11

Kinetics Modeling

11.1 Introduction

Because our general aim is to illustrate geochemical modeling as practised at the present
time, our goal in this chapter is limited by the capabilities of programs (widely) available
today. Therefore, we do not attempt to introduce the broad field of chemical kinetics,
but only the amount necessary to understand the kinetic capabilities of today's modeling
programs. We give examples using what we consider to be the most useful of these,
The Geochemist's Workbench™ and PHREEQC. As mentioned earlier, our treatment is
no substitute for a careful reading of the user's manuals for these programs.

11.2 Some Basic Theory

We need a mathematical expression involving the concentrations of reactants and prod-
ucts in a given chemical reaction, which relates how far the reaction has proceeded to
some time variable. First, we introduce a variable which tells us how far the reaction
has proceeded.

11.2.1 The Progress Variable

Consider a generalized chemical reaction

$$a\text{A} + b\text{B} = c\text{C} + d\text{D} \tag{11.1}$$

where A, B, C, and D are chemical formulae, and a, b, c, d are the stoichiometric
coefficients. We pointed out in §3.4.3 that when this reaction reaches equilibrium,

$$c\mu_\text{C} + d\mu_\text{D} = a\mu_\text{A} + b\mu_\text{B}$$

and

$$\Delta_r\mu = c\mu_\text{C} + d\mu_\text{D} - a\mu_\text{A} - b\mu_\text{B} \tag{11.2}$$
$$= 0$$

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Equation (11.1) can be generalized to

$$\sum_i v_i M_i = 0 \tag{11.3}$$

where M_i are the chemical formulae and v_i are the stoichiometric coefficients, with the stipulation that v_i is positive for products and negative for reactants. Equation (11.2) can then be generalized to

$$\sum_i v_i \mu_i = 0 \tag{11.4}$$

Up to now, we have been most interested in reactions that reach equilibrium. Now let's look at what happens before that point is reached, i.e., while the reaction is taking place. Let's say that the reaction proceeds from left to right as written. It doesn't matter for the moment whether all the reactants and products are in the same phase (a *homogeneous* reaction) or in different phases (a *heterogeneous* reaction). During the reaction, A and B disappear and C and D appear, but the *proportions* of A:B:C:D that appear and disappear are fixed by the stoichiometric coefficients. If the reaction is

$$A + 2B \rightarrow 3C + 4D \tag{11.5}$$

then for every mole of A that reacts (disappears), 2 moles of B must also disappear, while 3 moles of C and 4 moles of D must appear. This is simply a mass balance, independent of thermodynamics or kinetics, and can be expressed as

$$\frac{dn_A}{v_A} = \frac{dn_B}{v_B} = \frac{dn_C}{v_C} = \frac{dn_D}{v_D} = \frac{dn_i}{v_i} \tag{11.6}$$

where the differentials dn_A, dn_B, and so on, refer to a change in the amount of A, B, and so on, of any convenient magnitude. We can next imagine the reaction proceeding in a series of such changes, or reaction increments, from the beginning to the end of the reaction (either when equilibrium is reached, or when one of the reactants is used up), and write

$$\frac{dn_A}{v_A} = \frac{dn_B}{v_B} = \frac{dn_C}{v_C} = \frac{dn_D}{v_D} = d\xi \tag{11.7}$$

from which it appears that

$$\frac{dn_A}{d\xi} = v_A; \quad \frac{dn_B}{d\xi} = v_B; \quad \cdots \frac{dn_i}{d\xi} = v_i \tag{11.8}$$

where our new variable ξ is called the reaction progress variable, and in this case represents an arbitrary number of moles. Equation (11.8) says that in Reaction (11.5), $dn_A/d\xi = -1$, $dn_B/d\xi = -2$, $dn_C/d\xi = 3$, and so on, which simply means that for every mole of A that disappears, 2 moles of B also disappear, 3 moles of C appear, and so on.

11.2.2 The Reaction Rate

Having defined reaction increments $d\xi$, we can now define the *rate of reaction* as

$$\frac{d\xi}{dt} = \frac{1}{\nu_A}\frac{dn_A}{dt} = \frac{1}{\nu_B}\frac{dn_B}{dt} = \cdots = \frac{1}{\nu_i}\frac{dn_i}{dt} \qquad (11.9)$$

where dt is an increment of time, and $d\xi/dt$ is the derivative of ξ with respect to t, an expression of the amount of progress of the reaction as a function of time, or simply the rate of reaction.

This expression (11.9) is written in terms of the absolute number of moles of A, B, and so on, $(n_A, n_B, \ldots)$, but by considering a fixed volume we could change these to concentration terms. Thus,

$$\frac{d\xi}{dt} = \frac{1}{\nu_A}\frac{dC_A}{dt} = \frac{1}{\nu_B}\frac{dC_B}{dt} = \cdots = \frac{1}{\nu_i}\frac{dC_i}{dt} \qquad (11.10)$$

where C is in some unit of concentration such as moles per cubic centimeter.

So, evidently, the rate of reaction can be determined by measuring the concentration of *any* of the reactants or products as a function of time. With one important stipulation: the reaction we have written must be what is actually happening.

Elementary and Overall Reactions

If we measure the rate of change of concentration of products and reactants in many ordinary chemical reactions, we find that the relationship in (11.10) is often not obeyed. This is because the reaction does not actually proceed *as written*, at the molecular level. For example, Reaction (11.5), taken literally, indicates that a molecule of A reacts with 2 molecules of B, and at that instant, 3 molecules of C and 4 molecules of D are formed. But this might not be what happens at all, and in view of the improbability of three molecules $(A + 2\,B)$ meeting at a single point, it probably is not in this case. The reaction as written may well represent the *overall* result of a series of *elementary* reactions. Thus A and B may in fact react to form a number of *intermediate species* such as X and Y, which then react with each other or with A or B to form C and D. In thermodynamics, the existence of such intermediate species is not important to the study of the overall reaction, as long as equilibrium is attained, but, in kinetics, these intermediate species contribute to the overall rate of reaction and may actually be *rate-controlling*, even though their concentrations may be small.

The *reaction mechanism* is the description of an overall reaction in terms of the separate elementary reactions that are involved.

The Steady State

Of course, it is also possible that intermediate species do form, but they achieve a *steady-state* concentration, that is, they break up just as rapidly as they form. In this case, Equation (11.10) would be obeyed, even though it did not represent what actually happens at the molecular level. Steady-state conditions are common in experimental and natural settings. For example, the CO_2 concentration in the atmosphere is not

controlled by any equilibrium reaction, but is the net result of a balance between inputs and outputs from a variety of processes. The "steady-state" concentration may of course gradually change, but so slowly compared with other rates in the system that considering it a constant in kinetic models is correct (Lasaga, 1998, §1.3).

