

Home-work #4.

Problems: 4.2; 4.4; 4.7; 4.16; 4.25; 4.28; 5.7; 5.12; 5.15; 5.20; 5.23; 5.26

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:

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

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>$\Delta R\%$</u>	<u>Crystal Structure</u>	<u>ΔElectro-negativity</u>	<u>Valence</u>
Ni		FCC		2+
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.

4.7 In order to compute composition, in atom percent, of a 92.5 wt% Ag-7.5 wt% Cu alloy, we employ Equation 4.6 as

$$\begin{aligned}
 C'_{\text{Ag}} &= \frac{C_{\text{Ag}}^{\text{A}} C_{\text{Cu}}}{C_{\text{Ag}}^{\text{A}} C_{\text{Cu}} + C_{\text{Cu}}^{\text{A}} C_{\text{Ag}}} \times 100 \\
 &= \frac{(92.5)(63.55 \text{ g/mol})}{(92.5)(63.55 \text{ g/mol}) + (7.5)(107.87 \text{ g/mol})} \times 100 \\
 &= 87.9 \text{ at\%}
 \end{aligned}$$

$$\begin{aligned}
 C'_{\text{Cu}} &= \frac{C_{\text{Cu}}^{\text{A}} C_{\text{Ag}}}{C_{\text{Ag}}^{\text{A}} C_{\text{Cu}} + C_{\text{Cu}}^{\text{A}} C_{\text{Ag}}} \times 100 \\
 &= \frac{(7.5)(107.87 \text{ g/mol})}{(92.5)(63.55 \text{ g/mol}) + (7.5)(107.87 \text{ g/mol})} \times 100 \\
 &= 12.1 \text{ at\%}
 \end{aligned}$$

4.16 We are asked in this problem to determine the approximate density of a Ti-6Al-4V titanium alloy that has a composition of 90 wt% Ti, 6 wt% Al, and 4 wt% V. In order to solve this problem, Equation 4.10a is modified to take the following form:

$$\rho_{\text{ave}} = \frac{100}{\frac{C_{\text{Ti}}}{\rho_{\text{Ti}}} + \frac{C_{\text{Al}}}{\rho_{\text{Al}}} + \frac{C_{\text{V}}}{\rho_{\text{V}}}}$$

And, using the density values for Ti, Al, and V—i.e., 4.51 g/cm³, 2.71 g/cm³, and 6.10 g/cm³—(as taken from inside the front cover of the text), the density is computed as follows:

$$\begin{aligned}
 \rho_{\text{ave}} &= \frac{100}{\frac{90 \text{ wt\%}}{4.51 \text{ g/cm}^3} + \frac{6 \text{ wt\%}}{2.71 \text{ g/cm}^3} + \frac{4 \text{ wt\%}}{6.10 \text{ g/cm}^3}} \\
 &= 4.38 \text{ g/cm}^3
 \end{aligned}$$

4.28 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 3.54, the planar densities for BCC (100) and (110) are $\frac{3}{16R^2}$ and $\frac{3}{8R^2\sqrt{2}}$, respectively—that is $\frac{0.19}{R^2}$ and $\frac{0.27}{R^2}$. Thus, since the planar density for (110) is greater, it will have the lower surface energy.

4.25 This problem asks that we compute the unit cell edge length for a 90 wt% Fe-10 wt% V alloy. First of all, the atomic radii for Fe and V (using the table inside the front cover) are 0.124 and 0.132 nm, respectively. Also, using Equation 3.5 it is possible to compute the unit cell volume, and inasmuch as the unit cell is cubic, the unit cell edge length is just the cube root of the volume. However, it is first necessary to calculate the density and average atomic weight of this alloy using Equations 4.10a and 4.11a. Inasmuch as the densities of iron and vanadium are 7.87 g/cm^3 and 6.10 g/cm^3 , respectively, (as taken from inside the front cover), the average density is just

$$\begin{aligned}\rho_{\text{ave}} &= \frac{100}{\frac{C_{\text{V}}}{\rho_{\text{V}}} + \frac{C_{\text{Fe}}}{\rho_{\text{Fe}}}} \\ &= \frac{100}{\frac{10\text{ wt}\%}{6.10\text{ g/cm}^3} + \frac{90\text{ wt}\%}{7.87\text{ g/cm}^3}} \\ &= 7.65\text{ g/cm}^3\end{aligned}$$

And for the average atomic weight

$$\begin{aligned}A_{\text{ave}} &= \frac{100}{\frac{C_{\text{V}}}{A_{\text{V}}} + \frac{C_{\text{Fe}}}{A_{\text{Fe}}}} \\ &= \frac{100}{\frac{10\text{ wt}\%}{50.94\text{ g/mole}} + \frac{90\text{ wt}\%}{55.85\text{ g/mol}}} \\ &= 55.32\text{ g/mol}\end{aligned}$$

Now, V_C is determined from Equation 3.5 as

$$\begin{aligned}V_C &= \frac{nA_{\text{ave}}}{\rho_{\text{ave}}N_A} \\ &= \frac{(2\text{ atoms/unit cell})(55.32\text{ g/mol})}{(7.65\text{ g/cm}^3)(6.023 \times 10^{23}\text{ atoms/mol})}\end{aligned}$$

$$= 2.40 \times 10^{-23} \text{ cm}^3/\text{unit cell}$$

And, finally

$$\begin{aligned} a &= (V_C)^{1/3} \\ &= (2.40 \times 10^{-23} \text{ cm}^3/\text{unit cell})^{1/3} \\ &= 2.89 \times 10^{-8} \text{ cm} = 0.289 \text{ nm} \end{aligned}$$

