{2}R$
3. **(a)** cal/(g mol)(ΔK); **(b)** cal/(g mol)(ΔK)(K); **(c)** cal/(g mol)(ΔK)(K^2); **(d)** cal/(g mol)(ΔK)(K^3)
4. 7.11 cal/(g mol)(K)
5. **(a)** 0.58 cal/(g)(°C); **(b)** 0.49 cal/(g)(°C); experimental = 0.535 cal/(g)(°C)
6. $27{,}115 + 6.55T - 9.98 \times 10^{-4}T^2$

Section 4.3

1. 32,970 J (7880 cal)
2. 192 Btu for 2 lb
3. **(a)** Liquid; **(b)** two phase; **(c)** two phase; **(d)** vapor; **(e)** vapor
4. 13,900 Btu
5. 19,013 J/kg

Section 4.4

1. −334 Btu/lb
2. 6567 Btu

Section 4.5-1

1. (a) $T = 90.19$ K; (b) $m = 1.48 \times 10^7$ g; (c) $x = 3.02 \times 10^{-4}$; (d) 49.6 hr; (e) from a handbook, $T = 100$ K approx (for process at constant volume)
2. (a) Down; (b) probably up, depending on room temperature; (c) down
3. (a) $T_1 = 166.2$°C, $T_2 = 99.63$°C; (b) $Q = -6.40 \times 10^4$ J
4. 594 Btu
5. (a) 0; (b) 0; (c) 0; (d) if ideal gas $\Delta T = 0$, T_2 = room temperature; (e) 0.26 atm
6. 7m

Section 4.5-2

1. 12,200 lb/hr
2. 99°C
3. 1847 watts (2.48 hp)
4. −19.7 Btu/s

Section 4.6

1. (2)
2. Thermal—presumably internal energy or heat—not freely convertible to mechanical energy. The latter types of energy are freely convertible one to the other.
3. Process in which total of freely convertible forms of energy are not reduced.
4. $W = 27.6$ kJ; $Q = -27.6$ kJ; $\Delta E = \Delta H = 0$
5. 38.8 hp

Section 4.7-1

1. −74.83 kJ/g mol CH_4 (−17.88 kcal)
2. 597.32 kJ/g mol C_6H_6 (142.76 kcal)

Section 4.7-2

1. −148.53 k cal/g mol
2. No
3. 230 Btu/ft^3 at 60°F and 30.0 in. Hg

Section 4.7-3

1. No. The result depends on the values in Eq. (4.38) and may be positive or negative.
2. (a) $p \simeq 2$ atm; (b) $Q_v = -3.55$ kcal/g mol CO (evolved)

Section 4.7-4

1. 125 Btu/ft^3 at SC.

Section 4.7-5

1. −248,100 J (−59,299 kcal)
2. 6020 Btu/lb methane
3. 0.52 lb

Section 4.7-6

1. 975K

Section 4.8-1

1. Almost always
2. **(a)** HNO_3, HCl, or H_2SO_4 in water; **(b)** NaCl, KCl, NH_4NO_3 in water
3. **(a)** 25°C and 1 atm; **(b)** 0
4. −4,655 cal/g mol soln (heat transfer is from solution to surroundings)
5. $Q = -1.61 \times 10^6$ Btu

Section 4.8-2

1. $\omega_V = 0.85$; $\omega_L = 0.15$
2. 500 Btu/lb
4. Two phase; for the liquid $\omega_{H_2O} = 0.50$ and $\hat{H} = 8$ Btu/lb; for the vapor $\omega_{H_2O} = 1.00$ and $\hat{H} = 1174$ Btu/lb

Section 4.9

1. t_{DB} = gas temperature; t_{WB} = temperature registered at equilibrium between evaporating water around temperature sensor and surroundings at t_{DB}
2. No
3. See Eqs. (5.21)–(5.26).
4. **(a)** 0.03 kg/kg dry air; **(b)** 1.02 m^3/kg dry air; **(c)** 38°C_{in}; **(d)** 151 kJ/kg dry air; **(e)** 31.5°C
5. **(a)** $\mathcal{H} = 0.0808$ lb H_2O/lb dry air; **(b)** $H = 118.9$ Btu/lb dry air; **(c)** $V = 16.7$ ft^3/lb dry air; **(d)** $\mathcal{H} = 0.0710$ lb H_2O/lb dry air
6. 49,700 Btu
7. **(a)** 1.94×10^6 ft^3/hr; **(b)** 3.00×10^4 ft^3/hr; **(c)** 2.44×10^5 Btu/hr

Section 5.1

1. Yes. See Appendix L.
2. For one phase, $N_{sp} - 1 + 2$ intensive variable (from the phase rule) plus one extensive variable are needed to completely specify a stream.
3. 9
4. Any number from 7 to 11 may be acceptable, depending on assumptions concerning the relations among the pressures in the reactor and mixer streams.
5. Yes

Chapter 6

1. The solution of the differential equation requires the initial conditions to be able to predict the response at other times.
2. Independent
3. Let the derivatives vanish (delete them from the equations).
4. (a)
5. (1), (4), (7), (9), (11); (2), (8); (3), (5), (10), (12); (6)

Appendix B

ATOMIC WEIGHTS AND NUMBERS

TABLE B.1 Relative Atomic Weights, 1965 (Based on the Atomic Mass of $^{12}C = 12$)
The values for atomic weights given in the table apply to elements as they exist in nature, without artificial alteration of their isotopic composition, and, further, to natural mixtures that do not include isotopes of radiogenic origin.

Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	—	Mercury	Hg	80	200.59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	—	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	—
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85	—	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	—	Nobelium	No	102	—
Beryllium	Be	4	9.0122	Osmium	Os	75	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994
Boron	B	5	10.811	Palladium	Pd	46	106.4
Bromine	Br	35	79.904	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Caesium	Cs	55	132.905	Plutonium	Pu	94	—
Calcium	Ca	20	40.08	Polonium	Po	84	—
Californium	Cf	98	—	Potassium	K	19	39.102
Carbon	C	6	12.01115	Praseodym	Pr	59	140.907
Cerium	Ce	58	140.12	Promethium	Pm	61	—
Chlorine	Cl	17	35.453^b	Protactinium	Pa	91	—
Chromium	Cr	24	51.996^b	Radium	Ra	88	—
Cobalt	Co	27	58.9332	Radon	Rn	86	—
Copper	Cu	29	63.546^b	Rhenium	Re	75	186.2
Curium	Cm	96	—	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	84.57
Einsteinium	Es	99	—	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.956
Fermium	Fm	100	—	Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086
Francium	Fr	87	—	Silver	Ag	47	107.868
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.064
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	—
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	59	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lr	103	—	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium	Md	101	—				

SOURCE: *Comptes Rendus*, 23rd IUPAC Conference, 1965, Butterworth's, London, 1965, pp. 177–178.

Appendix C

STEAM TABLES

Note: **Tables in SI and American Engineering units for superheated steam are on the chart in the pocket in the back of the book.**

Absolute pressure = atmospheric pressure − vacuum.

Barometer and vacuum columns may be corrected to mercury at 32°F by subtracting $0.00009 \times (t - 32) \times$ column height, where t is the column temperature in °F.

One inch of mercury at 32°F = 0.4912 lb/in.^{2}

Example:

Barometer reads 30.17 in. at 70°F. Vacuum column reads 28.26 in. at 80°F. Pounds pressure = $(30.17 - 0.00009 \times 38 \times 30.17) - 28.26 - 0.00009 \times 48 \times 28.26) = 1.93$ in. of mercury at 32°F.

Saturation temperature (from table) = 100°F.

TABLE C.1 Saturated Steam: Temperature Table

	Absolute pressure			*Specific volume*			*Enthalpy*	
Temp. Fahr. t	Lb/in.^{2} p	In. Hg 32°F	Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g
32	0.0886	0.1806	0.01602	3305.7	3305.7	0	1075.1	1075.1
34	0.0961	0.1957	0.01602	3060.4	3060.4	2.01	1074.9	1076.0
36	0.1041	0.2120	0.01602	2836.6	2836.6	4.03	1072.9	1076.9
38	0.1126	0.2292	0.01602	2632.2	2632.2	6.04	1071.7	1077.7
40	0.1217	0.2478	0.01602	2445.1	2445.1	8.05	1070.5	1078.6
42	0.1315	0.2677	0.01602	2271.8	2271.8	10.06	1069.3	1079.4
44	0.1420	0.2891	0.01602	2112.2	2112.2	12.06	1068.2	1080.3
46	0.1532	0.3119	0.01602	1965.5	1965.5	14.07	1067.1	1081.2
48	0.1652	0.3364	0.01602	1829.9	1829.9	16.07	1065.9	1082.0
50	0.1780	0.3624	0.01602	1704.9	1704.9	18.07	1064.8	1082.9
52	0.1918	0.3905	0.01603	1588.4	1588.4	20.07	1063.6	1083.7
54	0.2063	0.4200	0.01603	1482.4	1482.4	22.07	1062.5	1084.6
56	0.2219	0.4518	0.01603	1383.5	1383.5	24.07	1061.4	1085.5
58	0.2384	0.4854	0.01603	1292.7	1292.7	26.07	1060.2	1086.3
60	0.2561	0.5214	0.01603	1208.1	1208.1	28.07	1059.1	1087.2
62	0.2749	0.5597	0.01604	1129.7	1129.7	30.06	1057.9	1088.0
64	0.2949	0.6004	0.01604	1057.1	1057.1	32.06	1056.8	1088.9

TABLE C.1 *(cont.)*

	Absolute pressure		*Specific volume*			*Enthalpy*		
Temp. Fahr. t	Lb/in.² p	In. Hg 32°F	Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g
68	0.3388	0.6898	0.01605	927.0	927.0	36.05	1054.5	1090.6
70	0.3628	0.7387	0.01605	868.9	868.9	38.05	1053.4	1091.5
72	0.3883	0.7906	0.01606	814.9	814.9	40.04	1052.3	1092.3
74	0.4153	0.8456	0.01606	764.7	764.7	42.04	1051.2	1093.2
76	0.4440	0.9040	0.01607	718.0	718.0	44.03	1050.1	1094.1
78	0.4744	0.9659	0.01607	674.4	674.4	46.03	1048.9	1094.9
80	0.5067	1.032	0.01607	633.7	633.7	48.02	1047.8	1095.8
82	0.5409	1.101	0.01608	595.8	595.8	50.02	1046.6	1096.6
84	0.5772	1.175	0.01608	560.4	560.4	52.01	1045.5	1097.5
86	0.6153	1.253	0.01609	527.6	527.6	54.01	1044.4	1098.4
88	0.6555	1.335	0.01609	497.0	497.0	56.00	1043.2	1099.2
90	0.6980	1.421	0.01610	468.4	468.4	58.00	1042.1	1100.1
92	0.7429	1.513	0.01611	441.7	441.7	59.99	1040.9	1100.9
94	0.7902	1.609	0.01611	416.7	416.7	61.98	1039.8	1101.8
96	0.8403	1.711	0.01612	393.2	393.2	63.98	1038.7	1102.7
98	0.8930	1.818	0.01613	371.3	371.3	65.98	1037.5	1103.5
100	0.9487	1.932	0.01613	350.8	350.8	67.97	1036.4	1104.4
102	1.0072	2.051	0.01614	331.5	331.5	69.96	1035.2	1105.2
104	1.0689	2.176	0.01614	313.5	313.5	71.96	1034.1	1106.1
106	1.1338	2.308	0.01615	296.5	296.5	73.95	1033.0	1107.0
108	1.2020	2.447	0.01616	280.7	280.7	75.94	1032.0	1107.9
110	1.274	2.594	0.01617	265.7	265.7	77.94	1030.9	1108.8
112	1.350	2.749	0.01617	251.6	251.6	79.93	1029.7	1109.6
114	1.429	2.909	0.01618	238.5	238.5	81.93	1028.6	1110.5
116	1.512	3.078	0.01619	226.2	226.2	83.92	1027.5	1111.4
118	1.600	3.258	0.01620	214.5	214.5	85.92	1026.4	1112.3
120	1.692	3.445	0.01620	203.45	203.47	87.91	1025.3	1113.2
122	1.788	3.640	0.01621	193.16	193.18	89.91	1024.1	1114.0
124	1.889	3.846	0.01622	183.44	183.46	91.90	1023.0	1114.9
126	1.995	4.062	0.01623	174.26	174.28	93.90	1021.8	1115.7
128	2.105	4.286	0.01624	165.70	165.72	95.90	1020.7	1116.6
130	2.221	4.522	0.01625	157.55	157.57	97.89	1019.5	1117.4
132	2.343	4.770	0.01626	149.83	149.85	99.89	1018.3	1118.2
134	2.470	5.029	0.01626	142.59	142.61	101.89	1017.2	1119.1
136	2.603	5.300	0.01627	135.73	135.75	103.88	1016.0	1119.9
138	2.742	5.583	0.01628	129.26	129.28	105.88	1014.9	1120.8
140	2.887	5.878	0.01629	123.16	123.18	107.88	1013.7	1121.6
142	3.039	6.187	0.01630	117.37	117.39	109.88	1012.5	1122.4
144	3.198	6.511	0.01631	111.88	111.90	111.88	1011.3	1123.2
146	3.363	6.847	0.01632	106.72	106.74	113.88	1010.2	1124.1
148	3.536	7.199	0.01633	101.82	101.84	115.87	1009.0	1124.9
150	3.716	7.566	0.01634	97.18	97.20	117.87	1007.8	1125.7
152	3.904	7.948	0.01635	92.79	92.81	119.87	1006.7	1126.6

TABLE C.1 *(cont.)*

	Absolute pressure		*Specific volume*			*Enthalpy*		
Temp. Fahr. t	Lb/in.^{2} p	In. Hg 32°F	Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g
154	4.100	8.348	0.01636	88.62	88.64	121.87	1005.5	1127.4
156	4.305	8.765	0.01637	84.66	84.68	123.87	1004.4	1128.3
158	4.518	9.199	0.01638	80.90	80.92	125.87	1003.2	1129.1
160	4.739	9.649	0.01639	77.37	77.39	127.87	1002.0	1129.9
162	4.970	10.12	0.01640	74.00	74.02	129.88	1000.8	1130.7
164	5.210	10.61	0.01642	70.79	70.81	131.88	999.7	1131.6
166	5.460	11.12	0.01643	67.76	67.78	133.88	998.5	1132.4
168	5.720	11.65	0.01644	64.87	64.89	135.88	997.3	1133.2
170	5.990	12.20	0.01645	62.12	62.14	137.89	996.1	1134.0
172	6.272	12.77	0.01646	59.50	59.52	139.89	995.0	1134.9
174	6.565	13.37	0.01647	57.01	57.03	141.89	993.8	1135.7
176	6.869	13.99	0.01648	56.64	54.66	143.90	992.6	1136.5
178	7.184	14.63	0.01650	52.39	52.41	145.90	991.4	1137.3
180	7.510	15.29	0.01651	50.26	50.28	147.91	990.2	1138.1
182	7.849	15.98	0.01652	48.22	48.24	149.92	989.0	1138.9
184	8.201	16.70	0.01653	46.28	46.30	151.92	987.8	1139.7
186	8.566	17.44	0.01654	44.43	44.45	153.93	986.6	1140.5
188	8.944	18.21	0.01656	42.67	42.69	155.94	985.3	1141.3
190	9.336	19.01	0.01657	40.99	41.01	157.95	984.1	1142.1
192	9.744	19.84	0.01658	39.38	39.40	159.95	982.8	1142.8
194	10.168	20.70	0.01659	37.84	37.86	161.96	981.5	1143.5
196	10.605	21.59	0.01661	36.38	36.40	163.97	980.3	1144.3
198	11.057	22.51	0.01662	34.98	35.00	165.98	979.0	1145.0
200	11.525	23.46	0.01663	33.65	33.67	167.99	977.8	1145.8
202	12.010	24.45	0.01665	32.37	32.39	170.01	976.6	1146.6
204	12.512	25.47	0.01666	31.15	31.17	172.02	975.3	1147.3
206	13.031	26.53	0.01667	29.99	30.01	174.03	974.1	1148.1
208	13.568	27.62	0.01669	28.88	28.90	176.04	972.8	1148.8
210	14.123	28.75	0.01670	27.81	27.83	178.06	971.5	1149.6
212	14.696	29.92	0.01672	26.81	26.83	180.07	970.3	1150.4
215	15.591		0.01674	25.35	25.37	186.10	968.3	1151.4
220	17.188		0.01677	23.14	23.16	188.14	965.2	1153.3
225	18.915		0.01681	21.15	21.17	193.18	961.9	1155.1
230	20.78		0.01684	19.371	19.388	198.22	958.7	1156.9
235	22.80		0.01688	17.761	17.778	203.28	955.3	1158.6
240	24.97		0.01692	16.307	16.324	208.34	952.1	1160.4
245	27.31		0.01696	15.010	15.027	213.41	948.7	1162.1
250	29.82		0.01700	13.824	13.841	218.48	945.3	1163.8
255	32.53		0.01704	12.735	12.752	223.56	942.0	1165.6
260	35.43		0.01708	11.754	11.771	228.65	938.6	1167.3

TABLE C.1 *(cont.)*

	Absolute pressure			*Specific volume*			*Enthalpy*	
Temp. Fahr. t	Lb/in.^{2} p	In. Hg 32°F	Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g
270	41.85		0.01717	10.053	10.070	238.84	931.8	1170.6
275	45.40		0.01721	9.313	9.330	243.94	928.2	1172.1
280	49.20		0.01726	8.634	8.651	249.06	924.6	1173.7
285	53.25		0.01731	8.015	8.032	254.18	921.0	1175.2
290	57.55		0.01735	7.448	7.465	259.31	917.4	1176.7
295	62.13		0.01740	6.931	6.948	264.45	913.7	1178.2
300	67.01		0.01745	6.454	6.471	269.60	910.1	1179.7
305	72.18		0.01750	6.014	6.032	274.76	906.3	1181.1
310	77.68		0.01755	5.610	5.628	279.92	902.6	1182.5
315	83.50		0.01760	5.239	5.257	285.10	898.8	1183.9
320	89.65		0.01765	4.897	4.915	290.29	895.0	1185.3
325	96.16		0.01771	4.583	4.601	295.49	891.1	1186.6
330	103.03		0.01776	4.292	4.310	300.69	887.1	1187.8
335	110.31		0.01782	4.021	4.039	305.91	883.2	1189.1
340	117.99		0.01788	3.771	3.789	311.14	879.2	1190.3
345	126.10		0.01793	3.539	3.557	316.38	875.1	1191.5
350	134.62		0.01799	3.324	3.342	321.64	871.0	1192.6
355	143.58		0.01805	3.126	3.144	326.91	866.8	1193.7
360	153.01		0.01811	2.940	2.958	332.19	862.5	1194.7
365	162.93		0.01817	2.768	2.786	337.48	858.2	1195.7
370	173.33		0.01823	2.607	2.625	342.79	853.8	1196.6
375	184.23		0.01830	2.458	2.476	348.11	849.4	1197.5
380	195.70		0.01836	2.318	2.336	353.45	844.9	1198.4
385	207.71		0.01843	2.189	2.207	358.80	840.4	1199.2
390	220.29		0.01850	2.064	2.083	364.17	835.7	1199.9
395	233.47		0.01857	1.9512	1.9698	369.56	831.0	1200.6
400	247.25		0.01864	1.8446	1.8632	374.97	826.2	1201.2
405	261.67		0.01871	1.7445	1.7632	380.40	821.4	1201.8
410	276.72		0.01878	1.6508	1.6696	385.83	816.6	1202.4
415	292.44		0.01886	1.5630	1.5819	391.30	811.7	1203.0
420	308.82		0.01894	1.4806	1.4995	396.78	806.7	1203.5
425	325.91		0.01902	1.4031	1.4221	402.28	801.6	1203.9
430	343.71		0.01910	1.3303	1.3494	407.80	796.5	1204.3
435	362.27		0.01918	1.2617	1.2809	413.35	791.2	1204.6
440	381.59		0.01926	1.1973	1.2166	418.91	785.9	1204.8
445	401.70		0.01934	1.1367	1.1560	424.49	780.4	1204.9
450	422.61		0.01943	1.0796	1.0990	430.11	774.9	1205.0
455	444.35		0.0195	1.0256	1.0451	435.74	769.3	1205.0
460	466.97		0.0196	0.9745	0.9941	441.42	763.6	1205.0
465	490.43		0.0197	0.9262	0.9459	447.10	757.8	1204.9
470	514.70		0.0198	0.8808	0.9006	452.84	751.9	1204.7
475	539.90		0.0199	0.8379	0.8578	458.59	745.9	1204.5
480	566.12		0.0200	0.7972	0.8172	464.37	739.8	1204.2

TABLE C.1 *(cont.)*

Temp. Fahr. t	*Absolute pressure* Lb/in.^{2} p	In. Hg 32°F	*Specific volume* Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	*Enthalpy* Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g
485	593.28		0.0201	0.7585	0.7786	470.18	733.6	1203.8
490	621.44		0.0202	0.7219	0.7421	476.01	727.3	1203.3
495	650.59		0.0203	0.6872	0.7075	481.90	720.8	1202.7
500	680.80		0.0204	0.6544	0.6748	487.80	714.2	1202.0
505	712.19		0.0206	0.6230	0.6436	493.8	707.5	1201.3
510	744.55		0.0207	0.5932	0.6139	499.8	700.6	1200.4
515	777.96		0.0208	0.5651	0.5859	505.8	693.6	1199.4
520	812.68		0.0209	0.5382	0.5591	511.9	686.5	1198.4
525	848.37		0.0210	0.5128	0.5338	518.0	679.2	1197.2
530	885.20		0.0212	0.4885	0.5097	524.2	671.9	1196.1
535	923.45		0.0213	0.4654	0.4867	530.4	664.4	1194.8
540	962.80		0.0214	0.4433	0.4647	536.6	656.7	1193.3
545	1003.6		0.0216	0.4222	0.4438	542.9	648.9	1191.8
550	1045.6		0.0218	0.4021	0.4239	549.3	640.9	1190.2
555	1088.8		0.0219	0.3830	0.4049	555.7	632.6	1188.3
560	1133.4		0.0221	0.3648	0.3869	562.2	624.1	1186.3
565	1179.3		0.0222	0.3472	0.3694	568.8	615.4	1184.2
570	1226.7		0.0224	0.3304	0.3528	575.4	606.5	1181.9
575	1275.7		0.0226	0.3143	0.3369	582.1	597.4	1179.5
580	1326.1		0.0228	0.2989	0.3217	588.9	588.1	1177.0
585	1378.1		0.0230	0.2840	0.3070	595.7	578.6	1174.3
590	1431.5		0.0232	0.2699	0.2931	602.6	568.8	1171.4
595	1486.5		0.0234	0.2563	0.2797	609.7	558.7	1168.4
600	1543.2		0.0236	0.2432	0.2668	616.8	548.4	1165.2
605	1601.5		0.0239	0.2306	0.2545	624.1	537.7	1161.8
610	1661.6		0.0241	0.2185	0.2426	631.5	526.6	1158.1
615	1723.4		0.0244	0.2068	0.2312	638.9	515.3	1154.2
620	1787.0		0.0247	0.1955	0.2202	646.5	503.7	1150.2
625	1852.4		0.0250	0.1845	0.2095	654.3	491.5	1145.8
630	1919.8		0.0253	0.1740	0.1993	662.2	478.8	1141.0
635	1989.0		0.0256	0.1638	0.1894	670.4	465.5	1135.9
640	2060.3		0.0260	0.1539	0.1799	678.7	452.0	1130.7
645	2133.5		0.0264	0.1441	0.1705	687.3	437.6	1124.9
650	2208.8		0.0268	0.1348	0.1616	696.0	422.7	1118.7
655	2286.4		0.0273	0.1256	0.1529	705.2	407.0	1112.2
660	2366.2		0.0278	0.1167	0.1445	714.4	390.5	1104.9
665	2448.0		0.0283	0.1079	0.1362	724.5	372.1	1096.6
670	2532.4		0.0290	0.0991	0.1281	734.6	353.3	1087.9
675	2619.2		0.0297	0.0904	0.1201	745.5	332.8	1078.3
680	2708.4		0.0305	0.0810	0.1115	757.2	310.0	1067.2
685	2800.4		0.0316	0.0716	0.1032	770.1	284.5	1054.6

TABLE C.1 *(cont.)*

Temp. Fahr. t	Absolute pressure Lb/in.^{2} p	In. Hg 32°F	Specific volume Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g	Enthalpy Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g
690	2895.0		0.0328	0.0617	0.0945	784.2	254.9	1039.1
695	2992.7		0.0345	0.0511	0.0856	801.3	219.1	1020.4
700	3094.1		0.0369	0.0389	0.0758	823.9	171.7	995.6
705	3199.1		0.0440	0.0157	0.0597	870.2	77.6	947.8
705.34*	3206.2		0.0541	0	0.0541	910.3	0	910.3

*Critical temperature. v = specific volume, ft^3/lb. h = enthalpy, Btu/lb.

