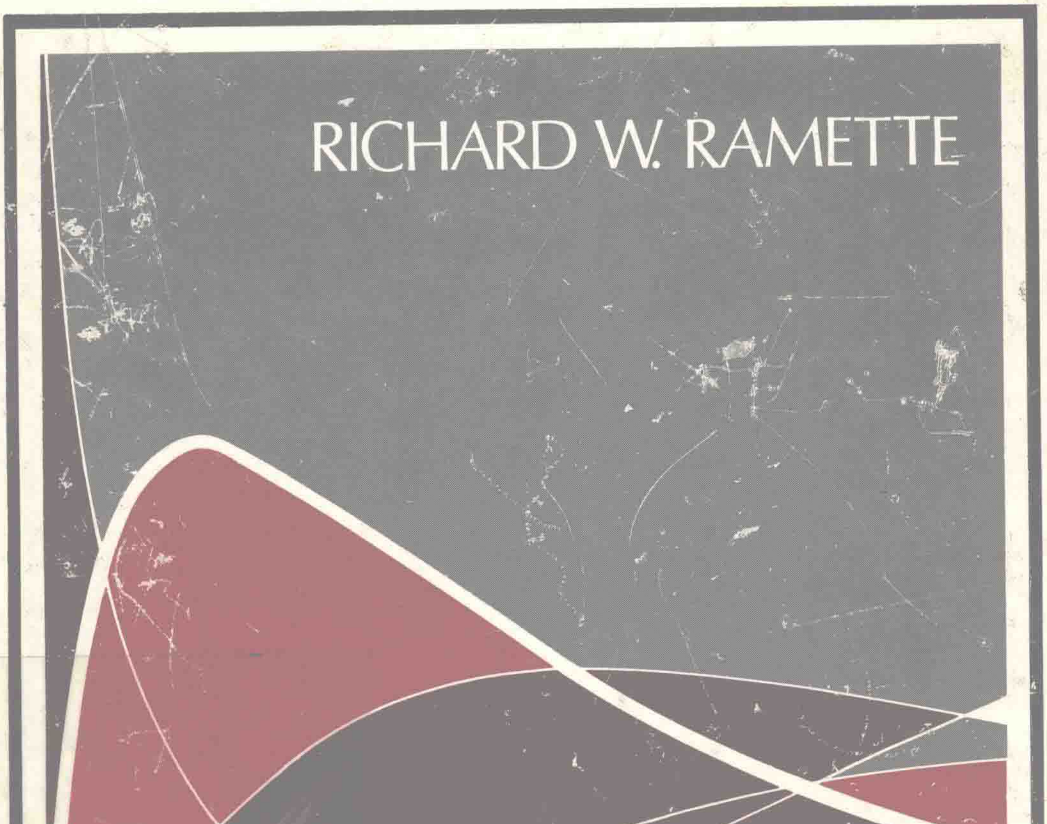
CHEMICAL EQUILIBRIUM AND ANALYSIS

RICHARD W. RAMETTE



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Richard W. Ramette
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ADDISON-WESLEY PUBLISHING COMPANY
Reading, Massachusetts • Menlo Park, California
London • Amsterdam • Don Mills, Ontario • Sydney

This book is in the ADDISON-WESLEY SERIES IN CHEMISTRY

Library of Congress Cataloging in Publication Data

Ramette, Richard W. 1927–
Chemical equilibrium and analysis.

Includes index.
1. Chemistry, Analytic. 2. Chemical equilibrium
I. Title.
QD75.2.R35 543 80-11937
ISBN 0-201-06107-4

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ISBN 0-201-06107-4
ABCDEFGHIJ-DO-8987654321

This book is gratefully dedicated to

David Leader, the biology teacher at Hartford Public High School who demonstrated the Fehling's analytical test for glucose one day and instantly transformed me into a boy chemist;

Alfred R. A. Brooks, HPHS science club adviser who encouraged us to fool around in the lab after school to learn how things work;

Joel and Grace Ramette, my patient parents who let me make those awful smells and bangs in the attic lab, and who sacrificed much in sending me to college;

Gil Burford and George Matsuyama, Wesleyan University professors who helped me through the initial bewilderments of analytical and physical chemistry;

Ernest B. Sandell, my thesis adviser at the University of Minnesota, who demonstrated so clearly in his research that chemical equilibrium and analysis are a single subject;

Isaac M. Kolthoff, who inspired all of us at Minnesota with a steady flow of principles and creative ideas including his favorite maxim: ''Theory guides, experiment decides'';

Laurence M. Gould, extraordinary President of Carleton College, who hired me on some sort of faith in 1954 and constantly encouraged the faculty to work toward excellence in college teaching in ''Science and the Other Humanities'';

My students, who have educated me while I have tried to teach them, and whose questions, anxieties, suggestions, and successes continue to provide a stimulating workshop;

My wife, Lee, whose understanding support and encouragement have helped tremendously to make this book-writing project possible.

