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Introduction

As geochemists, we frequently need to describe the chemical states of natural waters, including how dissolved mass is distributed among aqueous species, and to understand how such waters will react with minerals, gases, and fluids of the Earth's crust and hydrosphere. We can readily undertake such tasks when they involve simple chemical systems, in which the relatively few reactions likely to occur can be anticipated through experience and evaluated by hand calculation. As we encounter more complex problems, we must rely increasingly on quantitative models of solution chemistry and irreversible reaction to find solutions.

The field of geochemical modeling has grown rapidly since the early 1960s, when the first attempt was made to predict by hand calculation the concentrations of dissolved species in seawater. Today's challenges might be addressed by using computer programs to trace many thousands of reactions in order, for example, to predict the solubility and mobility of forty or more elements in buried radioactive waste.

Geochemists now use quantitative models to understand sediment diagenesis and hydrothermal alteration, explore for ore deposits, determine which contaminants will migrate from mine tailings and toxic waste sites, predict scaling in geothermal wells and the outcome of steam-flooding oil reservoirs, solve kinetic rate equations, manage injection wells, evaluate laboratory experiments, and study acid rain, among many examples. Teachers let their students use these models to learn about geochemistry by experiment and experience.

Many hundreds of scholarly articles have been written on the modeling of geochemical systems, giving mathematical, geochemical, mineralogical, and practical perspectives on modeling techniques. Dozens of computer programs, each with its own special abilities and prejudices, have been developed (and laboriously debugged) to analyze various classes of geochemical problems. In this book, I attempt to treat geochemical modeling as an integrated subject, progressing from the theoretical foundations and computational concerns to the ways in which models can be applied in practice. In doing so, I hope to convey, by principle and by example, the nature of modeling and the results and uncertainties that can be expected.

1.1 Development of Chemical Modeling

Hollywood may never make a movie about geochemical modeling, but the field has its roots in top-secret efforts to formulate rocket fuels in the 1940s and 1950s. Anyone who reads cheap novels knows that these efforts involved brilliant scientists endangered by spies, counter-spies, hidden microfilm, and beautiful but treacherous women.

The rocket scientists wanted to be able to predict the thrust that could be expected from a fuel of a certain composition (see historical sketches by Zeleznik and Gordon, 1968; van Zeggeren and Storey, 1970; Smith and Missen, 1982). The volume of gases exiting the nozzle of the rocket motor could be used to calculate the

expected thrust. The scientists recognized that by knowing the fuel's composition, the temperature at which it burned, and the pressure at the nozzle exit, they had uniquely defined the fuel's equilibrium volume, which they set about calculating.

Aspects of these early calculations carry through to geochemical modeling. Like rocket scientists, we define a system of known composition, temperature, and pressure in order to calculate its equilibrium state. Much of the impetus for carrying out the calculations remains the same, too. Theoretical models allowed rocket scientists to test fuels without the expense of launching rockets, and even to consider fuels that had been formulated only on paper. Similarly, they allow geoscientists to estimate the results of a hydrothermal experiment without spending time and money conducting it, test a chemical stimulant for an oil reservoir without risking damage to the oil field, or help evaluate the effectiveness of a scheme to immobilize contaminants leaking from buried waste before spending and perhaps wasting millions of dollars and years of effort.

Chemical modeling also played a role in the early development of electronic computers. Early computers were based on analog methods in which voltages represented numbers. Because the voltage could be controlled to within only the accuracy of the machine's components, numbers varied in magnitude over just a small range. Chemical modeling presented special problems because the concentrations of species vary over many orders of magnitude. Even species in small concentrations, such as H^+ in aqueous systems, must be known accurately, since concentrations appear not only added together in mass balance equations, but multiplied by each other in the mass action (equilibrium constant) equations. The mathematical nature of the chemical equilibrium problem helped to demonstrate the limitations of analog methods, providing impetus for the development of digital computers.

1.1.1 Controversy Over Free-Energy Minimization

Brinkley (1947) published the first algorithm to solve numerically for the equilibrium state of a multicomponent system. His method, intended for a desk calculator, was soon applied on digital computers. The method was based on evaluating equations for equilibrium constants, which, of course, are the mathematical expression of the minimum point in Gibbs free energy for a reaction.

In 1958, White *et al.* published an algorithm that used optimization theory to solve the equilibrium problem by "minimizing the free energy directly." Free-energy minimization became a field of study of its own, and the technique was implemented in a number of computer programs. The method had the apparent advantage of not requiring balanced chemical reactions. Soon, the chemical community was divided into two camps, each of which made extravagant claims about guarantees of convergence and the simplicity or elegance of differing algorithms (Zeleznik and Gordon, 1968).

According to Zeleznik and Gordon, tempers became so heated that a panel that was convened in 1959 to discuss equilibrium computation had to be split in two. Both sides seemed to have lost sight of the fact that the equilibrium constant is a mathematical expression of minimized free energy. As noted by Smith and Missen (1982), the working equations of Brinkley (1947) and White *et al.* (1958) are suspiciously similar. As well, the complexity of either type of formulation depends largely on the choice of components and independent variables, as described in Chapter 3.

Not surprisingly, Zeleznik and Gordon (1960, 1968) and Brinkley (1960) proved that the two methods were computationally and conceptually equivalent. The balanced reactions of the equilibrium constant method are counterparts to the species compositions required by the minimization technique; in fact, given the same choice of components, the reactions and expressions of species compositions take the same form.

