

# CHEMICAL EQUILIBRIUM

A PRACTICAL INTRODUCTION FOR THE  
PHYSICAL AND LIFE SCIENCES

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A PRACTICAL INTRODUCTION FOR THE  
PHYSICAL AND LIFE SCIENCES

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PLENUM PRESS • NEW YORK AND LONDON

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Library of Congress Cataloging in Publication Data

Guenther, William B

Chemical equilibrium.

Bibliography: p.

Includes index.

1. Chemical equilibrium. I. Title.

QD503.G8                    541'.392                    75-28028

ISBN-13: 978-1-4684-2165-1            e-ISBN-13: 978-1-4684-2163-7

DOI: 10.1007/978-1-4684-2163-7

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© 1975 Plenum Press, New York

Softcover reprint of the hardcover 1st edition 1975

A Division of Plenum Publishing Corporation

227 West 17th Street, New York, N. Y. 10011

United Kingdom edition published by Plenum Press, London

A Division of Plenum Publishing Company, Ltd.

Davis House (4th Floor), 8 Scrubs Lane, Harlesden, London, NW10 6SE, England

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## Preface

The present work is designed to provide a practical introduction to aqueous equilibrium phenomena for both students and research workers in chemistry, biochemistry, geochemistry, and interdisciplinary environmental fields. The pedagogical strategy I have adopted makes heavy use of detailed examples of problem solving from real cases arising both in laboratory research and in the study of systems occurring in nature. The procedure starts with mathematically complete equations that will provide valid solutions of equilibrium problems, instead of the traditional approach through approximate concentrations and idealized, infinite-dilution assumptions. There is repeated emphasis on the use of corrected, conditional equilibrium constants and on the checking of numerical results by substitution in complete equations and/or against graphs of species distributions. Graphical methods of calculation and display are used extensively because of their value in clarifying equilibria and in leading one quickly to valid numerical approximations.

The coverage of solution equilibrium phenomena is not, however, exhaustively comprehensive. Rather, I have chosen to offer fundamental and rigorous examinations of homogeneous step-equilibria and their interactions with solubility and redox equilibria. Many examples are worked out in detail to demonstrate the use of equilibrium calculations and diagrams in various fields of investigation. Over 100 other exercises are included, most with answers and hints for solution. I have tried to bridge the gap between the oversimplified treatment in general and analytical chemistry texts and the complexities of the advanced presentations of multiple competing equilibria in real systems found in the books by Butler, Garrels and Christ,

and Stumm and Morgan (see the Bibliography, Appendix A-6). Students and workers in modern biology and geology as well as in chemistry need more help than these works offer in using equilibrium calculations to deal correctly with important aqueous systems. In this emphasis, this book differs from other works in that they are directed more toward chemical analysis, often giving scant coverage to the earth and biosciences and to applications to nonideal solutions.

The present book differs also in its inclusion of varied pH diagrams, graphical solution methods, details of Gran plots, and the construction of  $E$ -pH diagrams. Descriptions of Gran (linear titration) plots in the literature often do not make clear their limitations in precisely those cases in which we want most to use them: extremes at which the approximate equations used to derive the linear functions do not apply. Finally, it is my hope that the gradual introduction of the complexities affecting solubility found in Chapter 10 will prove helpful in dealing with this difficult topic.

Throughout, I have attempted to adhere closely to standard IUPAC symbolism, as exemplified in the volumes of *Stability Constants* (see the Bibliography, Appendix A-6). The chief exception is in the use of acidity constants rather than the proton formation constants of anions; I do this because it seems still to be predominant usage, though I hope this will change.

I realize that many who are familiar with equilibrium calculations will find the complete equations, the log ratio,  $\log \alpha$ ,  $\log C$ , and  $\bar{n}$  diagrammatic methods new and strange. Nonetheless, I hope that they will persist in looking through this study, to discover how great are the gains in clarity and assurance when using these methods in preference to the guesswork of more traditional approaches.

