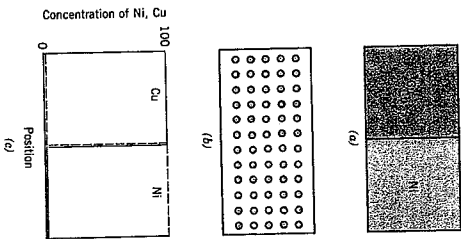


## 5.1 INTRODUCTION

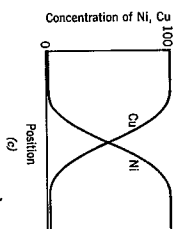
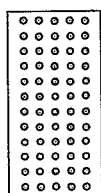
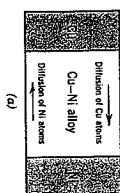
Many reactions and processes that are important in the treatment of materials rely on the transfer of mass either within a specific solid (ordinarily on a microscopic level) or from a liquid, a gas, or another solid phase. This is necessarily accomplished by **diffusion**, the phenomenon of material 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, as illustrated for copper and nickel in Figure 5.1, 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 5.2, namely, pure copper and nickel at the two extremes of the couple, separated by an alloyed region. Concentrations of both metals vary with position as shown in Figure 5.2c. 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.



**Figure 5.1** (a) A copper-nickel diffusion couple before a high-temperature heat treatment. (b) Schematic representations of Cu (colored circles) and Ni (black circles) atom locations within the diffusion couple. (c) Concentrations of copper and nickel as a function of position across the couple.



**Figure 5.2** (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 (black circles) atom locations within the couple. (c) Concentrations of copper and nickel as a function of position across the couple.

## 5.2 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 4.7). At a specific temperature some small fraction of the total number of atoms are 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 5.3a. 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 4.2). 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.

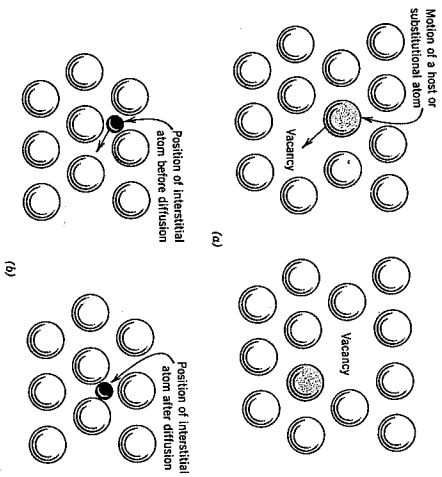


Figure 5.3 Schematic representations of (a) vacancy diffusion and (b) interstitial diffusion.

**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 5.3b).

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

**5.3 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

$$J = \frac{M}{At} \quad (5.1a)$$

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

$$J = \frac{1}{A} \frac{dM}{dt} \quad (5.1b)$$

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

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 5.4a.

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 point on this curve is the **concentration gradient**:

$$\text{concentration gradient} = \frac{dC}{dx} \quad (5.2a)$$

In the present treatment, the concentration profile is assumed to be linear, as depicted in Figure 5.4b, and

$$\text{concentration gradient} = \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B} \quad (5.2b)$$

For diffusion problems, it is usually most convenient to express concentration in terms of mass of diffusing species per unit volume of solid ( $\text{kg}/\text{m}^3$  or  $\text{g}/\text{cm}^3$ ).

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

$$J = -D \frac{dC}{dx} \quad (5.3)$$

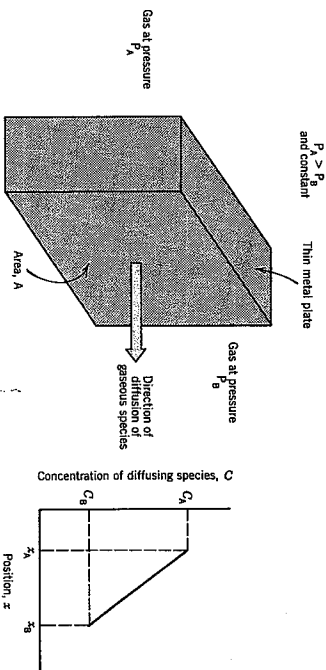


Figure 5.4 (a) Steady-state diffusion across a thin plate. (b) A linear concentration profile for the diffusion situation in (a).

