

PREFACE

OBJECTIVES AND TEXT ORGANIZATION

The past three decades have witnessed a virtual explosion in the range of topics gathered under the umbrella of environmental chemistry. Throughout this period, the basic principles of equilibrium chemistry, particularly as they apply to aquatic systems, have served as indispensable tools for understanding the composition of, and direction of change in, environmental systems. This fact, it seems to me, owes as much to the seminal book that established our current paradigm for studying and interpreting the chemistry of aquatic systems as to the centrality of the equilibrium principles themselves. That book, of course, is *Aquatic Chemistry*, by Stumm and Morgan, first published in 1970 and currently in its third edition. Since the publication of that text, the tools available for solving the equations that define and constrain the equilibrium composition of aquatic systems have been improved significantly, and those tools have been applied to an ever-expanding range of systems, but the basic approach for analyzing the systems has remained largely unaltered.

Though it is unarguably the definitive text in the field, *Aquatic Chemistry* is widely perceived as too advanced for students taking their first course in the subject area, particularly those with little background beyond an introductory course in general chemistry. As a result, over the years, a number of texts have emerged that attempt to convey the key concepts of equilibrium chemistry in a more accessible format. This text follows in that line, covering much of the same material but diverging in a few ways both substantive and stylistic. A brief outline of the text highlights both the similarities and differences.

The text starts with an overview of a few simple, well-known physical/chemical concepts: conservation of mass and energy, and the tendency for any system to change toward a more stable (less reactive) condition. In Chapter 1, a good deal of the vocabulary of equilibrium aquatic chemistry is defined, links between chemical parameters and reactivity are introduced, and the kinetic model for chemical equilibrium is developed.

Chapter 2 provides a more formalized approach to understanding and predicting chemical change, via the concepts of chemical thermodynamics. The presentation and level of coverage in this chapter, particularly the first half, differ substantially from those in most other texts in this field, and a case can be made that the presentation is beyond what is necessary or appropriate in an introductory course. Frankly, at times I have persuaded myself that this assessment is accurate. However, after deliberation, I always returned to the opinion that if I wanted students to understand how thermodynamics applies to aquatic systems, as opposed to simply understanding how to carry out useful thermodynamic calculations, I had to devote substantial space to the topic.

This decision reflects, in large part, my own frustration at having studied thermodynamics so often without quite seeing the connections among the various pieces. For instance, the relationships $\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S}$ and $\Delta\bar{G} = \Delta\bar{G}^{\circ} + RT \ln a$ make it clear that enthalpy and entropy must be related to chemical activity a , but until recently, I did not understand how. Similarly, I could calculate the redox potential of a solution (E_H) and the surface potential on a suspended colloid (Ψ), but I was never quite sure if, or how, these two electrical potentials were related.

Once I sorted out those issues, I found the insights they provided immensely satisfying, and found that several ideas and principles that I had previously thought disconnected could be interpreted coherently. This cohesiveness is the essential beauty of thermodynamics, and in Chapter 2 I have attempted to convey some of that cohesiveness to students.

In Chapters 3 through 5 and 7 through 10, applications of the chemical principles introduced in Chapters 1 and 2 are presented in the context of specific types of chemical reactions. The first such reactions described focus on acid/base chemistry, in a section that comprises Chapters 3 through 5. This section differs from the discussion of acid/base equilibria in other texts in two ways that are significant. First, in presenting an algorithm for solving for the equilibrium pH of solutions prepared with known inputs, I have chosen to introduce both the proton condition and the *TOTH* equation. In my experience, although students can rapidly master the use of the *TOTH* equation to solve an acid/base problem, they gain a firmer grasp of the qualitative chemistry and the quantitative analysis of equilibrium solutions by writing out the proton condition table. On the other hand, the *TOTH* equation provides an excellent introduction to the development of the tableau that is at the core of numerical solutions to such problems. The essential identity of these two equations for characterizing the proton mass balance is emphasized, so that students understand that both equations provide the same information.

