CHEMICAL EQUILIBRIUM

A PRACTICAL INTRODUCTION FOR THE PHYSICAL AND LIFE SCIENCES

By William B. Guenther

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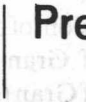


Preface

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 α, $\log \alpha$, 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.

William B. Guenther

Sewanee, Tennessee
August 1975

Contents

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 Li^+. Thus, the special ion 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 Li^+, can exist as entities in some crystal lattices, while no substances contain 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 H_3O^+ 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.[1]

In water, compounds having acidic protons (Brønsted acids) form hydronium H_3O^+ and higher hydrates, in which the proton is embedded in an unshared electron cloud on a water oxygen. Under

[1] J. O. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Plenum Press, New York, 1970, Vol. 1, Chapter 5, "Protons in Solution."

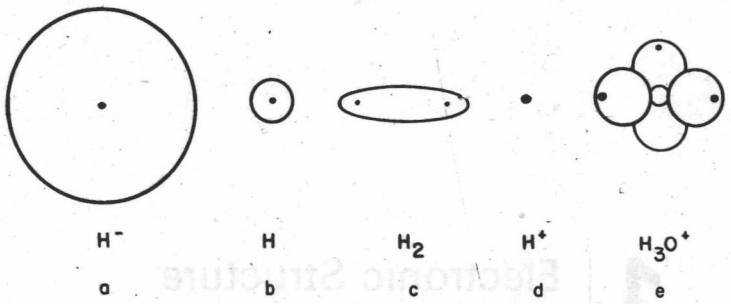


Figure 1-1. Drawings to scale of the forms of hydrogen. (a) The hydride ion, a proton with two electrons. (b) The hydrogen atom, a proton with one electron. (c) The hydrogen molecule, two separated protons in a cloud of two electrons. (d) The hydrogen core, or H^+ ion, a proton. (e) The hydronium ion, oxygen with four electron cloud pairs, three of which are protonated in H_3O^+.

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 $Al(H_2O)^{3+}$, can be seen to act like the Brønsted acids. The actual Lewis acid Al^{3+} withdraws electron cloud from the attached water molecules and also repels the H^+, which then jumps to neighboring water molecules. Either action increases the concentration of H_3O^+ and decreases the concentration

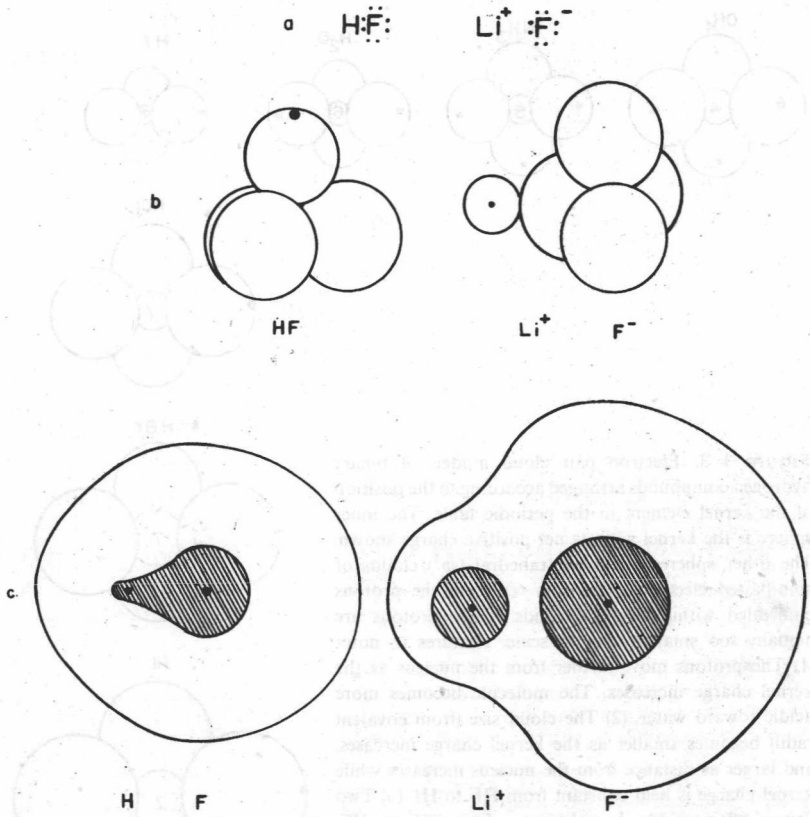


Figure 1-2. (a) Lewis dot structures for LiF and HF. (b) Electron pair cloud (tangent sphere) models of LiF and HF. [See H. A. Bent, *J. Chem. Ed.* **40**, 446 523 (1963).] (c) Contours of electron charge density calculated for LiF and HF. Inner contour is for 0.2 and the outer is for 0.002 atomic unit (6.7 e/Å^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 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

