

PHYSICAL CHEMISTRY

THIRD EDITION



ROBERT G. MORTIMER



Physical Chemistry

Third Edition

Physical Chemistry

Third Edition

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To my wife, Ann,
and to my late father, William E. Mortimer,
who was responsible for my taking my first chemistry course

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Preface

This is the third edition of a physical chemistry textbook designed for a two-semester undergraduate physical chemistry course. The physical chemistry course is often the first opportunity that a student has to synthesize descriptive, theoretical, and mathematical knowledge about chemistry into a coherent whole. To facilitate this synthesis, the book is constructed about the idea of defining a system, studying the states in which it might be found, and analyzing the processes by which it can change its state.

The book is divided into four parts. The first part focuses on the macroscopic properties of physical systems. It begins with the descriptive study of gases and liquids, and proceeds to the study of thermodynamics, which is a comprehensive macroscopic theory of the behavior of material systems. The second part focuses on dynamics, including gas kinetic theory, transport processes, and chemical reaction kinetics. The third part presents quantum mechanics and spectroscopy. The fourth part presents the relationship between molecular and macroscopic properties of systems through the study of statistical mechanics. This theory is applied to the structure of condensed phases. The book is designed so that the first three parts can be studied in any order, while the fourth part is designed to be a capstone in which the other parts are integrated into a cohesive whole.

In addition to the standard tables of integrals and numerical values of various properties, the book contains several appendices that expand on discussions in the body of the text, such as more detailed discussions of perturbation theory, group theory, and several mathematical topics. Each chapter begins with a statement of the principal facts and ideas that are presented in the chapter. There is a summary at the end of each chapter to assist in synthesizing the material of each chapter into a coherent whole. There are also marginal notes throughout the chapters that present biographical information and some comments. Each chapter contains examples that illustrate various kinds of calculations, as well as exercises placed within the chapter. Both these exercises and the problems at the end of each section are designed to provide practice in applying techniques and insights obtained through study of the chapter.

Answers to all of the numerical exercises and to the odd-numbered numerical problems are placed in Appendix K. A solutions manual, with complete solutions to all exercises and all odd-numbered problems, is available from the publisher. An instructor's manual with solutions to the even-numbered problems is available on-line to instructors. The instructor can choose whether to allow students to have access to the solutions manual, but can assign even-numbered problems when he or she wants the students to work problems without access to solutions.

The author encourages students and instructors to comment on any part of the book; please send comments and suggestions to the author's attention.

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It has been my pleasure to have studied with many dedicated and proficient teachers, and I acknowledge their influence, example, and inspiration. I am also grateful for the privilege of working with students, whose efforts to understand the workings of the physical universe make teaching the most desirable of all professions.

I have benefited from the expert advice of many reviewers. These include:

Jonas Goldsmith	Bryn Mawr College
Jason D. Hofstein	Sienna College
Daniel Lawson	University of Michigan–Dearborn
Jennifer Mihalick	University of Wisconsin–Oshkosh
Cynthia M. Woodbridge	Hillsdale College

and the reviewers of the previous editions. All of these reviewers gave sound advice, and some of them went beyond the call of duty in searching out errors and unclarities and in suggesting remedies. The errors that remain are my responsibility, not theirs.

I wish to thank the editorial staff of Elsevier/Academic Press for their guidance and help during a rather long and complicated project, and also wish to thank Erica Ellison, who was a valuable consultant. I thank my wife, Ann, for her patience, love, and support during this project.

1

Thermodynamics and the Macroscopic Description of Physical Systems

1

The Behavior of Gases and Liquids

PRINCIPAL FACTS AND IDEAS

1. The principal goal of physical chemistry is to understand the properties and behavior of material systems and to apply this understanding in useful ways.
2. The state of a system is specified by giving the values of a certain number of independent variables (state variables).
3. In an equilibrium one-phase fluid system of one substance, three macroscopic variables such as temperature, volume, and amount of substance can be independent variables and can be used to specify the macroscopic equilibrium state of the system. At least one of the variables used to specify the state of the system must be proportional to the size of the system (be extensive). Other macroscopic variables are mathematical functions of the independent variables.
4. The intensive state, which includes only intensive variables (variables that are independent of the size of the system), is specified by only two variables in the case of an equilibrium one-phase fluid system of one substance.
5. Nonideal gases and liquids are described mathematically by various equations of state.
6. The coexistence of phases can be described mathematically.
7. The liquid–gas coexistence curve terminates at the critical point, beyond which there is no distinction between liquid and gas phases.
8. The law of corresponding states asserts that in terms of reduced variables, all substances obey the same equation of state.

1.1

Introduction

This book is a textbook for a standard two-semester physical chemistry course at the undergraduate level. Physical chemistry involves both physics and chemistry. Physics has been defined as the study of the properties of matter that are shared by all substances, whereas chemistry has been defined as the study of the properties of individual substances. Chemistry grew out of the ancient occult art of alchemy, which involved among other things the attempted transmutation of cheaper materials into gold. Chemistry began as a completely experimental science. Substances were named and studied without reference to their molecular structures. Sulfuric acid was called “oil of vitriol,” and chemists memorized the fact that when copper was treated with oil of vitriol a solution of “blue vitriol” (now known as copper(II) sulfate) resulted. In the late 18th century, Lavoisier established the law of conservation of mass in chemical reactions, and Proust established the law of definite proportion. In order to explain these laws, Dalton proposed his atomic theory in 1803, as well as announcing the law of multiple proportions. With this theory, chemistry could evolve into a molecular science, with properties of substances tied to their molecular structures.

Antoine Laurent Lavoisier, 1743–1794, was a great French chemist who was called the “father of modern chemistry” because of his discovery of the law of conservation of mass. He was beheaded during the French Revolution because of his involvement in his father-in-law’s firm, which was employed by the royal government to collect taxes. It is said that he arranged with a friend to observe his head to see how long he could blink his eyes after his head was severed. He blinked for 15 seconds.

Joseph Proust, 1754–1826, was a French chemist who was the first to isolate sugar from grapes.

John Dalton, 1766–1844, was an English schoolmaster and chemist. After he became a famous chemist, he continued to teach at what we would now call the elementary school level.

Galileo Galilei, 1564–1642, was a great Italian mathematician and physicist. He refuted the assertion of Aristotle that a heavier object should fall faster than a lighter one and is said to have dropped two balls of different masses from the leaning tower of Pisa to demonstrate that they fell at the same rate. He supported the hypothesis of Copernicus that the earth revolves around the sun and was convicted of heresy in 1633 by the Roman Catholic Church for this belief. He spent the rest of his life under house arrest.

Systems

We call any object that we wish to study our *system*. A large system containing many atoms or molecules is called a *macroscopic system*, and a system consisting of a single atom or molecule is called a *microscopic system*. We consider two principal types of properties of systems. *Macroscopic properties* such as temperature and pressure apply only to a macroscopic system and are properties of the whole system. They can be observed and studied without reference to the molecular nature of matter. *Microscopic properties* such as kinetic energy and momentum are mechanical in nature. They apply to either macroscopic or microscopic systems.

The study of macroscopic properties involves thermodynamics, which is the major topic of this volume, along with gas kinetic theory, transport processes, and reaction kinetics. Quantum mechanics, spectroscopy, and statistical mechanics are molecular topics and are discussed in Parts 3 and 4 of this textbook.

Mathematics in Physical Chemistry

The study of any physical chemistry topics requires mathematics. Galileo once wrote, “The book of nature is written in the language of mathematics.” We will use mathematics in two different ways. First, we will use it to describe the behavior of systems without explaining the origin of the behavior. Second, we will use it to develop theories that explain why certain behaviors occur. This chapter is an example of the first usage, and the next chapter is an example of the second usage.

Much of the mathematical education that physical chemistry students have received has focused on mathematical theory rather than on practical applications. A student who was unable to apply an elementary calculus technique once said to the author, “I know that was in the calculus course, but nobody told me that I would ever have to use it.” Mathematical theory is not always important in physical chemistry, but you

need to be able to apply mathematical methods. There are several books that cover the application of mathematics to problems in physical chemistry.¹

Arithmetic is the principal branch of *numerical mathematics*. It involves carrying out operations such as addition, subtraction, multiplication, and division on actual numbers. Geometry, algebra, and calculus are parts of *symbolic mathematics*, in which symbols that represent numerical quantities and operations are manipulated without doing the numerical operations. Both kinds of mathematics are applied in physical chemistry.

Mathematical Functions

A mathematical function involves two kinds of variables: An *independent variable* is one to which we can assign a value. A *mathematical function* is a rule that delivers the value of a *dependent variable* when values are assigned to the independent variable or variables. A function can be represented by a formula, a graph, a table, a mathematical series, and so on. Consider the *ideal gas law*:

$$PV = nRT \quad (1.1-1)$$

In this equation P represents the pressure of the gas, V represents its volume, n represents the amount of substance in moles, T represents the absolute temperature, and R stands for the *ideal gas constant*. The ideal gas law does a good but not perfect job of representing the equilibrium behavior of real gases under ordinary conditions. It is more nearly obeyed if the pressure of the gas is made smaller. A gas that is at a sufficiently low pressure that it obeys the ideal gas law to an adequate approximation is called a *dilute gas*. An *ideal gas* is defined to obey this equation for all pressures and temperatures. An ideal gas does not exist in the real world, and we call it a *model system*. A model system is an imaginary system designed to resemble some real system. A model system is useful only if its behavior mimics that of a real system to a useful degree and if it can be more easily analyzed than the real system.

We can solve the ideal gas law for V by symbolically dividing by P :

$$V = \frac{nRT}{P} \quad (1.1-2)$$

The right-hand side of Eq. (1.1-2) is a formula that represents a mathematical function. The variables T , P , and n are independent variables, and V is the dependent variable. If you have the numerical values of T , P , and n , you can now carry out the indicated arithmetic operations to find the value of V . We can also solve Eq. (1.1-1) for P by symbolically dividing by V :

$$P = \frac{nRT}{V} \quad (1.1-3)$$

We have now reassigned V to be one of the independent variables and P to be the dependent variable. This illustrates a general fact: *If you have an equation containing*

¹Robert G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Academic Press, San Diego, CA, U.S.A., 2005; James R. Barrante, *Applied Mathematics for Physical Chemistry*, 3rd ed., Pearson Prentice Hall, Upper Saddle River, NJ, 2004; Donald A. McQuarrie, *Mathematical Methods for Scientists and Engineers*, University Science Books, 2003.

several variables, you can manipulate the equation symbolically to turn any one of them into the dependent variable.