Source: Combustion Engineering, Inc.

Appendix D

PHYSICAL PROPERTIES OF VARIOUS ORGANIC AND INORGANIC SUBSTANCES

General Sources of Data for Tables on the Physical Properties, Heat Capacities, and Thermodynamic Properties in Appendices D, E, and F

1. Kobe, Kenneth A., and Associates, "Thermochemistry of Petrochemicals," Reprint from *Petroleum Refiner,* Gulf Publishing Company, Houston, Jan. 1949–July 1958. (Enthalpy tables D.2–D. and heat capacities of several gases in Table E.1, Appendix E.)
2. Lange, N. A., *Handbook of Chemistry,* 12th ed., McGraw-Hill, New York, 1979.
3. Maxwell, J. B., *Data Book on Hydrocarbons,* Van Nostrand Reinhold, New York, 1950.
4. Perry, J. H., and C. H. Chilton, eds., *Chemical Engineers' Handbook,* 5th ed., McGraw-Hill, New York, 1973.
5. Rossini, Frederick D., et al., "Selected Values of Chemical Thermodynamic Properties," from *National Bureau of Standards Circular 500,* U.S. Government Printing Office, Washington, D.C., 1952.
6. Rossini, Frederick D., et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, 1953 and subsequent years.
7. Weast, Robert C., *Handbook of Chemistry and Physics,* 59th ed., CRC Press, Boca Raton, Florida, 1979.

TABLE D.1 Physical Properties of Various Organic and Inorganic Substances*

To convert to kcal/g mol multiply by 0.2390; to Btu/lb mol multiply by 430.2.

Compound	Formula	Formula Wt	Sp Gr	Melting Temp. (K)	$\Delta\hat{H}$ Fusion (kJ/g mol)	Normal b.p.(K)	$\Delta\hat{H}$ Vap. at b.p. (kJ/g mol)	T_c (°K)	p_c (atm)	$\hat{V}_c$ (cm³/g mol)	z_c
Acetaldehyde	C_2H_4O	44.05	$0.783^{18°/4°}$	149.5		293.2		461.0			
Acetic acid	CH_3CHO_2	60.05	1.049	289.9	12.09	390.4	24.4	594.8	57.1	171	0.200
Acetone	C_3H_6O	58.08	0.791	178.2	5.69	329.2	30.2	508.0	47.0	213	0.238
Acetylene	C_2H_2	26.04	0.9061(A)	191.7	3.7	191.7	17.5	309.5	61.6	113	0.274
Air			1.000					132.5	37.2		
Ammonia	NH_3	17.03	$0.817^{-79°}$ 0.597(A)	195.40	5.653	239.73	23.35	405.5	111.3	72.5	0.243
Ammonium carbonate	$(NH_4)_2CO_3 \cdot H_2O$	114.11			(decomposes at 331 K)						
Ammonium chloride	NH_4Cl	53.50	$2.53^{17°}$		(decomposes at 623 K)						
Ammonium nitrate	NH_4NO_3	80.05	$1.725^{25°}$	442.8	5.4	(decomposes at 483.2 K)					
Ammonium sulfate	$(NH_4)_2SO_4$	132.14	1.769	786		(decomposes at 786 K after melting)					
Aniline	C_6H_7N	93.12	1.022	266.9		457.4		699	52.4		
Benzaldehyde	C_6H_5CHO	106.12	1.046	247.16		452.16	38.40				
Benzene	C_6H_6	78.11	0.879	278.693	9.837	353.26	30.76	562.6	48.6	260	0.274
Benzoic acid	$C_7H_6O_2$	122.12	$1.316^{28°/4°}$	395.4		523.0					
Benzyl alcohol	C_7H_8O	108.13	1.045	257.8		478.4					
Boron oxide	B_2O_3	69.64	1.85	723	22.0						
Bromine	Br_2	159.83	$3.119^{20°}$ 5.87(A)	265.8	10.8	331.78	31.0	584	102	144	0.306
1, 2-Butadiene	C_4H_6	54.09	$0.652^{20°}$	136.7		283.3		446			
1, 3-Butadiene	C_4H_6	54.09	0.621	164.1		268.6		425	42.7	221	0.271
Butane	$n\text{-}C_4H_{10}$	58.12	0.579	134.83	4.661	272.66	22.31	425.17	37.47	255	0.374
iso-Butane	$\text{iso-}C_4H_{10}$	58.12	0.557	113.56	4.540	261.43	21.29	408.1	36.0	263	0.283

phthalate	see Dibutyl phthalate										
tyric acid	n-$C_4H_8O_2$	88.10	0.958	267		437.1		628	52.0	290	0.293
utyric d	iso-$C_4H_8O_2$	88.10	0.949	226		427.7		609			
um senate	$Ca_3(AsO_4)_2$	398.06		1723							
um rbide	Ca_2C_2	64.10	$2.22^{18°}$	2573							
um rbonate	$CaCO_3$	100.09	2.93	(decomposes at 1098 K)							
um oride	$CaCl_2$	110.99	$2.152^{15°}$	1055	28.4						
	$CaCl_2 \cdot H_2O$	129.01									
	$CaCl_2 \cdot 2H_2O$	147.03									
	$CaCl_2 \cdot 6H_2O$	219.09	$1.78^{17°}$	303.4	37.3	($-6H_2O$ at 473 K)					
um anamide	$CaCN_2$	80.11	2.29								
um nide	$Ca(CN)_2$	92.12									
um droxide	$Ca(OH)_2$	74.10	2.24	($-H_2O$ at 853 K)							
um oxide	CaO	56.08	2.62	2873	50	3123					
um osphate	$Ca_3(PO_4)_2$	310.19	3.14	1943							
um silicate	$CaSiO_3$	117.17	2.915	1803	48.62						
um sulfate ypsum)	$CaSO_4 \cdot 2H_2O$	172.18	2.32	($-1\frac{1}{2}H_2O$ at 301°K)							
on	C	12.010	2.26	3873	46.0	4473					
on dioxide	CO_2	44.01	1.53(A) 1.229 satd. liq. at 5162 kPa	$217.0^{5.2\ atm}$	8.32	(sublimes at 195 K)		304.2	72.9	94	0.275
on ulfide	CS_2	76.14	$1.261^{22°/20°}$ 2.63(A)	161.1	4.39	319.41	26.8	552.0	78.0	170	0.293
on noxide	CO	28.01	0.968(A)	68.10	0.837	81.66	6.042	133.0	34.5	93	0.294
on rachloride	CCl_4	153.84	1.595	250.3	2.5	349.9	30.0	556.4	45.0	276	0.272
ine	Cl_2	70.91	2.49(A)	172.16	6.406	239.10	20.41	417.0	76.1	124	0.276

ces of data are listed at the beginning of Appendix D.

= 20°C/4°C unless specified. Sp gr for gas referred to air (A).

TABLE D.1 *(cont.)*

Compound	Formula	Formula Wt	Sp Gr	Melting Temp. (K)	$\Delta\hat{H}$ Fusion (kJ/g mol)	Normal b.p.(K)	$\Delta\hat{H}$ Vap. at b.p. (kJ/g mol)	T_c (K)	p_c (atm)	$\hat{V}_c$ (cm^3/g mol)	z_c
Chlorobenzene	C_6H_5Cl	112.56	1.107	228		405.26	36.5	632.4	44.6	308	0.265
Chloroform	$CHCl_3$	119.39	1.489^{20°	209.5		334.2		536.0	54.0	240	0.294
Chromium	Cr	52.01	7.1								
Copper	Cu	63.54	8.92	1356.2	13.0	2855	305				
Cumene	C_9H_{12}	120.19	0.862	177.125	7.1	425.56	37.5	636	31.0	440	0.260
Cupric sulfate	$CuSO_4$	159.61	3.605^{15°	(decomposes at 873 K)							
Cyclohexane	C_6H_{12}	84.16	0.779	279.83	2.677	353.90	30.1	553.7	40.4	308	0.274
Cyclopentane	C_5H_{10}	70.13	0.745	179.71	0.6088	322.42	27.30	511.8	44.55	260	0.27
Decane	$C_{10}H_{22}$	142.28	0.730^{20°	243.3		447.0		619.0	20.8	602	0.2476
Dibutyl phthalate	$C_8H_{22}O_4$	278.34	1.045^{21°			613					
Diethyl ether	$(C_2H_5)_2O$	74.12	0.708^{25°	156.86	7.301	307.76	26.05	467	35.6	281	0.261
Ethane	C_2H_6	30.07	1.049(A)	89.89	2.860	184.53	14.72	305.4	48.2	148	0.285
Ethanol	C_2H_6O	46.07	0.789	158.6	5.021	351.7	38.6	516.3	63.0	167	0.248
Ethyl acetate	$C_4H_8O_2$	88.10	0.901	189.4		350.2		523.1	37.8	286	0.252
Ethyl benzene	C_8H_{10}	106.16	0.867	178.185	9.163	409.35	36.0	619.7	37.0	360	0.260
Ethyl bromide	C_2H_5Br	108.98	1.460	154.1		311.4		504	61.5	215	0.320
Ethyl chloride	CH_3CH_2Cl	64.52	0.903^{10°	134.83	4.452	285.43	25	460.4	52.0	199	0.274
3-Ethyl hexane	C_8H_{18}	114.22	0.7169			391.69	34.3	567.0	26.4	466	0.264
Ethylene	C_2H_4	28.05	0.975(A)	103.97	3.351	169.45	13.54	283.1	50.5	124	0.270
Ethylene glycol	$C_2H_6O_2$	62.07	1.113^{19°	260	11.23	470.4	56.9				
Ferric oxide	Fe_2O_3	159.70	5.12	1833		(decomposes at 1833 K)					
Ferric sulfide	Fe_2S_3	207.90	4.3	(decomposes)							
Ferrous sulfide	FeS	87.92	4.84	1466		(decomposes)					
Formaldehyde	H_2CO	30.03	0.815^{-20°	154.9		253.9	24.5				
Formic acid	CH_2O_2	46.03	1.220	281.46	12.7	373.7	22.3				
Glycerol	$C_3H_8O_3$	92.09	1.260^{50°	291.36	18.30	563.2					
Helium	He	4.00	0.1368(A)	3.5	0.02	4.216	0.084	5.26	2.26	58	0.304
Heptane	C_7H_{16}	100.20	0.684	182.57	14.03	371.59	31.69	540.2	27.0	426	0.260

ogen	H_2	2.016	0.06948(A)	13.96	0.12	20.39	0.904	33.3	12.8	65	0.304
ogen loride	HCl	36.47	1.268(A)	158.94	1.99	188.11	16.15	324.6	81.5	87	0.266
ogen oride	HF	20.01	1.15	238		293		503.2			
ogen fide	H_2S	34.08	1.1895(A)	187.63	2.38	212.82	18.67	373.6	88.9	98	0.284
e	I_2	253.8	$4.93^{20°}$	386.5		457.4		826.0			
	Fe	55.85	7.7	1808	15	3073	353				
oxide	Fe_3O_4	231.55	5.2	1867	138	(decomposes at 1867 K after melting)					
	Pb	207.21	$11.337^{20°}$	600.6	5.10	2023	180				
oxide	PbO	223.21	9.5	1159	11.7	1745	213				
nesium	Mg	24.32	1.74	923	9.2	1393	132				
nesium oride	$MgCl_2$	95.23	$2.325^{25°}$	987	43.1	1691	137				
nesium droxide	$Mg(OH)_2$	58.34	2.4	(decomposes at 623 K)							
nesium oxide	MgO	40.32	3.65	3173	77.4	3873					
ury	Hg	200.61	$13.546^{20°}$								
ane	CH_4	16.04	0.554(A)	90.68	0.941	111.67	8.180	190.7	45.8	99	0.290
anol	CH_3OH	32.04	0.792	175.26	3.17	337.9	35.3	513.2	78.5	118	0.222
yl acetate	$C_3H_6O_2$	74.08	0.933	174.3		330.3		506.7	46.3	228	0.254
yl amine	CH_5N	31.06	$0.699^{-11°}$	180.5		266.3^{758mm}		429.9	73.6		
yl oride	CH_3Cl	50.49	1.785(A)	175.3		249		416.1	65.8	143	0.276
yl ethyl tone	C_4H_8O	72.10	0.805	186.1		352.6					
yl clohexane	C_7H_{14}	98.18	0.769	146.58	6.751	374.10	31.7	572.2	34.32	344	0.251
bdenum	Mo	95.95	10.2								
halene	$C_{10}H_8$	128.16	1.145	353.2		491.0					
el	Ni	58.69	$8.90^{20°}$	1725		3173					
c acid	HNO_3	63.02	1.502	231.56	10.47	359	30.30				
benzene	$C_6H_5O_2N$	123.11	1.203	278.7		483.9					
gen	N_2	28.02	12.5(D)	63.15	0.720	77.34	5.577	126.2	33.5	90	0.291
gen xide	NO_2	46.01	1.448	263.86	7.334	294.46	14.73	431.0	100.0	82	0.232

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ces of data are listed at the beginning of Appendix D.

= 20°C/4°C unless specified. Sp gr for gas referred to air (A).

TABLE D.1 *(cont.)*

Compound	Formula	Formula Wt	Sp Gr	Melting Temp. (K)	$\Delta\hat{H}$ Fusion (kJ/g mol)	Normal b.p.(K)	$\Delta\hat{H}$ Vap. at b.p. (kJ/g mol)	T_c (K)	p_c (atm)	$\hat{V}_c$ (cm^3/g mol)	z_c
Nitrogen oxide	NO	30.01	1.0367(A)	109.51	2.301	121.39	13.78	19.2	65.0	58	0.256
Nitrogen pentoxide	N_2O_5	108.02	$1.63^{18°}$	303		320					
Nitrogen tetraoxide	N_2O_4	92	$1.448^{20°}$	263.7		294.3		431.0	99.0		
Nitrogen trioxide	N_2O_3	76.02	1.447^{20}	171		276.5					
Nitrous oxide	N_2O	44.02	$\left.\begin{matrix}1.226^{-89°}\\1.530(A)\end{matrix}\right\}$	182.1		184.4		309.5	71.7	96.3	0.272
n-Nonane	C_9H_{20}	128.25	0.718	219.4		423.8		595	23		
n-Octane	C_8H_{18}	114.22	0.703	216.2		398.7		595.0	22.5	543	0.250
Oxalic acid	$C_2H_2O_4$	90.04	1.90	(decomposes at 459 K)							
Oxygen	O_2	32.00	1.1053(A)	54.40	0.443	90.19	6.820	154.4	49.7	74	0.290
n-Pentane	C_5H_{12}	72.15	$0.630^{18°}$	143.49	8.393	309.23	25.77	469.8	33.3	311	0.269
iso-Pentane	iso-C_5H_{12}	72.15	$0.621^{19°}$	113.1		300.9		461.0	32.9	308	0.268
1-Pentane	C_5H_{10}	70.13	0.641	107.96	4.937	303.13		474	39.9		
Phenol	C_6H_5OH	94.11	$1.071^{25°}$	315.66	11.43	454.56		692.1	60.5		
Phenyl hydrazine	$C_6H_8N_2$	108.14	$1.097^{23°}$	292.76	16.43	51.66					
Phosphoric acid	H_3PO_4	98.00	$1.834^{18°}$	315.51	10.5	($-\frac{1}{2}H_2O$ at 486 K)					
Phosphorus (red)	P_4	123.90	2.20	863	81.17	863	41.84				
Phosphorus (white)	P_4	123.90	1.82	317.4	2.5	553	49.71				
Phosphorus pentoxide	P_2O_5	141.95	2.387	(sublimes at 523 K)							
Propane	C_3H_8	44.09	1.562(A)	85.47	3.524	231.09	18.77	369.9	42.0	200	0.277
Propene	C_3H_6	42.08	1.498(A)	87.91	3.002	225.46	18.42	365.1	45.4	181	0.274
Propionic acid	$C_3H_6O_2$	74.08	0.993	252.2		414.4		612.5	53.0		

hol											
opyl ohol	C_3H_8O	60.09	0.785	183.5		355.4		508.8	53.0	219	0.278
pyl benzene	C_9H_{12}	120.19	0.862	173.660	8.54	432.38	38.2	638.7	31.3	429	0.257
n dioxide	SiO_2	60.09	2.25	1883	8.54	2503					
m bisulfate	$NaHSO_4$	120.07	2.742	455							
m carbonate soda)	$Na_2CO_3 \cdot 10H_2O$	286.15	1.46	306.5		(−H_2O at 306.5 K)					
m carbonate la ash)	Na_2CO_3	105.99	2.533	1127	33.4	(decomposes)					
m chloride	NaCl	58.45	2.163	1081	28.5	1738	171				
m cyanide	NaCN	49.01		835	16.7	1770	155				
m hydorxide	NaOH	40.00	2.130	592	8.4	1663					
m nitrate	$NaNO_3$	85.00	2.257	583	15.9	(decomposes at 653 K)					
m nitrite	$NaNO_2$	69.00	2.168^{0°	544		(decomposes at 593 K)					
m sulfate	Na_2SO_4	142.05	2.698	1163	24.3						
m sulfide	Na_2S	78.05	1.856	1223	6.7						
m sulfite	Na_2SO_3	126.05	2.633^{15°	(decomposes)							
m sulfate	$Na_2S_2O_3$	158.11	1.667								
mbic)	S_8	256.53	2.07	386	10.0	717.76	84				
noclinic)	S_8	256.53	1.96	392	14.17	717.76	84				
chloride no)	S_2CL_2	135.05	1.687	193.0		411.2	36.0				
dioxide	SO_2	64.07	2.264(A)	197.68	7.402	263.14	24.92	430.7	77.8	122	0.269
trioxide	SO_3	80.07	2.75(A)	290.0	24.5	316.5	41.8	491.4	83.8	126	0.262
ic acid	H_2SO_4	98.08	1.834^{18°	283.51	9.87				(decomposes at 613 K)		
ie	$C_6H_5CH_3$	92.13	0.866	178.169	6.619	383.78	33.5	593.9	40.3	318	0.263
	H_2O	18.016	1.00^{4°	273.16	6.009	373.16	40.65	647.4	218.3	56	0.230
ene	C_8H_{10}	106.16	0.864	225.288	11.57	412.26	34.4	619	34.6	390	0.27
ne	C_8H_{10}	106.16	0.880	247.978	13.60	417.58	36.8	631.5	35.7	380	0.26
ne	C_8H_{10}	106.16	0.861	286.423	17.11	411.51	36.1	618	33.9	370	0.25
	Zn	65.38	7.140	692.7	6.673	1180	114.8				
ulfate	$ZnSO_4$	161.44	3.74^{15°	(decomposes at 1013 K)							

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ces of data are listed at the beginning of Appendix D.

= 20°C/4°C unless specified. Sp gr for gas referred to air (A).

TABLE D.2 Enthalpies of Paraffinic Hydrocarbons, C_1–C_6 (J/G MOL)

To convert to Btu/lb mol, multiply by 0.4306.

K	C_1	C_2	C_3	n-C_4	i-C_4	n-C_5	n-C_6
273	0						
291	630	912	1,264	1,709	1,658	2,125	2,545
298	879	1,277	1,771	2,394	2,328	2,976	3,563
300	950	1,383	1,919	2,592	2,522	3,222	3,858
400	4,740	7,305	10,292	13,773	13,623	17,108	20,463
500	9,100	14,476	20,685	27,442	27,325	34,020	40,622
600	14,054	22,869	32,777	43,362	43,312	53,638	64,011
700	19,585	32,342	46,417	61,186	61,220	75,604	90,123
800	25,652	42,718	61,337	80,600	80,767	99,495	118,532
900	32,204	53,931	77,404	101,378	101,754	125,101	148,866
1,000	39,204	65,814	94,432	123,428	123,971	152,213	181,041
1,100	46,567	78,408	112,340	146,607	147,234	180,665	214,764
1,200	54,308	91,504	131,042	170,707	171,418	210,246	249,868
1,300	62,383	105,143	150,331	195,727	196,480	240,872	286,143
1,400	70,709	119,202	170,205	221,375	222,212	272,378	323,465
1,500	79,244	133,678	190,581	247,650	248,571	304,595	361,539
1,600	88,031						
1,800	106,064						
2,000	124,725						
2,200	143,804						
2,500	173,050						

TABLE D.3 Enthalpies of Monoolefinic Hydrocarbons, C_2–C_4 (J/G MOL)

To convert to Btu/lb mol, multiply by 0.4306.

