# PHYSICAL CHEMISTRY

## SEVENTH EDITION

ROBERT A. ALBERTY

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# PREFACE

In this edition the text has been thoroughly revised and the number of chapters has been increased to twenty-five. The book's objective over the years has been to make physical ideas about chemistry accessible to students. As more physical chemistry has been taught in lower-level courses, it has been possible to eliminate certain elementary material and to add more advanced material.

The basic theory of chemistry is presented from the viewpoint of a physical chemist, but many applications of physical chemistry to practical problems are described. Thus the book provides an introduction to the uses of physical chemistry in chemical engineering, biophysical chemistry, and molecular biology.

A course in physical chemistry provides many opportunities for the immediate application of ideas and equations in solving problems. In this edition 182 calculations are written out as examples, in addition to the many calculations that are carried out in the body of the text. This edition contains 1134 problems, of which 200 are new. The new problems are mostly concerned with new material.

There are two parallel problem sets at the end of each chapter. The answers are given for the first set in the Appendix. The *Solutions Manual for Physical Chemistry*, 7th ed., Wiley, New York, 1987, contains worked-out solutions for all of the problems in the first set and answers for the second set.

This edition has the same four main sections as the sixth edition. First, the consideration of thermodynamics alone has the advantage of showing clearly the power, and limits, of this treatment of equilibrium. Then quantum mechanics is introduced to describe atoms and molecules. After that it is possible not only to treat chemical kinetics classically but also to show how rates of chemical reactions can be understood in terms of molecular structure. The last chapter of the book discusses crystal geometry, X-ray diffraction, semiconductors, and crystallinity in synthetic high polymers.

The number of chapters on thermodynamics has been increased from eight to ten in this edition. The first chapter of the previous edition has been split into Chapter 1 on the zeroth law of thermodynamics and equations of state and Chapter 2 on the first law. Thus this edition contains more information on equations of state, which are so important in calculating the thermodynamic properties of real substances. The chapter on chemical equilibrium has been moved ahead of the chapters on phase equilibrium in this edition because of the importance of reactions in chemical thermodynamics. The chapter on phase equilibrium of the previous edition has been split into two chapters so that nonideal systems can be discussed more completely and excess thermodynamic properties can be introduced. In general the treatment of thermodynamics has been upgraded in this edition.

In Part 2 the level of the treatment of quantum mechanics has been raised because of its importance for the understanding of chemical phenomena. Operators and the calculation of expectation values are more frequently used. Atomic and molecular term symbols are introduced because of their usefulness in using selection rules for atomic and molecular electronic spectra. There is more emphasis on molecular orbital theory and on transition dipole moments. The chapter on molecular spectroscopy of the previous edition has been split into two: Chapter 15, "Rotational and Vibrational Spectroscopy," and Chapter 16, "Electronic Spectroscopy of Molecules." The treatment of the electronic spectra of molecules has been expanded by including more on the Franck-Condon principle and lasers. Fourier transform NMR is described, and in the chapter on statistical mechanics more use is made of probabilities and probability densities.

The chapter on the kinetics of gas reactions has been extensively rewritten and divided into two chapters: Chapter 20, "Experimental Gas Kinetics," and Chapter 21, "Theory of the Rate of Gas Reactions." The treatment of the theory of gas reactions has been significantly expanded.

As a new Associate Member of the IUPAC Commission on Symbols and Nomenclature I have paid special attention in this edition to the symbols used for physical quantities. A list of symbols with references to the sections in which they are introduced is a new feature in this edition. This list also shows the SI units for each physical quantity. Although other units are used, the advantage of the SI system is that it is coherent; that is, when SI units are used in a calculation, the result comes out in SI units without any numerical factors. This feature of the SI system is particularly important for physical chemistry, which uses a wide range of physical quantities. The underlying unity of science is emphasized by the use of seven base units to represent all physical quantities.

Since 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.