The ideal gas law might not be accurate enough for some gases under some conditions. If so, we can find some other function that will give the value of the pressure to greater accuracy. It is an experimental fact that the pressure of a gas or liquid of one substance at equilibrium is given by a function that depends on only three independent variables. We represent such a function by

$$P = P(T, V, n) \quad (1.1-4)$$

A mathematician would write $P = f(T, V, n)$ for the functional relation in Eq. (1.1-4), using the letter P for the variable and the letter f for the function. Chemists have too many variables to use two letters for each variable, so we use the same letter for the variable and the function. A functional relation that relates P , V , T , and n for a gas or a liquid at equilibrium is called an *equation of state* and is said to represent the *volumetric behavior* of the gas or liquid. We will introduce several equations of state later in this chapter.

EXAMPLE 1.1

Assume that the volume of a liquid is a linearly decreasing function of P , is a linearly increasing function of T , and is proportional to n . Write a formula expressing this functional relationship.

Solution

Let V_0 represent the volume at some reference temperature T_0 , some reference pressure P_0 , and some reference amount of substance n_0 .

$$V = V_0 \frac{n}{n_0} [1 - k(P - P_0) + a(T - T_0)] = n V_{m0} [1 - k(P - P_0) + a(T - T_0)]$$

where k and a are constants and where V_m represents the molar volume, equal to V/n , and V_{m0} represents V_0/n_0 .

A two-dimensional graph can represent a function of one independent variable. You plot the value of the independent variable on the horizontal axis and represent the value of the dependent variable by the height of a curve in the graph. To make a two-dimensional graph that represents the ideal gas law, we must keep two of the three independent variables fixed. Figure 1.1a shows a set of graphical curves that represent the dependence of P on V for an ideal gas for $n = 1.000$ mol and for several fixed values of T .

A three-dimensional graph can represent a function of two independent variables. Figure 1.1b shows a perspective view of a graphical surface in three dimensions that represents the dependence of P on V and T for an ideal gas with a fixed value of n (1.000 mol). Just as the height of a curve in Figure 1.1a gives the value of P for a particular value of V , the height of the surface in Figure 1.1b gives the value of P for a particular value of T and a particular value of V . Such graphs are not very useful for numerical purposes, but help in visualizing the general behavior of a function of two independent variables.

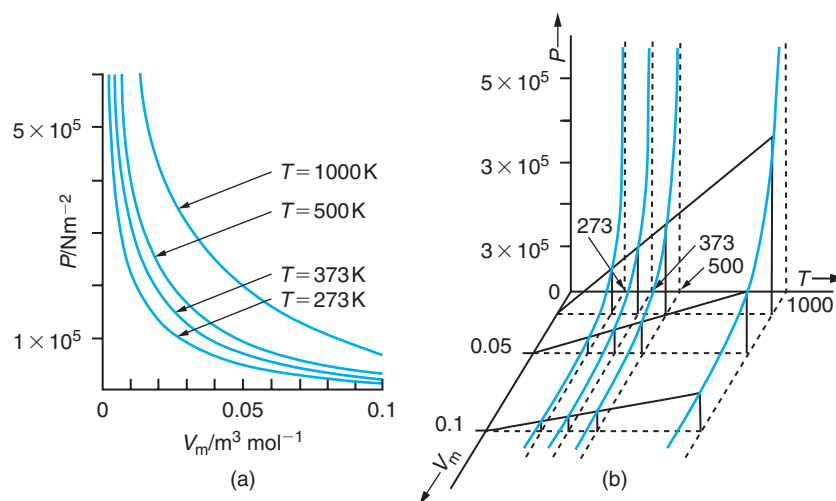


Figure 1.1 (a) The pressure of an ideal gas as a function of V at constant n and various constant values of T . (b) The pressure of an ideal gas as a function of V and T at constant n .

A function can also be represented by a table of values. For a function of one independent variable, a set of values of the independent variable is placed in one column. The value of the dependent variable corresponding to each value of the independent variable is placed in another column on the same line. A mathematician would say that we have a set of ordered pairs of numbers. Prior to the advent of electronic calculators, such tables were used to represent logarithms and trigonometric functions. Such a table provides values only for a finite number of values of the independent variable, but interpolation between these values can be used to obtain other values.

Units of Measurement

The values of most physical variables consist of two parts, a number and a unit of measurement. Various units of measurement exist. For example, the same distance could be expressed as 1.000 mile, 1609 meters, 1.609 kilometer, 5280 feet, 63360 inches, 1760 yards, 106.7 rods, 8.000 furlongs, and so on. A given mass could be expressed as 1.000 kilogram, 1000 grams, 2.205 pounds, 0.1575 stone, 195.3 ounces, and so on. There are sets of units that are consistent with each other. For example, pounds are used with feet, kilograms are used with meters, and grams are used with centimeters. Here is an important fact: *To carry out any numerical calculation correctly you must express all variables with consistent units.* If any quantities are expressed in inconsistent units, you will almost certainly get the wrong answer. In September 1999, a space probe optimistically named the “Mars Climate Orbiter” crashed into the surface of Mars instead of orbiting that planet. The problem turned out to be that some engineers had used “English” units such as feet and pounds, while physicists working on the same project had used metric units such as meters and kilograms. Their failure to convert units correctly caused the loss of a space vehicle that cost many millions of U.S. dollars. In another instance, when a Canadian airline converted from English units to metric units, a ground crew that was accustomed to English units incorrectly calculated how much fuel in kilograms to put into an airliner for a certain flight. The airplane ran out of

fuel before reaching its destination. Fortunately, the pilot was able to glide to a former military air field and make a “deadstick” landing on an unused runway. Some people who were having a picnic on the runway were fortunately able to get out of the way in time. There was even a movie made about this incident.

The official set of units that physicists and chemists use is the *International System of Units*, or *SI units*. The letters SI stand for *Système Internationale*, the French name for the set of units. In this system there are seven *base units*. The unit of length is the *meter* (m). The unit of mass is the *kilogram* (kg). The unit of time is the *second* (s). The unit of temperature is the *kelvin* (K). The unit of electric current is the *ampere* (A). The unit of luminous intensity is the *candela* (cd). The unit for the amount of a substance is the *mole* (mol). The SI units are called *MKS* (meter-kilogram-second) units. Prior to 1961, most chemists and some physicists used *cgs* (centimeter-gram-second) units, but we now use SI units to avoid confusion.

In addition to the seven base units, there are a number of *derived units*. The *newton* (N) is the SI unit of force:

$$1 \text{ N} = 1 \text{ kg m s}^{-2} \quad (\text{definition}) \quad (1.1-5)$$

The *pascal* (Pa) is the SI unit of pressure (force per unit area):

$$1 \text{ Pa} = 1 \text{ N m}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2} \quad (\text{definition}) \quad (1.1-6)$$

We have enclosed these defining equations in boxes, and will enclose the most important equations in boxes throughout the rest of the book.

A force exerted through a distance is equivalent to an amount of work, which is a form of energy. The SI unit of energy is the *joule* (J):

$$1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m}^2 \text{ s}^{-2} \quad (\text{definition}) \quad (1.1-7)$$

Multiples and submultiples of *SI units* are indicated by prefixes, such as “milli” for 1/1000, “centi” for 1/100, “deci” for 1/10, “kilo” for 1000, and so on. These prefixes are listed inside the cover of this book. We do not use double prefixes such as millikilogram for the gram or microkilogram for the milligram.

We will also use some non-SI units. The *calorie* (cal), which was originally defined as the amount of heat required to raise the temperature of 1 gram of water by 1°C, is now defined by:

$$1 \text{ cal} = 4.184 \text{ J} \quad (\text{exactly, by definition}) \quad (1.1-8)$$

We will use several non-SI units of pressure; the *atmosphere* (atm), the *torr*, and the *bar*.

$$1 \text{ atm} = 101325 \text{ Pa} \quad (\text{exactly, by definition}) \quad (1.1-9)$$

$$760 \text{ torr} = 1 \text{ atm} \quad (\text{exactly, by definition}) \quad (1.1-10)$$

$$1 \text{ bar} = 100000 \text{ Pa} \quad (\text{exactly, by definition}) \quad (1.1-11)$$

The angstrom (\AA , equal to 10^{-10} m or 10^{-8} cm) has been a favorite unit of length among chemists, because it is roughly equal to a typical atomic radius. Picometers are nearly as convenient, with 100 pm equal to 1 \AA . Chemists are also reluctant to abandon the *liter* (L), which is the same as 0.001 m^3 or 1 dm^3 (cubic decimeter).

The newton is named for Sir Isaac Newton, 1642–1727, the great English mathematician and physicist who invented classical mechanics and who was one of the inventors of calculus.

The pascal is named for Blaise Pascal, 1623–1662, a famous French philosopher, theologian, and mathematician.

The joule is named for James Prescott Joule, 1818–1889, a great English physicist who pioneered in the thermodynamic study of work, heat, and energy in a laboratory that he constructed in his family's brewery.

Lorenzo Romano Amadeo Carlo Avogadro, 1776–1856, was an Italian lawyer and professor of natural philosophy. He was the first to postulate that equal volumes of gases under the same conditions contained the same number of molecules.

Josef Loschmidt, 1821–1895, was an Austrian chemist who made various contributions, including being the first to propose using two line segments to represent a double bond and three line segments to represent a triple bond.

Boltzmann's constant is named for Ludwig Boltzmann, 1844–1906, an Austrian physicist who was one of the inventors of gas kinetic theory and statistical mechanics.

The Mole and Avogadro's Constant

The *formula unit* of a substance is the smallest amount of a substance that retains the identity of that substance. It can be an atom, a molecule, or an electrically neutral set of ions. A *mole* of any substance is an amount with the same number of formula units as the number of atoms contained in exactly 0.012 kg of the ^{12}C (carbon-12) isotope. The *atomic mass unit* (amu or u) is defined such that one atom of ^{12}C has a mass of exactly 12 amu. Therefore the mass of a mole of any substance expressed in grams is numerically equal to the mass of a formula unit expressed in atomic mass units.

