CHAPTER 2

ATOMIC STRUCTURE AND INTERATOMIC BONDING

PROBLEM SOLUTIONS

Fundamental Concepts
Electrons in Atoms

2.1 *Cite the difference between atomic mass and atomic weight.*

Solution

Atomic mass is the mass of an individual atom, whereas atomic weight is the average (weighted) of the atomic masses of an atom's naturally occurring isotopes.

2.2 *Silicon has three naturally occurring isotopes: 92.23% of* ^{28}Si*, with an atomic weight of 27.9769 amu, 4.68% of* ^{29}Si*, with an atomic weight of 28.9765 amu, and 3.09% of* ^{30}Si*, with an atomic weight of 29.9738 amu. On the basis of these data, confirm that the average atomic weight of Si is 28.0854 amu.*

Solution

The average atomic weight of silicon ($\bar{A}_{\text{Si}}$) is computed by adding fraction-of-occurrence/atomic weight products for the three isotopes—i.e., using Equation 2.2. (Remember: fraction of occurrence is equal to the percent of occurrence divided by 100.) Thus

$$\bar{A}_{\text{Si}} = f_{^{28}\text{Si}} A_{^{28}\text{Si}} + f_{^{29}\text{Si}} A_{^{29}\text{Si}} + f_{^{30}\text{Si}} A_{^{30}\text{Si}}$$

$$= (0.9223)(27.9769) + (0.0468)(28.9765) + (0.0309)(29.9738) = 28.0854$$

2.3 *Zinc has five naturally occurring isotopes: 48.63% of ^{64}Zn with an atomic weight of 63.929 amu; 27.90% of ^{66}Zn with an atomic weight of 65.926 amu; 4.10% of ^{67}Zn with an atomic weight of 66.927 amu; 18.75% of ^{68}Zn with an atomic weight of 67.925 amu; and 0.62% of ^{70}Zn with an atomic weight of 69.925 amu. Calculate the average atomic weight of Zn.*

Solution

The average atomic weight of zinc $\overline{A}_{Zn}$ is computed by adding fraction-of-occurrence—atomic weight products for the five isotopes—i.e., using Equation 2.2. (Remember: fraction of occurrence is equal to the percent of occurrence divided by 100.) Thus

$$\overline{A}_{Zn} = f_{^{64}Zn} A_{^{64}Zn} + f_{^{66}Zn} A_{^{66}Zn} + f_{^{67}Zn} A_{^{67}Zn} + f_{^{68}Zn} A_{^{68}Zn} + f_{^{70}Zn} A_{^{70}Zn}$$

Including data provided in the problem statement we solve for $\overline{A}_{Zn}$ as

$$\overline{A}_{Zn} = (0.4863)(63.929 \text{ amu}) + (0.2790)(65.926 \text{ amu})$$

$$+ (0.0410)(66.927 \text{ amu}) + (0.1875)(67.925 \text{ amu}) + (0.0062)(69.925)$$

$$= 65.400 \text{ amu}$$

2.4 *Indium has two naturally occurring isotopes:* ^{113}In *with an atomic weight of 112.904 amu, and* ^{115}In *with an atomic weight of 114.904 amu. If the average atomic weight for In is 114.818 amu, calculate the fraction-of-occurrences of these two isotopes.*

Solution

The average atomic weight of indium $(\bar{A}_{In})$ is computed by adding fraction-of-occurrence—atomic weight products for the two isotopes—i.e., using Equation 2.2, or

$$\bar{A}_{In} = f_{^{113}In} A_{^{113}In} + f_{^{115}In} A_{^{115}In}$$

Because there are just two isotopes, the sum of the fracture-of-occurrences will be 1.000; or

$$f_{^{113}In} + f_{^{115}In} = 1.000$$

which means that

$$f_{^{113}In} = 1.000 - f_{^{115}In}$$

Substituting into this expression the one noted above for $f_{^{113}In}$, and incorporating the atomic weight values provided in the problem statement yields

$$114.818 \text{ amu} = f_{^{113}In} A_{^{113}In} + f_{^{115}In} A_{^{115}In}$$

$$114.818 \text{ amu} = (1.000 - f_{^{113}In}) A_{^{113}In} + f_{^{115}In} A_{^{115}In}$$

$$114.818 \text{ amu} = (1.000 - f_{^{115}In})(112.904 \text{ amu}) + f_{^{115}In}(114.904 \text{ amu})$$

$$114.818 \text{ amu} = 112.904 \text{ amu} - f_{^{115}In}(112.904 \text{ amu}) + f_{^{115}In}(114.904 \text{ amu})$$

Solving this expression for $f_{^{115}In}$ yields $f_{^{115}In} = 0.957$. Furthermore, because

$$f_{^{113}In} = 1.000 - f_{^{115}In}$$

then

$$f_{^{113}In} = 1.000 - 0.957 = 0.043$$

2.5 *(a) How many grams are there in one amu of a material?*

(b) Mole, in the context of this book, is taken in units of gram-mole. On this basis, how many atoms are there in a pound-mole of a substance?

<u>Solution</u>

(a) In order to determine the number of grams in one amu of material, appropriate manipulation of the amu/atom, g/mol, and atom/mol relationships is all that is necessary, as

$$\#\text{g/amu} = \left(\frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}}\right)\left(\frac{1\ \text{g/mol}}{1\ \text{amu/atom}}\right)$$

$$= 1.66 \times 10^{-24}\ \text{g/amu}$$

(b) Since there are 453.6 g/lb_m,

$$1\ \text{lb-mol} = (453.6\ \text{g/lb}_m)(6.022\ ´\ 10^{23}\ \text{atoms/g-mol})$$

$$= 2.73 \times 10^{26}\ \text{atoms/lb-mol}$$

2.6 *(a) Cite two important quantum-mechanical concepts associated with the Bohr model of the atom.*

(b) Cite two important additional refinements that resulted from the wave-mechanical atomic model.

Solution

(a) Two important quantum-mechanical concepts associated with the Bohr model of the atom are (1) that electrons are particles moving in discrete orbitals, and (2) electron energy is quantized into shells.

(b) Two important refinements resulting from the wave-mechanical atomic model are (1) that electron position is described in terms of a probability distribution, and (2) electron energy is quantized into both shells and subshells--each electron is characterized by four quantum numbers.

2.7 *Relative to electrons and electron states, what does each of the four quantum numbers specify?*

Solution

The n quantum number designates the electron shell.

The l quantum number designates the electron subshell.

The m_l quantum number designates the number of electron states in each electron subshell.

The m_s quantum number designates the spin moment on each electron.

2.8 *Allowed values for the quantum numbers of electrons are as follows:*

$$n = 1, 2, 3, \ldots$$

$$l = 0, 1, 2, 3, \ldots, n - 1$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l$$

$$m_s = \pm \frac{1}{2}$$

The relationships between n and the shell designations are noted in Table 2.1. Relative to the subshells,

l = 0 corresponds to an s subshell

l = 1 corresponds to a p subshell

l = 2 corresponds to a d subshell

l = 3 corresponds to an f subshell

For the K shell, the four quantum numbers for each of the two electrons in the 1s state, in the order of nlm_lm_s*, are* $100(\frac{1}{2})$ *and* $100(-\frac{1}{2})$*. Write the four quantum numbers for all of the electrons in the L and M shells, and note which correspond to the s, p, and d subshells.*

Answer

For the *L* state, $n = 2$, and eight electron states are possible. Possible l values are 0 and 1, while possible m_l values are 0 and ±1; and possible m_s values are $\pm\frac{1}{2}$. Therefore, for the *s* states, the quantum numbers are $200(\frac{1}{2})$ and $200(-\frac{1}{2})$. For the *p* states, the quantum numbers are $210(\frac{1}{2})$, $210(-\frac{1}{2})$, $211(\frac{1}{2})$, $211(-\frac{1}{2})$, $21(-1)(\frac{1}{2})$, and $21(-1)(-\frac{1}{2})$.

For the *M* state, $n = 3$, and 18 states are possible. Possible l values are 0, 1, and 2; possible m_l values are 0, ±1, and ±2; and possible m_s values are $\pm\frac{1}{2}$. Therefore, for the *s* states, the quantum numbers are $300(\frac{1}{2})$, $300(-\frac{1}{2})$, for the *p* states they are $310(\frac{1}{2})$, $310(-\frac{1}{2})$, $311(\frac{1}{2})$, $311(-\frac{1}{2})$, $31(-1)(\frac{1}{2})$, and $31(-1)(-\frac{1}{2})$; for the *d* states they are $320(\frac{1}{2})$, $320(-\frac{1}{2})$, $321(\frac{1}{2})$, $321(-\frac{1}{2})$, $32(-1)(\frac{1}{2})$, $32(-1)(-\frac{1}{2})$, $322(\frac{1}{2})$, $322(-\frac{1}{2})$, $32(-2)(\frac{1}{2})$, and $32(-2)(-\frac{1}{2})$.

2.9 *Give the electron configurations for the following ions:* P^{5+}, P^{3-}, Sn^{4+}, Se^{2-}, I^{-}, *and* Ni^{2+}.

Solution

The electron configurations for the ions are determined using Table 2.2 (and Figure 2.8).

P^{5+}: From Table 2.2, the electron configuration for an atom of phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3$. In order to become an ion with a plus five charge, it must lose five electrons—in this case the three 3*p* and the two 3*s*. Thus, the electron configuration for a P^{5+} ion is $1s^2 2s^2 2p^6$.

P^{3-}: From Table 2.2, the electron configuration for an atom of phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3$. In order to become an ion with a minus three charge, it must acquire three electrons—in this case another three 3*p*. Thus, the electron configuration for a P^{3-} ion is $1s^2 2s^2 2p^6 3s^2 3p^6$.

Sn^{4+}: From the periodic table, Figure 2.8, the atomic number for tin is 50, which means that it has fifty electrons and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$. In order to become an ion with a plus four charge, it must lose four electrons—in this case the two 4*s* and two 5*p*. Thus, the electron configuration for an Sn^{4+} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$.

Se^{2-}: From Table 2.2, the electron configuration for an atom of selenium is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$. In order to become an ion with a minus two charge, it must acquire two electrons—in this case another two 4*p*. Thus, the electron configuration for an Se^{2-} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$.

I^{-}: From the periodic table, Figure 2.8, the atomic number for iodine is 53, which means that it has fifty three electrons and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$. In order to become an ion with a minus one charge, it must acquire one electron—in this case another 5*p*. Thus, the electron configuration for an I^{-} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$.

Ni^{2+}: From Table 2.2, the electron configuration for an atom of nickel is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$. In order to become an ion with a plus two charge, it must lose two electrons—in this case the two 4*s*. Thus, the electron configuration for a Ni^{2+} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$.

2.10 *Potassium iodide (KI) exhibits predominantly ionic bonding. The K^+ and I^- ions have electron structures that are identical to which two inert gases?*

Solution

The K^+ ion is just a potassium atom that has lost one electron; therefore, it has an electron configuration the same as argon (Figure 2.8).

The I^- ion is a iodine atom that has acquired one extra electron; therefore, it has an electron configuration the same as xenon.

2.11 *With regard to electron configuration, what do all the elements in Group IIA of the periodic table have in common?*

Solution

Each of the elements in Group IIA has two *s* electrons.

2.12 *To what group in the periodic table would an element with atomic number 112 belong?*

<u>Solution</u>

From the periodic table (Figure 2.8) the element having atomic number 112 would belong to group IIB. According to Figure 2.8, Ds, having an atomic number of 110 lies below Pt in the periodic table and in the right-most column of group VIII. Moving two columns to the right puts element 112 under Hg and in group IIB.

This element has been artificially created and given the name Copernicium with the symbol Cn. It was named after Nicolaus Copernicus, the Polish scientist who proposed that the earth moves around the sun (and not vice versa).

2.13 *Without consulting Figure 2.8 or Table 2.2, determine whether each of the following electron configurations is an inert gas, a halogen, an alkali metal, an alkaline earth metal, or a transition metal. Justify your choices.*

(a) $1s^2 2s^2 2p^6 3s^2 3p^5$

(b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

(c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2$

(f) $1s^2 2s^2 2p^6 3s^2$

Solution

(a) The $1s^2 2s^2 2p^6 3s^2 3p^5$ electron configuration is that of a halogen because it is one electron deficient from having a filled *p* subshell.

(b) The $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(c) The $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ electron configuration is that of an inert gas because of filled 4*s* and 4*p* subshells.

(d) The $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ electron configuration is that of an alkali metal because of a single *s* electron.

(e) The $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(f) The $1s^2 2s^2 2p^6 3s^2$ electron configuration is that of an alkaline earth metal because of two *s* electrons.

2.14 *(a) What electron subshell is being filled for the rare earth series of elements on the periodic table?*

(b) What electron subshell is being filled for the actinide series?

Solution

(a) The 4*f* subshell is being filled for the rare earth series of elements.

(b) The 5*f* subshell is being filled for the actinide series of elements.

Bonding Forces and Energies

2.15 Calculate the force of attraction between a Ca^{2+} and an O^{2-} ion whose centers are separated by a distance of 1.25 nm.

Solution

To solve this problem for the force of attraction between these two ions it is necessary to use Equation 2.13, which takes on the form of Equation 2.14 when values of the constants *e* and ε_0 are included—that is

$$F_A = \frac{(2.31 \times 10^{-28}\ \text{N-m}^2)\left(|Z_1|\right)\left(|Z_2|\right)}{r^2}$$

If we take ion 1 to be Ca^{2+} and ion 2 to be O^{2-}, then $Z_1 = +2$ and $Z_2 = -2$; also, from the problem statement $r = 1.25$ nm $= 1.25 \times 10^{-9}$ m. Thus, using Equation 2.14, we compute the force of attraction between these two ions as follows:

$$F_A = \frac{(2.31 \times 10^{-28}\ \text{N-m}^2)\left(|+2|\right)\left(|-2|\right)}{(1.25 \times 10^{-9}\ \text{m})^2}$$

$$5.91 \times 10^{-10}\ \text{N}$$

2.16 *The atomic radii of* Mg^{2+} *and* F^- *ions are 0.072 and 0.133 nm, respectively.*

(a) Calculate the force of attraction between these two ions at their equilibrium interionic separation (i.e., when the ions just touch one another).

(b) What is the force of repulsion at this same separation distance.

Solution

This problem is solved in the same manner as Example Problem 2.2.

(a) The force of attraction F_A is calculated using Equation 2.14 taking the interionic separation r to be r_0 the equilibrium separation distance. This value of r_0 is the sum of the atomic radii of the Mg^{2+} and F^- ions (per Equation 2.15)—that is

$$r_0 = r_{Mg^{2+}} + r_{F^-}$$

$$= 0.072 \text{ nm} + 0.133 \text{ nm} = 0.205 \text{ nm} = 0.205 \times 10^{-9} \text{ m}$$

We may now compute F_A using Equation 2.14. If was assume that ion 1 is Mg^{2+} and ion 2 is F^- then the respective charges on these ions are $Z_1 = Z_{Mg^{2+}} = +2$, whereas $Z_2 = Z_{F^-} = -1$. Therefore, we determine F_A as follows:

$$F_A = \frac{(2.31 \times 10^{-28} \text{ N-m}^2)\left(|Z_1|\right)\left(|Z_2|\right)}{r_0^2}$$

$$= \frac{(2.31 \times 10^{-28} \text{ N-m}^2)\left(|+2|\right)\left(|-1|\right)}{(0.205 \times 10^{-9} \text{ m})^2}$$

$$= 1.10 \times 10^{-8} \text{ N}$$

(b) At the equilibrium separation distance the sum of attractive and repulsive forces is zero according to Equation 2.4. Therefore

$$F_R = -F_A$$

$$= -(1.10 \times 10^{-8} \text{ N}) = -1.10 \times 10^{-8} \text{ N}$$

2.17 *The force of attraction between a divalent cation and a divalent anion is 1.67* $\times 10^{-8}$ *N. If the ionic radius of the cation is 0.080 nm, what is the anion radius?*

Solution

To begin, let us rewrite Equation 2.15 to read as follows:

$$r_0 = r_C + r_A$$

in which r_C and r_A represent, respectively, the radii of the cation and anion. Thus, this problem calls for us to determine the value of r_A. However, before this is possible, it is necessary to compute the value of r_0 using Equation 2.14, and replacing the parameter *r* with r_0. Solving this expression for r_0 leads to the following:

$$r_0 = \sqrt{\frac{(2.31 \times 10^{-28} \text{ N-m}^2)\left(|Z_C|\right)\left(|Z_A|\right)}{F_A}}$$

Here Z_C and Z_A represent charges on the cation and anion, respectively. Furthermore, inasmuch as both ion are divalent means that $Z_C = +2$ and $Z_A = -2$. The value of r_0 is determined as follows:

$$r_0 = \sqrt{\frac{(2.31 \times 10^{-28} \text{ N-m}^2)\left(|+2|\right)\left(|-2|\right)}{1.67 \times 10^{-8} \text{ N}}}$$

$$= 0.235 \times 10^{-9} \text{ m} = 0.235 \text{ nm}$$

Using the version of Equation 2.15 given above, and incorporating this value of r_0 and also the value of r_C given in the problem statement (0.080 nm) it is possible to solve for r_A:

$$r_A = r_0 - r_C$$

$$= 0.235 \text{ nm} - 0.080 \text{ nm} = 0.155 \text{ nm}$$

2.18 *The net potential energy between two adjacent ions, E_N, may be represented by the sum of Equations 2.9 and 2.11; that is,*

$$E_N = -\frac{A}{r} + \frac{B}{r^n} \qquad (2.17)$$

Calculate the bonding energy E_0 in terms of the parameters A, B, and n using the following procedure:

1. Differentiate E_N with respect to r, and then set the resulting expression equal to zero, since the curve of E_N versus r is a minimum at E_0.

2. Solve for r in terms of A, B, and n, which yields r_0, the equilibrium interionic spacing.

3. Determine the expression for E_0 by substitution of r_0 into Equation 2.17.

Solution

(a) Differentiation of Equation 2.17 yields

$$\frac{dE_N}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} + \frac{d\left(\frac{B}{r^n}\right)}{dr}$$

$$= \frac{A}{r^{(1 + 1)}} - \frac{nB}{r^{(n + 1)}} = 0$$

(b) Now, solving for r (= r_0)

$$\frac{A}{r_0^2} = \frac{nB}{r_0^{(n + 1)}}$$

or

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1 - n)}$$

(c) Substitution for r_0 into Equation 2.17 and solving for E (= E_0) yields

$$E_0 = -\frac{A}{r_0} + \frac{B}{r_0^n}$$

$$= -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1 - n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1 - n)}}$$

2.19 *For a Na^+–Cl^- ion pair, attractive and repulsive energies E_A and E_R, respectively, depend on the distance between the ions r, according to*

$$E_A = -\frac{1.436}{r}$$

$$E_R = \frac{7.32 \times 10^{-6}}{r^8}$$

For these expressions, energies are expressed in electron volts per Na^+–Cl^- pair, and r is the distance in nanometers. The net energy E_N is just the sum of the preceding two expressions.

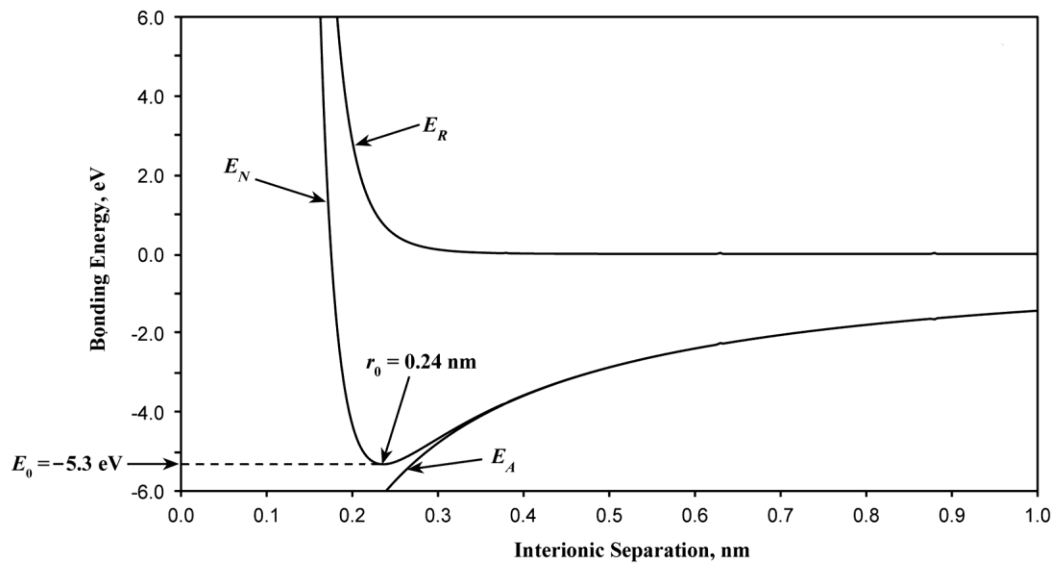
(a) Superimpose on a single plot E_N, E_R, and E_A versus r up to 1.0 nm.

(b) On the basis of this plot, determine (i) the equilibrium spacing r_0 between the Na^+ and Cl^- ions, and (ii) the magnitude of the bonding energy E_0 between the two ions.

(c) Mathematically determine the r_0 and E_0 values using the solutions to Problem 2.18, and compare these with the graphical results from part (b).

Solution

(a) Curves of E_A, E_R, and E_N are shown on the plot below.



(b) From this plot:

r_0 = 0.24 nm

E_0 = –5.3 eV

(c) From Equation 2.17 for E_N

$$A = 1.436$$

$$B = 7.32 \times 10^{-6}$$

$$n = 8$$

Thus,

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1 - n)}$$

$$= \left[\frac{1.436}{(8)(7.32 \times 10^{-6})}\right]^{1/(1 - 8)} = 0.236 \text{ nm}$$

and

$$E_0 = - \frac{1.436}{\left[\frac{1.436}{(8)(7.32 \times 10^{-6})}\right]^{1/(1 - 8)}} + \frac{7.32 \times 10^{-6}}{\left[\frac{1.436}{(8)(7.32 \times 10^{-6})}\right]^{8/(1 - 8)}}$$

$$= -5.32 \text{ eV}$$

2.20 *Consider a hypothetical X^+–Y^- ion pair for which the equilibrium interionic spacing and bonding energy values are 0.38 nm and –5.37 eV, respectively. If it is known that n in Equation 2.17 has a value of 8, using the results of Problem 2.18, determine explicit expressions for attractive and repulsive energies E_A and E_R of Equations 2.9 and 2.11.*

<u>Solution</u>

(a) This problem gives us, for a hypothetical X^+-Y^- ion pair, values for r_0 (0.38 nm), E_0 (– 5.37 eV), and n (8), and asks that we determine explicit expressions for attractive and repulsive energies of Equations 2.9 and 2.11. In essence, it is necessary to compute the values of A and B in these equations. Expressions for r_0 and E_0 in terms of n, A, and B were determined in Problem 2.18, which are as follows:

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1-n)}$$

$$E_0 = -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1-n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1-n)}}$$

Thus, we have two simultaneous equations with two unknowns (viz. A and B). Upon substitution of values for r_0 and E_0 in terms of n, the above two equations become

$$0.38 \text{ nm} = \left(\frac{A}{8B}\right)^{1/(1-8)} = \left(\frac{A}{8B}\right)^{-1/7}$$

and

$$-5.37 \text{ eV} = -\frac{A}{\left(\frac{A}{8B}\right)^{1/(1-8)}} + \frac{B}{\left(\frac{A}{8B}\right)^{8/(1-8)}}$$

$$= -\frac{A}{\left(\frac{A}{8B}\right)^{-1/7}} + \frac{B}{\left(\frac{A}{10B}\right)^{-8/7}}$$

We now want to solve these two equations simultaneously for values of A and B. From the first of these two equations, solving for $A/8B$ leads to

$$\frac{A}{8B} = (0.38 \text{ nm})^{-7}$$

Furthermore, from the above equation the A is equal to

$$A = 8B(0.38 \text{ nm})^{-7}$$

When the above two expressions for $A/8B$ and A are substituted into the above expression for E_0 (– 5.37 eV), the following results

$$-5.37 \text{ eV} = = -\frac{A}{\left(\frac{A}{8B}\right)^{-1/7}} + \frac{B}{\left(\frac{A}{10B}\right)^{-8/7}}$$

$$= -\frac{8B(0.38 \text{ nm})^{-7}}{\left[(0.38 \text{ nm})^{-7}\right]^{-1/7}} + \frac{B}{\left[(0.38 \text{ nm})^{-7}\right]^{-8/7}}$$

$$= -\frac{8B(0.38 \text{ nm})^{-7}}{0.38 \text{ nm}} + \frac{B}{(0.38 \text{ nm})^{8}}$$

Or

$$-5.37 \text{ eV} = = -\frac{8B}{(0.38 \text{ nm})^{8}} + \frac{B}{(0.38 \text{ nm})^{8}} = -\frac{7B}{(0.38 \text{ nm})^{8}}$$

Solving for B from this equation yields

$$B = 3.34 \times 10^{-4} \text{ eV-nm}^{8}$$

Furthermore, the value of A is determined from one of the previous equations, as follows:

$$A = 8B(0.38 \text{ nm})^{-7} = (8)\left(3.34 \times 10^{-4} \text{ eV-nm}^{8}\right)(0.38 \text{ nm})^{-7}$$

$$= 2.34 \text{ eV-nm}$$

Thus, Equations 2.9 and 2.11 become

$$E_A = -\frac{2.34}{r}$$

$$E_R = \frac{3.34 \times 10^{-4}}{r^{8}}$$

Of course these expressions are valid for r and E in units of nanometers and electron volts, respectively.

2.21 *The net potential energy* E_N *between two adjacent ions is sometimes represented by the expression*

$$E_N = -\frac{C}{r} + D\exp\left(-\frac{r}{r}\right) \qquad (2.18)$$

in which r is the interionic separation and C, D, and ρ are constants whose values depend on the specific material.

(a) Derive an expression for the bonding energy E_0 *in terms of the equilibrium interionic separation* r_0 *and the constants D and ρ using the following procedure:*

(i) Differentiate E_N *with respect to r, and set the resulting expression equal to zero.*

(ii) Solve for C in terms of D, ρ, and r_0.

(iii) Determine the expression for E_0 *by substitution for C in Equation 2.18.*

(b) Derive another expression for E_0 *in terms of* r_0, *C, and ρ using a procedure analogous to the one outlined in part* (a).

Solution

(a) Differentiating Equation 2.18 with respect to *r* yields

$$\frac{dE}{dr} = \frac{d\left(-\frac{C}{r}\right)}{dr} - \frac{d\left[D\exp\left(-\frac{r}{r}\right)\right]}{dr}$$

$$= \frac{C}{r^2} - \frac{D\exp\left(-\frac{r}{r}\right)}{r}$$

At $r = r_0$, $dE/dr = 0$, and

$$\frac{C}{r_0^2} = \frac{D\exp\left(-\frac{r_0}{r}\right)}{r} \qquad (2.18a)$$

Solving for *C* yields

$$C = \frac{r_0^2 D\exp\left(-\frac{r_0}{r}\right)}{r}$$

Substitution of this expression for C into Equation 2.18 yields an expression for E_0 as

$$E_0 = -\frac{\dfrac{r_0^2 D \exp\left(-\dfrac{r_0}{r}\right)}{\mathrm{r}}}{r_0} + D \exp\left(-\frac{r_0}{r}\right)$$

$$= -\frac{r_0 D \exp\left(-\dfrac{r_0}{r}\right)}{\mathrm{r}} + D \exp\left(-\frac{r_0}{r}\right)$$

$$= D\left(1 - \frac{r_0}{r}\right)\exp\left(-\frac{r_0}{r}\right)$$

(b) Now solving for D from Equation 2.18a above yields

$$D = \frac{C r \exp\left(\dfrac{r_0}{r}\right)}{r_0^2}$$

Substitution of this expression for D into Equation 2.18 yields an expression for E_0 as

$$E_0 = -\frac{C}{r_0} + \left[\frac{C r \exp\left(\dfrac{r_0}{r}\right)}{r_0^2}\right]\exp\left(-\frac{r_0}{r}\right)$$

$$= -\frac{C}{r_0} + \frac{C r}{r_0^2}$$

$$E_0 = \frac{C}{r_0}\left(\frac{r}{r_0} - 1\right)$$

Primary Interatomic Bonds

2.22 *(a) Briefly cite the main differences among ionic, covalent, and metallic bonding.*
(b) State the Pauli exclusion principle.

Solution

(a) The main differences between the various forms of primary bonding are:

Ionic--there is electrostatic attraction between oppositely charged ions.

Covalent--there is electron sharing between two adjacent atoms such that each atom assumes a stable electron configuration.

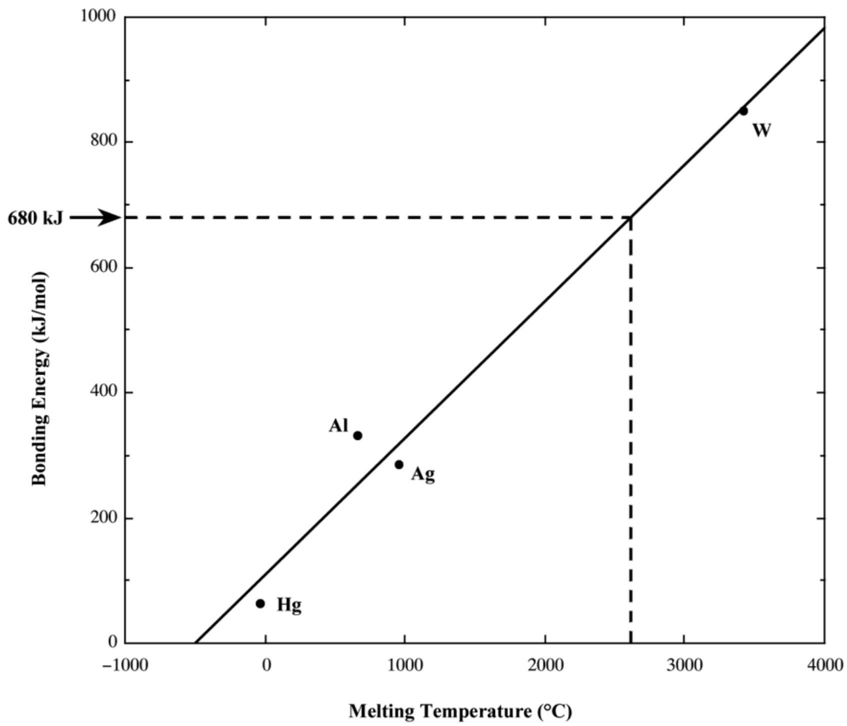
Metallic--the positively charged ion cores are shielded from one another, and also "glued" together by the sea of valence electrons.

(b) The Pauli exclusion principle states that each electron state can hold no more than two electrons, which must have opposite spins.

2.23 *Make a plot of bonding energy versus melting temperature for the metals listed in Table 2.3. Using this plot, approximate the bonding energy for molybdenum, which has a melting temperature of 2617°C.*

Solution

Below is plotted the bonding energy versus melting temperature for these four metals. From this plot, the bonding energy for molybdenum (melting temperature of 2617°C) should be approximately 680 kJ/mol. The experimental value is 660 kJ/mol.



Secondary Bonding or van der Waals Bonding

2.24 *Explain why hydrogen fluoride (HF) has a higher boiling temperature than hydrogen chloride (HCl) (19.4 vs. –85°C), even though HF has a lower molecular weight.*

Solution

The intermolecular bonding for HF is hydrogen, whereas for HCl, the intermolecular bonding is van der Waals. Since the hydrogen bond is stronger than van der Waals, HF will have a higher melting temperature.

Mixed Bonding

2.25 *Compute the %IC of the interatomic bond for each of the following compounds: MgO, GaP, CsF, CdS, and FeO.*

Solution

The percent ionic character is a function of the electron negativities of the ions X_A and X_B according to Equation 2.16. The electronegativities of the elements are found in Figure 2.9.

For MgO, X_{Mg} = 1.3 and X_O = 3.5, and therefore,

$$\%IC = \left[1 - \exp(-0.25)(3.5 - 1.3)^2\right] \times 100 = 70.1\%$$

For GaP, X_{Ga} = 1.8 and X_P = 2.1, and therefore,

$$\%IC = \left[1 - \exp(-0.25)(2.1 - 1.8)^2\right] \times 100 = 2.2\%$$

For CsF, X_{Cs} = 0.9 and X_F = 4.1, and therefore,

$$\%IC = \left[1 - \exp(-0.25)(4.1 - 0.9)^2\right] \times 100 = 92.3\%$$

For CdS, X_{Cd} = 1.5 and X_S = 2.4, and therefore,

$$\%IC = \left[1 - \exp(-0.25)(2.4 - 1.5)^2\right] \times 100 = 18.3\%$$

For FeO, X_{Fe} = 1.7 and X_O = 3.5, and therefore,

$$\%IC = \left[1 - \exp(-0.25)(3.5 - 1.7)^2\right] \times 100 = 55.5\%$$

2.26 *(a) Calculate %IC of the interatomic bonds for the intermetallic compound* Al_6Mn*. (b) On the basis of this result what type of interatomic bonding would you expect to be found in* Al_6Mn*?*

Solution

(a) The percent ionic character is a function of the electron negativities of the ions X_A and X_B according to Equation 2.16. The electronegativities for Al and Mn (Figure 2.9) are 1.5 and 1.6, respectively. Therefore the percent ionic character is determined using Equation 2.16 as follows:

$$\%IC = \left[1 - \exp(-0.25)(1.6 - 1.5)^2\right] \times 100 = 0.25\%$$

(b) Because the percent ionic character is exceedingly small (0.25%) and this intermetallic compound is composed of two metals, the bonding is completely metallic.

Bonding Type-Material Classification Correlations

2.27 *What type(s) of bonding would be expected for each of the following materials: solid xenon, calcium fluoride (CaF_2), bronze, cadmium telluride (CdTe), rubber, and tungsten?*

Solution

For solid xenon, the bonding is van der Waals since xenon is an inert gas.

For CaF_2, the bonding is predominantly ionic (but with some slight covalent character) on the basis of the relative positions of Ca and F in the periodic table.

For bronze, the bonding is metallic since it is a metal alloy (composed of copper and tin).

For CdTe, the bonding is predominantly covalent (with some slight ionic character) on the basis of the relative positions of Cd and Te in the periodic table.

For rubber, the bonding is covalent with some van der Waals. (Rubber is composed primarily of carbon and hydrogen atoms.)

For tungsten, the bonding is metallic since it is a metallic element from the periodic table.

Fundamentals of Engineering Questions and Problems

2.1FE *The chemical composition of the repeat unit for nylon 6,6 is given by the formula* $C_{12}H_{22}N_2O_2$*. Atomic weights for the constituent elements are* $A_C = 12$, $A_H = 1$, $A_N = 14$, *and* $A_O = 16$*. According to this chemical formula (for nylon 6,6), the percent (by weight) of carbon in nylon 6,6 is most nearly:*

(A) 31.6%

(B) 4.3%

(C) 14.2%

(D) 63.7%

Solution

The total atomic weight of one repeat unit of nylon 6,6, A_{total}, is calculated as

$$A_{total} = (12 \text{ atoms})(A_C) + (22 \text{ atoms})(A_H) + (2 \text{ atoms})(A_N) + (2 \text{ atoms})(A_O)$$

$$= (12 \text{ atoms})(12 \text{ g/mol}) + (22 \text{ atoms})(1 \text{ g/mol}) + (2 \text{ atoms})(14 \text{ g/mol}) + (2 \text{ atoms})(16 \text{ g/mol}) = 226 \text{ g/mol}$$

Therefore the percent by weight of carbon is calculated as

$$\text{C(wt\%)} = \frac{(12 \text{ atoms})(A_C)}{A_{\text{total}}} \times 100$$

$$= \frac{(12 \text{ atoms})(12 \text{ g/mol})}{226 \text{ g/mol}} \times 100 = 63.7\%$$

which is answer D.

2.2FE *Which of the following electron configurations is for an inert gas?*

(A) $1s^2 2s^2 2p^6 3s^2 3p^6$

(B) $1s^2 2s^2 2p^6 3s^2$

(C) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(D) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

Solution

The correct answer is A. The $1s^2 2s^2 2p^6 3s^2 3p^6$ electron configuration is that of an inert gas because of filled 3*s* and 3*p* subshells.

2.3FE *What type(s) of bonding would be expected for bronze (a copper-tin alloy)?*

(A) Ionic bonding

(B) Metallic bonding

(C) Covalent bonding with some van der Waals bonding

(D) van der Waals bonding

Solution

The correct answer is B. For bronze, the bonding is metallic because it is a metal alloy.

2.4FE *What type(s) of bonding would be expected for rubber?*

(A) Ionic bonding

(B) Metallic bonding

(C) Covalent bonding with some van der Waals bonding

(D) van der Waals bonding

<u>Solution</u>

The correct answer is C. For rubber, the bonding is covalent with some van der Waals bonding. (Rubber is composed primarily of carbon and hydrogen atoms.)

CHAPTER 3

THE STRUCTURE OF CRYSTALLINE SOLIDS

PROBLEM SOLUTIONS

Fundamental Concepts

3.1 *What is the difference between atomic structure and crystal structure?*

Solution

Atomic structure relates to the number of protons and neutrons in the nucleus of an atom, as well as the number and probability distributions of the constituent electrons. On the other hand, crystal structure pertains to the arrangement of atoms in the crystalline solid material.

Unit Cells

Metallic Crystal Structures

3.2 *If the atomic radius of lead is 0.175 nm, calculate the volume of its unit cell in cubic meters.*

Solution

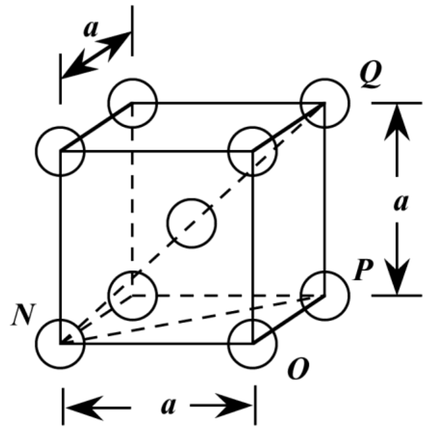
Lead has an FCC crystal structure and an atomic radius of 0.1750 nm (Table 3.1). The FCC unit cell volume may be computed from Equation 3.6 as

$$V_C = 16R^3\sqrt{2} = (16)\left(0.1750 \times 10^{-9} \text{ m}\right)^3\left(\sqrt{2}\right) = 1.213 \times 10^{-28} \text{ m}^3$$

3.3 *Show for the body-centered cubic crystal structure that the unit cell edge length a and the atomic radius R are related through* $a = 4R/\sqrt{3}$.

Solution

This problem calls for a demonstration of the relationship $a = \frac{4R}{\sqrt{3}}$ for BCC. Consider the BCC unit cell shown below



From the triangle *NOP*

$$(\overline{NP})^2 = a^2 + a^2 = 2a^2$$

And then for triangle *NPQ*,

$$(\overline{NQ})^2 = (\overline{QP})^2 + (\overline{NP})^2$$

But $\overline{NQ} = 4R$, R being the atomic radius. Also, $\overline{QP} = a$. Therefore,

$$(4R)^2 = a^2 + 2a^2$$

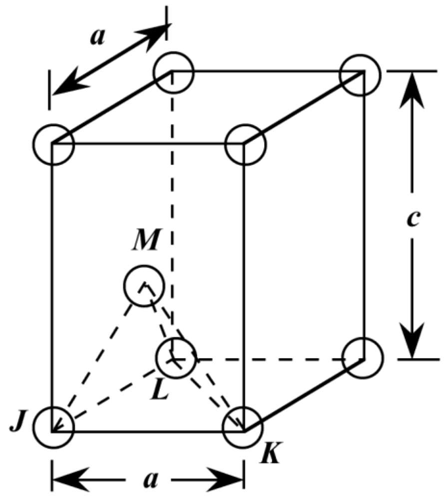
And solving for a:

$$a = \frac{4R}{\sqrt{3}}$$

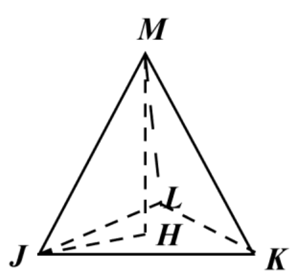
3.4 *For the HCP crystal structure, show that the ideal c/a ratio is 1.633.*

Solution

We are asked to show that the ideal *c/a* ratio for HCP is 1.633. A sketch of one-third of an HCP unit cell is shown below.



Consider the tetrahedron labeled as *JKLM*, which is reconstructed as follows:



The atom at point *M* is midway between the top and bottom faces of the unit cell--that is $\overline{MH} = c/2$. And, since atoms at points *J*, *K*, and *M*, all touch one another,

$$\overline{JM} = \overline{JK} = 2R = a$$

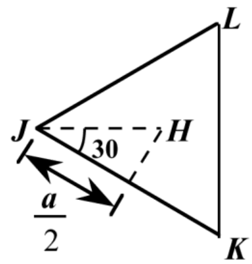
where *R* is the atomic radius. Furthermore, from triangle *JHM*,

$$(\overline{JM})^2 = (\overline{JH})^2 + (\overline{MH})^2$$

or

$$a^2 = (\overline{JH})^2 + \left(\frac{c}{2}\right)^2$$

Now, we can determine the $\overline{JH}$ length by consideration of triangle *JKL*, which is an equilateral triangle,



From this triangle it is the case that the angle subtended between the lines $\overline{JK}$ and $\overline{JH}$ is 30°, and

$$\cos 30° = \frac{a/2}{JH} = \frac{\sqrt{3}}{2}$$

which reduces to the following:

$$\overline{JH} = \frac{a}{\sqrt{3}}$$

Substitution of this value for $\overline{JH}$ into the above expression yields

$$a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

And when we solve for *c/a*

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

3.5 *Show that the atomic packing factor for BCC is 0.68.*

Solution

The atomic packing factor is defined as the ratio of sphere volume (V_S) to the total unit cell volume (V_C), or

$$\text{APF} = \frac{V_S}{V_C}$$

Because there are two spheres associated with each unit cell for BCC

$$V_S = 2(\text{sphere volume}) = 2\left(\frac{4\pi R^3}{3}\right) = \frac{8\pi R^3}{3}$$

Also, the unit cell has cubic symmetry, that is $V_C = a^3$. But a depends on R according to Equation 3.4, and

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

Thus,

$$\text{APF} = \frac{V_S}{V_C} = \frac{8\pi R^3/3}{64R^3/3\sqrt{3}} = 0.68$$

3.6 *Show that the atomic packing factor for HCP is 0.74.*

Solution

The APF is just the total sphere volume-unit cell volume ratio—i.e., (V_S/V_C). For HCP, there are the equivalent of six spheres per unit cell, and thus

$$V_S = 6\left(\frac{4\pi R^3}{3}\right) = 8\pi R^3$$

The unit cell volume (V_C) for the HCP unit cell was determined in Example Problem 3.3 and given in Equation 3.7b as

$$V_C = 6R^2c\sqrt{3}$$

And because $c = 1.633a = 2R(1.633)$

$$V_C = (6R^3\sqrt{3})(2)(1.633R) = 12\sqrt{3}(1.633)R^3$$

Thus,

$$\text{APF} = \frac{V_S}{V_C} = \frac{8\pi R^3}{12\sqrt{3}(1.633)R^3} = 0.74$$

Density Computations

3.7 *Molybdenum* (*Mo*) has *a BCC crystal structure, an atomic radius of 0.1363 nm, and an atomic weight of 95.94 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover of the book.*

Solution

This problem calls for a computation of the density of molybdenum. According to Equation 3.8

$$r = \frac{nA_{\text{Mo}}}{V_C N_{\text{A}}}$$

For BCC, n = 2 atoms/unit cell. Furthermore, because $V_C = a^3$, and $a = \frac{4R}{\sqrt{3}}$ (Equation 3.4), then

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3$$

Thus, realizing that A_{Mo} = 95.94 g/mol, using the above version of Equation 3.8, we compute the theoretical density for Mo as follows:

$$r = \frac{nA_{\text{Mo}}}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_{\text{A}}}$$

$$= \frac{\text{(2 atoms/unit cell)(95.94 g/mol)}}{\left[(4)\left(0.1363 \times 10^{-7}\text{ cm}\right)^3 / \sqrt{3}\right]^3 / \text{(unit cell)}\left(6.022 \times 10^{23}\text{ atoms/mol}\right)}$$

$$= 10.22 \text{ g/cm}^3$$

The value given inside the front cover is 10.22 g/cm^3.

3.8 *Strontium (Sr) has an FCC crystal structure, an atomic radius of 0.215 nm and an atomic weight of 87.62 g/mol. Calculate the theoretical density for Sr.*

Solution

According to Equation 3.8

$$\rho = \frac{nA_{\text{Sr}}}{V_C N_{\text{A}}}$$

For FCC, n = 4 atoms/unit cell. Furthermore, because $V_C = a^3$, and $a = 2R\sqrt{2}$ (Equation 3.1), then

$$V_C = \left(2R\sqrt{2}\right)^3$$

Thus, realizing that A_{Sr} = 87.62 g/mol, using the above version of Equation 3.8, we compute the theoretical density of Sr as follows:

$$\rho = \frac{nA_{\text{Sr}}}{\left(2R\sqrt{2}\right)^3 N_{\text{A}}}$$

$$= \frac{\text{(4 atoms/unit cell)(87.62 g/mol)}}{\left[(2)\left(0.215 \times 10^{-7}\text{ cm}\right)^3\sqrt{2}\right]^3\text{/(unit cell)}\left(6.022 \times 10^{23}\text{ atoms/mol}\right)}$$

$$= 2.59\text{ g/cm}^3$$

The experimental density for Sr is 2.54 g/cm^3.

3.9 *Calculate the radius of a palladium (Pd) atom, given that Pd has an FCC crystal structure, a density of 12.0 g/cm*^{3}*, and an atomic weight of 106.4 g/mol.*

Solution

We are asked to determine the radius of a palladium atom, given that Pd has an FCC crystal structure. For FCC, n = 4 atoms/unit cell, and $V_C = 16R^3\sqrt{2}$ (Equation 3.6). Now, the density of Pd may be expressed using a form of Equation 3.8 as follows:

$$r = \frac{nA_{\text{Pd}}}{V_C N_{\text{A}}}$$

$$= \frac{nA_{\text{Pd}}}{\left(16R^3\sqrt{2}\right)N_{\text{A}}}$$

Solving for R from the above expression yields

$$R = \left(\frac{nA_{\text{Pd}}}{16\,r\,N_{\text{A}}\sqrt{2}}\right)^{1/3}$$

Incorporation into this expression values for A_{Pd} , n, and ρ leads to the following value of R:

$$= \left[\frac{(4\text{ atoms/unit cell})\left(106.4\text{ g/mol}\right)}{(16)\left(12.0\text{ g/cm}^3\right)\left(6.022\times 10^{23}\text{ atoms/mol}\right)\left(\sqrt{2}\right)}\right]^{1/3}$$

$$= 1.38 \times 10^{-8}\text{ cm} = 0.138\text{ nm}$$

3.10 *Calculate the radius of a tantalum (Ta) atom, given that Ta has a BCC crystal structure, a density of 16.6 g/cm^3, and an atomic weight of 180.9 g/mol.*

<u>Solution</u>

It is possible to compute the radius of a Ta atom using a rearranged form of Equation 3.8. For BCC, n = 2 atoms/unit cell. Furthermore, because $V_C = a^3$ and $a = \frac{4R}{\sqrt{3}}$ (Equation 3.4) an expression for the BCC unit cell volume is as follows:

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

For Ta, Equation 3.8 takes the form

$$\rho = \frac{nA_{\text{Ta}}}{V_C N_A}$$

$$= \frac{nA_{\text{Ta}}}{\left(\frac{64R^3}{3\sqrt{3}}\right) N_A}$$

Solving for R in this equation yields

$$R = \left(\frac{3\sqrt{3}nA_{\text{Ta}}}{64\rho N_A}\right)^{1/3}$$

Upon incorporation of values of n, A_{Ta}, and ρ into this equation leads to the atomic radius of Ta as follows:

$$R = \left[\frac{(3\sqrt{3})(2 \text{ atoms/unit cell})(180.9 \text{ g/mol})}{(64)(16.6 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}\right]^{1/3}$$

$$= 1.43 \times 10^{-8} \text{ cm} = 0.143 \text{ nm}$$

3.11 *A hypothetical metal has the simple cubic crystal structure shown in Figure 3.3. If its atomic weight is 74.5 g/mol and the atomic radius is 0.145 nm, compute its density.*

Solution

For the simple cubic crystal structure (Figure 3.3), the value of n in Equation 3.8 is unity since there is only a single atom associated with each unit cell. Furthermore, for the unit cell edge length, $a = 2R$ (Figure 3.3); this means that the unit cell volume $V_C = a^3 = (2R)^3$. Therefore, Equation 3.8 takes the form

$$\rho = \frac{nA}{V_C N_A} = \frac{nA}{(2R)^3 N_A}$$

and incorporating values for R and A given in the problem statement, the density is determined as follows:

$$\rho = \frac{\text{(1 atom/unit cell)(74.5 g/mol)}}{\left\{\left[(2)(1.45 \times 10^{-8}\text{ cm})\right]^3\text{/unit cell}\right\}(6.022 \times 10^{23}\text{ atoms/mol})}$$

$$5.07\text{ g/cm}^3$$

3.12 *Titanium (Ti) has an HCP crystal structure and a density of 4.51 g/cm^3.*

(a) What is the volume of its unit cell in cubic meters?

(b) If the c/a ratio is 1.58, compute the values of c and a.

<u>Solution</u>

(a) The volume of the Ti unit cell may be computed using a rearranged form of Equation 3.8 as

$$V_C = \frac{nA_{\text{Ti}}}{\rho N_{\text{A}}}$$

For HCP, n = 6 atoms/unit cell, and the atomic weight for Ti, A_{Ti} = 47.9 g/mol. Thus,

$$V_C = \frac{(6\text{ atoms/unit cell})(47.9\text{ g/mol})}{\left(4.51\text{ g/cm}^3\right)\left(6.022 \times 10^{23}\text{ atoms/mol}\right)}$$

$$= 1.058 \times 10^{-22}\text{ cm}^3\text{/unit cell} = 1.058 \times 10^{-28}\text{ m}^3\text{/unit cell}$$

(b) From Equation 3.7a, for HCP the unit cell volume for is

$$V_C = \frac{3\sqrt{3}\,a^2 c}{2}$$

since, for Ti, $c = 1.58a$, then

$$V_C = \frac{3\sqrt{3}(1.58)\,a^3}{2} = 1.058 \times 10^{-22}\text{ cm}^3\text{/unit cell}$$

Now, solving for a

$$a = \left[\frac{(2)\left(1.058 \times 10^{-22}\text{ cm}^3\right)}{(3)\left(\sqrt{3}\right)(1.58)}\right]^{1/3}$$

$$= 2.96 \times 10^{-8}\text{ cm} = 0.296\text{ nm}$$

And finally, the value of c is

$$c = 1.58a = (1.58)(0.296\text{ nm}) = 0.468\text{ nm}$$

3.13 *Magnesium (Mg) has an HCP crystal structure and a density of 1.74 g/cm*^{3}.

(a) What is the volume of its unit cell in cubic centimeters?

(b) If the c/a ratio is 1.624, compute the values of c and a.

Solution

(a) The volume of the Mg unit cell may be computed using a rearranged form of Equation 3.8 as

$$V_C = \frac{nA_{\text{Mg}}}{\rho N_{\text{A}}}$$

Now, for HCP, n = 6 atoms/unit cell, and the atomic weight for Mg, A_{Mg} = 24.3 g/mol. Thus,

$$V_C = \frac{(6 \text{ atoms/unit cell})(24.3 \text{ g/mol})}{(1.74 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 1.39 \times 10^{-22} \text{ cm}^3\text{/unit cell} = 1.39 \times 10^{-28} \text{ m}^3\text{/unit cell}$$

(b) From Equation 3.7a, for HCP the unit cell volume for is

$$V_C = \frac{3\sqrt{3}\,a^2 c}{2}$$

but, since, for Mg, $c = 1.624a$, then

$$V_C = \frac{3\sqrt{3}(1.624)a^3}{2} = 1.39 \times 10^{-22} \text{ cm}^3\text{/unit cell}$$

Now, solving for a

$$a = \left[\frac{(2)(1.39 \times 10^{-22} \text{ cm}^3)}{(3)(\sqrt{3})(1.624)}\right]^{1/3}$$

$$= 3.21 \times 10^{-8} \text{ cm} = 0.321 \text{ nm}$$

And finally, the value of c is

$$c = 1.624a = (1.624)(0.321 \text{ nm}) = 0.521 \text{ nm}$$

3.14 *Using atomic weight, crystal structure, and atomic radius data tabulated inside the front cover of the book, compute the theoretical densities of aluminum (Al), nickel (Ni), magnesium (Mg), and tungsten (W), and then compare these values with the measured densities listed in this same table. The c/a ratio for magnesium is 1.624.*

Solution

This problem asks that we calculate the theoretical densities of Al, Ni, Mg, and W.