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 5.3 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 5.3, 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 5.1

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 ( $5 \times 10^{-3}$  and  $10^{-2}$  m) beneath the carburizing surface are 1.2 and 0.8 kg/m<sup>3</sup>, respectively. Assume a diffusion coefficient of  $3 \times 10^{-11}$  m<sup>2</sup>/s at this temperature.

**SOLUTION**  
Fick's first law, Equation 5.3, is utilized to determine the diffusion flux. Substitution of the values above into this expression yields

$$J = -D \frac{C_A - C_B}{x_A - x_B} = -(3 \times 10^{-11} \text{ m}^2/\text{s}) \frac{(1.2 - 0.8) \text{ kg/m}^3}{(5 \times 10^{-3} - 10^{-2}) \text{ m}} \\ = 2.4 \times 10^{-9} \text{ kg/m}^2\text{-s}$$

#### 5.4 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 5.5, which shows concentration profiles at three different

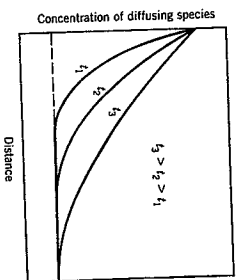


Figure 5.5 Concentration profiles for nonsteady-state diffusion taken at three different times,  $t_1$ ,  $t_2$ , and  $t_3$ .

diffusion times. Under conditions of nonsteady state, use of Equation 5.3 is no longer convenient; instead, the partial differential equation

$$\frac{\partial C}{\partial t} = D \left( D \frac{\partial^2 C}{\partial x^2} \right) \quad (5.4a)$$

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 5.4a simplifies to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (5.4b)$$

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<sup>1</sup> 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.
3. The time is taken to be zero the instant before the diffusion process begins.

These boundary conditions are simply stated as

$$\text{For } t = 0, C = C_0 \text{ at } 0 \leq x < \infty$$

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

$$C = C_0 \text{ at } x = \infty$$

Application of these boundary conditions to Equation 5.4b yields the solution

$$\frac{C_s - C_0}{C_s - C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \quad (5.5)$$

where  $C_s$  represents the concentration at depth  $x$  after time  $t$ . The expression  $\text{erf}(x/2\sqrt{Dt})$  is the Gaussian error function,<sup>2</sup> values of which are given in mathematical tables for various  $x/2\sqrt{Dt}$  values; a partial listing is given in Table 5.1.

<sup>1</sup> 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  $l > 10 \sqrt{Dt}$ .

<sup>2</sup> This Gaussian error function is defined by

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} d\eta$$

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

TABLE 5.1 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	0.9573
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

The concentration parameters that appear in Equation 5.5 are noted in Figure 5.6, a concentration profile taken at a specific time. Equation 5.5 thus demonstrates the relationship between concentration, position, and time, namely, that  $C_1$ , being a function of the dimensionless parameter  $x/\sqrt{Dt}$ , may be determined at any time and position if the parameters  $C_0$ ,  $C_1$ , 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 5.5 now becomes

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

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

$$\frac{x}{2\sqrt{Dt}} = \text{constant} \tag{5.6a}$$

or

$$\frac{x^2}{Dt} = \text{constant} \tag{5.6b}$$

Some diffusion computations are thus facilitated on the basis of this relationship, as demonstrated in Example Problem 5.3.

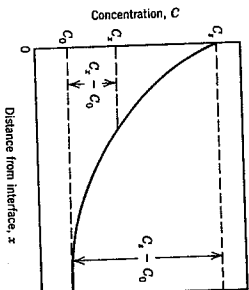


Figure 5.6 Concentration profile for nonsteady-state diffusion: concentration parameters relate to Equation 5.5.

EXAMPLE PROBLEM 5.2

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 ( $\text{CH}_4$ ).

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  $1.6 \times 10^{-11} \text{ m}^2/\text{s}$ ; assume that the steel piece is semi-infinite.

