CHAPTER 5: KINETICS: THE PACE OF THINGS

5.1 INTRODUCTION

Thermodynamics concerns itself with the distribution of components among the various phases and species of a system at equilibrium. *Kinetics* concerns itself with the *path* the system takes in achieving equilibrium. Thermodynamics allows us to predict the equilibrium state of a system. Kinetics, on the other hand, tells us how and how fast equilibrium will be attained. Although thermodynamics is a macroscopic science, we found it often useful to consider the microscopic viewpoint in developing thermodynamics models. Because kinetics concerns itself with the path a system takes, what we will call *reaction mechanisms*, the microscopic perspective becomes essential, and we will very often make use of it.

Our everyday experience tells one very important thing about reaction kinetics: they are generally slow at low temperature and become faster at higher temperature. For example, sugar dissolves much more rapidly in hot tea than it does in ice tea. Good instructions for making ice tea might then incorporate this knowledge of kinetics and include the instruction to be sure to dissolve the sugar in the hot tea before pouring it over ice. Because of this temperature dependence of reaction rates, low temperature geochemical systems are often not in equilibrium. A good example might be clastic sediments, which consist of a variety of phases. Some of these phases are in equilibrium with each other and with porewater, but most are not. Another example of this disequilibrium is the oceans. The surface waters of the oceans are everywhere oversaturated with respect to calcite, yet calcite precipitates from seawater only through biological activity. At a depth of 2500 m, the ocean is undersaturated with calcite, yet calcite shells of micro-organisms persist in sediments deposited at these depths (though they do dissolve at greater depths). Thus, great care must be used in applying thermodynamics to such systems. Even in the best of circumstances, thermodynamics will provide only a limited understanding of low temperature geochemical systems. A more complete understanding requires the application of kinetic theory. Indeed for such systems, kinetics is the deciding factor controlling their state and evolution. Even in metamorphic systems, with temperatures in the range of 300-700° C, kinetics factors are crucially important in determining their final states.

High temperature geochemical systems, such as magmas, are more likely to be in equilibrium, and thermodynamics provides a reasonable understanding of these systems. However, even at high temperatures, kinetic factors remain important and can inhibit equilibrium. One obvious example of disequilibrium at high temperature is the formation of volcanic glasses. Thermodynamics predicts that magmas should crystallize as they cool. But where cooling is rapid enough, this does not occur. Glasses, which in many ways are simply extremely viscous liquids, form instead.

It is perhaps ironic that it is kinetic factors, and a failure to achieve equilibrium, that in the end allow us to use thermodynamics to make statements about the Earth's interior. As we pointed out in the preceding chapter, if equilibrium were always achieved, the only rocks we could collect at the surface of the Earth (which is, after all, the only place we can collect them) would consist of quartz, clays, serpentine, etc.; their petrology would tell us nothing about their igneous or metamorphic histories. Fortunately, kinetic factors allow the original minerals and textures of gneisses, peridotites, lavas, etc. to be preserved for our study.

The foregoing might suggest that kinetics and thermodynamics are entirely unrelated subjects, and further, that what we have learned about thermodynamics is of little use in many instances. This is certainly not the case. As we shall see, transition state theory provides a very strong link between kinetics and thermodynamics. What we have learned about thermodynamics will prove very useful in our brief study of kinetics. Furthermore, chemical systems are always governed by a combination of thermodynamics and kinetics, so a full understanding of the Earth requires the use of both thermodynamic and kinetics tools. The goal of this chapter is to add the latter to our geochemical toolbox.

5.2 REACTION KINETICS

5.2.1 ELEMENTARY AND OVERALL REACTIONS

In thermodynamics, we found that the equilibrium state of a system is entirely independent of the path taken to reach that state. The goal of kinetics is a description of the manner in which the equilibrium state is achieved. This description is inherently path-dependent. Consider for example, the weathering of anorthite. We can write an *overall* reaction for this process as:

$$CaAl_2Si_2O_8 + 3H_2O + CO_{2(g)} \rightarrow CaCO_3 + 2Al(OH)_3 + 2SiO_{2(qz)} \quad 5.1$$

In nature, however, this process will involve several intermediate steps. These intermediate steps can include:

$$H_2O + CO_{2(g)} \rightarrow H_2CO_{3(aq)} \quad 5.2$$

$$H_2CO_3 \rightarrow HCO^-_{3(aq)} + H^+ \quad 5.3$$

$$CaAl_2Si_2O_8 + H_2O + 2H^+ \rightarrow Si_2Al_2O_5(OH)_4 + Ca^{2+}_{(aq)} \quad 5.4$$

$$H_2O + Si_2Al_2O_5(OH)_4 \rightarrow 2SiO_{2(qz)} + 2Al(OH)_3 \quad 5.5$$

$$HCO^-_{3(aq)} \rightarrow CO^{2-}_{3(aq)} + H^+ \quad 5.6$$

$$CO^{2-}_{3(aq)} + Ca^{2+}_{(aq)} \rightarrow CaCO_3 \quad 5.7$$

In thermodynamics, equation 5.1 is a perfectly adequate description of the reaction. In kinetics, a description of an *overall* reaction such as 5.1, requires a knowledge of the path taken, that is a knowledge of the steps involved. Reactions 5.2 through 5.7 thus describe the overall reaction 5.1. Reactions 5.2, 5.3, and 5.6 are *elementary reactions* in that they involve only one step and the reaction as written describes what occurs on the microscopic level. The remaining reactions are not elementary in that they each consist of a number of more elementary steps.

5.2.2 REACTION MECHANISMS

Reaction 5.4 describes the breakdown of anorthite to form kaolinite plus a free calcium ion. This reaction involves profound structural changes in the solid phase that are not described by equation 5.4. A full kinetic description of 5.4 will require some knowledge of the steps involved in these structural changes. One possibility is that all components are in solution at an intermediate state:

$$CaAl_2Si_2O_8 + 6H_2O + 2H^+ \rightarrow 2H_4SiO_{4(aq)} + 2Al(OH)^+_{2(aq)} + Ca^{2+}_{(aq)} + 2OH^- \quad 5.4a$$

$$2H_4SiO_{4(aq)} + 2Al(OH)^+_{2(aq)} + 2OH^- \rightarrow Si_2Al_2O_5(OH)_4 + 5H_2O \quad 5.4b$$

Reaction 5.5, the breakdown of kaolinite to quartz and gibbsite, could involve SiO_2 dissolving, subsequently precipitating as opaline silica, and later transforming to quartz:

$$Si_2Al_2O_5(OH)_4 + 5H_2O \rightarrow 2H_4SiO_{4(aq)} + 2Al(OH)_3 \quad 5.5a$$

$$H_4SiO_{4(aq)} \rightarrow SiO_{2(opal)} + 2H_2O \quad 5.5b$$

$$SiO_{2(opal)} \rightarrow SiO_{2(qz)} \quad 5.5c$$

The description of an overall reaction in terms of elementary reactions is called the *reaction mechanism*. The rates of truly elementary reactions are path-independent because there is only one possible path. In this sense, elementary reactions are somewhat analogous to state functions in thermodynamics. Clearly then, an important step in any kinetic study is determination of the reaction mechanism, that is, to describe the process in terms of elementary reactions. As we shall see, there may be more than one possible path for an overall reaction, and that several paths may be simultaneously involved. Kinetics can only provide an accurate description of a process if all these paths are known.

5.2.3 REACTION RATES

Consider a reaction such as the precipitation of dolomite from a solution. We can describe this as:

$$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \rightleftarrows CaMg(CO_3)_2$$

We *define* the *rate* of this reaction, $\Re$, as the rate at which dolomite is produced:

$$\Re \equiv \frac{d[CaMg(CO_3)_2]}{dt}$$

Clearly, if dolomite is to be formed, CO_3^{2-} must be consumed in this reaction twice as fast as Ca or Mg. For every mole of Ca or Mg consumed, exactly two moles of CO_3^{2-} will also be consumed and one mole of dolomite produced. This being the case, we could equally well express the reaction rate as:

$$\Re = -\frac{1}{2}\frac{d[CO_3^{2-}]}{dt} \qquad \text{or} \qquad \Re = -\frac{d[Ca^{2+}]}{dt} = -\frac{d[Mg^{2+}]}{dt}$$

We can now formulate the general rule. For any reaction such as:

$$aA + bB \rightarrow cC + dD \qquad 5.8$$

The *reaction rate*, $\Re$, is defined as the change in composition of the reaction mixture with time:

$$\boxed{\Re \equiv -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}} \qquad 5.9$$

The brackets denote the concentrations of the species and the negative sign indicates that reactants are consumed as the reaction proceeds. Thus *the rate of a reaction is simply the rate at which a reactant is consumed or product produced* divided by its stoichiometric coefficient.

5.2.3.1 THE REACTION RATE FOR AN ELEMENTARY REACTION: COMPOSITION DEPENDENCE

Reaction rates will, in general, depend on the concentration of the reactant. To understand this, consider the reaction:

$$N^\circ + O_2 \rightleftarrows NO + O \qquad 5.10$$

This reaction between free nitrogen atoms and oxygen molecules occurs in the stratosphere (where N° is produced by high energy collisions involving N_2) and contributes to the production of nitrous oxide. Let's assume that reaction 5.10 is an adequate description of this reaction. In other words, we are assuming that 5.10 is an elementary reaction and the reaction mechanism for the production of NO from nitrogen and oxygen gas is collision of a N° molecule and O_2 molecule. For the reaction to occur, the nitrogen and oxygen molecules must collide with enough kinetic energy that the mutual repulsion of the electron clouds is overcome and the electrons can be redistributed into new covalent orbits. The repulsive force represents an energy barrier, E_B, which will prevent low energy nitrogen and oxygen atoms from reacting. Figure 5.1 illustrates

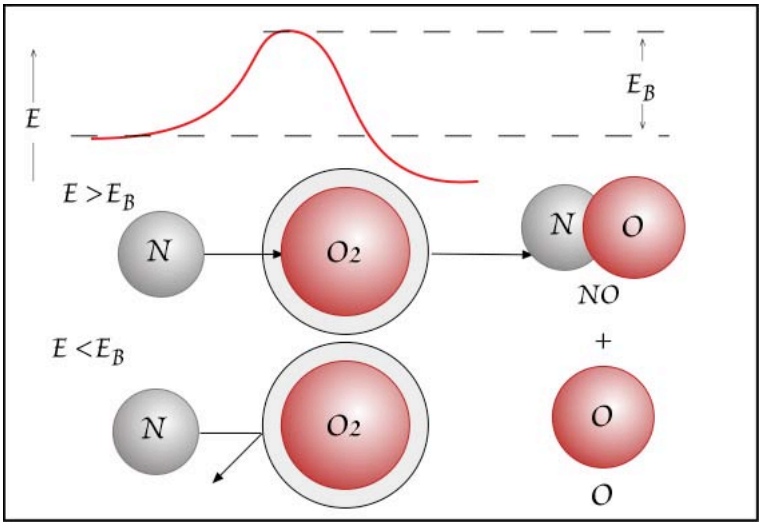


Figure 5.1. A nitrogen atom approaching an oxygen molecule must have enough kinetic energy to pass through the region where it is repelled by electrostatic repulsion of the electron cloud of the oxygen. Otherwise, it will not approach closely enough so that its electrons can combine with those of oxygen.

this point. The reaction rate will therefore depend on 1) the number of collisions per unit time, and 2) the fraction of N and O molecules having energy greater than the barrier energy.

Let's first consider the number of collisions per unit time. In order for a 'collision' to occur, the electron clouds must overlap, that is, they must approach within (r_N + r_{O_2}), where r_N and r_{O_2} are the radii of the nitrogen and oxygen molecules. To make things simple, imagine the oxygen to be fixed and the nitrogen in motion. In other words, our reference frame will be that of the oxygen molecules. We can imagine the nitrogen sweeping out a cross-section with radius (r_N + r_{O_2}) as it travels. If the nitrogen is travelling at velocity *v*, in time *t*, it will sweep out a cylindrical volume (Figure 5.2):

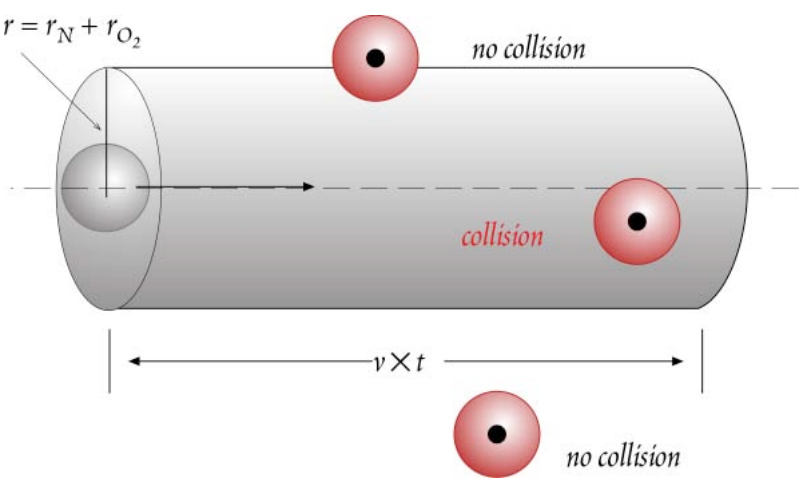


Figure 5.2. A nitrogen atom will sweep out a volume $V = v\pi(r_N + r_{O_2})^2 t$ in time *t*. Whether a collision occurs will depend on whether the center (indicated by black dot) of an oxygen atom falls within this volume.

$$V = v\pi(r_N + r_{O_2})^2 t \qquad 5.11$$

Whether a collision occurs will depend on whether the *center* of an oxygen molecule falls within this volume (Figure 5.2). The number of collisions that will occur in this time will be:

$$C = n_O v\pi(r_N + r_{O_2})^2 t \qquad 5.12$$

where n_O is the number of oxygen molecules per unit volume. The number of collisions per unit time is then simply:

$$\frac{C}{t} = n_O v\pi(r_N + r_{O_2})^2 \qquad 5.13$$

If there are n_N nitrogen atoms and the average velocity between nitrogen and oxygen molecules is $\bar{v}$, then the number of collisions per unit time is:

$$\dot{c} = n_N n_O \bar{v}\pi\left(r_N + r_{O_2}\right)^2 \qquad 5.14$$

If we let

$$k = \bar{v}\pi\left(r_N + r_{O_2}\right)^2$$

then the rate at which collisions occur is:

$$\dot{c} = k n_N n_{O_2} \qquad 5.15$$

Thus we see that *the reaction rate in this case will depend on the concentration of nitrogen, oxygen and a constant* that depends on the nature of the reactants. This is a general result.

5.2.3.2 The Reaction Rate for an Elementary Reaction: Temperature Dependence

We now need to estimate the fraction of nitrogen and oxygen atoms having at least the barrier energy, E_B. For simplicity, we will assume that oxygen and nitrogen molecules have an identical energy distribution. The Boltzmann Distribution Law, which we encountered in Section 2.6.4.1 (equ. 2.84), can be written to express the average number of molecules having energy level ε_i as:

$$n_i = Ae^{-\varepsilon_i / kT} \qquad 5.16$$

where k is Boltzmann's constant and A is a constant (comparing with equation 2.84, we see that $A = n/Q$ where n is the total number of molecules in the system and Q is the *partition function*). In plain English, this equation tells us that the number of molecules in some energy level i decreases exponentially as the energy of that level increases (Figure 2.9). We want to know the number of molecules with energy greater than E_B. In this case we are dealing with translational energy. The quantum spacings between translational energy levels are so small that they essentially form a continuum, allowing us to integrate equation 5.16. Fortunately for us, the integration of 5.16 from $\varepsilon = E_B$ to infinity has a simple solution:

$$A\int_{E_B}^{\infty} e^{-\varepsilon_i/\mathrm{k}T}\,d\varepsilon = A\mathrm{k}Te^{-E_B/\mathrm{k}T} \qquad 5.17$$

The *fraction* of molecules with energy greater than E_B is just:

$$\frac{A\int_{E_B}^{\infty} e^{-\varepsilon_i/\mathrm{k}T}\,d\varepsilon}{A\int_{0}^{\infty} e^{-\varepsilon_i/\mathrm{k}T}\,d\varepsilon} = \frac{A\mathrm{k}Te^{-E_B/\mathrm{k}T}}{A\mathrm{k}T} = e^{-E_B/\mathrm{k}T} \qquad 5.18$$

The rate of reaction will be the rate of collision times the fraction of molecules having energy greater than E_B:

$$\Re = n_N n_O \bar{v}\pi\left(r_N + r_{O_2}\right)^2 e^{-E_B/\mathrm{k}T} \qquad 5.19$$

Now we just need to find a value for velocity. The average velocity can be calculated from the Maxwell-Boltzmann Law*, which gives the distribution of velocities of molecules in a gas. Doing so, we find that the average velocity is:

$$\bar{v} = \sqrt{\frac{8\mathrm{k}T}{\pi\mu}} \qquad 5.20$$

where μ is the reduced mass, $\mu = m_N m_{O_2}/(m_N + m_{O_2})$. Substituting 5.20 into 5.19, our equation for the reaction rate is:

$$\Re = n_N n_O \pi\left(r_N + r_{O_2}\right)^2 \sqrt{\frac{8\mathrm{k}T}{\pi\mu}} e^{-E_B/\mathrm{k}T} \qquad 5.21$$

Redefining k as:

$$k = \pi\left(r_N + r_{O_2}\right)^2 \sqrt{\frac{8\mathrm{k}T}{\pi\mu}} e^{-E_B/\mathrm{k}T} \qquad 5.22$$

our reaction rate equation is:

$$\Re = k n_N n_{O_2} \qquad 5.23$$

Thus the reaction rate in this case depends on the concentration of nitrogen and oxygen and a constant k, called the *rate constant*†, which depends on temperature, properties of the reactants, and the barrier energy.

In a more rigorous analysis we would have to take into consideration atoms and molecules not being spherically symmetric and that, as a result, some orientations of the molecules are more likely to result in reaction than others. In addition, a head-on collision is more likely to result in reaction than a glancing blow, so the collision cross section will be less than $\pi(r_N + r_{O_2})^2$. These factors can, however, be accounted for by multiplying by a constant, called a *stearic factor*, so the form of our equation, and the temperature dependence, would not be affected. Values of stearic factors for various reactions range over many orders of magnitude and can be quite small. In rare circumstances, they can be greater than 1 (implying an effective collision cross section greater than the combined atomic radii).

* So-called because Maxwell proposed it and Boltzmann proved it rigorously.

† To distinguish the rate constant, k, from Boltzmann's constant, k, we will always write the former in lower case italics and the latter in roman typeface.

Temperature occurs in 2 places in equation 5.22; however, the square-root dependence is slight compared to the exponential one. For example, consider a temperature change of 300 K to 325 K. For a reaction with an activation energy of 25 kJ, the exponential temperature dependence results an increase in reaction rate of more than a factor of 2, whereas the square root dependence increases the reaction rate by only 4%. Hence the temperature dependence can be essentially expressed as:

$$k \propto e^{-E_B/\mathrm{kT}}$$ ‡

The temperature dependence of the rate constant is most often written as:

$$\boxed{k = Ae^{-E_B/\mathrm{kT}}} \qquad 5.24$$

which is the important *Arrhenius relation*¶. It expresses the rate constant in terms of the barrier, or *activation*, energy (also often written as E_A or E^*), and A, a proportionality constant sometimes called the *frequency factor* (because it depends on the frequency of collisions), and temperature. (We can replace k, Boltzmann's constant with R, the gas constant, if we deal in moles rather than atoms.)

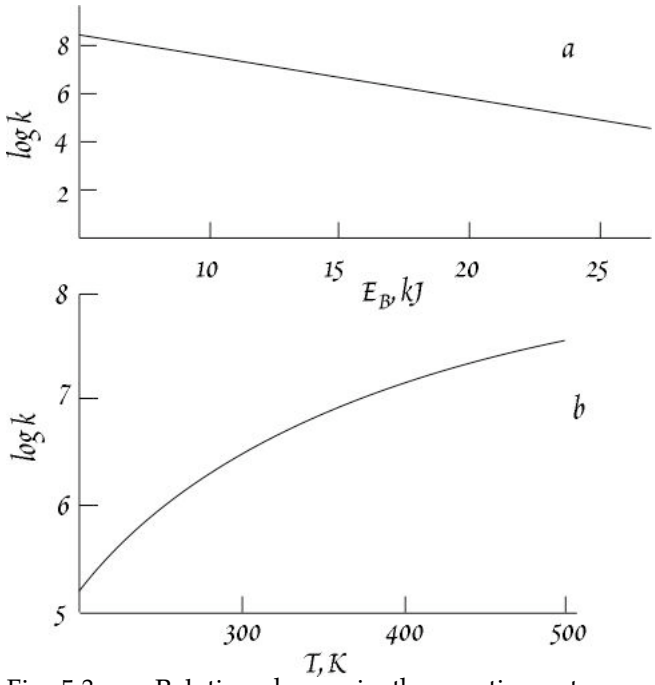


Fig. 5.3. a. Relative change in the reaction rate as a function of activation energy at 300 K. b. Change in the reaction rate for the same as a function of temperature with an activation energy of 15 kJ.

The temperature dependence of the rate constant is illustrated in Figure 5.3. We see that the reaction rate falls off by a factor of 10^2 as temperature is decreased from 500 to 200 K. This confirms our everyday experience that reaction rates are extremely temperature dependent. Table 5.1 lists some examples of activation energies for geochemical reactions.

The pre-exponential factor, A, is often assumed to be independent of temperature. Comparison of 5.24 with 5.23 shows, however, that it need not be. In the case of an elementary gas phase reaction, we would predict a dependence on the square root of temperature. Other kinds of reactions show other kinds temperature dependencies of the frequency factor, however. A more accurate expression of temperature dependence of the reaction rate is:

$$k = AT^n e^{-E_B/\mathrm{kT}} \qquad 5.25$$

where the exponent n can be any number. Nevertheless, the temperature dependence of the frequency factor is usually small and it can often be safely neglected, as in our example above.

‡ This form of the temperature dependence of reaction rate was first proposed by Jacobus H. Van't Hoff (1852-1911), who deduced it by analogy to equation 3.96, the *Van't Hoff equation*. Van't Hoff was born in Rotterdam and in 1878 was appointed professor of geology, mineralogy, and chemistry at the University of Amsterdam. In 1896 he moved to the University of Berlin, where he remained for the rest of his life. He won the Nobel Prize for Chemistry in 1901.

¶ Named for Svante August Arrhenius (1859-1927) because Arrhenius provided the theoretical justification for Van't Hoff's proposal. Arrhenius's PhD dissertation, completed in 1884 at the University of Uppsala in Sweden, was rated fourth class by the committee of examiners, implying great things were not expected of him. The old boys must have been a little surprised nineteen years later when Arrhenius won the Nobel Prize for chemistry. Among Arrhenius's other contributions were the ionic theory of electrolyte solutions and the greenhouse theory of climate: that the CO_2 concentration in the atmosphere could be an important control on global temperature, and that anthropogenic burning of fossil fuel could lead to global warming.

5.3.2.3 A General Form of the Rate Equation

In general, the rate of a reaction such as:

$$aA + bB \rightarrow cC + dD$$

can be expressed as:

$$\Re = k a_A^{n_A} a_B^{n_B} a_C^{n_C} a_D^{n_D} \qquad 5.26^{£}$$

where k is the *rate constant* and a_A, etc. are activities (we will often use the simplifying assumption of ideality and replace these by concentrations). The exponents n_A, n_B, etc. can be any number, including zero. The sum of the exponents n_A, n_B, ... is the *order of the reaction*. In general, the value of the exponents must be determined experimentally, though their values can be predicted if the reaction mechanism is known, as we saw in the above example.

Just as the mole fraction was the unit of choice for thermodynamics, *moles per volume, or moles per area in the case of reactions taking place on surfaces, is the unit of choice for kinetics*. Thus wherever more than one phase is involved, one concentration should be expressed in moles per unit area or volume.

There are several simplifications of equation 5.26 for *elementary reactions*. First, the rate of reaction is independent of the concentration of the products so the exponents of the products will be 0. Indeed, *one of the criteria for an elementary reaction is that the product not influence the reaction rate*. Second, *the values of the exponents for the reactants are the stoichiometric coefficients of the reactant species*. Thus if the reaction can be written in terms of a series of elementary reactions, then the exponents for the rate equation can be deduced from those of the component elementary reactions. For elementary reactions, the order of reaction will be equal to the sum of the stoichiometric coefficients of the products. For complex reac-

Example 5.1. Rate of hydration of $CO_{2(aq)}$

The rate for the hydration of CO_2 (i.e., $CO_2 + H_2O \rightleftarrows H_2CO_3$) has been found to follow the first order rate law:

$$-\frac{d[CO_{2(aq)}]}{dt} = k[CO_{2(aq)}] \qquad 5.27$$

At 25° C, k has been determined to be 0.014 sec^{-1}. Make a graph showing how the concentration of CO_2 will change with time as the reaction proceeds, assuming an equilibrium (i.e., final) CO_2 concentration of 0.

