CAMBRIDGE

Cambridge University Press
978-0-521-87554-7 - Geochemical and Biogeochemical Reaction Modeling, Second Edition
Craig M. Bethke
Excerpt
More information

1

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.

Cambridge University Press
978-0-521-87554-7 - Geochemical and Biogeochemical Reaction Modeling, Second Edition
Craig M. Bethke
Excerpt
More information

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 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

Cambridge University Press
978-0-521-87554-7 - Geochemical and Biogeochemical Reaction Modeling, Second Edition
Craig M. Bethke
Excerpt
More information

dissociated ions (Na^+, Ca^{++}, Mg^{++}, HCO_3^-, and so on), even though the solutes are distributed among complexes such as $MgSO_4$(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.

Cambridge University Press
978-0-521-87554-7 - Geochemical and Biogeochemical Reaction Modeling, Second Edition
Craig M. Bethke
Excerpt
More information

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 (1971), Anderson and Crerar (1993), and Nordstrom and Munoz (1994). 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), and Pitzer (1987); Anderson and Crerar (1993, Chapter 23) 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, Chapters 13 and 14) 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.

Cambridge University Press
978-0-521-87554-7 - Geochemical and Biogeochemical Reaction Modeling, Second Edition
Craig M. Bethke
Excerpt
More information

2

Modeling overview

A *model* is a simplified version of reality that is useful as a tool. A successful model strikes a balance between realism and practicality. Properly constructed, a model is neither so simplified that it is unrealistic nor so detailed that it cannot be readily evaluated and applied to the problem of interest.

Geologic maps constitute a familiar class of models. To map a sedimentary section, a geologist collects data at certain outcrops. He casts his observations in terms of the local stratigraphy, which is itself a model that simplifies reality by allowing groups of sediments to be lumped together into formations. He then interpolates among his data points (and projects beneath them) to infer positions for formation contacts, faults, and so on across his field area.

The final map is detailed enough to show the general arrangement of formations and major structures, but simplified enough, when drawn to scale, that small details do not obscure the overall picture. The map, despite its simplicity, is without argument a useful tool for understanding the area's geology. To be successful, a geochemical model should also portray the important features of the problem of interest without necessarily attempting to reproduce each chemical or mineralogical detail.

2.1 Conceptual models

The first and most critical step in developing a geochemical model is conceptualizing the system or process of interest in a useful manner. By *system*, we simply mean the portion of the universe that we decide is relevant. The composition of a *closed system* is fixed, but mass can enter and leave an *open system*. A system has an *extent*, which the modeler defines when he sets the amounts of fluid and mineral considered in the calculation. A system's extent might be a droplet of rainfall, the groundwater and sediments contained in a unit volume of an aquifer, or the world's oceans.

Cambridge University Press
978-0-521-87554-7 - Geochemical and Biogeochemical Reaction Modeling, Second Edition
Craig M. Bethke
Excerpt
More information

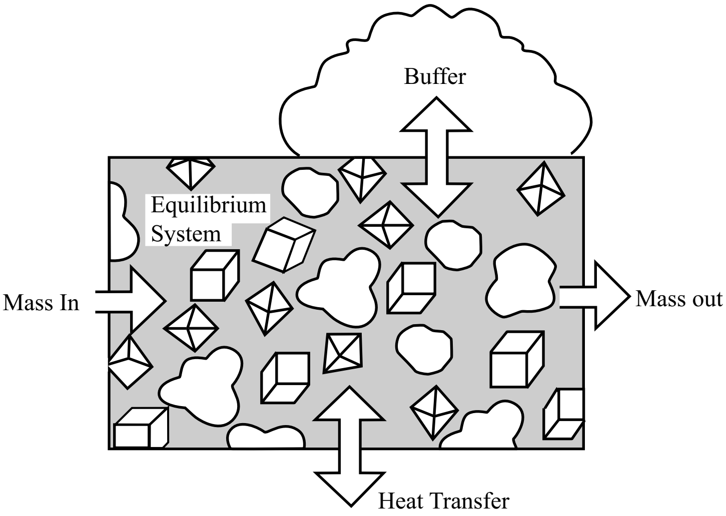

Fig. 2.1. Schematic diagram of a reaction model. The heart of the model is the equilibrium system, which contains an aqueous fluid and, optionally, one or more minerals. The system's constituents remain in chemical equilibrium throughout the calculation. Transfer of mass into or out of the system and variation in temperature drive the system to a series of new equilibria over the course of the reaction path. The system's composition may be buffered by equilibrium with an external gas reservoir, such as the atmosphere.