5.7 We are asked to determine the position at which the nitrogen concentration is 0.5 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 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

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

5.12 This problem asks that we determine the position at which the carbon concentration is 0.25 wt% after a 10-h heat treatment at 1325 K when $C_0 = 0.55$ wt% C. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.25 - 0.55}{0 - 0.55} = 0.5455 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus,

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4545$$

Using data in Table 5.1 and linear interpolation

z	$\operatorname{erf}(z)$
0.40	0.4284
z	0.4545
0.45	0.4755

$$\frac{z - 0.40}{0.45 - 0.40} = \frac{0.4545 - 0.4284}{0.4755 - 0.4284}$$

And,

$$z = 0.4277$$

Which means that

$$\frac{x}{2\sqrt{Dt}} = 0.4277$$

And, finally

$$\begin{aligned} x &= 2(0.4277)\sqrt{Dt} = (0.8554)\sqrt{(4.3 \times 10^{-11} \text{ m}^2/\text{s})(3.6 \times 10^4 \text{ s})} \\ &= 1.06 \times 10^{-3} \text{ m} = 1.06 \text{ mm} \end{aligned}$$

5.15 This problem calls for an estimate of the time necessary to achieve a carbon concentration of 0.35 wt% at a point 6.0 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,

$$\frac{(2.0 \text{ mm})^2}{15 \text{ h}} = \frac{(6.0 \text{ mm})^2}{t_2}$$

from which

$$t_2 = 135 \text{ h}$$

5.20 In this problem we are given Q_d for the diffusion of Cu in Ag (i.e., 193,000 J/mol) and asked to compute D at 1200 K given that the value of D at 1000 K is $1.0 \times 10^{-14} \text{ m}^2/\text{s}$. It first becomes necessary to solve for D_0 from Equation 5.8 as

$$\begin{aligned} D_0 &= D \exp\left(\frac{Q_d}{RT}\right) \\ &= (1.0 \times 10^{-14} \text{ m}^2/\text{s}) \exp\left[\frac{193,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1000 \text{ K})}\right] \\ &= 1.22 \times 10^{-4} \text{ m}^2/\text{s} \end{aligned}$$

Now, solving for D at 1200 K (again using Equation 5.8) gives

$$\begin{aligned} D &= (1.22 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{193,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1200 \text{ K})}\right] \\ &= 4.8 \times 10^{-13} \text{ m}^2/\text{s} \end{aligned}$$

5.23 This problem asks us to determine the values of Q_d and D_0 for the diffusion of Au in Ag 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 1.0×10^{-3} and $0.90 \times 10^{-3} \text{ K}^{-1}$, respectively, then the corresponding values of $\log D_1$ and $\log D_2$ are -14.68 and -13.57 . Therefore,

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

$$\begin{aligned} Q_d &= -2.3 R \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}} \\ &= -(2.3)(8.31 \text{ J/mol} \cdot \text{K}) \left[\frac{-14.68 - (-13.57)}{(1.0 \times 10^{-3} - 0.90 \times 10^{-3}) \text{ K}^{-1}} \right] \\ &= 212,200 \text{ J/mol} \end{aligned}$$

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, $D = 1.0 \times 10^{-14} \text{ m}^2/\text{s}$ at $T = 1064 \text{ K}$ ($1/T = 0.94 \times 10^{-3} \text{ K}^{-1}$). Therefore

$$\begin{aligned} D_0 &= D \exp\left(\frac{Q_d}{RT}\right) \\ &= (1.0 \times 10^{-14} \text{ m}^2/\text{s}) \exp\left[\frac{212,200 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1064 \text{ K})}\right] \\ &= 2.65 \times 10^{-4} \text{ m}^2/\text{s} \end{aligned}$$

5.26 To solve this problem it is necessary to employ Equation 5.7

$$Dt = \text{constant}$$

Which, for this problem, takes the form

$$D_{1000}t_{1000} = D_T t_T$$

At 1000°C, and using the data from Table 5.2, for the diffusion of carbon in γ -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

$$\begin{aligned} D_{1000} &= (2.3 \times 10^{-5} \text{ m}^2/\text{s}) \exp \left[-\frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K})(1000 + 273 \text{ K})} \right] \\ &= 1.93 \times 10^{-11} \text{ m}^2/\text{s} \end{aligned}$$

Thus, from the above equation

$$(1.93 \times 10^{-11} \text{ m}^2/\text{s})(12 \text{ h}) = D_T(4 \text{ h})$$

And, solving for D_T

$$D_T = \frac{(1.93 \times 10^{-11} \text{ m}^2/\text{s})(12 \text{ h})}{4 \text{ h}} = 5.79 \times 10^{-11} \text{ m}^2/\text{s}$$

Now, solving for T from Equation 5.9a gives

$$\begin{aligned} T &= -\frac{Q_d}{R(\ln D_T - \ln D_0)} \\ &= -\frac{148,000 \text{ J/mol}}{(8.31 \text{ J/mol} \cdot \text{K}) [\ln (5.79 \times 10^{-11} \text{ m}^2/\text{s}) - \ln (2.3 \times 10^{-5} \text{ m}^2/\text{s})]} \\ &= 1381 \text{ K} = 1108^\circ\text{C} \end{aligned}$$