Answer: Since we are not given the absolute concentrations, we cannot determine the absolute change. We can, however, determine relative change. To do so, we just integrate 5.27:

$$-\int \frac{d[CO_{2(aq)}]}{[CO_{2(aq)}]} = k\int_0^t dt$$

With some rearranging, we obtain:

$$\frac{[CO_{2(aq)}]}{[CO_{2(aq)}]_0} = e^{-kt} \qquad 5.28$$

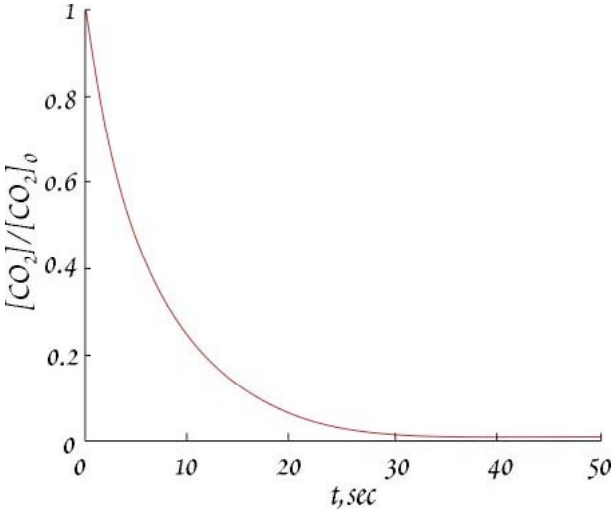


Figure 5.4. Progress in the reaction $CO_{2(aq)} + H_2O \rightarrow H_2CO_3$ with time, as measured by decrease in $[CO_2]$.

Figure 5.4 shows our result. It is apparent that this is a fast reaction. We can assume that equilibrium will prevail on most time scales of interest to us.

£ Don't confuse this equation, which expresses the way in which reaction rates depend on concentrations, with equation 5.9, which is the definition of the reaction rate.

tions, however, the order of reaction must be deduced, either experimentally, or from the component elementary reactions.

A further simplification may be made where one of the reactants is in sufficient abundance that its concentration is not affected by the progress of the reaction of interest. For instance, the hydration of CO_2 through:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

The rate of this reaction will be:

$$-\frac{d[CO_2]}{dt} = k[CO_2][H_2O]$$

which is a second order reaction. However, in aqueous solution, H_2O will always be present in great excess over CO_2 and its abundance will not be significantly changed by this reaction. This allows us to treat the reaction as if it were first order and to define a *pseudo-first order* rate constant, k^*, as:

$$k^* = k\,[H_2O]$$

Since $[H_2O]$ is constant, it follows that k^* is as well. The reaction rate can then be written as:

$$-\frac{d[CO_2]}{dt} = k^*[CO_2]$$

In Examples 5.1 and 5.2 we have used just such a *pseudo-first order* rate constant.

Table 5.1. Activation Energies of Some Geochemical Reactions

Reaction	E_A kJ/mol
$Mg_3Si_4O_{10}(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O$	371.8
$CaCO_3 + SiO_2 \rightarrow CaCO_3 + CO_2$	225.0
$2CaCO_3 + Mg^{2+} \rightarrow (CaMg)CO_3 + Ca^{2+}$	117.1
$NaAlSi_2O_6{\cdot}H_2O + SiO_2 \rightarrow NaAlSi_3O_8 + H_2O$	106.3
$C_2H_4 + H_2 \rightarrow C_2H_6$	102.8
$CaF_2 \rightarrow Ca^{2+} + 2F^+$	73.0
$MgSiO_3 + 2H^+ + H_2O \rightarrow Mg^{2+} + H_4SiO_4$	49.0
$SiO_{2\,(qz)} + 2\,H_2O \rightarrow H_2SiO_4$	40.6
$SiO_{2(am)} + 2\,H_2O \rightarrow H_2SiO_4$	35.8
$H_2SiO_4 \rightarrow SiO_{2(qz)} + 2\,H_2O$	28.4
$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + H_2SiO_4$	21.7
$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2+}$	20.1
$O + O_3 \rightarrow 2O_2$	13.4

5.2.4 Rates of Complex Reactions

Deciding whether a reaction is elementary is not always straightforward. Consider the reaction:

$$2NO_2 \rightarrow 2NO + O_2 \qquad 5.29$$

On a microscopic basis, we might describe this reaction as the collision of two NO_2 molecules to form two NO molecules and an O_2 molecule. Since no intermediate steps occur, this would appear to be an elementary reaction. The rate equation for this reaction has been experimentally determined to be:

$$-\frac{d[NO_2]}{dt} = 2k[NO_2]^2$$

This has the predicted form for an elementary reaction of second order; thus experiment confirms that reaction 5.29 is elementary.

Now consider the reaction: $2O_3 \rightarrow 3O_2$

We might reason that this reaction requires only the collision of two ozone molecules with no intermediate products and that the reaction is therefore primary. However, the experimentally determined rate law is:

$$\frac{1}{3}\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[O_3]}{dt} = k\frac{[O_3]^2}{[O_2]} \qquad 5.30$$

Since the rate depends on the concentration of the product, the reaction is not elementary and must involve intermediate steps.

EXAMPLE 5.2: OXIDATION OF FERROUS IRON

Given the adjacent equilibrium and pseudo-first order rate constants for the oxidation of three species of ferrous iron (Fe^{2+}, $Fe(OH)^+$, and $Fe(OH)_2$) to ferric iron in the adjacent table, calculate the overall rate of oxidation of ferrous iron at pH 2, 6, and 8 assuming a total Fe^{2+} concentration of 1×10^{-6} M.

Equilibrium Constants

Reaction	pK
$Fe^{2+} + H_2O \rightleftarrows FeOH^+ + H^+$	4.5
$FeOH^+ + H_2O \rightleftarrows Fe(OH)_2 + H^+$	7.4

Oxidation Rate Constants

Fe^{2+} Species	k (s^{-1})
Fe^{2+}	7.9×10^{-6}
$FeOH^+$	25
$Fe(OH)_2$	7.9×10^{6}

Answer: The overall oxidation rate can be written as:

$$\frac{d\Sigma Fe^{2+}}{dt} = k_1[Fe^{2+}] + k_2[FeOH^-] + k_3[Fe(OH)_2] \qquad 5.31$$

Thus to calculate the rate, we will have to calculate the concentrations of the various species. These are given by:

$$[FeOH^-] = K_1 \frac{[Fe^{2+}]}{[H^+]} \quad \text{and} \quad [Fe(OH)_2] = K_2 \frac{[Fe^{2+}]}{[H^+]^2}$$

We can substitute these expressions into 5.32 we have:

$$\frac{d\Sigma Fe^{2+}}{dt} = [Fe^{2+}]\left(k_1 + \frac{k_2 K_1}{[H^+]} + \frac{k_2 K_2}{[H^+]^2} \right) \qquad 5.32$$

Since the total Fe^{2+} is the same at all three pH's the concentration of the Fe^{2+} ion must vary. So we need to calculate the concentration of ionic Fe^{2+} at these pH's. The total Fe^{2+} is:

$$\Sigma Fe^{2+} = [Fe^{2+}] + [FeOH^-] + [Fe(OH)_2]$$

or:

$$\Sigma Fe^{2+} = [Fe^{2+}]\left(1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} \right)$$

so that:

$$[Fe^{2+}] = \frac{\Sigma Fe^{2+}}{1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2}}$$

We can now calculate the rates. Substituting in appropriate values into equ. 5.32, we find the rate is 0.0031 M/sec, 0.9371 M/sec, and 7.89 M/sec at a pH of 2, 4, and 8 respectively. Thus the combination of the different rate constants and the pH dependency of the Fe speciation results in a very strong pH dependence of the oxidation rate.

5.2.4.1 CHAIN REACTIONS AND BRANCHING

Many overall reactions involve a series of sequential elementary reactions, or steps, each of which must be completed before a subsequent reaction can occur. Such reactions are termed *chain reactions*. It is also possible that the path of an overall reaction may include two or more alternative elementary reactions, or sequences of elementary reactions, that occur simultaneously. These alternatives paths are called *branches*. The combustion of hydrogen is a good example because it is a chain reaction involving several branches.

Experiments have shown that the reaction rate for the combustion of hydrogen is not simply:

$$\frac{d[H_2O]}{dt}] = k[H_2]^2[O_2] \qquad 5.33$$

and therefore $2H_2 + O_2 \rightarrow 2H_2O$ is not an elementary reaction. If it were an elementary reaction, equation 5.33 predicts that its rate should continuously decrease through the course of the reaction (provided temperature is held constant!) since the reactants will be consumed and their concentrations will decrease. In actuality the rate of this reaction can increase rapidly, sometimes catastrophically (even at

constant temperature), as it proceeds. Evidently, the reaction mechanism is more complex. Indeed it appears to involve several steps. The final step of this reaction is:

$$OH + H_2 \rightarrow H_2O + H \qquad 5.34$$

This is an elementary reaction, depending only on the concentration of the two reactants. However, one of the reactants, OH, and one of the products, H, are not among the original constituents of the gas. Rather, they are created by intermediate steps. Species that do not appear in the overall reaction are termed *reactive intermediates*.

The first step in the combustion of hydrogen is breakup of the hydrogen molecule, forming highly reactive atomic H:

$$H_2 \rightarrow 2H \qquad 5.34a$$

The next step is reaction of the atomic hydrogen with an oxygen molecule:

$$H + O_2 \rightarrow OH + O \qquad 5.34b$$

Reactions 5.34a and 5.34b are an example of a *chain reaction*.

Since 5.34 is an elementary reaction, the reaction rate can be written as:

$$\frac{d[H_2O]}{dt} = k[OH][H_2]$$

This is also the rate of the overall reaction. Thus the overall reaction will depend on the availability of OH. What makes the combustion of hydrogen particularly interesting is that there are several ways in which OH may be created. Reaction 5.34b is one way. The monatomic oxygen created in this reaction, however, provides two alternate mechanisms for the creation of the OH complex:

$$H_2 + O \rightarrow OH + H \qquad 5.34c$$

and

$$H + O \rightarrow OH \qquad 5.34d$$

Reactions 5.34b through 5.34d represent alternative reaction paths or *branches*. Notice that the final step also provides an alternative mechanism, or branch, for the production of monatomic hydrogen.

The branching that occurs provides the potential for a "runaway" or explosive reaction. This is apparent if we simply sum reactions 5.34 and 5.34b through 5.34d:

$$\begin{aligned} & 4 \times [OH + H_2 \rightarrow H_2O + H] \\ + \quad & 2 \times [H + O_2 \rightarrow OH + O] \\ + \quad & H_2 + O \rightarrow OH + H \\ + \quad & H + O \rightarrow OH \\ \hline & 5H_2 + 2O_2 \rightarrow 4H_2O + 2H \end{aligned} \qquad 5.34e$$

Each cycle of these reactions produces four water molecules plus two hydrogens. Since the rate of the overall reaction, i.e., the production of water, depends on [OH], which in turn depends on [H], the reaction will accelerate with time. (Actually, the combustion of hydrogen is a *very* complex reaction. When all the elementary reactions are written down, including the reverse reactions and reactions with the container wall, they fill an entire page. Interestingly, it displays this runaway behavior only under certain combinations of T, P, and container size and shape. The latter dependence results from reactions with, or catalyzed by, the container wall. Under certain conditions, it will become steady state; i.e., the creation and consumption of water balance to produce a constant concentration of water.)

5.2.4.2 Rate-Determining Step

It often happens that the reaction rate of a chain, or sequential, reaction, is controlled by a single step that is very much slower than the other steps. For example, how quickly you can buy a pencil at the campus bookstore on the first day of class will probably be controlled entirely by how quickly you can get through the checkout line. Such a step is called the *rate-determining step*. Once the rate of this step is determined, the rates of all other steps are essentially irrelevant.

Now consider a reaction that can occur through two branches. For example,

$$A \xrightarrow{1} B \qquad \text{and} \qquad A \xrightarrow{2} B$$

The reaction rate is then:

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] \tag{5.35}$$

If one path is very much faster than the other, then the fastest of the two will always be taken. Thus for branched reactions, the fastest branch determines the reaction mechanism. Mathematically, we may say that if $k_1 >> k_2$ then $(k_1 + k_2) \approx k_1$ and therefore:

$$\frac{d[A]}{dt} \approx -k_1[A]$$

In our analogy above, if an express checkout is available, you would certainly take it. In this case, the slowness of the regular checkout line becomes irrelevant for determining how quickly you can buy your pencil. To sum up, we may say that when reactions occur *in series*, then *the slowest reaction is the rate determining step. When parallel*, or branched, reaction paths are available, then *the fastest path is rate-determining*.

5.2.5 Steady-State and Equilibrium

Many geochemical systems are steady state ones, that is, time-invariant systems, or approximately so. The equilibrium state is also a steady state, but not all steady state systems are necessarily equilibrium ones. We may say then that steady state is a necessary, but not sufficient, condition for *equilibrium*. Let's consider how a system will approach the steady-state and equilibrium.

Consider the elementary reaction: $A \rightarrow B$

Suppose that this reaction does not entirely consume A, but reaches a steady state where the concentration of A is $[A]_s$, the subscript *s* denoting the steady state. In this case, we can express the reaction rate as:

$$\frac{d[A]}{dt} \approx k([A]_s - [A]) \tag{5.36}$$

where $[A]_s$ is the steady state concentration of A. The reaction rate is 0 when $[A] = [A]_s$.

To see how the concentration will vary before steady state is achieved, we integrate 5.36:

$$\ln\left(\frac{[A]_s - [A]}{[A]_s - [A]^\circ}\right) = -kt$$

where $[A]^\circ$ is the initial concentration of A. This may be written as:

$$\frac{[A]_s - [A]}{[A]_s - [A]^\circ} = e^{-kt} \tag{5.37}$$

The denominator is a constant (for a given set of initial conditions), so we can rewrite 5.37 as:

$$[A]_s - [A] = Ce^{-kt}$$

The excess concentration of A, i.e., $[A]–[A]_S$ declines as e^{-t}, so that steady state is approached asymptotically. An effective steady state will be achieved when $t >> 1/k$. As in Example 5.1, the reaction rate decreases exponentially with time, i.e.:

$$\frac{d[A]}{dt} = kCe^{-kt}$$

Now suppose that in addition to the reaction: $A \rightarrow B$, the reaction $B \rightarrow A$ also occurs and that both are first order elementary reactions. The rates of reaction will be:

$$\frac{d[A]}{dt} = -k_+[A] + k_-[B] \tag{5.38}$$

Here we are using k_+ for the rate constant of the forward reaction and k_- for the rate constant of the reverse reaction. Assuming the system is closed and that no other processes affect the concentrations of A and B, then:

$$[A] + [B] = \Sigma AB$$

where ΣAB is the total of A and B and is a constant. Equ. 5.38 can therefore be written as:

$$\frac{d[A]}{dt} = -k_+[A] + k_-[\Sigma AB - A] = -(k_+ + k_-)[A] + k_-\Sigma AB \qquad 5.39$$

The concentration of at some time τ, $[A]_\tau$ is obtained by integrating 5.39:

$$\int_{A^\circ}^{A_\tau} \frac{d[A]}{-(k_+ + k_-)[A] + k_-\Sigma AB} = \int_0^\tau dt$$

which yields:

$$\frac{-(k_+ + k_-)[A]_\tau + k_-\Sigma AB}{-(k_+ + k_-)[A]^\circ + k_-\Sigma AB} = e^{-(k_+ + k_-)\tau}$$

Since $[A]^\circ + [B]^\circ = \Sigma AB$, we can also express this as:

$$\frac{-k_+[A]_\tau + k_-[B]_\tau}{-k_+[A]^\circ + k_-[B]^\circ} = e^{-(k_+ + k_-)\tau} \qquad 5.40$$

Thus in the general case, the concentrations of A and B will depend on their initial concentrations. However, for $\tau = \infty$, or as a practical matter when $\tau >> (k_+ + k_-)$, then a steady-state will be achieved where 5.40 reduces to:

$$k_+[A]_\infty = k_-[B]_\infty \qquad 5.41$$

5.3 Relationships between Kinetics and Thermodynamics

5.3.1 Principle of Detailed Balancing

Equation 5.41 describes the relation between the concentration of reactant and product of a reversible reaction after infinite time, i.e., in the steady state. This then is just the state the reaction will obtain in the absence of constraints and external disturbance. This is precisely the definition of equilibrium we decided on in Chapter 2. It follows that $[A]_\infty$ and $[B]_\infty$ are then also the equilibrium concentrations. Thus we see, as we stated in Chapter 2, that equilibrium is not necessarily a static state on the microscopic scale. Rather, it is a steady state where the forward rate of reaction is equal to the reverse rate. Formally, we may say that for an elementary reaction such as:

$$A \rightleftarrows B$$

at equilibrium the following relation must hold:

$$k_+[A]_{eq} = k_-[B]_{eq} \qquad 5.42$$

where k_+ and k_- are the rate constants for the forward and reverse reactions respectively. This is known as the *principle of detailed balancing*, and it establishes an essential link between thermodynamics and kinetics. This link is apparent when we combine equation 5.42 with equation 3.85 to obtain:

$$\boxed{\frac{k_+}{k_-} = \frac{[B]_{eq}}{[A]_{eq}} = K^{app}} \qquad 5.43$$

It is apparent from equation 5.43 that if the equilibrium constant and one of the rate constants for a reaction are known, the rate constant for the reverse reaction may be deduced. Furthermore, if the form of the rate law for either the forward or reverse reaction is known, the other can be deduced. This is a trivial point for elementary reactions since rate laws for such reactions are readily obtained in any

EXAMPLE 5.3: RACEMIZATION OF AMINO ACIDS

Amino-acids are nitrogen-containing organic molecules that are essential to life. The chemical properties of amino acids depend not only on their composition, but also on their structure. Twenty different amino acids are used in building proteins. Amino acid comes in two forms, which can be distinguished by the direction in which they rotate polarized light. Interestingly enough, organisms synthesize only the form that rotates polarized light in a counterclockwise manner, labeled the L-form (Fig. 5.5a). After death of the organism, however, the amino acid can spontaneously convert to its mirror image, the D-form (Fig. 5.5b), corresponding to clockwise rotation of light. This process is termed racemization. Racemization is a first order reaction and rate constants for this process have been determined for a number of amino acids in various substances. This provides a means of dating sediment. Given that the rate constant k_+ for the l-isoleucine → d-alloisoleucine reaction is 1.2×10^{-7} y^{-1} and for the d-alloisoleucine → l-isoleucine is 9.6×10^{-8} y^{-1}, what is the age of a sediment whose d-alloisoleucine/l-isoleucine ratio is 0 .1? Assume that the total isoleucine is conserved and an initial d-isoleucine concentration of 0.

Answer: This is a special case of equation 5.40 where [B]° is 0 and [A] + [B] = [A]°. L etting γ be the r atio [B]/[A] (d-alloisoleucine/l-isoleucine) and substituting into to 5.40, we obtain:

$$\frac{-k_+ + \gamma k_-}{-k_+(1+\gamma)} = e^{-(k_+ + k_-)t}$$

Substituting values and solving for t, we find the age is 8.27×10^3 yr. Of course, racemization rates, like all reaction rates depend on temperature, so this result assumes constant temperature.

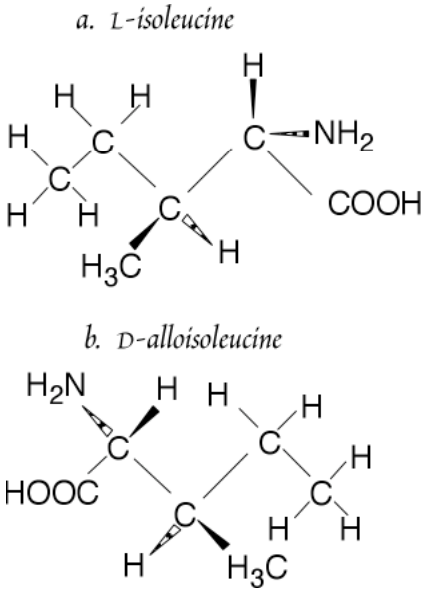


Figure 5.5. S tructure of L-isoleucine and D-alloisoleucine. Solid wedge shapes indicate bonds coming out of the plane of the paper, hashed wedge shapes indicate bonds behind the paper.

case. The importance of this point is that it holds for overall reactions as well as elementary ones. For example, consider the serpentinization of olivine:

$$2Mg_2SiO_4 + H_2O + 2H^+ \rightleftarrows Mg_3Si_2O_5(OH)_4 + Mg^{2+}$$

This is not an elementary reaction as several intermediate steps are involved, as in the example of the weathering of anorthite discussed earlier. Nevertheless, if olivine, serpentine and water can be assumed to be pure phases and have unit activity, the equilibrium constant for this reaction is:

$$K^{app} = \frac{[Mg^{2+}]}{[H^+]^2} \qquad 5.44$$

The relation between the forward and reverse reaction rate constants must be:

$$k_-[Mg^{2+}] = k_+[H^+]^2$$

Suppose that experiments show that the rate law for the forward reaction is:

$$\frac{d[Mg^{2+}]}{dt} = k[Ol][H^+]$$

where [*Ol*] is the specific area (area per solution volume) of olivine in the experiment. From equation 5.9, we can express the rate for the reverse reaction as:

$$\frac{d[Ol]}{dt} = -2\frac{d[Mg^{2+}]}{dt} = -k[Ol][H^+]$$

Using equation 5.43 to obtain a substitution for k, we find that the rate law for the reverse reaction, i.e., for the formation of olivine from serpentine must be:

$$\frac{d[Ol]}{dt} = -2k'\frac{[Mg^{2+}]}{[H^+]^2}[Ol][H^+] = -2k'\frac{[Mg^{2+}]}{[H^+]}[Ol] \qquad 5.45$$

where k' is the rate constant for the reverse reaction.

5.3.2 Enthalpy and Activation Energy

The principle of detailed balancing allows us to relate the activation energy in the Arrhenius relation (equation 5.24) to the heat (enthalpy) of reaction. Recall that the equilibrium constant is related to free energy change of reaction as:

$$K = e^{-\Delta G_r^o/RT} = e^{-\Delta H_r^o/RT + \Delta S/R} = e^{\Delta S/R}e^{-\Delta H_r^o/RT} \qquad 5.46$$

(For simplicity and clarity, here, and in the subsequent discussion of Transition State Theory, we assume ideal behavior, and therefore that activities equal concentrations and that $K^{app} = K$.) If we write the Arrhenius relations for the forward and reverse reactions and combine them with equations 5.43 we obtain:

$$\frac{k_+}{k_-} = \frac{A_+e^{-E_+/RT}}{A_-e^{-E_-/RT}} = \frac{A_+}{A_-}e^{-(E_+ - E_-)/RT} = K \qquad 5.47$$

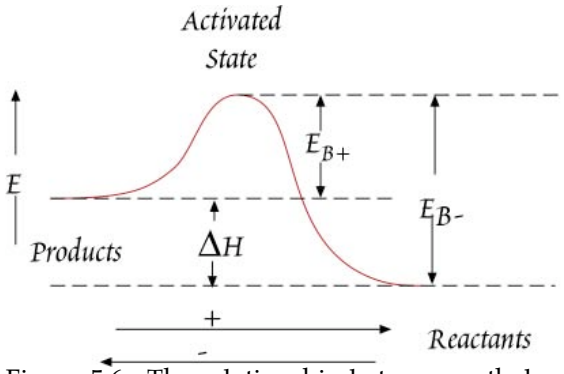


Figure 5.6. The relationship between enthalpy of reaction and the barrier energy for the forward and reverse reactions.

Comparing equations 4.46 and 4.47, we can see that:

and $$E_+ - E_- = \Delta H_r^o \qquad 5.48$$

This relationship is illustrated for the example of an exothermic reaction in Figure 5.6. In the process of converting products to reactants, an amount of energy ΔH is released. To reach that state, however, an energy barrier of E_{B+} must be overcome. It is apparent then that the enthalpy change of reaction is just the difference between the barrier energies of the forward and reverse reactions. We also see that:

$$\frac{A_+}{A_-} = e^{\Delta S/R} \qquad 5.49$$

Indeed, it can be shown that Arrhenius coefficient, or frequency factor, is related to entropy as:

$$A_+ = \frac{kT}{h}e^{\Delta S_+^*/R} \qquad 5.50$$

where ΔS_+^* is the entropy difference between the initial state and the activated state (discussed below) and h is Planck's constant. The ratio kT/h has units of time^{-1} and is called the *fundamental frequency*. At 298 K, it as a value of 6.21×10^{12} sec^{-1}.

5.3.3 Aspects of Transition State Theory

In the above discussion, we have already made implicit use of *Transition State Theory*. Transition State Theory postulates that an *elementary* reaction such as:

$$A + BC \rightarrow AC + B \qquad 5.51$$

proceeds through the formation of an *activated complex* ABC*, also called a reactive intermediate. Thus reaction 5.70 can be described by the mechanism:

$$A + BC \rightarrow ABC^* \qquad 5.52 \quad \text{and} \quad ABC^* \rightarrow AC + B \qquad 5.53$$

The activated complex ABC* is assumed to be in thermodynamic equilibrium with both reactants and products. Hence it is possible to define an equilibrium constant for 5.52 (assuming ideal behavior) as:

$$\mathrm{K}^* = \frac{[\mathrm{ABC}^*]}{[\mathrm{A}][\mathrm{BC}]}$$

as well as a free energy change: $\Delta G^* = -RT \ln \mathrm{K}^*$

and enthalpy and entropy changes: $\Delta G^* = \Delta H^* - T\,\Delta S^*$

Though do so here would take us too far afield, it can be shown from a statistical mechanical approach that the rate constant for 5.52 is:

$$k = \kappa \frac{\mathrm{k}T}{h} \mathrm{K}^* \qquad 5.54$$

where $\mathrm{k}T/h$ is the fundamental frequency as we defined it above, and κ is a constant, called the transmission coefficient, whose value is often close to 1. Equation 5.54 is known as the *Eyring Equation*£. It is then easily shown that the rate constant is:

$$k = \frac{\mathrm{k}T}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} = \frac{\mathrm{k}T}{h} e^{-\Delta G^*/RT} \qquad 5.55$$

Thus if the nature of the activated complex is understood, the rate constant can be calculated. For example, we saw that the partition function is related to entropy and energy (it is also easily shown that is related to Gibbs Free Energy and enthalpy as well). The rate constant can be calculated from partition functions of the activated complex and reactants.