*Outlines of Theoretical Chemistry*, as it was then entitled, was written in 1913 by Dr. Frederick Getman, who carried it through 1927 in four editions. The next four editions were written by Dr. Farrington Daniels. In 1955 I joined Dr. Daniels in the first edition of this book. We worked together on three editions and started working on the fourth before Dr. Daniels died on June 23, 1972. The seventh edition still owes much to the high standards and interest in students that Dr. Daniels always had. It is remarkable that this edition of *Physical Chemistry* traces its origins back 74 years.

Many individuals made helpful suggestions in the preparation of this edition. I am especially indebted to my colleagues at MIT for their advice: Sylvia T. Ceyer, John M. Deutch, Robert W. Field, Carl W. Garland, James L. Kinsey, Keith A. Nelson, Irwin Oppenheim, Philip L. Phillips, Paul R. Schimmel, Jeffrey I. Steinfeld, John S. Waugh, and Mark S. Wrighton. I am also indebted to David Garvin (National Bureau of Standards), Edward L. King (University of Colorado), and William R. Smith (University of Guelph) for their review of chapters.

Robert J. Silbey read the manuscript and proof for the whole book and made many useful suggestions.

Bruce Garetz (Polytechnic Institute of New York), George W. Murphy (University of Oklahoma), and George C. Schatz (Northwestern University) read the entire manuscript and made many useful suggestions. The manuscript was also read by two students, George Maalouf and Peter Coon, who found a number of errors.

I am indebted to John Wiley for its support and especially to my editor, Dennis Sawicki, for his advice.

I am also indebted to many users of previous editions who have pointed out errors and have made useful suggestions. This book has been improved significantly by numerous contacts with users.

I especially thank Lillian Alberty for the difficult job of typing the manuscript and for encouraging me in the preparation of this edition.

Cambridge, Massachusetts
January, 1987

**Robert A. Alberty**

# A NOTE TO THE STUDENT

A problems book containing worked-out solutions for the first set of problems and answers for the second set of problems is available as a companion to this text. Please ask for *Solutions Manual for Physical Chemistry*, by Robert A. Alberty.

R. A. A.

# CONTENTS

# PART 1

# 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 it involves, our first applications will be to the quantitative treatment of chemical equilibrium. These methods are then applied to equilibrium between different phases. This provides the basis for the quantitative treatment of distillation and for the interpretation of the phase changes in mixtures of solids. Then thermodynamics is applied to electrochemical cells and biochemical reactions.

Finally, the concepts and relationships of thermodynamics are applied to the equilibrium properties of surfaces. These include surface tension, surface pressure, adsorption, adhesion, and the effect of curvature of a surface on vapor pressure.

Equilibrium conditions are independent of mechanism; the great strength (and weakness) of thermodynamics is that it is not concerned with mechanisms or molecular models. In Part Two we will see how various thermodynamic quantities may be calculated from information about individual molecules using statistical mechanics. Statistical mechanics provides insight into thermodynamics and accurate predictions of many properties for simple systems of independent particles, but it is difficult to apply statistical mechanics to very complicated systems and to highly interactive systems.

# 1

# ZEROTH LAW OF THERMODYNAMICS AND EQUATIONS OF STATE

The chapter opens with a discussion of the thermodynamic concept of temperature. The principle involved in defining temperature was not recognized until after the establishment of the first and second laws of thermodynamics, and therefore it is referred to as the "zeroth" law. After discussing a perfect gas we consider the behavior of real gases. In doing that we will see the importance of the concept of the state of a system. The thermodynamic properties of a gas or liquid are represented by an equation of state, like the virial equation or the van der Waals equation. Equations of state find extensive use in thermodynamics. To represent the properties of a gas or liquid over a wide range of conditions the equation of state must incorporate the critical region.

## 1.1 SYSTEM, SURROUNDING, STATE OF A SYSTEM, AND STATE VARIABLES

A thermodynamic system is a part of the physical universe that is under consideration. A system is separated from the rest of the universe by a *boundary*. The part of the universe outside of the boundary is referred to as *surroundings*. 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 any interaction of the system with its surroundings, the system is called an *isolated* system.

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.

