

$$\begin{aligned} \frac{d[A]}{dt} &= -k_+[A] + k_-[\Sigma AB - A] \\ &= -(k_+ + k_-)[A] + k_- \Sigma AB \end{aligned} \quad (5.37)$$

The concentration at some time  $\tau$ ,  $[A]_\tau$ , is obtained by integrating 5.37:

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

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:

$$\frac{-k_+[A]_\tau + k_-[B]_\tau}{-k_+[A]^\circ + k_-[B]^\circ} = e^{-(k_+ + k_-)\tau} \quad (5.38)$$

Thus in the general case, the concentrations of A and B will depend on their initial concentrations (see Example 5.3). However, for

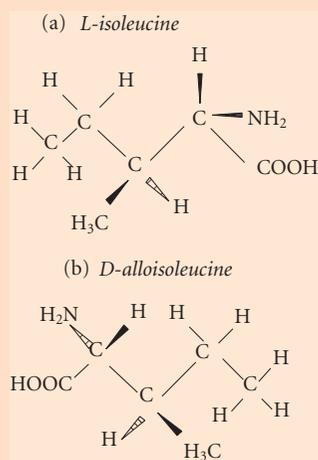
### Example 5.3 Racemization of amino acids

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 acids come 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 (Figure 5.5a). After death of the organism, however, the amino acid can spontaneously convert to its mirror image, the D-form (Figure 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  $\rightarrow$  d-alloisoleucine is  $9.6 \times 10^{-7} \text{y}^{-1}$  and for the d-alloisoleucine  $\rightarrow$  l-isoleucine is  $9.6 \times 10^{-8} \text{y}^{-1}$ , 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 eqn 5.38 where  $[B]^\circ$  is 0 and  $[A] + [B] = [A]^\circ$ . Letting  $\gamma$  be the ratio  $[B]/[A]$  (d-alloisoleucine/l-isoleucine) and substituting into 5.38, we obtain:

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

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



**Figure 5.5** Structure 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.

$\tau = \infty$ , or as a practical matter when  $\tau \gg (k_+ + k_-)$ , then a steady state will be achieved where eqn. 5.38 reduces to:

$$k_+[A]_\infty = k_-[B]_\infty \quad (5.39)$$

### 5.3 RELATIONSHIPS BETWEEN KINETICS AND THERMODYNAMICS

#### 5.3.1 Principle of detailed balancing

Equation 5.39 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 upon in Chapter 2. It follows that  $[A]_\infty$  and  $[B]_\infty$  are 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:



at equilibrium the following relation must hold:

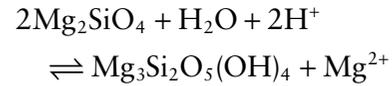
$$k_+[A]_{\text{eq}} = k_-[B]_{\text{eq}} \quad (5.40)$$

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 eqn. 5.40 with eqn. 3.85 to obtain:

$$\boxed{\frac{k_+}{k_-} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = K^{\text{app}}} \quad (5.41)$$

It is apparent from eqn. 5.41 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 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:



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:

$$K^{\text{app}} = \frac{[\text{Mg}^{2+}]}{[\text{H}^+]^2} \quad (5.42)$$

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

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

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

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

where  $[\text{Ol}]$  is the specific area (area per solution volume) of olivine in the experiment. From eqn. 5.7, we can express the rate for the reverse reaction as:

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

Using eqn. 5.41 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:

$$\frac{d[\text{Ol}]}{dt} = -2k' \frac{[\text{Mg}^{2+}]}{[\text{H}^+]^2} [\text{Ol}][\text{H}^+] \\ = -2k' \frac{[\text{Mg}^{2+}]}{[\text{H}^+]} [\text{Ol}] \quad (5.43)$$

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 (eqn. 5.22) to the heat (enthalpy) of reaction. Recall that the equilibrium constant is related to free energy change of reaction as:

$$K = e^{-\Delta G_r^\circ/RT} = e^{-\Delta H_r^\circ/RT + \Delta S_r/R} = e^{\Delta S_r/R} e^{-\Delta H_r^\circ/RT} \quad (5.44)$$

(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  $K^{\text{app}} = K$ .) If we write the Arrhenius relations for the forward and reverse reactions and combine them with eqn. 5.41 we obtain:

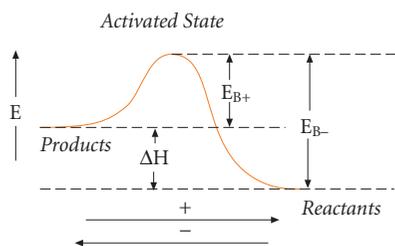
$$\frac{k_+}{k_-} = \frac{A_+ e^{-E_+/RT}}{A_- e^{-E_-/RT}} = \frac{A_+}{A_-} e^{-(E_+ - E_-)/RT} = K \quad (5.45)$$

Comparing equations 5.44 and 5.45, we can see that:

$$\text{and} \quad E_+ - E_- = \Delta H_r^\circ \quad (5.46)$$

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  $\Delta H$  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:

$$\frac{A_+}{A_-} = e^{\Delta S_r/R} \quad (5.47)$$



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

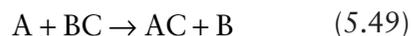
Indeed, it can be shown that Arrhenius coefficient, or frequency factor, is related to entropy as:

$$A_+ = \frac{kT}{h} e^{\Delta S_r^\ddagger/R} \quad (5.48)$$

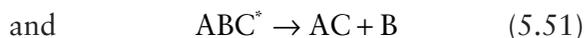
where  $\Delta S_r^\ddagger$  is the entropy difference between the initial state and the activated state (discussed below) and  $h$  is Planck's constant. The ratio  $kT/h$  has units of  $\text{time}^{-1}$  and is called the *fundamental frequency*. At 298 K, it has a value of  $6.21 \times 10^{12}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

### 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:



proceeds through the formation of an *activated complex*  $ABC^*$ , also called a reactive intermediate. Thus reaction 5.49 can be described by the mechanism:



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 reaction 5.50 (assuming ideal behavior) as:

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

as well as a free energy change:

$$\Delta G^* = -RT \ln K^*$$

and enthalpy and entropy changes:

$$\Delta G^* = \Delta H^* - T \Delta S^*$$

Though to do so here would take us too far afield, it can be shown from a statistical mechanical approach that the rate constant for 5.50 is:

$$k = \kappa \frac{kT}{h} K^* \quad (5.52)$$

where  $kT/h$  is the fundamental frequency as we defined it above, and  $\kappa$  is a constant, called the transmission coefficient, whose value is often close to 1. Equation 5.52 is known as the *Eyring Equation*.<sup>\*</sup> It is then easily shown that the rate constant is:

$$k = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \quad (5.53)$$

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 (see Example 5.4).