11.2.3 Rate Laws

A rate law is a statement about how the rate of a reaction depends on the concentrations of the participating species. If one thinks about chemical reactions as something that happens at the molecular level when molecules collide with one another, it makes sense that the number of collisions, and hence the rate of reaction, should depend on how many molecules of each type there are; that is, their concentrations.[1]

In most cases, a simple power function of concentrations is found to apply. For reaction (11.1) it is

$$\text{rate of reaction} = R = \frac{\mathrm{d}\xi}{\mathrm{d}t} = k \cdot C_A^{n_A} C_B^{n_B} C_C^{n_C} C_D^{n_D} \tag{11.11}$$

The constant of proportionality, k, is called the *rate constant*. The exponents $n_A \ldots n_D$ are often integers, but can be fractional or decimal numbers, especially in heterogeneous reactions where adsorption and other surface-related effects can influence reaction rates. They define the *order* of the reaction. If n_A is 2, the reaction is said to be second order in A. The sum of the exponents gives the overall order of the reaction.

If the reaction is heterogeneous (more than one phase is involved), one or more of the "concentrations" in (11.11) must refer to the *specific area* (surface area per unit volume of solution) or the *reactive* surface area of the solids involved, because obviously the rate of reaction will depend on how much of the solid is available to react. This is one of the most difficult parameters to quantify, especially in field situations.

Simple Rate Equations

Rate equations or rate laws are determined by analyzing one or more reactant or product species as a function of time as a reaction proceeds, and then inspecting the results to see what theoretical form best fits the data. The simplest examples are those for elementary reactions, but the kinetics of more complex (multi-step) reactions can often be expressed by the same equations in certain cases, such as by using suitable constraints.

Zeroth Order   A zeroth-order reaction obeys the relation

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = k \tag{11.12}$$

or

$$C = C^\circ - kt \tag{11.13}$$

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[1]In thermodynamics, we must use "corrected" concentrations, or activities. In kinetics it is the actual concentrations that are important.

where C° is the initial concentration. A plot of concentration vs. time will thus give a straight line. Bacterial reduction of sulfate in marine environments (where variables other than SO_4^{2-} are constant) appears to be zeroth order (Lasaga, 1998, p. 38).

First Order   Rate laws for elementary reactions are for the most part what one would expect. For example, a simple molecular (or nuclear) decomposition,

$$A \rightarrow \text{products}$$
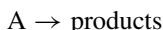
proceeds at a rate that depends only on the concentration of A; the more A, the more decomposition per unit time. If all exponents in Equation (11.11) are zero except for $n_A = 1$, the rate law becomes

$$\frac{d\xi}{dt} = -\frac{dC_A}{dt} = k \cdot C_A \tag{11.14}$$

and the reaction is first order. The decay of radioactive elements is an example of such reactions.

If we simplify C_A to C and let $C = C^\circ$ at time $t = 0$, integration of (11.14) gives

$$\int_{C^\circ}^{C} \frac{dC}{C} = -k \int_{0}^{t} dt \tag{11.15}$$

$$\ln \frac{C^\circ}{C} = kt \tag{11.16}$$

$$\ln C = \ln C^\circ - kt \tag{11.17}$$

$$C = C^\circ e^{-kt} \tag{11.18}$$

These equations suggest various ways of plotting data to see if they fit a first-order rate law. For example, a plot of $\ln(C^\circ/C)$ vs. t will give a straight line with a slope equal to the rate constant for concentration data from a first-order reaction.

Second Order   The most common type of elementary reaction resulting from bimolecular collisions is

$$A + B \rightarrow \text{products} \tag{11.19}$$

Here we expect the frequency of reaction to be proportional to the concentrations of the reactants and the concentration of products to have no effect, and so the rate law is

$$\frac{d\xi}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k \cdot C_A^1 C_B^1 \tag{11.20}$$

and the reaction is second order.

If the initial concentrations of A and B are C_A° and C_B°, the stoichiometry of (11.19) requires that

$$C_A^\circ - C_A = C_B^\circ - C_B$$

Solving this for C_B and substituting this result in (11.20) yields

$$-\frac{dC_A}{dt} = k \cdot C_A(C_A - C_A^\circ + C_B^\circ) \tag{11.21}$$

Integration of (11.21) then gives

$$\ln \left(\frac{C_A^\circ C_B}{C_B^\circ C_A} \right) = (C_B^\circ - C_A^\circ)kt \tag{11.22}$$

Therefore, a plot of

$$\left(\frac{1}{C_B^\circ - C_A^\circ} \right) \ln \left(\frac{C_A^\circ C_B}{C_B^\circ C_A} \right)$$

vs. time t will result in a straight line with a slope equal to the rate constant for concentrations taken from a second-order reaction. Similar equations can be derived for reactions with different stoichiometric coefficients.

There are a number of other rate laws, but this will suffice to give an idea of the procedures involved. However, it should be emphasized that most chemical reactions are "overall" reactions, and that understanding them in terms of their fundamental elementary reactions is a goal not often and not easily achieved.

Pseudo-Order Reactions   As mentioned above, complex reactions can often be expressed by the simple equations of zeroth-, first-, or second-order elementary reactions under certain conditions. For example, the dissolution of many minerals at conditions close to equilibrium is a strong function of the free energy of the reaction (Lasaga, 1998, §7.10), but far from equilibrium the rate becomes nearly independent of the free energy of reaction. In other words, the rate of dissolution will be virtually constant under these conditions, or pseudo-first-order.

Another example of a pseudo-first-order reaction is shown in Figure 11.1. These data are the result of a very complicated set of reactions, largely unknown, involving non-bacterial reduction of aqueous sulfate and slow release of hydrogen sulfide from organic material in a natural shale. Nevertheless, the data fit a simple first-order relationship.

In a reaction involving A and B which is truly second order, choosing conditions such that the concentration of B is held essentially constant (which might be done in several ways) reduces Equation (11.20) for second-order reactions to

$$-\frac{dC_A}{dt} = kC_B C_A = k_{app}C_A \tag{11.23}$$

which is the equation for a first-order reaction, where $k_{app} = kC_B$, is a pseudo-first-order rate constant, or apparent-first-order constant. If *all* reactant concentrations are held essentially constant, a pseudo-zeroth-order reaction is generated.

