PHYSICAL CHEMISTRY

SIXTH EDITION

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JOHN WILEY & SONS
New York Chichester Brisbane Sydney Toronto Singapore

Cover: Photography by Manfred Kage© Peter Arnold, Inc.
Designed by Ann Marie Renzi

Library of Congress Cataloging in Publication Data:

Alberty, Robert A.
Physical chemistry.

Includes bibliographies and index.
1. Chemistry, Physical and theoretical. I. Title.
QD453.2.D36 1983 541.3 82-11058
ISBN 0-471-09284-3

Printed in the United States of America

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PREFACE

This book was written for a comprehensive first course in physical chemistry, emphasizing the fundamentals that provide a basis for the understanding of chemistry. 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 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 immediate application of ideas and equations in solving problems. In this edition 147 calculations are written out as examples, in addition to the many calculations that are carried out in the body of the text. There are 1040 problems in this edition, of which 226 are new.

There are two parallel problem sets at the end of each chapter. The answers are given for the first set. The *Solutions Manual for Physical Chemistry*, 6th ed., John Wiley, New York, 1983, 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 fifth 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.

In this edition several changes have been made in the division of the material into chapters. The fifth edition chapter on the second and third laws of thermodynamics has been split so that there is now a separate chapter on Gibbs energy and chemical potential. In general the treatment of thermodynamics has been upgraded in this edition. The fifth edition chapter on quantum theory has been split, creating a separate chapter on atomic structure. The material in the fifth edition chapter on macromolecules has been incorporated into earlier chapters so that a separate chapter is not needed. The advantage in this is that various principles and methods are applied to synthetic high polymers and proteins as well as to small molecules. This approach has been advocated by the Polymer Education Committee of the American Chemical Society. New material is provided on the thermodynamics of rubberlike elasticity, the kinetics of step-growth and free radical polymerization, the spatial configuration of polymer chains, and crystallinity in synthetic polymers.

This edition uses SI units almost exclusively. There are real advantages in calculations because the SI system is coherent; that is, no additional numerical factors appear in equations relating different physical quantities. The SI system also uses the units ampere, coulomb, and volt. The mol L^{-1} is retained as a common unit of concentration, and the electron volt is often used as the unit of energy in atomic and molecular systems.

This year there has been a major improvement in the availability of tabulated thermodynamic data. *The NBS Table of Chemical Thermodynamic Properties* has been published with some 15,000 entries. This extends the data that had been available in *NBS Technical Notes 270-3 to 270-8*. The new table is especially welcome because there has not been a combined table of this type since *Circular 500* was published in 1952. As a part of the shift to SI units these tables are based on a standard-state pressure of 1 bar. Since these tables are such an important reference, and since SI units are used more and more, the standard-state pressure has been changed to the bar in this edition. The *JANAF Thermochemical Tables* will soon be available for this new standard-state pressure. Some data from both of these tables are given in the Appendix of this text.

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. This is the first edition without Dr. Daniel's name on it, but it 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 70 years.

Many individuals made helpful suggestions in the preparation of this edition. I especially acknowledge the suggestions provided by Malcolm W. Chase, John M. Deutch, Robert W. Field, Carl W. Garland, Edward L. King, James L. Kinsey, Read F. McFeeley, Irwin Oppenheim, Martin A. Paul, Paul R. Schimmel, Robert J. Silbey, Jeffrey I. Steinfeld, John S. Waugh, and Mark S. Wrighton.

Robert C. Dunbar, George C. Schatz, Leonard D. Spicer, and Philip H. Rieger read the entire manuscript and made many useful suggestions.

I am indebted to David Garvin for providing a prepublication copy of *The NBS Tables of Chemical Thermodynamic Properties*, and to Malcolm Chase for prepublication values from the forthcoming *JANAF Thermochemical Tables*.

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, 1982 **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.

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ADOPTION OF A STANDARD-STATE PRESSURE OF 1 BAR

Thermodynamic properties of pure substances are generally tabulated at a standard pressure and a standard temperature, or a series of temperatures. It has been the custom in physical chemistry to use a standard-state pressure of one atmosphere. The atmosphere is not part of the SI system, but, as we will see in Section 1.4, is equal to 101,325 pascals or 1.01325 bar.