The preparation of the large number of  $\alpha$ ,  $\log \alpha$ , and  $\bar{n}$  diagrams was facilitated by use of an  $X$ - $Y$  plotter and a computer program compiled by Dr. C. C. Ross, Jr., Mathematics Department, Director of Academic Computing, University of the South (see Appendices A-2-A-4). It seemed best not to retouch the small discontinuities, which arise from tolerances in the computation program and plotter in these plots.

I record my gratitude for the encouragement of many colleagues and for the inspiration of the writers of the books listed in the Bibliography, Appendix A-6. I thank the University of the

South for according to me a sabbatical in 1974–75 for the completion of the book.

*Sewanee, Tennessee*  
*August 1975*

**William B. Guenther**



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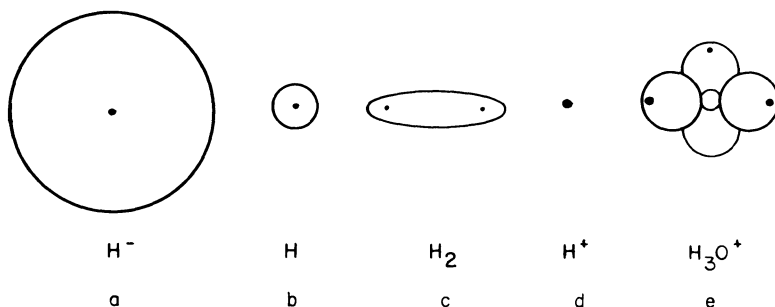
# 1 | Electronic Structure in Aqueous Acid–Base Chemistry

## 1. The Proton in Compounds

Modern theory supports the view that chemical change in matter is the process of rearrangement of negative electron clouds and positive atomic kernels to form a more stable mutual relation. The lightest element, hydrogen, is unique. All others retain a core of inner electrons throughout their reactions. But the core of hydrogen is only a proton. It is about  $10^{-5}$  the diameter of the lithium ion  $\text{Li}^+$ . Thus, the special ion  $\text{H}^+$  has exceptionally high positive charge density, the charge per unit volume. It associates with electron clouds in any matter available. Other ions, like the  $\text{Li}^+$ , can exist as entities in some crystal lattices, while no substances contain  $\text{H}^+$  as a separate entity or ion unit. It is important to be clear from the start about the vastly different species formed by hydrogen (Figure 1-1). When we speak of hydrogen ion and hydrogen compounds, we shall almost always mean the proton contained in an electron pair cloud as shown in the  $\text{H}_3\text{O}^+$  scheme in Figure 1-1. For a full discussion of evidence and the unique features of proton chemistry see Chapter 5 in the book by Bockris and Reddy.<sup>1</sup>

In water, compounds having acidic protons (Brønsted acids) form hydronium  $\text{H}_3\text{O}^+$  and higher hydrates, in which the proton is embedded in an unshared electron cloud on a water oxygen. Under

<sup>1</sup>J. O. BOCKRIS and A. K. N. REDDY, *Modern Electrochemistry*, Plenum Press, New York, 1970, Vol. 1, Chapter 5, "Protons in Solution."

