

CONCISE PHYSICAL CHEMISTRY

DONALD W. ROGERS

Department of Chemistry and Biochemistry
The Brooklyn Center
Long Island University
Brooklyn, NY

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.

Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data:

Rogers, Donald W.

Concise physical chemistry / by Donald W. Rogers.

p. cm.

Includes index.

Summary: "This book is a physical chemistry textbook that presents the essentials of physical chemistry as a logical sequence from its most modest beginning to contemporary research topics. Many books currently on the market focus on the problem sets with a cursory treatment of the conceptual background and theoretical material, whereas this book is concerned only with the conceptual development of the subject. It contains mathematical background, worked examples and problemsets. Comprised of 21 chapters, the book addresses ideal gas laws, real gases, the thermodynamics of simple systems, thermochemistry, entropy and the second law, the Gibbs free energy, equilibrium, statistical approaches to thermodynamics, the phase rule, chemical kinetics, liquids and solids, solution chemistry, conductivity, electrochemical cells, atomic theory, wave mechanics of simple systems, molecular orbital theory, experimental determination of molecular structure, and photochemistry and the theory of chemical kinetics"— Provided by publisher.

ISBN 978-0-470-52264-6 (pbk.)

1. Chemistry, Physical and theoretical—Textbooks. I. Title.

QD453.3.R63 2010

541—dc22

2010018380

Printed in Singapore

10 9 8 7 6 5 4 3 2 1

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FOREWORD

Among many advantages of being a professional researcher and teacher is the pleasure of reading a new and good textbook that concisely summarizes the fundamentals and progress in your research area. This reading not only gives you the enjoyment of looking once more at the whole picture of the edifice that many generations of your colleagues have meticulously build but, most importantly, also enhances your confidence that your choice to spend your entire life to promote and contribute to this structure is worthwhile. Clearly, the perception of the textbook by an expert in the field is quite different, to say the least, from the perception of a junior or senior undergraduate student who is about to register for a class. A simple look at a textbook that is jam-packed with complex integrals and differential equations may scare any prospective students to death. On the other hand, eliminating the mathematics entirely will inevitably eliminate the rigor of scientific statements. In this respect, the right compromise between simplicity and rigor in explaining complex scientific topics is an extremely rare talent. The task is especially large given the fact that the textbook is addressed to students for whom a particular area of science is not among their primary interests. In this respect, Professor Rogers's *Concise Physical Chemistry* is a textbook that ideally suits all of the above-formulated criteria of a new and good textbook.

Although the fundamental laws and basic principles of physical chemistry were formulated long ago, research in the area is continuously widening and deepening. As a result, the original boundaries of physical chemistry as a science become more and more vague and difficult to determine. During the last two decades, physical chemistry has made a tremendous progress mainly boosted by a spectacular increase in our computational capabilities. This is especially visible in quantum molecular modeling. For instance, on my first acquaintance with physical chemistry about 30 years ago, the only molecule that could be quantitatively treated with an accuracy close to

experimental data by wave mechanics was the hydrogen molecule. In a lifetime, I have witnessed a complete change of the research picture in which thermodynamic and kinetic data are theoretically obtained routinely with an accuracy often exceeding the experimental one. Quite obviously, to keep the pace with the progress in research, textbooks should be permanently updated and revised. In his textbook Professor Rogers sticks to the classical topics that are conventionally considered as part of physical chemistry. However, these classical topics are deciphered from a modern point of view, and here lies the main strength of this textbook as well as what actually makes this textbook different from many other similar textbooks.

Traditionally, physical chemistry is viewed as an application of physical principles in explaining and rationalizing chemical phenomena. As such, the powerful principles and theories that physical chemistry borrows from physics are accompanied by an advanced and mandatory set of mathematical tools. This makes the process of learning physical chemistry very difficult albeit challenging, exciting, and rewarding. The level of mathematics used by Professor Rogers to formulate and prove the physicochemical principles is remarkably consistent throughout the whole text. Thus, only the most general algebra and calculus concepts are required to understand the essence of the topics discussed. Professor Rogers's way of reasoning is succinct and easy to follow while the examples used to illustrate the theoretical developments are carefully selected and always make a good point. There is no doubt that this textbook is a work of great value, and I heartily recommend it for everybody who wants to enter the wonderful world of physical chemistry.