### Example 5.4 Estimating $\Delta G^\ddagger$ for the aragonite-calcite transition

Aragonite is the high-pressure form of  $\text{CaCO}_3$ . 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  $\Delta G^\ddagger$  for this reaction.

Aragonite to calcite transition rates

T °C	R (m/sec)
455	$7.45 \times 10^{-09}$
435	$3.36 \times 10^{-09}$
415	$1.61 \times 10^{-09}$
395	$6.24 \times 10^{-10}$
372	$2.72 \times 10^{-10}$

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

$$k_+ = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \quad (5.53)$$

From eqn. 5.58, the the rate of the net reaction is:

$$\mathfrak{R}_{net} = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} (1 - e^{\Delta G/RT})$$

This rate expression has units of  $\text{time}^{-1}$ , 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

<sup>\*</sup> 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.

distance in this case would be lattice spacing, which for aragonite is about  $5 \text{ \AA}$  (or  $5 \times 10^{-10} \text{ m}$ ). Thus if  $\lambda$  is the lattice spacing, we have

$$\mathfrak{R}_{net} = \frac{\lambda k T}{h} e^{-\Delta G^*/RT} (1 - e^{\Delta G/RT}) \text{ m/s}$$

Solving for  $\Delta G^*$ :

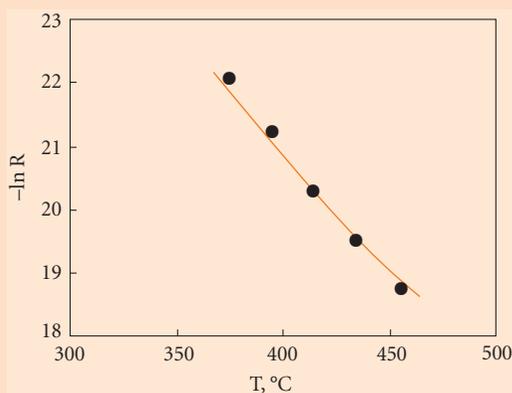
$$\Delta G^* = -RT \left[ \ln \mathfrak{R}_{net} - \ln \frac{\lambda k T}{h} - \ln(1 - e^{\Delta G/RT}) \right]$$

To determine  $\Delta G^*$ , we have to calculate  $\Delta G$ , which we can do using the thermodynamic data in Table 2.2 and eqn. 2.134. Our spreadsheet is shown below. Calculating the average  $\Delta G^*$  for the 4 measurements, we find  $\Delta G^* = 161 \text{ KJ}$ . We can then use  $\Delta G^*$  to predict the reaction rates. A comparison between the measured and predicted reaction rates is shown in Figure 5.7.

R	8.314	J/mol-K	h	6.63E-34	J-sec
k	1.38E-23	J/K	$\lambda$	5.00E-10	m
$\lambda k/h$	1.04E+01	m/K-sec			

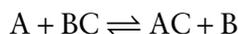
  

T °C	R m/sec	ln R	T, K	$\Delta G$ , J	$\ln(1 - \exp(\Delta G/RT))$	$\ln(\lambda k T/h)$	$\Delta G^*$ kJ	-ln Rcalc
455	7.45E-09	18.7152	728	-2828.8	-0.985	8.933	161.38	18.6485
435	3.63E-09	19.4352	708	-2709.3	-0.997	8.906	160.95	19.4397
415	1.61E-09	20.2452	688	-2592	-1.010	8.877	160.80	20.2756
395	6.24E-10	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
						$\Delta G^*$	<b>160.98</b>	ave



**Figure 5.7** Comparison of observed and predicted rates of the aragonite→calcite reaction. Data (circles) from Carlson (1980).

Now consider that reaction 5.49 is reversible so that:



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

The net rate of reaction is:

$$\mathfrak{R}_{net} = \mathfrak{R}_+ - \mathfrak{R}_- \quad (5.54)$$

If  $\Delta G$  is the free energy difference between product and reactant, then the free energy difference between the product and the activated complex must be  $\Delta G - \Delta G^*$ . From this it is readily shown (Problem 3) that the ratio of the forward and reverse reaction rates is:

$$\frac{\mathfrak{R}_+}{\mathfrak{R}_-} = e^{-\Delta G/RT} \quad (5.55)$$

where  $\Delta G$  is the actual free energy difference between products and reactants. The negative of  $\Delta G$  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  $\Delta G$ ). Substituting 5.55 into 5.54 and rearranging, we have:

$$\mathfrak{R}_{net} = \mathfrak{R}_+(1 - e^{\Delta G/RT}) \quad (5.56)$$

If the forward reaction is an elementary one, then  $\mathfrak{R}_+$  will be:

$$\mathfrak{R}_+ = k_+[A][BC]$$

where  $k$  will be as defined in 5.22.

It must be emphasized that *equations 5.55 and 5.56 apply to elementary reactions only*. However, a similar equation may be written for *overall* reactions:

$$\mathfrak{R}_{net} = \mathfrak{R}_+(1 - e^{n\Delta G/RT}) \quad (5.57)$$

where  $n$  can be any real number. Using the Arrhenius expression for  $k$  (eqn. 5.22), eqn. 5.57 becomes:

$$\mathfrak{R}_{net} = A_+ e^{-E_{A^+}/RT} (1 - e^{n\Delta G/RT}) [A]^{n_A} [B]^{n_B} \dots \quad (5.58)$$

where  $[A]$ ,  $[B]$ ,  $\dots$  are the concentrations (surface areas for solids) of the reactants and the  $n$ 's can be any real number (Lasaga,

1981b). Equation 5.58 links kinetics and thermodynamics and forms the basis of *irreversible thermodynamics*.