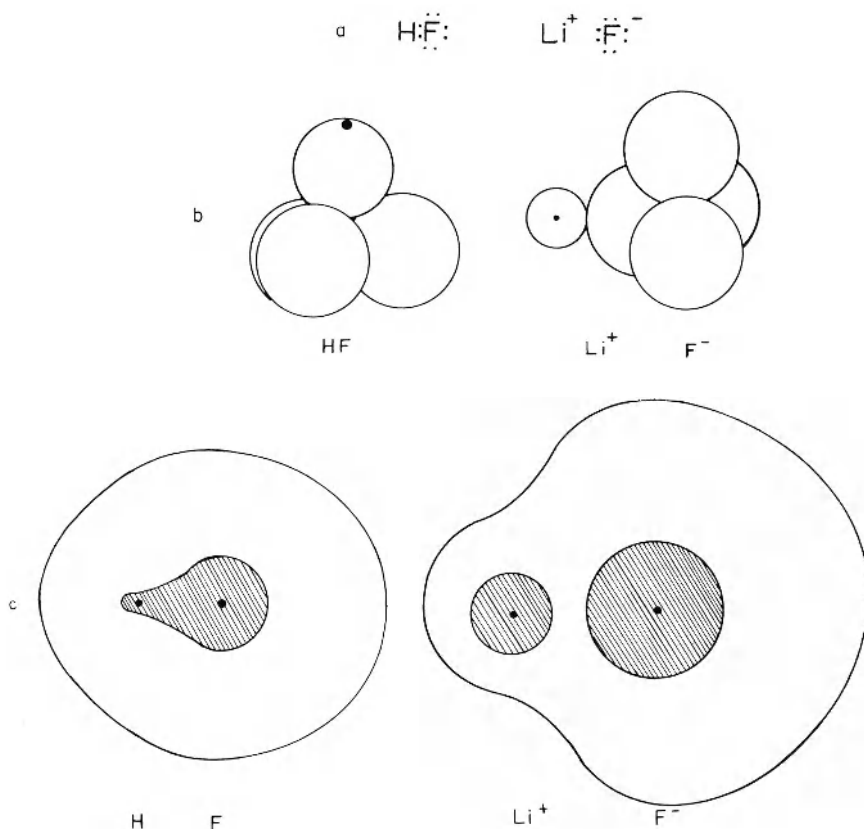


**Figure 1-1.** Drawings to scale of the forms of hydrogen. (a) The hydride ion, a proton with two electrons. (b) The hydrogen atom, a proton with one electron. (c) The hydrogen molecule, two separated protons in a cloud of two electrons. (d) The hydrogen core, or  $\text{H}^+$  ion, a proton. (e) The hydronium ion, oxygen with four electron cloud pairs, three of which are protonated in  $\text{H}_3\text{O}^+$ .

common conditions only the first row elements from B to F, and a few others like S, can hold protons in water. In addition, the three smallest, N, O, and F, exhibit the phenomenon of “hydrogen bonding,” which accounts for the unusual properties of water and many compounds of these elements.

The normal covalent bond, not the hydrogen bond, between other atoms and hydrogen differs from all other bonds in that the proton merges almost completely with a cloud on the other atom. This makes our traditional bond formulas of these compounds misleading. Let us compare HF and LiF in several formulations: Lewis dot structures (Figure 1-2a), electron pair cloud (tangent sphere) models (Figure 1-2b), and contour plots of electron cloud densities calculated with molecular orbital theory (Figure 1-2c). The orbital spheres in Figure 1-2b agree with the densities in Figure 1-2c far better than does the dot picture, Figure 1-2a. Ball-and-stick models are also seriously misleading with the hydrogen compounds.