SOLUTION

Since this a nonsteady-state diffusion problem in which the surface composition is held constant, Equation 5.5 is used. Values for all the parameters in this expression except time  $t$  are specified in the problem as follows:

- $C_0 = 0.25 \text{ wt\% C}$
- $C_1 = 1.20 \text{ wt\% C}$
- $C_2 = 0.80 \text{ wt\% C}$
- $x = 0.50 \text{ mm} = 5 \times 10^{-4} \text{ m}$
- $D = 1.6 \times 10^{-11} \text{ m}^2/\text{s}$

Thus,

$$\frac{C_2 - C_0}{C_2 - C_0} = \frac{0.80 - 0.25}{1.20 - 0.25} = 1 - \text{erf} \left[ \frac{(5 \times 10^{-4} \text{ m})}{2\sqrt{(1.6 \times 10^{-11} \text{ m}^2/\text{s})t}} \right]$$

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

We must now determine from Table 5.1 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 5.3**

The diffusion coefficients for copper in aluminum at 500 and 600°C are  $4.8 \times 10^{-14}$  and  $5.3 \times 10^{-13} \text{ m}^2/\text{s}$ , 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 5.6b may be employed. The composition in both diffusion situations will be equal at the same position (i.e.,  $x$  is also a constant), thus

$$D_1 t = \text{constant} \quad (5.7)$$

at both temperatures. That is,

$$(D_1 t)_{500} = (D_1 t)_{600}$$

or

$$t_{500} = \frac{(D_1 t)_{600}}{D_{500}} = \frac{(5.3 \times 10^{-13} \text{ m}^2/\text{s})(10 \text{ h})}{4.8 \times 10^{-14} \text{ m}^2/\text{s}} = 110.4 \text{ h}$$

**5.5 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 5.2. 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  $\alpha$ -iron at 500°C, the  $D$  value being greater for the carbon interdiffusion ( $1.1 \times 10^{-20}$  vs.  $2.3 \times 10^{-12} \text{ m}^2/\text{s}$ ). 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  $\alpha$ -Fe, the diffusion coefficient increases approximately five orders of magnitude (from  $1.1 \times 10^{-20}$  to  $3.9 \times 10^{-15} \text{ m}^2/\text{s}$ ) in rising temperature from 500 to 900°C (Table 5.2). The temperature dependence of diffusion coefficients is related to temperature according to

$$D = D_0 \exp \left( -\frac{Q_d}{RT} \right) \quad (5.8)$$

**TABLE 5.2** A Tabulation of Diffusion Data

Diffusing Species	Host Metal	$D_0$ ( $\text{m}^2/\text{s}$ )	Activation Energy $Q_d$		T (°C)	Calculated Values $D$ ( $\text{m}^2/\text{s}$ )
			kJ/mol	eV/atom		
Fe	$\alpha$ -Fe (BCC)	$2.0 \times 10^{-4}$	241	57.5	249	$1.1 \times 10^{-20}$ $900$ $3.9 \times 10^{-15}$
	$\gamma$ -Fe (FCC)	$5.0 \times 10^{-5}$	284	67.9	2.94	$1.1 \times 10^{-17}$ $900$ $7.8 \times 10^{-16}$
C	$\alpha$ -Fe	$6.2 \times 10^{-7}$	80	19.2	0.83	$2.3 \times 10^{-12}$ $500$ $1.6 \times 10^{-10}$ $900$ $2.6 \times 10^{-10}$
C	$\gamma$ -Fe	$1.0 \times 10^{-5}$	136	32.4	1.40	$9.2 \times 10^{-12}$ $900$ $7.0 \times 10^{-11}$
Cu	Cu	$7.8 \times 10^{-5}$	211	50.4	2.18	$4.4 \times 10^{-19}$ $500$ $4.3 \times 10^{-18}$
	Zn	$3.4 \times 10^{-5}$	191	45.6	1.98	$500$ $4.1 \times 10^{-14}$
Al	Al	$1.7 \times 10^{-4}$	142	34.0	1.47	$500$ $4.8 \times 10^{-14}$
	Cu	$6.5 \times 10^{-5}$	135	32.3	1.40	$500$ $1.8 \times 10^{-15}$
Mg	Al	$1.2 \times 10^{-4}$	131	31.2	1.35	$500$ $1.5 \times 10^{-22}$
	Ni	$2.7 \times 10^{-5}$	255	61.0	2.64	$500$ $1.5 \times 10^{-22}$

Source: C. J. Simbels and E. A. Brandes (Editors), *Metals Reference Book*, 5th edition, Butterworths, London, 1976.

where

$D_0$  = a temperature-independent preexponential ( $\text{m}^2/\text{s}$ )

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

$R$  = the gas constant, 8.31 J/mol·K, 1.987 cal/mol·K, or  $8.62 \times 10^{-5} \text{ eV/atom}$

$T$  = 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 5.2 also contains a listing of  $D_0$  and  $Q_d$  values for several diffusion systems.

