CHAPTER 2

ATOMIC STRUCTURE AND INTERATOMIC BONDING

PROBLEM SOLUTIONS

Fundamental Concepts

Electrons in Atoms

2.1 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 The average atomic weight of silicon ($\overline{A}_{\text{Si}}$) is computed by adding fraction-of-occurrence/atomic weight products for the three isotopes. Thus

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

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

2.3 (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

$$\# \text{ g/amu } = \left(\frac{1 \text{ mol}}{6.023 \text{ x } 10^{23} \text{ atoms}}\right)\left(\frac{1 \text{ g/mol}}{1 \text{ amu/atom}}\right)$$

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

(b) Since there are 453.6 g/lb$_m$,

$$1 \text{ lb-mol } = (453.6 \text{ g/lb}_m)(6.023 \text{ x } 10^{23} \text{ atoms/g-mol})$$

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

2.4 (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.

2.5 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.

2.6 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 $32(-2)(-\frac{1}{2})$.

2.7 The electron configurations for the ions are determined using Table 2.2 (and Figure 2.6).

P^{5+}: $1s^2 2s^2 2p^6$

P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$

Sn^{4+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$

Se^{2-}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

I^-: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

Ni^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

2.8 The K^+ ion is just a potassium atom that has lost one electron; therefore, it has an electron configuration the same as argon (Figure 2.6).

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

The Periodic Table

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

2.10 From the periodic table (Figure 2.6) the element having atomic number 112 would belong to group IIB. According to Figure 2.6, 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.

2.11 (a) The $1s^22s^22p^63s^23p^5$ electron configuration is that of a halogen because it is one electron deficient from having a filled *p* subshell.

(b) The $1s^22s^22p^63s^23p^63d^74s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(c) The $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$ electron configuration is that of an inert gas because of filled 4*s* and 4*p* subshells.

(d) The $1s^22s^22p^63s^23p^64s^1$ electron configuration is that of an alkali metal because of a single *s* electron.

(e) The $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^55s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(f) The $1s^22s^22p^63s^2$ electron configuration is that of an alkaline earth metal because of two *s* electrons.

2.12 (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

2.13 The attractive force between two ions F_A is just the derivative with respect to the interatomic separation of the attractive energy expression, Equation 2.8, which is just

$$F_A = \frac{dE_A}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} = \frac{A}{r^2}$$

The constant A in this expression is defined in footnote 3. Since the valences of the Ca^{2+} and O^{2-} ions (Z_1 and Z_2) are both 2, then

$$F_A = \frac{(Z_1 e)(Z_2 e)}{4\pi\varepsilon_0 r^2}$$

$$= \frac{(2)(2)(1.6 \text{ x } 10^{-19} \text{ C})^2}{(4)(\pi)(8.85 \text{ x } 10^{-12} \text{ F/m})(1.25 \text{ x } 10^{-9} \text{ m})^2}$$

$$= 5.89 \text{ x } 10^{-10} \text{ N}$$

2.14 (a) Differentiation of Equation 2.11 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

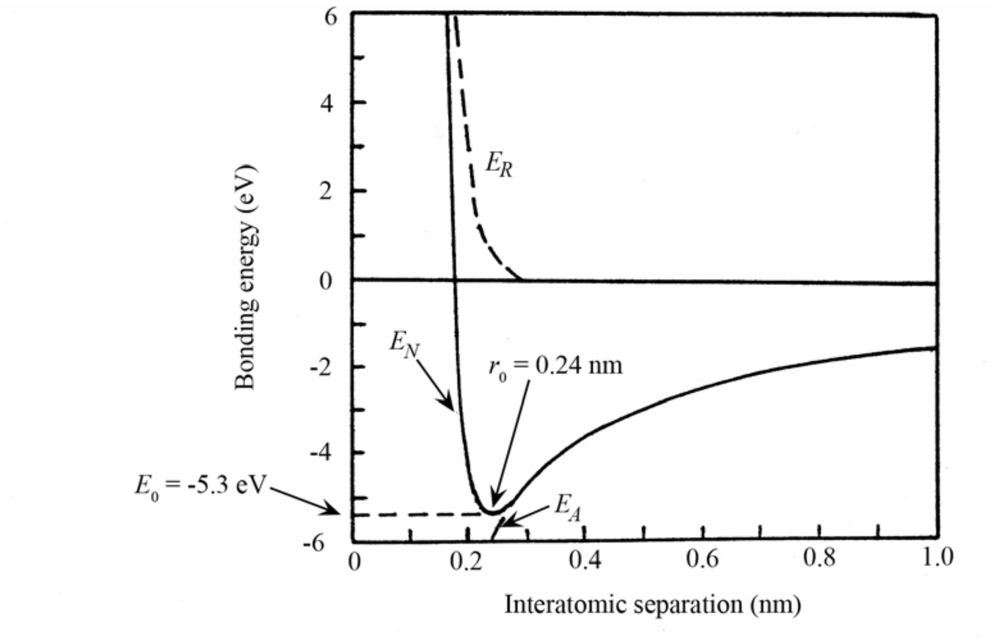
$$r_0 = \left(\frac{A}{nB}\right)^{1/(1\ -\ n)}$$

(c) Substitution for r_0 into Equation 2.11 and solving for E (= E_0)

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

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

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



(b) From this plot

$$r_0 = 0.24 \text{ nm}$$

$$E_0 = -5.3 \text{ eV}$$

(c) From Equation 2.11 for E_N

$$A = 1.436$$

$$B = 7.32 \text{ x } 10^{-6}$$

$$n = 8$$

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

$$E_0 = -\frac{1.436}{\left[\dfrac{1.436}{(8)\left(7.32\times10^{-6}\right)}\right]^{1/(1-8)}} + \frac{7.32\times10^{-6}}{\left[\dfrac{1.436}{(8)\left(7.32\times10^{-6}\right)}\right]^{8/(1-8)}}$$

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

2.16 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 2.8 and 2.9. 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 2.14, 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, these equations take the forms

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

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 2.8 and 2.9 become

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

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

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

2.17 (a) Differentiating Equation 2.12 with respect to *r* yields

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

$$= \frac{C}{r^2} - \frac{De^{-r/\rho}}{\rho}$$

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

$$\frac{C}{r_0^2} = \frac{De^{-(r_0/\rho)}}{\rho} \qquad (2.12b)$$

Solving for *C* and substitution into Equation 2.12 yields an expression for E_0 as

$$E_0 = De^{-(r_0/\rho)}\left(1 - \frac{r_0}{\rho}\right)$$

(b) Now solving for *D* from Equation 2.12b above yields

$$D = \frac{C\rho\, e^{(r_0/\rho)}}{r_0^2}$$

Substitution of this expression for *D* into Equation 2.12 yields an expression for E_0 as

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

Primary Interatomic Bonds

2.18 (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.

2.19 The percent ionic character is a function of the electron negativities of the ions X_A and X_B according to Equation 2.10. The electronegativities of the elements are found in Figure 2.7.

For MgO, X_{Mg} = 1.2 and X_{O} = 3.5, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(3.5-1.2)^2}\right] \times 100 = 73.4\%$$

For GaP, X_{Ga} = 1.6 and X_{P} = 2.1, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(2.1-1.6)^2}\right] \times 100 = 6.1\%$$

For CsF, X_{Cs} = 0.7 and X_{F} = 4.0, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(4.0-0.7)^2}\right] \times 100 = 93.4\%$$

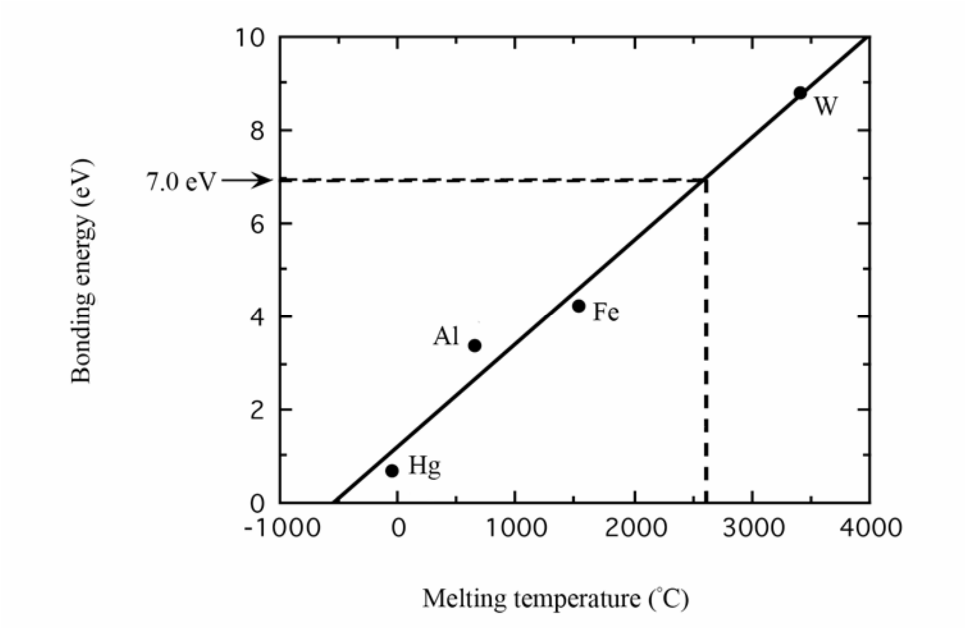
For CdS, X_{Cd} = 1.7 and X_{S} = 2.5, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(2.5-1.7)^2}\right] \times 100 = 14.8\%$$

For FeO, X_{Fe} = 1.8 and X_{O} = 3.5, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(3.5-1.8)^2}\right] \times 100 = 51.4\%$$

2.20 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 7.0 eV. The experimental value is 6.8 eV.



2.21 For silicon, having the valence electron structure $3s^2 3p^2$, N' = 4; thus, there are 8 – N' = 4 covalent bonds per atom.

For bromine, having the valence electron structure $4s^2 4p^5$, N' = 7; thus, there is 8 – N' = 1 covalent bond per atom.

For nitrogen, having the valence electron structure $2s^2 2p^3$, N' = 5; thus, there are 8 – N' = 3 covalent bonds per atom.

For sulfur, having the valence electron structure $3s^2 3p^4$, N' = 6; thus, there are 8 – N' = 2 covalent bonds per atom.

For neon, having the valence electron structure $2s^2 2p^6$, N' = 8; thus, there are 8 – N' = 0 covalent bonds per atom, which is what we would expect since neon is an inert gas.

2.22 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.

Secondary Bonding or van der Waals Bonding

2.23 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.

CHAPTER 3

THE STRUCTURE OF CRYSTALLINE SOLIDS

PROBLEM SOLUTIONS

Fundamental Concepts

3.1 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.

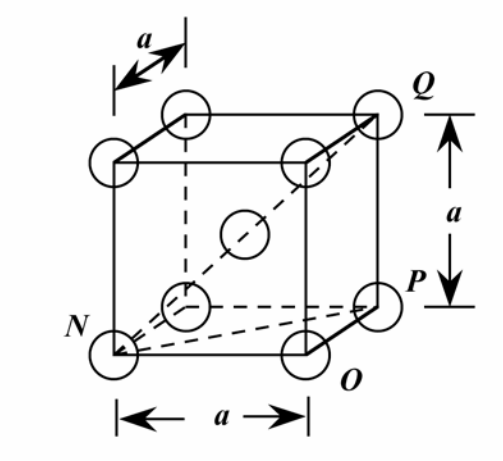
Unit Cells

Metallic Crystal Structures

3.2 For this problem, we are asked to calculate the volume of a unit cell of lead. Lead has an FCC crystal structure (Table 3.1). The FCC unit cell volume may be computed from Equation 3.4 as

$$V_C = 16R^3\sqrt{2} = (16)\left(0.175 \times 10^{-9}\text{ m}\right)^3\left(\sqrt{2}\right) = 1.213 \times 10^{-28}\text{ m}^3$$

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



Using the triangle *NOP*

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

And then for triangle *NPQ*,

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

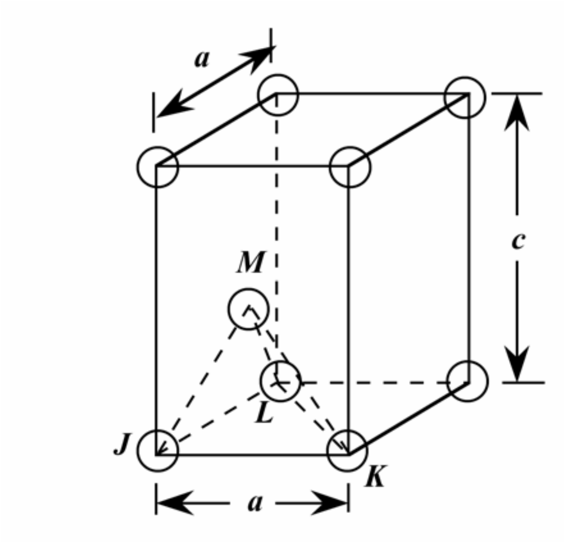
But $\overline{NQ} = 4R$, *R* being the atomic radius. Also, $\overline{QP} = a$. Therefore,

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

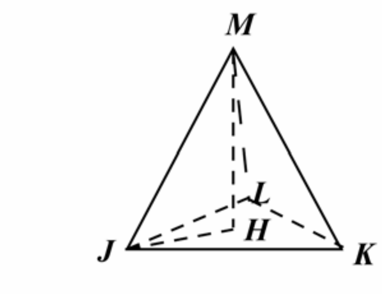
or

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

3.4 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



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,

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

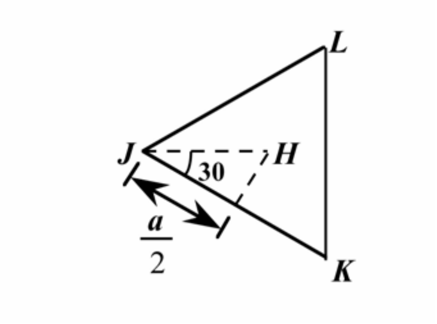
where *R* is the atomic radius. Furthermore, from triangle *JHM*,

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

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,



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

and

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

Substituting this value for $\overline{JH}$ in 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, solving for *c/a*

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

3.5 We are asked to show that the atomic packing factor for BCC is 0.68. The atomic packing factor is defined as the ratio of sphere volume to the total unit cell volume, or

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

Since 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 3.3, and

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

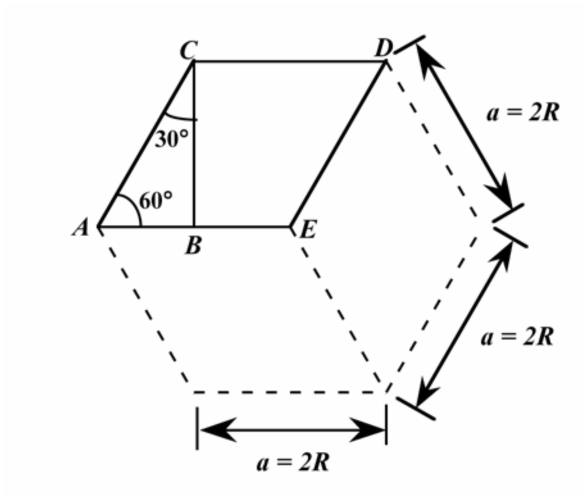
Thus,

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

3.6 This problem calls for a demonstration that the APF for HCP is 0.74. Again, the APF is just the total sphere volume-unit cell volume ratio. For HCP, there are the equivalent of six spheres per unit cell, and thus

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

Now, the unit cell volume is just the product of the base area times the cell height, *c*. This base area is just three times the area of the parallelepiped *ACDE* shown below.



The area of *ACDE* is just the length of $\overline{CD}$ times the height $\overline{BC}$. But $\overline{CD}$ is just *a* or 2*R*, and

$$\overline{BC} = 2R\cos(30°) = \frac{2R\sqrt{3}}{2}$$

Thus, the base area is just

$$\text{AREA} = (3)(\overline{CD})(\overline{BC}) = (3)(2R)\left(\frac{2R\sqrt{3}}{2}\right) = 6R^2\sqrt{3}$$

and since $c = 1.633a = 2R(1.633)$

$$V_C = (\text{AREA})(c) = 6R^2c\sqrt{3} = \left(6R^2\sqrt{3}\right)(2)(1.633)R = 12\sqrt{3}\,(1.633)\,R^3$$

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 This problem calls for a computation of the density of molybdenum. According to Equation 3.5

$$\rho = \frac{nA_{\mathrm{Mo}}}{V_C N_{\mathrm{A}}}$$

For BCC, n = 2 atoms/unit cell, and

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

Thus,

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

$$= \frac{\text{(2 atoms/unit cell)(95.94 g/mol)}}{\left[(4)\left(0.1363 \times 10^{-7}\ \text{cm}\right)^3/\sqrt{3}\right]^3/\text{(unit cell)}\left(6.023 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 10.21\ \text{g/cm}^3$$

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

3.8 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 3.4). Now,

$$\rho = \frac{nA_{\mathrm{Pd}}}{V_C N_{\mathrm{A}}}$$

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

And solving for R from the above expression yields

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

$$= \left[\frac{(4\ \text{atoms/unit cell})\,(106.4\ \text{g/mol})}{(16)(12.0\ \text{g/cm}^3)(6.023 \times 10^{23}\ \text{atoms/mol})(\sqrt{2})}\right]^{1/3}$$

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

3.9 This problem asks for us to calculate the radius of a tantalum atom. For BCC, n = 2 atoms/unit cell, and

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

Since, from Equation 3.5

$$\rho = \frac{nA_{\mathrm{Ta}}}{V_C N_{\mathrm{A}}}$$

$$= \frac{nA_{\mathrm{Ta}}}{\left(\dfrac{64R^3}{3\sqrt{3}}\right) N_{\mathrm{A}}}$$

and solving for R the previous equation

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

$$= \left[\frac{(3\sqrt{3})\,(2\text{ atoms/unit cell})\,(180.9\text{ g/mol})}{(64)\,(16.6\text{ g/cm}^3)(6.023\text{ x }10^{23}\text{ atoms/mol})}\right]^{1/3}$$

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

3.10 For the simple cubic crystal structure, the value of *n* in Equation 3.5 is unity since there is only a single atom associated with each unit cell. Furthermore, for the unit cell edge length, $a = 2R$ (Figure 3.23). Therefore, employment of Equation 3.5 yields

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

$$= \frac{\text{(1 atom/unit cell)(74.5 g/mol)}}{\left\{\left[(2)\left(1.45 \times 10^{-8}\ \text{cm}\right)\right]^3 /\text{(unit cell)}\right\}\left(6.023 \times 10^{23}\ \text{atoms/mol}\right)}$$

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

3.11 (a) The volume of the Ti unit cell may be computed using Equation 3.5 as

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

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

$$V_C = \frac{(6 \text{ atoms/unit cell})(47.9 \text{ g/mol})}{\left(4.51 \text{ g/cm}^3\right)\left(6.023 \text{ x } 10^{23} \text{ atoms/mol}\right)}$$

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

(b) From part of the solution to Problem 3.6, for HCP

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

But, since $a = 2R$, (i.e., $R = a/2$) then

$$V_C = 6\left(\frac{a}{2}\right)^2 c\sqrt{3} = \frac{3\sqrt{3}\,a^2c}{2}$$

but, since $c = 1.58a$

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

Now, solving for a

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

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

And finally

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

3.12 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 3.4). Also, $R = 0.143$ nm (1.43×10^{-8} cm) and $A_{\text{Al}} = 26.98$ g/mol. Employment of Equation 3.5 yields

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

$$= \frac{(4 \text{ atoms/unit cell})(26.98 \text{ g/mol})}{\left\{\left[(2)(1.43 \times 10^{-8} \text{ cm})(\sqrt{2})\right]^3/(\text{unit cell})\right\}(6.023 \times 10^{23} \text{ atoms/mol})}$$

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

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

Nickel also has an FCC crystal structure and therefore

$$\rho = \frac{(4 \text{ atoms/unit cell})(58.69 \text{ g/mol})}{\left\{\left[(2)(1.25 \times 10^{-8} \text{ cm})(\sqrt{2})\right]^3/(\text{unit cell})\right\}(6.023 \times 10^{23} \text{ atoms/mol})}$$

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

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

Magnesium has an HCP crystal structure, and from the solution to Problem 3.6,

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

and, since $c = 1.624a$ and $a = 2R = 2(1.60 \times 10^{-8} \text{ cm}) = 3.20 \times 10^{-8}$ cm

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

Also, there are 6 atoms/unit cell for HCP. Therefore the theoretical density is

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

$$= \frac{(6\text{ atoms/unit cell})(24.31\text{ g/mol})}{\left(1.38 \times 10^{-22}\text{ cm}^3\text{/unit cell}\right)\left(6.023 \times 10^{23}\text{ atoms/mol}\right)}$$

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

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

Tungsten has a BCC crystal structure for which $n = 2$ and $a = \frac{4R}{\sqrt{3}}$ (Equation 3.3); also $A_W = 183.85$ g/mol and $R = 0.137$ nm. Therefore, employment of Equation 3.5 leads to

$$\rho = \frac{(2\text{ atoms/unit cell})(183.85\text{ g/mol})}{\left\{\left[\frac{(4)\left(1.37 \times 10^{-8}\text{ cm}\right)}{\sqrt{3}}\right]^3 /(\text{unit cell})\right\}\left(6.023 \times 10^{23}\text{ atoms/mol}\right)}$$

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

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

3.13 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 2.6, its atomic weight is 92.91 g/mol. Thus, for FCC (employing Equation 3.5)

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

$$= \frac{(4 \text{ atoms/unit cell})(92.91 \text{ g/mol})}{\left\{\left[(2)(1.43 \times 10^{-8}\text{ cm})(\sqrt{2})\right]^3 /(\text{unit cell})\right\}(6.023 \times 10^{23}\text{ atoms/mol})}$$

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

For BCC, $n = 2$, and $a = \frac{4R}{\sqrt{3}}$ (Equation 3.3), thus

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

$$\rho = \frac{(2 \text{ atoms/unit cell})(92.91 \text{ g/mol})}{\left\{\left[\frac{(4)(1.43 \times 10^{-8}\text{ cm})}{\sqrt{3}}\right]^3 /(\text{unit cell})\right\}(6.023 \times 10^{23}\text{ atoms/mol})}$$

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

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

3.14 For each of these three alloys we need, by trial and error, to calculate the density using Equation 3.5, 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.

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

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

$$= \frac{(2\ \text{atoms/unit cell})(43.1\ \text{g/mol})}{\left\{\left[\frac{(4)(1.22 \times 10^{-8}\ \text{cm})}{\sqrt{3}}\right]^3 /(\text{unit cell})\right\}(6.023 \times 10^{23}\ \text{atoms/mol})}$$

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

Therefore, its crystal structure is BCC.

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

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

$$= \frac{(1\ \text{atom/unit cell})(184.4\ \text{g/mol})}{\left\{\left[(2)(1.46 \times 10^{-8}\ \text{cm})\right]^3 /(\text{unit cell})\right\}(6.023 \times 10^{23}\ \text{atoms/mol})}$$

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

Therefore, its crystal structure is simple cubic.

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

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

$$= \frac{\text{(2 atoms/unit cell)(91.6 g/mol)}}{\left\{\left[\frac{(4)(1.37 \times 10^{-8}\ \text{cm})}{\sqrt{3}}\right]^3 \text{/(unit cell)}\right\}(6.023 \times 10^{23}\ \text{atoms/mol})}$$

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

Therefore, its crystal structure is BCC.

3.15 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 Equation 3.5 as

$$n = \frac{\rho V_C N_\text{A}}{A_\text{U}}$$

$$= \frac{(19.05\ \text{g/cm}^3)(2.86)(5.87)(4.95)\left(\times\ 10^{-24}\ \text{cm}^3\right)\left(6.023\ \times\ 10^{23}\ \text{atoms/mol}\right)}{238.03\ \text{g/mol}}$$

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

Therefore

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

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

$$= 0.536$$

3.16 (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 3.5 as

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

$$= \frac{(4\ \text{atoms/unit cell})(114.82\ \text{g/mol})}{\left[\left(4.59 \times 10^{-8}\ \text{cm}\right)^2 \left(4.95 \times 10^{-8}\ \text{cm}\right)/\text{unit cell}\right]\left(6.023 \times 10^{23}\ \text{atoms/mol}\right)}$$

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

3. 17 (a) We are asked to calculate the unit cell volume for Be. For HCP, from the solution to Problem 3.6

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

But, $c = 1.568a$, and $a = 2R$, or $c = 3.14R$, and

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

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

(b) The theoretical density of Be is determined, using Equation 3.5, 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). Thus,

$$\rho = \frac{(6\ \text{atoms/unit cell})(9.01\ \text{g/mol})}{(4.87 \times 10^{-23}\ \text{cm}^3\text{/unit cell})(6.023 \times 10^{23}\ \text{atoms/mol})}$$

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

The value given in the literature is 1.85 g/cm^3.

3.18 This problem calls for us to compute the atomic radius for Mg. In order to do this we must use Equation 3.5, as well as the expression which relates the atomic radius to the unit cell volume for HCP; from Problem 3.6 it was shown that

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

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

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

And from Equation 3.5, the density is equal to

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

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

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

$$= \left[\frac{(6 \text{ atoms/unit cell})(24.31 \text{ g/mol})}{(1.624)(12\sqrt{3})(1.74 \text{ g/cm}^3)(6.023 \times 10^{23} \text{ atoms/mol})}\right]^{1/3}$$

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

3.19 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 a result of Problem 3.6, that is

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

The problem states that $c = 1.623a$, and $a = 2R$. Therefore

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

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

Crystal Systems

3.20 (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

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

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

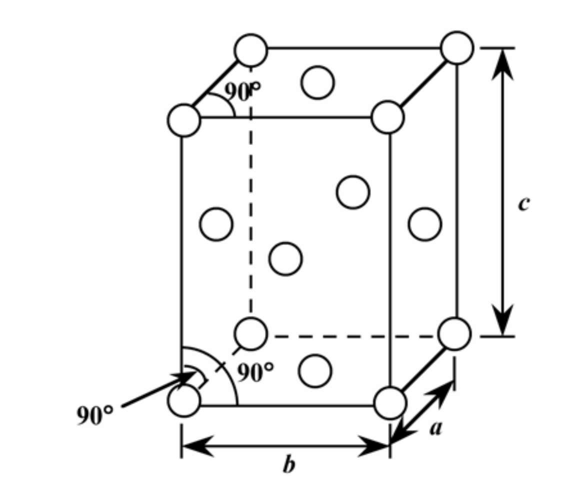
Thus, using Equation 3.5, the density is equal to

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

$$= \frac{(2\ \text{atoms/unit cell})(141\ \text{g/mol})}{(5.51 \times 10^{-23}\ \text{cm}^3/\text{unit cell})(6.023 \times 10^{23}\ \text{atoms/mol})}$$

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

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



Point Coordinates

3.22 This problem asks that we list the point coordinates for all of the atoms that are associated with the FCC unit cell. From Figure 3.1b, the atom located of the origin of the unit cell has the coordinates 000. Coordinates for other atoms in the bottom face are 100, 110, 010, and $\frac{1}{2}\frac{1}{2}0$. (The *z* coordinate for all these points is zero.)

For the top unit cell face, the coordinates are 001, 101, 111, 011, and $\frac{1}{2}\frac{1}{2}1$. (These coordinates are the same as bottom-face coordinates except that the "0" *z* coordinate has been replaced by a "1".)

Coordinates for those atoms that are positioned at the centers of both side faces, and centers of both front and back faces need to be specified. For the front and back-center face atoms, the coordinates are $1\frac{1}{2}\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$, respectively. While for the left and right side center-face atoms, the respective coordinates are $\frac{1}{2}0\frac{1}{2}$ and $\frac{1}{2}1\frac{1}{2}$.

3.23 Here we are asked list point coordinates for both sodium and chlorine ions for a unit cell of the sodium chloride crystal structure, which is shown in Figure 12.2.

In Figure 12.2, the chlorine ions are situated at all corners and face-centered positions. Therefore, point coordinates for these ions are the same as for FCC, as presented in the previous problem—that is, 000, 100, 110, 010, 001, 101, 111, 011, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}1$, $1\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}1\frac{1}{2}$.