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July 2010

ILIE FISHTIK

PREFACE

Shall I call that wise or foolish, now; if it be really wise it has a foolish look to it; yet, if it be really foolish, then has it a sort of wiseish look to it.

Moby-Dick (Chapter 99) —Herman Melville

Physical chemistry stands at the intersection of the power and generality of classical and quantum physics with the minute molecular complexity of chemistry and biology. Any molecular process that can be envisioned as a flow from a higher energy state to a lower state is subject to analysis by the methods of classical thermodynamics. Chemical thermodynamics tells us where a process is going. Chemical kinetics tells us how long it will take to get there.

Evidence for and application of many of the most subtle and abstract principles of quantum mechanics are to be found in the physical interpretation of chemical phenomena. The vast expansion of spectroscopy from line spectra of atoms well known in the nineteenth century to the magnetic resonance imaging (MRI) of today's diagnostic procedures is a result of our gradually enhanced understanding of the quantum mechanical interactions of energy with simple atomic or complex molecular systems.

Mathematical methods developed in the domain of physical chemistry can be successfully applied to very different phenomena. In the study of seemingly unrelated phenomena, we are astonished to find that electrical potential across a capacitor, the rate of isomerization of cyclopentene, and the growth of marine larvae either as individuals or as populations have been successfully modeled by the same first-order differential equation.

Many people in diverse fields use physical chemistry but do not have the opportunity to take a rigorous three-semester course or to master one of the several ~1000-page texts in this large and diverse field. *Concise Physical Chemistry* is

intended to meet (a) the needs of professionals in fields other than physical chemistry who need to be able to master or review a limited portion of physical chemistry or (b) the need of instructors who require a manageable text for teaching a one-semester course in the essentials of the subject. The present text is not, however, a diluted form of physical chemistry. Topics are treated as brief, self-contained units, graded in difficulty from a reintroduction to some of the concepts of general chemistry in the first few chapters to research-level computer applications in the later chapters.

I wish to acknowledge my obligations to Anita Lekhwani and Rebekah Amos of John Wiley and Sons, Inc. and to Tony Li of Scientific Computing, Long Island University. I also thank the National Center for Supercomputing Applications and the National Science Foundation for generous allocations of computer time, and the H. R. Whiteley Foundation of the University of Washington for summer research fellowships during which part of this book was written.

Finally, though many people have helped me in my attempts to better appreciate the beauty of this vast and variegated subject, this book is dedicated to the memory of my first teacher of physical chemistry, Walter Kauzmann.

DONALD W. ROGERS

1

IDEAL GAS LAWS

In the seventeenth and eighteenth centuries, thoughtful people, influenced by the success of early scientists like Galileo and Newton in the fields of mechanics and astronomy, began to look more carefully for quantitative connections among the phenomena around them. Among these people were the chemist Robert Boyle and the famous French balloonist Jacques Alexandre César Charles.

1.1 EMPIRICAL GAS LAWS

Many physical chemistry textbooks begin, quite properly, with a statement of Boyle's and Charles's laws of ideal gases:

$$pV = k_1 \quad (\text{Boyle, 1662})$$

and

$$V = k_2T \quad (\text{Charles, 1787})$$

The constants k_1 and k_2 can be approximated simply by averaging a series of experimental measurements, first of pV at constant temperature T for the Boyle equation, then of V/T at constant pressure p for Charles's law. All this can be done using simple manometers and thermometers.

1.1.1 The Combined Gas Law

These two laws can be combined to give a new constant

$$\frac{pV}{T} = k_3$$

Subsequently, it was found that if the quantity of gas taken is the number of grams equal to the atomic or molecular weight of the gas, the constant k_3 , now written R under the new stipulations, is given by

$$pV = RT$$

For the number of *moles* of a gas, n , we have

$$pV = nRT$$

The constant R is called the *universal gas constant*.

1.1.2 Units

The pressure of a confined gas is the sum of the force exerted by all of the gas molecules as they impact with the container walls of area A in unit time:

$$p = \frac{f \text{ in units of N}}{A \text{ in units of m}^2}$$

The summed force f is given in units of newtons (N), and the area is in square meters (m^2). The N m^{-2} is also called the pascal (Pa). The pascal is about five or six orders of magnitude smaller than pressures encountered in normal laboratory practice, so the convenient unit $1 \text{ bar} \equiv 10^5 \text{ Pa}$ was defined.