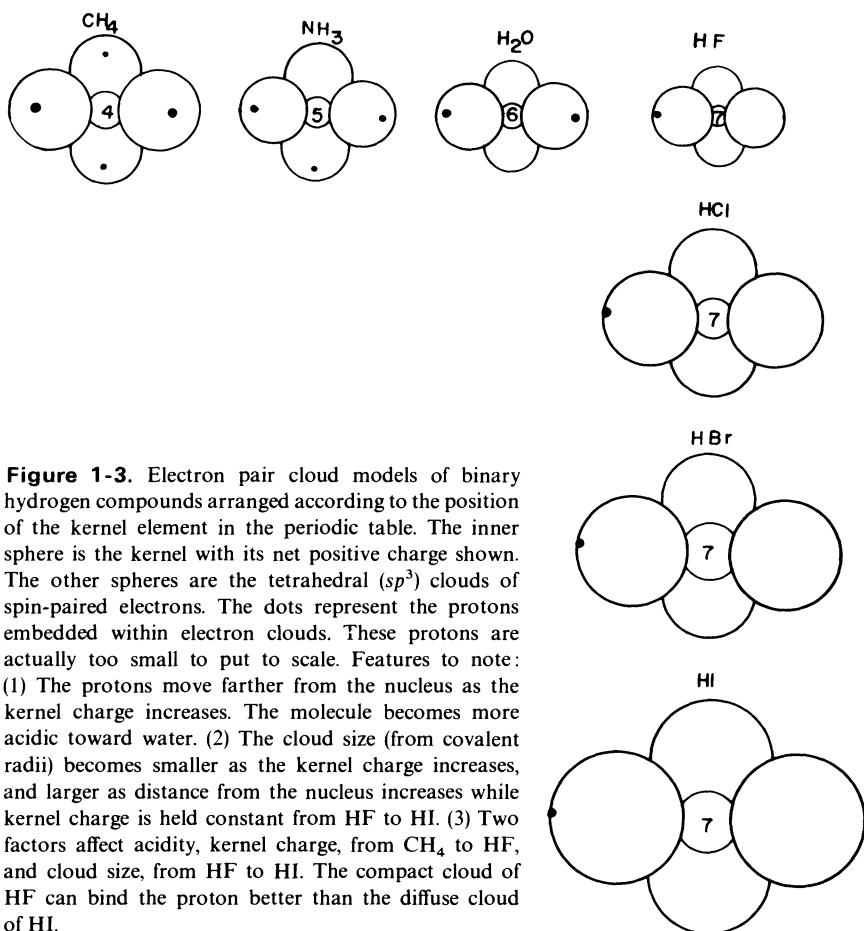
The ability of protons to migrate from cloud to cloud among the highly electronegative atoms is a major feature of acid–base chemistry. In water solution, a Brønsted acid, like HF, may donate protons to water molecules. A Lewis acid, like  $\text{Al}(\text{H}_2\text{O})^{3+}$ , can be seen to act like the Brønsted acids. The actual Lewis acid  $\text{Al}^{3+}$  withdraws electron cloud from the attached water molecules and also repels the  $\text{H}^+$ , which then jumps to neighboring water molecules. Either action increases the concentration of  $\text{H}_3\text{O}^+$  and decreases the concentration



**Figure 1-2.** (a) Lewis dot structures for LiF and HF. (b) Electron pair cloud (tangent sphere) models of LiF and HF. [See H. A. Bent, *J. Chem. Ed.* **40**, 446 523 (1963).] (c) Contours of electron charge density calculated for LiF and HF. Inner contour is for 0.2 and the outer is for 0.002 atomic unit ( $6.7 e/\text{\AA}^3$ ). This shows the ionic nature of LiF, while the nuclei of HF are both within the same inner cloud. [See R. F. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.* **47**, 3381 (1967); **49**, 1653 (1968); and A. C. Wahl, "Chemistry by Computer," *Sci. Am.* **1970** (April).]

of  $\text{OH}^-$ . The donor–acceptor nature of the solvent is central to our view of acid–base chemistry in water solutions.

Acid–base concepts share some features with seemingly different types of interactions: complexing, precipitation, and even redox. Comparison of these through theories of Brønsted, Lewis, Usanovich, and Lux–Flood extends our use of the electronic interpretations of



chemistry. Huheey surveys these theories.<sup>2</sup> Introductory surveys of structural and theoretical principles are available.<sup>3,4</sup>

Figure 1-3 shows the competing effects of nuclear repulsion and electron cloud attraction for a proton in binary hydrogen compounds.

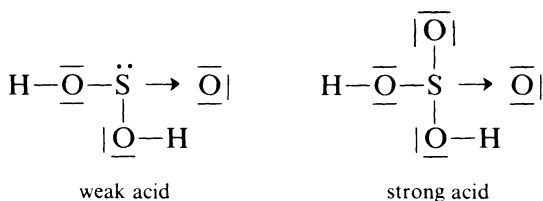
<sup>2</sup>J. E. HUHEEY, *Inorganic Chemistry*, Harper and Row, New York, 1972, Chapter 6.

