



# Ch05 Solution Manual Material Science and Engineering 8th Edition

Material Science & Engineering (HITEC University)



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## CHAPTER 5

### DIFFUSION

#### PROBLEM SOLUTIONS

##### **Introduction**

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

##### Solution

Self-diffusion is atomic migration in pure metals--i.e., when all atoms exchanging positions are of the same type. Interdiffusion is diffusion of atoms of one metal into another metal.

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.

Solution

Self-diffusion may be monitored by using radioactive isotopes of the metal being studied. The motion of these isotopic atoms may be monitored by measurement of radioactivity level.

## 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.

### Solution

(a) With vacancy diffusion, atomic motion is from one lattice site to an adjacent vacancy. Self-diffusion and the diffusion of substitutional impurities proceed via this mechanism. On the other hand, atomic motion is from interstitial site to adjacent interstitial site for the interstitial diffusion mechanism.

(b) Interstitial diffusion is normally more rapid than vacancy diffusion because: (1) interstitial atoms, being smaller than vacancies, have a higher probability of finding an empty adjacent interstitial site than a vacancy has of finding an empty adjacent vacancy site. (2) The probability of an empty adjacent interstitial site is greater than for a vacancy adjacent to a host (or substitutional impurity) atom.

## **Steady-State Diffusion**

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

### Solution

Steady-state diffusion is the situation wherein the rate of diffusion into a given system is just equal to the rate of diffusion out, such that there is no net accumulation or depletion of diffusing species--i.e., the diffusion flux is independent of time.

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

Solution

- (a) The driving force is that which compels a reaction to occur.  
(b) The driving force for steady-state diffusion is the concentration gradient.

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 5-mm-thick sheet of palladium having an area of  $0.20 \text{ m}^2$  at  $500^\circ\text{C}$ . Assume a diffusion coefficient of  $1.0 \times 10^{-8} \text{ m}^2/\text{s}$ , 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.

Solution

This problem calls for the mass of hydrogen, per hour, that diffuses through a Pd sheet. It first becomes necessary to employ both Equations 5.1a and 5.3. Combining these expressions and solving for the mass yields

$$\begin{aligned} M &= JAt = -DA \frac{\Delta C}{\Delta x} \\ &= - (1.0 \times 10^{-8} \text{ m}^2/\text{s}) (0.20 \text{ m}^2) (3600 \text{ s/h}) \left[ \frac{0.6 - 2.4 \text{ kg/m}^3}{5 \times 10^{-3} \text{ m}} \right] \\ &= 2.6 \times 10^{-3} \text{ kg/h} \end{aligned}$$

5.7 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  $6 \times 10^{-11} \text{ m}^2/\text{s}$ , and the diffusion flux is found to be  $1.2 \times 10^{-7} \text{ kg/m}^2\text{-s}$ . Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is  $4 \text{ kg/m}^3$ . How far into the sheet from this high-pressure side will the concentration be  $2.0 \text{ kg/m}^3$ ? Assume a linear concentration profile.

### Solution

This problem is solved by using Equation 5.3 in the form

$$J = -D \frac{C_A - C_B}{x_A - x_B}$$

If we take  $C_A$  to be the point at which the concentration of nitrogen is  $4 \text{ kg/m}^3$ , then it becomes necessary to solve for  $x_B$ , as

$$x_B = x_A + D \left[ \frac{C_A - C_B}{J} \right]$$

Assume  $x_A$  is zero at the surface, in which case

$$x_B = 0 + (6 \times 10^{-11} \text{ m}^2/\text{s}) \left[ \frac{4 \text{ kg/m}^3 - 2 \text{ kg/m}^3}{1.2 \times 10^{-7} \text{ kg/m}^2\text{-s}} \right]$$

$$= 1 \times 10^{-3} \text{ m} = 1 \text{ mm}$$



5.8 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  $1.4 \times 10^{-8} \text{ kg/m}^2\text{-s}$ . Hint: Use Equation 4.9 to convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.

Solution

Let us first convert the carbon concentrations from weight percent to kilograms carbon per meter cubed using Equation 4.9a. For 0.012 wt% C

$$C_C'' = \frac{C_C}{\frac{C_C}{\rho_C} + \frac{C_{Fe}}{\rho_{Fe}}} \times 10^3$$

$$= \frac{0.012}{\frac{0.012}{2.25 \text{ g/cm}^3} + \frac{99.988}{7.87 \text{ g/cm}^3}} \times 10^3$$

$$0.944 \text{ kg C/m}^3$$

Similarly, for 0.0075 wt% C

$$C_C'' = \frac{0.0075}{\frac{0.0075}{2.25 \text{ g/cm}^3} + \frac{99.9925}{7.87 \text{ g/cm}^3}} \times 10^3$$

$$= 0.590 \text{ kg C/m}^3$$

Now, using a rearranged form of Equation 5.3

$$D = -J \left[ \frac{x_A - x_B}{C_A - C_B} \right]$$

$$= - (1.40 \times 10^{-8} \text{ kg/m}^2\text{-s}) \left[ \frac{-10^{-3} \text{ m}}{0.944 \text{ kg/m}^3 - 0.590 \text{ kg/m}^3} \right]$$

$$= 3.95 \times 10^{-11} \text{ m}^2/\text{s}$$

5.9 When  $\alpha$ -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

$$C_H = 1.34 \times 10^{-2} \sqrt{p_{H_2}} \exp\left(-\frac{27.2 \text{ kJ/mol}}{RT}\right) \quad (5.14)$$

Furthermore, the values of  $D_0$  and  $Q_d$  for this diffusion system are  $1.4 \times 10^{-7} \text{ m}^2/\text{s}$  and  $13,400 \text{ J/mol}$ , respectively. Consider a thin iron membrane 1 mm thick that is at  $250^\circ\text{C}$ . 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).

### Solution

Ultimately we will employ Equation 5.3 to solve this problem. However, it first becomes necessary to determine the concentration of hydrogen at each face using Equation 5.14. At the low pressure (or B) side

$$C_{H(B)} = (1.34 \times 10^{-2}) \sqrt{0.15 \text{ MPa}} \exp\left[-\frac{27,200 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(250 + 273 \text{ K})}\right]$$

$$9.93 \times 10^{-6} \text{ wt\%}$$

Whereas, for the high pressure (or A) side

$$C_{H(A)} = (1.34 \times 10^{-2}) \sqrt{7.5 \text{ MPa}} \exp\left[-\frac{27,200 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(250 + 273 \text{ K})}\right]$$

$$7.02 \times 10^{-5} \text{ wt\%}$$

We now convert concentrations in weight percent to mass of hydrogen per unit volume of solid. At face B there are  $9.93 \times 10^{-6} \text{ g}$  (or  $9.93 \times 10^{-9} \text{ kg}$ ) of hydrogen in 100 g of Fe, which is virtually pure iron. From the density of iron ( $7.87 \text{ g/cm}^3$ ), the volume iron in 100 g ( $V_B$ ) is just

$$V_B = \frac{100 \text{ g}}{7.87 \text{ g/cm}^3} = 12.7 \text{ cm}^3 = 1.27 \times 10^{-5} \text{ m}^3$$

Therefore, the concentration of hydrogen at the B face in kilograms of H per cubic meter of alloy [ $C''_{H(B)}$ ] is just

$$C_{H(B)}'' = \frac{C_{H(B)}}{V_B}$$

$$= \frac{9.93 \times 10^{-9} \text{ kg}}{1.27 \times 10^{-5} \text{ m}^3} = 7.82 \times 10^{-4} \text{ kg/m}^3$$

At the A face the volume of iron in 100 g ( $V_A$ ) will also be  $1.27 \times 10^{-5} \text{ m}^3$ , and

$$C_{H(A)}'' = \frac{C_{H(A)}}{V_A}$$

$$= \frac{7.02 \times 10^{-8} \text{ kg}}{1.27 \times 10^{-5} \text{ m}^3} = 5.53 \times 10^{-3} \text{ kg/m}^3$$

Thus, the concentration gradient is just the difference between these concentrations of nitrogen divided by the thickness of the iron membrane; that is

$$\frac{\Delta C}{\Delta x} = \frac{C_{H(B)}'' - C_{H(A)}''}{x_B - x_A}$$

$$= \frac{7.82 \times 10^{-4} \text{ kg/m}^3 - 5.53 \times 10^{-3} \text{ kg/m}^3}{10^{-3} \text{ m}} = -4.75 \text{ kg/m}^4$$

At this time it becomes necessary to calculate the value of the diffusion coefficient at 250°C using Equation 5.8. Thus,

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

$$= (1.4 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left(-\frac{13,400 \text{ J/mol}}{(8.31 \text{ J/mol-K})(250 + 273 \text{ K})}\right)$$

$$= 6.41 \times 10^{-9} \text{ m}^2/\text{s}$$

And, finally, the diffusion flux is computed using Equation 5.3 by taking the negative product of this diffusion coefficient and the concentration gradient, as

$$J = -D \frac{\Delta C}{\Delta x}$$

$$= - (6.41 \times 10^{-9} \text{ m}^2/\text{s})(-4.75 \text{ kg/m}^4) = 3.05 \times 10^{-8} \text{ kg/m}^2 \cdot \text{s}$$

## 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.

### Solution

It can be shown that

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

is a solution to

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

simply by taking appropriate derivatives of the  $C_x$  expression. When this is carried out,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} = \frac{B}{2D^{1/2}t^{3/2}} \left( \frac{x^2}{2Dt} - 1 \right) \exp\left(-\frac{x^2}{4Dt}\right)$$

5.11 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  $\gamma$ -Fe in Table 5.2.