11.2.4   Temperature Dependence of Rate Constants

From the relations in §3.5.3 we see that the temperature dependence of the equilibrium constant K can be expressed as

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^\circ}{R}$$

or, alternatively,

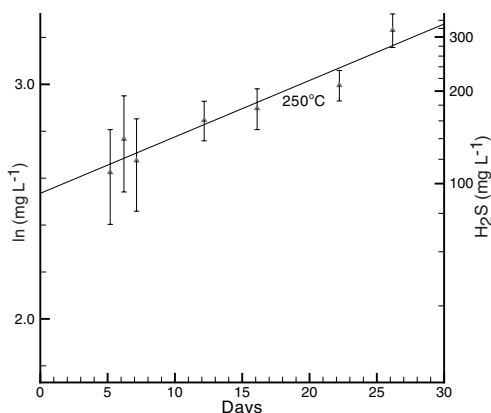$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

Figure 11.1. Concentration of H_2S in a solution in contact with gypsum and organic-rich shale at 250°C, as a function of time. The H_2S is being released from the organic shale, and is also being formed by reduction of aqueous sulfate (unpublished data of G.M. Anderson and T. M. Seward).

In 1889, Arrhenius proposed a similar equation for the temperature effect on rate constants,

$$\frac{d \ln k}{d(1/T)} = -\frac{E_a}{R} \tag{11.24}$$

or

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \tag{11.25}$$

where E_a is the Arrhenius activation energy, or just the activation energy, and turns out to be closely related to the "energy barrier" between products and reactants in chemical reactions.

Experimental data for a great many reactions over a large range of temperatures show that the Arrhenius equation is usually closely obeyed, showing that E_a is either a constant or a weak function of temperature, and so we can integrate the equation to give

$$\ln k = \ln A - \frac{E_a}{RT} \tag{11.26}$$

or

$$k = Ae^{-E_a/RT} \tag{11.27}$$

where A, which enters (11.26) as a constant of integration, is called the *pre-exponential factor*.

The activation energy of an overall reaction is made up of the individual contributions of the elementary reactions making up the overall reaction. The magnitude of the activation energy can vary from virtually zero to hundreds of kilojoules per mole and, besides controlling the temperature dependence of the rate constant, provides clues as

to the nature of the reaction mechanisms, because the energies involved in many types of diffusion, electron exchange, and bond-breaking processes are known.

11.3   Kinetics of Precipitation and Dissolution Reactions

A reasonable assumption about the rate of mineral precipitation or dissolution might be that the rate is proportional to the degree of super- or under-saturation. Expressing this idea mathematically, we would say that the rate R is

$$R \propto (1 - \Omega) \tag{11.28}$$

where Ω is defined as the ratio of the ion activity product (IAP) and the solubility product, K_{sp} (§3.5.2). If IAP $< K_{sp}$, the solution is underaturated, $\Omega < 1$, and R is positive (mineral dissolves). If IAP $> K_{sp}$, $\Omega > 1$, and R is negative (mineral precipitates). For added generality, we would use Q and K rather than IAP and K_{sp} (§3.5; §3.5.2).

The proportionality factor would include, at a minimum, the rate constant for the reaction, and the relative surface area of the mineral, i.e., the mineral surface area per unit volume of solution. We might also add a term, v, to account for cases in which the dissolution of one mole of solid phase gives rise to v moles of the component we are measuring. For example, if we measured the solubility of Mg_2SiO_4 by measuring aqueous Mg, $v = 2$.

Equation (11.28) then becomes

$$R = \frac{A}{V} v k \left(1 - \frac{Q}{K} \right) \tag{11.29}$$

where A and V are the mineral surface area and solution volume, respectively, and k is the rate constant of the dissolution reaction. Other options are the inclusion of an exponent n on the $(1 - \Omega)$ term, i.e., $(1 - \Omega)^n$, or on the Ω term itself, i.e., $(1 - \Omega^n)$. This equation is used in The Geochemist's Workbench™ to model the kinetics of dissolution and precipitation. Program PHREEQC uses a more flexible method, as explained below.

Examples

The Geochemist's Workbench™   In program REACT, part of The Geochemist's Workbench™, equation (11.29) is implemented by using the `kinetic` command to set the variables (key words) required. The format is

```
kinetic <mineral> <variable> = <value>
```

where `mineral` is an identifying label for the following variable, and `variable` is either `rate_con` for the rate constant in moles per square centimeter per second, or `surf` for the mineral surface area in square centimeters per gram.

For example, the rate constant for the dissolution of albite is $10^{-12.26}$ mol m^{-2} s^{-1}, or $10^{-16.26}$ mol cm^{-2} s^{-1} (Lasaga, 1998, Table 1.5). This is entered in REACT as

```
kinetic Albite rate_con 5.50e-17
```

```
T = 25
swap Kaolinite for Al+++
swap Quartz for SiO2(aq)
swap Muscovite for K+
pH = 6
Na+   = .3  molal
Ca++  = .05 molal
Cl-   = .3  molal
HCO3- = .02 molal
 10 free grams Kaolinite
 10 free grams Quartz
 10 free grams Muscovite
react 10 grams Albite
kinetic Albite pre-exp 18370 act_en 117200
kinetic Albite surf = 1e3
time begin 0 years, end 2000 years
suppress all
unsuppress Albite Quartz Muscovite Kaolinite
go
```

Table 11.1. Input script for program REACT, to model the dissolution of albite.

Alternatively, we can set the activation energy (E_a) and the pre-exponential factor (A), Equation (11.27), to let REACT calculate the rate constant at any temperature. Thus

```
kinetic Albite pre-exp 18370 act_en 117200
```

(using values from Lasaga, 1998).

To use a surface area of 1000 $\text{cm}^2\,\text{g}^{-1}$ (the solution volume V is known by the program), we enter

```
kinetic Albite surf 1000
```

The program then has enough information to use Equation (11.29). However, if some other rate equation is preferred, we can enter it in another part of the `kinetic` statement (see below). For example, to use Equation (11.29) to examine the kinetic dissolution of albite in water in equilibrium with kaolinite, muscovite, and quartz at 25°C and a pH of 6.0,[2] we would prepare a script similar to that shown in Table 11.1.

We suppress the effects of all minerals except those needed, to allow a better comparison with PHREEQC (below), with the `suppress all` and `unsuppress` commands.