Systems may also be classified according to whether they are homogeneous or heterogenous. A *homogeneous* system is uniform in all of its properties. Such a system consists of a single phase. *Heterogeneous* systems contain more than one phase. An observable property has the same value at any point in a homogeneous phase. Under special circumstances the effects of gravity, electric or magnetic fields, and surface effects may cause measurable properties to vary within a phase, but for systems of interest to chemists these effects are usually negligible and do not have to be taken into account.

When a system is at equilibrium under a given set of conditions, it is said to be in a definite *state*. The state of a system may be identified from the fact that when it is in a definite state, each of its properties has a definite value. It is found that, for a fixed amount of a pure material, the state is usually completely defined by any two of the three variables—pressure, volume, and temperature. Water has a temperature of maximum density at about 4 °C, and so in this region its state may not be specified by giving the pressure and the volume. However, the specification of the temperature and pressure or volume is always enough. Variables such as pressure, volume, and temperature are referred to as *state variables*.

If a thermodynamic system is at equilibrium its state is defined entirely by the state variables, *and not by the history of the system*.

A system may be taken through a series of changes in which work and heat pass through the boundary so that there is a change in the surroundings as well as the system. If the boundary does not permit the flow of heat, any process occurring in the system is said to be *adiabatic*, and the boundary is called an adiabatic wall.

## 1.2 EXTENSIVE AND INTENSIVE THERMODYNAMIC PROPERTIES

If the mass of a thermodynamic system is doubled without any other change, certain thermodynamic properties that are used to describe the system also double. Examples are the volume of the system and its energy. Such thermodynamic properties are referred to as *extensive*. Other thermodynamic properties, such as the temperature and pressure, are not affected by changing the mass of the system, so they are referred to as *intensive* properties.

When an extensive property of a homogeneous system is divided by mass an intensive property is obtained; for example, the volume per unit mass (the reciprocal of the density) is an intensive property. In chemistry it is generally more useful to divide by the amount of substance $n$. The amount of substance 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, $n = N/N_A$, where $N_A$ is the

Avogadro constant. The ratio of the volume to the amount of substance is referred to as the molar volume. The term molar volume is generally applied to a system containing a single component and so we will represent the molar volume by $V_i = V/n$, where the $i$ indicates the substance. In this equation $V$ represents the extensive property and $V_i$ the intensive property; $V$ has the SI units $\mathrm{m}^3$ and $V_i$ has the SI units $\mathrm{m}^3\ \mathrm{mol}^{-1}$. Thus the perfect gas law can be written

$$PV = nRT \tag{1.1a}$$

or

$$PV_i = RT \tag{1.1b}$$

When the context makes it clear that we are considering a mole of a substance, the perfect gas law may be written $PV = RT$. In this chapter we will use $V$ for molar volume because we will always be considering 1 mol of a substance.

## 1.3 THE ZEROTH LAW OF THERMODYNAMICS

If two closed systems 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. Thus we can readily determine whether two systems are at the same temperature by bringing them into contact and seeing whether observable changes take place in the properties of either system. If no change occurs, they are at the same temperature.

Now let us consider three systems A, B, and C. 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 necessarily be true, and so this empirical fact is referred to as the ***zeroth law of thermodynamics***.

This law puts the concept of temperature on a firm basis in the following way: if two systems are in thermal equilibrium they have the same temperature; if they are not in thermal equilibrium they have different temperatures. Now, how can a temperature scale be set up?

To establish a temperature scale we start with gas B in a state defined by volume $V_B$ and pressure $P_B$. The values of $V_A$ and $P_A$ of a system of gas A that is in equilibrium with B are determined experimentally. There are many combinations of $P_A$ and $V_A$ for which there is equilibrium, and these pairs of values may be plotted on a graph of $P_A$ versus $V_A$ such as that in Fig. 1.1. According to the zeroth law of thermodynamics, this curve at constant temperature (an isotherm) is independent of the nature of gas B, since the same result would be obtained by using instead of B any other gas in equilibrium with it. If the thermal state of B is changed and the experiment repeated, another isotherm for gas A will be obtained. Each isotherm obtained in this way may be assigned a temperature $\theta$, and in this way a temperature scale may be set up. All systems having the same temperature $\theta$ will remain unchanged in properties when they are brought into thermal contact with each other through a wall that allows the two systems to have different pressures and different chemical compositions.

