

4.2 Determination of the number of vacancies per cubic meter in gold at 900°C (1173 K) requires the utilization of Equations 4.1 and 4.2 as follows:

$$\begin{aligned}
 N_v &= N \exp\left(-\frac{Q_v}{kT}\right) = \frac{N_A \rho_{\text{Au}}}{A_{\text{Au}}} \exp\left(-\frac{Q_v}{kT}\right) \\
 &= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(18.63 \text{ g/cm}^3)}{196.9 \text{ g/mol}} \exp\left[-\frac{0.98 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1173 \text{ K})}\right] \\
 &= 3.52 \times 10^{18} \text{ cm}^{-3} = 3.52 \times 10^{24} \text{ m}^{-3}
 \end{aligned}$$

### Impurities in Solids

4.4 In this problem we are asked to cite which of the elements listed form with Ni the three possible solid solution types. For complete substitutional solubility the following criteria must be met: 1) the difference in atomic radii between Ni and the other element ( $\Delta R\%$ ) must be less than  $\pm 15\%$ , 2) the crystal structures must be the same, 3) the electronegativities must be similar, and 4) the valences should be the same, or nearly the same. Below are tabulated, for the various elements, these criteria.

<u>Element</u>	<u><math>\Delta R\%</math></u>	<u>Crystal Structure</u>	<u><math>\Delta</math>Electro-negativity</u>	<u>Valence</u>
<b>Ni</b>		<b>FCC</b>		<b>2+</b>
C	-43			
H	-63			
O	-52			
Ag	+16	FCC	+0.1	1+
Al	+15	FCC	-0.3	3+
Co	+0.6	HCP	0	2+
Cr	+0.2	BCC	-0.2	3+
Fe	-0.4	BCC	0	2+
Pt	+11	FCC	+0.4	2+
Zn	+7	HCP	-0.2	2+

(a) Pt is the only element that meets all of the criteria and thus forms a substitutional solid solution having complete solubility. At elevated temperatures Co and Fe experience allotropic transformations to the FCC crystal structure, and thus display complete solid solubility at these temperatures.

(b) Ag, Al, Co, Cr, Fe, and Zn form substitutional solid solutions of incomplete solubility. All these metals have either BCC or HCP crystal structures, and/or the difference between their atomic radii and that for Ni are greater than  $\pm 15\%$ , and/or have a valence different than 2+.

(c) C, H, and O form interstitial solid solutions. These elements have atomic radii that are significantly smaller than the atomic radius of Ni.

4.9 The concentration, in weight percent, of an element in an alloy may be computed using a modified form of Equation 4.3. For this alloy, the concentration of iron ( $C_{\text{Fe}}$ ) is just

$$C_{\text{Fe}} = \frac{m_{\text{Fe}}}{m_{\text{Fe}} + m_{\text{C}} + m_{\text{Cr}}} \times 100$$

$$= \frac{105 \text{ kg}}{105 \text{ kg} + 0.2 \text{ kg} + 1.0 \text{ kg}} \times 100 = 98.87 \text{ wt\%}$$

Similarly, for carbon

$$C_{\text{C}} = \frac{0.2 \text{ kg}}{105 \text{ kg} + 0.2 \text{ kg} + 1.0 \text{ kg}} \times 100 = 0.19 \text{ wt\%}$$

And for chromium

$$C_{\text{Cr}} = \frac{1.0 \text{ kg}}{105 \text{ kg} + 0.2 \text{ kg} + 1.0 \text{ kg}} \times 100 = 0.94 \text{ wt\%}$$

4.10 The concentration of an element in an alloy, in atom percent, may be computed using Equation 4.5. However, it first becomes necessary to compute the number of moles of both Cu and Zn, using Equation 4.4. Thus, the number of moles of Cu is just

$$n_{m_{\text{Cu}}} = \frac{m'_{\text{Cu}}}{A_{\text{Cu}}} = \frac{33 \text{ g}}{63.55 \text{ g/mol}} = 0.519 \text{ mol}$$

Likewise, for Zn

$$n_{m_{\text{Zn}}} = \frac{47 \text{ g}}{65.39 \text{ g/mol}} = 0.719 \text{ mol}$$

Now, use of Equation 4.5 yields

$$\begin{aligned} C'_{\text{Cu}} &= \frac{n_{m_{\text{Cu}}}}{n_{m_{\text{Cu}}} + n_{m_{\text{Zn}}}} \times 100 \\ &= \frac{0.519 \text{ mol}}{0.519 \text{ mol} + 0.719 \text{ mol}} \times 100 = 41.9 \text{ at\%} \end{aligned}$$

