Chapter 6 / Diffusion

*P*hotograph of a steel gear that has been "case hardened." The outer surface layer was selectively hardened by a high-temperature heat treatment during which carbon from the surrounding atmosphere diffused into the surface. The "case" appears as the dark outer rim of that segment of the gear that has been sectioned. Actual size. (Photograph courtesy of Surface Division Midland-Ross.)

Why Study *Diffusion?*

Materials of all types are often heat treated to improve their properties. The phenomena that occur during a heat treatment almost always involve atomic diffusion. Often an enhancement of diffusion rate is desired; on occasion measures are taken to reduce it. Heat-treating temperatures and times, and/or cooling rates are often predictable using the mathematics of diffusion and appropriate diffusion constants. The steel gear shown on this page has been case hardened (Section 9.14); that is, its hardness and resistance to failure by fatigue have been enhanced by diffusing excess carbon or nitrogen into the outer surface layer.

Learning Objectives

After studying this chapter you should be able to do the following:

1. Name and describe the two atomic mechanisms of diffusion.
2. Distinguish between steady-state and nonsteady-state diffusion.
3. (a) Write Fick's first and second laws in equation form, and define all parameters.
   (b) Note the kind of diffusion for which each of these equations is normally applied.
4. Write the solution to Fick's second law for diffusion into a semi-infinite solid when the concentration of diffusing species at the surface is held constant. Define all parameters in this equation.
5. Calculate the diffusion coefficient for some material at a specified temperature, given the appropriate diffusion constants.
6. Note one difference in diffusion mechanisms for metals and ionic solids.

6.1 INTRODUCTION

Many reactions and processes that are important in the treatment of materials rely on the transfer of mass either within a specific solid (ordinarily on a microscopic level) or from a liquid, a gas, or another solid phase. This is necessarily accomplished by **diffusion,** the phenomenon of material transport by atomic motion. This chapter discusses the atomic mechanisms by which diffusion occurs, the mathematics of diffusion, and the influence of temperature and diffusing species on the rate of diffusion.

The phenomenon of diffusion may be demonstrated with the use of a *diffusion couple,* which is formed by joining bars of two different metals together so that there is intimate contact between the two faces; this is illustrated for copper and nickel in Figure 6.1, which includes schematic representations of atom positions and composition across the interface. This couple is heated for an extended period at an elevated temperature (but below the melting temperature of both metals), and cooled to room temperature. Chemical analysis will reveal a condition similar to that represented in Figure 6.2, namely, pure copper and nickel at the two extremities of the couple, separated by an alloyed region. Concentrations of both metals vary with position as shown in Figure 6.2*c.* This result indicates that copper atoms have migrated or diffused into the nickel, and that nickel has diffused into copper. This process, whereby atoms of one metal diffuse into another, is termed **interdiffusion,** or **impurity diffusion.**

Interdiffusion may be discerned from a macroscopic perspective by changes in concentration which occur over time, as in the example for the Cu–Ni diffusion couple. There is a net drift or transport of atoms from high to low concentration regions. Diffusion also occurs for pure metals, but all atoms exchanging positions are of the same type; this is termed **self-diffusion.** Of course, self-diffusion is not normally subject to observation by noting compositional changes.

6.2 DIFFUSION MECHANISMS

From an atomic perspective, diffusion is just the stepwise migration of atoms from lattice site to lattice site. In fact, the atoms in solid materials are in constant motion, rapidly changing positions. For an atom to make such a move, two conditions must be met: (1) there must be an empty adjacent site, and (2) the atom must have sufficient energy to break bonds with its neighbor atoms and then cause some lattice distortion during the displacement. This energy is vibrational in nature (Section 5.10). At a specific temperature some small fraction of the total number of atoms
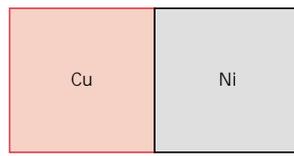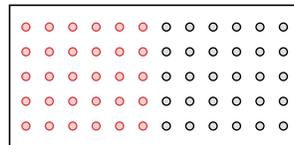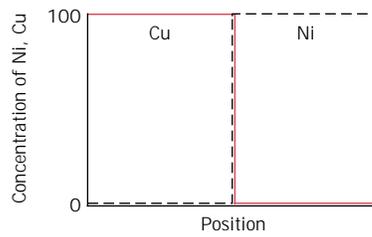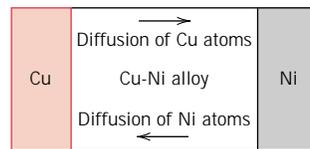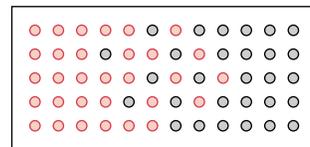
FIGURE 6.1 (*a*) A copper–nickel diffusion couple before a high-temperature heat treatment. (*b*) Schematic representations of Cu (colored circles) and Ni (gray circles) atom locations within the diffusion couple. (*c*) Concentrations of copper and nickel as a function of position across the couple.
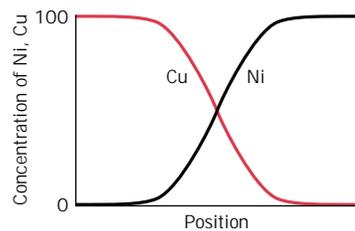
FIGURE 6.2 (*a*) A copper–nickel diffusion couple after a high-temperature heat treatment, showing the alloyed diffusion zone. (*b*) Schematic representations of Cu (colored circles) and Ni (gray circles) atom locations within the couple. (*c*) Concentrations of copper and nickel as a function of position across the couple.

is capable of diffusive motion, by virtue of the magnitudes of their vibrational energies. This fraction increases with rising temperature.

Several different models for this atomic motion have been proposed; of these possibilities, two dominate for metallic diffusion.
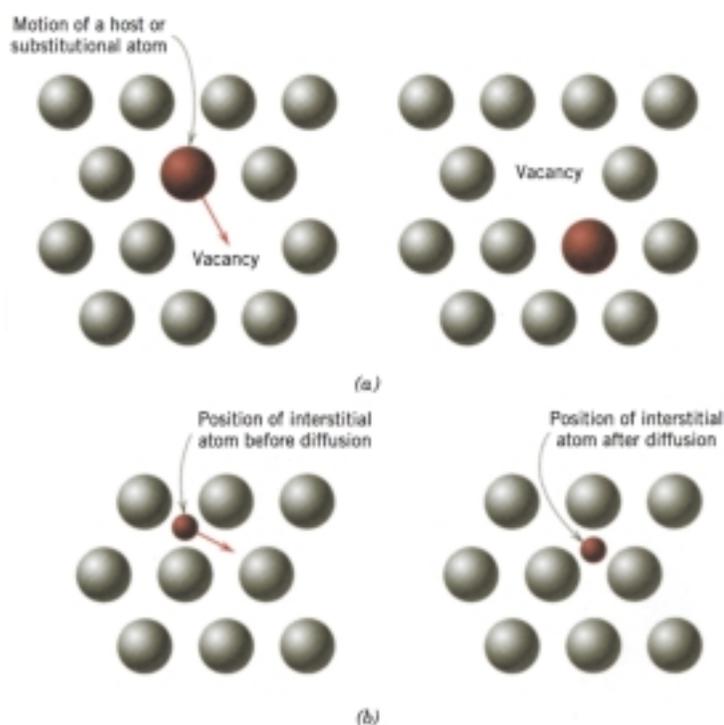
VACANCY DIFFUSION