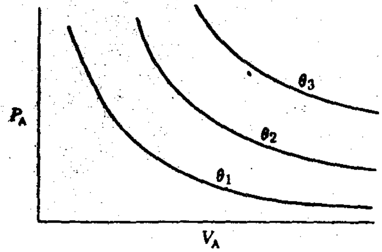

**Fig. 1.1** Isotherms for gas A. This plot, which is for a hypothetical gas A, might look quite different for some other gas.

## 1.4 THE PERFECT GAS TEMPERATURE SCALE

An empirical temperature scale can be set up using data on gas A in the following way. A thermometer can be based on the measurement of the pressure of a given mass of A at some constant volume. The simplest assumption that can be made about the relation between temperature $\theta$ and pressure $P_A$ is that it is linear.

$$\theta = a + bP_A \tag{1.2}$$

To define temperatures on this scale it is necessary to select two fixed points. On the Celsius scale, 0 °C is taken as the temperature of ice and liquid water in contact with air at 1 atm pressure, and 100 °C is taken as the temperature of equilibrium of liquid water and its vapor under a pressure of 1 atm. Measurements of the pressure of gas A in the thermometer referred to above make it possible to calculate $a$ and $b$ in equation 1.2. The problem with this approach is that different gases give different values of $\theta$. However, if $\lim_{P\to 0}(PV)$ is used, rather than pressure $P_A$, it is found that all gases yield the same temperatures. In this expression $V$ is the molar volume. Since all gases approach the same behavior as the pressure is reduced, we speak of gases under this limiting condition as perfect gases. Thus perfect gas thermometers are used in implementing the Celsius temperature scale. When Celsius temperature is represented by $t$, equation 1.2 may be written

$$\lim_{P\to 0}(PV) = (t - a)/b \tag{1.3}$$

Thus the limiting value for the $PV$ product for any gas is a linear function of the temperature. When the Celsius scale is used it is found that $a = -273.15$. Thus it is advantageous to introduce a new temperature scale $T$, the Kelvin scale, such that

$$T/\mathrm{K} = t/{}^\circ\mathrm{C} + 273.15 \tag{1.4}$$

The reason for writing the equation in this way is that temperatures $T$ on the Kelvin scale have the units K, and temperatures $t$ on the Celsius scale have units °C, which need to be divided out before numbers on the two scales are compared. Thus equation 1.3 can be written

$$\lim_{P\to 0}(PV) = T/b \tag{1.5}$$

It is further found experimentally that the same value of parameter $b$ is obtained using different gases and so equation 1.5 is written

$$\lim_{P \to 0} (PV) = RT \tag{1.6}$$

where $R$ is the *gas constant*. This equation is obeyed by all gases. Perfect gases obey equation 1.1 under all conditions.

The temperature scale developed in this way is called the perfect gas temperature scale. We will find later that this scale is identical with one based on the second law of thermodynamics, and that it is independent of the properties of any particular substance (see Section 3.4). In Chapter 18 the perfect gas temperature scale will be identified with that which arises in statistical mechanics.

The unit of temperature on the thermodynamic temperature scale is called the Kelvin because this temperature scale was introduced by Lord Kelvin in 1848. The K unit does not have a degree sign, but the degree sign is retained in the unit for the Celsius scale (°C).

Since it takes two fixed temperatures to define a temperature scale, these are now taken as absolute zero and the triple point of water, which is defined as 273.16 K. 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 0.010 0 °C lower because (1) the solubility of air in liquid water at 1 bar ($10^5$ N m$^{-2}$) pressure is sufficient to lower the freezing point 0.002 4 °C (Section 6.14), and (2) the increase of pressure from 611 Pa to 1 bar lowers the freezing point 0.007 5 °C, as shown in Example 6.3. Thus the ice point is at 273.15 K, and this is frequently taken as a standard temperature in thermodynamics.