Solution

In order to solve this problem it is first necessary to use Equation 5.5:

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

wherein,  $C_x = 0.45$ ,  $C_0 = 0.20$ ,  $C_s = 1.30$ , and  $x = 2 \text{ mm} = 2 \times 10^{-3} \text{ m}$ . Thus,

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.45 - 0.20}{1.30 - 0.20} = 0.2273 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

or

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - 0.2273 = 0.7727$$

By linear interpolation using data from Table 5.1

$z$	<u><math>\operatorname{erf}(z)</math></u>
0.85	0.7707
$z$	0.7727
0.90	0.7970

$$\frac{z - 0.850}{0.900 - 0.850} = \frac{0.7727 - 0.7707}{0.7970 - 0.7707}$$

From which

$$z = 0.854 = \frac{x}{2\sqrt{Dt}}$$

Now, from Table 5.2, at 1000°C (1273 K)

$$D = (2.3 \times 10^{-5} \text{ m}^2/\text{s}) \exp \left[ -\frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1273 \text{ K})} \right]$$

$$= 1.93 \times 10^{-11} \text{ m}^2/\text{s}$$

Thus,

$$0.854 = \frac{2 \times 10^{-3} \text{ m}}{(2)\sqrt{(1.93 \times 10^{-11} \text{ m}^2/\text{s})(t)}}$$

Solving for t yields

$$t = 7.1 \times 10^4 \text{ s} = 19.7 \text{ h}$$



5.12 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  $6.9 \times 10^{-11} \text{ m}^2/\text{s}$ .

### Solution

This problem asks that we determine the position at which the carbon concentration is 0.15 wt% after a 10-h heat treatment at 1325 K when  $C_0 = 0.35 \text{ wt\% C}$ . From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.15 - 0.35}{0 - 0.35} = 0.5714 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus,

$$\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4286$$

Using data in Table 5.1 and linear interpolation

$z$	<u>erf(z)</u>
0.40	0.4284
$z$	0.4286
0.45	0.4755

$$\frac{z - 0.40}{0.45 - 0.40} = \frac{0.4286 - 0.4284}{0.4755 - 0.4284}$$

And,

$$z = 0.4002$$

Which means that

$$\frac{x}{2\sqrt{Dt}} = 0.4002$$

And, finally

$$x = 2(0.4002)\sqrt{Dt} = (0.8004)\sqrt{(6.9 \times 10^{-11} \text{ m}^2/\text{s})(3.6 \times 10^4 \text{ s})}$$

$$= 1.26 \times 10^{-3} \text{ m} = 1.26 \text{ mm}$$

Note: this problem may also be solved using the “Diffusion” module in the VMSE software. Open the “Diffusion” module, click on the “Diffusion Design” submodule, and then do the following:

1. Enter the given data in left-hand window that appears. In the window below the label “D Value” enter the value of the diffusion coefficient—viz. “6.9e-11”.

2. In the window just below the label “Initial, C0” enter the initial concentration—viz. “0.35”.

3. In the window the lies below “Surface, Cs” enter the surface concentration—viz. “0”.

4. In the window below the label “Time, t” enter the time—viz. “36000”.  
h) = 36,000 s—so enter the value “3.6e4”.

5. Next, at the bottom of this window click on the button labeled “Add curve”.

6. On the right portion of the screen will appear a concentration profile for this particular diffusion situation. A diamond-shaped cursor will appear at the upper left-hand corner of the resulting curve. Click and drag this cursor down the curve to the point at which the number below “Concentration:” reads “0.15 wt%”. Then read the value under the “Distance:”. For this problem, this value (the solution to the problem) is ranges between 1.24 and 1.30 mm.

5.13 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  $2.5 \times 10^{-11} \text{ m}^2/\text{s}$ .

Solution

This problem asks us to compute the nitrogen concentration ( $C_x$ ) at the 1 mm position after a 10 h diffusion time, when diffusion is nonsteady-state. From Equation 5.5

$$\begin{aligned} \frac{C_x - C_0}{C_s - C_0} &= \frac{C_x - 0}{0.1 - 0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \\ &= 1 - \operatorname{erf}\left[\frac{10^{-3} \text{ m}}{(2)\sqrt{(2.5 \times 10^{-11} \text{ m}^2/\text{s})(10 \text{ h})(3600 \text{ s/h})}}\right] \\ &= 1 - \operatorname{erf}(0.527) \end{aligned}$$

Using data in Table 5.1 and linear interpolation

$z$	<u><math>\operatorname{erf}(z)</math></u>
0.500	0.5205
0.527	$y$
0.550	0.5633

$$\frac{0.527 - 0.500}{0.550 - 0.500} = \frac{y - 0.5205}{0.5633 - 0.5205}$$

from which

$$y = \operatorname{erf}(0.527) = 0.5436$$

Thus,

$$\frac{C_x - 0}{0.1 - 0} = 1.0 - 0.5436$$

This expression gives

$$C_x = 0.046 \text{ wt\% N}$$

Note: this problem may also be solved using the “Diffusion” module in the VMSE software. Open the “Diffusion” module, click on the “Diffusion Design” submodule, and then do the following:

1. Enter the given data in left-hand window that appears. In the window below the label “D Value” enter the value of the diffusion coefficient—viz. “2.5e-11”.

2. In the window just below the label “Initial, C0” enter the initial concentration—viz. “0”.

3. In the window the lies below “Surface, Cs” enter the surface concentration—viz. “0.1”.

h) = 36,000 s—so enter the value “3.6e4”.

5. Next, at the bottom of this window click on the button labeled “Add curve”.

6. On the right portion of the screen will appear a concentration profile for this particular diffusion situation. A diamond-shaped cursor will appear at the upper left-hand corner of the resulting curve. Click and drag this cursor down the curve to the point at which the number below “Distance:” reads “1.00 mm”. Then read the value under the “Concentration:”. For this problem, this value (the solution to the problem) is 0.05 wt%.

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:

$$C_x = \left( \frac{C_1 + C_2}{2} \right) - \left( \frac{C_1 - C_2}{2} \right) \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \quad (5.15)$$

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

A diffusion couple composed of two silver-gold alloys is formed; 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  $8.5 \times 10^{-5} \text{ m}^2/\text{s}$  and 202,100 J/mol, respectively.

#### Solution

For this platinum-gold diffusion couple for which  $C_1 = 5 \text{ wt\% Au}$  and  $C_2 = 2 \text{ wt\% Au}$ , we are asked to determine the diffusion time at 750°C that will give a composition of 2.5 wt% Au at the 50 μm position. Thus, for this problem, Equation 5.15 takes the form

$$2.5 = \left( \frac{5 + 2}{2} \right) - \left( \frac{5 - 2}{2} \right) \operatorname{erf} \left( \frac{50 \times 10^{-6} \text{ m}}{2\sqrt{Dt}} \right)$$

It now becomes necessary to compute the diffusion coefficient at 750°C (1023 K) given that  $D_0 = 8.5 \times 10^{-5} \text{ m}^2/\text{s}$  and  $Q_d = 202,100 \text{ J/mol}$ . From Equation 5.8 we have

$$\begin{aligned} D &= D_0 \exp \left( -\frac{Q_d}{RT} \right) \\ &= (8.5 \times 10^{-5} \text{ m}^2/\text{s}) \exp \left[ -\frac{202,100 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1023 \text{ K})} \right] \\ &= 4.03 \times 10^{-15} \text{ m}^2/\text{s} \end{aligned}$$

Substitution of this value into the above equation leads to

$$2.5 = \left( \frac{5 + 2}{2} \right) - \left( \frac{5 - 2}{2} \right) \operatorname{erf} \left[ \frac{50 \times 10^{-6} \text{ m}}{2\sqrt{(4.03 \times 10^{-15} \text{ m}^2/\text{s})(t)}} \right]$$

This expression reduces to the following form:

$$0.6667 = \operatorname{erf} \left( \frac{393.8 \sqrt{s}}{\sqrt{t}} \right)$$

Using data in Table 5.1, it is necessary to determine the value of  $z$  for which the error function is 0.6667. We use linear interpolation as follows:

$z$	$\operatorname{erf}(z)$
0.650	0.6420
$y$	0.6667
0.700	0.6778

$$\frac{y - 0.650}{0.700 - 0.650} = \frac{0.6667 - 0.6420}{0.6778 - 0.6420}$$

from which

$$y = 0.6844 = \frac{393.8 \sqrt{s}}{\sqrt{t}}$$

And, solving for  $t$  gives

$$t = 3.31 \times 10^5 \text{ s} = 92 \text{ h}$$

5.15 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.