One mechanism involves the interchange of an atom from a normal lattice position to an adjacent vacant lattice site or vacancy, as represented schematically in Figure 6.3a. This mechanism is aptly termed **vacancy diffusion.** Of course, this process necessitates the presence of vacancies, and the extent to which vacancy diffusion can occur is a function of the number of these defects that are present; significant concentrations of vacancies may exist in metals at elevated temperatures (Section 5.2). Since diffusing atoms and vacancies exchange positions, the diffusion of atoms in one direction corresponds to the motion of vacancies in the opposite direction. Both self-diffusion and interdiffusion occur by this mechanism; for the latter, the impurity atoms must substitute for host atoms.

INTERSTITIAL DIFFUSION

The second type of diffusion involves atoms that migrate from an interstitial position to a neighboring one that is empty. This mechanism is found for interdiffusion of impurities such as hydrogen, carbon, nitrogen, and oxygen, which have atoms that are small enough to fit into the interstitial positions. Host or substitutional impurity atoms rarely form interstitials and do not normally diffuse via this mechanism. This phenomenon is appropriately termed **interstitial diffusion** (Figure 6.3b).

In most metal alloys, interstitial diffusion occurs much more rapidly than diffusion by the vacancy mode, since the interstitial atoms are smaller, and thus more

FIGURE 6.3 Schematic representations of (a) vacancy diffusion and (b) interstitial diffusion.

mobile. Furthermore, there are more empty interstitial positions than vacancies; hence, the probability of interstitial atomic movement is greater than for vacancy diffusion.

6.3 STEADY-STATE DIFFUSION

Diffusion is a time-dependent process—that is, in a macroscopic sense, the quantity of an element that is transported within another is a function of time. Often it is necessary to know how fast diffusion occurs, or the rate of mass transfer. This rate is frequently expressed as a **diffusion flux** (J), defined as the mass (or, equivalently, the number of atoms) M diffusing through and perpendicular to a unit cross-sectional area of solid per unit of time. In mathematical form, this may be represented as

$$J = \frac{M}{At} \tag{6.1a}$$

where A denotes the area across which diffusion is occurring and t is the elapsed diffusion time. In differential form, this expression becomes

$$J = \frac{1}{A}\frac{dM}{dt} \tag{6.1b}$$

The units for J are kilograms or atoms per meter squared per second (kg/m^2-s or atoms/m^2-s).

If the diffusion flux does not change with time, a steady-state condition exists. One common example of **steady-state diffusion** is the diffusion of atoms of a gas through a plate of metal for which the concentrations (or pressures) of the diffusing species on both surfaces of the plate are held constant. This is represented schematically in Figure 6.4a.

When concentration C is plotted versus position (or distance) within the solid x, the resulting curve is termed the **concentration profile;** the slope at a particular

FIGURE 6.4
(a) Steady-state diffusion across a thin plate. (b) A linear concentration profile for the diffusion situation in (a).
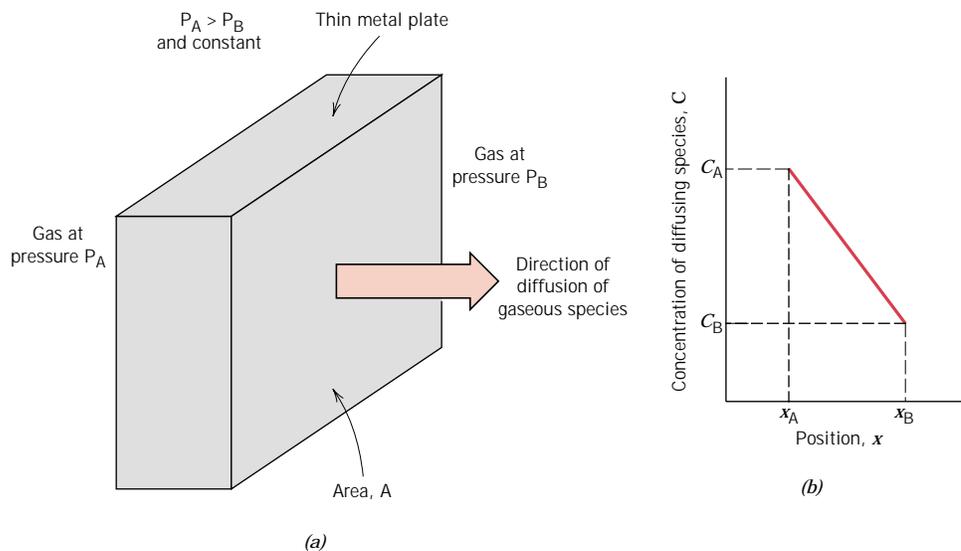
point on this curve is the **concentration gradient:**

$$\text{concentration gradient} = \frac{dC}{dx} \tag{6.2a}$$

In the present treatment, the concentration profile is assumed to be linear, as depicted in Figure 6.4*b*, and

$$\text{concentration gradient} = \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B} \tag{6.2b}$$

For diffusion problems, it is sometimes convenient to express concentration in terms of mass of diffusing species per unit volume of solid (kg/m^3 or g/cm^3).[1]

The mathematics of steady-state diffusion in a single (x) direction is relatively simple, in that the flux is proportional to the concentration gradient through the expression

$$J = -D\frac{dC}{dx} \tag{6.3}$$

The constant of proportionality D is called the **diffusion coefficient,** which is expressed in square meters per second. The negative sign in this expression indicates that the direction of diffusion is down the concentration gradient, from a high to a low concentration. Equation 6.3 is sometimes called **Fick's first law.**

Sometimes the term **driving force** is used in the context of what compels a reaction to occur. For diffusion reactions, several such forces are possible; but when diffusion is according to Equation 6.3, the concentration gradient is the driving force.

One practical example of steady-state diffusion is found in the purification of hydrogen gas. One side of a thin sheet of palladium metal is exposed to the impure gas composed of hydrogen and other gaseous species such as nitrogen, oxygen, and water vapor. The hydrogen selectively diffuses through the sheet to the opposite side, which is maintained at a constant and lower hydrogen pressure.

EXAMPLE PROBLEM 6.1

A plate of iron is exposed to a carburizing (carbon-rich) atmosphere on one side and a decarburizing (carbon-deficient) atmosphere on the other side at 700°C (1300°F). If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 and 10 mm (5×10^{-3} and 10^{-2} m) beneath the carburizing surface are 1.2 and 0.8 kg/m^3, respectively. Assume a diffusion coefficient of 3×10^{-11} m^2/s at this temperature.