K	Ethylene	Propylene	1-Butene	iso-Butene	*cis*-2-Butene	*trans*-2-Butene
273	0	0	0	0	0	0
291	753	1,104	1,536	1,538	1,354	1,520
298	1,054	1,548	2,154	2,154	1,895	2,125
300	1,125	1,665	2,313	2,322	2,020	2,263
400	6,008	8,882	12,455	12,367	11,070	12,112
500	11,890	17,572	24,765	24,468	22,346	23,995
600	18,648	27,719	38,911	38,425	35,614	37,668
700	26,158	39,049	54,643	53,889	50,542	53,011
800	34,329	51,379	71,755	70,793	66,985	69,705
900	43,053	64,642	89,997	88,826	84,684	87,654
1,000	52,258	78,742	109,286	107,947	103,470	106,692
1,100	61,923	93,470	129,494	123,846	123,260	126,649
1,200	71,964	108,825	150,456	148,866	143,845	147,402
1,300	82,341	124,683	172,087	170,414	165,184	168,824
1,400	92,968	141,000	194,304	188,363	187,150	190,874
1,500	103,888	157,736	217,065	215,183	209,702	213,467

TABLE D.4 Enthalpies of Nitrogen and Some of its Oxides (J/G MOL)

To convert to Btu/lb mol, multiply by 0.4306.

K	N_2	NO	N_2O	NO_2	N_2O_4
273	0	0	0	0	0
291	524	537	681	658	1,384
298	728	746	951	917	1,937
300	786	801	9,660	985	2,083
400	3,695	3,785	13,740	4,865	10,543
500	6,644	6,811	18,179	9,070	19,915
600	9,627	9,895	22,919	13,564	30,124
700	12,652	13,054	27,924	18,305	
800	15,756	16,292	33,154	23,242	
900	18,961	19,597	38,601	28,334	
1,000	22,171	22,970	44,258	33,551	
1,100	25,472	26,392	50,115	38,869	
1,200	28,819	29,861	56,170	44,266	
1,300	32,216	33,371	62,425	49,731	
1,400	35,639	36,915	68,868	55,258	
1,500	39,145	40,488	75,504	60,826	
1,750	47,940	49,505			
2,000	56,902	58,634			
2,250	65,981	67,856			
2,500	75,060	77,127			

TABLE D.5 Enthalpies of Sulfur Compounds (J/G MOL)

To convert to Btu/lb mol, multiply by 0.4306.

K	$S_2(g)$	SO_2	SO_3	H_2S	CS_2
273	0	0	0	0	0
291	579	706	899	607	807
298	805	984	1,255	845	1,125
300	869	1,064	1,338	909	1,217
400	4,196	5,234	6,861	4,372	5,995
500	7,652	9,744	13,033	7,978	11,108
600	11,192	14,514	19,832	11,752	16,455
700	14,790	19,501	27,154	15,706	21,974
800	18,426	24,647	34,748	19,840	27,631
900	22,087	29,915	42,676	24,145	33,388
1,000	25,769	35,275	50,835	28,610	39,220
1,100	29,463	40,706	59,203	33,216	45,103
1,200	33,174	46,191	67,738	37,953	51,044
1,300	36,898	51,714	76,399	42,802	57,027
1,400	40,630	57,320		47,739	63,052
1,500	44,371	62,927		52,802	69,119
1,600	48,116	68,533		57,906	75,186
1,700	51,881	74,182		63,094	81,295
1,800	55,605	79,872		68,324	87,361
1,900	59,370	85,520			

Appendix E

HEAT CAPACITY EQUATIONS

LE E.1 Heat Capacity Equations for Organic and Inorganic Compounds (at Low Pressures)[*]

s: (1) $C_p^\circ = a + b(T) + c(T)^2 + d(T)^3$;

(2) $C_p^\circ = a + b(T) + c(T)^{-2}$.

Units of C_p° are J/(g mol)(K or °C).

To convert to cal/(g mol)(K or °C) = Btu/(lb mol)(°R or °F), multiply by 0.2390.

Compound	Formula	Mol. Wt.	State	Form	T	a	$b \cdot 10^2$	$c \cdot 10^5$	$d \cdot 10^9$	Temp. Range (in T)
one	CH_3COCH_3	58.08	g	1	°C	71.96	20.10	−12.78	34.76	0–1200
ylene	C_2H_2	26.04	g	1	°C	42.43	6.053	−5.033	18.20	0–1200
		29.0	g	1	°C	28.94	0.4147	0.3191	−1.965	0–1500
			g	1	K	28.09	0.1965	0.4799	−1.965	273–1800
onia	NH_3	17.03	g	1	°C	35.15	2.954	0.4421	−6.686	0–1200
onium sulfate	$(NH_4)_2SO_4$	132.15	c	1	K	215.9				275–328
ene	C_6H_6	78.11	l	1	K	−7.27329	77.054	−164.82	1,897.9	279–350
			g	1	°C	74.06	32.95	−25.20	77.57	0–1200
tane	C_4H_{10}	58.12	g	1	°C	89.46	30.13	−18.91	49.87	0–1200
ane	C_4H_{10}	58.12	g	1	°C	92.30	27.88	−15.47	34.98	0–1200
tene	C_4H_8	56.10	g	1	°C	82.88	25.64	− 17.27	50.50	0–1200
um carbide	CaC_2	64.10	c	2	K	68.62	1.19	-8.66×10^{10}	—	298–720
um carbonate	$CaCO_3$	100.09	c	2	K	82.34	4.975	-12.87×10^{10}	—	273–1033
um hydroxide	$Ca(OH)_2$	74.10	c	1	K	89.5				276–373
um oxide	CaO	56.08	c	2	K	41.84	2.03	-4.52×10^{10}		10273–1173
on	C	12.01	$c^{\dagger}$	2	K	11.18	1.095	-4.891×10^{10}		273–1373
on dioxide	CO_2	44.01	g	1	°C	36.11	4.233	−2.887	7.464	0–1500
on monoxide	CO	28.01	g	1	°C	28.95	0.4110	0.3548	−2.220	0–1500
on tetrachloride	CCl_4	153.84	l	1	K	12.285	0.01095	−318.26	3,425.2	273–343
ine	Cl_2	70.91	g	1	°C	33.60	1.367	−1.607	6.473	0–1200
er	Cu	63.54	c	1	K	22.76	0.06117			273–1357
ene opropyl benzene)	C_9H_{12}	120.19	g	1	°C	139.2	53.76	−39.79	120.5	0–1200
exane	C_6H_{12}	84.16	g	1	°C	94.140	49.62	−31.90	80.63	0–1200

hite.

TABLE E.1 (*cont.*)

Compound	Formula	Mol. Wt.	State	Form	T	a	$b \cdot 10^2$	$c \cdot 10^5$	$d \cdot 10^9$	Temp. Range (in T)
Cylopentane	C_5H_{10}	70.13	g	1	°C	73.39	39.28	−25.54	68.66	0–1200
Ethane	C_2H_6	30.07	g	1	°C	49.37	13.92	−5.816	7.280	0–1200
Ethyl alcohol	C_2H_6O	46.07	l	1	K	−325.137	0.041379	−1,403.1	1.7035 × 10⁴	250–400
			g	1	°C	61.34	15.72	−8.749	19.83	0–1200
Ethylene	C_2H_4	28.05	g	1	°C	40.75	11.47	−6.891	17.66	0–1200
Ferric oxide	Fe_2O_3	159.70	c	2	K	103.4	6.711	−17.72 × 10¹⁰	—	273–1097
Formaldehyde	CH_2O	30.03	g	1	°C	34.28	4.268	0.0000	−8.694	0–1200
Helium	He	4.00	g	1	°C	20.8				All
n-Hexane	C_6H_{14}	86.17	l	1	K	31.421	0.97606	−235.37	3,092.7	273–400
			g	1	°C	137.44	40.85	−23.92	57.66	0–1200
Hydrogen	H_2	2.016	g	1	°C	28.84	0.00765	0.3288	−0.8698	0–1500
Hydrogen bromide	HBr	80.92	g	1	°C	29.10	−0.0227	0.9887	−4.858	0–1200
Hydrogen chloride	HCl	36.47	g	1	°C	29.13	−0.1341	0.9715	−4.335	0–1200
Hydrogen cyanide	HCN	27.03	g	1	°C	35.3	2.908	1.092		0–1200
Hydrogen sulfide	H_2S	34.08	g	1	°C	33.51	1.547	0.3012	−3.292	0–1500
Magnesium chloride	$MgCl_2$	95.23	c	1	K	72.4	1.58			273–991
Magnesium oxide	MgO	40.32	c	2	K	45.44	0.5008	−8.732 × 10¹⁰		273–2073
Methane	CH_4	16.04	g	1	°C	34.31	5.469	0.3661	−11.00	0–1200
			g	1	K	19.87	5.021	1.268	−11.00	273–1500
Methyl alcohol	CH_3OH	32.04	l	1	K	−259.25	0.03358	−1,1639	1.4052 × 10⁴	273–400
			g	1	°C	42.93	8.301	−1.87	−8.03	0–700

l cyclohexane	C_7H_{14}	98.18	g	1	°C	121.3	56.53	−37.72	100.8	0–1200
l cyclopentane	C_6H_{12}	84.16	g	1	°C	98.83	45.857	−30.44	83.81	0–1200
acid	HNO_3	63.02	l	1	°C	110.0				25
oxide	NO	30.01	g	1	°C	29.50	0.8188	−0.2925	0.3652	0–3500
en	N_2	28.02	g	1	°C	29.00	0.2199	0.5723	−2.871	0–1500
en dioxide	NO_2	46.01	g	1	°C	36.07	3.97	−2.88	7.87	0–1200
en tetraoxide	N_2O_4	92.02	g	1	°C	75.7	12.5	−11.3		0–300
s oxide	N_2O	44.02	g	1	°C	37.66	4.151	−2.694	10.57	0–1200
n	O_2	32.00	g	1	°C	29.10	1.158	−0.6076	1.311	0–1500
ane	C_5H_{12}	72.15	l	1	K	33.24	192.41	−236.87	17,944	270–350
			g	1	°C	114.8	34.09	−18.99	42.26	0–1200
e	C_3H_8	44.09	g	1	°C	68.032	22.59	−13.11	31.71	0–1200
ene	C_3H_6	42.08	g	1	°C	59.580	17.71	−10.17	24.60	0–1200
n carbonate	Na_2CO_3	105.99	c	1	K	121				288–371
n carbonate	Na_2CO_3 $\cdot 10H_2O$	286.15	c	1	K	535.6				298
	S	32.07	c[‡]	1	K	15.2	2.68			273–368
			c[§]	1	K	18.5	1.84			368–392
ic acid	H_2SO_4	98.08	l	1	°C	139.1	15.59			10–45
dioxide	SO_2	64.07	g	1	°C	38.91	3.904	−3.104	8.606	0–1500
trioxide	SO_3	80.07	g	1	°C	48.50	9.188	−8.540	32.40	0–1000
e	C_7H_8	92.13	l	1	K	1.8083	81.222	−151.27	1,630	270–370
			g	1	°C	94.18	38.00	−27.86	80.33	0–1200
	H_2O	18.016	l	1	K	18.2964	47.212	−133.88	1,314.2	273–373
			g	1	°C	33.46	0.6880	0.7604	−3.593	0–1500

bic. [§]Monoclinic.

TABLE E.2 Heat Capacity Equations for Organic and Inorganic Compounds (at Low Pressures)*

Form: (1) $C_p^\circ = a + b(T) + c(T)^2 + d(T)^3$;

The following relations have the units of cal/(g mol)(°C or K) = Btu/(lb mol)(°F or °R), and T is in °F or °R.

Compound	Formula	Mol. Wt.	State	Form	T	a	$b \cdot 10^2$	$c \cdot 10^5$	$d \cdot 10^9$	Temp. Range (in T)
Acetylene	C_2H_2	26.04								
			g	1	°F	9.89	0.8273	−0.3783	0.7457	32–2200
Air			g	1	°F	6.900	0.02884	0.02429	−0.08052	32–2700
			g	1	°R	6.713	0.02609	0.03540	−0.08052	492–3200
Ammonia	NH_3	17.03								
			g	1	°F	8.2765	0.39006	0.035245	−0.2740	32–2200
Nitrogen	N_2	28.02	g	1	°F	6.895	0.07624	−0.007009		
Oxygen	O_2	32.00	g	1	°F	7.104	0.07851	−0.005528		
Carbon dioxide	CO_2	44.01	g	1	°F	8.448	0.5757	−0.2159	0.3059	0–3500
Carbon monoxide	CO	28.01	g	1	°F	6.865	0.08024	−0.007367		
Cyclohexane	C_6H_{12}	84.16	l	1	°F	37.05				50
					°F	41.26				150
			g		°F	30.84				50
Cyclopentane	C_5H_{10}	70.13	l	1	°F	32.95				100
Toluene	$C_6H_5{\cdot}CH_3$			1	°F	20.869	5.293	−2 .086	3.929	32–2200

*Sources of data are listed at the beginning of Appendix D.

Appendix F

HEATS OF FORMATION AND COMBUSTION

TABLE F.1 Heats of Formation and Heats of Combustion of Compounds at 25°C[*†]

Standard states of products for $\Delta\hat{H}_c^\circ$ are $CO_2(g)$, $H_2O(l)$, $N_2(g)$, $SO_2(g)$, and HCl(aq). To convert to Btu/lb mol, multiply by 430.6.

Compound	Formula	Mol. wt.	State	$-\Delta\hat{H}_f^\circ$ (kJ/g mol)	$-\Delta\hat{H}_c^\circ$ (kJ/g mol)
Acetic acid	CH_3COOH	60.05	l	486.2	871.69
			g		919.73
Acetaldehyde	CH_3CHO	40.052	g	166.4	1192.36
Acetone	C_3H_6O	58.08	aq, 200	410.03	
			g	216.69	1821.38
Acetylene	C_2H_2	26.04	g	−226.75	1299.61
Ammonia	NH_3	17.032	l	67.20	
			g	46.191	382.58
Ammonium carbonate	$(NH_4)_2CO_3$	96.09	c		
			aq	941.86	
Ammonium chloride	NH_4Cl	53.50	c	315.4	
Ammonium hydroxide	NH_4OH	35.05	aq	366.5	
Ammonium nitrate	NH_4NO_3	80.05	c	366.1	
			aq	339.4	
Ammonium sulfate	$(NH_4)SO_4$	132.15	c	1179.3	
			aq	1173.1	
Benzaldehyde	C_6H_5CHO	106.12	l	88.83	
			g	40.0	
Benzene	C_6H_6	78.11	l	−48.66	3267.6

TABLE F.1 *(cont.)*

Compound	Formula	Mol. wt.	State	$-\Delta\hat{H}_f^\circ$ (kJ/g mol)	$-\Delta\hat{H}_c^\circ$ (kJ/g mol)
Bromine	Br_2	159.832	l	0	
			g	−30.7	
n-Butane	C_4H_{10}	58.12	l	147.6	2855.6
			g	124.73	2878.52
Isobutane	C_4H_{10}	58.12	l	158.5	2849.0
			g	134.5	2868.8
1-Butene	C_4H_8	56.104	g	−1.172	2718.58
Calcium arsenate	$Ca_3(AsO_4)_2$	398.06	c	3330.5	
Calcium carbide	CaC_2	64.10	c	62.7	
Calcium carbonate	$CaCO_3$	100.09	c	1206.9	
Calcium chloride	$CaCl_2$	110.99	c	794.9	
Calcium cyanamide	$CaCN_2$	80.11	c	352	
Calcium hydroxide	$Ca(OH)_2$	74.10	c	986.59	
Calcium oxide	CaO	56.08	c	635.6	
Calcium phosphate	$Ca_3(PO_4)_2$	310.19	c	4137.6	
Calcium silicate	$CaSiO_3$	116.17	c	1584	
Calcium sulfate	$CaSO_4$	136.15	c	1432.7	
			aq	1450.5	
Calcium sulfate (gypsum)	$CaSO_4 \cdot 2H_2O$	172.18	c	2021.1	
Carbon	C	12.01	c	0	393.51
			Graphite (β)		
Carbon dioxide	CO_2	44.01	g	393.51	
			l	412.92	
Carbon disulfide	CS_2	76.14	l	−87.86	1075.2
			g	−115.3	1102.6
Carbon monoxide	CO	28.01	g	110.52	282.99
Carbon tetrachloride	CCl_4	153.838	l	139.5	352.2
			g	106.69	384.9
Chloroethane	C_2H_5Cl	64.52	g	105.0	1421.1
			l	41.20	5215.44
Cumene (isopropylbenzene)	$C_6H_5CH(CH_3)_2$	120.19	g	−3.93	5260.59
			c	769.86	
Cupric sulfate	$CuSO_4$	159.61	aq	843.12	
			c	751.4	
Cyclohexane	C_6H_{12}	84.16	g	123.1	3953.0
Cyclopentane	C_5H_{10}	70.130	l	105.8	3290.9
			g	77.23	3319.5
Ethane	C_2H_6	30.07	g	84.667	1559.9
Ethyl acetate	$CH_3CO_2C_2H_5$	88.10	l	442.92	2274.48
Ethyl alcohol	C_2H_5OH	46.068	l	277.63	1366.91
			g	235.31	1409.25
Ethyl benzene	$C_6H_5 \cdot C_2H_5$	106.16	l	12.46	4564.87
			g	−29.79	4607.13
Ethyl chloride	C_2H_5Cl	64.52	g	105	
Ethylene	C_2H_4	28.052	g	−52.283	1410.99
Ethylene chloride	C_2H_3Cl	62.50	g	−31.38	1271.5

TABLE F.1 *(cont.)*

Compound	Formula	Mol. wt.	State	$-\Delta\hat{H}_f^\circ$ (kJ/g mol)	$-\Delta\hat{H}_c^\circ$ (kJ/g mol)
3-Ethyl hexane	C_8H_{18}	114.22	l	250.5	5470.12
			g	210.9	5509.78
Ferric chloride	$FeCl_3$		c	403.34	
Ferric oxide	Fe_2O_3	159.70	c	822.156	
Ferric sulfide	FeS_2	*see* Iron sulfide	*see* Iron sulfide		
Ferrosoferric oxide	Fe_3O_4	231.55	c	1116.7	
Ferrous chloride	$FeCl_2$		c	342.67	303.76
Ferrous oxide	FeO	71.85	c	267	
Ferrous sulfide	FeS	87.92	c	95.06	
Formaldehyde	H_2CO	30.026	g	115.89	563.46
n-Heptane	C_7H_{16}	100.20	l	224.4	4816.91
			g	187.8	4853.48
n-Hexane	C_6H_{14}	86.17	l	198.8	4163.1
			g	167.2	4194.753
Hydrogen	H_2	2.016	g	0	285.84
Hydrogen bromide	HBr	80.924	g	36.23	
Hydrogen chloride	HCl	36.465	g	92.311	
Hydrogen cyanide	HCN	27.026	g	−130.54	
Hydrogen sulfide	H_2S	34.082	g	20.15	562.589
Iron sulfide	FeS_2	119.98	c	177.9	
Lead oxide	PbO	223.21	c	219.2	
Magnesium chloride	$MgCl_2$	95.23	c	641.83	
Magnesium hydroxide	$Mg(OH)_2$	58.34	c	924.66	
Magnesium oxide	MgO	40.32	c	601.83	
Methane	CH_4	16.041	g	74.84	890.4
Methyl alcohol	CH_3OH	32.042	l	238.64	726.55
			g	201.25	763.96
Methyl chloride	CH_3Cl	50.49	g	81.923	766.63†
Methyl cyclohexane	C_7H_{14}	98.182	l	190.2	4565.29
			g	154.8	4600.68
Methyl cyclopentane	C_6H_{12}	84.156	l	138.4	3937.7
			g	106.7	3969.4
Nitric acid	HNO_3	63.02	l	173.23	
			aq	206.57	
Nitric oxide	NO	30.01	g	−90.374	
Nitrogen dioxide	NO_2	46.01	g	−33.85	
Nitrous oxide	N_2O	44.02	g	−81.55	
n-Pentane	C_5H_{12}	72.15	l	173.1	3509.5
			g	146.4	3536.15
Phosphoric acid	H_3PO_4	98.00	c	1281	
			aq ($1H_2O$)	1278	
Phosphorus	P_4	123.90	c	0	
Phosphorus pentoxide	P_2O_5	141.95	c	1506	

TABLE F.1 *(cont.)*

Compound	Formula	Mol. wt.	State	$-\Delta\hat{H}_f^\circ$ (kJ/g mol)	$-\Delta\hat{H}_c^\circ$ (kJ/g mol)
n-Propyl alcohol	C_3H_8O	60.09	g	255	2068.6
n-Propylbenzene	$C_6H_5{\cdot}CH_2{\cdot}C_2H_5$	120.19	l	38.40	5218.2
			g	−7.824	5264.5
Silicon dioxide	SiO_2	60.09	c	851.0	
Sodium bicarbonate	$NaHCO_3$	84.01	c	945.6	
Sodium bisulfate	$NaHSO_4$	120.07	c	1126	
Sodium carbonate	Na_2CO_3	105.99	c	1130	
Sodium chloride	$NaCl$	58.45	c	411.00	
Sodium cyanide	$NaCN$	49.01	c	89.79	
Sodium nitrate	$NaNO_3$	85.00	c	466.68	
Sodium nitrite	$NaNO_2$	69.00	c	359	
Sodium sulfate	Na_2SO_4	142.05	c	1384.5	
Sodium sulfide	Na_2S	78.05	c	373	
Sodium sulfite	Na_2SO_3	126.05	c	1090	
Sodium thiosulfate	$Na_2S_2O_3$	158.11	c	1117	
Sulfur	S	32.07	c (rhombic)	0	
			c (monoclinic)	−0.297	
Sulfur chloride	S_2Cl_2	135.05	l	60.3	
Sulfur dioxide	SO_2	64.066	g	296.90	
Sulfur trioxide	SO_3	80.066	g	395.18	
Sulfuric acid	H_2SO_4	98.08	l	811.32	
			aq	907.51	
Toluene	$C_6H_5{\cdot}CH_3$	92.13	l	−11.99	3909.9
			g	−50.000	3947.9
Water	H_2O	18.016	l	285.840	
			g	241.826	
m-Xylene	$C_6H_4(CH_3)_2$	106.16	l	25.42	4551.86
			g	−17.24	4594.53
o-Xylene	$C_6H_4(CH_3)_2$	106.16	l	24.44	4552.86
			g	−19.00	4596.29
p-Xylene	$C_6H_4(CH_3)_2$	106.16	l	24.43	4552.86
			g	−17.95	4595.25
Zinc sulfate	$ZnSO_4$	161.45	c	978.55	
			aq	1059.93	

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[*] Sources of data are given at the beginning of Appendix D, References 1, 4, and 5.

[†] Standard state HCl(g).