Solution

This problem calls for an estimate of the time necessary to achieve a carbon concentration of 0.45 wt% at a point 5.0 mm from the surface. From Equation 5.6b,

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

But since the temperature is constant, so also is  $D$  constant, and

$$\frac{x^2}{t} = \text{constant}$$

or

$$\frac{x_1^2}{t_1} = \frac{x_2^2}{t_2}$$

Thus,

$$\frac{(2.5 \text{ mm})^2}{10 \text{ h}} = \frac{(5.0 \text{ mm})^2}{t_2}$$

from which

$$t_2 = 40 \text{ h}$$

## 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.

### Solution

We are asked to compute the diffusion coefficients of C in both  $\alpha$  and  $\gamma$  iron at 900°C. Using the data in Table 5.2,

$$\begin{aligned} D_{\alpha} &= (6.2 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left[-\frac{80,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1173 \text{ K})}\right] \\ &= 1.69 \times 10^{-10} \text{ m}^2/\text{s} \end{aligned}$$

$$\begin{aligned} D_{\gamma} &= (2.3 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1173 \text{ K})}\right] \\ &= 5.86 \times 10^{-12} \text{ m}^2/\text{s} \end{aligned}$$

The  $D$  for diffusion of C in BCC  $\alpha$  iron is larger, the reason being that the atomic packing factor is smaller than for FCC  $\gamma$  iron (0.68 versus 0.74). Interstitial void space in the BCC Fe, and, therefore, the motion of the interstitial carbon atoms occurs more easily.



5.17 Using the data in Table 5.2, compute the value of  $D$  for the diffusion of zinc in copper at  $650^{\circ}\text{C}$ .

Solution

Incorporating the appropriate data from Table 5.2 into Equation 5.8 leads to

$$D = (2.4 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{189,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(650 + 273 \text{ K})}\right]$$
$$= 4.8 \times 10^{-16} \text{ m}^2/\text{s}$$

Note: this problem may also be solved using the “Diffusion” module in the VMSE software. Open the “Diffusion” module, click on the “D vs 1/T Plot” submodule, and then do the following:

1. In the left-hand window that appears, click on the “Zn-Cu” pair under the “Diffusing Species”-“Host Metal” headings.
2. Next, at the bottom of this window, click the “Add Curve” button.
3. A log  $D$  versus  $1/T$  plot then appears, with a line for the temperature dependence of the diffusion coefficient for Zn in Cu. Now under “Temp Range” in the boxes appearing below “T Max” change the temperature to either “650” C or “923” K. At the top of this curve is a diamond-shaped cursor. Click-and-drag this cursor down the line to the point at which the entry under the “Temperature (T):” label reads 923 K (inasmuch as this is the Kelvin equivalent of  $650^{\circ}\text{C}$ ). Finally, the diffusion coefficient value at this temperature is given under the label “Diff Coeff (D):”. For this problem, the value is  $4.7 \times 10^{-16} \text{ m}^2/\text{s}$ .

5.18 At what temperature will the diffusion coefficient for the diffusion of copper in nickel have a value of  $6.5 \times 10^{-17} \text{ m}^2/\text{s}$ . Use the diffusion data in Table 5.2.

Solution

Solving for T from Equation 5.9a

$$T = - \frac{Q_d}{R(\ln D - \ln D_0)}$$

and using the data from Table 5.2 for the diffusion of Cu in Ni (i.e.,  $D_0 = 2.7 \times 10^{-5} \text{ m}^2/\text{s}$  and  $Q_d = 256,000 \text{ J/mol}$ ), we get

$$\begin{aligned} T &= - \frac{256,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K}) [\ln (6.5 \times 10^{-17} \text{ m}^2/\text{s}) - \ln (2.7 \times 10^{-5} \text{ m}^2/\text{s})]} \\ &= 1152 \text{ K} = 879^\circ\text{C} \end{aligned}$$

Note: this problem may also be solved using the “Diffusion” module in the VMSE software. Open the “Diffusion” module, click on the “D vs 1/T Plot” submodule, and then do the following:

1. In the left-hand window that appears, there is a preset set of data for several diffusion systems. Click on the box for which Cu is the diffusing species and Ni is the host metal. Next, at the bottom of this window, click the “Add Curve” button.

2. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Cu in Ni. At the top of this curve is a diamond-shaped cursor. Click-and-drag this cursor down the line to the point at which the entry under the “Diff Coeff (D):” label reads  $6.5 \times 10^{-17} \text{ m}^2/\text{s}$ . The temperature at which the diffusion coefficient has this value is given under the label “Temperature (T):”. For this problem, the value is 1153 K.

5.19 The preexponential and activation energy for the diffusion of iron in cobalt are  $1.1 \times 10^{-5} \text{ m}^2/\text{s}$  and 253,300 J/mol, respectively. At what temperature will the diffusion coefficient have a value of  $2.1 \times 10^{-14} \text{ m}^2/\text{s}$ ?

### Solution

For this problem we are given  $D_0$  ( $1.1 \times 10^{-5}$ ) and  $Q_d$  (253,300 J/mol) for the diffusion of Fe in Co, and asked to compute the temperature at which  $D = 2.1 \times 10^{-14} \text{ m}^2/\text{s}$ . Solving for T from Equation 5.9a yields

$$T = \frac{Q_d}{R(\ln D_0 - \ln D)}$$

$$= \frac{253,300 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K}) [\ln (1.1 \times 10^{-5} \text{ m}^2/\text{s}) - \ln (2.1 \times 10^{-14} \text{ m}^2/\text{s})]}$$

$$= 1518 \text{ K} = 1245^\circ\text{C}$$

Note: this problem may also be solved using the “Diffusion” module in the VMSE software. Open the “Diffusion” module, click on the “D vs 1/T Plot” submodule, and then do the following:

1. In the left-hand window that appears, click on the “Custom1” box.
2. In the column on the right-hand side of this window enter the data for this problem. In the window under “D0” enter preexponential value—viz. “1.1e-5”. Next just below the “Qd” window enter the activation energy value—viz. “253.3”. It is next necessary to specify a temperature range over which the data is to be plotted. The temperature at which D has the stipulated value is probably between 1000°C and 1500°C, so enter “1000” in the “T Min” box that is beside “C”; and similarly for the maximum temperature—enter “1500” in the box below “T Max”.
3. Next, at the bottom of this window, click the “Add Curve” button.
4. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Fe in Co. At the top of this curve is a diamond-shaped cursor. Click-and-drag this cursor down the line to the point at which the entry under the “Diff Coeff (D):” label reads  $2.1 \times 10^{-14} \text{ m}^2/\text{s}$ . The temperature at which the diffusion coefficient has this value is given under the label “Temperature (T):”. For this problem, the value is 1519 K.

5.20 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  $6.25 \times 10^{-11} \text{ m}^2/\text{s}$ .

Solution

To solve this problem it first becomes necessary to solve for  $D_0$  from Equation 5.8 as

$$\begin{aligned} D_0 &= D \exp\left(\frac{Q_d}{RT}\right) \\ &= (6.25 \times 10^{-11} \text{ m}^2/\text{s}) \exp\left[\frac{111,000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1400 \text{ K})}\right] \\ &= 8.7 \times 10^{-7} \text{ m}^2/\text{s} \end{aligned}$$

Now, solving for D at 1100 K (again using Equation 5.8) gives

$$\begin{aligned} D &= (8.7 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left[-\frac{111,000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1100 \text{ K})}\right] \\ &= 4.6 \times 10^{-12} \text{ m}^2/\text{s} \end{aligned}$$

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

T (K)	D (m <sup>2</sup> /s)
1273	$9.4 \times 10^{-16}$
1473	$2.4 \times 10^{-14}$

- (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)?