The number of formula units, N , in a sample of any substance is proportional to the *amount of substance* measured in moles, denoted by n :

$$N = N_{\text{Av}}n \quad (1.1-12)$$

The proportionality constant N_{Av} is called *Avogadro's constant* in some countries and *Loschmidt's constant* in others. It is known from experiment to have the value

$$N_{\text{Av}} = 6.02214 \times 10^{23} \text{ mol}^{-1} \quad (1.1-13)$$

The ideal gas equation can be written in terms of the number of molecules, N :

$$V = \frac{nRT}{P} = \frac{nN_{\text{Av}}k_{\text{B}}T}{P} = \frac{Nk_{\text{B}}T}{p} \quad (1.1-14)$$

The *ideal gas constant* R is known from experiment to have the value $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$. In common non-SI units, it is equal to $0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$. The constant k_{B} is called *Boltzmann's constant*:

$$k_{\text{B}} = \frac{R}{N_{\text{Av}}} = \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{6.02214 \times 10^{23} \text{ mol}^{-1}} = 1.3807 \times 10^{-23} \text{ J K}^{-1} \quad (1.1-15)$$

Problem Solving Techniques

If you have a home repair or automotive repair to do, the work will go better if you have the necessary tools at hand when you start the job. The same thing is true for physical chemistry problems. You should analyze the problem and make sure that you know what formulas and techniques are needed and make sure that you have them at hand. Think of your supply of formulas and techniques as your tools, and try to keep your toolbox organized.

One of the most important things in problem solving is that you must use consistent units in any numerical calculation. The conversion to consistent units is conveniently done by the *factor-label method*, which is a straightforward use of proportionality factors. It is illustrated in the following example, and you can review this method in almost any general chemistry textbook.

EXAMPLE 1.2

Find the pressure in Pa and in atm of 20.00 g of neon gas (assumed to be ideal) at a temperature of 0.00°C and a volume of 22.400 L.

Solution

The Celsius temperature differs from the absolute temperature by 273.15 K, but the Celsius degree is the same size as the kelvin.

$$T = 273.15 \text{ K} + 0.00^\circ\text{C} = 273.15 \text{ K}$$

We convert amount of gas to moles and the volume to m^3 using the factor-label method:

$$n = (20.00 \text{ g}) \left(\frac{1 \text{ mol}}{20.179 \text{ g}} \right) = 0.9911 \text{ mol}$$

$$V = (22.400 \text{ L}) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) = 0.022400 \text{ m}^3$$

We now carry out the numerical calculation:

$$P = \frac{nRT}{V} = \frac{(0.9911 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{(0.022400 \text{ m}^3)}$$

$$= 1.005 \times 10^5 \text{ J m}^{-3} = 1.005 \times 10^5 \text{ N m}^{-2} = 1.005 \times 10^5 \text{ Pa}$$

You can see how the symbolic formula is used as a template for setting up the numerical calculation. The unit conversions can also be included in a single calculation:

$$P = \frac{(20.00 \text{ g})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{(22.400 \text{ L})} \left(\frac{1 \text{ mol}}{20.179 \text{ g}} \right) \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right)$$

$$= 1.005 \times 10^5 \text{ J m}^{-3} = 1.005 \times 10^5 \text{ N m}^{-2} = 1.005 \times 10^5 \text{ Pa}$$

The pressure can be expressed in atmospheres by another conversion:

$$P = (1.005 \times 10^5 \text{ Pa}) \left(\frac{1 \text{ atm}}{101325 \text{ Pa}} \right) = 0.9919 \text{ atm}$$

A calculator displayed 100,486.28725 Pa for the pressure in the previous example. The answer was then rounded to four digits to display only *significant digits*. In carrying out operations with a calculator, it is advisable to carry insignificant digits in intermediate steps in order to avoid round-off error and then to round off insignificant digits in the final answer. You can review significant digits in any elementary chemistry textbook. The main idea is that if the calculation produces digits that are probably incorrect, they are insignificant digits and should be rounded away. An important rule is that in a set of multiplications and divisions, the result generally has as many significant digits as the factor or divisor with the fewest significant digits.

Another important technique in problem solving is to figure out roughly how large your answer should be and what its units should be. For example, the author had a student under time pressure in an examination come up with an answer of roughly 10^{30} cm for a molecular dimension. A moment's thought should have revealed that this distance is greater than the size of the known universe and cannot be correct. Many common mistakes produce an answer that either has the wrong units or is obviously too large or too small, and you can spot these errors if you look for them. You should always write the units on every factor or divisor when setting up a numerical calculation so that you will be more likely to spot an error in units.

EXAMPLE 1.3

The speed of sound in dry air at a density of 1.293 g L^{-1} and a temperature of 0°C is 331.45 m s^{-1} . Convert this speed to miles per hour.

Solution

$$(331.45 \text{ m s}^{-1}) \left(\frac{1 \text{ in}}{0.0254 \text{ m}} \right) \left(\frac{1 \text{ ft}}{12 \text{ in}} \right) \left(\frac{1 \text{ mile}}{5280 \text{ ft}} \right) \left(\frac{3600 \text{ s}}{1 \text{ hour}} \right) = 741.43 \text{ miles hour}^{-1}$$

Note that the conversion ratios do not limit the number of significant digits because they are defined to be exact values.

Exercise 1.1

- Express the value of the ideal gas constant in $\text{cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$. Report only significant digits.
- Find the volume of 2.000 mol of helium (assume ideal) at a temperature of 298.15 K and a pressure of 0.500 atm.
- Find the pressure of a sample of 2.000 mol of helium (assume ideal) at a volume of 20.00 L and a temperature of 500.0 K. Express your answer in terms of Pa, bar, atm, and torr.

PROBLEMS**Section 1.1: Introduction**

- Express the speed of light in furlongs per fortnight. A furlong is $1/8$ mile, and a fortnight is 14 days.
- In the “cgs” system, lengths are measured in centimeters, masses are measured in grams, and time is measured in seconds. The cgs unit of energy is the erg and the cgs unit of force is the dyne.
 - Find the conversion factor between ergs and joules.
 - Find the conversion factor between dynes and newtons.
 - Find the acceleration due to gravity at the earth’s surface in cgs units.
- In one English system of units, lengths are measured in feet, masses are measured in pounds, abbreviated lb ($1 \text{ lb} = 0.4536 \text{ kg}$), and time is measured in seconds. The absolute temperature scale is the Rankine scale, such that 1.8°R corresponds to 1°C and to 1 K .
 - Find the acceleration due to gravity at the earth’s surface in English units.
 - If the pound is a unit of mass, then the unit of force is called the poundal. Calculate the value of the ideal gas constant in ft poundals $(^\circ\text{R})^{-1} \text{ mol}^{-1}$.
 - In another English system of units, the pound is a unit of force, equal to the gravitational force at the earth’s surface, and the unit of mass is the slug. Find the acceleration due to gravity at the earth’s surface in this set of units.
- A light-year is the distance traveled by light in one year.
 - Express the light-year in meters and in kilometers.
 - Express the light-year in miles.
 - If the size of the known universe is estimated to be 20 billion light-years (2×10^{10} light-years) estimate the size of the known universe in miles.
 - If the closest star other than the sun is at a distance of 4 light-years, express this distance in kilometers and in miles.
 - The mean distance of the earth from the sun is 149,599,000 km. Express this distance in light-years.

- 1.5** The parsec is a distance used in astronomy, defined to be a distance from the sun such that “the heliocentric parallax is 1 second of arc.” This means that the direction of observation of an object from the sun differs from the direction of observation from the earth by one second of arc.
- Find the value of 1 parsec in kilometers. Do this by constructing a right triangle with one side equal to 1 parsec and the other side equal to 1.49599×10^8 km, the distance from the earth to the sun. Make the angle opposite the short side equal to 1 second of arc.
 - Find the value of 1 parsec in light-years.
 - Express the distance from the earth to the sun in parsec.
- 1.6** Making rough estimates of quantities is sometimes a useful skill.
- Estimate the number of grains of sand on all of the beaches of all continents on the earth, excluding islands. Do this by making suitable estimates of: (1) the average width of a beach; (2) the average depth of sand on a beach; (3) the length of the coastlines of all of the continents; (4) the average size of a grain of sand.
 - Express your estimate in terms of moles of grains of sand, where a mole of grains of sand is 6.02214×10^{23} grains of sand.
- 1.7** Estimate the number of piano tuners in Chicago (or any other large city of your choice). Do this by estimating: (1) the number of houses, apartments, and other buildings in the city; (2) the fraction of buildings containing a piano; (3) the average frequency of tuning; (4) how many pianos a piano tuner can tune in 1 week.
- 1.8** Estimate the volume of the oceans of the earth in liters. Use the fact that the oceans cover about 71% of the earth’s area and estimate the average depth of the oceans. The greatest depth of the ocean is about 7 miles, slightly greater than the altitude of the highest mountain on the earth.
- 1.9** Find the volume of CO_2 gas produced from 100.0 g of CaCO_3 if the CO_2 is at a pressure of 746 torr and a temperature of 301.0 K. Assume the gas to be ideal.
- 1.10** According to Dalton’s law of partial pressures, the pressure of a mixture of ideal gases is the sum of the partial pressures of the gases. The partial pressure of a gas is defined to be the pressure that would be exerted if that gas were alone in the volume occupied by the gas mixture.
- A sample of oxygen gas is collected over water at 25°C at a total pressure of 748.5 torr, with a partial pressure of water vapor equal to 23.8 torr. If the volume of the collected gas is equal to 454 mL, find the mass of the oxygen. Assume the gas to be ideal.
 - If the oxygen were produced by the decomposition of KClO_3 , find the mass of KClO_3 .
- 1.11** The relative humidity is defined as the ratio of the partial pressure of water vapor to the pressure of water vapor at equilibrium with the liquid at the same temperature. The equilibrium pressure of water vapor at 25°C is 23.756 torr. If the relative humidity is 49%, estimate the amount of water vapor in moles contained in a room that is 8.0 m by 8.0 m and 3.0 m in height. Calculate the mass of the water.
- 1.12** Assume that the atmosphere is at equilibrium at 25°C with a relative humidity of 100% and assume that the barometric pressure at sea level is 1.00 atm. Estimate the total rainfall depth that could occur if all of this moisture is removed from the air above a certain area of the earth.

