4.2 *(a) Calculate the fraction of atom sites that are vacant for copper (Cu) at its melting temperature of 1084°C (1357 K). Assume an energy for vacancy formation of 0.90 eV/atom.*

(b) Repeat this calculation at room temperature (298 K).

(c) What is ratio of N_V/N(1357 K) and N_V/N(298 K)?

<u>Solution</u>

(a) In order to compute the fraction of atom sites that are vacant in copper at 1357 K, we must employ Equation 4.1. As stated in the problem, Q_v = 0.90 eV/atom. Thus,

$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.90\text{ eV/atom}}{(8.62\times10^{-5}\text{ eV/atom-K})(1357\text{ K})}\right]$$

$$= 4.56 \times 10^{-4} = N_v/N(1357\text{ K})$$

(b) We repeat this computation at room temperature (298 K), as follows:

$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.90\text{ eV/atom}}{(8.62\times10^{-5}\text{ eV/atom-K})(298\text{ K})}\right]$$

$$= 6.08 \times 10^{-16} = N_v/N(298\text{ K})$$

(c) And, finally the ratio of N_V/N(1357 K) and N_V/N(298 K) is equal to the following:

$$\frac{N_v/N(1357\text{ K})}{N_v/N(298\text{ K})} = \frac{4.56 \times 10^{-4}}{6.08 \times 10^{-16}} = 7.5 \times 10^{11}$$

4.4 Atomic radius, crystal structure, electronegativity, and the most common valence are given in the following table for several elements; for those that are nonmetals, only atomic radii are indicated.

Element	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Ni	*0.1246*	*FCC*	*1.8*	*+2*
C	*0.071*			
H	*0.046*			
O	*0.060*			
Ag	*0.1445*	*FCC*	*1.9*	*+1*
Al	*0.1431*	*FCC*	*1.5*	*+3*
Co	*0.1253*	*HCP*	*1.8*	*+2*
Cr	*0.1249*	*BCC*	*1.6*	*+3*
Fe	*0.1241*	*BCC*	*1.8*	*+2*
Pt	*0.1387*	*FCC*	*2.2*	*+2*
Zn	*0.1332*	*HCP*	*1.6*	*+2*

Which of these elements would you expect to form the following with nickel:

(a) a substitutional solid solution having complete solubility

(b) a substitutional solid solution of incomplete solubility

(c) an interstitial solid solution

Solution

For complete substitutional solubility the four Hume-Rothery rules must be satisfied: (1) the difference in atomic radii between Ni and the other element ($\Delta R\%$) must be less than ±15%; (2) the crystal structures must be the same; (3) the electronegativities must be similar; and (4) the valences should be the same.

Element	$\Delta R\%$	Crystal Structure	ΔElectro-negativity	Valence
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 ±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.

5.2 *(a) Compare interstitial and vacancy atomic mechanisms for diffusion.*

(b) Cite two reasons why interstitial diffusion is normally more rapid than vacancy diffusion.

Answer

(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, are more mobile; and (2) the probability of an empty adjacent interstitial site is greater than for a vacancy adjacent to a host (or substitutional impurity) atom.

5.16 *The diffusion coefficients for carbon in nickel are given at two temperatures are as follows:*

T (°C)	*D (m²/s)*
600	*5.5×10^{-14}*
700	*3.9×10^{-13}*

(a) Determine the values of D_0 and Q_d.

(b) What is the magnitude of D at 850°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 (873 K [600°C] and 973 K [700°C]) and D_1 and D_2 (5.5×10^{-14} and 3.9×10^{-13} m²/s), we get

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

$$= -\frac{(8.31\text{ J/mol-K})\left[\ln\left(5.5 \times 10^{-14}\right) - \ln\left(3.9 \times 10^{-13}\right)\right]}{\dfrac{1}{873\text{ K}} - \dfrac{1}{973\text{ K}}}$$

$$= 138{,}300\text{ J/mol}$$

Now, solving for D_0 from a rearranged form of Equation 5.8 (and using the 600°C value of D)

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

$$= \left(5.5 \times 10^{-14}\text{ m}^2/\text{s}\right)\exp\left[\frac{138{,}300\text{ J/mol}}{(8.31\text{ J/mol-K})(873\text{ K})}\right]$$

$$= 1.05 \times 10^{-5}\ \text{m}^2/\text{s}$$

(b) Using these values of D_0 and Q_d, D at 1123 K (850°C) is just

$$D = \left(1.05 \times 10^{-5}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{138{,}300\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1123\ \text{K})}\right]$$

$$= 3.8 \times 10^{-12}\ \text{m}^2/\text{s}$$