As a part of the shift to SI units the Commission on Thermodynamics of the International Union of Pure and Applied Chemistry has recently recommended that thermodynamic data should be reported for a standard-state pressure of 1 bar, which is 10^5 newtons per square meter or 10^5 pascals. The new *NBS Tables of Chemical Thermodynamic Properties* (1982), which is a new combined edition of Technical Note 270 of the National Bureau of Standards, is based on a standard-state pressure of 1 bar. In view of the importance of this new reference table (which provides data on some 15,000 chemical species) and the desirability of following the conventions of the International Union of Pure and Applied Chemistry, a standard-state pressure of 1 bar is adopted in this edition. This means that the atmosphere will not be used as a unit of pressure and the familiar value of the gas constant 0.082 06 L atm K^{-1} mol^{-1} is replaced by 0.083 14 L bar K^{-1} mol^{-1}.

The change of the standard-state pressure from 1 atm to 1 bar also changes the value of the equilibrium constant for a gas reaction. For example, for $H_2(g) = 2H(g)$, $K_P = (P_H/P^\circ)^2/(P_{H_2}/P^\circ) = P_H^2/P_{H_2}P^\circ$, where P° is the standard-state pressure. Thus when P° is changed from 1 atm to 1 bar, K_P is increased by a factor of 1.013 25.

The small decrease (1.3%) in pressure in going from 1 atm to 1 bar does not have a significant effect on the thermodynamic properties of liquids and solids. Also it does not affect the enthalpy of formation ΔH_f° of gases or condensed phases. However, going from a standard-state pressure of 1 atm to 1 bar increases the standard-state entropy S° by $R \ln (101{,}325/10^5) = 0.109$ J K^{-1} mol^{-1} at any temperature. The standard Gibbs energy of formation ΔG_f° at 25 °C is reduced by $0.033\ \Sigma\nu_i$ kJ mol^{-1}, where $\Sigma\nu_i$ is the difference between the number of moles of gaseous products and gaseous reactants in the formation reaction. Since these changes are not very large compared with the usual experimental uncertainties in $S°$ and $\Delta G_f°$, the mixing of data for 1 atm and for 1 bar will not cause big errors. It is, of course, best practice to make the conversion.

Appendix A.1 gives the chemical thermodynamic properties of a number of species at 25 °C and 1 bar taken from *The NBS Tables of Chemical Thermodynamic Properties*, and Appendix A.2 provides data at a series of temperatures for a smaller number of species from *JANAF Thermochemical Tables* for a standard-state pressure of 1 bar.

PART 1

THERMODYNAMICS

Thermodynamics deals with relationships between properties of systems at equilibrium and with differences in properties between various equilibrium states. It 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.

Here, the ideas of thermodynamics are first applied to equilibria between different phases. This provides the basis for the quantitative treatment of fractional distillation and for the interpretation of the phase changes in mixtures of solids. The ideas of thermodynamics are next applied to chemical reactions. The use of thermodynamic tables to calculate equilibrium compositions is discussed in detail. These methods are also applied to the reactions of electrochemical cells, which determine the maximum electromotive force that a cell can produce.

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

FIRST LAW OF THERMODYNAMICS

The quantitative concepts of temperature, work, internal energy, and heat play an important role in the understanding of chemical phenomena. These concepts will be developed in this chapter, and the relationship between heat and work as forms of energy will be emphasized. 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.

The first law is often called the law of conservation of energy. This concept first appeared in mechanics and was later extended to include electrostatics and electrodynamics. Joule performed experiments in 1840–1845 that showed how heat could also be included in the conservation of energy. The first law leads to the definitions of the internal energy *U* and enthalpy *H*. One of the important applications of the first law in chemistry is the determination of the heat evolved or absorbed in chemical reactions. Furthermore, if heat capacities of reactants and products are known, the heat of reaction may be calculated at other temperatures after it has been measured at one.

1.1 SYSTEM, SURROUNDINGS, 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 heterogeneous. 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 completely defined by any two of the three variables—pressure, volume, and temperature.* Such variables are referred to as *state variables*.

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*Water at about 4 °C is an exception to this statement. Specifying the volume and pressure is not enough to define the state of the system. However, specification of the pressure and temperature or volume and temperature is always enough.