<sup>3</sup>G. M. BARROW, *General Chemistry*, Wadsworth Publishing Co., Belmont, California, 1972, Chapters 7 and 11, "Structure" and "Equilibria."

<sup>4</sup>HENRY A. BENT, *The Second Law*, Oxford University Press, New York, 1965, Chapter 32, "Thermodynamics of Acid-Base Reactions."

## 2. The Oxy-Acid–Bases

The same arguments concerning size and charge effects in the binary hydrogen compounds of Figure 1-3 apply to the major class of acid–bases, the oxy-acid–bases. In these, a protonated oxygen is attached to other atoms, usually electron-withdrawing atoms or groups. The more withdrawing, the more acidic the proton, the more favorable is its transfer to the oxygen cloud on a water molecule, for example, compare sulfate(IV) and sulfate(VI) acids :

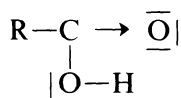


$\text{H}_2\text{SO}_4$  has one more coordinated oxide than  $\text{H}_2\text{SO}_3$ . This withdraws more electron cloud from the S, and through it, from the OH groups. Another way to approach this is to note that the oxidation state of S is six in  $\text{H}_2\text{SO}_4$ , so that the more exposed positive kernel of the S withdraws cloud more strongly from OH groups than does S(IV).

Similar reasoning can be applied to other series, for example :

Acid	$\text{HOCl}$	$\text{HOClO}$	$\text{HOClO}_2$	$\text{HOClO}_3$
$pK_a$	7.5	2.0	strong	strong

Carboxylic acids have the withdrawing coordinated oxide also,



The  $pK_a$  is 4–5 when R is aliphatic. But if other withdrawing groups are added in R, acidity increases :

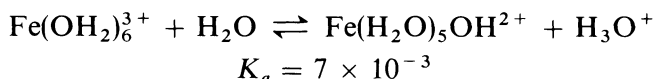
Acid	acetic	chloroacetic	dichloroacetic	trichloroacetic
$pK_a$	4.76	2.86	1.3	0.7

Thus we see that for most acids in water, the proton shifts between electron clouds on oxygen in water and in other molecules with slightly different environments.



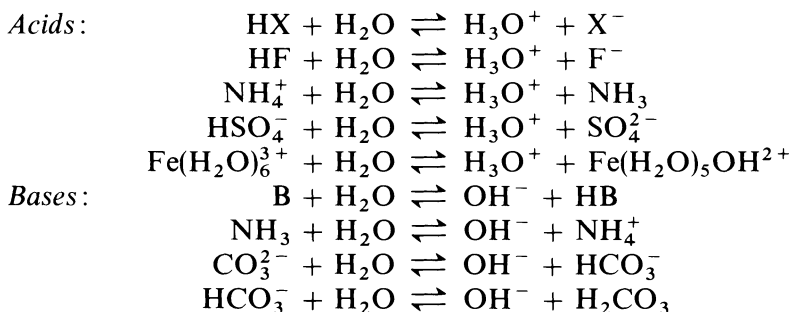
### 3. Brønsted Acid–Base Pairs versus “Hydrolysis”

Metal ions in solution are truly oxy-acids. Many of these have large kernels and use  $d^2sp^3$  orbitals for six-coordinate bonding. They can hold  $H_2O$  as well as  $OH^-$  or  $O^{2-}$  of the smaller oxy-acids. Ions like  $Fe^{3+}$  strongly hold six water molecules and withdraw electron cloud from the oxygen. This produces acid behavior in no way different from that of the other acids we have considered,