Taking natural logarithms of Equation 5.8 yields

$$\ln D = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T} \right) \quad (5.9)$$

Since  $D_0$ ,  $Q_d$ , and  $R$  are all constants, this expression takes on the form of an equation of a straight line:

$$y = b + mx$$

where  $y$  and  $x$  are analogous, respectively, to the variables in  $D$  and  $1/T$ . Thus, if  $\ln D$  is plotted versus the reciprocal of the absolute temperature, a straight line should result, having slope and intercept of  $-Q_d/R$  and  $\ln D_0$ , 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 5.7), it may be noted that linear relationships exist for all cases shown.

**EXAMPLE PROBLEM 5.4**

Using the data in Table 5.2, compute the diffusion coefficient for magnesium in aluminum at 400°C.

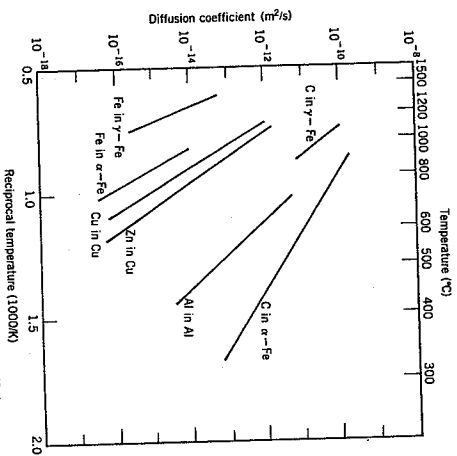


Figure 5.7 Plot of the logarithm of the diffusion coefficient versus the reciprocal of absolute temperature for several metals. Data taken from C. J. Smithells and E. A. Brandes (Editors), *Metals Reference Book*, 5th edition, Butterworths, London, 1976.]

**SOLUTION**  
This diffusion coefficient may be determined by applying Equation 5.8, the values of  $D_0$  and  $Q_d$  from Table 5.2 are  $1.2 \times 10^{-4} \text{ m}^2/\text{s}$  and  $131 \text{ kJ/mol}$ , respectively. Thus,

$$D = (1.2 \times 10^{-4} \text{ m}^2/\text{s}) \exp \left[ - \frac{(131,000 \text{ J/mol})}{(8.31 \text{ J/mol}\cdot\text{K})(400 + 273 \text{ K})} \right] \\ = 8.1 \times 10^{-15} \text{ m}^2/\text{s}$$

## 5.6 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.

## 5.7 MATERIALS PROCESSING AND DIFFUSION

Some properties of materials are subject to alteration and improvement as a result of processes and transformations that involve atomic diffusion. For these transformations to occur over reasonable time periods (usually on the order of hours),

they are ordinarily carried out at elevated temperatures at which diffusion rates are comparatively rapid. These high-temperature procedures, often termed *heat treatments*, are utilized at least once during the production of almost all common metallic, ceramic, and polymeric materials. For example, the strength of some steels is reliant on appropriate heat treatments (Chapter 11), as is also the mechanical integrity of many ceramics (Section 14.9).

## 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 non-steady 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.

## IMPORTANT TERMS AND CONCEPTS

Activation energy	Diffusion flux	Interstitial diffusion
Carburizing	Driving force	Nonsteady-state diffusion
Concentration gradient	Fick's first and second laws	Self-diffusion
Concentration profile	Interdiffusion (impurity diffusion)	Steady-state diffusion
Diffusion		Vacancy diffusion
Diffusion coefficient		

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## QUESTIONS AND PROBLEMS

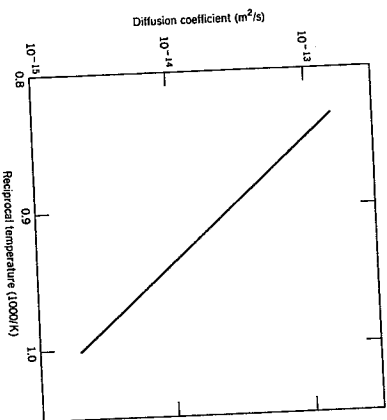
5.1 Briefly explain the difference between self-diffusion and interdiffusion.

5.2 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.