Solution

- (a) Using Equation 5.9a, we set up two simultaneous equations with  $Q_d$  and  $D_0$  as unknowns as follows:

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_1} \right)$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_2} \right)$$

Now, solving for  $Q_d$  in terms of temperatures  $T_1$  and  $T_2$  (1273 K and 1473 K) and  $D_1$  and  $D_2$  ( $9.4 \times 10^{-16}$  and  $2.4 \times 10^{-14}$  m<sup>2</sup>/s), we get

$$\begin{aligned} Q_d &= -R \frac{\ln D_1 - \ln D_2}{\frac{1}{T_1} - \frac{1}{T_2}} \\ &= - (8.31 \text{ J/mol} \cdot \text{K}) \frac{[\ln (9.4 \times 10^{-16}) - \ln (2.4 \times 10^{-14})]}{\frac{1}{1273 \text{ K}} - \frac{1}{1473 \text{ K}}} \\ &= 252,400 \text{ J/mol} \end{aligned}$$

Now, solving for  $D_0$  from Equation 5.8 (and using the 1273 K value of  $D$ )

$$D_0 = D_1 \exp \left( \frac{Q_d}{RT_1} \right)$$

$$= (9.4 \times 10^{-16} \text{ m}^2/\text{s}) \exp \left[ \frac{252,400 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1273 \text{ K})} \right]$$

$$= 2.2 \times 10^{-5} \text{ m}^2/\text{s}$$

(b) Using these values of  $D_0$  and  $Q_d$ ,  $D$  at 1373 K is just


$$D = (2.2 \times 10^{-5} \text{ m}^2/\text{s}) \exp \left[ -\frac{252,400 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1373 \text{ K})} \right]$$

$$= 5.4 \times 10^{-15} \text{ m}^2/\text{s}$$

Note: this problem may also be solved using the “Diffusion” module in the VMSE software. Open the “Diffusion” module, click on the “ $D_0$  and  $Q_d$  from Experimental Data” submodule, and then do the following:

1. In the left-hand window that appears, enter the two temperatures from the table in the book (viz. “1273” and “1473”, in the first two boxes under the column labeled “T (K)”. Next, enter the corresponding diffusion coefficient values (viz. “9.4e-16” and “2.4e-14”).

3. Next, at the bottom of this window, click the “Plot data” button.

4. A log  $D$  versus  $1/T$  plot then appears, with a line for the temperature dependence for this diffusion system. At the top of this window are given values for  $D_0$  and  $Q_d$    $10^{-5} \text{ m}^2/\text{s}$  and 252 kJ/mol, respectively

5. To solve the (b) part of the problem we utilize the diamond-shaped cursor that is located at the top of the line on this plot. Click-and-drag this cursor down the line to the point at which the entry under the “Temperature (T):” label reads “1373”. The value of the diffusion coefficient at this temperature is given under the label “Diff Coeff (D):”. For our problem, this value is  $5.4 \times 10^{-15} \text{ m}^2/\text{s}$ .

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

T (°C)	D (m <sup>2</sup> /s)
650	$5.5 \times 10^{-16}$
900	$1.3 \times 10^{-13}$

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

Solution

(a) Using Equation 5.9a, we set up two simultaneous equations with  $Q_d$  and  $D_0$  as unknowns as follows:

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_1} \right)$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_2} \right)$$

Solving for  $Q_d$  in terms of temperatures  $T_1$  and  $T_2$  (923 K [650°C] and 1173 K [900°C]) and  $D_1$  and  $D_2$  ( $5.5 \times 10^{-16}$  and  $1.3 \times 10^{-13}$  m<sup>2</sup>/s), we get

$$\begin{aligned} Q_d &= -R \frac{\ln D_1 - \ln D_2}{\frac{1}{T_1} - \frac{1}{T_2}} \\ &= - \frac{(8.31 \text{ J/mol} \cdot \text{K}) [\ln (5.5 \times 10^{-16}) - \ln (1.3 \times 10^{-13})]}{\frac{1}{923 \text{ K}} - \frac{1}{1173 \text{ K}}} \\ &= 196,700 \text{ J/mol} \end{aligned}$$

Now, solving for  $D_0$  from Equation 5.8 (and using the 650°C value of  $D$ )

$$D_0 = D_1 \exp \left( \frac{Q_d}{RT_1} \right)$$

$$= (5.5 \times 10^{-16} \text{ m}^2/\text{s}) \exp \left[ \frac{196,700 \text{ J/mol}}{(8.31 \text{ J/mol-K})(923 \text{ K})} \right]$$

$$= 7.5 \times 10^{-5} \text{ m}^2/\text{s}$$

(b) Using these values of  $D_0$  and  $Q_d$ ,  $D$  at 1148 K (875°C) is just

$$D = (7.5 \times 10^{-5} \text{ m}^2/\text{s}) \exp \left[ -\frac{196,700 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1148 \text{ K})} \right]$$

$$= 8.3 \times 10^{-14} \text{ m}^2/\text{s}$$

Note: this problem may also be solved using the “Diffusion” module in the VMSE software. Open the “Diffusion” module, click on the “ $D_0$  and  $Q_d$  from Experimental Data” submodule, and then do the following:

1. In the left-hand window that appears, enter the two temperatures from the table in the book (converted from degrees Celsius to Kelvins) (viz. “923” (650°C) and “1173” (900°C), in the first two boxes under the column labeled “T (K)”. Next, enter the corresponding diffusion coefficient values (viz. “5.5e-16” and “1.3e-13”).

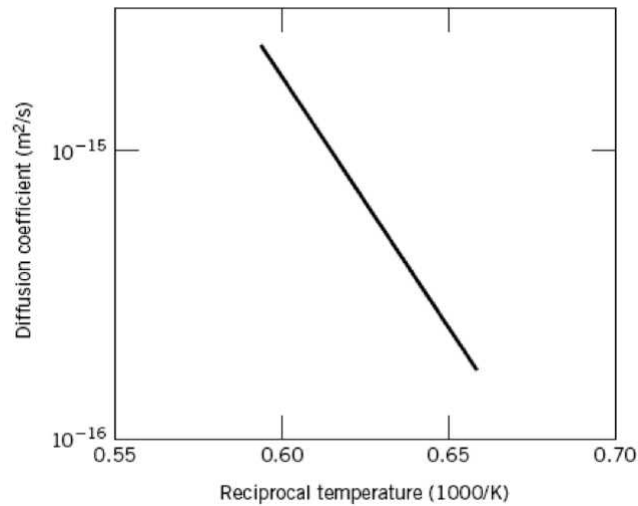
3. Next, at the bottom of this window, click the “Plot data” button.

4. A log  $D$  versus  $1/T$  plot then appears, with a line for the temperature dependence for this diffusion system. At the top of this window are given values for  $D_0$  and  $Q_d$   $10^{-5} \text{ m}^2/\text{s}$  and 196 kJ/mol, respectively

5. To solve the (b) part of the problem we utilize the diamond-shaped cursor that is located at the top of the line on this plot. Click-and-drag this cursor down the line to the point at which the entry under the “Temperature (T):” label reads “1148” (i.e., 875°C). The value of the diffusion coefficient at this temperature is given under the label “Diff Coeff (D):”. For our problem, this value is  $8.9 \times 10^{-14} \text{ m}^2/\text{s}$ .



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 iron in chromium. Determine values for the activation energy and preexponential.

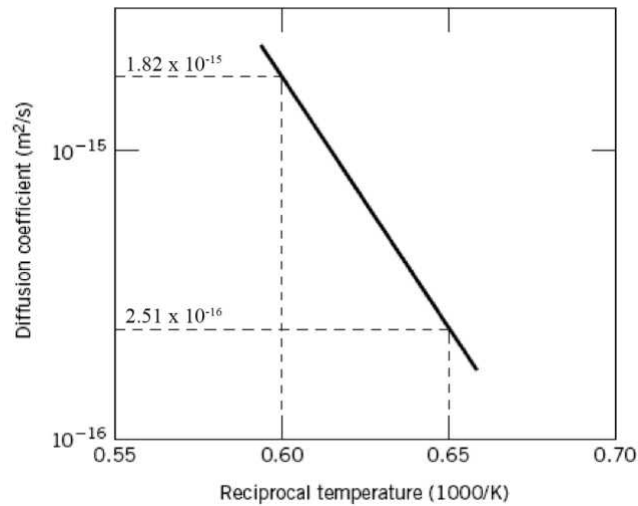


### Solution

This problem asks us to determine the values of  $Q_d$  and  $D_0$  for the diffusion of Fe in Cr from the plot of  $\log D$  versus  $1/T$ . According to Equation 5.9b the slope of this plot is equal to  $-\frac{Q_d}{2.3R}$  (rather than  $-\frac{Q_d}{R}$  since we are using  $\log D$  rather than  $\ln D$ ) and the intercept at  $1/T = 0$  gives the value of  $\log D_0$ . The slope is equal to

$$\text{slope} = \frac{\Delta(\log D)}{\Delta\left(\frac{1}{T}\right)} = \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Taking  $1/T_1$  and  $1/T_2$  as  $0.65 \times 10^{-3}$  and  $0.60 \times 10^{-3} \text{ K}^{-1}$ , respectively, then the corresponding values of  $D_1$  and  $D_2$  are  $2.81 \times 10^{-16}$  and  $1.82 \times 10^{-15}$ , as noted in the figure below.