Since Al has an FCC crystal structure, n = 4, and $V_C = 16R^3\sqrt{2}$ (Equation 3.6). From inside the front cover, for Al, R = 0.143 nm (1.43 × 10^{-8} cm) and A_{Al} = 26.98 g/mol. Employment of Equation 3.8 yields

$$\rho = \frac{nA_{\text{Al}}}{V_C N_{\text{A}}}$$

$$= \frac{(4 \text{ atoms/unit cell})(26.98 \text{ g/mol})}{\left\{\left[(16)(1.43 \times 10^{-8} \text{ cm})^3(\sqrt{2})\right]/(\text{unit cell})\right\}(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 2.71 \text{ g/cm}^3$$

The value given in the table inside the front cover is 2.71 g/cm^3.

Nickel also has an FCC crystal structure and R = 0.125 nm (1.25 × 10^{-8} cm) and A_{Ni} = 58.69 g/mol. (Again, for FCC, FCC crystal structure, n = 4, and $V_C = 16R^3\sqrt{2}$.) Therefore, we determine the density using Equation 3.8 as follows:

$$\rho = \frac{(4 \text{ atoms/unit cell})(58.69 \text{ g/mol})}{\left\{\left[(16)(1.25 \times 10^{-8} \text{ cm})^3(\sqrt{2})\right]/(\text{unit cell})\right\}(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 8.82 \text{ g/cm}^3$$

The value given in the table is 8.90 g/cm^3.

Magnesium has an HCP crystal structure, and from Equation 3.7a,

$$V_C = \frac{3a^2c\sqrt{3}}{2}$$

And, since $c = 1.624a$ and $a = 2R$ = 2(1.60 × 10^{-8} cm) = 3.20 × 10^{-8} cm, the unit cell volume is equal to

$$V_C = \frac{\left(3\sqrt{3}\right)(1.624)\left(3.20 \times 10^{-8}\ \text{cm}\right)^3}{2} = 1.38 \times 10^{-22}\ \text{cm}^3/\text{unit cell}$$

Also, there are 6 atoms/unit cell for HCP. Therefore the theoretical density is calculated using Equation 3.8 as

$$\rho = \frac{nA_{\text{Mg}}}{V_C N_{\text{A}}}$$

$$= \frac{\text{(6 atoms/unit cell)(24.31 g/mol)}}{\left(1.38 \times 10^{-22}\ \text{cm}^3/\text{unit cell}\right)\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 1.75\ \text{g/cm}^3$$

The value given in the table is 1.74 g/cm^3.

Tungsten has a BCC crystal structure for which $n = 2$ and $a = \dfrac{4R}{\sqrt{3}}$ (Equation 3.4); also $A_{\text{W}} = 183.84$ g/mol and $R = 0.137$ nm. Therefore, employment of Equation 3.8 (and realizing that $V_C = a^3$) yields the following value for the density:

$$\rho = \frac{\text{(2 atoms/unit cell)(183.84 g/mol)}}{\left\{\left[\dfrac{(4)\left(1.37 \times 10^{-8}\ \text{cm}\right)}{\sqrt{3}}\right]^3 /(\text{unit cell})\right\}\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 19.3\ \text{g/cm}^3$$

The value given in the table is 19.3 g/cm^3.

3.15 *Niobium (Nb) has an atomic radius of 0.1430 nm and a density of 8.57 g/cm*^{3}*. Determine whether it has an FCC or a BCC crystal structure.*

Solution

In order to determine whether Nb has an FCC or a BCC crystal structure, we need to compute its density for each of the crystal structures. For FCC, n = 4, and $a = 2R\sqrt{2}$ (Equation 3.1). Also, from Figure 2.8, its atomic weight is 92.91 g/mol. Thus, for FCC (employing Equation 3.8)

$$\rho = \frac{nA_{\text{Nb}}}{V_C N_{\text{A}}} = \frac{nA_{\text{Nb}}}{a^3 N_{\text{A}}} = \frac{nA_{\text{Nb}}}{(2R\sqrt{2})^3 N_{\text{A}}}$$

$$= \frac{\text{(4 atoms/unit cell)(92.91 g/mol)}}{\left\{\left[(2)(1.43 \times 10^{-8}\text{ cm})(\sqrt{2})\right]^3/\text{(unit cell)}\right\}(6.022 \times 10^{23}\text{ atoms/mol})}$$

$$= 9.33 \text{ g/cm}^3$$

For BCC, n = 2, and $a = \frac{4R}{\sqrt{3}}$ (Equation 3.4), thus

$$\rho = \frac{nA_{\text{Nb}}}{V_C N_{\text{A}}} = \frac{nA_{\text{Nb}}}{a^3 N_{\text{A}}} = \frac{nA_{\text{Nb}}}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_{\text{A}}}$$

$$\rho = \frac{\text{(2 atoms/unit cell)(92.91 g/mol)}}{\left\{\left[\frac{(4)(1.43 \times 10^{-8}\text{ cm})}{\sqrt{3}}\right]^3/\text{(unit cell)}\right\}(6.022 \times 10^{23}\text{ atoms/mol})}$$

$$= 8.57 \text{ g/cm}^3$$

which is the value provided in the problem statement. Therefore, Nb has the BCC crystal structure.

3.16 *The atomic weight, density, and atomic radius for three hypothetical alloys are listed in the following table. For each, determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination.*

Alloy	***Atomic Weight (g/mol)***	***Density (g/cm^3)***	***Atomic Radius (nm)***
A	*43.1*	*6.40*	*0.122*
B	*184.4*	*12.30*	*0.146*
C	*91.6*	*9.60*	*0.137*

Solution

For each of these three alloys we need, by trial and error, to calculate the density using Equation 3.8, and compare it to the value cited in the problem. For SC, BCC, and FCC crystal structures, the respective values of n are 1, 2, and 4, whereas the expressions for a (since $V_C = a^3$) are $2R$, $2R\sqrt{2}$, and $\frac{4R}{\sqrt{3}}$.

For alloy A, let us calculate ρ assuming a BCC crystal structure.

$$\rho = \frac{nA_\text{A}}{V_C N_\text{A}}$$

$$= \frac{nA_\text{A}}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_\text{A}}$$

$$= \frac{(2\text{ atoms/unit cell})(43.1\text{ g/mol})}{\left\{\left[\frac{(4)(1.22 \times 10^{-8}\text{ cm})}{\sqrt{3}}\right]^3 /(\text{unit cell})\right\}(6.022 \times 10^{23}\text{ atoms/mol})}$$

$$= 6.40\text{ g/cm}^3$$

Therefore, its crystal structure is BCC.

For alloy B, let us calculate ρ assuming a simple cubic crystal structure.

$$\rho = \frac{nA_\text{B}}{(2a)^3 N_\text{A}}$$

$$= \frac{(1\text{ atom/unit cell})(184.4\text{ g/mol})}{\left\{\left[(2)\left(1.46\times 10^{-8}\text{ cm}\right)\right]^3/(\text{unit cell})\right\}\left(6.022\times 10^{23}\text{ atoms/mol}\right)}$$

$$= 12.3\text{ g/cm}^3$$

Therefore, its crystal structure is simple cubic.

For alloy C, let us calculate ρ assuming a BCC crystal structure.

$$r = \frac{nA_C}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_A}$$

$$= \frac{(2\text{ atoms/unit cell})(91.6\text{ g/mol})}{\left\{\left[\frac{(4)\left(1.37\times 10^{-8}\text{ cm}\right)}{\sqrt{3}}\right]^3/(\text{unit cell})\right\}\left(6.022\times 10^{23}\text{ atoms/mol}\right)}$$

$$= 9.60\text{ g/cm}^3$$

Therefore, its crystal structure is BCC.

3.17 *The unit cell for uranium (U) has orthorhombic symmetry, with a, b, and c lattice parameters of 0.286, 0.587, and 0.495 nm, respectively. If its density, atomic weight, and atomic radius are 19.05 g/cm³, 238.03 g/mol, and 0.1385 nm, respectively, compute the atomic packing factor.*

Solution

In order to determine the APF for U, we need to compute both the unit cell volume (V_C) which is just the product of the three unit cell parameters, as well as the total sphere volume (V_S) which is just the product of the volume of a single sphere and the number of spheres in the unit cell (*n*). The value of *n* may be calculated from a rearranged form of Equation 3.8 as

$$n = \frac{\rho V_C N_A}{A_U}$$

$$= \frac{(19.05\ \text{g/cm}^3)(2.86)(5.87)(4.95)(\times\ 10^{-24}\ \text{cm}^3)(6.022 \times 10^{23}\ \text{atoms/mol})}{238.03\ \text{g/mol}}$$

$$= 4.01\ \text{atoms/unit cell}$$

Therefore, we determine the atomic packing factor using Equation 3.3 as

$$\text{APF} = \frac{V_S}{V_C} = \frac{(4)\left(\frac{4}{3}\pi R^3\right)}{(a)(b)(c)}$$

$$= \frac{(4)\left[\frac{4}{3}(\pi)(1.385 \times 10^{-8}\ \text{cm})^3\right]}{(2.86)(5.87)(4.95)(\times\ 10^{-24}\ \text{cm}^3)}$$

$$= 0.536$$

3.18 *Indium (In) has a tetragonal unit cell for which the a and c lattice parameters are 0.459 and 0.495 nm, respectively.*

(a) If the atomic packing factor and atomic radius are 0.693 and 0.1625 nm, respectively, determine the number of atoms in each unit cell.

(b) The atomic weight of indium is 114.82 g/mol; compute its theoretical density.

Solution

(a) For indium, and from the definition of the APF

$$\text{APF} = \frac{V_S}{V_C} = \frac{n\left(\frac{4}{3}\pi R^3\right)}{a^2 c}$$

we may solve for the number of atoms per unit cell, *n*, as

$$n = \frac{(\text{APF})\,a^2 c}{\frac{4}{3}\pi R^3}$$

$$= \frac{(0.693)(4.59)^2(4.95)\left(10^{-24}\ \text{cm}^3\right)}{\frac{4}{3}\pi\left(1.625 \times 10^{-8}\ \text{cm}\right)^3}$$

$$= 4.0 \text{ atoms/unit cell}$$

(b) In order to compute the density, we just employ Equation 3.8 as

$$\rho = \frac{nA_{\text{In}}}{a^2 c N_{\text{A}}}$$

$$= \frac{(4\ \text{atoms/unit cell})(114.82\ \text{g/mol})}{\left[\left(4.59 \times 10^{-8}\ \text{cm}\right)^2\left(4.95 \times 10^{-8}\ \text{cm}\right)/\text{unit cell}\right]\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 7.31\ \text{g/cm}^3$$

3.19 *Beryllium (Be) has an HCP unit cell for which the ratio of the lattice parameters c/a is 1.568. If the radius of the Be atom is 0.1143 nm, (a) determine the unit cell volume, and (b) calculate the theoretical density of Be and compare it with the literature value.*

Solution

(a) We are asked to calculate the unit cell volume for Be. The volume of an HCP unit cell is provided by Equation 3.7b as follows:

$$V_C = 6R^2c\sqrt{3}$$

But, c = 1.568a, and a = 2R, or c = (1.568)(2R) = 3.136R. Substitution of this expression for c into the above equation leads to

$$V_C = (6)(3.14)\ R^3\sqrt{3}$$

$$= (6)(3.14)\left(\sqrt{3}\right)\left[0.1143 \times 10^{-7}\ \text{cm}\right]^3 = 4.87 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

(b) The theoretical density of Be is determined, using Equation 3.8, as follows:

$$\rho = \frac{nA_{\text{Be}}}{V_C N_{\text{A}}}$$

For HCP, n = 6 atoms/unit cell, and for Be, A_{Be} = 9.01 g/mol (as noted inside the front cover)—and the value of V_C was determined in part (a). Thus, the theoretical density of Be is

$$\rho = \frac{(6\ \text{atoms/unit cell})(9.01\ \text{g/mol})}{\left(4.87 \times 10^{-23}\ \text{cm}^3/\text{unit cell}\right)\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 1.84\ \text{g/cm}^3$$

The literature value is 1.85 g/cm^3.

3.20 *Magnesium (Mg) has an HCP crystal structure, a c/a ratio of 1.624, and a density of 1.74 g/cm³. Compute the atomic radius for Mg.*

Solution

This problem calls for us to compute the atomic radius for Mg. In order to do this we must use Equation 3.8, as well as the expression that relates the atomic radius to the unit cell volume for HCP—Equation 3.7b—that is

$$V_C = 6R^2c\sqrt{3}$$

In this case $c = 1.624a$, but, for HCP, $a = 2R$, which means that

$$V_C = 6R^2(1.624)(2R)\sqrt{3} = (1.624)\left(12\sqrt{3}\right)R^3$$

And from Equation 3.8, the density is equal to

$$\rho = \frac{nA_{\text{Mg}}}{V_C N_{\text{A}}} = \frac{nA_{\text{Mg}}}{(1.624)\left(12\sqrt{3}\right)R^3 N_{\text{A}}}$$

And, solving for R from the above equation leads to the following:

$$R = \left[\frac{nA_{\text{Mg}}}{(1.624)\left(12\sqrt{3}\right)\rho N_{\text{A}}}\right]^{1/3}$$

For the HCP crystal structure, $n = 6$ and from the inside cover, the atomic weight of Mg is 24.31 g/mol. Upon incorporation of these values as well as the density of Mg provided in the problem statement, we compute the Mg's atomic radius as follows:

$$= \left[\frac{(6\text{ atoms/unit cell})(24.31\text{ g/mol})}{(1.624)\left(12\sqrt{3}\right)\left(1.74\text{ g/cm}^3\right)\left(6.022 \times 10^{23}\text{ atoms/mol}\right)}\right]^{1/3}$$

$$= 1.60 \times 10^{-8}\text{ cm} = 0.160\text{ nm}$$

3.21 *Cobalt (Co) has an HCP crystal structure, an atomic radius of 0.1253 nm, and a c/a ratio of 1.623. Compute the volume of the unit cell for Co.*

Solution

This problem asks that we calculate the unit cell volume for Co, which has an HCP crystal structure. In order to do this, it is necessary to use Equation 3.7b—an expression for the volume of an HCP unit cell in terms of the atomic radius *R* and the lattice parameter –that is

$$V_C = 6R^2c\sqrt{3}$$

The problem states that $c = 1.623a$; also, it is the case for HCP that $a = 2R$. Making these substitutions into the previous equation yields

$$V_C = (1.623)\left(12\sqrt{3}\right) R^3$$

And incorporation of the value of *R* provided in the problem statement leads to the following value for the unit cell volume:

$$V_C = (1.623)\left(12\sqrt{3}\right)\left(1.253 \times 10^{-8}\ \text{cm}\right)^3 = 6.64 \times 10^{-23}\ \text{cm}^3 = 6.64 \times 10^{-2}\ \text{nm}^3$$

Polymorphism and Allotropy

3.22 *Iron (Fe) undergoes an allotropic transformation at 912°C: upon heating from a BCC (*α *phase) to an FCC (*γ *phase). Accompanying this transformation is a change in the atomic radius of Fe—from* R_{BCC} *= 0.12584 nm to* R_{FCC} *= 0.12894 nm—and, in addition a change in density (and volume). Compute the percent volume change associated with this reaction. Does the volume increase or decrease?*

<u>Solution</u>

To solve this problem let us first compute the density of each phase using Equation 3.8, and then determine the volumes per unit mass (the reciprocals of densities). From these values it is possible to calculate the percent volume change.

The density of each phase may be computed using Equation 3.8—i.e.,

$$r = \frac{nA_{\mathrm{Fe}}}{V_C N_{\mathrm{A}}}$$

The atomic weight of Fe will be the same for both BCC and FCC structures (55.85 g/mol); however, values of n and V_C will be different.

For BCC iron, n = 2 atoms/unit cell, whereas the volume of the cubic unit cell is the cell edge length a cubed--$V_C = a^3$. However, a and the atomic radius (R_{BCC}) are related according to Equation 3.4—that is

$$a = \frac{4R_{\mathrm{BCC}}}{\sqrt{3}}$$

which means that

$$V_C = a^3 = \left(\frac{4R_{\mathrm{BCC}}}{\sqrt{3}}\right)^3$$

The value of R_{BCC} is given in the problem statement as 0.12584 nm = 1.2584×10^{-8} cm. It is now possible to calculate the density of BCC iron as follows:

$$r_{\mathrm{BCC}} = \frac{nA_{\mathrm{Fe}}}{\left(\frac{4R_{\mathrm{BCC}}}{\sqrt{3}}\right)^3 N_{\mathrm{A}}}$$

$$= \frac{(2 \text{ atoms/unit cell})(55.85 \text{ g/mol})}{\left[\frac{(4)(1.2584 \times 10^{-8} \text{ cm})}{\sqrt{3}}\right]^3 (6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 7.5572 \text{ g/cm}^3$$

For FCC iron, n = 4 atoms/unit cell, $V_C = 16\sqrt{2}R_{\text{FCC}}^3$ (Equation 3.6), and, as noted in the problem statement, R_{FCC} = 0.12894 nm = 1.2894 × 10^{-8} cm. We now calculate the density of FCC iron as follows:

$$r_{\text{FCC}} = \frac{nA_{\text{Fe}}}{\left(16\sqrt{2}R_{\text{FCC}}^3\right)N_{\text{A}}}$$

$$= \frac{(4 \text{ atoms/unit cell})(55.85 \text{ g/mol})}{\left[(16)(\sqrt{2})(1.2894 \times 10^{-8} \text{ cm})^3\right](6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 7.6479 \text{ g/cm}^3$$

Because we are interested in volumes of these two phases, for each we take the reciprocal of it density, which is equivalent to volume per unit mass (or specific volume), v. The percent volume change $\bar{v}$ experienced by iron during this phase transformation, upon heating is equal to

$$\bar{v} = \frac{v_{\text{BCC}} - v_{\text{FCC}}}{v_{\text{BCC}}} \times 100$$

$$= \frac{\frac{1}{7.5572 \text{ g/cm}^3} - \frac{1}{7.6479 \text{ g/cm}^3}}{\frac{1}{7.5572 \text{ g/cm}^3}} \times 100$$

$$1.19\%$$

The volume decreases because $v_{\text{FCC}} < v_{\text{BCC}}$ –i.e., since $r_{\text{FCC}} > r_{\text{BCC}}$.

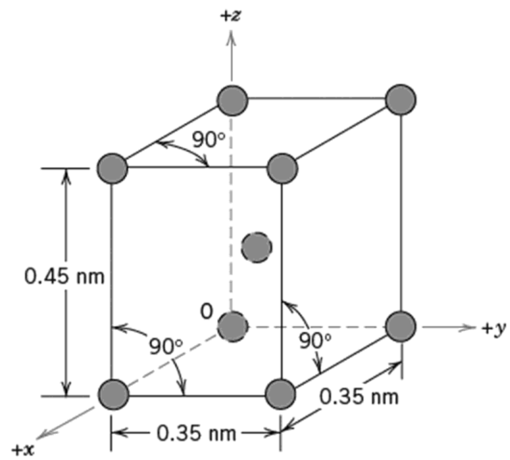
Crystal Systems

3.23 *The accompanying figure shows a unit cell for a hypothetical metal.*

(a) To which crystal system does this unit cell belong?

(b) What would this crystal structure be called?

(c) Calculate the density of the material, given that its atomic weight is 141 g/mol.



<u>Solution</u>

(a) The unit cell shown in the problem statement belongs to the tetragonal crystal system since $a = b = 0.35$ nm, $c = 0.45$ nm, and $\alpha = \beta = \gamma = 90°$.

(b) The crystal structure would be called *body-centered tetragonal*.

(c) As with BCC, $n = 2$ atoms/unit cell. Also, for this unit cell

$$V_C = (3.5 \times 10^{-8}\ \text{cm})^2 (4.5 \times 10^{-8}\ \text{cm})$$

$$= 5.51 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

Thus, using Equation 3.8, the density is equal to

$$\rho = \frac{nA}{V_C N_\text{A}}$$

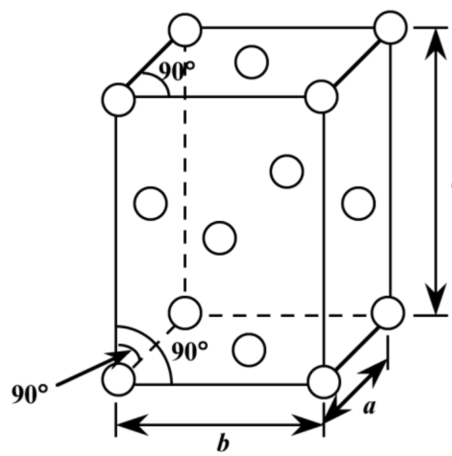
$$= \frac{(2\ \text{atoms/unit cell})(141\ \text{g/mol})}{(5.51 \times 10^{-23}\ \text{cm}^3/\text{unit cell})(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 8.49\ \text{g/cm}^3$$

3.24 *Sketch a unit cell for the face-centered orthorhombic crystal structure.*

Solution

A unit cell for the face-centered orthorhombic crystal structure is presented below.



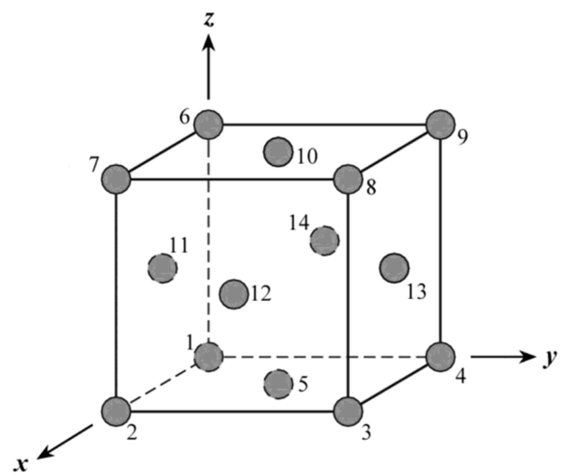
For the orthorhombic crystal system, $a \neq b \neq c$, and $\alpha = \beta = \gamma = 90°$. Also, for the face-centered orthorhombic crystal structure, atoms will be located at the centers of all 6 faces (in addition to all 8 corners).

Point Coordinates

3.25 *List the point coordinates for all atoms that are associated with the FCC unit cell (Figure 3.1).*

Solution

This problem asks that we list the point coordinates for all of the atoms associated with the FCC unit cell. The reduced-sphere FCC unit cell, Figure 3.1b, is shown below on which is superimposed an *x*-*y*-*z* coordinate axis system. Also, each atom in the unit cell is labeled with a number. Of course, because the unit cell is cubic, the unit cell edge length along each of the *x*, *y*, and *z* axes is *a*.



Coordinates for each of these points is determined in a manner similar to that demonstrated in Example Problem 3.6. For the atom labeled 1 in the FCC unit cell, we determine its point coordinates by using rearranged forms of Equations 3.9a, 3.9b, and 3.9c as follows:

The lattice position referenced to the *x* axis is $0a = qa$

The lattice position referenced to the *y* axis is $0a = ra$

The lattice position referenced to the *x* axis is $0a = sa$

Solving these expressions for the values of *q, r,* and *s* leads to

$q = 0$ $r = 0$ $s = 0$

Therefore, the *q r s* coordinates for point 1 are 0 0 0.

For point 10, which lies at the middle of the top unit cell face, its lattice position indices referenced to the *x*, *y*, and *z* axes are, respectively, $a/2$, $a/2$, and *a*, and

The lattice position referenced to the *x* axis is $a/2 = qa$

The lattice position referenced to the *y* axis is $a/2 = ra$

The lattice position referenced to the *x* axis is $a = sa$

Thus, values for the three point coordinates are

$q = 1/2$ $r = 1/2$ $s = 1$

and this point is $\frac{1}{2}\frac{1}{2}1$.

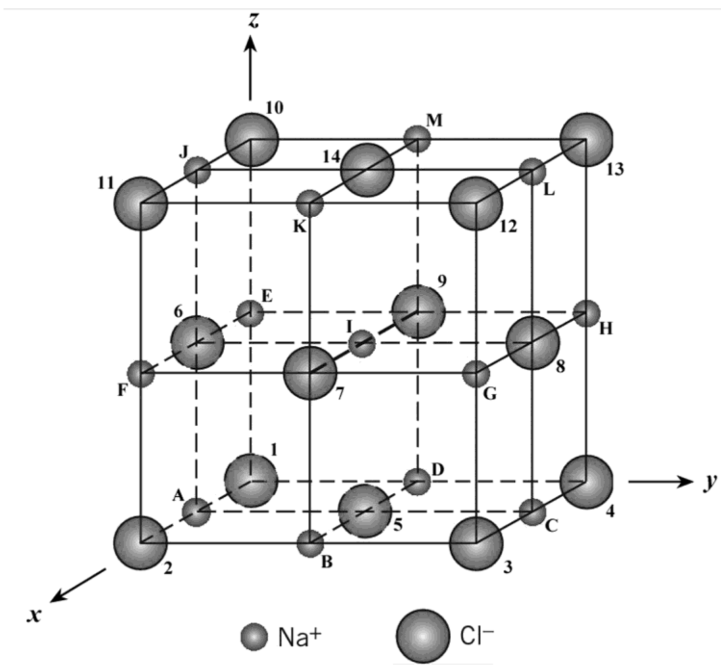
This same procedure is carried out for the remaining the points in the unit cell; indices for all fourteen points are listed in the following table.

Point number	*q*	*r*	*s*
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	0
6	0	0	1
7	1	0	1
8	1	1	1
9	0	1	1
10	$\frac{1}{2}$	$\frac{1}{2}$	1
11	$\frac{1}{2}$	0	$\frac{1}{2}$
12	1	$\frac{1}{2}$	$\frac{1}{2}$
13	$\frac{1}{2}$	1	$\frac{1}{2}$
14	0	$\frac{1}{2}$	$\frac{1}{2}$

3.26 *List the point coordinates of both the sodium (Na) and chlorine (Cl) ions for a unit cell of the sodium chloride (NaCl) crystal structure (Figure 12.2).*

Solution

This problem asks that we list the point coordinates for all sodium and chlorine ion associated with the NaCl unit cell. The NaCl unit cell, Figure 12.2, is shown below on which is superimposed an *x*-*y*-*z* coordinate axis system. Also, each Na ion in the unit cell is labeled with an uppercase letter; Cl ions are labeled with numbers. Of course, because the unit cell is cubic, the unit cell edge length along each of the *x*, *y*, and *z* axes is *a*.



Coordinates for each of these points is determined in a manner similar to that demonstrated in Example Problem 3.6. For the Cl ion labeled 5, we determine its point coordinates by using rearranged forms of Equations 3.9a, 3.9b, and 3.9c as follows:

The lattice position referenced to the *x* axis is $a/2 = qa$

The lattice position referenced to the *y* axis is $a/2 = ra$

The lattice position referenced to the *x* axis is $0a = sa$

Solving these expressions for the values of *q*, *r*, and *s* leads to

$$q = \frac{1}{2} \qquad r = \frac{1}{2} \qquad s = 0$$

Therefore, the $q\ r\ s$ coordinates for this point are $\frac{1}{2}\frac{1}{2}0$.

The Na ion labeled L, has lattice position indices referenced to the *x*, *y*, and *z* axes of *a*/2, *a*, and *a*, respectively. Therefore,

The lattice position referenced to the *x* axis is $a/2 = qa$

The lattice position referenced to the *y* axis is $a = ra$

The lattice position referenced to the *x* axis is $a = sa$

Thus, values for values of *q*, *r*, and *s* are as follows:

$q = 1/2$ $r = 1$ $s = 1$

and the coordinates for the location of this ion are $\frac{1}{2}11$.

This same procedure is carried out for determine point coordinates for both Na and Cl ions in the unit cell. Indices for all these points are listed in the following two tables.

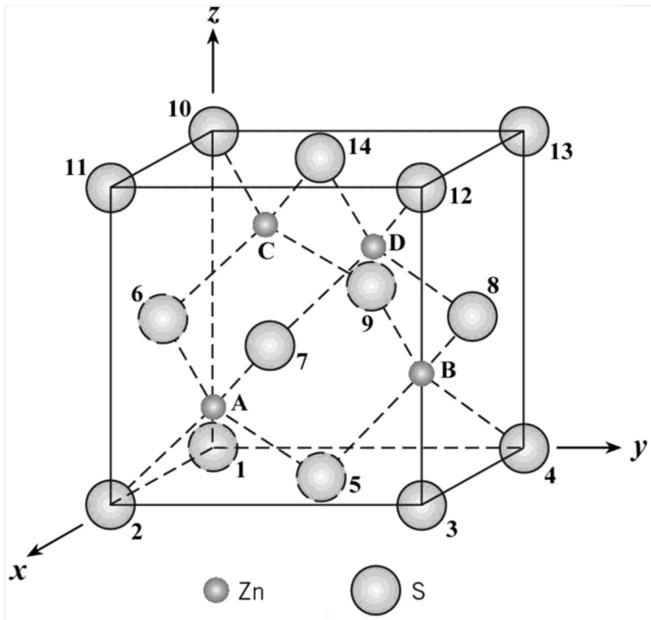
Cl ion point number	*q*	*r*	*s*
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	0
6	$\frac{1}{2}$	0	$\frac{1}{2}$
7	1	$\frac{1}{2}$	$\frac{1}{2}$
8	$\frac{1}{2}$	1	$\frac{1}{2}$
9	0	$\frac{1}{2}$	$\frac{1}{2}$
10	0	0	1
11	1	0	1
12	1	1	1
13	0	1	1
14	$\frac{1}{2}$	$\frac{1}{2}$	1

Na ion point letter	q	r	s
A	$\frac{1}{2}$	0	0
B	1	$\frac{1}{2}$	0
C	$\frac{1}{2}$	1	0
D	0	$\frac{1}{2}$	0
E	0	0	$\frac{1}{2}$
F	1	0	$\frac{1}{2}$
G	1	1	$\frac{1}{2}$
H	0	1	$\frac{1}{2}$
I	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
J	$\frac{1}{2}$	0	1
K	1	$\frac{1}{2}$	1
L	$\frac{1}{2}$	1	1
M	0	$\frac{1}{2}$	1

3.27 *List the point coordinates of both the zinc (Zn) and sulfur (S) atoms for a unit cell of the zinc blende (ZnS) crystal structure (Figure 12.4).*

Solution

The ZnS unit cell, Figure 12.4, is shown below on which is superimposed an *x*-*y*-*z* coordinate axis system. Also, each Zn atom in the unit cell is labeled with an uppercase letter; S atoms are labeled with numbers. Of course, because the unit cell is cubic, the unit cell edge length along each of the *x*, *y*, and *z* axes is *a*.



Coordinates for each of these points is determined in a manner similar to that demonstrated in Example Problem 3.6. For the S atom labeled 7, we determine its point coordinates by using rearranged forms of Equations 3.9a, 3.9b, and 3.9c as follows:

The lattice position referenced to the *x* axis is $a = qa$

The lattice position referenced to the *y* axis is $a/2 = ra$

The lattice position referenced to the *x* axis is $a/2 = sa$

Solving these expressions for the values of *q*, *r*, and *s* leads to

$$q = 1 \qquad r = \frac{1}{2} \qquad s = \frac{1}{2}$$

Therefore, the *q r s* coordinates for this point are $1\frac{1}{2}\frac{1}{2}$.

The S atom labeled C, has lattice position indices referenced to the x, y, and z axes of $a/4$, $a/4$, and $3a/4$, respectively. Therefore,

The lattice position referenced to the x axis is $a/4 = qa$

The lattice position referenced to the y axis is $a/4 = ra$

The lattice position referenced to the x axis is $3a/4 = sa$

Thus, values for values of q, r, and s are as follows:

$q = 1/4$ $r = 1/4$ $s = 3/4$

and the coordinates for the location of this atom are $\frac{1}{4}\frac{1}{4}\frac{3}{4}$.

This same procedure is carried out for determine point coordinates for both Zn and S atoms in the unit cell. Indices for all these points are listed in the following two tables.

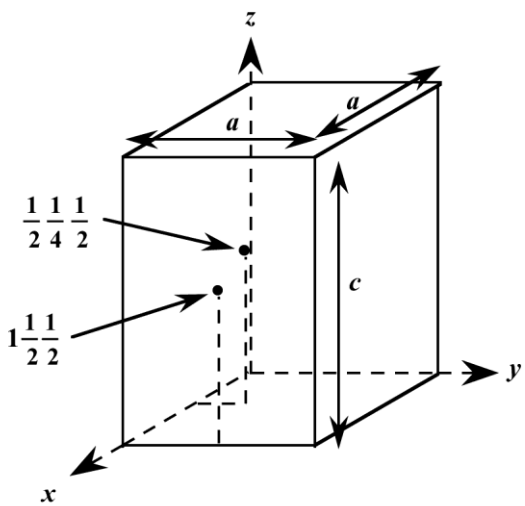
S atom point number	q	r	s
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	0
6	$\frac{1}{2}$	0	$\frac{1}{2}$
7	1	$\frac{1}{2}$	$\frac{1}{2}$
8	$\frac{1}{2}$	1	$\frac{1}{2}$
9	0	$\frac{1}{2}$	$\frac{1}{2}$
10	0	0	1
11	1	0	1
12	1	1	1
13	0	1	1
14	$\frac{1}{2}$	$\frac{1}{2}$	1

Zn atom point letter	q	r	s
A	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
B	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{4}$
C	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
D	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$

3.28 *Sketch a tetragonal unit cell, and within that cell indicate locations of the* $1\frac{1}{2}\frac{1}{2}$ *and* $\frac{1}{2}\frac{1}{4}\frac{1}{2}$ *point coordinates.*

Solution

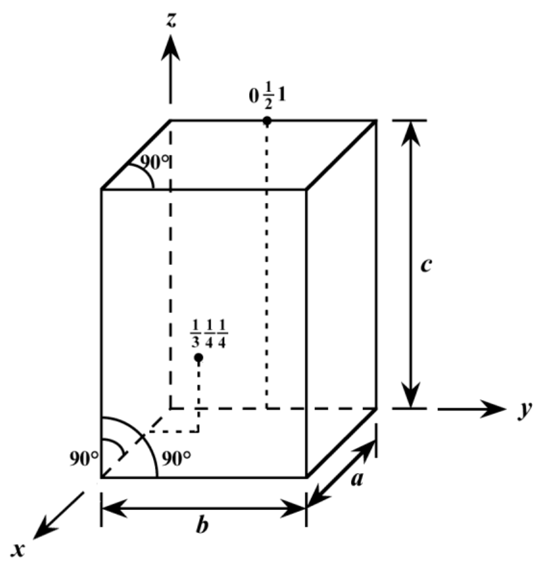
A tetragonal unit in which are shown the $1\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}\frac{1}{4}\frac{1}{2}$ point coordinates is presented below.



3.29 *Sketch an orthorhombic unit cell, and within that cell indicate locations of the* $0\ \frac{1}{2}\ 1$ *and* $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ *point coordinates.*

Solution

An orthorhombic unit in which are shown the $0\frac{1}{2}1$ and $\frac{1}{3}\frac{1}{4}\frac{1}{4}$ point coordinates is presented below.



3.30 *Using the Molecule Definition Utility found in the "Metallic Crystal Structures and Crystallography" and "Ceramic Crystal Structures" modules of VMSE, located on the book's web site [www.wiley.com/college/callister (Student Companion Site)], generate (and print out) a three-dimensional unit cell for β tin (Sn), given the following: (1) the unit cell is tetragonal with a =0.583 nm and c =0.318 nm, and (2) Sn atoms are located at the following point coordinates:*

0 0 0	0 1 1
1 0 0	$\frac{1}{2}\ 0\ \frac{3}{4}$
1 1 0	$\frac{1}{2}\ 1\ \frac{3}{4}$
0 1 0	$1\ \frac{1}{2}\ \frac{1}{4}$
0 0 1	$0\ \frac{1}{2}\ \frac{1}{4}$
1 0 1	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
1 1 1	

Solution

First of all, open the "Molecule Definition Utility"; it may be found in either of "Metallic Crystal Structures and Crystallography" or "Ceramic Crystal Structures" modules.

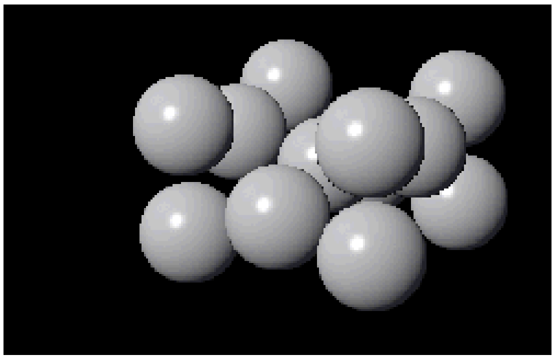
In the "Step 1" window, it is necessary to define the atom type, a color for the spheres (atoms), and specify an atom size. Let us enter "Sn" as the name of the atom type (since "Sn" the symbol for tin). Next it is necessary to choose a color from the selections that appear in the pull-down menu—for example, "LtBlue" (light blue). In the "Enter size (nm)" window, it is necessary to enter an atom size. In the instructions for this step, it is suggested that the atom diameter in nanometers be used. From the table found inside the front cover of the textbook, the atomic radius for tin is 0.151 nm, and, therefore, the atomic diameter is twice this value (i.e., 0.302 nm); therefore, we enter the value "0.302". Now click on the "Register Atom Type" button. A small sphere having the color you selected will appear to the right of the white Molecule Definition Utility box.

In the "Step 2" window we specify positions for all of the atoms within the unit cell; their point coordinates are specified in the problem statement. It is first necessary to select the Sn atom in order to specify its coordinates. This is accomplished by clicking on the small sphere that appeared in Step 1. At this time it is necessary to enter the X, Y, and Z coordinates for one of the Sn atoms. For example, the point coordinates for the first Sn atom in the list are 000; therefore, we enter a "0" (zero) in each of the "X", "Y", and "Z" atom position boxes, and then click on "Register Atom Position." An atom will be displayed at this position within the X-Y-Z coordinate axis system to the right of the white box. We next, enter the coordinates of another Sn atom—e.g., 1, 0, and 0. Inasmuch as this atom is located a distance of *a* units along the X-axis, the value of "0.583" is entered in the "X" atom position box (since this the value of *a* given in the problem statement); zeros are entered in each of "Y" and "Z" position boxes. Upon clicking on "Register Atom Position" this atom is also displayed within the coordinate system. This same procedure is repeated for all 13 of the point coordinates specified in the problem statement. For the atom having point coordinates of “111” respective values of “0.583”, “0.583”, and “0.318” are entered in the X, Y, and Z atom position boxes, since the unit cell edge length along the Y and Z axes are *a* (0.583) and *c* (0.318 nm), respectively. For fractional point coordinates, the appropriate *a* or *c* value is multiplied by the fraction. For example, the second point coordinate set in the right-hand column, $\frac{1}{2}0\frac{3}{4}$, the X, Y, and Z atom positions are $\frac{1}{2}(0.583) = 0.2915$, 0, and $\frac{3}{4}(0.318) = 0.2385$, respectively. The X, Y, and Z atom position entries for all 13 sets of point coordinates are as follows:

0, 0, and 0	0, 0.583, and 0.318
0.583, 0, and 0	0.2915, 0, and 0.2385
0.583, 0.583, and 0	0.2915, 0.583, and 0.2385
0, 0.583, and 0	0.583, 0.2915, and 0.0795
0, 0, and 0.318	0, 0.2915, 0.0795
0.583, 0, and 0.318	0.2915, 0.2915, and 0.159
0.583, 0.583, and 0.318	

In Step 3, we may specify which atoms are to be represented as being bonded to one another, and which type of bond(s) to use (single, double, triple, dashed, and dotted are possibilities), as well as bond color (e.g., light gray, white, cyan); or we may elect to not represent any bonds at all. If it is decided to show bonds, probably the best thing to do is to represent unit cell edges as bonds.

Your image should appear as



Finally, your image may be rotated by using mouse click-and-drag.

[Note: Unfortunately, with this version of the Molecular Definition Utility, it is not possible to save either the data or the image that you have generated. You may use screen capture (or screen shot) software to record and store your image.]

Crystallographic Directions

3.31 *Draw an orthorhombic unit cell, and within that cell a* $[2\bar{1}1]$ *direction.*

Solution

This problem calls for us to draw a $[2\bar{1}1]$ direction within an orthorhombic unit cell ($a \neq b \neq c$, $\alpha = \beta = \gamma =$ 90□). Such a unit cell with its origin positioned at point *O* is shown below. This direction may be plotted using the procedure outlined in Example Problem 3.8, with which rearranged forms of Equations 3.10a-3.10c are used. Let us position the tail of the direction vector at the origin of our coordinate axes; this means that tail vector coordinates for this $[2\bar{1}1]$ direction are

$u = 2$
$v = -1$
$w = 1$

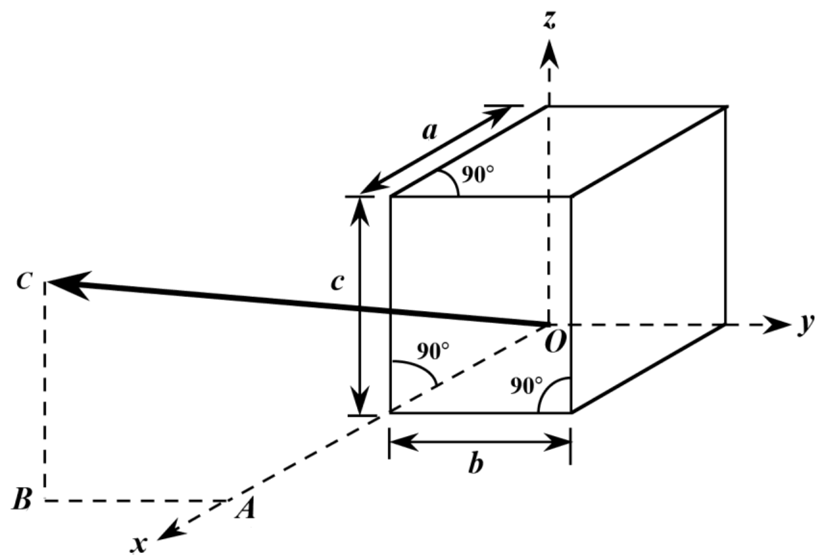
Because the tail of the direction vector is positioned at the origin, its coordinates are as follows:

$x_1 = 0a$
$y_1 = 0b$
$z_1 = 0c$

Head coordinates are determined using the rearranged forms of Equations 3.10a-3.10c, as follows:

$$x_2 = ua + x_1 = (2)a + 0a = 2a$$
$$y_2 = vb + y_1 = (-1)b + 0b = -b$$
$$z_2 = wc + z_1 = (1)c + 0c = c$$

Therefore, coordinates for the vector head are $2a$, $-b$, and c. To locate the vector head, we start at the origin, point *O*, and move along the +*x* axis $2a$ units (from point *O* to point *A*), then parallel to the +*y*-axis $-b$ units (from point *A* to point *B*). Finally, we proceed parallel to the *z*-axis *c* units (from point *B* to point *C*). The $[2\bar{1}1]$ direction is the vector from the origin (point *O*) to point *C* as shown.


z
a
90°
c
c
O
y
90°
90°
b
B
A
x

3.32 *Sketch a monoclinic unit cell, and within that cell a* $[\bar{1}01]$ *direction.*

Solution

This problem asks that a $[\bar{1}01]$ direction be drawn within a monoclinic unit cell ($a \neq b \neq c$, and $\alpha = \beta = 90° \neq \gamma$). Such a unit cell with its origin positioned at point *O* is shown below. This direction may be plotted using the procedure outlined in Example Problem 3.8, with which rearranged forms of Equations 3.10a-3.10c are used. Let us position the tail of the direction vector at the origin of our coordinate axes; this means that vector head indices for this $[\bar{1}01]$ direction are

$u = -1$

$v = 0$

$w = 1$

Because the tail of the direction vector is positioned at the origin, its coordinates are as follows:

$x_1 = 0a$

$y_1 = 0b$

$z_1 = 0c$

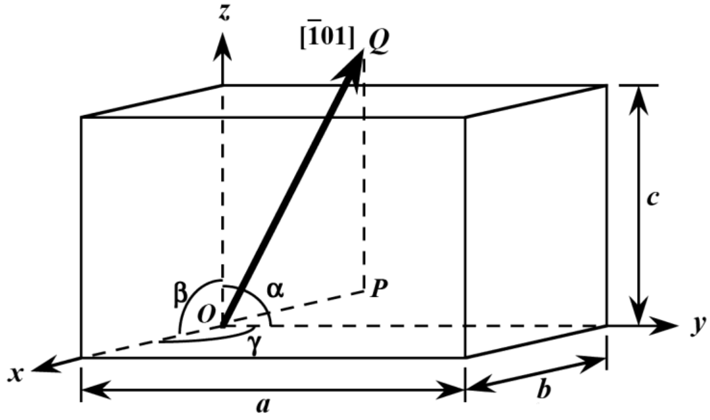
Head coordinates are determined using the rearranged forms of Equations 3.10a-3.10c, as follows:

$$x_2 = ua + x_1 = (-1)a + 0a = -a$$

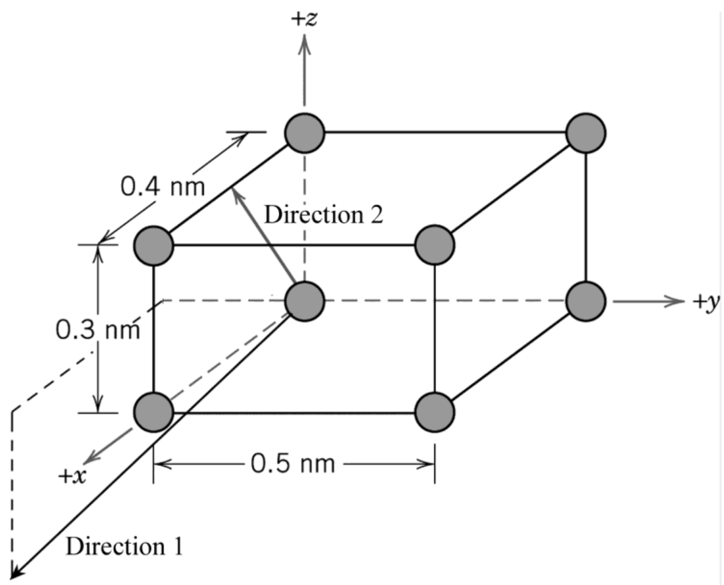
$$y_2 = vb + y_1 = (0)b + 0b = -0b$$

$$z_2 = wc + z_1 = (1)c + 0c = c$$

Therefore, coordinates for the vector head are $-a$, $0b$, and c. To locate the vector head, we start at the origin, point *O*, and move from the origin along the minus *x*-axis *a* units (from point *O* to point *P*). There is no projection along the *y*-axis since the next index is zero. Since the final coordinate is *c*, we move from point *P* parallel to the *z*-axis, *c* units (to point *Q*). Thus, the $[\bar{1}01]$ direction corresponds to the vector passing from the origin to point *Q*, as indicated in the figure.



3.33 *What are the indices for the directions indicated by the two vectors in the following sketch?*



Solution

We are asked for the indices of the two directions sketched in the figure. Unit cell edge lengths are a = 0.4 nm, b = 0.5 nm, and c = 0.3 nm. In solving this problem we will use the symbols a, b, and c rather than the magnitudes of these parameters

The tail of the Direction 1 vector passes through the origin, therefore, its tail coordinates are

$x_1 = 0a$

$y_1 = 0b$

$z_1 = 0c$

And the vector head coordinates are as follows:

$x_2 = a$

$y_2 = -b/2$

$z_2 = -c$

To determine the directional indices we employ Equations 3.10a, 3.10b, and 3.10c. Because there is a 2 in the denominator for y_2 we will assume n = 2. Hence

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a - 0a}{a}\right) = 2$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{-b/2 - 0b}{b}\right) = -1$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{-c \; - \; 0c}{c}\right) = -2$$

Therefore, Direction 1 is a $[2\overline{1}\overline{2}]$ direction.

We use the same procedure to determine the indices for Direction 2. Again, because the vector tail passes through the origin of the coordinate system, the values of x_1, y_1, and z_1 are the same as for Direction 1. Furthermore, vector head coordinates are as follows:

$x_2 = a/2$

$y_2 = 0b$

$z_2 = c$

We again choose a value of 2 for n because of the 2 in the denominator of the x_2 coordinate. Therefore,

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a/2 - 0a}{a}\right) = 1$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{0b \; - \; 0b}{b}\right) = 0$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{c \; - \; 0c}{c}\right) = 2$$

Therefore, Direction 2 is a [102] direction.

3.34 *Within a cubic unit cell, sketch the following directions:*

(a) $[101]$ *(e)* $[\bar{1}1\bar{1}]$

(b) $[211]$ *(f)* $[\bar{2}12]$

(c) $[10\bar{2}]$ *(g)* $[3\bar{1}2]$

(d) $[3\bar{1}3]$ *(h)* $[301]$

Solution

(a) For the [101] direction, it is the case that

$u = 1$ $v = 0$ $w = 1$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

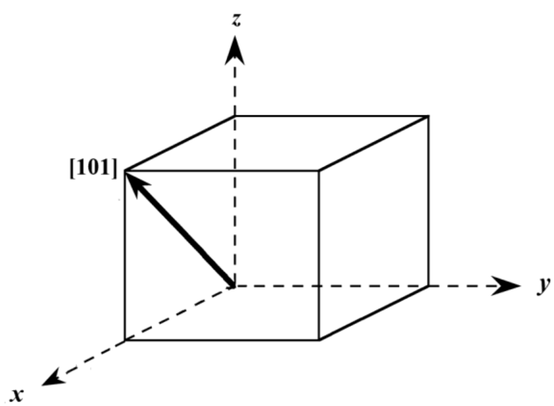
$$x_2 = ua + x_1 = (1)a + 0a = a$$

$$y_2 = vb + y_1 = (0)b + 0b = 0b$$

$$z_2 = wc + z_1 = (1)c + 0c = c$$

Thus, the vector head is located at a, $0b$, and c, and the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., a), in order to clarify construction of the direction vector, we have chosen to use b and c to designate edge lengths along y and z axes, respectively.]