Now consider that reaction 5.51 is reversible so that:

$$\mathrm{A} + \mathrm{BC} \rightleftarrows \mathrm{AC} + \mathrm{B}$$

and that the reverse reaction proceeds through the same activated complex ABC*.

The net rate of reaction is: $\Re_{net} = \Re_+ - \Re_-$ 5.56

If ΔG is the free energy difference between product and reactant, then the free energy difference between the product and the activated complex must be ΔG-ΔG^*. From this it is readily shown (Problem 5.3) that the ratio of the forward and reverse reaction rates is:

$$\frac{\Re_+}{\Re_-} = e^{-\Delta G/RT} \qquad 5.57$$

where ΔG is the actual free energy difference between products and reactants. The negative of ΔG in this context is often called the *affinity of reaction*, *reaction affinity*, or simply *affinity* and is designated A_r (for clarity, however, we shall continue to designate this quantity as ΔG). Substituting 5.57into 5.56 and rearranging, we have:

$$\Re_{net} = \Re_+ (1 - e^{\Delta G/RT}) \qquad 5.58$$

If the forward reaction is an elementary one, then $\Re_+$ will be:

$$\Re_+ = k_+[\mathrm{A}][\mathrm{BC}]$$

where k will be as defined in 5.24.

It must be emphasized that *equations 5.57 and 5.58 apply to elementary reactions only*. However, a similar equation may be written for *overall* reactions:

£ Named for Henry Eyring (1901-1981) who formulated transition state theory in 1935. It was evidently an idea whose time had come, because M. G. Evans and M. Polanyi independently developed the same theory in a paper published the same year. Eyring, who was born in Juarez, Mexico, received his PhD from the University of California at Berkeley in 1929. He worked in the University of Wisconsin, the Kaiser Wilhelm Institut in Berlin (working with Polanyi) and Princeton University before becoming professor of chemistry at the University of Utah in 1946, where he remained for the rest of his life.

$$\Re_{net} = \Re_{+}(1 - e^{n\Delta G/RT}) \qquad 5.59$$

where n can be any real number. Using the Arrhenius expression for k (equ. 5.24), equation 5.59 becomes:

$$\Re_{net} = A_{+}e^{-E_{A+}/RT}(1 - e^{n\Delta G/RT})[A]^{n_A}[B]^{n_B}\ldots \qquad 5.60$$

where [A], [B], ... are the concentrations (surface areas for solids) of the reactants and the *n's* can be any real number (Lasaga, 1981b.)Equation 5.60 links kinetics and thermodynamics and forms the basis of *irreversible thermodynamics*.

If the system is not far from equilibrium, then $\Delta G << RT$ and we may approximate e^x by $1 + x$, so that for an elementary reaction:

$$\Re_{net} \approx -\frac{\Re_{+}\Delta G}{RT} \qquad 5.61$$

Thus close to equilibrium, the reaction rate will vary linearly with ΔG, slowing as equilibrium is approached. Substituting A_r for $-\Delta G$, 5.61 can also be written as:

$$\Re_{net} \approx -\frac{\Re_{+}A_r}{RT} \qquad 5.62$$

At this point, you might think, "this is all fine and good, but how do I calculate ΔG?" There are several approaches to estimating the value of ΔG under non-equilibrium conditions. For the first method, let's return to the relationship between activities, ΔG°, and K. In Chapter 3, we found we could express the relationship between chemical potential and activities *at equilibrium* as:

$$\sum_i \nu_i \mu_i^o + RT \ln \prod_i a_i^{\nu_i} = 0 \qquad (3.84)$$

At equilibrium, the first term on the left is ΔG° and the second term is RT ln K. *Under non-equilibrium conditions*, however, the product of activities will not be equal to K and equation 3.84 will not be equal to 0. Rather, it will have some finite value, which is ΔG. We define a quantity Q as:

$$Q \equiv \prod_i a_i^{\nu_i} \qquad 5.63$$

Q is called the *reaction quotient* (Chapter 3). Though equation 5.63 has the same form as our definition of the equilibrium constant (equ. 3.85), there is an important difference. K defines the relationship between activities *at equilibrium*. In defining Q, we impose no such condition, so that Q is simply the product of activities. At equilibrium Q = K, but not otherwise. Under non-equilibrium conditions, we can express equation 3.86 as:

$$\Delta G^\circ + RT \ln Q = \Delta G \qquad 5.64$$

Since ΔG° is equal to $-RT$ ln K, equ. 5.64 can be written as:

$$RT \ln Q - RT \ln \mathrm{K} = \Delta G \qquad \text{or:} \qquad \frac{Q}{K} = e^{\Delta G/RT} \qquad 5.65$$

Substituting 5.65 into 5.58, we have for an elementary reaction:

$$\Re_{net} = \Re_{+}(1 - \frac{Q}{\mathrm{K}}) \qquad 5.66$$

Thus we expect reaction rates to decrease as $Q \rightarrow$ K.

To arrive at the second method of estimating ΔG, we recall that ΔG may be written as $\Delta H - T\Delta S$. At equilibrium:

$$\Delta G_{eq} = \Delta H_{eq} - T_{eq}\Delta S_{eq} = 0$$

EXAMPLE 5.4: ESTIMATING ΔG^* FOR THE ARAGONITE-CALCITE TRANSITION

Aragonite is the high-pressure form of $CaCO_3$. Upon heating at 1 atm, it will spontaneously revert to calcite. Carlson (1980) heated aragonite crystals containing calcite nuclei to a series of temperatures for fixed times on the heating stage of a microscope, then measured the growth of the calcite nuclei and from that calculated growth rates shown in the adjacent table. Using these data, determine the value of ΔG^* for this reaction.

ARAGONITE TO CALCITE TRANSITION RATES

T °C	R (m/sec)
455	7.45×10^{-09}
435	3.63×10^{-09}
415	1.61×10^{-09}
395	6.24×10^{-10}
375	2.72×10^{-10}

Answer: This is a reversible reaction, so we have to consider that both the forward and reverse of the aragonite → calcite reaction will occur. According to transition state theory, the rate constant for the forward reaction is

$$k_+ = \frac{kT}{h} e^{-\Delta G^*/RT} \qquad (5.55)$$

From equ. 5.60, the rate of the net reaction is:

$$\Re_{net} = \frac{kT}{h} e^{-\Delta G^{*}/RT} (1 - e^{\Delta G/RT})$$

This rate expression has units of time^{-1}, but Carlson's results are given in units of distance/time. How do we reconcile these? We might guess in this case that fundamental frequency, the pre-exponential term, ought to be multiplied by some sort of *fundamental distance*. A fundamental distance is this case would be lattice spacing, which for aragonite is about 5 Å (or 5×10^{-10} m). Thus if λ is the lattice spacing, we have

$$\Re_{net} = \frac{\lambda kT}{h} e^{-\Delta G^{*}/RT} (1 - e^{\Delta G/RT}) \text{ m/s}$$

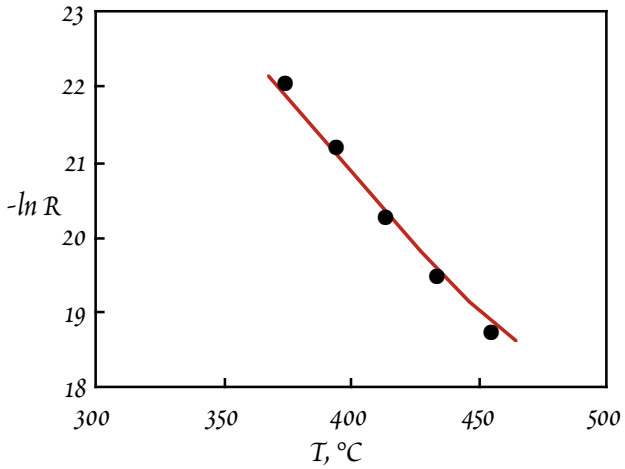


Figure 5.8. Comparison of observed and predicted rates of the aragonite → calcite reaction. Data (circles) from Carlson (1980).

Solving for ΔG^*:

$$\Delta G^* = -RT[\ln \Re_{net} - \ln \frac{\lambda kT}{h} - \ln(1 - e^{\Delta G/RT})]$$

To determine ΔG^*, we have to calculate ΔG, which we can do using the thermodynamic data in Table 2.2 and equation 2.133. Our spreadsheet is shown below. Calculating the average ΔG^* for the 4 measurements, we find ΔG^* = 161 kJ. We can then use ΔG^* to predict the reaction rates. A comparison between the measured and predicted reaction rates is shown in Figure 5.8.

R	8.314	J/mol-K		h	6.63E-34	J-sec		
k	1.38E-23	J/K		λ	5.00E-10	m		
lk/h	1.04E+01	m/K-sec						
					ln(1-exp			
T °C	R m/sec	ln R	T, K	ΔG, J	(ΔG/RT))	ln(lkT/h)	ΔG* kJ	-ln Rcalc
455	7.45E-09	18.7152	728	-2828.8	-0.985	8.933	161.38	18.6485
435	3.63E-09	19.4352	708	-2709.3	-0.997	8.906	160.95	19.4397
415	1.61E-09	20.2452	688	-2592	-1.010	8.877	160.80	20.2756
395	6.24E-10	21.1952	668	-2476.6	-1.022	8.847	161.17	21.1605
375	2.72E-10	22.0252	648	-2363	-1.035	8.817	160.58	22.0986
						ΔG*	**160.98**	ave

where the subscript *eq* denotes the quantity when products and reactants are at equilibrium. Under non-equilibrium conditions, ΔH –TΔS will have some finite value. We can make use of this and write:

$$\Delta G = \Delta H - T\Delta S - (\Delta H_{eq} - T_{eq}\Delta S_{eq}) = \Delta H - \Delta H_{eq} - (T\Delta S - T_{eq}\Delta S_{eq}) \qquad 5.67$$

For temperatures close to the equilibrium temperature, ΔH and ΔS may be considered constant, i.e., independent of temperature, so that 5.67 simplifies to:

$$A_r = -\Delta G = \Delta T \Delta S \qquad 5.68$$

where $\Delta T = (T - T_{eq})$ and is sometimes called the *temperature overstep*. This may be substituted into 5.61, so that close to equilibrium we have

$$\Re_{net} = \frac{-\Re_+ \Delta S(T - T_{eq})}{RT_{eq}} \qquad 5.69$$

Wood and Walther (1983) used this equation to analyze experimental reaction rate studies of a variety of silicate-aqueous fluid reactions. They found that essentially all the experimental data could be fit to this equation if $\Re_+$ is given by:

$$\Re_+ = -k\,A$$

where A is the surface area of the solid phase and *k* is the rate constant. Furthermore, the temperature dependence of the rate constant could be expressed as:

$$\log k = -2900/T - 6.85 \qquad 5.70$$

This is illustrated in Figure 5.7. The data show a scatter of >±1 order of magnitude about the line, so clearly the equation cannot be used for exact prediction of reaction rates. As Kerrick et al. (1991) point out, this approach has limits and cannot be applied to reactions involving carbonates. Nevertheless, Wood and Walther's work provides a useful way to estimate the order of magnitude of silicate dissolution rates.

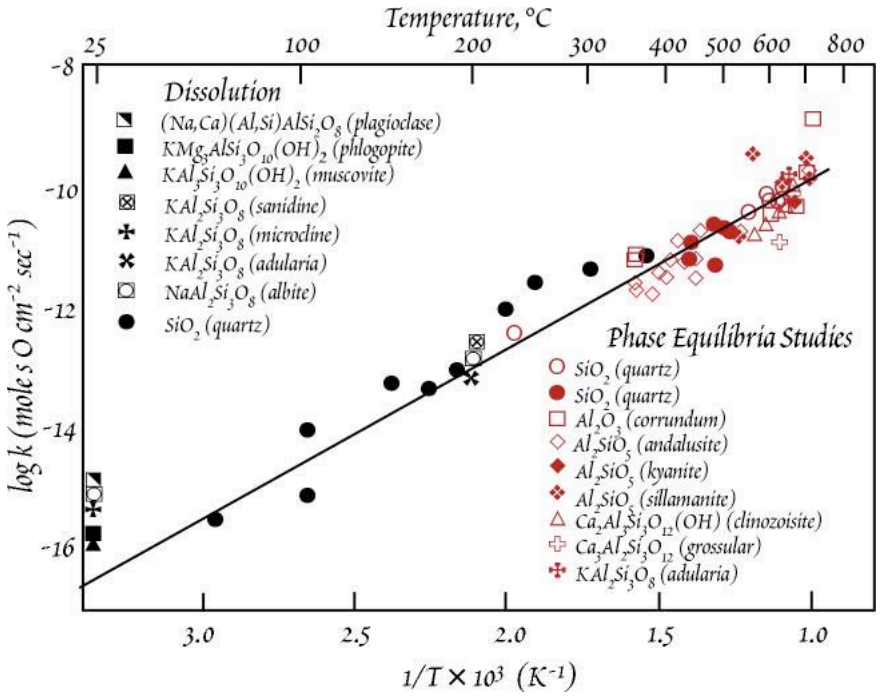


Figure 5.7. Log of the rate constant vs. inverse of temperature for a variety of silicate and aluminate dissolution reactions. Wood and Walther (1983) extracted reaction rate data from both studies of the rates of mineral dissolutions (labeled "Dissolution" and phase equilibria studies (labeled "Phase Equilibria Studies"). Notice that the rate constant has units of mole of oxygen per cc per second. From Wood and Walther (1983).

5.4 Diffusion

We can't stir geochemical reactions. However, nature often provides advection to transport components. In nature, the driving force of advection is gravity: fluids (including the mantle, which behaves as a fluid on geological time scales) move upward or downward because they are lighter or heavier than their surroundings. Just as it does when we stir the tea, advection serves to transport reactants and therefore speed reactions. However, advection is rarely effective on very small scales. On these scales, diffusion is usually the process responsible for transport of chemical components. Except in gases, diffusion is too slow to transport components more than a few meters (and generally less). Consequently, chemical transport generally involves both diffusion and advection: advection for large-scale transport and diffusion for small-scale transport. In this section, we discuss the nature of diffusion and develop the tools necessary to treat it. Because advection depends on the physical properties of materials (density, viscosity), we will not treat it here.

5.4.1 Diffusion Flux and Fick's Laws

Fick's Law[§], or *Fick's First Law*, states that at steady state, the *flux*, *J*, of some species through a plane is proportional to the concentration gradient normal to that plane:

$$\boxed{J = -D\frac{\partial c}{\partial x}} \qquad 5.71$$

The minus sign indicates diffusion is toward the region of lower concentration. The proportionality coefficient, *D*, is the *diffusion coefficient*. *J* has units of mass/area-time, e.g., moles/m^2-sec. If concentration is expressed per unit volume, as is often preferred in kinetics, the diffusion coefficient has units of $m^{-1}sec^{-1}$. The diffusion coefficient must be empirically determined and will depend on the nature of the diffusing species, the material properties of the system in which diffusion is taking place and, as usual, temperature.

Strictly speaking, equation 5.71 is applicable to diffusion in only one dimension. A more general expression of Fick's First Law, applicable in 3 dimensional space is:

$$\mathbf{J} = -D\vec{\nabla}\mathbf{c} \qquad 5.72$$

where ∇c is:

$$\vec{\nabla}c = \frac{\partial c}{\partial x}\mathbf{x} + \frac{\partial c}{\partial y}\mathbf{y} + \frac{\partial c}{\partial z}\mathbf{z}$$

and **x**, **y**, and **z** are unit vectors in the respective directions. Provided the concentration gradient is unidirectional (this will be the case, for example, in an accumulating sequence of sediments), equation 5.72 can be reduced to equation 5.71 simply by choosing the x-direction to be the direction of the concentration gradient.

Now let's consider how concentration will change with time as a consequence of diffusion. Imagine a volume enclosed in a cube of dimension *dx* (Fig. 5.10). Further imagine a diffusion flux of a species of interest through the plane and into the volume at *x* and a flux out of the volume through the plane at *x*+*dx*. Suppose n_x atoms per second pass through the plane at *x* and n_{x+dx} atoms per second pass through

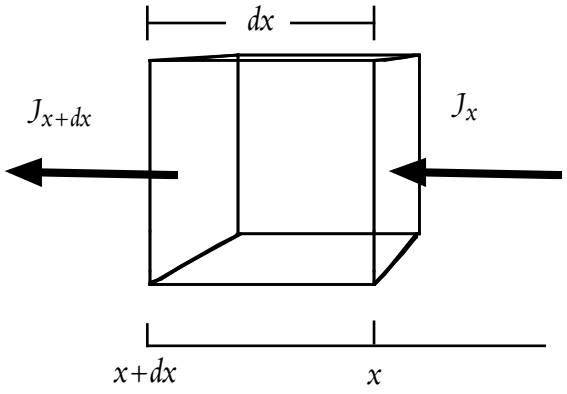


Figure 5.10. A volume of dimension *dx* with fluxes through the planes at *x* and *dx*.

[§]Named for Adolf Fick (1829-1901). Fick was born in Kassel, Germany and earned an MD from the University of Marburg in 1851. Fisk's interest in diffusion through cell membranes led him to formulate the laws that bear his name. It was actually the second law that was published first, in an 1855 paper titled *Über Diffusion*. Fick deduced it by analogy to Fourier's equation for thermal diffusion.

the plane at $x+dx$. The fluxes at the two planes are thus $J_x = n_x/dx^2\text{-}sec$ and $J_{x+dx} = n_{x+dx}/dx^2\text{-}sec$. Conservation of mass dictates that the increase in the number of atoms, dn, within the volume is just what goes in less what goes out. Over an increment of time dt this will be $dn = (J_x - J_{x+dx})dt$. The change in the concentration over this time is just this change in the number of atoms per unit volume:

$$dc = \frac{(J_x - J_{x+dx})dt}{dx}$$

and the rate of change of concentration is:

$$\frac{dc}{dt} = -\frac{(J_{x+dx} - J_x)}{dx}$$

If we specify that we are interested in the change in concentration at some fixed point x and some fixed time t, in the limit of infinitesimal dt and dx, this equation can be written as:

$$\left(\frac{\partial c}{\partial t}\right)_x = -\left(\frac{\partial J}{\partial x}\right)_t \qquad 5.73$$

Equation 5.73 is called the equation of continuity since it follows from mass conservation. Now since the flux is given by Fick's First Law, we can write:

$$\left(\frac{\partial c}{\partial t}\right)_x = -\left(\frac{\partial\left(-D\partial c/\partial x\right)}{\partial x}\right)_t$$

Simplifying, we arrive at *Fick's Second Law:*

$$\boxed{\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t} \qquad 5.74$$

Equation 5.74 tells us that rate of change with time of the concentration at any point is proportional to the second differential of the diffusion profile. Fick's second law is illustrated in Figure 5.11.

5.4.1.1 Solutions to Fick's Second Law

There is no single solution (i.e., function expressing $c(t,x)$) for equation 5.74; rather there are a number of possible solutions, and the solution appropriate to a particular problem will depend on the boundary conditions. Let's consider a few of the simpler ones. In all cases, we assume that the system is uniform in composition in the y and z directions so diffusion occurs only in the x direction.

As a first case, consider a thin film of some diffusing species sandwiched between layers of infinite length having concentration c=0. This might represent a 'doped' layer in a diffusion experiment in the laboratory. In nature, it might represent a thin sedimentary horizon enriched in some species such as iridium (such as the iridium-enriched layer in many sediments at the Cretaceous-Tertiary Bound-

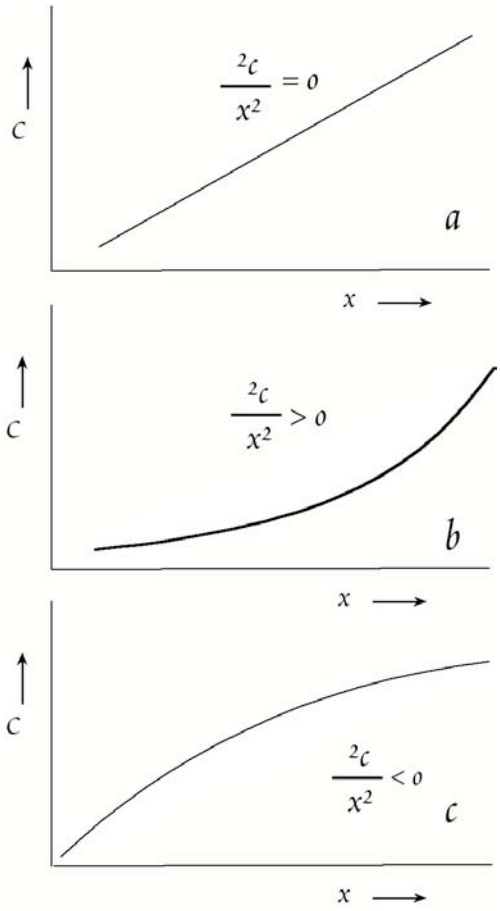


Figure 5.11. Three possible concentration gradients. In a, $\partial^2 c/\partial x^2 = 0$ and therefore $\partial c/\partial t = 0$. Thus for a gradient that is straight, the concentration at any point remains constant (even though there is diffusion along the gradient). This is therefore the steady state case. In case b, $\partial^2 c/\partial x^2 > 0$ and hence the concentration at any point increases with time. In case c, $\partial^2 c/\partial x^2 < 0$ and therefore the concentration at any point decreases with time. Both cases b and c will tend, with time, toward the steady state case, a.

ary). Diffusion will cause the species to migrate away from $x = 0$ as time passes. Mathematically, this situation imposes certain boundary conditions on the solution of 5.74. We take the position of enriched horizon to be 0, and we seek a solution to 5.74 such that at $t = 0$ $c = 0$ everywhere except $x = 0$. At some time $t > 0$, our function should have the property that c approaches 0 as x approaches infinity. We further require that the total amount of the species remain constant, i.e.:

$$M = \int_{-\infty}^{+\infty} c\,dx$$

where M is the total amount of substance in a cylinder of unit cross section and length x.

The solution is given by Crank (1975) as:

$$c(x,t) = \frac{M}{2(\pi Dt)^{1/2}} e^{-x^2/4Dt} \qquad 5.75$$

Figure 5.12 shows how the concentration profile changes with time under these circumstances. It is interesting to note that these profiles are the same as those of a "normal" statistical distribution error curve with a standard deviation $\sigma = (2Dt)^{1/2}$.

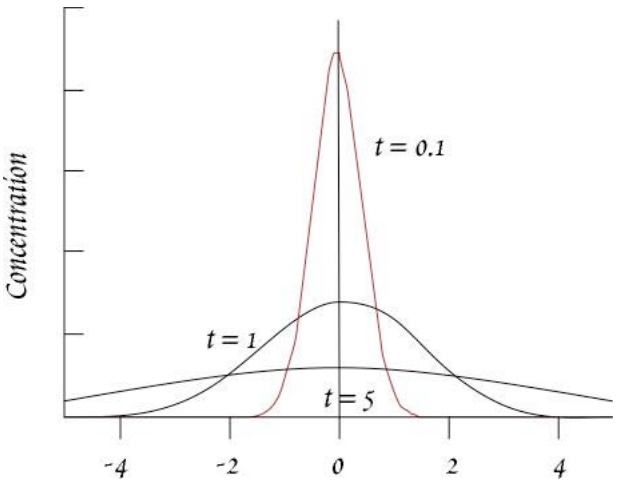


Figure 5.12. Concentration profiles at 3 different times resulting from outward diffusion from an thin film of the diffusing species. Note that the area under the curve remains constant through time.

Suppose a boundary condition is imposed that diffusion can occur only in the positive direction. We can treat this case as if the diffusion in the negative direction is reflected at the plane x = 0. The solution is obtained by superimposing the solution for the negative case on the positive one:

$$c(x,t) = \frac{M}{(\pi Dt)^{1/2}} e^{-x^2/4Dt} \qquad 5.76$$

Now consider a situation where the diffusing species has an initial uniform concentration C_o between $x = 0$ and $x = -\infty$, and 0 concentration between $x = 0$ and $x = \infty$. In the laboratory, this circumstance might arise if we place 2 experimental charges adjacent one and other: one having been 'doped' with the species of interest. In nature, a somewhat analogous situation might be a layer of fresh water overlying a formation brine in an aquifer, or river water overlying seawater in an estuary, or two adjacent crystals.