Because we entered the values of E_a and A for Equation (11.27) rather than a value for the rate constant itself, we can use the same script for other temperatures simply

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[2]This example is modified from one in the GWB User's Guide (Bethke, 1994). Program REACT in The Geochemist's Workbench™ also implements several other equations for rate laws, catalyzing and inhibiting species, nucleation, catalysis, and so on.
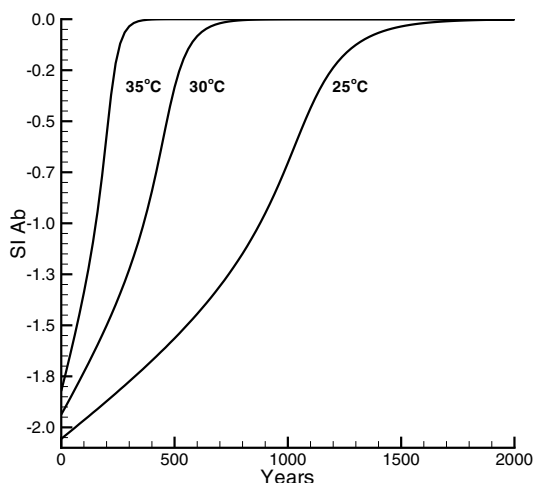
Figure 11.2. The Saturation Index of albite as a function of time at various temperatures, as calculated by REACT.

by changing the statement $T = 25$ to $T = 30$ or $T = 35$, etc. The results of this calculation are shown in Figure 11.2.

It is not difficult to see that although we have successfully modeled a kinetic reaction, there are complicating factors to be considered before we could model a natural or realistic situation. For example, the rate constants for many minerals such as albite are strongly pH dependent. Also, the rates of some reactions will affect the rates of others, because the same solute species may be involved. In a sense, everything that happens affects everything else.

PHREEQC   To illustrate how PHREEQC handles kinetics, we will consider the same reactions. In PHREEQC the user must program the rate equation in a series of statements in a subset of the BASIC language, an option that gives great flexibility, now also available in REACT. For example, to calculate the Saturation Index of albite dissolving in the same solution as shown in Table 11.1, the PHREEQC input script would be similar to that in Table 11.2.

There are two keywords in this script which are unique to kinetic calculations –
KINETICS and RATES.

KINETICS   This keyword begins a block of data which identifies kinetic reactions and supplies parameters used in each reaction, such as activation energies, duration of reactions, number of steps, etc. In Table 11.2 only one kinetic reaction is specified, for albite dissolution. For comparison with the REACT example, we use the same amount of mineral, and the same kinetic parameters. The current amount (moles) of mineral, which will decrease during dissolution, is identified as -m, and the initial amount of mineral, in this case the same quantity, is identified as -m0. PHREEQC measures

```
TITLE Albite dissolution kinetics
SOLUTION 1
        temp        25
        units       mol/kgw
        ph          6
        Na          0.3
        Ca          0.05
        Cl          . 3         charge
        C(4)        0.02
EQUILIBRIUM_PHASES 1
        Quartz          0.0
        Kaolinite       0.0
        Muscovite       0.0
KINETICS 1 Define Albite parameters
        Albite
                -m          0.03814  # 10 grams albite
                -m0         0.03814
                -parms      18370   117200
        -steps      6311385e4 in 100 steps
INCREMENTAL_REACTIONS true
RATES
        Albite
        -start
        1       rem M = current no. moles of Ab
        2       rem at start, M (= m) = M0 = .03814
        3       rem Initial area (A0) is 1000 [cm^2/g] for 10 g (=1e4 cm^2)
        4       rem so A0/V [cm^-1] is 10
        5       rem pre-exp const A [mol/cm^2.s] is 18370 = PARM(1)
        6       rem act energy Ea [J/mol] is 117200 = PARM(2)
        7       rem this gives rate const of 5.50e-17 mol/[cm^2.s] at 25C
        10       A0 = 1e4
        15       V = 1000
        20       sr_ab = SR("Albite")
        25       if (M <= 0) then goto 200
        30       R = 8.31451
        35       T = 298.15
        45       area = (M/M0)^(2/3)*A0
        50       rate_const = PARM(1)*EXP(-PARM(2)/(R*T))
        55       rate = (area/V)*rate_const*(1-sr_ab)
        60       rem multiply by 1000 to change mol/(cm^3.s) to mol/(L.s)
        65       rate = rate*1000
        70       moles = rate*TIME
        75       PUT(area,1)
        80       PUT(rate,2)
        200       SAVE moles
        -end
SELECTED_OUTPUT
        -file       albite.sel
        -reset      false
USER_PUNCH
        -headings  Ab_left   area   rate   Time(years)  a_Na+  SI(Albite)
        -start
        10  PUNCH  M  GET(1) GET(2) TOTAL_TIME/31556925 10^(LA("Na+")) SI("Albite")
        -end
END
```

Table 11.2. A PHREEQC script for the kinetic dissolution of albite.

time in seconds, so a duration of 2000 years is quite a large number. The keyword INCREMENTAL_REACTIONS is made true so that each reaction step begins where the last one ended. The default, false, means that each step begins at time zero.

RATES   This data block supplies a program written in BASIC which defines the rate reactions, using parameters specified in the KINETICS block. In addition to most of the usual BASIC commands, several commands unique to PHREEQC are also available, which allow access to parameters calculated by PHREEQC. Using a BASIC program means a bit more work for the user, but the results are worth it, in the sense that virtually any kinetic rate law may be introduced.

In the example in Table 11.2,

- two parameters are imported from KINETICS, PARM(1) and PARM(2),

- a command special to PHREEQC, SR(''ALBITE''), gives the saturation ratio Q/K.

- the initial surface area, A0, is 1000 cm^2, but this decreases as albite dissolves. It is assumed here that albite occurs as uniform spheres or cubes, so that the surface area decreases as the 2/3 power of the decrease in mass. As noted before, this is one of the most difficult parameters to quantify in kinetic studies.

- another keyword not previously mentioned is USER_PUNCH, which is much like SELECTED_OUTPUT, but which allows the user to define his/her own output variables. If these occur in a BASIC program, they must be saved in an array with PUT statements, and accessed in USER_PUNCH with GET statements.