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

$$\mathfrak{R}_{net} \approx -\frac{\mathfrak{R}_+\Delta G}{RT} \quad (5.59)$$

Thus close to equilibrium, the reaction rate will vary linearly with  $\Delta G$ , slowing as equilibrium is approached. Substituting  $A_r$  for  $-\Delta G$ , eqn. 5.59 can also be written as:

$$\mathfrak{R}_{net} \approx \frac{\mathfrak{R}_+ A_r}{RT} \quad (5.60)$$

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

$$\sum_i v_i \mu_i^\circ + RT \ln \prod_i a_i^{v_i} = 0 \quad (3.84)$$

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

$$Q \equiv \prod_i a_i^{v_i} \quad (5.61)$$

$Q$  is called the *reaction quotient* (Chapter 3). Though eqn. 5.61 has the same form as our definition of the equilibrium constant (eqn. 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 eqn. 3.86 as:

$$\Delta G^\circ + RT \ln Q = \Delta G \quad (5.62)$$

Since  $\Delta G^\circ$  is equal to  $-RT \ln K$ , eqn. 5.62 can be written as:

$$RT \ln Q - RT \ln K = \Delta G \quad \text{or:} \quad \frac{Q}{K} = e^{\Delta G/RT} \quad (5.63)$$

Substituting 5.63 into 5.56, we have for an elementary reaction:

$$\mathfrak{R}_{net} = \mathfrak{R}_+ \left(1 - \frac{Q}{K}\right) \quad (5.64)$$

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

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

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

where the subscript *eq* denotes the quantity when products and reactants are at equilibrium. Under non-equilibrium conditions,  $\Delta H - T\Delta S$  will have some finite value. We can make use of this and write:

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S - (\Delta H_{eq} - T_{eq}\Delta S_{eq}) \\ &= \Delta H - \Delta H_{eq} - (T\Delta S - T_{eq}\Delta S_{eq}) \end{aligned} \quad (5.65)$$

For temperatures close to the equilibrium temperature,  $\Delta H$  and  $\Delta S$  may be considered

constant (i.e., independent of temperature), so that eqn. 5.65 simplifies to:

$$A_r = -\Delta G = \Delta T\Delta S \quad (5.66)$$

where  $\Delta T = (T - T_{eq})$  and is sometimes called the *temperature overstep* (see Example 5.5). This may be substituted into eqn. 5.59, so that close to equilibrium we have

$$\mathfrak{R}_{net} = \frac{-\mathfrak{R}_+^2 \Delta S (T - T_{eq})}{RT_{eq}} \quad (5.67)$$

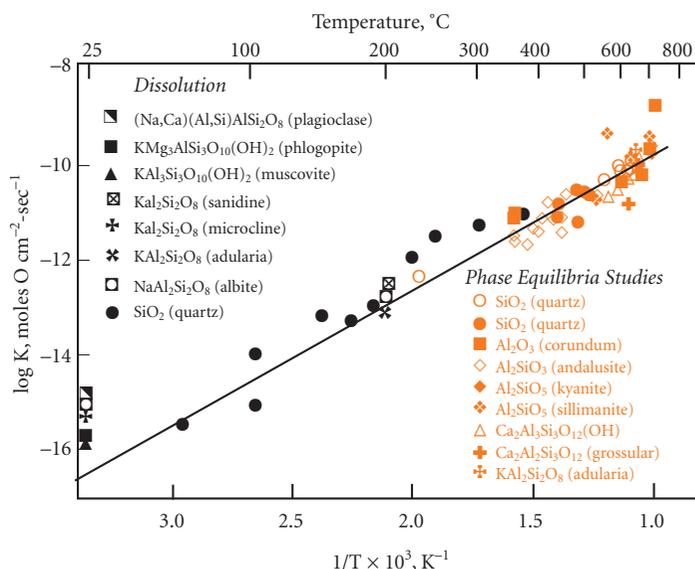
Wood and Walther (1983) used this equation to analyze experimental reaction rate studies of a variety of silicate–aqueous fluid reactions. They found that essentially all the experimental data could be fit to this equation if  $\mathfrak{R}_+$  is given by:

$$\mathfrak{R}_+ = -kA$$

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:

$$\log k = -2900/T - 6.85 \quad (5.68)$$

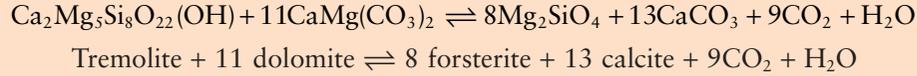
This is illustrated in Figure 5.8. The data show a scatter of more than 1 order of magnitude about the line, so clearly the equation cannot be used for exact prediction of reaction rates.



**Figure 5.8** 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). Reprinted with permission from AAAS.

### Example 5.5 Predicting rates of reversible metamorphic reactions

Consider the reaction:



Assume  $T = 625^\circ\text{C}$ ,  $\Delta S_r = 1.140\text{ kJ/K}$ ,  $E_A = 579\text{ kJ}$ ,  $A = 1.54 \times 10^{27}\text{ sec}^{-1}$  (Heinrich *et al.*, 1989), an overstep of the equilibrium temperature of  $5^\circ\text{C}$ , and that the dolomite crystals are perfect cubes, i.e.,  $V_{D_o} = (S_{D_o})^{2/3}$  where  $V_{D_o}$  and  $S_{D_o}$  are the volume and surface area respectively of dolomite. Assume further that the initial assemblage contains only tremolite plus dolomite and that the reaction rate can be expressed as in eqn. 5.58, i.e.:

$$\frac{-dV_{D_o} / V_{D_{o0}}}{dt} = k(1 - e^{\Delta G/RT}) S_{D_o} / S_{D_{o0}}$$

where  $V_{D_{o0}}$  and  $S_{D_{o0}}$  are the initial dolomite volume and surface areas respectively and  $k$  is the rate constant with the usual Arrhenius temperature dependence (the minus sign occurs because dolomite is a reactant). Calculate the extent of conversion of dolomite (i.e., volume relative to initial volume  $V_o$ ) as a function of time.