The solution to this case may be found by imagining the volume between $x = 0$ and $x = -\infty$ as being composed of an infinite number of thin films of thickness $\delta\xi$ (Fig, 5.13). The concentration of the diffusing species at some point x_p at time t is then the sum of the contributions of each imaginary thin film (Crank, 1975). The mathematical solution is obtained by integrating the contribution of all such films:

$$c(x,t) = \frac{C_o}{2(\pi Dt)^{1/2}} \int_x^{\infty} e^{-\xi^2/4Dt} d\xi \qquad 5.77$$

or defining $\eta = \xi / 2\sqrt{Dt}$:

$$c(x,t) = \frac{C_o}{\pi^{1/2}} \int_{x/2\sqrt{Dt}}^{\infty} e^{-\eta^2} d\eta \qquad 5.78$$

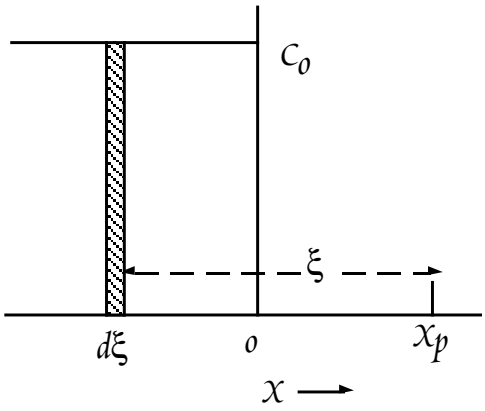


Figure 5.13. An extended initial distribution can be thought of as consisting of an infinite number of thin films of thickness $\delta\xi$. The concentration of a diffusing species at some point x_p is the contribution from each film from distances x to infinity (after Crank, 1975).

The integral in 5.78 may be written as:

$$\int_{\frac{x}{2\sqrt{Dt}}}^{\infty} e^{-\eta^2} d\eta = \int_0^{\infty} e^{-\eta^2} d\eta - \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\eta^2} d\eta \quad 5.79$$

This integral has the form of a standard mathematical function called the *error function*, which is defined as:

$$erf(x) = \frac{2}{\pi^{1/2}} \int_0^x e^{-\eta^2} d\eta \quad 5.80$$

Substituting 5.80 into 5.78 and since erf(∞) = 1, equation 5.78 becomes:

$$c(x,t) = \frac{C_o}{2}\left\{1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right\} \quad 5.81$$

Values for the error function may be found in mathematical tables. The error function is also a standard function in some spreadsheets such as Microsoft Excel™*. Alternatively, it may be approximated as:

$$erf(x) \cong \sqrt{1 - \exp(-4x^2/\pi)} \quad 5.82$$

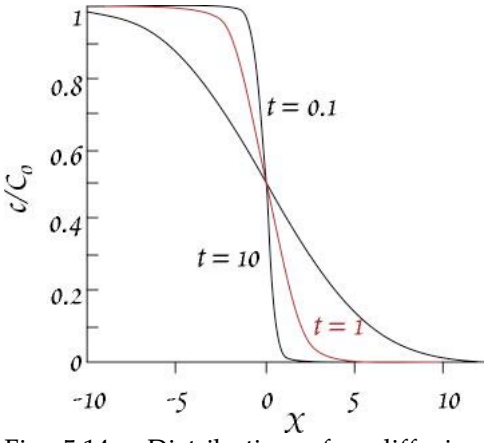


Fig. 5.14. Distribution of a diffusing species initially confined to $-\infty < x < 0$ at three times after diffusion begins.

Figure 5.15 shows how the concentration profile will appear at different times. Since erf (0) = 0, the profiles have the interesting property that $c = C_o/2$ at $x = 0$ at all times.

A similar approach can be used for a diffusing species initially confined to a distinct region, for example: $-h < x < +h$. Examples might be sedimentary or metamorphic layers of finite thickness or a compositionally zoned crystal (Example 5.6). Again, the layer is treated as a series of thin films, but the integration in equation 5.77 is carried out from $-h$ to $+h$. The result is:

$$c(x,t) = \frac{C_0}{2}\left\{erf\left(\frac{h-x}{2\sqrt{Dt}}\right) + erf\left(\frac{h+x}{2\sqrt{Dt}}\right)\right\} \quad 5.83$$

5.4.2 The Diffusion Coefficient and Diffusion in Multicomponent Systems

There are 2 important constraints on diffusion that we have thus far ignored. First, diffusion differs from other kinds of transport in that we specify that there is *no net transport of material across the boundary of interest*. If there is net transport, we are, by definition, dealing with flow or advection rather than diffusion. If this constraint is to be satisfied, movement of one species through a plane must be accompanied by movement of one or more other species in the opposite direction.

The second constraint is electrical neutrality. Diffusion of even small quantities of an ion will quickly lead to the development of a large electric potential. The force associated with the potential would prevent any further diffusion of that ion in that direction. Thus diffusion of an ionic species must be coupled with diffusion of an equal quantity of charge in the opposite direction. In addition to these constraints, we must recognize that diffusion in some cases will lead to non-ideal mixing and the finite enthalpy and volume changes that accompany such situations.

With this in mind, we can recognize four classes of situations and four kinds of diffusion coefficients:

1.) T*racer, or Self- Diffusion*, in which the net mass and charge fluxes associated with the diffusing species is sufficiently small that they can be safely ignored. There maybe no significant concentration gradient. This situation occurs when, for example, an experimental charge is doped with a radioactive

* The error function in Excel, ERF(), is an add-in function found among the "analysis tools". ERF() does not properly treat the case where x < 0. The error function has the property that erf(-x) = -erf (x). In working with Excel, test for a negative value of x and where x is <0 replace ERF (-X) with –ERF(X). IF functions in Excel have the format "IF(logical_test, value_if_true, value_if_false)". So, for example, us a statement such as "=IF(X<0,-ERF(-X),ERF(X))".

isotope in sufficiently small amounts such that the concentration of the element, and hence its chemical potential, does not vary significantly. This is the simplest situation, and the one that we have dealt with thus far.

2.) *Chemical Diffusion* refers to non-ideal situations where chemical potential rather than concen-

EXAMPLE 5.6. DIFFUSION IN A CRYSTAL

Igneous crystals are often zoned as a result of changes in the composition of the magma. Suppose an olivine crystal of 2 mm diameter with a concentration of 2000 ppm Ni suddenly comes in contact with a magma in which its equilibrium concentration should be 500 ppm Ni. How long would it take for diffusion to homogenize the crystal at a temperature of 1250° C, assuming instantaneous equilibration at the crystal-liquid boundary?

Answer: We can treat the olivine crystal as a sphere. Radial symmetry then allows us to consider the problem as a function of radius. We need only consider the variation of concentration along 1 radial direction with $0 < x < r$. Our boundary condition is that at $x = r$ (the edge of the crystal) concentration is held constant by reaction with the liquid. We'll call this concentration C_r. The initial distribution is $c = C_i$ for $0 < x < r$. According to Crank (1975), the solution is:

$$\frac{c - C_i}{C_r - C_i} = 1 + \frac{2r}{\pi x}\sum_{n=1}^{\infty}\frac{-1^n}{n}\sin\left(\frac{n\pi x}{r}\right)\exp\left(\frac{-Dn^2\pi^2 t}{r^2}\right) \qquad 5.84$$

and the concentration at $x = 0$, C_0, is:

$$C_0 = (C_r - C_i)\left\{1 + 2\sum_{n=1}^{\infty} -1^n \exp\left(\frac{-Dn^2\pi^2 t}{r^2}\right)\right\} + C_i \qquad 5.85$$

From equation 5.71, we see that as the concentration gradient disappears, the rate of diffusion goes to 0. So the crystal approaches homogeneity only asymptotically, becoming homogeneous only at $t = \infty$, but it will become *essentially* homogeneous more quickly. *Essentially homogeneous* implies we could not detect a gradient. If our analytical precision is only 5%, we could not detect a gradient of less than 5%. So let's rephrase the question to ask, how will it take before the concentration gradient is less than 5%? We set $C_0/C_r = 1.05$ and substituting into 5.85 and rearranging, we obtain:

$$0.05 \le \left(1 - \frac{C_i}{C_r}\right)2\sum_{n=1}^{\infty} -1^n \exp\left(\frac{-Dn^2\pi^2 t}{r^2}\right) \qquad 5.86$$

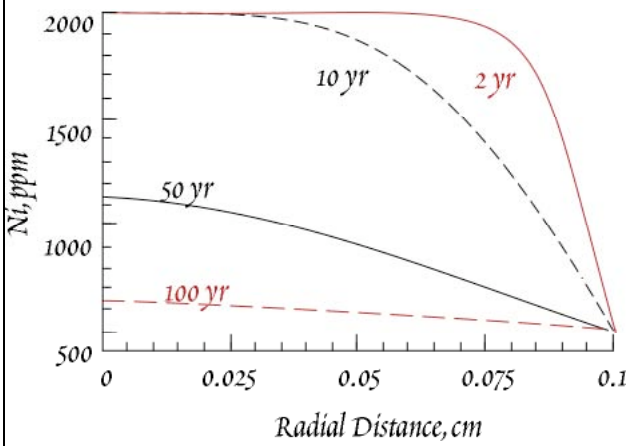


Fig. 5.15. Distribution of Ni in a spherical olivine grain with an initial concentration of 2000 ppm and a rim concentration fixed at 500 ppm.

As it turns out, for relatively large values of t ($Dt/r^2 > 0.1$), the summation converges within 0.05% after the first term, so that 5.86 may be approximated by:

$$t \cong \frac{-r^2}{D\pi^2}\ln\left(\frac{0.05}{2(C_i / C_r - 1)}\right)$$

For the value of $D = 10^{-12}$ cm^2/sec given by Morioka and Nagasawa (1991), we find that about 154 years is required before the olivine homogenizes. If the olivine spent less than this time in contact with the magma, we would expect it to be zoned in Ni concentration. Figure 5.15 shows how the concentration profile of Ni would vary with time.

tration must be considered. In this circumstance, Fick's Laws can be rewritten as:

$$J = -L\frac{\partial \mu}{\partial x} \qquad 5.87 \qquad \text{and} \qquad \left(\frac{\partial c}{\partial t}\right)_t = L\left(\frac{\partial^2 \mu}{\partial x^2}\right)_t \qquad 5.87a$$

L is called the *chemical* or *phenomenological coefficient*. These equations must be used in situations where there is a significant change in composition of the material through which diffusion is occurring, such a chemically zoned liquid or solid, or across a phase boundary. For example, consider an olivine crystal in equilibrium with a surrounding basaltic liquid. There would be a significant change in the concentration of a species such as Mg at the phase boundary, and hence equation 5.71 would predict that, even at equilibrium, diffusion of Mg out of the olivine and into the liquid should occur, but, of course, this will not be the case. However, by specifying that the olivine and the basalt are in equilibrium, we are specifying that the chemical potential of Mg is the same in the olivine and in the melt, and thus equation 5.87 correctly predicts that no diffusion will occur at equilibrium.

Example 5.7. Equilibration between a Mineral Grain and Pore Water

Imagine a grain of calcite in an accumulating sediment surrounded by pore water. Assume that the distribution coefficient of Sr between calcite and water is 100, that the calcite has an initial Sr concentration of 2000 ppm and that a constant Sr concentration of 10ppm is maintained in the water, and that the grain is spherical. If the diffusion coefficient for Sr in calcite is 10^{-15} cm^2/sec and radius of the calcite grain is 1 mm, how will the average concentration of Sr in the grain change with time?

Answer: This problem is similar to the previous example (Example 5.6). This time, however, we want to know the average concentration of the grain. The mass of Sr at time t in a spherical shell of thickness dr is:

$$M(t) = c(r,t)4\pi r^2 dr$$

The average concentration of Sr in the grain at time t is then obtained by integrating and dividing by the volume:

$$\overline{C}(t) = \frac{1}{\frac{4}{3}\pi a^3}\int_0^a c(r,t)4\pi r^2 dr \qquad 5.88$$

where $c(r,t)$ is given by equation 5.85 in Example 5.6. The solution is (Albarède, 1995):

$$\overline{C}(t) = \frac{6C_i}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n}e^{-n^2\pi^2 Dt/a^2} + C_0 \qquad 5.89*$$

where C_i is the initial concentration in the calcite and C_0 is the concentration at the edge of the crystal, which will be in equilibrium with the pore water. The solution is shown Figure 5.16. The grain reaches equilibrium with the pore water within 100,000 to 200,000 years.

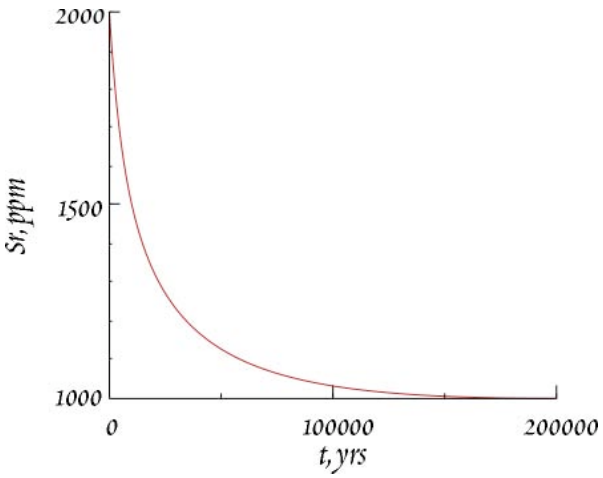


Figure 5.16. Change in the bulk concentration of Sr in a 2 mm diameter calcite grain assuming and initial concentration of 2000 ppm, a constant concentration in the porewater of 10 ppm and a calcite/water distribution coefficient of 100.

* The summation in equation 5.89 is slow if Dt/a^2 is small. An alternative solution to equ. 5.89 is:

$$\overline{C}(t) = 1 - \frac{6\sqrt{Dt}}{a}\left[\sum_{n=1}^{\infty}\frac{e^{-na/\sqrt{Dt}}}{\sqrt{\pi}} - \frac{na}{\sqrt{Dt}}\left\{1 - erf\left(\frac{na}{\sqrt{Dt}}\right)\right\}\right] + 3\frac{Dt}{a^2} \qquad 5.90$$

The two solutions give identical results. They differ only in the ease of computation. For large values of Dt/a^2 the summation in 589 is preferred. For small values of Dt/a^2 5.90 is preferred.

3.) *Multicomponent Diffusion* refers to situations where the concentration of the species of interest is sufficiently large that its diffusion must be coupled with diffusion of other species in the opposite direction to maintain electrical neutrality and/or constant volume. In such a circumstance, the diffusion of any one species is related to the diffusion of all other species. For example, had we considered the diffusion of Mg in olivine in Example 5.6, it would have been necessary to consider the diffusion of Fe in the opposite direction. Under such circumstances, the flux of species *i* is computed as:

$$J_i = -\sum_{k=1}^{n} D_{i,k} \frac{\partial c_k}{\partial x} \qquad 5.91$$

where D_{ik} is the *interdiffusion coefficient* describing the interaction of species *i* and *k*, and *n* is the number of components in the system. Equation 5.91 is known as the *Fick-Onsager Law*. The interdiffusion coefficient is related to the tracer diffusion coefficient as:

$$D_{i,k} = \frac{n_i D_i + n_k D_k}{n_i + n_k} \qquad 5.92$$

where n_i is the mole fraction of *i* and D_i is the tracer diffusion coefficient for *i*. For i = *k*, equation 5.92 reduces to $D_{i,I} = D_i$.

The complete solution for diffusion flux in the system is:

$$\mathbf{J = DC} \qquad 5.93$$

where **J** is the flux vector, **D** is the diffusion coefficient matrix, or tensor, and **C** is the concentration gradient vector:

$$\begin{bmatrix} J_1 \\ J_2 \\ \vdots \\ J_{n-1} \end{bmatrix} = \begin{bmatrix} D_{11} & D_{12} & \cdots & D_{1n-1} \\ D_{21} & D_{22} & \cdots & D_{2n-1} \\ \vdots & \vdots & & \vdots \\ D_{n-11} & D_{n-12} & \cdots & D_{n-1n-1} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_{n-1} \end{bmatrix}$$

where C_i is $\partial c_i/\partial x$ (this is the same as equation 5.93, but in matrix notation). Interdiffusion can result in diffusion up a concentration gradient, because as we can see from equation 5.91, the flux of species *i* depends on the concentration gradients of all species, not just its own.

4.) *Multicomponent Chemical Diffusion* refers to situations where both the chemical potential and the diffusion of other species must be considered. In this case, the diffusion flux is calculated according to equation 5.93, but the diffusion coefficient matrix, **D**, must be calculated as:

$$\mathbf{D = LG} \qquad 5.94$$

Where **L** is the matrix of phenomenological coefficients and the elements of **G**, the thermodynamic matrix, are functions of the derivatives of activity with respect to concentration. The paper of Liang et al. (1997) provides an excellent review of the theory, and the experiments of Watson (1982) provides a good example of the complexity and non-intuitive nature of multicomponent chemical diffusion. In this experiment, a quartz sphere was dissolved in

Example 5.8. Interdiffusion Coefficients

Calculate the diffusion flux for Mn in a garnet given the interdiffusion coefficient matrix below if the concentration gradients are .023 mol/cm, -0.009 mol/cm and -.015 mol/cm for Mn^{2+}, Mg^{2+}, and Fe^{2+} respectively.

Diffusion Coefficient Matrix for Garnet

	Mn	Mg	Fe
Mn	8.38×10^{-20}	-9.91×10^{-20}	-4.68×10^{-21}
Mg	-2.78×10^{-20}	7.26×10^{-21}	-8.81×10^{-23}
Fe	-7.16×10^{-20}	-4.81×10^{-23}	1.19×10^{-20}

from Demspter (1975).

Answer: we calculate the diffusion flux for Mn using equation 5.91. We find that J_{Mn} is 3×10^{-21} mole/cm^2-sec.

molten basalt. All elements except SiO_2 were diffusing out of the basalt into SiO_2-rich liquid. Figure 5.17 shows concentration profiles in which Na and K are actually diffusing in the direction of higher concentration.

Although diffusion is treated differently in different circumstances, it is important to bear in mind that the mechanism on a microscopic scale is always the same: it results from the random motion of atoms or molecules. Reference is sometimes made to the 'driving force' of diffusion, taken either as the concentration or chemical potential gradient. While it may sometimes be convenient to think in terms of 'driving forces', these forces are not real.

To demonstrate this point, we can derive Fick's first law just from a consideration of random atomic motion. Consider two adjacent lattice planes in a crystal spaced a distance dx apart. Let the number of atoms of the element of interest at the first plane be n_1 and the number of atoms at the second be n_2. We assume that atoms can change position randomly by jumping to an adjacent plane and that this occurs with an average frequency ν (i.e., 1 jump of distance dx every $1/\nu$ sec). We further assume that there are no external forces, so that a jump in any direction has equal probability. At the first plane there will be $\nu n_1/6$ atoms that jump to the second plane (we divide by 6 because there are 6 possible jump directions: up, down, back, front, right, left). At the second plane there will be $\nu n_2/6$ atoms that jump to first plane. The net flux from the first plane to the second is then:

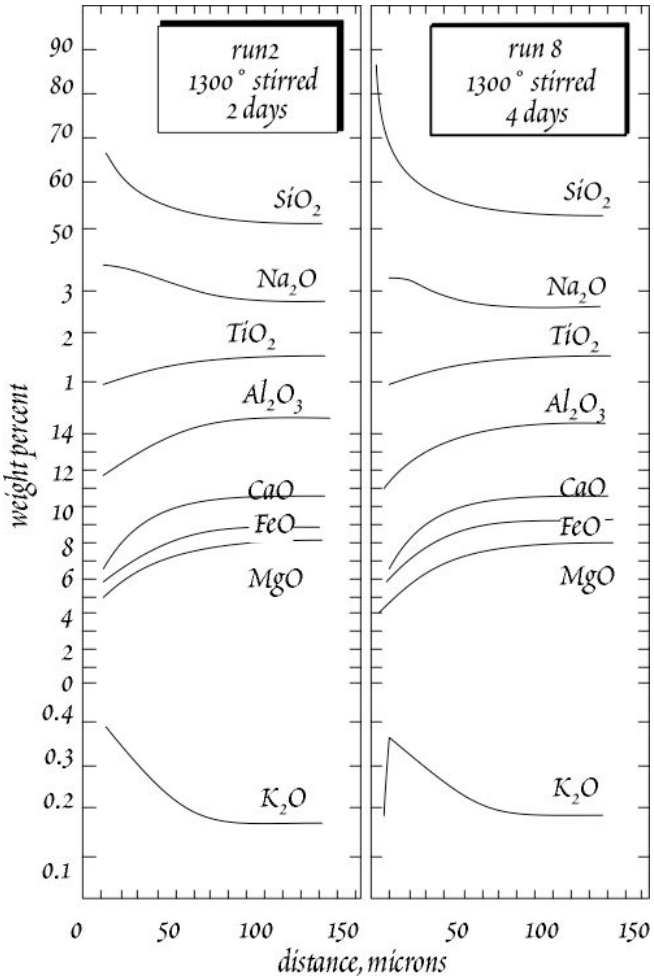


Figure 5.17. Electron microprobe traverses across boundary layers of melt in contact with dissolving quartz spheres. Quartz is to the left at zero microns. Note that K_2O and Na_2O are diffusing 'uphill', that is, toward higher K_2O and Na_2O concentrations in the SiO_2-rich liquid. From Watson (1982).

$$J = \frac{\nu n_1/6 - \nu n_2/6}{dx^2} = \frac{\nu}{6}\frac{(n_1 - n_2)}{dx^2} \qquad 5.95$$

The concentration, c, is the number of atoms of interest per unit volume, i.e., n/dx^3, so we may substitute cdx^3 for the number of atoms in 5.95:

$$J = \frac{\nu}{6}\frac{(c_1 - c_2)dx^3}{dx^2} = \frac{\nu}{6}(c_1 - c_2)dx$$

Letting $dc = -(c_1 - c_2)$, we can rewrite this equation as:

$$J = -\frac{\nu dx^2}{6}\frac{dc}{dx}$$

If we let $D = \nu dx^2/6$ then we have Fick's first law:

$$J = -D\frac{dc}{dx}$$

Hence D is related to the jump frequency, ν, and square of the jump distance (dx).

We see that there is a net diffusion, not because of the presence of a force, but only because there are more atoms at one point than at an adjacent one. In the absence of a concentration gradient (i.e., n_1 and n_2 the same, there would be $nv/6$ atoms moving from the first to the second plane and $nv/6$ atoms moving from second to the first plane. But if we cannot distinguish atoms originally at the first plane from those originally at the second, these fluxes balance and go unnoticed. If we could distinguish the atoms, we could detect a flux even in the absence of a concentration gradient. Other factors, such as pressure or stress gradient, presence of an electromagnetic field, a temperature gradient, or concentration gradients of other species may make a jump in one direction more probable than another, as can differences in chemical potential between the two planes. Such 'forces' will affect the diffusion flux and terms must be added to the diffusion equations to account for them. The point we are stressing here is that diffusion can occur in the absence of all such forces.

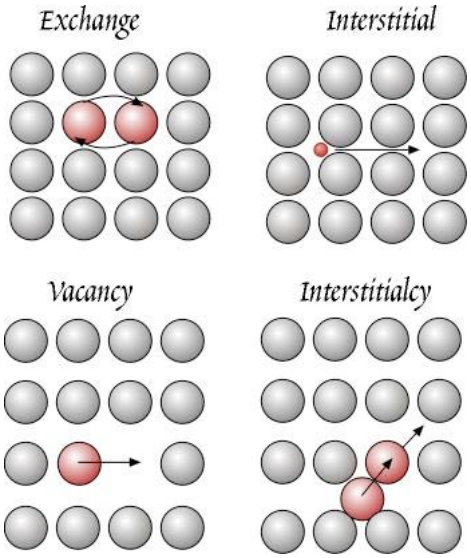


Figure 5.18. Four types of diffusion mechanisms in solids. After Broecker and Oversby (1971).

5.4.3 Diffusion in Solids and the Temperature Dependence of the Diffusion Coefficient

We can imagine four ways in which diffusion might take place in solids (Figure 5.18):

1.) *Exchange*: the interchange of position of two atoms in adjacent sites.

2.) *Interstitial*: in which an atom moves from one interstitial site to another.

3.) *Interstitialcy*: in which an atom is displaced from a lattice site into an interstitial site.

4.) *Vacancy*: in which an atom moves from a lattice site to a vacancy, creating a vacancy behind it.

Mechanisms 1 and 3 involve displacement of two atoms and therefore have high activation energies. Since interstitial sites are likely to be small, mechanism 2 will apply mainly to small atoms (H and He, for example). Thus we are left with mechanism four as a principal mechanism of diffusion in solids.

Hence, diffusion in solids is a bit like a game of checkers: an atom can generally only travel by moving from lattice site to lattice site. Furthermore, it can only move to a vacant lattice site (and one of the correct type). In general, lattice vacancies are of two types: permanent and temporary. Permanent vacancies can arise from defects or through the presence of impurities, for example through substitution of a doubly charged ion for a singly charged one with a vacancy providing charge balance. Temporary sites arise from thermal agitation causing the volume of the solid to be slightly greater than the ideal volume by forcing atoms onto the surface. The number of the former is temperature independent, the latter are temperature dependent.

Let's attempt to calculate a diffusion coefficient *ab initio* for the simple one-dimensional case of tracer diffusion in a solid occurring through the vacancy mechanism. Since a certain minimum energy is required to get an ion out of the lattice site 'energy well' we would expect the number of the temporary vacancies to have a temperature dependence of the form of equation 5.16, the Boltzmann distribution law. Thus the number of lattice vacancies can be written as:

$$N_{vac} = N_{perm} + ke^{-E_H/RT}$$

where k is some constant and E_H is an activation energy needed to create a vacancy or 'hole'.