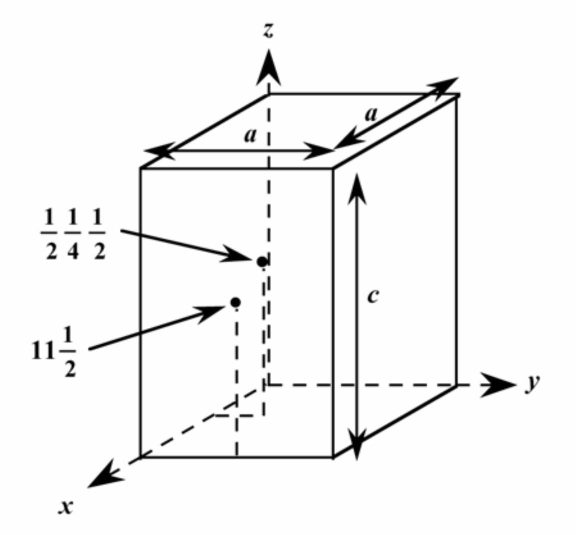
Furthermore, the sodium ions are situated at the centers of all unit cell edges, and, in addition, at the unit cell center. For the bottom face of the unit cell, the point coordinates are as follows: $\frac{1}{2}00$, $1\frac{1}{2}0$, $\frac{1}{2}10$, $0\frac{1}{2}0$. While, for the horizontal plane that passes through the center of the unit cell (which includes the ion at the unit cell center), the coordinates are $00\frac{1}{2}$, $1\,0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $1\,1\frac{1}{2}$, and $01\frac{1}{2}$. And for the four ions on the top face $\frac{1}{2}01$, $1\,\frac{1}{2}1$, $\frac{1}{2}1\,1$, and $0\frac{1}{2}1$.

3.24 This problem calls for us to list the point coordinates of both the zinc and sulfur atoms for a unit cell of the zinc blende structure, which is shown in Figure 12.4.

First of all, the sulfur atoms occupy the face-centered positions in the unit cell, which from the solution to Problem 3.22, are as follows: 000, 100, 110, 010, 001, 101, 111, 011, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}1$, $1\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}1\frac{1}{2}$.

Now, using an *x*-*y*-*z* coordinate system oriented as in Figure 3.4, the coordinates of the zinc atom that lies toward the lower-left-front of the unit cell has the coordinates $\frac{3}{4}\frac{1}{4}\frac{1}{4}$, whereas the atom situated toward the lower-right-back of the unit cell has coordinates of $\frac{1}{4}\frac{3}{4}\frac{1}{4}$. Also, the zinc atom that resides toward the upper-left-back of the unit cell has the $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ coordinates. And, the coordinates of the final zinc atom, located toward the upper-right-front of the unit cell, are $\frac{3}{4}\frac{3}{4}\frac{3}{4}$.

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



3.26 First of all, open the "Molecular 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 "Atom Size" 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" button, followed by clicking on the "Go to Step 2" button.

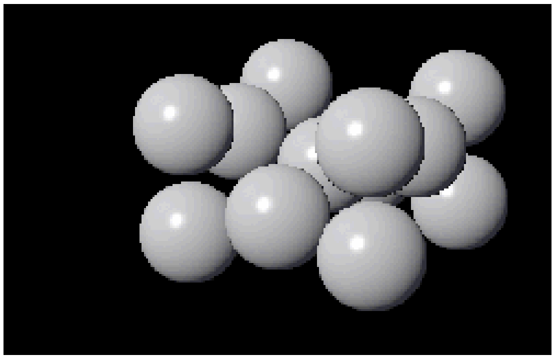
In the "Step 2" window we specify positions for all of the atoms within the unit cell; their point coordinates are specified in the problem statement. Now we must enter a name in the box provided for each of the atoms in the unit cell. For example, let us name the first atom "Sn1". Its point coordinates are 000, and, therefore, we enter a "0" (zero) in each of the "x", "y", and "z" atom position boxes. Next, in the "Atom Type" pull-down menu we select "Sn", our only choice, and the name we specified in Step 1. For the next atom, which has point coordinates of 100, let us name it "Sn2"; since it 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 is the value of *a* given in the problem statement); zeros are entered in each of the "y" and "z" position boxes. We next click on the "Register" button. 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
0.583, 0, and 0
0.583, 0.583, and 0
0, 0.583, and 0
0, 0, and 0.318
0.583, 0, and 0.318
0.583, 0.583, and 0.318
0, 0.583, and 0.318
0.2915, 0, and 0.2385
0.2915, 0.583, and 0.2385
0.583, 0.2915, and 0.0795
0, 0.2915, 0.0795
0.2915, 0.2915, and 0.159

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 solid, single dashed, double, and triple are possibilities), or we may elect to not represent any bonds at all (in which case we click on the "Go to Step 4" button). If it is decided to show bonds, probably the best thing to do is to represent unit cell edges as bonds.

The window in Step 4 presents all the data that have been entered; you may review these data for accuracy. If any changes are required, it is necessary to close out all windows back to the one in which corrections are to be made, and then reenter data in succeeding windows. When you are fully satisfied with your data, click on the "Generate" button, and the image that you have defined will be displayed. The image may then be rotated by using mouse click-and-drag.

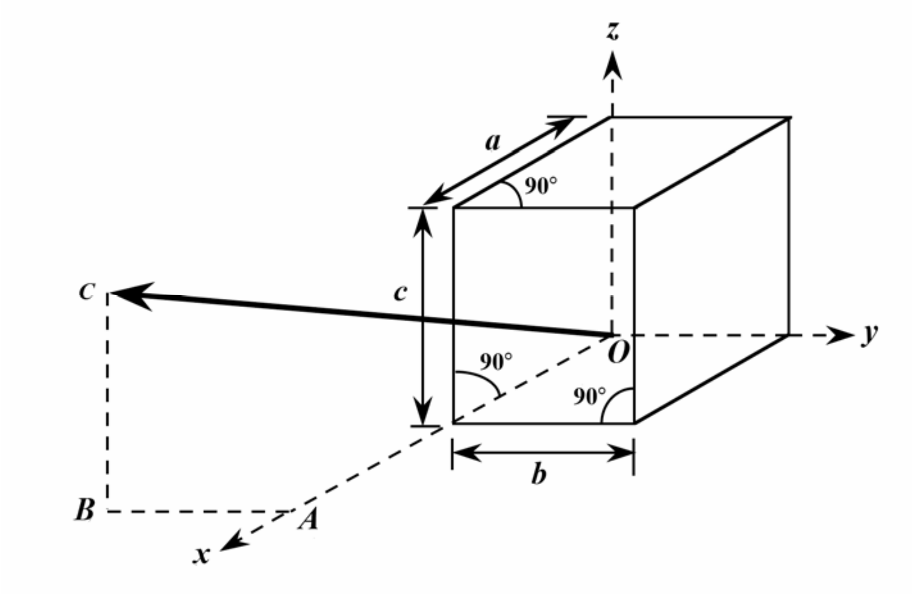
Your image should appear as



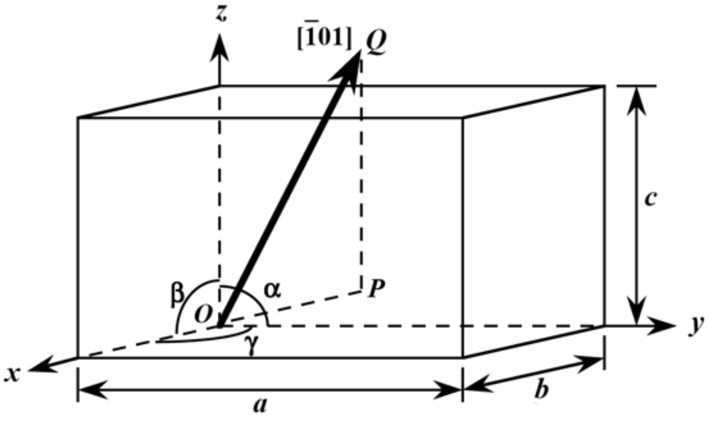
[Note: Unfortunately, with this version of the Molecular Definition Utility, it is not possible to save either the data or the image that you have generated. You may use screen capture (or screen shot) software to record and store your image.]

Crystallographic Directions

3.27 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. We first move along the +*x*-axis 2*a* 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.



3.28 This problem asks that a $[\bar{1}01]$ direction be drawn within a monoclinic unit cell ($a \neq b \neq c$, and $\alpha = \beta = 90° \neq \gamma$). One such unit cell with its origin at point *O* is sketched below. For this direction, we 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 index is a one, 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.



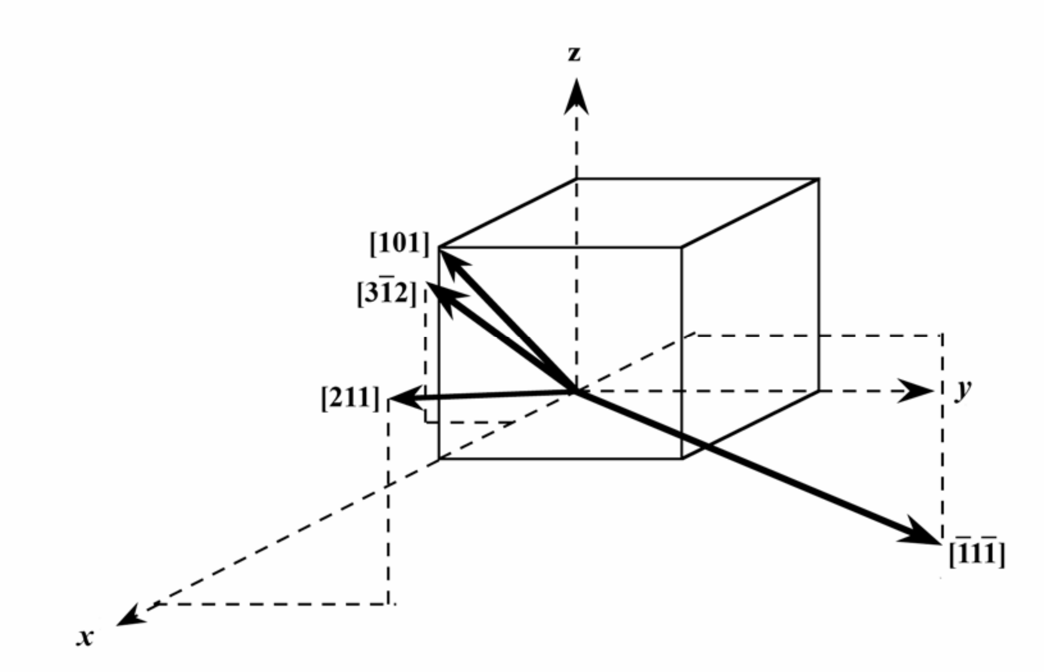
3.29 We are asked for the indices of the two directions sketched in the figure. For direction 1, the projection on the x-axis is a, while projections on the y- and z-axes are $-b/2$ and $-c$, respectively. This is a $[2\bar{1}\bar{2}]$ direction as indicated in the summary below.

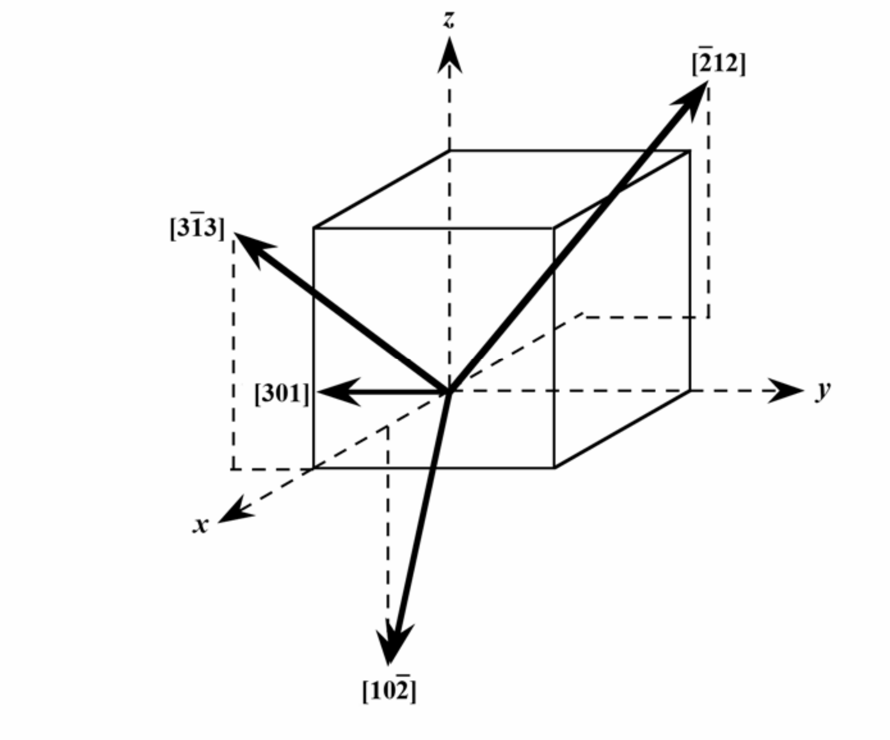
	$\underline{x}$	$\underline{y}$	$\underline{z}$
Projections	a	$-b/2$	$-c$
Projections in terms of a, b, and c	1	-1/2	-1
Reduction to integers	2	-1	-2
Enclosure		$[2\bar{1}\bar{2}]$	

Direction 2 is [102] as summarized below.

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Projections	$a/2$	$0b$	c
Projections in terms of a, b, and c	1/2	0	1
Reduction to integers	1	0	2
Enclosure		[102]	

3.30 The directions asked for are indicated in the cubic unit cells shown below.





3.31 Direction A is a $[\bar{1}10]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$-a$	b	$0c$
Projections in terms of a, b, and c	–1	1	0
Reduction to integers		not necessary	
Enclosure		$[\bar{1}10]$	

Direction B is a [121] direction, which determination is summarized as follows. The vector passes through the origin of the coordinate system and thus no translation is necessary. Therefore,

	x	y	z
Projections	$\frac{a}{2}$	b	$\frac{c}{2}$
Projections in terms of a, b, and c	$\frac{1}{2}$	1	$\frac{1}{2}$
Reduction to integers	1	2	1
Enclosure		[121]	

Direction C is a $[0\bar{1}\bar{2}]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$0a$	$-\frac{b}{2}$	$-c$
Projections in terms of a, b, and c	0	$-\frac{1}{2}$	–1
Reduction to integers	0	–1	–2
Enclosure		$[0\bar{1}\bar{2}]$	

Direction D is a $[1\bar{2}1]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$\frac{a}{2}$	$-b$	$\frac{c}{2}$
Projections in terms of a, b, and c	$\frac{1}{2}$	–1	$\frac{1}{2}$
Reduction to integers	1	–2	1
Enclosure		$[1\bar{2}1]$	

3.32 Direction A is a $[33\bar{1}]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	a	b	$-\frac{c}{3}$
Projections in terms of a, b, and c	1	1	$-\frac{1}{3}$
Reduction to integers	3	3	–1
Enclosure		$[33\bar{1}]$	

Direction B is a $[\bar{4}0\bar{3}]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$-\frac{2a}{3}$	$0b$	$-\frac{c}{2}$
Projections in terms of a, b, and c	$-\frac{2}{3}$	0	$-\frac{1}{2}$
Reduction to integers	–4	0	–3
Enclosure		$[\bar{4}0\bar{3}]$	

Direction C is a $[\bar{3}61]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$-\frac{a}{2}$	b	$\frac{c}{6}$
Projections in terms of a, b, and c	$-\frac{1}{2}$	1	$\frac{1}{6}$
Reduction to integers	–3	6	1
Enclosure		$[\bar{3}61]$	

Direction D is a $[\bar{1}1\bar{1}]$ direction, which determination is summarized as follows. We first of all position the origin of the coordinate system at the tail of the direction vector; then in terms of this new coordinate system

	x	y	z
Projections	$-\frac{a}{2}$	$\frac{b}{2}$	$-\frac{c}{2}$
Projections in terms of a, b, and c	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
Reduction to integers	–1	1	–1
Enclosure		$[\bar{1}1\bar{1}]$	

3.33 For tetragonal crystals $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$; therefore, projections along the x and y axes are equivalent, which are not equivalent to projections along the z axis.

(a) Therefore, for the [011] direction, equivalent directions are the following: [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) Also, for the [100] direction, equivalent directions are the following: $[\bar{1}00]$, [010], and $[0\bar{1}0]$.

3.34 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 3.6

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

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

$$w = w' = 0$$

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 $[00\overline{1}]$, $u' = 0$, $v' = 0$, and $w' = -1$; therefore,

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

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

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

$$w = -1$$

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

3.35 This problem asks for the determination of indices for several directions in a hexagonal unit cell.

For direction A, projections on the a_1, a_2, and z axes are $-a$, $-a$, and c, or, in terms of a and c the projections are –1, –1, and 1. This means that

$u' = -1$

$v' = -1$

$w' = 1$

Now, from Equations 3.6, the u, v, t, and w indices become

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}\left[(2)(-1) - (-1)\right] = -\frac{1}{3}$$

$$v = \frac{1}{3}(2v\tilde{O} - u\tilde{O}) = \frac{1}{3}\left[(2)(-1) - (-1)\right] = -\frac{1}{3}$$

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

$$w = w' = 1$$

Now, in order to get the lowest set of integers, it is necessary to multiply all indices by the factor 3, with the result that the direction A is a $[\overline{1}\,\overline{1}23]$ direction.

For direction B, projections on the a_1, a_2, and z axes are $-a$, $0a$, and $0c$, or, in terms of a and c the projections are –1, 0, and 0. This means that

$u' = -1$

$v' = 0$

$w' = 0$

Now, from Equations 3.6, the u, v, t, and w indices become

$$u = \frac{1}{3}(2u' - v) = \frac{1}{3}\left[(2)(-1) - 0\right] = -\frac{2}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}\left[(2)(0) - (-1)\right] = \frac{1}{3}$$

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

$$w = w' = 0$$

Now, in order to get the lowest set of integers, it is necessary to multiply all indices by the factor 3, with the result that the direction B is a $[\bar{2}110]$ direction.

For direction C projections on the a_1, a_2, and z axes are a, $a/2$, and $0c$, or, in terms of a and c the projections are 1, 1/2, and 0, which when multiplied by the factor 2 become the smallest set of integers: 2, 1, and 0. This means that

$u' = 2$

$v' = 1$

$w' = 0$

Now, from Equations 3.6, the u, v, t, and w indices become

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}\left[(2)(2) - 1\right] = \frac{3}{3} = 1$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}\left[(2)(1) - 2\right] = 0$$

$$t = -(u+v) = -\left(1 - 0\right) = -1$$

$$w = w' = 0$$

No reduction is necessary inasmuch as all the indices are integers. Therefore, direction C is a $[10\bar{1}0]$.

For direction D projections on the a_1, a_2, and z axes are a, $0a$, and $c/2$, or, in terms of a and c the projections are 1, 0, and 1/2, which when multiplied by the factor 2 become the smallest set of integers: 2, 0, and 1. This means that

$u' = 2$

$v' = 0$

$w' = 1$

Now, from Equations 3.6, the u, v, t, and w indices become

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}\left[(2)(2) - 0\right] = \frac{4}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}\left[(2)(0) - (2)\right] = -\frac{2}{3}$$

3.36 This problem asks for us to derive expressions for each of the three primed indices in terms of the four unprimed indices.

It is first necessary to do an expansion of Equation 3.6a 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 3.6b gives

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}\left[(2)(2u' - 3u) - u'\right] = u' - 2u$$

Or

$$u' = v + 2u$$

And, solving for *v* from Equation 3.6c 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 3.6c gives

$$u = -v - t$$

which, when substituted in the previous equation results in the following expression for v'

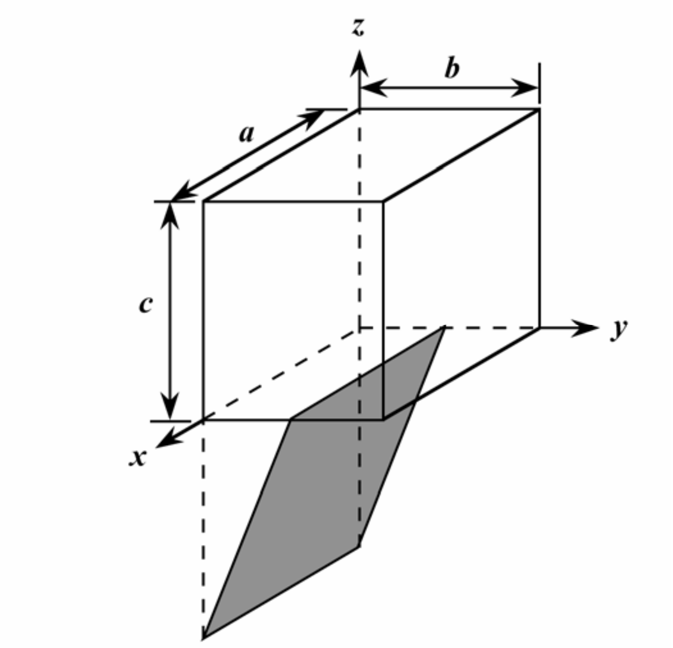
$$v' = -u - 2t = -(-v - t) - 2t = v - t$$

And, of course from Equation 3.6d

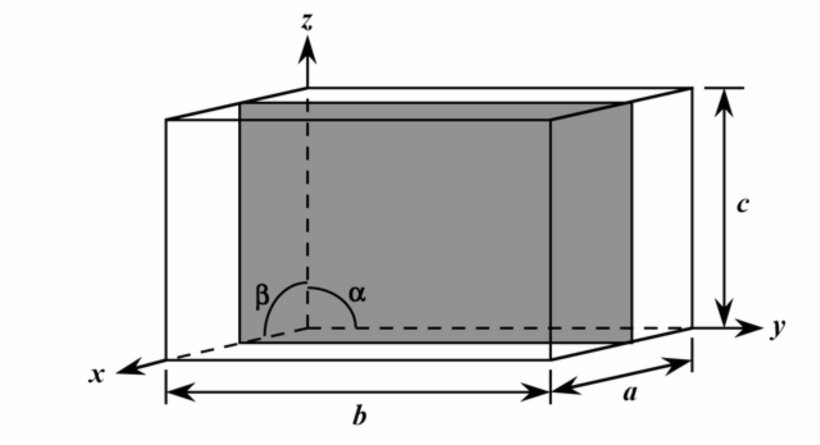
$$w' = w$$

Crystallographic Planes

3.37 (a) We are asked to draw a $(02\overline{1})$ plane within an orthorhombic unit cell. First remove the three indices from the parentheses, and take their reciprocals--i.e., ∞, 1/2, and -1. This means that the plane parallels the *x*-axis, intersects the *y*-axis at *b*/2, and intersects the *z*-axis at -*c*. The plane that satisfies these requirements has been drawn within the orthorhombic unit cell below. (For orthorhombic, $a \neq b \neq c$, and $\alpha = \beta = \gamma = 90°$.)



(b) A (200) plane is drawn within the monoclinic cell shown below. We first remove the parentheses and take the reciprocals of the indices; this gives 1/2, ∞, and ∞,. Thus, the (200) plane parallels both *y*- and *z*-axes, and intercepts the *x*-axis at *a*/2, as indicated in the drawing. (For monoclinic, $a \neq b \neq c$, and $\alpha = \gamma = 90° \neq \beta$.)



3.38 This problem calls for specification of the indices for the two planes that are drawn in the sketch.

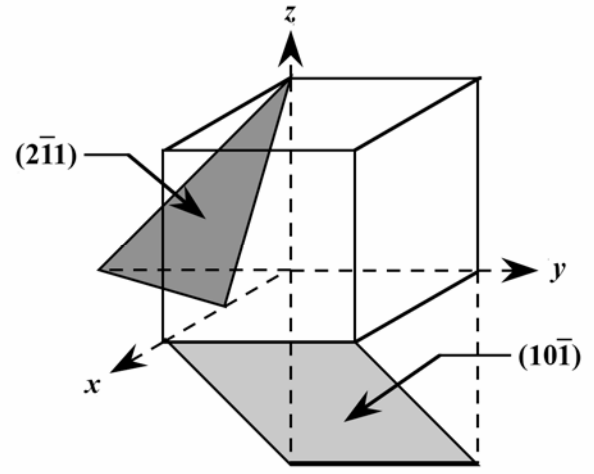
Plane 1 is a (211) plane. The determination of its indices is summarized below.

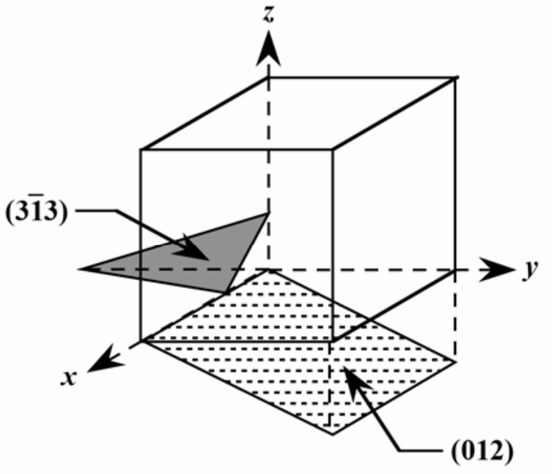
	x	y	z
Intercepts	*a*/2	*b*	*c*
Intercepts in terms of *a*, *b*, and *c*	1/2	1	1
Reciprocals of intercepts	2	1	1
Enclosure		(211)	

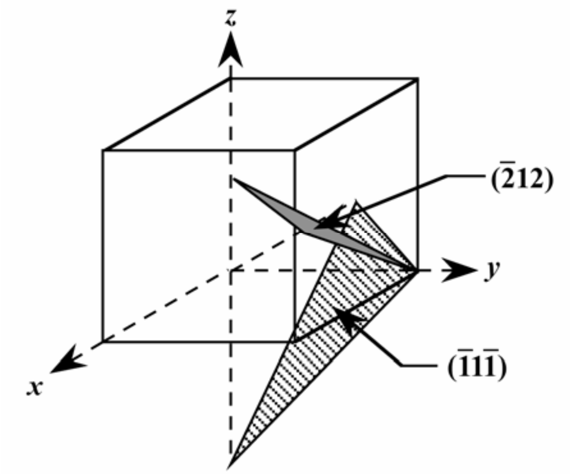
Plane 2 is a $(0\overline{2}0)$ plane, as summarized below.

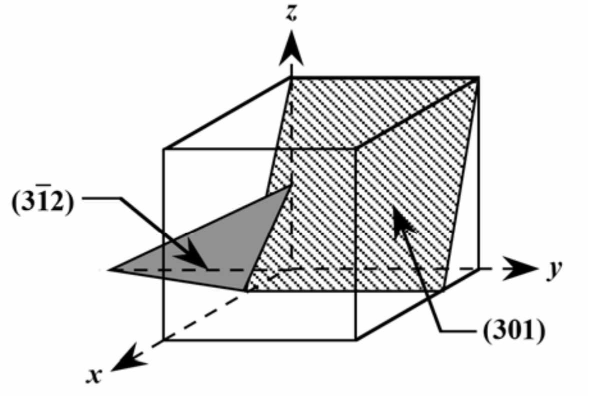
	x	y	z
Intercepts	∞*a*	-*b*/2	∞*c*
Intercepts in terms of *a*, *b*, and *c*	∞	-1/2	∞
Reciprocals of intercepts	0	-2	0
Enclosure		$(0\overline{2}0)$	

3.39 The planes called for are plotted in the cubic unit cells shown below.









3.40 For plane A we will leave the origin at the unit cell as shown. If we extend this plane back into the plane of the page, then it is a $(11\bar{1})$ plane, as summarized below.

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Intercepts	a	b	$-c$
Intercepts in terms of a, b, and c	1	1	-1
Reciprocals of intercepts	1	1	-1
Reduction		not necessary	
Enclosure		$(11\bar{1})$	

[*Note:* If we move the origin one unit cell distance parallel to the x axis and then one unit cell distance parallel to the y axis, the direction becomes $(\bar{1}\bar{1}1)$].

For plane B we will leave the origin of the unit cell as shown; this is a (230) plane, as summarized below.

