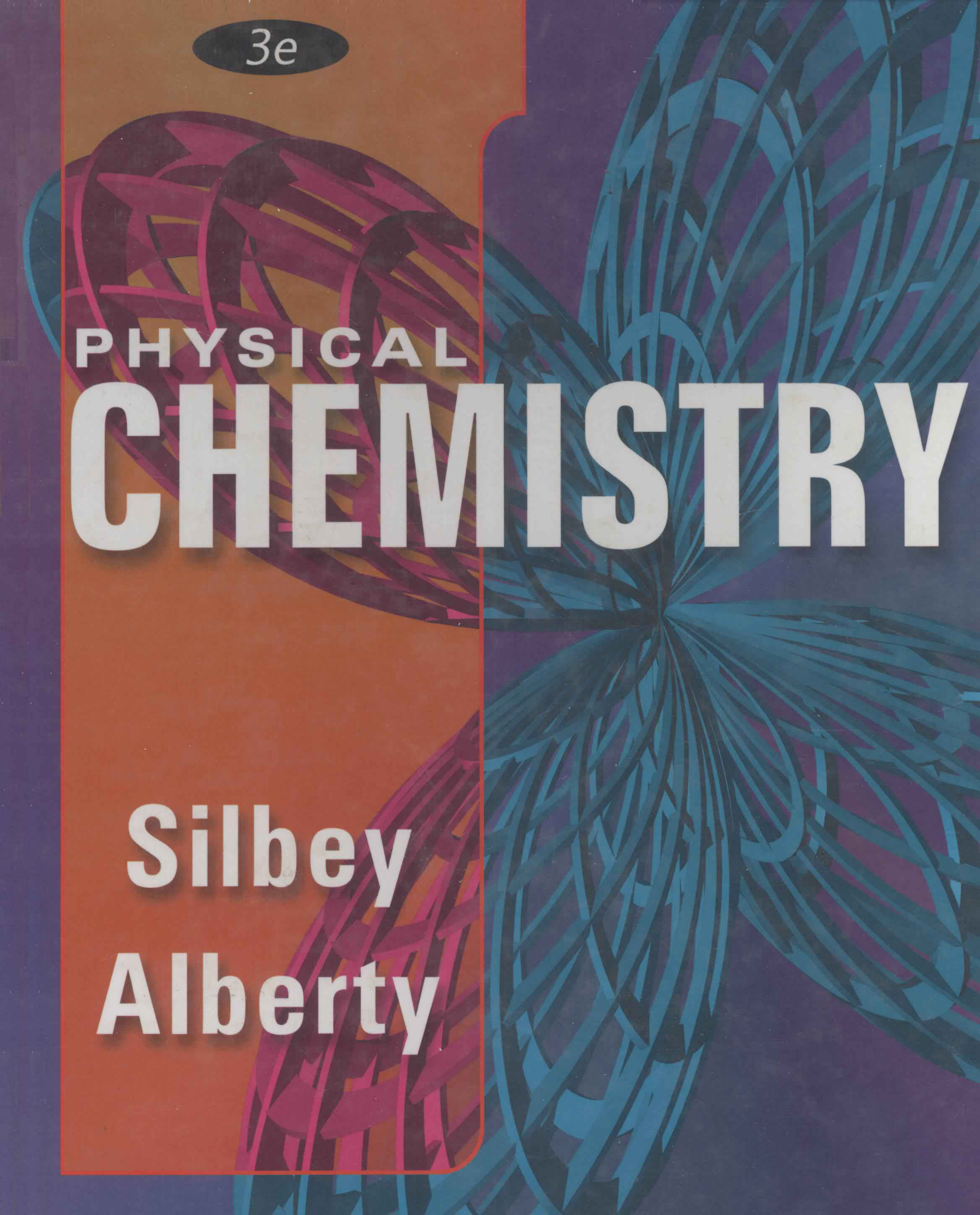

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# PHYSICAL
# CHEMISTRY

**Silbey**
**Alberty**

# Physical Chemistry

## Third Edition

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# PREFACE

The objective of this book is to make the concepts and methods of physical chemistry clear and interesting to students who have had a year of calculus and a year of physics. The underlying theory of chemical phenomena is complicated, and so it is a challenge to make the most important concepts and methods understandable to undergraduate students. However, these basic ideas are accessible to students, and they will find them useful whether they are chemistry majors, biologists, engineers, or earth scientists. The basic theory of chemistry is presented from the viewpoint of academic physical chemists, but many applications of physical chemistry to practical problems are described.