- 5.3. (a) Compare interstitial and vacancy atomic mechanisms for diffusion. (b) Cite two reasons why interstitial diffusion is normally more rapid than vacancy diffusion.
- 5.4 Briefly explain the concept of steady state as it applies to diffusion.
- 5.5 (a) Briefly explain the concept of a driving force. (b) What is the driving force for steady-state diffusion?
- 5.6 The purification of hydrogen gas by diffusion through a palladium sheet was discussed in Section 5.3. Compute the number of kilograms of hydrogen that pass per hour through a 6-mm-thick sheet of palladium having an area of 0.25 m<sup>2</sup> at 600°C. Assume a diffusion coefficient of  $1.7 \times 10^{-8}$  m<sup>2</sup>/s, that the concentrations at the high- and low-pressure sides of the plate are 2.0 and 0.4 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.
- 5.7 A sheet of steel 2.5 mm thick has nitrogen atmospheres on both sides at 900°C and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is  $1.2 \times 10^{-10}$  m<sup>2</sup>/s, and the diffusion flux is found to be  $1.0 \times 10^{-7}$  kg/m<sup>2</sup>·s. Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is 2 kg/m<sup>3</sup>. How far into the sheet from this high-pressure side will the concentration be 0.5 kg/m<sup>3</sup>? Assume a linear concentration profile.
- 5.8 A sheet of BCC iron 2 mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at 675°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 0.015 and 0.0068 wt%. Compute the diffusion coefficient if the diffusion flux is  $7.36 \times 10^{-9}$  kg/m<sup>2</sup>·s. Hint: Convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.
- 5.9 Show that Fick's second law (Equation 5.4b) takes on the form of Fick's first law (Equation 5.3) for conditions of steady state, that is,
- $$\frac{\partial C}{\partial t} = 0$$
- 5.10 Show that
- $$C_x = \frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$
- is also a solution to Equation 5.4b. The parameter  $B$  is a constant, being independent of both  $x$  and  $t$ .
- 5.11 Determine the carburizing time necessary to achieve a carbon concentration of 0.30 wt% at a position 4 mm into an iron-carbon alloy that initially contains 0.10 wt% C. The surface concentration is to be maintained at 0.90 wt% C, and the treatment is to be conducted at 1100°C. Use the diffusion data for  $\gamma$ -Fe in Table 5.2.
- 5.12 An FCC iron-carbon alloy initially containing 0.55 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1325 K (1052°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 0.25 wt% after a 10-h treatment? The value of  $D$  at 1325 K is  $4.3 \times 10^{-11}$  m<sup>2</sup>/s.
- 5.13 Nitrogen from a gaseous phase is to be diffused into pure iron at 675°C. If the surface concentration is maintained at 0.2 wt% N, what will be the concentration 2 mm from the surface after 25 h? The diffusion coefficient for nitrogen in iron at 675°C is  $1.9 \times 10^{-11}$  m<sup>2</sup>/s.
- 5.14 Simplify Equation 5.5 for the situation when  $C_1$  is halfway between  $C_2$  and  $C_0$ .
- 5.15 For a steel alloy it has been determined that a carburizing heat treatment of 15 h duration will raise the carbon concentration to 0.35 wt% at a point 2.0 mm from the surface. Estimate the time necessary to achieve the same concentration at a 6.0-mm position for an identical steel and at the same carburizing temperature.
- 5.16 Cite the values of the diffusion coefficients for the interdiffusion of carbon in both  $\alpha$ -iron (BCC) and  $\gamma$ -iron (FCC) at 900°C. Which is larger? Explain why this is the case.
- 5.17 Using the data in Table 5.2, compute the value of  $D$  for the diffusion of magnesium in aluminum at 400°C.
- 5.18 At what temperature will the diffusion coefficient for the diffusion of zinc in copper have a value of  $2.6 \times 10^{-16}$  m<sup>2</sup>/s? Use the diffusion data in Table 5.2.
- 5.19 The preexponential and activation energy for the diffusion of chromium in nickel are  $1.1 \times 10^{-4}$  m<sup>2</sup>/s and 272,000 J/mol, respectively. At what temperature will the diffusion coefficient have a value of  $1.2 \times 10^{-14}$  m<sup>2</sup>/s?
- 5.20 The activation energy for the diffusion of copper in silver is 193,000 J/mol. Calculate the diffusion coefficient at 1200 K (927°C), given that  $D$  at 1000 K (727°C) is  $1.0 \times 10^{-14}$  m<sup>2</sup>/s.
- 5.21 The diffusion coefficients for nickel in iron are given at two temperatures:
- | $T$ (K) | $D$ (m <sup>2</sup> /s) |
|---------|-------------------------|
| 1473    | $2.2 \times 10^{-15}$   |
| 1673    | $4.8 \times 10^{-14}$   |
- (a) Determine the values of  $D_0$  and the activation energy  $Q_d$ .
- (b) What is the magnitude of the  $D$  at 1300°C (1573 K)?
- 5.22 The diffusion coefficients for carbon in nickel are given at two temperatures:
- | $T$ (°C) | $D$ (m <sup>2</sup> /s) |
|----------|-------------------------|
| 600      | $5.5 \times 10^{-14}$   |
| 700      | $3.9 \times 10^{-13}$   |
- (a) Determine the values of  $D_0$  and  $Q_d$ .
- (b) What is the magnitude of  $D$  at 850°C?
- 5.23 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