SOLUTION

Fick's first law, Equation 6.3, is utilized to determine the diffusion flux. Substitution of the values above into this expression yields

$$J = -D\frac{C_A - C_B}{x_A - x_B} = -(3 \times 10^{-11}\ m^2/s)\frac{(1.2 - 0.8)\ kg/m^3}{(5 \times 10^{-3} - 10^{-2})\ m}$$

$$= 2.4 \times 10^{-9}\ kg/m^2\text{-s}$$

---

[1] Conversion of concentration from weight percent to mass per unit volume (in kg/m^3) is possible using {Equation 5.9.}

6.4 NONSTEADY-STATE DIFFUSION

Most practical diffusion situations are nonsteady-state ones. That is, the diffusion flux and the concentration gradient at some particular point in a solid vary with time, with a net accumulation or depletion of the diffusing species resulting. This is illustrated in Figure 6.5, which shows concentration profiles at three different diffusion times. Under conditions of nonsteady state, use of Equation 6.3 is no longer convenient; instead, the partial differential equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{6.4a}$$

known as **Fick's second law,** is used. If the diffusion coefficient is independent of composition (which should be verified for each particular diffusion situation), Equation 6.4a simplifies to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{6.4b}$$

Solutions to this expression (concentration in terms of both position and time) are possible when physically meaningful boundary conditions are specified. Comprehensive collections of these are given by Crank, and Carslaw and Jaeger (see References).

One practically important solution is for a semi-infinite solid[2] in which the surface concentration is held constant. Frequently, the source of the diffusing species is a gas phase, the partial pressure of which is maintained at a constant value. Furthermore, the following assumptions are made:

1. Before diffusion, any of the diffusing solute atoms in the solid are uniformly distributed with concentration of C_0.

2. The value of x at the surface is zero and increases with distance into the solid.
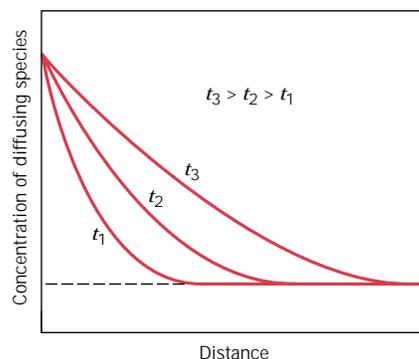

FIGURE 6.5 Concentration profiles for nonsteady-state diffusion taken at three different times, t_1, t_2, and t_3.

---

[2] A bar of solid is considered to be semi-infinite if none of the diffusing atoms reaches the bar end during the time over which diffusion takes place. A bar of length l is considered to be semi-infinite when $l > 10\sqrt{Dt}$.

3. The time is taken to be zero the instant before the diffusion process begins.

These boundary conditions are simply stated as

For $t = 0$, $C = C_0$ at $0 \leq x \leq \infty$

For $t > 0$, $C = C_s$ (the constant surface concentration) at $x = 0$

$C = C_0$ at $x = \infty$

Application of these boundary conditions to Equation 6.4b yields the solution

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{6.5}$$

where C_x represents the concentration at depth x after time t. The expression $\text{erf}(x/2\sqrt{Dt})$ is the Gaussian error function,[3] values of which are given in mathematical tables for various $x/2\sqrt{Dt}$ values; a partial listing is given in Table 6.1. The concentration parameters that appear in Equation 6.5 are noted in Figure 6.6, a concentration profile taken at a specific time. Equation 6.5 thus demonstrates the relationship between concentration, position, and time, namely, that C_x, being a function of the dimensionless parameter $x/\sqrt{Dt}$, may be determined at any time and position if the parameters C_0, C_s, and D are known.

Suppose that it is desired to achieve some specific concentration of solute, C_1, in an alloy; the left-hand side of Equation 6.5 now becomes

$$\frac{C_1 - C_0}{C_s - C_0} = \text{constant}$$

Table 6.1 **Tabulation of Error Function Values**

z	erf(z)	z	erf(z)	z	erf(z)
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

---

[3] This Gaussian error function is defined by

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} \, dy$$

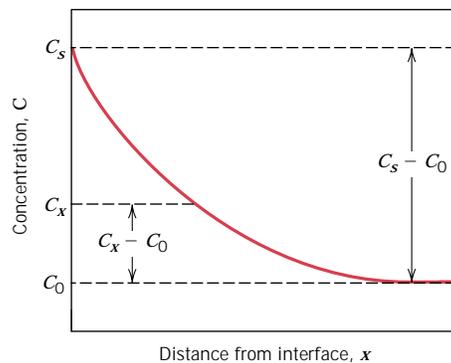where $x/2\sqrt{Dt}$ has been replaced by the variable z.

FIGURE 6.6 Concentration profile for nonsteady-state diffusion; concentration parameters relate to Equation 6.5.

This being the case, the right-hand side of this same expression is also a constant, and subsequently

$$\frac{x}{2\sqrt{Dt}} = \text{constant} \tag{6.6a}$$

or

$$\frac{x^2}{Dt} = \text{constant} \tag{6.6b}$$

Some diffusion computations are thus facilitated on the basis of this relationship, as demonstrated in Example Problem 6.3.

EXAMPLE PROBLEM 6.2

For some applications, it is necessary to harden the surface of a steel (or iron-carbon alloy) above that of its interior. One way this may be accomplished is by increasing the surface concentration of carbon in a process termed **carburizing**; the steel piece is exposed, at an elevated temperature, to an atmosphere rich in a hydrocarbon gas, such as methane (CH_4).

Consider one such alloy that initially has a uniform carbon concentration of 0.25 wt% and is to be treated at 950°C (1750°F). If the concentration of carbon at the surface is suddenly brought to and maintained at 1.20 wt%, how long will it take to achieve a carbon content of 0.80 wt% at a position 0.5 mm below the surface? The diffusion coefficient for carbon in iron at this temperature is 1.6×10^{-11} m^2/s; assume that the steel piece is semi-infinite.

SOLUTION

Since this is a nonsteady-state diffusion problem in which the surface composition is held constant, Equation 6.5 is used. Values for all the parameters in this expression except time t are specified in the problem as follows:

$$C_0 = 0.25 \text{ wt\% C}$$

$$C_s = 1.20 \text{ wt\% C}$$

$$C_x = 0.80 \text{ wt\% C}$$

$$x = 0.50 \text{ mm} = 5 \times 10^{-4} \text{ m}$$

$$D = 1.6 \times 10^{-11} \text{ m}^2/\text{s}$$

Thus,

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.80 - 0.25}{1.20 - 0.25} = 1 - \text{erf}\left[\frac{(5 \times 10^{-4}\,\text{m})}{2\sqrt{(1.6 \times 10^{-11}\,\text{m}^2/\text{s})(t)}}\right]$$

$$0.4210 = \text{erf}\left(\frac{62.5\,\text{s}^{1/2}}{\sqrt{t}}\right)$$

We must now determine from Table 6.1 the value of z for which the error function is 0.4210. An interpolation is necessary, as

z	erf(z)
0.35	0.3794
z	0.4210
0.40	0.4284

$$\frac{z - 0.35}{0.40 - 0.35} = \frac{0.4210 - 0.3794}{0.4284 - 0.3794}$$

or

$$z = 0.392$$

Therefore,

$$\frac{62.5\,\text{s}^{1/2}}{\sqrt{t}} = 0.392$$

and solving for t,

$$t = \left(\frac{62.5\,\text{s}^{1/2}}{0.392}\right)^2 = 25{,}400\,\text{s} = 7.1\,\text{h}$$

EXAMPLE PROBLEM 6.3

The diffusion coefficients for copper in aluminum at 500 and 600°C are 4.8×10^{-14} and 5.3×10^{-13} m²/s, respectively. Determine the approximate time at 500°C that will produce the same diffusion result (in terms of concentration of Cu at some specific point in Al) as a 10-h heat treatment at 600°C.