One of the important objectives of a course in physical chemistry is to learn how to solve numerical problems. The problems in physical chemistry help emphasize features in the underlying theory, and they illustrate practical applications.

## FEATURES NEW TO THIS EDITION

In this edition there are two types of problems: problems that can be solved with a hand-held calculator and a new set of **COMPUTER PROBLEMS** that require a personal computer with a mathematical application installed. There are two sets of problems of the first type. The answers to problems in the first set are given in the back of the textbook, and worked-out solutions to these problems are given in the *Solutions Manual for Physical Chemistry*. The answers for the second set of problems are given in the *Solutions Manual*. In the two sets of problems that can be solved using hand-held calculators, some problems are marked with an icon to indicate that they may be more conveniently solved on a personal computer with a mathematical program. But the 136 new COMPUTER PROBLEMS are problems that require a personal computer with a mathematical application such as Mathematica™, MathCad™, MATLAB™, or MAPLE™ installed. The recent development of these mathematical applications makes it possible to undertake problems that were previously too difficult or too time consuming. This is particularly true for two- and three-dimensional plots, integration and differentiation of complicated functions, and solving differential equations. The *Solutions Manual for Physical Chemistry* provides Mathematica$^{\text{TM}}$ programs and printouts for the 136 COMPUTER PROBLEMS.

The Mathematica$^{\text{TM}}$ solutions of the 136 COMPUTER PROBLEMS in digital form are available on the web at http://www.wiley.com/college/silbey. They can be downloaded into a personal computer with Mathematica$^{\text{TM}}$ installed. Students can obtain Mathematica at a reduced price from Wolfram Research, 100 Trade Center Drive, Champaign, Illinois, 61820-7237. A password is required and will be available in the *Solutions Manual,* along with further information about how to access the Mathematica solutions in digital form. Emphasis in the COMPUTER PROBLEMS has been put on problems that do not require complicated programming, but do make it possible for students to explore important topics more deeply. Suggestions are made as to how to vary parameters and how to apply these programs to other substances and systems. As an aid to showing how commands are used, there is an index in the *Solutions Manual* of the major commands used.

A related change in this edition is the use of Mathematica$^{\text{TM}}$ plots in some 50 figures in the textbook. The figure legends for these figures indicate the COMPUTER PROBLEM where the program is given. These programs make it possible for students to explore changes in the ranges of variables in plots and to make calculations on other substances and systems.

Another new feature of this third edition is a list of Key Ideas at the end of each chapter. In this edition, the Examples have been given titles and the mathematical review in the Appendix has been expanded.

Because the number of credits in physical chemistry courses, and therefore the need for more advanced material, varies at different universities and colleges, more topics have been included in this edition than can be covered in some courses.

The Appendix provides an alphabetical list of symbols for physical quantities and their units. The use of nomenclature and units is uniform throughout the book. SI (Système International d'Unités) units are used because of their advantage as a coherent system of units. That means that when SI units are used with all of the physical quantities in a calculation, the result comes out in SI units without having to introduce numerical factors. The underlying unity of science is emphasized by the use of seven base units to represent all physical quantities.

## HISTORY

*Outlines of Theoretical Chemistry,* as it was then entitled, was written in 1913 by Frederick Getman, who carried it through 1927 in four editions. The next four editions were written by Farrington Daniels. In 1955, Robert Alberty joined Farrington Daniels. At that time, the name of the book was changed to *Physical Chemistry,* and the numbering of the editions was started over. The collaboration ended in 1972 when Farrington Daniels died. The current edition is the third by R. A. Alberty and R. J. Silbey. It is remarkable that this textbook traces its origins back 87 years.

Over the years this book has profited tremendously from the advice of physical chemists all over the world. Many physical chemists who care how their subject is presented have written to us with their comments, and we hope that will continue. We are especially indebted to colleagues at MIT who have reviewed various sections and given us the benefit of advice. These include Sylvia T. Ceyer, Robert W. Field, Carl W. Garland, Mario Molina, Keith Nelson, and Irwin Oppenheim.