The values of  $\log D_1$  and  $\log D_2$  are  $-15.60$  and  $-14.74$ , and therefore,

$$Q_d = -2.3 R (\text{slope})$$

$$Q_d = -2.3 R \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= -(2.3)(8.31 \text{ J/mol} \cdot \text{K}) \left[ \frac{-15.60 - (-14.74)}{(0.65 \times 10^{-3} - 0.60 \times 10^{-3}) \text{ K}^{-1}} \right]$$

$$= 329,000 \text{ J/mol}$$

Rather than trying to make a graphical extrapolation to determine  $D_0$ , a more accurate value is obtained analytically using Equation 5.9b taking a specific value of both  $D$  and  $T$  (from  $1/T$ ) from the plot given in the problem; for example,  $D = 1.0 \times 10^{-15} \text{ m}^2/\text{s}$  at  $T = 1626 \text{ K}$  ( $1/T = 0.615 \times 10^{-3} \text{ K}^{-1}$ ). Therefore

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

$$= (1.0 \times 10^{-15} \text{ m}^2/\text{s}) \exp\left[\frac{329,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1626 \text{ K})}\right]$$

$$= 3.75 \times 10^{-5} \text{ m}^2/\text{s}$$

5.24 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<sup>3</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  $1.43 \times 10^{-9}$  kg/m<sup>2</sup>-s.

Solution

Combining Equations 5.3 and 5.8 yields

$$J = -D \frac{\Delta C}{\Delta x}$$

$$= -D_0 \frac{\Delta C}{\Delta x} \exp\left(-\frac{Q_d}{RT}\right)$$

Solving for T from this expression leads to

$$T = \left(\frac{Q_d}{R}\right) \frac{1}{\ln\left(-\frac{D_0 \Delta C}{J \Delta x}\right)}$$

And incorporation of values provided in the problem statement yields

$$= \left(\frac{80,000 \text{ J/mol}}{8.31 \text{ J/mol} \cdot \text{K}}\right) \frac{1}{\ln\left[\frac{(6.2 \times 10^{-7} \text{ m}^2/\text{s})(0.65 \text{ kg/m}^3 - 0.30 \text{ kg/m}^3)}{(1.43 \times 10^{-9} \text{ kg/m}^2 \cdot \text{s})(15 \times 10^{-3} \text{ m})}\right]}$$

$$= 1044 \text{ K} = 771^\circ\text{C}$$

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

Solution

In order to solve this problem, we must first compute the value of  $D_0$  from the data given at  $727^\circ\text{C}$  and 1000 K. this requires the combining of both Equations 5.3 and 5.8 as

$$\begin{aligned} J &= -D \frac{\Delta C}{\Delta x} \\ &= -D_0 \frac{\Delta C}{\Delta x} \exp\left(-\frac{Q_d}{RT}\right) \end{aligned}$$

Solving for  $D_0$  from the above expression gives

$$\begin{aligned} D_0 &= -\frac{J}{\frac{\Delta C}{\Delta x}} \exp\left(\frac{Q_d}{RT}\right) \\ &= -\left(\frac{5.4 \times 10^{-10} \text{ kg/m}^2\text{-s}}{-350 \text{ kg/m}^4}\right) \exp\left[\frac{125,000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1000 \text{ K})}\right] \\ &= 5.26 \times 10^{-6} \text{ m}^2/\text{s} \end{aligned}$$

The value of the diffusion flux at 1300 K may be computed using these same two equations as follows:

$$\begin{aligned} J &= -D_0 \left(\frac{\Delta C}{\Delta x}\right) \exp\left(-\frac{Q_d}{RT}\right) \\ &= -(5.26 \times 10^{-6} \text{ m}^2/\text{s})(-350 \text{ kg/m}^4) \exp\left[-\frac{125,000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1300 \text{ K})}\right] \\ &= 1.74 \times 10^{-8} \text{ kg/m}^2\text{-s} \end{aligned}$$

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

Solution

To solve this problem it is necessary to employ Equation 5.7

$$Dt = \text{constant}$$

Which, for this problem, takes the form

$$D_{900}t_{900} = D_T t_T$$

At 900°C, and using the data from Table 5.2, for the diffusion of carbon in  $\gamma$ -iron—i.e.,

$$D_0 = 2.3 \times 10^{-5} \text{ m}^2/\text{s}$$

$$Q_d = 148,000 \text{ J/mol}$$

the diffusion coefficient is equal to

$$\begin{aligned} D_{900} &= (2.3 \times 10^{-5} \text{ m}^2/\text{s}) \exp \left[ -\frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(900 + 273 \text{ K})} \right] \\ &= 5.9 \times 10^{-12} \text{ m}^2/\text{s} \end{aligned}$$

Thus, from the above equation

$$(5.9 \times 10^{-12} \text{ m}^2/\text{s})(15 \text{ h}) = D_T(2 \text{ h})$$

And, solving for  $D_T$

$$D_T = \frac{(5.9 \times 10^{-12} \text{ m}^2/\text{s})(15 \text{ h})}{2 \text{ h}} = 4.43 \times 10^{-11} \text{ m}^2/\text{s}$$

Now, solving for T from Equation 5.9a gives

$$T = -\frac{Q_d}{R(\ln D_T - \ln D_0)}$$

$$= - \frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K}) [\ln (4.43 \times 10^{-11} \text{ m}^2/\text{s}) - \ln (2.3 \times 10^{-5} \text{ m}^2/\text{s})]}$$

$$= 1353 \text{ K} = 1080^\circ\text{C}$$

5.27 (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?

Solution

(a) We are asked to calculate the diffusion coefficient for Cu in Al at 500°C. Using the data in Table 5.2 and Equation 5.8

$$\begin{aligned} D &= D_0 \exp\left(-\frac{Q_d}{RT}\right) \\ &= (6.5 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{136,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(500 + 273 \text{ K})}\right] \\ &= 4.15 \times 10^{-14} \text{ m}^2/\text{s} \end{aligned}$$

(b) This portion of the problem calls for the time required at 600°C to produce the same diffusion result as for 10 h at 500°C. Equation 5.7 is employed as

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

Now, from Equation 5.8 the value of the diffusion coefficient at 600°C is calculated as

$$\begin{aligned} D_{600} &= (6.5 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{136,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(600 + 273 \text{ K})}\right] \\ &= 4.69 \times 10^{-13} \text{ m}^2/\text{s} \end{aligned}$$

Thus,

$$\begin{aligned} t_{600} &= \frac{D_{500}t_{500}}{D_{600}} \\ &= \frac{(4.15 \times 10^{-14} \text{ m}^2/\text{s})(10 \text{ h})}{(4.69 \times 10^{-13} \text{ m}^2/\text{s})} = 0.88 \text{ h} \end{aligned}$$

5.28 A copper-nickel diffusion couple similar to that shown in Figure 5.1a 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 5.2.

Solution

In order to determine the temperature to which the diffusion couple must be heated so as to produce a concentration of 2.5 wt% Ni at the 2.0-mm position, we must first utilize Equation 5.6b with time  $t$  being a constant. That is

$$\frac{x^2}{D} = \text{constant}$$

Or

$$\frac{x_{I100}^2}{D_{1100}} = \frac{x_T^2}{D_T}$$

Now, solving for  $D_T$  from this equation, yields

$$D_T = \frac{x_T^2 D_{1100}}{x_{I100}^2}$$

and incorporating the temperature dependence of  $D_{1100}$  utilizing Equation (5.8), realizing that for the diffusion of Cu in Ni (Table 5.2)

$$D_0 = 2.7 \times 10^{-5} \text{ m}^2/\text{s}$$

$$Q_d = 256,000 \text{ J/mol}$$

then

$$D_T = \frac{(x_T^2) \left[ D_0 \exp\left(-\frac{Q_d}{RT}\right) \right]}{x_{I100}^2}$$

$$= \frac{(2 \text{ mm})^2 \left[ (2.7 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left(-\frac{256,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1373 \text{ K})}\right) \right]}{(3 \text{ mm})^2}$$



$$= 2.16 \times 10^{-15} \text{ m}^2/\text{s}$$

We now need to find the T at which D has this value. This is accomplished by rearranging Equation 5.9a and solving for T as

$$\begin{aligned} T &= \frac{Q_d}{R (\ln D_0 - \ln D)} \\ &= \frac{256,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K}) [\ln (2.7 \times 10^{-5} \text{ m}^2/\text{s}) - \ln (2.16 \times 10^{-15} \text{ m}^2/\text{s})]} \\ &= 1325 \text{ K} = 1052^\circ\text{C} \end{aligned}$$

5.29 A diffusion couple similar to that shown in Figure 5.1a 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  $1.8 \times 10^{-5} \text{ m}^2/\text{s}$  and 152,000 J/mol, respectively.