The logical unit of volume in the MKS (meter, kilogram, second) system is the m^3 , but this also is not commensurate with routine laboratory practice where the liter is used. One thousand liters equals 1 m^3 , so the MKS name for this cubic measure is the cubic decimeter—that is, one-tenth of a meter cubed (1 dm^3). Because there are 1000 cubic decimeters in a cubic meter and 1000 liters in a cubic meter, it is evident that $1 \text{ L} = 1 \text{ dm}^3$.

The unit of temperature is the kelvin (K), and the unit of weight is the kilogram (kg). Formally, there is a difference between weight and mass, which we shall ignore for the most part. Chemists are fond of expressing the *amount* of a pure substance in

terms of the number of moles n (a pure, unitless number), which is the mass in kg divided by an experimentally determined unit molar mass M , also in kg:¹

$$n = \frac{\text{kg}}{M}$$

If the pressure is expressed as N m^{-2} and volume is in m^3 , then pV has the unit N m , which is a unit of energy called the *joule* (J). From this, the expression

$$R = \frac{pV}{nT}$$

gives the unit of R as $\text{J K}^{-1} \text{mol}^{-1}$. Experiment revealed that

$$R = 8.314 \text{ J K}^{-1} \text{mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{mol}^{-1}$$

which also defines the *atmosphere*, an older unit of pressure that still pervades the literature.

1.2 THE MOLE

The concept of the *mole* (gram molecular weight in early literature) arises from the deduction by Avogadro in 1811 that equal volumes of gas at the same pressure and temperature contain the same number of particles. This somewhat intuitive conclusion was drawn from a picture of the gaseous state as being characterized by repulsive forces between gaseous particles whereby doubling, tripling, and so on, the weight of the sample taken will double, triple, and so on, its number of particles, hence its volume. It was also known at the time that electrolysis of water produced *two* volumes of hydrogen for every volume of oxygen, so Avogadro deduced the formula H_2O for water on the basis of his hypothesis of equal volume for equal numbers of particles in the gaseous state.

By Avogadro's time, it was also known that the number of grams of oxygen obtained by electrolysis of water is 8 times the number of grams of hydrogen. By his 2-for-1 hypothesis, Avogadro reasoned that the less numerous oxygen atoms must be $2(8) = 16$ times as heavy as the more numerous hydrogen atoms. This theoretical vision led directly to the concept of atomic and molecular weight and to the mass of pure material equal to its atomic weight or molecular weight, which we now call the mole.² Various experimental methods have been used to determine the number of particles comprising one mole of a pure substance with the result

¹General practice is to write experimentally determined quantities in italics and units in Roman letters, but there is some overlap and we shall not be strict in this observance.

²The word is mole, but the unit is mol.

6.022×10^{23} , which is now appropriately called Avogadro's number, N_A . One mole of an ideal gas contains N_A particles and occupies 24.79 dm^3 at 1 bar pressure and 298.15 K.

1.3 EQUATIONS OF STATE

The equation $pV = RT$ with the stipulation of one mole of a pure gas is an *equation of state*. Given that R is a constant, the combined gas law equation can be written in a more general way:

$$p = f(V, T)$$

which suggests that there are other ways of writing an equation of state. Indeed, many equations of state are used in various applications (Metiu, 2006). The common feature of these equations is that only two *independent variables* are combined with constants in such a way as to produce a third *dependent* variable. We can write the general form as $p = f(V, T)$, or

$$V = f(p, T)$$

or

$$T = f(p, V)$$

so long as there are two independent variables and one dependent variable. One mole of a pure substance always has two *degrees of freedom*. Other observable properties of the sample can be expressed in the most general form:

$$z = f(x_1, x_2)$$

The variables in the general equation may seem unconnected to p and V , but there always exists, in principle, an equation of state, with two and only two independent variables, connecting them.

An infinitesimal change in a state function z for a system with two degrees of freedom is the sum of the infinitesimal changes in the two dependent variables, each multiplied by a sensitivity coefficient $(\partial z / \partial x_1)_{x_2}$ or $(\partial z / \partial x_2)_{x_1}$ which may be large if the dependent variable is very sensitive to independent variable x_i or small if dz is insensitive to x_i :

$$dz = \left(\frac{\partial z}{\partial x_1} \right)_{x_2} dx_1 + \left(\frac{\partial z}{\partial x_2} \right)_{x_1} dx_2$$