gold in silver. Determine values for the activation energy and preexponential.



- 5.24** Carbon is allowed to diffuse through a steel plate 10 mm thick. The concentrations of carbon at the two faces are 0.85 and 0.40 kg C/cm<sup>2</sup> Fe, which are maintained constant. If the preexponential and activation energy are  $6.2 \times 10^{-7}$  m<sup>2</sup>/s and 80,000 J/mol, respectively, compute the temperature at which the diffusion flux is  $6.3 \times 10^{-10}$  kg/m<sup>2</sup>·s.
- 5.25** The steady-state diffusion flux through a metal plate is  $7.8 \times 10^{-8}$  kg/m<sup>2</sup>·s at a temperature of 1200°C (1473 K) and when the concentration gradient is  $-500$  kg/m<sup>4</sup>. Calculate the diffusion flux at 1000°C (1273 K) for the same concentration gradient and assuming an activation energy for diffusion of 145,000 J/mol.
- 5.26** At approximately what temperature would a specimen of  $\gamma$ -iron have to be carburized for 4 h to produce the same diffusion result as at 1000°C for 12 h?
- 5.27** (a) Calculate the diffusion coefficient for magnesium in aluminum at 450°C. (b) What time will be required at 550°C to produce the same diffusion result (in terms of concentration at a specific point) as for 15 h at 450°C?
- 5.28** A copper-nickel diffusion couple similar to that shown in Figure 5.1a is fashioned. After a 500-h heat treatment at 1000°C (1273 K) the concentration of Ni is 3.0 wt% at the 1.0-mm position within the copper. At what temperature must the diffusion couple need to be heated to produce this same concentration (i.e., 3.0 wt% Ni) at a 2.0-mm position after 500 h? The preexponential and activation energy for the diffusion of Ni in Cu are  $2.7 \times 10^{-4}$  m<sup>2</sup>/s and 236,000 J/mol, respectively.
- 5.29** A diffusion couple similar to that shown in Figure 5.1a is prepared using two hypothetical metals A and B. After a 20-h heat treatment at 800°C (and subsequently cooling to room temperature) the concentration of B in A is 2.5 wt% at the 5.0-mm position within metal A. If another heat treatment is conducted on an identical diffusion couple, only at 1000°C for 20 h, at what position will the composition be 2.5 wt% B? Assume that the preexponential and activation energy for the diffusion coefficient are  $1.5 \times 10^{-4}$  m<sup>2</sup>/s and 125,000 J/mol, respectively.
- 5.30** 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 600°C (873 K) for 100 min increases the carbon concentration to 0.75 wt% at a position 0.5 mm below the surface. Estimate the diffusion time required at 900°C (1173 K) to achieve this same concentration also at a 0.5-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 5.2 for C diffusion in  $\alpha$ -Fe.
- 5.31** An FCC iron-carbon alloy initially containing 0.10 wt% C is carburized at an elevated temperature and in an atmosphere wherein the surface carbon concentration is maintained at 1.10 wt%. If after 48 h the concentration of carbon is 0.30 wt% at a position 3.5 mm below the surface, determine the temperature at which the treatment was carried out.
- 5.32** A diffusion couple was formed between pure copper and a copper-nickel alloy. After heating the couple to 1273 K (1000°C) for 30 days, the concentration of nickel in the copper is 10.0 wt% at a position 0.50 mm from the initial copper-alloy interface. What is the original composition of the copper-nickel alloy? The preexponential and activation energy for the diffusion of Ni in Cu are  $2.7 \times 10^{-4}$  m<sup>2</sup>/s and 236,000 J/mol, respectively.



# AI Introduction

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**THIRD EDITION**

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