SOLUTION

This is a diffusion problem in which Equation 6.6b may be employed. The composition in both diffusion situations will be equal at the same position (i.e., x is also a constant), thus

$$Dt = \text{constant} \tag{6.7}$$

at both temperatures. That is,

$$D_{500}\,t_{500} = D_{600}\,t_{600}$$

or

$$t_{500} = \frac{D_{600}\,t_{600}}{D_{500}} = \frac{(5.3 \times 10^{-13}\,\text{m}^2/\text{s})(10\,\text{h})}{4.8 \times 10^{-14}\,\text{m}^2/\text{s}} = 110.4\,\text{h}$$

6.5 FACTORS THAT INFLUENCE DIFFUSION

DIFFUSING SPECIES

The magnitude of the diffusion coefficient D is indicative of the rate at which atoms diffuse. Coefficients, both self- and interdiffusion, for several metallic systems are listed in Table 6.2. The diffusing species as well as the host material influence the diffusion coefficient. For example, there is a significant difference in magnitude between self- and carbon interdiffusion in α iron at 500°C, the D value being greater for the carbon interdiffusion (3.0×10^{-21} vs. 2.4×10^{-12} m²/s). This comparison also provides a contrast between rates of diffusion via vacancy and interstitial modes as discussed above. Self-diffusion occurs by a vacancy mechanism, whereas carbon diffusion in iron is interstitial.

TEMPERATURE

Temperature has a most profound influence on the coefficients and diffusion rates. For example, for the self-diffusion of Fe in α-Fe, the diffusion coefficient increases approximately six orders of magnitude (from 3.0×10^{-21} to 1.8×10^{-15} m²/s) in rising temperature from 500 to 900°C (Table 6.2). The temperature dependence of diffusion coefficients is related to temperature according to

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \tag{6.8}$$

where

D_0 = a temperature-independent preexponential (m²/s)

Q_d = the **activation energy** for diffusion (J/mol, cal/mol, or eV/atom)

Table 6.2   A Tabulation of Diffusion Data

Diffusing Species	Host Metal	D_0(m²/s)	Activation Energy Q_d		Calculated Values	
			kJ/mol	eV/atom	T(°C)	D(m²/s)
Fe	α-Fe (BCC)	2.8×10^{-4}	251	2.60	500	3.0×10^{-21}
					900	1.8×10^{-15}
Fe	γ-Fe (FCC)	5.0×10^{-5}	284	2.94	900	1.1×10^{-17}
					1100	7.8×10^{-16}
C	α-Fe	6.2×10^{-7}	80	0.83	500	2.4×10^{-12}
					900	1.7×10^{-10}
C	γ-Fe	2.3×10^{-5}	148	1.53	900	5.9×10^{-12}
					1100	5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.0×10^{-18}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

Source: E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book,* 7th edition, Butterworth-Heinemann, Oxford, 1992.

R = the gas constant, 8.31 J/mol-K, 1.987 cal/mol-K, or 8.62×10^{-5} eV/atom-K

T = absolute temperature (K)

The activation energy may be thought of as that energy required to produce the diffusive motion of one mole of atoms. A large activation energy results in a relatively small diffusion coefficient. Table 6.2 also contains a listing of D_0 and Q_d values for several diffusion systems.

Taking natural logarithms of Equation 6.8 yields

$$\ln D = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T}\right) \qquad (6.9a)$$

Or in terms of logarithms to the base 10

$$\log D = \log D_0 - \frac{Q_d}{2.3R}\left(\frac{1}{T}\right) \qquad (6.9b)$$

Since D_0, Q_d, and R are all constants, Equation 6.9b takes on the form of an equation of a straight line:

$$y = b + mx$$

where y and x are analogous, respectively, to the variables $\log D$ and $1/T$. Thus, if $\log D$ is plotted versus the reciprocal of the absolute temperature, a straight line should result, having slope and intercept of $-Q_d/2.3R$ and $\log D_0$, respectively. This is, in fact, the manner in which the values of Q_d and D_0 are determined experimentally. From such a plot for several alloy systems (Figure 6.7), it may be noted that linear relationships exist for all cases shown.
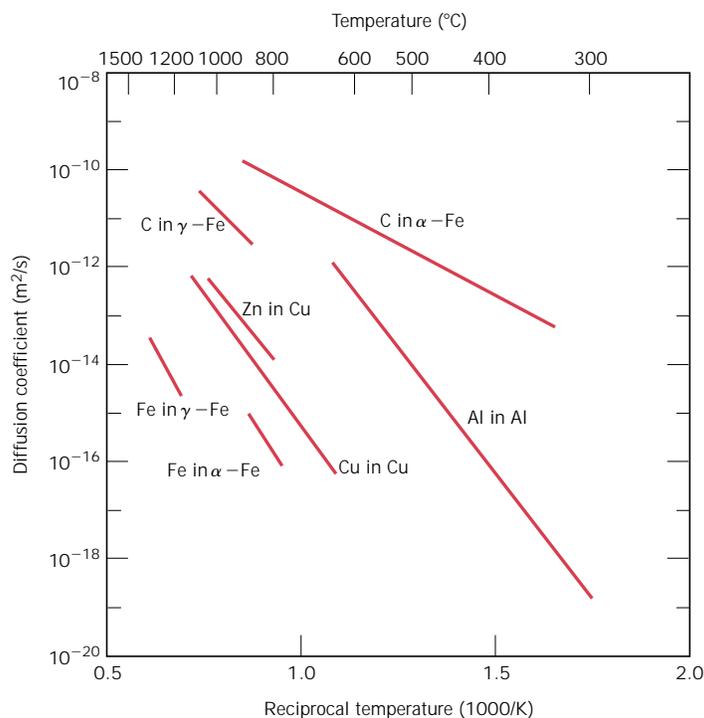

FIGURE 6.7 Plot of the logarithm of the diffusion coefficient versus the reciprocal of absolute temperature for several metals. [Data taken from E. A. Brandes and G. B. Brook (Editors), *Smithells Metals Reference Book,* 7th edition, Butterworth-Heinemann, Oxford, 1992.]

EXAMPLE PROBLEM 6.4

Using the data in Table 6.2, compute the diffusion coefficient for magnesium in aluminum at 550°C.