The probability, $\mathcal{P}$, of an atom making a successful jump to a vacant site is found by multiplying the number of attempts, $\aleph$, by the fractions of atoms having sufficient energy to get out of the well:

$$\mathcal{P} = \aleph e^{-E_B/RT} \qquad 5.96$$

The number of attempts is simply the vibration rate, ν, times the number of holes:

$$\aleph = \nu[N_{vac}] = \nu\left[N_{perm} + ke^{-E_H/RT}\right] \qquad 5.97$$

Combining 5.96 and 5.97 we have:

$$\mathcal{P} = vN_{perm}e^{-E_B/RT} + vke^{-(E_H+E_B)/RT}$$

The diffusion rate should be the number of jumps times the distance per jump, d:

$$\Re = vdN_{perm}e^{-E_B/RT} + vdke^{-(E_H+E_B)/RT} \quad 5.98$$

or

$$\Re = me^{-E_B/RT} + ne^{-(E_H+E_B)/RT} \quad 5.99$$

where n and m are simply two constants replacing the corresponding terms in equation 5.98. Thus diffusion rates generally will have a temperature dependence similar to equation 5.24. At low temperature, the permanent vacancies will dominate and diffusion rate equation will look like:

$$\Re \cong me^{-E_B/RT} \quad 5.100$$

At higher temperature where thermally generated vacancies come into play, the latter term in 5.99 dominates and the diffusion rate equation will look like:

$$\Re \cong ne^{-(E_H+E_B)/RT} \quad 5.101$$

Diffusion that depends on thermally created vacancies is sometimes called *intrinsic* diffusion, while that depending on permanent vacancies is called *extrinsic* diffusion. The boundary between these regions will vary, depending on the nature of the material and the impurities present. For NaCl, the transition occurs around 500° C, for silicates it generally occurs above 1000° C. Where the diffusion mechanism changes, a break in slope can be observed on a plot of ln D vs. 1/T. For example, Figure 5.19 shows how the diffusion coefficient might change based on equations 5.100 and 5.101.

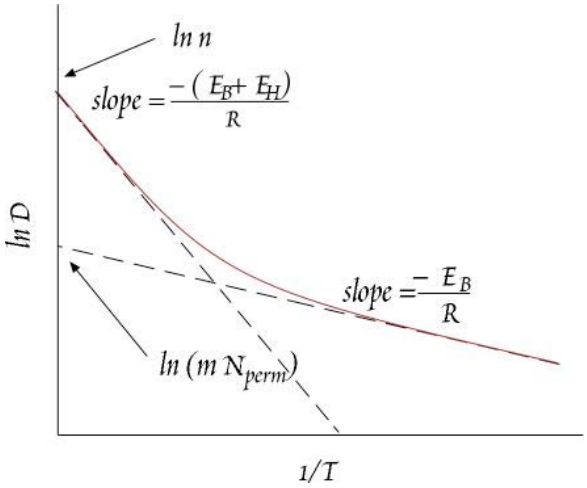


Fig. 5.19. Arrhenius plot illustrating how the change in diffusion mechanism from intrinsic to extrinsic can result in a break in slope.

Combining E_B and E_H into a single activation energy term, E_A, which is the energy necessary to create the vacancy and move another atom into it, a typical expression for temperature dependence of the diffusion coefficient in solids is:

$$\boxed{D = D_o e^{-E_a/RT}} \quad 5.102$$

where D_o is again called the frequency factor. As we have seen, it will depend on vibrational frequency and the distance of the interatomic jump.

Experimental observation supports our theoretical expectation of an exponential temperature dependence of diffusion, for example, in a series of measurements of the diffusion coefficient, D, at various temperatures (Figure 5.19). Taking the log of both sides of equation 5.102, we obtain:

$$\ln D = \ln D_o - \frac{E_A}{RT}$$

Thus on a plot of ln D versus reciprocal temperature, data for diffusion of a given element in a given substance should plot alone a line with slope E_A/R and intercept D_0 (Figure 5.20). Values for the activation energy are generally similar for most ele-

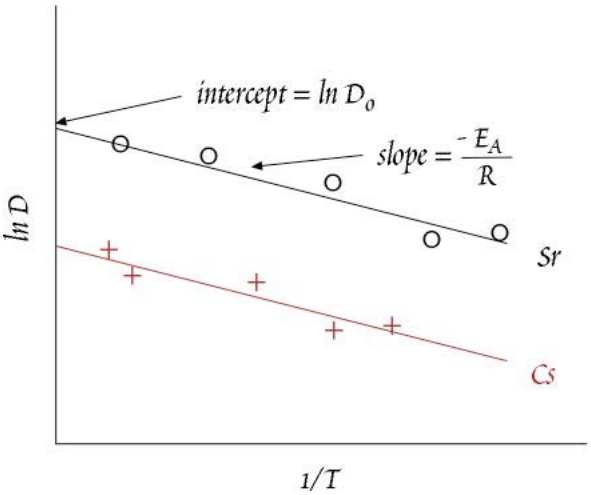


Figure 5.20. Schematic plot of log diffusion rate against inverse of temperature (Arrhenius plot) for two elements: Cs and Sr.

ments (typically 50 to 200 kJ), but the frequency factor varies widely. Table 5.2 list frequency factors and activation energies for several elements in various geological materials.

The pressure dependence of the diffusion coefficient is:

$$D = D_o e^{-(E_A + (P - P_{ref})\Delta V)/RT} \quad 5.103$$

where ΔV is the "activation volume".

5.4.4 Diffusion in Liquids

In both liquids and solids, diffusion coefficients depend on both the nature of the diffusing species and the nature of the media. As you might expect, small atoms generally diffuse more rapidly than large ions. The value of the diffusion coefficient in liquids can be estimated in a number of ways. Based on a model of molecular motion in a *non-ionic* liquid composed of molecules of diameter *d*, and assuming a kinetic energy per atom of 3k*T*/2 and a mean free path length of 2α*dT*, where α is the coefficient of thermal expansion, *m* is molecular mass and k is Boltzmann's constant, the diffusion coefficient may be estimated as (Kirkaldy and Young, 1985):

$$D \cong \alpha d \sqrt{\frac{8k}{\pi m}} T^{3/2} \quad 5.104$$

This predicts a diffusion coefficient near the melting point of 10^{-4} cm/sec.

Diffusion coefficients in liquids are also commonly expressed in terms of viscosity. For uncharged species, the dependence of the diffusion coefficient on molecular radius and viscosity is expressed by the *Stokes-Einstein Equation*:

$$D = \frac{kT}{6\pi\eta r} \quad 5.105$$

where *r* is molecular radius and η is viscosity. From this equation, we see that diffusion becomes more difficult as the liquid becomes more structured (polymerized) because the viscosity increases with increasing polymerization.

Table 5.2: Frequency Factors & Activation Energies

Species	Phase	Temp. Range ° C	D_o cm^2/sec	E_A kJ/mol
Fe	Olivine	1125-1200	5.59×10^{-02}	264
Fe	Olivine	1000-1125	5.90×10^{-07}	133
Mg	Olivine	1000-1150	1.82×10^{-08}	143
Mn	garnet	750-1475	5.15×10^{-04}	145
Fe	garnet	750-1475	6.39×10^{-04}	157
O	β-Qz	1010-1220	3.70×10^{-13}	230
O	Anorthite	800-1300	9.00×10^{-10}	234
Cr	Spinel	1200-1600	2.40×10^{-06}	337
Sr	Basaltic melt	1250-1450	0.278	104
Ca	Basaltic melt	1250-1450	0.535	105
Ba	Basaltic melt	1250-1450	0.059	94
Cs	Basaltic melt	1300-1400	110	272
Co	Basaltic melt	1250-1450	0.053	86
Ba	Andesitic melt	1300-1400	0.44	209
Sr	Andesitic melt	1300-1400	3.5	213
Co	Andesitic melt	1300-1400	160	280
Pb	Plagioclase	700-1050	1.86×10^{-03}	266
Pb	K-feldspar	700-1050	1.82×10^{-01}	309
Sr	Plagioclase	700-1050	1.78×10^{-03}	265
Na	albite	600-800	1.25×10^{-01}	100
Sr	orthoclase	800-870	6.00×10^{-06}	98
H_2O	obsidian	500-980	1.50×10^{-08}	27

Table 5.3 Trace Diffusion Coefficients for Ions in Infinitely Dilution Solution at 25°C.

Cation	D°	Anion	D°
	$10^{-6}cm^{-2}sec^{-1}$		$10^{-6}cm^{-2}sec^{-1}$
H^+	93.1	OH^-	52.7
Na^+	13.3	Cl^-	20.3
K^+	19.6	I^-	20.0
Mg^{2+}	7.05	SO_4^{2-}	10.7
Ca^{2+}	7.93	CO_3^{2-}	9.55
Sr^{2+}	7.94	HCO_3^{2-}	11.8
Ba^{2+}	8.48	NO_3^-	19.0
Fe^{2+}	7.19		
La^{3+}	6.17		

From Lasaga (1997).

Because of the electrical neutrality effect, ion charge is important in diffusion of ions. In aqueous electrolytes, tracer diffusion coefficients depend on ion charge as:

$$D^o = \frac{RT\lambda^o}{|z|\mathcal{F}^2} \qquad 5.106$$

where λ° is the limiting ionic conductance (conductance extrapolated to infinite dilution) of the ion (in $cm^2/ohm\text{-}equivalent$), $\mathcal{F}$ is Faraday's constant, and z is the charge of the ion. The limiting ionic conductance is itself a function of temperature, which leads to a strong dependence of D° on temperature. The naught (°) denotes the standard state of infinite dilution. Table 5.3 lists values of D° for a few ions of geochemical interest. In dilution solution, diffusion coefficients depend approximately on the square root of ionic strength. In more concentrated solutions, diffusion coefficients show a complex dependence on ionic strength, the treatment of which is beyond the scope of this book. Discussions of this problem may be found in Anderson (1981), Tyrell and Harris (1984), and Lasaga (1997).

5.5 Surfaces, Interfaces, and Interface Processes

The properties of a phase at its surface are different from the bulk properties of the phase. This difference arises from the difference between the local environment of atoms on a surface or interface and those in the interior of a phase. An atom at the surface of a crystal is not surrounded by the same bonds and distribution of charges as it would be in the interior of the crystal lattice. Its potential energy must therefore be different. Here we define *surface* as the exterior boundary of a condensed phase (a solid or liquid) in a vacuum or gas. An *interface* is the boundary between two condensed phases, for example, between 2 crystals or between a mineral and water (the term 'surface' is, however, often used for what we have just defined as an interface). Surfaces, surface energies, and interfaces play an important role in many geochemical processes. All heterogeneous reactions, i.e., those involving more than 1 phase, must always involve interfaces or surfaces. Dissolution, melting, exsolution, and precipitation are examples of processes that, on an atomic scale, occur entirely at or near the interface between two phases. Surfaces can also play important roles as catalysts in many geochemical reactions.

On a microscopic scale, the reactivity of mineral surfaces will vary locally for several reasons. The first is the microtopography of the surface (Figure 5.21). For example, a single growth unit (which might be a single atom, an ion, or molecule and called an *adatom*), located on an otherwise flat surface will be particularly unstable because it is bonded to other units on only one side. A *step* (which might be formed through growth, dissolution, or *screw dislocation*) provides a more favorable growth site because the new unit is bound to other units on 2 sides. An even better site for growth is at a *kink*, where bonds may be formed on 3 sides. Conversely, a unit at a kink (with 3 exposed sides) is less stable than one at a step (with 2 exposed sides), which in turn is less stable than a unit on a flat surface, with only 1 exposed side. The point is, kinks and steps will be more reactive than other features, so surface reactions rates will depend in part on the density of these features.

Properties of mineral surfaces will also vary depending on the orientation of the surface relative to crystallographic axes. Most minerals grow or dissolve faster in one direction than in another. Most surface reactions involve the formation of new bonds between atoms of a mineral and atoms of the adjacent phase; the nature of the bonds that are possible will depend on the orientation of the surface relative to crystallographic axes. Reaction rates measured for one crystal face may not be representative of other faces.

Finally, almost all minerals have a variety of atoms and crystallographic sites, hence there will be a variety of bonds that are possible on any surface. We will discuss this aspect of surfaces in slightly more detail below.

5.5.1 The Surface Free Energy

In Chapters 2 and 3, we introduced the concept of molar quantities and partial molar quantities. For example, the molar volume of a substance was:

$$\overline{V} = \frac{V}{n}$$

and we defined the partial molar volume as:

$$v_i^\phi = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \tag{3.11}$$

We now define 2 new quantities, the *molar surface area*:

$$\overline{A} = \frac{A}{n} \tag{5.107}$$

and the *partial molar surface area*:

$$a_i^\phi = \left(\frac{\partial A}{\partial n_i}\right)_{T,P,n_j} \tag{5.108}$$

where A is the surface area of the phase. The molar volume or the molar Gibbs Free Energy of pure quartz depends only on temperature and pressure. Thus the molar volume of each (pure) quartz crystal is the same as that of every other (pure) quartz crystal at that temperature and pressure. Unlike other molar quantities, the *molar surface area and partial molar surface area depend on shape and size*, and are therefore not intrinsic properties of the substance. For a sphere, for example, the partial molar surface area is related to molar volume as:

$$a = \frac{\partial A}{\partial V}\frac{\partial V}{\partial n} = \frac{2v}{r} \tag{5.109}$$

For other shapes, the relationship between a and v will be different.

Finally, we define the *surface free energy* of phase ϕ as:

$$\sigma^\phi \equiv \left(\frac{\partial G}{\partial A}\right)^\phi_{T,P,n} \tag{5.110}$$

The surface free energy represents those energetic effects that arise because of the difference in atomic environment on the surface of a phase. Surface free energy is closely related to surface tension. The total surface free energy of a phase is minimized by minimizing the phase's surface area. Thus a water drop in the absence of other forces will tend to form a sphere, the shape that minimizes surface area. When surface effects must be considered we can revise the Gibbs Free Energy equation (equ. 3.14) to be:

$$dG = VdP - SdT + \sum_i \mu_i dn_i + \sum_k \sigma_k dA_k \tag{5.111}$$

where the last sum is taken over all the interfaces of a system. In this sense different crystallographic faces have different surface free energies. The last term in 5.111 increases in importance as size decreases. This is because the surface area for a given volume or mass of a phase will be greatest when particle size is small.

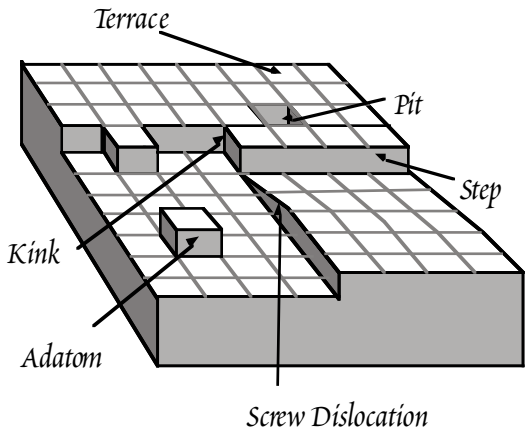


Figure 5.21. On a microscopic scale, the surface of a mineral exhibits a number of features. As a result, the local reactivity of the surface will be quite variable.

5.5.2 The Kelvin Effect

When the size of phases involved is sufficiently small, surface free energy can have the effect of displacing equilibrium. For an equilibrium system at constant temperature and pressure, equation 5.111 becomes:

$$0 = \sum_i \nu_i \mu_i^o + RT\sum_i \nu_i \ln a_i + \sum_k \sigma_k dA_k$$

The first term on the right is ΔG°, which according to 3.86 is equal to $-RT$ ln K. This is the 'normal' equilibrium constant, uninfluenced by surface free energy, so we'll call it K°. We will call the summation in the second term

K^s, the equilibrium influenced by surface free energy. Making these substitutions and rearranging, we have:

$$\ln K^s = \ln K^\circ - \frac{\sum \sigma_k dA_k}{RT} \qquad 5.112$$

Thus we predict that equilibrium can be shifted due to surface free energy, and the shift will depend on the surface or interfacial area. This is known as the *Kelvin Effect*.

There are a number of examples of this effect. For example, fine, and therefore high surface area, particles are more soluble than coarser particles of the same composition. Water has a surface free energy of about 70 mJ/m^2. Consequently, humidity in clouds and fogs can reach 110% when droplet size is small.

5.5.3 Nucleation and Crystal Growth

5.5.3.1 Nucleation

Liquids often become significantly oversaturated with respect to some species before crystallization begins. This applies to silicate liquids as well as aqueous solutions (surface seawater is several times oversaturated with respect to calcite). However, crystallization of such supersaturated solutions will often begin as soon as seed crystals are added. This suggests that nucleation is an important barrier to crystallization. This barrier arises because the formation of a crystal requires a local increase in free energy due to the surface free energy at the solid-liquid interface.

Let's explore how nucleation can be inhibited a bit further. For a crystal growing in a liquid, we can express the complete free energy change as:

$$dG_{tot} = \sigma dA + dG_{xt} \qquad 5.113$$

where dG_{xt} refers to the free energy change of the crystallization reaction that apply throughout the volume of the crystal (i.e., free energy in the usual sense, neglecting surface effects).

Let's consider a more specific example, that of a spherical crystal of phase ϕ growing from a liquid solution of component ϕ. The free energy change over some finite growth interval is:

$$\Delta G_{tot} = 4\pi r^2\sigma + \frac{4}{3}\pi r^3 \frac{\Delta G_{xt}}{\bar{V}} \qquad 5.114$$

where r is the radius (we divide by $\bar{V}$ to convert joules per mole to joules per unit volume). The first term is on the right is the surface free energy, and, although small, *is always positive*. At the point where the solution is exactly saturated ΔG will be 0. The net free energy, ΔG_{tot}, is thus positive, so the crystal will tend to dissolve. In order for spontaneous nucleation to occur, the second term on the right must be negative and its absolute value must exceed that of the first term on the right of 5.114, i.e., the liquid must be supersaturated for nucleation to occur. Solving 5.114 for r, we find that ΔG_{tot} is ≤ 0 when $r \ge -3\sigma/\Delta G$.

How will ΔG vary with r up to this point? To answer this, we differentiate 5.114 with respect to r:

$$\frac{\partial \Delta G_{tot}}{\partial r} = 8\pi r\sigma + 4\pi r^2 \frac{\Delta G_{xt}}{\bar{V}} \qquad 5.115$$

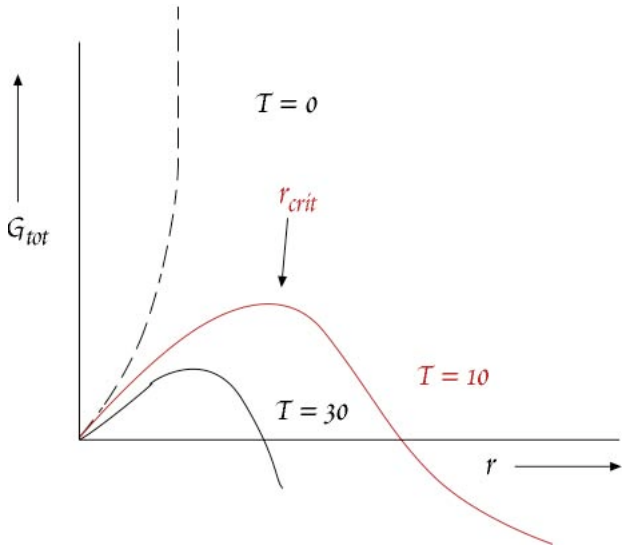


Figure 5.22. Free energy as a function of crystal radius for small crystals forming near the saturation point. ΔT is the amount of undercooling (difference between temperature and saturation temperature).

Since the volume free energy term is proportional to r^2 and the surface free energy term to r, the latter necessarily dominates at very small values of r. For small values of r, ΔG_{tot} will increase with increasing r because σ is always positive. In other words, near the saturation point where ΔG is small, very small crystals will become increasingly unstable as they grow. The critical value of r, that is the value at which ΔG will decrease upon further growth, occurs where $\partial G/\partial r = 0$. Solving equation 5.115, we find that

$$r_{crit} = -\frac{2\sigma}{\Delta G_{xt}/\overline{V}} \qquad 5.116$$

For a solution that undergoes cooling and becomes increasingly saturated as a result (e.g., a magma or a cooling hydrothermal solution), we can use equation 5.68 to approximate the ΔG term (i.e., $\Delta G \cong -\Delta T \Delta S$, where ΔT is the difference between actually temperature and the temperature at which saturation occurs and ΔS is the entropy change of crystallization). Figure 5.22 shows the total free energy calculated in this way as a function of r for various amounts of undercooling.

The surface free energy term correlates with viscosity. Thus nucleation should require less supersaturation for aqueous solutions than silicate melts. Among silicate melts, nucleation should occur more readily in basaltic ones, which have low viscosities, than in rhyolitic ones, which have high viscosities. This is what one observes. Also, we might expect rapid cooling to lead to greater supersaturation than slow cooling. This is because there is an element of chance involved in formation of a crystal nucleus (the chance of bringing enough of the necessary components together in the liquid so that r exceeds r_{crit}). Slow cooling provides time for this statistically unlikely event to occur, and prevents high degrees of supersaturation from arising. With rapid cooling, crystallization is postponed until ΔG_r is large, when many nuclei will be produced. Let's briefly consider nucleation rates in more detail.

5.5.3.2 Nucleation Rate

The first step in crystallization from a liquid is the formation of small clusters of atoms having the composition of the crystallizing phase. These so-called *heterophase fluctuations* arise purely because of statistical fluctuations in the distribution of atoms and molecules in the liquid. These fluctuations cause local variations in the free energy of the liquid, and therefore their distribution can be described by the Boltzmann distribution law:

$$N_i = N_v e^{-\Delta G_{xt}/kT}$$

where N_i is the number of clusters per unit volume containing i atoms, N_v is the number of atoms per unit volume of the cluster, and ΔG_i is the difference between the free energy of the cluster and that of the liquid as a whole. The number of clusters having the critical size (r_{crit}) is:

$$N_{crit} = N_v e^{-\Delta G_{crit}/kT}$$

where ΔG_{crit} is the total free energy (ΔG_{tot}) of clusters with critical radius obtained by solving equation 5.113 when $r = r_{crit}$. For spherical clusters, this is:

$$\Delta G_{crit} = \frac{16\pi}{3}\frac{\sigma^3 \overline{V}}{\Delta G_{xt}^2} \qquad 5.117$$

Substituting equation 5.68 for ΔG_r, we have:

$$\Delta G_{crit} = \frac{16\pi}{3}\frac{\sigma^3 \overline{V}}{(\Delta T \Delta S_{xt})^2} \qquad 5.118$$

If E_A is the activation energy associated with attachment of an additional atom to a cluster, then the probability of an atom having this energy is again given by the Boltzmann distribution law:

$$\mathcal{P} = e^{-E_A/kT}$$

Now according to transition state theory, the frequency of attempts, ν, to overcome this energy is simply the fundamental frequency $\nu = kT/h$. The attachment frequency is then the number of atoms adjacent to the cluster, N^*, times the number of attempts times the probability of success:

$$N^* \nu \mathcal{P} = N^* \frac{kT}{h} e^{-E_A/kT} \quad 5.119$$

The nucleation rate, *I*, is then the attachment frequency times the number of clusters of critical radius:

$$I = N_{crit} N^* \nu \mathcal{P} = N^* \frac{kT}{h} e^{-E_A/kT} e^{-\Delta G_{crit}/kT} \quad 5.120$$

Combining the frequency of attachment terms into a pre-exponential frequency factor A, and substituting 5.118 into 5.120 we have:

$$I = Ae^{-16\pi\sigma^3 \bar{V}^2/(3\Delta G^2 kT)} \quad 5.121$$

which is the usual expression for nucleation rate (e.g., McLean, 1965). If we substitute 5.68 into 5.121, we see that:

$$I = Ae^{-16\pi\sigma^3 \bar{V}^2/3(\Delta S \Delta T)^2 kT} \quad \text{or} \quad I \propto e^{-1/\Delta T^2} \quad 5.122$$

Example 5.9. Nucleation of Diopside

The enthalpy of fusion of diopside is 138 kJ/mol and its melting temperature is 1665 K. Assuming an activation energy of 1 × 10^{-18} J, how will the nucleation rate of diopside crystals in a diopside melt vary with temperature for surface free energies of 0.02, 0.06, and 0.12 J/m^2?

Answer: The one additional piece of information we need here is the molar volume, which we find to be 66 cc/mol from Table 2.2. We can calculate ΔS_m from the relation:

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

Assuming ΔS_m, σ, and E_A are indepe ndent of temperature, we can use equations 5.120 and 5.118 to calculate the nucleation rate. The calculation for the 3 surface free en ergies is shown in Figure 5.23a. Nucleation will be experimentally observable when the nucleation rate reaches ≈10^{-10} m^{-2}, which corresponds roughly to 1 nuclei/cm^2/hr. For a surface free energy of 0.02 J/m^2, the rate is reached only a few kelvins below the melting point. Further undercooling results in very high nucleation rates. For a surface energy of 0.06 J/m^2, an undercooling of 35 K is required, and an u ndercooling of 130 K is required at the highest value of surface energy. In the latter case, the rise in nucleation rate with undercooling is not nearly as steep.