The following individuals made very useful suggestions as to how to improve this third edition: Carl W. David (University of Connecticut), Mark D. Ediger (University of Wisconsin-Madison), Robert N. Goldberg (National Institute of Standards and Technology), Jerry Goodisman (Syracuse University), Christopher Grayce (University of California-Irvine), Mark R. Hoffmann (University of North Dakota), Richard Mendelsohn (Rutgers University), Worth E. Vaughan (University of of Wisconsin-Madison), and D. Zeroka (Lehigh University). We are also indebted to reviewers of earlier editions and to people who wrote us about the second edition.

The following individuals made very useful suggestions as to how to improve the Mathematica$^{\text{TM}}$ solutions to COMPUTER PROBLEMS: Ian Brooks (Wolfram Research), Carl W. David (U. Connecticut), Robert N. Goldberg (NIST), Mark R. Hoffman (University of North Dakota), Andre Kuzniarek (Wolfram Research), W. Martin McClain (Wayne State University), Kathryn Tomasson (University of North Dakota), and Worth E. Vaughan (University of Wisconsin-Madison).

We are indebted to Wiley editors Nedah Rose, Marian Provenzano, and David Harris for their advice and support. We are also indebted to Elizabeth Swain for her management of the production process and to Connie Parks for her copy editing. We are indebted to Martin Batey for making available the web site, and to many others at Wiley who were involved in the production of this third edition.

*Cambridge, Massachusetts* **Robert J. Silbey**
*January, 2000* **Robert A. Alberty**

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# PART
# ONE

# *Thermodynamics*

Thermodynamics deals with the interconversion of various kinds of energy and the changes in physical properties that are involved. Thermodynamics is concerned with equilibrium states of matter and has nothing to do with time. Even so, it is one of the most powerful tools of physical chemistry; because of its importance, the first part of this book is devoted to it. The first law of thermodynamics deals with the amount of work that can be done by a chemical or physical process and the amount of heat that is absorbed or evolved. On the basis of the first law it is possible to build up tables of enthalpies of formation that may be used to calculate enthalpy changes for reactions that have not yet been studied. With information on heat capacities of reactants and products also available, it is possible to calculate the heat of a reaction at a temperature where it has not previously been studied.

The second law of thermodynamics deals with the natural direction of processes and the question of whether a given chemical reaction can occur by itself. The second law was formulated initially in terms of the efficiencies of heat engines, but it also leads to the definition of entropy, which is important in determining the direction of chemical change. The second law provides the basis for the definition of the equilibrium constant for a chemical reaction. It provides an answer to the question, "To what extent will this particular reaction go before equilibrium is reached?" It also provides the basis for reliable predictions of the effects of temperature, pressure, and concentration on chemical and physical equilibrium. The third law provides the basis for calculating equilibrium constants from calorimetric measurements only. This is an illustration of the way in which thermodynamics interrelates apparently unrelated measurements on systems at equilibrium.

After discussing the laws of thermodynamics and the various physical quantities involved, our first applications will be to the quantitative treatment of chemical equilibria. These methods are then applied to equilibria between different phases. This provides the basis for the quantitative treatment of distillation and for the interpretation of phase changes in mixtures of solids. Then thermodynamics is applied to electrochemical cells and biochemical reactions.

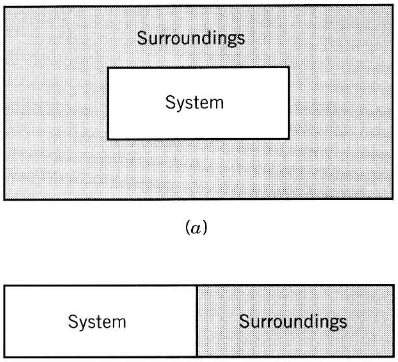
# 1

# Zeroth Law of Thermodynamics and Equations of State

The principle involved in defining temperature was not recognized until the establishment of the first and second laws of thermodynamics, and so it is referred to as the zeroth law. This leads to a discussion of the thermodynamic properties of gases and liquids. After discussing the ideal gas, we consider the behavior of real gases. The thermodynamic properties of a gas or liquid are represented by an equation of state, such as the virial equation or the van der Waals equation. The latter has the advantage that it provides a description of the critical region, but much more complicated equations are required to provide an accurate quantitative description. Since calculus is used so much in thermodynamics, the chapter ends with the chain rule, the cyclic rule, and partial molar properties.