(b) For a [211] direction, it is the case that

$u = 2$ $v = 1$ $w = 1$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

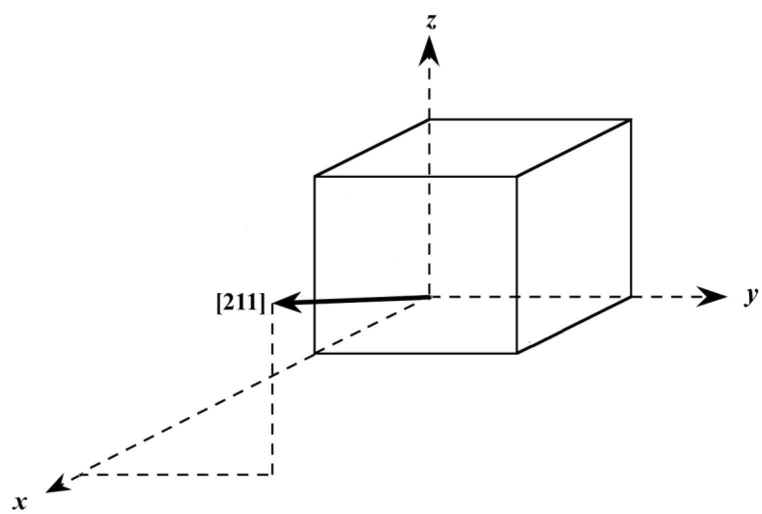
$$x_2 = ua + x_1 = (2)a + 0a = 2a$$

$$y_2 = vb + y_1 = (1)b + 0b = b$$

$$z_2 = wc + z_1 = (1)c + 0c = c$$

Thus, the vector head is located at 2*a*, *b*, and *c*, and the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(c) For the $[10\bar{2}]$ direction, it is the case that

$u = 1$ $\quad v = 0$ $\quad w = -2$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $\quad y_1 = 0b$ $\quad z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

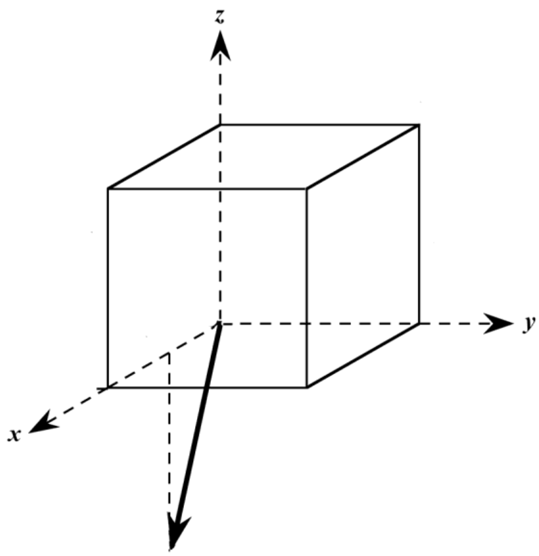
$$x_2 = ua + x_1 = (1)a + 0a = a$$

$$y_2 = vb + y_1 = (0)b + 0b = 0b$$

$$z_2 = wc + z_1 = (-2)c + 0c = -2c$$

Thus, the vector head is located at *a*, 0*b*, and *c*. However, in order to reduce the vector length, we have divided these coordinates by ½, which gives the new set of head coordinates as *a*/2, 0*b*, and –*c*; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(d) For the $[3\bar{1}3]$ direction, it is the case that

$u = 3$ $v = -1$ $w = 3$

If we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

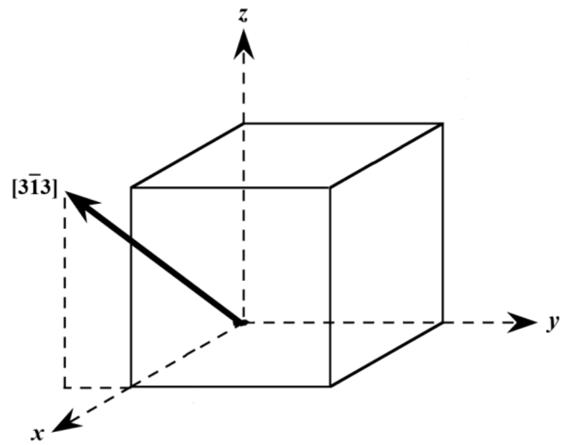
$$x_2 = ua + x_1 = (3)a + 0a = 3a$$

$$y_2 = vb + y_1 = (-1)b + 0b = -b$$

$$z_2 = wc + z_1 = (3)c + 0c = 3c$$

Thus, the vector head is located at 3*a*, –*b*, and 3*c*. However, in order to reduce the vector length, we have divided these coordinates by 1/3, which gives the new set of head coordinates as *a*, –*b*/3, and *c*; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(e) For the $[\bar{1}1\bar{1}]$ direction, it is the case that

$u = -1 \qquad v = 1 \qquad w = -1$

If we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a \qquad y_1 = 0b \qquad z_1 = 0c$

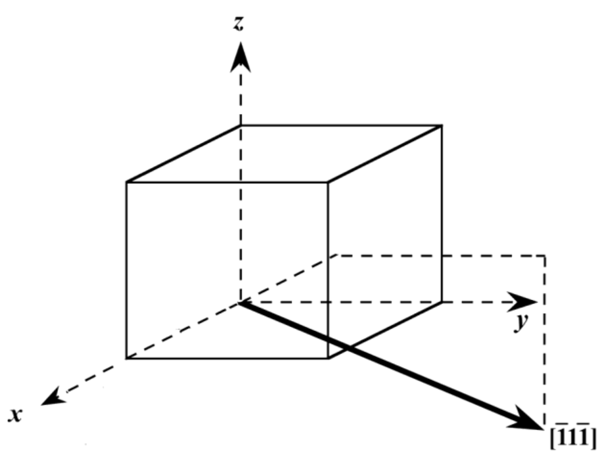
It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

$$x_2 = ua + x_1 = (-1)a + 0a = -a$$

$$y_2 = vb + y_1 = (1)b + 0b = b$$

$$z_2 = wc + z_1 = (-1)c + 0c = -c$$

Thus, the vector head is located at $-a$, b, and $-c$, and the direction vector having these head coordinates is plotted below.



[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]

(f) For the $[\bar{2}12]$ direction, it is the case that

$u = -2$ $\quad v = 1$ $\quad w = 2$

If we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $\quad y_1 = 0b$ $\quad z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

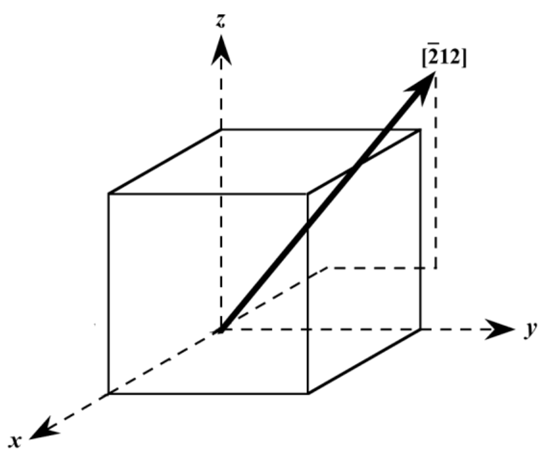
$$x_2 = ua + x_1 = (-2)a + 0a = -2a$$

$$y_2 = vb + y_1 = (1)b + 0b = b$$

$$z_2 = wc + z_1 = (2)c + 0c = 2c$$

Thus, the vector head is located at $-2a$, b, and $2c$. However, in order to reduce the vector length, we have divided these coordinates by 1/2, which gives the new set of head coordinates as $-a$, $b/2$, and c; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(g) For the $[3\bar{1}2]$ direction, it is the case that

$u = 3$ $\quad v = -1$ $\quad w = 2$

If we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $\quad y_1 = 0b$ $\quad z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

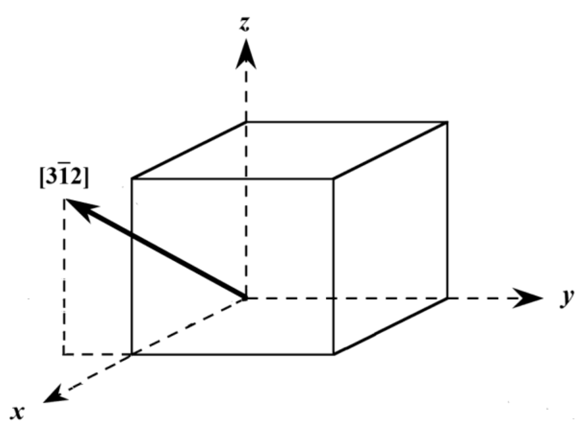
$$x_2 = ua + x_1 = (3)a + 0a = 3a$$

$$y_2 = vb + y_1 = (-1)b + 0b = -b$$

$$z_2 = wc + z_1 = (2)c + 0c = 2c$$

Thus, the vector head is located at 3*a*, –*b*, and 2*c*. However, in order to reduce the vector length, we have divided these coordinates by 1/3, which gives the new set of head coordinates as *a*, –*b/*3, and 2*c/*3; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(g) For the [301] direction, it is the case that

$u = 3$ $v = 0$ $w = 1$

If we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

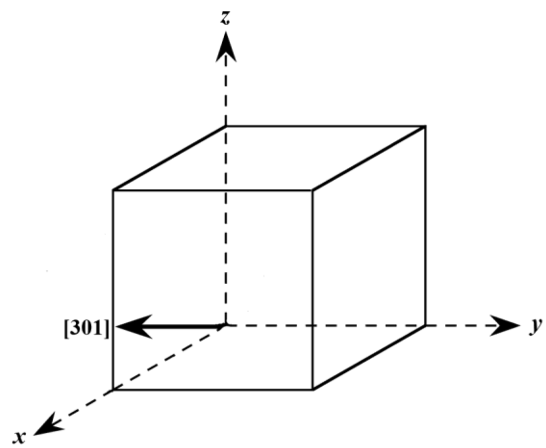
$$x_2 = ua + x_1 = (3)a + 0a = 3a$$

$$y_2 = vb + y_1 = (0)b + 0b = 0b$$

$$z_2 = wc + z_1 = (1)c + 0c = c$$

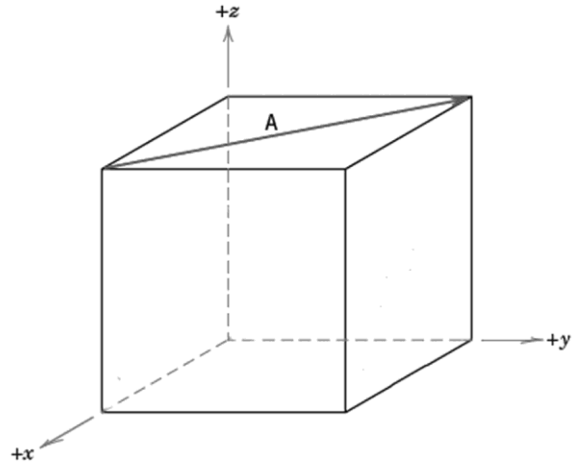
Thus, the vector head is located at 3*a*, 0*b*, and *c*. However, in order to reduce the vector length, we have divided these coordinates by 1/3, which gives the new set of head coordinates as *a*, 0*b*, and *c/*3; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



3.35 *Determine the indices for the directions shown in the following cubic unit cell:*

For Direction A



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = a$ $y_1 = 0b$ $z_1 = c$

Whereas head coordinates are as follows:

$x_2 = 0a$ $y_2 = b$ $z_2 = c$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 1 for the parameter n

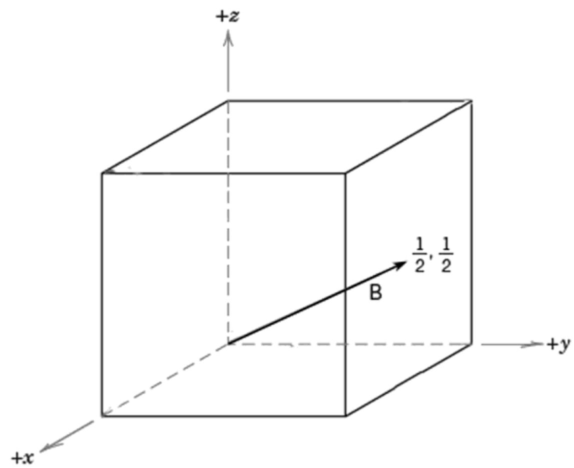
$$u = n\left(\frac{x_2 - x_1}{a}\right) = (1)\left(\frac{0a - a}{a}\right) = -1$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (1)\left(\frac{b - 0b}{b}\right) = 1$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (1)\left(\frac{c - c}{c}\right) = 0$$

Therefore, Direction A is $[\bar{1}10]$.

For Direction B



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Because the tail passes through the origin of the unit cell, its coordinates are as follows:

$x_1 = 0a$ $\qquad y_1 = 0b$ $\qquad z_1 = 0c$

Whereas head coordinates are as follows:

$x_2 = a/2$ $\qquad y_2 = b$ $\qquad z_2 = c/2$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 2 for the parameter *n*

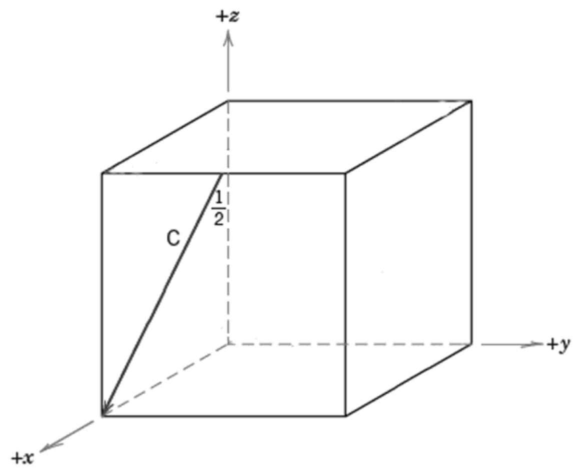
$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a/2 - 0a}{a}\right) = 1$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{b - 0b}{b}\right) = 2$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{c/2 - 0c}{c}\right) = 1$$

Therefore, Direction B is [121].

For direction C



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. The tail coordinates are as follows:

$x_1 = a$ $y_1 = b/2$ $z_1 = c$

Whereas head coordinates are as follows:

$x_2 = a$ $y_2 = 0b$ $z_2 = 0c$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 2 for the parameter n

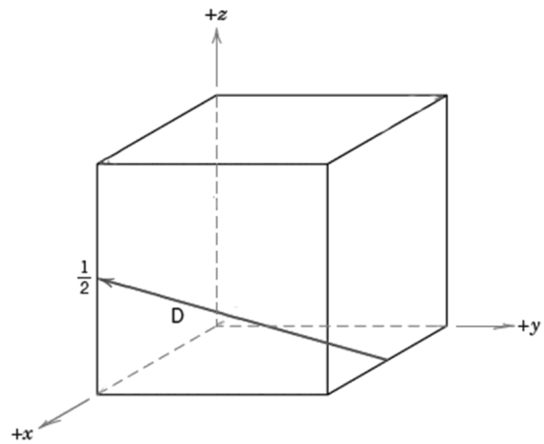
$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a - a}{a}\right) = 0$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{0b - b/2}{b}\right) = -1$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{0c - c}{c}\right) = -2$$

Therefore, Direction C is $[0\overline{1}\overline{2}]$.

For direction D



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = a/2$ $y_1 = b$ $z_1 = 0c$

Whereas head coordinates are as follows:

$x_2 = a$ $y_2 = 0b$ $z_2 = c/2$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 2 for the parameter n

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a - a/2}{a}\right) = 1$$

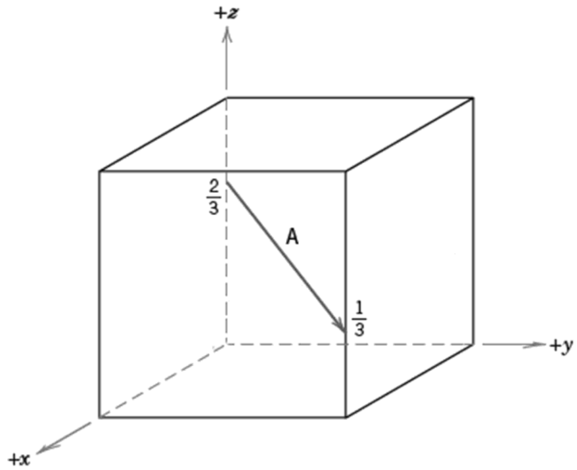
$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{0b - b}{b}\right) = -2$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{c/2 - 0c}{c}\right) = 1$$

Therefore, Direction D is $[1\overline{2}1]$.

3.36 *Determine the indices for the directions shown in the following cubic unit cell:*

Direction A



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = 0a$ $\qquad y_1 = 0b$ $\qquad z_1 = 2c/3$

Whereas head coordinates are as follows:

$x_2 = a$ $\qquad y_2 = b$ $\qquad z_2 = c/3$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 3 for the parameter *n*

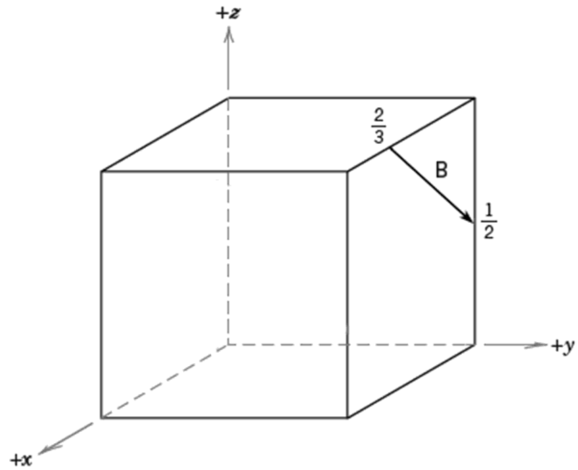
$$u = n\left(\frac{x_2 - x_1}{a}\right) = (3)\left(\frac{a - 0a}{a}\right) = 3$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (3)\left(\frac{b - 0b}{b}\right) = 3$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (3)\left(\frac{c/3 - 2c/3}{c}\right) = -1$$

Therefore, Direction A is $[33\overline{1}]$.

Direction B:



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = 2a/3$ $\quad$ $y_1 = b$ $\quad$ $z_1 = c$

Whereas head coordinates are as follows:

$x_2 = 0a$ $\quad$ $y_2 = b$ $\quad$ $z_2 = c/2$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 3 for the parameter n

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (3)\left(\frac{0a - 2a/3}{a}\right) = -2$$

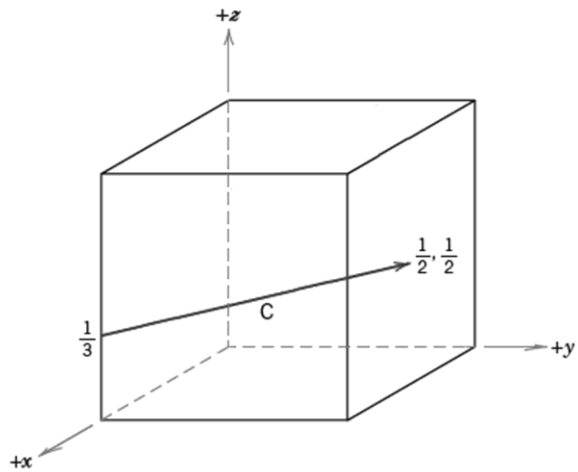
$$v = n\left(\frac{y_2 - y_1}{b}\right) = (3)\left(\frac{b - b}{b}\right) = 0$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (3)\left(\frac{c/2 - c}{c}\right) = -\frac{3}{2}$$

In order to reduce these values to the lowest set of integers, we multiply each by the factor 2.

Therefore, Direction B is $[\bar{4}0\bar{3}]$.

Direction C:



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = a$ $\qquad y_1 = 0b$ $\qquad z_1 = c/3$

Whereas head coordinates are as follows:

$x_2 = a/2$ $\qquad y_2 = b$ $\qquad z_2 = c/2$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 3 for the parameter n

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (3)\left(\frac{a/2 - a}{a}\right) = -\frac{3}{2}$$

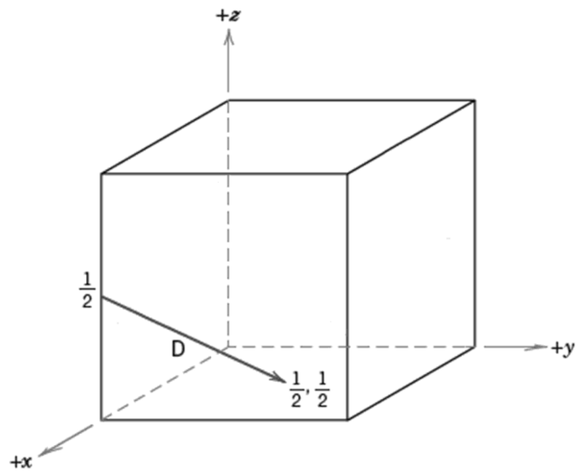
$$v = n\left(\frac{y_2 - y_1}{b}\right) = (3)\left(\frac{b - 0b}{b}\right) = 3$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (3)\left(\frac{c/2 - c/3}{c}\right) = \frac{1}{2}$$

In order to reduce these values to the lowest set of integers, we multiply each by the factor 2.

Therefore, Direction C is $[\bar{3}61]$.

Direction D:



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = a$ $\quad y_1 = 0b$ $\quad z_1 = c/2$

Whereas head coordinates are as follows:

$x_2 = a/2$ $\quad y_2 = b/2$ $\quad z_2 = 0c$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 2 for the parameter *n*

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a/2 - a}{a}\right) = -1$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{b/2 - 0b}{b}\right) = 1$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{0c - c/2}{c}\right) = -1$$

Therefore, Direction D is $[\bar{1}1\bar{1}]$.

3.37 (a) *What are the direction indices for a vector that passes from point* $\frac{1}{4}0\frac{1}{2}$ *to point* $\frac{3}{4}\frac{1}{2}\frac{1}{2}$ *in a cubic unit cell?*

(b) *Repeat part (a) for a monoclinic unit cell.*

Solution

(a) Point coordinate indices for the vector tail, $\frac{1}{4}0\frac{1}{2}$, means that

$$q = \frac{1}{4} \qquad r = 0 \qquad s = \frac{1}{2}$$

or that. using Equations 3.9a-3.9c, lattice positions references to the three axis are determine as follows:

$$\text{lattice position referenced to the } x \text{ axis} = qa = \left(\frac{1}{4}\right)a = \frac{a}{4} = x_1$$

$$\text{lattice position referenced to the } y \text{ axis} = rb = (0)b = 0b = y_1$$

$$\text{lattice position referenced to the } z \text{ axis} = sc = \left(\frac{1}{2}\right)c = \frac{c}{2} = z_1$$

Similarly for the vector head:

$$q = \frac{3}{4} \qquad r = \frac{1}{2} \qquad s = \frac{1}{2}$$

And we determine lattice positions for using Equations 3.9a-3.9c, in a similar manner:

$$\text{lattice position referenced to the } x \text{ axis} = qa = \left(\frac{3}{4}\right)a = \frac{3a}{4} = x_2$$

$$\text{lattice position referenced to the } y \text{ axis} = rb = \left(\frac{1}{2}\right)b = \frac{b}{2} = y_2$$

$$\text{lattice position referenced to the } z \text{ axis} = sc = \left(\frac{1}{2}\right)c = \frac{c}{2} = z_2$$

And, finally, determination of the *u*, *v*, and *w* direction indices is possible using Equations 3.10a-3.10c; because there is a 4 in the denominators of two of the lattice positions, let us assume a value of 4 for the parameter *n* in these equations. Therefore,

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (4)\left(\frac{\frac{3a}{4} - \frac{a}{4}}{a}\right) = 2$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (4)\left(\frac{\frac{b}{2} - 0b}{b}\right) = 2$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (4)\left(\frac{\frac{c}{2} - \frac{c}{2}}{c}\right) = 0$$

Because it is possible to reduce these indices to the smallest set of integers by dividing each by the factor 2, this vector points in a [110] direction.

(b) For a monoclinic unit cell, the direction indices will also be [110]. Lattice position coordinates for both vector head and tail will be the same as for cubic. Likewise, incorporating these lattice position coordinates into Equations 3.10a-3.10c also yield

$u = 1$

$v = 1$

$w = 0$

3.38 *(a) What are the direction indices for a vector that passes from point* $\frac{1}{3}\frac{1}{2}0$ *to point* $\frac{2}{3}\frac{3}{4}\frac{1}{2}$ *in a tetragonal unit cell?*

(b) Repeat part (a) for a rhombohedral unit cell.

Solution

(a) Point coordinate indices for the vector tail, $\frac{1}{3}\frac{1}{2}0$, means that

$$q = \frac{1}{3} \qquad r = \frac{1}{2} \qquad s = 0$$

or that. using Equations 3.9a-3.9c, lattice positions references to the three axis are determine as follows:

$$\text{lattice position referenced to the } x \text{ axis} = qa = \left(\frac{1}{3}\right)a = \frac{a}{3} = x_1$$

$$\text{lattice position referenced to the } y \text{ axis} = rb = \left(\frac{1}{2}\right)b = \frac{b}{2} = y_1$$

$$\text{lattice position referenced to the } z \text{ axis} = sc = (0)c = 0c = z_1$$

Similarly for the vector head:

$$q = \frac{2}{3} \qquad r = \frac{3}{4} \qquad s = \frac{1}{2}$$

And we determine lattice positions for using Equations 3.9a-3.9c, in a similar manner:

$$\text{lattice position referenced to the } x \text{ axis} = qa = \left(\frac{2}{3}\right)a = \frac{2a}{3} = x_2$$

$$\text{lattice position referenced to the } y \text{ axis} = rb = \left(\frac{3}{4}\right)b = \frac{3b}{4} = y_2$$

$$\text{lattice position referenced to the } z \text{ axis} = sc = \left(\frac{1}{2}\right)c = \frac{c}{2} = z_2$$

And, finally, determination of the *u*, *v*, and *w* direction indices is possible using Equations 3.10a-3.10c; because there is a 4 in one lattice position denominator, and 3 in two others, let us assume a value of 12 for the parameter *n* in these equations. Therefore,

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (12)\left(\frac{\frac{2a}{3} - \frac{a}{3}}{a}\right) = 4$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (12)\left(\frac{\frac{3b}{4} - \frac{b}{2}}{b}\right) = 3$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (12)\left(\frac{\frac{c}{2} - 0c}{c}\right) = 6$$

Therefore, the direction of the vector passing between these two points is a [436].

(b) For a rhombohedral unit cell, the direction indices will also be [436]. Lattice position coordinates for both vector head and tail will be the same as for tetragonal. Likewise, incorporating these lattice position coordinates into Equations 3.10a-3.10c also yield

$u = 4$

$v = 3$

$w = 6$

3.39 *For tetragonal crystals, cite the indices of directions that are equivalent to each of the following directions:*

(a) [011]

(b) [100]

Solution

(a) For tetragonal crystals, lattice parameter relationships are as follows: $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$. One way to determine indices of directions that are equivalent to [011] is to find indices for all direction vectors that have the same length as the vector for the [011] direction. Let us assign vector tail coordinates to the origin of the coordinate system, then $x_1 = y_1 = z_1 = 0$. Under these circumstances, vector length $\bar{V}$ is equal to

$$\bar{V} = \sqrt{x_2^2 + y_2^2 + z_2^2}$$

For the [011] direction

$x_2 = 0a$

$y_2 = b = a$ (since, for tetragonal $a = b$)

$z_2 = c$

Therefore, the vector length for the [011] direction $(\bar{V}_{011})$ is equal to

$$\bar{V}_{011} == \sqrt{x_2^2 + y_2^2 + z_2^2}$$

$$= \sqrt{(0a)^2 + a^2 + c^2}$$

$$= \sqrt{a^2 + c^2}$$

It is now necessary to find all combinations of x_2, y_2, and z_2 that yield the above expression for $(\bar{V}_{011})$. First of all, only values of $+c$ and $-c$, when squared yield c^2. This means that for the index w (of $[uvw]$) only values of +1 and −1 are possible.

With regard to values of the u and v indices, the sum of x_2^2 and y_2^2 must equal a^2. Therefore one of either u or v must be zero, whereas the other may be either +1 or −1. Therefore, in addition to [011] there are seven combinations u, v, and w indices that meet these criteria, which are listed as follows: [101], $[\bar{1}0\bar{1}]$, $[\bar{1}01]$, $[10\bar{1}]$, $[01\bar{1}]$, $[0\bar{1}1]$, and $[0\bar{1}\bar{1}]$.

(b) As with part (a), if we assign the vector tail coordinates to the origin of the coordinate system, then for the [100] direction vector head coordinates are as follows:

$x_2 = a$

$y_2 = 0b = 0a$ (since, for tetragonal $a = b$)

$z_2 = 0c$

Therefore, the vector length for the [100] direction $(\overline{V}_{100})$ is equal to

$$\overline{V}_{100} == \sqrt{x_2^2 + y_2^2 + z_2^2}$$

$$= \sqrt{(a)^2 + (0a)^2 + (0c)^2}$$

$$= \sqrt{a^2} = a$$

It is now necessary to find all combinations of x_2, y_2, and z_2 that yield the above expression for $(\overline{V}_{100})$. First of all, for all directions $c = 0$ because c is not included in the expression for $\overline{V}_{100}$. This means that for the index w (of [uvw]) for all directions must be zero.

With regard to values of the u and v indices, the sum of x_2^2 and y_2^2 must equal a^2. Therefore one of either u or v must be zero, whereas the other may be either +1 or –1. Therefore, in addition to [100] there are three combinations u, v, and w indices that meet these criteria, which are listed as follows: $[\overline{1}00]$, [010], and $[0\overline{1}0]$.

3.40 *Convert the [110] and $[00\overline{1}]$ directions into the four-index Miller–Bravais scheme for hexagonal unit cells.*

Solution

We are asked to convert [110] and $[00\overline{1}]$ directions into the four-index Miller-Bravais scheme for hexagonal unit cells. For [110]

$$U = 1$$

$$V = 1$$

$$W = 0$$

From Equations 3.11a-3.11d

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$v = \frac{1}{3}(2V - U) = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$t = -(U + V) = -\left(\frac{1}{3} + \frac{1}{3}\right) = -\frac{2}{3}$$

$$w = W = 0$$

It is necessary to multiply these numbers by 3 in order to reduce them to the lowest set of integers. Thus, the direction is represented as [*uvtw*] = $[11\overline{2}0]$.

For the $[00\overline{1}]$ direction

$$U = 0$$

$$V = 0$$

$$W = -1$$

Therefore, conversion to the four-index scheme is accomplished as follows:

$$U = \frac{1}{3}[(2)(0) - 0] = 0$$

$$V = \frac{1}{3}[(2)(0) - 0] = 0$$

$$t = -(0 + 0) = 0$$

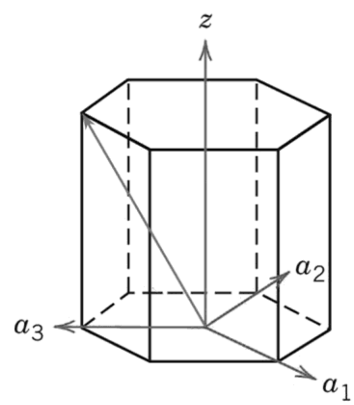
$$w = -1$$

Thus, the direction is represented as $[uvtw] = [000\overline{1}]$.

3.41 *Determine the indices for the directions shown in the following hexagonal unit cells:*

Solutions

(a)



One way solve this problem is to begin by determining the *U*, *V*, and *W* indices for the vector referenced to the three-axis scheme; this is possible using Equations 3.13a through 3.13c. Because the tail of the vector passes through the origin, $a_1'' = a_2'' = 0a$, and $z'' = 0c$ Furthermore, coordinates for the vector head are as follows:

$$a_1' = -a \qquad a_2' = -a \qquad z' = c$$

Now, solving for *U*, *V*, and *W* using Equations 3.13a, 3.13b, and 3.13c assuming a value of 1 for the parameter *n*

$$U = n\left(\frac{a_1' - a_1''}{a}\right) = (1)\left(\frac{-a - 0a}{a}\right) = -1$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) = (1)\left(\frac{-a - 0a}{a}\right) = -1$$

$$W = n\left(\frac{z' - z''}{c}\right) = (1)\left(\frac{c - 0c}{c}\right) = 1$$

Now, it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a through 3.11d, as follows:

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}\left[(2)(-1) - (-1)\right] = -\frac{1}{3}$$

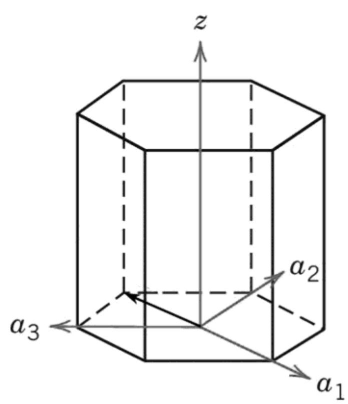
$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\left[(2)(-1) - (-1)\right] = -\frac{1}{3}$$

$$t = -(u + v) = -\left(-\frac{1}{3} - \frac{1}{3}\right) = \frac{2}{3}$$

$$w = W = 1$$

Multiplication of these three indices by the factor 3 reduces them to the lowest set, which equals values for *u*, *v*, *t*, and *w* of –1, –1, 2, and 3. Therefore the vector represents the $[\overline{1}\overline{1}23]$ direction.

(b)



This problem is to begin by determining the *U*, *V*, and *W* indices for the vector referenced to the three-axis scheme; this is possible using Equations 3.13a through 3.13c. Because the tail of the vector passes through the origin, $a_1' = a_2' = 0a$, and $z' = 0c$ Furthermore, coordinates for the vector head are as follows:

$a_1' = -a$ $\quad$ $a_2' = 0a$ $\quad$ $z' = 0c$

Now, solving for *U*, *V*, and *W* using Equations 3.13a, 3.13b, and 3.13c assuming a value of 1 for the parameter *n*

$$U = n\left(\frac{a_1' - a_1''}{a}\right) = (1)\left(\frac{-a - 0a}{a}\right) = -1$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) = (1)\left(\frac{0a - 0a}{a}\right) = 0$$

$$w = n\left(\frac{z' - z''}{c}\right) = (1)\left(\frac{0c - 0c}{c}\right) = 0$$

Now, it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a through 3.11d, as follows:

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}\left[(2)(-1) - (0)\right] = -\frac{2}{3}$$

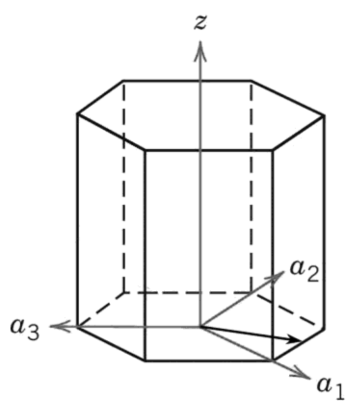
$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\left[(2)(0) - (-1)\right] = \frac{1}{3}$$

$$t = -(u + v) = -\left(-\frac{2}{3} + \frac{1}{3}\right) = \frac{1}{3}$$

$$w = W = 0$$

Multiplication of these three indices by the factor 3 reduces them to the lowest set, which equals values for *u*, *v*, *t*, and *w* of –2, 1, 1, and 0. Therefore the vector represents the $[\overline{2}110]$ direction.

(c)



This problem is to begin by determining the *U*, *V*, and *W* indices for the vector referenced to the three-axis scheme; this is possible using Equations 3.13a through 3.13c. Because the tail of the vector passes through the origin, $a_1'' = a_2'' = 0a$, and $z'' = 0c$ Furthermore, coordinates for the vector head are as follows:

$a_1' = a$ $\quad a_2' = a/2$ $\quad z' = 0c$

Now, solving for *U*, *V*, and *W* using Equations 3.13a, 3.13b, and 3.13c assuming a value of 1 for the parameter *n*

$$U = n\left(\frac{a_1' - a_1''}{a}\right) = (1)\left(\frac{a - 0a}{a}\right) = 1$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) = (1)\left(\frac{a/2 - 0a}{a}\right) = \frac{1}{2}$$

$$W = n\left(\frac{z' - z''}{c}\right) = (1)\left(\frac{0c - 0c}{c}\right) = 0$$

Multiplying these integers by the factor 2, reduces them to the following indices:

$U = 2$ $\quad\quad V = 1$ $\quad\quad W = 0$

Now, it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a through 3.11d, as follows:

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}\left[(2)(2) - (1)\right] = \frac{3}{3} = 1$$

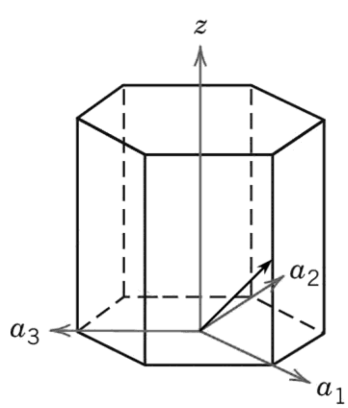
$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\left[(2)(1) - 2\right] = 0$$

$$t = -(u + v) = -\left(1 + 0\right) = -1$$

$$w = W = 0$$

Therefore, the values for *u*, *v*, *t*, and *w* are 1, 0, –1, and 0, and the vector represents the $[10\bar{1}0]$ direction.

(d)



We begin by determining the *U*, *V*, and *W* indices for the vector referenced to the three-axis scheme; this is possible using Equations 3.13a through 3.13c. Because the tail of the vector passes through the origin, $a_1' = a_2' = 0a$, and $z' = 0c$ Furthermore, coordinates for the vector head are as follows:

$$a_1' = a \qquad a_2' = 0a \qquad z' = c/2$$

Now, solving for *U*, *V*, and *W* using Equations 3.13a, 3.13b, and 3.13c assuming a value of 1 for the parameter *n*

$$U = n\left(\frac{a_1' - a_1''}{a}\right) = (1)\left(\frac{a - 0a}{a}\right) = 1$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) = (1)\left(\frac{0a - 0a}{a}\right) = 0$$

$$W = n\left(\frac{z' - z''}{c}\right) = (1)\left(\frac{c/2 - 0c}{c}\right) = \frac{1}{2}$$

Multiplying these integers by the factor 2, reduces them to the following indices:

$$U = 2 \qquad V = 0 \qquad W = 1$$

Now, it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a through 3.11d, as follows:

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}\left[(2)(2) - (0)\right] = \frac{4}{3}$$

$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\left[(2)(0) - (2)\right] = -\frac{2}{3}$$

$$t = -(u + v) = -\left(\frac{4}{3} - \frac{2}{3}\right) = -\frac{2}{3}$$

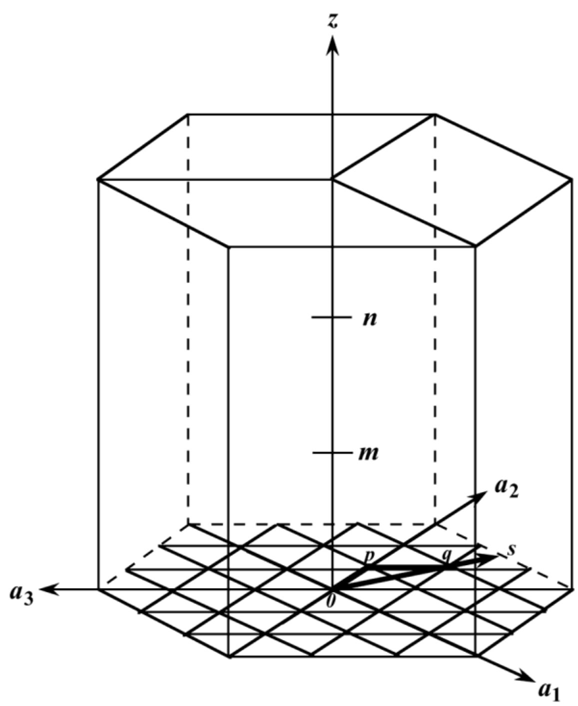
$$w = W = 1$$

Multiplication of these three indices by the factor 3 reduces them to the lowest set, which equals values for *u, v, t*, and *w* of 4, –2, –2, and 3. Therefore, this vector represents the $[4\overline{2}\overline{2}3]$ direction.

3.42 *Sketch the* $[01\bar{1}0]$ *and* $[\bar{2}\bar{2}43]$ *directions in a hexagonal unit cell.*

Solution

The first portion of this problem asks that we plot the $[01\bar{1}0]$ within a hexagonal unit cell. Below is shown this direction plotted within a hexagonal unit cell having a ruled-net coordinate scheme.



For the sake of convenience we will position the vector tail at the origin of the coordinate system. This means that $a_1'' = a_2'' = a_3'' = 0a$ and $z'' = 0c$. Coordinates for the vector head (a_1', a_2', a_3' and z') may be determined using rearranged forms of Equations 3.12a through 3.12d, taking the value of n to be unity, and since, for this $[01\bar{1}0]$ direction

$$u = 0 \qquad v = 1 \qquad t = -1 \qquad w = 0$$

Thus, vector head coordinates are determined as follows:

$$a_1' = \frac{ua}{3n} + a_1'' = \frac{0a}{3(1)} + 0a = 0a$$

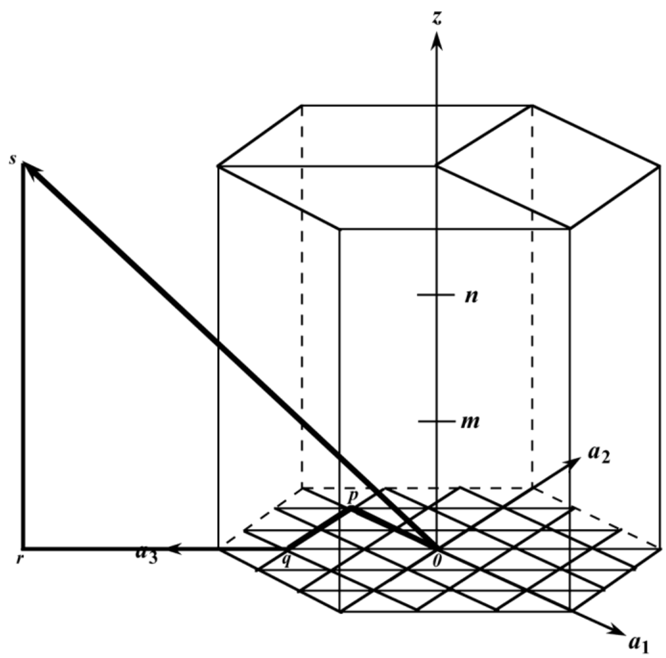
$$a_2' = \frac{va}{3n} + a_2'' = \frac{a}{3(1)} + 0a = \frac{a}{3}$$

$$a_3' = \frac{ta}{3n} + a_3'' = \frac{-a}{3(1)} + 0a = -\frac{a}{3}$$

$$z' = \frac{wc}{3n} + z' = \frac{0c}{3(1)} + 0c = 0c$$

In constructing this vector, we begin at the origin of the coordinate system, point *o*. Because $a_1' = 0a$, we do not move in the direction of the a_1 axis. However, because $a_2' = \frac{a}{3}$, we proceed from point *o*, $\frac{a}{3}$ units distance along the a_2, from point *o* to point *p*, and from here $-\frac{a}{3}$ units parallel to the a_3 axis, from point *p* to point *q*. Since the *z'* is zero, it is not necessary to proceed from point *q* parallel to the *z* axis. Thus, the $[01\bar{1}0]$ direction corresponds to the vector that extends from point *o* to point *s* as shown.

For the second portion of the problem, we are asked to plot the $[\bar{2}\bar{2}43]$ direction, which is shown below.



For the sake of convenience we will position the vector tail at the origin of the coordinate system. This means that $a_1'' = a_2'' = a_3'' = 0a$ and $z'' = 0c$. Coordinates for the vector head (a_1', a_2', a_3' and z') may be determined using rearranged forms of Equations 3.12a through 3.12d, taking the value of *n* to be unity, and since, for this $[\bar{2}\bar{2}43]$ direction

$u = -2$ $v = -2$ $t = 4$ $w = 3$

Thus, vector head coordinates are determined as follows:

$$a_1' = \frac{ua}{3n} + a_1'' = \frac{-2a}{3(1)} + 0a = -\frac{2a}{3}$$

$$a_2' = \frac{va}{3n} + a_2'' = \frac{-2a}{3(1)} + 0a = -\frac{2a}{3}$$

$$a_3' = \frac{ta}{3n} + a_3'' = \frac{4a}{3(1)} + 0a = \frac{4a}{3}$$

$$z' = \frac{wc}{3n} + z'' = \frac{3c}{3(1)} + 0c = c$$

In constructing this vector, we begin at the origin of the coordinate system, point *o*. Because $a_1' = -\frac{2a}{3}$, we move $-\frac{2a}{3}$ along the a_1 axis, from point *o* to point *p*. From here we proceed $-\frac{2a}{3}$ units parallel to the a_2 axis ($a_2' = -\frac{2a}{3}$), from point *p* to point *q*. Next we proceed $\frac{4a}{3}$ units parallel to the a_3 axis, from point *q* to point *r*, and, finally, from point *r*, *c* units parallel to the *z* axis to point *s*. Hence, this $[\bar{2}\bar{2}43]$ direction corresponds to the vector that extends from point *o* to point *s*, as shown in the above diagram.

3.43 *Using Equations 3.11a, 3.11b, 3.11c, and 3.11d, derive expressions for each of the three U, V, and W indices in terms of the four u, v, t, and w indices.*

Solution

It is first necessary to do an expansion of Equation 3.11a as

$$u = \frac{1}{3}(2U - V) = \frac{2U}{3} - \frac{V}{3}$$

And solving this expression for *V* yields

$$V = 2U - 3u$$

Now, substitution of this expression into Equation 3.11b gives

$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\Big[(2)(2U - 3u) - U\Big] = U - 2u$$

Or

$$U = v + 2u$$

And, solving for *v* from Equation 3.11c leads to

$$v = -(u + t)$$

which, when substituted into the above expression for *U*, yields

$$U = v + 2u = -u - t + 2u = u - t$$

In solving for an expression for *V*, we begin with the one of the above expressions for this parameter—i.e.,

$$V = 2U - 3u$$

Now, substitution of the above expression for *U* into this equation leads to

$$V = 2U - 3u = (2)(u - t) - 3u = -u - 2t$$

And solving for *u* from Equation 3.11c gives

$$u = -v - t$$

which, when substituted in the previous equation results in the following expression for V

$$V = -u - 2t = -(-v - t) - 2t = v - t$$

And, from Equation 3.11d

$$W = w$$

Crystallographic Planes

3.44 *(a) Draw an orthorhombic unit cell, and within that cell a* $(02\bar{1})$ *plane.*

(b) Draw a monoclinic unit cell, and within that cell a (200) plane.

Solution

(a) We are asked to draw a $(02\bar{1})$ plane within an orthorhombic unit cell. For the orthorhombic crystal system, relationships among the lattice parameters are as follows:

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

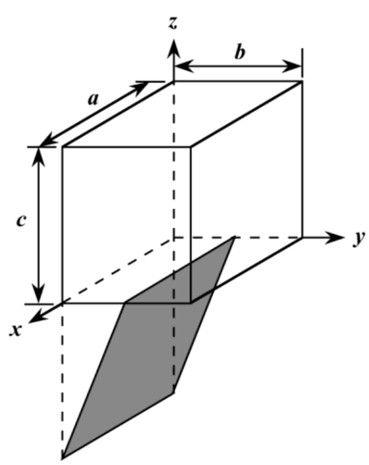
Thus, the three coordinate axes are parallel to one another. In order to construct the $(02\bar{1})$ plane it is necessary to determine intersections with the coordinate axes. The *A*, *B*, and *C* intercepts are computed using rearranged forms of Equations 3.14a, 3.14b, and 3.14c with $h = 0$, $k = 2$, and $l = -1$. Thus, intercept values are as follows (assuming $n = 1$):

$$A = \frac{na}{h} = \frac{(1)a}{0} = \infty a$$

$$B = \frac{nb}{k} = \frac{(1)b}{2} = \frac{b}{2}$$

$$C = \frac{nc}{l} = \frac{(1)c}{-1} = -c$$

Thus, intercepts with the *x*, *y*, and *z* axes are respectively, ∞a, $b/2$, and $-c$; this plane parallels the *x* axis inasmuch as its intercept is infinity. The plane that satisfies these requirements has been drawn within the orthorhombic unit cell below.



(b) In this part of the problem we are asked to draw a (200) plane within a monoclinic unit cell. For the monoclinic crystal system, relationships among the lattice parameters are as follows:

$a \neq b \neq c$

$\alpha = \gamma = 90° \neq \beta$

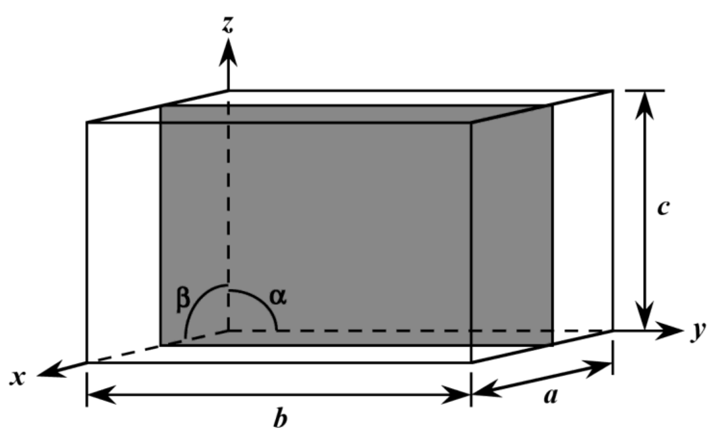
In order to construct the (200) plane it is necessary to determine intersections with the coordinate axes. The *A*, *B*, and *C* intercepts are computed using rearranged forms of Equations 3.14a, 3.14b, and 3.14c with $h = 2$, $k = 0$, and $l = 0$. Thus, intercept values are as follows (assuming $n = 1$):

$$A = \frac{na}{h} = \frac{(1)a}{2} = \frac{a}{2}$$

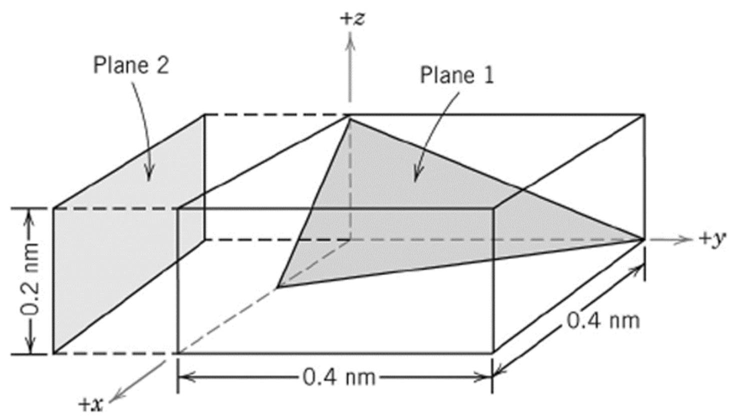
$$B = \frac{nb}{k} = \frac{(1)b}{0} = ¥ b$$

$$C = \frac{nc}{l} = \frac{(1)c}{0} = ¥ c$$

Thus, intercepts with the *x*, *y*, and *z* axes are respectively, *a*/2, ∞*b*, and ∞*c;* this plane parallels both the *y* and *z* axes inasmuch their intercepts are infinity. The plane that satisfies these requirements has been drawn within the monoclinic unit cell below.



3.45 *What are the indices for the two planes drawn in the following sketch?*



Solution

In order to solve for the *h, k,* and *l* indices for these two crystallographic planes it is necessary to use Equations 3.14a, 3.14b, and 3.14c.

For Plane 1, the intercepts with the *x, y,* and *z* axes are *a*/2 (0.2 nm), *b* (0.4 nm), and *c* (0.2 nm)—that is

$A = a/2 \qquad B = b \qquad C = c$

Thus, from Equations 3.14a-3.14c (assuming $n = 1$) we have the following:

$$h = \frac{na}{A} = \frac{(1)a}{a/2} = 2$$

$$k = \frac{nb}{B} = \frac{(1)b}{b} = 1$$

$$l = \frac{nc}{C} = \frac{(1)c}{c} = 1$$

Therefore, Plane 1 is a (211) plane.

Plane 2 is parallel to both the *x* and *z* axes, which means that the respective intercepts are ∞a and ∞c. The intercept with the *y* axis is at $-b/2$ (0.2 nm). Thus, values of the intercepts are as follows:

$A = \infty a \qquad B = -b/2 \qquad C = \infty c$

And when we incorporate these values into Equations 3.14a, 3.14b, and 3.14c, computations of the *h, k,* and *l* indices are as follows (assuming that $n = 1$):

$$h = \frac{na}{A} = \frac{(1)a}{\infty a} = 0$$

$$k = \frac{nb}{B} = \frac{(1)b}{-b/2} = -2$$

$$l = \frac{nc}{C} = \frac{(1)c}{\infty c} = 0$$

Therefore, Plane 2 is a $(0\bar{2}0)$ plane, which is also parallel to a $(0\bar{1}0)$ plane.

3.46 *Sketch within a cubic unit cell the following planes:*

(a) $(10\bar{1})$	*(e)* $(\bar{1}1\bar{1})$
(b) $(2\bar{1}1)$	*(f)* $(\bar{2}12)$
(c) (012)	*(g)* $(3\bar{1}2)$
(d) $(3\bar{1}3)$	*(h)* (301)

<u>Solutions</u>

In order to plot each of these planes it is necessary to determine the axial intercepts using rearranged forms of Equations 3.14a, 3.14b, and 3.14c.