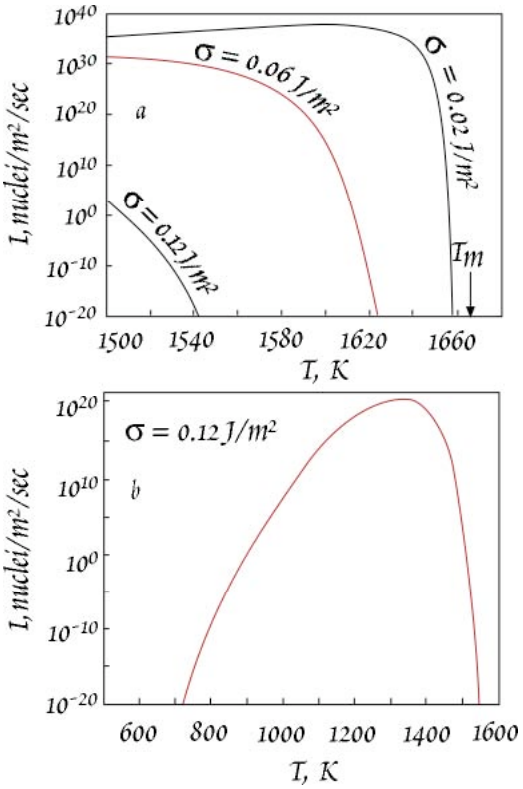


Figure 5.23. Calculated nucleation rate of diopside in diopside melt as a function of temperature.

In Figure 5.23b, we see that the nucleation rate passes through a maximum and as undercooling proceeds further, the rate decreases. This decrease reflects the 1/T dependence of both exponential terms in equation 5.120, i.e., the formation and growth of h eterophase fluctuations will fall as temperatures falls. Observed nucleation rates show this maximum, but the "bell" is generally more symmetric and considerably narrower. This reflects the increasing viscosity of the melt, and therefore the decreasing mobility of atoms, i.e., diffusion of atoms to the proto-nuclei slows.

This implies nucleation rate will be a very strong function of "temperature overstepping" for relatively small values of ΔT, but will level off at higher values of ΔT. At low degrees of overstepping, nucleation rate will be nil, but will increase rapidly once a critical temperature is achieved, as is demonstrated in Example 5.9. A more detailed treatment of nucleation and growth of crystals in cooling magmas can be found in Toramaru (1991).

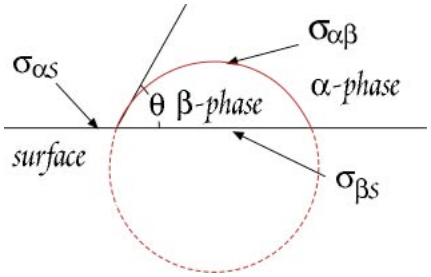


Figure 5.24. Illustration of the balance of forces as a spherical crystal or droplet of phase β crystallizes or condenses from phase α on a surface.

5.5.3.3 Heterogeneous Nucleation

The nucleation of diopside crystals from diopside melt is an example of homogenous nucleation, i.e., nucleation in a system where initially only one phase is present. Heterogeneous nucleation refers to the nucleation of a phase on a pre-existing one. Often the surface free energy between the nucleating phase and the pre-existing surface is lower than between the nucleating phase and the phase from which it is growing. Hence heterogeneous nucleation is often favored over homogeneous nucleation. Perhaps the most familiar example is dew. Dew droplets appears on surfaces, such as those of grass, at significant lower relative humidity than necessary for fog or mist to form. The reason is that the surface free energy between grass and water is lower than between water and air. Another example is the clusters of crystals seen in igneous rocks. These result from one crystal nucleating on the other, again because the free energy of the crystal-crystal interface is lower than that of the crystal-magma interface.

Let's examine this in a more quantitative fashion. Consider a spherical cap of phase β nucleating from phase α on a flat surface, *s* (Figure 5.24). The balance of surface forces at the three-phase contact is:

$$\sigma_{\alpha s} = \sigma_{\beta s} + \sigma_{\alpha\beta}\cos\theta \qquad 5.123$$

and solving for θ

$$\cos\theta = \frac{\sigma_{\alpha s} - \sigma_{\beta s}}{\sigma_{\alpha\beta}}$$

If the interfacial energy between the nucleating phase, β, and the surface ($\sigma_{\beta s}$) is smaller than that between phase α and the surface($\sigma_{\beta s}$), then the angle of intersection, θ, will be small so as to maximize the interfacial surface area between β and *s* for a given volume of β. In the limit where $\sigma_{\beta s} << \sigma_{\alpha s}$ then θ will approach 0 and β will form a film coating the surface. As $\sigma_{\beta s}$ approaches $\sigma_{\alpha s}$ the nucleating phase will form more spherical droplets. If $\sigma_{\beta s} \geq \sigma_{\alpha s}$ then θ will be 90° or greater, and heterogeneous nucleation will not occur. To take account of the reduced interfacial energy between β and *s*, equation 5.117 becomes:

$$\Delta G_{crit} = \frac{16\pi}{3}\frac{\sigma_{\alpha\beta}^3 \overline{V}}{\Delta G_{xt}^2}\left(2 - 3\cos\theta + \cos^3\theta\right) \qquad 5.124$$

In metamorphic reactions, nucleation will necessarily always be heterogeneous. Provided the necessary components of the nucleating phase are available and delivered rapidly enough by fluid transport and diffusion, interfacial energy will dictate where new phases will nucleate, nucleation being favored on phases where the interfacial energy is lowest. Where transport of components limit growth, however, this may not be the case, as phases will nucleate where the components necessary for growth are available. For example, experimental investigation of the reaction calcite + quartz ⇄ wollastonite + CO_2 revealed that in the absence of water, wollastonite nucleated on quartz. In experiments where water was present, it nucleated on calcite. SiO_2 is not significantly soluble in CO_2, so it could not be transported in the H_2O free experiments, hence nucleation could only occur where SiO_2 was available, i.e., at the surface of quartz, despite a probable higher interfacial energy.

Unfortunately, agreement between observed and predicted nucleation rates is often poor (Kirkpatrick, 1981; Kerrick et al., 1991). Equation 5.121 and Figure 5.23 show that the nucleation rate is a very

strong function of the surface free energy ($I \propto \exp(\sigma^3)$), and the poor agreement between theory and observation may reflect the lack of accurate data on surface free energy as well as the activation energy, E_A. However, it may also indicate that further work on the nucleation theory is required.

5.5.3.4 Diffusion-Limited and Heat-Flow Limited Growth

Two other kinetic factors affect crystallization. These are the local availability of energy and local availability of components necessary for crystal growth. The latter can be important where the crystal is of different composition than the liquid (almost always the case in nature except freezing of fresh water). Crystals can grow only as fast as the necessary chemical components are delivered to their surfaces. Where diffusion is not rapid enough to supply these components, diffusion will limit growth.

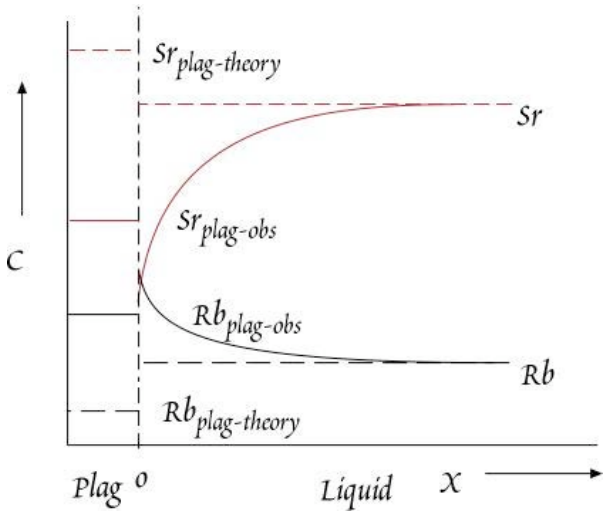


Figure 5.25. Variation of Sr and Rb concentrations from a plagioclase liquid interface. Solid curves show the variation of concentration. The crystal-liquid interface is at 0. Dashed lines show the concentrations at infinite distance from the interface (Sr_∞, Rb_∞). Sr_{plag} and Rb_{plag} are the concentrations in the crystal.

A second effect of slow diffusion is to change the *apparent* distribution coefficient, because the crystal 'sees' the concentrations in the adjacent boundary layer rather than the average concentrations in the liquid. Thus the crystal may become less depleted in elements excluded from the crystal, and less enriched in elements preferentially incorporated in it, than equilibrium thermodynamics would predict. For example, suppose a crystal of plagioclase is crystallizing from a silicate melt. Plagioclase preferentially incorporates Sr and excludes Rb. If diffusion of Sr and Rb to the crystal is slow compared with the crystal growth rate, the liquid in the boundary layer immediately adjacent the crystal will become impoverished in Sr and enriched in Rb. The crystal will grow in equilibrium with this boundary layer liquid, not the average magma composition, thus will be poorer in Sr and richer in Rb than if it grew in equilibrium with the average magma. Figure 5.25 illustrates this point. If however, growth rate of the crystal is very much slower than the transport of components to the crystal-liquid interface, this circumstance will not arise.

When crystals grow from a magma there will be a local increase in temperature at the crystal-liquid boundary, due to release of latent heat of fusion, ΔH_m, which will retard crystal grow. In most cases, however, advection and conduction of heat is probably sufficiently rapid that this is at best a minor effect. The effect is probably more important in prograde metamorphic reactions (e.g., dehydration reactions), which are usually endothermic and hence require a continuous supply of energy to maintain crystal growth. Where crystal growth and transport of components is sufficiently rapid, heat flow may limit rates of crystal growth. This is more likely to occur at high temperatures and in late stages of metamorphism when structures are already large (Fisher, 1978). We will explore the effects of crystal growth rates, diffusion rates, and heat flow on metamorphic processes in a subsequent chapter.

5.5.4 Adsorption

Many geochemically important reactions take place at the interface between solid and fluid phases, and inevitably involve adsorption and desorption of species onto or from the surface of the solid. Two types of adsorption are possible: physical and chemical. Physical adsorption involves the attachment of an ion or molecule to a surface through intermolecular or van der Waals forces. Such forces are relatively weak and heat of adsorption (ΔH_{ad}) relatively low (typically 4-12 kJ/mol). Chemical adsorption involves the formation of a new chemical bond between the adsorbed species and atoms on the surface of the solid. Heats of chemical adsorption are relatively large (>40 kJ/mol).

Adsorption of ions and molecules on a solid surface or interface affects the surface free energy. The relationship between surface free energy and adsorbed ions can be expressed as:

$$d\sigma = -\sum_i \frac{n_{i,s}}{A} d\mu_i = -\sum_i \Gamma_i d\mu_i \qquad 5.125$$

where $n_{i,s}$ is the number of mole of species *i* adsorbed at the surface, A is the surface area, and we define Γ_i as the *Gibbs adsorption density*. Because silicates and oxides generally have positive surface free energies, we can see that adsorption will decrease this energy and is therefore strongly favored.

5.5.4.1 The Relation between Concentration and Adsorption: Langmuir and Freundlich Isotherm

Consider the adsorption of aqueous species *M* at a surface site which we will denote as *S*. The reaction may be written as:

$$M + S \rightleftarrows M{\cdot}S$$

We will denote the fraction of surface sites occupied by M as Θ_M, the rate constant for adsorption as k_+, and that for desorption as k_-. The fraction of free sites is then $(1 - \Theta_M)$, and we explicitly assume that *M* is the only species adsorbed from solution. Assuming the reaction is elementary, the rate of adsorption is then:

$$\frac{dM}{dt} = k_+ [M](1 - \Theta_M) \qquad 5.126$$

The rate of desorption is:

$$\frac{d\Theta_M}{dt} = k_- \Theta_M \qquad 5.127$$

At equilibrium, the rate of adsorption and desorption will be equal, so

$$k_- \Theta_M = k_+ [M](1 - \Theta_M) \qquad 5.128$$

Solving 5.128 for Θ_M, we obtain:

$$\Theta_M = \frac{k_+/k_- [M]}{1 + k_+/k_- [M]} \qquad 5.129$$

which expresses the fraction of site occupied by *M* as a function of the concentration of *M*. Since at equilibrium:

$$K_{ad} = \frac{[M]_{ads}}{[M]_{aq}} = \frac{k_+}{k_-} \qquad (5.43)$$

where K_{ad} is the equilibrium constant for adsorption, equation 5.129 becomes:

$$\boxed{\Theta_M = \frac{K_{ad}[M]}{1 + K_{ad}[M]}} \qquad 5.130$$

Equation 5.130 is known as the *Langmuir Isotherm**. Since this is a chapter on kinetics, we have derived it using a kinetic approach, but it is a statement of thermodynamic equilibrium and can be readily derived from thermodynamics as well. From the definition of Θ_M, we may also write the Langmuir isotherm as:

$$\Gamma_M = \Gamma_M^{max} \frac{K_{ad}[M]}{1 + K_{ad}[M]} \qquad 5.131$$

* An admittedly odd name for this equation. It is named for Irving Langmuir (1881-1957). Langmuir obtained a PhD from the University of Göttingen and spent most of his career working for General Electric Company. While trying extending the life of light bulbs, Langmuir carried out experiments on the adsorption of gases by metals. He developed this equation to describe his results. He won the Nobel Prize for Chemistry in 1932. The term "Isotherm" arises because such descriptions of adsorption are valid only for 1 temperature (i.e., K_{ads} is temperature dependent, as we would expect).

EXAMPLE 5.10. THE LANGMUIR ISOTHERM

Consider a suspension of 1 mol/l of FeOH. Assuming an adsorption site density of 0.1 mol/mol and K for adsorption of Sr on FeOH of 10^5, how will the Sr adsorption density vary with the concentration of Sr in the solution? Assume that no other ions are present in the solution.

Answer: We can use equation 5.131 to solve this problem. Γ_M^{max} in this case is 0.1 mol/mol. Using this value and K_{ads} of 10^5 in this equation, we obtain the result shown in Figure 5.26. The inset shows that at concentrations less than about 4 μM, the adsorption density rises linearly with concentration. At higher concentrations, the adsorption density asymptotically approaches the maximum value of 0.1 mol.

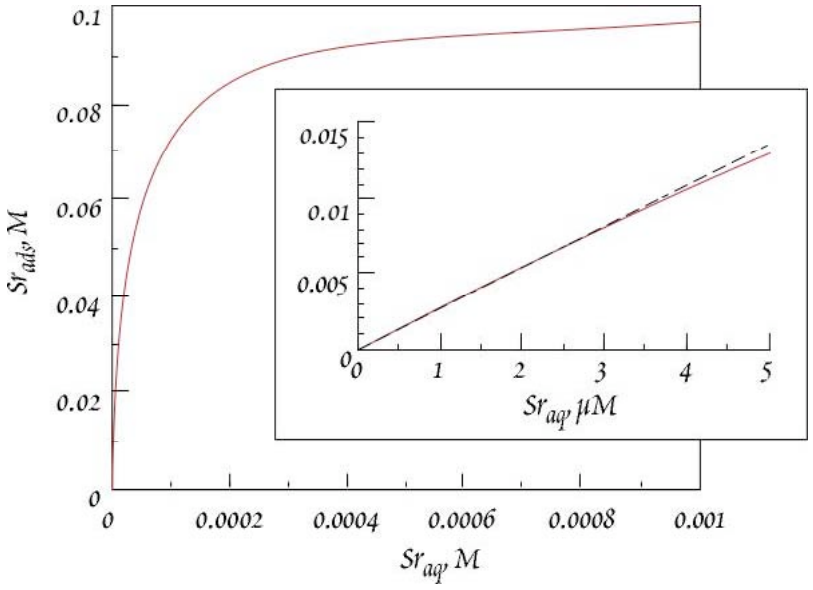


Figure 5.26. Variation of adsorption density of Sr on FeOH as a function of Sr concentration of the solution.

where Γ_M^{max} is the maximum observed adsorption. Thus the Langmuir Isotherm predicts a maximum adsorption when all available sites are occupied by *M*. At large concentrations of *M*, then:

$$\Gamma_M = \Gamma_M^{max} \qquad 5.132$$

Where the concentration of *M* is small such that $K_{ad}[M] << 1$, equation 5.130 reduces to:

$$\Theta_M \cong K_{ad}[M] \qquad 5.133$$

This equation simply says that *the fraction of sites occupied by M is proportional to the concentration of M in solution*.

The *Freundlich Isotherm*, which is purely empirical, is:

$$\boxed{\Theta_M = K_{ad}[M]^n} \qquad 5.134$$

where *n* is any number. At low concentrations of M, the Langmuir isotherm reduces to the Freundlich isotherm with $n = 1$, i.e., the amount adsorbed is a linear function of the concentration in solution.

5.5.5 Catalysis

The International Union of Pure and Applied Chemistry (IUPAC) defines *catalyst* as follows:

> *A catalyst is a substance that increases the rate without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis, and a reaction in which a catalyst in involved is known as a catalyzed reaction.*

Another definition of a catalyst is a *chemical species that appears in the rate law with a reaction order greater than its stoichiometric coefficient*. This latter definition makes is clear that a catalyst may be involved in the reaction as a reactant, a product, or neither. If it is a reactant or product, its presence affects the reaction rate to a greater extent than would be predicted from the stoichiometry of the reaction.

We can distinguish two kinds of catalysis. Homogeneous catalysis refers to a situation in which the catalyst is present in the same phase in which the reaction is occurring (necessarily a solution). Examples of homogeneous catalysts of geochemical reactions include acids and a collection of organic mole-

cules called enzymes. Catalysis that occurs at the interface between two phases is referred to as heterogeneous catalysis. We will focus primarily on heterogeneous catalysis here. Heterogeneous catalysts are commonly simply surfaces of some substance. A familiar, but non-geochemical, example is the platinum in the catalytic converter of an automobile, which catalyzes the further oxidation of gasoline combustion products.

Catalysts work by providing an alternative reaction path with lower activation energy. In many cases, the lowering of the activation energy arises when reacting species are adsorbed. The heat liberated by the adsorption (ΔH_{ads}) is available to contribute toward the activation energy. For example, consider the reaction:

$$A + B \rightarrow C$$

having an activation energy E_A. A solid catalyst of this reaction would provide the following alternate reaction mechanism:

$$A + S \rightarrow A{\cdot}S$$
$$B + S \rightarrow B{\cdot}S$$
$$B{\cdot}S + A{\cdot}S \rightarrow C{\cdot}S$$
$$C{\cdot}S \rightarrow C + S$$

The net heat of adsorption for this process is:

$$\Delta H_{ad} = \Delta H_{ad}^{A} + \Delta H_{ad}^{B} - \Delta H_{ad}^{C}$$

Recalling that enthalpy is related to activation energy, we can write the activation energy for the catalyzed reaction as:

$$E_A^{cat} = E_A + \Delta H_{ad} \qquad 5.135$$

If ΔH_{ad} is negative (i.e., heat liberated by adsorption), the activation energy is lowered and the reaction proceeds at a faster rate than it otherwise would.

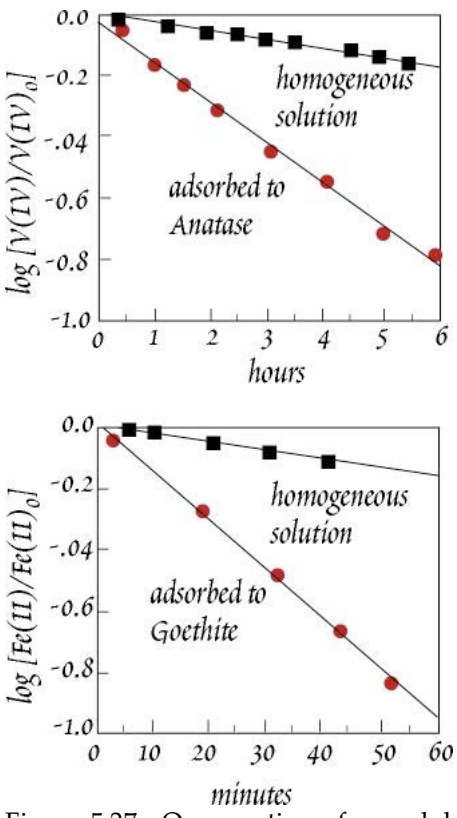


Figure 5.27. Oxygenation of vanadyl at pH 4 and P_{O_2} = 1 atm in experiments of Wehrli and Stumm (1988). After Wehrli et al. (1989).

As we noted earlier, a surface will have a variety of sites for adsorption/desorption and surface reactions on a microscopic scale. Each site will have particular activation energy for each of these reactions. The activation energies for these processes will, however, be related. Sites with large negative adsorption energies also will be sites with low activation energies for surface reactions. On the other hand, if a site has a large negative adsorption energy, the desorption energy will be large and positive and desorption inhibited. If either the activation energy or the desorption energy is too large, catalysis of the overall reaction will be inhibited. What is required for fast overall reaction rates is a site where some compromise is achieved. In general, reaction and desorption energies will be related as:

$$\Delta G_r = -n\Delta G_d \qquad 5.136$$

where n is some constant. The presence of several sites on a solid surface results in several possible reaction paths. The fastest reaction path, that is the path that optimizes n, will dominate the reaction.

Surfaces of semiconductors (metal oxides and sulfides) can catalyze oxidation-reduction reactions (e.g., Wehrli, et al., 1989). For example, both TiO_2 and Al_2O_3 can catalyze the oxidation of vanadyl, V(IV), to vanadate, V(V). Figure 5.27 compares the rate of reaction in the presence of TiO_2 solid to the homogeneous reaction, demonstrating the reaction is substantially faster in the presence of TiO_2. The reaction mechanism for the surface catalyzed reaction may be described as follows (Figure 5.28):

$$2{>}TiOH + VO^{2+} \rightleftarrows {>}(TiO)_2VO + 2H^+$$
$${>}(TiO)_2VO + TiOH \rightleftarrows {>}(Ti)_3VO_4^{2-} + H^+$$

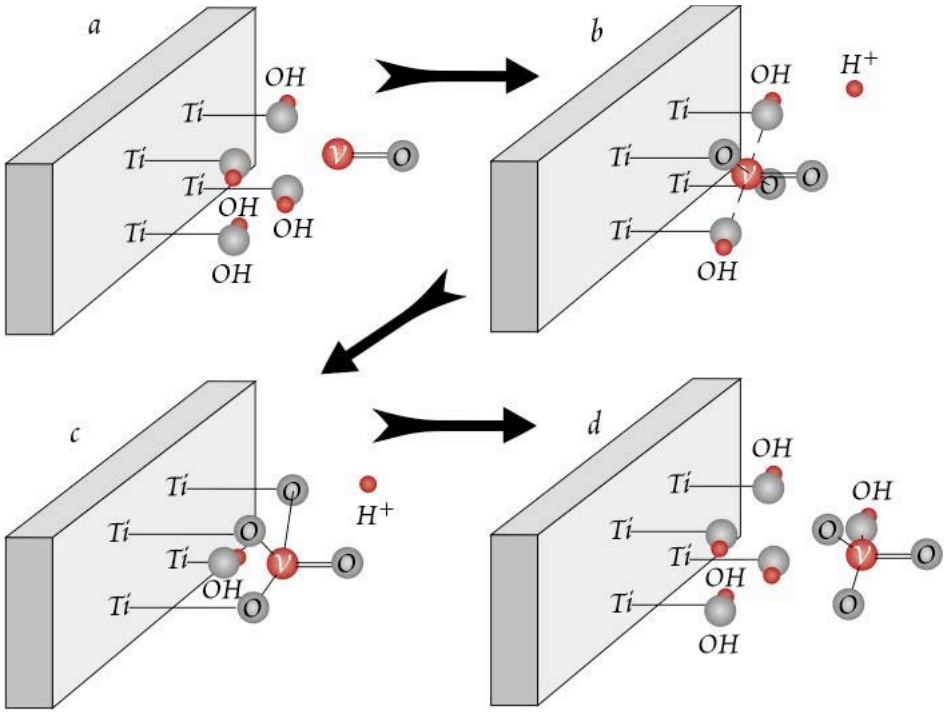


Figure 5.28. Mechanism of oxygenation of surface-bound vanadyl. In step (1) vanadyl is adsorbed at a TiO_2 surface (a → b). Note that the vanadium is bound to two surface TiO groups. In step (2), the vanadium binds to a third surface oxygen, releasing an H^+ ion (b → c). In step (3), the vandate ion is replaced at the surface by 3 H^+ ions (c → d) (at intermediate pH, most vanadate will remain bound to the surface).

$$(Ti)_3VO_4^{2-} + H_2O + 2OH^- \rightleftarrows 3{>}TiOH + HVO_4^{2-}$$

where >Ti indicates the Ti atom is part of a surface. The rate law for this reaction as determined by Wehrli and Stumm (1988) is:

$$-\frac{d\{V(IV)\}}{dt} = k\{VO(OTi<)\}[O_2]$$

where the {} brackets denote surface concentrations. The reaction is thus second order, depending on the concentration of surface bound V(IV) and dissolved O_2. Wehrli and Stumm (1988) determined the rate constant for this reaction to be 0.051 $M_{-1}s_{-1}$ and the activation energy to be 56.5 kJ/mol at pH 7.

The surface catalyzed reaction is essentially independent of pH, whereas the reaction in homogeneous solution is strongly pH dependent. The rate law for the latter can be written as:

$$-\frac{d\{V(IV)\}}{dt} = k\{VO^+\}[O_2][H^+]$$

The apparent rate constant for this reaction is 1.87×10^{-6} s^{-1} and the apparent activation energy is 140 kJ/mol. Part of the difference in the activation energies can be accounted for as the energy of the hydrolysis reaction:

$$VO^{2+} + H_2O \rightleftarrows VO(OH)^+ + H^+$$

which is the first step in the homogeneous reaction. This energy is 54.4 kJ/mol. Wehrli and Stumm (1988) speculated that the remainder of the difference in activation energy is the energy required for the transition from the octahedral structure of the dissolved $VO(OH)^+$ ion to the tetrahedral structure of the dissolved vanadate ion.