1.2

Systems and States in Physical Chemistry

Figure 1.2 depicts a typical macroscopic system, a sample of a single gaseous substance that is contained in a cylinder with a movable piston. The cylinder is immersed in a constant-temperature bath that can regulate the temperature of the system. The volume of the system can be adjusted by moving the piston. There is a valve between the cylinder and a hose that leads to the atmosphere or to a tank of gas. When the valve is closed so that no matter can pass into or out of the system, the system is called a *closed system*. When the valve is open so that matter can be added to or removed from the system, it is called an *open system*. If the system were insulated from the rest of the universe so that no heat could pass into or out of the system, it would be called an *adiabatic system* and any process that it undergoes would be called an *adiabatic*

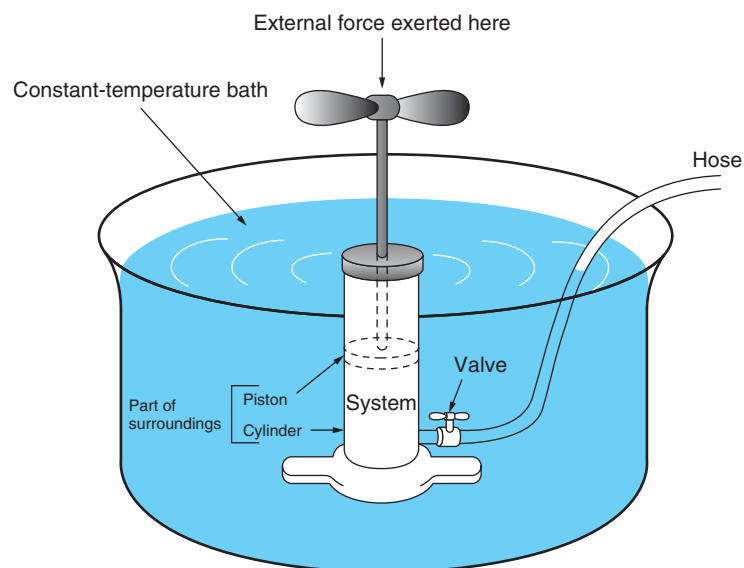


Figure 1.2 A Typical Fluid System Contained in a Cylinder with Variable Volume.

process. If the system were completely separated from the rest of the universe so that no heat, work, or matter could be transferred to or from the system, it would be called an *isolated system*.

The portion of the universe that is outside of the system is called the *surroundings*. We must specify exactly what parts of the universe are included in the system. In this case we define the system to consist only of the gas. The cylinder, piston, and constant-temperature bath are parts of the surroundings.

The State of a System

Specifying the *state of a system* means describing the condition of the system by giving the values of a sufficient set of numerical variables. We have already asserted that for an equilibrium one-phase liquid or gaseous system of one substance, the pressure is a function of three independent variables. We now assert as an experimental fact *that for any equilibrium one-phase fluid system (gas or liquid system) of one substance, there are only three macroscopic independent variables, at least one of which must be proportional to the size of the system*. All other equilibrium macroscopic variables are dependent variables, with values given as functions of the independent variables. We say that *three independent variables specify the equilibrium macroscopic state of a gas or liquid of one substance*. We can generally choose which three independent variables to use so long as one is proportional to the size of the system. For fluid system of one substance, we could choose T , V , and n to specify the equilibrium state. We could also choose T , P , and n , or we could choose T , P , and V .

All other equilibrium macroscopic variables must be dependent variables that are functions of the variables chosen to specify the state of the system. We call both the independent variables and the dependent variables *state functions* or *state variables*. There are two principal classes of macroscopic variables. *Extensive variables* are proportional to the size of the system if P and T are constant, whereas *intensive variables* are independent of the size of the system if P and T are constant. For example, V , n , and m

(the mass of the system) are extensive variables, whereas P and T are intensive variables. The quotient of two extensive variables is an intensive variable. The *density* ρ is defined as m/V , and the *molar volume* V_m is defined to equal V/n . These are intensive variables. One test to determine whether a variable is extensive or intensive is to imagine combining two identical systems, keeping P and T fixed. Any variable that has twice the value for the combined system as for one of the original systems is extensive, and any variable that has the same value is intensive. In later chapters we will define a number of extensive thermodynamic variables, such as the internal energy U , the enthalpy H , the entropy S , and the Gibbs energy G .

We are sometimes faced with systems that are not at equilibrium, and the description of their states is more complicated. However, there are some nonequilibrium states that we can treat as though they were equilibrium states. For example, if liquid water at atmospheric pressure is carefully cooled below 0°C in a smooth container it can remain in the liquid form for a relatively long time. The water is said to be in a *metastable state*. At ordinary pressures, carbon in the form of diamond is in a metastable state, because it spontaneously tends to convert to graphite (although very slowly).

Differential Calculus and State Variables

Because a dependent variable depends on one or more independent variables, a change in an independent variable produces a corresponding change in the dependent variable. If f is a differentiable function of a single independent variable x ,

$$f = f(x) \quad (1.2-1)$$

then an infinitesimal change in x given by dx (the *differential* of x) produces a change in f given by

$$df = \frac{df}{dx} dx \quad (1.2-2)$$

where df/dx represents the *derivative* of f with respect to x and where df represents the *differential* of the dependent variable f . The derivative df/dx gives the rate of change of f with respect to x and is defined by

$$\frac{df}{dx} = \lim_{h \rightarrow 0} \frac{f(x+h) - f(x)}{h} \quad (1.2-3)$$

if the limit exists. If the derivative exists, the function is said to be *differentiable*. There are standard formulas for the derivatives of many functions. For example, if $f = a \sin(bx)$, where a and b represent constants, then

$$\frac{df}{dx} = ab \cos(x) \quad (1.2-4)$$

If a function depends on several independent variables, each independent variable makes a contribution like that in Eq. (1.2-2). If f is a differentiable function of x , y , and z , and if infinitesimal changes dx , dy , and dz are imposed, then the differential df is given by

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz \quad (1.2-5)$$

where $(\partial f/\partial x)_{y,z}$, $(\partial f/\partial y)_{x,z}$, and $(\partial f/\partial z)_{x,y}$ are *partial derivatives*. If the function is represented by a formula, a partial derivative with respect to one independent variable is obtained by the ordinary procedures of differentiation, treating the other independent variables as though they were constants. The independent variables that are held constant are usually specified by subscripts.

We assume that our macroscopic equilibrium state functions are differentiable except possibly at isolated points. For an equilibrium gas or liquid system of one phase and one substance, we can write

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n}\right)_{T,P} dn \quad (1.2-6)$$

This equation represents the value of an infinitesimal change in volume that is produced when we impose arbitrary infinitesimal changes dT , dP , and dn on the system, making sure that the system is at equilibrium after we make the changes. For an ideal gas

$$dV = \frac{nR}{P} dT - \frac{nRT}{P^2} dP + \frac{RT}{P} dn \quad (\text{ideal gas}) \quad (1.2-7)$$

A *mathematical identity* is an equation that is valid for all values of the variables contained in the equation. There are several useful identities involving partial derivatives. Some of these are stated in Appendix B. An important identity is the *cycle rule*, which involves three variables such that each can be expressed as a differentiable function of the other two:

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \quad (\text{cycle rule}) \quad (1.2-8)$$

If there is a fourth variable, it is held fixed in all three of the partial derivatives. Some people are surprised by the occurrence of the negative sign in this equation. See Appendix B for further discussion.

EXAMPLE 1.4

Take $z = xy$ and show that the three partial derivatives conform to the cycle rule.

Solution

$$\begin{aligned} \left(\frac{\partial z}{\partial x}\right)_y &= y \\ \left(\frac{\partial x}{\partial y}\right)_z &= -\frac{z}{y^2} \\ \left(\frac{\partial y}{\partial z}\right)_x &= \frac{1}{x} \\ \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x &= -y \frac{z}{y^2} \frac{1}{x} = -\frac{z}{xy} = -1 \end{aligned}$$

Exercise 1.2

Take $z = ax \ln(y/b)$, where a and b are constants.

a. Find the partial derivatives $(\partial z/\partial x)_y$, $(\partial x/\partial y)_z$, and $(\partial y/\partial z)_x$.

b. Show that the derivatives of part a conform to the cycle rule.

A *second partial derivative* is a partial derivative of a partial derivative. Both derivatives can be with respect to the same variable:

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial x}\right)_y\right)_y \quad (1.2-9)$$

The following is called a *mixed second partial derivative*:

$$\frac{\partial^2 f}{\partial y \partial x} = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x}\right)_y\right)_x \quad (1.2-10)$$

The reciprocity relation is named for its discoverer, Leonhard Euler, 1707–1783, a great Swiss mathematician who spent most of his career in St. Petersburg, Russia, and who is considered by some to be the father of mathematical analysis. The base of natural logarithms is denoted by e after his initial.

Euler's reciprocity relation states that the two mixed second partial derivatives of a differentiable function must be equal to each other:

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y} \quad (1.2-11)$$

Exercise 1.3

Show that the three pairs of mixed partial derivatives that can be obtained from the derivatives in Eq. (1.2-7) conform to Euler's reciprocity relation.

Processes

A process is an occurrence that changes the state of a system. Every macroscopic process has a *driving force* that causes it to proceed. For example, a temperature difference is the driving force that causes a flow of heat. A larger value of the driving force corresponds to a larger rate of the process. A zero rate must correspond to zero value of the driving force. A *reversible process* is one that can at any time be reversed in direction by an infinitesimal change in the driving force. The driving force of a reversible process must be infinitesimal in magnitude since it must reverse its sign with an infinitesimal change. A reversible process must therefore occur infinitely slowly, and the system has time to relax to equilibrium at each stage of the process. The system passes through a sequence of equilibrium states during a reversible process. A reversible process is sometimes called a *quasi-equilibrium process* or a *quasi-static process*. There can be no truly reversible processes in the real universe, but we can often make calculations for them and apply the results to real processes, either exactly or approximately.

An approximate version of Eq. (1.2-6) can be written for a finite reversible process corresponding to increments ΔP , ΔT , and Δn :

$$\Delta V \approx \left(\frac{\partial V}{\partial T}\right)_{P,n} \Delta T + \left(\frac{\partial V}{\partial P}\right)_{T,n} \Delta P + \left(\frac{\partial V}{\partial n}\right)_{T,P} \Delta n \quad (1.2-12)$$

where \approx means “is approximately equal to” and where we use the common notation

$$\Delta V = V(\text{final}) - V(\text{initial}) \quad (1.2-13)$$

and so on. Calculations made with Eq. (1.2-12) will usually be more nearly correct if the finite increments ΔT , ΔP , and Δn are small, and less nearly correct if the increments are large.