The indices for plane (a) are as follows:

$$h = 1 \qquad k = 0 \qquad l = -1$$

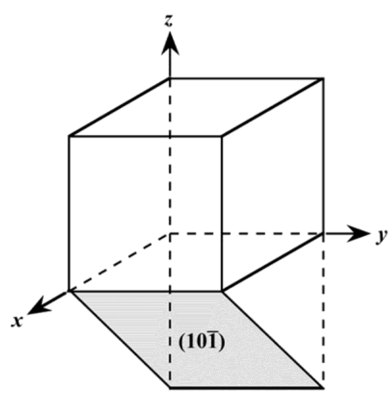
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{1} = a$$

$$B = \frac{nb}{k} = \frac{(1)b}{0} = \infty b$$

$$C = \frac{nc}{l} = \frac{(1)c}{-1} = -c$$

Thus, this plane intersects the *x* and *z* axes at *a* and –*c*, respectively, and parallels the *y* axis. This plane has been drawn in the following sketch.



The indices for plane (b) are as follows:

$$h = 2 \qquad k = -1 \qquad l = 1$$

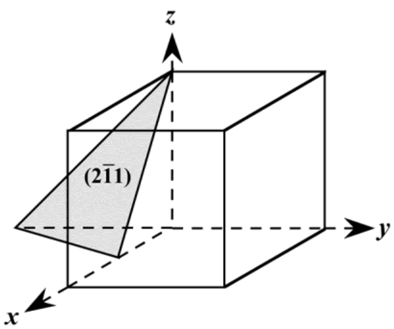
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{2} = \frac{a}{2}$$

$$B = \frac{nb}{k} = \frac{(1)b}{-1} = -b$$

$$C = \frac{nc}{l} = \frac{(1)c}{1} = c$$

Thus, this plane intersects the *x*, *y*, and *z* axes at *a*/2, –*b*, and *c*, respectively. This plane has been drawn in the following sketch.



The indices for plane (c) are as follows:

$h = 0$ $k = 1$ $l = 2$

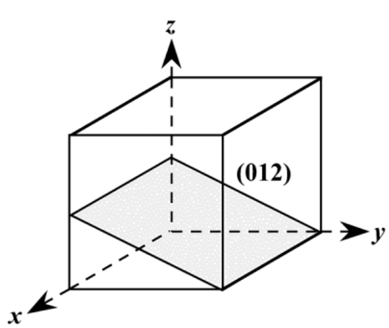
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that $n = 1$):

$$A = \frac{na}{h} = \frac{(1)a}{0} = \infty a$$

$$B = \frac{nb}{k} = \frac{(1)b}{1} = b$$

$$C = \frac{nc}{l} = \frac{(1)c}{2} = \frac{c}{2}$$

Thus, this plane intersects the *y*, and *z* axes at *b* and *c*/2, respectively, and parallels the *x* axis. This plane has been drawn in the following sketch.



The indices for plane (d) are as follows:

$h = 3 \qquad k = -1 \qquad l = 3$

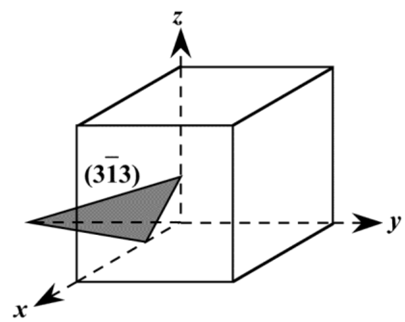
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{3} = \frac{a}{3}$$

$$B = \frac{nb}{k} = \frac{(1)b}{-1} = -b$$

$$C = \frac{nc}{l} = \frac{(1)c}{3} = \frac{c}{3}$$

Thus, this plane intersects the *x*, *y*, and *z* axes at *a*/3, –*b* and *c*/3, respectively. This plane has been drawn in the following sketch.



The indices for plane (e) are as follows:

$h = -1 \qquad k = 1 \qquad l = -1$

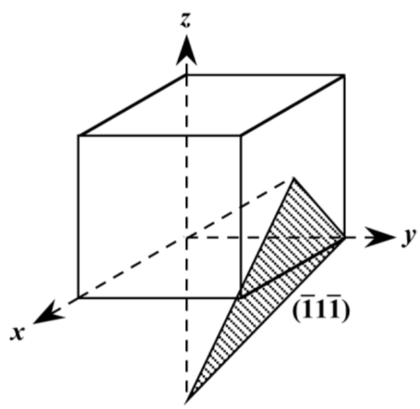
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{-1} = -a$$

$$B = \frac{nb}{k} = \frac{(1)b}{1} = b$$

$$C = \frac{nc}{l} = \frac{(1)c}{-1} = -c$$

Thus, this plane intersects the *x*, *y*, and *z* axes at –*a*, *b* and –*c*, respectively. This plane has been drawn in the following sketch.



The indices for plane (f) are as follows:

$h = -2$ $\quad k = 1$ $\quad l = 2$

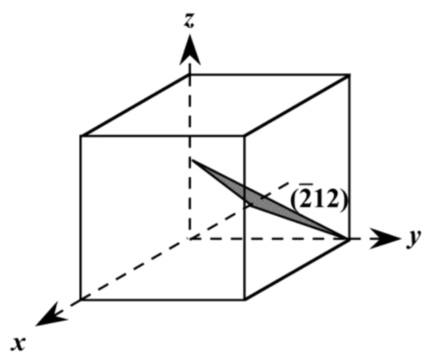
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{-2} = -\frac{a}{2}$$

$$B = \frac{nb}{k} = \frac{(1)b}{1} = b$$

$$C = \frac{nc}{l} = \frac{(1)c}{2} = \frac{c}{2}$$

Thus, this plane intersects the *x*, *y*, and *z* axes at –*a*/2, *b* and *c*/2, respectively. This plane has been drawn in the following sketch.



The indices for plane (g) are as follows:

$h = 3$ $\quad k = -1$ $\quad l = 2$

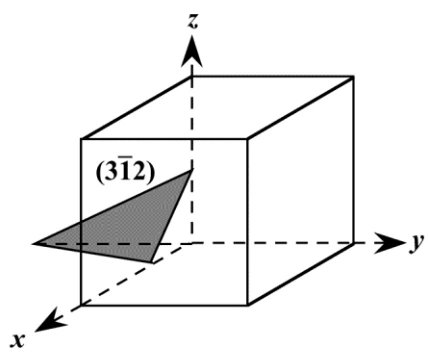
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{3} = \frac{a}{3}$$

$$B = \frac{nb}{k} = \frac{(1)b}{-1} = -b$$

$$C = \frac{nc}{l} = \frac{(1)c}{2} = \frac{c}{2}$$

Thus, this plane intersects the *x*, *y*, and *z* axes at *a*/3, –*b* and *c*/2, respectively. This plane has been drawn in the following sketch.



The indices for plane (h) are as follows:

$h = 3 \qquad k = 0 \qquad l = 1$

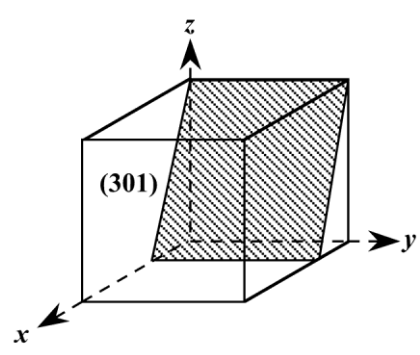
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{3} = \frac{a}{3}$$

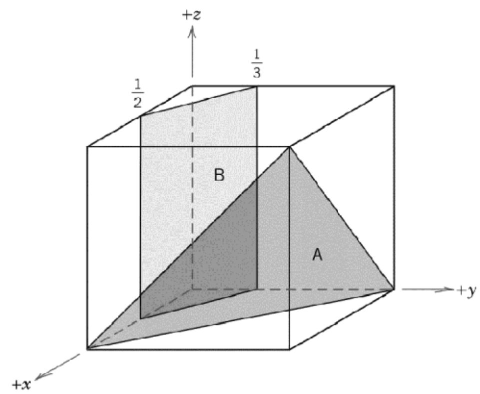
$$B = \frac{nb}{k} = \frac{(1)b}{0} = \infty b$$

$$C = \frac{nc}{l} = \frac{(1)c}{1} = c$$

Thus, this plane intersects the *x* and *z* axes at *a*/3 and *c*, respectively, and parallels the *y* axis. This plane has been drawn in the following sketch.



3.47 *Determine the Miller indices for the planes shown in the following unit cell:*



Solution

For plane A, the first thing we need to do is determine the intercepts of this plane with the *x, y,* and *z* axes. If we extend the plane back into the plane of the page, it will intersect the *z* axis at $-c$. Furthermore, intersections with the *x* and *y* axes are, respectively, *a* and *b*. The is, values of the intercepts *A*, *B*, and *C*, are *a, b,* and $-c$. If we assume that the value of *n* is 1, the values of *h, k,* and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{a} = 1$$

$$k = \frac{nb}{B} = \frac{(1)b}{b} = 1$$

$$l = \frac{nc}{C} = \frac{(1)c}{-c} = -1$$

Therefore, the A plane is a $(11\bar{1})$ plane.

For plane B, its intersections with with the *x, y,* and *z* axes are *a*/2, *b*/3, and ∞c (because this plane parallels the *z* axis)—these three values are equal to *A, B,* and *C,* respectively. If we assume that the value of *n* is 1, the values of *h, k,* and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

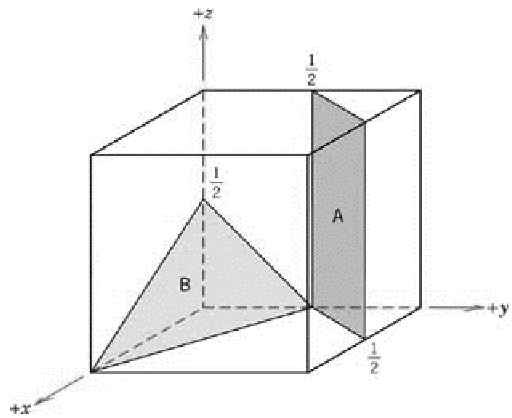
$$h = \frac{na}{A} = \frac{(1)a}{a/2} == 2$$

$$k = \frac{nb}{B} = \frac{(1)b}{b/3} = 3$$

$$l = \frac{nc}{C} = \frac{(1)c}{¥c} = 0$$

Therefore, the B plane is a (230) plane.

3.48 *Determine the Miller indices for the planes shown in the following unit cell:*



For plane A, we will move the origin of the coordinate system one unit cell distance to the right along the *y* axis. Referenced to this new origin, the plane's intersections with with the *x* and *y* axes are *a*/2, –*b*/2; since it is parallel to the *z* axis, the intersections is taken as and ∞*c*—these three values are equal to *A, B,* and *C*, respectively. If we assume that the value of *n* is 1/2 (because of the *a*/2 and –*b*/2 intercepts), the values of *h*, *k*, and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1/2)a}{a/2} = 1$$

$$k = \frac{nb}{B} = \frac{(1/2)b}{-b/2} = -1$$

$$l = \frac{nc}{C} = \frac{(1/2)c}{\infty c} = 0$$

Therefore, plane A is a $(1\bar{1}0)$ plane.

For plane B, its intersections with with the *x, y,* and *z* axes are *a*, *b*/2, and *c/*2; therefore, these three values are equal to *A*, *B*, and *C*, respectively. If we assume that the value of *n* is 1, the values of *h*, *k*, and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

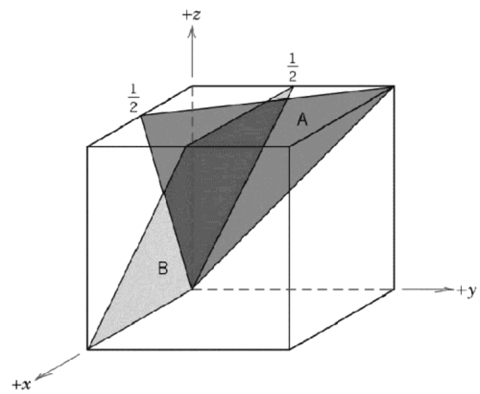
$$h = \frac{na}{A} = \frac{(1)a}{a} == 1$$

$$k = \frac{nb}{B} = \frac{(1)b}{b/2} = 2$$

$$l = \frac{nc}{C} = \frac{(1)c}{c/2} = 2$$

Therefore, the B plane is a (122) plane.

3.49 *Determine the Miller indices for the planes shown in the following unit cell:*



Solution

Since Plane A passes through the origin of the coordinate system as shown, we will move the origin of the coordinate system one unit cell distance vertically along the *z* axis. Referenced to this new origin, intercepts with the *x*, *y*, and *z* axes are, respectively, *a*/2, *b*, and –*c*. If we assume that the value of *n* is 1, the values of *h*, *k*, and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{a/2} = 2$$

$$k = \frac{nb}{B} = \frac{(1)b}{b} = 1$$

$$l = \frac{nc}{C} = \frac{(1)c}{-c} = -1$$

Therefore, the A plane is a $(21\overline{1})$ plane.

For plane B, since the plane passes through the origin of the coordinate system as shown, we will move the origin one unit cell distance up vertically along the *z* axis. Referenced to this new origin, intercepts with the *y* and *z* axes are, respectively, *b*/2 and –*c*. Because the plane is parallel to the *x* axis, its intersections is taken as and ∞*a*. Thus, values of *A*, *B*, and *C*, respectively, correspond to ∞*a*, *b/*2, and –*c*. If we assume that the value of *n* is 1, the values of *h*, *k*, and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{\infty a} = 0$$

$$k = \frac{nb}{B} = \frac{(1)b}{b/2} = 2$$

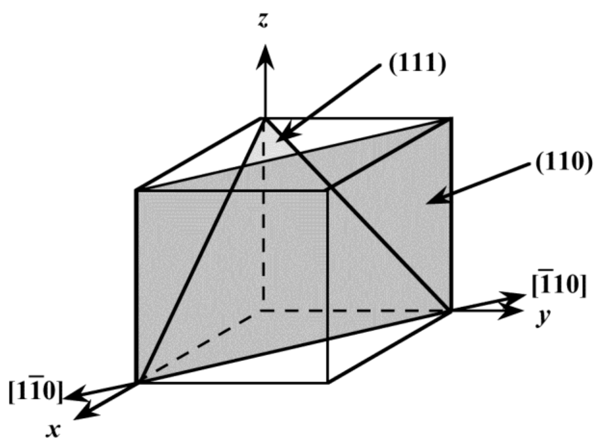
$$l = \frac{nc}{C} = \frac{(1)c}{-c} = -1$$

Therefore, the B plane is a $(02\bar{1})$ plane.

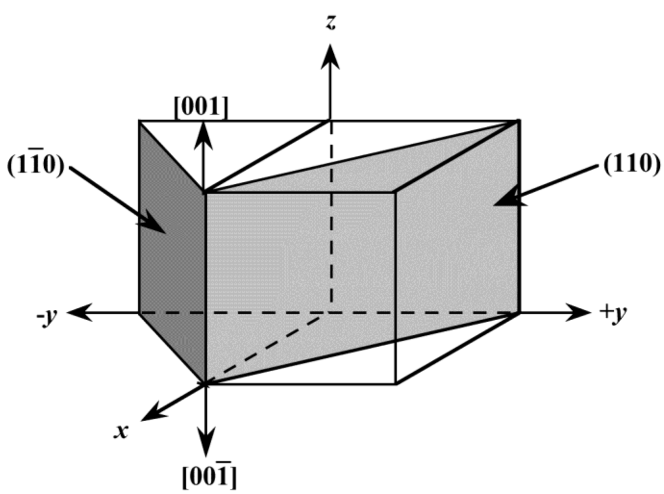
3.50 *Cite the indices of the direction that results from the intersection of each of the following pairs of planes within a cubic crystal: (a) the (110) and (111) planes, (b) the (110) and $(1\bar{1}0)$ planes, and (c) the $(11\bar{1})$ and (001) planes.*

Solution

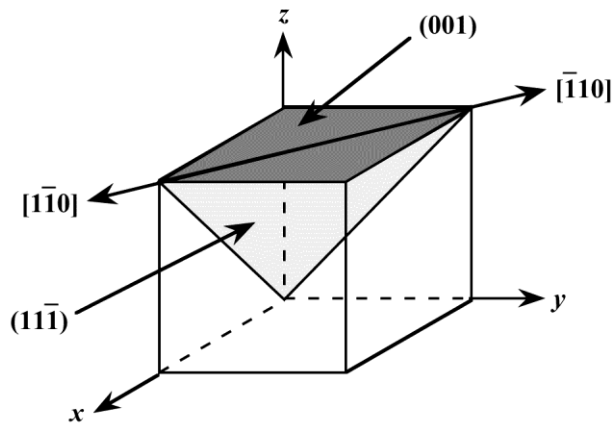
(a) In the figure below is shown (110) and (111) planes, and, as indicated, their intersection results in a $[\bar{1}10]$, or equivalently, a $[1\bar{1}0]$ direction.



(b) In the figure below is shown (110) and $(1\bar{1}0)$ planes, and, as indicated, their intersection results in a [001], or equivalently, a $[00\bar{1}]$ direction.



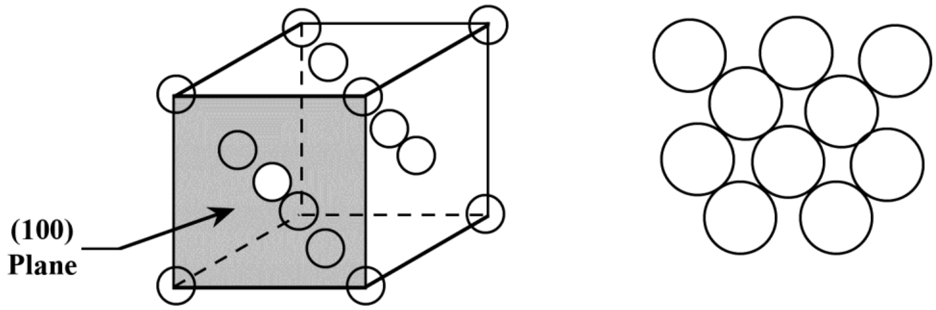
(c) In the figure below is shown $(11\bar{1})$ and (001) planes, and, as indicated, their intersection results in a $[\bar{1}10]$, or equivalently, a $[1\bar{1}0]$ direction.



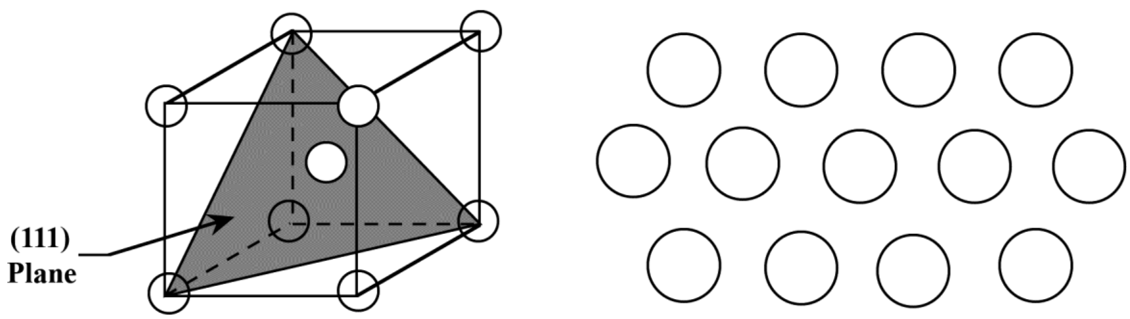
3.51 *Sketch the atomic packing of (a) the (100) plane for the FCC crystal structure, and (b) the (111) plane for the BCC crystal structure (similar to Figures 3.12b and 3.13b).*

<u>Solution</u>

(a) An FCC unit cell, its (100) plane, and the atomic packing of this plane are indicated below.



(b) A BCC unit cell, its (111) plane, and the atomic packing of this plane are indicated below.



3.52 *Consider the reduced-sphere unit cell shown in Problem 3.23, having an origin of the coordinate system positioned at the atom labeled O. For the following sets of planes, determine which are equivalent:*

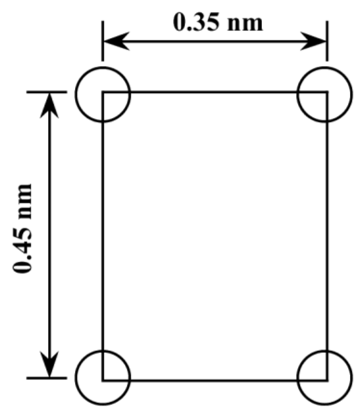
(a) (100), $(0\bar{1}0)$, *and* (001)

(b) (110), (101), (011), *and* $(\bar{1}01)$

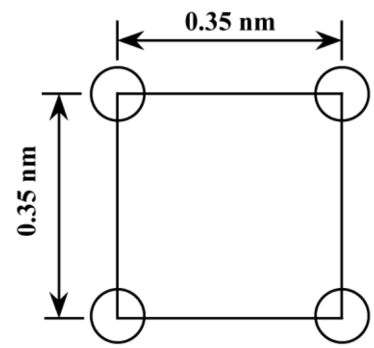
(c) (111), $(1\bar{1}1)$, $(11\bar{1})$), *and* $(\bar{1}1\bar{1})$

<u>Solution</u>

(a) The unit cell in Problem 3.20 is body-centered tetragonal. Of the three planes given in the problem statement the (100) and $(0\bar{1}0)$ are equivalent—that is, have the same atomic packing. The atomic packing for these two planes as well as the (001) are shown in the figure below.

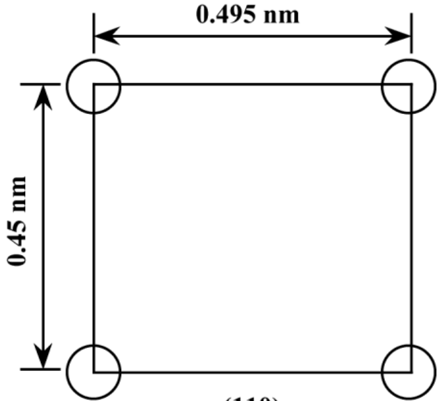


(100), (0$\bar{1}$0)

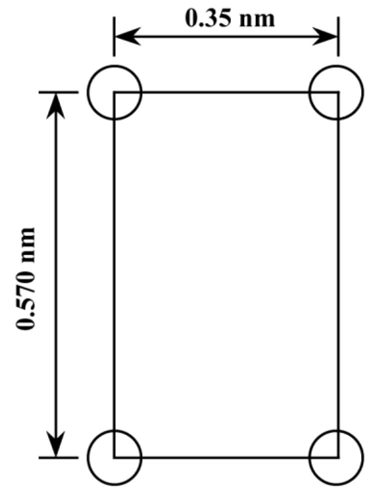


(001)

(b) Of the four planes cited in the problem statement, only (101), (011), and $(\bar{1}01)$ are equivalent—have the same atomic packing. The atomic arrangement of these planes as well as the (110) are presented in the figure below. *Note:* the 0.495 nm dimension for the (110) plane comes from the relationship $\left[(0.35 \text{ nm})^2 + (0.35 \text{ nm})^2\right]^{1/2}$. Likewise, the 0.570 nm dimension for the (101), (011), and $(\bar{1}01)$ planes comes from $\left[(0.35 \text{ nm})^2 + (0.45 \text{ nm})^2\right]^{1/2}$.

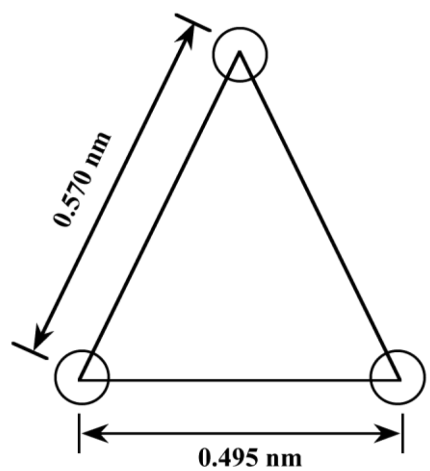


(110)

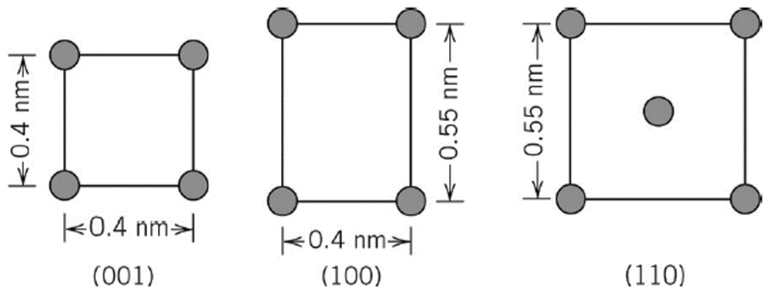


(101), (011), ($\bar{1}$01)

(c) All of the (111), ($1\bar{1}1$), ($11\bar{1}$), and ($\bar{1}1\bar{1}$) planes are equivalent, that is, have the same atomic packing as illustrated in the following figure:



3.53 *The accompanying figure shows three different crystallographic planes for a unit cell of a hypothetical metal. The circles represent atoms:*

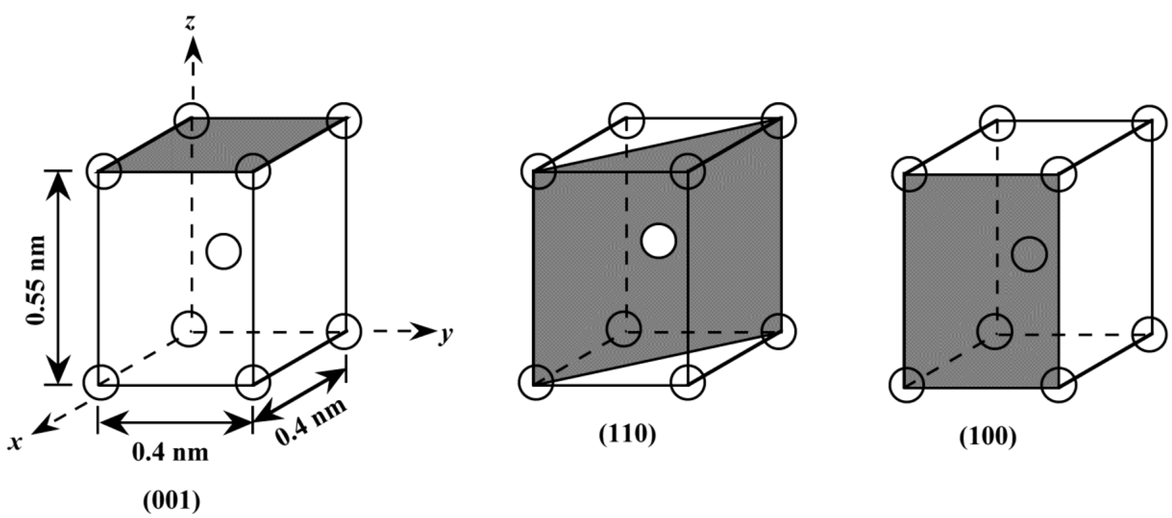


(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

Solution

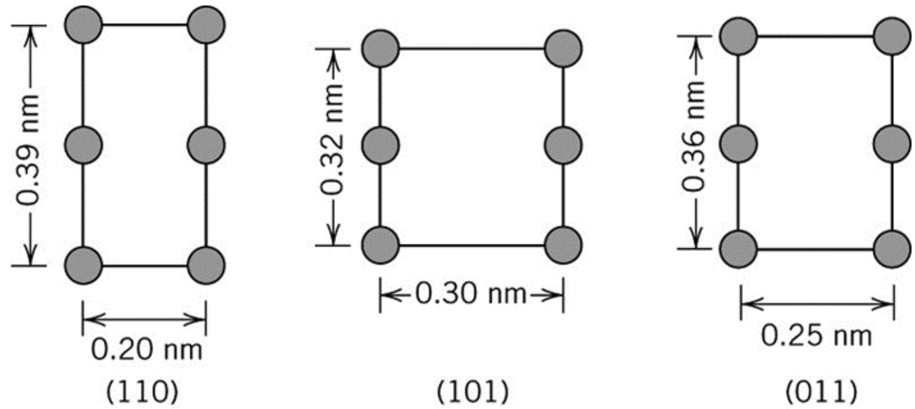
Unit cells are constructed below from the three crystallographic planes provided in the problem statement.



(a) This unit cell belongs to the *tetragonal system* since $a = b = 0.40$ nm, $c = 0.55$ nm, and $\alpha = \beta = \gamma = 90°$.

(b) This crystal structure would be called *body-centered tetragonal* since the unit cell has tetragonal symmetry, and an atom is located at each of the corners, as well as the cell center.

3.54 *The accompanying figure shows three different crystallographic planes for a unit cell of some hypothetical metal. The circles represent atoms:*



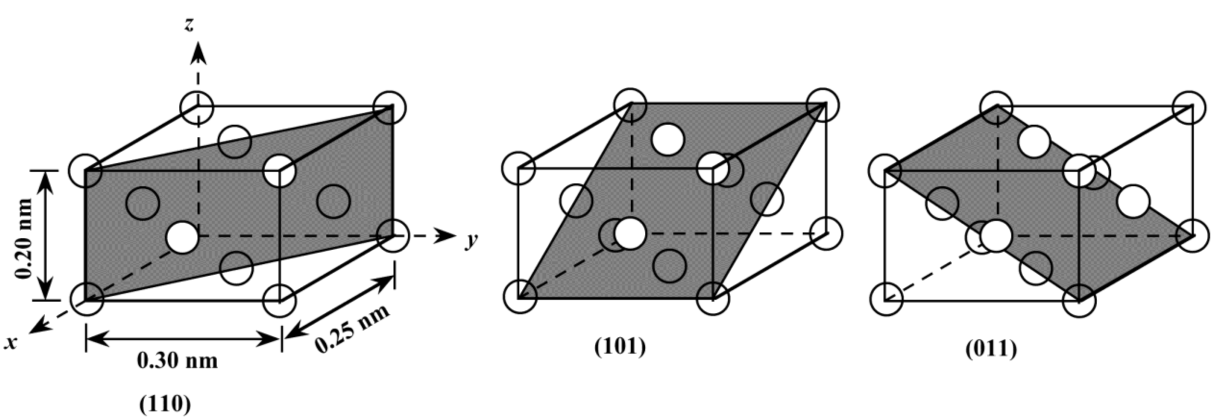
(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

(c) If the density of this metal is 18.91 g/cm³, determine its atomic weight.

Solution

The unit cells constructed below show the three crystallographic planes that were provided in the problem statement.



(a) This unit cell belongs to *the orthorhombic crystal system* since a = 0.25 nm, b = 0.30 nm, c = 0.20 nm, and $\alpha = \beta = \gamma = 90°$.

(b) This crystal structure would be called *face-centered orthorhombic* since the unit cell has orthorhombic symmetry, and an atom is located at each of the corners, as well as at each of the face centers.

(c) In order to compute its atomic weight, we employ a rearranged form of Equation 3.8, with n = 4; thus

$$A = \frac{\rho V_C N_\mathrm{A}}{n}$$

$$= \frac{(18.91\ \mathrm{g/cm^3})\ (2.0)(2.5)(3.0)\ (\times\ 10^{-24}\ \mathrm{cm^3/unit\ cell})(6.022\ \times\ 10^{23}\ \mathrm{atoms/mol})}{4\ \mathrm{atoms/unit\ cell}}$$

$$= 42.7\ \mathrm{g/mol}$$

3.55 *Convert the (111) and* $(0\bar{1}2)$ *planes into the four-index Miller–Bravais scheme for hexagonal unit cells.*

Solution

This problem asks that we convert (111) and $(0\bar{1}2)$ planes into the four-index Miller-Bravais scheme, (*hkil*), for hexagonal cells. For (111), *h* = 1, *k* = 1, and *l* = 1, and, from Equation 3.15, the value of *i* is equal to

$$i = -(h + k) = -(1 + 1) = -2$$

Therefore, the (111) plane becomes $(11\bar{2}1)$.

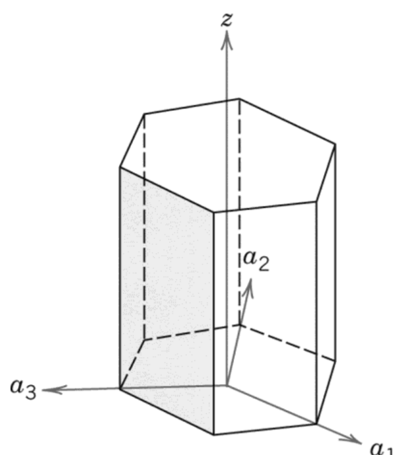
Now for the $(0\bar{1}2)$ plane, *h* = 0, *k* = –1, and *l* = 2, and computation of *i* using Equation 3.15 leads to

$$i = -(h + k) = -[0 + (-1)] = 1$$

such that $(0\bar{1}2)$ becomes $(0\bar{1}12)$.

3.56 *Determine the indices for the planes shown in the following hexagonal unit cells:*

<u>Solutions</u>



(a)

For this plane, intersections with a_1, a_2, and z axes are ∞a, $-a$, and ∞c (the plane parallels both a_1 and z axes). Therefore, these three values are equal to A, B, and C, respectively. If we assume that the value of n is 1, the values of h, k, and l are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{\infty a} = 0$$

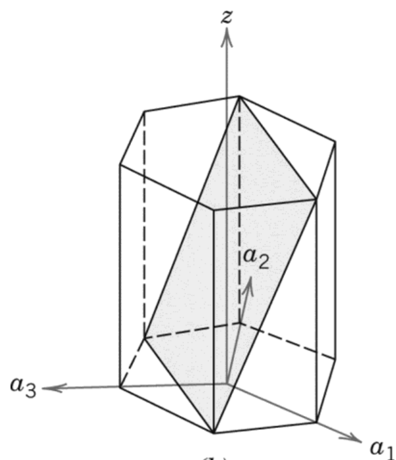
$$k = \frac{na}{B} = \frac{(1)a}{-a} = -1$$

$$l = \frac{nc}{C} = \frac{(1)c}{\infty c} = 0$$

Now, from Equation 3.15, the value of i is

$$i = -(h + k) = -[0 + (-1)] = 1$$

Hence, this is a $(0\bar{1}10)$ plane.



(b)

For this plane, intersections with a_1, a_2, and z axes are $-a$, $-a$, and $c/2$. Therefore, these three values are equal to A, B, and C, respectively. If we assume that the value of n is 1, the values of h, k, and l are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{-a} = -1$$

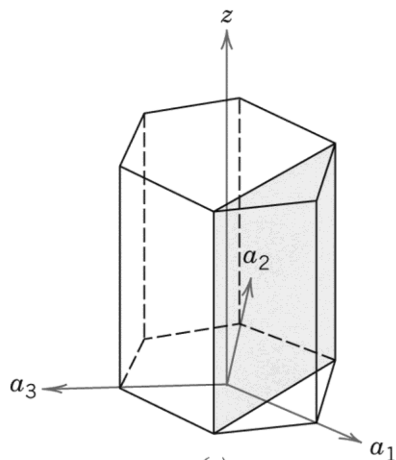
$$k = \frac{na}{B} = \frac{(1)a}{-a} = -1$$

$$l = \frac{nc}{C} = \frac{(1)c}{c/2} = 2$$

Now, from Equation 3.15, the value of i is

$$i = -(h + k) = -[-1 - 1)] = 2$$

Hence, this is a $(\bar{1}\bar{1}22)$ plane.



(c)

For this plane, intersections with a_1, a_2, and z axes are $a/2$, $-a$, and ∞c (the plane parallels the z axis). Therefore, these three values are equal to A, B, and C, respectively. If we assume that the value of n is 1, the values of h, k, and l are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{a/2} = 2$$

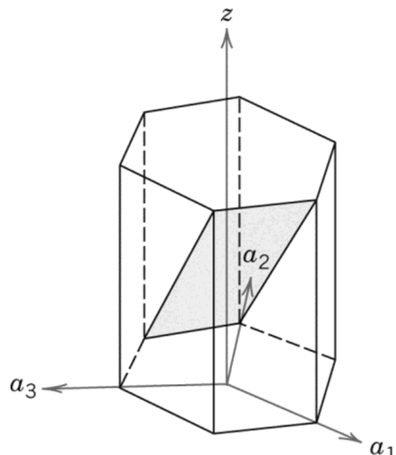
$$k = \frac{na}{B} = \frac{(1)a}{-a} = -1$$

$$l = \frac{nc}{C} = \frac{(1)c}{\infty c} = 0$$

Now, from Equation 3.15, the value of i is

$$i = -(h + k) = -(2 - 1) = -1$$

Hence, this is a $(2\bar{1}\bar{1}0)$ plane.



(d)

For this plane, intersections with a_1, a_2, and z axes are $-a$, a, and $c/2$. Therefore, these three values are equal to A, B, and C, respectively. If we assume that the value of n is 1, the values of h, k, and l are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{-a} = -1$$

$$k = \frac{na}{B} = \frac{(1)a}{a} = 1$$

$$l = \frac{nc}{C} = \frac{(1)c}{c/2} = 2$$

Now, from Equation 3.15, the value of i is

$$i = -(h + k) = -(-1 + 1) = 0$$

Hence, this is a $(\overline{1}102)$ plane.

3.57 *Sketch the $(01\bar{1}1)$ and $(2\bar{1}\bar{1}0)$ planes in a hexagonal unit cell.*

Solution

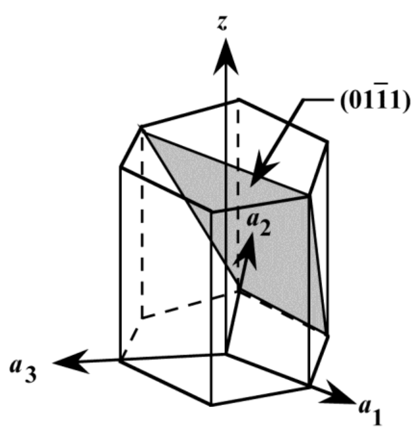
For $(01\bar{1}1)$ the values of *h*, *k*, *i*, and *l* are, respectively, 0, 1, –1, and 1. Now, for *h, k,* and *l,* we solve for values of intersections with the a_1, a_2, and *z* axes (i.e., *A, B,* and *C*) using rearranged forms of Equations 3.14a, 3.14b, and 3.14c (assuming a value of 1 for the parameter *n*) as follows:

$$A = \frac{na}{h} = \frac{(1)a}{0} = \text{¥}\, a$$

$$B = \frac{na}{k} = \frac{(1)a}{1} = a$$

$$C = \frac{nc}{l} = \frac{(1)c}{1} = c$$

Hence, this plane is parallel to the a_1 axis, and intersects the a_2 axis at *a*, the a_3 axis at –*a*, and the *z*-axis at *c*. The plane having these intersections is shown in the figure below.



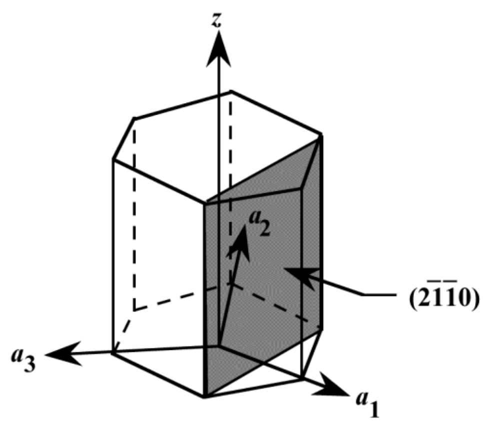
For the $(2\bar{1}\bar{1}0)$ plane, the values of *h*, *k*, *i*, and *l* are, respectively, 2, –1, –1, and 0. Now, for *h*, *k*, and *l*, we solve for values of intersections with the a_1, a_2, and *z* axes (i.e., *A*, *B*, and *C*) using rearranged forms of Equations 3.14a, 3.14b, and 3.14c (assuming a value of 1 for the parameter *n*) as follows:

$$A = \frac{na}{h} = \frac{(1)a}{2} = \frac{a}{2}$$

$$B = \frac{na}{k} = \frac{(1)a}{-1} = -a$$

$$C = \frac{nc}{l} = \frac{(1)c}{0} = \infty c$$

Thus, this plane is parallel to the *c* axis, and intersects the a_1 axis at *a*/2 and the a_2 axis at –*a*. The plane having these intersections is shown in the figure below.



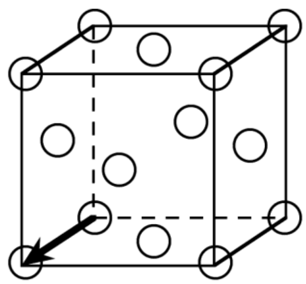
Linear and Planar Densities

3.58 *(a) Derive linear density expressions for FCC [100] and [111] directions in terms of the atomic radius R.*

(b) Compute and compare linear density values for these same two directions for copper (Cu).

Solution

(a) In the figure below is shown a [100] direction within an FCC unit cell.

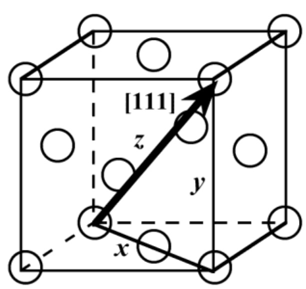


For this [100] direction there is one atom at each of the two unit cell corners, and, thus, there is the equivalent of 1 atom that is centered on the direction vector. The length of this direction vector is just the unit cell edge length, $2R\sqrt{2}$ (Equation 3.1). Therefore, the expression for the linear density of this plane is

$$\mathrm{LD}_{100} = \frac{\text{number of atoms centered on [100] direction vector}}{\text{length of [100] direction vector}}$$

$$= \frac{1 \text{ atom}}{2R\sqrt{2}} = \frac{1}{2R\sqrt{2}}$$

An FCC unit cell within which is drawn a [111] direction is shown below.



For this [111] direction, the vector shown passes through only the centers of the single atom at each of its ends, and, thus, there is the equivalence of 1 atom that is centered on the direction vector. The length of this direction vector is denoted by z in this figure, which is equal to

$$z = \sqrt{x^2 + y^2}$$

where x is the length of the bottom face diagonal, which is equal to $4R$. Furthermore, y is the unit cell edge length, which is equal to $2R\sqrt{2}$ (Equation 3.1). Thus, using the above equation, the length z may be calculated as follows:

$$z = \sqrt{(4R)^2 + (2R\sqrt{2})^2} = \sqrt{24R^2} = 2R\sqrt{6}$$

Therefore, the expression for the linear density of this direction is

$$\mathrm{LD}_{111} = \frac{\text{number of atoms centered on [111] direction vector}}{\text{length of [111] direction vector}}$$

$$= \frac{1 \text{ atom}}{2R\sqrt{6}} = \frac{1}{2R\sqrt{6}}$$

(b) From the table inside the front cover, the atomic radius for copper is 0.128 nm. Therefore, the linear density for the [100] direction is

$$\mathrm{LD}_{100}(\mathrm{Cu}) = \frac{1}{2R\sqrt{2}} = \frac{1}{(2)(0.128\text{ nm})\sqrt{2}} = 2.76 \text{ nm}^{-1} = 2.76 \times 10^9 \text{ m}^{-1}$$

While for the [111] direction

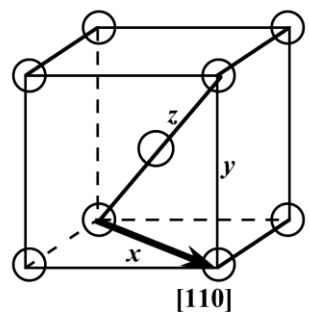
$$\mathrm{LD}_{111}(\mathrm{Cu}) = \frac{1}{2R\sqrt{6}} = \frac{1}{(2)(0.128\text{ nm})\sqrt{6}} = 1.59 \text{ nm}^{-1} = 1.59 \times 10^9 \text{ m}^{-1}$$

3.59 *(a) Derive linear density expressions for BCC [110] and [111] directions in terms of the atomic radius R.*

(b) Compute and compare linear density values for these same two directions for iron (Fe).

Solution

(a) In the figure below is shown a [110] direction within a BCC unit cell.



For this [110] direction there is one atom at each of the two unit cell corners, and, thus, there is the equivalence of 1 atom that is centered on the direction vector. The length of this direction vector is denoted by *x* in this figure, which is equal to

$$x = \sqrt{z^2 - y^2}$$

where *y* is the unit cell edge length, which, from Equation 3.4 is equal to $\frac{4R}{\sqrt{3}}$. Furthermore, *z* is the length of the unit cell diagonal, which is equal to 4*R* Thus, using the above equation, the length *x* may be calculated as follows:

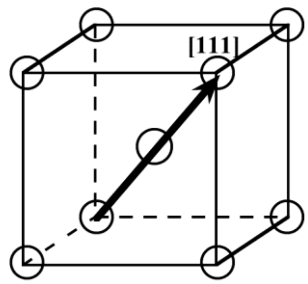
$$x = \sqrt{(4R)^2 - \left(\frac{4R}{\sqrt{3}}\right)^2} = \sqrt{\frac{32R^2}{3}} = 4R\sqrt{\frac{2}{3}}$$

Therefore, the expression for the linear density of this direction is

$$\text{LD}_{110} = \frac{\text{number of atoms centered on [110] direction vector}}{\text{length of [110] direction vector}}$$

$$= \frac{1 \text{ atom}}{4R\sqrt{\frac{2}{3}}} = \frac{\sqrt{3}}{4R\sqrt{2}}$$

A BCC unit cell within which is drawn a [111] direction is shown below.



For although the [111] direction vector shown passes through the centers of three atoms, there is an equivalence of only two atoms associated with this unit cell—one-half of each of the two atoms at the end of the vector, in addition to the center atom belongs entirely to the unit cell. Furthermore, the length of the vector shown is equal to 4*R*, since all of the atoms whose centers the vector passes through touch one another. Therefore, the linear density is equal to

$$LD_{111} = \frac{\text{number of atoms centered on [111] direction vector}}{\text{length of [111] direction vector}}$$

$$= \frac{2 \text{ atoms}}{4R} = \frac{1}{2R}$$

(b) From the table inside the front cover, the atomic radius for iron is 0.124 nm. Therefore, the linear density for the [110] direction is

$$LD_{110}(\text{Fe}) = \frac{\sqrt{3}}{4R\sqrt{2}} = \frac{\sqrt{3}}{(4)(0.124 \text{ nm})\sqrt{2}} = 2.47 \text{ nm}^{-1} = 2.47 \times 10^9 \text{ m}^{-1}$$

While for the [111] direction

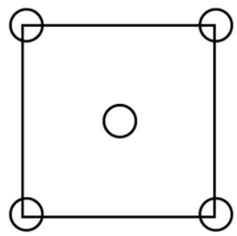
$$LD_{111}(\text{Fe}) = \frac{1}{2R} = \frac{1}{(2)(0.124 \text{ nm})} = 4.03 \text{ nm}^{-1} = 4.03 \times 10^9 \text{ m}^{-1}$$

3.60 *(a) Derive planar density expressions for FCC (100) and (111) planes in terms of the atomic radius R.*

(b) Compute and compare planar density values for these same two planes for aluminum (Al).

Solution

(a) In the figure below is shown a (100) plane for an FCC unit cell.

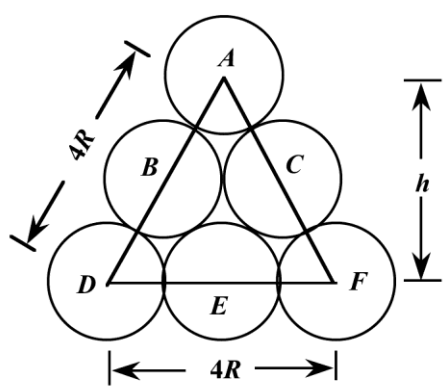


For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the equivalence of 2 atoms associated with this FCC (100) plane. The planar section represented in the above figure is a square, wherein the side lengths are equal to the unit cell edge length, $2R\sqrt{2}$ (Equation 3.1); and, thus, the area of this square is just $(2R\sqrt{2})^2 = 8R^2$. Hence, the planar density for this (100) plane is just

$$\mathrm{PD}_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{2 \text{ atoms}}{8R^2} = \frac{1}{4R^2}$$

That portion of an FCC (111) plane contained within a unit cell is shown below.



There are six atoms whose centers lie on this plane, which are labeled *A* through *F*. One-sixth of each of atoms *A*, *D*, and *F* are associated with this plane (yielding an equivalence of one-half atom), with one-half of each of atoms *B*, *C*, and *E* (or an equivalence of one and one-half atoms) for a total equivalence of two atoms. Now, the area of the triangle shown in the above figure is equal to one-half of the product of the base length and the height, *h*. If we consider half of the triangle, then

$$(2R)^2 + h^2 = (4R)^2$$

which leads to $h = 2R\sqrt{3}$. Thus, the area is equal to

$$\text{Area} = \frac{4R(h)}{2} = \frac{(4R)\left(2R\sqrt{3}\right)}{2} = 4R^2\sqrt{3}$$

And, thus, the planar density is

$$\text{PD}_{111} = \frac{\text{number of atoms centered on (111) plane}}{\text{area of (111) plane}}$$

$$= \frac{2\text{ atoms}}{4R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

(b) From the table inside the front cover, the atomic radius for aluminum is 0.143 nm. Therefore, the planar density for the (100) plane is

$$\text{PD}_{100}(\text{Al}) = \frac{1}{4R^2} = \frac{1}{4(0.143\text{ nm})^2} = 12.23\text{ nm}^{-2} = 1.223 \times 10^{19}\text{ m}^{-2}$$

While for the (111) plane

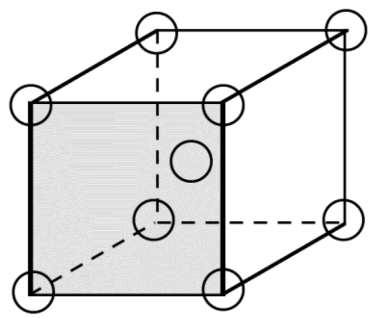
$$\text{PD}_{111}(\text{Al}) = \frac{1}{2R^2\sqrt{3}} = \frac{1}{2\sqrt{3}(0.143\text{ nm})^2} = 14.12\text{ nm}^{-2} = 1.412 \times 10^{19}\text{ m}^{-2}$$

3.61 *(a) Derive planar density expressions for BCC (100) and (110) planes in terms of the atomic radius R.*

(b) Compute and compare planar density values for these same two planes for molybdenum (Mo).

Solution

(a) A BCC unit cell within which is drawn a (100) plane is shown below.

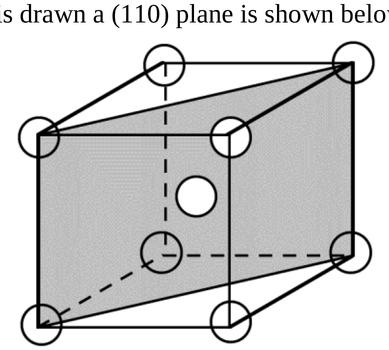


For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells. Thus, there is the equivalence of 1 atom associated with this BCC (100) plane. The planar section represented in the above figure is a square, wherein the side lengths are equal to the unit cell edge length, $\frac{4R}{\sqrt{3}}$ (Equation 3.4); thus, the area of this square is just $\left(\frac{4R}{\sqrt{3}}\right)^2 = \frac{16R^2}{3}$. Hence, the planar density for this (100) plane is just

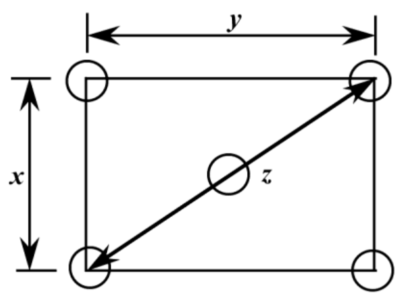
$$\mathrm{PD}_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{1 \text{ atom}}{\frac{16\,R^2}{3}} = \frac{3}{16\,R^2}$$

A BCC unit cell within which is drawn a (110) plane is shown below.



For this (110) plane there is one atom at each of the four cube corners through which it passes, each of which is shared with four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the equivalence of 2 atoms associated with this BCC (110) plane. The planar section represented in the above figure is a rectangle, as noted in the figure below.