*Answer:* To solve this problem, we need to integrate the equation above. First, we substitute eqn. 5.22 for  $k$  and  $(V/V_{D_{o0}})^{2/3}$  for  $S_{D_o}/S_{D_{o0}}$ . Upon integration, we obtain:

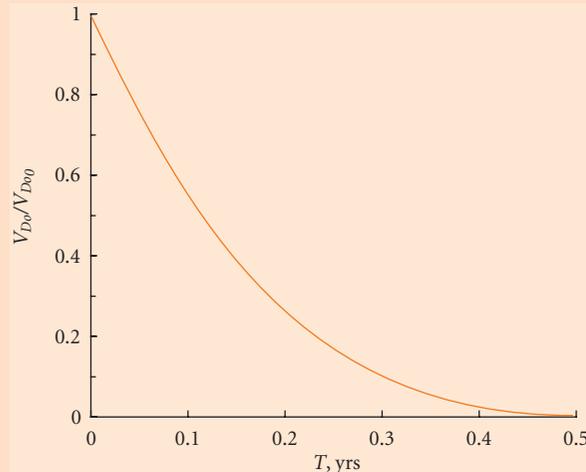
$$\frac{V_{D_o}}{V_{D_{o0}}} = \left[ 1 - \frac{A}{3} e^{-E_A/RT} (1 - e^{\Delta G/RT}) t \right]^3$$

Making use of  $-\Delta T \Delta S \approx \Delta G$  (where  $\Delta T$  is the temperature overstep; eqn. 5.66), we have:

$$\frac{V_{D_o}}{V_{D_{o0}}} = \left[ 1 - \frac{A}{3} e^{-E_A/RT} (1 - e^{\Delta T \Delta S/RT}) t \right]^3$$

The result is shown in Figure 5.9. On geological time-scales, this reaction is clearly quite fast, going to completion within half a year ( $1.5 \times 10^7$  sec), even with a relatively small temperature overstep of  $5^\circ\text{C}$ . We also see in Figure 5.9 that the rate of reaction decreases as time progresses. This occurs because of the decreasing dolomite surface area.

The temperature conditions we chose for this example, a constant  $5^\circ\text{C}$  overstep, are not geologically realistic. A more realistic assumption would be that of steady temperature increase, such as would occur around an igneous intrusion or as a result of burial or underthrusting. That situation is addressed in Problem 8 at the end of this chapter.



**Figure 5.9** Relative volume of dolomite as a function of time predicted at  $625^\circ\text{C}$ .

As Kerrick *et al.* (1991) pointed 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.

## 5.4 DIFFUSION

We cannot 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 geologic 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:

$$J = -D \frac{\partial c}{\partial x} \quad (5.69)$$

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<sup>2</sup>-sec. If concentration is expressed per unit volume, as is often preferred in kinetics, the diffusion coefficient has units of m<sup>2</sup>-sec<sup>-1</sup>. The

diffusion coefficient must be empirically determined and will depend upon the nature of the diffusing species, the material properties of the system in which diffusion is taking place and, as usual, temperature.

Strictly speaking, eqn. 5.69 is applicable to diffusion in only one dimension, and in our brief treatment here, we will consider only the one-dimensional case. A more general expression of Fick's First Law, applicable in three-dimensional space is:

$$\mathbf{J} = -D \nabla c \quad (5.70)$$

where  $\nabla c$  is:  $\nabla c = \frac{\partial c}{\partial x} \mathbf{x} + \frac{\partial c}{\partial y} \mathbf{y} + \frac{\partial c}{\partial z} \mathbf{z}$

and  $\mathbf{x}$ ,  $\mathbf{y}$ , and  $\mathbf{z}$  are unit vectors in the respective directions. In many cases, a three-dimensional case can be reduced to a one-dimensional one by choosing our  $x$ -direction to be the direction of the concentration gradient or by assuming that diffusion is radial. However, many materials, and in particular most minerals, are anisotropic so that diffusion will proceed more rapidly in one direction than in others (this effect can be as large as several orders of magnitude). In that case, eqn. 5.70 becomes:

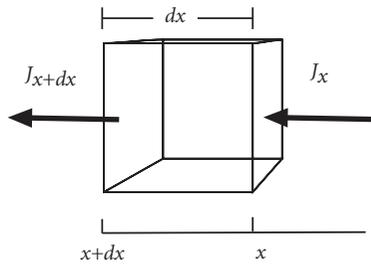
$$\mathbf{J} = -\mathbf{D} \times \nabla c \quad (5.70a)$$

where  $\mathbf{D}$  is a tensor represented by symmetric 3×3 matrix:

$$D = \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{12} & D_{22} & D_{23} \\ D_{13} & D_{23} & D_{33} \end{pmatrix}$$

Now let's consider how concentration will change with time as a consequence of diffusion. Imagine a volume enclosed in a cube of dimension  $dx$  (Figure 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 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

\* Named for Adolf Fick (1829–1901). Fick was born in Kassel, Germany, and earned an MD from the University of Marburg in 1851. Fick'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.



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

atoms,  $dn$ , within the volume is just what goes in minus what comes 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:

$$\left(\frac{\partial c}{\partial t}\right)_x = -\left(\frac{\partial J}{\partial x}\right)_t \quad (5.71)$$

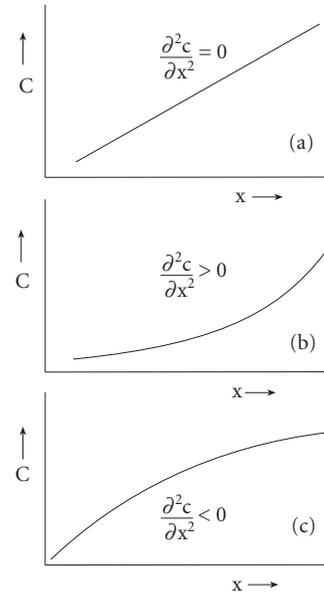
Equation 5.71 is called the equation of continuity since it follows from mass conservation. Now since the flux is given by Fick's First Law, we can write:

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

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

$$\boxed{\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t} \quad (5.72)$$

Equation 5.72 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.