Appendix G

VAPOR PRESSURES

TABLE G.1 Vapor Pressures of Various Substances

Antoine equation:

$$\ln(p^*) = A - \frac{B}{C + T}$$

where p^* = vapor pressure, mm Hg
T = temperature, K
A, B, C = constants

Name	Formula	Range (K)	*A*	*B*	*C*
Acetic acid	$C_2H_4O_2$	290–430	16.8080	3405.57	−56.34
Acetone	C_3H_6O	241–350	16.6513	2940.46	−35.93
Ammonia	NH_3	179–261	16.9481	2132.50	−32.98
Benzene	C_6H_6	280–377	15.9008	2788.51	−52.36
Carbon disulfide	CS_2	288–342	15.9844	2690.85	−31.62
Carbon tetrachloride	CCl_4	253–374	15.8742	2808.19	−45.99
Chloroform	$CHCl_3$	260–370	15.9732	2696.79	−46.16
Cyclohexane	C_6H_{12}	280–380	15.7527	2766.63	−50.50
Ethyl acetate	$C_4H_8O_2$	260–385	16.1516	2790.50	−57.15
Ethyl alcohol	C_2H_6O	270–369	18.5242	3578.91	−50.50
Ethyl bromide	$C_2H_5B_r$	226–333	15.9338	2511.68	−41.44
n-Heptane	C_7H_{16}	270–400	15.8737	2911.32	−56.51
n-Hexane	C_6H_{14}	245–370	15.8366	2697.55	−48.78
Methyl alcohol	CH_4O	257–364	18.5875	3626.55	−34.29
n-Pentane	C_5H_{12}	220–330	15.8333	2477.07	−39.94
Sulfur dioxide	SO_2	195–280	16.7680	2302.35	−35.97
Toluene	$C_6H_5CH_3$	280–410	16.0137	3096.52	−53.67
Water	H_2O	284–441	18.3036	3816.44	−46.13

Appendix H

HEATS OF SOLUTION AND DILUTION

TABLE H.1 Integral Heats of Solution and Dilution at 25°c

Formula	Description	State	$-\Delta\hat{H}_f^\circ$ (kJ/g mol)	$-\Delta\hat{H}^\circ_{\text{soln}}$ (kJ/g mol)	$-\Delta\hat{H}^\circ_{\text{dil}}$ (kJ/g mol)
NaOH	crystalline II		426.726		
	in 3 H_2O	aq	455.612	28.869	28.869
	4 H_2O	aq	461.156	34.434	5.564
	5 H_2O	aq	464.486	37.739	3.305
	10 H_2O	aq	469.227	42.509	4.769
	20 H_2O	aq	469.591	42.844	.334
	30 H_2O	aq	469.457	42.718	.125
	40 H_2O	aq	469.340	42.593	.125
	50 H_2O	aq	469.252	42.509	.083
	100 H_2O	aq	469.059	42.342	.167
	200 H_2O	aq	469.026	42.258	.083
	300 H_2O	aq	469.047	42.300	.041
	500 H_2O	aq	469.097	42.383	.083
	1,000 H_2O	aq	469.189	42.467	.083
	2,000 H_2O	aq	469.285	42.551	.083
	10,000 H_2O	aq	469.448	42.718	.041
	50,000 H_2O	aq	469.528	42.802	.083
	∞ H_2O	aq	469.595	42.886	.083
H_2SO_4		liq	811.319		
	in 0.5 H_2O	aq	827.051	15.731	15.731
	1.0 H_2O	aq	839.394	28.074	12.343
	1.5 H_2O	aq	848.222	36.902	8.823
	2 H_2O	aq	853.243	41.923	5.021
	3 H_2O	aq	860.314	48.994	7.071
	4 H_2O	aq	865.376	54.057	5.063
	5 H_2O	aq	869.351	58.032	3.975
	10 H_2O	aq	878.347	67.027	8.995
	25 H_2O	aq	883.618	72.299	5.272
	50 H_2O	aq	884.664	73.345	1.046
	100 H_2O	aq	885.292	73.973	0.628
	500 H_2O	aq	888.054	76.734	2.761
	1,000 H_2O	aq	889.894	78.575	1.841
	10,000 H_2O	aq	898.388	87.069	2.636
	100,000 H_2O	aq	904.957	93.637	6.568
	500,000 H_2O	aq	906.630	95.311	1.674
	∞ H_2O	aq	907.509	96.190	0.879

SOURCE: F. D. Rossini et al., "Selected Values of Chem. Thermo. Properties," *Natl. Bur. Std. Circ. 500,* U.S. Government Printing Office, Washington, D.C., 1952.

Appendix I

ENTHALPY-CONCENTRATION DATA

TABLE I.1 Enthalpy-concentration Data for the Single-phase Liquid Region and Also the Saturated Vapor of the Acetic Acid-water System at 1 Atmosphere

Reference state: Liquid water at 32°F and 1 atm; solid acid at 32°F and 1 atm.

Liquid or Vapor		Enthalpy—Btu/lb Liquid Solution						Enthalpy Saturated Vapor Btu/lb
Mole Fraction Water	Weight Fraction Water	20°C 68°F	40°C 104°F	60°C 140°F	80°C 176°F	100°C 212°F	Saturated Liquid	
0.00	0.00	93.54	111.4	129.9	149.1	169.0	187.5	361.8
0.05	0.01555	93.96	112.2	130.9	150.4	170.6	186.9	
0.10	0.03225	93.82	112.3	131.5	151.3	172.0	186.5	374.6
0.20	0.0698	92.61	111.9	131.7	152.2	173.8	185.2	395.3
0.30	0.1140	90.60	110.7	131.3	152.6	175.0	183.8	423.7
0.40	0.1667	87.84	108.9	130.6	152.9	176.1	182.9	461.4
0.50	0.231	83.96	106.3	129.1	152.7	177.1	182.4	510.5
0.55	0.268	81.48	104.5	128.1	152.5	177.5	182.3	
0.60	0.3105	78.53	102.5	126.9	152.1	178.0	182.0	573.4
0.65	0.358	75.36	100.2	125.5	151.6	178.3	181.9	
0.70	0.412	71.72	97.71	123.9	151.1	178.8	181.7	656.0
0.75	0.474	67.59	94.73	122.2	149.9	179.3	182.1	
0.80	0.545	62.88	91.43	120.2	149.7	179.9	181.6	767.3
0.85	0.630	57.44	87.56	117.8	148.9	180.5	181.6	
0.90	0.730	51.03	83.02	115.1	147.8	180.8	181.7	921.6
0.95	0.851	43.74	77.65	111.7	146.4	181.2	181.5	
1.00	1.00	36.06	71.91	107.7	143.9	180.1	180.1	1150.4

SOURCE: Data calculated from miscellaneous literature sources and smoothed.

TABLE I.2 Vapor-liquid Equilibrium Data for the Acetic Acid-water System; Pressure = 1 Atmosphere

x Mole Fraction Water in the Liquid	y Mole Fraction Water in the Vapor
0.020	0.035
0.040	0.069
0.060	0.103
0.080	0.135
0.100	0.165
0.200	0.303
0.300	0.425
0.400	0.531
0.500	0.627
0.600	0.715
0.700	0.796
0.800	0.865
0.900	0.929
0.940	0.957
0.980	0.985

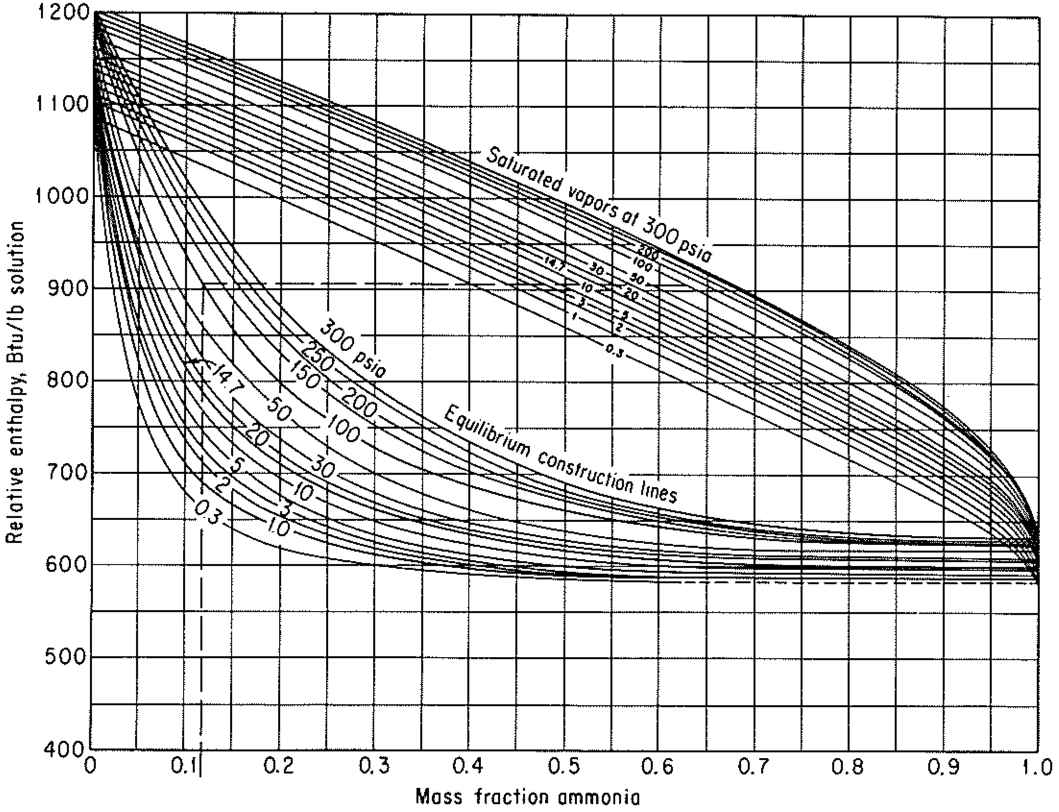
Saturated vapors at 300 psia
200
100
50
30
20
14.7
10
5
3
2
1
0.5
300 psia
250
200
150
100
50
30
20
14.7
10
5
3
2
1.0
0.3
Equilibrium construction lines
Relative enthalpy, Btu/lb solution
1200
1100
1000
900
800
700
600
500
400
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mass fraction ammonia

Figure I.1

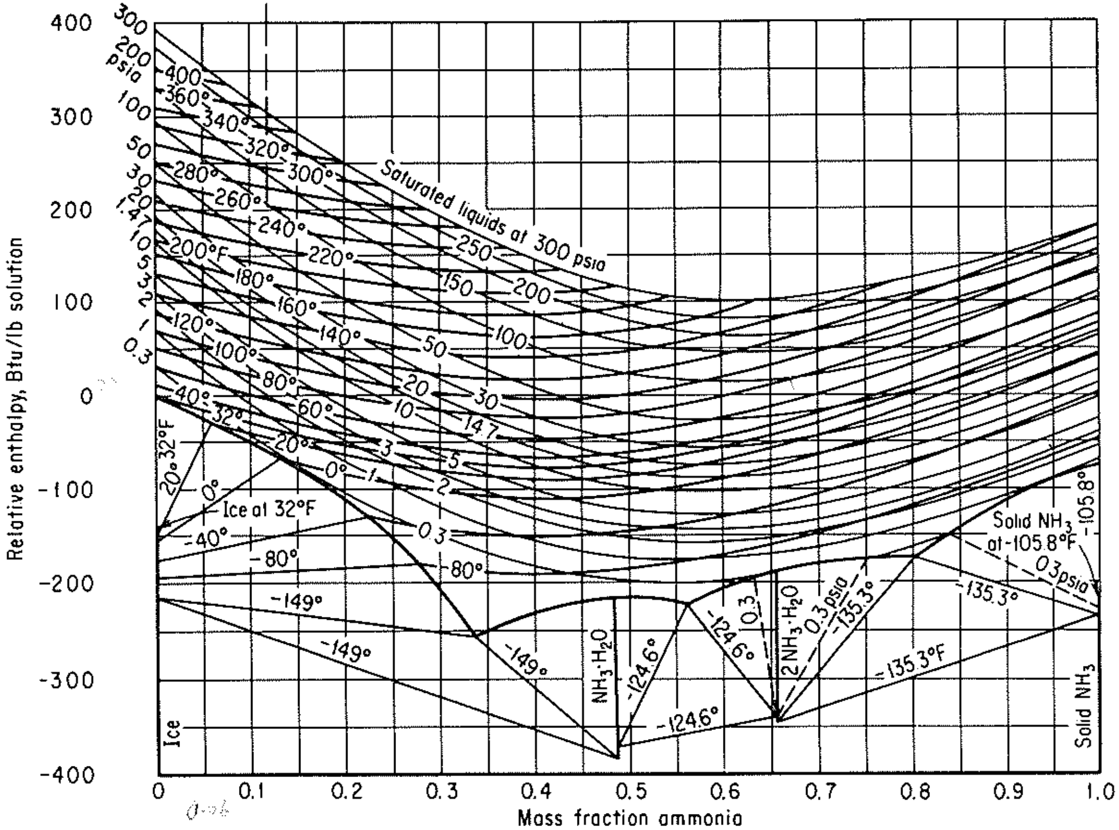

Figure I.1 Enthalpy-concentration chart for NH_3-H_2O.

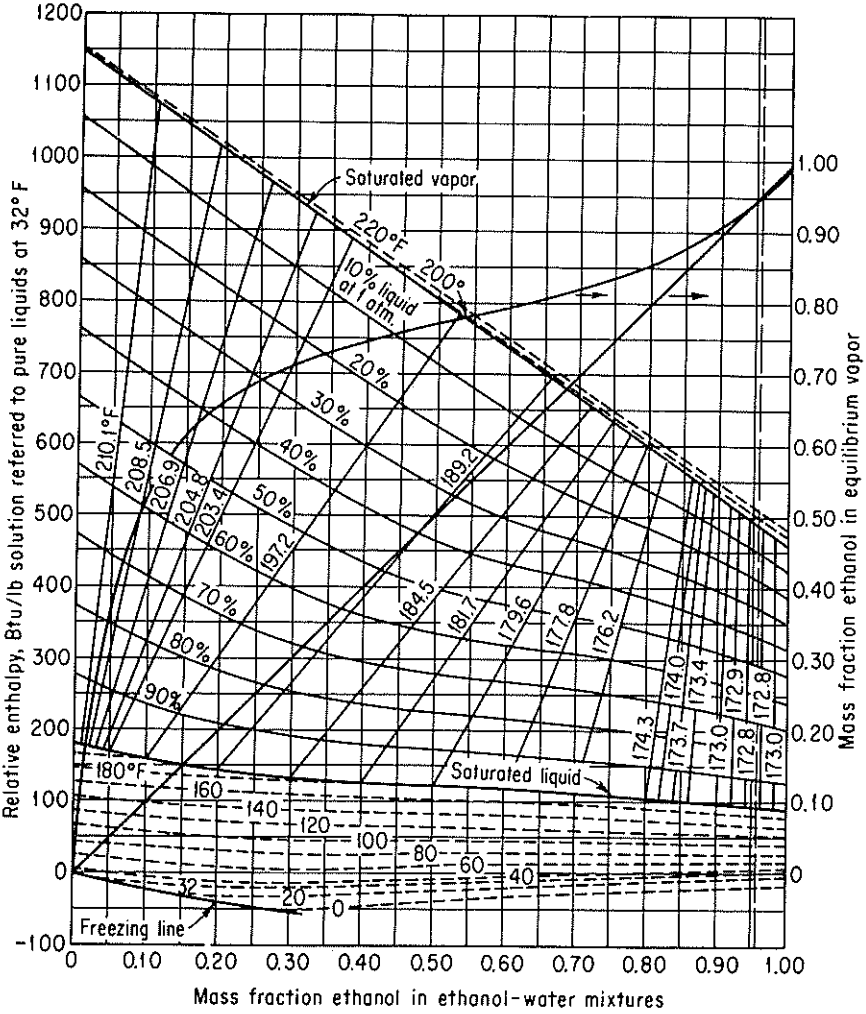

Figure I.2 Enthalpy-composition diagram for the ethanol-water system, showing liquid and vapor phases in equilibrium at 1 atm.

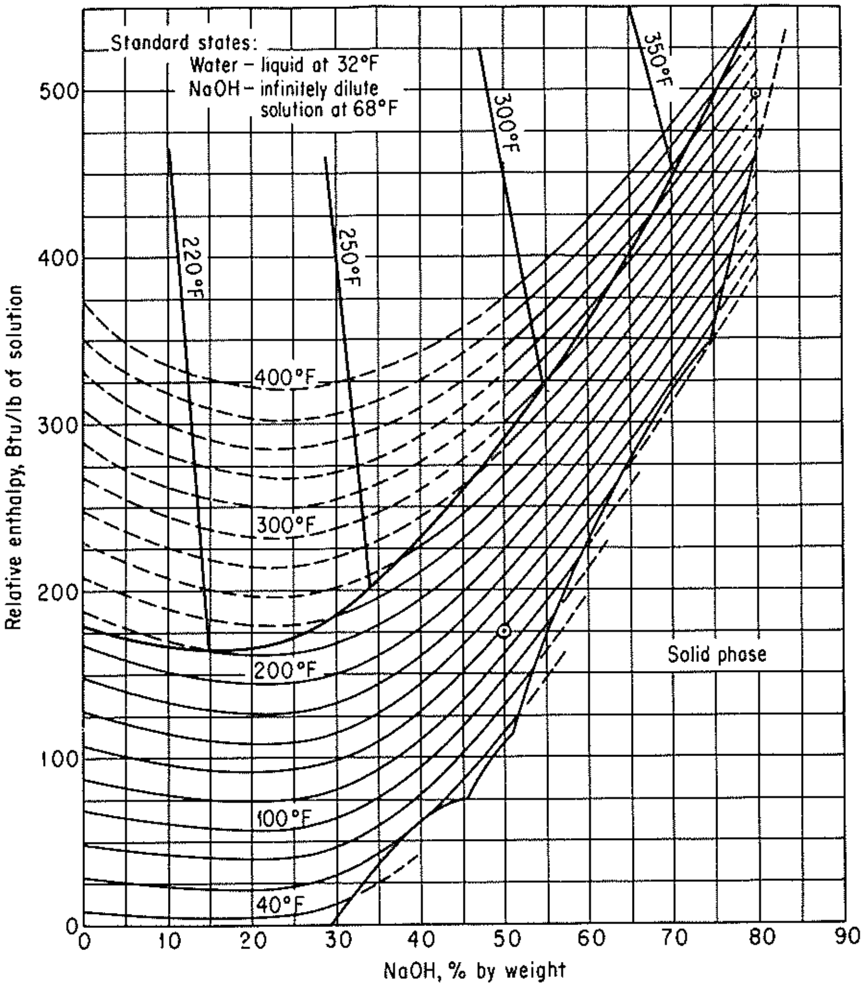

Figure I.3 Enthalpy-concentration chart for sodium hydroxide-water.

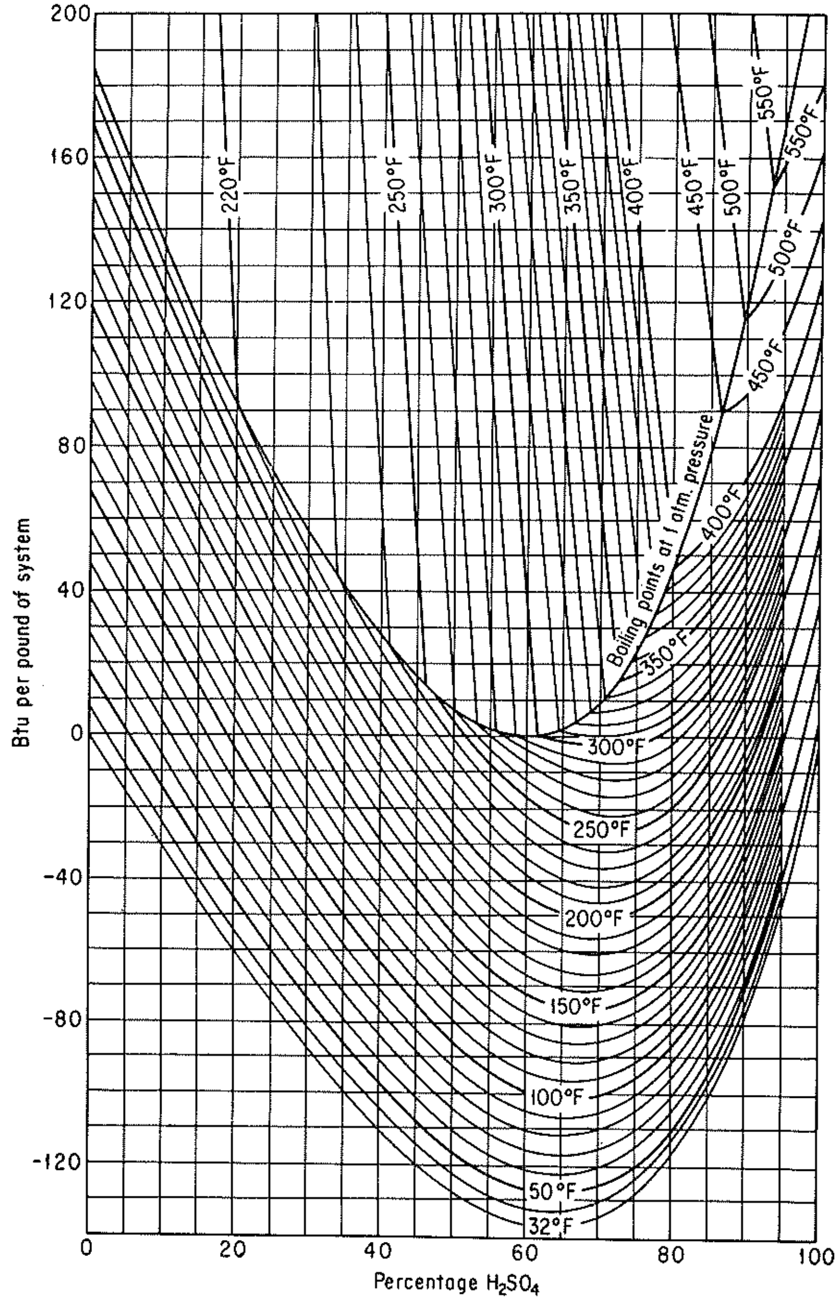

Figure I.4 Enthalpy-concentration of sulfuric acid-water system relative to pure components. (Water and H_2SO_4 at 32°F and own vapor pressure.) (Data from International Critical Tables, © 1943 O. A. Hougen and K. M. Watson.)