Variables Related to Partial Derivatives

The *isothermal compressibility* κ_T is defined by

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right) \quad \text{(definition of the isothermal compressibility)} \quad (1.2-14)$$

The factor $1/V$ is included so that the compressibility is an intensive variable. The fact that T and n are fixed in the differentiation means that measurements of the isothermal compressibility are made on a closed system at constant temperature. It is found experimentally that the compressibility of any system is positive. That is, every system decreases its volume when the pressure on it is increased.

The *coefficient of thermal expansion* is defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,n} \quad \text{(definition of the coefficient of thermal expansion)} \quad (1.2-15)$$

The coefficient of thermal expansion is an intensive quantity and is usually positive. That is, if the temperature is raised the volume usually increases. There are a few systems with negative values of the coefficient of thermal expansion. For example, liquid water has a negative value of α between 0°C and 3.98°C . In this range of temperature the volume of a sample of water decreases if the temperature is raised. Values of the isothermal compressibility for a few pure liquids at several temperatures and at two different pressures are given in Table A.1 of Appendix A. The values of the coefficient of thermal expansion for several substances are listed in Table A.2. Each value applies only to a single temperature and a single pressure, but the dependence on temperature and pressure is not large for typical liquids, and these values can usually be used over fairly wide ranges of temperature and pressure.

For a closed system (constant n) Eq. (1.2-12) can be written

$$\Delta V \approx V\alpha\Delta T - V\kappa_T\Delta P \quad (1.2-16)$$

EXAMPLE 1.5

The isothermal compressibility of liquid water at 298.15 K and 1.000 atm is equal to $4.57 \times 10^{-5} \text{ bar}^{-1} = 4.57 \times 10^{-10} \text{ Pa}^{-1}$. Find the fractional change in the volume of a sample of water if its pressure is changed from 1.000 bar to 50.000 bar at a constant temperature of 298.15 K.

Solution

The compressibility is relatively small in magnitude so we can use Eq. (1.2-16):

$$\Delta V \approx -V\kappa_T\Delta P \quad (1.2-17)$$

The fractional change is

$$\frac{\Delta V}{V} \approx -\kappa_T \Delta P = -(4.57 \times 10^{-5} \text{ bar}^{-1})(49.00 \text{ bar}) = -2.24 \times 10^{-3}$$

EXAMPLE 1.6

For liquid water at 298.15 K and 1.000 atm, $\alpha = 2.07 \times 10^{-4} \text{ K}^{-1}$. Find the fractional change in the volume of a sample of water at 1.000 atm if its temperature is changed from 298.15 K to 303.15 K.

Solution

To a good approximation,

$$\Delta V \approx V\alpha\Delta T$$

The fractional change in volume is

$$\frac{\Delta V}{V} \approx \alpha\Delta T = (2.07 \times 10^{-4} \text{ K}^{-1})(5.000 \text{ K}) = 1.04 \times 10^{-3}$$

Exercise 1.4

- Find expressions for the isothermal compressibility and coefficient of thermal expansion for an ideal gas.
- Find the value of the isothermal compressibility in atm^{-1} , in bar^{-1} , and in Pa^{-1} for an ideal gas at 298.15 K and 1.000 atm. Find the ratio of this value to that of liquid water at the same temperature and pressure, using the value from Table A.1.
- Find the value of the coefficient of thermal expansion of an ideal gas at 20°C and 1.000 atm. Find the ratio of this value to that of liquid water at the same temperature and pressure, using the value from Table A.2.

In addition to the coefficient of thermal expansion there is a quantity called the *coefficient of linear thermal expansion*, defined by

$$\alpha_L = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_P \quad \begin{array}{l} \text{(definition of the coefficient} \\ \text{of linear thermal expansion)} \end{array} \quad (1.2-18)$$

where L is the length of the object. This coefficient is usually used for solids, whereas the coefficient of thermal expansion in Eq. (1.2-15) is used for gases and liquids. Unfortunately, the subscript L is sometimes omitted on the symbol for the coefficient of linear thermal expansion, and the name “coefficient of thermal expansion” is also sometimes used for it. Because the units of both coefficients are the same (reciprocal temperature) there is opportunity for confusion between them.

We can show that the linear coefficient of thermal expansion is equal to one-third of the coefficient of thermal expansion. Subject a cubical object of length L to an infinitesimal change in temperature, dT . The new length of the object is

$$L(T + dT) = L(T) + \left(\frac{\partial L}{\partial T} \right)_P dT = L(T)(1 + \alpha_L dT) \quad (1.2-19)$$

The volume of the object is equal to L^3 , so

$$\begin{aligned} V(T + dT) &= L(T)^3 (1 + \alpha_L dT)^3 \\ &= L(T)^3 (1 + 3\alpha_L dT + 3(\alpha_L dT)^2 + (\alpha_L dT)^3) \end{aligned} \quad (1.2-20)$$

Since dT is small, the last two terms are insignificant compared with the term that is proportional to dT .

$$V(T + dT) = L(T)^3 (1 + 3\alpha_L dT) \quad (1.2-21)$$

The volume at temperature $T + dT$ is given by

$$V(T + dT) = V(T) + \left(\frac{\partial V}{\partial T}\right) dT = V(T)(1 + \alpha dT) \quad (1.2-22)$$

Comparison of Eq. (1.2-22) with Eq. (1.2-21) shows that

$$\alpha = 3\alpha_L \quad (1.2-23)$$

This relationship holds for objects that are not necessarily shaped like a cube.

EXAMPLE 1.7

The linear coefficient of expansion of borosilicate glass, such as Pyrex[®] or Kimax[®], is equal to $3.2 \times 10^{-6} \text{ K}^{-1}$. If a volumetric flask contains 2.000000 L at 20.0°C, find its volume at 25.0°C.

Solution

$$\begin{aligned} V(25^\circ\text{C}) &= V(20^\circ\text{C})(1 + 3\alpha_L(5.0^\circ\text{C})) \\ &= (2.000000 \text{ L})(1 + 3(3.2 \times 10^{-6})(5.0^\circ\text{C})) = 2.000096 \text{ L} \end{aligned}$$

Exercise 1.5

Find the volume of the volumetric flask in Example 1.7 at 100.0°C.

Moderate changes in temperature and pressure produce fairly small changes in the volume of a liquid, as in the examples just presented. The volumes of most solids are even more nearly constant. We therefore recommend the following practice: *For ordinary calculations, assume that liquids and solids have fixed volumes. For more precise calculations, calculate changes in volume proportional to changes in pressure or temperature as in Examples 1.5 and 1.6.*

Exercise 1.6

The compressibility of acetone at 20°C is $12.39 \times 10^{-10} \text{ Pa}^{-1}$, and its density is 0.7899 g cm^{-3} at 20°C and 1.000 bar.

- Find the molar volume of acetone at 20°C and a pressure of 1.000 bar.
- Find the molar volume of acetone at 20°C and a pressure of 100.0 bar.

PROBLEMS

Section 1.2: Systems and States in Physical Chemistry

1.13 Show that the three partial derivatives obtained from $PV = nRT$ with n fixed conform to the cycle rule, Eq. (B-15) of Appendix B.

1.14 For 1.000 mol of an ideal gas at 298.15 K and 1.000 bar, find the numerical value of each of the three partial derivatives in the previous problem and show numerically that they conform to the cycle rule.

1.15 Finish the equation for an ideal gas and evaluate the partial derivatives for $V = 22.4$ L, $T = 273.15$ K, and $n = 1.000$ mol.

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + ?$$

1.16 Take $z = aye^{x/b}$, where a and b are constants.

- Find the partial derivatives $(\partial z/\partial x)_y$, $(\partial x/\partial y)_z$, and $(\partial y/\partial z)_x$.
- Show that the derivatives of part a conform to the cycle rule, Eq. (B-15) of Appendix B.

1.17 a. Find the fractional change in the volume of a sample of liquid water if its temperature is changed from 20.00°C to 30.00°C and its pressure is changed from 1.000 bar to 26.000 bar.

- Estimate the percent change in volume of a sample of benzene if it is heated from 0°C to 45°C at 1.000 atm.
- Estimate the percent change in volume of a sample of benzene if it is pressurized at 55°C from 1.000 atm to 50.0 atm.

1.18 a. Estimate the percent change in the volume of a sample of carbon tetrachloride if it is pressurized from 1.000 atm to 10.000 atm at 25°C.

- Estimate the percent change in the volume of a sample of carbon tetrachloride if its temperature is changed from 20°C to 40°C.

1.19 Find the change in volume of 100.0 cm³ of liquid carbon tetrachloride if its temperature is changed from 20.00°C to 25.00°C and its pressure is changed from 1.000 atm to 10.000 atm.

1.20 Let $f(u) = \sin(au^2)$ and $u = x^2 + y^2$, where a is a constant. Using the chain rule, find $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$. (See Appendix B.)

1.21 Show that for any system,

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$$

1.22 The coefficient of linear expansion of borosilicate glass is equal to $3.2 \times 10^{-6} \text{ K}^{-1}$.

- Calculate the pressure of a sample of helium (assumed ideal) in a borosilicate glass vessel at 150°C if its pressure at 0°C is equal to 1.000 atm. Compare with the value of the pressure calculated assuming that the volume of the vessel is constant.
- Repeat the calculation of part a using the virial equation of state truncated at the B_2 term. The value of B_2 for helium is 11.8 cm³mol⁻¹ at 0°C and 11.0 cm³mol⁻¹ at 150°C.

1.23 Assuming that the coefficient of thermal expansion of gasoline is roughly equal to that of benzene, estimate the fraction of your gasoline expense that could be saved by purchasing gasoline in the morning instead of in the afternoon, assuming a temperature difference of 5°C.

1.24 The volume of a sample of a liquid at constant pressure can be represented by

$$V_m(t_C) = V_m(0^\circ\text{C})(1 + \alpha' t_C + \beta' t_C^2 + \gamma' t_C^3)$$

where α' , β' , and γ' are constants and t_C is the Celsius temperature.