SOLUTION

This diffusion coefficient may be determined by applying Equation 6.8; the values of D_0 and Q_d from Table 6.2 are 1.2×10^{-4} m²/s and 131 kJ/mol, respectively. Thus,

$$D = (1.2 \times 10^{-4} \text{ m}^2/\text{s}) \exp \left[- \frac{(131{,}000 \text{ J/mol})}{(8.31 \text{ J/mol-K})(550 + 273 \text{ K})} \right]$$

$$= 5.8 \times 10^{-13} \text{ m}^2/\text{s}$$

EXAMPLE PROBLEM 6.5

In Figure 6.8 is shown a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of absolute temperature, for the diffusion of copper in gold. Determine values for the activation energy and the preexponential.
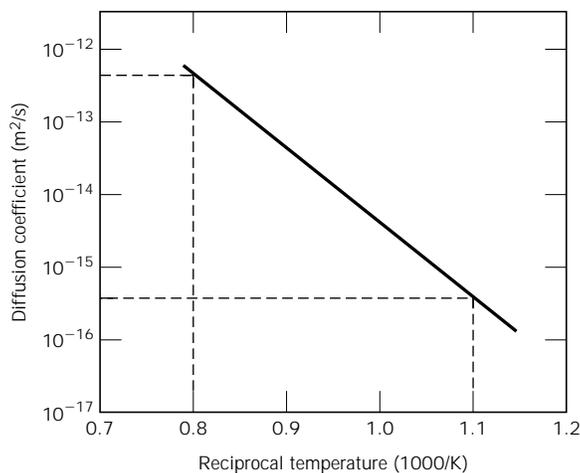

FIGURE 6.8 Plot of the logarithm of the diffusion coefficient versus the reciprocal of absolute temperature for the diffusion of copper in gold.

SOLUTION

From Equation 6.9b the slope of the line segment in Figure 6.8 is equal to $-Q_d/2.3R$, and the intercept at $1/T = 0$ gives the value of log D_0. Thus, the activation energy may be determined as

$$Q_d = -2.3R \text{ (slope)} = -2.3R \left[\frac{\Delta (\log D)}{\Delta \left(\dfrac{1}{T} \right)} \right]$$

$$= -2.3R \left[\frac{\log D_1 - \log D_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} \right]$$

where D_1 and D_2 are the diffusion coefficient values at $1/T_1$ and $1/T_2$, respectively. Let us arbitrarily take $1/T_1 = 0.8 \times 10^{-3}$ (K)$^{-1}$ and $1/T_2 = 1.1 \times 10^{-3}$ (K)$^{-1}$. We may now read the corresponding $\log D_1$ and $\log D_2$ values from the line segment in Figure 6.8.

[Before this is done, however, a parenthetic note of caution is offered. The vertical axis in Figure 6.8 is scaled logarithmically (to the base 10); however, the actual diffusion coefficient values are noted on this axis. For example, for $D = 10^{-14}$ m^2/s, the logarithm of D is -14.0 *not* 10^{-14}. Furthermore, this logarithmic scaling affects the readings between decade values; for example, at a location midway between 10^{-14} and 10^{-15}, the value is not 5×10^{-15}, but rather, $10^{-14.5} = 3.2 \times 10^{-15}$].

Thus, from Figure 6.8, at $1/T_1 = 0.8 \times 10^{-3}$ (K)$^{-1}$, $\log D_1 = -12.40$, while for $1/T_2 = 1.1 \times 10^{-3}$ (K)$^{-1}$, $\log D_2 = -15.45$, and the activation energy, as determined from the slope of the line segment in Figure 6.8, is

$$Q_d = -2.3R \left[\frac{\log D_1 - \log D_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} \right]$$

$$= -2.3\,(8.31 \text{ J/mol-K}) \left[\frac{-12.40 - (-15.45)}{0.8 \times 10^{-3} \text{ (K)}^{-1} - 1.1 \times 10^{-3} \text{ (K)}^{-1}} \right]$$

$$= 194{,}000 \text{ J/mol} = 194 \text{ kJ/mol}$$

Now, rather than trying to make a graphical extrapolation to determine D_0, a more accurate value is obtained analytically using Equation 6.9b, and a specific value of D (or $\log D$) and its corresponding T (or $1/T$) from Figure 6.8. Since we know that $\log D = -15.45$ at $1/T = 1.1 \times 10^{-3}$ (K)$^{-1}$, then

$$\log D_0 = \log D + \frac{Q_d}{2.3R} \left(\frac{1}{T} \right)$$

$$= -15.45 + \frac{(194{,}000 \text{ J/mol})(1.1 \times 10^{-3} \text{ [K]}^{-1})}{(2.3)(8.31 \text{ J/mol-K})}$$

$$= -4.28$$

Thus, $D_0 = 10^{-4.28}$ m^2/s $= 5.2 \times 10^{-5}$ m^2/s.

DESIGN EXAMPLE 6.1

The wear resistance of a steel gear is to be improved by hardening its surface. This is to be accomplished by increasing the carbon content within an outer surface layer as a result of carbon diffusion into the steel; the carbon is to be supplied from an external carbon-rich gaseous atmosphere at an elevated and constant temperature. The initial carbon content of the steel is 0.20 wt%, whereas the surface concentration is to be maintained at 1.00 wt%. In order for this treatment to be effective, a carbon content of 0.60 wt% must be established at a position 0.75 mm below the surface. Specify an appropriate heat treatment in terms of temperature and time for temperatures between 900°C and 1050°C. Use data in Table 6.2 for the diffusion of carbon in γ-iron.

***S*OLUTION**

Since this is a nonsteady-state diffusion situation, let us first of all employ Equation 6.5, utilizing the following values for the concentration parameters:

$$C_0 = 0.20 \text{ wt\% C}$$
$$C_s = 1.00 \text{ wt\% C}$$
$$C_x = 0.60 \text{ wt\% C}$$

Therefore

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.60 - 0.20}{1.00 - 0.20} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

And thus

$$0.5 = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Using an interpolation technique as demonstrated in Example Problem 6.2 and the data presented in Table 6.1

$$\frac{x}{2\sqrt{Dt}} = 0.4747 \qquad (6.10)$$

The problem stipulates that $x = 0.75$ mm $= 7.5 \times 10^{-4}$ m. Therefore

$$\frac{7.5 \times 10^{-4} \text{ m}}{2\sqrt{Dt}} = 0.4747$$

This leads to

$$Dt = 6.24 \times 10^{-7} \text{ m}^2$$

Furthermore, the diffusion coefficient depends on temperature according to Equation 6.8; and, from Table 6.2 for the diffusion of carbon in γ-iron, $D_0 = 2.3 \times 10^{-5}$ m²/s and $Q_d = 148,000$ J/mol. Hence

$$Dt = D_0 \exp\left(-\frac{Q_d}{RT}\right)(t) = 6.24 \times 10^{-7} \text{ m}^2$$

$$(2.3 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(T)}\right](t) = 6.24 \times 10^{-7} \text{ m}^2$$

And solving for the time t

$$t \text{ (in s)} = \frac{0.0271}{\exp\left(-\dfrac{17,810}{T}\right)}$$

Thus, the required diffusion time may be computed for some specified temperature (in K). Below are tabulated t values for four different temperatures that lie within the range stipulated in the problem.