From this figure, the area of the rectangle is the product of x and y. The length x is just the unit cell edge length, which for BCC (Equation 3.4) is $\frac{4R}{\sqrt{3}}$. Now, the diagonal length z is equal to 4R. For the triangle bounded by the lengths x, y, and z

$$y = \sqrt{z^2 - x^2}$$

Or

$$y = \sqrt{(4R)^2 - \left(\frac{4R}{\sqrt{3}}\right)^2} = \frac{4R\sqrt{2}}{\sqrt{3}}$$

Thus, in terms of R, the area of this (110) plane is just

$$\text{Area}(110) = xy = \left(\frac{4R}{\sqrt{3}}\right)\left(\frac{4R\sqrt{2}}{\sqrt{3}}\right) = \frac{16R^2\sqrt{2}}{3}$$

And, finally, the planar density for this (110) plane is just

$$\text{PD}_{110} = \frac{\text{number of atoms centered on (110) plane}}{\text{area of (110) plane}}$$

$$= \frac{2 \text{ atoms}}{\frac{16R^2\sqrt{2}}{3}} = \frac{3}{8R^2\sqrt{2}}$$

(b) From the table inside the front cover, the atomic radius for molybdenum is 0.136 nm. Therefore, the planar density for the (100) plane is

$$\mathrm{PD}_{100}(\mathrm{Mo}) = \frac{3}{16R^2} = \frac{3}{16(0.136\ \mathrm{nm})^2} = 10.14\ \mathrm{nm}^{-2} = 1.014 \times 10^{19}\ \mathrm{m}^{-2}$$

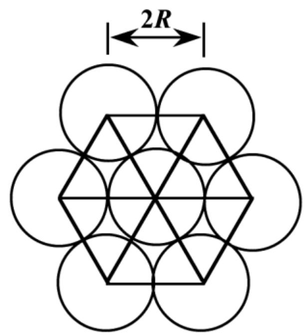
While for the (110) plane

$$\mathrm{PD}_{110}(\mathrm{Mo}) = \frac{3}{8R^2\sqrt{2}} = \frac{3}{8(0.136\ \mathrm{nm})^2\sqrt{2}} = 14.34\ \mathrm{nm}^{-2} = 1.434 \times 10^{19}\ \mathrm{m}^{-2}$$

3.62 *(a) Derive the planar density expression for the HCP (0001) plane in terms of the atomic radius R.*
(b) Compute the planar density value for this same plane for titanium (Ti).

Solution

(a) A (0001) plane for an HCP unit cell is show below.



Each of the 6 perimeter atoms in this plane is shared with three other unit cells, whereas the center atom is shared with no other unit cells; this gives rise to three equivalent atoms belonging to this plane.

In terms of the atomic radius *R*, the area of each of the 6 equilateral triangles that have been drawn is $R^2\sqrt{3}$, or the total area of the plane shown is $6R^2\sqrt{3}$. And the planar density for this (0001) plane is equal to

$$\mathrm{PD}_{0001} = \frac{\text{number of atoms centered on (0001) plane}}{\text{area of (0001) plane}}$$

$$= \frac{3 \text{ atoms}}{6R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

(b) From the table inside the front cover, the atomic radius for titanium is 0.145 nm. Therefore, the planar density for the (0001) plane is

$$\mathrm{PD}_{0001}(\mathrm{Ti}) = \frac{1}{2R^2\sqrt{3}} = \frac{1}{2\sqrt{3}(0.145\text{ nm})^2} = 13.73\text{ nm}^{-2} = 1.373 \times 10^{19}\text{ m}^{-2}$$

Polycrystalline Materials

3.63 *Explain why the properties of polycrystalline materials are most often isotropic.*

Solution

Although each individual grain in a polycrystalline material may be anisotropic, if the grains have random orientations, then the solid aggregate of the many anisotropic grains will behave isotropically.

X-Ray Diffraction: Determination of Crystal Structures

3.64 *The interplanar spacing* d_{hkl} *for planes in a unit cell having orthorhombic geometry is given by*

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where a, b, and c are the lattice parameters.

(a) To what equation does this expression reduce for crystals having cubic symmetry?

(b) For crystals having tetragonal symmetry?

Solution

(a) For the crystals having cubic symmetry, $a = b = c$. Making this substitution into the above equation leads to

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}$$

$$= \frac{h^2 + k^2 + l^2}{a^2}$$

(b) For crystals having tetragonal symmetry, $a = b \neq c$. Replacing b with a in the equation found in the problem statement leads to

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{c^2}$$

$$= \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

3.65 *Using the data for aluminum in Table 3.1, compute the interplanar spacing for the (110) set of planes.*

Solution

From the Table 3.1, aluminum has an FCC crystal structure and an atomic radius of 0.1431 nm. Using Equation 3.1, the lattice parameter a may be computed as

$$a = 2R\sqrt{2} = (2)(0.1431\text{ nm})\sqrt{2} = 0.4045\text{ nm}$$

Now, the interplanar spacing d_{110} is determined using Equation 3.22 as

$$d_{110} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (0)^2}} = \frac{0.4045\text{ nm}}{\sqrt{2}} = 0.2860\text{ nm}$$

3.66 *Using the data for α-iron in Table 3.1, compute the interplanar spacings for the (111) and (211) sets of planes.*

Solution

From the table, α-iron has a BCC crystal structure and an atomic radius of 0.1241 nm. Using Equation 3.4 the lattice parameter, a, may be computed as follows:

$$a = \frac{4R}{\sqrt{3}} = \frac{(4)(0.1241 \text{ nm})}{\sqrt{3}} = 0.2866 \text{ nm}$$

Now, the d_{111} interplanar spacing may be determined using Equation 3.22 as

$$d_{111} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = \frac{0.2866 \text{ nm}}{\sqrt{3}} = 0.1655 \text{ nm}$$

And, similarly for d_{211}

$$d_{211} = \frac{a}{\sqrt{(2)^2 + (1)^2 + (1)^2}} = \frac{0.2866 \text{ nm}}{\sqrt{6}} = 0.1170 \text{ nm}$$

3.67 *Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC chromium (Cr) when monochromatic radiation of wavelength 0.0711 nm is used.*

Solution

We first calculate the lattice parameter using Equation 3.4 and the value of *R* (0.1249 nm) cited in Table 3.1, as follows:

$$a = \frac{4R}{\sqrt{3}} = \frac{(4)(0.1249\ \text{nm})}{\sqrt{3}} = 0.2884\ \ \text{nm}$$

Next, the interplanar spacing for the (310) set of planes may be determined using Equation 3.22 according to

$$d_{310} = \frac{a}{\sqrt{(3)^2 + (1)^2 + (0)^2}} = \frac{0.2884\ \text{nm}}{\sqrt{10}} = 0.0912\ \ \text{nm}$$

And finally, employment of Equation 3.21 yields the diffraction angle as

$$\sin \theta = \frac{n\lambda}{2d_{310}} = \frac{(1)(0.0711\ \text{nm})}{(2)(0.0912\ \text{nm})} = 0.390$$

Which leads to

$$\theta = \sin^{-1}(0.390) = 22.94°$$

And, finally

$$2\theta = (2)(22.94°) = 45.88°$$

3.68 *Determine the expected diffraction angle for the first-order reflection from the (111) set of planes for FCC nickel (Ni) when monochromatic radiation of wavelength 0.1937 nm is used.*

Solution

We first calculate the lattice parameter using Equation 3.1 and the value of R (0.1246 nm) cited in Table 3.1, as follows:

$$a = 2R\sqrt{2} = (2)(0.1246 \text{ nm})\sqrt{2} = 0.3524 \text{ nm}$$

Next, the interplanar spacing for the (111) set of planes may be determined using Equation 3.22 according to

$$d_{111} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = \frac{0.3524 \text{ nm}}{\sqrt{3}} = 0.2035 \text{ nm}$$

And finally, employment of Equation 3.21 yields the diffraction angle as

$$\sin \theta = \frac{n\lambda}{2d_{111}} = \frac{(1)(0.1937 \text{ nm})}{(2)(0.2035 \text{ nm})} = 0.476$$

Which leads to

$$\theta = \sin^{-1}(0.476) = 28.42°$$

And, finally

$$2\theta = (2)(28.42°) = 56.84°$$

3.69 *The metal rhodium (Rh) has an FCC crystal structure. If the angle of diffraction for the (311) set of planes occurs at 36.12° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.0711 nm is used, compute the following: (a) the interplanar spacing for this set of planes and (b) the atomic radius for a Rh atom.*

Solution

(a) From the data given in the problem, and realizing that 36.12° = 2θ, the interplanar spacing for the (311) set of planes for rhodium may be computed using Equation 3.21 as

$$d_{311} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.0711 \text{ nm})}{(2)\left(\sin \dfrac{36.12°}{2}\right)} = 0.1147 \text{ nm}$$

(b) In order to compute the atomic radius we must first determine the lattice parameter, *a*, using Equation 3.22, and then *R* from Equation 3.1 since Rh has an FCC crystal structure. Therefore,

$$a = d_{311}\sqrt{(3)^2 + (1)^2 + (1)^2} = (0.1147 \text{ nm})\left(\sqrt{11}\right) = 0.3804 \text{ nm}$$

And, from Equation 3.1

$$R = \frac{a}{2\sqrt{2}} = \frac{0.3804 \text{ nm}}{2\sqrt{2}} = 0.1345 \text{ nm}$$

3.70 *The metal niobium (Nb) has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at 75.99° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute the following: (a) the interplanar spacing for this set of planes and (b) the atomic radius for the Nb atom.*

Solution

(a) From the data given in the problem statement, and realizing that 75.99° = 2θ, the interplanar spacing for the (211) set of planes for Nb may be computed using Equation 3.21 as follows:

$$d_{211} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1659 \text{ nm})}{(2)\left(\sin \frac{75.99°}{2}\right)} = 0.1348 \text{ nm}$$

(b) In order to compute the atomic radius we must first determine the lattice parameter, a, using Equation 3.22, and then R from Equation 3.4 since Nb has a BCC crystal structure. Therefore,

$$a = d_{211}\sqrt{(2)^2 + (1)^2 + (1)^2} = (0.1347 \text{ nm})(\sqrt{6}) = 0.3300 \text{ nm}$$

And, from a rearranged form Equation 3.4

$$R = \frac{a\sqrt{3}}{4} = \frac{(0.3300 \text{ nm})\sqrt{3}}{4} = 0.1429 \text{ nm}$$

3.71 *For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 44.53° for FCC nickel (Ni) when monochromatic radiation having a wavelength of 0.1542 nm is used?*

Solution

The first step to solve this problem is to compute the value of θ in Equation 3.21. Because the diffraction angle, 2θ, is equal to 44.53°, θ = 44.53°/2 = 22.27°. We can now determine the interplanar spacing using Equation 3.21; thus

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.1542\ \text{nm})}{(2)\left(\sin 22.27°\right)} = 0.2035\ \text{nm}$$

Now, employment of both Equations 3.22 and 3.1 (since Ni's crystal structure is FCC), and the value of R for nickel from Table 3.1 (0.1246 nm) leads to

$$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{2R\sqrt{2}}{d_{hkl}}$$

$$= \frac{(2)(0.1246\ \text{nm})\sqrt{2}}{(0.2035\ \text{nm})} = 1.732$$

This means that

$$h^2 + k^2 + l^2 = (1.732)^2 = 3.0$$

From Table 3.5 and for the FCC crystal structure, the only three integers the sum of the squares of which equals 3.0 are 1, 1, and 1. Therefore, the set of planes responsible for this diffraction peak is the (111) set.

3.72 *For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 136.15° for BCC tantalum (Ta) when monochromatic radiation having a wavelength of 0.1937 nm is used?*

Solution

The first step to solve this problem is to compute the value of θ in Equation 3.21. Because the diffraction angle, 2θ, is equal to 136.15°, θ = 136.15°/2 = 68.08°. We can now determine the interplanar spacing using Equation 3.21; thus

$$d_{hkl} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1937\ \text{nm})}{(2)(\sin 68.08°)} = 0.1044\ \text{nm}$$

Now, employment of both Equations 3.22 and 3.4 (since Ta's crystal structure is BCC), and the value of R for Ta from Table 3.1 (0.1430 nm) leads to

$$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{\frac{4R}{\sqrt{3}}}{d_{hkl}} = \frac{4R}{d_{hkl}\sqrt{3}}$$

$$= \frac{(4)(0.1430\ \text{nm})}{(0.1044\ \text{nm})\sqrt{3}} = 3.163$$

This means that

$$h^2 + k^2 + l^2 = (3.163)^2 = 10.0$$

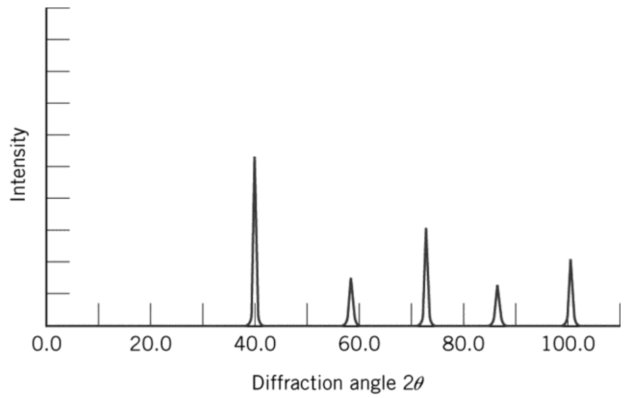
From Table 3.5 and for the BCC crystal structure, the only three integers the sum of the squares of which equals 10.0 are 3, 1, and 0. Therefore, the set of planes responsible for this diffraction peak is the (310) set.

3.73 *Figure 3.26 shows the first five peaks of the x-ray diffraction pattern for tungsten (W), which has a BCC crystal structure; monochromatic x-radiation having a wavelength of 0.1542 nm was used.*

(a) Index (i.e., give h, k, and l indices) for each of these peaks.

(b) Determine the interplanar spacing for each of the peaks.

(c) For each peak, determine the atomic radius for W, and compare these with the value presented in Table 3.1.



Solution

(a) Since W has a BCC crystal structure, and using information in Table 3.5, indices for the first five peaks are (110), (200), (211), (220), and (310).

(b) For each peak, in order to calculate the interplanar spacing we must employ Equation 3.21. For the first peak, which occurs at 40.2°= 2θ, then θ = 40.2°/2 =20.1°.

$$d_{110} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1542 \text{ nm})}{(2)(\sin 20.1°)} = 0.2244 \text{ nm}$$

(c) Employment of Equations 3.22 and 3.4 is necessary for the computation of R for W as

$$R = \frac{a\sqrt{3}}{4} = \frac{(d_{hkl})(\sqrt{3})\sqrt{(h)^2 + (k)^2 + (l)^2}}{4}$$

$$= \frac{(0.2244 \text{ nm})(\sqrt{3})\sqrt{(1)^2 + (1)^2 + (0)^2}}{4}$$

$$= 0.1374 \text{ nm}$$

Similar computations are made for the other peaks which results are tabulated below:

Peak Index	2θ	d_{hkl}(nm)	R (nm)
200	58.4	0.1580	0.1369
211	73.3	0.1292	0.1370
220	87.0	0.1120	0.1371
310	100.7	0.1001	0.1371

The atomic radius for tungsten cited in Table 3.1 is 0.1371 nm.

3.74 *The following table lists diffraction angles for the first four peaks (first-order) of the x-ray diffraction pattern for platinum (Pt), which has an FCC crystal structure; monochromatic x-radiation having a wavelength of 0.0711 nm was used.*

Plane Indices	*Diffraction Angle (2θ)*
(111)	*18.06°*
(200)	*20.88°*
(220)	*26.66°*
(311)	*31.37°*

(a) Determine the interplanar spacing for each of the peaks.

(b) For each peak, determine the atomic radius for Pt, and compare these with the value presented in Table 3.1.

Solution

(a) For each peak, in order to calculate the interplanar spacing we must employ Equation 3.21. For the first peak [which occurs by diffraction from the (111) set of planes] and occurs at 18.06°––that is, 2θ = 18.06°, which means that θ = 18.06°/2 =9.03°. Using Equation 3.21, the interplanar spacing is computed as follows:

$$d_{111} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.0711 \text{ nm})}{(2)(\sin 9.03°)} = 0.2265 \text{ nm}$$

(b) Employment of Equations 3.22 and 3.1 is necessary for the computation of R for Pt as

$$R = \frac{a}{2\sqrt{2}} = \frac{(d_{hkl})\sqrt{(h)^2 + (k)^2 + (l)^2}}{2\sqrt{2}}$$

$$= \frac{(d_{111})\sqrt{(1)^2 + (1)^2 + (1)^2}}{2\sqrt{2}}$$

$$= \frac{(0.2265 \text{ nm})\sqrt{(1)^2 + (1)^2 + (1)^2}}{2\sqrt{2}}$$

$$= 0.1387 \text{ nm}$$

Similar computations are made for the other peaks which results are tabulated below:

Peak Index	2θ	d_{hkl}(nm)	R (nm)
200	20.88	0.1962	0.1387
220	29.72	0.1386	0.1386
311	34.93	0.1185	0.1390

The atomic radius for platinum cited in Table 3.1 is 0.1387 nm.

3.75 *The following table lists diffraction angles for the first three peaks (first-order) of the x-ray diffraction pattern for some metal. Monochromatic x-radiation having a wavelength of 0.1397 nm was used.*

(a) Determine whether this metal's crystal structure is FCC, BCC or neither FCC or BCC, and explain the reason for your choice.

(b) If the crystal structure is either BCC or FCC, identify which of the metals in Table 3.1 gives this diffraction pattern. Justify your decision.

Peak Number	Diffraction Angle (2θ)
1	34.51°
2	40.06°
3	57.95°

Solution

(a) The steps in solving this part of the problem are as follows:

1. For each of these peaks compute the value of d_{hkl} using Equation 3.21 in the form

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \qquad \text{(P.1)}$$

taking $n = 1$ since this is a first-order reflection, and $\lambda = 0.1397$ nm (as given in the problem statement).

2. Using the value of d_{hkl} for each peak, determine the value of a from Equation 3.22 for both BCC and FCC crystal structures—that is

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad \text{(P.2)}$$

For BCC the planar indices for the first three peaks are (110), (200), and (211), which yield the respective $h^2 + k^2 + l^2$ values of 2, 4, and 6. On the other hand, for FCC planar indices for the first three peaks are (111), (200), and (220), which yield the respective $h^2 + k^2 + l^2$ values of 3, 4, and 8.

3. If the three values of a are the same (or nearly the same) for either BCC or FCC then the crystal structure is which of BCC or FCC has the same a value.

4. If none of the set of a values for both FCC and BCC are the same (or nearly the same) then the crystal structure is neither BCC or FCC.

Step 1

Using Equation P.1, the three values of d_{hkl} are computed as follows:

$$d_1 = \frac{n\lambda}{2\sin\theta_1} = \frac{(1)(0.1397\text{ nm})}{(2)\sin\left(\frac{34.51°}{2}\right)} = 0.2355\text{ nm}$$

$$d_2 = \frac{n\lambda}{2\sin\theta_2} = \frac{(1)(0.1397\text{ nm})}{(2)\sin\left(\frac{40.06°}{2}\right)} = 0.2039\text{ nm}$$

$$d_3 = \frac{n\lambda}{2\sin\theta_3} = \frac{(1)(0.1397\text{ nm})}{(2)\sin\left(\frac{57.95°}{2}\right)} = 0.1442\text{ nm}$$

Step 2

Using Equation P.2 let us first compute values of *a* for BCC.

For the (110) set of planes

$$a_1(\text{BCC}) = d_1\sqrt{h^2+k^2+l^2} = (0.2355\text{ nm})\sqrt{1^2+1^2+0^2} = 0.3330\text{ nm}$$

For the (200) set of planes:

$$a_2(\text{BCC}) = d_2\sqrt{h^2+k^2+l^2} = (0.2039\text{ nm})\sqrt{2^2+0^2+0^2} = 0.4078\text{ nm}$$

And for the (211) set of planes:

$$a_3(\text{BCC}) = d_3\sqrt{h^2+k^2+l^2} = (0.1442\text{ nm})\sqrt{2^2+1^2+1^2} = 0.3532\text{ nm}$$

Inasmuch as these three values of *a* are not nearly the same, the crystal structure is not BCC.

We now repeat this procedure for the FCC crystal structure.

For the (111) set of planes:

$$a_1(\text{FCC}) = d_1\sqrt{h^2+k^2+l^2} = (0.2355\text{ nm})\sqrt{1^2+1^2+1^2} = 0.4079\text{ nm}$$

Whereas for the (200) set of planes:

$$a_2(\text{FCC}) = d_2\sqrt{h^2+k^2+l^2} = (0.2039\text{ nm})\sqrt{2^2+0^2+0^2} = 0.4078\text{ nm}$$

And, finally, for the (220) set of planes:

$$a_3(\text{FCC}) = d_3\sqrt{h^2 + k^2 + l^2} = (0.1442 \text{ nm})\sqrt{2^2 + 2^2 + 0^2} = 0.4079 \text{ nm}$$

Inasmuch as $a_1 = a_2 = a_3$ the crystal structure is FCC.

(b) Since we know the value of a for this FCC crystal structure, it is possible to calculate the value of the atomic radius R using a rearranged form of Equation 3.1; and once we know the value of R, we just find that metal in Table 3.1 that has this atomic radius. Thus, we calculate the value of R as follows (using a value of 0.4079 for a):

$$R = \frac{a}{2\sqrt{2}} = \frac{0.4079 \text{ nm}}{2\sqrt{2}} = 0.1442 \text{ nm}$$

From Table 3.1 the only FCC metal that has this atomic radius is *gold* (although both aluminum, and silver have an FCC crystal structure and R values close to this value).

3.76 *The following table lists diffraction angles for the first three peaks (first-order) of the x-ray diffraction pattern for some metal. Monochromatic x-radiation having a wavelength of 0.0711 nm was used.*

(a) Determine whether this metal's crystal structure is FCC, BCC or neither FCC or BCC and explain the reason for your choice.

(b) If the crystal structure is either BCC or FCC, identify which of the metals in Table 3.1 gives this diffraction pattern. Justify your decision.

Peak Number	*Diffraction Angle* *(2θ)*
1	*18.27°*
2	*25.96°*
3	*31.92°*

Solution

(a) The steps in solving this part of the problem are as follows:

1. For each of these peaks compute the value of d_{hkl} using Equation 3.21 in the form

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \qquad \text{(P.1)}$$

taking n = 1 since this is a first-order reflection, and λ = 0.0711 nm (as given in the problem statement).

2. Using the value of d_{hkl} for each peak, determine the value of a from Equation 3.22 for both BCC and FCC crystal structures—that is

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad \text{(P.2)}$$

For BCC the planar indices for the first three peaks are (110), (200), and (211), which yield the respective $h^2 + k^2 + l^2$ values of 2, 4, and 6. On the other hand, for FCC planar indices for the first three peaks are (111), (200), and (220), which yield the respective $h^2 + k^2 + l^2$ values of 3, 4, and 8.

3. If the three values of a are the same (or nearly the same) for either BCC or FCC then the crystal structure is which of BCC or FCC has the same a value.

4. If none of the set of a values for both FCC and BCC are the same (or nearly the same) then the crystal structure is neither BCC or FCC.

Step 1

Using Equation P.1, the three values of d_{hkl} are computed as follows:

$$d_1 = \frac{n\lambda}{2\sin\theta_1} = \frac{(1)(0.0711 \text{ nm})}{(2)\sin\left(\frac{18.27°}{2}\right)} = 0.2239 \text{ nm}$$

$$d_2 = \frac{n\lambda}{2\sin\theta_2} = \frac{(1)(0.0711 \text{ nm})}{(2)\sin\left(\frac{25.96°}{2}\right)} = 0.1583 \text{ nm}$$

$$d_3 = \frac{n\lambda}{2\sin\theta_3} = \frac{(1)(0.0711 \text{ nm})}{(2)\sin\left(\frac{31.92°}{2}\right)} = 0.1293 \text{ nm}$$

Step 2

Using Equation P.2 let us first compute values of *a* for BCC.

For the (110) set of planes

$$a_1(\text{BCC}) = d_1\sqrt{h^2 + k^2 + l^2} = (0.2239 \text{ nm})\sqrt{1^2 + 1^2 + 0^2} = 0.3166 \text{ nm}$$

For the (200) set of planes:

$$a_2(\text{BCC}) = d_2\sqrt{h^2 + k^2 + l^2} = (0.1583 \text{ nm})\sqrt{2^2 + 0^2 + 0^2} = 0.3166 \text{ nm}$$

And for the (211) set of planes:

$$a_3(\text{BCC}) = d_3\sqrt{h^2 + k^2 + l^2} = (0.1293 \text{ nm})\sqrt{2^2 + 1^2 + 1^2} = 0.3167 \text{ nm}$$

Inasmuch as $a_1 = a_2 \cong a_3$ the crystal structure is BCC, and it is not necessary to pursue the possibility of FCC.

(b) Since we know the value of *a* for this BCC crystal structure, it is possible to calculate the value of the atomic radius *R* using a rearranged form of Equation 3.4; and once we know the value of *R*, we just find that metal in Table 3.1 that has this atomic radius. Thus, we calculate the value of *R* as follows (using a value of 0.3166 for *a*):

$$R = \frac{a\sqrt{3}}{4} = \frac{(0.3166 \text{ nm})\sqrt{3}}{4} = 0.1371 \text{ nm}$$

From Table 3.1 the BCC metal that has this atomic radius is *tungsten* (although molybdenum has a BCC crystal structure and an *R* close to this value).

Noncrystalline Solids

3.77 *Would you expect a material in which the atomic bonding is predominantly ionic in nature to be more or less likely to form a noncrystalline solid upon solidification than a covalent material? Why? (See Section 2.6.)*

Solution

A material in which atomic bonding is predominantly ionic in nature is less likely to form a noncrystalline solid upon solidification than a covalent material because covalent bonds are directional whereas ionic bonds are nondirectional; it is more difficult for the atoms in a covalent material to assume positions giving rise to an ordered structure.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

3.1FE *A hypothetical metal has the BCC crystal structure, a density of 7.24 g/cm³, and an atomic weight of 48.9 g/mol. The atomic radius of this metal is:*

(A) 0.122 nm *(C) 0.0997 nm*

(B) 1.22 nm *(D) 0.154 nm*

<u>Solution</u>

The volume of a BCC unit cell is calculated using Equation 3.4 as follows

$$V_C = a^3 = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

Now, using Equation 3.8, we may determine the density as follows:

$$r = \frac{nA}{V_C N_A}$$

$$= \frac{nA}{\left(\frac{64R^3}{3\sqrt{3}}\right)N_A} = \frac{\left(3\sqrt{3}\right)nA}{64R^3 N_A}$$

And, from this expression, solving for *R*, leads to

$$R = \left[\frac{\left(3\sqrt{3}\right)nA}{64 r N_A}\right]^{1/3}$$

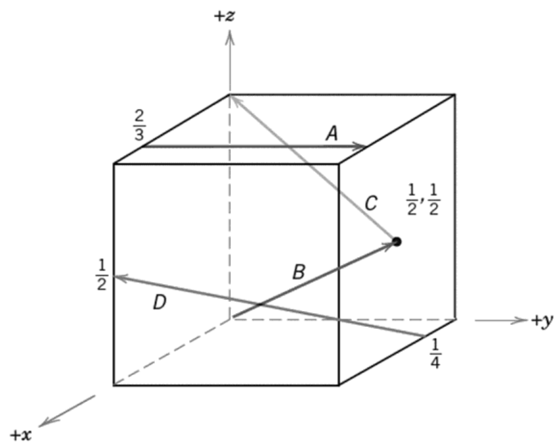
Since there are two atoms per unit cell ($n = 2$) and incorporating values for the density (ρ) and atomic weight (A) provided in the problem statement, we calculate the value of *R* as follows:

$$= \left[\frac{(3\sqrt{3})(2 \text{ atoms/unit cell})(48.9 \text{ g/mol})}{(64)(7.24 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}\right]^{1/3}$$

$$= 1.22 \times 10^{-8} \text{ cm} = 0.122 \text{ nm}$$

which is answer A.

3.2FE *In the following unit cell, which vector represents the [121] direction?*



Solution

In order to solve this problem, let us take the position of the [121] direction vector as the origin of the coordinate system, and then, using Equations 3.10a, 3.10b, and 3.10c, determine the head coordinates of the vector. The vector in the illustration that coincides with this vector or is parallel to it corresponds to the [121] direction.

Using this scheme, vector tail coordinates are as follows:

$x_1 = 0a \qquad y_1 = 0b \qquad z_1 = 0c$

For this direction, values of the *u*, *v*, and *w* indices are as follows:

$u = 1 \qquad v = 2 \qquad w = 1$

Now, assuming a value of 1 for the parameter *n*, values of the head coordinates (x_2, y_2 , and z_2) are determined (using Equations 3.10) as follows:

$$x_2 = ua + x_1 = (1)a + 0a = a$$

$$y_2 = vb + y_1 = (2)b + 0b = 2b$$

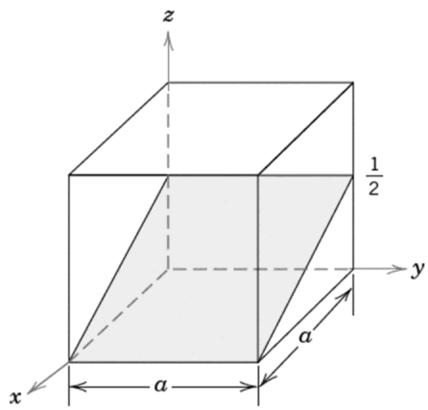
$$z_2 = wc + z_1 = (1)c + 0c = c$$

If we now divide these three head coordinates by a factor of 2, it is possible, in a stepwise manner, locate the location of the vector head as follows: move *a*/2 units along the *x* axis, then *b* units parallel to the *y* axis, and from here *c*/2 units parallel to the *z* axis. The vector from the origin to this point corresponds to B.

3.3FE *What are the Miller indices for the plane shown in the following cubic unit cell?*

(A) (201) *(C)* $(10\frac{1}{2})$

(B) $\left(1\,\infty\,\frac{1}{2}\right)$ *(D) (102)*



Solution

The Miller indices for this direction may be determined using Equations 3.14a, 3.14b, and 3.14c. However, it is first necessary to note intersections of this plane with the *x*, *y*, and *z* coordinate axes. These respective intercepts are *a*, ∞*a* (since the plane is parallel to the *y* axis), and *a*/2; that is

$A = a$ $B = \infty a$ $C = a/2$

Thus, using Equations 3.14, values of the *h*, *k*, and *l* indices (assuming that *n* = 1)are as follows:

$$h = \frac{na}{A} = \frac{(1)a}{a} = 1$$

$$k = \frac{na}{B} = \frac{(1)a}{\text{¥}a} = 0$$

$$l = \frac{nc}{C} = \frac{(1)c}{c/2} = 2$$

Therefore this is a (102) plane, which means that D is the correct answer.

CHAPTER 4

IMPERFECTIONS IN SOLIDS

PROBLEM SOLUTIONS

Vacancies and Self-Interstitials

4.1 *The equilibrium fraction of lattice sites that are vacant in silver (Ag) at 700°C is 2 × 10^{-6}. Calculate the number of vacancies (per meter cubed) at 700°C. Assume a density of 10.35 g/cm^3 for Ag.*

Solution

This problem is solved using two steps: (1) calculate the total number of lattice sites in silver, N_{Ag}, using Equation 4.2; and (2) multiply this number by fraction of lattice that are vacant, 2 × 10^{-6}. The parameter N_{Ag} is related to the density, (ρ), Avogadro's number (N_A), and the atomic weight (A_{Ag}=107.87 g/mol, from inside the front cover) according to Equation 4.2 as

$$N_{Ag} = \frac{N_A \rho_{Ag}}{A_{Ag}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(10.35\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{107.87\ \text{g/mol}}$$

$$= 5.78 \times 10^{28}\ \text{atoms/m}^3$$

The number of vacancies per meter cubed in silver at 700°C, N_v, is determined as follows:

$$N_v = (2 \times 10^{-6})N_{Ag}$$

$$= (2 \times 10^{-6})(5.78 \times 10^{28}\ \text{atoms/m}^3) = 1.156 \times 10^{23}\ \text{vacancies/m}^3$$

4.2 *For some hypothetical metal, the equilibrium number of vacancies at 900°C is 2.3 × 10^{25} m^{-3}. If the density and atomic weight of this metal are 7.40 g/cm^3 and 85.5 g/mol, respectively, calculate the fraction of vacancies for this metal at 900°C.*

Solution

This problem is solved using two steps: (1) calculate the total number of lattice sites in silver, N, using Equation 4.2, and (2) take the ratio of the equilibrium number of vacancies given in the problem statement (N_v = 2.3 × 10^{25} m^{-3}) and this value of N. From Equation 4.2

$$N = \frac{N_A \rho}{A}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(7.40 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{85.5 \text{ g/mol}}$$

$$= 5.21 \times 10^{28} \text{ atoms/m}^3$$

The fraction of vacancies is equal to the N_v/N ratio, which is computed as follows:

$$\frac{N_v}{N} = \frac{2.3 \times 10^{25} \text{ m}^{-3}}{5.21 \times 10^{28} \text{ atoms/m}^3}$$

$$= 4.41 \times 10^{-4}$$

4.3 *(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)?

Solution

(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,

$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.90\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1357\ \text{K})}\right]$$

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

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

$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.90\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(298\ \text{K})}\right]$$

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

(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 *Calculate the number of vacancies per cubic meter in gold (Au) at 900°C. The energy for vacancy formation is 0.98 eV/atom. Furthermore, the density and atomic weight for Au are 18.63 g/cm^3 (at 900°C) and 196.9 g/mol, respectively.*

Solution

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:

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) = \frac{N_A \rho_{Au}}{A_{Au}} \exp\left(-\frac{Q_v}{kT}\right)$$

Inserting into this expression he density and atomic weight values for gold leads to the following:

$$N_v = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(18.63 \text{ g/cm}^3)}{196.9 \text{ g/mol}} \exp\left[-\frac{0.98 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1173 \text{ K})}\right]$$

$$= 3.52 \times 10^{18} \text{ cm}^{-3} = 3.52 \times 10^{24} \text{ m}^{-3}$$

4.5 *Calculate the energy for vacancy formation in nickel (Ni), given that the equilibrium number of vacancies at 850°C (1123 K) is 4.7 × 10^{22} m^{-3}. The atomic weight and density (at 850°C) for Ni are, respectively, 58.69 g/mol and 8.80 g/cm^3.*

Solution

This problem calls for the computation of the activation energy for vacancy formation in nickel. 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), Avogadro's number (N_A), and the atomic weight (A) according to Equation 4.2 as

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

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(8.80 \text{ g/cm}^3)}{58.69 \text{ g/mol}}$$

$$= 9.03 \times 10^{22} \text{ atoms/cm}^3 = 9.03 \times 10^{28} \text{ atoms/m}^3$$

Now, taking natural logarithms of both sides of Equation 4.1, yields he following

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

We make Q_v the dependent variable after some algebraic manipulation as

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

Incorporation into this expression, values for N_v (determined above as 9.03 × 10^{28} atoms/m^3), N (provided in the problem statement, 4.7 × 10^{22} m^{-3}). T (850°C = 1123 K) and k, leads to the following:

$$Q_v = -\left(8.62 \times 10^{-5} \text{ eV/atom-K}\right)(1123 \text{ K}) \ln\left[\frac{4.7 \times 10^{22} \text{ m}^{-3}}{9.03 \times 10^{28} \text{ m}^{-3}}\right]$$

$$= 1.40 \text{ eV/atom}$$

Impurities in Solids

4.6 *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*	*1.4*	*+1*
Al	*0.1431*	*FCC*	*1.5*	*+3*
Co	*0.1253*	*HCP*	*1.7*	*+2*
Cr	*0.1249*	*BCC*	*1.6*	*+3*
Fe	*0.1241*	*BCC*	*1.7*	*+2*
Pt	*0.1387*	*FCC*	*1.5*	*+2*
Zn	*0.1332*	*HCP*	*1.7*	*+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 (ΔR**%**) 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	ΔR%	Crystal Structure	ΔElectro-negativity	Valence
Ni		**FCC**		**2+**
C	–43			
H	–63			
O	–52			
Ag	+16	FCC	-0.4	1+
Al	+15	FCC	-0.3	3+
Co	+0.6	HCP	-0.1	2+
Cr	+0.2	BCC	-0.2	3+
Fe	-0.4	BCC	-0.1	2+
Pt	+11	FCC	-0.3	2+
Zn	+7	HCP	-0.1	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.

4.7 *Which of the following systems (i.e., pair of metals) would you expect to exhibit complete solid solubility? Explain your answers.*

(a) Cr-V

(b) Mg-Zn

(c) Al-Zr

(d) Ag-Au

(e) Pb-Pt

Solution

In order for there to be complete solubility (substitutional) for each pair of metals, the four Hume-Rothery rules must be satisfied: (1) the difference in atomic radii between Ni and the other element (ΔR**%**) 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.

(a) A comparison of these four criteria for the Cr-V system is given below:

Metal	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Cr	0.125	BCC	1.6	+3
V	0.132	BCC	1.5	+5 (+3)

For chromium and vanadium, the percent difference in atomic radii is approximately 6%, the crystal structures are the same (BCC), and there is very little difference in their electronegativities. The most common valence for Cr is +3; although the most common valence of V is +5, it can also exist as +3. Therefore, chromium and vanadium are completely soluble in one another.

(b) A comparison of these four criteria for the Mg-Zn system is given below:

Metal	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Mg	0.160	HCP	1.3	+2
Zn	0.133	HCP	1.7	+2

For magnesium and zinc, the percent difference in atomic radii is approximately 17%, the crystal structures are the same (HCP), and there is some difference in their electronegativities (1.3 vs. 1.7). The most common valence for both Mg and Zn is +2. Magnesium and zinc are not completely soluble in one another, primarily because of the difference in atomic radii.

(c) A comparison of these four criteria for the Al-Zr system is given below:

Metal	*Atomic Radius (nm)*	*Crystal Structure*	*Electronegativity*	*Valence*
Al	0.143	FCC	1.5	+3
Zr	0.159	HCP	1.2	+4

For aluminum and zirconium, the percent difference in atomic radii is approximately 11%, the crystal structures are different (FCC and HCP), there is some difference in their electronegativities (1.5 vs. 1.2). The most common valences for Al and Zr are +3 and +4, respectively. Aluminum and zirconium are not completely soluble in one another, primarily because of the difference in crystal structures.

(d) A comparison of these four criteria for the Ag-Au system is given below:

Metal	*Atomic Radius (nm)*	*Crystal Structure*	*Electronegativity*	*Valence*
Ag	0.144	FCC	1.4	+1
Au	0.144	FCC	1.4	+1

For silver and gold, the atomic radii are the same, the crystal structures are the same (FCC), their electronegativities are the same (1.4), and their common valences are +1. Silver and gold are completely soluble in one another because all four criteria are satisfied.

(d) A comparison of these four criteria for the Pb-Pt system is given below:

Metal	*Atomic Radius (nm)*	*Crystal Structure*	*Electronegativity*	*Valence*
Pb	0.175	FCC	1.6	+2
Pt	0.139	FCC	1.5	+2

For lead and platinum, the percent difference in atomic radii is approximately 20%, the crystal structures are the same (FCC), their electronegativities are nearly the same (1.6 vs. 1.5), and the most common valence for both of them is +2. Lead and platinum are not completely soluble in one another, primarily because of the difference in atomic radii.

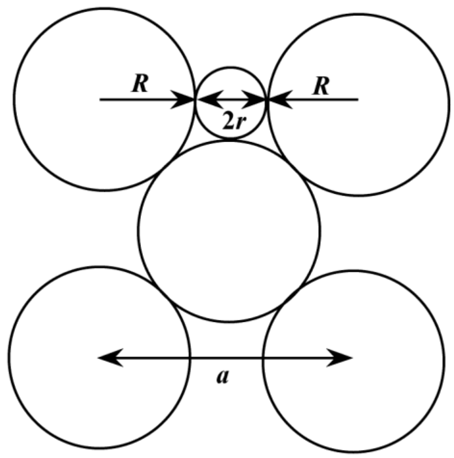
4.8 *(a) Compute the radius r of an impurity atom that will just fit into an FCC octahedral site in terms of the atomic radius R of the host atom (without introducing lattice strains).*

(b) Repeat part (a) for the FCC tetrahedral site.

(Note: You may want to consult Figure 4.3a.)

<u>Solution</u>

(a) In the drawing below is shown the atoms on the (100) face of an FCC unit cell; the small circle represents an impurity atom that just fits within the octahedral interstitial site that is located at the center of the unit cell edge.



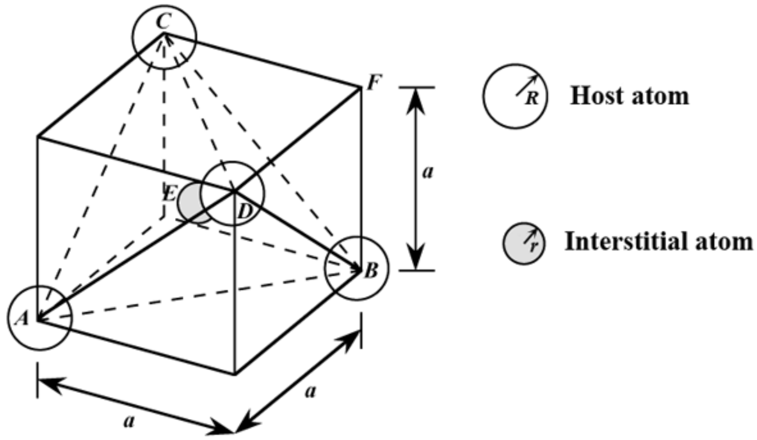
The diameter of an atom that will just fit into this site (2*r*) is just the difference between that unit cell edge length (*a*) and the radii of the two host atoms that are located on either side of the site (*R*); that is

$$2r = a - 2R$$

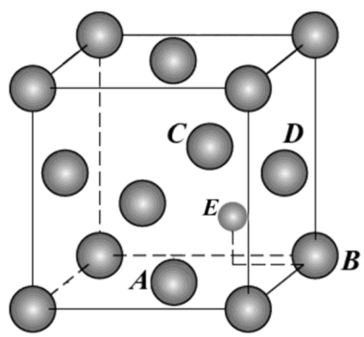
However, for FCC *a* is related to *R* according to Equation 3.1 as $a = 2R\sqrt{2}$; therefore, solving for *r* from the above equation gives

$$r = \frac{a - 2R}{2} = \frac{2R\sqrt{2} - 2R}{2} = 0.414R$$

(b) Drawing (*a*) below shows one quadrant of an FCC unit cell, which is a cube; corners of the tetrahedron correspond to atoms that are labeled *A*, *B*, *C*, and *D*. These corresponding atom positions are noted in the FCC unit cell in drawing (*b*). In both of these drawings, atoms have been reduced from their normal sizes for clarity. The interstitial atom resides at the center of the tetrahedron, which is designated as point *E*, in both (*a*) and (*b*).



(*a*)



(*b*)

Let us now express the host and interstitial atom radii in terms of the cube edge length, designated as *a*. From Figure (*a*), the spheres located at positions *A* and *B* touch each other along the bottom face diagonal. Thus,

$$\overline{AB} = 2R$$

But

$$(\overline{AB})^2 = a^2 + a^2 = 2a^2$$

or

$$\overline{AB} = a\sqrt{2} = 2R$$

And

$$a = \frac{2R}{\sqrt{2}}$$

There will also be an anion located at the corner, point *F* (not drawn), and the cube diagonal $\overline{AEF}$ will be related to the atomic radii as

$$\overline{AEF} = 2(r + R)$$

(The line *AEF* has not been drawn to avoid confusion.) From the triangle *ABF*

$$(\overline{AB})^2 + (\overline{FB})^2 = (\overline{AEF})^2 \qquad \text{(P4.8a)}$$

But,

$$\overline{FB} = a = \frac{2R}{\sqrt{2}}$$

and

$$\overline{AB} = 2R$$

from above. Substitution of the parameters involving *r* and *R* noted above into Equation P4.8a leads to the following:

$$(2R)^2 + \left(\frac{2R}{\sqrt{2}}\right)^2 = \left[2(r + R)\right]^2$$

Solving for *r* leads to

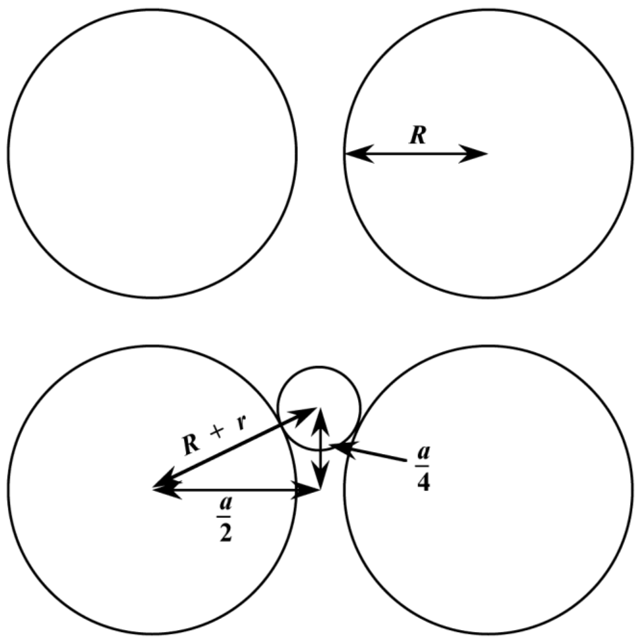
$$r = R\left(\frac{\sqrt{6} - 2}{2}\right) = 0.225R$$

4.9 *Compute the radius r of an impurity atom that will just fit into a BCC tetrahedral site in terms of the atomic radius R of the host atom (without introducing lattice strains).*

(Note: You may want to consult Figure 4.3b.)

Solution

A (100) face of a BCC unit cell is shown below.



The interstitial atom that just fits into this interstitial site is shown by the small circle. It is situated in the plane of this (100) face, midway between the two vertical unit cell edges, and one quarter of the distance between the bottom and top cell edges. From the right triangle` defined by the three arrows we may write

$$\left(\frac{a}{2}\right)^2 + \left(\frac{a}{4}\right)^2 = (R + r)^2$$

However, from Equation 3.4, $a = \frac{4R}{\sqrt{3}}$, and, therefore, making this substitution, the above equation takes the form

$$\left(\frac{4R}{2\sqrt{3}}\right)^2 + \left(\frac{4R}{4\sqrt{3}}\right)^2 = R^2 + 2Rr + r^2$$

After rearrangement the following quadratic equation results in:

$$r^2 + 2Rr - 0.667R^2 = 0$$

And upon solving for *r:*

$$r = \frac{-(2R) \pm \sqrt{(2R)^2 - (4)(1)(-0.667R^2)}}{2}$$

$$= \frac{-2R \pm 2.582R}{2}$$

And, finally

$$r(+) = \frac{-2R + 2.582R}{2} = 0.291R$$

$$r(-) = \frac{-2R - 2.582R}{2} = -2.291R$$

Of course, only the $r(+)$ root is possible, and, therefore, $r = 0.291R$.

4.10 *(a) Using the result of Problem 4.8(a), compute the radius of an octahedral interstitial site in FCC iron.*

(b) On the basis of this result and the answer to Problem 4.9, explain why a higher concentration of carbon will dissolve in FCC iron than in iron that has a BCC crystal structure.

Solution

(a) From Problem 4.8(a), the radius of an octahedral interstitial site, r, is related to the atomic radius of the host material according to $r = 0.414R$. The atomic radius of an iron atom is 0.124 nm; therefore, the radius of this octahedral site in iron is

$$r_{\text{Fe(Oct)}} = 0.414R_{\text{Fe}} = (0.414)(0.124 \text{ nm}) = 0.051 \text{ nm}$$

(b) Carbon atoms are situated in octahedral sites in FCC iron, and, for BCC iron, in tetrahedral sites. The relationship between r and R for BCC iron, as determined in problem 4.9 is $r = 0.291R$. Therefore, in BCC iron, the radius of the tetrahedral site is

$$r_{\text{Fe(Tet)}} = 0.291R_{\text{Fe}} = (0.291)(0.124 \text{ nm}) = 0.036 \text{ nm}$$

Because the radius of the octahedral site in FCC iron (0.051 nm) is greater the radius of the tetrahedral site in BCC iron (0.036 nm), a higher concentration of carbon will dissolve in FCC.

4.11 *(a) For BCC iron, compute the radius of a tetrahedral interstitial site. (See the result of Problem 4.9.)*

(b) Lattice strains are imposed on iron atoms surrounding this site when carbon atoms occupy it. Compute the approximate magnitude of this strain by taking the difference between the carbon atom radius and the site radius and then dividing this difference by the site radius.

Solution

(a) The relationship between r and R for BCC iron, as determined in problem 4.9 is $r = 0.291R$. Therefore, in BCC iron, the radius of the tetrahedral site is

$$r_{\mathrm{Fe(Tet)}} = 0.291R_{\mathrm{Fe}} = (0.291)(0.124 \text{ nm}) = 0.036 \text{ nm}$$

(b) The radius of a carbon atom (r_C) is 0.071 nm (as taken from the inside cover of the book). The lattice strain introduced by a carbon atom the is situated on a BCC tetrahedral site is determined as follows:

$$\text{Lattice strain} = \frac{r_C - r_{\mathrm{Fe(Tet)}}}{r_{\mathrm{Fe(Tet)}}} = \frac{0.071 \text{ nm} - 0.036 \text{ nm}}{0.036 \text{ nm}} = 0.97$$

Specification of Composition

4.12 *Derive the following equations:*

(a) Equation 4.7a

(b) Equation 4.9a

(c) Equation 4.10a

(d) Equation 4.11b

Solution

(a) This problem asks that we derive Equation 4.7a. To begin, C_1 is defined according to Equation 4.3a as

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

or, equivalently

$$C_1 = \frac{m'_1}{m'_1 + m'_2} \times 100$$

where the primed *m*'s indicate masses in grams. From Equation 4.4 we may write

$$m'_1 = n_{m1} A_1$$

$$m'_2 = n_{m2} A_2$$

And, substitution into the C_1 expression above

$$C_1 = \frac{n_{m1} A_1}{n_{m1} A_1 + n_{m2} A_2} \times 100$$

From Equation 4.5a it is the case that

$$n_{m1} = \frac{C'_1 (n_{m1} + n_{m2})}{100}$$

$$n_{m2} = \frac{C'_2 (n_{m1} + n_{m2})}{100}$$

And substitution of these expressions into the above equation (for C_1) leads to

$$C_1 = \frac{C_1'' A_1}{C_1'' A_1 + C_2'' A_2} \times 100$$

which is just Equation 4.7a.

(b) This part of the problem asks that we derive Equation 4.9a. To begin, C_1'' is defined as the mass of component 1 per unit volume of alloy, or

$$C_1'' = \frac{m_1}{V}$$

If we assume that the total alloy volume V is equal to the sum of the volumes of the two constituents--i.e., $V = V_1 + V_2$—then

$$C_1'' = \frac{m_1}{V_1 + V_2}$$

Furthermore, the volume of each constituent is related to its density and mass as

$$V_1 = \frac{m_1}{\rho_1}$$

$$V_2 = \frac{m_2}{\rho_2}$$

This leads to

$$C_1'' = \frac{m_1}{\dfrac{m_1}{\rho_1} + \dfrac{m_2}{\rho_2}}$$

From Equation 4.3a, m_1 and m_2 may be expressed as follows:

$$m_1 = \frac{C_1 (m_1 + m_2)}{100}$$

$$m_2 = \frac{C_2 (m_1 + m_2)}{100}$$

Substitution of these equations into the preceding expression (for C_1'') yields

$$C_1' = \frac{\dfrac{C_1(m_1 + m_2)}{100}}{\dfrac{\dfrac{C_1(m_1 + m_2)}{100}}{\rho_1} + \dfrac{\dfrac{C_2(m_1 + m_2)}{100}}{\rho_2}}$$

$$= \frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}$$

If the densities ρ_1 and ρ_2 are given in units of g/cm^3, then conversion to units of kg/m^3 requires that we multiply this equation by 10^3, inasmuch as

$$1 \text{ g/cm}^3 = 10^3 \text{ kg/m}^3$$

Therefore, the previous equation takes the form

$$C_1' = \frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \times 10^3$$

the desired expression.