Appendix J

THERMODYNAMIC CHARTS

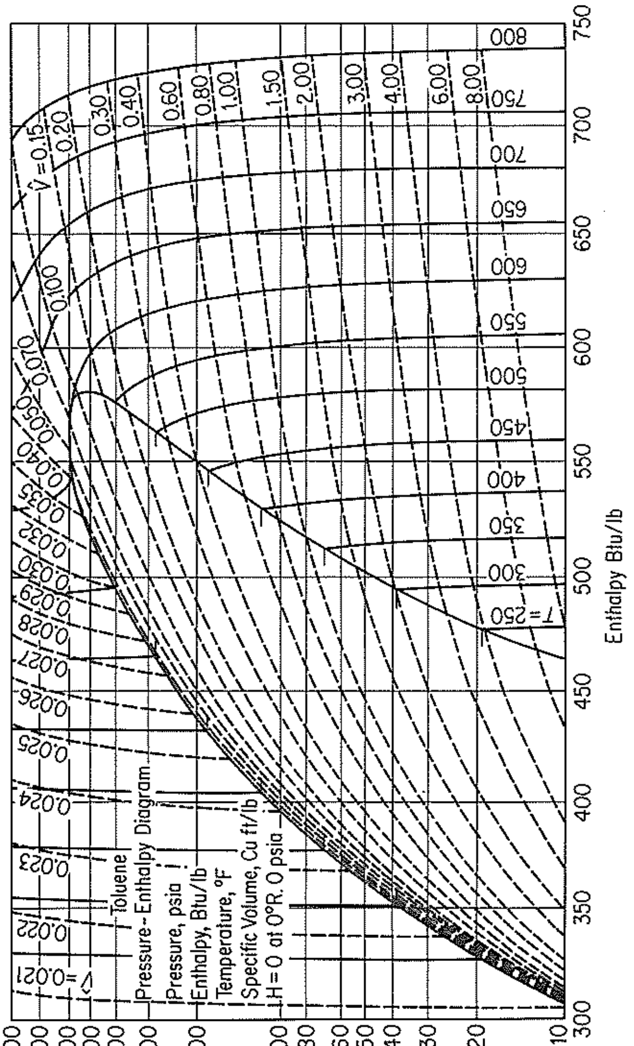

Figure J.1 Enthalpy-pressure chart for toluene.

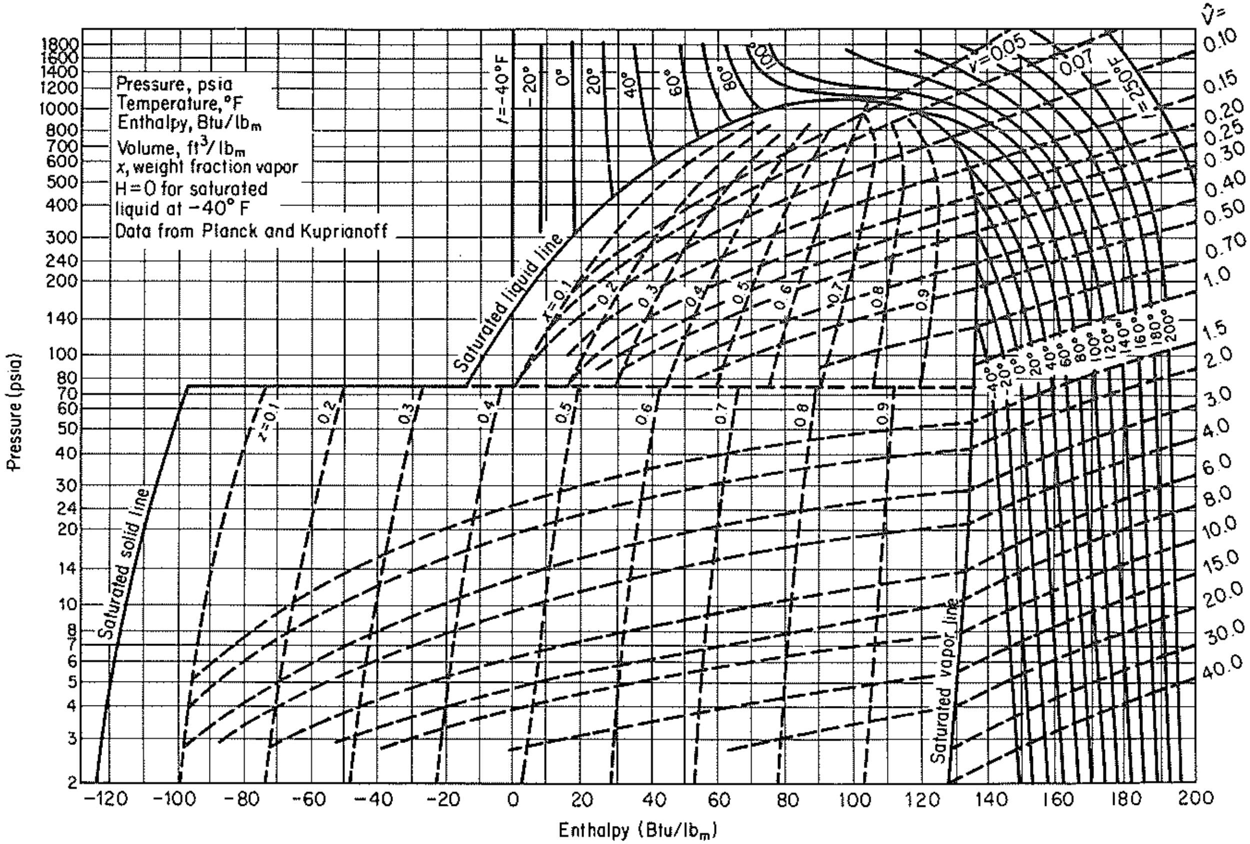

Figure J.2 Pressure-enthalpy chart for carbon dioxide.

Appendix K

PHYSICAL PROPERTIES OF PETROLEUM FRACTIONS

In the early 1930s, tests were developed which characterized petroleum oils and petroleum fractions, so that various physical characteristics of petroleum products could be related to these tests. Details of the tests can be found in *Petroleum Products and Lubricants,* an annual publication of the Committee D-2 of the American Society for Testing Materials.[1] These tests are not scientifically exact, and hence the procedure used in the tests must be followed faithfully if reliable results are to be obtained. However, the tests have been adopted because they are quite easy to perform in the ordinary laboratory and because the properties of petroleum fractions can be predicted from the results. The specifications for fuels, oils, and so on, are set out in terms of these tests plus many other properties, such as the flashpoint, the percent sulfur, and the viscosity.

Over the years various phases of the initial work have been extended and development of a new characterization scheme using the pseudocompound approach is evolving. Daubert[2] summarizes the traditional and new methods insofar as predicting molecular weights, pseudocritical temperature and pressure, acentric factor, and characterization factors.

In this appendix we present the results of the work of Smith and Watson and associates,[3–5] who related petroleum properties to a factor known as the *characterization factor* (sometimes called the *UOP characterization factor*). It is defined as

$$K = \frac{(T_B)^{1/3}}{S}$$

where K = *UOP* characterization factor
T = cubic average boiling point, °R
S = specific gravity at 60°F/60°F

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[1] Report of Committee D-2, ASTM, Philadelphia, annually.

[2] T. E. Daubert, "Property Predictions," *Hydrocarbon Proc.*, pp. 107–110 (March 1980).

[3] R. L. Smith and K. M. Watson, *Ind. Eng. Chem.*, v. 29, p. 1408 (1937).

Other averages for boiling points are used in evaluating K and the other physical properties in this Appendix. (Refer to Danbert or Maxwell[6] for details.) This factor has been related to many of the other simple tests and properties of petroleum fractions, such as viscosity, molecular weight, critical temperature, and percentage of hydrogen, so that it is quite easy to estimate the factor for any particular sample. Furthermore, tables of the UOP characterization factor are available for a wide variety of common types of petroleum fractions as shown in Table K.1 for typical liquids.

Van Winkle[7] discusses the relationships among the volumetric average boiling point, the molal average boiling point, the cubic average boiling point, the weight average boiling point, and the mean average boiling point, and illustrates how the K and other properties of petroleum fractions can be evaluated from experimental data. In Table K.2 are shown the source, boiling-point basis, and any special limitations of the various charts in this appendix.

TABLE K.1 Typical UOP Characterization Factors

Type of stock	K	Type of stock	K
Pennsylvania crude	12.2–12.5	Propane	14.7
Mid-Continent crude	11.8–12.0	Hexane	12.8
Gulf Coast crude	11.0–11.8	Octane	12.7
East Texas crude	11.9	Natural gasoline	12.7–12.8
California crude	10.98–11.9	Light gas oil	10.5
Benzene	9.5	Kerosene	10.5–11.5

Riazi[8] has proposed an equation to predict the basic properties of crude and products based on the equation

$$\text{value of property} = aT_B^b S^c$$

where T_B is the normal boiling point in °R and S is the specific gravity at 60°F; a, b, and c are empirical constants.

For use in computer-aided calculations, the following empirical correlations can be of assistance. Refer to the original references and Daubert[9] for an assessment of the accuracy of each relation with respect to any material.

Heat capacity of hydrogen vapor[10]

$$C_p = (0.0450K - 0.233) + (0.440 + 0.0177K)(10^{-3}t) - 0.1520(10^{-6}t^2)$$

where C_p = specific heat of vapor, Btu/(lb$_m$)(°F)
t = temperature, °F
K = characterization factor

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[6] J. B. Maxwell, *Data Book on Hydrocarbons*, New York; Van Nostrand, 1950.

[7] M. Van Winkle, *Pet. Refiner*, v. 34, pp. 136–138 (June 1955).

[8] M. R. Riazi, Ph.D. dissertation, Pennsylvania State University, 1980.

[9] Daubert, *Hydrocarbon Process.*, p. 107.

[10] J. F. Fallon and K. M. Watson, "Thermal Properties of Hydrocarbons," *Nat. Pet. News (Tech. Sec.)*, p. R-372 (June 7, 1944).

TABLE K.2 Information Concerning Charts in Appendix K

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1. *Specific heats of hydrocarbon liquids*
   Source: J. B. Maxwell, *Data Book on Hydrocarbons,* Van Nostrand Reinhold, New York, 1950, p. 93 (original from M. W. Kellogg Co.).
   Description: A chart of C_p (0.4 to 0.8) vs. t (0 to 1000°F) for petroleum fractions from 0 to 120° API.
   Boiling-point basis: Volumetric average boiling point, which is equal to graphical integration of the differential ASTM distillation curve (Van Winkle's "exact method").
   Limitations: This chart is not valid at temperatures within 50°F of the pseudocritical temperatures.
2. *Vapor pressure of hydrocarbons*
   Source: Maxwell, *Data Book on Hydrocarbons,* p. 42.
   Description: Vapor pressure (0.002 to 100 atm) vs. temperature (50 to 1200°F) for hydrocarbons with normal boiling point of 100 to 1200°F (C_4H_{10} and C_5H_{12} lines shown).
   Boiling-point basis: Normal boiling points (pure hydrocarbons).
   Limitations: These charts apply well to all hydrocarbon series except the lowest-boiling members of each series.
3. *Heat of combustion of fuel oils and petroleum fractions*
   Source: Maxwell, *Data Book on Hydrocarbons,* p. 180.
   Description: Heats of combustion above 60°F (17,000 to 25,000 Btu/lb) vs. gravity (0 to 60°API) with correction for sulfur and inerts included (as shown on chart).
4. *Properties of petroleum fractions*
   Source: O. A. Hougen and K. M. Watson, *Chemical Process Principles Charts,* Wiley, New York, 1946, Chart 3.
   Description: °API(−10 to 90°API) vs. boiling point (100 to 1000°F) with molecular weight, critical temperature, and K factors as parameters.
   Boiling-point basis: Use cubic average boiling point when using the K values; use mean average boiling point when using the molecular weights.
5. *Heats of vaporization of hydrocarbons and petroleum fractions at* 1.0 *atm pressure*
   Source: Hougen and Watson, *Chemical Process Principles Chart,* Chart 68.
   Description: Heats of vaporization (60 to 180 Btu/lb) vs. mean average boiling point (100 to 1000°F) with molecular weight and API gravity as parameters.
   Boiling-point basis: Mean average boiling point.

Heat capacity of hydrocarbon liquids[11]

$$C_p = [(0.355 + 0.128 \times 10^{-2}\text{API}) + (0.503 + 0.117 \times 10^{-2}\text{API})(10^{-3}t)] \times (0.05K + 0.41)$$

where API = gravity degrees API and the other units are the same as for vapor heat capacity.

Specific gravity

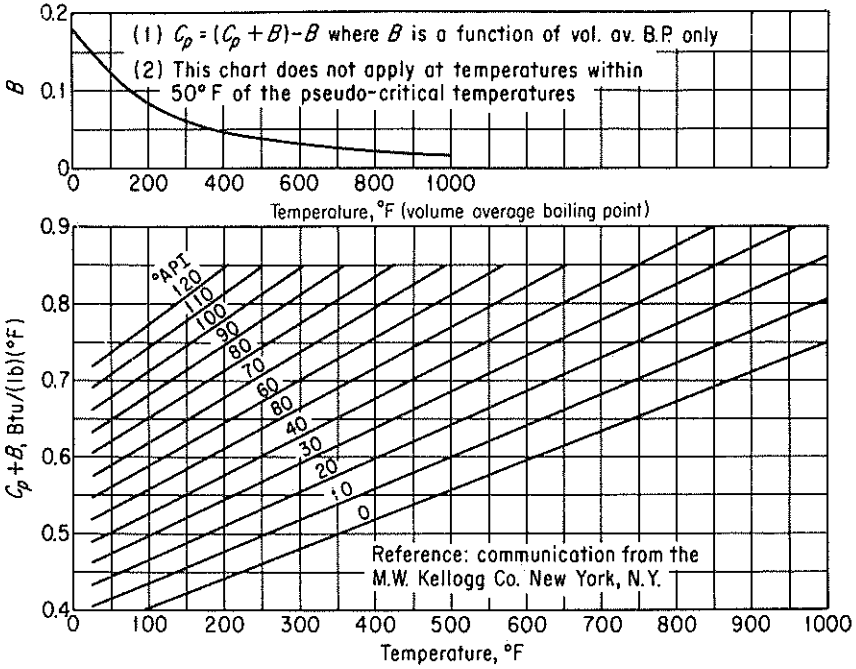

Figure K.1 Specific heats of hydrocarbon liquids.

where sp gr = specific gravity, 60/60°F
°API = degrees API

Pseudo critical temperature[12]

$$t'_c = a_0 + a_1T + a_2T^2 + a_3AT + a_4T^3 + a_5T^2 + a_6A^2T^2$$

where t'_c = pseudo-critical temperature, °R
T = molal average boiling point, °F
A = degrees API
a_i = constants in the correlation (see Table K.3)

Pseudo critical pressure[13]

$$p'_c = b_0 + b_1T + b_2T^2 + b_3AT + b_4T^3 + b_5AT^2 + b_6A^2T + b_7A^2T^2$$

where p'_c = pseudo-critical pressure psia
T = mean average boiling point, °F
A = degrees API
b_i = constants in the correlation (see Table K.3)

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[12] R. H. Cavett. "Physical Data for Distillation Calculations-Vapor-Liquid Equilibria," *Proc. Am. Pet. Inst. Div. Refining.* v. 42, p. 351 (1962).

[13] Ibid.

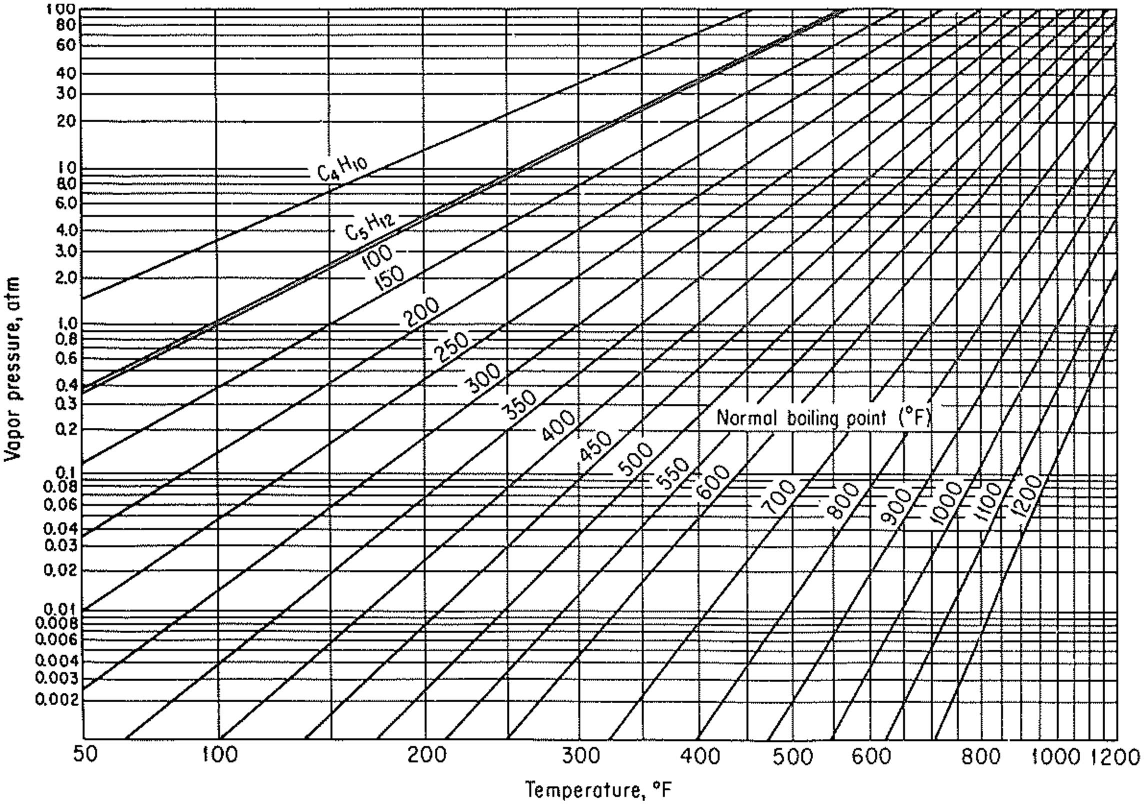


Figure K.2 Vapor pressure of hydrocarbons.

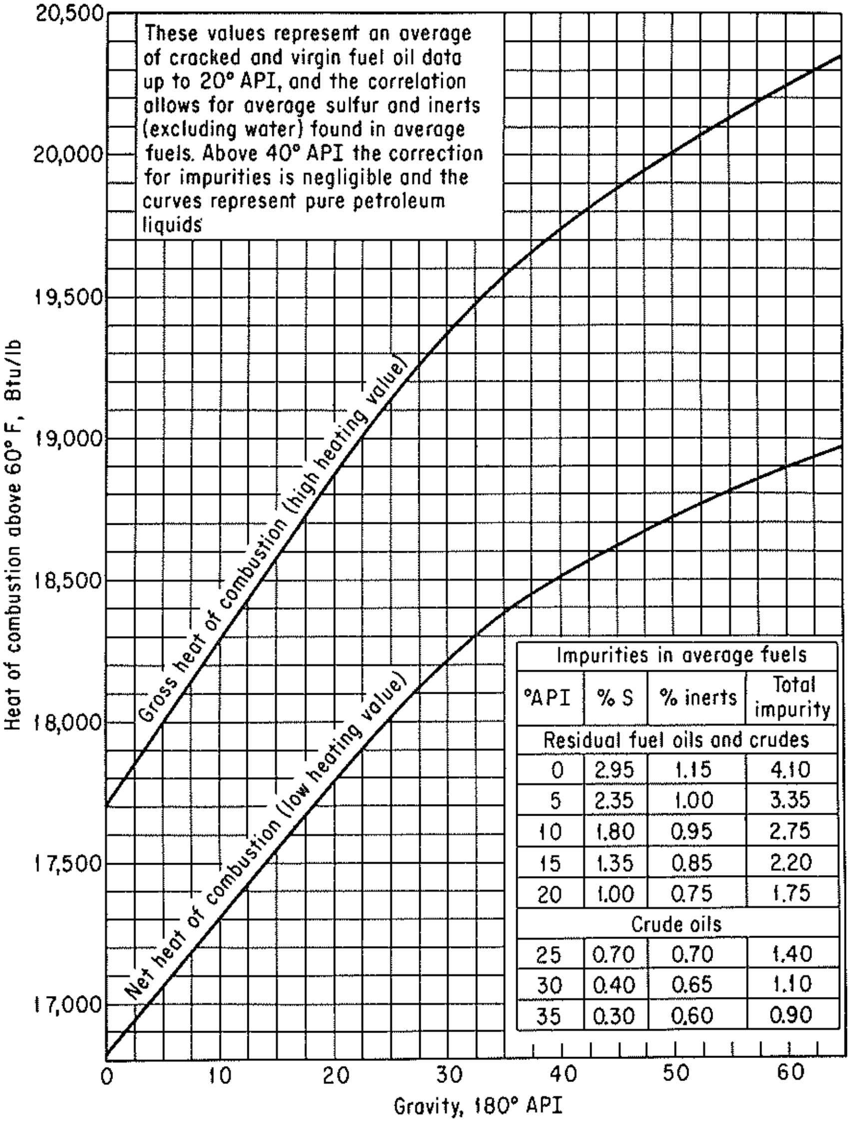
Enthalpy. Calculated as

$$\Delta H = \int_{T_{\text{ref}}}^{\bar{T}_1} C_{p_{\text{liq}}}\,dt + \Delta H_{\text{vaporization at}\,\bar{T}_1} + \int_{\bar{T}_1}^{T} C_{p_{\text{vap}}}\,dt$$

where $\overline{T_1}$ is the mean average boiling point.

TABLE K.3 Constants for Cavett Correlations

i	a_i	b_i
0	768.07121	2.8290406
1	(0.17133693) (10)	(0.94120109) (10^{-3})
2	(−0.10834003) (10^{-2})	(−0.30474749) (10^{-5})
3	(−0.89212579) (10^{-2})	(−0.20876110) (10^{-4})
4	(0.38890584) (10^{-6})	(0.15184103) (10^{-8})
5	(0.53094920) (10^{-5})	(0.11047899) (10^{-7})



These values represent an average of cracked and virgin fuel oil data up to 20° API, and the correlation allows for average sulfur and inerts (excluding water) found in average fuels. Above 40° API the correction for impurities is negligible and the curves represent pure petroleum liquids

Impurities in average fuels

°API	% S	% inerts	Total impurity
Residual fuel oils and crudes			
0	2.95	1.15	4.10
5	2.35	1.00	3.35
10	1.80	0.95	2.75
15	1.35	0.85	2.20
20	1.00	0.75	1.75
Crude oils			
25	0.70	0.70	1.40
30	0.40	0.65	1.10
35	0.30	0.60	0.90

Figure K.3 Heat of combustion of fuel oils and petroleum fractions.