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Intercepts	$\frac{a}{2}$	$\frac{b}{3}$	∞c
Intercepts in terms of a, b, and c	$\frac{1}{2}$	$\frac{1}{3}$	∞
Reciprocals of intercepts	2	3	0
Enclosure		(230)	

3.41 For plane A we will move the origin of the coordinate system one unit cell distance to the right along the *y* axis; thus, this is a $(1\bar{1}0)$ plane, as summarized below.

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Intercepts	$\frac{a}{2}$	$-\frac{b}{2}$	$\infty\, c$
Intercepts in terms of *a*, *b*, and *c*	$\frac{1}{2}$	$-\frac{1}{2}$	∞
Reciprocals of intercepts	2	– 2	0
Reduction	1	– 1	0
Enclosure		$(1\bar{1}0)$	

For plane B we will leave the origin of the unit cell as shown; thus, this is a (122) plane, as summarized below.

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Intercepts	*a*	$\frac{b}{2}$	$\frac{c}{2}$
Intercepts in terms of *a*, *b*, and *c*	1	$\frac{1}{2}$	$\frac{1}{2}$
Reciprocals of intercepts	1	2	2
Reduction		not necessary	
Enclosure		(122)	

$$t = -(u+v) = -\left(\frac{4}{3} - \frac{2}{3}\right) = -\frac{2}{3}$$

$$w = w' = 1$$

Now, in order to get the lowest set of integers, it is necessary to multiply all indices by the factor 3, with the result that the direction D is a $[4\bar{2}\bar{2}3]$ direction.

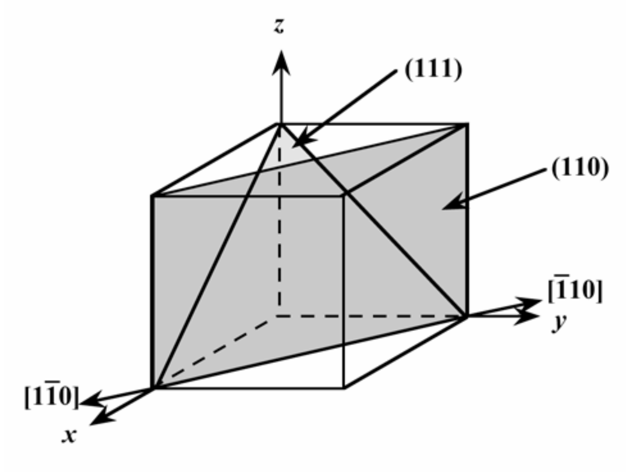
3.42 For plane A since the plane passes through the origin of the coordinate system as shown, we will move the origin of the coordinate system one unit cell distance vertically along the z axis; thus, this is a $(21\overline{1})$ plane, as summarized below.

	x	y	z
Intercepts	$\frac{a}{2}$	b	$-c$
Intercepts in terms of a, b, and c	$\frac{1}{2}$	1	– 1
Reciprocals of intercepts	2	1	– 1
Reduction		not necessary	
Enclosure		$(21\overline{1})$	

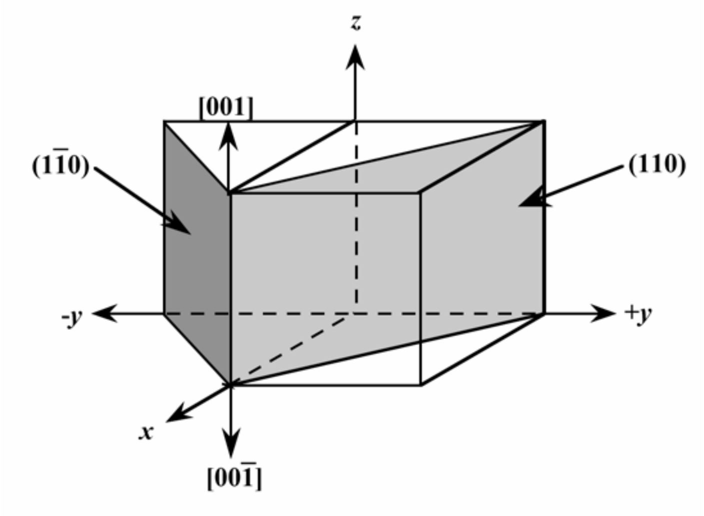
For plane B, since the plane passes through the origin of the coordinate system as shown, we will move the origin one unit cell distance vertically along the z axis; this is a $(02\overline{1})$ plane, as summarized below.

	x	y	z
Intercepts	$\infty\, a$	$\frac{b}{2}$	$-c$
Intercepts in terms of a, b, and c	∞	$\frac{1}{2}$	– 1
Reciprocals of intercepts	0	2	– 1
Reduction		not necessary	
Enclosure		$(02\overline{1})$	

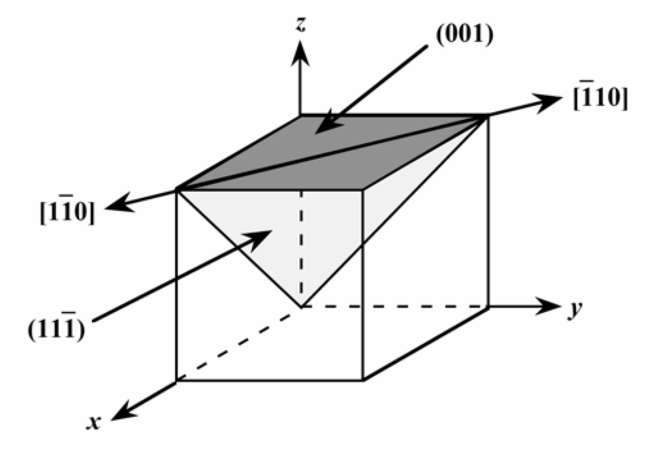
3.43 (a) In the figure below is shown (110) and (111) planes, and, as indicated, their intersection results in a $[\overline{1}10]$, or equivalently, a $[1\overline{1}0]$ direction.



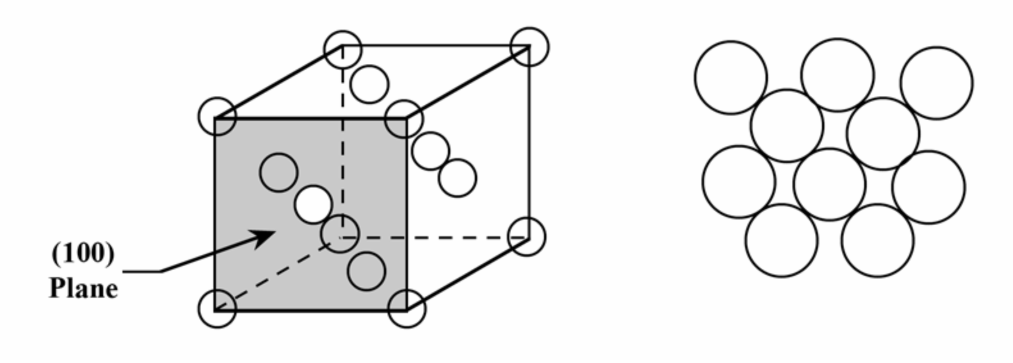
(b) In the figure below is shown (110) and $(1\overline{1}0)$ planes, and, as indicated, their intersection results in a [001], or equivalently, a $[00\overline{1}]$ direction.



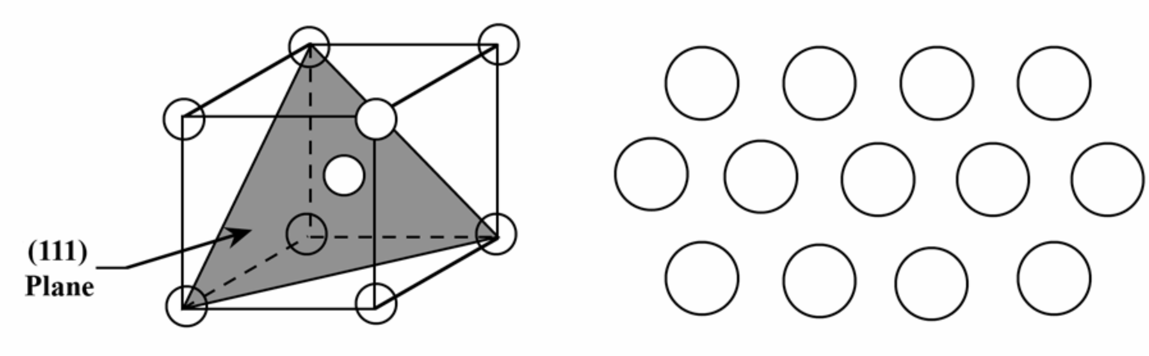
(c) In the figure below is shown $(11\overline{1})$ and (001) planes, and, as indicated, their intersection results in a $[\overline{1}10]$, or equivalently, a $[1\overline{1}0]$ direction.


z
(001)
[$\bar{1}$10]
[1$\bar{1}$0]
(11$\bar{1}$)
y
x

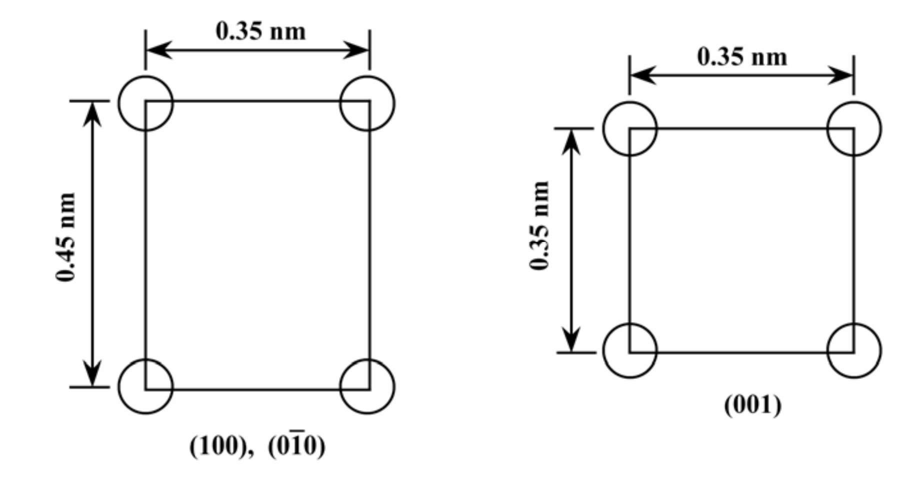
3.44 (a) The atomic packing of the (100) plane for the FCC crystal structure is called for. An FCC unit cell, its (100) plane, and the atomic packing of this plane are indicated below.



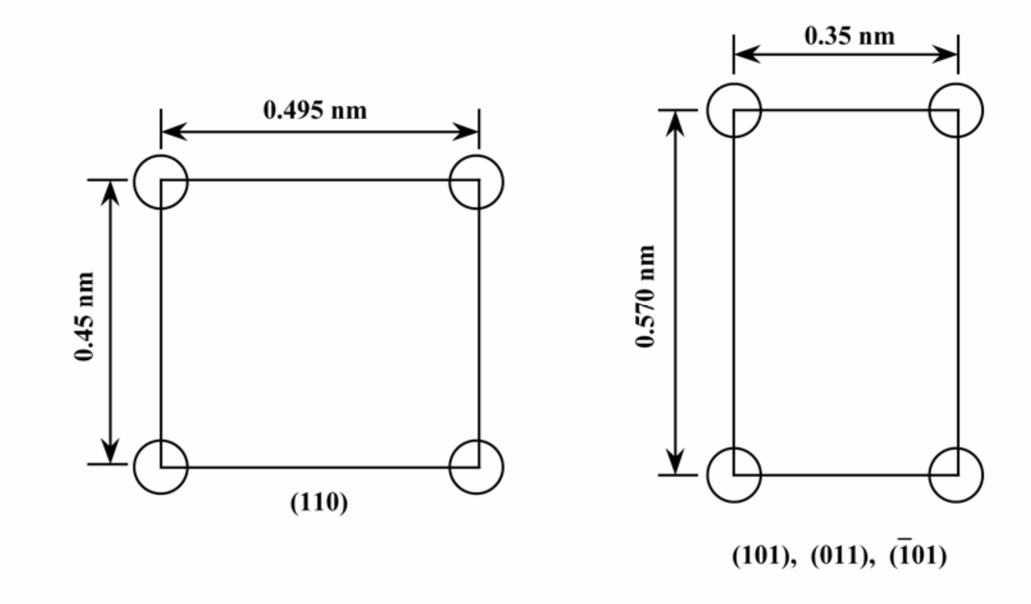
(b) For this part of the problem we are to show the atomic packing of the (111) plane for the BCC crystal structure. A BCC unit cell, its (111) plane, and the atomic packing of this plane are indicated below.



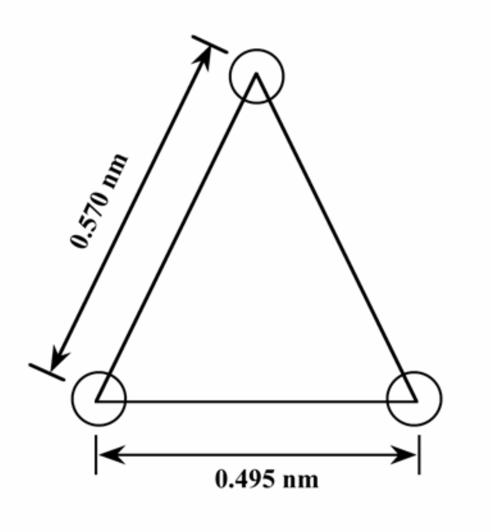
3.45 (a) The unit cell in Problem 3.20 is body-centered tetragonal. Of the three planes given in the problem statement the (100) and $(0\bar{1}0)$ are equivalent—that is, have the same atomic packing. The atomic packing for these two planes as well as the (001) are shown in the figure below.



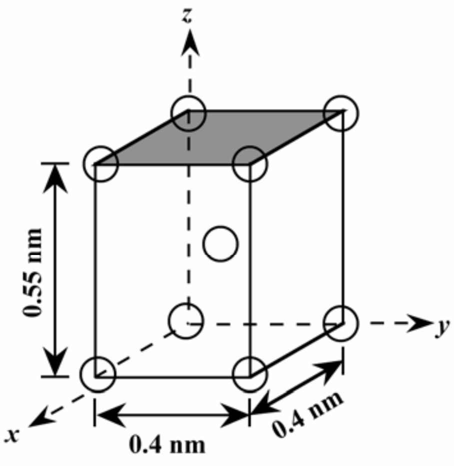
(b) Of the four planes cited in the problem statement, only (101), (011), and $(\bar{1}01)$ are equivalent—have the same atomic packing. The atomic arrangement of these planes as well as the (110) are presented in the figure below. *Note:* the 0.495 nm dimension for the (110) plane comes from the relationship $\left[(0.35 \text{ nm})^2 + (0.35 \text{ nm})^2\right]^{1/2}$. Likewise, the 0.570 nm dimension for the (101), (011), and $(\bar{1}01)$ planes comes from $\left[(0.35 \text{ nm})^2 + (0.45 \text{ nm})^2\right]^{1/2}$.



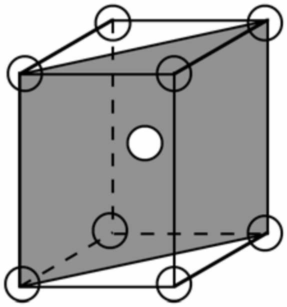
(c) All of the (111), $(1\bar{1}1)$, $(11\bar{1})$, and $(\bar{1}1\bar{1})$ planes are equivalent, that is, have the same atomic packing as illustrated in the following figure:



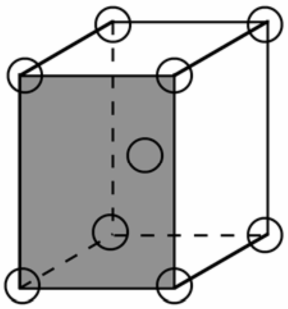
3.46 Unit cells are constructed below from the three crystallographic planes provided in the problem statement.



(001)



(110)

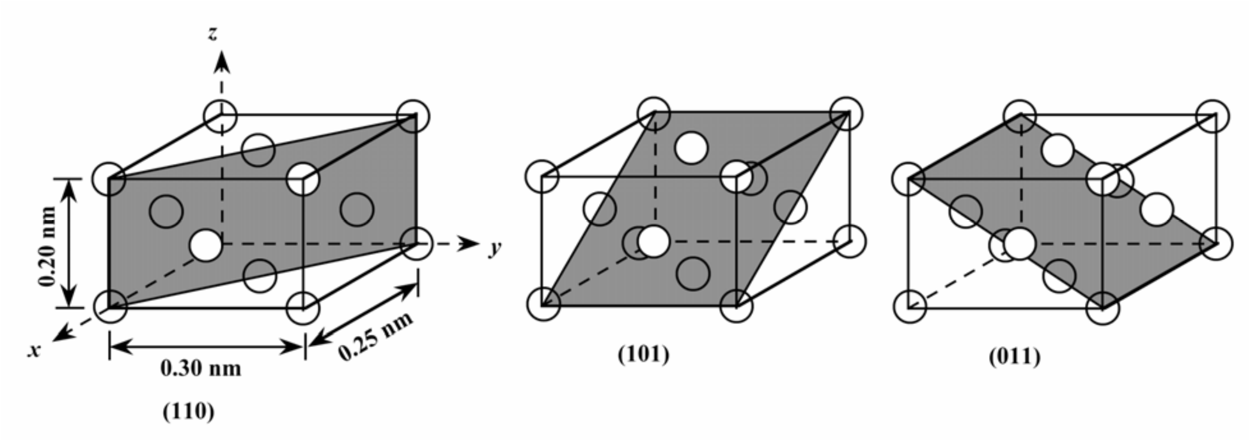


(100)

(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.

3.47 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 Equation 3.5, with n = 4; thus

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

$$= \frac{(18.91 \text{ g/cm}^3)\ (2.0)(2.5)(3.0)\ (\times\ 10^{-24}\ \text{cm}^3\text{/unit cell})(6.023\ \times\ 10^{23}\ \text{atoms/mol})}{4 \text{ atoms/unit cell}}$$

$$= 42.7 \text{ g/mol}$$

3.48 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 3.7, 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 3.7 leads to

$$i = -(h + k) = -[0 + (-1)] = 1$$

such that $(0\bar{1}2)$ becomes $(0\bar{1}12)$.

3.49 This problem asks for the determination of Bravais-Miller indices for several planes in hexagonal unit cells.

(a) For this plane, intersections with the a_1, a_2, and z axes are ∞a, $-a$, and ∞c (the plane parallels both a_1 and z axes). In terms of a and c these intersections are ∞, -1, and ∞, the respective reciprocals of which are 0, -1, and 0. This means that

$h = 0$

$k = -1$

$l = 0$

Now, from Equation 3.7, 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 the a_1, a_2, and z axes are $-a$, $-a$, and $c/2$, respectively. In terms of a and c these intersections are -1, -1, and 1/2, the respective reciprocals of which are -1, -1, and 2. This means that

$h = -1$

$k = -1$

$l = 2$

Now, from Equation 3.7, 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 the a_1, a_2, and z axes are $a/2$, $-a$, and ∞c (the plane parallels the z axis). In terms of a and c these intersections are 1/2, -1, and ∞, the respective reciprocals of which are 2, -1, and 0. This means that

$h = 2$

$k = -1$

$l = 0$

Now, from Equation 3.7, 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 the a_1, a_2, and z axes are $-a$, a, and $c/2$, respectively. In terms of a and c these intersections are –1, 1, and 1/2, the respective reciprocals of which are –1, 1, and 2. This means that

$h = -1$

$k = 1$

$l = 2$

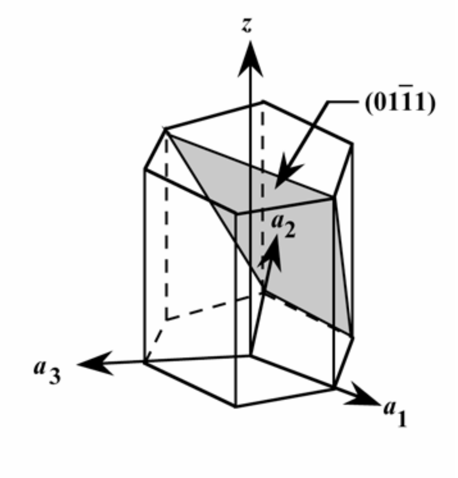
Now, from Equation 3.7, the value of i is

$$i = -(h + k) = -(-1 + 1) = 0$$

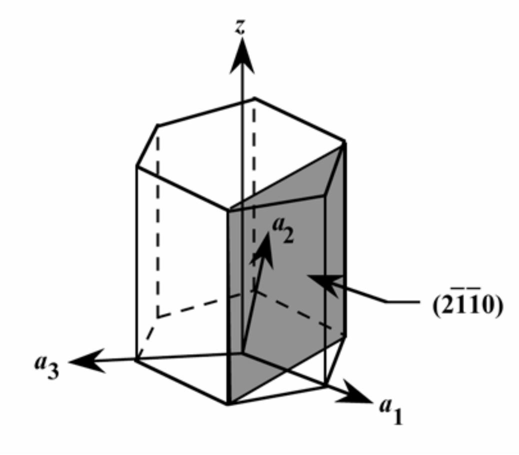
Therefore, this is a $(\bar{1}102)$ plane.

3.50 This problem asks that we draw $(01\bar{1}1)$ and $(2\bar{1}\bar{1}0)$ planes within hexagonal unit cells.

For $(01\bar{1}1)$ the reciprocals of *h*, *k*, *i*, and *l* are, respectively, ∞, 1, –1, and 1; thus, 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

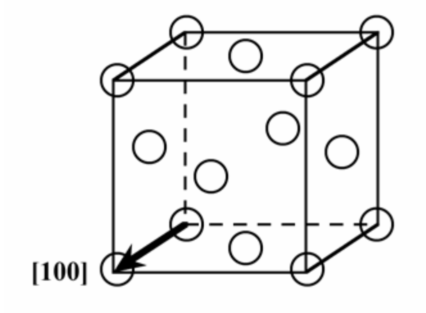


For $(2\bar{1}\bar{1}0)$ the reciprocals of *h*, *k*, *i*, and *l* are, respectively, 1/2, –1, –1, and ∞; thus, this plane is parallel to the *c* axis, and intersects the a_1 axis at *a*/2, the a_2 axis at –*a*, and the a_3 axis at –*a*. The plane having these intersections is shown in the figure below.



Linear and Planar Densities

3.51 (a) In the figure below is shown a [100] direction within an FCC unit cell.

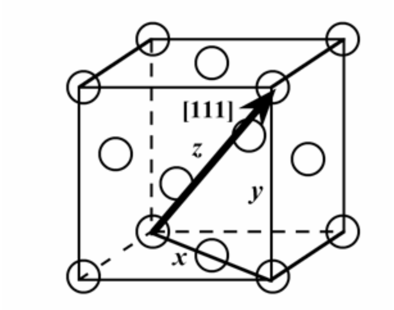


For this [100] direction there is one atom at each of the two unit cell corners, and, thus, there is the equivalent of 1 atom that is centered on the direction vector. The length of this direction vector is just the unit cell edge length, $2R\sqrt{2}$ (Equation 3.1). Therefore, the expression for the 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

$$\mathrm{LD}_{111} = \frac{\text{number of atoms centered on [111] direction vector}}{\text{length of [111] direction vector}}$$

$$= \frac{1 \text{ atom}}{2R\sqrt{6}} = \frac{1}{2R\sqrt{6}}$$

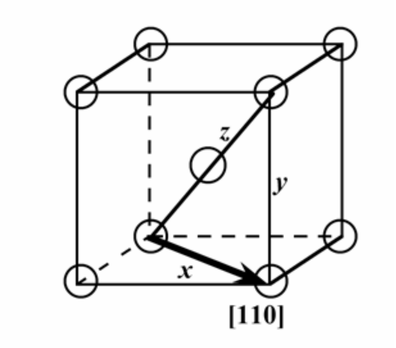
(b) From the table inside the front cover, the atomic radius for copper is 0.128 nm. Therefore, the linear density for the [100] direction is

$$\mathrm{LD}_{100}(\mathrm{Cu}) = \frac{1}{2R\sqrt{2}} = \frac{1}{(2)(0.128 \text{ nm})\sqrt{2}} = 2.76 \text{ nm}^{-1} = 2.76 \times 10^9 \text{ m}^{-1}$$

While for the [111] direction

$$\mathrm{LD}_{111}(\mathrm{Cu}) = \frac{1}{2R\sqrt{6}} = \frac{1}{(2)(0.128 \text{ nm})\sqrt{6}} = 1.59 \text{ nm}^{-1} = 1.59 \times 10^9 \text{ m}^{-1}$$

3.52 (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 3.3 is equal to $\frac{4R}{\sqrt{3}}$. Furthermore, z is the length of the unit cell diagonal, which is equal to $4R$ Thus, using the above equation, the length x may be calculated as follows:

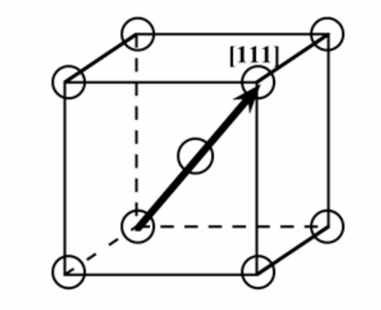
$$x = \sqrt{(4R)^2 - \left(\frac{4R}{\sqrt{3}}\right)^2} = \sqrt{\frac{32R^2}{3}} = 4R\sqrt{\frac{2}{3}}$$

Therefore, the expression for the linear density of this direction is

$$\mathrm{LD}_{110} = \frac{\text{number of atoms centered on [110] direction vector}}{\text{length of [110] direction vector}}$$

$$= \frac{1 \text{ atom}}{4R\sqrt{\frac{2}{3}}} = \frac{\sqrt{3}}{4R\sqrt{2}}$$

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

$$\mathrm{LD}_{111} = \frac{\text{number of atoms centered on [111] direction vector}}{\text{length of [111] direction vector}}$$

$$= \frac{2 \text{ atoms}}{4R} = \frac{1}{2R}$$

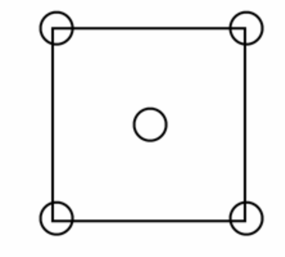
(b) From the table inside the front cover, the atomic radius for iron is 0.124 nm. Therefore, the linear density for the [110] direction is

$$\mathrm{LD}_{110}(\mathrm{Fe}) = \frac{\sqrt{3}}{4R\sqrt{2}} = \frac{\sqrt{3}}{(4)(0.124 \text{ nm})\sqrt{2}} = 2.47 \text{ nm}^{-1} = 2.47 \times 10^{9} \text{ m}^{-1}$$

While for the [111] direction

$$\mathrm{LD}_{111}(\mathrm{Fe}) = \frac{1}{2R} = \frac{1}{(2)(0.124 \text{ nm})} = 4.03 \text{ nm}^{-1} = 4.03 \times 10^{9} \text{ m}^{-1}$$

3.53 (a) In the figure below is shown a (100) plane for an FCC unit cell.