A second skill that is developed in this section is the ability to predict a priori the dominant acid/base species expected to be present at equilibrium, even when a complicated mixture of acids and bases has been used to prepare a solution. I derived this algorithm almost two decades ago, with a good deal of assistance from Dimitri Spyridakis. It has been very gratifying and more than a little surprising to see how enthusiastically other instructors have adopted the algorithm, now that I have begun to publicize what I had assumed was a widespread approach.

Chapter 6 diverges from the preceding and subsequent chapters, being devoted to a presentation of the most common features of some currently available software for solving chemical equilibrium problems. I have emphasized the solution approach taken in the MINEQL family of programs, without tying the discussion to any particular software package. While some instructors may choose to skip this chapter or to have students start using the software packages without going into the solution algorithms, I believe that understanding the basics of those algorithms is valuable, both pedagogically and to ease the learning of the

program mechanics when applied to some important systems that are not covered in the manuals.

Chapters 7 through 10 describe, respectively, equilibrium between solutions and a gas phase, reactions of metals in aqueous systems (both complexation and precipitation/dissolution), equilibrium in systems where oxidation-reduction reactions are occurring, and equilibrium between solutions and solid surfaces (adsorption). In each of these chapters, the presentation includes both a formal mathematical analysis of the reactions of interest and a discussion of how those reactions are analyzed by using chemical equilibrium software. All these chapters also refer to the thermodynamic developments in Chapter 2, and the last two chapters rely heavily on that development in the analysis of how the local electrical potential can affect chemical behavior. It is particularly in these latter chapters that, I hope, the detailed discussion of electrical potential and activity coefficients in Chapter 2 pays dividends.

A COMMENT ON THE TEXT LENGTH AND A PHILOSOPHY OF INSTRUCTION

One of the most difficult parts of writing this text has been finding the right balance between attention to fundamental concepts and problem-solving techniques. In striking that balance, I have been guided by my experience teaching water chemistry courses over the past 20 years, which has convinced me that students want and can handle more fundamentals than most instructors (including myself) have been providing. Ironically, in my opinion, what frustrates these students and sometimes leads them to believe that water chemistry is overwhelmingly difficult is that, as instructors, we have tried too hard to *simplify* the concepts. Too often, the simplifications we offer provide students the tools to derive correct answers to numerical problems, but only by following algorithms that they do not fully understand. Then, they feel intimidated and lost when faced with a problem for which the algorithm is inapplicable (or worse, they fail to realize that the algorithm is inapplicable and so apply it inappropriately).

I have therefore chosen to write longer and more detailed explanations of both the relevant chemistry and mathematics than are found in most other texts. Undeniably, this decision has lengthened the text, perhaps to the dismay of those who are perusing it for the first time. However, the range of topics covered is no greater than in other water chemistry texts, so the added length does not represent an increase in the conceptual material that readers are asked to master. To the contrary, my belief is that the extra explanatory material will actually *reduce* the time that students need to devote to learning the course content, while simultaneously facilitating a deeper understanding of the subject matter.

Having said that, I recognize that water chemistry courses are taught in many different formats—as semester courses, quarter courses, with and without laboratory components, etc.—and that many instructors will choose to cover only a

portion of the text in their courses. In such cases, I believe that a successful course could be taught by omitting coverage of Chapters 10, 9, and 2, in that order, depending on the severity of the time constraints. While an understanding of chemical thermodynamics (Chapter 2) is certainly helpful for interpreting all types of chemical reactions, it is more central to discussions of redox and adsorption reactions (Chapters 9 and 10, respectively) than the reactions covered in earlier chapters. Alternatively, an instructor might consider omitting coverage of chemical equilibrium software packages (Chapter 6 and easily identifiable sections of Chapters 7 through 10).

One of my goals throughout the writing of the text has been to integrate the material within each chapter and between chapters as seamlessly as possible. The benefits of such integration are self-evident, but the integration does impair any effort to fashion a course based on reading of disparate sections. Therefore, my personal preference is not to respond to time constraints by eliminating coverage of selected, isolated sections of the text. I believe that, in the end, students are better served by reading and mastering Chapters 1 and 3 through 8 in their entirety, than by being exposed to all 10 chapters but feeling unsure about their mastery of any of them. However, I realize that different courses have different objectives, and I hope that instructors will experiment freely with various ways to use the text and provide feedback to me on how well those approaches work.