The results from PHREEQC look much like those in Figure 11.2, with some differences in the Saturation Indices, because of the different data used. A more complex example of albite dissolution based on the work of Sverdrup (1990) involving temperature effects, CO_2 concentration, and organic decomposition is included in the database supplied with PHREEQC.[3]

11.4   Kinetics of Acetate Decomposition

An example of the use of the rate constant and activation energy in a homogeneous reaction is the work of Palmer and Drummond (1986) on the kinetics of the decomposition of acetate compounds such as acetic acid and sodium acetate at elevated temperatures. Organic compounds are generally quite unstable at elevated temperatures, but some persist for surprisingly long times. Just how long is an important geological question, because these compounds may be involved in many important processes, such as the generation of natural gas and transport of base metals. To find out how long acetates could be expected to persist at various temperatures, Palmer and Drummond measured the concentration of acetate remaining after various times at several temperatures, using

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[3]A recent release of The Geochemist's Workbench™ adds the ability to program any rate law, much as in this PHREEQC example.
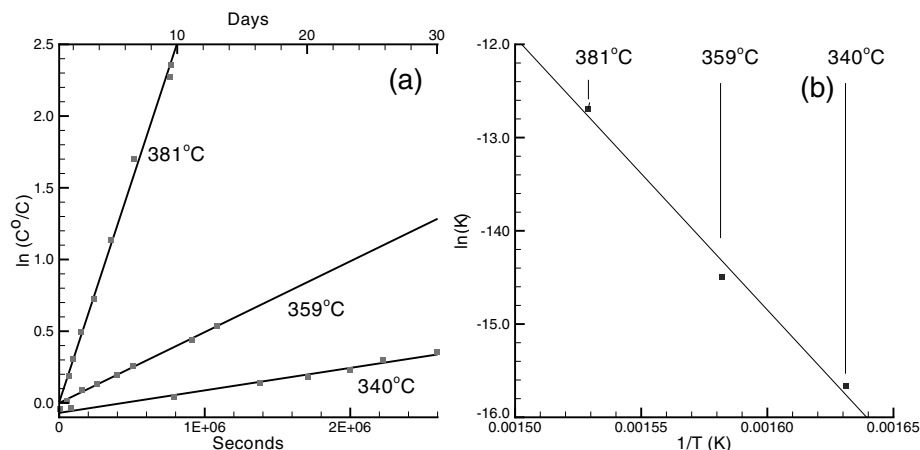
Figure 11.3. (a) The results of experiments by Palmer and Drummond (1986) on the decomposition of sodium acetate at three temperatures. (b) Rate constants derived from the slopes of the lines in (a), in an Arrhenius plot.

several different containing surfaces, because it is found that surfaces play a catalytic role. That is, the rate of reaction depends on the surface available to the reaction. Some of their data are shown in Table 11.3 and Figure 11.3.

The experimental data in Figure 11.3(a) are plotted according to Equation (11.16), so that the slope of each line gives the rate constant at that temperature. These constants are listed in Table 11.4, and plotted in Figure 11.3(b). Assuming that this Arrhenius relationship continues to hold at other temperatures (which implies that the reaction mechanism remains the same at these other temperatures), we can now calculate the rate constant at other temperatures, and therefore calculate how much acetate will remain after various lengths of time. Some typical results are shown in Table 11.5. The rate constant at 200°C from Figure 11.3(b) is $1.0734 \times 10^{-13}\,\text{s}^{-1}$. Using this in Equation (11.16) we find that there will still be appreciable acetate concentrations after thousands of years.

Acetate Example Using PHREEQC The acetate calculation can also be performed using PHREEQC, using a simple BASIC program in the RATES data block as before. The script would be similar to that in Table 11.6.

Part of almost all homogeneous kinetic calculations will be some method to *decouple* the reactive species, which are often redox species. In kinetic calculations, the species are obviously not at equilibrium with each other, at least at the start of the calculation; they approach equilibrium during the calculation. But speciation programs such as PHREEQC and REACT assume all species to be at equilibrium unless told otherwise. In this case we want CH_4 to not react with other species, partly to see what it is doing during the reaction, and partly because in nature it is extremely unreactive. We also want acetate to be decoupled because it is metastable and will not even exist in the solution at equilibrium. At the time of writing, this is not necessary in PHREEQC, because the

| Time | | | |
hours	seconds	Acetate molality	$\ln(C^o/C)$
Experiment 26, 340°C			
22.0	79 200	0.04E+010	−0.036
219.0	788 400	9.59E−01	0.042
382.5	1 377 000	8.71E−01	0.138
475.5	1 711 800	8.37E−01	0.178
554.5	1 996 200	7.92E−01	0.233
618.0	2 224 800	7.42E−01	0.298
721.0	2 595 600	7.03E−01	0.352
Experiment 27, 359°C			
14.0	50 400	9.89E−01	0.011
43.5	156 600	9.15E−01	0.089
73.0	262 800	8.78E−01	0.130
109.5	394 200	8.22E−01	0.196
140.5	505 800	7.75E−01	0.255
253.5	912 600	6.43E−01	0.442
301.0	1 083 600	5.84E−01	0.538
Experiment 28, 381°C			
1.0	3 600	1.05E+00	−0.044
18.5	66 600	8.28E−01	0.189
26.5	95 400	7.38E−01	0.304
41.5	149 400	6.11E−01	0.493
66.0	237 600	4.84E−01	0.726
98.0	352 800	3.21E−01	1.136
142.0	511 200	1.82E−01	1.704
211.0	759 600	1.03E−01	2.273
213.5	768 600	9.50E−02	2.354

Table 11.3. Data from Palmer and Drummond (1986) on the breakdown of sodium acetate on titanium surfaces at three temperatures.

Expmt	T(°C)	Rate const. (s^{-1})	1/T (K)	ln K
26	340	1.570E−07	0.001631	−15.764
27	359	4.937E−07	0.001582	−14.332
28	381	3.087E−06	0.001529	−12.778

Table 11.4. Rate constants derived from the slopes of the curves in Figure 11.3.

t (years)	t (seconds)	$\ln(C^o/C)$	C (molal)
10	3.156E+08	3.3874E−05	0.099997
100	3.156E+09	3.3874E−04	0.099966
1 000	3.156E+10	3.3874E−03	0.099662
10 000	3.156E+11	3.3874E−02	0.096669
100 000	3.156E+12	3.3874E−01	0.071267
500 000	1.578E+13	1.6937E+00	0.018384
1 000 000	3.156E+13	3.3874E+00	0.003380

Table 11.5. The concentration of sodium acetate remaining after various lengths of time at 200°C, starting with 0.1 molal.

database does not contain a redox reaction for acetate, so while it will ionize and react with metals, forming acetate complexes, it will not decompose. This will undoubtedly be changed in future versions.

In PHREEQC, decoupling is achieved by defining new species and, if desired, their reactions with other species. In this case we simply define `Methane` to be a new species, and give it no reactions; it is inert. In REACT (below), decoupling is achieved with a `decouple` statement.

The reaction rate is calculated (in statement 40) according to Equation (11.14), and we increase the duration to 10^6 years. The activation energy E_a (`PARM(1)`) and the pre-exponential constant A (`PARM(2)`) are obtained from the linear fit coefficients of Figure 11.3(b); see Equation (11.26). The results of both the PHREEQC output and Equation (11.16) (Table 11.5) are shown in Figure 11.4. They are identical.