Heat of vaporization[14]

$$\Delta H_{vap} = 2.303\ \{(z_g - z_l)R(T_c)[A + 40T_r^2(T_r - b)e^{-20}(T_r - b)^2]\}$$

where H_{vap} = latent heat of vaporization, Btu/lb_{m}

$z_g - z_l$ = pressure correction (see Fallon and Watson for table of values)

R = universal gas constant

T_c = critical temperature, °R

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[14] Fallon and Watson, "Thermal Properties," p. R-372.

T_r = reduced temperature
A, b = constants (see Fallon and Watson for ways to calculate values)

or (a somewhat less accurate equation)[15]

$$\Delta H_{\text{vap}} = 0.95RT_B\left(\frac{T_B}{T_B - 43}\right)^2\left(\frac{1 - T_r}{1 - T_{rB}}\right)^{0.38}$$

where T_B = molal average boiling point, °R
T_r = reduced temperature
T_{rB} = reduced T_B

Boiling-point relations

(a)

$$\bar{t}_v = \sum_{i=1}^{n} X_{vi}t_{bi}$$

where X_{vi} = volume fraction of the ith component of the petroleum fraction
t_{bi} = normal boiling point of the midpoint of the ith volume fraction, °F or °R
n = number of volume fractions in the distillation curve to characterize the petroleum product

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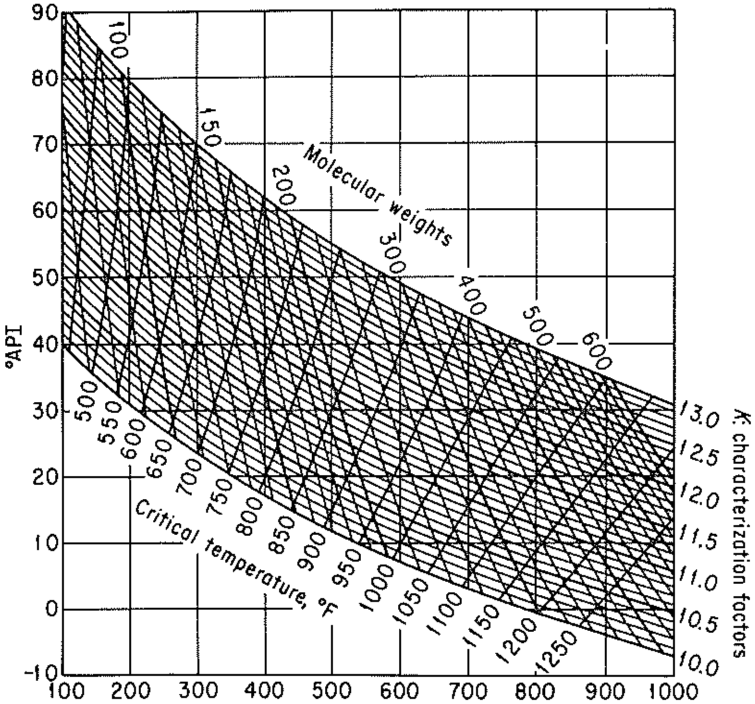
[15] K. M. Watson, "Thermodynamics of the Liquid State," *Ind. Eng. Chem.*, v. 35, p. 398 (1943).



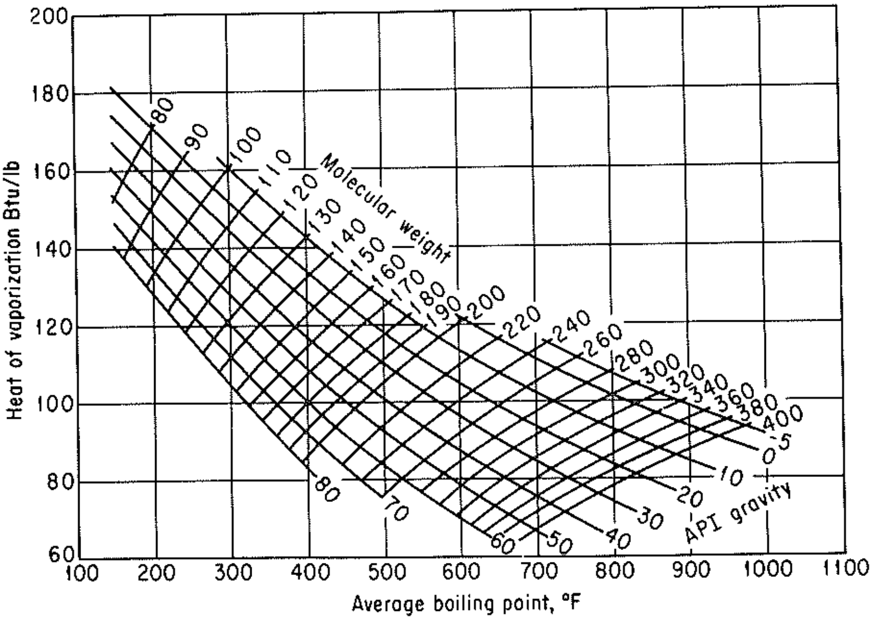


Figure K.5 Heats of vaporization of hydrocarbon and petroleum fractions at 1.0 atmosphere pressure.

(b) $$\bar{t} = (V_1 t_1^{1/3} + V_2 t_2^{1/3} + \cdots + V_n t_n^{1/3})^3$$

where $\bar{t}$ = cubic average boiling point, °F

V_i = volume fraction i of a petroleum product having a normal boiling point of t_i

t_i = temperature, °F

(c) $$\bar{t}_x = x_1 t_1 + x_2 t_2 + \cdots + x_n t_n$$

where $\bar{t}_x$ = molar average boiling point, °F

x_i = the mole fractions of the narrow boiling range with normal boiling points t_i

t_i = temperature, °F

(d) $$\bar{t}_M = \frac{\bar{t}_x + \bar{t}}{2}$$

where $\bar{t}_M$ is the mean average boiling point, °F.

SUPPLEMENTARY REFERENCES

BEHAR, E., "Natural Gas and Crude Oil Characterization," *Proceedings Use of Computers in Chemical Engineering,* April 26–30, 1987, Taormina, Sicily, Pergamon Press, New York, 1988.

DAUBERT, T. E., "Property Predictions," *Hydrocarbon Process.,* p. 107 (March 1980).

Appendix L

SOLUTION OF SETS OF EQUATIONS

L.1 INDEPENDENT LINEAR EQUATIONS

This appendix contains a brief summary of methods of solving linear and nonlinear equations. It is only a summary; for details consult one of the numerous texts on numerical analysis that can be found in any library.

If you write several *linear* material balances, say m in number, they will take the form

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n &= b_1 \\ a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n &= b_2 \\ &\cdots \\ a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mn}x_n &= b_m \end{aligned} \tag{L.1}$$

or in compact matrix notation

$$\mathbf{ax} = \mathbf{b} \tag{L.1a}$$

where $x_1, x_2, \ldots, x_n$ represent the unknown variables, and the a_{ij} and b_i represent the constants and known variables. As an example of Eq. (L.1), we can write the three component mass balances corresponding to Fig. L.1:

$$\begin{aligned} 0.50(100) &= 0.80(P) + 0.05(W) \\ 0.40(100) &= 0.05(P) + 0.925(W) \\ 0.10(100) &= 0.15(P) + 0.025(W) \end{aligned} \tag{L.2}$$

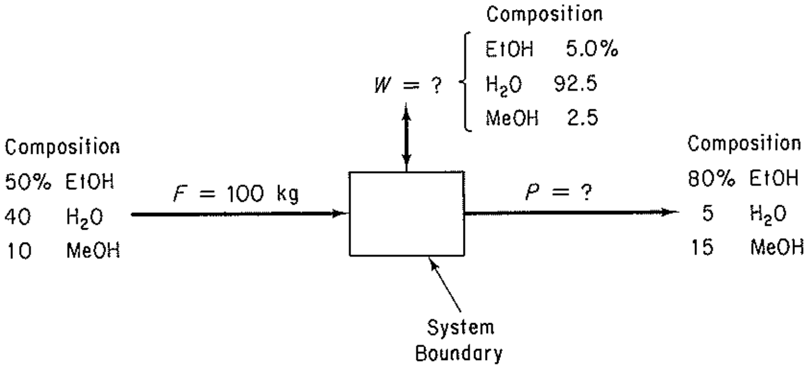


Figure L.1. Data for a material balance.

- **(a)** There is no set of x's that satisfies Eq. (L.1).
- **(b)** There is a unique set of x's that satisfies Eq. (L.1).
- **(c)** There is an infinite number of sets of x's that satisfy Eq. (L.1).

Figure L.2 represents each of the three cases geometrically in two dimensions. Case 1 is usually termed inconsistent, whereas cases 2 and 3 are consistent; but to an engineer who is interested in the solution of practical problems, case 3 is as unsatisfying as case 1. Hence case 2 will be termed *determinate*, and case 3 will be termed *indeterminate*.

To ensure that a system of equations represented by (L.1) has a unique solution, it is necessary to first show that (L.1) is consistent, that is, that the coefficient

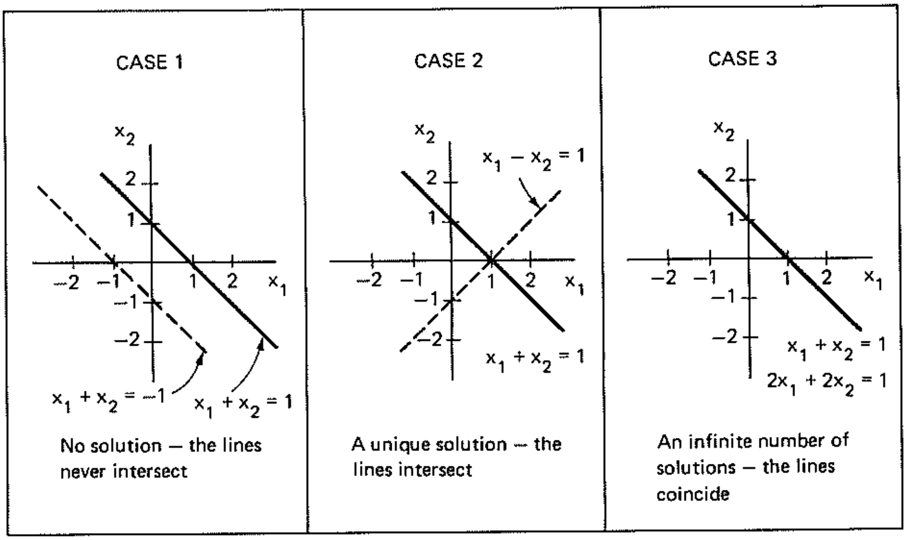


Figure L.2. Types of solutions of linear equations.

matrix **a** and the augmented matrix [**a**, **b**] must have the same rank r. Then, if $n = r$, the system (L.1) is determinate, whereas if $r < n$, as may be the case, then the number $(n - r)$ variables must be specified in some manner or determined by optimization procedures. If the equations are independent, $m = r$.

As an illustration of these ideas, consider the case of the three equations corresponding to the set of Eqs. (L.2) in which we have more equations than unknowns $(m > n)$. The matrix [**a**, **b**] is

$$[\mathbf{a}, \mathbf{b}] = \left[\begin{array}{cc|c} 0.80 & 0.05 & 50 \\ 0.05 & 0.925 & 40 \\ 0.15 & 0.025 & 10 \end{array}\right]$$

Note how the rank of **a** (the rank of a matrix is given by the size of the largest nonzero determinant that can be formed from the matrix), the matrix composed of the first two columns, can at the most be 2 and that the rank of [**a**, **b**] is also 2 because the determinant of [**a**, **b**] is zero. To obtain a consistent set of equations, one of the three material balances must be eliminated, leaving two equations in two unknowns, P and W, that have a unique solution ($m = r = 2$ and $n = 2$). The third equation is a redundant equation. It would probably be best to pick the two equations in which the coefficients were known with the greatest precision.

As another example, consider a set of 10 equations involving 16 unknowns $(m < n)$ so that $(n - m) = 6$. Consequently, six more variables must be specified in some manner before the system of equations becomes determinate.

Next, suppose that you are interested in solving n linear independent equations in n unknown variables:

$$\left.\begin{array}{l} a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n = b_1 \\ a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n = b_2 \\ \qquad \cdots \\ a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n = b_n \end{array}\right\} \mathbf{ax} = \mathbf{b} \tag{L.3}$$

In general there are two ways to solve Eq. (L.3) for $x_1, \ldots, x_n$: elimination techniques and iterative techniques. Both are easily executed by computer programs. In the pocket in the back cover of this book you will find a disk containing Fortran computer programs that can be used in solving sets of linear equations. We shall illustrate the Gauss–Jordan elimination method. Other techniques can be found in texts on matrices, linear algebra, and numerical analysis.

The essence of the Gauss–Jordan method is to transform Eq. (L.3) into Eq. (L.4) by sequential nonunique elementary operations on Eq. (L.3):

$$\begin{array}{l} x_1 + 0 + \cdots + 0 = b_1' \\ 0 + x_2 + \cdots + 0 = b_2' \\ \qquad \cdots \\ 0 + 0 + \cdots + x_n = b_n' \end{array} \tag{L.4}$$

Equation (L.4) has a solution for $x_1, \ldots, x_n$ that can be obtained by inspection.

EXAMPLE L.1

To illustrate the elementary operations that are required to execute the Gauss–Jordan method, consider the following independent set of three equations in three unknowns:

$$4x_1 + 2x_2 + x_3 = 15 \tag{1}$$

$$20x_1 + 5x_2 - 7x_3 = 0 \tag{2}$$

$$8x_1 - 3x_2 + 5x_3 = 24 \tag{3}$$

The augmented matrix is

$$\left[\begin{array}{ccc|c} 4 & 2 & 1 & 15 \\ 20 & 5 & -7 & 0 \\ 8 & -3 & 5 & 24 \end{array}\right]$$

Take the a_{11} element as a pivot. To make it 1 and the other elements in the first column zero, carry out the following elementary operations shown in order for each row:

(a) Subtract $(\frac{20}{4})$ Eq. (1), from Eq. (2).
(b) Subtract $(\frac{8}{4})$ Eq. (1), from Eq. (3).
(c) Multiply Eq. (1) by $\frac{1}{4}$.

to get

$$\left[\begin{array}{ccc|c} 1 & \frac{1}{2} & \frac{1}{4} & \frac{15}{4} \\ 0 & -5 & -12 & -75 \\ 0 & -7 & 3 & -6 \end{array}\right] \qquad \begin{array}{c} \textit{new eq. no.} \\ (1a) \\ (2a) \\ (3a) \end{array}$$

Carry out the following elementary operations to make the pivot element a_{22} equal to 1 and the other elements in the second column equal to zero:

(d) subtract $[(\frac{1}{2})/-5]$ of Eq. (2a), from Eq. (1a).
(e) Subtract $(-7/-5)$ of Eq. (2a), from Eq. (3a).
(f) Multiply Eq. (2a) by $(1/-5)$.

to obtain

$$\left[\begin{array}{ccc|c} 1 & 0 & -\frac{19}{20} & -\frac{15}{4} \\ 0 & 1 & \frac{12}{5} & 15 \\ 0 & 0 & \frac{99}{5} & 99 \end{array}\right] \qquad \begin{array}{c} \textit{new eq. no.} \\ (1b) \\ (2b) \\ (3b) \end{array}$$

Another series of elementary operations (left for you to propose) leads to a 1 for the element a_{33} and zeros for the other two elements in the third column:

$$\left[\begin{array}{ccc|c} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 3 \\ 0 & 0 & 1 & 5 \end{array}\right]$$

The solution to the original set of equations is

$$x_1 = 1$$

$$x_2 = 3$$

$$x_3 = 5$$

as can be observed from the augmentation column.

To obtain good accuracy and avoid numerical errors, the choice of the pivot should be made by scanning all the eligible coefficients and choosing the one with the greatest magnitude for the next pivot. For example, you might choose a_{21} for the first pivot, and then find that a_{31} would be the next pivot and finally a_{22} the last pivot to give

$$\left[\begin{array}{ccc|c} 0 & 1 & 0 & 3 \\ 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 5 \end{array}\right]$$

By exchanging rows 1 and 2, you get exactly the form as (L.4).

EXAMPLE L.2

Determine the number of independent components (which is the same as the number of independent material balances) for a process involving the following two competing reactions:

$$CO + 2H_2 \longrightarrow CH_3OH$$

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

Solution

Prepare a matrix in which the rows are the atomic species for which the balances are to be made and the columns are chemical compounds entering and leaving the process. Each element in the matrix is the number of atoms in the chemical compound.

$$\begin{array}{cc} & \begin{array}{ccccc} H_2 & H_2O & CO & CH_4 & CH_3OH \end{array} \\ \begin{array}{c} H \\ O \\ C \end{array} & \left[\begin{array}{ccccc} 2 & 2 & 0 & 4 & 4 \\ 0 & 1 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 & 1 \end{array}\right] \end{array}$$

Transform the matrix by elementary operations so that there are 1's on the main diagonal starting at the a_{11} position, and only zeros below the main diagonal. The sum of the diagonal elements [starting at the a_{11} position] is the *rank* of the matrix that is equivalent to the number of components. Do you get three for the matrix above?

The number of independent components is not always equal to the number of atomic species, as shown in the next example.

EXAMPLE L.3

Determine the number of independent components for a process involving the following reaction:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Solution

Form the species matrix and determine its rank.

$$\begin{array}{c|ccc} & H_2O & SO_3 & H_2SO_4 \\ \hline H & 2 & 0 & 2 \\ S & 0 & 1 & 1 \\ O & 1 & 3 & 4 \end{array}$$

Are you able to make the transformation to

$$\begin{array}{c|ccc} & H_2O & SO_3 & H_2SO_4 \\ \hline H & 1 & 0 & 1 \\ S & 0 & 1 & 1 \\ O & 0 & 0 & 0 \end{array}$$

Note that the rank of the matrix is 2, not 3; hence only two independent components exist for independent material balances.

To summarize, you will find the information flow diagram in Fig. L.3 helpful. Linear equations can also be solved by the iterative methods described in the next section.

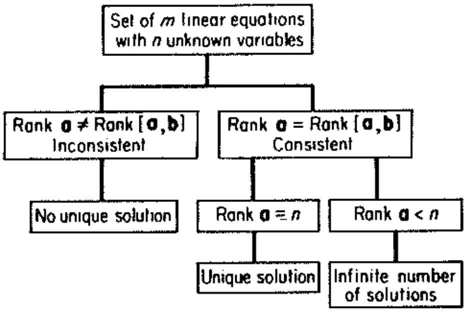


Figure L.3. **a** is the $m \times n$ matrix of the coefficients in the equations, and **[a, b]** is the $m \times (n + 1)$ augmented matrix.

L.2 NONLINEAR INDEPENDENT EQUATIONS

The precise criteria used to ascertain if a linear system of equations is determinate cannot be neatly extended to nonlinear systems of equations. Furthemore, the solution of sets of nonlinear equations requires the use of computer codes that may fail to solve your problem for one or more of a variety of reasons, a few of which are mentioned below. The problem to be solved can be written as

$$\left.\begin{aligned} f_1(x_1, \ldots, x_n) &= 0 \\ f_2(x_1, \ldots, x_n) &= 0 \\ &\cdots \\ f_n(x_1, \ldots, x_n) &= 0 \end{aligned}\right\} \quad \mathbf{f}(\mathbf{x}) = \mathbf{0} \tag{L.5}$$

where each function $f_i(x_1, \ldots, x_n)$ corresponds to a nonlinear function containing one or more of the variable whose values are unknown.

Figure L.4 classifies the major general methods of solving systems of nonlinear equations. Within each category and as combinations of categories you can find innumerable variations and submethods in the literature and available as computer codes. Table L.1 lists several of the computer codes that can be found in most computer center libraries and can be used to solve sets of nonlinear equations. In the disk in the pocket in the back of this book is a simple Fortran code that makes use of the

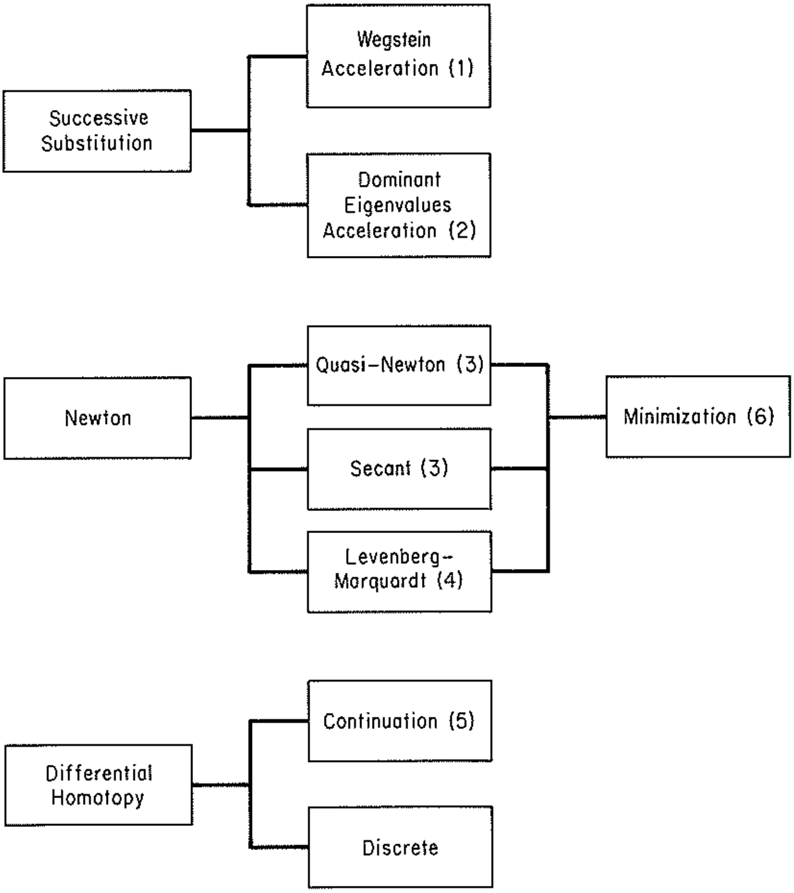


Figure L.4. General categories of techniques to solve nonlinear equations.

References for Figure AL.4

1. Wegstein, J. H., *Commu. ACM*. vol. 1, p. 9 (1958)
2. Orbach, O., and C. M. Crowe, *Can. J. Chem. Eng.*, vol. 49, p. 509 (1971).
3. Dennis, J. E. and R. B. Schnabel, *Numerical Methods for Unconstrained Optimization and Nonlinear Equations*, Prentice-Hall, Englewood Cliffs, N.J., 1983.
4. Marquardt, D., *SIAM J Appld. Math.*, vol. 11, p. 431 (1963).
5. Davidenko, D., *Ukrain Math.*, vol. 5, p. 196 (1953).
6. Edgar, T. F. and D. M. Himmelblau, *Optimization of Chemical Processes*, McGraw-Hill, New York, 1988.

