understanding chemistry

CHEMICAL EQUILIBRIA

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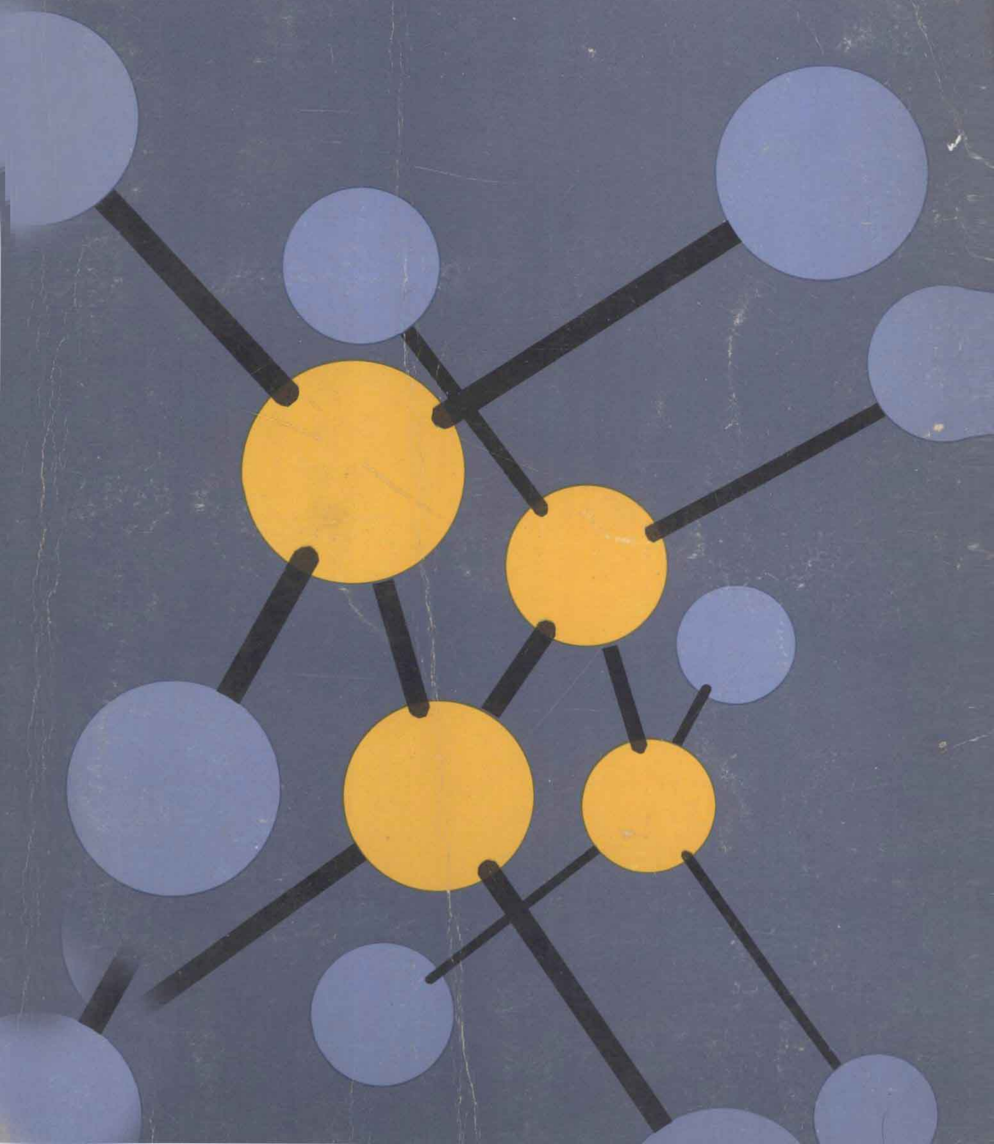

Understanding Chemistry IV

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1967 W. A. Benjamin, Inc.
New York Amsterdam

Understanding Chemistry **IV**

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Library of Congress Catalog Card Number 66-29689
Manufactured in the United States of America

*This manuscript was put into production on April 15, 1966;
this volume was published on January 3, 1967.*