Acetate Example Using REACT In REACT, kinetic information is provided in the `kinetic` statement, as mentioned above. This time, we use the `rxn` and `rate_law` parts of the `kinetic` statement to enter the reaction and the rate equation explicitly. REACT parses the `rxn` statement to assess what the reaction is, and uses `rate_law` as the rate equation. The script is shown in Table 11.7.[4] The results are shown, along with those for PHREEQC, in Figure 11.4.

Well, one could say, if the calculation can be done on a spreadsheet, or even a calculator, why should we use a complicated program? It depends on how much we want to know. If we only want to know the amount of acetate as a function of time, a calculator is quite sufficient. However, the PHREEQC and REACT results include data on many solution species besides acetate, the solution pH, Saturation Indices, oxidation states, and so on, which would be of interest in many situations. We could also calculate the effects of adding other components, although this would be subject to experimental confirmation.

Acetate Example Using CKS At this point a mention of a different kind of program seems appropriate. CKS (Chemical Kinetics Simulator) is a program distributed

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[4]Note that in `rate_law` we include the molality of each species individually in order to get the total acetate concentration. In a later release, this is accomplished with a single term.

```
DATABASE llnl.dat
TITLE Kinetic decomposition of sodium acetate
definition of Methane decouples CO2 and CH4

SOLUTION_MASTER_SPECIES
    Methane Methane 0.0 CH4 16.0432
SOLUTION_SPECIES
    Methane = Methane
    log_k = 0
SOLUTION 1
    temp    200
    units   mol/kgw
    ph  7
    Na   .1
    Acetate .1
    Cl   .001     charge
KINETICS 1 Define Acetate parameters
    NaAc
#   reaction is NaCH3COO(aq)  + H+  -> Na+  + CH4(aq)  + CO2(aq)
#     or in phreeqc NaAcetate(aq) + H+  -> Na+  + Methane  + HCO3-
        -formula   Acetate -1 H -1 Methane 1 C 1  O 2
        -m    .1
        -m0   .1
        -parms    242908  7.0244e13
# these parameters give a rate constant at 200 C = 1.0734e-13.
    -steps  3.1556925e13 in 100 steps
INCREMENTAL_REACTIONS true
RATES
    NaAc
    -start
    1   rem PARM(1) is Ea
    2   rem PARM(2) is A
    10  R = 8.31451
    20  T = 473.15
    30  rate_const = PARM(2)*EXP(-PARM(1)/(R*T))
    40  rate = rate_const*TOT("Acetate")
    50  moles = rate*TIME
    60  PUT(rate,1)
    200 SAVE moles
    -end
SELECTED_OUTPUT
    -file   acetate.sel
    -reset  false
USER_PUNCH
    -headings    Time(yrs) rate  Acetate C(4) Methane
    -start
    10  PUNCH  TOTAL_TIME/31556925 GET(1) TOT("Acetate") TOT("C(4)") TOT("Methane")
    -end
END
```

Table 11.6. A PHREEQC script for the kinetic decomposition of sodium acetate at 200°C.

```
time start = 0 days, end = 1e6 years
temperature = 200
decouple Acetic\_acid(aq)
decouple Methane(aq)
swap CO2(aq) for HCO3-
1 kg free H2O
total molality CO2(aq) = 1e-10
total molality Methane(aq) = 1e-10
total molality Na+ = .1
total molality Acetic\_acid(aq) = .1
total molality Cl- = .001
pH = 7
kinetic redox-1 \
rxn = "Acetate  + H+  -> Methane(aq)  + CO2(aq)" \
rate\_con = 1.073e-13 \
rate\_law = 'rate\_con * (molality("Acetate") \
+ molality("NaCH3COO(aq)") + molality("Na(CH3COO)2-") \
+ molality("Acetic\_acid(aq)"))'
```

Table 11.7. A REACT script for the kinetic decomposition of sodium acetate at 200°C.
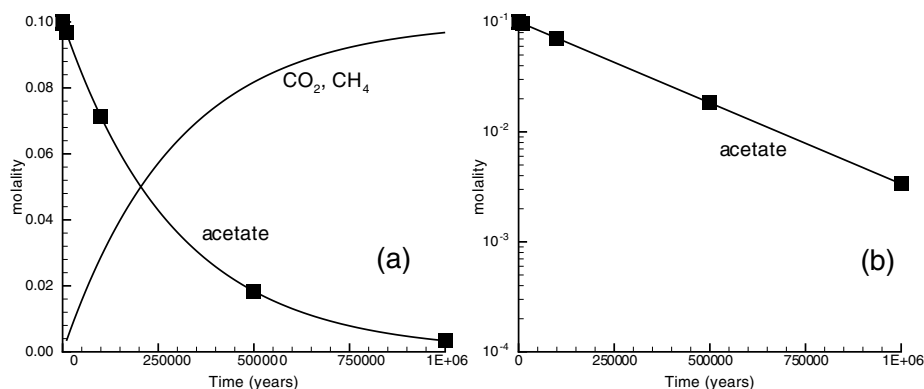
Figure 11.4. (a) Concentration of sodium acetate remaining as a function of time at 200°C, using data of Palmer and Dummond (1986). The solid line is calculated by PHREEQC, by REACT, and by program CKS, which all give virtually the same results. The square points are from Table 11.5. (b) The same data using a log scale for the acetate concentrations.

free by IBM (http://www.almaden.ibm.com/st/msim/) that models kinetic reactions by considering a large number of particles and a reaction or series of reactions between "species", which are simply labeled particles. Changes in the system are modeled by randomly selecting among probability-related reaction steps, where the probabilities are related to the reaction rate constants. It is ideally suited to trying out various reaction schemes in complex systems, and comparing the results with experimental data. In our acetate decomposition example, the results are virually indistinguishable from those of PHREEQC and REACT. However, it is more of a research tool than an environmental modeling tool, and will not be discussed further.

11.5   Coupled Aqueous Speciation and Biological Processes

A good example of interactions among inorganic chemistry, organic compounds degradation, and microbial activities is formation and destruction of metal–chelate complexes. At many defense facilities in the USA, radionuclides and chelating agents are buried together (mixed wastes). The formation of radionuclide–chelate complexes greatly increases radionuclide mobility and poses significantly more risks to humans and the environment. Microbial degradation of chelating agents has the apparent benefits of reducing the mobility and risk.