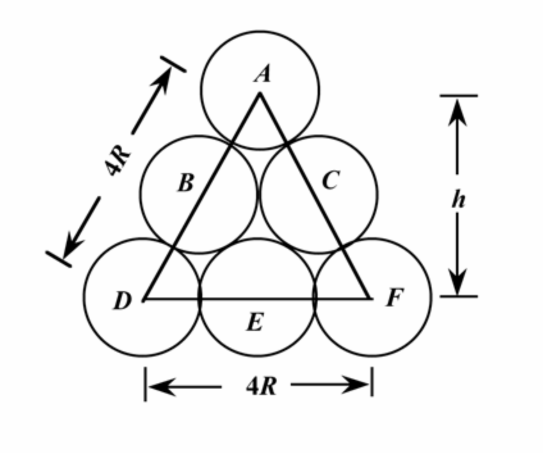


For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the equivalence of 2 atoms associated with this FCC (100) plane. The planar section represented in the 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

$$\text{PD}_{111} = \frac{\text{number of atoms centered on (111) plane}}{\text{area of (111) plane}}$$

$$= \frac{2 \text{ atoms}}{4R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

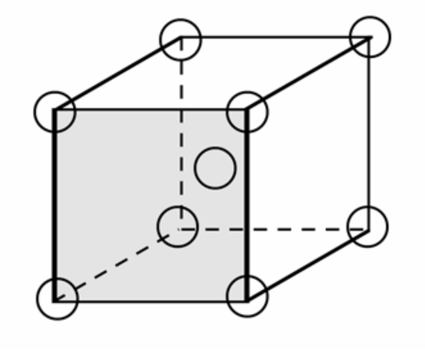
(b) From the table inside the front cover, the atomic radius for aluminum is 0.143 nm. Therefore, the planar density for the (100) plane is

$$\text{PD}_{100}(\text{Al}) = \frac{1}{4R^2} = \frac{1}{4(0.143 \text{ nm})^2} = 12.23 \text{ nm}^{-2} = 1.223 \times 10^{19} \text{ m}^{-2}$$

While for the (111) plane

$$\text{PD}_{111}(\text{Al}) = \frac{1}{2R^2\sqrt{3}} = \frac{1}{2\sqrt{3}(0.143 \text{ nm})^2} = 14.12 \text{ nm}^{-2} = 1.412 \times 10^{19} \text{ m}^{-2}$$

3.54 (a) A BCC unit cell within which is drawn a (100) plane is shown below.

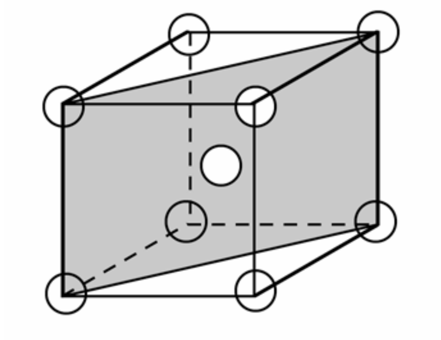


For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells. Thus, there is the equivalence of 1 atom associated with this BCC (100) plane. The planar section represented in the above figure is a square, wherein the side lengths are equal to the unit cell edge length, $\frac{4R}{\sqrt{3}}$ (Equation 3.3); and, 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

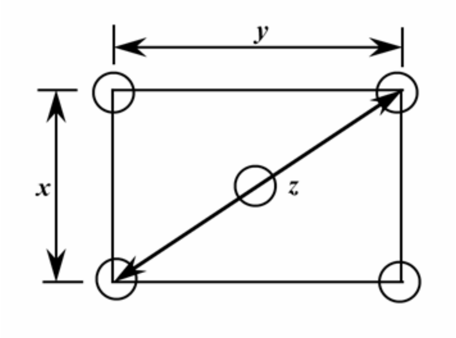
$$\mathrm{PD}_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{1 \text{ atom}}{\frac{16\ R^2}{3}} = \frac{3}{16\ R^2}$$

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 3.3) 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

$$\text{PD}_{110} = \frac{\text{number of atoms centered on (110) plane}}{\text{area of (110) plane}}$$

$$= \frac{2 \text{ atoms}}{\frac{16R^2\sqrt{2}}{3}} = \frac{3}{8R^2\sqrt{2}}$$

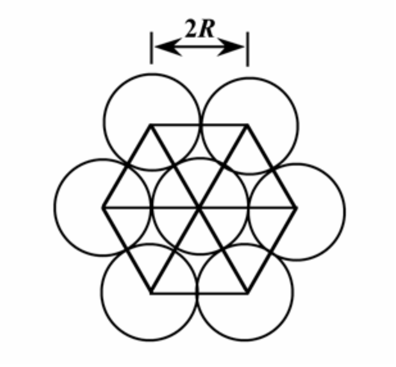
(b) From the table inside the front cover, the atomic radius for molybdenum is 0.136 nm. Therefore, the planar density for the (100) plane is

$$\mathrm{PD}_{100}(\mathrm{Mo}) = \frac{3}{16R^2} = \frac{3}{16(0.136\ \mathrm{nm})^2} = 10.14\ \mathrm{nm}^{-2} = 1.014 \times 10^{19}\ \mathrm{m}^{-2}$$

While for the (110) plane

$$\mathrm{PD}_{110}(\mathrm{Mo}) = \frac{3}{8R^2\sqrt{2}} = \frac{3}{8(0.136\ \mathrm{nm})^2\sqrt{2}} = 14.34\ \mathrm{nm}^{-2} = 1.434 \times 10^{19}\ \mathrm{m}^{-2}$$

3.55 (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

3.56 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

3.57 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

$$a = 2R\sqrt{2} = (2)(0.1431\ \text{nm})\sqrt{2} = 0.4048\ \text{nm}$$

Now, the interplanar spacing d_{110} maybe determined using Equation 3.14 as

$$d_{110} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (0)^2}} = \frac{0.4048\ \text{nm}}{\sqrt{2}} = 0.2862\ \text{nm}$$

3.58 We first calculate the lattice parameter using Equation 3.3 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 3.14 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 3.13 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

$$2\theta = (2)(22.94°) = 45.88°$$

3.59 From the table, α-iron has a BCC crystal structure and an atomic radius of 0.1241 nm. Using Equation 3.3 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 3.14 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}

$$d_{211} = \frac{a}{\sqrt{(2)^2 + (1)^2 + (1)^2}} = \frac{0.2866 \text{ nm}}{\sqrt{6}} = 0.1170 \text{ nm}$$

3.60 (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 3.13 as

$$d_{311} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.0711\ \text{nm})}{(2)\left(\sin\frac{36.12^\circ}{2}\right)} = 0.1147\ \text{nm}$$

(b) In order to compute the atomic radius we must first determine the lattice parameter, *a*, using Equation 3.14, 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

$$R = \frac{a}{2\sqrt{2}} = \frac{0.3804\ \text{nm}}{2\sqrt{2}} = 0.1345\ \text{nm}$$

3.61 (a) From the data given in the problem, and realizing that 75.99° = 2θ, the interplanar spacing for the (211) set of planes for Nb may be computed using Equation 3.13 as follows:

$$d_{211} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.1659\ \text{nm})}{(2)\left(\sin\dfrac{75.99°}{2}\right)} = 0.1348\ \text{nm}$$

(b) In order to compute the atomic radius we must first determine the lattice parameter, *a*, using Equation 3.14, and then *R* from Equation 3.3 since Nb has a BCC crystal structure. Therefore,

$$a = d_{211}\sqrt{(2)^2 + (1)^2 + (1)^2} = (0.1347\ \text{nm})\left(\sqrt{6}\right) = 0.3300\ \text{nm}$$

And, from Equation 3.3

$$R = \frac{a\sqrt{3}}{4} = \frac{(0.3300\ \text{nm})\sqrt{3}}{4} = 0.1429\ \text{nm}$$

3.62 The first step to solve this problem is to compute the interplanar spacing using Equation 3.13. Thus,

$$d_{hkl} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1542 \ \text{nm})}{(2)\left(\sin \frac{44.53°}{2}\right)} = 0.2035 \ \text{nm}$$

Now, employment of both Equations 3.14 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

$$h^2 + k^2 + l^2 = (1.732)^2 = 3.0$$

By trial and error, the only three integers that are all odd or even, 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.

3.63 For each peak, in order to compute the interplanar spacing and the lattice parameter we must employ Equations 3.14 and 3.13, respectively. The first peak of Figure 3.21, which results from diffraction by the (111) set of planes, occurs at $2\theta = 31.3°$; the corresponding interplanar spacing for this set of planes, using Equation 3.13, is equal to

$$d_{111} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1542 \text{ nm})}{(2)\left(\sin \dfrac{31.3°}{2}\right)} = 0.2858 \text{ nm}$$

And, from Equation 3.14, the lattice parameter a is determined as

$$a = d_{hkl}\sqrt{(h)^2 + (k)^2 + (l)^2} = d_{111}\sqrt{(1)^2 + (1)^2 + (1)^2}$$

$$= (0.2858 \text{ nm})\sqrt{3} = 0.4950 \text{ nm}$$

Similar computations are made for the other peaks which results are tabulated below:

Peak Index	2θ	d_{hkl}(nm)	a (nm)
200	36.6	0.2455	0.4910
220	52.6	0.1740	0.4921
311	62.5	0.1486	0.4929
222	65.5	0.1425	0.4936

3.64 The first four diffraction peaks that will occur for BCC consistent with *h* + *k* + *l* being even are (110), (200), (211), and (220).

3.65 (a) Since W has a BCC crystal structure, only those peaks for which $h + k + l$ are even will appear. Therefore, the first peak results by diffraction from (110) planes.

(b) For each peak, in order to calculate the interplanar spacing we must employ Equation 3.13. For the first peak which occurs at 40.2°

$$d_{110} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.1542 \text{ nm})}{(2)\left(\sin \frac{40.2°}{2}\right)} = 0.2244 \text{ nm}$$

(c) Employment of Equations 3.14 and 3.3 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

Noncrystalline Solids

3.66 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.

CHAPTER 4

IMPERFECTIONS IN SOLIDS

PROBLEM SOLUTIONS

Vacancies and Self-Interstitials

4.1 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,

$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.90 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1357 \text{ K})}\right]$$

$$= 4.56 \times 10^{-4}$$

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

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) = \frac{N_A \rho_{Au}}{A_{Au}} \exp\left(-\frac{Q_v}{kT}\right)$$

$$= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(18.63 \text{ g/cm}^3)}{196.9 \text{ g/mol}} \exp\left[-\frac{0.98 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom}-\text{K})(1173 \text{ K})}\right]$$

$$= 3.52 \times 10^{18} \text{ cm}^{-3} = 3.52 \times 10^{24} \text{ m}^{-3}$$

4.3 This problem calls for the computation of the activation energy for vacancy formation in silver. 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

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

$$= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(9.5 \text{ g/cm}^3)}{107.9 \text{ g/mol}}$$

$$= 5.30 \text{ x } 10^{22} \text{ atoms/cm}^3 = 5.30 \text{ x } 10^{28} \text{ atoms/m}^3$$

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

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

and, after some algebraic manipulation

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

$$= -(8.62 \times 10^{-5} \text{ eV/atom-K})(800°\text{C} + 273 \text{ K}) \ln\left[\frac{3.60 \times 10^{23} \text{ m}^{-3}}{5.30 \times 10^{28} \text{ m}^{-3}}\right]$$

$$= 1.10 \text{ eV/atom}$$

Impurities in Solids

4.4 In this problem we are asked to cite which of the elements listed form with Ni the three possible solid solution types. For complete substitutional solubility the following criteria must be met: 1) the difference in atomic radii between Ni and the other element (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, or nearly the same. Below are tabulated, for the various elements, these criteria.

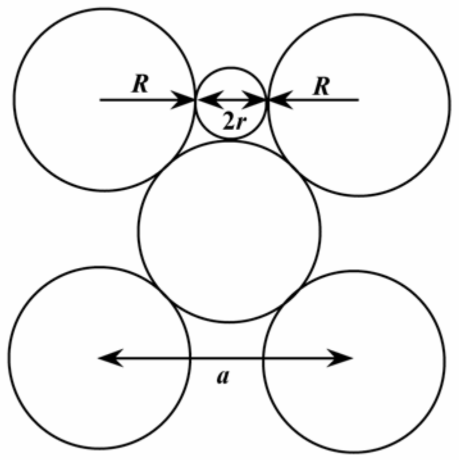
Element	ΔR%	Crystal Structure	ΔElectro-negativity	Valence
Ni		**FCC**		**2+**
C	–43			
H	–63			
O	–52			
Ag	+16	FCC	+0.1	1+
Al	+15	FCC	-0.3	3+
Co	+0.6	HCP	0	2+
Cr	+0.2	BCC	-0.2	3+
Fe	-0.4	BCC	0	2+
Pt	+11	FCC	+0.4	2+
Zn	+7	HCP	-0.2	2+

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

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

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

4.5 In the drawing below is shown the atoms on the (100) face of an FCC unit cell; the interstitial site is at the center of the edge.



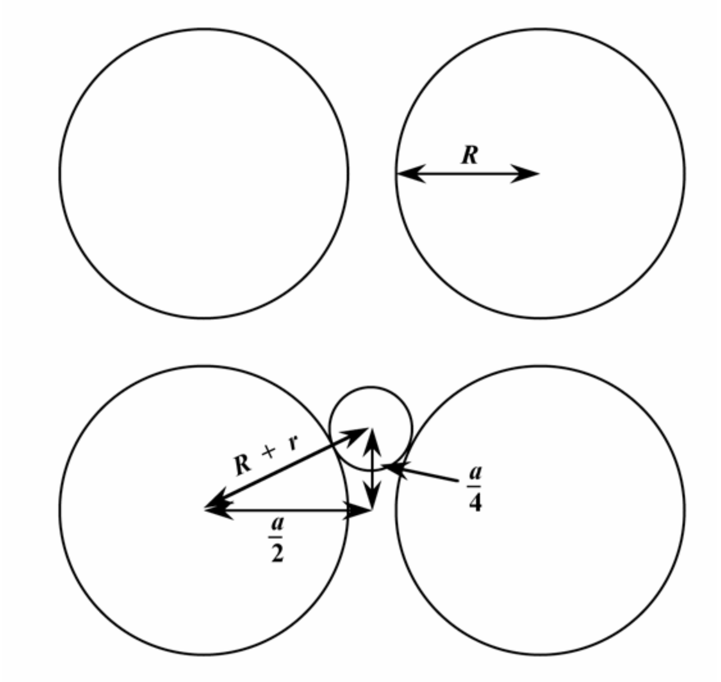
The diameter of an atom that will just fit into this site (2r) is just the difference between that unit cell edge length (a) and the radii of the two host atoms that are located on either side of the site (R); that is

$$2r = a - 2R$$

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

$$r = \frac{a - 2R}{2} = \frac{2R\sqrt{2} - 2R}{2} = 0.41R$$

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 that is 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 3.3, $a = \frac{4R}{\sqrt{3}}$, 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:

$$r^2 + 2Rr - 0.667R^2 = 0$$

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, $r = 0.291R$.

Thus, for a host atom of radius R, the size of an interstitial site for FCC is approximately 1.4 times that for BCC.

Specification of Composition

4.6 (a) This problem asks that we derive Equation 4.7a. To begin, C_1 is defined according to Equation 4.3 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

$$m_1' = \mathrm{n}_{m1} A_1$$

$$m_2' = \mathrm{n}_{m2} A_2$$

And, substitution into the C_1 expression above

$$C_1 = \frac{\mathrm{n}_{m1} A_1}{\mathrm{n}_{m1} A_1 + \mathrm{n}_{m2} A_2} \times 100$$

From Equation 4.5 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 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 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

$$C_1'' = \frac{m_1}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2}}$$

From Equation 4.3, 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 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

$$C_1'' = \frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \text{ x } 10^3$$

which is 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, we get

$$\rho_{\text{ave}} = \frac{m_1 + m_2}{\dfrac{m_1}{\rho_1} + \dfrac{m_2}{\rho_2}}$$

Furthermore, from Equation 4.3

$$m_1 = \frac{C_1 (m_1 + m_2)}{100}$$

$$m_2 = \frac{C_2 (m_1 + m_2)}{100}$$

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

$$= \frac{100}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}$$

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

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

$$= \frac{(92.5)(63.55 \text{ g/mol})}{(92.5)(63.55 \text{ g/mol}) + (7.5)(107.87 \text{ g/mol})} \times 100$$

$$= 87.9 \text{ at\%}$$

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

$$= \frac{(7.5)(107.87 \text{ g/mol})}{(92.5)(63.55 \text{ g/mol}) + (7.5)(107.87 \text{ g/mol})} \times 100$$

$$= 12.1 \text{ at\%}$$

4.8 In order to compute composition, in weight percent, of a 5 at% Cu-95 at% Pt alloy, we employ Equation 4.7 as

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

$$= \frac{(5)(63.55\ \mathrm{g/mol})}{(5)(63.55\ \mathrm{g/mol}) + (95)(195.08\ \mathrm{g/mol})} \times 100$$

$$= 1.68\ \mathrm{wt\%}$$

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

$$= \frac{(95)(195.08\ \mathrm{g/mol})}{(5)(63.55\ \mathrm{g/mol}) + (95)(195.08\ \mathrm{g/mol})} \mathrm{x}\ 100$$

$$= 98.32\ \mathrm{wt\%}$$

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

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

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

Similarly, for carbon

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

And for chromium

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

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

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

Likewise, for Zn

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

Now, use of Equation 4.5 yields

$$C'_{\mathrm{Cu}} = \frac{n_{m_{\mathrm{Cu}}}}{n_{m_{\mathrm{Cu}}} + n_{m_{\mathrm{Zn}}}} \times 100$$

$$= \frac{0.519\ \mathrm{mol}}{0.519\ \mathrm{mol} + 0.719\ \mathrm{mol}} \times 100 = 41.9\ \mathrm{at\%}$$

Also,

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

4.11 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 a modified form of Equation 4.5, gives

$$C'_{\text{Ag}} = \frac{n_{m_{\text{Ag}}}}{n_{m_{\text{Ag}}} + n_{m_{\text{Au}}} + n_{m_{\text{Cu}}}} \times 100$$

$$= \frac{187.1 \text{ mol}}{187.1 \text{ mol} + 192.8 \text{ mol} + 37.8 \text{ mol}} \times 100 = 44.8 \text{ at\%}$$

$$C'_{\text{Au}} = \frac{192.8 \text{ mol}}{187.1 \text{ mol} + 192.8 \text{ mol} + 37.8 \text{ mol}} \times 100 = 46.2 \text{ at\%}$$

$$C'_{\text{Cu}} = \frac{37.8 \text{ mol}}{187.1 \text{ mol} + 192.8 \text{ mol} + 37.8 \text{ mol}} \times 100 = 9.0 \text{ at\%}$$

4.12 We are asked to compute the composition of a Pb-Sn alloy in atom percent. Employment of Equation 4.6 leads to

$$C'_{\mathrm{Pb}} = \frac{C_{\mathrm{Pb}} A_{\mathrm{Sn}}}{C_{\mathrm{Pb}} A_{\mathrm{Sn}} + C_{\mathrm{Sn}} A_{\mathrm{Pb}}} \times 100$$

$$= \frac{5.5(118.69 \text{ g/mol})}{5.5(118.69 \text{ g/mol}) + 94.5(207.2 \text{ g/mol})} \times 100$$

$$= 3.2 \text{ at\%}$$

$$C'_{\mathrm{Sn}} = \frac{C_{\mathrm{Sn}} A_{\mathrm{Pb}}}{C_{\mathrm{Sn}} A_{\mathrm{Pb}} + C_{\mathrm{Pb}} A_{\mathrm{Sn}}} \times 100$$

$$= \frac{94.5(207.2 \text{ g/mol})}{94.5(207.2 \text{ g/mol}) + 5.5(118.69 \text{ g/mol})} \times 100$$

$$= 96.8 \text{ at\%}$$

4.13 This problem calls for a conversion of composition in atom percent to composition in weight percent. The composition in atom percent for Problem 4.11 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

$$C_{\text{Ag}} = \frac{C'_{\text{Ag}}A_{\text{Ag}}}{C'_{\text{Ag}}A_{\text{Ag}} + C'_{\text{Au}}A_{\text{Au}} + C'_{\text{Cu}}A_{\text{Cu}}} \times 100$$

$$= \frac{(44.8)(107.87\ \text{g/mol})}{(44.8)(107.87\ \text{g/mol}) + (46.2)(196.97\ \text{g/mol}) + (9.0)(63.55\ \text{g/mol})} \times 100$$

= 33.3 wt%

$$C_{\text{Au}} = \frac{C'_{\text{Au}}A_{\text{Au}}}{C'_{\text{Ag}}A_{\text{Ag}} + C'_{\text{Au}}A_{\text{Au}} + C'_{\text{Cu}}A_{\text{Cu}}} \times 100$$

$$= \frac{(46.2)(196.97\ \text{g/mol})}{(44.8)(107.87\ \text{g/mol}) + (46.2)(196.97\ \text{g/mol}) + (9.0)(63.55\ \text{g/mol})} \times 100$$

= 62.7 wt%

$$C_{\text{Cu}} = \frac{C'_{\text{Cu}}A_{\text{Cu}}}{C'_{\text{Ag}}A_{\text{Ag}} + C'_{\text{Au}}A_{\text{Au}} + C'_{\text{Cu}}A_{\text{Cu}}} \times 100$$

$$= \frac{(9.0)(63.55\ \text{g/mol})}{(44.8)(107.87\ \text{g/mol}) + (46.2)(196.97\ \text{g/mol}) + (9.0)(63.55\ \text{g/mol})} \times 100$$

= 4.0 wt%

4.14 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,

$$N = \frac{N_{\mathrm{A}}\,\rho_{\mathrm{Pb}}}{A_{\mathrm{Pb}}}$$

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,

$$N = \frac{(6.023 \text{ x } 10^{23} \text{ atoms/mol})(11.35 \text{ g/cm}^3)}{207.2 \text{ g/mol}}$$

$$= 3.30 \text{ x } 10^{22} \text{ atoms/cm}^3 = 3.30 \text{ x } 10^{28} \text{ atoms/m}^3$$

4.15 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; and, therefore

$$C''_{\mathrm{Si}} = \frac{0.25}{\dfrac{0.25}{2.33 \ \mathrm{g/cm^3}} + \dfrac{99.75}{7.87 \ \mathrm{g/cm^3}}} \times 10^3$$

$$= 19.6 \ \mathrm{kg/m^3}$$

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

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

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:

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

$$= 4.38\ \text{g/cm}^3$$

4.17 This problem asks that we determine the unit cell edge length for a 80 wt% Ag-20 wt% Pd alloy. In order to solve this problem it is necessary to employ Equation 3.5; 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 107.9 and 106.4 g/mol, respectively (Figure 2.6), 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

$$a = \left[\frac{(4\ \text{atoms/unit cell})\left(\dfrac{100}{\dfrac{80\ \text{wt\%}}{107.9\ \text{g/mol}} + \dfrac{20\ \text{wt\%}}{106.4\ \text{g/mol}}}\right)}{\left(\dfrac{100}{\dfrac{80\ \text{wt\%}}{10.49\ \text{g/cm}^3} + \dfrac{20\ \text{wt\%}}{12.02\ \text{g/cm}^3}}\right)\left(6.023 \times 10^{23}\ \text{atoms/mol}\right)}\right]^{1/3}$$

$$= 4.050 \times 10^{-8}\ \text{cm} = 0.4050\ \text{nm}$$

4.18 This problem asks that we determine, for a hypothetical alloy that is composed of 25 wt% of metal A and 75 wt% of metal B, whether the crystal structure is simple cubic, face-centered cubic, or body-centered cubic. We are given the densities of the these metals (ρ_A = 6.17 g/cm^3 and ρ_B = 8.00 g/cm^3 for B), their atomic weights (A_A = 171.3 g/mol and A_B = 162.0 g/mol), and that the unit cell edge length is 0.332 nm (i.e., 3.32 x 10^{-8} cm). In order to solve this problem it is necessary to employ Equation 3.5; in this expression density and atomic weight will be averages for the alloy—that is

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{V_C N_A}$$

Inasmuch as for each of the possible crystal structures, the unit cell is cubic, then $V_C = a^3$, or

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{a^3 N_A}$$

And, 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:

$$n = \frac{\rho_{\text{ave}} a^3 N_A}{A_{\text{ave}}}$$

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

$$n = \frac{\left(\dfrac{100}{\dfrac{C_A}{\rho_A} + \dfrac{C_B}{\rho_B}}\right) a^3 N_A}{\left(\dfrac{100}{\dfrac{C_A}{A_A} + \dfrac{C_B}{A_B}}\right)}$$

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

$$n = \frac{\left(\dfrac{100}{\dfrac{25\ \text{wt\%}}{6.17\ \text{g/cm}^3} + \dfrac{75\ \text{wt\%}}{8.00\ \text{g/cm}^3}}\right)(3.32 \times 10^{-8}\ \text{nm})^3 (6.023 \times 10^{23}\ \text{atoms/mol})}{\left(\dfrac{100}{\dfrac{25\ \text{wt\%}}{171.3\ \text{g/mol}} + \dfrac{75\ \text{wt\%}}{162.0\ \text{g/mol}}}\right)}$$

$$= 1.00\ \text{atom/unit cell}$$

Therefore, on the basis of this value, the crystal structure is *simple cubic*.

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

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

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

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

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:

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

4.20 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 4.18 is necessary, using the following values:

$C_1 = C_{\text{Mo}} = 16.4$ wt%
$\rho_1 = \rho_{\text{Mo}} = 10.22\ \text{g/cm}^3$
$\rho_2 = \rho_{\text{W}} = 19.3\ \text{g/cm}^3$
$A_1 = A_{\text{Mo}} = 95.94$ g/mol

Thus

$$N_{\text{Mo}} = \frac{N_{\text{A}} C_{\text{Mo}}}{\dfrac{C_{\text{Mo}} A_{\text{Mo}}}{\rho_{\text{Mo}}} + \dfrac{A_{\text{Mo}}}{\rho_{\text{W}}}\left(100 - C_{\text{Mo}}\right)}$$

$$= \frac{\left(6.023 \times 10^{23}\ \text{atoms/mol}\right)(16.4\ \text{wt\%})}{\dfrac{(16.4\ \text{wt\%})(95.94\ \text{g/mol})}{10.22\ \text{g/cm}^3} + \dfrac{95.94\ \text{g/mol}}{19.3\ \text{g/cm}^3}\left(100 - 16.4\ \text{wt\%}\right)}$$

$$= 1.73 \text{ x } 10^{22}\ \text{atoms/cm}^3$$

4.21 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 4.18 is necessary, using the following values:

$C_1 = C_{\mathrm{Nb}} = 24$ wt%
$\rho_1 = \rho_{\mathrm{Nb}} = 8.57\ \mathrm{g/cm^3}$
$\rho_2 = \rho_{\mathrm{V}} = 6.10\ \mathrm{g/cm^3}$
$A_1 = A_{\mathrm{Nb}} = 92.91$ g/mol

Thus

$$N_{\mathrm{Nb}} = \frac{N_{\mathrm{A}} C_{\mathrm{Nb}}}{\dfrac{C_{\mathrm{Nb}} A_{\mathrm{Nb}}}{\rho_{\mathrm{Nb}}} + \dfrac{A_{\mathrm{Nb}}}{\rho_{\mathrm{V}}}\left(100 - C_{\mathrm{Nb}}\right)}$$

$$= \frac{\left(6.023 \times 10^{23}\ \text{atoms/mol}\right)(24\ \text{wt\%})}{\dfrac{(24\ \text{wt\%})(92.91\ \text{g/mol})}{8.57\ \text{g/cm}^3} + \dfrac{92.91\ \text{g/mol}}{6.10\ \text{g/cm}^3}(100 - 24\ \text{wt\%})}$$

$$= 1.02 \times 10^{22}\ \text{atoms/cm}^3$$

4.22 This problem asks that we derive Equation 4.19, 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, 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

$$N_1 = \frac{c_1' N_A \rho_{ave}}{A_{ave}}$$

$$= \frac{N_A C_1' \rho_1 \rho_2}{C_1' \rho_2 A_1 + \left(100 - C_1'\right) \rho_1 A_2}$$

And, solving for C_1'

$$C_1' = \frac{100 N_1 \rho_1 A_2}{N_A \rho_1 \rho_2 - N_1 \rho_2 A_1 + N_1 \rho_1 A_2}$$

Substitution of this expression for C_1' into Equation 4.7a, which may be written in the following form

$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100$$

$$= \frac{C_1' A_1}{C_1' A_1 + \left(100 - C_1'\right) A_2} \times 100$$

yields

$$C_1 = \frac{100}{1 + \frac{N_A \rho_2}{N_1 A_1} - \frac{\rho_2}{\rho_1}}$$

the desired expression.