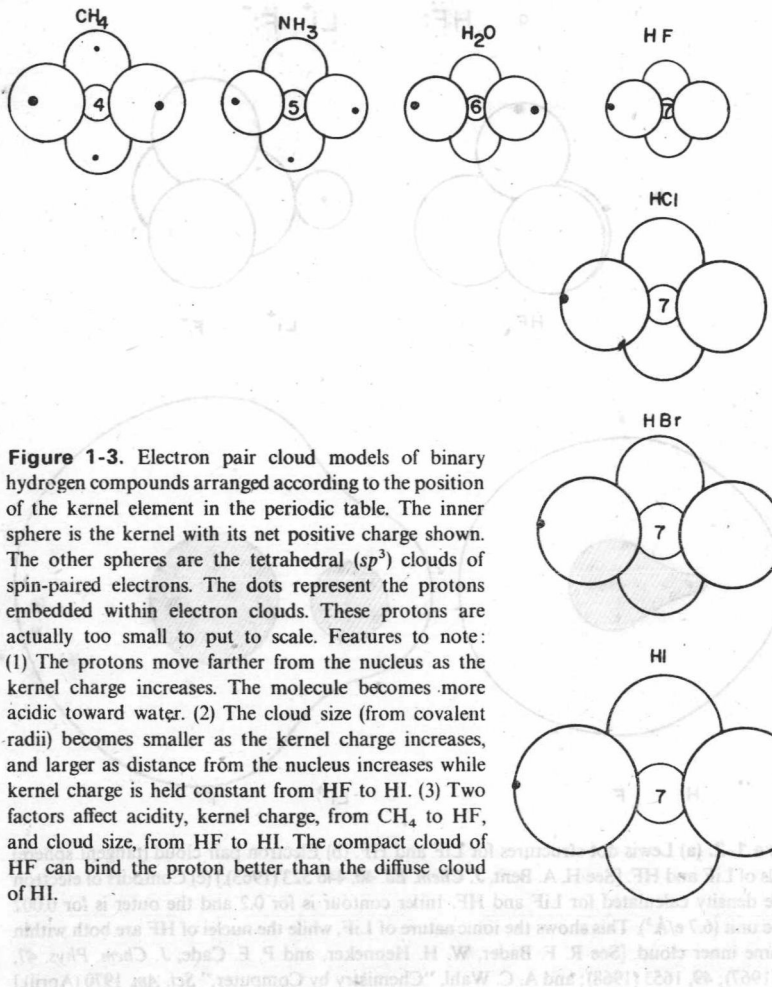


Figure 1-3. Electron pair cloud models of binary hydrogen compounds arranged according to the position of the kernel element in the periodic table. The inner sphere is the kernel with its net positive charge shown. The other spheres are the tetrahedral (sp^3) clouds of spin-paired electrons. The dots represent the protons embedded within electron clouds. These protons are actually too small to put to scale. Features to note: (1) The protons move farther from the nucleus as the kernel charge increases. The molecule becomes more acidic toward water. (2) The cloud size (from covalent radii) becomes smaller as the kernel charge increases, and larger as distance from the nucleus increases while kernel charge is held constant from HF to HI. (3) Two factors affect acidity, kernel charge, from CH_4 to HF, and cloud size, from HF to HI. The compact cloud of HF can bind the proton better than the diffuse cloud of HI.

chemistry. Huheey surveys these theories.[2] Introductory surveys of structural and theoretical principles are available.[3,4]

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

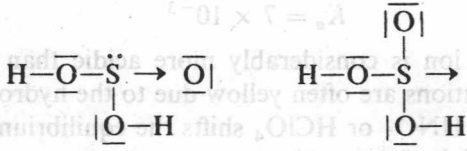
[2]J. E. HUHEEY, *Inorganic Chemistry*, Harper and Row, New York, 1972, Chapter 6.

[3]G. M. BARROW, *General Chemistry*, Wadsworth Publishing Co., Belmont, California, 1972, Chapters 7 and 11, "Structure" and "Equilibria."

[4]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:



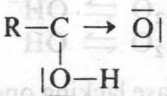
weak acid strong acid

H_2SO_4 has one more coordinated oxide than H_2SO_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 H_2SO_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	HOCl	HOClO	$HOClO_2$	$HOClO_3$
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.