However, complex interactions or feedback loops exist among the different components of the system:

- bacteria can use the chelate as the substrate, and thus accomplish the goal of reducing the mobility of radionuclides by increase of sorption and less solubility;

- on the other hand, biodegradation of organic compounds builds up the bicarbonate content of the system, and forms mobile actinide–carbonate complexes;

- actinides when present at micro-molar per liter levels can be toxic to microorganisms and hence inhibit microbial growth;

- microbiological degradation reactions cause changes of pH and hence change of the speciation, sorption, and solubility of actinides;

- most actinides have multiple valence states, and microbial activities can change the redox states of the radionuclides and change their mobility.

With all these complex interactions, it is desirable to build a model that can quantitatively evaluate all the components of the system. Rittmann and VanBriesen (1996) and VanBriesen and Rittmann (1999) developed the code CCBATCH to do just that. CCBATCH, which stands for "co-contaminant batch reactor", has three components.

Aqueous speciation   This is in line with traditional speciation code like MINTEQA2 and PHREEQC. Instantaneous equilibrium is assumed for all homogenous aqueous complexation reactions.
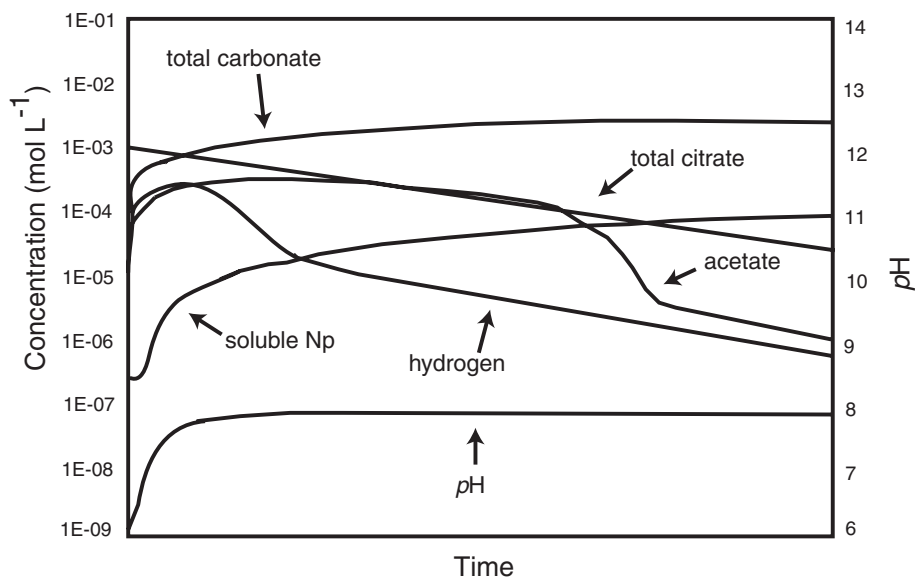
Figure 11.5. Simulated fate of Np during the mineralization of citrate by an anaerobic microbial consortium. After Banaszak *et al.* (1998).

Biodegradation   Degradation of organic compounds is treated as a kinetic process and described by the dual Monod kinetics formulation (Bae and Rittmann, 1996).

Cell growth and decay   The growth and decay of the biomass (cells) are also simulated as a mass balance.

CCBTACH solves the aqueous speciation equations and the Monod kinetics sequentially. Biodegradation reactions are solved in the biodegradation subroutine or submodel. The products from biodegradation reactions are brought into the speciation subroutine, where the speciation is changed accordingly due to the changes of, for example, total H^+ and CO_3^{2-}.

An example calculation was given in Banaszak *et al.* (1998) for anaerobic degradation of citric–Np complexes by a consortium of bacteria. The initial conditions are *p*H 6, total carbonate concentration of 10^{-5} M, fixed redox potential of -250 mV, and equilibrium with amorphous $Np(OH)_4$. The modeling results are shown in Figure 11.5. The initial degradation of citrate results in an increase of *p*H and a slight decrease of Np in solution. However, degradation of citrate and acetate produces carbonate, and that leads to the formation of carbon–Np complexes and an increase of 2–3 orders of magnitude in total dissolved Np concentrations. The results are somewhat counter-intuitive – degradation of organic chelate in a reducing environment may not necessarily reduce actinide mobility. These modeling results are difficult to verify with laboratory and field data. Nevertheless, it illustrates the importance of considering the interplay of various processes, and the complexity in this relatively simple system.

$Mn^{2+} + 0.5O_2 + H_2O \rightarrow MnO_2 + 2H^+$	1
$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 + 2H^+$	2
$2Fe^{2+} + MnO_2 + 4H_2O \rightarrow 2Fe(OH)_3 + Mn^{2+} + 2H^+$	3
$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$	4
$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$	5
$H_2S + MnO_2 + 2H^+ \rightarrow Mn^{2+} + S^o + 2H_2O$	6
$H_2S + 2Fe(OH)_3 + 4H^+ \rightarrow 2Fe^{2+} + S^o + 6H_2O$	7
$FeS + 2O_2 \rightarrow Fe^{2+} + SO_4^{2-}$	8
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	9
$CH_4 + SO_4^{2-} + 2H^+ \rightarrow H_2S + CO_2 + 2H_2O$	10

Table 11.8. Secondary redox reactions in the model presented by Hunter *et al.* (1998).

The Geochemist's Workbench™ program REACT now includes procedures to calculate reaction kinetics of biotransformations, and the PHREEQC documentation gives an example of similar calculations in PHREEQC.

11.6 Application to Landfill Leachate into Aquifers

Municipal landfill leachate usually contains high concentrations of dissolved organic carbon (DOC), and hence intrusion of leachate into aquifers can result in development of redox zones due to microbial activities. Redox zones developed in oxic aquifers show a sequence, from landfill to downgradient areas, methanogenic/sulfate-reducing, iron-reducing, manganese-reducing, nitrate-reducing, to aerobic zones (Amirbrahman *et al.*, 1998; Baedecker and Back, 1979; Baedecker *et al.*, 1993; Bjerg *et al.*, 1995). These microbiallly mediated redox reactions have significant influence on inorganic pore fluid chemistry, natural attenuation, and fate and transport of toxic elements and compounds in the leachate.

Hunter *et al.* (1998) used a kinetic model to simulate reactive transport and groundwater evolution upon the intrusion of landfill leachate into an oxic aquifer. Most interestingly, they found that the patterns of redox fronts are similar to what have been seen in marine sediments. Hunter *et al.* (1998) first developed a one-dimensional multicomponent reactive transport model BIORXNTRN and then conducted a numerical experiment using this code. The actual model is quite complex; we describe here the essentials of it so that we can see what can be done.

