4.3 *Calculate the activation energy for vacancy formation in aluminum, given that the equilibrium number of vacancies at 500°C (773 K) is 7.57 × 10²³ m⁻³. The atomic weight and density (at 500°C) for aluminum are, respectively, 26.98 g/mol and 2.62 g/cm³.*

<u>Solution</u>

Upon examination of Equation 4.1, all parameters besides Q_v are given except N, the total number of atomic sites. However, N is related to the density, (ρ_{Al}), Avogadro's number (N_A), and the atomic weight (A_{Al}) according to Equation 4.2 as

$$N = \frac{N_A \rho_{Al}}{A_{Al}}$$

$$= \frac{(6.022 \times 10^{23} \ \text{atoms/mol})(2.62 \ \text{g/cm}^3)}{26.98 \ \text{g/mol}}$$

$$= 5.85 \times 10^{22} \ \text{atoms/cm}^3 = 5.85 \times 10^{28} \ \text{atoms/m}^3$$

Now, taking natural logarithms of both sides of Equation 4.1,

$$\ln N_v = \ln N - \frac{Q_v}{kT}$$

and, after some algebraic manipulation

$$Q_v = -kT \ln\left(\frac{N_v}{N}\right)$$

$$= -\left(8.62 \times 10^{-5} \ \text{eV/atom-K}\right)(500°\text{C} + 273 \ \text{K}) \ \ln\left[\frac{7.57 \times 10^{23} \ \text{m}^{-3}}{5.85 \times 10^{28} \ \text{m}^{-3}}\right]$$

$$= 0.75 \ \text{eV/atom}$$

4.7 *What is the composition, in atom percent, of an alloy that consists of 30 wt% Zn and 70 wt% Cu?*

In order to compute composition, in atom percent, of a 30 wt% Zn-70 wt% Cu alloy, we employ Equation 4.6 as

$$C'_{Zn} = \frac{C_{Zn}A_{Cu}}{C_{Zn}A_{Cu} + C_{Cu}A_{Zn}} \times 100$$

$$= \frac{(30)(63.55 \text{ g}/\text{mol})}{(30)(63.55 \text{ g}/\text{mol}) + (70)(65.41 \text{ g}/\text{mol})} \times 100$$

$$= 29.4 \text{ at\%}$$

$$C'_{Cu} = \frac{C_{Cu}A_{Zn}}{C_{Zn}A_{Cu} + C_{Cu}A_{Zn}} \times 100$$

$$= \frac{(70)(65.41 \text{ g}/\text{mol})}{(30)(63.55 \text{ g}/\text{mol}) + (70)(65.41 \text{ g}/\text{mol})} \times 100$$

$$= 70.6 \text{ at\%}$$

4.16 *Determine the approximate density of a high-leaded brass that has a composition of 64.5 wt% Cu, 33.5 wt% Zn, and 2.0 wt% Pb.*

Solution

In order to solve this problem, Equation 4.10a is modified to take the following form:

$$\rho_{ave} = \frac{100}{\dfrac{C_{Cu}}{\rho_{Cu}} + \dfrac{C_{Zn}}{\rho_{Zn}} + \dfrac{C_{Pb}}{\rho_{Pb}}}$$

And, using the density values for Cu, Zn, and Pb—i.e., 8.94 g/cm³, 7.13 g/cm³, and 11.35 g/cm³—(as taken from inside the front cover of the text), the density is computed as follows:

$$\rho_{ave} = \frac{100}{\dfrac{64.5 \text{ wt\%}}{8.94 \text{ g}/\text{cm}^3} + \dfrac{33.5 \text{ wt\%}}{7.13 \text{ g}/\text{cm}^3} + \dfrac{2.0 \text{ wt\%}}{11.35 \text{ g}/\text{cm}^3}}$$

$$= 8.27 \text{ g/cm}^3$$

4.19 *For a solid solution consisting of two elements (designated as 1 and 2), sometimes it is desirable to determine the number of atoms per cubic centimeter of one element in a solid solution, N_1, given the concentration of that element specified in weight percent, C_1. This computation is possible using the following expression:*

$$N_1 = \frac{N_A C_1}{\dfrac{C_1 A_1}{\rho_1} + \dfrac{A_1}{\rho_2}(100 - C_1)} \qquad (4.18)$$

where

      N_A *= Avogadro's number*

      ρ_1 *and ρ_2 = densities of the two elements*

      A_1 *= the atomic weight of element 1*

Derive Equation 4.18 using Equation 4.2 and expressions contained in Section 4.4.