TABLE L.1 Computer Codes to Solve Sets of Nonlinear Equations

Code	Method	Source
CO5NAF	Powell's hybrid	NAG, 1101 31st St., Suite 100, Downers Grove, IL 60515
DEPAR	Homotopy plus Newton	Algorithm 502, *ACM Trans. Math. Software,* v. 2, p. 98 (1976)
HYBRD	Powell's hybrid	MINIPACK, Argonne Natl. Lab., Argonne, IL 60439.
	Homotopy	J. D. Seader, Dept. Chem. Eng., University of Utah, Salt Lake City, UT 84112.
SOSNLE	Brown's method	Numerical Math. Div., Sandia Natl. Lab., Albuquerque, NM 87185
Various	Newton, secant	J. E. Dennis, and R. B. Schnabel, *Numerical Methods for Unconstrained Optimization and Nonlinear Equations,* 1983, Appendix A, Prentice-Hall, Englewood Cliffs, NJ 07632
ZSYSTM	Brent's method	IMSL, 7500 Bellaire Blvd., Houston, TX 77036

basic Newton method. However, it is only a simplified code, and for professional work a more robust code should be employed.

Newton's Method

Refer to equations (L.5). For a single equation (and variable), $f(x) = 0$, Newton's method uses the expansion of $f(x)$ in a first-order Taylor series about a reference point (a starting guess for the solution) x_0.

$$f(x) \approx f(x_0) + \frac{df(x_0)}{dx}(x - x_0) \tag{L.6}$$

Note that Eq. (L.6) is a *linear equation* which is tangent to $f(x)$ at x_0. Examine Fig. L.5. The right-hand side of Eq. (L.6) is equated to zero and the resulting equation solved for $(x - x_0)$.

$$x - x_0 = -\frac{f(x_0)}{df(x_0)/dx} \tag{L.7}$$

For example, suppose that $f(x) = 4x^3 - 1 = 0$, hence $df(x)/dx = 12x^2$. The sequence of steps to apply Newton's method using Eq. (L.7) starting at $x_0 = 3$ would be

$$\begin{aligned} x_1 &= x_0 - \frac{4x^3 - 1}{12x^2} \\ &= 3 - \frac{107}{108} = 2.009259 \end{aligned}$$

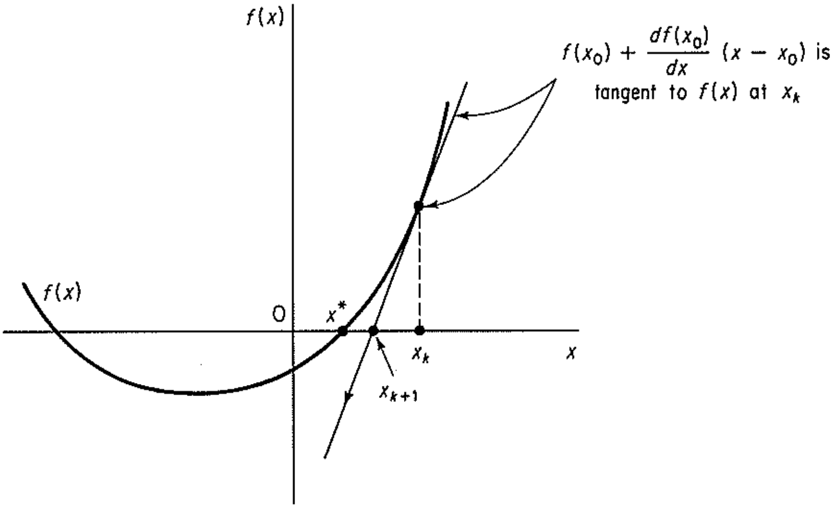


Figure L.5. Newton's Method applied to the solution of $f(x) = 0$ starting at x_k. x_{k+1} is the next reference point for linearization. x^* is the solution.

$$x_2 = 2.00926 - \frac{31.4465}{48.4454} = 1.36015$$

Additional iterations yield the following values for x_k:

k	x_k
0	3.00000
1	2.009259
2	1.3601480
3	0.9518103
4	0.7265254
5	0.6422266
6	0.6301933
7	0.6299606
8	0.6299605
9	0.6299605

so that the solution is given with increasing precision as k increases.

Suppose that two independent equations in two variables whose values are to be determined are

$$\begin{aligned} f_1(x_1, x_2) &= 0 \\ f_2(x_1, x_2) &= 0 \end{aligned} \qquad \text{(L.8)}$$

To apply Newton's method, expand each equation as a first-order Taylor series to get a set of linear equations at the point (x_{10}, x_{20}).

$$
\begin{aligned}
f_1(x_1, x_2) &\simeq f_1(x_{10}, x_{20}) + \frac{\partial f_1(x_{10}, x_{20})}{\partial x_1}(x_1 - x_{10}) + \frac{\partial f_1(x_{10}, x_{20})}{\partial x_2}(x_2 - x_{20}) \\
f_2(x_1, x_2) &\simeq f_2(x_{10}, x_{20}) + \frac{\partial f_2(x_{10}, x_{20})}{\partial x_1}(x_1 - x_{10}) + \frac{\partial f_2(x_{10}, x_{20})}{\partial x_2}(x_2 - x_{20})
\end{aligned}
\tag{L.9}
$$

Let the partial derivatives be designed by the constants $a_{ij} = \partial f_i/\partial x_j$ to simplify the notation, and let $(x_i - x_{i0}) = \Delta x_i$. Then, after equating the right-hand side of Eqs. (L.9) to zero, they become

$$
\begin{aligned}
a_{11}\,\Delta x_1 + a_{12}\,\Delta x_2 &= -f_1(x_{10}, x_{20}) \\
a_{21}\,\Delta x_1 + a_{22}\,\Delta x_2 &= -f_2(x_{10}, x_{20})
\end{aligned}
\tag{L.10}
$$

These equations are linear and can be solved by a linear equation solver to get the next reference point (x_{11}, x_{21}). Iteration is continued until a solution of satisfactory precison is reached. Of course, a solution may not be reached, as illustrated in Fig. L.6c, or may not be reached because of round-off or truncation errors. If the Jacobian matrix [see Eq. (L.11) below] is singular, the linearized equations may have no solution or a whole family of solutions, and Newton's method probably will fail to obtain a solution. It is quite common for the Jacobian matrix to become ill-conditioned because if x_0 is far from the solution or the nonlinear equations are badly scaled, the correct solution will not be obtained.

The analog of (L.10) in matrix notation is

$$
\mathbf{J}_k(\mathbf{x} - \mathbf{x}_k) = -\mathbf{f}(\mathbf{x}_k) \tag{L.11}
$$

where $\mathbf{J}$ is the Jacobian matrix (the matrix whose elements are composed of the first partial derivatives of the equations with respect to the variables). For two equations

$$
\mathbf{J} = \begin{bmatrix} \partial f_1(\mathbf{x})/\partial x_1 & \partial f_1(\mathbf{x})/\partial x_2 \\ \partial f_2(\mathbf{x})/\partial x_1 & \partial f_2(\mathbf{x})/\partial x_2 \end{bmatrix} \qquad \begin{aligned} \mathbf{x} &= \begin{bmatrix} \Delta x_1 \\ \Delta x_2 \end{bmatrix} \\ \mathbf{f} &= \begin{bmatrix} f_1 \\ f_2 \end{bmatrix} \end{aligned}
$$

Quasi-Newton Methods

A quasi-Newton method in general is one that imitates Newton's method. If $f(x)$ is not given by a formula, or the formula is so complicted that analytical derivatives cannot be formulated, you can replace df/dx in Eq. (L.7) with a finite difference approximation

$$
x_{k+1} = x_k - \frac{f(x)}{[f(x + h) - f(x - h)]/2h} \tag{L.12}
$$

A central difference has been used in Eq. (L.12) but forward differences or any other difference scheme would suffice *as long as the step size h is selected to match the difference formula and the computer (machine) precision* for the computer on which the calculations are to be executed.

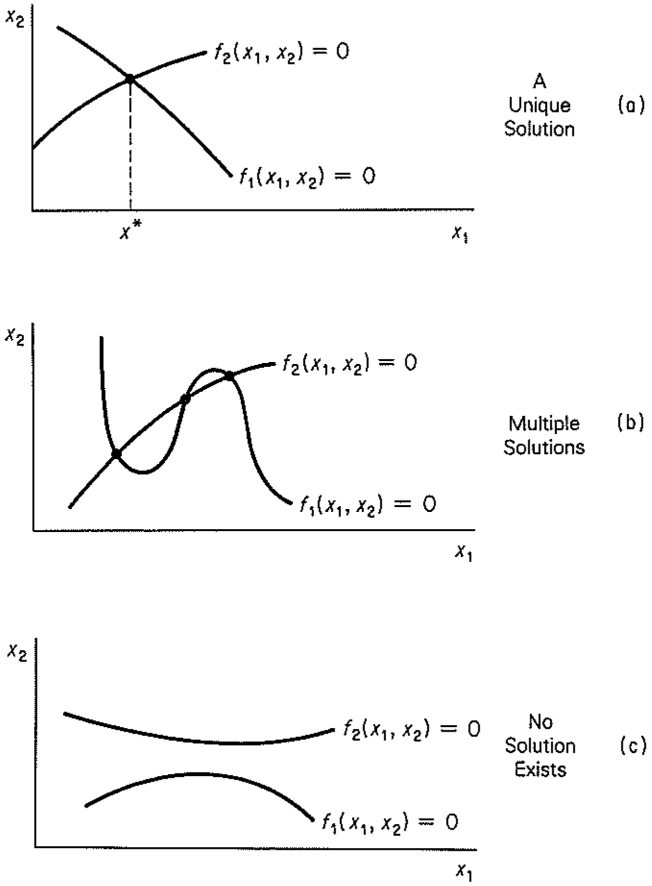


Figure L.6. Possible cases for the solution of two independent nonlinear equations $f_1(x_1, x_2) = 0$ and $f_2(x_1, x_2) = 0$ in two unknown variables.

Other than the problem of the selection of the value of h, the only additional disadvantage of a quasi-Newton method is that additional function evaluations are needed on each iteration k. Eq. (L.12) can be applied to sets of equations if the partial derivatives are replaced by finite difference approximations.

Secant Methods

In the secant method the approximate model analogous to the right hand side of Eq. (4.6) (equated to zero) is

$$f(x_k) + m(x - x_k) = 0 \tag{L.13}$$

where m is the slope of the line connecting the a point x_k and a second point x_q, given by

$$m = \frac{f(x_q) - f(x_k)}{x_q - x_k}$$

Thus the secant method, imitates Newton's method (in this sense the secant method is also a quasi-Newton method (see Figure L.7)

Secant methods start out by using two points x_k and x_q spanning the interval of x, points at which the values of $f(x)$ are of opposite sign. The zero of $f(x)$ is predicted by

$$\tilde{x} = x_q - \frac{f(x_q)}{\dfrac{f(x_q) - f(x_k)}{x_q - x_k}} \tag{L.14}$$

The two points retained for the next step are $\tilde{x}$ and either x_q or x_k, the choice being made so that the pair of values $f(\tilde{x})$, and either $f(x_k)$ or $f(x_q)$, have opposite signs to maintain the bracket on x^*. (This variation is called "regula falsi" or the method of false position.) In Figure L.7, for the $(k + 1)$st stage, $\tilde{x}$ and x_q would be selected as the end points of the secant line. Secant methods may seem crude, but they work well in practice. The details of the computational aspects of a sound algorithm to solve multiple equations by the secant method are too lengthy to outline here (particularly the calculation of a new Jacobian matrix from the former one; instead refer to Dennis and Schnabel[a]).

The application of Eq. (L.14) yields the following results for $f(x) = 4x^3 - 1 = 0$ starting at $x_k = -3$ and $x_q = 3$. Some of the values of $f(x)$ and x during the search are shown below; note that x_q remains unchanged in order to maintain the bracket with $f(x) > 0$.

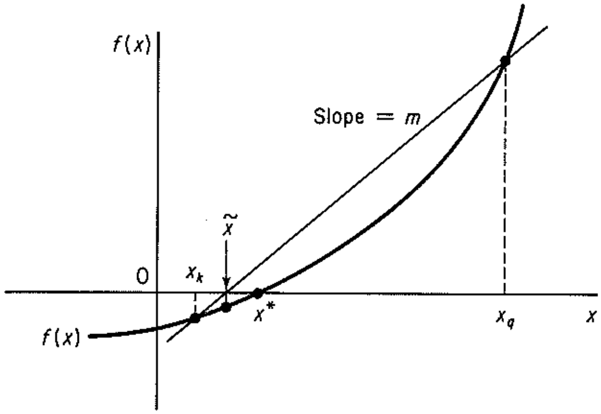


Figure L.7. Secant Method for the solution of $f(x) = 0$. x^* is the solution, $\tilde{x}$ the approximate to x^*, and x_q and x_k the starting points for iteration k of the secant method.

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[a] Dennis, J. E. and R. B. Schnabel, *Numerical Methods for Unconstrained Optimization and Nonlinear Equations* (1983, Appendix A) Prentice-Hall, Englewood Cliffs, NJ 07632.

k	x_q	x_k	$f(x_k)$
0	3	-3	-109.0000
1	3	0.0277778	$-$ 0.9991
2	3	0.055296	$-$ 0.9992
3	3	0.0825434	$-$ 0.9977
4	3	0.1094966	$-$ 0.9899
5	3	0.1361213	$-$ 0.9899
20	3	0.4593212	$-$ 0.6124
50	3	0.6223007	$-$ 0.0360
100	3	0.6299311	$- 1.399 \times 10^{-4}$
132	3	0.6299597	$- 3.952 \times 10^{-6}$

Brent's and Brown's Methods

Brent's[b] and Brown's[c] methods are variations of Newton's method that improve convergence. The calculation of the elements in $\mathbf{J}_k$ in Eq. (L.11) and the solving of the linear equations are intermingled. Each row of $\mathbf{J}_k$ is obtained as needed using the latest information available. Then one more step in the solution of the linear equations is executed. Brown's method is an extension of Gaussian elimination; Brent's method is an extension of QR factorization. Computer codes are generally implemented by using numerical approximations for the partial derivatives in $\mathbf{J}_k$.

Powell Hybrid and Levenberg-Marquardt Methods

Powell[d] and Levenberg[e]-Marquardt[f] calculated a new point $\mathbf{x}^{(k+1)}$ from the old one $\mathbf{x}^{(k)}$ by (note in the next two equations the superscript (k) is used instead of a subscript k to denote the stage of iteration so that the notation is less confusing)

$$\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \Delta x^{(k)} \tag{L.15}$$

where $\Delta x^{(k)}$ was obtained by solving the set of linear equations

$$\sum_{j=1}^{n} [\mu^{(k)} I_{ij} + \sum_{t=1}^{n} J_{ti}^{(k)} J_{tj}^{(k)}]\Delta x_j^{(k)} = -\sum_{t=1}^{n} J_{ti}^{(k)} f_t(x^{(k)}) \qquad i=1, \ldots, n \quad (L.16)$$

where I_{ij} is an element of the unit matrix $\mathbf{I}$ and $\mu^{(k)}$ is a non-negative parameter whose value is chosen to reduce the sum of squares of the deviations (f_i- 0) on each stage of the calculations. Powell used numerical approximations for the elements of $\mathbf{J}$. In matrix notation Eq. (L.16) can be derived by premultiplying Eq. (L.11) by $\mathbf{J}_k^T$.

$$\mathbf{J}_k^T \mathbf{J}_k \Delta\mathbf{x}_k = -\mathbf{J}_k^T \mathbf{f}(\mathbf{x}_k)$$

and adding a weighting factor $\mu_k \mathbf{I}$ to the left hand side to insure $\mathbf{J}_k^T \mathbf{J}$ is positive definite.

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[b] Brent, R. P., *SIAM J. Num. Anal.*, vol. 10, p. 327 (1973).

[c] Brown, K. M., PhD Dissertation, Purdue University, 1966.

[d] Powell, M.J.D. in *Numerical Methods for Nonlinear Algebraic Equations*, ed. P. Rabinowitz, Chapt. 6, Gordon Breach, New York, 1970.

[e] Levenberg, K., *Quart. Appld. Math.*, vol. 2, p. 164 (1944).

[f] Marquardt, D. W., *J. SIAM*, vol. 11, p. 431 (1963).

Minimization Methods

The solution of a set of nonlinear equations can be accomplished by minimizing the sum of squares of the deviations between the function values and zero.

$$\text{Minimize } F = \sum_{i=1}^{n} f_i^2(\mathbf{x}) \qquad i = 1, \ldots, m$$

Edgar and Himmelblau[g] list a number of codes to minimize F including codes that enable you to place constraints on the variables.

Method of Successive Substitutions

Successive substitution (or resubstitution) starts by solving each equation $f_i(x)$ for a single (different) output variable. For example, for three equations, you solve for an output variable (f_2 for x_1, f_3 for x_3, and f_1 for x_2)

$$\begin{aligned} f_1(x) &= 3x_1 + x_2 + 2x_3 - 3 = 0 \\ f_2(x) &= -3x_1 + 5x_2^2 + 2x_1x_3 - 1 = 0 \\ f_3(x) &= 25x_1x_2 + 20x_3 + 12 = 0 \end{aligned}$$

and rearrange them as follows

$$\left.\begin{aligned} x_1 &= F_1(x) = \frac{5x_2^2}{3} + \frac{2x_3x_1}{3} - \frac{1}{3} \\ x_2 &= F_2(x) = -3x_1 - 2x_3 + 3 \\ x_3 &= F_3(x) = -\frac{25x_1x_2}{20} - \frac{12}{20} \end{aligned}\right\} \quad \mathbf{x} = \mathbf{F}(\mathbf{x}) \tag{L.17}$$

An initial vector (x_{10}, x_{20}, x_{30}) is guessed and then introduced into the right hand side of (L.17) to get the next vector (x_{11}, x_{21}, x_{31}), which is in turn introduced into the right hand side and so on. In matrix notation the iteration from k to $k+1$ is

$$\mathbf{x}_{k+1} = \mathbf{F}(\mathbf{x}_k) \tag{L.18}$$

For the procedure of successive substitution to be guaranteed to converge, the value of the largest absolute eigenvalue of the Jacobian matrix of $\mathbf{F}(\mathbf{x})$ evaluated at each iteration point must be less than (or equal to) one. If more than one solution exists for Eqs. (L.17), the starting vector and the selection of the variable to solve for in an equation controls the solution located. Also, different arrangements of the equations and different selection of the variable to solve for may yield different convergence results.

The Wegstein and Dominant Eigenvalue methods listed in Figure L.3 are useful techniques to speed up convergence (or avoid non-convergence) of the method of

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[g] Edgar, T. F., and D. M. Himmelblau, *Optimization of Chemical Processes*, Chapters 6 and 8, McGraw-Hill, New York, 1988.

successive substitutions. Consult the references cited in Figure L.3 for the specific details.

Wegstein's method, which is used in many flowsheeting codes, accelerates the convergence of the method of successive substitutions on each iteration. In the secant method, the approximate slope is

$$m = \frac{f(x_k) - f(x_{k-1})}{x_k - x_{k-1}},$$

where x_k is the value of x on the kth (current) iteration and x_{k-1} is the value of x on the $(k - 1)st$ (previous) iteration. The equation of a line through x_k and $f(x_k)$ with slope m is

$$f(x) - f(x_k) = m(x - x_k).$$

In successive substitutions we solve $x = f(x)$. Introduce $x = f(x)$ into the equation for the line

$$x - f(x_k) = m(x - x_k)$$

and solve for x:

$$x = \frac{1}{1 - m} f(x_k) - \frac{m}{1 - m} x_k.$$

Let $t = \dfrac{1}{1 - m}$. Then for the $(k + 1)st$ (next) iteration,

$$x_{k+1} = (1 - t)x_k + tf(x_k).$$

For the solution of several equations simultaneously, each x is treated independently, a procedure that may possibly cause some instability if the x's interact. In such cases, an upper limit should be placed on t, say $0 \leq t \leq 1$. The Wegstein algorithm is for stage k.

1. Calculate x_k from the previous stage.
2. Evaluate $f(x_k)$.
3. Calculate m and t.
4. Calculate x_{k+1}.
5. Set $x_k \rightarrow x_{k+1}$ and repeat the above, starting with 2.
6. Terminate when $x_{k+1} - x_k <$ tolerance assigned.

Homotopy (Continuation) Methods

Homotopy methods[h,i] can be viewed as methods that widen the domain of conver-

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[h] M. Kubicek, "Algorithm 502," *ACM Trans. Math. Software*, v. 2, p. 98 (1976).

[i] W. J. Lin, J. D. Seader, and T. L. Wayburn, *AIChE J.*, v. 33, p. 886 (1987).

gence of any particular method of solving nonlinear equations, or, alternatively, as a method of obtaining starting guesses satisfactorily close to the desired solution. A set of functions $\mathbf{F}(\mathbf{x})$ is modified as follows to be a linear combination of a parameter t:

$$\mathbf{F}(\mathbf{x}, t) = \mathbf{F}(\mathbf{x}) + (1 - t)\mathbf{F}(\mathbf{x}_0) = \mathbf{0} \qquad 0 \leq t \leq 1 \tag{L.19}$$

where t is a scalar parameter such that when t is a fixed number the trajectory $\mathbf{F}(\mathbf{x}, t) = 0$ occurs [a mapping of $\mathbf{F}(\mathbf{x})$] and when $t = 1$ the trajectory of the set of equations reaches the desired solution $\mathbf{F}(\mathbf{x}^*) = 0$. With this definition $\mathbf{x}$ describes a curve in space (a continuous mapping called a homotopy) with one end point at a known value (the starting guess) for $\mathbf{x}$, namely $\mathbf{x}_0$, and the other end point at a solution of $\mathbf{F}(\mathbf{x}) = \mathbf{0}$, $\mathbf{x}^*$.

Lin et al. outline the procedure, which is first to determine $\mathbf{x}$ and t as functions of the arc length of the homotopy trajectory. Then Eq. (L.19) is differentiated with respect to the arc length to yield an initial value problem in ordinary differential equations. Starting at $\mathbf{x}_0$ and t_0, the initial value problem is transformed by using Euler's method to a set of linear algebraic equations that yield the next step in the trajectory. The trajectory may reach some or all of the solutions of $\mathbf{F}(\mathbf{x}) = \mathbf{0}$; hence several starting points may have to be selected to create paths to all the solutions, and many undesired solutions (from a physical viewpoint) will be obtained. A number of practical matters to make the technique work can be found in the review by Seydel and Hlavacek.[j]

SUPPLEMENTARY REFERENCE

RHEINBOLT, W. C., *Numerical Analysis of Parameterized Nonlinear Equations,* Wiley-Interscience, New York, 1986.