- Find an expression for the coefficient of thermal expansion as a function of t_C .
- Evaluate the coefficient of thermal expansion of benzene at 20.00°C, using $\alpha' = 1.17626 \times 10^{-3}(\text{°C})^{-1}$, $\beta' = 1.27776 \times 10^{-6}(\text{°C})^{-2}$, and $\gamma' = 0.80648 \times 10^{-8}(\text{°C})^{-3}$. Compare your value with the value in Table A.2.

1.25 The coefficient of thermal expansion of ethanol equals $1.12 \times 10^{-3} \text{ K}^{-1}$ at 20°C and 1.000 atm. The density at 20°C is equal to 0.7893 g cm⁻³.

- Find the volume of 1.000 mol of ethanol at 10.00°C and 1.000 atm.
- Find the volume of 1.000 mol of ethanol at 30.00°C and 1.000 atm.

1.3

Real Gases

The van der Waals equation of state is named for Johannes Diderik van der Waals, 1837–1923, a Dutch physicist who received the 1910 Nobel Prize in physics for his work on equations of state.

Most gases obey the ideal gas law to a good approximation when near room temperature and at a moderate pressure. At higher pressures one might need a better description. Several equations of state have been devised for this purpose. The *van der Waals equation of state* is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (1.3-1)$$

The symbols a and b represent constant parameters that have different values for different substances. Table A.3 in Appendix A gives values of van der Waals parameters for several substances.

We solve the van der Waals equation for P and note that P is actually a function of only two intensive variables, the temperature T and the molar volume V_m , defined to equal V/n .

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (1.3-2)$$

This dependence illustrates the fact that *intensive variables such as pressure cannot depend on extensive variables* and that *the intensive state of a gas or liquid of one substance is specified by only two intensive variables*.

EXAMPLE 1.8

Use the van der Waals equation to calculate the pressure of nitrogen gas at 273.15 K and a molar volume of 22.414 L mol⁻¹. Compare with the pressure of an ideal gas at the same temperature and molar volume.

Solution

$$\begin{aligned} P &= \frac{(8.134 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{0.022414 \text{ m}^3 \text{ mol}^{-1} - 0.0000391 \text{ m}^3 \text{ mol}^{-1}} - \frac{0.1408 \text{ Pa m}^3 \text{ mol}^{-1}}{(0.022414 \text{ m}^3 \text{ mol}^{-1})^2} \\ &= 1.0122 \times 10^5 \text{ Pa} = 0.9990 \text{ atm} \end{aligned}$$

For the ideal gas

$$P = \frac{RT}{V_m} = \frac{(8.134 \text{ J K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})}{0.022414 \text{ m}^3 \text{ mol}^{-1}} = 1.0132 \times 10^5 \text{ Pa} = 1.0000 \text{ atm}$$

Exercise 1.7

- Show that in the limit that V_m becomes large, the van der Waals equation becomes identical to the ideal gas law.
- Find the pressure of 1.000 mol of nitrogen at a volume of 24.466 L and a temperature of 298.15 K using the van der Waals equation of state. Find the pressure of an ideal gas under the same conditions.

- c. Find the pressure of 1.000 mol of nitrogen at a volume of 1.000 L and a temperature of 298.15 K using the van der Waals equation of state. Find the pressure of an ideal gas under the same conditions.

Another common equation of state is the *virial equation of state*:

$$\frac{PV_m}{RT} = 1 + \frac{B_2}{V_m} + \frac{B_3}{V_m^2} + \frac{B_4}{V_m^3} + \dots \quad (1.3-3)$$

which is a power series in the independent variable $1/V_m$. The B coefficients are called *virial coefficients*. The first virial coefficient, B_1 , is equal to unity. The other virial coefficients must depend on temperature in order to provide an adequate representation. Table A.4 gives values of the second virial coefficient for several gases at several temperatures.

An equation of state that is a power series in P is called the *pressure virial equation of state*:

$$PV_m = RT + A_2P + A_3P^2 + A_4P^3 + \dots \quad (1.3-4)$$

The coefficients A_2, A_3 , etc., are called *pressure virial coefficients* and also must depend on the temperature. It can be shown that A_2 and B_2 are equal.

EXAMPLE 1.9

Show that $A_2 = B_2$.

Solution

We solve Eq. (1.3-3) for P and substituting this expression for each P in Eq. (1.3-4).

$$P = \frac{RT}{V_m} + \frac{RT B_2}{V_m^2} + \frac{RT B_3}{V_m^3} + \dots$$

We substitute this expression into the left-hand side of Eq. (1.3-4).

$$PV_m = RT + \frac{RT B_2}{V_m} + \frac{RT B_3}{V_m^2} + \dots$$

We substitute this expression into the second term on the right-hand side of Eq. (1.3-4).

$$PV_m = RT + A_2 \frac{RT}{V_m} + \frac{RT B_2}{V_m^2} + \frac{RT B_3}{V_m^3} + \dots$$

If two power series in the same variable are equal to each other for all values of the variable, the coefficients of the terms of the same power of the variable must be equal to each other. We equate the coefficients of the $1/V_m$ terms and obtain the desired result:

$$A_2 = B_2$$

Exercise 1.8

Show that $A_3 = \frac{1}{RT}(B_3 - B_2^2)$.

Table 1.1 displays several additional equations of state, and values of parameters for several gases are found in Table A.3. The parameters for a given gas do not necessarily have the same values in different equations even if the same letters are used. The accuracy of several of the equations of state has been evaluated.² The *Redlich–Kwong equation of state* seemed to perform better than the other two-parameter equations, with the van der Waals equation coming in second best. The Gibbons–Laughton modification of the Redlich–Kwong equation (with four parameters) is more accurate than the two-parameter equations.

Table 1.1 Some Equations of State

The letters a and b stand for constant parameters that have different values for different substances. These parameters do not necessarily have the values for the same substance in different equations of state.

The Berthelot Equation of State

$$\left(P + \frac{a}{TV_m^2}\right)(V_m - b) = RT$$

The Dieterici Equation of State

$$Pe^{a/V_m RT}(V_m - b) = RT$$

The Redlich–Kwong Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a}{T^{1/2}V_m(V_m + b)}$$

The Soave Modification of the Redlich–Kwong Equation of State

$$P = \frac{RT}{V_m - b} - \frac{\alpha\alpha(T)}{V_m(V_m + b)}$$

where $\alpha(T) = \{1 + m[1 - (T/T_c)^{1/2}]\}^2$, where m is a constant parameter and where T_c is the critical temperature. See the article by Soave for values of the parameter m .

The Gibbons–Laughton Modification of the Redlich–Kwong–Soave Equation of State

The equation is the same as the Soave modification, but $\alpha(T)$ is given by

$$\alpha(T) = 1 + X(T/T_c) - 1 + Y(T/T_c)^{1/2} - 1$$

where X and Y are constant parameters. See the article by Gibbons and Laughton for values of these parameters.

Other equations of state can be found in the book by Hirschfelder, Curtiss, and Bird, including the Beattie–Bridgeman equation, with five parameters, and the Benedict–Webb–Rubin equation, with eight parameters.

²J. B. Ott, J. R. Goates, and H. T. Hall, Jr., *J. Chem. Educ.*, **48**, 515 (1971); M. W. Kemp, R. E. Thompson, and D. J. Zigrang, *J. Chem. Educ.*, **52**, 802 (1975).

Graphical Representation of Volumetric Data for Gases

The *compression factor*, denoted by Z , is sometimes used to describe the behavior of real gases:

$$Z = \frac{PV_m}{RT} \quad (1.3-5)$$

Some authors call Z the *compressibility factor*. We avoid this name because it might be confused with the compressibility. The compression factor equals unity for an ideal gas. Figure 1.3 shows a graph of the compression factor of nitrogen gas as a function of pressure at several temperatures. At low temperatures, the value of Z is less than unity for moderate pressures, but rises above unity for larger pressures. At higher temperatures, the value of Z is greater than unity for all pressures. Attractions between the molecules tend to reduce the value of Z and repulsions between the molecules tend to increase the value of Z . Attractions are more important at lower temperatures and smaller pressures, and repulsions are more important at higher temperatures and higher pressures. The temperature at which the curve has zero slope at zero pressure is called the *Boyle temperature*. This is the temperature at which the gas most nearly approaches ideality for small pressures.

For a van der Waals gas, the compression factor is given by

$$Z = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} = \frac{1}{1 - by} - \frac{ay}{RT} \quad (1.3-6)$$

where we let $y = 1/V_m$. Since a and b are both positive for all gases, the first term on the right-hand side of Eq. (1.3-6) gives a positive contribution to Z , and the second term gives a negative contribution. The parameter b describes the effect of repulsive

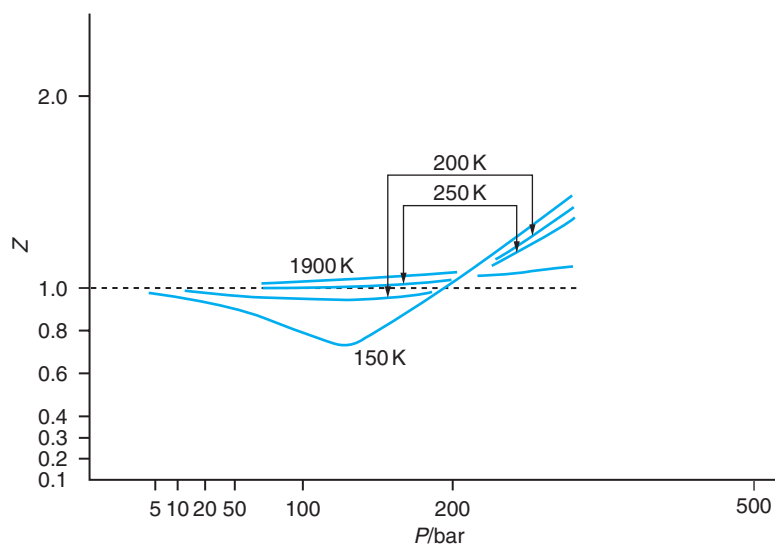


Figure 1.3 The Compression Factor of Nitrogen as a Function of Pressure at Several Temperatures.

intermolecular forces and the parameter a describes the effect of attractive intermolecular forces. For higher temperatures the second term is relatively unimportant, and the compression factor will exceed unity for all values of y . For temperatures below the Boyle temperature the second term becomes relatively more important, and a value of Z less than unity will occur if y is not too large.