W. A. Benjamin, Inc.
New York, New York 10016

UNDERSTANDING CHEMISTRY

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Understanding Chemistry IV

Chemical equilibria

Preface

Any introductory course in general chemistry must have as one of its objectives the effective presentation of a wide variety of topics. An overall view of chemistry at this level is generally regarded as desirable both for the students who will not proceed further with chemistry and for those who will continue with more detailed and specialized studies of the various areas of science. The general chemistry course must introduce to its students the current theories and unifying concepts of the subject. For the student to achieve a real familiarity with the subject, he must also acquire skill in the solution of the many typical chemical problems; he can then, for example, better appreciate the experimental basis for chemistry because he can do some of the calculations that relate experimental quantities to derived properties and relations.

The lecturer in such a course is, therefore, faced with the problem of dividing his available time between two kinds of topics. On the one hand, he can limit his discussion to rather general principles and run the risk of leaving the average student unable to apply the principles to specific cases. On the other hand, he can include in his lectures the details of problem-solving procedures and risk the loss of interest that often accompanies such material.

In the first-year chemistry course at Case Institute we are trying to resolve this common problem by using this instructional material to supplement the course lectures and recitations. We have found that such supplementary material allows the student, on his own, to acquire sound techniques for applying to specific problems the general principles developed in lectures or in assigned reading. In this way the student acquires the ability to handle the manipulations and calculations that are such a necessary part of chemistry. Moreover, when this is accomplished with the aid of these supplements, the lecturer is freed of detailed drill and repetition and is able to function in his proper role—that of providing the general principles and background, of showing the unifying features of the topics studied, and of generally conveying the exciting story that can be told, at this stage, about the developing field of chemistry. Our experience, as we have developed and used this material, is that it provides a valuable course supplement that aids both student and lecturer.

Material presented in the manner of these volumes is said to be "programmed." Programmed instruction, provided by books or mechanical devices, is already in widespread use in a number of areas and at various levels; its use in chemistry instruction, although of more recent origin, is growing; and there is clear indication that, when properly used, it is an efficient and effective teaching aid. Briefly stated, programmed instruction consists of a logically organized, carefully sequenced series of items (questions). Each item provides information to be learned and also requires the student to answer a question, carry out a calculation, or insert a word or a number. In this way the student is led to the goal of each programmed unit. You will notice, if you are inspecting programmed material for the first time, that individual items taken out of context seem perhaps trivial, or pointless, or too difficult. To evaluate programmed material you must follow through a sequence of items, as does the student, to see how topics are developed. The ultimate objective of each chapter is stated in the opening discussion. These statements of objectives serve not only to describe the chapter but also to allow students who have already mastered the material of the chapter to recognize this and to proceed with other work.

The material in this book and its companion volumes is supplementary. Topics are not treated exhaustively, and some knowledge of the concepts and terminology pertinent to each topic is assumed.

It is important to recognize that these programmed supplements do not themselves constitute a course and that all the general unifying material necessary for the complete development of the subject must be provided by the lecturer or through reading assignments. Some of this preparatory information is best given before the students are assigned a chapter, and some further discussion of the topic is valuable after the students have developed the familiarity with the topics that comes from working through the chapter.

Proceeding as outlined in the introduction, each chapter will require one to two hours to complete. Thus each chapter provides a convenient assignment unit.

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Cleveland, Ohio
August 1966

Introduction

Although in preparative chemistry one tries to use reactions that "go to completion," one finds that one deals in chemical systems with reactions that proceed only to a state of equilibrium. When this equilibrium state is reached, the system may contain mostly products, mostly reactants, or any intermediate proportion of products and reactants.

Under given conditions, the position of the equilibrium in a chemical system can sometimes be deduced from an expression relating the concentrations of all reagents to a constant for the reaction. Here it will be assumed that the basis for such expressions has been established and the way in which such expressions are used to obtain information on the concentrations of the reagents, at equilibrium, will be developed.