[j] R. Seydel, and V. Hlavacek, *Chem. Eng. Sci.,* v. 42, p. 1281 (1987).

Appendix M

FITTING FUNCTIONS TO DATA

Frequently, you would like to estimate the best values of the coefficients in an equation from experimental data. The equation might be a theoretical law or just a polynomial, but the procedure is the same. Let y be the dependent variable in the equation, b_i be the coefficients in the equation, and x_i be the independent variables in the equation so that the model is of the form

$$y = f(b_0, b_1, \ldots; x_0, x_1, \ldots) \tag{M.1}$$

Let ϵ represent the error between the observation of y, Y, and the predicted value of y using the values of x_i and the estimated values of the coefficients b_i:

$$Y = y + \epsilon \tag{M.2}$$

The classical way to get the best estimates of the coefficients is by least squares, that is, by minimizing the sum of the squares of the errors (of the deviations) between Y and y for all the j sets of experimental data:

$$\text{Minimize } F = \sum_{j=1}^{p} (\epsilon_j)^2 = \sum_{j=1}^{p} (Y_j - f_j)^2 \tag{M.3}$$

Let us use a model linear in the coefficients with one independent variable x

$$y = b_0 + b_1 x \tag{M.4}$$

(in which x_0 associated with b_0 always equals 1 in order to have an intercept) to illustrate the principal features of the least-squares method to estimate the model coefficients. The objective function is

$$F = \sum_{j=1}^{p} (Y_j - y_j)^2 = \sum_{j=1}^{p} (Y_j - b_0 - b_1 x_j)^2 \tag{M.5}$$

There are two unknown coefficients, b_0 and b_1, and p known pairs of experimental values of Y_j and x_j. We want to minimize F with respect to b_0 and b_1. Recall from calculus that you take the first partial derivatives of F and equate them to zero to get the necessary conditions for a minimum.

$$\frac{\partial F}{\partial b_0} = 0 = 2\sum_{j=1}^{p}(Y_j - b_0 - b_1x_j)(-1) \tag{M.6a}$$

$$\frac{\partial F_0}{\partial b_1} = 0 = 2\sum_{j=1}^{p}(Y_j - b_0 - b_1x_j)(-x_j) \tag{M.6b}$$

Rearrangement yields a set of linear equations in two unknowns, b_0 and b_1:

$$\sum_{j=1}^{p} b_0 + \sum_{j=1}^{p} b_1x_j = \sum_{j=1}^{p} Y_j$$

$$\sum_{j=1}^{p} b_0x_j + \sum_{j=1}^{p} b_1x_j^2 = \sum_{j=1}^{p} x_jY_j$$

The summation $\Sigma_{j=1}^{p} b_0$ is $(p)(b_0)$ and in the other summations the constants b_0 and b_1 can be removed from within the summation signs so that

$$b_0(p) + b_1\sum_{j=1}^{p} x_j = \sum_{j=1}^{p} Y_j \tag{M.7a}$$

$$b_0\sum_{j=1}^{p} x_j + b_1\sum_{j=1}^{p} x_j^2 = \sum_{j=1}^{p} x_jY_j \tag{M.7b}$$

The two linear equations above in two unknowns, b_0 and b_1, can be solved quite easily for b_0 the intercept and b_1 the slope.

EXAMPLE M.1 Application of Least Squares

Fit the model $y = \beta_0 + \beta_1 x$ to the following data (Y is the measured response and x the independent variable).

x	Y
0	0
1	2
2	4
3	6
4	8
5	10

Solution

The computations needed to solve Eqs. (M.7) are

$$\sum x_j = 15 \qquad \sum x_jY_j = 110$$

$$\sum Y_j = 30 \qquad \sum x_j^2 = 55$$

Then

$$6b_0 + 15b_1 = 30$$

$$15b_0 + 55b_1 = 110$$

Solution of these two equations yields

$$b_0 = 0 \qquad b_1 = 2$$

and the model becomes $\hat{Y} = 2x$, where $\hat{Y}$ is the predicted value for a given x.

The least-squares procedure outlined above can be extended to any number of variables as long as the model is linear in the coefficients. For example, a polynomial

$$y = a + bx + cx^2$$

is linear in the coefficients (but not in x), and would be represented as

$$y = b_0 + b_1x_1 + b_2x_2$$

where $a = b_0$, $b = b_1$, $c = b_2$, $x_1 = x$, and $x_2 = x^2$. Linear equations equivalent to Eqs. (M.7) with several independent variables can be solved via a computer. If the equation you want to fit is nonlinear in the coefficients such as

$$y = b_0e^{b_1x} + b_2x^2$$

you can minimize F in Eq. (M.3) directly by the computer program on the disk in the back of this book, or by using a nonlinear least-squares computer code taken from a library of computer codes.

Additional useful information can be extracted from a least-squares analysis if four basic assumptions are made in addition to the presumed linearity of y in x:

1. The x's are deterministic variables (not random).
2. The variance of ϵ_j is constant or varies only with the x's.
3. The observations Y_j are mutually statistically independent.
4. The distribution of Y_j about y_j given x_j is a normal distribution.

For further details, see Box, Hunter, and Hunter[1] or Box and Draper[2].

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[1] G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters*, Wiley-Interscience, New York, 1978.

[2] G. E. P. Box and N. R. Draper, *Empirical Model Building and Response Surfaces*, Wiley, New York, 1987.

Appendix N

ANSWERS TO SELECTED PROBLEMS

Chapter 1

1.2 **(a)** 6.707 × 10^8; **(b)** 116.45; **(c)** 96.6; **(d)** 91.44
1.7 5.86 W; 17.58 W
1.12 **(a)** 40; **(b)** 30; **(c)** 2293; **(d)** 8; **(e)** 400; **(f)** 2
1.18 J/(s)(m^2)(°C)
1.21 No
1.22 1: 1.248 × 10^6; 2: 2.10 × 10^7
1.30 **(a)** 9.9 × 10^3 g; **(b)** 408.3 lb; **(c)** 22.6 lb
1.31 **(a)** 11.45 lb; **(b)** 201 lb; **(c)** 41,100 lb
1.38 0.0311 lb mol H_2SO_4/gal
1.42 59.29 lb/ft^3 and 7.93 lb/gal
1.45 He: 0.167; N_2: 0.389; 0_2: 0.444
1.49 Yes
1.51 **(a)** 42.412 L/min
1.54 **(a)** 34; **(b)** 0.125
1.58 CH_4: 8.5%; C_2H_6 4.0%; CO_2; 87.5%
1.62 Analysis: A: 32.2%; B: 27.2%; C: 40.6% mol
1.66 **(a)** 21.1°C, 294 K, 530°R
1.67 −321.4°F; 138.6°R for N_2; −268.8°C, 4.4 K for He
1.72 **(a)** 6.9 × 10^4 N/m^2, 69 kN/m^2, 69 kPa; **(b)** 1 atm, 101.3 kN/m^2, 0.1013 MN/m^2
1.74 63.8 psia
1.80 **(a)** 115 ft; **(b)** No
1.84 655 mm Hg
1.94 0.42 kPa

1.97 Yes, yes, yes

1.101 (b) 4.47 g; (d) 3.41 g; (f) 6.08 lb; (h) 8.21 lb

1.104 30.8 lb O_2

1.109 (a) 609 ton S; (b) 913.5 ton O_2; (c) 342.6 ton H_2O

1.115 (a) 33% excess C; (b) 86.0% Fe_2O_3

1.119 (a) C; (b) $Ca_3(PO_4)_2$ and SiO_2; (c) 0.170

Chapter 2

2.2 Yes

2.5 (a) unsteady state, open

2.8 4 balances including total material balance; 3 are independent

2.11 No stream values; 2 compositions; no.

2.13 CO_2(13%), H_2O(14.3%), N_2(67.6%), O_2(5.1%)

2.16 (a) CO_2(14.1%), SO_2(0.32%), H_2O(6.5%), N_2(75.8%), O_2(3.37%)
(b) H_2O(6.40%), SO_2(0.32%), CO_2(11.4%), CO(2.08%), O_2(5.07%), N_2(74.96%)

2.22 CO_2(8.2%), CO(3.5%), O_2(5.4%), N_2(82.3%)

2.25 47.8 kg

2.31 (a) 33%; (b) 8.0

2.36 0.801 ton

2.39 417 spent acid, 176 lb concentrated HNO_3, 407 lb concentrated H_2SO_4

2.45 (a) A(0.600), B(0.350), C(0.05); (b) an infinite number of solutions exist

2.50 7980 gal/hr

2.53 0.236 mol air/mol exhaust gas

2.55 2

2.59 8 unknowns (C, D, E, F, G, H, x_{F,C_2}, x_{F,C_3}; balances: unit 1-3, unit 2-2, unit 3-3 for a total of 8. Note: $1 - x_{F,C_2} - x_{F,C_3}$ can be added by including one more unknown

2.62 $P = 35.9$; $X_{C3} = 0.504$, $X_{C4} = 0.496$

2.67 (a) 53%

2.68 ratio = 0.199 mol R/mol $SiCl_4$ exiting

2.69 R = 7670 kg/hr

2.74 (a) B = 586 lb/hr; (b) D = 414 lb/hr; (c) Fraction = 0.551

2.80 80.8%

2.85 (a) 14.25 kg mol; (b) 29.7 kg mol

Chapter 3

3.1 1.026 L

3.5 1.46×10^{-2} kg H_2O

3.11 (a) 0.107 ft^3 at 125 psia and T; (b) 1.017 ft^3 at 14.7 psia and T

3.16 0.325 ft^3

3.20 3.56 ft^3 at 70° F, 29.4 in. Hg/ft^3 gas at 90°F, 35 in. Hg

3.25 (a) 0.080; (b) 15.47 m^3 at 300 K and 101.4 kPa/kg fuel

3.29 C_3H_6

3.34 (a) 0.0952 kg/m^3; (b) 0.069 = sp.gr.

3.37 pressure CO_2 = 17.7 mm Hg

3.41 **(a)** N_2 (83.35%), CO_2 (11.06%), H_2(5.59%); **(b)** 2.187; **(c)** 28.26

3.44 van der Waals: 10.60 g mol; Redlich-Kwong: 10.61 g mol

3.49 **(a)** 26.5 atm; **(b)** 26.5 atm; **(c)** 25.95 atm

3.51 500°R

3.54 24.6 lb

3.58 435 K

3.63 $(n_2/n_1) = 0.291$ for the real gas

3.67 31.9 kg/m^3 at 393 K and 3500 kPa

3.71 **(a)** 194.6 mm Hg vs. 199.1 from handbook; T = 316.4°K (43.4°C) vs. 42.7 from handbook

3.74 27 atm at 100°C

3.79 **(a)** 47.6 ft^3 at 90°F and 29.80 in. Hg; **(b)** 0.107 lb H_2O

3.83 O_2: 296 ft^3 at 745 mm, 25°C; C_2H_2: 54 ft^3 at 745 mm, 25°C

3.87 T ~ 82°C; mol fr. C_6H_4 ~ 0.73, hence condensation occurs starting at ~ 88°C

3.91 Bubble point: 375.1 K; Dewpoint: 381.5 K

3.96 561.6 total mol liquid and 566.4 total mol vapor

3.100 **(a)** 12.3%; **(b)** 14.9%; **(c)** 75°F

3.104 **(a)** 2.75×10^{-3} mol Bz/mol gas; **(b)** 2.758×10^{-3} mol Bz/mol Bz free gas **(c)** 0.0074; **(d)** 0.023

3.110 717 ft^3 at 30°C and 750 mm Hg

3.115 47.4°C

3.119 **(a)** CO_2 (6.7%), CO(12.4%), O_2(18.1%), N_2(62.8%); **(b)** 35.8 ft^3 air at T and p/lb $H_2C_2O_4$; **(c)** 106.2 ft^3 at T and p/lb $H_2C_2O_4$, **(d)** 111°F

3.122 **(a)** 89 ft^3/min; **(b)** 1180 mm Hg

3.125 37,920 ft^3 at 70°F and 760 mm Hg

3.129 2

3.131 (1):1; (2):1, (3):4

3.133 (1):1

Chapter 4

4.1 **(a)** 2.5×10^4 cal/kg; **(b)** 1.048×10^5 J/kg; **(c)** 2.91×10^{-2} (kW)(hr)/kg; **(d)** 3.5×10^4 (ft)(lb_f)/(lb_m)

4.4 8.56×10^{-4}; 6.20×10^{-2} if the units of D are cm and Gg/(min)(cm^2)

4.12 1.55 (ft)(lb_f)

4.17 4.4 kW

4.21 5×10^8 W

4.24 -2.50×10^6 J/g mol

4.27 All yes except internal energy ($\Delta\hat{U}$ would be yes).

4.29 $C_p = 36.7 + 0.0403T - 0.0000221\ T^2$

4.33 **(a)** $C_p = 6.852 + 1.62 \times 10^{-3}T_{°C} - 0.26 \times 10^{-6}T^2_{°C}$

4.34 **(a)** Kopp's rule: 33.8 cal/(g mol)(°C); 32.8 cal/(g mol)(°C) from Perry; **(b)** 62.4; 65.41 from Perry **(c)** 133.0 cal/(g mol)(°C)

4.37 3759 cal/g mol

4.43 2.563×10^3 J/g mol

4.47 26.8 kJ/kg

4.50 10,590 cal/g mol Cl_2

4.53 117,950 J/g mol (28,190 cal/g mol)

4.59 **(a)** 8640 Btu/lb mol; the data appear valid as they yield a straight line for $\log_{10} p$ vs. $1/T$; **(b)** 9110 Btu/lb mol; **(c)** 8770 Btu/lb mol

4.60 **(a)** 3576 Btu; **(b)** 3576 Btu; **(c)** 1173.35 Btu; **(d)** 182 Btu/lb; **(e)** −964.2 Btu/lb; **(f)** 788.9 Btu/lb

4.64 Use CO_2 chart or tables: −73.4 Btu/lb

4.69 **(a)** $W = 0$; $Q = \Delta U = C_V\Delta T \approx C_p\Delta T = 10$ Btu; **(b)** $Q = 0$, $-W = \Delta U \cong \Delta H = C_p\Delta T = 10$ Btu

4.73 **(a)** 2.120 Btu/lb; **(b)** 2.131 Btu/lb

4.78 2.47 lb steam/lb mol waste gas

4.82 0.1171

4.87 **(a)** 86°C; **(b)** 7,887 kg H_2O

4.91 **(a)** CO_2 is at 800 psia and **(b)** is all liquid; **(c)** $\Delta V \approx 3$ ft^3/lb

4.95 No.

4.96 **(a)** 2.72 kJ/kg **(b)** No. (Q is not known)

4.100 **(a)** Initial volume: 0; **(b)** final volume: 0.218 ft^3

4.105 6.62 hp

4.112 **(a)** \$2.21/10^6 Btu; **(b)** \$6.45/10^6 Btu

4.116 **(a)** −123.94 k cal/g mol; **(b)** 43.200 k cal/g mol; **(c)** −90.434 k cal/g mol

4.123 −199.5 kJ/g mol

4.127 141 Btu/ft^3 at SC of NGI

4.129 a1. −23,600 Btu/lb; b1. −21,500 Btu/lb

4.135 **(a)** 35.84 lb; **(b)** 53,600 Btu output

4.141 -9.92×10^6 kJ/1000 kg

4.144 16.60 kJ/100 g charge or 0.166 kJ/g charge

4.146 2180 K

4.149 C_4H_8 if equilibrium is ignored

4.151 **(a)** 1.70×10^6 Btu; **(b)** 168°F

4.153 **(a)** −33,000 Btu/lb mol; **(b)** −289.65 k cal/g mol $CaCl_2$; **(c)** −1440 Btu/lb mol $CaCl_2$

4.160 28%

4.161 **(a)** 465 lb of 73% NaOH added

4.165 **(a)** 0.079 kg mol H_2O/kg mol air; **(b)** 87.1 kPa; **(c)** 37°C

4.168 **(a)** 0.01813 lb H_2O/lb air; **(b)** 0.031 lb H_2O/lb air; **(c)** 1.14%

Chapter 5

5.1 Degrees of freedom = C + 4

5.5 Degrees of freedom = 2C + 2N + 5; specify p(N), Q(N), F(C + 2), S(C + 2), N(1) for each stage

5.12 Degrees of freedom = 16

5.19 1,129.5 kg/feed

5.21 B = 240,270, C = 95,930, D = 10,270, E = 44,750, F = 4,480, A = 336,200 all lb/hr

5.24 **(a)** 90°F; **(b)** 2,800 lb of 40% NaCl produced/hr.

5.29 **(a)** 3000 lb (NH_3), 11,000 lb $(NH_4)_2SO_4$, 7,500 lb Benzol, 2,500 lb Toluol, 1,500 lb Pyridine; **(c)** 2660 lb 40% NaOH; **(d)** 3720 lb 50% H_2SO_4

5.33 Heat duty for exchangers (in MM kJ/hr): No. 1 = 82.04, No. 2 = 120.33, No. 3 = 165.35 (all temperatures 60°C)

Chapter 6

6.2 230.5 min

6.8 37,700 lb

6.11 121.5 s

6.17 moles $C_6H_{12} = e^{-kt}$

6.21 28 min

6.24 **(b)** 129°F for half-full

NOMENCLATURE*

A = area
A = constant
a = acceleration
$\mathbf{a}$ = coefficient matrix
a = constant in general
a = constant in van der Waals' equation, (Eq. 3.11)
a, b, c = constants in heat capacity equation
$\mathcal{AS}$ = absolute saturation
°API = specific gravity of oil defined in Eq. (1.9)
B = constant
b = constant in van der Waals' equation, Eq. (3.11)
$\dot{B}$ = rate of energy transfer accompanying $\dot{w}$
(c) = crystalline
C = constant in Eq. (1.1)
C = number of chemical components in the phase rule
c^* = rank of the atom matrix
C_p = heat capacity at constant pressure
C_{p_m} = mean heat capacity
C_s = humid heat
C_v = heat capacity at constant volume
D = diameter
D = distillate product
E = total energy in system = $U + K + P$
E_v = irreversible conversion of mechanical energy to internal energy
F = force
F = number of degrees of freedom in the phase rule
F = feed stream
(g) = gas
g = acceleration due to gravity
g_c = conversion factor of $\dfrac{32.174(\text{ft})(\text{lb}_\text{m})}{(\text{sec}^2)(\text{lb}_\text{f})}$
$\hat{H}$ = enthalpy per unit mass or mole
h = distance above reference plane
h = number of stoichiometric constraints
H = enthalpy, with appropriate subscripts, relative to a reference enthalpy
$\mathcal{H}$ = humidity, lb water vapor/lb dry air
(l) = liquid
h_c = heat transfer coefficient
$\Delta\hat{H}$ = enthalpy change per unit mass or mole
ΔH = enthalpy change, with appropriate subscripts
ΔH_0 = constant
ΔH_{rxn} = heat of reaction
ΔH_{soln} = heat of solution
ΔH_c° = standard heat of combustion

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*Units are discussed in text.

ΔH_f° = standard heat of formation
K = characterization factor
K = degree Kelvin
K = kinetic energy
k_g' = mass transfer coefficient
K_j = vapor/liquid equilibrium, Eq. (3.39)
L = moles of liquid, Eq. (3.44)
l = distance
lb = pound, as a mass
lb_f = pound, as a force
lb_m = pound, as a mass
m = mass of material
m = number of equations
$\dot{m}$ = rate of mass transport through defined surfaces
mol. wt. = molecular weight
n = number of moles
n = number of unknown variables
N_d = degrees of freedom
N_p = number of equipment parameters
N_Q = number of heat transfer variables
N_{Re} = Reynolds number
N_r = number of independent constraints
N_s = number of streams
N_{sp} = number of chemical species
N_v = total number of variables
N_w = number of work variables
$\mathcal{P}$ = number of phases in the phase rule
p = partial pressure (with a suitable subscript for p)
p = pressure
p_c' = pseudocritical pressure
p^* = vapor pressure
p_c = critical pressure
P = potential energy
P = product
p_r' = pseudoreduced pressure
p_r = reduced pressure = p/p_c
p_t = total pressure in a system
Q = heat transferred
$\dot{Q}$ = rate of heat transferred (per unit time)
q = volumetric flow rate
Q_p = heat evolved in a constant pressure process
Q_v = heat evolved in a constant volume process
(s) = solid
R = recycle stream
R = universal gas constant

r = rank of a matrix in Chap. 2
$\dot{r}_A$ = rate of generation of consumption of component A (by chemical reaction)
$\mathcal{RH}$ = relative humidity
$\mathcal{RS}$ = relative saturation
S = cross-sectional area perpendicular to material flow
s = second
sp gr = specific gravity
T = absolute temperature or temperature in general
t = temperature in °C or °F
t = time
T'_c = pseudocritical temperature
T'_r = pseudoreduced temperature
T_b = normal boiling point (in K or °R)
T_c = critical temperature (absolute)
T_{DB} = dry-bulb temperature
T_f = melting point (in K)
T_r = reduced temperature = T/T_c
T_{WB} = wet-bulb temperature
U = internal energy
$\hat{V}$ = humid volume
$\hat{V}$ = specific volume (volume per unit mass or mole)
V = system volume of fluid volume in general
v = velocity
V_c = critical volume
$\hat{V}_{ci}$ = ideal critical volume = RT_c/p_c
$\hat{V}_{ci}$ = pseudocritical ideal volume
V_g = volume of gas
V_l = volume of liquid
V_r = reduced volume = V/V_c
V_{ri} = ideal reduced volume = V/V_{ci}
$\dot{W}$ = rate of work done by system (per unit time)
W = waste stream
W = work done by the system
$\dot{w}_A$, $\dot{w}$ = rate of mass flow of component A and total mass flow, respectively, through system boundary other than a defined surface
x = mass or mole fraction in general
x = mass or mole fraction in the liquid phase for two-phase systems
x = unknown variable
y = mass or mole fraction in the vapor phase for two-phase systems
z = compressibility factor
z'_c = pseudocritical compressibility factor
z_c = critical compressibility factor
z_j = mole fraction of j
z_m = mean compressibility factor

Greek letters:

α, β, γ = constants in heat capacity equation
γ = constant in Eq. (3.17)
Δ = difference between exit and entering stream; also used for final minus initial times or small time increments
λ = molal heat of vaporization
λ_f = molal latent heat of fusion at the melting point
ρ = density
ρ_A, ρ = mass of component A, or total mass, respectively, per unit volume
ρ_L = liquid density
μ = viscosity
ϵ = error
ρ_V = vapor density
ω = mass fraction

Subscripts:

A, B = components in a mixture
c = critical
i = any component
i = ideal state
r = reduced state
t = at constant temperature
t = total
1, 2 = system boundaries

Superscript:
$\hat{}$ = per unit mass or per mole
$\cdot$ = per unit time (a rate)

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