PREFACE

This is a textbook for an introductory course in analytical chemistry that enrolls premedical, biology, and geology students as well as chemistry majors. I believe that such courses should treat the subject as a fundamental science, with a central focus on the healthy symbiosis between applied chemical analysis and theoretical models of aqueous equilibrium systems. Traditional analytical texts have made good use of tabulated values of equilibrium constants and electrode potentials, but students have a tendency to think of these tables as exact and unchanging. Most textbooks have not encouraged students to think about the origin of equilibrium data, which therefore take on the character of carved-stone tablets handed down by some forgotten scientific ancestor. Over the years I have tried to find many ways to convince my students that such ''constants'' are still subject to revision, that even the identities of solution species may be questioned, and that studies of new equilibrium systems are important in many research areas. Progress in all fields of chemical science, including oceanography, geochemistry, and environmental science, depends strongly on current and past research on chemical equilibrium and analysis, including studies of speciation.

I have chosen the important classical methods of analysis: titration, gravimetry, spectrophotometry, and potentiometry, and have discussed them in conjunction with the chief types of aqueous equilibria: acid–base, oxidation–reduction, metal–ligand complexes, precipitation–solubility, and distribution. I believe we should teach chemical equilibrium and analysis as complementary facets of a single subject. The treatment in this text is a blend of theoretical principles with practical applications, of descriptive chemistry with precision measurements, and of algebraic derivations with numerical calculations. In some sections hypothetical chemical models are translated into their mathematical counterparts, while elsewhere the anatomy of analytical methods is revealed by discussion of underlying equilibria.

One unique feature of this book is the liberal use of Case Studies based on data taken from the research literature. This approach not only places ideas in a realistic context but minimizes our natural tendency to oversimplify. For example, the effect of ionic strength on equilibria becomes obvious when we deal with

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real data, and we learn quickly that the assumption ''activity coefficients can be neglected for our purposes'' is not always valid. Very soon the students become uncomfortable about ignoring such important effects and, much to their credit, they would rather not have to find out later that their instruction was inadequate. As Alfred North Whitehead said: ''They should feel that they are studying something and are not merely executing intellectual minuets.''

The first chapter describes the main concepts of chemical analysis and defines common terms and methods. In Chapter 2, I have provided a practical approach to aqueous solution stoichiometry that will serve as a strong bridge from the basic ideas of the freshman course to the precise calculations of analysis. In Chapter 3, I have kept simple the statistical treatment of experimental data. Chapter 4 on chemical equilibrium and reaction tendency is especially important in showing how to handle the nonideal chemical systems that are so common in experimental work. I have demonstrated the need for activity coefficients and introduced a useful distinction between the equilibrium constant K and its molarity counterpart Q. The topics of spectrophotometry and galvanic cells are placed early in the book, so they may be used to advantage in the equilibrium discussions that follow. Acid–base systems are treated before other equilibria because they are relatively simple and because pH effects are so important in systems involving complexes and solubility. Considerable space is given to metal–ligand complexes because of their great significance in many areas of chemistry in addition to their value in chemical analysis. It is logical to delay the discussion of solubility equilibria because it depends strongly on both acid–base and metal–ligand reactions. I believe that the traditional overdependence on the simple solubility-product model has hampered chemists' understanding of solubility. The metal–ligand complexes and the solubility chapters offer rich opportunities to integrate all of the topics treated earlier in the book.

The concluding chapter on distribution equilibria and solvent extraction is optional in an introductory course. Further, when time is short, an instructor may choose to omit various parts of Chapters 7, 11, 13, 15, and 18.

The Appendixes are novel and instructive in the way they summarize data on equilibrium constants and reduction potentials. By grouping information about each element we gain an overview of important properties. A great deal of descriptive chemistry is implicit in these data summaries.

Another unusual feature of this book is its Laboratory Program. It includes some experiments of a more traditional type together with several experiments that support the main theme of the book. The laboratory work may readily be scheduled to correlate closely with the lectures. In comparison with the common ''quant unknowns,'' some experiments will be more difficult for the instructor to grade. For example, it may not be the student's fault that, due to tarnish, the response of the silver-wire electrode departs from the Nernst equation. However, these experiments are worthwhile because of the gain in understanding achieved when students interpret their own laboratory data in terms of the same fundamental principles they are struggling with in homework.

The first version of the manuscript took shape in 1975–1976, mainly during a sabbatical leave in Gainesville, Florida, and I thank Carleton College, the University of Florida, and Roger G. Bates for encouraging support. Much of the later writing was done during summers in Madison, Wisconsin, and it is a pleasure to acknowledge the excellent professional environment at the University of Wisconsin and the creative help given by Robert Lavine. I also appreciate the secretarial talents of Wendy Zimmerman and the duplicating skills of Marion Leidner and Loretta Springer, while the manuscript evolved through ten revisions in five years. Among the many reviewers who offered valuable suggestions I am grateful to Wilmer Stratton (Earlham College), Dennis Evans (University of Wisconsin/Madison), William Guenther (University of the South), Thomas Dunne (Reed College), Arthur Hubbard (University of California/Santa Barbara), Dennis Johnson (Iowa State University), and my colleagues at Carleton, Delores Bowers and David Smith, who actually taught from the manuscript. The excellent editorial contributions by Rima Zolina at Addison-Wesley have been remarkably valuable in the final metamorphosis. Finally, I am indebted to the many students in Northfield and Madison who studied from the preliminary editions. Their tolerance and helpful suggestions during the prolonged process of testing and revision have stimulated many improvements in the book.