## 1.1 STATE OF A SYSTEM

A thermodynamic system is that part of the physical universe that is under consideration. A system is separated from the rest of the universe by a real or imaginary **boundary.** The part of the universe outside the boundary of the system is referred to as **surroundings,** as illustrated by Fig. 1.1. Even though a system is enclosed by a boundary, heat may be transferred between system and surroundings, and the surroundings may do work on the system, or vice versa. If the boundary around a system prevents interaction of the system with its surroundings, the system is called an **isolated** system.



(*a*)

(*b*)

**Figure 1.1** (*a*) A system is separated from its surroundings by a boundary, real or imaginary. (*b*) As a simplification we can imagine the system to be separated from the surroundings by a single wall that may be an insulator or a heat conductor. Later (Section 6.8) we will consider semipermeable boundaries so that the system is open to the transfer of matter.

If matter can be transferred from the surroundings to the system, or vice versa, the system is referred to as an **open** system; otherwise, it is a **closed** system.

When a system is under discussion it must be described precisely. A system is **homogeneous** if its properties are uniform throughout; such a system consists of a single phase. If a system contains more than one phase, it is **heterogeneous.** A simple example of a two-phase system is liquid water in equilibrium with ice. Water can also exist as a three-phase system: liquid, ice, and vapor, all in equilibrium.

Experience has shown that the macroscopic state of a system at equilibrium can be specified by the values of a small number of macroscopic variables. These variables, which include, for example, temperature $T$, pressure $P$, and volume $V$, are referred to as **state variables** or **thermodynamic variables.** They are called state variables because they specify the state of a system. Two samples of a substance that have the same state variables are said to be in the same state. It is remarkable that the state of a homogeneous system at equilibrium can be specified by so few variables. When a sufficient number of state variables are specified, all of the other properties of the system are fixed. It is even more remarkable that these state variables follow all of the rules of calculus; that is, they can be treated as mathematical functions that can be differentiated and integrated. Thermodynamics leads to the definition of additional properties, like internal energy and entropy, that can also be used to describe the state of a system, and are themselves state variables.

Note that the description of the microscopic state of a system containing many molecules requires the specification of a very large number of variables. For example, to describe the microscopic state of a system using classical mechanics, we would have to give the three coordinates and three components of the momentum of each molecule, plus information about its vibrational and rotational motion. For one mole of gas molecules, this would mean more than $6 \times 10^{23}$ numbers. An important thing to notice is that we can use a small number of state variables to describe the equilibrium state of a system that is too complicated to describe in a microscopic way.

Thermodynamic variables are either intensive or extensive. **Intensive variables** are independent of the size of the system; examples are pressure, density, and temperature. **Extensive variables** do depend on the size of the system and double if the system is duplicated and added to itself; examples are volume, mass, internal energy, and entropy. Note that the ratio of two extensive variables is an intensive variable; density is an example. Thus we can talk about the **intensive state of the system,** which is described by intensive variables, or the **extensive state of a system,** which is described by intensive variables plus at least one extensive variable. The intensive state of the gas helium is described by specifying its pressure and density. The extensive state of a certain amount of helium is described by specifying the amount, the pressure, and the density; the extensive state of one mole of helium might be represented by 1 mol He($P$, $\rho$), where $P$ and $\rho$ represent the pressure and density, respectively.

To describe the intensive state of a homogeneous binary mixture, we have to specify the relative amounts of the two species, and so it is necessary to specify three intensive properties. This can be generalized by saying that for a system in which there are no chemical reactions, the intensive state can be specified by $N_s+1$ intensive variables, where $N_s$ is the number of species.

In chemistry it is generally more useful to express the size of a system in terms of the amount of substance it contains, rather than its mass. **The amount of substance $n$ is the number of entities (atoms, molecules, ions, electrons, or specified groups of such particles) expressed in terms of moles.** If a system contains $N$ molecules, the amount of substance $n = N/N_A$, where $N_A$ is the Avogadro constant ($6.022 \times 10^{23}$ mol$^{-1}$). The ratio of the volume $V$ to the amount of substance is referred to as the molar volume: $\overline{V} = V/n$. The volume $V$ is expressed in SI units of m$^3$, and the molar volume $\overline{V}$ is expressed in SI units of m$^3$ mol$^{-1}$. We will use the overbar regularly to indicate molar thermodynamic quantities.