The gas constant $R$ can be expressed in various units, but we will emphasize the use of SI units. They are the international standard, and they also have the advantage of being coherent. This means that if all quantities in an equation are expressed in SI base units, the result will be expressed in SI base units without including any numerical factors. The unit of pressure in the SI system is the pascal Pa, which is the pressure produced by a force of 1 N on an area of a square meter. In addition to using the prefixes listed in the front 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, represented by atm, had been used as a unit of pressure.

A standard atmosphere is equal to the pressure required to support 76 cm of mercury at 0 °C at a point on earth where the acceleration of gravity $g$ is 9.806 65 m s$^{-2}$. The density of mercury at 0 °C is 13.5951 g cm$^{-3}$, or $13.5951 \times 10^3$ kg m$^{-3}$. Thus the pressure of a standard atmosphere may be expressed in the SI system as follows:

$$\begin{aligned} 1 \text{ atm} &= (0.76 \text{ m})(13.5951 \times 10^3 \text{ kg m}^{-3})(9.806\,65 \text{ m s}^{-2}) \\ &= 101{,}325 \text{ N m}^{-2} = 101{,}325 \text{ Pa} = 1.01325 \text{ bar} \end{aligned}$$

The conversion factor to remember is 1.013 25 bar atm$^{-1}$.

In order to determine the value of the gas constant we also need the definition of a mole. The 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 $n$, which is expressed in mole . The molar mass $M$ must be expressed in kg $mol^{-1}$ if SI units are used in the calculation.*

The molar mass of molecular oxygen is $31.9988 \times 10^{-3}$ kg $mol^{-1}$ or 31.9988 g $mol^{-1}$. Very careful experiments with molecular oxygen show that as the pressure is reduced indefinitely the $PV$ product for oxygen approaches 2271.08 Pa $m^3$ $mol^{-1}$ at 0 °C (273.15 K). We may calculate the gas constant using equation 1.6.

$$R = \frac{\lim_{P\to 0}(PV)}{T} = \frac{2271.08 \text{ Pa m}^3 \text{ mol}^{-1}}{273.15 \text{ K}}$$

$$= 8.314\,41 \text{ J K}^{-1} \text{ mol}^{-1} \tag{1.7}$$

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 SI units.

**Example 1.1** Calculate the value of $R$ in cal $K^{-1}$ $mol^{-1}$, L bar $K^{-1}$ $mol^{-1}$, and L atm $K^{-1}$ $mol^{-1}$.

Since the calorie is defined as 4.184 J,

$$R = 8.314\,41 \text{ J K}^{-1} \text{ mol}^{-1}/4.184 \text{ J cal}^{-1}$$

$$= 1.987\,19 \text{ cal K}^{-1} \text{ mol}^{-1}$$

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

$$R = (8.314\,41 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1})(10^3 \text{ L m}^{-3})(10^{-5} \text{ bar Pa}^{-1})$$

$$= 0.083\,144\,1 \text{ L bar K}^{-1} \text{ mol}^{-1}$$

Since 1 atm is 1.013 25 bar,

$$R = (0.083\,144\,1 \text{ L bar K}^{-1} \text{ mol}^{-1})/(1.013\,25 \text{ bar atm}^{-1})$$

$$= 0.082\,056 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

## 1.5 COMPRESSIBILITY FACTOR

Real gases behave like perfect gases in the limits of low pressures and high temperatures, but they deviate significantly at high pressures and low temperatures. The compressibility factor $Z = PV/RT$ is a convenient measure of the deviation from perfect behavior. Figure 1.2 shows the compressibility factors of a variety of gases as a function of pressure at 0 °C. As the pressure is reduced to zero, the compressibility factor approaches unity as expected. At very high pressures the compressibility factor is always greater than unity. This can be understood in terms of the finite size of molecules. At very high pressures the molecules of the gas are pushed close together, and the volume of the gas is larger than expected for a perfect gas because a significant fraction of the volume is occupied by the molecules themselves. At low

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*The molar mass $M$ is the mass of a mole of a substance, and the molecular mass $m$ is the mass of a single molecule. Thus $M = N_A m$, where $N_A$ is the Avogadro constant.