In this volume you will learn how to do such calculations for several representative types of systems. First, some simple gas phase reactions will be considered. Then, reactions in which the equilibrium is established between two phases will be illustrated by the treatment of the solubility of salts in aqueous solutions. Finally, the equilibria associated with the ionization of acids and bases in aqueous solution will be studied.

The topics dealt with are those usually encountered in an introductory general chemistry course; but the procedure for this book–it is a programmed instruction book, not a textbook or problem manual–may be new to you. The material is divided into chapters, and the objectives of each chapter are clearly stated at the beginning. Within each chapter, the material is presented in short numbered items (one or more sentences) that require you to supply a missing word, perform a calculation, or answer a question. Thus, as you are guided through a topic, you are obliged to participate in its development all the way.

For this book to be most valuable, you must write your answer in the blanks provided; only then should you turn over the page to see whether you are on the right track. The instructions are simple: Read and complete the items in numerical order. You will find on the following right-hand page the correct answer, or answers, for each item. The understanding of each item depends upon your understanding of the ideas in the previous items; therefore you should not go ahead unless your answer is the same or equivalent to the answer given. (Your answer need not be precisely the same as long as the meaning is essentially the same.) If your answer is incorrect, do not go on to the next item until you know why it is wrong and have corrected it. Answers to problems may be calculated with a slide rule. The answers given have been rounded off to the correct number of significant figures.

You will find that each chapter builds up to questions which are, in effect, summary problems that will illustrate whether you have mastered the material at hand. The average completion time for each chapter is between one and two hours.

		I A	II A	III B	IV B	V B	VI B	VII B	VIII	VIII	VIII	I B	II B	III A	IVA	VA	VI A	VII A	
										1 **H** 1.008									2 **He** 4.003
2	Period 2	3 **Li** 6.940	4 **Be** 9.013											5 **B** 10.82	6 **C** 12.010	7 **N** 14.008	8 **O** 16.0000	9 **F** 19.00	10 **Ne** 20.183
2 8	Period 3	11 **Na** 22.991	12 **Mg** 24.32											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.98	16 **S** 32.066	17 **Cl** 35.457	18 **Ar** 39.944
2 8 8	Period 4	19 **K** 39.100	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.95	24 **Cr** 52.01	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.94	28 **Ni** 58.71	29 **Cu** 63.54	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.60	33 **As** 74.91	34 **Se** 78.96	35 **Br** 79.916	36 **Kr** 83.80
2 8 18 8	Period 5	37 **Rb** 85.48	38 **Sr** 87.63	39 **Y** 88.92	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc*** [99]	44 **Ru** 101.1	45 **Rh** 102.91	46 **Pd** 106.4	47 **Ag** 107.880	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.70	51 **Sb** 121.76	52 **Te** 127.61	53 **I** 126.91	54 **Xe** 131.30
2 8 18 18 8	Period 6	55 **Cs** 132.91	56 **Ba** 137.36	57 **La** 138.9 ¦ 58 to 71	72 **Hf** 178.50	73 **Ta** 180.95	74 **W** 183.86	75 **Re** 186.22	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.09	79 **Au** 197.0	80 **Hg** 200.61	81 **Tl** 204.39	82 **Pb** 207.21	83 **Bi** 209.00	84 **Po*** 210	85 **At*** [210]	86 **Rn*** 222
2 8 18 32 18 8	Period 7	87 **Fr*** [223]	88 **Ra*** 226.05	89 **Ac*** 227	90 **Th*** 232.05	91 **Pa*** ¦ 92 to 103													

*All isotopes are radioactive.

[ ] Indicates mass number of longest known half-life.

Note: The small figures at far left show electron distribution in preceding noble gas.