### Solution

In order to determine the position within the diffusion couple at which the concentration of A in B is 3.2 wt%, we must employ Equation 5.6b with  $t$  constant. That is

$$\frac{x^2}{D} = \text{constant}$$

Or

$$\frac{x_{800}^2}{D_{800}} = \frac{x_{1000}^2}{D_{1000}}$$

It is first necessary to compute values for both  $D_{800}$  and  $D_{1000}$

$$D_{800} = (1.8 \times 10^{-5} \text{ m}^2/\text{s}) \exp \left[ -\frac{152,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(800 \text{ K})} \right]$$

$$= 2.12 \times 10^{-15} \text{ m}^2/\text{s}$$

$$D_{1000} = (1.8 \times 10^{-5} \text{ m}^2/\text{s}) \exp \left[ -\frac{152,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1000 \text{ K})} \right]$$

$$= 2.05 \times 10^{-13} \text{ m}^2/\text{s}$$

Now, solving the above expression for  $x_{800}$  yields

$$x_{800} = x_{1000} \sqrt{\frac{D_{800}}{D_{1000}}}$$

$$= (15.5 \text{ mm}) \sqrt{\frac{2.12 \times 10^{-15} \text{ m}^2/\text{s}}{2.05 \times 10^{-13} \text{ m}^2/\text{s}}}$$

$$= 1.6 \text{ mm}$$

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 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 5.2 for C diffusion in  $\alpha$ -Fe.

### Solution

In order to compute the diffusion time at 650°C to produce a carbon concentration of 0.90 wt% at a position 1.0 mm below the surface we must employ Equation 5.6b with position (x) constant; that is

$$Dt = \text{constant}$$

Or

$$D_{850}t_{850} = D_{650}t_{650}$$

In addition, it is necessary to compute values for both  $D_{850}$  and  $D_{650}$  using Equation 5.8. From Table 5.2, for the diffusion of C in  $\alpha$ -Fe,  $Q_d = 80,000$  J/mol and  $D_0 = 6.2 \times 10^{-7}$  m<sup>2</sup>/s. Therefore,

$$D_{850} = (6.2 \times 10^{-7} \text{ m}^2/\text{s}) \exp \left[ -\frac{80,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(850 + 273 \text{ K})} \right]$$

$$= 1.17 \times 10^{-10} \text{ m}^2/\text{s}$$

$$D_{650} = (6.2 \times 10^{-7} \text{ m}^2/\text{s}) \exp \left[ -\frac{80,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(650 + 273 \text{ K})} \right]$$

$$= 1.83 \times 10^{-11} \text{ m}^2/\text{s}$$

Now, solving the original equation for  $t_{650}$  gives

$$t_{650} = \frac{D_{850}t_{850}}{D_{650}}$$

$$= \frac{(1.17 \times 10^{-10} \text{ m}^2/\text{s})(10 \text{ min})}{1.83 \times 10^{-11} \text{ m}^2/\text{s}}$$

$$= 63.9 \text{ min}$$

5.31 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.

Solution

This problem asks us to compute the temperature at which a nonsteady-state 49.5 h diffusion anneal was carried out in order to give a carbon concentration of 0.35 wt% C in FCC Fe at a position 4.0 mm below the surface. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.35 - 0.20}{1.0 - 0.20} = 0.1875 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Or

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.8125$$

Now it becomes necessary, using the data in Table 5.1 and linear interpolation, to determine the value of  $\frac{x}{2\sqrt{Dt}}$ .

Thus

$z$	<u><math>\operatorname{erf}(z)</math></u>
0.90	0.7970
$y$	0.8125
0.95	0.8209

$$\frac{y - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$$

From which

$$y = 0.9324$$

Thus,

$$\frac{x}{2\sqrt{Dt}} = 0.9324$$

And since  $t = 49.5 \text{ h}$  ( $178,200 \text{ s}$ ) and  $x = 4.0 \text{ mm}$  ( $4.0 \times 10^{-3} \text{ m}$ ), solving for  $D$  from the above equation yields

$$D = \frac{x^2}{(4t)(0.9324)^2}$$

$$= \frac{(4.0 \times 10^{-3} \text{ m})^2}{(4)(178,200 \text{ s})(0.9324)^2} = 2.58 \times 10^{-11} \text{ m}^2/\text{s}$$

Now, in order to determine the temperature at which  $D = 2.58 \times 10^{-11} \text{ m}^2/\text{s}$ , this equation for  $T$  yields

$$T = \frac{Q_d}{R (\ln D_0 - \ln D)}$$

From Table 5.2,  $D_0$  and  $Q_d$  for the diffusion of C in FCC Fe are  $2.3 \times 10^{-5} \text{ m}^2/\text{s}$  and  $148,000 \text{ J/mol}$ , respectively. Therefore

$$T = \frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K}) [\ln (2.3 \times 10^{-5} \text{ m}^2/\text{s}) - \ln (2.58 \times 10^{-11} \text{ m}^2/\text{s})]}$$

$$= 1300 \text{ K} = 1027^\circ\text{C}$$

## Diffusion in Semiconducting Materials

5.32 Phosphorus atoms are to be diffused into a silicon wafer using both predeposition and drive-in heat treatment. The predeposition treatment is carried out at 950°C for a period of 2.5 h. The surface concentration of P is maintained at a constant level of  $1.5 \times 10^{26}$  atoms/m<sup>3</sup>. Drive-in diffusion will be carried out at 1200°C for a period of 2.5 h. For the diffusion of P in Si, values of  $Q_d$  and  $D_0$  are 3.40 eV and  $1.1 \times 10^{-4}$  m<sup>2</sup>/s, respectively.

- (a) Calculate the value of  $Q_0$ .
- (b) Determine the value of  $x_j$  for the drive-in diffusion treatment.
- (c) Also for the drive-in treatment, compute the position  $x$  at which the concentration of P atoms is  $10^{24}$  m<sup>-3</sup>.

### Solution

(a) For this portion of the problem we are asked to determine the value of  $Q_0$ . This is possible using Equation 5.12. However, it is first necessary to determine the value of  $D$  for the predeposition treatment [ $D_p$  at  $T_p = 950^\circ\text{C}$  (1223 K)] using Equation 5.8. Thus

$$\begin{aligned} D_p &= D_0 \exp\left(-\frac{Q_d}{kT_p}\right) \\ &= (1.1 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{3.40 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1223 \text{ K})}\right] \\ &= 1.08 \times 10^{-18} \text{ m}^2/\text{s} \end{aligned}$$

The value of  $Q_0$  may be determined as follows:

$$\begin{aligned} Q_0 &= 2C_s \sqrt{\frac{D_p t_p}{\pi}} \\ &= (2)(1.5 \times 10^{26} \text{ atoms/m}^3) \sqrt{\frac{(1.08 \times 10^{-18} \text{ m}^2/\text{s})(45 \text{ min})(60 \text{ s/min})}{\pi}} \\ &= 9.14 \times 10^{18} \text{ atoms/m}^2 \end{aligned}$$



(b) Computation of the junction depth requires that we use Equation 5.13. However, before this is possible it is necessary to calculate  $D$  at the temperature of the drive-in treatment [ $D_d$  at  $1200^\circ\text{C}$  ( $1473\text{ K}$ )]. Thus,

$$D_d = (1.1 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{3.40 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1473 \text{ K})}\right]$$

$$= 2.58 \times 10^{-16} \text{ m}^2/\text{s}$$

Now from Equation 5.13

$$x_j = \left[ (4D_d t_d) \ln\left(\frac{Q_0}{C_B \sqrt{\pi D_d t_d}}\right) \right]^{1/2}$$

$$= \left\{ (4)(2.58 \times 10^{-16} \text{ m}^2/\text{s})(9000 \text{ s}) \ln\left[\frac{9.14 \times 10^{18} \text{ atoms/m}^2}{(5 \times 10^{19} \text{ atoms/m}^3)\sqrt{(\pi)(2.58 \times 10^{-16} \text{ m}^2/\text{s})(9000 \text{ s})}}\right] \right\}^{1/2}$$

$$= 1.21 \times 10^{-5} \text{ m} = 12.1 \text{ }\mu\text{m}$$

(c) For a concentration of  $10^{24}$  P atoms/ $\text{m}^3$  for the drive-in treatment, we compute the value of  $x$  using Equation 5.11. However, it is first necessary to manipulate Equation 5.11 so that  $x$  is the dependent variable. Taking natural logarithms of both sides leads to

$$\ln C(x, t) = \ln\left(\frac{Q_0}{\sqrt{\pi D_d t_d}}\right) - \frac{x^2}{4D_d t_d}$$

Now, rearranging and solving for  $x$  leads to

$$x = \left\{ (4D_d t_d) \ln\left[\frac{Q_0}{C(x, t)\sqrt{\pi D_d t_d}}\right] \right\}^{1/2}$$

Now, incorporating values for  $Q_0$  and  $D_d$  determined above and taking  $C(x, t) = 10^{24}$  P atoms/ $\text{m}^3$  yields

$$\begin{aligned}
 x &= \left\{ (4)(2.58 \times 10^{-16})(9000) \ln \left[ \frac{9.14 \times 10^{18}}{(10^{24}) \sqrt{(\pi)(2.58 \times 10^{-16})(9000)}} \right] \right\}^{1/2} \\
 &= 3.36 \times 10^{-6} \text{ m} = 3.36 \text{ } \mu\text{m}
 \end{aligned}$$

5.33 Aluminum atoms are to be diffused into a silicon wafer using both predeposition and drive-in heat treatments; the background concentration of Al in this silicon material is known to be  $3 \times 10^{19}$  atoms/m<sup>3</sup>. The drive-in diffusion treatment is to be carried out at 1050°C for a period of 4.0 h, which gives a junction depth  $x_j$  of 3.0  $\mu\text{m}$ . Compute the predeposition diffusion time at 950°C if the surface concentration is maintained at a constant level of  $2 \times 10^{25}$  atoms/m<sup>3</sup>. For the diffusion of Al in Si, values of  $Q_d$  and  $D_0$  are 3.41 eV and  $1.38 \times 10^{-4}$  m<sup>2</sup>/s, respectively.