**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 (b),  $\partial^2 c/\partial x^2 > 0$  and hence the concentration at any point increases with time. In (c),  $\partial^2 c/\partial x^2 < 0$  and therefore the concentration at any point decreases with time. Both (b) and (c) will tend, with time, toward the steady-state case (a).

#### 5.4.1.1 Solutions to Fick's Second Law

There is no single solution (i.e., function expressing  $c(t,x)$ ) for eqn. 5.72; 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 Boundary). 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 eqn. 5.72. We take the position of enriched horizon to be 0, and we seek a solution to 5.72 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:

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

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

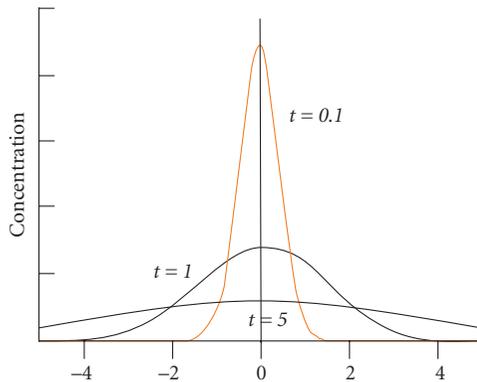
The solution is given by Crank (1975) as:

$$c(x, t) = \frac{M}{2(\pi Dt)^{1/2}} e^{-x^2/4Dt} \quad (5.73)$$

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  $\sigma = (2Dt)^{1/2}$ .

Suppose a boundary condition is imposed such 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:

$$c(x, t) = \frac{M}{(\pi Dt)^{1/2}} e^{-x^2/4Dt} \quad (5.74)$$



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

Now consider a situation where the diffusing species has an initial uniform concentration  $C_0$  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 two experimental charges adjacent to one another, 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  $\Delta\xi$  (Figure 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:

$$c(x, t) = \frac{C_0}{2(\pi Dt)^{1/2}} \int_x^{\infty} e^{-\xi^2/4Dt} d\xi \quad (5.75)$$

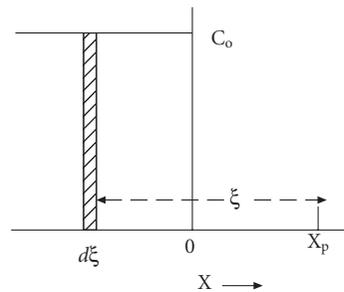
or defining

$$\eta = \xi / 2\sqrt{Dt} \quad (5.76)$$

$$c(x, t) = \frac{C_0}{\pi^{1/2}} \int_{x/2\sqrt{Dt}}^{\infty} e^{-\eta^2} d\eta$$

The integral in eqn. 5.76 may be written as:

$$\int_{\frac{x}{2\sqrt{Dt}}}^{\infty} e^{-\eta^2} d\eta = \int_0^{\infty} e^{-\eta^2} d\eta - \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\eta^2} d\eta \quad (5.77)$$



**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). By permission of Oxford University Press.

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

$$\text{erf}(x) = \frac{2}{\pi^{1/2}} \int_0^x e^{-\eta^2} d\eta \quad (5.78)$$

Substituting eqn. 5.78 into 5.76, and since  $\text{erf}(\infty) = 1$ , eqn. 5.78 becomes:

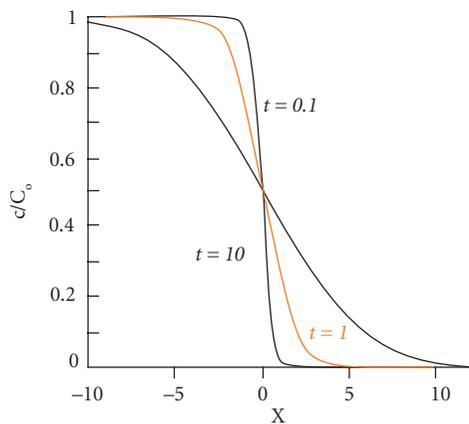
$$c(x, t) = \frac{C_0}{2} \left\{ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right\} \quad (5.79)$$

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:

$$\text{erf}(x) \cong \sqrt{1 - \exp(-4x^2 / \pi)} \quad (5.80)$$

Figure 5.14 shows how the concentration profile will appear at different times. Since  $\text{erf}(0) = 0$ , the profiles have the interesting property that  $c = C_0/2$  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



**Figure 5.14** Distribution of a diffusing species initially confined to  $-\infty < x < 0$  at three time intervals after diffusion begins.

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 eqn. 5.75 is carried out from  $-h$  to  $+h$ . The result is:

$$c(x, t) = \frac{C_0}{2} \left\{ \text{erf} \left( \frac{h-x}{2\sqrt{Dt}} \right) + \text{erf} \left( \frac{h+x}{2\sqrt{Dt}} \right) \right\} \quad (5.81)$$

#### 5.4.2 The diffusion coefficient and diffusion in multicomponent systems

There are two 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) *Tracer, or self-diffusion*, in which the net mass and charge fluxes associated with the diffusing species are sufficiently small that they can be safely ignored. There may be no significant concentration gradient. This situation occurs when, for example, an experimental charge is doped with a radioactive isotope in suf-

\*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  $\text{erf}(-x) = -\text{erf}(x)$ . In working with Excel, test for a negative value of  $x$  and where  $x < 0$  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, use a statement such as “=IF(X<0,-ERF(-X),ERF(X))”.