(c) Now we are asked to derive Equation 4.10a. The density of an alloy ρ_{ave} is just the total alloy mass M divided by its volume V

$$\rho_{\text{ave}} = \frac{M}{V}$$

Or, in terms of the component elements 1 and 2

$$\rho_{\text{ave}} = \frac{m_1 + m_2}{V_1 + V_2}$$

[*Note:* Here it is assumed that the total alloy volume is equal to the separate volumes of the individual components, which is only an approximation; normally V will not be exactly equal to $(V_1 + V_2)$].

Each of V_1 and V_2 may be expressed in terms of its mass and density as,

$$V_1 = \frac{m_1}{\rho_1}$$

$$V_2 = \frac{m_2}{\rho_2}$$

When these expressions are substituted into the above equation (for ρ_{ave}), we get

$$\rho_{\text{ave}} = \frac{m_1 + m_2}{\dfrac{m_1}{\rho_1} + \dfrac{m_2}{\rho_2}}$$

Furthermore, from Equation 4.3a

$$m_1 = \frac{C_1(m_1 + m_2)}{100}$$

$$m_2 = \frac{C_2(m_1 + m_2)}{100}$$

Which, when substituted into the above ρ_{ave} expression yields

$$\rho_{\text{ave}} = \frac{m_1 + m_2}{\dfrac{\dfrac{C_1(m_1 + m_2)}{100}}{\rho_1} + \dfrac{\dfrac{C_2(m_1 + m_2)}{100}}{\rho_2}}$$

And, finally, this equation reduces to

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}$$

(d) And, finally, the derivation of Equation 4.11b for A_{ave} is requested. The alloy average molecular weight is just the ratio of total alloy mass in grams M' and the total number of moles in the alloy N_m. That is

$$A_{\text{ave}} = \frac{M'}{N_m} = \frac{m'_1 + m'_2}{n_{m1} + n_{m2}}$$

But using Equation 4.4 we may write

$$m'_1 = n_{m1} A_1$$

$$m'_2 = n_{m2} A_2$$

Which, when substituted into the above A_{ave} expression yields

$$A_{\text{ave}} = \frac{M'}{N_m} = \frac{n_{m1} A_1 + n_{m2} A_2}{n_{m1} + n_{m2}}$$

Furthermore, from Equation 4.5a

$$n_{m1} = \frac{C'_1(n_{m1} + n_{m2})}{100}$$

$$n_{m2} = \frac{C'_2(n_{m1} + n_{m2})}{100}$$

Thus, substitution of these expressions into the above equation for A_{ave} yields

$$A_{\text{ave}} = \frac{\dfrac{C'_1 A_1 (n_{m1} + n_{m2})}{100} + \dfrac{C'_2 A_2 (n_{m1} + n_{m2})}{100}}{n_{m1} + n_{m2}}$$

$$= \frac{C'_1 A_1 + C'_2 A_2}{100}$$

which is the desired result.

4.13 *What is the composition, in atom percent, of an alloy that consists of 92.5 wt% Ag and 7.5 wt% Cu?*

Solution

In order to compute composition, in atom percent, of a 92.5 wt% Ag-7.5 wt% Cu alloy, we employ Equation 4.6 given the atomic weights of silver and copper (found on the inside of the book's cover):

A_{Ag} = 107.87 g/mol

A_{Cu} = 63.55 g/mol

These compositions in atom percent are determined as follows:

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

$$= \frac{(92.5)(63.55\text{ g/mol})}{(92.5)(63.55\text{ g/mol}) + (7.5)(107.87\text{ g/mol})} \times 100$$

$$= 87.9\text{ at\%}$$

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

$$= \frac{(7.5)(107.87\text{ g/mol})}{(92.5)(63.55\text{ g/mol}) + (7.5)(107.87\text{ g/mol})} \times 100$$

$$= 12.1\text{ at\%}$$

4.14 *What is the composition, in atom percent, of an alloy that consists of 5.5 wt% Pb and 94.5 wt% Sn?*

Solution

In order to compute composition, in atom percent, of a 5.5 wt% Pb-94.5 wt% Sn alloy, we employ Equation 4.6 given the atomic weights of lead and tin (found on the inside of the book's cover):

A_{Pb} = 207.2 g/mol

A_{Sn} = 118.71 g/mol

These compositions in atom percent are determined as follows:

$$C'_{Pb} = \frac{C_{Pb}A_{Sn}}{C_{Pb}A_{Sn} + C_{Sn}A_{Pb}} \times 100$$

$$= \frac{(5.5)(118.71\text{ g/mol})}{(5.5)(118.71\text{ g/mol}) + (94.5)(207.2\text{ g/mol})} \times 100$$

$$= 3.23\text{ at\%}$$

$$C'_{Sn} = \frac{C_{Sn}A_{Pb}}{C_{Pb}A_{Sn} + C_{Sn}A_{Pb}} \times 100$$

$$= \frac{(94.5)(207.2\text{ g/mol})}{(5.5)(118.71\text{ g/mol}) + (94.5)(207.2\text{ g/mol})} \times 100$$

$$= 96.77\text{ at\%}$$

4.15 *What is the composition, in weight percent, of an alloy that consists of 5 at% Cu and 95 at% Pt?*

Solution

In order to compute composition, in weight percent, of a 5 at% Cu-95 at% Pt alloy, we employ Equation 4.7 given the atomic weights of copper and platinum (found on the inside of the book's cover):

A_{Cu} = 63.55 g/mol

A_{Pt} = 195.08 g/mol

These compositions in weight percent are determined as follows:

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

$$= \frac{(5)(63.55 \text{ g/mol})}{(5)(63.55 \text{ g/mol}) + (95)(195.08 \text{ g/mol})} \times 100$$

= 1.68 wt%

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

$$= \frac{(95)(195.08 \text{ g/mol})}{(5)(63.55 \text{ g/mol}) + (95)(195.08 \text{ g/mol})} \times 100$$

= 98.32 wt%

4.16 *Calculate the composition, in weight percent, of an alloy that contains 105 kg of iron, 0.2 kg of carbon, and 1.0 kg of chromium.*

Solution

The concentration, in weight percent, of an element in an alloy may be computed using Equation 4.3b. For this alloy, the concentration of iron (C_{Fe}) is just

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

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

Similarly, for carbon

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

And for chromium

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

4.17 *What is the composition, in atom percent, of an alloy that contains 33 g of copper and 47 g of zinc?*

Solution

The concentration of an element in an alloy, in atom percent, may be computed using Equation 4.5a. However, it first becomes necessary to compute the number of moles of both Cu and Zn, using Equation 4.4. Atomic weights of copper and zinc (found on the inside of the book's cover) are as follows:

A_{Cu} = 63.55 g/mol

A_{Zn} = 65.41 g/mol

Thus, the number of moles of Cu is just

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

Likewise, for Zn

$$n_{m_{Zn}} = \frac{47\text{ g}}{65.41\text{ g/mol}} = 0.719 \text{ mol}$$

Now, use of Equation 4.5a yields

$$C'_{Cu} = \frac{n_{m_{Cu}}}{n_{m_{Cu}} + n_{m_{Zn}}} \times 100$$

$$= \frac{0.519\text{ mol}}{0.519\text{ mol} + 0.719\text{ mol}} \times 100 = 41.9 \text{ at\%}$$

Also,

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

4.18 *What is the composition, in atom percent, of an alloy that contains 44.5 lb_m of Ag, 83.7 lb_m of Au, and 5.3 lb_m of Cu?*

Solution

In this problem we are asked to determine the concentrations, in atom percent, of the Ag-Au-Cu alloy. It is first necessary to convert the amounts of Ag, Au, and Cu into grams.

$$m'_{\text{Ag}} = (44.5\ \text{lb}_\text{m})(453.6\ \text{g/lb}_\text{m}) = 20{,}185\ \text{g}$$

$$m'_{\text{Au}} = (83.7\ \text{lb}_\text{m})(453.6\ \text{g/lb}_\text{m}) = 37{,}966\ \text{g}$$

$$m'_{\text{Cu}} = (5.3\ \text{lb}_\text{m})(453.6\ \text{g/lb}_\text{m}) = 2{,}404\ \text{g}$$

These masses must next be converted into moles (Equation 4.4), as

$$n_{m_{\text{Ag}}} = \frac{m'_{\text{Ag}}}{A_{\text{Ag}}} = \frac{20{,}185\ \text{g}}{107.87\ \text{g/mol}} = 187.1\ \text{mol}$$

$$n_{m_{\text{Au}}} = \frac{37{,}966\ \text{g}}{196.97\ \text{g/mol}} = 192.8\ \text{mol}$$

$$n_{m_{\text{Cu}}} = \frac{2{,}404\ \text{g}}{63.55\ \text{g/mol}} = 37.8\ \text{mol}$$

Now, employment of Equation 4.5b, gives

$$C'_{\text{Ag}} = \frac{n_{m_{\text{Ag}}}}{n_{m_{\text{Ag}}} + n_{m_{\text{Au}}} + n_{m_{\text{Cu}}}} \times 100$$

$$= \frac{187.1\ \text{mol}}{187.1\ \text{mol} + 192.8\ \text{mol} + 37.8\ \text{mol}} \times 100 = 44.8\ \text{at\%}$$

$$C'_{\text{Au}} = \frac{192.8\ \text{mol}}{187.1\ \text{mol} + 192.8\ \text{mol} + 37.8\ \text{mol}} \times 100 = 46.2\ \text{at\%}$$

$$C'_{Cu} = \frac{37.8\ \text{mol}}{187.1\ \text{mol} + 192.8\ \text{mol} + 37.8\ \text{mol}} \times 100 = 9.0\ \text{at\%}$$

4.19 *Convert the atom percent composition in Problem 4.18 to weight percent.*

Solution

This problem calls for a conversion of composition in atom percent to composition in weight percent. The composition in atom percent for Problem 4.18 is 44.8 at% Ag, 46.2 at% Au, and 9.0 at% Cu. Modification of Equation 4.7 to take into account a three-component alloy leads to the following

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

$$= \frac{(44.8)(107.87 \text{ g/mol})}{(44.8)(107.87 \text{ g/mol}) + (46.2)(196.97 \text{ g/mol}) + (9.0)(63.55 \text{ g/mol})} \times 100$$

= 33.3 wt%

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

$$= \frac{(46.2)(196.97 \text{ g/mol})}{(44.8)(107.87 \text{ g/mol}) + (46.2)(196.97 \text{ g/mol}) + (9.0)(63.55 \text{ g/mol})} \times 100$$

= 62.7 wt%

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

$$= \frac{(9.0)(63.55 \text{ g/mol})}{(44.8)(107.87 \text{ g/mol}) + (46.2)(196.97 \text{ g/mol}) + (9.0)(63.55 \text{ g/mol})} \times 100$$

= 4.0 wt%

4.20 *Calculate the number of atoms per cubic meter in Pb.*

Solution

This problem calls for a determination of the number of atoms per cubic meter for lead. In order to solve this problem, one must employ Equation 4.2,

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

The density of Pb (from the table inside of the front cover) is 11.35 g/cm^3, while its atomic weight is 207.2 g/mol. Thus,

$$N = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(11.35 \text{ g/cm}^3)}{207.2 \text{ g/mol}}$$

$$= 3.30 \times 10^{22} \text{ atoms/cm}^3 = 3.30 \times 10^{28} \text{ atoms/m}^3$$

4.21 *Calculate the number of atoms per cubic meter in Cr.*

Solution

This problem calls for a determination of the number of atoms per cubic meter for chromium. In order to solve this problem, one must employ Equation 4.2,

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

The density of Cr (from the table inside of the front cover) is 7.19 g/cm^3, while its atomic weight is 52.00 g/mol. Thus,

$$N = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(7.19 \text{ g/cm}^3)}{52.00 \text{ g/mol}}$$

$$= 8.33 \times 10^{22} \text{ atoms/cm}^3 = 8.33 \times 10^{28} \text{ atoms/m}^3$$

4.22 *The concentration of Si in an Fe-Si alloy is 0.25 wt%. What is the concentration in kilograms of Si per cubic meter of alloy?*

<u>Solution</u>

In order to compute the concentration in kg/m^3 of Si in a 0.25 wt% Si-99.75 wt% Fe alloy we must employ Equation 4.9 as

$$C''_{\mathrm{Si}} = \frac{C_{\mathrm{Si}}}{\dfrac{C_{\mathrm{Si}}}{\rho_{\mathrm{Si}}} + \dfrac{C_{\mathrm{Fe}}}{\rho_{\mathrm{Fe}}}} \times 10^3$$

From inside the front cover, densities for silicon and iron are 2.33 and 7.87 g/cm^3, respectively; therefore

$$C''_{\mathrm{Si}} = \frac{0.25}{\dfrac{0.25}{2.33\ \mathrm{g/cm^3}} + \dfrac{99.75}{7.87\ \mathrm{g/cm^3}}} \times 10^3$$

$$= 19.6\ \mathrm{kg/m^3}$$

4.23 *The concentration of phosphorus in silicon is 1.0 × 10⁻⁷ at%. What is the concentration in kilograms of phosphorus per cubic meter?*

Solution

Strategy for solving:

Step 1: Convert the concentration of P from at% to wt% using Equation 4.7a

Step 2: Compute the concentration of kilograms per cubic meter using Equation 4.9a

Step 1: From Equation 4.7a, the concentration of P in weight percent is determined as follows:

$$C_P = \frac{C'_P A_P}{C'_P A_P + C'_{Si} A_{Si}} \times 100$$

where

$C'_{Fe} = 1.0 \times 10^{-7}$ at%

$C'_{Si} = 100.00$ at% $- 1.0 \times 10^{-7}$ at% $= 99.9999999$ at%

A_P = 30.97 g/mol (from inside front cover)

A_{Si} = 28.09 g/mol (from inside front cover)

Now, solve for C_P using the above equation

$$C_P = \frac{(1.0 \times 10^{-7} \text{ at\%})(30.97 \text{ g/mol})}{(1.0 \times 10^{-7} \text{ at\%})(30.97 \text{ g/mol}) + (99.9999999 \text{ at\%})(28.09 \text{ g.mol})} \times 100$$

$$= 1.103 \times 10^{-7} \text{ wt\%}$$

Step 2

We now compute the number of kilograms per meter cubed (Equation 4.9a) with

ρ_{Si} = 2.33 g/cm^3 (from inside front cover)

ρ_P = 1.82 g/cm^3 (from inside front cover)

$C_{Si} = 100.00 \text{ wt\%} - 1.103 \times 10^{-7} \text{ wt\%} = 99.999999890$

Therefore

$$C''_P = \left(\frac{C_P}{\frac{C_P}{\rho_P} + \frac{C_{Si}}{\rho_{Si}}} \right) \times 10^3$$

$$= \left(\frac{1.103 \times 10^{-7}\ \text{wt\%}}{\dfrac{1.103 \times 10^{-7}\ \text{wt\%}}{1.82\ \text{g/cm}^3} + \dfrac{99.999999890\ \text{wt\%}}{2.33\ \text{g/cm}^3}} \right) \times 10^3$$

$$2.57 \times 10^{-6}\ \text{kg/m}^3$$

4.24 *Determine the approximate density of a Ti-6Al-4V titanium (Ti) alloy that has a composition of 90 wt% Ti, 6 wt% Al, and 4 wt% V.*

Solution

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

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

And, using the density values for Ti, Al, and V—i.e., 4.51 g/cm^3, 2.71 g/cm^3, and 6.10 g/cm^3—(as taken from inside the front cover of the text), the density is computed as follows:

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

$$= 4.38\text{ g/cm}^3$$

4.25 *Calculate the unit cell edge length for an 80 wt% Ag–20 wt% Pd alloy. All of the palladium is in solid solution, the crystal structure for this alloy is FCC, and the room-temperature density of Pd is 12.02 g/cm*^{3}.

<u>Solution</u>

In order to solve this problem it is necessary to employ Equation 3.8; in this expression density and atomic weight will be averages for the alloy—that is

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{V_C N_{\text{A}}}$$

Inasmuch as the unit cell is cubic, then $V_C = a^3$, then

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{a^3 N_{\text{A}}}$$

And solving this equation for the unit cell edge length, leads to

$$a = \left(\frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}\right)^{1/3}$$

Expressions for A_{ave} and ρ_{ave} are found in Equations 4.11a and 4.10a, respectively, which, when incorporated into the above expression yields

$$a = \left[\frac{n\left(\dfrac{100}{\dfrac{C_{\text{Ag}}}{A_{\text{Ag}}} + \dfrac{C_{\text{Pd}}}{A_{\text{Pd}}}}\right)}{\left(\dfrac{100}{\dfrac{C_{\text{Ag}}}{\rho_{\text{Ag}}} + \dfrac{C_{\text{Pd}}}{\rho_{\text{Pd}}}}\right) N_{\text{A}}}\right]^{1/3}$$

Since the crystal structure is FCC, the value of n in the above expression is 4 atoms per unit cell. The atomic weights for Ag and Pd are 107.87 and 106.4 g/mol, respectively (Figure 2.8), whereas the densities for the Ag and Pd are 10.49 g/cm^3 (inside front cover) and 12.02 g/cm^3. Substitution of these, as well as the concentration values stipulated in the problem statement, into the above equation gives

$$a = \left[\frac{(4 \text{ atoms/unit cell}) \left(\dfrac{100}{\dfrac{80 \text{ wt\%}}{107.87 \text{ g/mol}} + \dfrac{20 \text{ wt\%}}{106.4 \text{ g/mol}}} \right)}{\left(\dfrac{100}{\dfrac{80 \text{ wt\%}}{10.49 \text{ g/cm}^3} + \dfrac{20 \text{ wt\%}}{12.02 \text{ g/cm}^3}} \right) \left(6.022 \times 10^{23} \text{ atoms/mol}\right)} \right]^{1/3}$$

$$= 4.050 \times 10^{-8} \text{ cm} = 0.4050 \text{ nm}$$

4.26 *Some hypothetical alloy is composed of 25 wt% of metal A and 75 wt% of metal B. If the densities of metals A and B are 6.17 and 8.00 g/cm³, respectively, and their respective atomic weights are 171.3 and 162.0 g/mol, determine whether the crystal structure for this alloy is simple cubic, face-centered cubic, or body-centered cubic. Assume a unit cell edge length of 0.332 nm.*

Solution

In order to solve this problem it is necessary to employ Equation 3.8; in this expression density and atomic weight will be averages for the alloy—that is

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{V_C N_{\text{A}}}$$

Inasmuch as for each of the possible crystal structures, the unit cell is cubic, then $V_C = a^3$, or

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{a^3 N_{\text{A}}}$$

Now, in order to determine the crystal structure it is necessary to solve for n, the number of atoms per unit cell. For $n = 1$, the crystal structure is simple cubic, whereas for n values of 2 and 4, the crystal structure will be either BCC or FCC, respectively. When we solve the above expression for n the result is as follows:

$$n = \frac{\rho_{\text{ave}} a^3 N_{\text{A}}}{A_{\text{ave}}}$$

Expressions for A_{ave} and ρ_{ave} are found in Equations 4.11a and 4.10a, respectively, which, when incorporated into the above expression yields

$$n = \frac{\left(\dfrac{100}{\dfrac{C_{\text{A}}}{\rho_{\text{A}}} + \dfrac{C_{\text{B}}}{\rho_{\text{B}}}}\right) a^3 N_{\text{A}}}{\left(\dfrac{100}{\dfrac{C_{\text{A}}}{A_{\text{A}}} + \dfrac{C_{\text{B}}}{A_{\text{B}}}}\right)}$$

Substitution of the concentration values (i.e., C_{A} = 25 wt% and C_{B} = 75 wt%) as well as values for the other parameters given in the problem statement, into the above equation gives

$$n = \frac{\left(\dfrac{100}{\dfrac{25\text{ wt\%}}{6.17\text{ g/cm}^3} + \dfrac{75\text{ wt\%}}{8.00\text{ g/cm}^3}}\right)(3.32 \times 10^{-8}\text{ nm})^3(6.022 \times 10^{23}\text{ atoms/mol})}{\left(\dfrac{100}{\dfrac{25\text{ wt\%}}{171.3\text{ g/mol}} + \dfrac{75\text{ wt\%}}{162.0\text{ g/mol}}}\right)}$$

$$= 1.00 \text{ atom/unit cell}$$

Therefore, on the basis of this value, the crystal structure is *simple cubic*.

4.27 *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:*

$$N_1 = \frac{N_A C_1}{\dfrac{C_1 A_1}{\rho_1} + \dfrac{A_1}{\rho_2}(100 - C_1)} \qquad (4.21)$$

where N_A is Avogadro's number, ρ_1 and ρ_2 are the densities of the two elements, and A_1 is the atomic weight of element 1.

Derive Equation 4.21 using Equation 4.2 and expressions contained in Section 4.4.

Solution

This problem asks that we derive Equation 4.21, 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:

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

4.28 *Molybdenum (Mo) forms a substitutional solid solution with tungsten (W). Compute the number of molybdenum atoms per cubic centimeter for a molybdenum-tungsten alloy that contains 16.4 wt% Mo and 83.6 wt% W. The densities of pure molybdenum and tungsten are 10.22 and 19.30 g/cm^3, respectively.*

Solution

This problem asks us to determine the number of molybdenum atoms per cubic centimeter for a 16.4 wt% Mo-83.6 wt% W solid solution. To solve this problem, employment of Equation 4.21 is necessary, using the following values:

$C_1 = C_{\text{Mo}} = 16.4 \text{ wt\%}$
$\rho_1 = \rho_{\text{Mo}} = 10.22 \text{ g/cm}^3$
$\rho_2 = \rho_{\text{W}} = 19.30 \text{ g/cm}^3$
$A_1 = A_{\text{Mo}} = 95.94 \text{ g/mol}$

Thus

$$N_{\text{Mo}} = \frac{N_{\text{A}} C_{\text{Mo}}}{\dfrac{C_{\text{Mo}} A_{\text{Mo}}}{\rho_{\text{Mo}}} + \dfrac{A_{\text{Mo}}}{\rho_{\text{W}}}(100 - C_{\text{Mo}})}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(16.4 \text{ wt\%})}{\dfrac{(16.4 \text{ wt\%})(95.94 \text{ g/mol})}{10.22 \text{ g/cm}^3} + \dfrac{95.94 \text{ g/mol}}{19.3 \text{ g/cm}^3}(100 - 16.4 \text{ wt\%})}$$

$$= 1.73 \times 10^{22} \text{ atoms/cm}^3$$

4.29 *Niobium forms a substitutional solid solution with vanadium. Compute the number of niobium atoms per cubic centimeter for a niobium-vanadium alloy that contains 24 wt% Nb and 76 wt% V. The densities of pure niobium and vanadium are 8.57 and 6.10 g/cm³, respectively.*

Solution

This problem asks us to determine the number of niobium atoms per cubic centimeter for a 24 wt% Nb-76 wt% V solid solution. To solve this problem, employment of Equation 4.21 is necessary, using the following values:

$C_1 = C_{Nb} = 24$ wt%
$\rho_1 = \rho_{Nb} = 8.57$ g/cm^3
$\rho_2 = \rho_V = 6.10$ g/cm^3
$A_1 = A_{Nb} = 92.91$ g/mol

Thus

$$N_{Nb} = \frac{N_A C_{Nb}}{\frac{C_{Nb} A_{Nb}}{\rho_{Nb}} + \frac{A_{Nb}}{\rho_V}\left(100 - C_{Nb}\right)}$$

$$= \frac{\left(6.022 \times 10^{23} \text{ atoms/mol}\right)(24 \text{ wt\%})}{\frac{(24 \text{ wt\%})(92.91 \text{ g/mol})}{8.57 \text{ g/cm}^3} + \frac{92.91 \text{ g/mol}}{6.10 \text{ g/cm}^3}(100 - 24 \text{ wt\%})}$$

$$= 1.02 \times 10^{22} \text{ atoms/cm}^3$$

4.30 *Consider an iron-carbon alloy that contains 0.2 wt% C, in which all the carbon atoms reside in tetrahedral interstitial sites. Compute the fraction of these sites that are occupied by carbon atoms.*

Solution

The following strategy will be used to solve this problem:

Step 1: compute the number of Fe atoms per centimeter cubed using Equation 4.21

Step 2: compute the number of C atoms per centimeter cubed also using Equation 4.21

Step 3: compute the number of unit cells per centimeter cubed by dividing the number of Fe atoms per centimeter cubed (Step 1) by two since there are two Fe atoms per BCC unit cell

Step 4: compute the number of total interstitial sites per centimeter cubed by multiplying the number of tetrahedral interstitial sites by the number of unit cells per cubic centimeter (from Step 3)

Step 5: The fraction of tetrahedral sites occupied by carbon atoms is computed by dividing the number of carbon atoms per centimeter cubed (Step 3) by the total number of interstitial sites per cubic centimeter

The solution to this problem involves using the following values:

$C_C = 0.2$ wt%

$C_{Fe} = 99.8$ wt%

$\rho_C = 2.25$ g/cm^3

$\rho_{Fe} = 7.87$ g/cm^3

$A_C = 12.01$ g/mol

$A_{Fe} = 55.85$ g/mol

Step 1: We compute the number of Fe atoms per cubic centimeter using Equation 4.21 as:

$$N_{Fe} = \frac{N_A C_{Fe}}{\dfrac{C_{Fe} A_{Fe}}{\rho_{Fe}} + \dfrac{A_{Fe}}{\rho_C}(100 - C_{Fe})}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(99.8 \text{ wt\% Fe})}{\dfrac{(99.8 \text{ wt\% Fe})(55.85 \text{ g/mol})}{7.87 \text{ g/cm}^3} + \dfrac{(55.85 \text{ g/mol})}{2.25 \text{ g/cm}^3}(100 \text{ wt\%} - 99.8 \text{ wt\%})}$$

$$8.43 \times 10^{22} \text{ Fe atoms/cm}^3$$

Step 2: We can compute the number of C atoms per cubic centimeter also using Equation 4.21 as follows:

$$N_C = \frac{N_A C_C}{\dfrac{C_C A_C}{\rho_C} + \dfrac{A_C}{\rho_{Fe}}(100 - C_C)}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/cm}^3)(0.2\ \text{wt\%})}{\dfrac{(0.2\ \text{wt\%})(12.01\ \text{g/mol})}{2.25\ \text{g/cm}^3} + \dfrac{12.01\ \text{g/mol}}{7.87\ \text{g/cm}^3}(100\ \text{wt\%} - 0.2\ \text{wt\%})}$$

$$= 7.85 \times 10^{20}\ \text{C atoms/cm}^3$$

Step 3: the number of unit cells per centimeter cubed is determined by dividing the number of Fe atoms per centimeter cubed (Step 1) by two since there are two Fe atoms per BCC unit cell—that is

$$\text{no. unit cells/cm}^3 = \frac{N_{Fe}}{2}$$

$$= \frac{8.43 \times 10^{22}\ \text{Fe atoms/cm}^3}{2} = 4.22 \times 10^{22}$$

Step 4: We compute the number of total interstitial sites per centimeter cubed by multiplying the number of tetrahedral interstitial sites per unit cell by the number of unit cells per cubic centimeter (from Step 3). From Figure 4.3*b*, there are 4 tetrahedral sites located on the front face plane of the unit cell—one site for each of the unit cell edges in this plane. Inasmuch as there are 6 faces on this unit cell there are 6 × 4 = 24 interstitial sites for this unit cell. However, each of these sites is shared by 2 unit cells, which means that only 12 sites belong to each unit cell. Therefore the number of tetrahedral sites per centimeter cubed corresponds to 12 times the number of unit cells per cubic centimeter (n_s)—that is

$$n_s = (12\ \text{sites/unit cell})(4.22 \times 10^{22}\ \text{unit cells/cm}^3)$$

$$= 5.06 \times 10^{23}\ \text{sites/cm}^3$$

Step 5: The fraction of tetrahedral sites occupied by carbon atoms is computed by dividing the number of carbon atoms per centimeter cubed (Step 3) by the total number of interstitial sites per cubic centimeter, that is

$$\text{fraction sites occupied} = \frac{N_C}{n_s}$$

$$= \frac{7.85 \times 10^{20} \text{ C atoms/cm}^3}{5.06 \times 10^{23} \text{ sites/cm}^3} = 1.55 \times 10^{-3}$$

4.31 *For a BCC iron-carbon alloy that contains 0.1 wt% C, calculate the fraction of unit cells that contain carbon atoms.*

Solution

It is first necessary to compute the number of carbon atoms per cubic centimeter of alloy using Equation 4.21. For this problem

$A_1 = A_C$ = 12.011 g/mol (from inside the front cover)

$C_1 = C_C$ = 0.1 wt%

$\rho_1 = \rho_C$ = 2.25 g/cm^3 (from inside front cover)

$\rho_2 = \rho_{Fe}$ = 7.87 g/cm^3 (from inside front cover)

Now using from Equation 4.21

$$N_C = \frac{N_A C_C}{\dfrac{C_C A_C}{\rho_C} + \dfrac{A_C}{\rho_{Fe}}(100 - C_C)}$$

$$= \frac{(6.022 \times 10^{23} \text{atoms/mol})(0.1 \text{ wt\%})}{\dfrac{(0.1 \text{ wt\%})(12.011 \text{ g/mol})}{2.25 \text{ g/cm}^3} + \dfrac{(12.011 \text{ g/mol})}{7.87 \text{ g/cm}^3}(100 - 0.1 \text{ wt\%})}$$

$$= 3.94 \times 10^{20} \text{ C atoms/cm}^3$$

We now perform the same calculation for iron atoms, where

$A_1 = A_{Fe}$ = 55.85 g/mol (from inside the front cover)

$C_1 = C_{Fe}$ = 100% – 0.1 wt% = 99.9 wt%

$\rho_1 = \rho_{Fe}$ = 7.87 g/cm^3 (from inside front cover)

$\rho_2 = \rho_C$ = 2.25 g/cm^3 (from inside front cover)

Therefore,

$$= \frac{(6.022 \times 10^{23} \text{atoms/mol})(99.9 \text{ wt\%})}{\dfrac{(99.9 \text{ wt\%})(55.85 \text{ g/mol})}{7.87 \text{ g/cm}^3} + \dfrac{(55.85 \text{ g/mol})}{2.25 \text{ g/cm}^3}(100 - 99.9 \text{ wt\%})}$$

$$= 8.46 \times 10^{22} \text{ Fe atoms/cm}^3$$

From Section 3.4 there are two Fe atoms associated with each unit cell; hence, the number of unit cells in a centimeter cubed, n_i, is equal to

$$n_i = \frac{\text{No. Fe atoms/cm}^3}{\text{No. atoms/unit cell}}$$

$$= \frac{8.46 \times 10^{22} \text{ atoms/cm}^3}{2 \text{ atoms/unit cell}} = 4.23 \times 10^{22} \text{ unit cells/cm}^3$$

Now, the fraction of unit cells that contain carbon atoms, n_f , is just the number of carbon atoms per centimeter cubed (3.94×10^{20}) divided by the number of unit cells per centimeter cubed (4.23×10^{22}), or

$$n_f = \frac{3.94 \times 10^{20} \text{ C atoms/cm}^3}{4.23 \times 10^{22} \text{ unit cells/cm}^3}$$

$$= 9.31 \times 10^{-3} \text{ atoms/unit cell}$$

The reciprocal of n_f is the number of unit cells per atom—viz.

$$\frac{1}{n_f} = \frac{1}{9.31 \times 10^{-3} \text{ atoms/unit cell}}$$

$$= 107.5 \text{ unit cells/atom}$$

That is, there is one carbon atom per 107.5 unit cells.

4.32 *For Si to which has had added 1.0 × 10^{-5} at% of aluminum (Al), calculate the number of Al atoms per cubic meter.*

Solution

To make this computation we need to use Equation 4.21. However, because the concentration of Al is given in atom percent, it is necessary to convert 1.0 × 10^{-5} at% to weight percent using Equation 4.7a. For this computation

$C_1 = C_{Al}$ = concentration of Al in wt%

$C'_1 = C'_{Al}$ = atom percent of Al = 1.0 × 10^{-5} at%

$C'_2 = C'_{Si}$ = atom percent of Si = 100 at% – 1.0 × 10^{-5} at% = 99.99999 at%

$A_1 = A_{Al}$ = atomic weight of Al = 26.98 g/mol (from inside front cover)

$A_2 = A_{Si}$ = atomic weight of Si = 28.09 g/mol (from inside front cover)

Now using Equation 4.7a we compute the value of C_1 (or C_{Al}) as follows:

$$C_1 = \frac{C'_1 A_1}{C'_1 A_1 + C'_2 A_2} \times 100$$

$$= \frac{(1.0 \times 10^{-5} \text{ wt\%})(26.98 \text{ g/mol})}{(1.0 \times 10^{-5} \text{ wt\%})(26.98 \text{ g/mol}) + (99.99999 \text{ wt\%})(28.09 \text{ g/mol})} \times 100$$

$$9.60 \times 10^{-6} \text{ wt\%}$$

Now employment of Equation 4.21 with

N_1= number of Al atoms per meter cubed

C_1 = concentration of Al in weight percent = 9.60 × 10^{-6} wt%

A_1 = atomic weight of Al = 26.98 g/mol (inside front cover)

ρ_1 = density of Al = 2.71 g/cm^3 (inside front cover)

ρ_2 = density of silicon = 2.33 g/cm^3 (inside front cover)

leads to

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

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(9.60 \times 10^{-6}\ \text{wt\%})}{\dfrac{(9.60 \times 10^{-6}\ \text{wt\%})(26.98\ \text{g/mol})}{2.71\ \text{g/cm}^3} + \dfrac{(26.98\ \text{g/mol})}{2.33\ \text{g/cm}^3}(100 - 9.60 \times 10^{-6}\ \text{wt\%})}$$

$$= 4.99 \times 10^{15}\ \text{Al atoms/cm}^3$$

4.33 *Sometimes it is desirable to determine the weight percent of one element, C_1, that will produce a specified concentration in terms of the number of atoms per cubic centimeter, N_1, for an alloy composed of two types of atoms. This computation is possible using the following expression:*

$$C_1 = \frac{100}{1 + \frac{N_A \rho_2}{N_1 A_1} - \frac{\rho_2}{\rho_1}} \qquad (4.22)$$

where N_A is Avogadro's number, ρ_1 and ρ_2 are the densities of the two elements, and A_1 is the atomic weight of element 1.

Derive Equation 4.22 using Equation 4.2 and expressions contained in Section 4.4.

Solution

This problem asks that we derive Equation 4.22, using other equations given in the chapter. The number of atoms of component 1 per cubic centimeter is just equal to the atom fraction of component 1 (c'_1) times the total number of atoms per cubic centimeter in the alloy (N). Thus, using the equivalent of Equation 4.2 for N, we may write

$$N_1 = c'_1 N = \frac{c'_1 N_A \rho_{ave}}{A_{ave}}$$

Realizing that

$$c'_1 = \frac{C'_1}{100}$$

and

$$C'_2 = 100 - C'_1$$

and substitution of the expressions for ρ_{ave} and A_{ave}, Equations 4.10b and 4.11b, respectively, leads to

$$N_1 = \frac{c'_1 N_A \rho_{ave}}{A_{ave}}$$

$$= \frac{(c'_1 N_A)\left(\frac{C'_1 A_1 + C'_2 A_2}{\frac{C'_1 A_1}{\rho_1} + \frac{C'_2 A_2}{\rho_2}}\right)}{\frac{C' A_1 + C'_2 A_2}{100}}$$

$$= \frac{N_A C'_1 r_1 r_2}{C'_1 r_2 A_1 + (100 - C'_1) r_1 A_2}$$

And, solving for C'_1 leads to

$$C'_1 = \frac{100\, N_1 r_1 A_2}{N_A r_1 r_2 - N_1 r_2 A_1 + N_1 r_1 A_2}$$

Substitution of this expression for C'_1 into Equation 4.7a, which may be written in the following form

$$C_1 = \frac{\left(\frac{100\, N_1 r_1 A_2}{N_A r_1 r_2 - N_1 r_2 A_1 + N_1 r_1 A_2}\right) A_1}{\left(\frac{100\, N_1 r_1 A_2}{N_A r_1 r_2 - N_1 r_2 A_1 + N_1 r_1 A_2}\right) A_1 + \left[100 - \left(\frac{100\, N_1 r_1 A_2}{N_A r_1 r_2 - N_1 r_2 A_1 + N_1 r_1 A_2}\right)\right] A_2} \times 100$$

which simplifies to

$$C_1 = \frac{100}{1 + \frac{N_A r_2}{N_1 A_1} - \frac{r_2}{r_1}}$$

the desired expression.

4.34 *Gold (Au) forms a substitutional solid solution with silver (Ag). Compute the weight percent of gold that must be added to silver to yield an alloy that contains 5.5 × 10^{21} Au atoms per cubic centimeter. The densities of pure Au and Ag are 19.32 and 10.49 g/cm^3, respectively.*

Solution

To solve this problem, employment of Equation 4.22 is necessary, using the following values:

$N_1 = N_{\text{Au}} = 5.5 \times 10^{21}$ atoms/cm^3
$\rho_1 = \rho_{\text{Au}} = 19.32$ g/cm^3
$\rho_2 = \rho_{\text{Ag}} = 10.49$ g/cm^3
$A_1 = A_{\text{Au}} = 196.97$ g/mol (found inside front cover)
$A_2 = A_{\text{Ag}} = 107.87$ g/mol (found inside from cover)

Thus

$$C_{\text{Au}} = \frac{100}{1 + \dfrac{N_{\text{A}} r_{\text{Ag}}}{N_{\text{Au}} A_{\text{Au}}} - \dfrac{r_{\text{Ag}}}{r_{\text{Au}}}}$$

$$= \frac{100}{1 + \dfrac{(6.022 \times 10^{23} \text{ atoms/mol})(10.49 \text{ g/cm}^3)}{(5.5 \times 10^{21} \text{ atoms/cm}^3)(196.97 \text{ g/mol})} - \left(\dfrac{10.49 \text{ g/cm}^3}{19.32 \text{ g/cm}^3}\right)}$$

$$= 15.9 \text{ wt\%}$$

4.35 *Germanium (Ge) forms a substitutional solid solution with silicon (Si). Compute the weight percent of germanium that must be added to silicon to yield an alloy that contains 2.43 × 10^{21} Ge atoms per cubic centimeter. The densities of pure Ge and Si are 5.32 and 2.33 g/cm^3, respectively.*

Solution

To solve this problem, employment of Equation 4.22 is necessary, using the following values:

$N_1 = N_{\text{Ge}} = 2.43 \times 10^{21}$ atoms/cm^3
$\rho_1 = \rho_{\text{Ge}} = 5.32$ g/cm^3
$\rho_2 = \rho_{\text{Si}} = 2.33$ g/cm^3
$A_1 = A_{\text{Ge}} = 72.64$ g/mol (found inside front cover)
$A_2 = A_{\text{Si}} = 28.09$ g/mol (found inside front cover)

Thus

$$C_{\text{Ge}} = \frac{100}{1 + \dfrac{N_{\text{A}}\, r_{\text{Si}}}{N_{\text{Ge}} A_{\text{Ge}}} - \dfrac{r_{\text{Si}}}{r_{\text{Ge}}}}$$

$$= \frac{100}{1 + \dfrac{(6.022 \times 10^{23}\ \text{atoms/mol})(2.33\ \text{g/cm}^3)}{(2.43 \times 10^{21}\ \text{atoms/cm}^3)(72.64\ \text{g/mol})} - \left(\dfrac{2.33\ \text{g/cm}^3}{5.32\ \text{g/cm}^3}\right)}$$

$$= 11.7\ \text{wt\%}$$

4.36 *Electronic devices found in integrated circuits are composed of very high purity silicon to which has been added small and very controlled concentrations of elements found in Groups IIIA and VA of the periodic table. For Si to which has had added 6.5 $\times 10^{21}$ atoms per cubic meter of phosphorus, compute (a) the weight percent and (b) the atom percent of P present.*

Solution

(a) This part of the problem is solved using Equation 4.22, in which

C_1 = concentration of P in wt%

N_1 = number of P atoms per cubic centimeter = $(6.5 \times 10^{21}$ atoms/m$^3)(1$ m$^3/10^6$ cm$^3)$

= 6.5×10^{15} atoms/cm^3

A_1 = atomic weight of P = 30.97 g/mol (inside front cover)

ρ_1 = density of P = 1.82 g/cm^3 (inside front cover)

ρ_2 = density of silicon = 2.33 g/cm^3 (inside front cover)

And, from Equation 4.22

$$C_1 = \frac{100}{1 + \frac{N_A \rho_2}{N_1 A_1} - \frac{\rho_2}{\rho_1}}$$

$$= \frac{100}{1 + \frac{(6.022 \times 10^{23} \text{ atoms/mol})(2.33 \text{ g/cm}^3)}{(6.5 \times 10^{15} \text{ atoms/cm}^3)(30.97 \text{ g/mol})} - \frac{2.33 \text{ g/cm}^3}{1.82 \text{ g/cm}^3}}$$

$$= 1.43 \times 10^{-5} \text{ wt\%}$$

(b) To convert from weight percent to atom percent we use Equation 4.6a where

C_1' = atom percent of P

C_1 = weight percent of P = 1.43×10^{-5} wt%

C_2 = weight percent of Si = 100 wt% – 1.43×10^{-5} wt% = 99.9999857

A_1 = atomic weight of P = 30.97 g/mol

A_2 = atomic weight of Si = 28.09 g/mol

And from Equation 4.6a we obtain the following:

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

$$= \frac{(1.43 \times 10^{-5}\ \text{wt\%})(28.09\ \text{g/mol})}{(1.43 \times 10^{-5}\ \text{wt\%})(28.09\ \text{g/mol}) + (99.9999857\ \text{wt\%})(30.97\ \text{g/mol})} \times 100$$

$$= 1.30 \times 10^{-5}\ \text{at\%}$$

4.37 *Iron and vanadium both have the BCC crystal structure, and V forms a substitutional solid solution for concentrations up to approximately 20 wt% V at room temperature. Compute the unit cell edge length for a 90 wt% Fe–10 wt% V alloy.*

Solution

This problems 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 3.8 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 7.87g/cm^3 and 6.10 g/cm^3, respectively, (as taken from inside the front cover), the average density is just

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{V}}}{\rho_{\text{V}}} + \dfrac{C_{\text{Fe}}}{\rho_{\text{Fe}}}}$$

$$= \frac{100}{\dfrac{10 \text{ wt\%}}{6.10 \text{ g/cm}^3} + \dfrac{90 \text{ wt\%}}{7.87 \text{ g/cm}^3}}$$

$$= 7.65 \text{ g/cm}^3$$

And for the average atomic weight

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{V}}}{A_{\text{V}}} + \dfrac{C_{\text{Fe}}}{A_{\text{Fe}}}}$$

$$= \frac{100}{\dfrac{10 \text{ wt\%}}{50.94 \text{ g/mol}} + \dfrac{90 \text{ wt\%}}{55.85 \text{ g/mol}}}$$

$$= 55.32 \text{ g/mol}$$

Now, V_C is determined from Equation 3.8 as (taking the number of atoms per unit cell, n = 2, since the crystal structure of the alloy is BCC)

$$V_C = \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= \frac{(2 \text{ atoms/unit cell})(55.32 \text{ g/mol})}{(7.65 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}$$

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

And, finally, because the unit cell is of cubic symmetry

$$a = (V_C)^{1/3}$$

$$= (2.40 \times 10^{-23} \text{ cm}^3\text{/unit cell})^{1/3}$$

$$= 2.89 \times 10^{-8} \text{ cm} = 0.289 \text{ nm}$$

Dislocations—Linear Defects

4.38 *Cite the relative Burgers vector–dislocation line orientations for edge, screw, and mixed dislocations.*

Answer

The Burgers vector and dislocation line are perpendicular for edge dislocations, parallel for screw dislocations, and neither perpendicular nor parallel for mixed dislocations

Interfacial Defects

4.39 *For an FCC single crystal, would you expect the surface energy for a (100) plane to be greater or less than that for a (111) plane? Why? (Note: You may want to consult the solution to Problem 3.60 at the end of Chapter 3.)*

Answer

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 3.60, 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.

4.40 *For a BCC single crystal, would you expect the surface energy for a (100) plane to be greater or less than that for a (110) plane? Why? (Note: You may want to consult the solution to Problem 3.61 at the end of Chapter 3.)*

Answer

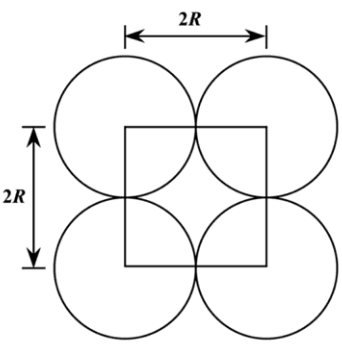
The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solution to Problem 3.61, 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.

4.41 *For a single crystal of some hypothetical metal that has the simple cubic crystal structure (Figure 3.3), would you expect the surface energy for a (100) plane to be greater, equal to, or less than a (110) plane. Why?*

Answer

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.

It becomes necessary to determine the packing densities of the (100) and (110) planes for the simple cubic crystal structure. Below is shown a (100) plane for simple cubic.



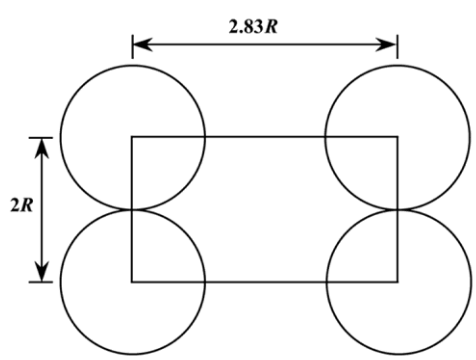
(100)

For this plane there is one atom at each of the four corners, which is shared with four adjacent unit cells. Thus there is the equivalence of one atom associated with this (100) plane. The planar section is a square, where in the side lengths are equal to the unit cell edge length, 2*R*. Thus the area of this square is $4R^2$, which yields a planar density of

$$PD_{100} = \frac{\text{number of atoms centered on the (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{1 \text{ atom}}{4R^2} = \frac{0.25}{R^2}$$

We now repeat this procedure for a (110) plane, which is shown below.



(110)

Because each of these atoms is shared with four other unit cells, there is the equivalence of 1 atom associated with the plane. This planar section is a rectangle with dimensions of $2R \times 2R\sqrt{2}$ (Note: $2\sqrt{2} = 2.83$). Thus the area of this rectangle is $4R^2\sqrt{2} = 5.66R^2$. The planar density for the (110) plane is, therefore,

$$\mathrm{PD}_{110} = \frac{1 \text{ atom}}{5.66R^2} = \frac{0.18}{R^2}$$

Thus, because the planar density for (100) is greater, it will have the lower surface energy.

4.42 *(a) For a given material, would you expect the surface energy to be greater than, the same as, or less than the grain boundary energy? Why?*

(b) The grain boundary energy of a small-angle grain boundary is less than for a high-angle one. Why is this so?

Answer

(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.

4.43 *(a) Briefly describe a twin and a twin boundary.*

(b) Cite the difference between mechanical and annealing twins.

Answer

(a) A twin boundary is an interface such that atoms on one side are located at mirror image positions of those atoms situated on the other boundary side. The region on one side of this boundary is called a twin.

(b) Mechanical twins are produced as a result of mechanical deformation and generally occur in BCC and HCP metals. Annealing twins form during annealing heat treatments, most often in FCC metals.

4.44 *For each of the following stacking sequences found in FCC metals, cite the type of planar defect that exists:*

(a) . . . A B C A B C B A C B A . . .

(b) . . . A B C A B C B C A B C . . .

Copy the stacking sequences, and indicate the position(s) of planar defect(s) with a vertical dashed line.

<u>Answer</u>

(a) The interfacial defect that exists for this stacking sequence is a twin boundary, which occurs at the indicated position.

A B C A B C B A C B A

The stacking sequence on one side of this position is mirrored on the other side.

(b) The interfacial defect that exists within this FCC stacking sequence is a stacking fault, which occurs between the two lines.

A B C A B C B C A B C

Within this region, the stacking sequence is HCP.

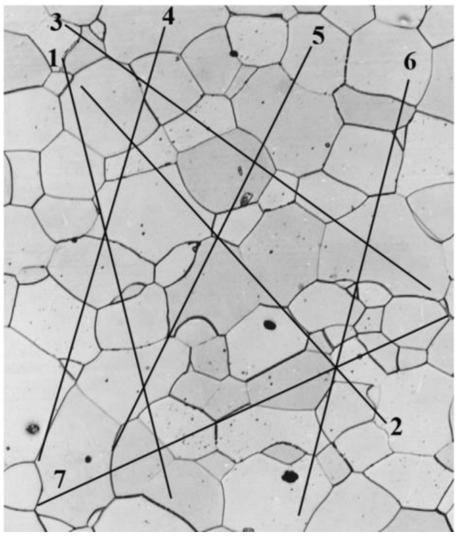
Grain Size Determination

4.45 *(a) Using the intercept method determine the mean intercept length, in millimeters, of the specimen whose microstructure is shown in Figure 4.15b; 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 4.15*b*, on which seven straight line segments, each of which is 60 mm long has been constructed; these lines are labeled "1" through "7".



Since the length of each line is 60 mm and there are 7 lines, the total line length (L_T in Equation 4.16) is 420 mm. Tabulated below is the number of grain-boundary intersections for each line:

Line Number	No. Grains Intersected
1	11
2	10
3	9
4	8.5
5	7
6	10
7	8
Total	63.5

Because L_T = 420 mm, P = 63.5 grain-boundary intersections, and the magnification M = 100×, the mean intercept length $\bar{\ell}$ is computed using Equation 4.16 as follows:

$$\bar{\ell} = \frac{L_T}{PM} = \frac{420 \text{ mm}}{(63.5 \text{ intersections})(100\times)}$$

$$= 0.066 \text{ mm}$$

(b) The ASTM grain size number G is computed by substitution of this value for $\bar{\ell}$ into Equation 4.19a as follows:

$$G = -6.6457 \log \bar{\ell} - 3.298$$

$$= (-6.6457)[\log(0.066 \text{ mm})] - 3.298$$

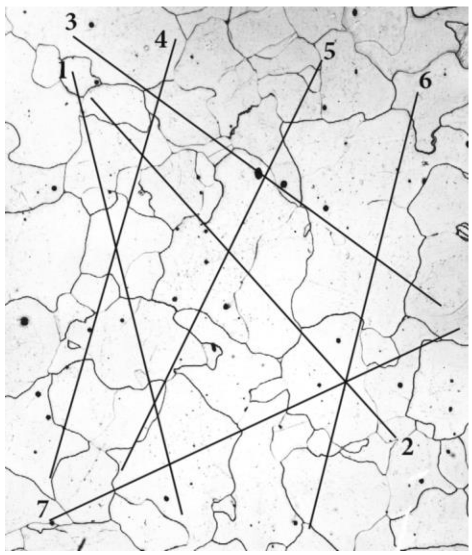
$$= 4.55$$

4.46 *(a) Employing the intercept technique, determine the mean intercept length for the steel specimen whose microstructure is shown in Figure 9.25a; 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 9.25*a*, on which seven straight line segments, each of which is 60 mm long has been constructed; these lines are labeled "1" through "7".



Since the length of each line is 60 mm and there are 7 lines, the total line length (L_T in Equation 4.16) is 420 mm. Tabulated below is the number of grain-boundary intersections for each line:

Line Number	No. Grains Intersected
1	7
2	7
3	7
4	8
5	10
6	6
7	8
Total	53

Because L_T = 420 mm, P = 56 grain-boundary intersections, and the magnification M = 90×, the mean intercept length $\overline{\ell}$ is computed using Equation 4.16 as follows:

$$\overline{\ell} = \frac{L_T}{PM} = \frac{420 \text{ mm}}{(53 \text{ intersections})(90\times)}$$

$$= 0.088 \text{ mm}$$

(b) The ASTM grain size number G is computed by substitution of this value for $\overline{\ell}$ into Equation 4.19a as follows:

$$G = -6.6457 \log \overline{\ell} - 3.298$$

$$= (-6.6457)[\log(0.088 \text{ mm})] - 3.298$$

$$= 3.72$$

4.47 *For an ASTM grain size of 6, approximately how many grains would there be per square inch under each of the following conditions?*

(a) At a magnification of 100×

(b) Without any magnification?