### Solution

This problem asks that we compute the time for the predeposition heat treatment for the diffusion of Al in Si. In order to do this it is necessary to determine the value of  $Q_0$  from Equation 5.13. However, before doing this we must first calculate  $D_d$ , using Equation 5.8. Therefore

$$\begin{aligned} D_d &= D_0 \exp\left(-\frac{Q_d}{kT_d}\right) \\ &= (1.38 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{3.41 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1050^\circ\text{C} + 273 \text{ K})}\right] \\ &= 1.43 \times 10^{-17} \text{ m}^2/\text{s} \end{aligned}$$

Now, solving for  $Q_0$  in Equation 5.13 leads to

$$Q_0 = (C_B \sqrt{\pi D_d t_d}) \exp\left(\frac{x_j^2}{4 D_d t_d}\right)$$

In the problem statement we are given the following values:

$$C_B = 3 \times 10^{19} \text{ atoms/m}^3$$

$$t_d = 4 \text{ h (14,400 s)}$$

$$x_j = 3.0 \mu\text{m} = 3.0 \times 10^{-6} \text{ m}$$

Therefore, incorporating these values into the above equation yields

$$Q_0 = \left[ (3 \times 10^{19} \text{ atoms/m}^3) \sqrt{(\pi)(1.43 \times 10^{-17} \text{ m}^2/\text{s})(14,400 \text{ s})} \right] \exp\left[\frac{(3.0 \times 10^{-6} \text{ m})^2}{(4)(1.43 \times 10^{-17} \text{ m}^2/\text{s})(14,400 \text{ s})}\right]$$

$$= 1.34 \times 10^{18} \text{ atoms/m}^2$$

We may now compute the value of  $t_p$  using Equation 5.12. However, before this is possible it is necessary to determine  $D_p$  (at 950°C) using Equation 5.8. Thus

$$D_p = (1.38 \times 10^{-4} \text{ m}^2/\text{s}) \exp \left[ -\frac{3.41 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(950^\circ\text{C} + 273 \text{ K})} \right]$$

$$= 1.24 \times 10^{-18} \text{ m}^2/\text{s}$$

Now, solving for  $t_p$  in Equation 5.12 we get

$$t_p = \frac{\pi Q_0^2}{4C_s^2 D_p}$$

And incorporating the value of  $C_s$  provided in the problem statement ( $2 \times 10^{25} \text{ atoms/m}^3$ ) as well as values for  $Q_0$  and  $D_p$  determined above, leads to

$$t_p = \frac{\pi (1.34 \times 10^{18} \text{ atoms/m}^2)^2}{(4)(2 \times 10^{25} \text{ atoms/m}^3)^2 (1.24 \times 10^{-18} \text{ m}^2/\text{s})}$$

$$= 2.84 \times 10^3 \text{ s} = 47.4 \text{ min}$$

## DESIGN PROBLEMS

### **Steady-State 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 0.0709 MPa (0.7 atm) and 0.02026 MPa (0.2 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:

$$C_H = 2.5 \times 10^3 \sqrt{p_{H_2}} \exp\left(-\frac{27.8 \text{ kJ/mol}}{RT}\right) \quad (5.16a)$$

$$C_N = 2.75 \times 10^{-3} \sqrt{p_{N_2}} \exp\left(-\frac{37.6 \text{ kJ/mol}}{RT}\right) \quad (5.16b)$$

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

$$D_H (\text{m}^2/\text{s}) = 1.4 \times 10^{-7} \exp\left(-\frac{13.4 \text{ kJ/mol}}{RT}\right) \quad (5.17a)$$

$$D_N (\text{m}^2/\text{s}) = 3.0 \times 10^{-7} \exp\left(-\frac{76.15 \text{ kJ/mol}}{RT}\right) \quad (5.17b)$$

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.

### Solution

This problem calls for us to ascertain whether or not a hydrogen-nitrogen gas mixture may be enriched with respect to hydrogen partial pressure by allowing the gases to diffuse through a metal sheet at an elevated temperature. If this is possible, the temperature and sheet thickness are to be specified; if such is not possible, then we are to state the reasons why. Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.3. Inasmuch as the partial pressures on the high-pressure side of the sheet are the same, and the pressure of hydrogen on the low pressure side is 3.5 times that of nitrogen, and concentrations are proportional to the square

root of the partial pressure, the diffusion flux of hydrogen  $J_H$  is the square root of 3.5 times the diffusion flux of nitrogen  $J_N$ --i.e.

$$J_H = \sqrt{3.5} J_N$$

Thus, equating the Fick's law expressions incorporating the given equations for the diffusion coefficients and concentrations in terms of partial pressures leads to the following

$$\begin{aligned} J_H &= \frac{1}{\Delta x} \times \\ & (2.5 \times 10^3) \left( \sqrt{0.1013 \text{ MPa}} - \sqrt{0.0709 \text{ MPa}} \right) \exp\left(-\frac{27.8 \text{ kJ}}{RT}\right) (1.4 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left(-\frac{13.4 \text{ kJ}}{RT}\right) \\ &= \sqrt{3.5} J_N \\ &= \frac{\sqrt{3.5}}{\Delta x} \times \\ & (2.75 \times 10^3) \left( \sqrt{0.1013 \text{ MPa}} - \sqrt{0.02026 \text{ MPa}} \right) \exp\left(-\frac{37.6 \text{ kJ}}{RT}\right) (3.0 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left(-\frac{76.15 \text{ kJ}}{RT}\right) \end{aligned}$$

The  $\Delta x$ 's cancel out, which means that the process is independent of sheet thickness. Now solving the above expression for the absolute temperature  $T$  gives

$$T = 3237 \text{ K}$$

which value is extremely high (surely above the melting point of the metal). Thus, such a diffusion process is not possible.

5.D2 A gas mixture is found to contain two diatomic A and B species for which the partial pressures of both are 0.05065 MPa (0.5 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 0.02026 MPa (0.2 atm) for gas A, and 0.01013 MPa (0.1 atm) for gas B. The concentrations of A and B ( $C_A$  and  $C_B$ , in mol/m<sup>3</sup>) are functions of gas partial pressures ( $p_{A_2}$  and  $p_{B_2}$ , in MPa) and absolute temperature according to the following expressions:

$$C_A = 200 \sqrt{p_{A_2}} \exp \left( -\frac{25.0 \text{ kJ/mol}}{RT} \right) \quad (5.18a)$$

$$C_B = 1.0 \times 10^{-3} \sqrt{p_{B_2}} \exp \left( -\frac{30.0 \text{ kJ/mol}}{RT} \right) \quad (5.18b)$$

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

$$D_A (\text{m}^2/\text{s}) = 4.0 \times 10^{-7} \exp \left( -\frac{15.0 \text{ kJ/mol}}{RT} \right) \quad (5.19a)$$

$$D_B (\text{m}^2/\text{s}) = 2.5 \times 10^{-6} \exp \left( -\frac{24.0 \text{ kJ/mol}}{RT} \right) \quad (5.19b)$$

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.