Temperature (°C)	Time s	h
900	106,400	29.6
950	57,200	15.9
1000	32,300	9.0
1050	19,000	5.3

6.6 OTHER DIFFUSION PATHS

Atomic migration may also occur along dislocations, grain boundaries, and external surfaces. These are sometimes called "*short-circuit*" *diffusion paths* inasmuch as rates are much faster than for bulk diffusion. However, in most situations short-circuit contributions to the overall diffusion flux are insignificant because the cross-sectional areas of these paths are extremely small.

6.7 DIFFUSION IN IONIC AND POLYMERIC MATERIALS

We now extrapolate some of the diffusion principles discussed above to ionic and polymeric materials.

IONIC MATERIALS

For ionic compounds, the situation is more complicated than for metals inasmuch as it is necessary to consider the diffusive motion of two types of ions that have opposite charges. Diffusion in these materials occurs by a vacancy mechanism (Figure 6.3*a*). And, as we noted in Section 5.3, in order to maintain charge neutrality in an ionic material, the following may be said about vacancies: (1) ion vacancies occur in pairs [as with Schottky defects (Figure 5.3)], (2) they form in nonstoichiometric compounds (Figure 5.4), and (3) they are created by substitutional impurity ions having different charge states than the host ions (Example Problem 5.2). In any event, associated with the diffusive motion of a single ion is a transference of electrical charge. And in order to maintain localized charge neutrality in the vicinity of this moving ion, it is necessary that another species having an equal and opposite charge accompany the ion's diffusive motion. Possible charged species include another vacancy, an impurity atom, or an electronic carrier [i.e., a free electron or hole (Section 12.6)]. It follows that the rate of diffusion of these electrically charged couples is limited by the diffusion rate of the slowest moving species.

When an external electric field is applied across an ionic solid, the electrically charged ions migrate (i.e., diffuse) in response to forces that are brought to bear on them. And, as we discuss in Section 12.15, this ionic motion gives rise to an electric current. Furthermore, the electrical conductivity is a function of the diffusion coefficient (Equation 12.26). Consequently, much of the diffusion data for ionic solids comes from electrical conductivity measurements.

POLYMERIC MATERIALS

For polymeric materials, we are more interested in the diffusive motion of small foreign molecules (e.g., O_2, H_2O, CO_2, CH_4) between the molecular chains than in the diffusive motion of atoms within the chain structures. A polymer's permeability and absorption characteristics relate to the degree to which foreign substances diffuse into the material. Penetration of these foreign substances can lead to swelling and/or chemical reactions with the polymer molecules, and often to a depreciation of the material's mechanical and physical properties {(Section 16.11).}

Rates of diffusion are greater through amorphous regions than through crystalline regions; the structure of amorphous material is more "open." This diffusion mechanism may be considered to be analogous to interstitial diffusion in metals—that is, in polymers, diffusive movement from one open amorphous region to an adjacent open one.

Foreign molecule size also affects the diffusion rate: smaller molecules diffuse faster than larger ones. Furthermore, diffusion is more rapid for foreign molecules that are chemically inert than for those that react with the polymer.

For some applications low diffusion rates through polymeric materials are desirable, as with food and beverage packaging and with automobile tires and inner tubes. Polymer membranes are often used as filters to selectively separate one chemical species from another (or others) (e.g., the desalinization of water). In such instances it is normally the case that the diffusion rate of the substance to be filtered is significantly greater than that for the other substance(s).

SUMMARY

Solid-state diffusion is a means of mass transport within solid materials by stepwise atomic motion. The term ''self-diffusion'' refers to the migration of host atoms; for impurity atoms, the term ''interdiffusion'' is used. Two mechanisms are possible: vacancy and interstitial. For a given host metal, interstitial atomic species generally diffuse more rapidly.

For steady-state diffusion, the concentration profile of the diffusing species is time independent, and the flux or rate is proportional to the negative of the concentration gradient according to Fick's first law. The mathematics for nonsteady state are described by Fick's second law, a partial differential equation. The solution for a constant surface composition boundary condition involves the Gaussian error function.

The magnitude of the diffusion coefficient is indicative of the rate of atomic motion, being strongly dependent on and increasing exponentially with increasing temperature.

Diffusion in ionic materials occurs by a vacancy mechanism; localized charge neutrality is maintained by the coupled diffusive motion of a charged vacancy and some other charged entity. In polymers, small molecules of foreign substances diffuse between molecular chains by an interstitial-type mechanism from one amorphous region to an adjacent one.

IMPORTANT TERMS AND CONCEPTS

Activation energy
Carburizing
Concentration gradient
Concentration profile
Diffusion
Diffusion coefficient

Diffusion flux
Driving force
Fick's first and second laws
Interdiffusion (impurity diffusion)

Interstitial diffusion
Nonsteady-state diffusion
Self-diffusion
Steady-state diffusion
Vacancy diffusion

REFERENCES

Borg, R. J. and G. J. Dienes (Editors), *An Introduction to Solid State Diffusion,* Academic Press, San Diego, 1988.

Brandes, E. A. and G. B. Brook (Editors), *Smithells Metals Reference Book,* 7th edition, Butterworth-Heinemann Ltd., Oxford, 1992.

Carslaw, H. S. and J. C. Jaeger, *Conduction of Heat in Solids,* 2nd edition, Clarendon Press, Oxford, 1986.

Crank, J., *The Mathematics of Diffusion,* 2nd edition, Clarendon Press, Oxford, 1980.

Girifalco, L. A., *Atomic Migration in Crystals,* Blaisdell Publishing Company, New York, 1964.

Shewmon, P. G., *Diffusion in Solids,* McGraw-Hill Book Company, New York, 1963. Reprinted by The Minerals, Metals and Materials Society, Warrendale, PA, 1989.

QUESTIONS AND PROBLEMS

Note: To solve those problems having an asterisk (*) by their numbers, consultation of supplementary topics [appearing only on the CD-ROM (and not in print)] will probably be necessary.

6.1 Briefly explain the difference between self-diffusion and interdiffusion.

6.2 Self-diffusion involves the motion of atoms that are all of the same type; therefore it is not subject to observation by compositional changes, as with interdiffusion. Suggest one way in which self-diffusion may be monitored.

6.3 **(a)** Compare interstitial and vacancy atomic mechanisms for diffusion.
(b) Cite two reasons why interstitial diffusion is normally more rapid than vacancy diffusion.

6.4 Briefly explain the concept of steady state as it applies to diffusion.

6.5 **(a)** Briefly explain the concept of a driving force.
(b) What is the driving force for steady-state diffusion?