### 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 into 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 one 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:

$$\frac{c - C_i}{C_r - C_i} = 1 + \frac{2r}{\pi x} \sum_{n=1}^{\infty} \frac{-1^n}{n} \sin\left(\frac{n\pi x}{r}\right) \exp\left(\frac{-Dn^2\pi^2 t}{r^2}\right) \quad (5.82)$$

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

$$C_0 = (C_r - C_i) \left\{ 1 + 2 \sum_{n=1}^{\infty} -1^n \exp\left(\frac{-Dn^2\pi^2 t}{r^2}\right) \right\} + C_i \quad (5.83)$$

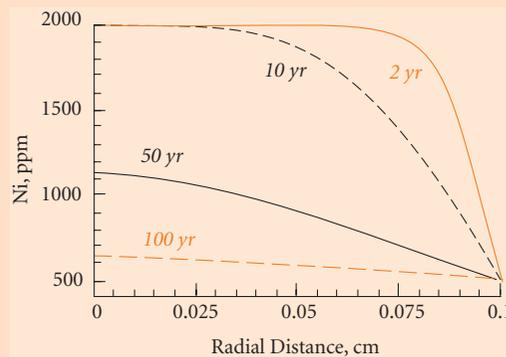
From eqn. 5.69, we see that as the concentration gradient disappears, the rate of diffusion goes to 0. So the crystal approaches homogeneity only asymptotically, becoming homogenous only at  $t = \infty$ , but it will become *essentially* homogenous more quickly. *Essentially homogenous* implies we could 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 long will it take before the concentration gradient is less than 5%? We set  $C_0/C_r = 1.05$  and substituting into eqn. 5.83 and rearranging, we obtain:

$$0.05 \leq \left(1 - \frac{C_i}{C_r}\right) 2 \sum_{n=1}^{\infty} -1^n \exp\left(\frac{-Dn^2\pi^2 t}{r^2}\right) \quad (5.84)$$

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 eqn. 5.84 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  $D = 10^{-12} \text{ cm}^2/\text{sec}$  given by Morioka and Nagasawa (1990), 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.



**Figure 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.

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

$$J = -L \frac{\partial \mu}{\partial x} \quad (5.85)$$

and

$$\left( \frac{\partial c}{\partial t} \right)_t = L \left( \frac{\partial^2 \mu}{\partial x^2} \right)_t \quad (5.85a)$$

$L$  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 as a chemically zoned liquid or solid, or across a phase boundary. For

### 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, that a constant Sr concentration of 10 ppm is maintained in the water, and that the grain is spherical. If the diffusion coefficient for Sr in calcite is  $10^{-15}$  cm<sup>2</sup>/sec and the 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:

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

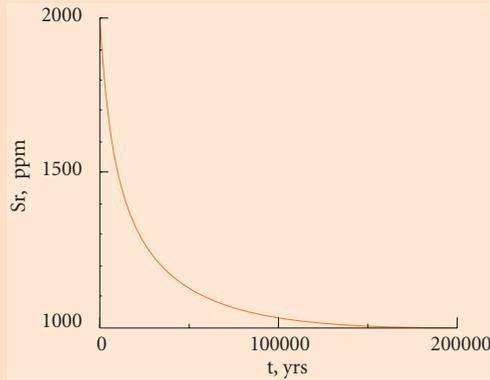
The average concentration of Sr in the grain at time  $t$  is then obtained by integrating and dividing by the volume:

$$\bar{C}(t) = \frac{1}{\frac{4}{3}\pi a^3} \int_0^a c(r, t) 4\pi r^2 dr \quad (5.86)$$

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

$$\bar{C}(t) = \frac{6C_i}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n} e^{-n^2 \pi^2 \frac{Dt}{a^2}} + C_0 \quad (5.87)^*$$

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 an initial concentration of 2000 ppm, a constant concentration in the pore water of 10 ppm and a calcite/water distribution coefficient of 100.

\* The summation in eqn. 5.87 is slow if  $Dt/a^2$  is small. An alternative solution to eqn. 5.87 is:

$$\bar{C}(t) = 1 - \frac{6\sqrt{Dt}}{a} \left[ \sum_{n=1}^{\infty} \frac{e^{-\frac{na}{\sqrt{Dt}}}}{\sqrt{\pi}} - \frac{na}{\sqrt{Dt}} \left\{ 1 - \operatorname{erf} \left( \frac{na}{\sqrt{Dt}} \right) \right\} \right] + 3 \frac{Dt}{a^2} \quad (5.88)$$

The two solutions give identical results. They differ only in the ease of computation. For large values of  $Dt/a^2$  the summation in eqn. 5.87 is preferred. For small values of  $Dt/a^2$  5.88 is preferred.

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 eqn. 5.69 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 eqn. 5.85 correctly predicts that no diffusion will occur at equilibrium.

- (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:

$$J_i = - \sum_{k=1}^n D_{i,k} \frac{\partial c_k}{\partial x} \quad (5.89)$$

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 5.89 is known as the *Fick-Onsager Law*. The interdiffusion coefficient is related to the tracer diffusion coefficient as:

$$D_{i,k} = \frac{n_i D_i + n_k D_k}{n_i + n_k} \quad (5.90)$$

where  $n_i$  is the mole fraction of  $i$  and  $D_i$  is the tracer diffusion coefficient for  $i$  (see Example 5.8). For  $i = k$ , eqn. 5.90 reduces to  $D_{i,i} = D_i$ . The complete solution for diffusion flux in the system is:

$$\mathbf{J} = \mathbf{D}\mathbf{C} \quad (5.91)$$

where  $\mathbf{J}$  is the flux vector,  $\mathbf{D}$  is the diffusion coefficient matrix, or tensor, and  $\mathbf{C}$  is the concentration gradient vector:

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

where  $C_i$  is  $\partial c_i / \partial x$  (this is the same as eqn. 5.91, but in matrix notation). Interdiffusion can result in diffusion up a concentration gradient, because as we can see from eqn. 5.89, the flux of species  $i$  depends on the concentration gradients of all species, not just its own.