***Comment:***

*Since this is our first use of physical quantities, we should note that the value of a physical quantity is equal to the product of a numerical factor and a unit:*

$$\textit{physical quantity} = \textit{numerical value} \times \textit{unit}$$

*The values of all physical quantities can be expressed in terms of SI base units (see Appendix A). However, some physical quantities are dimensionless, and so the symbol for the SI unit is taken as one because this is what you get when units cancel. Note that, in print, physical quantities are represented by italic type and units are represented by roman type.*

When a system is in a certain state with its properties independent of time and having no fluxes (e.g., no heat flowing through the system), then the system is said to be at **equilibrium.** When a thermodynamic system is at equilibrium its state is defined entirely by the state variables, and **not by the history of the system.** By history of the system, we mean the previous conditions under which it has existed.

Since the state of a system at equilibrium can be specified by a small number of state variables, it should be possible to express the value of a variable that has not been specified as a function of the values of other variables that have been specified. The simplest example of this is the ideal gas law.

For some systems, more than two intensive variables must be stated to specify the state of the system. If there is more than one species, the composition has to be given. If a liquid system is in the form of small droplets, the surface area has to be given. If the system is in an electric or magnetic field, this may have an effect on its properties, and then the electric field strength and magnetic field strength become state variables. We will generally ignore the effect of the earth's gravitational field on a system, although this can be important, as we will see in the special topic at the end of this chapter.

The pressure of the atmosphere is measured with a barometer, as shown in Fig. 1.2*a*, and the pressure of a gaseous system is measured with a closed-end manometer, as shown in Fig. 1.2*b*.

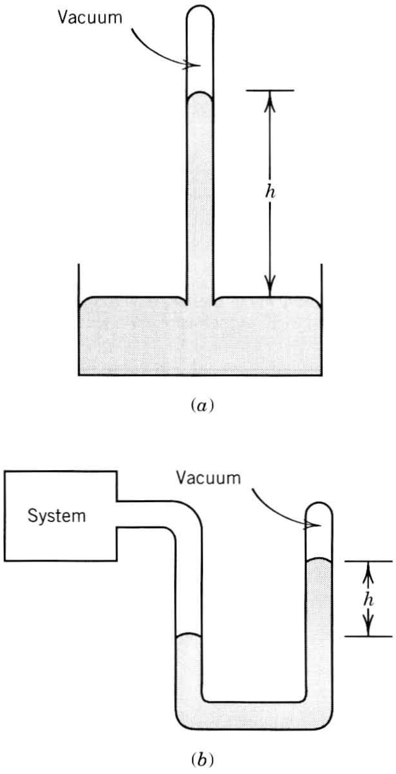
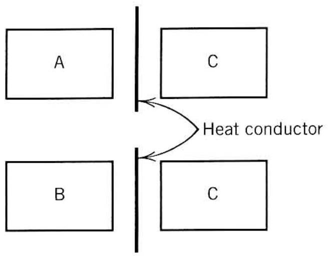


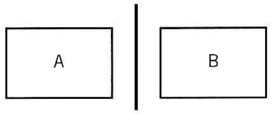
**Figure 1.2** (*a*) The pressure exerted by the atmosphere on the surface of mercury in a cup is given by $P = h\rho g$ (see Example 1.1). (*b*) The pressure of a system is given by the same equation when a closed-end manometer is used.

## 1.2 THE ZEROTH LAW OF THERMODYNAMICS

Although we all have a commonplace notion of what temperature is, we must define it very carefully so that it is a useful concept in thermodynamics. If two closed systems with fixed volumes are brought together so that they are in thermal contact, changes may take place in the properties of both. Eventually a state is reached in which there is no further change, and this is the state of **thermal equilibrium.** In this state, the two systems have the same temperature. Thus, we can readily determine whether two systems are at the same temperature by bringing them into thermal contact and seeing whether observable changes take place in the properties of either system. If no change occurs, the systems are at the same temperature.



If A and C are in thermal equilibrium, and B and C are in thermal equilibrium, then



A and B will be found to be in thermal equilibrium when connected by a heat conductor.