4.23 This problem asks us to determine the weight percent of Au that must be added to Ag such that the resultant alloy will contain 5.5 x 10^{21} Au atoms per cubic centimeter. To solve this problem, employment of Equation 4.19 is necessary, using the following values:

$N_1 = N_{\mathrm{Au}} = 5.5 \times 10^{21}$ atoms/cm^3
$\rho_1 = \rho_{\mathrm{Au}} = 19.32$ g/cm^3
$\rho_2 = \rho_{\mathrm{Ag}} = 10.49$ g/cm^3
$A_1 = A_{\mathrm{Au}} = 196.97$ g/mol
$A_2 = A_{\mathrm{Ag}} = 107.87$ g/mol

Thus

$$C_{\mathrm{Au}} = \frac{100}{1 + \dfrac{N_{\mathrm{A}}\rho_{\mathrm{Ag}}}{N_{\mathrm{Au}}A_{\mathrm{Au}}} - \dfrac{\rho_{\mathrm{Ag}}}{\rho_{\mathrm{Au}}}}$$

$$= \frac{100}{1 + \dfrac{(6.023 \times 10^{23} \text{ atoms/mol})(10.49 \text{ g/cm}^3)}{(5.5 \times 10^{21} \text{ atoms/cm}^3)(196.97 \text{ g/mol})} - \left(\dfrac{10.49 \text{ g/cm}^3}{19.32 \text{ g/cm}^3}\right)}$$

$$= 15.9 \text{ wt\%}$$

4.24 This problem asks us to determine the weight percent of Ge that must be added to Si such that the resultant alloy will contain 2.43 x10^{21} Ge atoms per cubic centimeter. To solve this problem, employment of Equation 4.19 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
$A_2 = A_{\text{Si}} = 28.09$ g/mol

Thus

$$C_{\text{Ge}} = \frac{100}{1 + \dfrac{N_{\text{A}}\rho_{\text{Si}}}{N_{\text{Ge}}A_{\text{Ge}}} - \dfrac{\rho_{\text{Si}}}{\rho_{\text{Ge}}}}$$

$$= \frac{100}{1 + \dfrac{(6.023 \times 10^{23} \text{ atoms/mol})(2.33 \text{ g/cm}^3)}{(2.43 \times 10^{21} \text{ atoms/cm}^3)(72.64 \text{ g/mol})} - \left(\dfrac{2.33 \text{ g/cm}^3}{5.32 \text{ g/cm}^3}\right)}$$

$$= 11.7 \text{ wt\%}$$

4.25 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 3.5 it is possible to compute the unit cell volume, and inasmuch as the unit cell is cubic, the unit cell edge length is just the cube root of the volume. However, it is first necessary to calculate the density and average atomic weight of this alloy using Equations 4.10a and 4.11a. Inasmuch as the densities of iron and vanadium are 7.87g/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

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{V}}}{A_{\text{V}}} + \dfrac{C_{\text{Fe}}}{A_{\text{Fe}}}}$$

$$= \frac{100}{\dfrac{10 \text{ wt\%}}{50.94 \text{ g/mole}} + \dfrac{90 \text{ wt\%}}{55.85 \text{ g/mol}}}$$

$$= 55.32 \text{ g/mol}$$

Now, V_C is determined from Equation 3.5 as

$$V_C = \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= \frac{(2 \text{ atoms/unit cell})(55.32 \text{ g/mol})}{\left(7.65 \text{ g/cm}^3\right)\left(6.023 \times 10^{23} \text{ atoms/mol}\right)}$$

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

And, finally

$$a = (V_C)^{1/3}$$

$$= \left(2.40 \times 10^{-23} \text{cm}^3/\text{unit cell}\right)^{1/3}$$

$$= 2.89 \times 10^{-8} \text{ cm} = 0.289 \text{ nm}$$

Dislocations—Linear Defects

4.26 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

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

4.28 The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solution to Problem 3.54, the planar densities for BCC (100) and (110) are $\frac{3}{16R^2}$ and $\frac{3}{8R^2\sqrt{2}}$, respectively—that is $\frac{0.19}{R^2}$ and $\frac{0.27}{R^2}$. Thus, since the planar density for (110) is greater, it will have the lower surface energy.

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

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

4.30 (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.

4.31 (a) The interfacial defect that exists for this stacking sequence is a twin boundary, which occurs at the indicated position.

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.

Within this region, the stacking sequence is HCP.

Grain Size Determination

4.32 (a) This problem calls for a determination of the average grain size of the specimen which microstructure is shown in Figure 4.14(b). Seven line segments were drawn across the micrograph, each of which was 60 mm long. The average number of grain boundary intersections for these lines was 8.7. Therefore, the average line length intersected is just

$$\frac{60 \text{ mm}}{8.7} = 6.9 \text{ mm}$$

Hence, the average grain diameter, *d*, is

$$d = \frac{\text{ave. line length intersected}}{\text{magnification}} = \frac{6.9 \text{ mm}}{100} = 6.9 \times 10^{-2} \text{ mm}$$

(b) This portion of the problem calls for us to estimate the ASTM grain size number for this same material. The average grain size number, *n*, is related to the number of grains per square inch, *N*, at a magnification of 100x according to Equation 4.16. Inasmuch as the magnification is 100x, the value of *N* is measured directly from the micrograph, which is approximately 12 grains. In order to solve for *n* in Equation 4.16, it is first necessary to take logarithms as

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

From which *n* equals

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

$$= \frac{\log 12}{\log 2} + 1 = 4.6$$

4.33 (a) This portion of the problem calls for a determination of the average grain size of the specimen which microstructure is shown in Figure 9.25(a). Seven line segments were drawn across the micrograph, each of which was 60 mm long. The average number of grain boundary intersections for these lines was 6.3. Therefore, the average line length intersected is just

$$\frac{60 \text{ mm}}{6.3} = 9.5 \text{ mm}$$

Hence, the average grain diameter, *d*, is

$$d = \frac{\text{ave. line length intersected}}{\text{magnification}} = \frac{9.5 \text{ mm}}{90} = 0.106 \text{ mm}$$

(b) This portion of the problem calls for us to estimate the ASTM grain size number for this same material. The average grain size number, *n*, is related to the number of grains per square inch, *N*, at a magnification of 100x according to Equation 4.16. However, the magnification of this micrograph is not 100x, but rather 90x. Consequently, it is necessary to use Equation 4.17

$$N_M \left(\frac{M}{100}\right)^2 = 2^{n-1}$$

where N_M = the number of grains per square inch at magnification *M*, and *n* is the ASTM grain size number. Taking logarithms of both sides of this equation leads to the following:

$$\log N_M + 2 \log \left(\frac{M}{100}\right) = (n - 1) \log 2$$

Solving this expression for *n* gives

$$n = \frac{\log N_M + 2 \log \left(\frac{M}{100}\right)}{\log 2} + 1$$

From Figure 9.25(a), N_M is measured to be approximately 4, which leads to

$$n = \frac{\log 4 + 2 \log \left(\frac{90}{100}\right)}{\log 2} + 1$$

$$= 2.7$$

4.34 (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 100x. All we need do is solve for the parameter N in Equation 4.16, inasmuch as $n = 6$. Thus

$$N = 2^{n-1}$$

$$= 2^{6-1} = 32 \text{ grains/in.}^2$$

(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 4.17:

$$N_M \left(\frac{M}{100}\right)^2 = 2^{n-1}$$

where N_M = the number of grains per square inch at magnification M, and n 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}.

4.35 This problem asks that we determine the ASTM grain size number if 30 grains per square inch are measured at a magnification of 250. In order to solve this problem we make use of Equation 4.17:

$$N_M \left(\frac{M}{100}\right)^2 = 2^{n-1}$$

where N_M = the number of grains per square inch at magnification M, and n is the ASTM grain size number. Solving the above equation for n, and realizing that $N_M = 30$, while $M = 250$, we have

$$n = \frac{\log N_M + 2\log\left(\frac{M}{100}\right)}{\log 2} + 1$$

$$= \frac{\log 30 + 2\log\left(\frac{250}{100}\right)}{\log 2} + 1 = 2.5$$

4.36 This problem asks that we determine the ASTM grain size number if 25 grains per square inch are measured at a magnification of 75. In order to solve this problem we make use of Equation 4.17—viz.

$$N_M \left(\frac{M}{100}\right)^2 = 2^{n-1}$$

where N_M = the number of grains per square inch at magnification M, and n is the ASTM grain size number. Solving the above equation for n, and realizing that N_M = 25, while M = 75, we have

$$n = \frac{\log N_M + 2 \log \left(\frac{M}{100}\right)}{\log 2} + 1$$

$$= \frac{\log 25 + 2 \log \left(\frac{75}{100}\right)}{\log 2} + 1 = 4.8$$

DESIGN PROBLEMS

Specification of Composition

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

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

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 solving for C_{Li} from the above equation, we get

$$C_{\text{Li}} = \frac{100\,\rho_{\text{Li}}\left(\rho_{\text{Al}} - \rho_{\text{ave}}\right)}{\rho_{\text{ave}}\left(\rho_{\text{Al}} - \rho_{\text{Li}}\right)}$$

$$= \frac{(100)\left(0.534\ \text{g/cm}^3\right)\left(2.71\ \text{g/cm}^3 - 2.47\ \text{g/cm}^3\right)}{\left(2.47\ \text{g/cm}^3\right)\left(2.71\ \text{g/cm}^3 - 0.534\ \text{g/cm}^3\right)}$$

$$= 2.38\ \text{wt\%}$$

4.D2 This problem asks that we determine the concentration (in weight percent) of Cu that must be added to Pt so as to yield a unit cell edge length of 0.390 nm. To begin, it is necessary to employ Equation 3.5, 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

$$V_C = a^3 = (0.390 \text{ nm})^3$$

$$\left(3.90 \times 10^{-8} \text{ cm}\right)^3 = 5.932 \times 10^{-23} \text{ cm}^3$$

It is now necessary to construct expressions for A_{ave} and ρ_{ave} in terms of the concentration of vanadium, C_{Cu}, using Equations 4.11a and 4.10a. For A_{ave} we have

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{Cu}}}{A_{\text{Cu}}} + \dfrac{(100 - C_{\text{Cu}})}{A_{\text{Pt}}}}$$

$$= \frac{100}{\dfrac{C_{\text{Cu}}}{63.55 \text{ g/mol}} + \dfrac{(100 - C_{\text{Cu}})}{195.08 \text{ g/mol}}}$$

whereas for ρ_{ave}

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{Cu}}}{\rho_{\text{Cu}}} + \dfrac{(100 - C_{\text{Cu}})}{\rho_{\text{Pt}}}}$$

$$= \frac{100}{\dfrac{C_{\text{Cu}}}{8.94 \text{ g/cm}^3} + \dfrac{(100 - C_{\text{Cu}})}{21.45 \text{ g/cm}^3}}$$

Within the FCC unit cell there are 4 equivalent atoms, and thus, the value of *n* in Equation 3.5 is 4; hence, this expression may be written in terms of the concentration of Cu in weight percent as follows:

$$V_C = 5.932 \text{ x } 10^{-23} \text{ cm}^3$$

$$= \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= \frac{(4 \text{ atoms/unit cell})\left[\dfrac{100}{\dfrac{C_{\text{Cu}}}{63.55 \text{ g/mol}} + \dfrac{(100 - C_{\text{Cu}})}{195.08 \text{ g/mol}}}\right]}{\left[\dfrac{100}{\dfrac{C_{\text{Cu}}}{8.94 \text{ g/cm}^3} + \dfrac{(100 - C_{\text{Cu}})}{21.45 \text{ g/cm}^3}}\right](6.023 \times 10^{23} \text{ atoms/mol})}$$

And solving this expression for C_{Cu} leads to C_{Cu} = 2.825 wt%.

CHAPTER 5

DIFFUSION

PROBLEM SOLUTIONS

Introduction

5.1 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 may be monitored by using radioactive isotopes of the metal being studied. The motion of these isotopic atoms may be monitored by measurement of radioactivity level.

Diffusion Mechanisms

5.3 (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.

Steady-State Diffusion

5.4 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.

5.5 (a) The driving force is that which compels a reaction to occur.

(b) The driving force for steady-state diffusion is the concentration gradient.

5.6 This problem calls for the mass of hydrogen, per hour, that diffuses through a Pd sheet. It first becomes necessary to employ both Equations 5.1a and 5.3. Combining these expressions and solving for the mass yields

$$M = JAt = -DAt\frac{\Delta C}{\Delta x}$$

$$= -\left(1.7 \times 10^{-8}\ \mathrm{m^2/s}\right)\left(0.25\ \mathrm{m^2}\right)(3600\ \mathrm{s/h})\left[\frac{0.4 - 2.0\ \mathrm{kg/m^3}}{6 \times 10^{-3}\ \mathrm{m}}\right]$$

$$= 4.1 \text{ x } 10^{-3}\ \mathrm{kg/h}$$

5.7 We are asked to determine the position at which the nitrogen concentration is 0.5 kg/m^3. This problem is solved by using Equation 5.3 in the form

$$J = -D\frac{C_A - C_B}{x_A - x_B}$$

If we take C_A to be the point at which the concentration of nitrogen is 2 kg/m^3, then it becomes necessary to solve for x_B, as

$$x_B = x_A + D\left[\frac{C_A - C_B}{J}\right]$$

Assume x_A is zero at the surface, in which case

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

$$= 1.8 \text{ x } 10^{-3} \text{ m} = 1.8 \text{ mm}$$

5.8 This problem calls for computation of the diffusion coefficient for a steady-state diffusion situation. Let us first convert the carbon concentrations from weight percent to kilograms carbon per meter cubed using Equation 4.9a. For 0.015 wt% C

$$C''_{\mathrm{C}} = \frac{C_{\mathrm{C}}}{\dfrac{C_{\mathrm{C}}}{\rho_{\mathrm{C}}} + \dfrac{C_{\mathrm{Fe}}}{\rho_{\mathrm{Fe}}}} \times 10^3$$

$$= \frac{0.015}{\dfrac{0.015}{2.25\ \mathrm{g/cm^3}} + \dfrac{99.985}{7.87\ \mathrm{g/cm^3}}} \times 10^3$$

$$1.18\ \mathrm{kg\ C/m^3}$$

Similarly, for 0.0068 wt% C

$$C''_{\mathrm{C}} = \frac{0.0068}{\dfrac{0.0068}{2.25\ \mathrm{g/cm^3}} + \dfrac{99.9932}{7.87\ \mathrm{g/cm^3}}} \times 10^3$$

$$= 0.535\ \mathrm{kg\ C/m^3}$$

Now, using a rearranged form of Equation 5.3

$$D = -J\left[\frac{x_{\mathrm{A}} - x_{\mathrm{B}}}{C_{\mathrm{A}} - C_{\mathrm{B}}}\right]$$

$$= -\left(7.36 \times 10^{-9}\ \mathrm{kg/m^2\text{-}s}\right)\left[\frac{-2 \times 10^{-3}\ \mathrm{m}}{1.18\ \mathrm{kg/m^3} - 0.535\ \mathrm{kg/m^3}}\right]$$

$$= 2.3 \times 10^{-11}\ \mathrm{m^2/s}$$

5.9 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 5.3 to solve this problem. However, it first becomes necessary to determine the concentration of hydrogen at each face using Equation 5.11. At the low pressure (or B) side

$$C_{\mathrm{N(B)}} = \left(4.90 \times 10^{-3}\right)\sqrt{0.10 \ \mathrm{MPa}} \ \exp\left[-\frac{37{,}600 \ \mathrm{J/mol}}{(8.31 \ \mathrm{J/mol\text{-}K})(300 + 273 \ \mathrm{K})}\right]$$

$$5.77 \times 10^{-7} \ \mathrm{wt\%}$$

Whereas, for the high pressure (or A) side

$$C_{\mathrm{N(A)}} = \left(4.90 \times 10^{-3}\right)\sqrt{5.0 \ \mathrm{MPa}} \ \exp\left[-\frac{37{,}600 \ \mathrm{J/mol}}{(8.31 \ \mathrm{J/mol\text{-}K})(300 + 273 \ \mathrm{K})}\right]$$

$$4.08 \times 10^{-6} \ \mathrm{wt\%}$$

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/cm^3), the volume iron in 100 g (V_{B}) is just

$$V_{\mathrm{B}} = \frac{100 \ \mathrm{g}}{7.87 \ \mathrm{g/cm^3}} = 12.7 \ \mathrm{cm^3} = 1.27 \times 10^{-5} \ \mathrm{m^3}$$

Therefore, the concentration of hydrogen at the B face in kilograms of N per cubic meter of alloy [$C''_{\mathrm{N(B)}}$] 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 1.27×10^{-5} m^3, and

$$C''_{\mathrm{N(A)}} = \frac{C_{\mathrm{N(A)}}}{V_{\mathrm{A}}}$$

$$= \frac{4.08 \times 10^{-9}\ \text{kg}}{1.27 \times 10^{-5}\ \text{m}^3} = 3.21 \text{ x } 10^{-4}\ \text{kg/m}^3$$

Thus, the concentration gradient is just the difference between these concentrations of nitrogen divided by the thickness of the iron membrane; that is

$$\frac{\Delta C}{\Delta x} = \frac{C''_{\text{N(B)}} - C''_{\text{N(A)}}}{x_{\text{B}} - x_{\text{A}}}$$

$$= \frac{4.54 \text{ x } 10^{-5}\ \text{kg/m}^3 - 3.21 \text{ x } 10^{-4}\ \text{kg/m}^3}{1.5 \times 10^{-3}\ \text{m}} = -\ 0.184\ \ \text{kg/m}^4$$

At this time it becomes necessary to calculate the value of the diffusion coefficient at 300°C using Equation 5.8. Thus,

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

$$= (3.0 \times 10^{-7}\ \text{m}^2/\text{s})\ \exp\left(-\frac{76{,}150\ \text{J/mol}}{(8.31\ \text{J/mol} - \text{K})(300 + 273\ \text{K})}\right)$$

$$= 3.40 \text{ x } 10^{-14}\ \text{m}^2/\text{s}$$

And, finally, the diffusion flux is computed using Equation 5.3 by taking the negative product of this diffusion coefficient and the concentration gradient, as

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -(3.40 \times 10^{-14}\ \text{m}^2/\text{s})(-\ 0.184\ \ \text{kg/m}^4) = 6.26 \times 10^{-15}\ \text{kg/m}^2\text{-s}$$

Nonsteady-State Diffusion

5.10 It can be shown that

$$C_x = \frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

is a solution to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

simply by taking appropriate derivatives of the C_x expression. When this is carried out,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} = \frac{B}{2D^{1/2}t^{3/2}}\left(\frac{x^2}{2Dt} - 1\right)\exp\left(-\frac{x^2}{4Dt}\right)$$

5.11 We are asked to compute the carburizing (i.e., diffusion) time required for a specific nonsteady-state diffusion situation. It is first necessary to use Equation 5.5:

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

wherein, $C_x = 0.30$, $C_0 = 0.10$, $C_s = 0.90$, and $x = 4$ mm $= 4 \times 10^{-3}$ 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

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

From which

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

Now, from Table 5.2, at 1100°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,

$$0.814 = \frac{4 \times 10^{-3} \text{ m}}{(2)\sqrt{(5.35 \times 10^{-11} \text{ m}^2/\text{s})(t)}}$$

Solving for *t* yields

$$t = 1.13 \text{ x } 10^5 \text{ s} = 31.3 \text{ h}$$

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

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

Thus,

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

Using data in Table 5.1 and linear interpolation

z	erf (z)
0.40	0.4284
z	0.4545
0.45	0.4755

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

And,

$$z = 0.4277$$

Which means that

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

And, finally

$$x = 2(0.4277)\sqrt{Dt} = (0.8554)\sqrt{(4.3 \times 10^{-11}\ \text{m}^2/\text{s})(3.6 \times 10^4\ \text{s})}$$

$$= 1.06 \text{ x } 10^{-3} \text{ m} = 1.06 \text{ mm}$$

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. “4.3e-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 1.05 mm.

5.13 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

$$\frac{C_x - C_0}{C_s - C_0} = \frac{C_x - 0}{0.2 - 0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= 1 - \operatorname{erf}\left[\frac{2 \times 10^{-3}\text{ m}}{(2)\sqrt{(1.9 \times 10^{-11}\text{ m}^2/\text{s})(25\text{ h})(3600\text{ s/h})}}\right]$$

$$= 1 - \operatorname{erf}\,(0.765)$$

Using data in Table 5.1 and linear interpolation

z	erf (z)
0.750	0.7112
0.765	y
0.800	0.7421

$$\frac{0.765 - 0.750}{0.800 - 0.750} = \frac{y - 0.7112}{0.7421 - 0.7112}$$

from which

$$y = \operatorname{erf}\,(0.765) = 0.7205$$

Thus,

$$\frac{C_x - 0}{0.2 - 0} = 1.0 - 0.7205$$

This expression gives

$$C_x = 0.056\text{ wt\% N}$$

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. “1.9e-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 0.06 wt%.

5.14 For this platinum-gold diffusion couple for which C_1 = 1 wt% Au and C_2 = 4 wt% Au, we are asked to determine the diffusion time at 1000°C that will give a composition of 2.8 wt% Au at the 10 μm position. Thus, for this problem, Equation 5.12 takes the form

$$2.8 = \left(\frac{1 + 4}{2}\right) - \left(\frac{1 - 4}{2}\right) \text{erf}\left(\frac{10 \times 10^{-6}\ \text{m}}{2\sqrt{Dt}}\right)$$

It now becomes necessary to compute the diffusion coefficient at 1000°C (1273 K) given that $D_0 = 1.3 \text{ x } 10^{-5}\ \text{m}^2/\text{s}$ and Q_d = 252,000 J/mol. From Equation 5.8 we have

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

$$= \left(1.3 \times 10^{-5}\ \text{m}^2/\text{s}\right) \exp\left[-\frac{252{,}000\ \text{J/mol}}{(8.31\ \text{J/mol} - \text{K})(1273\ \text{K})}\right]$$

$$= 5.87 \text{ x } 10^{-16}\ \text{m}^2/\text{s}$$

Substitution of this value into the above equation leads to

$$2.8 = \left(\frac{1 + 4}{2}\right) - \left(\frac{1 - 4}{2}\right) \text{erf}\left[\frac{10 \times 10^{-6}\ \text{m}}{2\sqrt{(5.87 \times 10^{-16}\ \text{m}^2/\text{s})\,(t)}}\right]$$

This expression reduces to the following form:

$$0.2000 = \text{erf}\left[\frac{206.4\sqrt{\text{s}}}{\sqrt{t}}\right]$$

Using data in Table 5.1, it is necessary to determine the value of z for which the error function is 0.2000. We use linear interpolation as follows:

z	erf (z)
0.150	0.1680
y	0.2000
0.200	0.2227

$$\frac{y - 0.150}{0.200 - 0.150} = \frac{0.2000 - 0.1680}{0.2227 - 0.1680}$$

from which

$$y = 0.1793 = \frac{206.4\sqrt{\mathrm{s}}}{\sqrt{t}}$$

And, solving for t gives

$$t = 1.33 \text{ x } 10^6 \text{ s} = 368 \text{ h} = 15.3 \text{ days}$$

5.15 This problem calls for an estimate of the time necessary to achieve a carbon concentration of 0.35 wt% at a point 6.0 mm from the surface. From Equation 5.6b,

$$\frac{x^2}{Dt} = \text{constant}$$

But since the temperature is constant, so also is *D* constant, and

$$\frac{x^2}{t} = \text{constant}$$

or

$$\frac{x_1^2}{t_1} = \frac{x_2^2}{t_2}$$

Thus,

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

from which

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

Factors That Influence Diffusion

5.16 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,

$$D_{\alpha} = (6.2 \times 10^{-7} \text{ m}^2\text{/s}) \exp\left[-\frac{80{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1173 \text{ K})}\right]$$

$$= 1.69 \text{ x } 10^{-10} \text{ m}^2\text{/s}$$

$$D_{\gamma} = (2.3 \times 10^{-5} \text{ m}^2\text{/s}) \exp\left[-\frac{148{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1173 \text{ K})}\right]$$

$$= 5.86 \text{ x } 10^{-12} \text{ m}^2\text{/s}$$

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.

5.17 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 into Equation 5.8 leads to

$$D = \left(1.2 \times 10^{-4}\ \mathrm{m^2/s}\right) \exp\left[-\frac{131{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(673\ \mathrm{K})}\right]$$

$$= 8.1 \times 10^{-15}\ \mathrm{m^2/s}$$

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 7.8 x 10^{-15} $\mathrm{m^2/s}$.

5.18 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 x 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 x 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. However, the temperature range does not extend to conditions specified in the problem statement. Thus, 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. In the window under "D0" enter preexponential value from Table 5.2—viz. "2.4e-5". Next just below the "Qd" window enter the activation energy value—viz. "189". It is next necessary to specify a temperature range over which the data is to be plotted. The temperature at which *D* has the stipulated value is probably between 500ºC and 1000ºC, so enter "500" in the "T Min" box that is beside "C"; and similarly for the maximum temperature—enter "1000" in the box below "T Max".

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. Click-and-drag this cursor down the line to the point at which the entry under the "Diff Coeff (D):" label reads 2.6 x 10^{-16} m^2/s. The temperature at which the diffusion coefficient has this value is given under the label "Temperature (T):". For this problem, the value is 903 K.

5.19 For this problem we are given D_0 (1.1 x 10^{-4}) and Q_d (272,000 J/mol) for the diffusion of Cr in Ni, and asked to compute the temperature at which D = 1.2 x 10^{-14} m^2/s. Solving for T from Equation 5.9a yields

$$T = \frac{Q_d}{R(\ln D_0 - \ln D)}$$

$$= \frac{272{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(1.1 \times 10^{-4} \text{ m}^2\text{/s}\right) - \ln\left(1.2 \times 10^{-14} \text{ m}^2\text{/s}\right)\right]}$$

$$= 1427 \text{ K} = 1154°\text{C}$$

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, click on the “Custom1” box.

2. In the column on the right-hand side of this window enter the data for this problem. In the window under “D0” enter preexponential value—viz. “1.1e-4”. Next just below the “Qd” window enter the activation energy value—viz. “272”. It is next necessary to specify a temperature range over which the data is to be plotted. The temperature at which D has the stipulated value is probably between 1000ºC and 1500ºC, so enter “1000” in the “T Min” box that is beside “C”; and similarly for the maximum temperature—enter “1500” in the box below “T Max”.

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. Click-and-drag this cursor down the line to the point at which the entry under the “Diff Coeff (D):” label reads 1.2 x 10^{-14} m^2/s. The temperature at which the diffusion coefficient has this value is given under the label “Temperature (T):”. For this problem, the value is 1430 K.

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

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

$$= \left(1.0 \times 10^{-14} \ \mathrm{m^2/s}\right) \exp\left[\frac{193{,}000 \ \mathrm{J/mol}}{(8.31 \ \mathrm{J/mol\text{-}K})(1000 \ \mathrm{K})}\right]$$

$$= 1.22 \text{ x } 10^{-4} \ \mathrm{m^2/s}$$

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

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

$$= 4.8 \text{ x } 10^{-13} \ \mathrm{m^2/s}$$

5.21 (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 x 10^{-15} and 4.8 x 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 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

$$D = \left(3.5 \times 10^{-4}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{315{,}700\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1573\ \text{K})}\right]$$

$$= 1.1 \text{ x } 10^{-14} \text{ m}^2/\text{s}$$

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 “Add Curve” 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 x 10^{-4} m^2/s and 315 kJ/mol, 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 x 10^{-14} m^2/s.

5.22 (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 Equation 5.8 (and using the 600°C value of D)

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

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

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

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

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

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

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 “Add Curve” 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 x 10^{-5} m^2/s and 138 kJ/mol, 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 “1123” (i.e., 850ºC). 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 x 10^{-14} m^2/s.