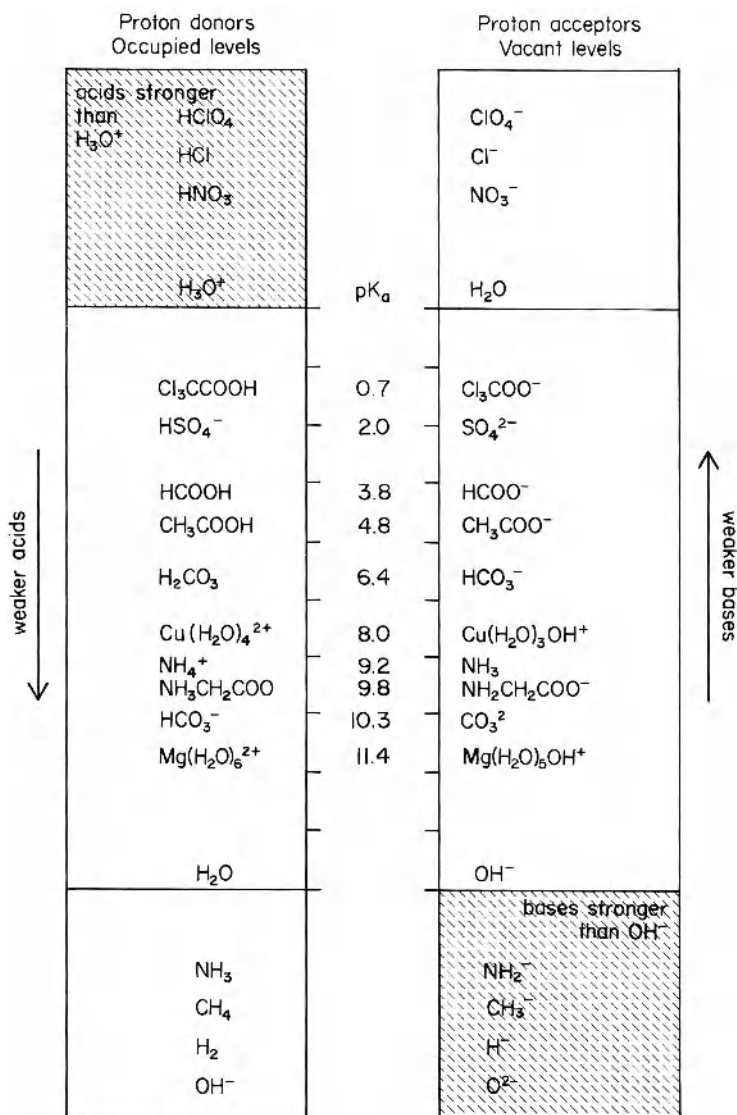
Thus, the ferric ion is considerably more acidic than acetic acid. Dilute ferric solutions are often yellow due to the hydroxopentaquo ion. Addition of  $HNO_3$  or  $HClO_4$  shifts the equilibrium to the left, giving the pale violet hexaquo ion.

Note that we do not ever need to refer to “hydrolysis” to explain acid–base behavior in water. It only confuses the issue. All the Brønsted acids and bases follow identical patterns of proton transfer. There is no chemical reason to call some of these examples dissociation and some hydrolysis:



Each acid has a conjugate base lacking one proton, and each base has a conjugate acid having one added proton. Thus, we speak of an acid–base pair, since they must exist together at equilibrium.

The relative strengths of acid–base pairs have been estimated and are shown diagrammatically in Figure 1-4. An acid can protonate, to an equilibrium concentration, the conjugate base of any acid below it. Thus, the strong acids protonate water to give  $H_3O^+$ , and the strong bases are protonated by water to form  $OH^-$ . Further discussions of these large topics can be found in general texts and in the references cited in footnotes 1–4 as well as in the figure legends.



**Figure 1-4.** Aqueous proton levels shown as free energy levels. [See Henry A. Bent, *The Second Law*, Oxford University Press, New York, 1965, Chapter 32; and R. W. Gurney, *Ionic Processes in Solution*, McGraw-Hill, New York, 1953 (reprinted Dover, 1962), p. 133.]