R. W. Ramette,
Laurence McKinley Gould
Professor of Chemistry

Northfield, Minnesota
September, 1980

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CONCEPTS OF CHEMICAL ANALYSIS

1

I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of *Science*, whatever the matter may be.

Lord Kelvin

I like analytical chemistry. It not only uses and nourishes other fields of natural science and mathematics, but is a constantly growing blend of elegant theory, precise technique, and practical relevance. Analytical chemistry is so varied in content and so broad in scope that no one can master it fully or ignore it completely.

Although this textbook concentrates on the classical approaches of gravimetric, titrimetric, spectrophotometric, and potentiometric determinations, the underlying concepts apply to all of the modern and sophisticated procedures as well. Such concepts will be identified in this chapter and then used repeatedly in examples throughout the text. As I.M. Kolthoff said*:

> . . . The aims and objectives of analytical chemistry are to determine the composition of any simple or complex compound or mixture of compounds . . . The progress and advance of analytical chemistry depend to a great extent upon an intelligent application of the fundamentals of physical chemistry and the close relation between physical and analytical chemistry.

Perhaps the first famous chemical analysis was performed by Archimedes in ancient Greece. The King had given an artisan some gold for making a beautiful crown but suspected (without proof) that the goldsmith had cheated by replacing part of the gold with silver. Archimedes was the head scientist and the King wanted an answer. After considerable fretting without the slightest idea of how to test the crown, Archimedes decided to take a bath and, as he lowered his body into the tub, the water flowed over the edge. The answer came in an intuitive flash. "Eureka!" (I have found it!), cried Archimedes as he leaped from the tub and ran naked into the street.

Archimedes went to the King and got some pure gold that weighed as much as the crown and also some pure silver that weighed the same. When carefully lowered into a vessel full of water, the pure gold caused less overflow than did the pure silver (gold is almost twice as dense as silver). Then came the key step—he submerged the crown and noticed that the water overflow was intermediate between that caused by the gold and by the silver. This proved to the King's satisfaction that the artisan had made an alloy which still looked like gold but contained a substantial amount of silver. Archimedes went on to further discoveries and fame, but there is no record of what happened to the goldsmith. We still make regular use of Archimedes' Principle in the modern form: a body immersed in a fluid is buoyed up with a force equal to the weight of the displaced fluid.

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*I. M. Kolthoff, "Analytical Chemistry as a Technique and as a Science," *Chemical and Engineering News, 28,* p. 2882, August 21, 1950.

1.1 MAIN STEPS IN CHEMICAL ANALYSIS

The story of Archimedes illustrates the main steps in analytical procedure:

1. Statement of the problem.
2. Obtaining the sample for analysis.
3. Preparation of materials, including reference standards.
4. Sample treatment, including separations if necessary.
5. The determinative step.
6. Interpretation and conclusions.
7. Actions.

Each of these steps deserves some discussion to establish concepts and to define important terms:

1. Proper Statement of the Problem

Suppose you run an analytical service and have two customers who want you to determine the percentage of mercury in some material. The statements of their problems might be very different.

Customer A wants to bid on a boatload of high-grade mercury-containing ore, can provide you with as large a sample as you wish, states that the mercury is a major constituent at about the 5% level, and wants a representative figure of high accuracy for the mercury content of the load.

By contrast, customer B has one specimen of an ancient copper coin, suspects that the mercury content is at the part-per-million level, and tells you that the coin is not to be damaged, but that the determination need be accurate only to one significant digit.

Even though the overall problem is identical (determining the amount of mercury), the analytical approaches will have great differences. The ore will require statistical sampling techniques, and has enough mercury to permit the accurate methods of gravimetric analysis or titration to be used. The coin might be subjected to neutron bombardment followed by gamma-ray spectroscopy.

Proper statement of the problem is helpful as a guide to the analytical chemist who must choose from an arsenal of methods. It is also important to the person seeking information, so that the right sort of results are obtained. Further discussion at this stage may rule against the determination being carried out: for example, money may be no barrier to the mercury ore buyer, but the archaeologist with the rare coin must ask, "Is it really so vital for me to know the trace mercury content of this coin, given that the neutron activation analysis will cost about $500?"

As another example, suppose a physical chemist wants to know the concentration of chlorine in a mixture of gases used in a kinetics study. It makes a great difference if the determination must be carried out at 10-millisecond intervals following compression by a shock wave compared to the

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