EXAMPLE 1.10

- Find an expression for the Boyle temperature of a van der Waals gas.
- Find the value of the Boyle temperature of nitrogen gas as predicted by the van der Waals equation.

Solution

- Since y is proportional to P for small values of P , we seek the temperature at which

$$\left(\frac{\partial Z}{\partial y}\right)\Big|_{y=0} = 0 = \left(\frac{b}{(1-by)^2} - \frac{a}{RT}\right)\Big|_{y=0} = b - \frac{a}{RT}$$

where the subscript $y = 0$ indicates the value of y at which the derivative is evaluated. The Boyle temperature is

$$T_{\text{Boyle}} = a/Rb$$

- For nitrogen,

$$T_{\text{Boyle}} = \frac{0.1408 \text{ Pa m}^2 \text{ mol}^{-1}}{(8.134 \text{ J K}^{-1} \text{ mol}^{-1})(3.913 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})} = 433 \text{ K}$$

Exercise 1.9

- Find an expression for the Boyle temperature of a gas obeying the Dieterici equation of state.
- Find the value of the Boyle temperature of nitrogen according to the Dieterici equation of state.
- Find the expression for the molar volume at which $Z = 1$ for the van der Waals gas for a given temperature below the Boyle temperature. Hint: Find the nonzero value of y in Eq. (1.3-6) that makes $Z = 1$.
- Find the value of the molar volume and the pressure at which $Z = 1$ for nitrogen at 273.15 K, according to the van der Waals equation.

PROBLEMS**Section 1.3: Real Gases**

1.26 For the van der Waals equation of state, obtain formulas for the partial derivatives $(\partial P/\partial T)_{V,n}$, $(\partial P/\partial V)_{T,n}$, and $(\partial P/\partial n)_{T,V}$.

1.27 For the virial equation of state,

- Find the expressions for $(\partial P/\partial V)_{T,n}$ and $(\partial P/\partial T)_{V,n}$.
- Show that $(\partial^2 P/\partial V \partial T)_n = (\partial^2 P/\partial T \partial V)_n$.

- 1.28** Evaluate each of the partial derivatives in Problem 1.26 for carbon dioxide at 298.15 K and 10.000 bar.
- 1.29** a. Derive an expression for the isothermal compressibility of a gas obeying the van der Waals equation of state. Hint: Use the reciprocal identity, Eq. (B-8).
b. Evaluate the isothermal compressibility of carbon dioxide gas at a temperature of 298.15 K and a molar volume of $0.01000 \text{ m}^3 \text{ mol}^{-1}$. Compare with the value obtained from the ideal gas law.
- 1.30** Write the expressions giving the compression factor Z as a function of temperature and molar volume for the van der Waals, Dieterici, and Redlich–Kwong equations of state.
- 1.31** a. For the van der Waals equation of state at temperatures below the Boyle temperature, find an expression for a value of the pressure other than $P = 0$ for which $PV_m = RT$.
b. Find the value of this pressure for nitrogen gas at 298.15 K.
- 1.32** a. By differentiation, find an expression for the isothermal compressibility of a gas obeying the Dieterici equation of state.
b. Find the value of the isothermal compressibility of nitrogen gas at 298.15 K and $V_m = 24.4 \text{ L}$. Compare with that of an ideal gas.
- 1.33** a. By differentiation, find an expression for the coefficient of thermal expansion of a gas obeying the van der Waals equation of state.
b. Find the value of the coefficient of thermal expansion of nitrogen gas at 298.15 K and $V_m = 24.4 \text{ L mol}^{-1}$.
- 1.34** By differentiation, find an expression for the coefficient of thermal expansion of a gas obeying the Dieterici equation of state.
- 1.35** Manipulate the Dieterici equation of state into the virial form. Use the identity
- $$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \cdots + (-1)^n \frac{x^n}{n!} + \cdots$$
- where $n! = n(n-1)(n-2)(n-3)\cdots(3)(2)(1)$. Write expressions for the second, third, and fourth virial coefficients.
- 1.36** Write an expression for the isothermal compressibility of a nonideal gas obeying the Redlich–Kwong equation of state.
- 1.37** The experimental value of the compression factor $Z = PV_m/RT$ for hydrogen gas at $T = 273.15 \text{ K}$ and

$V_m = 0.1497 \text{ L mol}^{-1}$ is 1.1336. Find the values of Z predicted by the van der Waals, Dieterici, and Redlich–Kwong equations of state for these conditions. Calculate the percent error for each.

- 1.38** The parameters for the van der Waals equation of state for a mixture of gases can be approximated by use of the *mixing rules*:

$$a = a_1x_1^2 + a_{12}x_1x_2 + a_2x_2^2$$

$$b = b_1x_1^2 + b_{12}x_1x_2 + b_2x_2^2$$

where x_1 and x_2 are the mole fractions of the two substances and where a_1 , b_1 , a_2 , and b_2 are the van der Waals parameters of the two substances. The quantities a_{12} and b_{12} are defined by

$$a_{12} = (a_1a_2)^{1/2}$$

and

$$b_{12} = \left(\frac{b_1^{1/3} + b_2^{1/3}}{3} \right)^3$$

- a. Using these mixing rules and the van der Waals equation of state, find the pressure of a mixture of 0.79 mol of N_2 and 0.21 mol of O_2 at 298.15 K and at a *mean molar volume* (defined as V/n_{total}) of $0.00350 \text{ m}^3 \text{ mol}^{-1}$. Compare your answer with the pressure of an ideal gas under the same conditions.
- b. Using the van der Waals equation of state, find the pressure of pure N_2 at 298.15 K and at a molar volume of $0.00350 \text{ m}^3 \text{ mol}^{-1}$.
- c. Using the van der Waals equation of state, find the pressure of pure O_2 at 298.15 K and at a molar volume of $0.00350 \text{ m}^3 \text{ mol}^{-1}$.
- 1.39** Find the value of the isothermal compressibility of carbon dioxide gas at 298.15 K and a molar volume of 24.4 L mol^{-1} ,
a. According to the ideal gas law.
b. According to the truncated virial equation of state
- $$\frac{PV_m}{RT} = 1 + \frac{B_2}{V_m}$$
- For carbon dioxide at 298.15 K,
 $B_2 = -12.5 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$.
- 1.40** Considering P to be a function of T , V , and n , obtain the expression for dP for a gas obeying the van der Waals equation of state.

1.4

The Coexistence of Phases and the Critical Point

Transitions from a gaseous state to a liquid state or from a liquid state to a solid state, and so forth, are called *phase transitions* and the samples of matter in the different states are called *phases*. Such transitions can take place abruptly. If a gas is initially at a temperature slightly above its condensation temperature, a small decrease in the temperature can produce a liquid phase that coexists with the gas phases, and a further small decrease in the temperature can cause the system to become a single liquid phase. This remarkable behavior is an exception to the general rule that in nature small changes produce small effects and large changes produce large effects.

It is an experimental fact that for any pure substance the pressure at which two phases can coexist at equilibrium is a smooth function of the temperature. Equivalently, the temperature is a smooth function of the pressure. Figure 1.4 shows schematic curves representing these functions for a typical substance. The curves are called *coexistence curves* and the figure is called a *phase diagram*. The three curves shown are the solid–gas (sublimation) curve at the bottom of the figure, the liquid–gas (vaporization) curve at the upper right, and the solid–liquid (fusion, melting, or freezing) curve at the upper left. The three curves meet at a point called the *triple point*. This point corresponds to

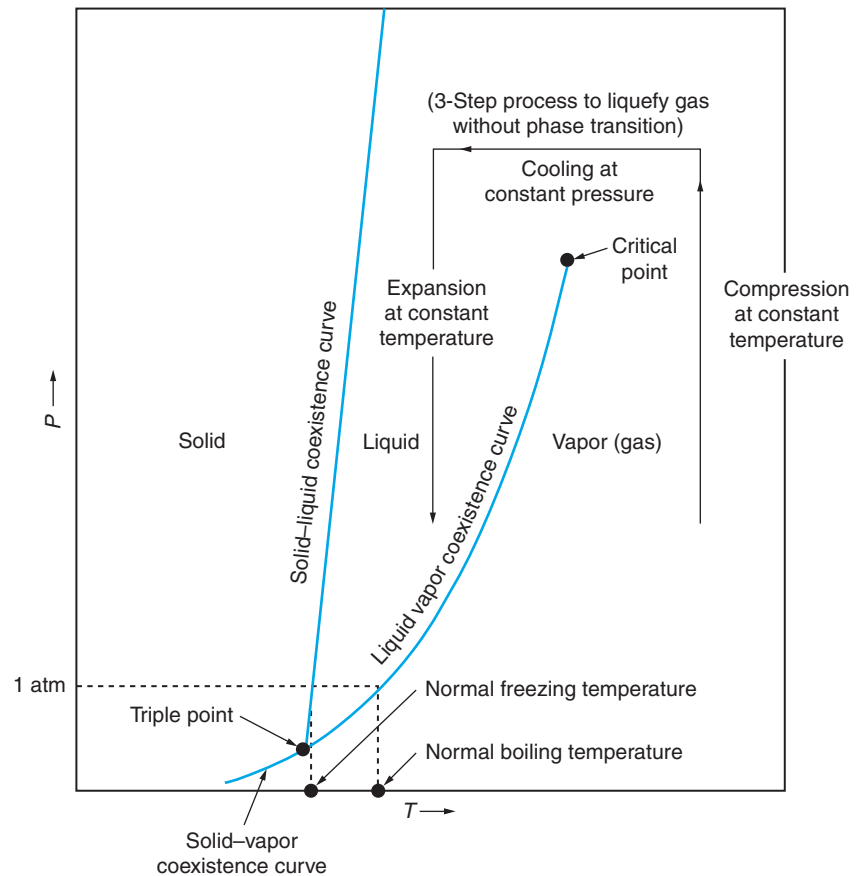


Figure 1.4 The Coexistence Curves for a Typical Pure Substance (Schematic).

the unique value of the pressure and the unique value of the temperature at which all three phases can coexist.