The "art" of geochemical modeling is conceptualizing the model in a useful way. Figure 2.1 shows schematically the basis for constructing a geochemical model. The heart of the model is the *equilibrium system*, which remains in some form of chemical equilibrium, as described below, throughout the calculation. The equilibrium system contains an aqueous fluid and optionally one or more minerals. The temperature and composition of the equilibrium system are known at the beginning of the model, which allows the system's equilibrium state to be calculated. Pressure also affects the equilibrium state, but usually in a minor way under the near-surface conditions considered in this book (e.g., Helgeson, 1969; but also see Hemley *et al.*, 1986), unless a gas phase is present.

In the simplest class of geochemical models, the equilibrium system exists as a closed system at a known temperature. Such equilibrium models predict the distribution of mass among species and minerals, as well as the species' activities, the fluid's saturation state with respect to various minerals, and the fugacities of different gases that can exist in the chemical system. In this case, the initial equilibrium system constitutes the entire geochemical model.

More complicated models account for the transport of mass or heat into or out of the system, so that its composition or temperature, or both, vary over the course of the calculation. The system's initial equilibrium state provides the starting point for this class of reaction path models. From this point, the model traces how mass entering and leaving the system, or changes in temperature, affect the system's equilibrium state.

Conceptualizing a geochemical model is a matter of defining (1) the nature of equilibrium to be maintained, (2) the initial composition and temperature of the equilibrium system, and (3) the mass transfer or temperature variation to occur over the course of the reaction process envisioned.

2.1.1 Types of equilibrium

It is useful at this point to differentiate among the ways in which we can define equilibrium. In a classic sense (e.g., Pitzer and Brewer, 1961; Denbigh, 1971), a system is in equilibrium when it occupies a specific region of space within which there is no spontaneous tendency for change to occur. In this case, which we will call *complete equilibrium*, all possible chemical reactions are in equilibrium. Assuming complete equilibrium, for example, we can predict the distribution of dissolved species in a sample of river water, if the water is not supersaturated with respect to any mineral.

Geochemical models can be conceptualized in terms of certain false equilibrium states (Barton *et al.*, 1963; Helgeson, 1968). A system is in *metastable equilibrium* when one or more reactions proceed toward equilibrium at rates that are vanishingly small on the time scale of interest. Metastable equilibria commonly figure in geochemical models. In calculating the equilibrium state of a natural water from a reliable chemical analysis, for example, we may find that the water is supersaturated with respect to one or more minerals. The calculation predicts that the water exists in a metastable state because the reactions to precipitate these minerals have not progressed to equilibrium.

In tracing a reaction path, likewise, we may find a mineral in the calculation results that is unlikely to form in a real system. Quartz, for example, would be likely to precipitate too slowly to be observed in a laboratory experiment conducted at room temperature. A model can be instructed to seek metastable solutions by not considering (*suppressing*, in modeling parlance) certain minerals in the calculation, as would be necessary to model such an experiment.

A system in complete equilibrium is spatially continuous, but this requirement can be relaxed as well. A system can be in internal equilibrium but, like Swiss cheese, have holes. In this case, the system is in *partial equilibrium*. The fluid in a sandstone, for example, might be in equilibrium itself, but may not be in equilibrium with the mineral grains in the sandstone or with just some of the grains. This concept has provided the basis for many published reaction paths, beginning

Cambridge University Press
978-0-521-87554-7 - Geochemical and Biogeochemical Reaction Modeling, Second Edition
Craig M. Bethke
Excerpt
More information

with the work of Helgeson *et al.* (1969), in which a rock gradually reacts with its pore fluid.