5.23 This problem asks us to determine the values of Q_d and D_0 for the diffusion of Au in Ag from the plot of log *D* versus 1/*T*. According to Equation 5.9b the slope of this plot is equal to $-\frac{Q_d}{2.3R}$ (rather than $-\frac{Q_d}{R}$ since we are using log *D* rather than ln *D*) and the intercept at 1/*T* = 0 gives the value of log D_0. The slope is equal to

$$\text{slope} = \frac{\Delta(\log D)}{\Delta\left(\frac{1}{T}\right)} = \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Taking $1/T_1$ and $1/T_2$ as 1.0 x 10^{-3} and 0.90 x 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 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 x 10^{-14} m^2/s at *T* = 1064 K (1/*T* = 0.94 x 10^{-3} K^{-1}). Therefore

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

$$= \left(1.0 \times 10^{-14}\ \text{m}^2/\text{s}\right) \exp\left[\frac{212{,}200\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1064\ \text{K})}\right]$$

$$= 2.65 \text{ x } 10^{-4}\ \text{m}^2/\text{s}$$

5.24 This problem asks that we compute the temperature at which the diffusion flux is 6.3 x 10^{-10} kg/m^2-s. Combining Equations 5.3 and 5.8 yields

$$J = -D \frac{\Delta C}{\Delta x}$$

$$= -D_0 \frac{\Delta C}{\Delta x} \exp\left(-\frac{Q_d}{RT}\right)$$

Solving for *T* from this expression leads to

$$T = \left(\frac{Q_d}{R}\right) \frac{1}{\ln\left(-\frac{D_0 \Delta C}{J \, \Delta x}\right)}$$

$$= \left(\frac{80{,}000 \text{ J/mol}}{8.31 \text{ J/mol-K}}\right) \frac{1}{\ln\left[\frac{(6.2 \times 10^{-7} \text{ m}^2\text{/s})(0.85 \text{ kg/m}^3 - 0.40 \text{ kg/m}^3)}{(6.3 \times 10^{-10} \text{ kg/m}^2\text{-s})(10 \times 10^{-3} \text{ m})}\right]}$$

$$= 900 \text{ K} = 627°\text{C}$$

5.25 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 5.3 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

$$D_0 = -\frac{J}{\dfrac{\Delta C}{\Delta x}}\exp\left(\frac{Q_d}{RT}\right)$$

$$= -\left(\frac{7.8 \times 10^{-8}\ \mathrm{kg/m^2\text{-}s}}{-500\ \mathrm{kg/m^4}}\right)\exp\left[\frac{145{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(1200 + 273\ \mathrm{K})}\right]$$

$$= 2.18 \text{ x } 10^{-5}\ \mathrm{m^2/s}$$

The value of the diffusion flux at 1273 K may be computed using these same two equations as follows:

$$J = -D_0\left(\frac{\Delta C}{\Delta x}\right)\exp\left(-\frac{Q_d}{RT}\right)$$

$$= -\left(2.18 \times 10^{-5}\ \mathrm{m^2/s}\right)\left(-500\ \mathrm{kg/m^4}\right)\exp\left[-\frac{145{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(1273\ \mathrm{K})}\right]$$

$$= 1.21 \text{ x } 10^{-8}\ \mathrm{kg/m^2\text{-}s}$$

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

$$Dt = \text{constant}$$

Which, for this problem, takes the form

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

At 1000°C, and using the data from Table 5.2, for the diffusion of carbon in γ-iron—i.e.,

$D_0 = 2.3 \text{ x } 10^{-5} \text{ m}^2/\text{s}$

$Q_d = 148{,}000 \text{ J/mol}$

the diffusion coefficient is equal to

$$D_{1000} = \left(2.3 \text{ x } 10^{-5} \text{ m}^2/\text{s}\right) \exp\left[-\frac{148{,}000 \text{ J/mol}}{(8.31 \text{ J/mol - K})(1000 + 273 \text{ K})}\right]$$

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

Thus, from the above equation

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

And, solving for D_T

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

Now, solving for T from Equation 5.9a gives

$$T = -\frac{Q_d}{R\left(\ln D_T - \ln D_0\right)}$$

$$= -\frac{148{,}000 \text{ J/mol}}{(8.31 \text{ J/mol - K})\left[\ln\left(5.79 \times 10^{-11} \text{ m}^2/\text{s}\right) - \ln\left(2.3 \text{ x } 10^{-5} \text{ m}^2/\text{s}\right)\right]}$$

$$= 1381 \text{ K} = 1108°\text{C}$$

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

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

$$= \left(1.2 \times 10^{-4} \text{ m}^2/\text{s}\right) \exp\left[-\frac{131{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(450 + 273 \text{ K})}\right]$$

$$= 4.08 \text{ x } 10^{-14} \text{ m}^2/\text{s}$$

(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

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

$$= 5.76 \text{ x } 10^{-13} \text{ m}^2/\text{s}$$

Thus,

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

$$= \frac{\left(4.08 \times 10^{-14} \text{ m}^2/\text{s}\right)(15 \text{ h})}{\left(5.76 \times 10^{-13} \text{ m}^2/\text{s}\right)} = 1.06 \text{ h}$$

5.28 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

$$\frac{x^2}{D} = \text{constant}$$

Or

$$\frac{x_{1000}^2}{D_{1000}} = \frac{x_{\mathrm{T}}^2}{D_{\mathrm{T}}}$$

Now, solving for D_{T} from this equation, yields

$$D_{\mathrm{T}} = \frac{x_{\mathrm{T}}^2 D_{1000}}{x_{1000}^2}$$

and incorporating the temperature dependence of D_{1000} utilizing Equation (5.8), yields

$$D_{\mathrm{T}} = \frac{\left(x_{\mathrm{T}}^2\right)\left[D_0 \exp\left(-\frac{Q_d}{RT}\right)\right]}{x_{1000}^2}$$

$$= \frac{(2\ \mathrm{mm})^2\left[\left(2.7 \times 10^{-4}\ \mathrm{m^2/s}\right)\exp\left(-\frac{236{,}000\ \ \mathrm{J/mol}}{(8.31\ \ \mathrm{J/mol\text{-}K})(1273\ \ \mathrm{K})}\right)\right]}{(1\ \mathrm{mm})^2}$$

$$= 2.21 \times 10^{-13}\ \mathrm{m^2/s}$$

We now need to find the *T* at which *D* has this value. This is accomplished by rearranging Equation 5.9a and solving for *T* as

$$T = \frac{Q_d}{R\left(\ln D_0 - \ln D\right)}$$

$$= \frac{236{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})\left[\ln\left(2.7 \times 10^{-4}\ \mathrm{m^2/s}\right) - \ln\left(2.21 \times 10^{-13}\ \mathrm{m^2/s}\right)\right]}$$

$$= 1357\ \mathrm{K} = 1084^\circ\mathrm{C}$$

5.29 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:

$$D_{800} = \left(1.5 \times 10^{-4} \text{ m}^2\text{/s}\right)\exp\left[-\frac{125{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(800 + 273 \text{ K})}\right]$$

$$= 1.22 \text{ x } 10^{-10} \text{ m}^2\text{/s}$$

$$D_{1000} = \left(1.5 \times 10^{-4} \text{ m}^2\text{/s}\right)\exp\left[-\frac{125{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1000 + 273 \text{ K})}\right]$$

$$= 1.11 \text{ x } 10^{-9} \text{ m}^2\text{/s}$$

Now, solving the above expression for x_{1000} yields

$$x_{1000} = x_{800}\sqrt{\frac{D_{1000}}{D_{800}}}$$

$$= (5 \text{ mm})\sqrt{\frac{1.11 \times 10^{-9} \text{ m}^2\text{/s}}{1.22 \times 10^{-10} \text{ m}^2\text{/s}}}$$

$$= 15.1 \text{ mm}$$

5.31 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

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.30 - 0.10}{1.10 - 0.10} = 0.2000 = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Or

$$\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.8000$$

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 x 10^{-3} m), solving for D from the above equation yields

$$D = \frac{x^2}{(4t)(0.9063)^2}$$

$$= \frac{\left(3.5 \times 10^{-3} \text{ m}\right)^2}{(4)(172{,}800 \text{ s})(0.821)} = 2.16 \times 10^{-11} \text{ m}^2/\text{s}$$

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

$$T = \frac{Q_d}{R\left(\ln D_0 - \ln D\right)}$$

From Table 5.2, D_0 and Q_d for the diffusion of C in FCC Fe are 2.3 x 10^{-5} m^2/s and 148,000 J/mol, respectively. Therefore

$$T = \frac{148{,}000 \text{ J/mol}}{(8.31 \text{ J/mol - K})\left[\ln\left(2.3 \times 10^{-5} \text{ m}^2/\text{s}\right) - \ln\left(2.16 \times 10^{-11} \text{ m}^2/\text{s}\right)\right]}$$

$$= 1283 \text{ K} = 1010°\text{C}$$

5.30 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

$$Dt = \text{constant}$$

Or

$$D_{600}t_{600} = D_{900}t_{900}$$

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 = 80,000 J/mol and D_0 = 6.2 x 10^{-7} m^2/s. Therefore,

$$D_{600} = \left(6.2 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{80{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(600 + 273\ \text{K})}\right]$$

$$= 1.01 \times 10^{-11}\ \text{m}^2/\text{s}$$

$$D_{900} = \left(6.2 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left[-\frac{80{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(900 + 273\ \text{K})}\right]$$

$$= 1.69 \times 10^{-10}\ \text{m}^2/\text{s}$$

Now, solving the original equation for t_{900} gives

$$t_{900} = \frac{D_{600}t_{600}}{D_{900}}$$

$$= \frac{\left(1.01 \times 10^{-11}\ \text{m}^2/\text{s}\right)(100\ \text{min})}{1.69 \times 10^{-10}\ \text{m}^2/\text{s}}$$

$$= 5.98\ \text{min}$$

DESIGN PROBLEMS

Steady-State Diffusion

5.D1 This problem calls for us to ascertain whether or not a hydrogen-nitrogen gas mixture may be enriched with respect to hydrogen partial pressure by allowing the gases to diffuse through an iron sheet at an elevated temperature. If this is possible, the temperature and sheet thickness are to be specified; if such is not possible, then we are to state the reasons why. Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.3. 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 five 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.

$$J_H = \sqrt{5}\, J_N$$

Thus, equating the Fick's law expressions incorporating the given equations for the diffusion coefficients and concentrations in terms of partial pressures leads to the following

$$J_H$$

$$= \frac{1}{\Delta x} \times$$

$$\left(2.5 \times 10^{-3}\right)\left(\sqrt{0.1013\ \text{MPa}} - \sqrt{0.051\ \text{MPa}}\right)\exp\left(-\frac{27.8\ \text{kJ}}{RT}\right)\left(1.4 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left(-\frac{13.4\ \text{kJ}}{RT}\right)$$

$$= \sqrt{5}\, J_N$$

$$= \frac{\sqrt{5}}{\Delta x} \times$$

$$\left(2.75 \times 10^{3}\right)\left(\sqrt{0.1013\ \text{MPa}} - \sqrt{0.01013\ \text{MPa}}\right)\exp\left(-\frac{37.6\ \text{kJ}}{RT}\right)\left(3.0 \times 10^{-7}\ \text{m}^2/\text{s}\right)\exp\left(-\frac{76.15\ \text{kJ}}{RT}\right)$$

The Δx's cancel out, which means that the process is independent of sheet thickness. Now solving the above expression for the absolute temperature T gives

$$T = 3467\ \text{K}$$

which value is extremely high (surely above the vaporization point of iron). Thus, such a diffusion process is *not possible*.

5.D2 This problem calls for us to ascertain whether or not an A_2-B_2 gas mixture may be enriched with respect to the A partial pressure by allowing the gases to diffuse through a metal sheet at an elevated temperature. If this is possible, the temperature and sheet thickness are to be specified; if such is not possible, then we are to state the reasons why. Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.3. 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.

$$J_A = \sqrt{2.5}\, J_B$$

Thus, equating the Fick's law expressions incorporating the given equations for the diffusion coefficients and concentrations in terms of partial pressures leads to the following

$$J_A$$

$$= \frac{1}{\Delta x} \times$$

$$\left(1.5 \times 10^3\right)\left(\sqrt{0.1013 \text{ MPa}} - \sqrt{0.051 \text{ MPa}}\right) \exp\left(-\frac{20.0 \text{ kJ}}{RT}\right)\left(5.0 \times 10^{-7} \text{ m}^2/\text{s}\right) \exp\left(-\frac{13.0 \text{ kJ}}{RT}\right)$$

$$= \sqrt{2.5}\, J_B$$

$$= \frac{\sqrt{2.5}}{\Delta x} \times$$

$$\left(2.0 \times 10^3\right)\left(\sqrt{0.1013 \text{ MPa}} - \sqrt{0.0203 \text{ MPa}}\right) \exp\left(-\frac{27.0 \text{ kJ}}{RT}\right)\left(3.0 \times 10^{-6} \text{ m}^2/\text{s}\right) \exp\left(-\frac{21.0 \text{ kJ}}{RT}\right)$$

The Δx's cancel out, which means that the process is independent of sheet thickness. Now solving the above expression for the absolute temperature T gives

$$T = 568 \text{ K } (295°\text{C})$$

5.D4 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

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.75 - 0.15}{1.20 - 0.15}$$

$$= 0.5714 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

And 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 stipulates that x = 0.65 mm = 6.5 x 10^{-4} m. Therefore

$$\frac{6.5 \times 10^{-4}\ \text{m}}{2\sqrt{Dt}} = 0.4002$$

Which leads to

$$Dt = 6.59 \text{ x } 10^{-7} \text{ m}^2$$

Furthermore, the diffusion coefficient depends on temperature according to Equation 5.8; and, as noted in Design Example 5.1, D_0 = 2.3 x 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

$$t \text{ (in s)} = \frac{2.86 \times 10^{-2}}{\exp\left(-\frac{17{,}810}{T}\right)}$$

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	Time 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	h
1.3	1000	26,700	7.4
	1100	9,600	2.7
	1200	4,000	1.1
1.4	1000	21,100	6.1
	1100	7,900	2.2
	1200	1,500	0.9

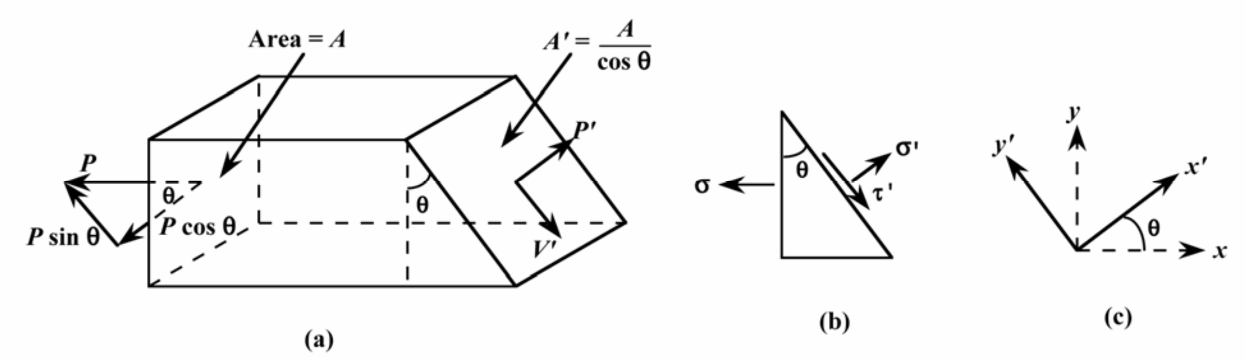
CHAPTER 6

MECHANICAL PROPERTIES OF METALS

PROBLEM SOLUTIONS

Concepts of Stress and Strain

6.1 This problem asks that we derive Equations 6.4a and 6.4b, using mechanics of materials principles. In Figure (a) below is shown a block element of material of cross-sectional area *A* that is subjected to a tensile force *P*. Also represented is a plane that is oriented at an angle θ referenced to the plane perpendicular to the tensile axis; the area of this plane is $A' = A/\cos\theta$. In addition, and the forces normal and parallel to this plane are labeled as *P′* and *V′*, respectively. Furthermore, on the left-hand side of this block element are shown force components that are tangential and perpendicular to the inclined plane. In Figure (b) are shown the orientations of the applied stress σ, the normal stress to this plane σ', as well as the shear stress τ' taken parallel to this inclined plane. In addition, two coordinate axis systems in represented in Figure (c): the primed *x* and *y* axes are referenced to the inclined plane, whereas the unprimed *x* axis is taken parallel to the applied stress.



Normal and shear stresses are defined by Equations 6.1 and 6.3, respectively. However, we now chose to express these stresses in terms (i.e., general terms) of normal and shear forces (*P* and *V*) as

$$\sigma = \frac{P}{A}$$

$$\tau = \frac{V}{A}$$

For static equilibrium in the *x′* direction the following condition must be met:

$$\sum F_{x'} = 0$$

which means that

$$P\tilde{O} - P\cos\theta = 0$$

Or that

$$P' = P\cos\theta$$

Now it is possible to write an expression for the stress σ' in terms of P' and A' using the above expression and the relationship between A and A' [Figure (a)]:

$$\sigma' = \frac{P\hat{C}}{A\hat{C}}$$

$$= \frac{P\cos\theta}{\dfrac{A}{\cos\theta}} = \frac{P}{A}\cos^2\theta$$

However, it is the case that $P/A = \sigma$; and, after making this substitution into the above expression, we have Equation 6.4a--that is

$$\sigma' = \sigma\cos^2\theta$$

Now, for static equilibrium in the y' direction, it is necessary that

$$\sum F_{y\tilde{O}} = 0$$

$$= -V\tilde{O} + P\sin\theta$$

Or

$$V' = P\sin\theta$$

We now write an expression for τ' as

$$\tau' = \frac{V'}{A'}$$

And, substitution of the above equation for V' and also the expression for A' gives

$$\tau' = \frac{V'}{A'}$$

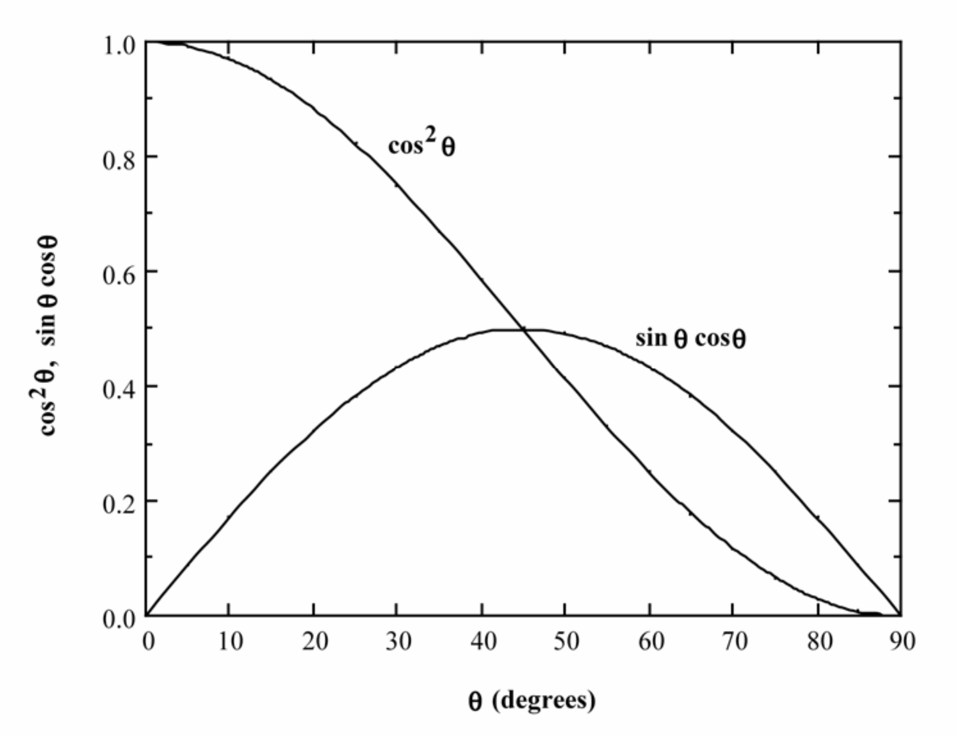
$$= \frac{P\sin\theta}{\dfrac{A}{\cos\theta}}$$

$$= \frac{P}{A}\sin\theta\cos\theta$$

$$= \sigma\sin\theta\cos\theta$$

which is just Equation 6.4b.

6.2 (a) Below are plotted curves of $\cos^2\theta$ (for σ') and $\sin\theta\cos\theta$ (for τ') versus θ.



(b) The maximum normal stress occurs at an inclination angle of 0°.

(c) The maximum shear stress occurs at an inclination angle of 45°.

Stress-Strain Behavior

6.3 This problem calls for us to calculate the elastic strain that results for a copper specimen stressed in tension. The cross-sectional area is just (15.2 mm) x (19.1 mm) = 290 mm^2 (= 2.90 x 10^{-4} m^2 = 0.45 in.^2); also, the elastic modulus for Cu is given in Table 6.1 as 110 GPa (or 110 x 10^9 N/m^2). Combining Equations 6.1 and 6.5 and solving for the strain yields

$$\varepsilon = \frac{\sigma}{E} = \frac{F}{A_0 E} = \frac{44{,}500 \text{ N}}{(2.90 \times 10^{-4} \text{ m}^2)(110 \times 10^9 \text{ N/m}^2)} = 1.39 \text{ x } 10^{-3}$$

6.4 We are asked to compute the maximum length of a cylindrical nickel specimen (before deformation) that is deformed elastically in tension. For a cylindrical specimen

$$A_0 = \pi\left(\frac{d_0}{2}\right)^2$$

where d_0 is the original diameter. Combining Equations 6.1, 6.2, and 6.5 and solving for l_0 leads to

$$l_0 = \frac{\Delta l}{\varepsilon} = \frac{\Delta l}{\frac{\sigma}{E}} \acute{\not{Z}} \frac{\Delta l\, E}{\frac{F}{A_0}} \acute{Z}= \frac{\Delta l\, E\pi\left(\frac{d_0}{2}\right)^2}{F} = \frac{\Delta l\, E\pi\, d_0^2}{4F}$$

$$= \frac{(0.25 \times 10^{-3}\,\text{m})(207 \times 10^9\,\text{N/m}^2)\,(\pi)\,(10.2 \times 10^{-3}\,\text{m})^2}{(4)(8900\ \ \text{N})}$$

$$= 0.475\ \text{m} = 475\ \text{mm}\ (18.7\ \text{in.})$$

6.5 This problem asks us to compute the elastic modulus of aluminum. For a square cross-section, $A_0 = b_0^2$, where b_0 is the edge length. Combining Equations 6.1, 6.2, and 6.5 and solving for E, leads to

$$E = \frac{\sigma}{\varepsilon} = \frac{\dfrac{F}{A_0}}{\dfrac{\Delta l}{l_0}} = \frac{F l_0}{b_0^2 \Delta l}$$

$$= \frac{(66{,}700 \ \mathrm{N})\left(125 \times 10^{-3}\,\mathrm{m}\right)}{\left(16.5 \times 10^{-3}\,\mathrm{m}\right)^2 \left(0.43 \times 10^{-3}\,\mathrm{m}\right)}$$

$$= 71.2 \times 10^9 \ \mathrm{N/m^2} = 71.2 \ \mathrm{GPa} \ \ (10.4 \times 10^6 \ \mathrm{psi})$$

6.6 In order to compute the elongation of the Ni wire when the 300 N load is applied we must employ Equations 6.1, 6.2, and 6.5. Solving for Δl and realizing that for Ni, E = 207 GPa (30 x 10^6 psi) (Table 6.1),

$$\Delta l = l_0 \varepsilon = l_0 \frac{\sigma}{E} = \frac{l_0 F}{E A_0} = \frac{l_0 F}{E\pi\left(\frac{d_0}{2}\right)^2} = \frac{4 l_0 F}{E\pi d_0^2}$$

$$= \frac{(4)(30\ \text{m})(300\ \text{N})}{\left(207 \times 10^9\ \text{N/m}^2\right)(\pi)\left(2 \times 10^{-3}\ \text{m}\right)^2} = 0.0138\ \text{m} = 13.8\ \text{mm}\ (0.53\ \text{in.})$$

6.7 (a) This portion of the problem calls for a determination of the maximum load that can be applied without plastic deformation (F_y). Taking the yield strength to be 345 MPa, and employment of Equation 6.1 leads to

$$F_y = \sigma_y A_0 = \left(345 \text{ x } 10^6 \text{ N/m}^2\right)\left(130 \text{ x } 10^{-6} \text{ m}^2\right)$$

$$= 44{,}850 \text{ N} \quad (10{,}000 \text{ lb}_\text{f})$$

(b) The maximum length to which the sample may be deformed without plastic deformation is determined from Equations 6.2 and 6.5 as

$$l_i = l_0\left(1 + \frac{\sigma}{E}\right)$$

$$= (76 \text{ mm})\left[1 + \frac{345 \text{ MPa}}{103 \text{ x } 10^3 \text{ MPa}}\right] = 76.25 \text{ mm} \quad (3.01 \text{ in.})$$

6.8 This problem asks us to compute the diameter of a cylindrical specimen of steel in order to allow an elongation of 0.38 mm. Employing Equations 6.1, 6.2, and 6.5, assuming that deformation is entirely elastic

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0^2}{4}\right)} = E\,\frac{\Delta l}{l_0}$$

Or, solving for d_0

$$d_0 = \sqrt{\frac{4\,l_0 F}{\pi E \Delta l}}$$

$$= \sqrt{\frac{(4)\left(500 \text{ x } 10^{-3}\text{ m}\right)(11{,}100 \text{ N})}{(\pi)\left(207 \text{ x } 10^{9} \text{ N/m}^2\right)\left(0.38 \text{ x } 10^{-3}\text{ m}\right)}}$$

$$= 9.5 \text{ x } 10^{-3} \text{ m} = 9.5 \text{ mm (0.376 in.)}$$

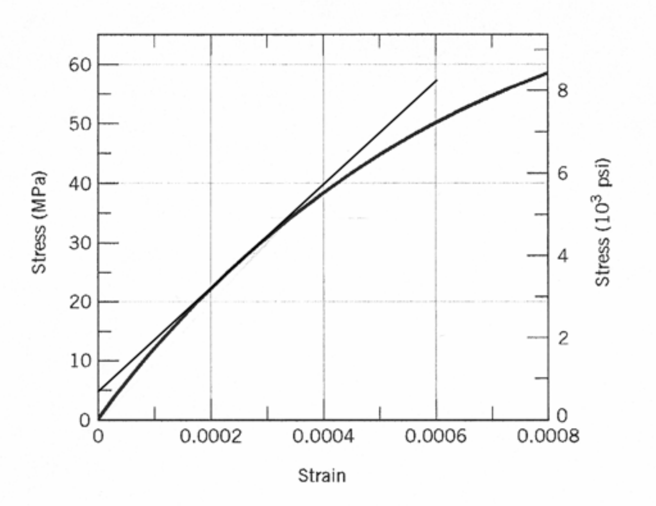
6.9 This problem asks that we calculate the elongation Δl of a specimen of steel the stress-strain behavior of which is shown in Figure 6.21. First it becomes necessary to compute the stress when a load of 65,250 N is applied using Equation 6.1 as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{65{,}250 \text{ N}}{\pi\left(\frac{8.5 \text{ x } 10^{-3} \text{ m}}{2}\right)^2} = 1150 \text{ MPa} \ \ (170{,}000 \text{ psi})$$

Referring to Figure 6.21, at this stress level we are in the elastic region on the stress-strain curve, which corresponds to a strain of 0.0054. Now, utilization of Equation 6.2 to compute the value of Δl

$$\Delta l = \varepsilon l_0 = (0.0054)(80 \text{ mm}) = 0.43 \text{ mm} \ \ (0.017 \text{ in.})$$

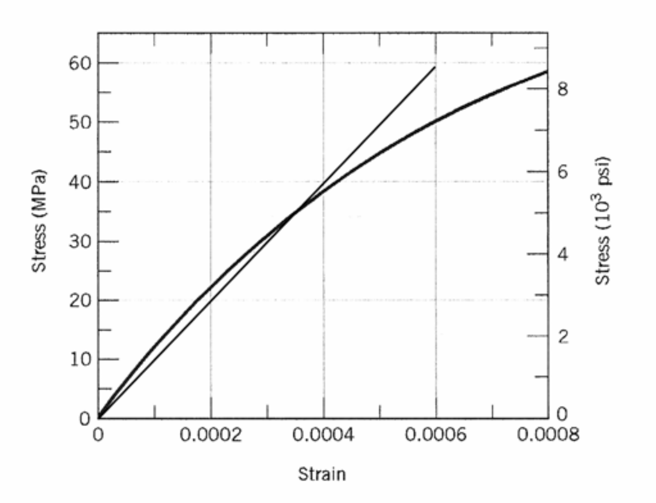
6.10 (a) This portion of the problem asks that the tangent modulus be determined for the gray cast iron, the stress-strain behavior of which is shown in Figure 6.22. In the figure below is shown a tangent draw on the curve at a stress of 25 MPa.