5.6 Kinetics of Dissolution and Leaching

5.6.1 Simple Oxides

The rate of dissolution of non-ionic solids are generally controlled by surface reactions at the solid-water interface. Absorption of ions to the surface of the solid play a critical role in the dissolution process. Adsorption of H^+ and OH^- ions at the surface appears to dominate dissolution reactions; however, adsorption of other species, particularly organic ones such as carboxylic acids, can be important as well.

Consider the example of a simple oxide (e.g., Al_2O_3) illustrated in Figure 5.29. As we noted earlier, "dangling" oxygens on surfaces in contact with aqueous solution will be protonated under most circumstances, i.e., an H^+ ion will react with one of the surface O ligands to form a surface hydroxyl. Bonding of a single proton to a surface oxygen merely replaces the bond that the oxygen would have formed with a metal ion had it been located in the crystal interior. Addition of a second proton, i.e., protonation of the surface hydroxyl, however, has the consequence of weakening metal-oxides bonds.

In the case of a trivalent ion such as Al_2O_3, protonation of three such bonds effectively frees the ion from the lattice structure. We can expect, therefore, that the dissolution rate will be proportional to finding 3 protonated ligands surround a single surface metal ion.

The concentration of surface-bound protons, $[H^+]_s$ can be related to the concentration of H^+ in solution through an absorption equilibrium constant K_{ad}, so that:

$$[H^+]_s/S = K_{ad}[H^+]_{aq}$$

where S is the density of surface sites. The probability of finding a metal surrounded with three protonated ligands is then proportional $([H^+]_s/S)^3$. Thus we expect the dissolution rate to be proportional to the third power of the surface protonation:

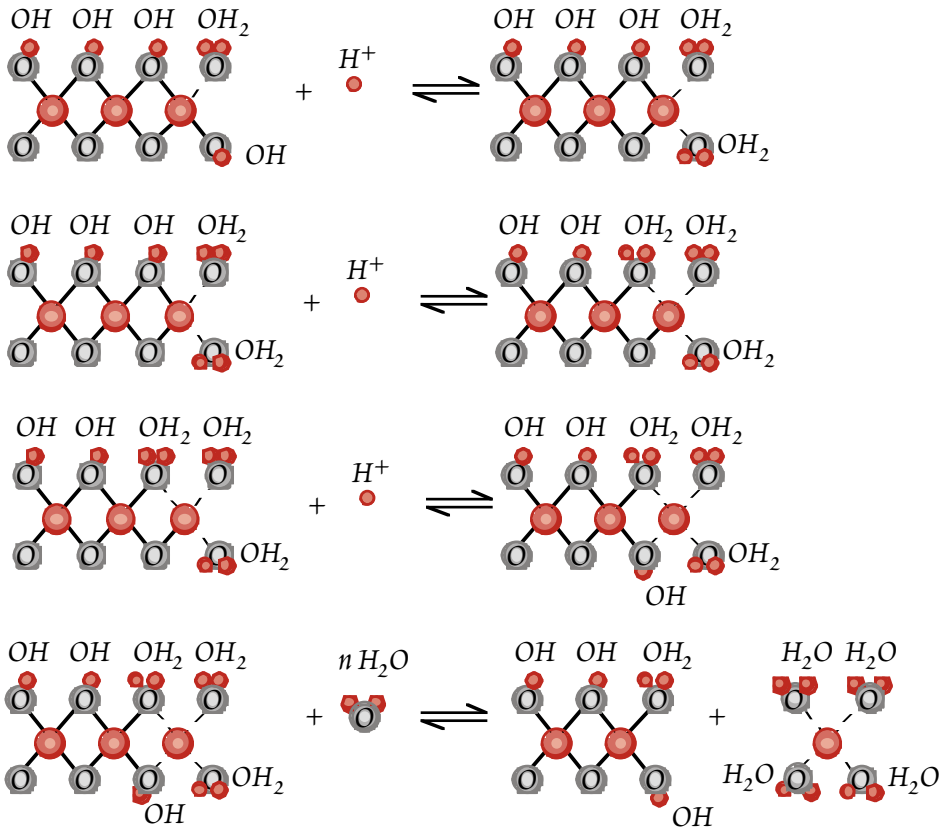


Figure 5.29. Cartoon of proton-promoted dissolution of an oxide such as Al_2O_3 at a surface step. After Stumm and Wollast (1990).

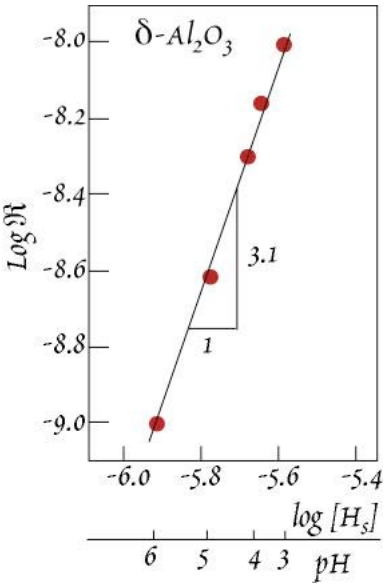


Figure 5.30. Log of the rate of Al_2O_3 dissolution plotted against the log of the concentration of surface protons. The slope of 3 indicates a rate law with third order dependence on the surface concentration of protons. From Stumm and Wollast (1990).

Figure 5.30 shows that this is indeed the case for Al_2O_3.

Deprotonation of surface OH groups will occur at high pH through the following reaction:

$$\text{S—OH} + OH^- \rightleftarrows \text{S—}O^- + H_2O \qquad 5.137$$

where S—O denotes a surface-bound oxygen. This deprotonation disrupts metal-oxygen bonds through polarization of electron orbitals. As a result, dissolution rates will also increase with increasing pH in alkaline solutions. Adsorption of protons at the surface is thought to be fast, hence equilibrium between adsorbed and aqueous protons is quickly attained. Thus detachment of the metal species becomes the rate-determining step. Other ligands, particularly organic ones such as oxalates, will have a similar effect. The overall dissolution rate is given by (Stumm and Wollast, 1990) as:

$$\Re = k_H\left\{[H_s^+]/S\right\}^i + k_{OH}\left\{[OH_s^-]/S\right\}^i + k_L\left\{[L_s]/S\right\}^i + k_{H_2O}$$

where i is the charge on the metal ion.

6.5.2 Silicates

Surface protonation and deprotonation also play a dominant role in silicate dissolution (e.g., Blum and Lasaga, 1988). However, the dissolution of silicates is somewhat more complex than that of simple oxides because they typically contain several metals bound in different ways. This can result in incongruent dissolution, i.e., some metal ions may be released to solution more rapidly than others (though experiments suggest dissolution is most often congruent). A related, and particularly important, factor is lattice structure, in particular the degree to which the individual silica tetrahedra share oxygens. There is a complete range among silicates in this respect, from orthosilicates, such as olivine, in which no oxygens are shared, to the tecto-, or framework-, silicates, such as quartz and the feldspars, in which all oxygens are shared. As we discussed in Chapter 4, shared oxygens are termed bridging, and non-shared ones *non-bridging* oxygens. Sharing of oxygens increases the degree of *polymerization* of the structure.

The degree of polymerization is important in the context of dissolution because the non-bridging bonds are much more reactive than the bridging ones. Minerals with highly polymerized structures, such as feldspars, dissolve slowly and are subject to leaching, as components (particularly the network-modifiers) may be dissolved out leaving the silicate framework still partially intact. Silicates with a low fraction of shared oxygens dissolve more rapidly and more uniformly. An example is olivine, whose structure is illustrated in Figure 5.31a. Once the Mg ions surrounding it are removed, the individual silica tetrahedra are no longer bound to the

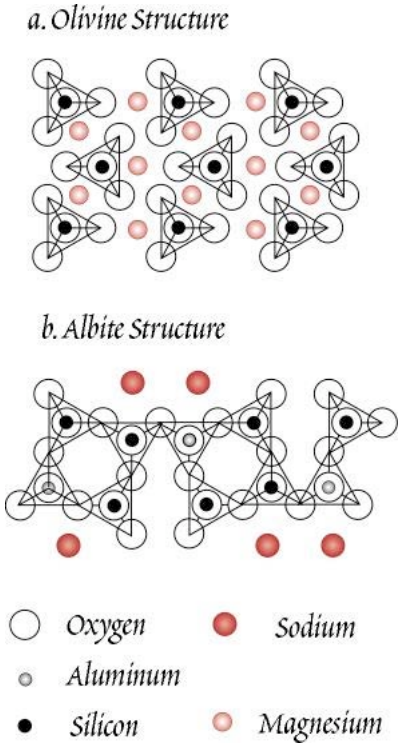


Figure 5.31. Comparison of olivine (forsterite) and feldspar (albite) structures. In feldspar, all oxygens are shared by adjacent tetrahedra, in olivine none are; instead the excess charge of the SiO_4^{4-} units is compensated by 2 Mg^{2+}.

mineral, and are free to form H_4SiO_4 complexes in the solution (a more likely mode of dissolution is replacement of Mg^{2+} by $2H^+$; in essence, this produces a free H_4SiO_4 molecule). In contrast, removal of Na^+ by H^+ in albite (Figure 5.31b) leaves the framework of tetrahedra largely intact. The rate of weathering can also be affected by the Al/Si ratio, as the silicate groups are less reactive than the aluminate ones. Thus the dissolution rate of plagioclase depends on the ratio of the anorthite ($CaAl_2Si_2O_8$) to albite ($NaAlSi_3O_8$) components, with calcic plagioclase weathering more rapidly (e.g., Oxburgh, et al., 1994).

Some idea of the role these factors play can be obtained from Table 5.3, which lists the mean lifetimes of a 1 mm crystal for a variety of minerals in contact with a solution of pH 5 based on experimentally determined dissolution rates.

Table 5.3. Dissolution Rates and Mean Lifetimes of Crystals at 25°C and pH 5

Mineral	Log Rate (mol/m²/s)	Mean Lifetime years
Quartz	-13.39	34,000,000
Kaolinite	-13.28	6,000,000
Muscovite	-13.07	2,600,000
Epidote	-12.61	923,000
Microcline	-12.50	579,000
Albite	-12.26	-575,000
Sanidine	-12.00	291,000
Gibbsite	-11.45	276,000
Enstatite	-10.00	10,100
Diopside	-10.15	6,800
Forsterite	-9.50	2,300
Nepheline	-8.55	211
Anorthite	-8.55	112
Wollastonite	-8.00	79

From Lasaga et al. (1994).

There are four important classes of reactions involved in silicate dissolution and leaching: hydration, ion exchange, leaching, and hydrolysis.

Hydration simply implies the addition of water to the structure. The effect of hydration may range from simply relaxation of the polymeric structure (e.g., swelling of vermiculite) to disruption of bridging bonds, to dissolution of polymeric fragments.

Ion exchange involves replacement of a network-modifying cation by hydrogen ions. For example, Wollast and Chou (1992) showed that when freshly ground albite is mixed with water, there is an increase in Na^+_{aq} and an increase in pH, corresponding to the consumption of H^+_{aq}. This reaction may be represented as:

$$NaAlSi_3O_8 + H^+ \rightleftarrows HAlSi_3O_8 + Na^+$$

This reaction, as well as the replacement of Mg^{2+} by H^+ in forsterite, has been shown to be largely reversible. Wollast and Chou (1992) found that ion exchange occurs to a depth of about 20 Å in albite, corresponding to a depth of 2 or 3 unit cells.

Leaching involves the removal of an ion without replacement by an ion from solution. The consumption of H^+ observed by Wollast and Chou (1992) was less than the production of Na^+, so that much of the Na^+ loss from the albite appears to result from leaching rather than ion exchange, i.e.:

$$NaAlSi_3O_8 \rightleftarrows AlSi_3O_8^- + Na^+$$

This reaction, of course, results in the production of negative charge on the surface. Wollast and Chou (1992) found that the extent of leaching could be related to both pH and Na^+_{aq} concentration:

$$X_{X^-} \approx 10^{-5.01} a_{H^+}^{-0.35} a_{Na^+}^{-0.65} \qquad 5.138$$

where X_{X^-} is the mole fraction of negatively charged surface species. Thus according to equ. 5.138, leaching increases with increasing pH and decreases with increasing aqueous Na concentration.

As we noted, structure affects the rate and degree of leaching. Sheet silicates (micas, clays, talc, serpentine) have relatively open structures though which water and solutes can be transported deeply into the structure, resulting in leaching of cations, including octahedrally coordinated Al and Mg. While the feldspar structure is not open, preferential removal of aluminate groups and charge-balance cations produces a porous structure, allowing penetration of water. Thus deep (400 Å) Na-, Ca-, and Al-poor, and Si-, H-rich layers have been observed on experimentally reacted plagioclase (Casey and Bunker, 1990).

Hydrolysis refers to the surface protonation and deprotonation reactions we have already discussed in the context of oxide dissolution. Hydrolysis has the effect of breaking of covalent metal-oxide bonds

in the polymer structure by replacing them with an O–H bonds. The effect is the same as replacing one of the oxygens in the tetrahedron by an OH group. Where a bridging oxygen is involved, hydrolysis decreases the degree of polymerization of the structure and eventually leads to its destruction. Complete hydrolysis of a silica tetrahedron results in the formation of a free H_4SiO_4 molecule.

This process appears to be of critical importance in the dissolution of silicates, as was the case for oxides. Many silicate dissolution experiments have shown a dependence of dissolution rate on pH of the form:

$$\Re = k a_{H^+}^n \qquad 5.139$$

with the value of n less than one. Blum and Lasaga (1988, 1991) showed that the dissolution rate of albite can be directly related to the surface concentration of positive species ($S—OH_2^+$) under acidic conditions and to the concentration of negative surface species ($S—O^-$) under basic regions. In other words:

under acidic conditions: $$\Re = k_1[S—OH_2^+] \qquad 5.140a$$

and under basic conditions:

$$\Re = k_2[S—O^-] \qquad 5.140b$$

This dependence explains the fractional dependence of dissolution rate on pH. The reason is that the concentrations of $S—OH_2^+$ and $S—O^-$ species can be related to pH through Freundlich isotherms (equation 5.134). In the case of albite dissolution, Blum and Lasaga (1991) found:

$$\left[S-OH_2^+\right] = \mathrm{K}_1 a_{H^+}^{0.52} \qquad 5.141a$$

$$\left[S-O^-\right] = \mathrm{K}_2 a_{OH^-}^{0.37} = \mathrm{K}_3 a_{H^+}^{-0.37} \qquad 5.141b$$

for acidic and basic conditions respectively. This relationship is shown in Figure 5.32a. Substituting 5.141a and b into 5.140a and b, we expect:

$$\Re = k_3 a_{H^+}^{-0.52} \qquad 5.142a$$

and $$\Re = k_4 a_{H^+}^{-0.37} \qquad 5.142b$$

This matches well the pH dependencies determined experimentally by Chou and Wollast (1985), who found the exponents in equations 5.136 were 0.49 and -0.30 for the acidic and basic conditions respectively, as is shown in Figure 5.32b. Although the experimental data have been questioned, a similar relationship between abundance of surface species and dissolution rate has been claimed for olivine.

Ganor et al. (1995) demonstrated that the dissolution rate of kaolinite ($Al_2Si_2O_5[OH]_4$) also shows a fractional

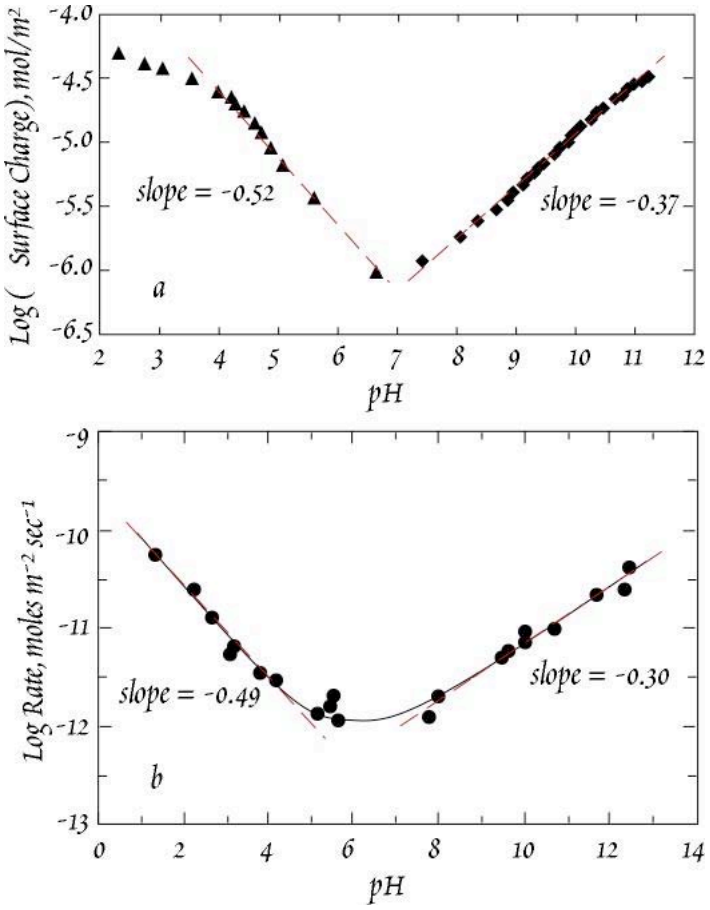


Figure 5.32. (a) Relationship between pH and the absolute value of net surface charge on dissolving albite particles. A Freundlich isotherm (dashed red lines) can be fit to the data. (b) Relationship between log of the albite dissolution rate and pH determined by Chou and Wollast (1985). The slope passing through the step parts of the curve (dashed red lines) is similar to slopes in (a), indicating adsorption and desorption of protons controls the dissolution rate. From Blum and Lasaga (1991).

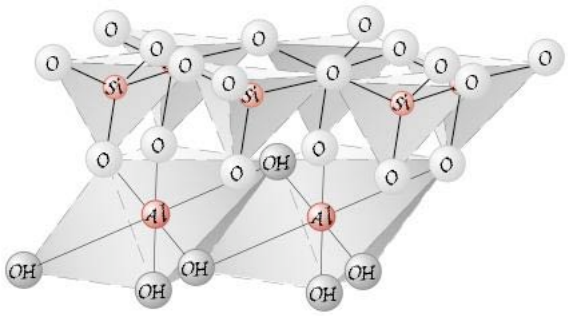


Figure 5.33. The structure of kaolinite. Kaolinite consist of a layer of Si-tetrahedra linked to a layer of Al-Octahedra through a shared oxygen.

exponential dependence on pH (equation 5.140) with the value of the exponent, n, being 0.4±0.2 for the pH range 3 to 4. Consistent with earlier studies, they concluded the form of the rate equation reflected the equilibrium adsorption of protons on the mineral surface. Their interpretation of the details of the reaction mechanism, however, was somewhat different than the interpretation of the mechanism of Al_2O_3 dissolution of Stumm and Wollast (1990) discussed above. Ganor et al. (1995) argued that simultaneous protonation of all metal-oxide bonds was unlikely and furthermore unnecessary, since stepwise breaking of metal oxide bonds would do the job. They argued that hydrogen ion–mediated breaking of Al–O–Si bonds was the critical and rate-determining step in kaolinite dissolution. In support of this hypothesis, they point out that *ab initio* (i.e., from first principles) calculations show that the activation energy for hydrolysis of this bond is lower than that of Si–O–Si bonds. The kaolinite structure (Figure 5.33) consists of alternating sheets of Si-tetrahedra and Al-octahedra, with each Si-tetrahedron sharing an oxygen with an Al in the octahedral layer. Breaking these Al–O–Si bonds effectively "unzips" the octahedral and tetrahedral sheets. Subsequent hydrolysis of the individual metal-oxygen bonds is then fast.

In focussing on the effects of pH in our discussion of dissolution thus far, we have implicitly assumed that dissolution reactions take place far from equilibrium. We have also ignored the effects of temperature. Clearly, temperature and the approach to equilibrium must be taken into account in a full treatment of dissolution. Furthermore, other dissolved species might either catalyze or inhibit dissolution reactions. Lasaga et al. (1994) have proposed the following rate equation to take account of these additional factors:

$$\Re = k_0 e^{-E_A/RT} f(\Delta G) A_{\min} a_{H^+}^n \prod_i a_i^{m_i} \qquad 5.143$$

The $k_0 e^{-E_A/RT}$ term is the usual Arrhenius expression for temperature dependence. A_{min} is the surface area of the dissolving mineral, the term $a_{H^+}^n$ takes account of the pH dependence, and the $a_i^{m_i}$ terms take account of the inhibitory or catalytic effects of other ions; n and m_i may take any value. The $f(\Delta G)$ term is some function of ΔG that expresses the dependence of the rate on the deviation from equilibrium. For instance, we saw that transition state theory predicts that $f(\Delta G)$ for an elementary reaction takes the form of equation 5.59, i.e.:

Table 5.4. Apparent Activation Energies for Dissolution Reactions

Mineral	E_a kJ//mol	pH
Albite	54.4	neutral
Albite	32.2	Basic
Albite	117.2	<3
Epidote	82.9	1.4
Kaolinite	29.3	3–4
Microcline	52.3	3
Quartz	71.2	7
Sanadine	54.0	3
Wollastonite	79.1	3-8

modified from Lasaga et al. (1994).

For an overall reaction, $f(\Delta G)$ might have the form (equation 5.60):

Even if the exact form of the rate equation is not known, an apparent activation energy can be calculated to express the temperature dependence of reaction rate. In that case, however, the activation energy is valid only under a specific set of conditions. Values of such apparent activation energies for a few minerals are listed in Table 5.4.

Equation 5.143 predicts that the dissolution rate will slow as equilibrium between mineral and solution is approached, i.e., as the concentration of dissolved

components increases. This will occur when the rate of dissolution exceeds the rate of transport because the concentrations of dissolution products will build up at the mineral-water interface. In the steady-state, mass balance requires that the rate of dissolution (i.e., the rate at which aqueous species are produced at the surface) and transport (the rate at which components are removed from the solution adjacent the dissolving surface) must be equal. Thus overall weathering rates are controlled by a combination of surface kinetics and transport kinetics. In each individual situation, one or the other can be the rate-limiting step.

Surface reactions are most often rate-limiting in dissolution and weathering of silicate minerals at low temperature (25°C). Dissolution of readily soluble minerals (e.g., halite) and even moderately soluble minerals (e.g., gypsum) are, by contrast, usually limited by the rate at which the dissolving components can be transported away from the mineral-water interface. by advection and diffusion. As temperature increases, transport is increasingly likely to become rate-limiting. This is because the activation energy of diffusion in aqueous solution, typically 5-10 kJ/mol, is generally less than the activation energy of surface reactions (typically >30 kJ/mol; Table 5.4). Thus the diffusion rates increase more slowly with temperature than surface reaction rates. This point is illustrated for the case of calcite in Figure 5.33. At temperatures less than 75° C, growth and dissolution of calcite, a moderately soluble mineral, is effectively controlled by the surface reaction rate, while at temperatures greater than 125° C, diffusion is the rate-controlling step. Dissolution under hydrothermal and metamorphic conditions is most likely to be diffusion-controlled for most minerals (Guy and Schott, 1989).

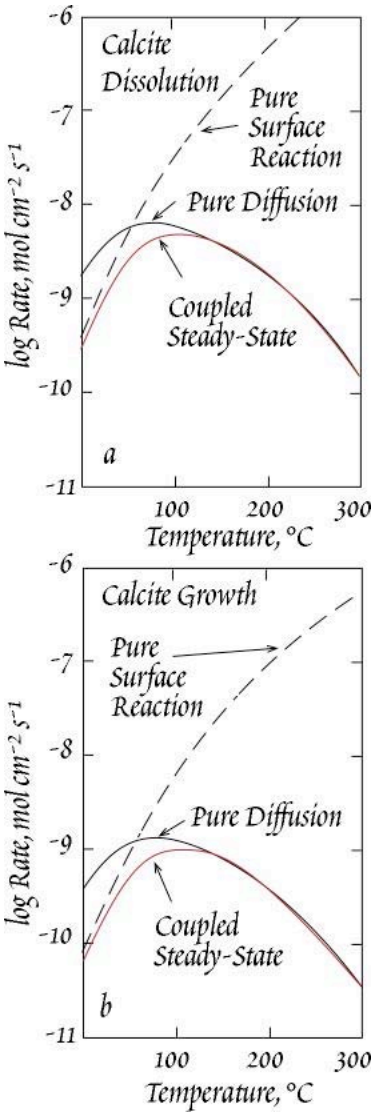


Figure 5.34. Log of steady state growth (a) and dissolution (b) of calcite as a function of temperature, comparing diffusion-controlled and surface reaction-controlled kinetics. The model assumes a 1 μ hydrodynamic boundary layer and saturation in the case of growth. From Murphy et al. (1989).

5.7 Diagenesis

An introductory geology text might define *diagenesis* as the process through which a sediment is converted to a sedimentary rock. We will use diagenesis to refer to a number of physical and chemical processes that occur subsequent to deposition of a sediment, including compaction and expulsion of pore water, consumption of organic matter, and resulting changes in $p\varepsilon$. Some of the originally deposited phases dissolve in the pore water during diagenesis, other phases crystallize from the pore water. Some of these changes begin immediately after deposition, some only as a result of later deformation. Some occur as a result of moderately elevated temperature and pressure, though processes occurring at much higher temperature and pressure would be called metamorphism. Diagenesis and metamorphism form a continuum; though a geologist might volunteer a definite opinion on whether a particular specimen had been diagenetically or metamorphically altered, he would be hard pressed to come up with criteria to distinguish diagenesis from metamorphism that was not arbitrary. Here, we will briefly consider a few of these processes.