      <u>Solution</u>

This problem asks that we derive Equation 4.18, using other equations given in the chapter. The concentration of component 1 in atom percent (C_1') is just $100\, c_1'$ where c_1' is the atom fraction of component 1. Furthermore, c_1' is defined as $c_1' = N_1/N$ where N_1 and N are, respectively, the number of atoms of component 1 and total number of atoms per cubic centimeter. Thus, from the above discussion the following holds:

$$N_1 = \frac{C_1'\, N}{100}$$

Substitution into this expression of the appropriate form of N from Equation 4.2 yields

$$N_1 = \frac{C_1'\, N_A\, \rho_{ave}}{100\, A_{ave}}$$

And, finally, substitution into this equation expressions for C_1' (Equation 4.6a), ρ_{ave} (Equation 4.10a), A_{ave} (Equation 4.11a), and realizing that $C_2 = (C_1 - 100)$, and after some algebraic manipulation we obtain the desired expression:
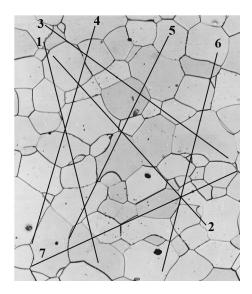
$$N_1 = \frac{N_A C_1}{\dfrac{C_1 A_1}{\rho_1} + \dfrac{A_1}{\rho_2}(100 - C_1)}$$

4.32 *(a) Using the intercept method, determine the average grain size, in millimeters, of the specimen whose microstructure is shown in Figure 4.14(b); use at least seven straight-line segments.*

(b) Estimate the ASTM grain size number for this material.

Solution

(a) Below is shown the photomicrograph of Figure 4.14(*b*), on which seven straight line segments, each of which is 60 mm long has been constructed; these lines are labeled "1" through "7".

In order to determine the average grain diameter, it is necessary to count the number of grains intersected by each of these line segments. These data are tabulated below.

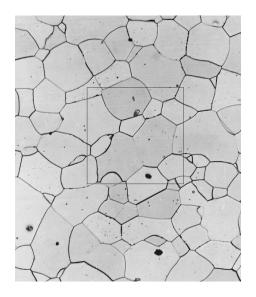| Line Number	No. Grains Intersected
1	11
2	10
3	9
4	8.5
5	7
6	10
7	8

The average number of grain boundary intersections for these lines was 9.1. Therefore, the average line length intersected is just

$$\frac{60 \text{ mm}}{9.1} = 6.59 \text{ mm}$$

Hence, the average grain diameter, d, is

$$d = \frac{\text{ave. line length intersected}}{\text{magnification}} = \frac{6.59 \text{ mm}}{100} = 6.59 \times 10^{-2} \text{ mm}$$

(b) This portion of the problem calls for us to estimate the ASTM grain size number for this same material. The average grain size number, n, is related to the number of grains per square inch, N, at a magnification of 100× according to Equation 4.16. Inasmuch as the magnification is 100×, the value of N is measured directly from the micrograph. The photomicrograph on which has been constructed a square 1 in. on a side is shown below.

The total number of complete grains within this square is approximately 10 (taking into account grain fractions). Now, in order to solve for n in Equation 4.16, it is first necessary to take logarithms as

$$\log N = (n - 1) \log 2$$

From which n equals

$$n = \frac{\log N}{\log 2} + 1$$

$$= \frac{\log 10}{\log 2} + 1 = 4.3$$

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

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 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

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

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

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 γ-Fe in Table 5.2.*

Solution

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

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

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

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

or

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

By linear interpolation using data from Table 5.1

z	$\mathrm{erf}(z)$
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)

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

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

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

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

5.14 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:

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

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 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 mm position into the 2 wt% Au side of the diffusion couple. Preexponential and activation energy values for Au diffusion in Ag are 8.5×10^{-5} m²/s and 202,100 J/mol, respectively.**

Solution

For this platinum-gold diffusion couple for which C_1 = 5 wt% Au and C_2 = 2 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

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

It now becomes necessary to compute the diffusion coefficient at 750°C (1023 K) given that $D_0 = 8.5 \times 10^{-5}$ m²/s and Q_d = 202,100 J/mol. From Equation 5.8 we have

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

$$= (8.5 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{202{,}100 \text{ J/mol}}{(8.31 \text{ J/mol}-\text{K})(1023 \text{ K})}\right]$$

$$= 4.03 \times 10^{-15} \text{ m}^2/\text{s}$$

Substitution of this value into the above equation leads to

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

This expression reduces to the following form:

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

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	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

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

And, solving for t gives

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

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

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

(a) Determine the values of D_0 and the activation energy Q_d.

(b) What is the magnitude of D at 1100°C (1373 K)?

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 (9.4×10^{-16} and 2.4×10^{-14} m²/s), we get

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

$$= -(8.31 \text{ J/mol-K})\frac{\left[\ln\left(9.4 \times 10^{-16}\right) - \ln\left(2.4 \times 10^{-14}\right)\right]}{\frac{1}{1273 \text{ K}} - \frac{1}{1473 \text{ K}}}$$

$$= 252{,}400 \text{ J/mol}$$

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

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

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

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

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

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

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