### Solution

This problem calls for us to ascertain whether or not an A<sub>2</sub>-B<sub>2</sub> gas mixture may be enriched with respect to the A partial pressure by allowing the gases to diffuse through a metal sheet at an elevated temperature. If this is possible, the temperature and sheet thickness are to be specified; if such is not possible, then we are to state the reasons why. Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.3. Inasmuch as the partial pressures on the high-pressure side of the sheet are the same, and the pressure of A<sub>2</sub> on the low pressure side is 2.0 times that of B<sub>2</sub>, and concentrations are proportional to the square root of the partial pressure, the diffusion flux of A,  $J_A$ , is the square root of 2.0 times the diffusion flux of nitrogen  $J_B$ --i.e.

$$J_A = \sqrt{2.0} J_B$$

Thus, equating the Fick's law expressions incorporating the given equations for the diffusion coefficients and concentrations in terms of partial pressures leads to the following

$$\begin{aligned}
& J_A \\
&= \frac{1}{\Delta x} \times \\
& (200) \left( \sqrt{0.05065 \text{ MPa}} - \sqrt{0.02026 \text{ MPa}} \right) \exp\left(-\frac{25.0 \text{ kJ}}{RT}\right) (4.0 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left(-\frac{15.0 \text{ kJ}}{RT}\right) \\
&= \sqrt{2.0} J_B \\
&= \frac{\sqrt{2.0}}{\Delta x} \times \\
& (1.0 \times 10^3) \left( \sqrt{0.05065 \text{ MPa}} - \sqrt{0.01013 \text{ MPa}} \right) \exp\left(-\frac{30.0 \text{ kJ}}{RT}\right) (2.5 \times 10^{-6} \text{ m}^2/\text{s}) \exp\left(-\frac{24.0 \text{ kJ}}{RT}\right)
\end{aligned}$$

The  $\Delta x$ 's cancel out, which means that the process is independent of sheet thickness. Now solving the above expression for the absolute temperature T gives

$$T = 401 \text{ K (128}^\circ\text{C)}$$

Thus, it is possible to carry out this procedure at 401 K or 128°C.



## Nonsteady-State Diffusion

5.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%. 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  $3 \times 10^{-7} \text{ m}^2/\text{s}$  and 76,150 J/mol, respectively, over this temperature range.

### Solution

This is a nonsteady-state diffusion problem. The following values for the concentration parameters:

$$C_0 = 0.002 \text{ wt\% N}$$

$$C_s = 0.50 \text{ wt\% N}$$

$$C_x = 0.10 \text{ wt\% N}$$

Therefore

$$\begin{aligned} \frac{C_x - C_0}{C_s - C_0} &= \frac{0.10 - 0.002}{0.50 - 0.002} \\ &= 0.1968 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \end{aligned}$$

And thus

$$1 - 0.1968 = 0.8032 = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Using linear interpolation and the data presented in Table 5.1

$z$	$\text{erf}(z)$
0.9000	0.7970
$y$	0.8032
0.9500	0.8209

$$\frac{0.8032 - 0.7970}{0.8209 - 0.7970} = \frac{y - 0.9000}{0.9500 - 0.9000}$$

From which

$$y = \frac{x}{2\sqrt{Dt}} = 0.9130$$

The problem stipulates that  $x = 0.40 \text{ mm} = 4.0 \times 10^{-4} \text{ m}$ . Therefore

$$\frac{4.0 \times 10^{-4} \text{ m}}{2\sqrt{Dt}} = 0.9130$$

Which leads to

$$Dt = 4.80 \times 10^{-8} \text{ m}^2$$

Furthermore, the diffusion coefficient  $D_0$  is given in the problem statement,  $D_0 = 3 \times 10^{-7} \text{ m}^2/\text{s}$  and  $Q_d = 76,150 \text{ J/mol}$ . Hence

$$Dt = D_0 \exp\left(-\frac{Q_d}{RT}\right)(t) = 4.80 \times 10^{-8} \text{ m}^2$$

$$(3.0 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left[-\frac{76,150 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(T)}\right](t) = 4.80 \times 10^{-8} \text{ m}^2$$

And solving for the time  $t$

$$t \text{ (in s)} = \frac{0.160}{\exp\left(-\frac{9163.7}{T}\right)}$$

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

Temperature (°C)	Time	
	s	h
500	22,500	6.3
550	11,000	3.1
600	5800	1.6

## Diffusion in Semiconducting Materials

5.D4 One integrated circuit design calls for the diffusion of arsenic into silicon wafers; the background concentration of As in Si is  $2.5 \times 10^{20}$  atoms/m<sup>3</sup>. The predeposition heat treatment is to be conducted at 1000°C for 45 minutes, with a constant surface concentration of  $8 \times 10^{26}$  As atoms/m<sup>3</sup>. At a drive-in treatment temperature of 1100°C, determine the diffusion time required for a junction depth of 1.2 μm. For this system, values of  $Q_d$  and  $D_0$  are 4.10 eV and  $2.29 \times 10^{-3}$  m<sup>2</sup>/s, respectively.

### Solution

This problem asks that we compute the drive-in diffusion time for arsenic diffusion in silicon. It is first necessary to determine the value of  $Q_0$  using Equation 5.12. But before this is possible, the value of  $D_p$  at 1000°C must be computed with the aid of Equation 5.8. Thus,

$$\begin{aligned} D_p &= D_0 \exp\left(-\frac{Q_d}{kT_p}\right) \\ &= (2.29 \times 10^{-3} \text{ m}^2/\text{s}) \exp\left[-\frac{4.10 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1000^\circ\text{C} + 273 \text{ K})}\right] \\ &= 1.36 \times 10^{-19} \text{ m}^2/\text{s} \end{aligned}$$

Now for the computation of  $Q_0$  using Equation 5.12:

$$\begin{aligned} Q_0 &= 2C_s \sqrt{\frac{D_p t_p}{\pi}} \\ &= (2)(8 \times 10^{26} \text{ atoms/m}^3) \sqrt{\frac{(1.36 \times 10^{-19} \text{ m}^2/\text{s})(45 \text{ min})(60 \text{ s/min})}{\pi}} \\ &= 1.73 \times 10^{19} \text{ atoms/m}^2 \end{aligned}$$

We now desire to calculate  $t_d$  in Equation 5.13. Algebraic manipulation and rearrangement of this expression leads to

$$\exp\left(\frac{x_j^2}{4D_d t_d}\right) = \frac{Q_0}{C_B \sqrt{\pi D_d t_d}}$$

At this point it is necessary to determine the value of  $D_d$  (at 1100°C). Thus

$$\begin{aligned} D_d &= (2.29 \times 10^{-3} \text{ m}^2/\text{s}) \exp\left[-\frac{4.10 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1100^\circ\text{C} + 273 \text{ K})}\right] \\ &= 2.06 \times 10^{-18} \text{ m}^2/\text{s} \end{aligned}$$

And incorporation of values of all parameters except  $t_d$  in the above expression yields

$$\exp\left[\frac{(1.2 \times 10^{-6} \text{ m})^2}{(4)(2.06 \times 10^{-18} \text{ m}^2/\text{s})t_d}\right] = \frac{1.73 \times 10^{19} \text{ atoms/m}^2}{(2.5 \times 10^{20} \text{ atoms/m}^3)\sqrt{(\pi)(2.06 \times 10^{-18} \text{ m}^2/\text{s})t_d}}$$

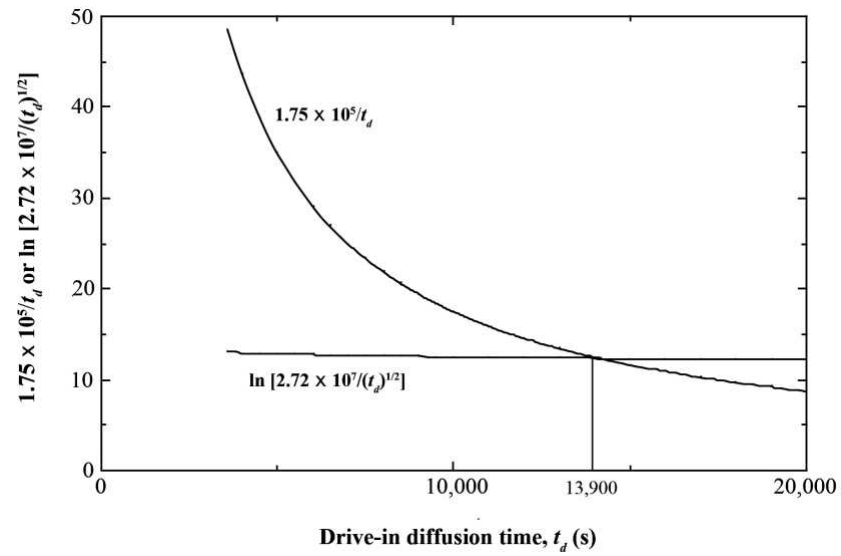
which expression reduces to

$$\exp\left(\frac{1.75 \times 10^5 \text{ s}}{t_d}\right) = \frac{2.72 \times 10^7 \text{ s}^{1/2}}{\sqrt{t_d}}$$

Solving for  $t_d$  is not a simple matter. One possibility is to use a graphing technique. Let us take the logarithm of both sides of the above equation, which gives

$$\frac{1.75 \times 10^5 \text{ s}}{t_d} = \ln\left(\frac{2.72 \times 10^7 \text{ s}^{1/2}}{\sqrt{t_d}}\right)$$

Now if we plot the terms on both left and right hand sides of this equation versus  $t_d$ , the value of  $t_d$  at the point of intersection of the two resulting curves is correct answer. Below is such a plot:



As noted, the two curves intersect at about 13,900 s, which corresponds to  $t_d = 3.86$  h.