**Figure 1.3** The zeroth law of thermodynamics is concerned with thermal equilibrium between three bodies.

Now let us consider three systems, A, B, and C, as shown in Fig. 1.3. It is an experimental fact that if system A is in thermal equilibrium with system C, and system B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other. It is not obvious that this should be true, and so this empirical fact is referred to as the **zeroth law of thermodynamics.**

To see how the zeroth law leads to the definition of a temperature scale, we need to consider thermal equilibrium between systems A, B, and C in more detail. Assume that A, B, and C each consist of a certain mass of a different fluid. We use the word **fluid** to mean either a gas or a compressible liquid. Our experience is that if the volume of one of these systems is held constant, its pressure may vary over a range of values, and if the pressure is held constant, its volume may vary over a range of values. Thus, the pressure and the volume are independent thermodynamic variables. Furthermore, suppose that the experience with these systems is that their intensive states are specified completely when the pressure and volume are specified. That is, when one of the systems reaches equilibrium at a certain pressure and volume, all of its macroscopic properties have certain characteristic values. It is quite remarkable and fortunate that the macroscopic state of a given mass of fluid of a given composition can be fixed by specifying only the pressure and the volume.*

If there are further constraints on the system, there will be a smaller number of independent variables. An example of an additional constraint is thermal equilibrium with another system. Experience shows that if a fluid is in thermal equilibrium with another system, it has only one independent variable. In other words, if we set the pressure of system A at a particular value $P_A$, we find that there is thermal equilibrium with system C, in a specified state, only at a particular value of $V_A$. Thus, system A in thermal equilibrium with system C is characterized by a **single** independent variable, pressure or volume; one or the other can be set arbitrarily, but not both. The plot of all the values of $P_A$ and $V_A$ for which there is equilibrium with system C is called an **isotherm.** Figure 1.4 gives this isotherm, which we label $\Theta_1$. Since system A is in thermal equilibrium with system C at any $P_A$, $V_A$ on the isotherm, we can say that each of the pairs $P_A$, $V_A$ on this isotherm corresponds with the same temperature $\Theta_1$.

When heat is added to system C and the experiment is repeated, a different isotherm is obtained for system A. In Fig. 1.4, the isotherm for the second experiment is labeled $\Theta_2$. If still more heat is added to system C and the experiment is repeated again, the isotherm labeled $\Theta_3$ is obtained.

Figure 1.4 illustrates Boyle's law that states that $PV = \text{constant}$ for a specified amount of gas at a specified temperature. Experimentally, this is strictly true only in the limit of zero pressure. Charles and Gay-Lussac found that the volume of a gas varies linearly with the temperature at specified pressure when the temperature is measured with a mercury in glass thermometer, for example. Since it would be preferable to have a temperature scale that is independent of the properties of

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*This is not true for water in the neighborhood of 4 °C, but the state is specified by giving the temperature and the volume or the temperature and the pressure. See Section 6.1.

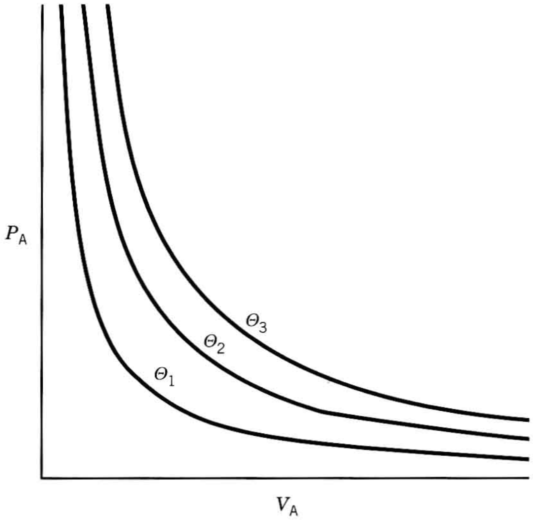

**Figure 1.4** Isotherms for fluid A. This plot, which is for a hypothetical fluid, might look quite different for some other fluid.

particular materials like mercury and glass, it is better to say that the ratio of the $P_2V_2$ product at temperature $\Theta_2$ to $P_1V_1$ at temperature $\Theta_1$ depends only on the two temperatures:

$$\frac{P_2V_2}{P_1V_1} = \phi(\Theta_1, \Theta_2) \tag{1.1}$$

where $\phi$ is an unspecified function. The simplest thing to do is to take the ratio of the $PV$ products to be equal to the ratio of the temperatures, thus defining a temperature scale:

$$\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1} \quad \text{or} \quad \frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1} \tag{1.2}$$

Here we have introduced a new symbol $T$ for the temperature because we have made a specific assumption about the function $\phi$. Equations 1.1 and 1.2 are exact only in the limit of zero pressure, and so $T$ is referred to as the ideal gas temperature.