6.6 The purification of hydrogen gas by diffusion through a palladium sheet was discussed in Section 6.3. Compute the number of kilograms of hydrogen that pass per hour through a 5-mm thick sheet of palladium having an area of 0.20 m^2 at 500°C. Assume a diffusion coefficient of 1.0×10^{-8} m^2/s, that the concentrations at the high- and low-pressure sides of the plate are 2.4 and 0.6 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.

6.7 A sheet of steel 1.5 mm thick has nitrogen atmospheres on both sides at 1200°C and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is 6×10^{-11} m^2/s, and the diffusion flux is found to be 1.2×10^{-7} kg/m^2-s. Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is 4 kg/m^3. How far into the sheet from this high-pressure side will the concentration be 2.0 kg/m^3? Assume a linear concentration profile.

6.8* A sheet of BCC iron 1 mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at 725°C. After having reached steady state, the iron was quickly cooled to room temperature. The carbon concentrations at the two surfaces of the sheet were determined to be 0.012 and 0.0075 wt%. Compute the diffusion coefficient if the diffusion flux is 1.4×10^{-8} kg/m^2-s. *Hint:* Use Equation 5.9 to convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.

6.9 When α-iron is subjected to an atmosphere of hydrogen gas, the concentration of hydrogen in the iron, C_H (in weight percent), is a function of hydrogen pressure, p_{H_2} (in MPa), and absolute temperature (T) according to

$$C_H = 1.34 \times 10^{-2} \sqrt{p_{H_2}} \exp\left(-\frac{27.2 \text{ kJ/mol}}{RT}\right)$$
(6.11)

Furthermore, the values of D_0 and Q_d for this diffusion system are 1.4×10^{-7} m^2/s and 13,400 J/mol, respectively. Consider a thin iron membrane 1 mm thick that is at 250°C. Compute the diffusion flux through this membrane if the hydrogen pressure on one side of the membrane is 0.15 MPa (1.48 atm), and on the other side 7.5 MPa (74 atm).

6.10 Show that

$$C_x = \frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

is also a solution to Equation 6.4b. The parameter B is a constant, being independent of both x and t.

6.11 Determine the carburizing time necessary to achieve a carbon concentration of 0.45 wt% at a position 2 mm into an iron–carbon alloy that initially contains 0.20 wt% C. The surface concentration is to be maintained at 1.30 wt% C, and the treatment is to be conducted at 1000°C. Use the diffusion data for γ-Fe in Table 6.2.

6.12 An FCC iron–carbon alloy initially containing 0.35 wt% C is exposed to an oxygen-

rich and virtually carbon-free atmosphere at 1400 K (1127°C). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere; that is, the carbon concentration at the surface position is maintained essentially at 0 wt% C. (This process of carbon depletion is termed *decarburization*.) At what position will the carbon concentration be 0.15 wt% after a 10-h treatment? The value of D at 1400 K is 6.9×10^{-11} m²/s.

6.13 Nitrogen from a gaseous phase is to be diffused into pure iron at 700°C. If the surface concentration is maintained at 0.1 wt% N, what will be the concentration 1 mm from the surface after 10 h? The diffusion coefficient for nitrogen in iron at 700°C is 2.5×10^{-11} m²/s.

6.14 **(a)** Consider a diffusion couple composed of two semi-infinite solids of the same metal. Each side of the diffusion couple has a different concentration of the same elemental impurity; furthermore, each impurity level is constant throughout its side of the diffusion couple. Solve Fick's second law for this diffusion situation assuming that the diffusion coefficient for the impurity is independent of concentration, and for the following boundary conditions:

$$C = C_1 \text{ for } x < 0, \text{ and } t = 0$$
$$C = C_2 \text{ for } x > 0, \text{ and } t = 0$$

Here we take the $x = 0$ position to be at the initial diffusion couple boundary.

(b) Using the result of part a, consider a diffusion couple composed of two silver-gold alloys; these alloys have compositions of 98 wt% Ag-2 wt% Au and 95 wt% Ag-5 wt% Au. Determine the time this diffusion couple must be heated at 750°C (1023 K) in order for the composition to be 2.5 wt% Au at the 50 μm position into the 2 wt% Au side of the diffusion couple. Preexponential and activation energy values for Au diffusion in Ag are 8.5×10^{-5} m²/s and 202,100 J/mol, respectively.

6.15 For a steel alloy it has been determined that a carburizing heat treatment of 10 h duration will raise the carbon concentration to 0.45 wt% at a point 2.5 mm from the surface. Estimate the time necessary to achieve the same concentration at a 5.0-mm position for an identical steel and at the same carburizing temperature.

6.16 Cite the values of the diffusion coefficients for the interdiffusion of carbon in both α-iron (BCC) and γ-iron (FCC) at 900°C. Which is larger? Explain why this is the case.

6.17 Using the data in Table 6.2, compute the value of D for the diffusion of zinc in copper at 650°C.

6.18 At what temperature will the diffusion coefficient for the diffusion of copper in nickel have a value of 6.5×10^{-17} m²/s? Use the diffusion data in Table 6.2.

6.19 The preexponential and activation energy for the diffusion of iron in cobalt are 1.1×10^{-5} m²/s and 253,300 J/mol, respectively. At what temperature will the diffusion coefficient have a value of 2.1×10^{-14} m²/s?

6.20 The activation energy for the diffusion of carbon in chromium is 111,000 J/mol. Calculate the diffusion coefficient at 1100 K (827°C), given that D at 1400 K (1127°C) is 6.25×10^{-11} m²/s.

6.21 The diffusion coefficients for iron in nickel are given at two temperatures:

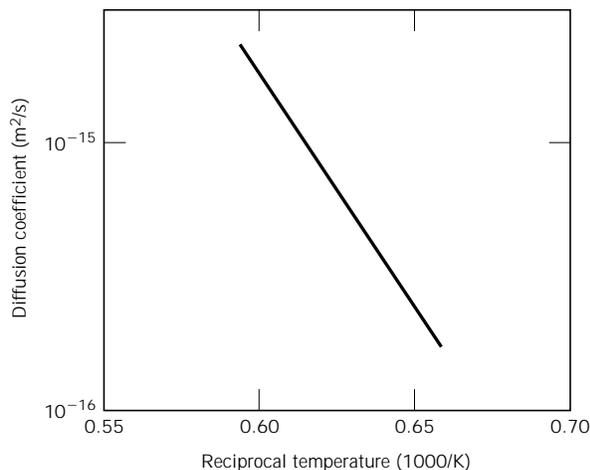| T(K)	D(m²/s)
1273	9.4×10^{-16}
1473	2.4×10^{-14}

(a) Determine the values of D_0 and the activation energy Q_d.
(b) What is the magnitude of D at 1100°C (1373 K)?

6.22 The diffusion coefficients for silver in copper are given at two temperatures:

T(°C)	D(m²/s)
650	5.5×10^{-16}
900	1.3×10^{-13}

(a) Determine the values of D_0 and Q_d.
(b) What is the magnitude of D at 875°C?

6.23 Below is shown a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of the absolute temperature, for the diffusion of iron in chromium. Deter-

mine values for the activation energy and preexponential.