Also,

$$C'_{\text{Zn}} = \frac{0.719 \text{ mol}}{0.519 \text{ mol} + 0.719 \text{ mol}} \times 100 = 58.1 \text{ at\%}$$

## Interfacial Defects

4.27 The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solution to Problem 3.53, planar densities for FCC (100) and (111) planes are  $\frac{1}{4R^2}$  and  $\frac{1}{2R^2\sqrt{3}}$ , respectively—that is  $\frac{0.25}{R^2}$  and  $\frac{0.29}{R^2}$  (where  $R$  is the atomic radius). Thus, since the planar density for (111) is greater, it will have the lower surface energy.

4.29 (a) The surface energy will be greater than the grain boundary energy. For grain boundaries, some atoms on one side of a boundary will bond to atoms on the other side; such is not the case for surface atoms. Therefore, there will be fewer unsatisfied bonds along a grain boundary.

(b) The small-angle grain boundary energy is lower than for a high-angle one because more atoms bond across the boundary for the small-angle, and, thus, there are fewer unsatisfied bonds.

## DESIGN PROBLEMS

### **Specification of Composition**

4.D1 This problem calls for us to compute the concentration of lithium (in wt%) that, when added to aluminum, will yield a density of  $2.47 \text{ g/cm}^3$ . Solution of this problem requires the use of Equation 4.10a, which takes the form

$$\rho_{\text{ave}} = \frac{100}{\frac{C_{\text{Li}}}{\rho_{\text{Li}}} + \frac{100 - C_{\text{Li}}}{\rho_{\text{Al}}}}$$

inasmuch as  $C_{\text{Li}} + C_{\text{Al}} = 100$ . According to the table inside the front cover, the respective densities of Li and Al are  $0.534$  and  $2.71 \text{ g/cm}^3$ . Upon solving for  $C_{\text{Li}}$  from the above equation, we get

$$\begin{aligned} C_{\text{Li}} &= \frac{100 \rho_{\text{Li}} (\rho_{\text{Al}} - \rho_{\text{ave}})}{\rho_{\text{ave}} (\rho_{\text{Al}} - \rho_{\text{Li}})} \\ &= \frac{(100)(0.534 \text{ g/cm}^3)(2.71 \text{ g/cm}^3 - 2.47 \text{ g/cm}^3)}{(2.47 \text{ g/cm}^3)(2.71 \text{ g/cm}^3 - 0.534 \text{ g/cm}^3)} \\ &= 2.38 \text{ wt\%} \end{aligned}$$

5.7 We are asked to determine the position at which the nitrogen concentration is  $0.5 \text{ kg/m}^3$ . 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  $2 \text{ kg/m}^3$ , 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

$$\begin{aligned} x_B &= 0 + (1.2 \times 10^{-10} \text{ m}^2/\text{s}) \left[ \frac{2 \text{ kg/m}^3 - 0.5 \text{ kg/m}^3}{1.0 \times 10^{-7} \text{ kg/m}^2 \cdot \text{s}} \right] \\ &= 1.8 \times 10^{-3} \text{ m} = 1.8 \text{ mm} \end{aligned}$$



5.11 We are asked to compute the carburizing (i.e., diffusion) time required for a specific nonsteady-state diffusion situation. 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,  $C_x = 0.30$ ,  $C_0 = 0.10$ ,  $C_s = 0.90$ , and  $x = 4 \text{ mm} = 4 \times 10^{-3} \text{ m}$ . Thus,

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.30 - 0.10}{0.90 - 0.10} = 0.2500 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

or

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - 0.2500 = 0.7500$$

By linear interpolation using data from Table 5.1

$z$	$\operatorname{erf}(z)$
0.80	0.7421
$z$	0.7500
0.85	0.7707

$$\frac{z - 0.800}{0.850 - 0.800} = \frac{0.7500 - 0.7421}{0.7707 - 0.7421}$$

From which

$$z = 0.814 = \frac{x}{2\sqrt{Dt}}$$

Now, from Table 5.2, at  $1100^\circ\text{C}$  (1373 K)

$$\begin{aligned} D &= (2.3 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol}\cdot\text{K})(1373 \text{ K})}\right] \\ &= 5.35 \times 10^{-11} \text{ m}^2/\text{s} \end{aligned}$$