Since, according to equation 1.2, $PV/T$ is a constant for a fixed mass of gas and since $V$ is an extensive property,

$$PV/T = nR \tag{1.3}$$

where $n$ is the amount of gas and $R$ is referred to as the **gas constant.** Equation 1.3 is called the ideal gas **equation of state.** An equation of state is the relation between the thermodynamic properties of a substance at equilibrium.

## 1.3 THE IDEAL GAS TEMPERATURE SCALE

The ideal gas temperature scale can be defined more carefully by taking the temperature $T$ to be proportional to $P\overline{V} = PV/n$ in the limit of zero pressure. Since different gases give slightly different scales when the pressure is about one bar (1 bar = $10^5$ pascal = $10^5$ Pa = $10^5$ N m$^{-2}$), it is necessary to use the limit of

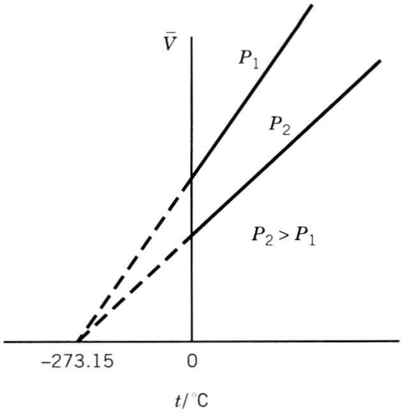

**Figure 1.5** Plots of $\overline{V}$ versus temperature for a given amount of a real gas at two low pressures $P_1$ and $P_2$, as given by Gay-Lussac's law.

the $P\overline{V}$ product as the pressure approaches zero. When this is done, all gases yield the same temperature scale. We speak of gases under this limiting condition as **ideal.** Thus, the **ideal gas temperature** $T$ is defined by

$$T = \lim_{P\to 0}(P\overline{V}/R) \tag{1.4}$$

The proportionality constant is called the gas constant $R$. The unit of thermodynamic temperature, 1 kelvin or 1 K, is defined as the fraction 1/273.16 of the temperature of the triple point of water. * Thus, the temperature of an equilibrium system consisting of liquid water, ice, and water vapor is 273.16 K. The temperature 0 K is called absolute zero. According to the current best measurements, the freezing point of water at one atmosphere (101 325 Pa, see below) is 273.15 K, and the boiling point at 1 atmosphere is 373.12 K; however, these are experimental values and may be determined more accurately in the future. The Celsius scale $t$ is formally defined by

$$t/°\text{C} = T/\text{K} - 273.15 \tag{1.5}$$

The reason for writing the equation in this way is that temperature $T$ on the Kelvin scale has the unit K, and temperature $t$ on the Celsius scale has the unit °C, which need to be divided out before temperatures on the two scales are compared. In Fig. 1.5, the molar volume of an ideal gas is plotted versus the Celsius temperature $t$ at two pressures.

We will find later that the ideal gas temperature scale is identical with one based on the second law of thermodynamics, which is independent of the properties of any particular substance (see Section 3.9). In Chapter 16 the ideal gas temperature scale will be identified with that which arises in statistical mechanics.

The gas constant $R$ can be expressed in various units, but we will emphasize the use of SI units. The SI unit of **pressure** ($P$), is the pascal, Pa, which is the pressure produced by a force of 1 N on an area of 1 $\text{m}^2$. In addition to using the prefixes listed in the back cover of the book to express larger and smaller pressures, it is convenient to have a unit that is approximately equal to the atmospheric pressure. This unit is the bar, which is $10^5$ Pa. Earlier the atmosphere, which is defined as 101 325 Pa, had been used as a unit of pressure.

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### Example 1.1 *Express one atmosphere pressure in SI units*

Calculate the pressure of the earth's atmosphere at a point where the barometer reads 76 cm of mercury at 0 °C and the acceleration of gravity $g$ is 9.806 65 m $\text{s}^{-2}$. The density of mercury at 0 °C is 13.5951 g $\text{cm}^{-3}$, or $13.5951 \times 10^3$ kg $\text{m}^{-3}$.