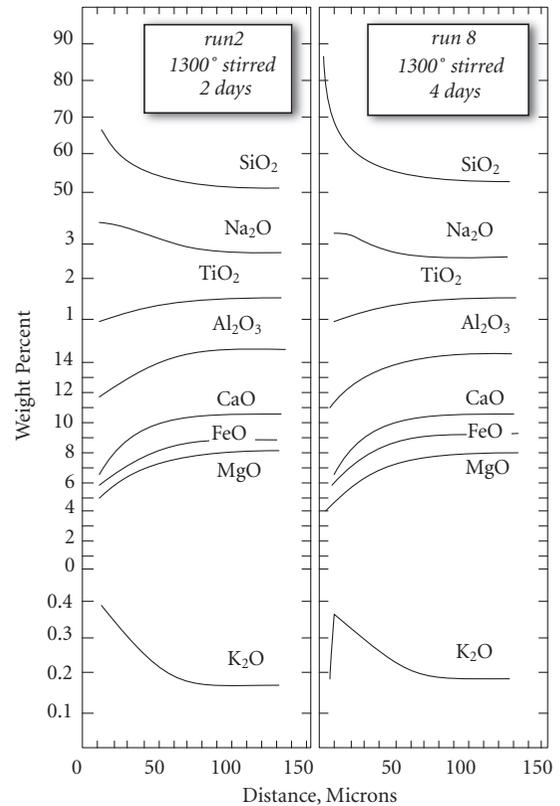
- (4) *Multicomponent chemical diffusion* refers to situations where both the chemical potential and the diffusion of other species must be considered. In this case, the diffusion flux is calculated according to equation 5.93, but the diffusion coefficient matrix,  $\mathbf{D}$ , must be calculated as:

$$\mathbf{D} = \mathbf{L}\mathbf{G} \quad (5.92)$$

where  $\mathbf{L}$  is the matrix of phenomenological coefficients and the elements of  $\mathbf{G}$ , 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) provide a good example of the complexity and non-intuitive nature of multicomponent chemical diffusion. In this experiment, a quartz sphere was dissolved in molten basalt. All elements except  $\text{SiO}_2$  were diffusing out of the basalt into  $\text{SiO}_2$ -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



**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  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  are diffusing “uphill”, that is, toward higher  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  concentrations in the  $\text{SiO}_2$ -rich liquid. From Watson (1982). With kind permission of Springer Science+Business Media.

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  $\nu$  (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:

### Example 5.8 Interdiffusion coefficients

Calculate the diffusion flux for Mn in a garnet given the interdiffusion coefficient matrix below (in  $\text{cm}^2/\text{sec}$ ) and the concentration gradients of  $0.023 \text{ mol/cm}$ ,  $-0.009 \text{ mol/cm}$  and  $-0.015 \text{ mol/cm}$  for  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$ , respectively.

Diffusion coefficient matrix for garnet

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

From Dempster (1975).

*Answer:* We calculate the diffusion flux for Mn using eqn. 5.89. We find that  $J_{\text{Mn}}$  is  $3 \times 10^{-21}$  mole/ $\text{cm}^2\text{-sec}$ .

$$J = \frac{vn_1/6 - vn_2/6}{dx^2} = \frac{v(n_1 - n_2)}{6 dx^2} \quad (5.93)$$

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 eqn. 5.93:

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

Letting  $dc = -(c_1 - c_2)$  and multiplying by  $dx/dx$ , we can rewrite this equation as:

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

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

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

Hence  $D$  is related to the jump frequency,  $v$ , 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 unno-

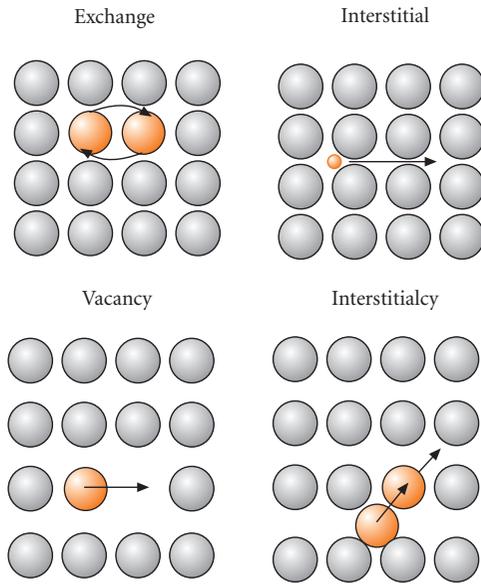
ticed. If we could distinguish the atoms, we could detect a flux even in the absence of a concentration gradient. Other factors, such as pressure or stress gradient, presence of an electromagnetic field, a temperature gradient, or concentration gradients of other species may make a jump in one direction 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.

#### 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



**Figure 5.18** Four types of diffusion mechanisms in solids. After Henderson (1986).

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 while 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 eqn. 5.14, 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:

$$\mathcal{P} = \aleph e^{-E_B/RT} \quad (5.94)$$

The number of attempts is simply the vibration rate,  $\nu$ , times the number of holes:

$$\aleph = \nu[N_{vac}] = \nu[N_{perm} + ke^{-E_H/RT}] \quad (5.95)$$

Combining eqns. 5.94 and 5.95 we have:

$$\mathcal{P} = \nu N_{perm} e^{-E_B/RT} + \nu k e^{-(E_H+E_B)/RT}$$

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

$$\aleph = \nu d N_{perm} e^{-E_B/RT} + \nu d k e^{-(E_H+E_B)/RT} \quad (5.96)$$

or

$$\aleph = m e^{-E_B/RT} + n e^{-(E_H+E_B)/RT} \quad (5.97)$$

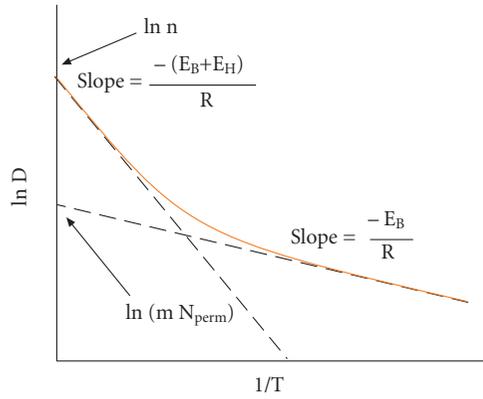
where  $n$  and  $m$  are simply two constants replacing the corresponding terms in eqn. 5.96. Thus diffusion rates generally will have a temperature dependence similar to eqn. 5.22. At low temperature, the permanent vacancies will dominate and the diffusion rate equation will look like:

$$\aleph \cong m e^{-E_B/RT} \quad (5.98)$$

At higher temperature where thermally generated vacancies come into play, the latter term in 5.97 dominates, and the diffusion rate equation will look like:

$$\aleph \cong n e^{-(E_H+E_B)/RT} \quad (5.99)$$

Diffusion that depends on thermally created vacancies is sometimes called *intrinsic* diffusion,



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

while that depending on permanent vacancies is called *extrinsic* diffusion. The boundary between these regions will vary, depending upon the nature of the material and the impurities present. For NaCl, the transition occurs around 500°C, while 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 eqns. 5.98 and 5.99.