The slope of this line (i.e., $\Delta\sigma/\Delta\varepsilon$), the tangent modulus, is computed as follows:

$$\frac{\Delta\sigma}{\Delta\varepsilon} = \frac{57\text{ MPs} - 0\text{ MPa}}{0.0006 - 0} = 95{,}000\text{ MPa} = 95\text{ GPa} \ (13.8 \text{ x } 10^6 \text{ psi})$$

(b) The secant modulus taken from the origin is calculated by taking the slope of a secant drawn from the origin through the stress-strain curve at 35 MPa (5,000 psi). This secant modulus is drawn on the curve shown below:



The slope of this line (i.e., $\Delta\sigma/\Delta\varepsilon$), the secant modulus, is computed as follows:

$$\frac{\Delta\sigma}{\Delta\varepsilon} = \frac{60 \text{ MPs} - 0 \text{ MPa}}{0.0006 - 0} = 100,000 \text{ MPa} = 100 \text{ GPa} \ (14.5 \text{ x } 10^6 \text{ psi})$$

6.11 We are asked, using the equation given in the problem statement, to verify that the modulus of elasticity values along [110] directions given in Table 3.3 for aluminum, copper, and iron are correct. The α, β, and γ parameters in the equation correspond, respectively, to the cosines of the angles between the [110] direction and [100], [010] and [001] directions. Since these angles are 45°, 45°, and 90°, the values of α, β, and γ are 0.707, 0.707, and 0, respectively. Thus, the given equation takes the form

$$\frac{1}{E_{<110>}}$$

$$= \frac{1}{E_{<100>}} - 3\left(\frac{1}{E_{<100>}} - \frac{1}{E_{<111>}}\right)\Big[(0.707)^2(0.707)^2 + (0.707)^2(0)^2 + (0)^2(0.707)^2\Big]$$

$$= \frac{1}{E_{<100>}} - (0.75)\left(\frac{1}{E_{<100>}} - \frac{1}{E_{<111>}}\right)$$

Utilizing the values of $E_{<100>}$ and $E_{<111>}$ from Table 3.3 for Al

$$\frac{1}{E_{<110>}} = \frac{1}{63.7\text{ GPa}} - (0.75)\left[\frac{1}{63.7\text{ GPa}} - \frac{1}{76.1\text{ GPa}}\right]$$

Which leads to, $E_{<110>}$ = 72.6 GPa, the value cited in the table.

For Cu,

$$\frac{1}{E_{<110>}} = \frac{1}{66.7\text{ GPa}} - (0.75)\left[\frac{1}{66.7\text{ GPa}} - \frac{1}{191.1\text{ GPa}}\right]$$

Thus, $E_{<110>}$ = 130.3 GPa, which is also the value cited in the table.

Similarly, for Fe

$$\frac{1}{E_{<110>}} = \frac{1}{125.0\text{ GPa}} - (0.75)\left[\frac{1}{125.0\text{ GPa}} - \frac{1}{272.7\text{ GPa}}\right]$$

And $E_{<110>}$ = 210.5 GPa, which is also the value given in the table.

6.12 This problem asks that we derive an expression for the dependence of the modulus of elasticity, *E*, on the parameters *A*, *B*, and *n* in Equation 6.25. It is first necessary to take dE_N/dr in order to obtain an expression for the force *F*; this is accomplished as follows:

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

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

The second step is to set this dE_N/dr expression equal to zero and then solve for r (= r_0). The algebra for this procedure is carried out in Problem 2.14, with the result that

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

Next it becomes necessary to take the derivative of the force (*dF/dr*), which is accomplished as follows:

$$\frac{dF}{dr} = \frac{d\left(\frac{A}{r^2}\right)}{dr} + \frac{d\left(-\frac{nB}{r^{(n+1)}}\right)}{dr}$$

$$= -\frac{2A}{r^3} + \frac{(n)(n+1)B}{r^{(n+2)}}$$

Now, substitution of the above expression for r_0 into this equation yields

$$\left(\frac{dF}{dr}\right)_{r_0} = -\frac{2A}{\left(\frac{A}{nB}\right)^{3/(1-n)}} + \frac{(n)(n+1)B}{\left(\frac{A}{nB}\right)^{(n+2)/(1-n)}}$$

which is the expression to which the modulus of elasticity is proportional.

6.13 This problem asks that we rank the magnitudes of the moduli of elasticity of the three hypothetical metals X, Y, and Z. From Problem 6.12, it was shown for materials in which the bonding energy is dependent on the interatomic distance r according to Equation 6.25, that the modulus of elasticity E is proportional to

$$E \propto -\frac{2A}{\left(\dfrac{A}{nB}\right)^{3/(1-n)}} + \frac{(n)(n+1)B}{\left(\dfrac{A}{nB}\right)^{(n+2)/(1-n)}}$$

For metal X, A = 1.5, B = 7 x 10^{-6}, and n = 8. Therefore,

$$E \propto -\frac{(2)(1.5)}{\left[\dfrac{1.5}{(8)\left(7 \text{ x } 10^{-6}\right)}\right]^{3/(1-8)}} + \frac{(8)(8+1)\left(7 \text{ x } 10^{-6}\right)}{\left[\dfrac{1.5}{(8)\left(7 \text{ x } 10^{-6}\right)}\right]^{(8+2)/(1-8)}}$$

$$= 830$$

For metal Y, A = 2.0, B = 1 x 10^{-5}, and n = 9. Hence

$$E \propto -\frac{(2)(2.0)}{\left[\dfrac{2.0}{(9)\left(1 \text{ x } 10^{-5}\right)}\right]^{3/(1-9)}} + \frac{(9)(9+1)\left(1 \text{ x } 10^{-5}\right)}{\left[\dfrac{2.0}{(9)\left(1 \text{ x } 10^{-5}\right)}\right]^{(9+2)/(1-9)}}$$

$$= 683$$

And, for metal Z, A = 3.5, B = 4 x 10^{-6}, and n = 7. Thus

$$E \propto -\frac{(2)(3.5)}{\left[\dfrac{3.5}{(7)\left(4 \text{ x } 10^{-6}\right)}\right]^{3/(1-7)}} + \frac{(7)(7+1)\left(4 \text{ x } 10^{-6}\right)}{\left[\dfrac{3.5}{(7)\left(4 \text{x } 10^{-6}\right)}\right]^{(7+2)/(1-7)}}$$

$$= 7425$$

Therefore, metal Z has the highest modulus of elasticity.

Elastic Properties of Materials

6.14 (a) We are asked, in this portion of the problem, to determine the elongation of a cylindrical specimen of steel. Combining Equations 6.1, 6.2, and 6.5, leads to

$$\sigma = E\varepsilon$$

$$\frac{F}{\pi\left(\frac{d_0^2}{4}\right)} = E\,\frac{\Delta l}{l_0}$$

Or, solving for Δl (and realizing that E = 207 GPa, Table 6.1), yields

$$\Delta l = \frac{4F\,l_0}{\pi\,d_0^2 E}$$

$$= \frac{(4)(48{,}900\ \text{N})\left(250 \text{ x } 10^{-3}\,\text{m}\right)}{(\pi)\left(15.2 \text{ x } 10^{-3}\,\text{m}\right)^2\left(207 \text{ x } 10^{9}\ \text{N/m}^2\right)} = 3.25 \text{ x } 10^{-4}\ \text{m} = 0.325\ \text{mm}\ \ (0.013\ \text{in.})$$

(b) We are now called upon to determine the change in diameter, Δd. Using Equation 6.8

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\Delta d/d_0}{\Delta l/l_0}$$

From Table 6.1, for steel, $\nu = 0.30$. Now, solving the above expression for Δd yields

$$\Delta d = -\frac{\nu\,\Delta l\,d_0}{l_0} = -\frac{(0.30)(0.325\ \text{mm})(15.2\ \text{mm})}{250\ \text{mm}}$$

$$= -5.9 \text{ x } 10^{-3}\ \text{mm}\ \ (-2.3 \text{ x } 10^{-4}\ \text{in.})$$

The diameter will decrease.

6.15 This problem asks that we calculate the force necessary to produce a reduction in diameter of 2.5 x 10^{-3} mm for a cylindrical bar of aluminum. For a cylindrical specimen, the cross-sectional area is equal to

$$A_0 = \frac{\pi d_0^2}{4}$$

Now, combining Equations 6.1 and 6.5 leads to

$$\sigma = \frac{F}{A_0} = \frac{F}{\dfrac{\pi d_0^2}{4}} = E\varepsilon_z$$

And, since from Equation 6.8

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{\dfrac{\Delta d}{d_0}}{\nu} = -\frac{\Delta d}{\nu d_0}$$

Substitution of this equation into the above expression gives

$$\frac{F}{\dfrac{\pi d_0^2}{4}} = E\left(-\frac{\Delta d}{\nu d_0}\right)$$

And, solving for F leads to

$$F = -\frac{d_0 \Delta d\, \pi E}{4\nu}$$

From Table 6.1, for aluminum, $\nu = 0.33$ and $E = 69$ GPa. Thus,

$$F = -\frac{\left(19 \text{ x } 10^{-3}\text{ m}\right)\left(-2.5 \text{ x } 10^{-6}\text{ m}\right)(\pi)\left(69 \text{ x } 10^{9}\text{ N/m}^2\right)}{(4)(0.33)}$$

$$= 7{,}800 \text{ N} \quad (1785 \text{ lb}_\text{f})$$

6.16 This problem asks that we compute Poisson's ratio for the metal alloy. From Equations 6.5 and 6.1

$$\varepsilon_z = \frac{\sigma}{E} = \frac{F}{A_0 E} = \frac{F}{\pi\left(\dfrac{d_0}{2}\right)^2 E} = \frac{4F}{\pi\, d_0^2\, E}$$

Since the transverse strain ε_x is just

$$\varepsilon_x = \frac{\Delta d}{d_0}$$

and Poisson's ratio is defined by Equation 6.8, then

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\Delta d / d_0}{\left(\dfrac{4F}{\pi\, d_0^2 E}\right)} = -\frac{d_0 \Delta d\, \pi\, E}{4F}$$

$$= -\frac{\left(10 \text{ x } 10^{-3} \text{ m}\right)\left(-7 \text{ x } 10^{-6} \text{ m}\right)(\pi)\left(100 \text{ x } 10^{9} \text{ N/m}^2\right)}{(4)(15{,}000 \text{ N})} = 0.367$$

6.17 This problem asks that we compute the original length of a cylindrical specimen that is stressed in compression. It is first convenient to compute the lateral strain ε_x as

$$\varepsilon_x = \frac{\Delta d}{d_0} = \frac{30.04 \text{ mm} - 30.00 \text{ mm}}{30.00 \text{ mm}} = 1.33 \text{ x } 10^{-3}$$

In order to determine the longitudinal strain ε_z we need Poisson's ratio, which may be computed using Equation 6.9; solving for ν yields

$$\nu = \frac{E}{2G} - 1 = \frac{65.5 \text{ x } 10^3 \text{ MPa}}{(2)\left(25.4 \text{ x } 10^3 \text{ MPa}\right)} - 1 = 0.289$$

Now ε_z may be computed from Equation 6.8 as

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{1.33 \text{ x } 10^{-3}}{0.289} = -4.60 \text{ x } 10^{-3}$$

Now solving for l_0 using Equation 6.2

$$l_0 = \frac{l_i}{1 + \varepsilon_z}$$

$$= \frac{105.20 \text{ mm}}{1 - 4.60 \text{ x } 10^{-3}} = 105.69 \text{ mm}$$

6.18 This problem asks that we calculate the modulus of elasticity of a metal that is stressed in tension. Combining Equations 6.5 and 6.1 leads to

$$E = \frac{\sigma}{\varepsilon_z} = \frac{F}{A_0 \varepsilon_z} = \frac{F}{\varepsilon_z \pi \left(\frac{d_0}{2}\right)^2} = \frac{4F}{\varepsilon_z \pi d_0^2}$$

From the definition of Poisson's ratio, (Equation 6.8) and realizing that for the transverse strain, $\varepsilon_x = \frac{\Delta d}{d_0}$

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{\Delta d}{d_0 \nu}$$

Therefore, substitution of this expression for ε_z into the above equation yields

$$E = \frac{4F}{\varepsilon_z \pi d_0^2} = \frac{4F\nu}{\pi d_0 \Delta d}$$

$$= \frac{(4)(1500 \ \text{N})(0.35)}{\pi \left(10 \times 10^{-3} \text{m}\right)\left(6.7 \times 10^{-7} \text{m}\right)} = 10^{11} \text{ Pa} = 100 \text{ GPa} \ \ (14.7 \text{ x } 10^{6} \text{ psi})$$

6.19 We are asked to ascertain whether or not it is possible to compute, for brass, the magnitude of the load necessary to produce an elongation of 1.9 mm (0.075 in.). It is first necessary to compute the strain at yielding from the yield strength and the elastic modulus, and then the strain experienced by the test specimen. Then, if

$$\varepsilon(\text{test}) < \varepsilon(\text{yield})$$

deformation is elastic, and the load may be computed using Equations 6.1 and 6.5. However, if

$$\varepsilon(\text{test}) > \varepsilon(\text{yield})$$

computation of the load is not possible inasmuch as deformation is plastic and we have neither a stress-strain plot nor a mathematical expression relating plastic stress and strain. We compute these two strain values as

$$\varepsilon(\text{test}) = \frac{\Delta l}{l_0} = \frac{1.9 \text{ mm}}{380 \text{ mm}} = 0.005$$

and

$$\varepsilon(\text{yield}) = \frac{\sigma_y}{E} = \frac{240 \text{ MPa}}{110 \text{ x } 10^3 \text{ MPa}} = 0.0022$$

Therefore, computation of the load is *not possible* since ε(test) > ε(yield).

6.20 (a) This part of the problem asks that we ascertain which of the metals in Table 6.1 experience an elongation of less than 0.072 mm when subjected to a tensile stress of 50 MPa. The maximum strain that may be sustained, (using Equation 6.2) is just

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{0.072 \text{ mm}}{150 \text{ mm}} = 4.8 \times 10^{-4}$$

Since the stress level is given (50 MPa), using Equation 6.5 it is possible to compute the minimum modulus of elasticity which is required to yield this minimum strain. Hence

$$E = \frac{\sigma}{\varepsilon} = \frac{50 \text{ MPa}}{4.8 \times 10^{-4}} = 104.2 \text{ GPa}$$

Which means that those metals with moduli of elasticity greater than this value are acceptable candidates--namely, Cu, Ni, steel, Ti and W.

(b) This portion of the problem further stipulates that the maximum permissible diameter decrease is 2.3 x 10^{-3} mm when the tensile stress of 50 MPa is applied. This translates into a maximum lateral strain ε_x (max) as

$$\varepsilon_x(\text{max}) = \frac{\Delta d}{d_0} = \frac{-2.3 \times 10^{-3} \text{ mm}}{15.0 \text{ mm}} = -1.53 \times 10^{-4}$$

But, since the specimen contracts in this lateral direction, and we are concerned that this strain be less than 1.53 x 10^{-4}, then the criterion for this part of the problem may be stipulated as $-\frac{\Delta d}{d_0} < 1.53 \times 10^{-4}$.

Now, Poisson's ratio is defined by Equation 6.8 as

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z}$$

For each of the metal alloys let us consider a possible lateral strain, $\varepsilon_x = \frac{\Delta d}{d_0}$. Furthermore, since the deformation is elastic, then, from Equation 6.5, the longitudinal strain, ε_z is equal to

$$\varepsilon_z = \frac{\sigma}{E}$$

Substituting these expressions for ε_x and ε_z into the definition of Poisson's ratio we have

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\dfrac{\Delta d}{d_0}}{\dfrac{\sigma}{E}}$$

which leads to the following:

$$-\frac{\Delta d}{d_0} = \frac{\nu \sigma}{E}$$

Using values for ν and E found in Table 6.1 for the six metal alloys that satisfy the criterion for part (a), and for σ = 50 MPa, we are able to compute a $-\frac{\Delta d}{d_0}$ for each alloy as follows:

$$-\frac{\Delta d}{d_0}(\text{brass}) = \frac{(0.34)(50 \text{ x } 10^6 \text{ N/m}^2)}{97 \text{ x } 10^9 \text{ N/m}^2} = 1.75 \text{ x } 10^{-4}$$

$$-\frac{\Delta d}{d_0}(\text{copper}) = \frac{(0.34)(50 \text{ x } 10^6 \text{ N/m}^2)}{110 \text{ x } 10^9 \text{ N/m}^2} = 1.55 \text{ x } 10^{-4}$$

$$-\frac{\Delta d}{d_0}(\text{titanium}) = \frac{(0.34)(50 \text{ x } 10^6 \text{ N/m}^2)}{107 \text{ x } 10^9 \text{ N/m}^2} = 1.59 \text{ x } 10^{-4}$$

$$-\frac{\Delta d}{d_0}(\text{nickel}) = \frac{(0.31)(50 \text{ x } 10^6 \text{ N/m}^2)}{207 \text{ x } 10^9 \text{ N/m}^2} = 7.49 \text{ x } 10^{-5}$$

$$-\frac{\Delta d}{d_0}(\text{steel}) = \frac{(0.30)(50 \text{ x } 10^6 \text{ N/m}^2)}{207 \text{ x } 10^9 \text{ N/m}^2} = 7.25 \text{ x } 10^{-5}$$

$$-\frac{\Delta d}{d_0}(\text{tungsten}) = \frac{(0.28)(50 \text{ x } 10^6 \text{ N/m}^2)}{407 \text{ x } 10^9 \text{ N/m}^2} = 3.44 \text{ x } 10^{-5}$$

Thus, the brass, copper, and titanium alloys will experience a negative transverse strain greater than 1.53 x 10^{-4}. This means that the following alloys satisfy the criteria for both parts (a) and (b) of this problem: nickel, steel, and tungsten.

6.21 (a) This portion of the problem asks that we compute the elongation of the brass specimen. The first calculation necessary is that of the applied stress using Equation 6.1, as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{10{,}000\ \text{N}}{\pi\left(\frac{10 \text{ x } 10^{-3}\,\text{m}}{2}\right)^2} = 127 \text{ MPa} \quad (17{,}900 \text{ psi})$$

From the stress-strain plot in Figure 6.12, this stress corresponds to a strain of about 1.5 x 10^{-3}. From the definition of strain, Equation 6.2

$$\Delta l = \varepsilon l_0 = \left(1.5 \text{ x } 10^{-3}\right)(101.6 \text{ mm}) = 0.15 \text{ mm} \quad (6.0 \text{ x } 10^{-3} \text{ in.})$$

(b) In order to determine the reduction in diameter Δd, it is necessary to use Equation 6.8 and the definition of lateral strain (i.e., $\varepsilon_x = \Delta d/d_0$) as follows

$$\Delta d = d_0 \varepsilon_x = -d_0 \nu \varepsilon_z = -(10 \text{ mm})(0.35)\left(1.5 \text{ x } 10^{-3}\right)$$

$$= -5.25 \text{ x } 10^{-3} \text{ mm } (-2.05 \text{ x } 10^{-4} \text{ in.})$$

6.22 This problem asks that we assess the four alloys relative to the two criteria presented. The first criterion is that the material not experience plastic deformation when the tensile load of 35,000 N is applied; this means that the stress corresponding to this load not exceed the yield strength of the material. Upon computing the stress

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{35{,}000 \text{ N}}{\pi\left(\frac{15 \text{ x } 10^{-3} \text{ m}}{2}\right)^2} = 200 \text{ x } 10^6 \text{ N/m}^2 = 200 \text{ MPa}$$

Of the alloys listed, the Al, Ti and steel alloys have yield strengths greater than 200 MPa.

Relative to the second criterion (i.e., that Δd be less than $1.2 \text{ x } 10^{-2}$ mm), it is necessary to calculate the change in diameter Δd for these three alloys. From Equation 6.8

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\frac{\Delta d}{d_0}}{\frac{\sigma}{E}} = -\frac{E\,\Delta d}{\sigma\, d_0}$$

Now, solving for Δd from this expression,

$$\Delta d = -\frac{\nu \sigma d_0}{E}$$

For the aluminum alloy

$$\Delta d = -\frac{(0.33)(200 \text{ MPa})(15 \text{ mm})}{70 \text{ x } 10^3 \text{ MPa}} = -1.41 \text{ x } 10^{-3} \text{ mm}$$

Therefore, the Al alloy is not a candidate.

For the steel alloy

$$\Delta d = -\frac{(0.27)(200 \text{ MPa})(15 \text{ mm})}{205 \text{ x } 10^3 \text{ MPa}} = -0.40 \text{ x } 10^{-2} \text{ mm}$$

Therefore, the steel is a candidate.

For the Ti alloy

$$\Delta d = -\frac{(0.36)(200 \text{ MPa})(15 \text{ mm})}{105 \times 10^3 \text{ MPa}} = -1.0 \times 10^{-2} \text{ mm}$$

Hence, the titanium alloy is also a candidate.

6.23 This problem asks that we ascertain which of four metal alloys will not (1) experience plastic deformation, and (2) elongate more than 1.3 mm when a tensile load of 29,000 N is applied. It is first necessary to compute the stress using Equation 6.1; a material to be used for this application must necessarily have a yield strength greater than this value. Thus,

$$\sigma = \frac{F}{A_0} = \frac{29{,}000 \text{ N}}{\pi \left(\dfrac{12.7 \text{ x } 10^{-3} \text{ m}}{2}\right)^2} = 230 \text{ MPa}$$

Of the metal alloys listed, aluminum, brass and steel have yield strengths greater than this stress.

Next, we must compute the elongation produced in aluminum, brass, and steel using Equations 6.2 and 6.5 in order to determine whether or not this elongation is less than 1.3 mm. For aluminum

$$\Delta l = \frac{\sigma l_0}{E} = \frac{(230 \text{ MPa})(500 \text{ mm})}{70 \text{ x } 10^3 \text{ MPa}} = 1.64 \text{ mm}$$

Thus, aluminum is not a candidate.

For brass

$$\Delta l = \frac{\sigma l_0}{E} = \frac{(230 \text{ MPa})(500 \text{ mm})}{100 \text{ x } 10^3 \text{ MPa}} = 1.15 \text{ mm}$$

Thus, brass is a candidate. And, for steel

$$\Delta l = \frac{\sigma l_0}{E} = \frac{(230 \text{ MPa})(500 \text{ mm})}{207 \text{ x } 10^3 \text{ MPa}} = 0.56 \text{ mm}$$

Therefore, of these four alloys, only brass and steel satisfy the stipulated criteria.

Tensile Properties

6.24 Using the stress-strain plot for a steel alloy (Figure 6.21), we are asked to determine several of its mechanical characteristics.

(a) The elastic modulus is just the slope of the initial linear portion of the curve; or, from the inset and using Equation 6.10

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{(1300 - 0)\ \text{MPa}}{\left(6.25 \times 10^{-3} - 0\right)} = 210 \times 10^3\ \text{MPa} = 210\ \text{GPa} \quad (30.5 \times 10^6\ \text{psi})$$

The value given in Table 6.1 is 207 GPa.

(b) The proportional limit is the stress level at which linearity of the stress-strain curve ends, which is approximately 1370 MPa (200,000 psi).

(c) The 0.002 strain offset line intersects the stress-strain curve at approximately 1570 MPa (228,000 psi).

(d) The tensile strength (the maximum on the curve) is approximately 1970 MPa (285,000 psi).

6.25 We are asked to calculate the radius of a cylindrical brass specimen in order to produce an elongation of 5 mm when a load of 100,000 N is applied. It first becomes necessary to compute the strain corresponding to this elongation using Equation 6.2 as

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{5 \text{ mm}}{100 \text{ mm}} = 5 \text{ x } 10^{-2}$$

From Figure 6.12, a stress of 335 MPa (49,000 psi) corresponds to this strain. Since for a cylindrical specimen, stress, force, and initial radius r_0 are related as

$$\sigma = \frac{F}{\pi r_0^2}$$

then

$$r_0 = \sqrt{\frac{F}{\pi \sigma}} = \sqrt{\frac{100{,}000 \text{ N}}{\pi \left(335 \text{ x } 10^6 \text{ N/m}^2\right)}} = 0.0097 \text{ m} = 9.7 \text{ mm} \text{ (0.38 in.)}$$

6.26 This problem asks us to determine the deformation characteristics of a steel specimen, the stress-strain behavior for which is shown in Figure 6.21.

(a) In order to ascertain whether the deformation is elastic or plastic, we must first compute the stress, then locate it on the stress-strain curve, and, finally, note whether this point is on the elastic or plastic region. Thus, from Equation 6.1

$$\sigma = \frac{F}{A_0} = \frac{140{,}000 \text{ N}}{\pi \left(\dfrac{10 \text{ x } 10^{-3} \text{ m}}{2} \right)^2} = 1782 \text{ MPa} \quad (250{,}000 \text{ psi})$$

The 1782 MPa point is beyond the linear portion of the curve, and, therefore, the deformation will be both elastic and plastic.

(b) This portion of the problem asks us to compute the increase in specimen length. From the stress-strain curve, the strain at 1782 MPa is approximately 0.017. Thus, from Equation 6.2

$$\Delta l = \varepsilon l_0 = (0.017)(500 \text{ mm}) = 8.5 \text{ mm} \quad (0.34 \text{ in.})$$

6.27 (a) We are asked to compute the magnitude of the load necessary to produce an elongation of 2.25 mm for the steel displaying the stress-strain behavior shown in Figure 6.21. First, calculate the strain, and then the corresponding stress from the plot.

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{2.25 \text{ mm}}{375 \text{ mm}} = 0.006$$

This is within the elastic region; from the inset of Figure 6.21, this corresponds to a stress of about 1250 MPa (180,000 psi). Now, from Equation 6.1

$$F = \sigma A_0 = \sigma b^2$$

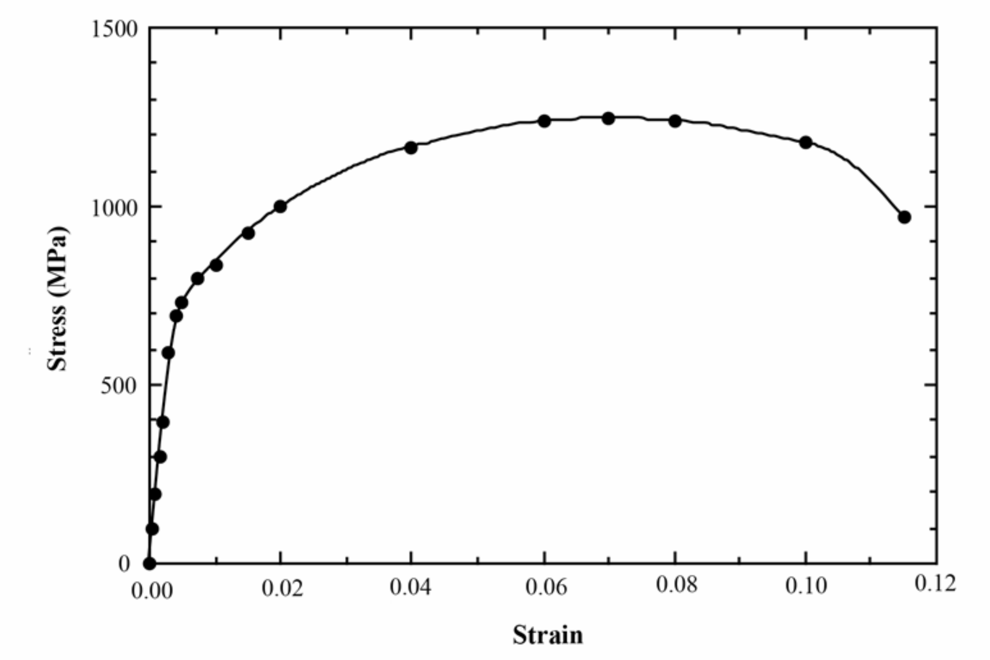
in which b is the cross-section side length. Thus,

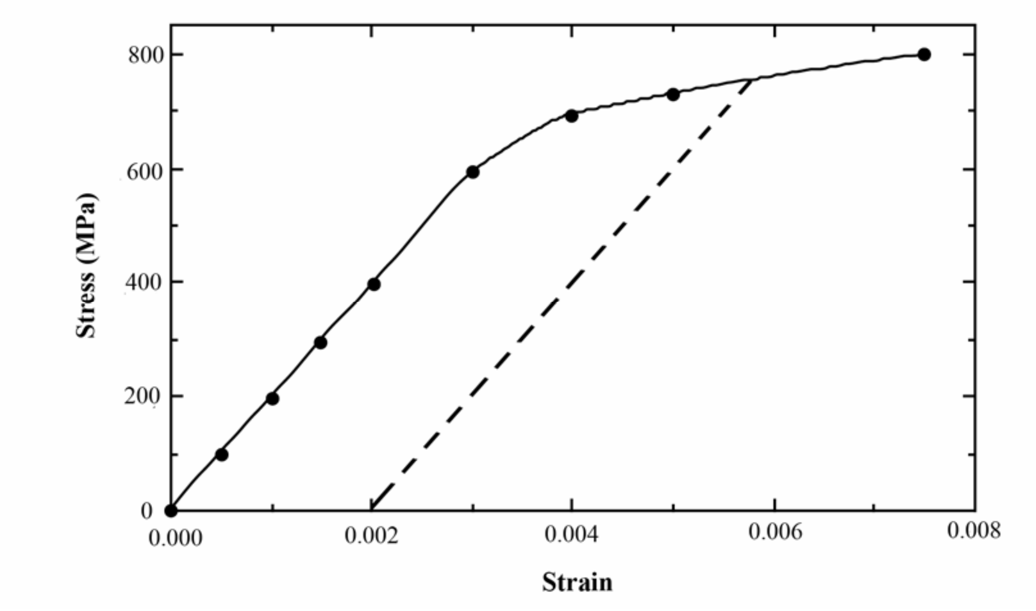
$$F = \left(1250 \text{ x } 10^6 \text{ N/m}^2\right)\left(5.5 \text{ x } 10^{-3} \text{ m}\right)^2 = 37{,}800 \text{ N} \quad (8500 \text{ lb}_\text{f})$$

(b) After the load is released there will be no deformation since the material was strained only elastically.