6.24 Carbon is allowed to diffuse through a steel plate 15 mm thick. The concentrations of carbon at the two faces are 0.65 and 0.30 kg C/m^3 Fe, which are maintained constant. If the preexponential and activation energy are 6.2×10^{-7} m^2/s and 80,000 J/mol, respectively, compute the temperature at which the diffusion flux is 1.43×10^{-9} kg/m^2-s.

6.25 The steady-state diffusion flux through a metal plate is 5.4×10^{-10} kg/m^2-s at a temperature of 727°C (1000 K) and when the concentration gradient is -350 kg/m^4. Calculate the diffusion flux at 1027°C (1300 K) for the same concentration gradient and assuming an activation energy for diffusion of 125,000 J/mol.

6.26 At approximately what temperature would a specimen of γ-iron have to be carburized for 2 h to produce the same diffusion result as at 900°C for 15 h?

6.27 **(a)** Calculate the diffusion coefficient for copper in aluminum at 500°C.
(b) What time will be required at 600°C to produce the same diffusion result (in terms of concentration at a specific point) as for 10 h at 500°C?

6.28 A copper-nickel diffusion couple similar to that shown in Figure 6.1a is fashioned. After a 700-h heat treatment at 1100°C (1373 K) the concentration of Cu is 2.5 wt% at the 3.0-mm position within the nickel. At what

temperature must the diffusion couple need to be heated to produce this same concentration (i.e., 2.5 wt% Cu) at a 2.0-mm position after 700 h? The preexponential and activation energy for the diffusion of Cu in Ni are given in Table 6.2.

6.29 A diffusion couple similar to that shown in Figure 6.1a is prepared using two hypothetical metals A and B. After a 30-h heat treatment at 1000 K (and subsequently cooling to room temperature) the concentration of A in B is 3.2 wt% at the 15.5-mm position within metal B. If another heat treatment is conducted on an identical diffusion couple, only at 800 K for 30 h, at what position will the composition be 3.2 wt% A? Assume that the preexponential and activation energy for the diffusion coefficient are 1.8×10^{-5} m^2/s and 152,000 J/mol, respectively.

6.30 The outer surface of a steel gear is to be hardened by increasing its carbon content. The carbon is to be supplied from an external carbon-rich atmosphere, which is maintained at an elevated temperature. A diffusion heat treatment at 850°C (1123 K) for 10 min increases the carbon concentration to 0.90 wt% at a position 1.0 mm below the surface. Estimate the diffusion time required at 650°C (923 K) to achieve this same concentration also at a 1.0-mm position. Assume that the surface carbon content is the same for both heat treatments, which is maintained constant. Use the diffusion data in Table 6.2 for C diffusion in α-Fe.

6.31 An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere wherein the surface carbon concentration is maintained at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.

Design Problems

6.D1 It is desired to enrich the partial pressure of hydrogen in a hydrogen-nitrogen gas mixture for which the partial pressures of both gases are 0.1013 MPa (1 atm). It has been proposed to accomplish this by passing both gases

through a thin sheet of some metal at an elevated temperature; inasmuch as hydrogen diffuses through the plate at a higher rate than does nitrogen, the partial pressure of hydrogen will be higher on the exit side of the sheet. The design calls for partial pressures of 0.051 MPa (0.5 atm) and 0.01013 MPa (0.1 atm), respectively, for hydrogen and nitrogen. The concentrations of hydrogen and nitrogen (C_H and C_N, in mol/m³) in this metal are functions of gas partial pressures (p_{H_2} and p_{N_2}, in MPa) and absolute temperature and are given by the following expressions:

$$C_H = 584 \sqrt{p_{H_2}} \exp\left(-\frac{27.8 \text{ kJ/mol}}{RT}\right)$$
(6.12a)

$$C_N = 2.75 \times 10^3 \sqrt{p_{N_2}} \exp\left(-\frac{37.6 \text{ kJ/mol}}{RT}\right)$$
(6.12b)

Furthermore, the diffusion coefficients for the diffusion of these gases in this metal are functions of the absolute temperature as follows:

$$D_H \text{ (m}^2\text{/s)} = 1.4 \times 10^{-7} \exp\left(-\frac{13.4 \text{ kJ/mol}}{RT}\right)$$
(6.13a)

$$D_N \text{ (m}^2\text{/s)} = 3.0 \times 10^{-7} \exp\left(-\frac{76.15 \text{ kJ/mol}}{RT}\right)$$
(6.13b)

Is it possible to purify hydrogen gas in this manner? If so, specify a temperature at which the process may be carried out, and also the thickness of metal sheet that would be required. If this procedure is not possible, then state the reason(s) why.

6.D2 A gas mixture is found to contain two diatomic A and B species for which the partial pressures of both are 0.1013 MPa (1 atm). This mixture is to be enriched in the partial pressure of the A species by passing both gases through a thin sheet of some metal at an elevated temperature. The resulting enriched mixture is to have a partial pressure of 0.051 MPa (0.5 atm) for gas A, and 0.0203 MPa (0.2 atm) for gas B. The concentrations of A and B (C_A and C_B, in mol/m³) are functions

of gas partial pressures (p_{A_2} and p_{B_2}, in MPa) and absolute temperature according to the following expressions:

$$C_A = 500 \sqrt{p_{A_2}} \exp\left(-\frac{20.0 \text{ kJ/mol}}{RT}\right)$$
(6.14a)

$$C_B = 2.0 \times 10^3 \sqrt{p_{B_2}} \exp\left(-\frac{27.0 \text{ kJ/mol}}{RT}\right)$$
(6.14b)

Furthermore, the diffusion coefficients for the diffusion of these gases in the metal are functions of the absolute temperature as follows:

$$D_A \text{ (m}^2\text{/s)} = 5.0 \times 10^{-7} \exp\left(-\frac{13.0 \text{ kJ/mol}}{RT}\right)$$
(6.15a)

$$D_B \text{ (m}^2\text{/s)} = 3.0 \times 10^{-6} \exp\left(-\frac{21.0 \text{ kJ/mol}}{RT}\right)$$
(6.15b)

Is it possible to purify the A gas in this manner? If so, specify a temperature at which the process may be carried out, and also the thickness of metal sheet that would be required. If this procedure is not possible, then state the reason(s) why.

6.D3 The wear resistance of a steel shaft is to be improved by hardening its surface. This is to be accomplished by increasing the nitrogen content within an outer surface layer as a result of nitrogen diffusion into the steel. The nitrogen is to be supplied from an external nitrogen-rich gas at an elevated and constant temperature. The initial nitrogen content of the steel is 0.002 wt%, whereas the surface concentration is to be maintained at 0.50 wt%. In order for this treatment to be effective, a nitrogen content of 0.10 wt% must be established at a position 0.40 mm below the surface. Specify appropriate heat treatments in terms of temperature and time for temperatures between 475°C and 625°C. The preexponential and activation energy for the diffusion of nitrogen in iron are 3×10^{-7} m²/s and 76,150 J/mol, respectively, over this temperature range.