

**IMPORTANT TERMS AND CONCEPTS**

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

**REFERENCES**

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**QUESTIONS AND PROBLEMS***Introduction*

- 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.

*Diffusion Mechanisms*

- 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.

*Steady-State 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  $0.25 \text{ m}^2$  at  $600^\circ\text{C}$ . Assume a diffusion coefficient of  $1.7 \times 10^{-8} \text{ m}^2/\text{s}$ , 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  $900^\circ\text{C}$  and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is  $1.2 \times 10^{-10} \text{ m}^2/\text{s}$ , and the diffusion flux is found to be  $1.0 \times 10^{-7} \text{ kg/m}^2\cdot\text{s}$ . Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is  $2 \text{ kg/m}^3$ . How far into the sheet from this high-pressure side will the concentration be  $0.5 \text{ kg/m}^3$ ? 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  $675^\circ\text{C}$ . 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

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coefficient if the diffusion flux is  $7.36 \times 10^{-9}$  kg/m<sup>2</sup>-s. *Hint:* Use Equation 4.9 to convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.

- 5.9** When  $\alpha$ -iron is subjected to an atmosphere of nitrogen gas, the concentration of nitrogen in the iron,  $C_N$  (in weight percent), is a function of hydrogen pressure,  $p_{N_2}$  (in MPa), and absolute temperature ( $T$ ) according to

$$C_N = 4.90 \times 10^{-3} \sqrt{p_{N_2}} \exp\left(-\frac{37.6 \text{ kJ/mol}}{RT}\right) \quad (5.11)$$

Furthermore, the values of  $D_0$  and  $Q_d$  for this diffusion system are  $3.0 \times 10^{-7}$  m<sup>2</sup>/s and 76,150 J/mol, respectively. Consider a thin iron membrane 1.5 mm thick that is at 300°C. Compute the diffusion flux through this membrane if the nitrogen pressure on one side of the membrane is 0.10 MPa (0.99 atm), and on the other side 5.0 MPa (49.3 atm).

## Nonsteady-State Diffusion

- 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** Consider a diffusion couple composed of two semi-infinite solids of the same metal, and that each side of the diffusion couple has a different concentration of the same elemental impurity; furthermore, assume each impurity level is constant throughout its side of the diffusion couple. For this situation, the solution to Fick's second law (assuming that the diffusion coefficient for the impurity is independent of concentration), is as follows:

$$C_x = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (5.12)$$

In this expression, when the  $x = 0$  position is taken as the initial diffusion couple interface, then  $C_1$  is the impurity concentration for  $x < 0$ ; likewise,  $C_2$  is the impurity content for  $x > 0$ .

A diffusion couple composed of two platinum-gold alloys is formed; these alloys have compositions of 99.0 wt% Pt-1.0 wt% Au and 96.0 wt% Pt-4.0 wt% Au. Determine the time this diffusion couple must be heated at 1000°C (1273 K) in order for the composition to be 2.8 wt% Au at the 10  $\mu$ m position into the 4.0 wt% Au side of the diffusion couple. Preexponential and activation energy values for Au diffusion in Pt are  $1.3 \times 10^{-5}$  m<sup>2</sup>/s and 252,000 J/mol, respectively.

- 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.

## Factors That Influence Diffusion

- 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.

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**5.18** At what temperature will the diffusion coefficient for the diffusion of zinc in copper have a value of  $2.6 \times 10^{-16} \text{ m}^2/\text{s}$ ? Use the diffusion data in Table 5.2.



**5.19** The preexponential and activation energy for the diffusion of chromium in nickel are  $1.1 \times 10^{-4} \text{ m}^2/\text{s}$  and 272,000 J/mol, respectively. At what temperature will the diffusion coefficient have a value of  $1.2 \times 10^{-14} \text{ m}^2/\text{s}$ ?



**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  $1.0 \times 10^{-14} \text{ m}^2/\text{s}$ .

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



$T(\text{K})$	$D(\text{m}^2/\text{s})$
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  $D$  at 1300°C (1573 K)?

**5.22** The diffusion coefficients for carbon in nickel are given at two temperatures:

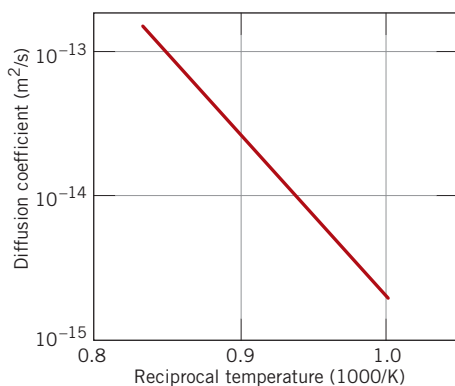


$T(^{\circ}\text{C})$	$D(\text{m}^2/\text{s})$
600	$5.5 \times 10^{-14}$
700	$3.9 \times 10^{-13}$

(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>3</sup> Fe, which are maintained constant. If the preexponential and activation energy are  $6.2 \times 10^{-7} \text{ m}^2/\text{s}$  and 80,000 J/mol, respectively, compute the temperature at which the diffusion flux is  $6.3 \times 10^{-10} \text{ kg/m}^2\text{-s}$ .

**5.25** The steady-state diffusion flux through a metal plate is  $7.8 \times 10^{-8} \text{ kg/m}^2\text{-s}$  at a temperature of 1200°C (1473 K) and when the concentration gradient is  $-500 \text{ kg/m}^4$ . 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 should the diffusion couple 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  $2.7 \times 10^{-4} \text{ m}^2/\text{s}$  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

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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  $1.5 \times 10^{-4} \text{ m}^2/\text{s}$  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 that 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.

## DESIGN PROBLEMS

*Steady-State Diffusion  
(Factors That Influence Diffusion)*

- 5.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/m<sup>3</sup>) 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:

$$C_H = 2.5 \times 10^3 \sqrt{p_{H_2}} \exp\left(-\frac{27.8 \text{ kJ/mol}}{RT}\right) \quad (5.13a)$$

$$C_N = 2.75 \times 10^3 \sqrt{p_{N_2}} \exp\left(-\frac{37.6 \text{ kJ/mol}}{RT}\right) \quad (5.13b)$$

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

$$D_H(\text{m}^2/\text{s}) = 1.4 \times 10^{-7} \exp\left(-\frac{13.4 \text{ kJ/mol}}{RT}\right) \quad (5.14a)$$

$$D_N(\text{m}^2/\text{s}) = 3.0 \times 10^{-7} \exp\left(-\frac{76.15 \text{ kJ/mol}}{RT}\right) \quad (5.14b)$$

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.

- 5.D2** A gas mixture is found to contain two diatomic A and B species ( $A_2$  and  $B_2$ ) 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