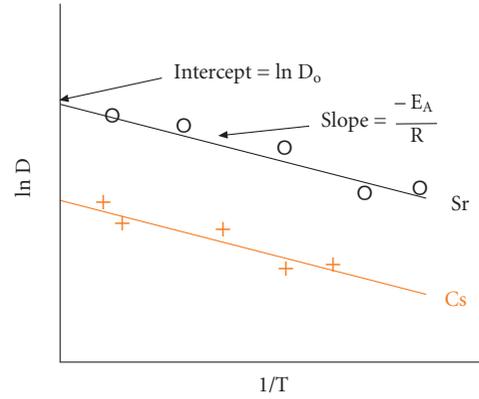
Combining  $E_B$  and  $E_H$  into a single activation energy term,  $E_A$ , which is the energy necessary to create the vacancy and move another atom into it, a typical expression for temperature dependence of the diffusion coefficient in solids is:

$$D = D_o e^{-E_A/RT} \quad (5.100)$$

where  $D_o$  is again called the frequency factor. As we have seen, it will depend upon 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 5.20). Taking the log of both sides of eqn. 5.100, we obtain:

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



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

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

$$D = D_o e^{-(E_A + (P - P_{ref})\Delta V)/RT} \quad (5.101)$$

where  $\Delta V$  is the “activation volume”.

#### 5.4.4 Diffusion in liquids

In both liquids and solids, diffusion coefficients depend upon 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  $3kT/2$  and a mean free path length of  $2\alpha dT$ , where  $\alpha$  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):

**Table 5.2** Self-diffusion frequency factors and activation energies.

Species	Phase	D <sub>0</sub> m <sup>2</sup> /sec	E <sub>A</sub> kJ/mol
Ar	Basaltic melt	8.05 × 10 <sup>-02</sup>	253
Ar	Orthoclase	3.74 × 10 <sup>-06</sup>	198
Ba	Basaltic melt	4.21 × 10 <sup>-07</sup>	130
Ca	Basaltic melt	1.22 × 10 <sup>-05</sup>	159
Co	Basaltic melt	1.59 × 10 <sup>-05</sup>	168
Fe	Garnet	6.4 × 10 <sup>-08</sup>	275
Mg	Olivine	9.6 × 10 <sup>-04</sup>	400
Mn	Garnet	5.1 × 10 <sup>-08</sup>	253
Na	Plagioclase	7.94 × 10 <sup>-04</sup>	268
Nd	Basaltic melt	4.07 × 10 <sup>-05</sup>	200
Nd	Andesitic melt	1.08 × 10 <sup>-05</sup>	169
O	Olivine	4.57 × 10 <sup>-09</sup>	338
O	Anorthite	1.50 × 10 <sup>-10</sup>	217
Pb	K-feldspar	1.81 × 10 <sup>-05</sup>	309
Rb	Rhyolitic melt	2.01 × 10 <sup>-07</sup>	127
Sr	Diopside a-axis	6.4 × 10 <sup>-04</sup>	452
Sr	Diopside b-axis	1.2 × 10 <sup>01</sup>	565
Sr	Diopside c-axis	1.2 × 10 <sup>-01</sup>	511
Sr	Basaltic melt	1.12 × 10 <sup>-05</sup>	169
Sr	Rhyolitic melt	3.74 × 10 <sup>-05</sup>	156
Sr	Plagioclase	1.1 × 10 <sup>-06</sup>	295
Sr	Calcite	2.1 × 10 <sup>-13</sup>	132
Zr	Basaltic melt	1.40 × 10 <sup>-05</sup>	189

Data from Zhang and Cherniak (2010)

$$D \cong \alpha d \sqrt{\frac{8k}{\pi m}} T^{3/2} \quad (5.102)$$

This predicts a diffusion coefficient near the melting point of 10<sup>-4</sup> cm<sup>2</sup>/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*:

$$D = \frac{kT}{6\pi\eta r} \quad (5.103)$$

where  $r$  is molecular radius and  $\eta$  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.

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:

$$D^\circ = \frac{RT\lambda^\circ}{|z|\mathcal{F}^2} \quad (5.104)$$

where  $\lambda^\circ$  is the limiting ionic conductance (conductance extrapolated to infinite dilution) of the ion (in cm<sup>2</sup>/ohm-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  $D^\circ$  on temperature. The nought (°) denotes the standard state of infinite dilution. Table 5.3 lists values of  $D^\circ$  for

**Table 5.3** Trace diffusion coefficients for ions in infinitely dilute solution at 25°C.

Cation	D <sup>°</sup> 10 <sup>-6</sup> cm <sup>2</sup> sec <sup>-1</sup>	Anion	D <sup>°</sup> 10 <sup>-6</sup> cm <sup>2</sup> sec <sup>-1</sup>
H <sup>+</sup>	93.1	OH <sup>-</sup>	52.7
Na <sup>+</sup>	13.3	Cl <sup>-</sup>	20.3
K <sup>+</sup>	19.6	I <sup>-</sup>	20.0
Mg <sup>2+</sup>	7.05	SO <sub>4</sub> <sup>2-</sup>	10.7
Ca <sup>2+</sup>	7.93	CO <sub>3</sub> <sup>2-</sup>	9.55
Sr <sup>2+</sup>	7.94	HCO <sub>3</sub> <sup>2-</sup>	11.8
Ba <sup>2+</sup>	8.48	NO <sub>3</sub> <sup>-</sup>	19.0
Fe <sup>2+</sup>	7.19		
La <sup>3+</sup>	6.17		