Solution

(a) This part of problem asks that we compute the number of grains per square inch for an ASTM grain size of 6 at a magnification of 100×. All we need do is solve for the parameter n in Equation 4.17, inasmuch as G = 6. Thus

$$n = 2^{G-1}$$

$$= 2^{6-1} = 32 \text{ grains/in.}^2$$

(b) Now it is necessary to compute the value of n for no magnification. In order to solve this problem it is necessary to use Equation 4.18:

$$n_M \left(\frac{M}{100}\right)^2 = 2^{G-1}$$

where n_M = the number of grains per square inch at magnification M, and G is the ASTM grain size number. Without any magnification, M in the above equation is 1, and therefore,

$$n_1 \left(\frac{1}{100}\right)^2 = 2^{6-1} = 32$$

And, solving for n_1, n_1 = 320,000 grains/in.^{2}.

4.48 *Determine the ASTM grain size number if 30 grains per square inch are measured at a magnification of 250×.*

Solution

In order to solve this problem we make use of Equation 4.18:

$$n_M \left(\frac{M}{100}\right)^2 = 2^{G-1}$$

where n_M = the number of grains per square inch at magnification M, and G is the ASTM grain size number. Solving the above equation for G, and realizing that n_M = 30, while M = 250. Some algebraic manipulation of Equation 4.18 is necessary. Taking logarithms of both sides of this equation leads to

$$\log\left[n_M \left(\frac{M}{100}\right)^2\right] = \log\left(2^{G-1}\right)$$

Or

$$\log n_M + 2\log\left(\frac{M}{100}\right) = (G - 1)\log 2$$

And solving this equation for G

$$\frac{\log n_M + 2\log\left(\frac{M}{100}\right)}{\log 2} = G - 1$$

or

$$G = \frac{\log n_M + 2\log\left(\frac{M}{100}\right)}{\log 2} + 1$$

From the problem statement:

$n_M = 30$

$M = 250$

And, therefore

$$G = \frac{\log 30 + 2\log\left(\frac{250}{100}\right)}{\log 2} + 1 = 8.6$$

4.49 *Determine the ASTM grain size number if 25 grains per square inch are measured at a magnification of 75×.*

Solution

In order to solve this problem we make use of Equation 4.18—viz.

$$n_M \left(\frac{M}{100}\right)^2 = 2^{G-1}$$

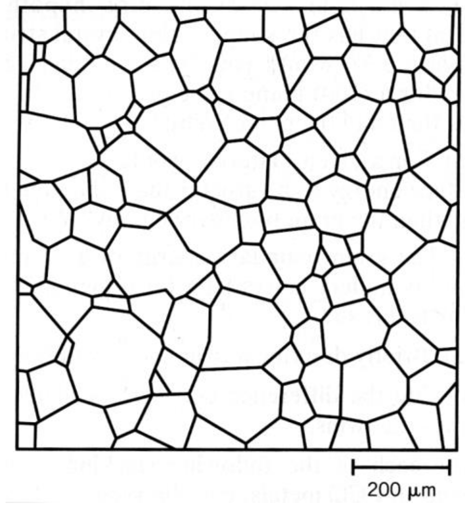
where n_M = the number of grains per square inch at magnification M, and G is the ASTM grain size number. By algebraic manipulation of Equation 4.18 (as outlined in Problem 4.48) we make G the dependent variable, which leads to the following expression:

$$G = \frac{\log n_M + 2 \log \left(\frac{M}{100}\right)}{\log 2} + 1$$

For n_M = 25 and M = 75, the value of G is

$$G = \frac{\log 25 + 2 \log \left(\frac{75}{100}\right)}{\log 2} + 1 = 4.8$$

4.50 *The following is a schematic micrograph that represents the microstructure of some hypothetical metal.*



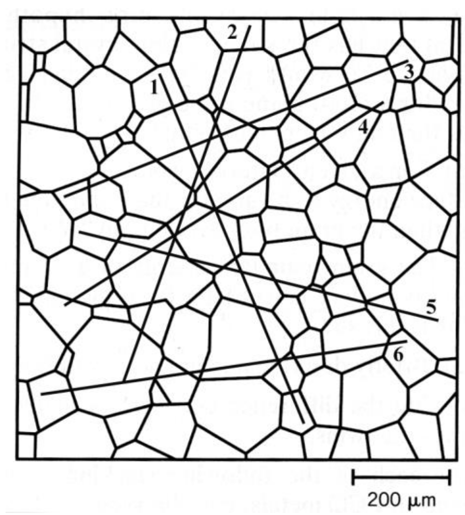
Determine the following:

(a) Mean intercept length

(b) ASTM grain size number, G

Solution

(a) Below is shown this photomicrograph on which six straight line segments, each of which is 50 mm long has been constructed; these lines are labeled "1" through "6".



Since the length of each line is 50 mm and there are 6 lines, the total line length (L_T in Equation 4.16) is 300 mm. Tabulated below is the number of grain-boundary intersections for each line:

Line Number	No. Grains Intersected
1	7
2	8
3	8
4	8
5	8
6	8
Total	47

Because L_T = 300 mm, P = 47 grain-boundary intersections, and the magnification M = 200×, the mean intercept length $\bar{\ell}$ is computed using Equation 4.16 as follows:

$$\bar{\ell} = \frac{L_T}{PM} = \frac{300 \text{ mm}}{(47 \text{ intersections})(200\times)}$$

$$= 0.032 \text{ mm}$$

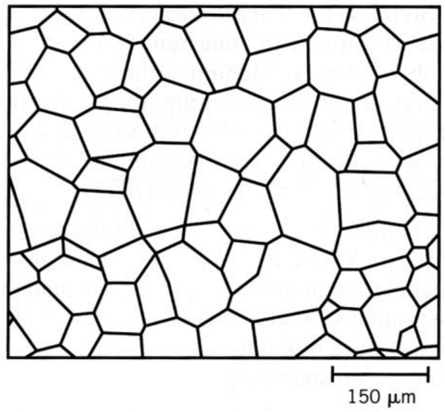
(b) The ASTM grain size number G is computed by substitution of this value for $\bar{\ell}$ into Equation 4.19a as follows:

$$G = -6.6457 \log \bar{\ell} - 3.298$$

$$= (-6.6457)[\log(0.032 \text{ mm})] - 3.298$$

$$= 6.64$$

4.51 *The following is a schematic micrograph that represents the microstructure of some hypothetical metal.*



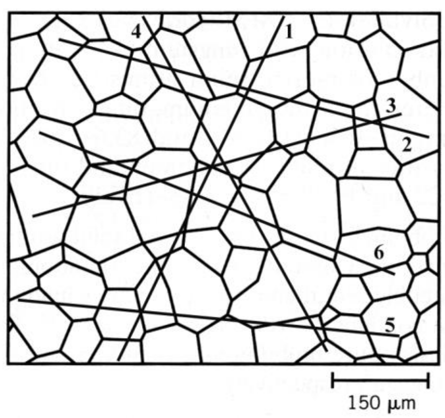
Determine the following:

(a) Mean intercept length

(b) ASTM grain size number, G

Solution

(a) Below is shown this photomicrograph on which six straight line segments, each of which is 50 mm long has been constructed; these lines are labeled "1" through "6".



Since the length of each line is 50 mm and there are 6 lines, the total line length (L_T in Equation 4.16) is 300 mm. Tabulated below is the number of grain-boundary intersections for each line:

Line Number	No. Grains Intersected
1	8
2	9
3	10
4	8
5	9
6	8
Total	52

Because L_T = 300 mm, P = 52 grain-boundary intersections, and the magnification M = 150×, the mean intercept length $\overline{\ell}$ is computed using Equation 4.16 as follows:

$$\overline{\ell} = \frac{L_T}{PM} = \frac{300 \text{ mm}}{(52 \text{ intersections})(150\times)}$$

$$= 0.038 \text{ mm}$$

(b) The ASTM grain size number G is computed by substitution of this value for $\overline{\ell}$ into Equation 4.19a as follows:

$$G = -6.6457 \log \overline{\ell} - 3.298$$

$$= (-6.6457)[\log(0.038 \text{ mm})] - 3.298$$

DESIGN PROBLEMS

Specification of Composition

4.D1 *Aluminum–lithium (Al-Li) alloys have been developed by the aircraft industry to reduce the weight and improve the performance of its aircraft. A commercial aircraft skin material having a density of 2.47 g/cm^3 is desired. Compute the concentration of Li (in wt%) that is required.*

Solution

Solution of this problem requires the use of Equation 4.10a, which takes the form

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

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 g/cm^3. Upon algebraic manipulation of the above equation and solving for C_{Li} leads to

$$C_{\text{Li}} = \frac{100\,\rho_{\text{Li}}(\rho_{\text{Al}} - \rho_{\text{ave}})}{\rho_{\text{ave}}(\rho_{\text{Al}} - \rho_{\text{Li}})}$$

Incorporation of values for ρ_{ave}, ρ_{Al}, and ρ_{Li} yields the following value for C_{Li}:

$$C_{\text{Li}} = \frac{(100)(0.534\text{ g/cm}^3)(2.71\text{ g/cm}^3 - 2.47\text{ g/cm}^3)}{(2.47\text{ g/cm}^3)(2.71\text{ g/cm}^3 - 0.534\text{ g/cm}^3)}$$

$$= 2.38\text{ wt\%}$$

4.D2 *Copper (Cu) and platinum (Pt) both have the FCC crystal structure, and Cu forms a substitutional solid solution for concentrations up to approximately 6 wt% Cu at room temperature. Determine the concentration in weight percent of Cu that must be added to Pt to yield a unit cell edge length of 0.390 nm.*

<u>Solution</u>

To begin, it is necessary to employ Equation 3.8, and solve for the unit cell volume, V_C, as

$$V_C = \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

where A_{ave} and ρ_{ave} are the atomic weight and density, respectively, of the Pt-Cu alloy. Inasmuch as both of these materials have the FCC crystal structure, which has cubic symmetry, V_C is just the cube of the unit cell length, a. That is

$$V_C = a^3 = (0.390 \text{ nm})^3$$

$$= (3.90 \times 10^{-8} \text{ cm})^3 = 5.932 \times 10^{-23} \text{ cm}^3$$

It is now necessary to construct expressions for A_{ave} and ρ_{ave} in terms of the concentration of copper, C_{Cu}, using Equations 4.11a and 4.10a. For A_{ave} we have

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{Cu}}}{A_{\text{Cu}}} + \dfrac{(100 - C_{\text{Cu}})}{A_{\text{Pt}}}}$$

$$= \frac{100}{\dfrac{C_{\text{Cu}}}{63.55 \text{ g/mol}} + \dfrac{(100 - C_{\text{Cu}})}{195.08 \text{ g/mol}}}$$

since the atomic weights for Cu and Pt are, respectively, 63.55 and 195.08 g/mol (as noted inside the front cover). Now, the expression for ρ_{ave} is as follows:

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{Cu}}}{\rho_{\text{Cu}}} + \dfrac{(100 - C_{\text{Cu}})}{\rho_{\text{Pt}}}}$$

$$= \frac{100}{\dfrac{C_{\text{Cu}}}{8.94\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{Cu}})}{21.45\ \text{g/cm}^3}}$$

given the densities of 8.94 and 21.45 g/cm^3 for the respective metals. Within the FCC unit cell there are 4 equivalent atoms, and thus, the value of n in Equation 3.8 is 4; hence, the expression for V_C may be written in terms of the concentration of Cu in weight percent as follows:

$$V_C = 5.932 \times 10^{-23}\ \text{cm}^3$$

$$= \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= \frac{(4\ \text{atoms/unit cell})\left[\dfrac{100}{\dfrac{C_{\text{Cu}}}{63.55\ \text{g/mol}} + \dfrac{(100 - C_{\text{Cu}})}{195.08\ \text{g/mol}}}\right]}{\left[\dfrac{100}{\dfrac{C_{\text{Cu}}}{8.94\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{Cu}})}{21.45\ \text{g/cm}^3}}\right](6.022 \times 10^{23}\ \text{atoms/mol})}$$

And solving this expression for C_{Cu} leads to C_{Cu} = 2.825 wt%.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

4.1FE *Calculate the number of vacancies per cubic meter at 1000°C for a metal that has an energy for vacancy formation of 1.22 eV/atom, a density of 6.25 g/cm³, and an atomic weight of 37.4 g/mol.*

(A) $1.49 \times 10^{18}\ m^{-3}$

(B) $7.18 \times 10^{22}\ m^{-3}$

(C) $1.49 \times 10^{24}\ m^{-3}$

(D) $2.57 \times 10^{24}\ m^{-3}$

<u>Solution</u>

Determination of the number of vacancies per cubic meter at 1000°C (1273 K) requires the utilization of Equations 4.1 and 4.2 as follows:

$$N_v = N\ \exp\left(-\frac{Q_v}{kT}\right) = \frac{N_A \rho}{A} \exp\left(-\frac{Q_v}{kT}\right)$$

Incorporation into this expression values for Q_v, ρ, and A provided in the problem statement yields the following for N_v:

$$N_v = \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(6.25\ \text{g/cm}^3)}{37.4\ \text{g/mol}} \exp\left[-\frac{1.22\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1273\ \text{K})}\right]$$

$$= 1.49 \times 10^{18}\ \text{cm}^{-3} = 1.49 \times 10^{24}\ \text{m}^{-3}$$

which is answer C.

4.2FE *What is the composition, in atom percent, of an alloy that consists of 4.5 wt% Pb and 95.5 wt% Sn? The atomic weights for Pb and Sn are 207.19 g/mol and 118.71 g/mol, respectively.*

(A) 2.6 at% Pb and 97.4 at% Sn

(B) 7.6 at% Pb and 92.4 at% Sn

(C) 97.4 at% Pb and 2.6 at% Sn

(D) 92.4 at% Pb and 7.6 at% Sn

Solution

We are asked to compute the composition of an alloy in atom percent. Employment of Equation 4.6a leads to

$$C'_{Pb} = \frac{C_{Pb}A_{Sn}}{C_{Pb}A_{Sn} + C_{Sn}A_{Pb}} \times 100$$

$$= \frac{(4.5)(118.71\text{ g/mol})}{(4.5)(118.71\text{ g/mol}) + (95.5)(207.19\text{ g/mol})} \times 100$$

$$= 2.6\text{ at\%}$$

$$C'_{Sn} = \frac{C_{Sn}A_{Pb}}{C_{Sn}A_{Pb} + C_{Pb}A_{Sn}} \times 100$$

$$= \frac{(95.5)(207.19\text{ g/mol})}{(95.5)(207.19\text{ g/mol}) + (4.5)(118.71\text{ g/mol})} \times 100$$

$$= 97.4\text{ at\%}$$

which is answer A (2.6 at% Pb and 97.4 at% Sn).

4.3FE *What is the composition, in weight percent, of an alloy that consists of 94.1 at% Ag and 5.9 at% Cu? The atomic weights for Ag and Cu are 107.87 g/mol and 63.55 g/mol, respectively.*

(A) 9.6 wt% Ag and 90.4 wt% Cu

(B) 3.6 wt% Ag and 96.4 wt% Cu

(C) 90.4 wt% Ag and 9.6 wt% Cu

(D) 96.4 wt% Ag and 3.6 wt% Cu

Solution

To compute composition, in weight percent, of a 94.1 at% Ag-5.9 at% Cu alloy, we employ Equation 4.7 as follows:

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

$$= \frac{(94.1)(107.87 \text{ g/mol})}{(94.1)(107.87 \text{ g/mol}) + (5.9)(63.55 \text{ g/mol})} \times 100$$

$$= 96.4 \text{ wt\%}$$

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

$$= \frac{(5.9)(63.55 \text{ g/mol})}{(94.1)(107.87 \text{ g/mol}) + (5.9)(63.55 \text{ g/mol})} \times 100$$

$$= 3.6 \text{ wt\%}$$

which is answer D (96.4 wt% Ag and 3.6 wt% Cu).

CHAPTER 5

DIFFUSION

PROBLEM SOLUTIONS

Introduction

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

Answer

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.*

Answer

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

Answer

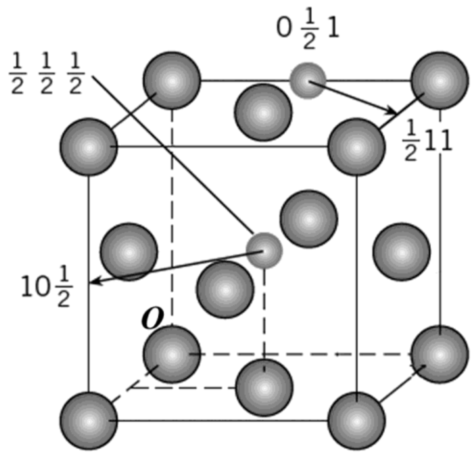
(a) With vacancy diffusion, atomic motion is from one lattice site to an adjacent vacancy. Self-diffusion and the diffusion of substitutional impurities proceed via this mechanism. On the other hand, atomic motion is from interstitial site to adjacent interstitial site for the interstitial diffusion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

5.4 *Carbon diffuses in iron via an interstitial mechanism—for FCC iron from one octahedral site to an adjacent one. In Section 4.3 (Figure 4.3a), we note that two general sets of point coordinates for this site are* $0\frac{1}{2}1$ *and* $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. *Specify the family of crystallographic directions in which this diffusion of carbon in FCC iron takes place.*

Solution

Below is shown a schematic FCC unit cell, and in addition representations of interstitial atoms located in both $0\frac{1}{2}1$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ octahedral sites. In addition, arrows have been drawn from each of these atoms to a nearest octahedral site: from $0\frac{1}{2}1$ to $\frac{1}{2}11$, and from $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ to $10\frac{1}{2}$. (*Note*: These point coordinates are referenced to the coordinate system having its origin located at the center of the bottom, rear atom, the one labeled with an *O*.)



Using the procedure detailed in Section 3.9 for determining the crystallographic direction of a vector (i.e., subtraction of vector tail coordinates from head coordinates) coordinates for the $0\frac{1}{2}1$ to $\frac{1}{2}11$ vector are as follows:

x coordinate: $\frac{1}{2} - 0 = \frac{1}{2}$

y coordinate: $1 - \frac{1}{2} = \frac{1}{2}$

z coordinate: $1 - 1 = 0$

In order to reduce these coordinates to integers it is necessary to multiply each by the factor "2". Therefore, this vector points in a [110] direction.

Applying this same procedure to the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ to $10\frac{1}{2}$ vector we obtain the following:

x coordinate: $1 - \frac{1}{2} = \frac{1}{2}$

y coordinate: $0 - \frac{1}{2} = -\frac{1}{2}$

z coordinate: $\frac{1}{2} - \frac{1}{2} = 0$

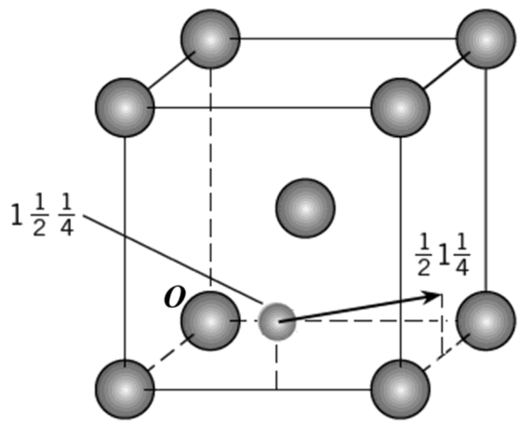
Again, multiplying these indices by 2 leads to the $[1\bar{1}0]$ direction.

Therefore, the family of crystallographic directions for the diffusion of interstitial atoms in FCC metals is $\langle 110 \rangle$.

5.5 *Carbon diffuses in iron via an interstitial mechanism—for BCC iron from one tetrahedral site to an adjacent one. In Section 4.3 (Figure 4.3b) we note that a general set of point coordinates for this site are* $1\frac{1}{2}\frac{1}{4}$. *Specify the family of crystallographic directions in which this diffusion of carbon in BCC iron takes place.*

Solution

Below is shown a schematic BCC unit cell, and in addition the representation of an interstitial atom located in a $1\frac{1}{2}\frac{1}{4}$ tetrahedral site. In addition, an arrow has been drawn from this atom to a nearest tetrahedral site: from $1\frac{1}{2}\frac{1}{4}$ to $\frac{1}{2}1\frac{1}{4}$. (*Note*: These point coordinates are referenced to the coordinate system having its origin located at the center of the bottom, rear atom, the one labeled with an *O*.)



Using the procedure detailed in Section 3.9 for determining the crystallographic direction of a vector (i.e., subtraction of vector tail coordinates from head coordinates) coordinates for this $1\frac{1}{2}\frac{1}{4}$ to $\frac{1}{2}1\frac{1}{4}$ vector are as follows:

x coordinate: $\frac{1}{2} - 1 = -\frac{1}{2}$

y coordinate: $1 - \frac{1}{2} = \frac{1}{2}$

z coordinate: $\frac{1}{4} - \frac{1}{4} = 0$

In order to reduce these coordinates to integers it is necessary to multiply each by the factor "2". Therefore, this vector points in a $[\bar{1}10]$ direction.

Thus, the family of crystallographic directions for the diffusion of interstitial atoms in BCC metals is $\langle 110 \rangle$.

Fick's First Law

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

Answer

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.

5.7 *(a) Briefly explain the concept of a driving force.*

(b) What is the driving force for steady-state diffusion?

Answer

(a) The driving force is that which compels a reaction to occur.

(b) The driving force for steady-state diffusion is the concentration gradient.

5.8 *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 6-mm thick sheet of palladium having an area of 0.25* m^2 *at 600°C. Assume a diffusion coefficient of* 1.7×10^{-8} m^2/s*, that the respective concentrations at the high- and low-pressure sides of the plate are 2.0 and 0.4 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 5.1 and 5.2. Combining these expressions and solving for the mass yields

$$M = JAt = -DAt\frac{\Delta C}{\Delta x}$$

$$= -(1.7 \times 10^{-8}\ \text{m}^2/\text{s})(0.25\ \text{m}^2)(3600\ \text{s/h})\left[\frac{0.4 - 2.0\ \text{kg/m}^3}{6 \times 10^{-3}\ \text{m}}\right]$$

$$= 4.1 \times 10^{-3}\ \text{kg/h}$$

5.9 *A sheet of steel 2.5-mm thick has nitrogen atmospheres on both sides at 900°C and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is 1.85 × 10^{-10} m^2/s, and the diffusion flux is found to be 1.0 × 10^{-7} $kg/m^2 \cdot s$. Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is 2 kg/m^3. How far into the sheet from this high-pressure side will the concentration be 0.5 kg/m^3? Assume a linear concentration profile.*

Solution

This problem is solved by using Equation 5.2 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 the above equation 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

$$x_B = 0 + (1.85 \times 10^{-10} \text{ m}^2/\text{s})\left[\frac{2 \text{ kg/m}^3 - 0.5 \text{ kg/m}^3}{1.0 \times 10^{-7} \text{ kg/m}^2\text{-s}}\right]$$

$$= 2.78 \times 10^{-3} \text{ m} = 2.78 \text{ mm}$$

5.10 *A sheet of BCC iron 2-mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at 675°C. After reaching steady state, the iron was quickly cooled to room temperature. The carbon concentrations at the two surfaces of the sheet were determined to be 0.015 and 0.0068 wt%, respectively. Compute the diffusion coefficient if the diffusion flux is 7.36 × 10^{-9} kg/m^2·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; the densities of carbon and iron are 2.25 g/cm^3 and 7.87 g/cm^3. For 0.015 wt% C

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

$$= \frac{0.015}{\dfrac{0.015}{2.25\ \text{g/cm}^3} + \dfrac{99.985}{7.87\ \text{g/cm}^3}} \times 10^3$$

$$1.18\ \text{kg C/m}^3$$

Similarly, for 0.0068 wt% C

$$C''_{C} = \frac{0.0068}{\dfrac{0.0068}{2.25\ \text{g/cm}^3} + \dfrac{99.9932}{7.87\ \text{g/cm}^3}} \times 10^3$$

$$= 0.535\ \text{kg C/m}^3$$

Now, using a rearranged form of Equation 5.2

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

and incorporating values of plate thickness and diffusion flux, provided in the problem statement, as well as the two concentrations of carbon determined above, the diffusion coefficient is computed as follows:

$$D = -\left(7.36 \times 10^{-9}\ \text{kg/m}^2\text{-s}\right)\left[\frac{2 \times 10^{-3}\ \text{m}}{0.535\ \text{kg/m}^3 - 1.18\ \text{kg/m}^3}\right]$$

$$= 2.3 \times 10^{-11}\ \text{m}^2/\text{s}$$

5.11 *When α-iron is subjected to an atmosphere of nitrogen gas, the concentration of nitrogen in the iron, C_N (in weight percent), is a function of hydrogen pressure, p_{N_2}(in MPa), and absolute temperature (T) according to*

$$C_N = 4.90 \times 10^{-3}\sqrt{p_{N_2}}\exp\left(-\frac{37,600\text{ J/mol}}{RT}\right) \qquad (5.14)$$

Furthermore, the values of D_0 and Q_d for this diffusion system are 5.0×10^{-7} m²/s and 77,000 J/mol, respectively. Consider a thin iron membrane 1.5-mm thick that is at 300°C. Compute the diffusion flux through this membrane if the nitrogen pressure on one side of the membrane is 0.10 MPa (0.99 atm) and that on the other side is 5.0 MPa (49.3 atm).

Solution

This problems asks for us to compute the diffusion flux of nitrogen gas through a 1.5-mm thick plate of iron at 300°C when the pressures on the two sides are 0.10 and 5.0 MPa. Ultimately we will employ Equation 5.2 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

$$C_{N(B)} = (4.90 \times 10^{-3})\sqrt{0.10\text{ MPa}}\exp\left[-\frac{37,600\text{ J/mol}}{(8.31\text{ J/mol-K})(300+273\text{ K})}\right]$$

$$5.77 \times 10^{-7}\text{ wt\%}$$

Whereas, for the high pressure (or A) side

$$C_{N(A)} = (4.90 \times 10^{-3})\sqrt{5.0\text{ MPa}}\exp\left[-\frac{37,600\text{ J/mol}}{(8.31\text{ J/mol-K})(300+273\text{ K})}\right]$$

$$4.08 \times 10^{-6}\text{ wt\%}$$

We now convert concentrations in weight percent to mass of nitrogen per unit volume of solid. At face B there are 5.77×10^{-7} g (or 5.77×10^{-10} kg) of hydrogen in 100 g of Fe, which is virtually pure iron. From the density of iron (7.87 g/cm³), 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 N per cubic meter of alloy [$C''_{N(B)}$] is just

$$C'_{\mathrm{N(B)}} = \frac{C_{\mathrm{N(B)}}}{V_{\mathrm{B}}}$$

$$= \frac{5.77 \times 10^{-10}\ \mathrm{kg}}{1.27 \times 10^{-5}\ \mathrm{m}^3} = 4.54 \times 10^{-5}\ \mathrm{kg/m}^3$$

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

$$C'_{\mathrm{N(A)}} = \frac{C_{\mathrm{N(A)}}}{V_{\mathrm{A}}}$$

$$= \frac{4.08 \times 10^{-9}\ \mathrm{kg}}{1.27 \times 10^{-5}\ \mathrm{m}^3} = 3.21 \times 10^{-4}\ \mathrm{kg/m}^3$$

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

$$\frac{\Delta C}{\Delta x} = \frac{C''_{\mathrm{N(B)}} - C''_{\mathrm{N(A)}}}{x_{\mathrm{B}} - x_{\mathrm{A}}}$$

$$= \frac{4.54 \times 10^{-5}\ \mathrm{kg/m}^3 - 3.21 \times 10^{-4}\ \mathrm{kg/m}^3}{1.5 \times 10^{-3}\ \mathrm{m}} = -0.184\ \mathrm{kg/m}^4$$

At this time it becomes necessary to calculate the value of the diffusion coefficient at 300°C using Equation 5.8. Thus,

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

$$= (5.0 \times 10^{-7}\ \mathrm{m}^2/\mathrm{s}) \exp\left[-\frac{77{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(300 + 273\ \mathrm{K})}\right]$$

$$= 4.74 \times 10^{-14}\ \mathrm{m}^2/\mathrm{s}$$

And, finally, the diffusion flux is computed using Equation 5.2 by taking the negative product of this diffusion coefficient and the concentration gradient, as

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

$$= -\left(4.74 \times 10^{-14}\ \text{m}^2/\text{s}\right)\left(-0.184\ \text{kg/m}^4\right) = 8.72 \times 10^{-15}\ \text{kg/m}^2\text{-s}$$

Fick's Second Law—Nonsteady-State Diffusion

5.12 *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. Hint: from Equation 5.4b, demonstrate that

$$\frac{\partial\left[\frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)\right]}{\partial t}$$

is equal to

$$D\left\{\frac{\partial^2\left[\frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)\right]}{\partial x^2}\right\}$$

Solution

When these differentiations are carried out, both are equal to the following expression:

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

5.13 *Determine the carburizing time necessary to achieve a carbon concentration of 0.30 wt% at a position 4 mm into an iron–carbon alloy that initially contains 0.10 wt% C. The surface concentration is to be maintained at 0.90 wt% C, and the treatment is to be conducted at 1100°C. Use the diffusion data for γ-Fe in Table 5.2.*

Solution

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 mm = 4×10^{-3} 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	erf(z)
0.80	0.7421
z	0.7500
0.85	0.7707

which leads to the following:

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

From which

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

Now, from Table 5.2, data for the diffusion of carbon into γ-iron are as follows:

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

Q_d = 148,000 J/mol

Therefore at 1100°C (1373 K)

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

$$= 5.35 \times 10^{-11} \text{ m}^2/\text{s}$$

Thus,

$$0.814 = \frac{4 \times 10^{-3} \text{ m}}{(2)\sqrt{\left(5.35 \times 10^{-11} \text{ m}^2/\text{s}\right)(t)}}$$

Solving for *t* yields

$$t = \frac{(4 \times 10^{-3} \text{ m})^2}{(2)^2(0.814)^2(5.35 \times 10^{-11} \text{ m}^2/\text{s})}$$

$$t = 1.13 \times 10^5 \text{ s} = 31.3 \text{ h}$$

5.14 *An FCC iron–carbon alloy initially containing 0.55 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1325 K (1052°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 0.25 wt% after a 10-h treatment? The value of D at 1325 K is* 3.3×10^{-11} *m²/s.*

Solution

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

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

Thus,

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

Using data in Table 5.1 and linear interpolation

z	erf (z)
0.40	0.4284
z	0.4545
0.45	0.4755

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

which leads to,

$$z = 0.4277$$

This means that

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

And, finally

$$x = 2(0.4277)\sqrt{Dt} = (0.8554)\sqrt{(3.3 \times 10^{-11}\ \mathrm{m^2/s})(3.6 \times 10^4\ \mathrm{s})}$$

$$= 9.32 \times 10^{-4} \text{ m} = 0.932 \text{ mm}$$

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. “3.3e-11”.

2. In the window just below the label “Initial, C0” enter the initial concentration—viz. “0.55”.

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

4. Then in the “Diffusion Time t” window enter the time in seconds; in 10 h there are (60 s/min)(60 min/h)(10 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 “0.25 wt%”. Then read the value under the “Distance:”. For this problem, this value (the solution to the problem) is 0.91 mm.

5.15 *Nitrogen from a gaseous phase is to be diffused into pure iron at 675°C. If the surface concentration is maintained at 0.2 wt% N, what will be the concentration 2 mm from the surface after 25 h? The diffusion coefficient for nitrogen in iron at 675°C is 2.8 × 10^{–11} m^2/s.*

Solution

This problem asks us to compute the nitrogen concentration (C_x) at the 2 mm position after a 25 h diffusion time, when diffusion is nonsteady-state. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{C_x - 0}{0.2 - 0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= 1 - \operatorname{erf}\left[\frac{2 \times 10^{-3}\text{ m}}{(2)\sqrt{(2.8 \times 10^{-11}\text{ m}^2/\text{s})(25\text{ h})(3600\text{ s/h})}}\right]$$

$$= 1 - \operatorname{erf}(0.630)$$

Using data in Table 5.1 and linear interpolation

z	erf (z)
0.600	0.6039
0.630	y
0.650	0.6420

$$\frac{0.630 - 0.600}{0.650 - 0.600} = \frac{y - 0.6039}{0.6420 - 0.6039}$$

from which

$$y = \operatorname{erf}(0.630) = 0.6268$$

Thus,

$$\frac{C_x - 0}{0.2 - 0} = 1.0 - 0.6268$$

And solving for C_x gives

$$C_x = 0.075\text{ wt\% N}$$

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. "2.8e-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. "0.2".

4. Then in the "Diffusion Time t" window enter the time in seconds; in 25 h there are (60 s/min)(60 min/h)(25 h) = 90,000 s—so enter the value "9e4".

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 "2.00 mm". Then read the value under the "Concentration:". For this problem, this value (the solution to the problem) is 0.07 wt%.

5.16 *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:*

$$C_x = C_2 + \left(\frac{C_1 - C_2}{2}\right)\left[1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad (5.15)$$

The schematic diffusion profile in Figure 5.13 shows these concentration parameters as well as concentration profiles at times t = 0 and t > 0. Please note that at t = 0, the x = 0 position is taken as the initial diffusion couple interface, whereas C_1 *is the impurity concentration for x < 0, and* C_2 *is the impurity content for x > 0.*

Consider a diffusion couple composed of pure nickel and a 55 wt% Ni-45 wt% Cu alloy (similar to the couple shown in Figure 5.1). Determine the time this diffusion couple must be heated at 1000°C (1273 K) in order to achieve a composition of 56.5 wt% Ni a distance of 15 μm into the Ni-Cu alloy referenced to the original interface. Values for the preexponential and activation energy for this diffusion system are 2.3×10^{-4} m^2/s *and 252,000 J/mol.*

Solution

This problem calls for us to determine the value of time t in Equation 5.15 given the following values:

C_1 = 100 wt% Ni

C_2 = 55 wt% Ni

C_x = 56.5 wt% Ni

T = 1273 K

$x = 15\ \mu\text{m} = 15 \times 10^{-6}$ m

$D_0 = 2.3 \times 10^{-4}\ \text{m}^2/\text{s}$

Q_d = 252,000 J/mol

Let us first of all compute the value of the diffusion coefficient D using Equation 5.8:

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

$$= (2.3 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{252{,}000\ \text{J/mol}}{(8.31\ \text{J/mol}\cdot\text{K})(1273\ \text{K})}\right]$$

$$= 1.04 \times 10^{-14} \text{ m}^2/\text{s}$$

Now incorporating values for all of the parameters except *t* into Equation 5.12 leads to

$$56.5 \text{ wt\% Ni} = 55 \text{ wt\% Ni} + \left(\frac{100 \text{ wt\% Ni} - 55 \text{ wt\% Cu}}{2}\right)\left[1 - \text{erf}\left(\frac{15 \times 10^{-6} \text{ m}}{2\sqrt{(1.04 \times 10^{-14} \text{ m}^2/\text{s})(t)}}\right)\right]$$

This expression reduces to the following:

$$0.9333 = \text{erf}\left(\frac{73.54 \text{ s}^{1/2}}{\sqrt{t}}\right)$$

From Table 5.1 to determine the value of *z* when erf(*z*) = 0.9333 an interpolation procedure is necessary as follows:

z	erf(*z*)
1.2	0.9103
z	0.9333
1.3	0.9340

$$\frac{z - 1.2}{1.3 - 1.2} = \frac{0.9333 - 0.9103}{0.9340 - 0.9103}$$

And solving for *z* we have

$$z = 1.297$$

Which means that

$$\frac{73.54 \text{ s}^{1/2}}{\sqrt{t}} = 1.297$$

Or that

$$t = \left(\frac{73.54}{1.297} \text{ s}^{1/2}\right)^2$$

$$= 3215 \text{ s} = 53.6 \text{ min} = 0.89 \text{ h}$$

5.17 *Consider a diffusion couple composed of two cobalt-iron alloys; one has a composition of 75 wt% Co-25 wt% Fe; the other alloy composition is 50 wt% Co-50 wt% Fe. If this couple is heated to a temperature of 800°C (1073 K) for 20,000 s, determine how far from the original interface into the 50 wt% Co-50 wt% Fe alloy the composition has increased to 52 wt%Co-48 wt% Fe. For the diffusion coefficient, assume values of 6.6 × 10^{-6} m^2/s and 247,000 J/mol, respectively, for the preexponential and activation energy.*

Solution

This problem calls for us to determine the value of the distance, *x*, in Equation 5.15 given the following values:

C_1 = 75 wt% Co

C_2 = 50 wt% Co

C_x = 52 wt% Co

T = 1073 K

t = 20,000 s

D_0 = 6.6 × 10^{-6} m^2/s

Q_d = 247,000 J/mol

Let us first of all compute the value of the diffusion coefficient *D* using Equation 5.8:

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

$$= (6.6 \times 10^{-6}\ \text{m}^2/\text{s}) \exp\left[-\frac{247{,}000\ \text{J/mol}}{(8.31\ \text{J/mol}\cdot\text{K})(1073\ \text{K})}\right]$$

$$= 6.15 \times 10^{-18}\ \text{m}^2/\text{s}$$

Now incorporating values for all of the parameters except *x* into Equation 5.15 leads to

$$52\ \text{wt\% Co} = 50\ \text{wt\% Co} + \left(\frac{75\ \text{wt\% Co} - 50\ \text{wt\% Co}}{2}\right)\left[1 - \text{erf}\left(\frac{x}{2\sqrt{(6.15 \times 10^{-18}\ \text{m}^2/\text{s})(20{,}000\ \text{s})}}\right)\right]$$

This expression reduces to the following:

$$0.8400 = \operatorname{erf}\left(\frac{x}{7.01 \times 10^{-7}\ \text{m}}\right)$$

From Table 5.1 to determine the value of *z* when erf(*z*) = 0.8400 an interpolation procedure is necessary as follows:

z	erf(*z*)
0.95	0.8209
z	0.8400
1.0	0.8427

$$\frac{z - 0.95}{1.0 - 0.95} = \frac{0.8400 - 0.8209}{0.8427 - 0.8209}$$

And solving for *z* we have

$$z = 0.994$$

Which means that

$$\frac{x}{7.01 \times 10^{-7}\ \text{m}} = 0.994$$

Or that

$$x = (7.01 \times 10^{-7}\ \text{m})(0.994)$$

$$= 6.97 \times 10^{-7}\ \text{m} = 0.697\ \mu\text{m}$$

5.18 *Consider a diffusion couple between silver and a gold alloy that contains 10 wt% silver. This couple is heat treated at an elevated temperature and it was found that after 850 s the concentration of silver had increased to 12 wt% at 10 μm from the interface into the Ag-Au alloy. Assuming preexponential and activation energy values of 7.2 × 10^{-6} m^2/s and 168,000 J/mol, compute the temperature of this heat treatment. (Note: you may find Figure 5.13 and Equation 5.15 helpful.)*

Solution

This problem calls for us to determine the value of time t in Equation 5.15 given the following values:

C_1 = 100 wt% Ag

C_2 = 10 wt Ag

C_x = 12 wt% Ag

t = 850 s

x = 10 μm = 10 × 10^{-6} m

D_0 = 7.2 × 10^{-6} m^2/s

Q_d = 168,000 J/mol

We first of all substitute values for all of the above parameters—except for D_0 and Q_d. This leads to the following expressions:

$$C_x = C_2 + \left(\frac{C_1 - C_2}{2}\right)\left[1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

$$12 \text{ wt\%} = 10 \text{ wt\%} + \left(\frac{100 \text{ wt\%} - 10 \text{ wt\%}}{2}\right)\left[1 - \text{erf}\left(\frac{10 \times 10^{-6} \text{ m}}{2\sqrt{D(850 \text{ s})}}\right)\right]$$

This equation reduces to the following:

$$0.9556 = \text{erf}\left(\frac{1.715 \times 10^{-7}}{\sqrt{D}}\right)$$

Or

$$0.9556 = \text{erf}\left(z\right)$$

It is now necessary to determine using the data in Table 5.1 the value of z for which the error function has a value of 0.9556. This requires an interpolation using the following data:

z	erf(z)
1.4	0.9523
z	0.9556
1.5	0.9661

The interpolation equation is

$$\frac{1.5 - z}{1.5 - 1.4} = \frac{0.9661 - 0.9556}{0.9661 - 0.9523}$$

Solving for z from this equation gives

$$z = 1.424$$

Incorporating this value into the above equation yields

$$1.424 = \frac{1.715 \times 10^{-7}}{\sqrt{D}}$$

from which D is equal to

$$D = 1.45 \times 10^{-14} \text{ m}^2/\text{s}$$

We may now compute the temperature at which the diffusion coefficient has this value using Equation 5.8. Taking natural logarithms of both sides of Equation 5.8 leads to

$$\ln D - \ln D_0 - \frac{Q_d}{RT}$$

And, solving for T

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

Into which we insert values of D, D_0, and Q_d as follows:

$$T = -\frac{168{,}000 \text{ J/m}}{(8.31 \text{ J/mol} \cdot \text{K})\left[\ln(1.45 \times 10^{-14} \text{ m}^2/\text{s}) - \ln(7.2 \times 10^{-6} \text{ m}^2/\text{s})\right]}$$

$$= 1010 \text{ K } (737°\text{C})$$

5.19 *For a steel alloy it has been determined that a carburizing heat treatment of 15 h duration will raise the carbon concentration to 0.35 wt% at a point 2.0 mm from the surface. Estimate the time necessary to achieve the same concentration at a 6.0-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 0.35 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, which means that

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

or

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

Thus, if we assign x_1 = 0.2 mm, x_2 = 0.6 mm, and t_1 15 h, then

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

from which

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

Factors That Influence Diffusion

5.20 *Cite the values of the diffusion coefficients for the interdiffusion of carbon in both α-iron (BCC) and γ-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 α and γ iron at 900°C. Using the data in Table 5.2,

$$D_\alpha = (1.1 \times 10^{-6}\ \text{m}^2/\text{s}) \exp\left[-\frac{87{,}400\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1173\ \text{K})}\right]$$

$$= 1.40 \times 10^{-10}\ \text{m}^2/\text{s}$$

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

$$= 5.86 \times 10^{-12}\ \text{m}^2/\text{s}$$

The D for diffusion of C in BCC α iron is larger, the reason being that the atomic packing factor is smaller than for FCC γ iron (0.68 versus 0.74—Section 3.4); this means that there is slightly more interstitial void space in the BCC Fe, and, therefore, the motion of the interstitial carbon atoms occurs more easily.

5.21 *Using the data in Table 5.2, compute the value of D for the diffusion of magnesium in aluminum at 400°C.*

Solution

This problem asks us to compute the magnitude of *D* for the diffusion of Mg in Al at 400°C (673 K). Incorporating the appropriate data from Table 5.2—i.e.,

$D_0 = 1.2 \times 10^{-4}\ \text{m}^2/\text{s}$

$Q_d = 130{,}000\ \text{J/mol}$

into Equation 5.8 leads to

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

$$= (1.2 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{130{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(673\ \text{K})}\right]$$

$$= 9.64 \times 10^{-15}\ \text{m}^2/\text{s}$$

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

1. In the left-hand window that appears, click on the "Mg-Al" 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 Mg in Al. 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 673 K (inasmuch as this is the Kelvin equivalent of 400ºC). Finally, the diffusion coefficient value at this temperature is given under the label "Diff Coeff (D):". For this problem, the value is $8.0 \times 10^{-15}\ \text{m}^2/\text{s}$.

5.22 *Using the data in Table 5.2 compute the value of D for the diffusion of nitrogen in FCC iron at 950°C.*

Solution

This problem asks us to compute the magnitude of *D* for the diffusion of N in FCC Fe at 950°C. Incorporating the appropriate data from Table 5.2—i.e.,

$D_0 = 9.1 \times 10^{-5}$ m^2/s

$Q_d = 168{,}000$ J/mol

into Equation 5.8 leads to

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

$$= \left(9.1 \times 10^{-5} \text{ m}^2/\text{s}\right) \exp\left[-\frac{168{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(950°\text{C} + 273)}\right]$$

$$= 6.0 \times 10^{-12} \text{ m}^2/\text{s}$$

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 "Custom 1 under the “Diffusing Species” heading (since none of the preset systems is for the diffusion of nitrogen in FCC iron).

2. Under "D_0" within the "Diffusion Coefficients" box enter "9.1e-5"; and under "Q_d" enter "168".

3. It is necessary to enter maximum and minimum temperatures within the "Temperature Range" box. Because our temperature of interest is 950°C, enter "900" in the "T Min" "C" box, and "1000" in the T Max "C" box.

3. Upon clicking on the "Add Curve" box, a log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for N in FCC iron. 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 1223 K (inasmuch as this is the Kelvin equivalent of 950ºC). Finally, the diffusion coefficient value at this temperature is given under the label “Diff Coeff (D):”. For this problem, the value is 6.0×10^{-12} m^2/s.

5.23 *At what temperature will the diffusion coefficient for the diffusion of zinc in copper have a value of 2.6×10^{-16} m²/s? Use the diffusion data in Table 5.2.*

Solution

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Zn in Cu has a value of 2.6×10^{-16} m^2/s. 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 Zn in Cu (i.e., $D_0 = 2.4 \times 10^{-5}$ m^2/s and Q_d = 189,000 J/mol) , we get

$$T = -\frac{189{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(2.6 \times 10^{-16} \text{ m}^2/\text{s}\right) - \ln\left(2.4 \times 10^{-5} \text{ m}^2/\text{s}\right)\right]}$$

$$= 901 \text{ K} = 628°\text{C}$$

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, there is a preset set of data for the diffusion of Zn in Cu system. Therefore, click on the "Cu-Ni" box.

2. In the column on the right-hand side of this window the activation energy-preexponential data for this problem. In the window under “D0” the preexponential value, “2.4e-5”, is displayed. Next just below the “Qd” the activation energy value (in KJ/mol), “189” is displayed. In the "Temperature Range" window minimum ("T Min") and maximum ("T Max") temperatures are displayed, in both °C and K. The default values for minimum and maximum temperatures are 800ºC and 1140ºC, respectively.

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 Zn in Cu. At the top of this curve is a diamond-shaped cursor. We want to click-and-drag this cursor down the line (to the right) to the point at which the entry under the “Diff Coeff (D):” label reads 2.6×10^{-16} m^2/s. As we drag the cursor to the right, the value of the diffusion coefficient continues to decrease, but only to about 1.5

$\times\ 10^{-14}\ m^2/s$. This means that the temperature at which the diffusion coefficient is $2.6 \times 10^{-16}\ m^2/s$ is lower than 800ºC. Therefore, let us change the T Min value to 600ºC. After this change is made click again on the "Add Curve", and a new curve appears. Now click and drag the cursor to the right until "$2.6 \times 10^{-16}\ m^2/s$ " is displayed under "Diff Coeff (D)". At this time under the "Temperature (T)" label is displayed the temperature—in this case "902 K".

5.24 *At what temperature will the diffusion coefficient for the diffusion of nickel in copper have a value of 4.0×10^{-17} m²/s? Use the diffusion data in Table 5.2.*

Solution

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Ni in Cu has a value of 4.0×10^{-17} m^2/s. 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 Ni in Cu (i.e., $D_0 = 1.9 \times 10^{-4}$ m^2/s and Q_d = 230,000 J/mol) , we get

$$T = -\frac{230{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(4.0 \times 10^{-17} \text{ m}^2/\text{s}\right) - \ln\left(1.9 \times 10^{-4} \text{ m}^2/\text{s}\right)\right]}$$

$$= 948 \text{ K} = 675°\text{C}$$

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, there is a preset set of data, but none for the diffusion of Ni in Cu. This requires us specify our settings by clicking on the “Custom1” box.

2. In the column on the right-hand side of this window enter the data for this problem, which are taken from Table 5.2. In the window under “D0” the preexponential value, enter “1.9e-4”. Next just below in the “Qd” window enter the activation energy value (in KJ/mol), in this case "230". It is now necessary to specify a temperature range over which the data is to be plotted—let us arbitrarily pick 500°C to be the miminum, which is entered in the "T Min" under "Temperature Range" window; we will also select 1000°C to be the maximum temperature, which is entered in the "T Max" window.

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 Ni in Cu. At the top of this curve is a diamond-shaped cursor. We next click-and-drag this cursor

down the line to the point at which the entry under the "Diff Coeff (D):" label reads 4.0×10^{-17} m^2/s. The temperature that appears under the "Temperature (T)" label is 949 K, which is the solution.

5.25 *The preexponential and activation energy for the diffusion of chromium in nickel are 1.1 × 10^{-4} m^2/s and 272,000 J/mol, respectively. At what temperature will the diffusion coefficient have a value of 1.2 × 10^{-14} m^2/s?*

Solution

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Cr in Ni has a value of 1.2 × 10^{-14} m^2/s. Solving for T from Equation 5.9a

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

and using the data the problem statement (i.e., D_0 = 1.1 × 10^{-4} m^2/s and Q_d = 272,000 J/mol) , we get

$$T = -\frac{272{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln(1.2 \times 10^{-14} \text{ m}^2/\text{s}) - \ln(1.1 \times 10^{-4} \text{ m}^2/\text{s})\right]}$$

$$= 1427 \text{ K} = 1154°\text{C}$$

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, there is a preset set of data, but none for the diffusion of Cr in Ni. This requires us specify our settings by clicking on the “Custom1” box.

2. In the column on the right-hand side of this window enter the data for this problem, which are given in the problem statement. In the window under “D0” enter “1.1e-4”. Next just below in the “Qd” window enter the activation energy value (in KJ/mol), in this case "272". It is now necessary to specify a temperature range over which the data is to be plotted—let us arbitrarily pick 1000°C to be the miminum, which is entered in the "T Min" under "Temperature Range" window; we will also select 1500°C to be the maximum temperature, which is entered in the "T Max" window.

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 Cr in Ni. At the top of this curve is a diamond-shaped cursor. We next click-and-drag this cursor

down the line to the point at which the entry under the “Diff Coeff (D):” label reads 1.2×10^{-14} m^2/s. The temperature that appears under the "Temperature (T)" label is 1430 K.

5.26 *The activation energy for the diffusion of copper in silver is 193,000 J/mol. Calculate the diffusion coefficient at 1200 K (927°C), given that D at 1000 K (727°C) is* 1.0×10^{-14} m^2/s.

Solution

To solve this problem it first becomes necessary to solve for D_0 from a rearranged form of Equation 5.8 and using 1000 K diffusion data:

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

$$= (1.0 \times 10^{-14} \text{ m}^2/\text{s}) \exp\left[\frac{193{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1000 \text{ K})}\right]$$

$$1.22 \times 10^{-4} \text{m}^2/\text{s}$$

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

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

$$4.8 \times 10^{-13} \text{ m}^2/\text{s}$$

5.27 *The diffusion coefficients for nickel in iron are given at two temperatures, as follows:*

T (K)	*D (m^2/s)*
1473	*2.2×10^{-15}*
1673	*4.8×10^{-14}*

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

(b) What is the magnitude of D at 1300°C (1573 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 (1473 K and 1673 K) and D_1 and D_2 (2.2×10^{-15} and 4.8×10^{-14} m^2/s), we get

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

$$= - (8.31 \text{ J/mol-K}) \frac{\left[\ln\left(2.2 \times 10^{-15}\right) - \ln\left(4.8 \times 10^{-14}\right)\right]}{\dfrac{1}{1473 \text{ K}} - \dfrac{1}{1673 \text{ K}}}$$

$$= 315{,}700 \text{ J/mol}$$

Now, solving for D_0 from a rearranged form of Equation 5.8 (and using the 1473 K value of D)

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

$$= \left(2.2 \times 10^{-15} \text{ m}^2\text{/s}\right)\exp\left[\frac{315{,}700 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1473 \text{ K})}\right]$$

$$= 3.5 \times 10^{-4} \text{ m}^2/\text{s}$$

(b) Using these values of D_0 and Q_d, D at 1573 K is just

$$D = (3.5 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{315{,}700 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1573 \text{ K})} \right]$$

$$= 1.1 \times 10^{-14} \text{ m}^2/\text{s}$$

Note: This problem may also be solved using the “Diffusion” module in the *VMSE* software. Open the “Diffusion” module, click on the “D0 and Qd 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. “1473” and “1673”, in the first two boxes under the column labeled “T (K)”. Next, enter the corresponding diffusion coefficient values (viz. “2.2e-15” and “4.8e-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 give values for D_0 and Q_d; for this specific problem these values are 3.49×10^{-4} m^2/s ("Do=3.49E-04") and 315 kJ/mol ("Qd=315"), 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 “1573”. The value of the diffusion coefficient at this temperature is given under the label “Diff Coeff (D):”. For our problem, this value is 1.2×10^{-14} m^2/s ("1.2E-14 m^2/s").