In the model, an anoxic leachate from a landfill has infiltrated into an oxic aquifer for 20 years. The flow velocity is 10 m yr^{-1}, and longitudinal dispersivity is 4 m. The leachate is rich in organic carbon. Degradation of organic carbon via microbial activities causes drastic changes in pore fluid inorganic chemistry and mineralogy. Several zones are developed (Figure 11.6).

Within the first 20 m, all dissolved and solid oxidants are depleted (Figure 11.6b,c). Microbial metabolism uses DOC and electron acceptors in the sequence O_2, NO_3^-, SO_4^{2-}, then methanogenesis becomes the dominant pathway for biodegradation. When
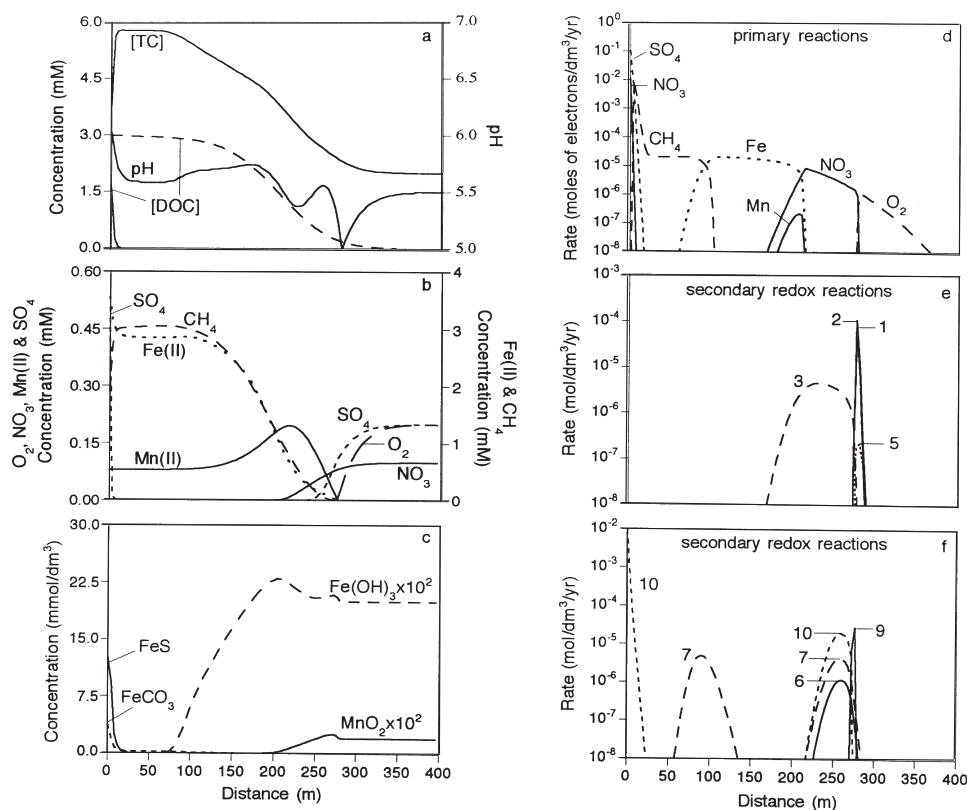
Figure 11.6. Chemical zonation in an aquifer after 20 years leachate contamination. Groundwater flows from left to right. (a) and (b) Dissolved species distribution; (c) Solid species; (d) Primary pathways for DOC biodegradation. (e) and (f) Rates of secondary reactions listed in Table 11.8. After Hunter *et al.* (1998).

DOC is depleted at about 280 m, a reverse zonation occurs before it returns back to aerobic conditions of the uncontaminated aquifer.

Accompanying the biodegradation, pH drops about one unit from 6 to 5. $Fe(OH)_3$ and MnO_2 are reduced and dissolved. The pore fluids begin to be supersaturated with $FeCO_3$ and $FeCO_3$ begins to precipitate. Reduction of SO_4^{2-} also produces H_2S and causes super-saturation and precipitation of FeS. These patterns of change have been observed in the field and compare well with marine sediment diagenesis (Stumm and Morgan, 1996).

We should note how Hunter *et al.* (1998) treat the kinetics in their model. They first divided reactions into different types.

- *Primary Redox Reactions*. Hunter *et al.* referred to the reactions of the redox sensitive species with DOC via microbial activities. A first-order rate law with respect to organic carbon concentration is used for these reactions. Two fractions of organic matter with different degradation rates are used.

- *Secondary Redox Reactions*. These are the redox reactions that involve products of the primary redox reactions and are essentially abiotic. They use a second-order, bimolecular rate expressions for these reactions.

- *Precipitation and Dissolution Reactions*. The apparent rate constants are a function of saturation state.

- *Aqueous speciation, Acid–base Reactions, and Sorption of* NH_4^+. These reactions are treated as being at equilibrium.

These modeling results show complex coupling and feedback mechanisms between biogeochemical reactions and inorganic chemistry. Hunter *et al.* (1998) relate this to a reaction network. Unlike the local equilibrium models we described in the preceding chapters, kinetically controlled reactions are pathway dependent and there may exist multiple pathways. Our understanding of these systems is limited. One difficulty for practical applications of such models is determination of a realistic rate constant. Hunter *et al.* (1998) noted that the *in situ* organic degradation rates reported in the literature span over ten orders of magnitude, which makes field application of this kind of kinetic model difficult. They conducted numerical experiments using various rates, and the results are quite different.

11.7   Conclusions

We have already stated (§1.4.2 and §2.5) that the subject of chemical reaction kinetics is both important and poorly understood in geochemical modeling. The problem is that this subject is much more difficult than equilibrium thermodynamics. The kinetics of a few reactions are fairly well understood, but a great many more have completely unknown kinetics. Furthermore, those that are understood have usually been studied in fairly "clean" systems, and the effect of added components is uncertain. Even if some reactions were perfectly understood, the usefulness of including the kinetics of

only some of the large number of reactions present in any realistic modeling study is questionable.

One way of getting around this is to use what seem to be reasonable estimates of rate laws and rate constants, as in some of our examples. This has the very useful effect of showing the importance of including kinetics in modeling studies, but the absence of reliable data for each reaction certainly renders the results of questionable usefulness.

It is safe to say that, at the present time, no realistic modeling study (that is, one based on a natural situation) has been carried out with realistic kinetics for all reactions involved. This is one of the factors used in evaluating the results of modeling studies, whether based entirely on equilibrium theory or whether they use some kinetics. There is a great deal of work to be done in this challenging field.