The equilibrium temperature for coexistence of the liquid and solid at a pressure equal to 1 atmosphere is called the *normal melting temperature* or *normal freezing temperature*. The equilibrium temperature for coexistence of the liquid and gas phases at a pressure equal to 1 atmosphere is called the *normal boiling temperature*. These temperatures are marked on Figure 1.4. If the triple point is at a higher pressure than 1 atmosphere the substance does not have a normal freezing temperature or a normal boiling temperature, but has a *normal sublimation temperature* at which the solid and gas coexist at a pressure equal to 1 atmosphere. The triple point of carbon dioxide occurs at a pressure of 5.112 atm and a temperature of 216.55 K (-56.60°C) and its normal sublimation temperature is equal to 194.6 K (-78.5°C). Equilibrium liquid carbon dioxide can be observed only at pressures greater than 5.112 atm. At lower pressures the solid sublimates directly into the vapor phase.

The Critical Point

There is a remarkable feature that is shown in Figure 1.4. The liquid–vapor coexistence curve terminates at a point that is called the *critical point*. The temperature, molar volume, and pressure at this point are called the *critical temperature*, denoted by T_c , the *critical molar volume*, denoted by V_{mc} , and the *critical pressure*, denoted by P_c . These three quantities are called *critical constants*. Table A.5 in the appendix gives values of the critical constants for several substances. At temperatures higher than the critical temperature and pressures higher than the critical pressure there is no transition between liquid and gas phases. It is possible to heat a gas to a temperature higher than the critical temperature, then to compress it until its density is as large as that of a liquid, and then to cool it until it is a liquid without ever having passed through a phase transition. A path representing this kind of process is drawn in Figure 1.4. Fluids at supercritical temperatures are often referred to as gases, but it is better to refer to them as *supercritical fluids*. Some industrial extractions, such as the decaffeination of coffee, are carried out with supercritical fluids such as carbon dioxide.³ Supercritical carbon dioxide is also used as a solvent in some HPLC applications.⁴ Using a chiral stationary phase, enantiomers can be separated. The liquid–solid coexistence curve apparently does not terminate at a critical point. Nobody has found such a termination, and it seems reasonable that the presence of a lattice structure in the solid, which makes it qualitatively different from the liquid, makes the existence of such a point impossible.

Figure 1.5 schematically shows the pressure of a fluid as a function of molar volume for several fixed temperatures, with one curve for each fixed temperature. These constant-temperature curves are called *isotherms*. For temperatures above the critical temperature there is only one fluid phase, and the isotherms are smooth curves. The liquid branch is nearly vertical since the liquid is almost incompressible while the gas branch of the curve is similar to the curve for an ideal gas. For subcritical temperatures, the isotherm consists of two smooth curves (branches) and a horizontal line segment, which is called a *tie line*. A tie line connects the two points representing the molar volumes of the coexisting liquid and gas phases. As subcritical temperatures closer and closer to the critical temperature are chosen the tie lines become shorter and shorter

³Chem. Eng. Sci., **36**(11), 1769(1981); Env. Sci. Technol., **20**(4), 319 (1986); Chemtech., **21**(4), 250 (1991), Anal. Chem., **66**(12), 106R (1994).

⁴A.M. Thayer, Chem. Eng. News, **83**, 49 (September 5, 2005).

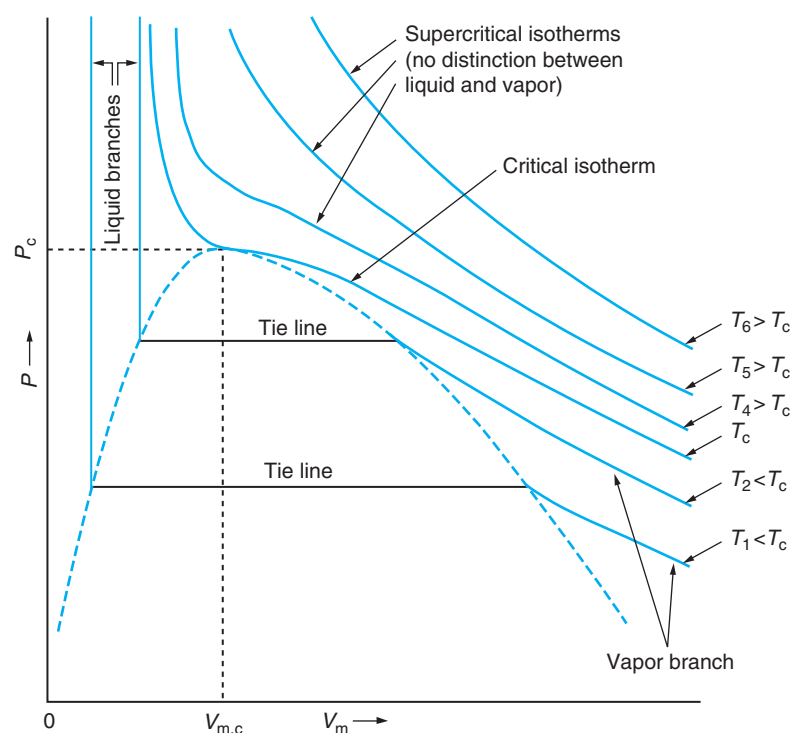


Figure 1.5 Isotherms for a Typical Pure Substance (Schematic).

until they shrink to zero length at the critical point. No two isotherms can intersect, so the isotherm that passes through the critical point must have a horizontal tangent line at the critical point. This point on the critical isotherm is an *inflection point*, with a zero value of $(\partial P / \partial V_m)_T$ and a zero value of $(\partial^2 P / \partial V_m^2)_T$.

At the critical point, a fluid exhibits some unusual properties such as strong scattering of light, infinite heat capacity, and infinite compressibility. If a sample of a pure fluid is confined in a rigid closed container such that the average molar volume is equal to that of the critical state and if the temperature is raised through the critical temperature, the meniscus between the liquid and gas phases becomes diffuse and then disappears at the critical temperature. Figure 1.6 shows photographs illustrating this behavior in carbon dioxide.⁵ The system contains three balls that are slightly different in density, with densities close to the critical density of carbon dioxide.

Figure 1.7 depicts a perspective view of a three-dimensional graph with a surface representing the pressure of a fluid as a function of temperature and molar volume. The isotherms in Figure 1.5 are produced by passing planes of constant temperature through the surface of this graph. Several isotherms are drawn on the surface in Figure 1.7. The liquid–gas tie lines are seen in the tongue-shaped region. When the three-dimensional graph is viewed in a direction perpendicular to the T – P plane each liquid–gas tie line is seen as a point. The set of all such points makes up the gas–liquid coexistence curve seen in Figure 1.4.

⁵J. V. Sengers and A. L. Sengers, *Chem. Eng. News.*, **46**, 54 (June 10, 1968). This figure can be seen on the Web at <http://sfu.ca/chemcai/critical.html>, courtesy of Dr. Steven Lower of Simon Fraser University.

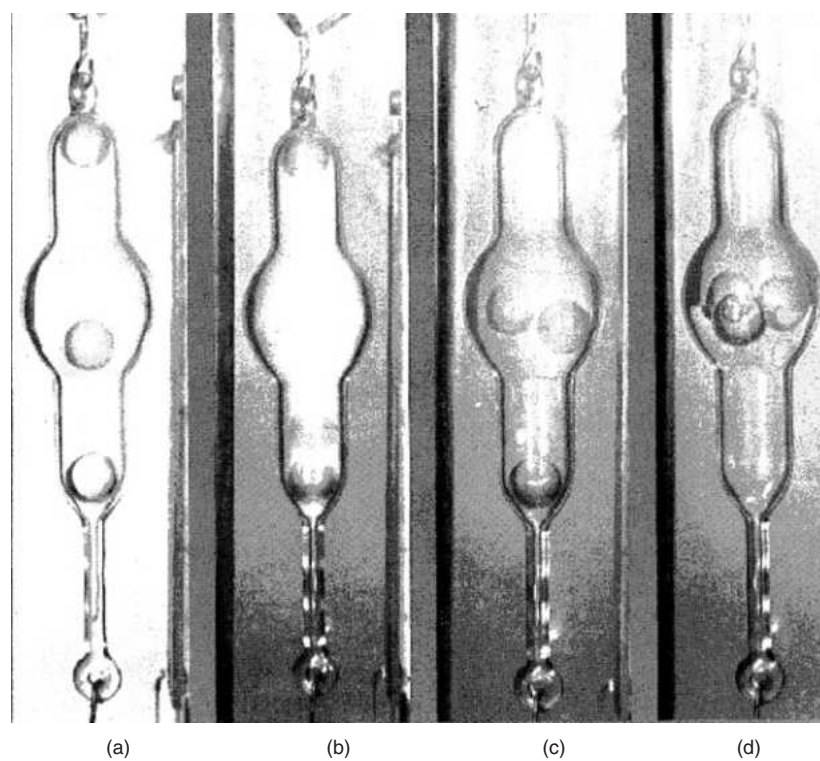


Figure 1.6 Liquid–Gas Equilibrium near the Critical Point. (a) At a temperature slightly above the critical temperature. The density of the fluid depends slightly on height, due to gravity. (b) At the critical temperature, and showing the scattering of light known as critical opalescence. (c) and (d) At subcritical temperatures, showing a definite meniscus. From J. V. Sengers and A. L. Sengers, *Chem. Eng. News*, June 10, 1968, p. 104. Used by permission of the copyright holder.

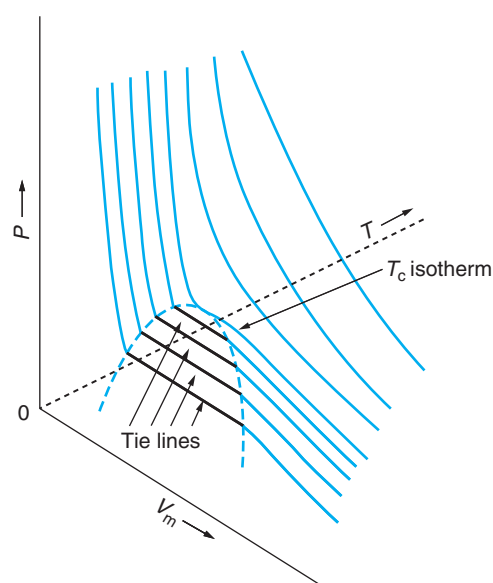


Figure 1.7 Surface Giving Pressure as a Function of Molar Volume and Temperature for a Typical Pure Substance in the Liquid–Vapor Region (Schematic).



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