Nonetheless, controversy continues even today among geochemical modelers. Colleagues sometimes take sides on the issue, and claims of simplified formulations and guaranteed convergence by minimization are still heard. In this book, I formalize the discussion in terms of equilibrium constants, which are familiar to geochemists and widely reported in the literature. Quite properly, I treat minimization methods as being computationally equivalent to the equilibrium constant approach, and do not discuss them as a separate group.

1.1.2 Application in Geochemistry

When they calculated the species distribution in seawater, Garrels and Thompson (1962) were probably the first to apply chemical modeling in the field of geochemistry. Modern chemical analyses give the composition of seawater in terms of dissociated ions (Na^+ , Ca^{++} , Mg^{++} , HCO_3^- , and so on), even though the solutes are distributed among complexes such as $\text{MgSO}_4(\text{aq})$ and CaCl^+ as well as the free ions. Before advent of the theory of electrolyte dissociation, seawater analyses were reported, with equal validity, in terms of the constituent salts NaCl , MgCl_2 , and so on. Analyses can, in fact, be reported in many ways, depending on the analyst's choice of chemical components.

Garrels and Thompson's calculation, computed by hand, is the basis for a class of geochemical models that predict species distributions, mineral saturation states, and gas fugacities from chemical analyses. This class of models stems from the distinction between a chemical analysis, which reflects a solution's bulk composition, and the actual distribution of species in a solution. Such *equilibrium models* have become widely applied, thanks in part to the dissemination of reliable computer programs such as SOLMNEQ (Kharaka and Barnes, 1973) and WATEQ (Truesdell and Jones, 1974).

Garrels and Mackenzie (1967) pioneered a second class of models when they simulated the reactions that occur as a spring water evaporates. They began by calculating the distribution of species in the spring water, and then repeatedly removed an aliquot of water and recomputed the species distribution. From concepts of equilibrium and mass transfer, the *reaction path model* was born. This class of calculation is significant in that it extends geochemical modeling from considering state to simulating process.

Helgeson (1968) introduced computerized modeling to geochemistry. Inspired by Garrels and Mackenzie's work, he realized that species distributions and the effects of mass transfer could be represented by general equations that can be coded into computer programs. Helgeson and colleagues (Helgeson *et al.*, 1969, 1970) demonstrated a generalized method for tracing reaction paths, which they automated with their program PATHI ("path-one") and used to study weathering, sediment diagenesis, evaporation, hydrothermal alteration, and ore deposition.

Two conceptual improvements have been made since this early work. First, Helgeson *et al.* (1970) posed the reaction path problem as the solution to a system of ordinary differential equations. Karpov and Kaz'min (1972) and Karpov *et al.* (1973) recast the problem algebraically so that a reaction path could be traced by repeatedly solving for a system's equilibrium state as the system varied in composition or temperature. Wolery's (1979) EQ3/EQ6, the first software package for geochemical modeling to be documented and distributed, and Reed's (1977, 1982) SOLVEQ and CHILLER programs used algebraic formulations. This refinement simplified the formulations and codes, separated consideration of mass and heat transfer from the chemical equilibrium calculations, and eliminated the error implicit in integrating differential equations numerically.

Second, modelers took a broader view of the choice of chemical components. Aqueous chemists traditionally think in terms of elements (and electrons) as components, and this choice carried through to the formulations of PATHI and EQ3/EQ6. Morel and Morgan (1972), in calculating species distributions, described

composition by using aqueous species for components (much like the seawater analysis described at the beginning of this section; see also Morel, 1983). Reed (1982) formulated the reaction path problem similarly, and Perkins and Brown's (1982) PATH program also used species and minerals as components. Chemical reactions now served double duty by giving the compositions of species and minerals in the system in terms of the chosen component set. This choice, which allowed models to be set up without even acknowledging the existence of elements, simplified the governing equations and provided for easier numerical solutions.

1.2 Scope of This Book

In setting out to write this book, I undertook to describe reaction modeling both in its conceptual underpinnings and its applications. Anything less would not be acceptable. Lacking a thorough introduction to underlying theory, the result would resemble a cookbook, showing the how but not the why of modeling. A book without detailed examples spanning a range of applications, on the other hand, would be sterile and little used.

Of necessity, I limited the scope of the text to discussing reaction modeling itself. I introduce the thermodynamic basis for the equations I derive, but do not attempt a complete development of the field of thermodynamics. A number of texts already present this beautiful body of theory better than I could aspire to in these pages. Among my favorites: Prigogine and Defay (1954), Pitzer and Brewer (1961), Denbigh (1981), Anderson and Crerar (1993), Nordstrom and Munoz (1994), Anderson (2017), and Ganguly (2020). I present (in Chapter 8) but do not derive models for estimating activity coefficients in electrolyte solutions. The reader interested in more detail may refer to Robinson and Stokes (1968), Helgeson *et al.* (1981), Pitzer (1987), and Grenthe *et al.* (1997); Anderson and Crerar (1993, their chapter 17) present a concise but thorough overview of the topic.

Finally, I do not discuss questions of the measurement, estimation, evaluation, and compilation of the thermodynamic data upon which reaction modeling depends. Nordstrom and Munoz (1994, their chapters 11 and 12) provide a summary and overview of this topic, truly a specialty in its own right. Haas and Fisher (1976), Helgeson *et al.* (1978), and Johnson *et al.* (1991) treat aspects of the subject in detail.