5.27 (a) We are asked to calculate the diffusion coefficient for Mg in Al at 450°C. Using the data in Table 5.2 and Equation 5.8

$$\begin{aligned}
 D &= D_0 \exp\left(-\frac{Q_d}{RT}\right) \\
 &= (1.2 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{131,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(450 + 273 \text{ K})}\right] \\
 &= 4.08 \times 10^{-14} \text{ m}^2/\text{s}
 \end{aligned}$$

(b) This portion of the problem calls for the time required at 550°C to produce the same diffusion result as for 15 h at 450°C. Equation 5.7 is employed as

$$D_{450}t_{450} = D_{550}t_{550}$$

Now, from Equation 5.8 the value of the diffusion coefficient at 550°C is calculated as

$$\begin{aligned}
 D_{550} &= (1.2 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{131,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(550 + 273 \text{ K})}\right] \\
 &= 5.76 \times 10^{-13} \text{ m}^2/\text{s}
 \end{aligned}$$

Thus,

$$\begin{aligned}
 t_{550} &= \frac{D_{450}t_{450}}{D_{550}} \\
 &= \frac{(4.08 \times 10^{-14} \text{ m}^2/\text{s})(15 \text{ h})}{(5.76 \times 10^{-13} \text{ m}^2/\text{s})} = 1.06 \text{ h}
 \end{aligned}$$

## Problem 1

- a) The diffusion types in solid phase are: i) vacancy diffusion og ii) interstitial diffusion.

i) **Vacancy diffusion**

Vacancy diffusion takes place when an atom in a normal lattice position move to a neighbouring vacancy. The rate of this diffusion increases with increasing concentration of vacancies and the mobility of atoms in the lattice. When the temperature increases the concentration of vacancies increases together with the mobility of atoms (increasing the vibration). Further, other processes that increases the concentration of vacancies, e.g. deformation, increases the diffusion rate. Both self- and inter-diffusion can follow this mechanism.

ii) **Interstitial diffusion**

Interstitial diffusion is migration of an atom from an interstitial position to an empty neighbouring interstitial position. This type of diffusion is typical for small atoms/impurities in a lattice/matrix of bigger atoms (e.g. H<sub>2</sub> in Iron). The reason that this type of diffusion is more common for small atoms is that they can fit in interstitial positions in the lattice without expanding the lattice considerably. Usually the rate of interstitial diffusion is substantially higher than the rate of vacancy diffusion since smaller atoms have higher mobility and the concentration of interstitial vacancies is substantially higher than lattice vacancies.

- b) The process described is a classical time dependent diffusion process, and we have to use Ficks 2nd law:

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

where  $C_x$  is the concentration at the distance  $x$ ,  $C_0$  is the bulk concentration and  $C_s$  is the concentration at the surface.

In the problem we get the information:

The surface concentration,  $C_s = 0,1 \text{ weight\%} = 4,5 \text{ kg/m}^3$ , bulk concentration  $C_0 = 0,0001 \text{ weight\%} = 0,0045 \text{ kg/m}^3$  and the concentration at  $x = 0,1 \text{ mm}$ ;  $C_x = 0,01 \text{ weight\%} = 0,45 \text{ kg/m}^3$ . From Ficks 2nd law we see that we know all the values except the time, and we put them in the expression for the time dependent diffusion:

$$\frac{(0,45 - 0,0045)}{(4,5 - 0,0045)} = 1 - \operatorname{erf}(Q) = 0,0991, \text{ where } Q \text{ is } \frac{x}{2(Dt)^{1/2}}$$

$\Rightarrow \text{erf}(Q) = 1 - 0,0991 = 0,901$ . We put in the value for  $x$  ( $10^{-4}$  m) and the diffusion coefficient ( $10^{-12}$  m<sup>2</sup>/s) and find that  $\text{erf}\left(\frac{50}{t^{1/2}}\right) = 0,901$ . Values for the error function is given below. We see that there is no value that agree with our value (0,901). By interpolation between  $z = 1.1$  og  $z = 1.2$  we find that  $\text{erf}(Q) = 0,901$  which gives  $Q = 1,169$  and  $t = \left(\frac{50}{1,169}\right)^2$ . Necessary time to produce this layer is therefore 1829 s (= 0,51 hours).

**Verdier for feil(error)-funksjonen /Values for the error function**

z	erf(z)	z	erf(z)	z	erf(z)
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.00	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999