The species dissolved in a fluid may be in partial equilibrium, as well. Many redox reactions equilibrate slowly in natural waters (e.g., Lindberg and Runnells, 1984). The oxidation of methane

$$CH_4(aq) + 2\,O_2(aq) \rightarrow HCO_3^- + H^+ + H_2O \tag{2.1}$$

is notorious in this regard. Shock (1988), for example, found that although carbonate species and organic acids in oil-field brines appear to be in equilibrium with each other, these species are clearly out of equilibrium with methane. To model such a system, the modeler can *decouple* redox pairs such as $HCO_3^- - CH_4$ (e.g., Wolery, 1983), denying the possibility that oxidized species react with reduced species.

A third variant is the concept of *local equilibrium*, sometimes called mosaic equilibrium (Thompson, 1959, 1970; Valocchi, 1985; Knapp, 1989). This idea is useful when temperature, mineralogy, or fluid chemistry vary across a system of interest. By choosing a small enough portion of a system, according to this assumption, we can consider that portion to be in equilibrium. The concept of local equilibrium can also be applied to model reactions occurring in systems open to groundwater flow, using the "flow-through" and "flush" models described in the next section. The various types of equilibrium can sometimes be combined in a single model. A modeler, for example, might conceptualize a system in terms of partial and local equilibrium.

2.1.2 The initial system

Calculating a model begins by computing the initial equilibrium state of the system at the temperature of interest. By convention but not requirement, the initial system contains a kilogram of water and so, accounting for dissolved species, a somewhat greater mass of fluid. The modeler can alter the system's extent by prescribing a greater or lesser water mass. Minerals may be included as desired, up to the limit imposed by the phase rule, as described in the next chapter. Each mineral included will be in equilibrium with the fluid, thus providing a constraint on the fluid's chemistry.

The modeler can constrain the initial equilibrium state in many ways, depending on the nature of the problem, but the number of pieces of information required is firmly set by the laws of thermodynamics. In general, the modeler sets the temperature and provides one compositional constraint for each chemical component in the system. Useful constraints include

- The mass of solvent water (1 kg by default),

Cambridge University Press
978-0-521-87554-7 - Geochemical and Biogeochemical Reaction Modeling, Second Edition
Craig M. Bethke
Excerpt
More information

- The amounts of any minerals in the equilibrium system,
- The fugacities of any gases at known partial pressure,
- The amount of any component dissolved in the fluid, such as Na^+ or HCO_3^-, as determined by chemical analysis, and
- The activities of a species such as H^+, as would be determined by pH measurement, or the oxidation state given by an Eh determination.

Unfortunately, the required number of constraints is not negotiable. Regardless of the difficulty of determining these values in sufficient number or the apparent desirability of including more than the allowable number, the system is mathematically underdetermined if the modeler uses fewer constraints than components, or overdetermined if he sets more.

Sometimes the calculation predicts that the fluid as initially constrained is supersaturated with respect to one or more minerals, and hence, is in a metastable equilibrium. If the supersaturated minerals are not suppressed, the model proceeds to calculate the equilibrium state, which it needs to find if it is to follow a reaction path. By allowing supersaturated minerals to precipitate, accounting for any minerals that dissolve as others precipitate, the model determines the stable mineral assemblage and corresponding fluid composition. The model output contains the calculated results for the supersaturated system as well as those for the system at equilibrium.

2.1.3 Mass and heat transfer: The reaction path

Once the initial equilibrium state of the system is known, the model can trace a reaction path. The reaction path is the course followed by the equilibrium system as it responds to changes in composition and temperature (Fig. 2.1). The measure of reaction progress is the variable ξ, which varies from zero to one from the beginning to end of the path. The simplest way to specify mass transfer in a reaction model (Chapter 13) is to set the mass of a reactant to be added or removed over the course of the path. In other words, the reaction rate is expressed in reactant mass per unit ξ. To model the dissolution of feldspar into a stream water, for example, the modeler would specify a mass of feldspar sufficient to saturate the water. At the point of saturation, the water is in equilibrium with the feldspar and no further reaction will occur. The results of the calculation are the fluid chemistry and masses of precipitated minerals at each point from zero to one, as indexed by ξ.

Any number of reactants may be considered, each of which can be transferred at a positive or negative rate. Positive rates cause mass to be added to the system; at negative rates it is removed. Reactants may be minerals, aqueous species (in charge-balanced combinations), oxide components, or gases. Since the role of a