5.7.1 Compositional Gradients in Accumulating Sediment

Let's turn our attention to the early stages of diagenesis in a slowly accumulating sediment. Our first task is to decide upon a reference frame. There are two choices: we could choose a reference frame

fixed to a specific layer. In this case, the sediment-water interface will appear to move upward with time. Alternatively, we can choose a reference frame that is fixed relative to the sediment-water interface, thus depth always refers to distance downward from that interface. As sediment accumulates, a given layer of sediment will appear to move downward in this reference frame. In this reference frame, we can express the change in concentration at some depth, x, as the sum of changes in the composition due to diagenesis plus the change in the composition of sediment flowing downward past our fixed reference point:

$$\left(\frac{\partial C}{\partial t}\right)_x = \frac{dC_i}{dt} - \omega\left(\frac{\partial C_i}{\partial x}\right)_t \qquad 5.144$$

where C_i is concentration some species i, and ω is the burial rate. The partial derivative on the left hand side refers to changes *at some fixed depth*, and the total derivative refers to diagenetic changes occurring in given layer, or horizon, undergoing burial. $(\partial C_i/\partial x)_t$ is the concentration gradient of i at some fixed time t. This equation allows us to convert a reference frame that is fixed relative to the sediment-water interface to one that is fixed relative to some sedimentary layer.

Now let's consider two extremes where equation 5.144 is particularly simple. In the first, steady-state is reached and there is no change with time, hence:

$$\left(\frac{\partial C}{\partial t}\right)_x = 0 \qquad 5.145$$

In other words, the concentration of i at some fixed depth below the water-sediment interface is constant. Under these circumstances then,

$$\frac{dC_i}{dt} = \omega\left(\frac{\partial C_i}{\partial x}\right)_t \qquad 5.146$$

This case is illustrated in Figure 5.35.

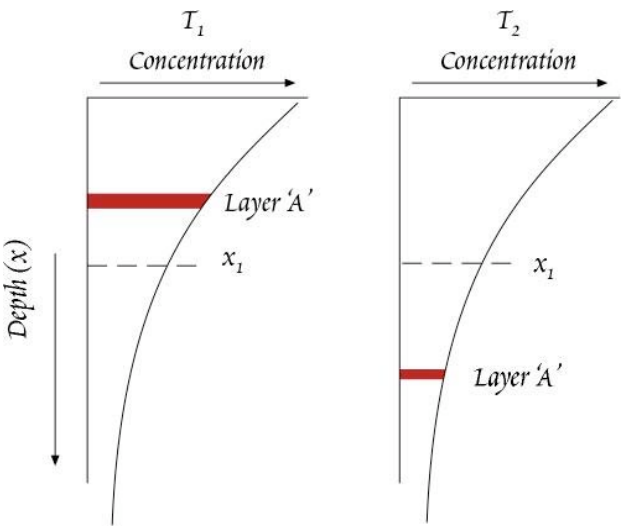


Figure 5.35. Steady-state diagenesis. Concentration at a fixed depth x_1 below the surface remains constant, but layer A, whose depth increases with time due to burial, experiences a decreasing concentration with time. After Berner (1980).

In the second extreme, there is no diagenesis and the composition of a given layer is determined only by what is initially deposited, thus:

$$\frac{dC_i}{dt} = 0 \qquad 5.147$$

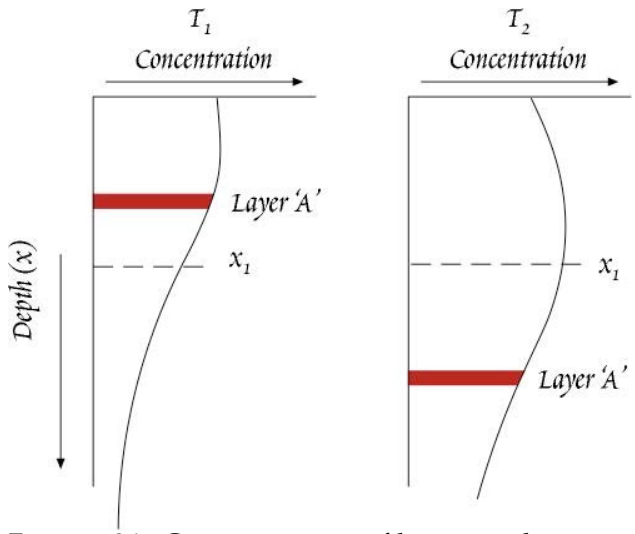


Figure 5.36. Concentration profiles in a sediment in which the composition of the material changes with time, but there is no diagenesis. The composition of any given layer is fixed, but the composition at some fixed depth relative to the water-sediment interface, such as x_1, changes with time. After Berner (1980).

The concentration change with time at some fixed depth is then due to change in the composition of the sediment moving downward past that point. Thus:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = \omega\left(\frac{\partial C_i}{\partial x}\right)_t \qquad 5.148$$

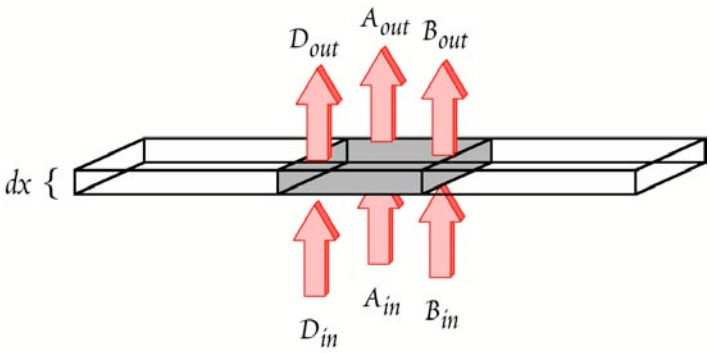


Figure 5.37. Fluxes through a box in a sedimentary layer of unit lateral dimensions and thickness *dx*. Arrows labeled A, B, and D indicate advective, biodiffusive, and molecular diffusive fluxes. Loss or gain by the box due to these processes depends on the difference in the flux into and out of the box: dF/dx.

This case is illustrated in Figure 5.36.

The sediment consists both of solid particles and the water buried with the particles, the pore water. Assuming no other fluid is present (e.g., gas, petroleum) then the volume fraction of water in the sediment is equal to the porosity ϕ. The volume fraction of solids is then simply $1 - \phi$. Most sediments will undergo compaction as they are buried. This is due to the weight of overlying sediment (gravitational compaction). Gravitational compaction results in expulsion of pore water and in decrease in porosity with depth. In addition, dissolution and cementation will also affect porosity. Since the molar volume of a phase precipitating or dissolving (the most important such phase is $CaCO_3$) will be different from its partial molar volume in solution, these processes will also result in motion of the pore water. When compaction occurs, the rate of burial of a sediment will not be equal to the sedimentation rate.

Now consider a box of sediment of thickness *dx* and unit length and width embedded within some sedimentary layer (Figure 5.37). We assume that the layer is of uniform composition in the lateral dimension, and therefore that there is no lateral diffusion, and that there is also no lateral advection of fluid. Within the box there are *C* moles of species *i*. If we chose our concentration units to be moles per volume, then the concentration is simply C_i.

Let's consider the processes that can affect the concentration of species *i* within the box. First of all, reactions occurring within the box might affect *i*. For example, oxidation and reduction will affect species such as Fe^{3+}, SO_4^{2-}, and Mn^{2+}, etc. If we are interested in the concentration of a dissolved species, then dissolution, crystallization, leaching, etc. will all change this concentration.

In addition to reactions occurring within the box, diffusion, advection, and bioturbation will also affect the concentration of *i* if there is a difference between the fluxes into and out of the box. Bioturbation is the stirring effect produced by the activity of animals that live in the sediment (the infauna). From a geochemical perspective, bioturbation is much like diffusion in that it results from the random motion of particles (even if these particles are of very different size from atoms and ions) and acts to reduce compositional gradients. Mathematically, we can treat the effect of bioturbation in a way similar to diffusion, i.e., we can define a bioturbation flux as:

$$J_B = -D_B\left(\frac{\partial C_i}{\partial x}\right)_t \qquad 5.149$$

where D_B is the biodiffusion coefficient. Values of D_B for solid phases range from 10^{-6} cm^2/sec in near shore clays to 10^{-11} in deep-sea pelagic sediments. The bioturbation coefficient will generally be different for solid species than for liquid ones. Since most animals live only in the upper few cm's or 10's of cm's, D_B will be a function of depth. In those circumstances, the time dependence of concentration is given by:

$$\left(\frac{\partial C}{\partial t}\right)_x = \left\{\frac{\partial(D_B(\partial C_i/\partial x))}{\partial x}\right\}_t \qquad 5.150$$

Since molecular diffusion through solids is much lower than through liquids, one can generally neglect diffusion in the solid and deal only with diffusion through the pore water. Because pore water

only occupies a fraction, ϕ, of the total volume of sediment, the flux will be reduced accordingly. Thus the diffusion of a dissolved species will be:

$$J_M = -\phi D_M \left(\frac{\partial C_i}{\partial x} \right) \quad 5.151$$

where we have adopted the subscript M to denote molecular diffusion. Fick's second law becomes:

$$\left(\frac{\partial C_i}{\partial t} \right)_x = \frac{1}{\phi} \frac{\partial \left(\partial \phi D_M \left(\partial C_i / \partial x \right) \right)}{\partial x} \quad 5.152$$

The advective flux is the product of the fluid (i.e., pore water) velocity times the concentration:

$$J_A = vC_i \quad 5.153$$

To describe the rate of change in concentration in the box, we want to know the rate of reactions within it and the change in flux across it, as it is the change in flux that dictates what is lost or gained by the box. Combining all the fluxes into a single term, F_i, the rate of change of species *i* in the box is:

$$\frac{dC_i}{dt} = -\frac{\partial F_i}{\partial x} + \sum R_i \quad 5.154$$

where the second term is the sum of the rates of all reactions affecting *i*. The flux term is negative because any decrease in flux over *dx* results in an increase in concentration within the box.

We can then use equation 5.144 to transform to a reference frame fixed relative to the sediment surface:

$$\left(\frac{\partial C_i}{\partial t} \right)_x = -\left(\frac{\partial F_i}{\partial x} \right)_t - \omega \frac{\partial C_i}{\partial x} + \sum R_i \quad 5.155$$

The downward burial of sediment past point *x* can also be considered a flux. Combining this with the other flux terms, we have:

$$\boxed{\left(\frac{\partial C_i}{\partial t} \right)_x = -\left(\frac{\partial F_i}{\partial x} \right)_t + \sum R_i} \quad 5.156$$

where F is the *net* flux of *i* in and out of the box and the last term is the rate of all internal changes, including chemical, biochemical, and radioactive, occurring within the box. Equation 5.156 is called the *Diagenetic Equation* (Berner, 1980). Let's now consider an example that demonstrates how this equation can be applied.

5.7.2 Reduction of Sulfate in Accumulating Sediment

Organic matter buried with the sediment will be attacked by aerobic bacteria until all dissolved O_2 is consumed. When O_2 is exhausted, often within tens of centimeters of the surface, consumption will continue anaerobically with sulfur in sulfate acting as the electron acceptor:

$$2\alpha CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad 5.157$$

where CH_2O represents organic matter generally and α is the number of organic matter carbon atoms reduced per sulfur atom. Let's assume that the rate of sulfate reduction depends only on the supply of organic matter and not on the abundance of sulfate. In this case:

$$\frac{d[CH_2O]}{dt} = -k[CH_2O] \quad 5.158$$

We are greatly simplifying matters since there are a great variety of organic compounds in sediments each of which will have a different rate constant. To further simplify matters, we will assume (1) that conditions become anaerobic at the sediment-water interface, (2) that all consumption of organic matter occurs anaerobically, (3) that steady-state is achieved (i.e., $(\partial C/\partial t)_x = 0$), and (4) there is no compaction (and therefore no pore water advection) or bioturbation. Substituting 5.158 into 5.148, we have:

$$-k[CH_2O] = \omega\left(\frac{\partial[CH_2O]}{\partial x}\right)_t \qquad 5.159$$

Integrating, we obtain the concentration of organic matter as a function of depth:

$$[CH_2O](x) = [CH_2O]^\circ e^{-kx/\omega} \qquad 5.160$$

where $[CH_2O]^\circ$ is the organic matter concentration at the sediment-water interface (x = 0).

We can now also solve for the variation in concentration sulfate in the pore water. According to equation 5.9, the rate of sulfate reduction is related to the organic matter consumption rate as:

$$\frac{d\left[SO_4^{2-}\right]}{dt} = \frac{1}{2\alpha}\frac{d[CH_2O]}{dt} = \frac{k[CH_2O]^\circ}{2\alpha}e^{-kx/\omega} \qquad 5.161$$

Whereas the organic matter can be considered fixed in sediment, the sulfate is a dissolved species, so we must also consider diffusion. Making appropriate substitutions into 5.156, we have:

$$\phi D\left(\frac{\partial^2\left[SO_4^{2-}\right]}{\partial x^2}\right) - \omega\left(\frac{\partial\left[SO_4^{2-}\right]}{\partial x}\right)_t - \frac{k[CH_2O]^\circ}{2\alpha}e^{-kx/\omega} = 0 \qquad 5.162$$

This is a second order differential equation and its solution will depend on the boundary conditions. Our boundary condition is that at x = 0, C = C°. The solution under these conditions is:

$$[SO_4^{2-}] = \frac{\omega^2[CH_2O]^\circ}{2\alpha(\omega^2 + kD)\phi}\left(e^{kx/\omega} - 1\right) + [SO_4^{2-}]^\circ \qquad 5.163$$

where $[SO_4^{2-}]^\circ$ is the sulfate concentration at the surface.

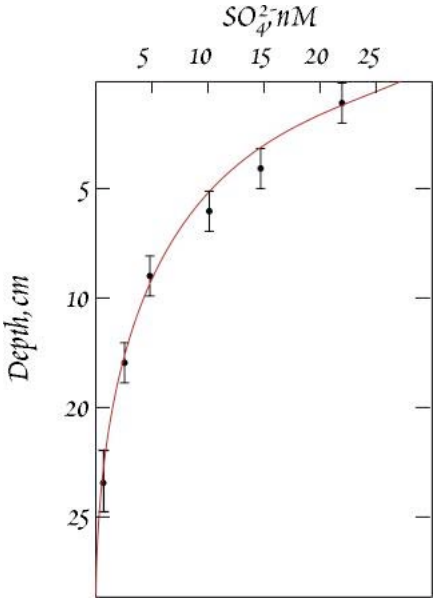


Fig. 5.38. Dissolved sulfate concentrations in sediments from the Saanich Inlet. Data are shown as open circles with error bars. Curve is fitted using equation 5.163 and parameters given in the text. From Murray et al. (1978).

Murray et al. (1978) applied this model to data from sediment cores taken from Saanich Inlet of British Columbia (Figure 5.38). Sedimentation rate, ω, was determined using ^{210}Pb (see Chapter 8) to be about 1 cm/yr, the factor α was independently estimated to be 0.5, and average porosity of 0.927. The value of D was taken to be 2.6×10^{-6} cm^2/sec. They fit an exponential curve of the form $c = a\,e^{-bx}$ to the data and found $a = 26.6$ and $b = 0.184$. From this they determined the rate constant to be 6.1×10^{-9} sec^{-1}, and the initial concentration of metabolizable organic matter to be 380 mM/cm^3 total sediment. The latter was somewhat larger than the value determined from the profile of total organic carbon in the core. To explain the discrepancy, the authors suggested methane is produced below the depth where sulfate is depleted. Methane then diffuses upward and is oxidized by sulfate-reducing bacteria.

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PROBLEMS

1. (a) Assuming that the precipitation of calcite from aqueous solution occurs only through the reaction:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)}$$

and that this reaction is *elementary*, write an equation for the rate of calcite precipitation.

(b) Assuming that the reaction above is reversible, i.e.:

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_{3(s)}$$

and still assuming that it is *elementary*, write an equation for the dependence of *net* rate of calcite precipitation on concentration and free energy change of reaction.

2. Zhong and Mucci (1993) found that at constant concentration of dissolved Ca^{2+} ($[Ca^{2+}] \approx 10.5$ mmol/kg), the rate of calcite precipitation in seawater obeyed the following rate law:

$$\Re = K_f [\, CO_3^{2-}]^3 - k_-$$

where $K_f = k_+ (a_{Ca^{2+}})^n \gamma^3_{CO_3} = 10^{3.5}$ and $k_- = 0.29$ ($\Re$ is in units of μmol m^{-2} h^{-1}).

(a) Is this rate law consistent with the mechanism of calcite precipitation in seawater being the elementary one described in problem 5.1 or with a more complex reaction mechanism? Justify your answer.

(b) Using this rate law, predict the rate of calcite precipitation for concentrations of CO_3^{2-} of 0.04, 0.066, and 0.3 mmol/kg.

3. Oxidation of methane in the atmosphere occurs through a number of mechanisms, including reaction with the hydroxyl radical:

$$OH + CH_4 \rightleftarrows H_2O + CH_3$$

The rate of this reaction for a series of temperatures is shown in the adjacent table. Based on these data, estimate the activation energy and frequency factor for this reaction. (*HINT*: Try using linear regression).

RATES OF METHANE-HYDROXYL REACTION

T, °C	k
25	$6.60\times^{-15}$
10	$4.76\times^{-15}$
0	$3.76\times^{-15}$
-10	$2.93\times^{-15}$
-25	$1.93\times^{-15}$

4. Schrott et al. (1981) found that dependence on pH of the rate of dissolution of enstatite could be expressed as:

$$\Re = k\, a_{H^+}^n$$

where *k* shows a typical Arrhenius temperature dependence.

a.) Reaction rates were measured at a series of pH values at constant temperature (22° C). These data are shown in the adjacent table. Using these data, estimate values of *k* and *n* for this temperature (*HINT*: try using linear regression).

RATE OF ENSTATITE DISSOLUTION

pH	Rate moles Si/g-sec
1	2.75×10^{-10}
2	7.08×10^{-11}
6	2.82×10^{-13}

b.) Reaction rates were also determined at various temperatures at constant pH (6). Using these data, estimate the activation energy and frequency factor for the rate constant.

T ° C	Rate moles Si/g-sec
20	3.72×10^{-13}
50	2.34×10^{-12}
60	4.07×10^{-12}
75	8.13×10^{-12}

c.) Using your results from (a) and (b), estimate the rate of reaction (in moles Si released per sec per gram enstatite) at pH 4 and 30° C.

5. Marcasite and pyrite are polymorphs of FeS_2. Though pyrite has a lower ΔG_f than marcasite, the latter often forms metastably. Lennie and Vaughan (1992) found that the kinetics of the marcasite to pyrite transformation follows a simple first order rate law:

$$-\frac{d\alpha}{dt} = k\alpha$$

where α is the volume fraction of marcasite and *k* has the usual Arrhenius temperature dependence with $A = 2.76 \times 10^{17}$ sec^{-1} and $E_A = 253$ kJ/mol. Assuming a system consisting initially of pure marcasite, calculate the time required for one half of the marcasite to convert to pyrite (i.e., $\alpha = 0.5$) at 300° C and 350° C.

6. If ΔG is the free energy of reaction for the reaction:

$$A + BC \rightarrow AC + B \qquad (1)$$

and assuming (1) this is an elementary reaction, (2) ideal behavior, and (3) it is a reversible reaction, show that the ratio of the forward and reverse rates of (1) is:

$$\frac{\Re_+}{\Re_-} = e^{-\Delta G/RT} \qquad (5.57)$$

(*HINT, start with equation 5.43*).

7. On a temperature-pressure diagram, draw a line such that the time required for complete conversion of a 1 mm aragonite crystal to calcite will be complete within 10^5 years. Assume spherically symmetric growth of calcite from a single nucleus in the center. Use the thermodynamic data in Table 2.2 and $\Delta G^* = 184$ kJ (see Example 5.4).

8. Using the data given in Example 5.5 for the reaction:

$$Ca_2Mg_5Si_8O_{22}(OH) + 11CaMg(CO_3)_2 \rightleftarrows 8Mg_2SiO_4 + 13\ CaCO_3 + 9CO_2 + H_2O$$

Tremolite + 11 Dolomite $\rightleftarrows$ 8 Forsterite + 13 Calcite + 9 CO_2 + H_2O

make a plot of the relative volume of dolomite (V_{Do}/V_{Do_0}) as a function of time assuming an initial temperature of 620° C (the equilibrium temperature) and a heating rate of 0.1° per year.
(*HINT:* Because the reaction is fast, the overall temperature change will be small, so you may assume that T (i.e. absolute temperature) is constant. However, because the temperature is close to the equilibrium temperature, the change in the temperature overstep, ΔT, will be significant. Approximate ΔG in equation 5.72 as $\Delta S \Delta T$ and express ΔT as a function of time, $\Delta T = R_H t$ where R_H is the heating rate, then integrate.)

9. The transformation of kaolinite to illite (muscovite) may be written as:

$$K^+ + 1.5Al_2Si_2O_5(OH)_4 \rightleftarrows H^+ + KAl_3Si_3O_{10}(OH)_2 + 1.5H_2O$$

Chermack and Rimstidt (1990) determined that the forward rate of reaction was:

$$-\frac{d[K^+]}{dt} = k_+[K^+]$$

Forward and reverse rate constants for the reaction were determined to be:

$$\ln k_+ = 12.90 - 1.87 \times 10^4/T \qquad \text{and} \qquad \ln k_- = 6.03 - 1.21 \times 10^4/T$$

a.) What are the activation energies for the forward and reverse reactions?
b.) What is the equilibrium constant for this reaction at 275 ° C ?
c.) Make a plot of log $\Re_{net}$ vs. log ($[H^+]/[K^+]$) at 250° C assuming a K^+ concentration of 2.0 x 10^{-6} M, ideal solution, that muscovite and kaolinite are pure phases, and that the forward and reverse reactions are elementary.

10. Using the data in Table 5.2, determine the diffusion coefficient for diffusion of Ba in an andesitic melt for T = 1200°, 1100°, 1000°, and 900°C (assume the parameters are valid over this temperature range; remember to use thermodynamic temperature).

11. Using the data in Example 5.8, calculate the diffusion flux for Mg and Fe in garnet.

12. A remarkable feature of sediments recording the Cretaceous-Tertiary Boundary is an enrichment in iridium (Ir) at the boundary, which is often marked by a boundary clay. Imagine a boundary clay 5 cm thick that initially has a uniform Ir concentration of 20 ppb. Assume and that sediments above and below the boundary clay contain negligible Ir. If the detection limit for Ir is 2 ppb, how thick would the Ir-enriched layer be after 60 million years if the diffusion coefficient for Ir is 10^{-15} cm^2/sec?

13. Assuming a surface free energy of 10^{-4} J/cm^2, $\bar{V}$ = 101 cc/mol, ΔH_m = 54.84 kJ/mol, and T_m = 1118° C, what is the critical radius for a spherical albite crystal growing in a pure albite melt that has been undercooled by 10°, 20°, and 30°?
Make a plot of ΔG_{tot} as a function of crystal radius for each of these temperatures. (*HINT*: your scale should span only 10 or 20 use microns.)

14. Crystal growth and dissolution are reactions that involve both diffusion and surface reactions occurring in series (i.e., a component of a growing crystal must first be delivered to the surface, then incorporated in the growing crystal). Either of these processes can be the rate-limiting step at 25° C. Diffusion in aqueous solutions typically has an activation energy of 20 kJ/mol whereas surface reactions in aqueous solution typically have activation energies of 60-80 kJ/mol. Assuming the rates of diffusion and surface reaction for growth of a certain mineral from aqueous solution are approximately equal at 25° C, will diffusion or surface reaction be rate-limiting at 200°C?

15. Some anaerobic bacteria can utilize Mn^{4+} to oxidize organic matter. The reaction may be represented as:

$$2MnO_2(s) + CH_2O + H_2O \rightleftarrows 2Mn^{2+} + CO_2 + 4OH^-$$

In its oxidized form, Mn is highly insoluble and effectively immobile in sediment. However, in its reduced form, Mn is soluble and mobile. Imagine that at a depth of 50 cm in actively depositing marine sediments conditions become sufficiently reducing so that the reaction above occurs. Furthermore, assume that reaction is such that a constant concentration of 0.02 mM of Mn^{2+} is maintained at this depth and below. Above this depth, Mn^{2+} is oxidized and precipitated through reactions such as:

$$Mn^{2+} + 2OH^- + \frac{1}{2}O_2 \rightleftarrows MnO_2(s) + H_2O$$

Assuming (1) that the rate of the above reaction may be written as:

$$-\frac{d[Mn^{2+}]}{dt} = k[Mn^{2+}]$$

(2) k for this reaction is 1×10^{-8} sec^{-1}, (3) the concentration of Mn^{2+} at the sediment-water interface is 0 and that diffusion from below is the sole source of Mn^{2+} between 0 and 50 cm, (4) D is 5×10^{-6} cm/sec, (5) a sedimentation rate of 1 cm/yr, (6) there is no advection, compaction, or bioturbation, and (7) a porosity of 0.85, make a plot of the concentration of dissolved Mn^{2+} vs. depth at steady state.

16. Diamond is remarkably stable at the surface of the Earth. Pearson et al. (1995) estimated that to convert 1 cc of diamond to graphite at 0.1MPa and 1000°C would require 1 billion years, but only a million years would be required at 1200°C. From the difference in these rates, estimate the activation energy for the diamond-graphite transition.