Problems<sup>5</sup>

- Classify the following substances as to their behavior in dilute water solutions as strong acid or base, weak acid or base, practically neutral. Use Figure 1-4 and analogies based on the periodic table:  
 $\text{HBr}$ ,  $\text{KOH}$ ,  $\text{KBr}$ ,  $\text{KNH}_2$ ,  $\text{C}_4\text{H}_7\text{OOH}$  (butyric acid),  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  
 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
  - Write chemical equations for the net ionic reactions occurring when:
    - Trisodium phosphate in water produces a very basic solution.
    - Dilute solutions of ammonium chloride and sodium hydroxide are mixed.
    - Ammonia acts weakly acidic when passed into saturated  $\text{NaOH}_{\text{aq}}$ .
    - Acetic acid can be a base (proton acceptor) in pure liquid  $\text{H}_2\text{SO}_4$ .
    - Strong acids form  $\text{H}_3\text{O}_{\text{aq}}^+$  in water, and  $\text{NH}_4^+$  in liquid  $\text{NH}_3$ .
    - Sodium reacts with either water or methanol to give  $\text{H}_2$  gas. What might be the self-ionization reaction of methanol?
- 
- Each of these groups is arranged from the strongest to the weakest acid in water solutions. Draw Lewis dot structures and explain these trends on the bases of size and charge effects.
 

a. $\text{H}_2\text{Te}$ , $\text{H}_2\text{Se}$ , $\text{H}_2\text{S}$ , $\text{H}_2\text{O}$ .	b. $\text{H}_2\text{CO}_3$ , $\text{H}_2\text{SiO}_3$ .
c. $\text{HOCl}$ , $\text{HOBr}$ , $\text{HOI}$ .	d. $\text{HNO}_3$ , $\text{HNO}_2$ , $\text{H}_2\text{CO}_3$ , $\text{HBO}_2$ .
  - When solutions of Fe(III) compounds are mixed with solutions of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , or  $\text{NaC}_2\text{H}_3\text{O}_2$ , similar precipitates of hydrated ferric oxide [ $“\text{Fe}(\text{OH})_3”$ ] form. Explain.
  - Each of the following groups is arranged from strong to weak acid. Explain the opposite trends.  $\text{H}_2\text{Te}$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{S}$ ; and  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SeO}_4$ ,  $\text{H}_2\text{TeO}_4$ .
  - When solutions of chromium(III) nitrate and potassium bicarbonate are mixed, a gas bubbles off and a light-green precipitate forms. Write a net ionic equation and explain the acid-base reactions.

<sup>5</sup>The problems after most chapters will be divided into two or three groups: (a) up to the single line: drill on basic ideas and operations; (b) from the single to the double line: more advanced or more complex situations; (c) after the double line: applications to special fields, not necessarily more difficult than sets (a) or (b).

# 2 | Chemical Equilibrium Relations and the pH System

## 1. The Equilibrium Constant

Chemists developed sufficiently sensitive methods of analysis in the 19th century to discover that many reactions “stop” somewhere short of completion. Berthelot and St. Gilles in 1862 showed that esterification reaches such a limit:



Their experimental yields for various mixtures were later shown to give a roughly constant quotient of the form

$$Q = \frac{[\text{ethyl acetate}][\text{water}]}{[\text{ethanol}][\text{acetic acid}]} = 4$$

From a modern reinvestigation of this equilibrium without strong acid catalysts present,<sup>1</sup> the two experiments summarized in Table 2-1 demonstrate how different mixtures achieve this quotient after reacting until an equilibrium state is reached. The figures are given on the basis of 100 moles of materials (mole percentage) at 25°C. Note that even though the proportions differ, the quotient at equilibrium is about the same. (The medium here is not a dilute water solution, and the quotients found did differ with the medium, varying from 1.9 to 4.6; see reference cited in footnote 1.)

<sup>1</sup>A. DARLINGTON and W. B. GUENTHER, *J. Chem. Eng. Data* **12**, 605 (1967).