Pressure $P$ is force $f$ divided by area $A$:

$$P = f/A$$

The force exerted by a column of air over an area $A$ is equal to the mass $m$ of mercury in a vertical column with a cross section $A$ times the acceleration of gravity $g$:

$$f = mg$$

---

*The triple point of water is the temperature and pressure at which ice, liquid, and vapor are in equilibrium with each other in the absence of air. The pressure at the triple point is 611 Pa. The freezing point in the presence of air at 1 atm is 0.0100 °C lower because (1) the solubility of air in liquid water at 1 atm (101 325 Pa) is sufficient to lower the freezing point 0.0024 °C (Section 6.8), and (2) the increase of pressure from 611 to 101 325 Pa lowers the freezing point 0.0075 °C, as shown in Example 6.2. Thus, the ice point is at 273.15 K, and this is frequently taken as a standard temperature in thermodynamics.

The mass of mercury raised above the flat surface in Fig. 1.2*a* is $\rho A h$ so that

$$f = \rho A h g$$

Thus, the pressure of the atmosphere is

$$P = h \rho g$$

If $h$, $\rho$, and $g$ are expressed in SI units, the pressure $P$ is expressed in pascals. Thus, the pressure of a standard atmosphere may be expressed in SI units as follows:

$$\begin{aligned} 1\ \text{atm} &= (0.76\ \text{m})(13.5951 \times 10^3\ \text{kg m}^{-3})(9.806\,65\ \text{m s}^{-2}) \\ &= 101\,325\ \text{N m}^{-2} = 101\,325\ \text{Pa} = 1.013\,25\ \text{bar} \end{aligned}$$

This equality is expressed by the conversion factor 1.013 25 bar $\text{atm}^{-1}$.

To determine the value of the gas constant we also need the definition of a mole. A **mole** is the amount of substance that has as many atoms or molecules as 0.012 kg (exactly) of $^{12}$C. The **molar mass** $M$ of a substance is the mass divided by the amount of substance $n$, and so its SI unit is kg $\text{mol}^{-1}$. Molar masses can also be expressed in g $\text{mol}^{-1}$, but it is important to remember that in making calculations in which all other quantities are expressed in SI units, the molar mass must be expressed in kg $\text{mol}^{-1}$. The molar mass $M$ is related to the molecular mass $m$ by $M = N_A m$, where $N_A$ is the **Avogadro constant** and $m$ is the mass of a single molecule.

Until 1986 the recommended value of the gas constant was based on measurements of the molar volumes of oxygen and nitrogen at low pressures. The accuracy of such measurements is limited by problems of sorption of gas on the walls of the glass vessels used. In 1986 the recommended value* of the gas constant

$$R = 8.314\,51\ \text{J K}^{-1}\ \text{mol}^{-1} \tag{1.6}$$

was based on measurements of the speed of sound in argon. The equation used is discussed in Section 17.4. Since pressure is force per unit area, the product of pressure and volume has the dimensions of force times distance, which is work or energy. Thus, the gas constant is obtained in joules if pressure and volume are expressed in pascals and cubic meters; note that 1 J = 1 Pa $\text{m}^3$.

**Example 1.2** ***Express the gas constant in various units***

Calculate the value of $R$ in cal $\text{K}^{-1}$ $\text{mol}^{-1}$, L bar $\text{K}^{-1}$ $\text{mol}^{-1}$, and L atm $\text{K}^{-1}$ $\text{mol}^{-1}$.

Since the calorie is defined as 4.184 J,

$$\begin{aligned} R &= 8.314\,51\ \text{J K}^{-1}\ \text{mol}^{-1}/4.184\ \text{J cal}^{-1} \\ &= 1.987\,22\ \text{cal K}^{-1}\ \text{mol}^{-1} \end{aligned}$$

Since the liter is $10^{-3}$ $\text{m}^3$ and the bar is $10^5$ Pa,

$$\begin{aligned} R &= (8.314\,51\ \text{Pa m}^3\ \text{K}^{-1}\ \text{mol}^{-1})(10^3\ \text{L m}^{-3})(10^{-5}\ \text{bar Pa}^{-1}) \\ &= 0.083\,145\,1\ \text{L bar K}^{-1}\ \text{mol}^{-1} \end{aligned}$$

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*E. R. Cohen and B. N. Taylor, The 1986 Adjustment of the Fundamental Physical Constants, *CODATA Bull.* **63**:1 (1986); *J. Phys. Chem. Ref. Data* **17**:1795 (1988).