4f series	58 **Ce** 140.13	59 **Pr** 140.92	60 **Nd** 144.27	61 **Pm*** [145]	62 **Sm** 150.35	63 **Eu** 152.0	64 **Gd** 157.26	65 **Tb** 158.93	66 **Dy** 162.51	67 **Ho** 164.94	68 **Er** 167.27	69 **Tm** 168.94	70 **Yb** 173.04	71 **Lu** 174.99

5f series	91 **Pa*** 231	92 **U*** 238.07	93 **Np*** [237]	94 **Pu*** [242]	95 **Am*** [243]	96 **Cm*** [248]	97 **Bk*** [247]	98 **Cf*** [251]	99 **Es***	100 **Fm***	101 **Md***	102 **—***	103 **Lw***

Contents

1 *Equilibrium calculations: homogeneous gas reactions*

Chemical reactions tend to proceed until they reach a state of equilibrium. For example, if $N_2O_4(g)$ is introduced into a container, dissociation to $NO_2(g)$ occurs, and the reaction $N_2O_4(g) = 2NO_2(g)$ continues until some definite fraction is converted to NO_2 and equilibrium is established. The concentrations of the reagents at equilibrium are related by an expression that has, for this example, the form $K = [NO_2]^2/[N_2O_4]$, K being the *equilibrium constant* for this reaction. (In later studies you will see that this is an approximation and is valid for *ideal* behavior in much the same way that the expression $PV = nRT$ is really valid only for *ideal* gases.)

This chapter deals with the equilibria established by gases in a container having a fixed volume and temperature. In the following chapters equilibria in systems containing liquids and solids will be treated.

It is assumed in this chapter that you know how to write the expression for the equilibrium constant for a reaction if the equation for the reaction is given, and that you are able to solve quadratic equations of the form $ax^2 + bx + c = 0$.

A typical problem that you will learn to solve is the following: "Calculate the equilibrium concentrations when 0.060 mole of PCl_5 and 0.020 mole of PCl_3 are allowed to come to equilibrium, according to the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, in a 4.7-liter container at 250°C. The equilibrium constant at this temperature is 0.042 mole/liter."

When you have finished this chapter, you will be able to solve, without difficulty, this problem and those in items 75-78.

1 At 250°C, phosphorus pentachloride dissociates according to the equation at the right. If 1.00 mole of PCl_5 is introduced into a container at 250°C, at a later time there will be (less, more) ______ than 1.00 mole of PCl_5 present.

28 In one experiment, PCl_5 was heated at 250°C until its concentration remained constant. The equilibrium concentration of each reagent was found to be as given at the right. Calculate the value of K at 250°: $K =$ ______.

At equilibrium

$[PCl_5] = 0.015$
$[PCl_3] = 0.025$
$[Cl_2] = 0.025$

$V = 5.0$ liters

55 For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K = 0.0579$ at 500°C. Write the equation from which x may be calculated.

27 $\frac{[PCl_3][Cl_2]}{[PCl_5]}$

54

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons 2NH_3(g)$
Initial conc.	0		0	6.00
Final conc.	$\frac{1}{2}x$		$\frac{3}{2}x$	$6.00 - x$

2 Each mole of PCl_5 that dissociates produces ___one___ mole(s) of PCl_3 and ___one___ mole(s) of Cl_2.

29 If the cell had originally been filled with pure PCl_5, its concentration before dissociation must have been ________ and the total number of moles of PCl_5 before dissociation must have been ________.

At equilibrium
$[PCl_5] = 0.015$
$[PCl_3] = 0.025$
$[Cl_2] = 0.025$

$V = 5.0$ liters

56 Solution of the fourth-power equation gives $x = 3.07$ moles per liter. What are the equilibrium concentrations of N_2, H_2, and NH_3?

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Equil. conc.	$0.5x$		$1.5x$		$6.00 - x$

1 less

28 $\frac{(0.025)(0.025)}{0.015} = 0.042$

55 $0.0579 = \frac{(6.00 - x)^2}{(0.500x)(1.50x)^3}$

$= \frac{(6.00 - x)^2}{1.69x^4}$

3 As the reaction proceeds, the number of moles of PCl_5 will ____de____ crease and the number of moles of PCl_3 will ____in____ crease until a state of equilibrium is attained.

30 Write the expression for the equilibrium constant, *K*, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

57 What is the percentage dissociation of NH_3 in the preceding problem?

2 1
1

29 0.040 mole/liter
(0.040) (5.0) = 0.20

56 $[N_2] = 1.54$
$[H_2] = 4.61$
$[NH_3] = 2.93$