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

T (°C)	*D (m^2/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} m^2/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

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

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

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "D0 and Qd 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. "873" (600ºC) and "973" (700ºC), in the first two boxes under the column labeled "T (K)". Next, enter the corresponding diffusion coefficient values (viz. "5.5e-14" and "3.9e-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 give values for D_0 and Q_d; for this specific problem these values are 1.04×10^{-5} m^2/s ("Do=1.04E-05") and 138 kJ/mol ("Qd=138"), respectively

5. It is not possible to solve part (b) of this problem using this submodule—data plotted do not extend to 850ºC. Therefore, it necessary to utilize the "D vs 1/T Plot" submodule.

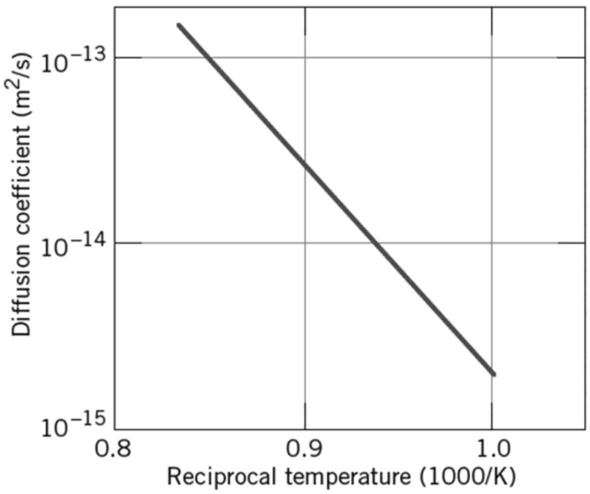
6. Open this submoduile, and in the left-hand window that appears, there is a preset set of data, but none for the diffusion of C in Ni. This requires us specify our settings by clicking on the "Custom1" box.

7. In the column on the right-hand side of this window enter the data for this problem, which have already been determined. In the window under "D0" the preexponential value, enter "1.04e-5". Next just below in the "Qd" window enter the activation energy value (in KJ/mol), in this case "138". It is now necessary to specify a temperature range over which the data is to be plotted—since we are interested in the value of *D* at 850ºC let us arbitrarily pick 600°C to be the miminum, which is entered in the "T Min" under "Temperature Range" window; let us also select 900°C to be the maximum temperature, which is entered in the "T Max" window.

8. Next, at the bottom of this window, click the "Add Curve" button.

9. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for C in Ni. At the top of this curve is a diamond-shaped cursor. We next click-and-drag this cursor down the line to the point at which the entry under the "Temperature (T)" label reads 1123 K. The value of the diffusion coefficient at this temperature is displayed below the “Diff Coeff (D)” label, which is 3.9×10^{-12} m^2/s.

5.29 *The accompanying figure shows a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of the absolute temperature for the diffusion of gold in silver. 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 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); furthermore, 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 0.90×10^{-3} K^{-1}, respectively, then the corresponding values of log D_1 and log D_2 are –14.68 and –13.57. Therefore,

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

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

$$= -(2.3)(8.31 \text{ J/mol-K})\left[\frac{-14.68 - (-13.57)}{\left(1.0 \times 10^{-3} - 0.90 \times 10^{-3}\right) \text{K}^{-1}}\right]$$

$$= 212{,}200 \text{ J/mol}$$

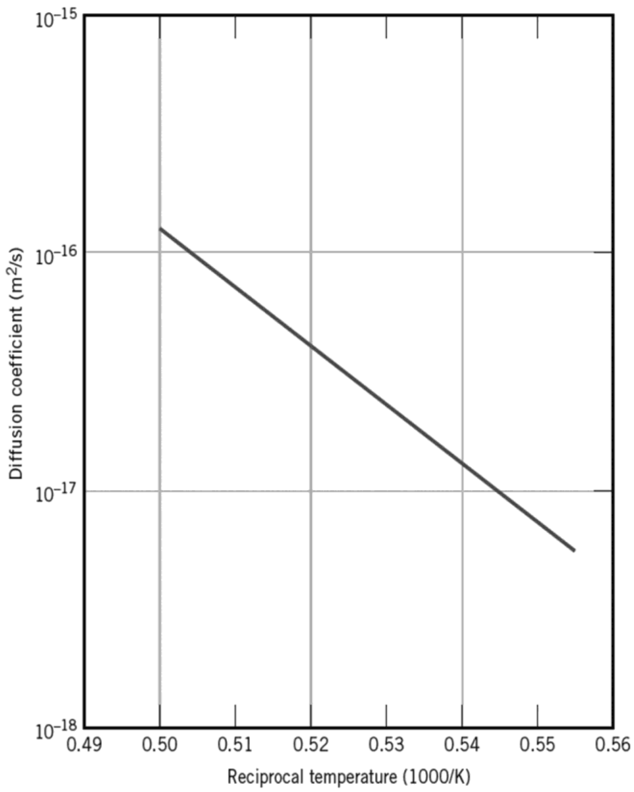
Rather than trying to make a graphical extrapolation to determine D_0, a more accurate value is obtained analytically using a rearranged form of Equation 5.9b taking a specific value of both D and T (from $1/T$) from the plot given in the problem; for example, $D = 1.0 \times 10^{-14}$ m^2/s at $T = 1064$ K ($1/T = 0.94 \times 10^{-3}$ K^{-1}). Therefore

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

$$= \left(1.0 \times 10^{-14} \text{ m}^2\text{/s}\right)\exp\left[\frac{212{,}200 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1064 \text{ K})}\right]$$

$$= 2.65 \times 10^{-4} \text{ m}^2\text{/s}$$

5.30 The accompanying figure shows a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of the absolute temperature for the diffusion of vanadium in molybdenum. 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 V in Mo 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*); furthermore, 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 0.50×10^{-3} and 0.55×10^{-3} K^{-1}, respectively, then the corresponding values of log D_1 and log D_2 are –15.90 and –17.13. Therefore,

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

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

$$= -(2.3)(8.31\text{ J/mol-K})\left[\frac{-15.90 - (-17.13)}{\left(0.50 \times 10^{-3} - 0.55 \times 10^{-3}\right)\text{ K}^{-1}}\right]$$

$$= 470{,}200\text{ J/mol}$$

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, $D = 1.26 \times 10^{-16}$ m^2/s at T = 2000 K (1/T = 0.50×10^{-3} K^{-1}). Therefore

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

$$= \left(1.26 \times 10^{-16}\text{ m}^2\text{/s}\right)\exp\left[\frac{470{,}200\text{ J/mol}}{(8.31\text{ J/mol-K})(2000\text{ K})}\right]$$

$$= 2.44 \times 10^{-4}\text{ m}^2\text{/s}$$

5.31 *From Figure 5.12 calculate activation energy for the diffusion of*

(a) copper in silicon, and

(b) aluminum in silicon

(c) How do these values compare?

Solution

(a) In order to determine the activation energy for the diffusion of copper in silicon, it is necessary to take the slope of its log D versus $1/T$ curve. The activation energy Q_d is equal to the equation cited in Example Problem 5.5—viz.

$$Q_d = -2.3R\left[\frac{\log D_1 - \log D_2}{\dfrac{1}{T_1} - \dfrac{1}{T_1}}\right]$$

On the plot of Figure 5.12, for copper, let us arbitrarily take

$1/T_1 = 1.5 \times 10^{-3}\ (\mathrm{K}^{-1})$

$1/T_2 = 0.6 \times 10^{-3}\ (\mathrm{K}^{-1})$

Their corresponding log D values are

$\log D_1 = -9.6$

$\log D_2 = -7.7$

Thus,

$$Q_d = -(2.3)(8.31\ \mathrm{J/mol \cdot K})\left[\frac{-9.6 - (-7.7)}{1.5 \times 10^{-3}\ \mathrm{K}^{-1} - 0.6 \times 10^{-3}\ \mathrm{K}^{-1}}\right]$$

$$= 40{,}350\ \mathrm{J/mol}$$

(b) For aluminum in silicon, let us use the following two log D versus $1/T$ values:

$1/T_1 = 1.5 \times 10^{-3}\ (\mathrm{K}^{-1})$

$1/T_2 = 0.6 \times 10^{-3}\ (\mathrm{K}^{-1})$

Their corresponding log D values are

$\log D_1 = -29.0$

$\log D_2 = -13.5$

Therefore, the activation energy is equal to

$$Q_d = -(2.3)(8.31 \text{ J/mol} \cdot \text{K}) \left[\frac{-29.0 - (-13.5)}{1.5 \times 10^{-3} \text{ K}^{-1} - 0.6 \times 10^{-3} \text{ K}^{-1}} \right]$$

$$= 330{,}000 \text{ J/mol}$$

(c) The activation energy for the diffusion of Al in Si (330,000 J/mol) is approximately eight times the value for the diffusion of Cu in Si (40,350 J/mol).

5.32 *Carbon is allowed to diffuse through a steel plate 10 mm thick. The concentrations of carbon at the two faces are 0.85 and 0.40 kg C/cm*^{3} *Fe, which are maintained constant. If the preexponential and activation energy are 5.0 × 10*$^{-7}$ *m*^{2}*/s and 77,000 J/mol, respectively, compute the temperature at which the diffusion flux is 6.3 × 10*$^{-10}$ *kg/m*^{2}*·s.*

Solution

This problem asks that we compute the temperature at which the diffusion flux is 6.3 × 10^{-10} kg/m^2-s. Combining Equations 5.2 and 5.8 yields

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

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

Taking natural logarithms of both sides of this equation yields the following expression:

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

Or

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

And solving for T from this expression leads to

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

Now, incorporating values of the parameters in this equation provided in the problem statement leads to the following:

$$T = \left(\frac{77,000 \text{ J/mol}}{8.31 \text{ J/mol-K}}\right) \frac{1}{\ln\left[- \frac{(5.0 \times 10^{-7} \text{ m}^2\text{/s})(0.40 \text{ kg/m}^3 - 0.85 \text{ kg/m}^3)}{(6.3 \times 10^{-10} \text{ kg/m}^2\text{-s})(10 \times 10^{-3} \text{ m})}\right]}$$

$$= 884 \text{ K} = 611°\text{C}$$

5.33 *The steady-state diffusion flux through a metal plate is 7.8 × 10^{-8} kg/m^2·s at a temperature of 1200°C (1473 K) and when the concentration gradient is –500 kg/m^4. Calculate the diffusion flux at 1000°C (1273 K) for the same concentration gradient and assuming an activation energy for diffusion of 145,000 J/mol.*

Solution

In order to solve this problem, we must first compute the value of D_0 from the data given at 1200°C (1473 K); this requires the combining of both Equations 5.2 and 5.8 as

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

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

Solving for D_0 from the above expression gives

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

And incorporating values of the parameters in this expressions provided in the problem statement yields the following:

$$D_0 = -\left(\frac{7.8 \times 10^{-8}\ \text{kg/m}^2\text{-s}}{-500\ \text{kg/m}^4}\right)\exp\left[\frac{145{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1200 + 273\ \text{K})}\right]$$

$$= 2.18 \times 10^{-5}\ \text{m}^2/\text{s}$$

The value of the diffusion flux at 1273 K may be computed using these same two equations as follows:

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

$$= -(2.18 \times 10^{-5}\ \text{m}^2/\text{s})(-500\ \text{kg/m}^4)\exp\left[-\frac{145{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1273\ \text{K})}\right]$$

$$= 1.21 \times 10^{-8}\ \text{kg/m}^2\text{-s}$$

5.34 *At approximately what temperature would a specimen of γ-iron have to be carburized for 4 h to produce the same diffusion result as carburization at 1000°C for 12 h?*

Solution

To solve this problem it is necessary to employ Equation 5.7

$$Dt = \text{constant}$$

which, for this problem, takes the form

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

At 1000°C, and using the data from Table 5.2, for the diffusion of carbon in γ-iron—i.e.,

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

Q_d = 148,000 J/mol

the diffusion coefficient is equal to

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

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

Thus, from the above for of Equation 5.7

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

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

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

$$= -\frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})\left[\ln(5.79 \times 10^{-11}\ \text{m}^2/\text{s}) - \ln(2.3 \times 10^{-5}\ \text{m}^2/s)\right]}$$

$$= 1381\ \text{K} = 1108°\text{C}$$

5.35 *(a) Calculate the diffusion coefficient for magnesium in aluminum at 450°C.*

(b) What time will be required at 550°C to produce the same diffusion result (in terms of concentration at a specific point) as for 15 h at 450°C?

Solution

(a) We are asked to calculate the diffusion coefficient for Mg in Al at 450°C. From Table 5.2, for this diffusion system

$D_0 = 1.2 \times 10^{-4}$ m²/s

Q_d =130,000 J/mol

Thus, from Equation 5.8

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

$$= (1.2 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{130{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(450 + 273 \text{ K})}\right]$$

$$= 4.81 \times 10^{-14} \text{ m}^2/\text{s}$$

(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

$$D_{550} = (1.2 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{130{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(550 + 273 \text{ K})}\right]$$

$$= 6.67 \times 10^{-13} \text{ m}^2/\text{s}$$

Thus, solving for the diffusion time at 550°C yields

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

$$= \frac{(4.81 \times 10^{-14} \text{ m}^2/\text{s})(15 \text{ h})}{(6.67 \times 10^{-13} \text{ m}^2/\text{s})} = 1.08 \text{ h}$$

5.36 *A copper–nickel diffusion couple similar to that shown in Figure 5.1a is fashioned. After a 500-h heat treatment at 1000°C (1273 K) the concentration of Ni is 3.0 wt% at the 1.0-mm position within the copper. At what temperature should the diffusion couple be heated to produce this same concentration (i.e., 3.0 wt% Ni) at a 2.0-mm position after 500 h? The preexponential and activation energy for the diffusion of Ni in Cu are 1.9 × 10^{-4} m^2/s and 230,000 J/mol, respectively.*

Solution

In order to determine the temperature to which the diffusion couple must be heated so as to produce a concentration of 3.0 wt% Ni at the 2.0-mm position, we must first utilize Equation 5.6b with time *t* being a constant. That is, because time (*t*) is a constant, then

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

Or

$$\frac{x_{1000}^2}{D_{1000}} = \frac{x_T^2}{D_T}$$

Now, solving for D_T from this equation, yields

$$D_T = \frac{x_T^2 D_{1000}}{x_{1000}^2}$$

and incorporating into this expressions the temperature dependence of D_{1000} utilizing Equation 5.8, yields

$$D_T = \frac{\left(x_T^2\right)\left[D_0 \exp\left(-\frac{Q_d}{RT}\right)\right]}{x_{1000}^2}$$

$$= \frac{(2\text{ mm})^2\left[\left(1.9 \times 10^{-4}\text{ m}^2/\text{s}\right)\exp\left(-\frac{230{,}000\text{ J/mol}}{(8.31\text{ J/mol-K})(1273\text{ K})}\right)\right]}{(1\text{ mm})^2}$$

$$= 2.74 \times 10^{-13}\text{ m}^2/\text{s}$$

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

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

$$= \frac{230{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(1.9 \times 10^{-4} \text{ m}^2/\text{s}\right) - \ln\left(2.74 \times 10^{-13} \text{ m}^2/\text{s}\right)\right]}$$

$$= 1360 \text{ K} = 1087°\text{C}$$

5.37 *A diffusion couple similar to that shown in Figure 5.1a is prepared using two hypothetical metals A and B. After a 20-h heat treatment at 800°C (and subsequently cooling to room temperature) the concentration of B in A is 2.5 wt% at the 5.0-mm position within metal A. If another heat treatment is conducted on an identical diffusion couple, but at 1000°C for 20 h, at what position will the composition be 2.5 wt% B? Assume that the preexponential and activation energy for the diffusion coefficient are 1.5 × 10⁻⁴ m²/s and 125,000 J/mol, respectively.*

Solution

In order to determine the position within the diffusion couple at which the concentration of A in B is 2.5 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}; this is accomplished using Equation 5.8 as follows:

$$D_{800} = (1.5 \times 10^{-4}\ \text{m}^2/\text{s})\exp\left[-\frac{125{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(800 + 273\ \text{K})}\right]$$

$$1.22 \times 10^{-10}\ \text{m}^2/\text{s}$$

$$D_{1000} = (1.5 \times 10^{-4}\ \text{m}^2/\text{s})\exp\left[-\frac{125{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1000 + 273\ \text{K})}\right]$$

$$1.11 \times 10^{-9}\ \text{m}^2/\text{s}$$

Now, solving the above expression for x_{1000} yields

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

$$= (5\ \text{mm})\sqrt{\frac{1.11 \times 10^{-9}\ \text{m}^2/\text{s}}{1.22 \times 10^{-10}\ \text{m}^2/\text{s}}}$$

$= 15.1$ mm

5.38 *Consider the diffusion of some hypothetical metal Y into another hypothetical metal Z at 950°C; after 10 h the concentration at the 0.5 mm position (in metal Z) is 2.0 wt% Y. At what position will the concentration also be 2.0 wt% Y after a 17.5 h heat treatment again at 950°C? Assume preexponential and activation energy values of* 4.3×10^{-4} *m^2/s and 180,000 J/mol, respectively, for this diffusion system.*

Solution

In order to determine the position within this diffusion system at which the concentration of X in Y is 2.0 wt% after 17.5 h, we must employ Equation 5.6b with *D* constant (since the temperature is constant). (Inasmuch as *D* is constant it is not necessary to employ preexponential and activation energy values cited in the problem statement.) Under these circumstances, Equation 5.6b takes the form

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

Or

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

If we assume the following:

$x_1 = 0.5$ mm

$t_1 = 10$ h

$t_2 = 17.5$ h

Now upon solving the above expression for x_2 and incorporation of these values we have

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

$$= \sqrt{\frac{(0.5 \text{ mm})^2 (17.5 \text{ h})}{10 \text{ h}}}$$

$$= 0.66 \text{ mm}$$

5.39 *A diffusion couple similar to that shown in Figure 5.1a is prepared using two hypothetical metals R and S. After a 2.5-h heat treatment at 750°C the concentration of R is 4 at% at the 4-mm position within S. Another heat treatment is conducted on an identical diffusion couple at 900°C and the time required to produce this same diffusion result (viz., 4 at% R at the 4-mm position within S) is 0.4 h. If it is known that the diffusion coefficient at 750°C is* 2.6×10^{-17} *m²/s determine the activation energy for the diffusion of R in S.*

Solution

In order to determine the activation energy for this diffusion system it is first necessary to compute the diffusion coefficient at 900°C. Inasmuch as x is the same for both heat treatments, Equation 5.6b takes the form

$$Dt = \text{constant}$$

Or that

$$D_{750}t_{750} = D_{900}t_{900}$$

It is possible to solve for D_{900} inasmuch as values for the other parameters are provided in the problem statement; i.e.,

$t_{750} = 2.5$ h
$D_{750} = 2.6 \times 10^{-17}$ m^2/s
$t_{900} = 0.4$ h

Solving for D_{900} from the above equation leads to

$$D_{900} = \frac{D_{750}t_{750}}{t_{900}}$$

$$= \frac{(2.6 \times 10^{-17}\ \text{m}^2/\text{s})(2.5\ \text{h})}{0.4\ \text{h}}$$

$$1.6 \times 10^{-16}\ \text{m}^2/\text{s}$$

Inasmuch as we know the values of D at both 750°C and 900°C—viz.,

$D_{750} = 2.6 \times 10^{-17}$ m^2/s
$D_{900} = 1.6 \times 10^{-16}$ m^2/s

it is possible to solve for the activation energy Q_d using the following equation, which is derived in Example Problem 5.5. In this expression, if we assign $D_{750} = D_1$ and $D_{900} = D_2$, then the activation energy is equal to

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

$$= -(2.3)(8.31\text{ J/mol}\cdot\text{K})\left[\frac{\log(2.6 \times 10^{-17}\text{ m}^2/\text{s}) - \log(1.6 \times 10^{-16}\text{ m}^2/\text{s})}{\frac{1}{(750 + 273\text{ K})} - \frac{1}{(900 + 273\text{ K})}}\right]$$

$$= 120{,}700\text{ J/mol}$$

5.40 *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 maintained at an elevated temperature. A diffusion heat treatment at 600°C (873 K) for 100 min increases the carbon concentration to 0.75 wt% at a position 0.5 mm below the surface. Estimate the diffusion time required at 900°C (1173 K) to achieve this same concentration also at a 0.5-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 α-Fe.*

Solution

In order to compute the diffusion time at 900°C to produce a carbon concentration of 0.75 wt% at a position 0.5 mm below the surface we must employ Equation 5.6b with position constant; that is

$$Dt = \text{constant}$$

since x is a constant (0.5 mm). This means that

$$D_{600}t_{600} = D_{900}t_{900}$$

In addition, it is necessary to compute values for both D_{600} and D_{900} using Equation 5.8. From Table 5.2, for the diffusion of C in α-Fe, Q_d = 87,400 J/mol and $D_0 = 1.1 \times 10^{-6}$ m^2/s. Therefore,

$$D_{600} = \left(1.1 \times 10^{-6}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{87{,}400\ \text{J/mol}}{(8.31\ \text{J/mol-K})(600 + 273\ \text{K})}\right]$$

$$6.45 \times 10^{-12}\ \text{m}^2/\text{s}$$

$$D_{900} = \left(1.1 \times 10^{-6}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{87{,}400\ \text{J/mol}}{(8.31\ \text{J/mol-K})(900 + 273\ \text{K})}\right]$$

$$1.40 \times 10^{-10}\ \text{m}^2/\text{s}$$

Now, solving the original equation for t_{900} gives

$$t_{900} = \frac{D_{600}t_{600}}{D_{900}}$$

$$= \frac{\left(6.45 \times 10^{-12}\ \text{m}^2/\text{s}\right)(100\ \text{min})}{1.40 \times 10^{-10}\ \text{m}^2/\text{s}}$$

$$= 4.61 \text{ min}$$

5.41 *An FCC iron–carbon alloy initially containing 0.10 wt% C is carburized at an elevated temperature and in an atmosphere in which the surface carbon concentration is maintained at 1.10 wt%. If after 48 h the concentration of carbon is 0.30 wt% at a position 3.5 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 48 h diffusion anneal was carried out in order to give a carbon concentration of 0.30 wt% C in FCC Fe at a position 3.5 mm below the surface. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.30 - 0.10}{1.10 - 0.10} = 0.2000 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Or

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.8000$$

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	erf (z)
0.90	0.7970
y	0.8000
0.95	0.8209

$$\frac{y - 0.90}{0.95 - 0.90} = \frac{0.8000 - 0.7970}{0.8209 - 0.7970}$$

From which

$$y = 0.9063$$

Thus,

$$\frac{x}{2\sqrt{Dt}} = 0.9063$$

And since t = 48 h (172,800 s) and x = 3.5 mm (3.5×10^{-3} m), solving for D from the above equation yields

$$D = \frac{x^2}{(4t)(0.9063)^2}$$

$$= \frac{(3.5 \times 10^{-3}\ \text{m})^2}{(4)(172{,}800\ \text{s})(0.821)} = 2.16 \times 10^{-11}\ \text{m}^2/\text{s}$$

Now, in order to determine the temperature at which D has the above value, we must employ Equation 5.9a; solving 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 2.3×10^{-5} m^2/s and 148,000 J/mol, respectively. Therefore

$$T = \frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})\left[\ln(2.3 \times 10^{-5}\ \text{m}^2/\text{s}) - \ln(2.16 \times 10^{-11}\ \text{m}^2/\text{s})\right]}$$

$$= 1283\ \text{K} = 1010°\text{C}$$

Diffusion in Semiconducting Materials

5.42 *For the predeposition heat treatment of a semiconducting device, gallium atoms are to be diffused into silicon at a temperature of 1150°C for 2.5 h. If the required concentration of Ga at a position 2 μm below the surface is 8 × 10^{23} atoms/m^3, compute the required surface concentration of Ga. Assume the following:*

(i) The surface concentration remains constant

(ii) The background concentration is 2 × 10^{19} Ga atoms/m^3

(iii) Preexponential and activation energy values are 3.74 × 10^{-5} m^2/s and 3.39 eV/atom, respectively.

Solution

This problem requires that we solve for the surface concentration, C_s of Equation 5.5 given the following:

$C_x = 8 \times 10^{23}$ atoms/m^3

$C_0 = 2 \times 10^{19}$ atoms/m^3

$x = 2$ μm $= 2 \times 10^{-6}$ m

$T = 1150$°C

$t = 2.5$ h $= 9000$ s

$D_0 = 3.74 \times 10^{-5}$ m^2/s

$Q_d = 3.39$ eV/atom

Equation 5.5 calls for a value of the diffusion coefficient D, which is determined at 1150°C using Equation 5.8. Thus

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

$$= (3.74 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{3.39 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom}\cdot\text{K})(1150°\text{C} + 273 \text{ K})}\right]$$

$$= 3.72 \times 10^{-17} \text{ m}^2/\text{s}$$

Now it is required that we solve for C_s in Equation 5.5:

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

And solving for C_s from this expression and incorporation of values for all of the other parameters leads to

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

$$= (2 \times 10^{19} \text{ atoms/m}^3) + \frac{(8 \times 10^{23} \text{ atoms/m}^3) - (2 \times 10^{19} \text{ atoms/m}^3)}{1 - \operatorname{erf}\left[\dfrac{2 \times 10^{-6} \text{ m}}{2\sqrt{(3.72 \times 10^{-17} \text{ m}^2/\text{s})(9000 \text{ s})}}\right]}$$

$$= (2 \times 10^{19} \text{ atoms/m}^3) + \frac{(8 \times 10^{23} \text{ atoms/m}^3)}{1 - \operatorname{erf}(1.7283)}$$

At this point it becomes necessary to conduct an interpolation—we know the z and need to determine the value of erf(z). This interpolation is conducted using data found in Table 5.1 as follows:

erf(z)	z
0.9838	1.7
erf(z)	1.7283
0.9891	1.8

$$\frac{1.8000 - 1.7283}{1.8000 - 1.7000} = \frac{0.9891 - \operatorname{erf}(z)}{0.9891 - 0.9838}$$

And solving this expression for erf(z) leads to

$$\operatorname{erf}(z) = 0.9853$$

Inserting this value into the above equation in which we are solving for C_s yields

$$C_s = (2 \times 10^{19} \text{ atoms/m}^3) + \frac{(8 \times 10^{23} \text{ atoms/m}^3)}{1 - \operatorname{erf}(1.7283)}$$

$$= (2 \times 10^{19} \text{ atoms/m}^3) + \frac{(8 \times 10^{23} \text{ atoms/m}^3)}{1 - 0.9853}$$

$$= 5.44 \times 10^{25} \text{ Ga atoms/m}^3$$

5.43 *Antimony atoms are to be diffused into a silicon wafer using both predeposition and drive-in heat treatments; the background concentration of Sb in this silicon material is known to be 2 × 10^{20} atoms/m^3. The predeposition treatment is to be conducted at 900°C for 1 h; the surface concentration of Sb is to be maintained at a constant level of 8.0 × 10^{25} atoms/m^3. Drive-in diffusion will be carried out at 1200°C for a period of 1.75 h. For the diffusion of Sb in Si, values of Q_d and D_0 are 3.65 eV/atom and 2.14 × 10^{-5} m^2/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 Sb atoms is 5 × 10^{23}/m^3.

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 = 900°C (1173 K)] using Equation 5.8. Thus

$$D_p = D_0 \exp\left(-\frac{Q_d}{kT_p}\right)$$

$$= (2.14 \times 10^{-5}\ \text{m}^2/\text{s}) \exp\left[-\frac{3.65\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom} \cdot \text{K})(1173\ \text{K})}\right]$$

$$= 4.5 \times 10^{-21}\ \text{m}^2/\text{s}$$

The value of Q_0 is determined (using Equation 5.12) as follows:

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

$$= (2)(8.0 \times 10^{25}\ \text{atoms/m}^3) \sqrt{\frac{(4.5 \times 10^{-21}\ \text{m}^2/\text{s})(1\ \text{h})(60\ \text{min/h})(60\ \text{s/min})}{\pi}}$$

$$= 3.63 \times 10^{17}\ \text{atoms/m}^2$$

(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°C (1473 K)]. Thus,

$$D_d = D_0 \exp\left(-\frac{Q_d}{kT_d}\right)$$

$$= (2.14 \times 10^{-5}\ \text{m}^2/\text{s}) \exp\left[-\frac{3.65\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom} \cdot \text{K})(1473\ K)}\right]$$

$$= 7.02 \times 10^{-18}\ \text{m}^2/\text{s}$$

Now from Equation 5.13

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

$$= \left\{(4)(7.02 \times 10^{-18}\ \text{m}^2/\text{s})(1.75\ \text{h})(60\ \text{min/h})(60\ \text{s/min}) \ln\left[\frac{3.63 \times 10^{17}\ \text{atoms/m}^2}{(2 \times 10^{20}\ \text{atoms/m}^3)\sqrt{(\pi)(7.02 \times 10^{-18}\ \text{m}^2/\text{s})(1.75\ \text{h})(60\ \text{min/h})(60\ \text{s/min})}}\right]\right\}^{1/2}$$

$$= 1.23 \times 10^{-6}\ \text{m} = 1.23\ \mu\text{m}$$

(c) For a concentration of 5×10^{23} Sb atoms/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 $C(x,t) = 5 \times 10^{23}$ Sb atoms/m^3 yields

$$x = \left\{ (4)(7.02 \times 10^{-18})(6300) \ln \left[\frac{3.63 \times 10^{17}}{(5 \times 10^{23})\sqrt{(\pi)(7.02 \times 10^{-18})(6300)}} \right] \right\}^{1/2}$$

$$= 3.43 \times 10^{-7} \text{ m} = 0.343 \ \mu\text{m}$$

5.44 *Indium atoms are to be diffused into a silicon wafer using both predeposition and drive-in heat treatments; the background concentration of In in this silicon material is known to be 2 $\times$ 10^{20} atoms/m^3. The drive-in diffusion treatment is to be carried out at 1175°C for a period of 2.0 h, which gives a junction depth x_j of 2.35 μm. Compute the predeposition diffusion time at 925°C if the surface concentration is maintained at a constant level of 2.5 $\times$ 10^{26} atoms/m^3. For the diffusion of In in Si, values of Q_d and D_0 are 3.63 eV/atom and 7.85 $\times$ 10^{-5} m^2/s, respectively.*

<u>Solution</u>

This problem asks that we compute the time for the predeposition heat treatment for the diffusion of In in Si. In order to do this it is first 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

$$D_d = D_0 \exp\left(-\frac{Q_d}{kT_d}\right)$$

$$= (7.85 \times 10^{-5}\ \text{m}^2/\text{s}) \exp\left[-\frac{3.63\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom}\cdot\text{K})(1175°\text{C} + 273\ \text{K})}\right]$$

$$= 1.84 \times 10^{-17}\ \text{m}^2/\text{s}$$

Now, solving for Q_0 in Equation 5.13 leads to

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

In the problem statement we are given the following values:

C_B = 2 × 10^{20} atoms/m^3

t_d = 2 h (7,200 s)

x_j = 2.35 μm = 2.35 × 10^{-6} m

Therefore, incorporating these values into the above equation yields

$$Q_0 = \left[(2 \times 10^{20}\ \text{atoms/m}^3)\sqrt{(\pi)(1.84 \times 10^{-17}\ \text{m}^2/\text{s})(7{,}200\ \text{s})}\right] \exp\left[\frac{(2.35 \times 10^{-6}\ \text{m})^2}{(4)(1.84 \times 10^{-17}\ \text{m}^2/\text{s})(7{,}200\ \text{s})}\right]$$

$$= 4.33 \times 10^{18}\ \text{atoms/m}^2$$

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 925°C) using Equation 5.8. Thus

$$D_p = (7.85 \times 10^{-5} \text{ m}^2/\text{s})\exp\left[-\frac{3.63 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom}\cdot\text{K})(925°\text{C} + 273 \text{ K})}\right]$$

$$= 4.25 \times 10^{-20} \text{ m}^2/\text{s}$$

Now, solving for t_p in Equation 5.12 we get

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

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

$$t_p = \frac{\pi \left(4.33 \times 10^{18} \text{ atoms/m}^2\right)^2}{(4)\left(2.5 \times 10^{26} \text{ atoms/m}^3\right)^2 (4.25 \times 10^{-20} \text{ m}^2/\text{s})}$$

$$= 5.54 \times 10^3 \text{ s} = 92.3 \text{ min} = 1.53 \text{ h}$$

DESIGN PROBLEMS

Fick's First Law

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 0.051 MPa (0.5 atm) and 0.01013 MPa (0.1 atm), respectively, for hydrogen and nitrogen. The concentrations of hydrogen and nitrogen (C_H and C_N, in mol/m^3) 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:*

$$C_H = 2.5 \times 10^3 \sqrt{p_{H_2}} \exp\left(-\frac{27{,}800 \text{ J/mol}}{RT}\right) \qquad (5.16a)$$

$$C_N = 2.75 \times 10^3 \sqrt{p_{N_2}} \exp\left(-\frac{37{,}600 \text{ J/mol}}{RT}\right) \qquad (5.16b)$$

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

$$D_H (\text{m}^2/\text{s}) = 1.4 \times 10^{-7} \exp\left(-\frac{13{,}400 \text{ J/mol}}{RT}\right) \qquad (5.17a)$$

$$D_N (\text{m}^2/\text{s}) = 3.0 \times 10^{-7} \exp\left(-\frac{76{,}150 \text{ J/mol}}{RT}\right) \qquad (5.17b)$$

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

Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.2. 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 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 5 times the diffusion flux of nitrogen J_N--i.e.

$$J_H = \sqrt{5} J_N$$

Let us begin by producing expressions for the diffusion flux of both hydrogen and nitrogen, and then use them to satisfy the above equation. Fick's first law describing the flux of hydrogen, J_H, is as follows:

$$J_H = - D_H \frac{\Delta C_H}{\Delta x}$$

$$= - \left(\frac{1}{\Delta x}\right)(1.4 \times 10^{-7})\left[\exp\left(- \frac{13{,}400 \text{ J/mol}}{RT}\right)\right]\left[C_H(\text{Lo}) - C_H(\text{Hi})\right]$$

where $C_H(\text{Lo})$ and $C_H(\text{Hi})$ designate values of the concentrations of hydrogen on low and high pressure sides of the plate. Expressions for these two parameters, as determined using Equation 5.16a, are as follows:

$$C_H(\text{Lo}) = (2.5 \times 10^3)(\sqrt{0.051 \text{ MPa}})\left[\exp\left(- \frac{27{,}800 \text{ J/mol}}{RT}\right)\right]$$

$$C_H(\text{Hi}) = (2.5 \times 10^3)(\sqrt{0.1013 \text{ MPa}})\left[\exp\left(- \frac{27{,}800 \text{ J/mol}}{RT}\right)\right]$$

Now, the expression for $C_H(\text{Lo}) - C_H(\text{Hi})$ may be written as follows:

$$C_H(\text{Lo}) - C_H(\text{Hi}) = (2.5 \times 10^3)(\sqrt{0.051 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}})\left[\exp\left(- \frac{27{,}800 \text{ J/mol}}{RT}\right)\right]$$

Hence, the expression for J_H reads as follows

$$J_H = - \left(\frac{1}{\Delta x}\right)(1.4 \times 10^{-7})\left[\exp\left(- \frac{13{,}400 \text{ J/mol}}{RT}\right)\right](2.5 \times 10^3)(\sqrt{0.051 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}})\left[\exp\left(- \frac{27{,}800 \text{ J/mol}}{RT}\right)\right]$$

A Fick's first law expression for the diffusion flux of nitrogen may be formulated in a similar manner, which reads as follows:

$$J_N = -D_N \frac{\Delta C_N}{\Delta x}$$

$$= -\left(\frac{1}{\Delta x}\right)(3.0 \times 10^{-7})\left[\exp\left(-\frac{76{,}150 \text{ J/mol}}{RT}\right)\right](2.75 \times 10^{3})(\sqrt{0.01013 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}})\left[\exp\left(-\frac{37{,}600 \text{ J/mol}}{RT}\right)\right]$$

And, finally, as noted above, we want to equate these two expressions such that they satisfy the following relationship:

$$J_H = \sqrt{5}\, J_N$$

and then solve this relationship for the temperature T (taking the value of R to be 8.31 J/mol-K). Following through this procedure results in a temperature of

$$T = 3467 \text{ K}$$

which value is extremely high (surely above the vaporization point of most metals). Thus, such a diffusion process is *not possible*.

5.D2 *A gas mixture is found to contain two diatomic A and B species (A_2 and B_2), the partial pressures of both of which are 0.1013 MPa (1 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 0.051 MPa (0.5 atm) for gas A and 0.0203 MPa (0.2 atm) for gas B. The concentrations of A and B (C_A and C_B, in mol/m^3) are functions of gas partial pressures (p_{A_2} and p_{B_2}, in MPa) and absolute temperature according to the following expressions:*

$$C_\mathrm{A} = 1.5 \times 10^3 \sqrt{p_{\mathrm{A}_2}}\, \exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right) \qquad (5.18a)$$

$$C_\mathrm{B} = 2.0 \times 10^3 \sqrt{p_{\mathrm{B}_2}}\, \exp\left(-\frac{27{,}000 \text{ J/mol}}{RT}\right) \qquad (5.18b)$$

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

$$D_\mathrm{A}(\mathrm{m}^2/\mathrm{s}) = 5.0 \times 10^{-7} \exp\left(-\frac{13{,}000 \text{ J/mol}}{RT}\right) \qquad (5.19a)$$

$$D_\mathrm{B}(\mathrm{m}^2/\mathrm{s}) = 3.0 \times 10^{-6} \exp\left(-\frac{21{,}000 \text{ J/mol}}{RT}\right) \qquad (5.19b)$$

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

Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.2. Inasmuch as the partial pressures on the high-pressure side of the sheet are the same, and the pressure of A_2 on the low pressure side is 2.5 times that of B_2, and concentrations are proportional to the square root of the partial pressure, the diffusion flux of A, J_A, is the square root of 2.5 times the diffusion flux of nitrogen J_B--i.e.

$$J_\mathrm{A} = \sqrt{2.5}\, J_\mathrm{B}$$

Let us begin by producing expressions for the diffusion flux of both A and B, and then use them to satisfy the above equation. Fick's first law describing the flux of A, J_A, is as follows:

$$J_A = -D_A \frac{\Delta C_A}{\Delta x}$$

$$= -\left(\frac{1}{\Delta x}\right)(5.0 \times 10^{-7})\left[\exp\left(-\frac{13{,}000 \text{ J/mol}}{RT}\right)\right]\left[C_A(\text{Lo}) - C_A(\text{Hi})\right]$$

where $C_A(\text{Lo})$ and $C_A(\text{Hi})$ designate values of the concentrations of species A on low and high pressure sides of the plate, respectively. Expressions for these two parameters, as determined using Equation 5.18a, are as follows:

$$C_A(\text{Lo}) = (1.5 \times 10^3)(\sqrt{0.051 \text{ MPa}})\left[\exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right)\right]$$

$$C_A(\text{Hi}) = (1.5 \times 10^3)(\sqrt{0.1013 \text{ MPa}})\left[\exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right)\right]$$

Now, the expression for $C_A(\text{Lo}) - C_A(\text{Hi})$ may be written as follows:

$$C_A(\text{Lo}) - C_A(\text{Hi}) = (1.5 \times 10^3)(\sqrt{0.051 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}})\left[\exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right)\right]$$

Hence, the expression for J_A reads as follows

$$J_A = -\left(\frac{1}{\Delta x}\right)(5.0 \times 10^{-7})\left[\exp\left(-\frac{13{,}000 \text{ J/mol}}{RT}\right)\right](1.5 \times 10^3)(\sqrt{0.051 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}})\left[\exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right)\right]$$

An expression for the diffusion flux for species B may be formulated in a similar manner, which reads as follows:

$$J_B = -D_B \frac{\Delta C_B}{\Delta x}$$

$$= -\left(\frac{1}{\Delta x}\right)(3.0 \times 10^{-6})\left[\exp\left(-\frac{21{,}000 \text{ J/mol}}{RT}\right)\right](2.0 \times 10^3)(\sqrt{0.0203 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}})\left[\exp\left(-\frac{27{,}000 \text{ J/mol}}{RT}\right)\right]$$

And, finally, as noted above, we want to equate these two expressions such that they satisfy the following relationship:

$$J_A = \sqrt{2.5}\, J_B$$

and then solve this relationship for the temperature T (taking the value of R to be 8.31 J/mol-K). Following through this procedure results in a temperature of

$$T = 568 \text{ K } (295°\text{C})$$

Thus, this purification *process is possible*, which may be carried out at 568 K; furthermore, it is independent of sheet thickness.

Fick's Second Law—Nonsteady-State Diffusion

5.D3 *The wear resistance of a steel shaft is to be improved by hardening its surface 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 0.0025 wt%, whereas the surface concentration is to be maintained at 0.45 wt%. For this treatment to be effective, a nitrogen content of 0.12 wt% must be established at a position 0.45 mm below the surface. Specify an appropriate heat treatment in terms of temperature and time for a temperature between 475°C and 625°C. The preexponential and activation energy for the diffusion of nitrogen in iron are* 5×10^{-7} m^2/s *and 77,000 J/mol, respectively, over this temperature range.*

Solution

In order to specify time-temperature combinations for this nonsteady-state diffusion situation, it is necessary to employ Equation 5.5, utilizing the following values for the concentration parameters:

$$C_0 = 0.0025 \text{ wt\% N}$$
$$C_s = 0.45 \text{ wt\% N}$$
$$C_x = 0.12 \text{ wt\% N}$$

Therefore, Equation 5.5

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

takes the form

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.12 - 0.0025}{0.45 - 0.0025}$$

$$= 0.2626 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus

$$1 - 0.2626 = 0.7374 = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Using linear interpolation and the data presented in Table 5.1

z	erf (z)
0.7500	0.7112
y	0.7374
0.8000	0.7421

$$\frac{0.7374 - 0.7112}{0.7421 - 0.7112} = \frac{y - 0.7500}{0.8000 - 0.7500}$$

From which

$$y = \frac{x}{2\sqrt{Dt}} = 0.7924$$

The problem stipulates that x = 0.45 mm = 4.5×10^{-4} m. Therefore

$$\frac{4.5 \times 10^{-4}\ \text{m}}{2\sqrt{Dt}} = 0.7924$$

Which leads to

$$Dt = 8.06 \times 10^{-8}\ \text{m}^2$$

Furthermore, the diffusion coefficient depends on temperature according to Equation 5.8; and, as stipulated in the problem statement, $D_0 = 5 \times 10^{-7}$ m^2/s and Q_d = 77,000 J/mol. Hence

$$Dt = D_0 \exp\left(-\frac{Q_d}{RT}\right)(t) = 8.06 \times 10^{-8}\ \text{m}^2$$

$$\left(5.0 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{77{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(T)}\right](t) = 8.06 \times 10^{-8}\ \text{m}^2$$

And solving for the time t

$$t\ (\text{in s}) = \frac{0.161}{\exp\left(-\frac{9265.9}{T}\right)}$$

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	Time h
500	25,860	7.2
550	12,485	3.5
600	6,550	1.8

5.D4 *The wear resistance of a steel gear is to be improved by hardening its surface, as described in Design Example 5.1. However, in this case the initial carbon content of the steel is 0.15 wt%, and a carbon content of 0.75 wt% is to be established at a position 0.65 mm below the surface. Furthermore, the surface concentration is to be maintained constant, but may be varied between 1.2 and 1.4 wt% C. Specify an appropriate heat treatment in terms of surface carbon concentration and time, and for a temperature between 1000°C and 1200°C.*

Solution

This is a nonsteady-state diffusion situation; thus, it is necessary to employ Equation 5.5, utilizing values/value ranges for the following parameters:

$$C_0 = 0.15 \text{ wt\% C}$$

$$1.2 \text{ wt\% C} \le C_s \le 1.4 \text{ wt\% C}$$

$$C_x = 0.75 \text{ wt\% C}$$

$$x = 0.65 \text{ mm}$$

$$1000^\circ\text{C} \le T \le 1200^\circ\text{C}$$

Let us begin by assuming a specific value for the surface concentration within the specified range—say 1.2 wt% C. Therefore, Equation 5.5 takes the form

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.75 - 0.15}{1.20 - 0.15}$$

$$= 0.5714 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus

$$1 - 0.5714 = 0.4286 = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Using linear interpolation and the data presented in Table 5.1

z	erf (z)
0.4000	0.4284
y	0.4286
0.4500	0.4755

$$\frac{0.4286 - 0.4284}{0.4755 - 0.4284} = \frac{y - 0.4000}{0.4500 - 0.4000}$$

from which

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

The problem statement stipulates that x = 0.65 mm = 6.5×10^{-4} m. Therefore

$$\frac{6.5 \times 10^{-4}\text{ m}}{2\sqrt{Dt}} = 0.4002$$

Which leads to

$$Dt = 6.59 \times 10^{-7}\text{ m}^2$$

Furthermore, the diffusion coefficient depends on temperature according to Equation 5.8; and, as noted in Design Example 5.1, $D_0 = 2.3 \times 10^{-5}$ m^2/s and Q_d = 148,000 J/mol. Hence

$$Dt = D_0 \exp\left(-\frac{Q_d}{RT}\right)(t) = 6.59 \times 10^{-7}\text{ m}^2$$

$$= \left(2.3 \times 10^{-5}\text{ m}^2/\text{s}\right)\exp\left[-\frac{148{,}000\text{ J/mol}}{(8.31\text{ J/mol-K})(T)}\right](t) = 6.59 \times 10^{-7}\text{ m}^2$$

And solving for the time t

$$t\text{ (in s)} = \frac{2.86 \times 10^{-2}}{\exp\left(-\dfrac{17{,}810}{T}\right)}$$

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
1000	34,100	9.5
1100	12,300	3.4
1200	5,100	1.4

Now, let us repeat the above procedure for two other values of the surface concentration, say 1.3 wt% C and 1.4 wt% C. Below is a tabulation of the results, again using temperatures of 1000°C, 1100°C, and 1200°C.

C_s (wt% C)	Temperature (°C)	Time (s)	Time (h)
	1000	26,700	7.4
1.3	1100	9,600	2.7
	1200	4,000	1.1
	1000	21,100	6.1
1.4	1100	7,900	2.2
	1200	1,500	0.9

Diffusion in Semiconducting Materials

5.D5 *One integrated circuit design calls for the diffusion of aluminum into silicon wafers; the background concentration of Al in Si is 1.75 × 10^{19} atoms/m^3. The predeposition heat treatment is to be conducted at 975°C for 1.25 h, with a constant surface concentration of 4 × 10^{26} Al atoms/m^3. At a drive-in treatment temperature of 1050°C, determine the diffusion time required for a junction depth of 1.75 μm. For this system, values of Q_d and D_0 are 3.41 eV/atom and 1.38 × 10^{-4} m^2/s, respectively.*

Solution

This problem asks that we compute the drive-in diffusion time for aluminum diffusion in silicon. Values of parameters given in the problem statement are as follows:

C_B = 1.75 × 10^{19} atoms/m^3

C_s = 4 × 10^{26} atoms/m^3

x_j = 1.75 μm = 1.75 × 10^{-6} m

T_p = 975°C = 1248 K

T_d = 1050°C = 1323 K

t_p = 1.25 h = 4500 s

Q_d = 3.41 eV/atom

D_0 = 1.38 × 10^{-4} m^2/s

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 975°C must be computed with the aid of Equation 5.8. Thus,

$$D_p = D_0 \exp\left(-\frac{Q_d}{kT_p}\right)$$

$$= (1.38 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{3.41\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom}\cdot\text{K})(975°\text{C} + 273\ \text{K})}\right]$$

$$= 2.36 \times 10^{-18}\ \text{m}^2/\text{s}$$

Now for the computation of Q_0 using Equation 5.12:

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

$$= (2)(4 \times 10^{26} \text{ atoms/m}^3)\sqrt{\frac{(2.36 \times 10^{-18} \text{ m}^2\text{/s})(1.25 \text{ h})(60 \text{ min/h})(60 \text{ s/min})}{\pi}}$$

$$= 4.65 \times 10^{19} \text{ atoms/m}^2$$

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 1050°C). This possible using Equation 5.8 as follows:

$$D_d = (1.38 \times 10^{-4} \text{ m}^2\text{/s})\exp\left[-\frac{3.41 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom}\cdot\text{K})(1050°\text{C} + 273 \text{ K})}\right]$$

$$= 1.426 \times 10^{-17} \text{ m}^2\text{/s}$$

And incorporation of values of all parameters except t_d in the expression cited above—i.e.,

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

yields

$$\exp\left[\frac{(1.75 \times 10^{-6} \text{ m})^2}{(4)(1.426 \times 10^{-17} \text{ m}^2\text{/s})t_d}\right] = \frac{4.65 \times 10^{19} \text{ atoms/m}^2}{(1.75 \times 10^{19} \text{ atoms/m}^3)\sqrt{(\pi)(1.426 \times 10^{-17} \text{ m}^2\text{/s})t_d}}$$

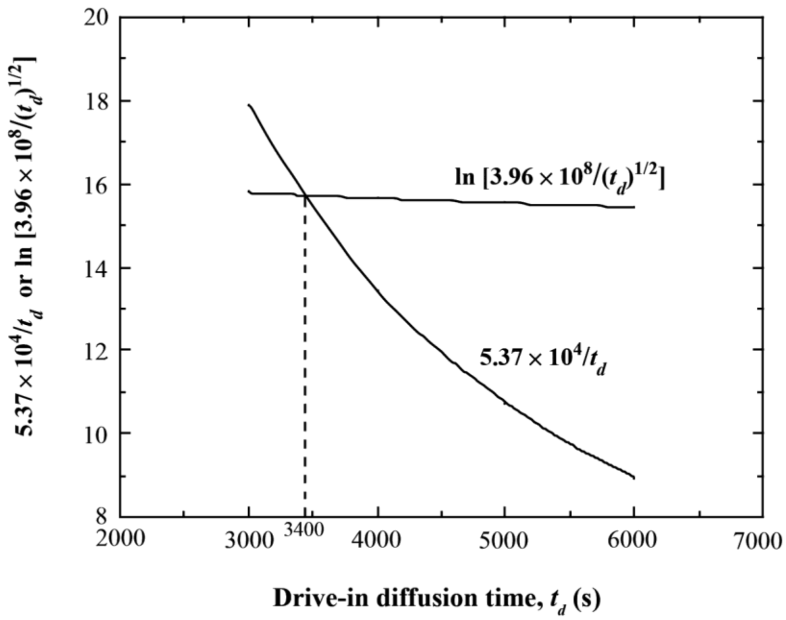
which expression reduces to

$$\exp\left(\frac{5.37 \times 10^4 \text{ s}}{t_d}\right) = \frac{3.96 \times 10^8 \text{ s}^{1/2}}{\sqrt{t_d}}$$

Solving for t_d is this expression 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

$$\frac{5.37 \times 10^4 \text{ s}}{t_d} = \ln\left(\frac{3.96 \times 10^8 \text{ s}^{1/2}}{\sqrt{t_d}}\right)$$

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 3400 s, which corresponds to t_d = 0.94 h.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

5.1FE *Atoms of which of the following elements will diffuse most rapidly in iron?*

(A) Mo	*(C) Cr*
(B) C	*(D) W*

<u>Solution</u>

The correct answer is B. Carbon atoms diffuse most rapidly because they are smaller than atoms of Mo, Cr, and W. Furthermore, diffusion of C in Fe is via an interstitial mechanism, whereas for Mo, Cr, and W the mechanism is vacancy diffusion.

5.2FE *Calculate the diffusion coefficient for copper in aluminum at 600°C. Preexponential and activation energy values for this system are* 6.5×10^{-5} *m²/s and 136,000 J/mol, respectively.*

(A) 5.7×10^{-2} m^2/s *(C)* 4.7×10^{-13} m^2/s

(B) 9.4×10^{-17} m^2/s *(D)* 3.9×10^{-2} m^2/s

Solution

We are asked to calculate the diffusion coefficient for Cu in Al at 600°C, given values for D_0 and Q_d. This determination is possible using Equation 5.8 as follows:

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

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

$$= 4.7 \times 10^{-13}\ \text{m}^2/\text{s}$$

Therefore, the correct answer is C.