6.28 This problem calls for us to make a stress-strain plot for stainless steel, given its tensile load-length data, and then to determine some of its mechanical characteristics.

(a) The data are plotted below on two plots: the first corresponds to the entire stress-strain curve, while for the second, the curve extends to just beyond the elastic region of deformation.





(b) The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{400 \text{ MPa} - 0 \text{ MPa}}{0.002 - 0} = 200 \text{ x } 10^3 \text{ MPa} = 200 \text{ GPa} \quad (29 \text{ x } 10^6 \text{ psi})$$

(c) For the yield strength, the 0.002 strain offset line is drawn dashed. It intersects the stress-strain curve at approximately 750 MPa (112,000 psi).

(d) The tensile strength is approximately 1250 MPa (180,000 psi), corresponding to the maximum stress on the complete stress-strain plot.

(e) The ductility, in percent elongation, is just the plastic strain at fracture, multiplied by one-hundred. The total fracture strain at fracture is 0.115; subtracting out the elastic strain (which is about 0.003) leaves a plastic strain of 0.112. Thus, the ductility is about 11.2%EL.

(f) From Equation 6.14, the modulus of resilience is just

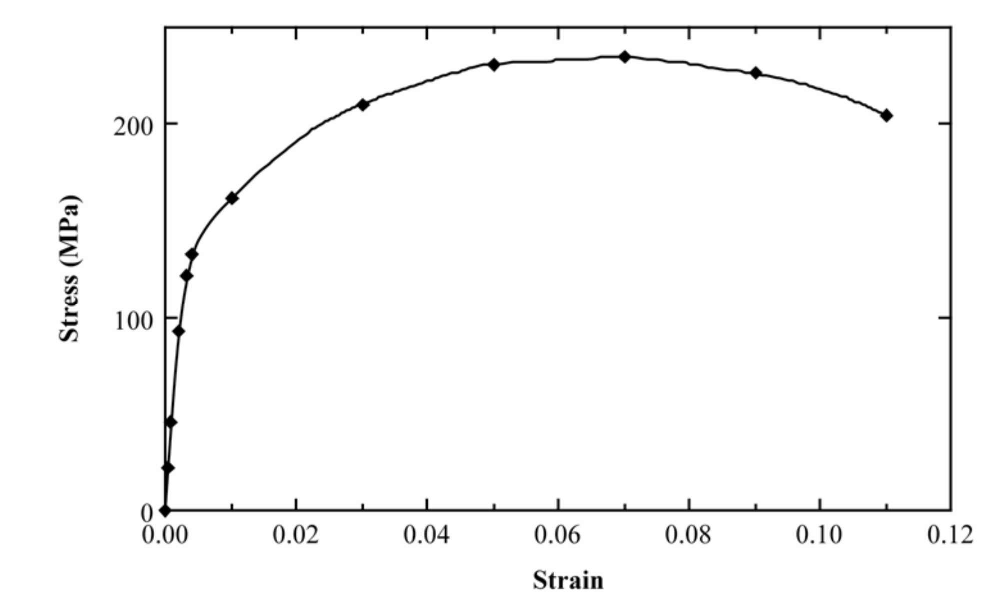
$$U_r = \frac{\sigma_y^2}{2E}$$

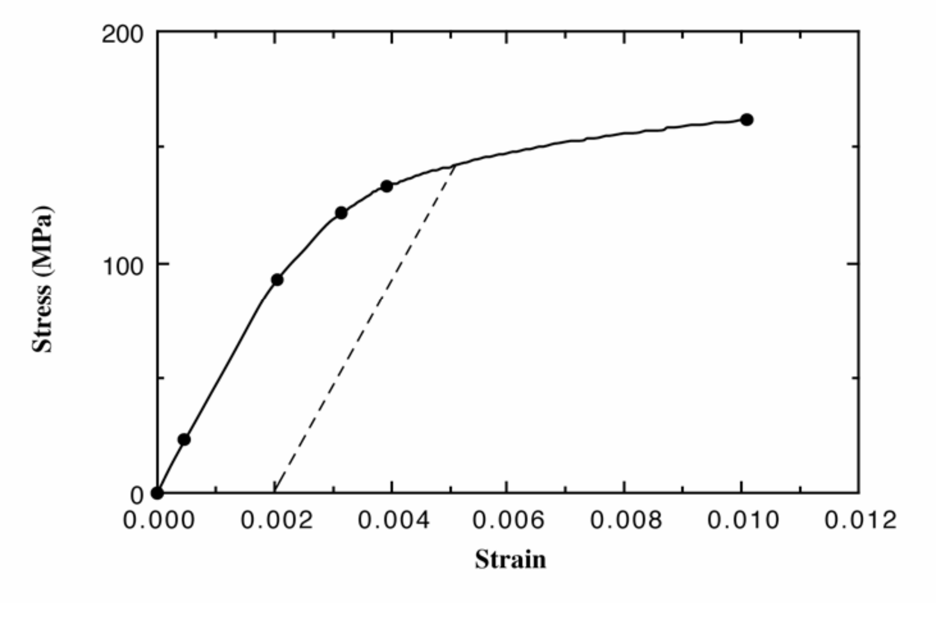
which, using data computed above gives a value of

$$U_r = \frac{(750 \text{ MPa})^2}{(2)\left(200 \text{ x } 10^3 \text{ MPa}\right)} = 1.40 \text{ x } 10^6 \text{ J/m}^3 \quad \left(210 \text{ in.-lb}_\text{f}/\text{in.}^3\right)$$

6.29 This problem calls for us to make a stress-strain plot for a magnesium, given its tensile load-length data, and then to determine some of its mechanical characteristics.

(a) The data are plotted below on two plots: the first corresponds to the entire stress-strain curve, while for the second, the curve extends just beyond the elastic region of deformation.





(b) The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{50 \text{ MPa} - 0 \text{ MPa}}{0.001 - 0} = 50 \text{ x } 10^3 \text{ MPa} = 50 \text{ GPa} \quad (7.3 \text{ x } 10^6 \text{ psi})$$

(c) For the yield strength, the 0.002 strain offset line is drawn dashed. It intersects the stress-strain curve at approximately 140 MPa (20,300 psi).

(d) The tensile strength is approximately 230 MPa (33,350 psi), corresponding to the maximum stress on the complete stress-strain plot.

(e) From Equation 6.14, the modulus of resilience is just

$$U_r = \frac{\sigma_y^2}{2E}$$

which, using data computed above, yields a value of

$$U_r = \frac{(140 \text{ x } 10^6 \text{ N/m}^2)^2}{(2)(50 \text{ x } 10^9 \text{ N/m}^2)} = 1.96 \text{ x } 10^5 \text{ J/m}^3 \quad (28.4 \text{ in.-lb}_\text{f}/\text{in.}^3)$$

(f) The ductility, in percent elongation, is just the plastic strain at fracture, multiplied by one-hundred. The total fracture strain at fracture is 0.110; subtracting out the elastic strain (which is about 0.003) leaves a plastic strain of 0.107. Thus, the ductility is about 10.7%EL.

6.30 This problem calls for the computation of ductility in both percent reduction in area and percent elongation. Percent reduction in area is computed using Equation 6.12 as

$$\%\mathrm{RA} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_f}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \text{ x } 100$$

in which d_0 and d_f are, respectively, the original and fracture cross-sectional areas. Thus,

$$\%\mathrm{RA} = \frac{\pi\left(\frac{12.8 \text{ mm}}{2}\right)^2 - \pi\left(\frac{8.13 \text{ mm}}{2}\right)^2}{\pi\left(\frac{12.8 \text{ mm}}{2}\right)^2} \text{ x } 100 = 60\%$$

While, for percent elongation, we use Equation 6.11 as

$$\%\mathrm{EL} = \left(\frac{l_f - l_0}{l_0}\right) \text{ x } 100$$

$$= \frac{74.17 \text{ mm} - 50.80 \text{ mm}}{50.80 \text{ mm}} \text{ x } 100 = 46\%$$

6.31 This problem asks us to calculate the moduli of resilience for the materials having the stress-strain behaviors shown in Figures 6.12 and 6.21. According to Equation 6.14, the modulus of resilience U_r is a function of the yield strength and the modulus of elasticity as

$$U_r = \frac{\sigma_y^2}{2E}$$

The values for σ_y and E for the brass in Figure 6.12 are determined in Example Problem 6.3 as 250 MPa (36,000 psi) and 93.8 GPa (13.6 x 10^6 psi), respectively. Thus

$$U_r = \frac{(250 \text{ MPa})^2}{(2)\left(93.8 \text{ x } 10^3 \text{ MPa}\right)} = 3.32 \text{ x } 10^5 \text{ J/m}^3 \quad \left(48.2 \text{ in.-lb}_\text{f}/\text{in.}^3\right)$$

Values of the corresponding parameters for the steel alloy (Figure 6.21) are determined in Problem 6.24 as 1570 MPa (228,000 psi) and 210 GPa (30.5 x 10^6 psi), respectively, and therefore

$$U_r = \frac{(1570 \text{ MPa})^2}{(2)\left(210 \text{ x } 10^3 \text{ MPa}\right)} = 5.87 \text{ x } 10^6 \text{ J/m}^3 \quad \left(867 \text{ in.-lb}_\text{f}/\text{in.}^3\right)$$

6.32 The moduli of resilience of the alloys listed in the table may be determined using Equation 6.14. Yield strength values are provided in this table, whereas the elastic moduli are tabulated in Table 6.1.

For steel

$$U_r = \frac{\sigma_y^2}{2E}$$

$$= \frac{(830 \text{ x } 10^6 \text{ N/m}^2)^2}{(2)\left(207 \text{ x } 10^9 \text{ N/m}^2\right)} = 16.6 \text{ x } 10^5 \text{ J/m}^3 \quad \left(240 \text{ in.-lb}_\text{f}/\text{in.}^3\right)$$

For the brass

$$U_r = \frac{(380 \text{ x } 10^6 \text{ N/m}^2)^2}{(2)\left(97 \text{ x } 10^9 \text{ N/m}^2\right)} = 7.44 \text{ x } 10^5 \text{ J/m}^3 \quad \left(108 \text{ in.-lb}_\text{f}/\text{in.}^3\right)$$

For the aluminum alloy

$$U_r = \frac{(275 \text{ x } 10^6 \text{ N/m}^2)^2}{(2)\left(69 \text{ x } 10^9 \text{ N/m}^2\right)} = 5.48 \text{ x } 10^5 \text{ J/m}^3 \quad \left(80.0 \text{ in.-lb}_\text{f}/\text{in.}^3\right)$$

And, for the titanium alloy

$$U_r = \frac{(690 \text{ x } 10^6 \text{ N/m}^2)^2}{(2)\left(107 \text{ x } 10^9 \text{ N/m}^2\right)} = 22.2 \text{ x } 10^5 \text{ J/m}^3 \quad \left(323 \text{ in.-lb}_\text{f}/\text{in.}^3\right)$$

6.33 The modulus of resilience, yield strength, and elastic modulus of elasticity are related to one another through Equation 6.14; the value of *E* for steel given in Table 6.1 is 207 GPa. Solving for σ_y from this expression yields

$$\sigma_y = \sqrt{2U_r E} = \sqrt{(2)(2.07\ \text{MPa})\left(207\ \text{x}\ 10^3\ \text{MPa}\right)}$$

$$= 925\ \text{MPa}\ \ (134{,}000\ \text{psi})$$

True Stress and Strain

6.34 To show that Equation 6.18a is valid, we must first rearrange Equation 6.17 as

$$A_i = \frac{A_0 l_0}{l_i}$$

Substituting this expression into Equation 6.15 yields

$$\sigma_T = \frac{F}{A_i} = \frac{F}{A_0}\left(\frac{l_i}{l_0}\right) = \sigma\left(\frac{l_i}{l_0}\right)$$

But, from Equation 6.2

$$\varepsilon = \frac{l_i}{l_0} - 1$$

Or

$$\frac{l_i}{l_0} = \varepsilon + 1$$

Thus,

$$\sigma_T = \sigma\left(\frac{l_i}{l_0}\right) = \sigma(\varepsilon + 1)$$

For Equation 6.18b

$$\varepsilon_T = \ln(1 + \varepsilon)$$

is valid since, from Equation 6.16

$$\varepsilon_T = \ln\left(\frac{l_i}{l_0}\right)$$

and

$$\frac{l_i}{l_0} = \varepsilon + 1$$

from above.

6.35 This problem asks us to demonstrate that true strain may also be represented by

$$\varepsilon_T = \ln\left(\frac{A_0}{A_i}\right)$$

Rearrangement of Equation 6.17 leads to

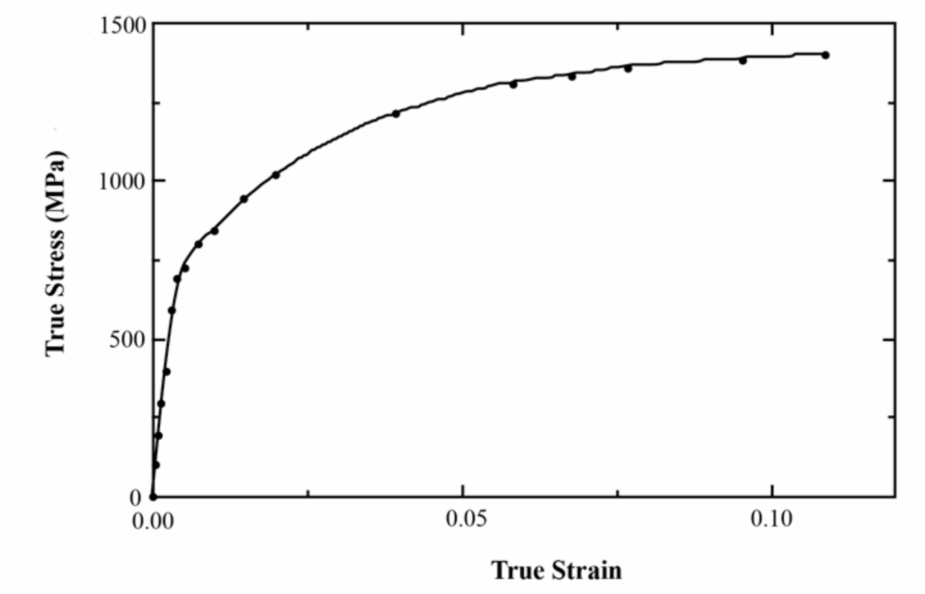
$$\frac{l_i}{l_0} = \frac{A_0}{A_i}$$

Thus, Equation 6.16 takes the form

$$\varepsilon_T = \ln\left(\frac{l_i}{l_0}\right) = \ln\left(\frac{A_0}{A_i}\right)$$

The expression $\varepsilon_T = \ln\left(\frac{A_0}{A_i}\right)$ is more valid during necking because A_i is taken as the area of the neck.

6.36 These true stress-strain data are plotted below.



6.37 We are asked to compute the true strain that results from the application of a true stress of 600 MPa (87,000 psi); other true stress-strain data are also given. It first becomes necessary to solve for *n* in Equation 6.19. Taking logarithms of this expression and after rearrangement we have

$$n = \frac{\log \sigma_T - \log K}{\log \varepsilon_T}$$

$$= \frac{\log (500 \text{ MPa}) - \log (825 \text{ MPa})}{\log (0.16)} = 0.273$$

Expressing ε_T as the dependent variable (Equation 6.19), and then solving for its value from the data stipulated in the problem statement, leads to

$$\varepsilon_T = \left(\frac{\sigma_T}{K}\right)^{1/n} = \left(\frac{600 \text{ MPa}}{825 \text{ MPa}}\right)^{1/0.273} = 0.311$$

6.38 We are asked to compute how much elongation a metal specimen will experience when a true stress of 415 MPa is applied, given the value of n and that a given true stress produces a specific true strain. Solution of this problem requires that we utilize Equation 6.19. It is first necessary to solve for K from the given true stress and strain. Rearrangement of this equation yields

$$K = \frac{\sigma_T}{(\varepsilon_T)^n} = \frac{345 \text{ MPa}}{(0.02)^{0.22}} = 816 \text{ MPa } (118{,}000 \text{ psi})$$

Next we must solve for the true strain produced when a true stress of 415 MPa is applied, also using Equation 6.19. Thus

$$\varepsilon_T = \left(\frac{\sigma_T}{K}\right)^{1/n} = \left(\frac{415 \text{ MPa}}{816 \text{ MPa}}\right)^{1/0.22} = 0.0463 = \ln\left(\frac{l_i}{l_0}\right)$$

Now, solving for l_i gives

$$l_i = l_0 e^{0.0463} = (500 \text{ mm})\, e^{0.0463} = 523.7 \text{ mm } (20.948 \text{ in.})$$

And finally, the elongation Δl is just

$$\Delta l = l_i - l_0 = 523.7 \text{ mm} - 500 \text{ mm} = 23.7 \text{ mm } (0.948 \text{ in.})$$

6.39 For this problem, we are given two values of ε_T and σ_T, from which we are asked to calculate the true stress which produces a true plastic strain of 0.21. Employing Equation 6.19, we may set up two simultaneous equations with two unknowns (the unknowns being K and n), as

$$\log (60,000 \text{ psi}) = \log K + n \log (0.15)$$

$$\log (70,000 \text{ psi}) = \log K + n \log (0.25)$$

Solving for n from these two expressions yields

$$n = \frac{\log (60{,}000) - \log (70{,}000)}{\log (0.15) - \log (0.25)} = 0.302$$

and for K

$$\log K = 5.027 \text{ or } K = 10^{5.027} = 106{,}400 \text{ psi}$$

Thus, for $\varepsilon_T = 0.21$

$$\sigma_T = K (\varepsilon_T)^n = (106{,}400 \text{ psi})(0.21)^{0.302} = 66{,}400 \text{ psi} \ \ (460 \text{ MPa})$$

6.40 For this problem we first need to convert engineering stresses and strains to true stresses and strains so that the constants K and n in Equation 6.19 may be determined. Since $\sigma_T = \sigma(1 + \varepsilon)$ then,

$$\sigma_{T1} = (315 \text{ MPa})(1 + 0.105) = 348 \text{ MPa}$$

$$\sigma_{T2} = (340 \text{ MPa})(1 + 0.220) = 415 \text{ MPa}$$

Similarly for strains, since $\varepsilon_T = \ln(1 + \varepsilon)$ then

$$\varepsilon_{T1} = \ln(1 + 0.105) = 0.09985$$

$$\varepsilon_{T2} = \ln(1 + 0.220) = 0.19885$$

Taking logarithms of Equation 6.19, we get

$$\log \sigma_T = \log K + n \log \varepsilon_T$$

which allows us to set up two simultaneous equations for the above pairs of true stresses and true strains, with K and n as unknowns. Thus

$$\log(348) = \log K + n \log(0.09985)$$

$$\log(415) = \log K + n \log(0.19885)$$

Solving for these two expressions yields $K = 628$ MPa and $n = 0.256$.

Now, converting $\varepsilon = 0.28$ to true strain

$$\varepsilon_T = \ln(1 + 0.28) = 0.247$$

The corresponding σ_T to give this value of ε_T (using Equation 6.19) is just

$$\sigma_T = K\varepsilon_T^n = (628 \text{ MPa})(0.247)^{0.256} = 439 \text{ MPa}$$

Now converting this value of σ_T to an engineering stress using Equation 6.18a gives

$$\sigma = \frac{\sigma_T}{1 + \varepsilon} = \frac{439 \text{ MPa}}{1 + 0.28} = 343 \text{ MPa}$$

6.41 This problem calls for us to compute the toughness (or energy to cause fracture). The easiest way to do this is to integrate both elastic and plastic regions, and then add them together.

$$\text{Toughness} = \int \sigma \, d\varepsilon$$

$$= \int_0^{0.007} E\varepsilon \, d\varepsilon + \int_{0.007}^{0.60} K\varepsilon^n \, d\varepsilon$$

$$= \left.\frac{E\varepsilon^2}{2}\right|_0^{0.007} + \left.\frac{K}{(n+1)}\varepsilon^{(n+1)}\right|_{0.007}^{0.60}$$

$$= \frac{103 \text{ x } 10^9 \text{ N/m}^2}{2}(0.007)^2 + \frac{1520 \text{ x } 10^6 \text{ N/m}^2}{(1.0 + 0.15)}\left[(0.60)^{1.15} - (0.007)^{1.15}\right]$$

$$= 7.33 \text{ x } 10^8 \text{ J/m}^3 \ \left(1.07 \text{ x } 10^5 \text{ in.-lb}_f/\text{in.}^3\right)$$

6.42 This problem asks that we determine the value of ε_T for the onset of necking assuming that necking begins when

$$\frac{d\sigma_T}{d\varepsilon_T} = \sigma_T$$

Let us take the derivative of Equation 6.19, set it equal to σ_T, and then solve for ε_T from the resulting expression. Thus

$$\frac{d\left[K(\varepsilon_T)^n\right]}{d\varepsilon_T} = Kn(\varepsilon_T)^{(n-1)} = \sigma_T$$

However, from Equation 6.19, $\sigma_T = K(\varepsilon_T)^n$, which, when substituted into the above expression, yields

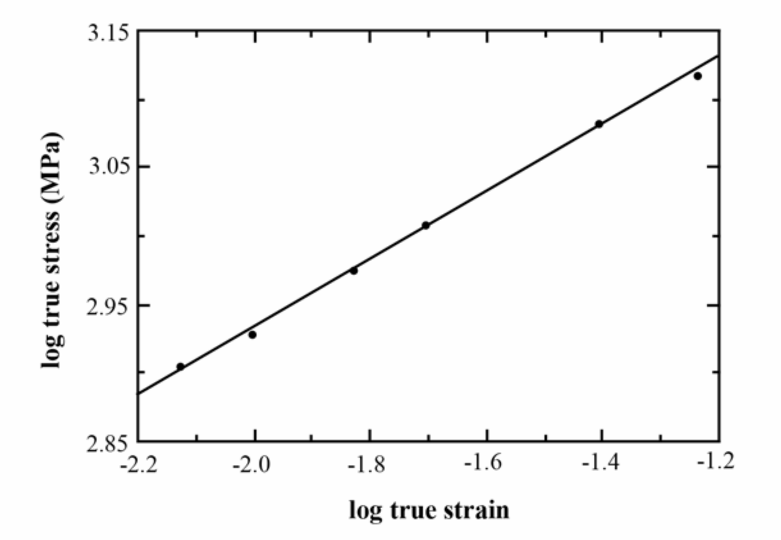
$$Kn(\varepsilon_T)^{(n-1)} = K(\varepsilon_T)^n$$

Now solving for ε_T from this equation leads to

$$\varepsilon_T = n$$

as the value of the true strain at the onset of necking.

6.43 This problem calls for us to utilize the appropriate data from Problem 6.28 in order to determine the values of *n* and *K* for this material. From Equation 6.27 the slope and intercept of a log σ_T versus log ε_T plot will yield *n* and log *K*, respectively. However, Equation 6.19 is only valid in the region of plastic deformation to the point of necking; thus, only the 8th, 9th, 10th, 11th, 12th, and 13th data points may be utilized. The log-log plot with these data points is given below.



The slope yields a value of 0.246 for *n*, whereas the intercept gives a value of 3.424 for log *K*, and thus $K = 10^{3.424}$ = 2655 MPa.

Elastic Recovery After Plastic Deformation

6.44 (a) In order to determine the final length of the brass specimen when the load is released, it first becomes necessary to compute the applied stress using Equation 6.1; thus

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{11{,}750\ \text{N}}{\pi\left(\frac{10\ \text{x}\ 10^{-3}\ \text{m}}{2}\right)^2} = 150\ \text{MPa}\ \ (22{,}000\ \text{psi})$$

Upon locating this point on the stress-strain curve (Figure 6.12), we note that it is in the linear, elastic region; therefore, when the load is released the specimen will return to its original length of 120 mm (4.72 in.).

(b) In this portion of the problem we are asked to calculate the final length, after load release, when the load is increased to 23,500 N (5280 lb_f). Again, computing the stress

$$\sigma = \frac{23{,}500\ \text{N}}{\pi\left(\frac{10\ \text{x}\ 10^{-3}\ \text{m}}{2}\right)^2} = 300\ \text{MPa}\ \ (44{,}200\ \text{psi})$$

The point on the stress-strain curve corresponding to this stress is in the plastic region. We are able to estimate the amount of permanent strain by drawing a straight line parallel to the linear elastic region; this line intersects the strain axis at a strain of about 0.012 which is the amount of plastic strain. The final specimen length l_i may be determined from a rearranged form of Equation 6.2 as

$$l_i = l_0(1 + \varepsilon) = (120\ \text{mm})(1 + 0.012) = 121.44\ \text{mm}\ (4.78\ \text{in.})$$

6.45 (a) We are asked to determine both the elastic and plastic strain values when a tensile force of 110,000 N (25,000 lb_f) is applied to the steel specimen and then released. First it becomes necessary to determine the applied stress using Equation 6.1; thus

$$\sigma = \frac{F}{A_0} = \frac{F}{b_0 d_0}$$

where b_0 and d_0 are cross-sectional width and depth (19 mm and 3.2 mm, respectively). Thus

$$\sigma = \frac{110{,}000 \text{ N}}{\left(19 \text{ x } 10^{-3} \text{ m}\right)\left(3.2 \text{ x } 10^{-3} \text{ m}\right)} = 1.810 \text{ x } 10^{9} \text{ N/m}^2 = 1810 \text{ MPa} \ \ (265{,}000 \text{ psi})$$

From Figure 6.21, this point is in the plastic region so the specimen will be both elastic and plastic strains. The total strain at this point, ε_t, is about 0.020. We are able to estimate the amount of permanent strain recovery ε_e from Hooke's law, Equation 6.5 as

$$\varepsilon_e = \frac{\sigma}{E}$$

And, since E = 207 GPa for steel (Table 6.1)

$$\varepsilon_e = \frac{1810 \text{ MPa}}{207 \text{ x } 10^3 \text{ MPa}} = 0.0087$$

The value of the plastic strain, ε_p is just the difference between the total and elastic strains; that is

$$\varepsilon_p = \varepsilon_t - \varepsilon_e = 0.020 - 0.0087 = 0.0113$$

(b) If the initial length is 610 mm (24.0 in.) then the final specimen length l_i may be determined from a rearranged form of Equation 6.2 using the plastic strain value as

$$l_i = l_0\left(1 + \varepsilon_p\right) = (610 \text{ mm})(1 + 0.0113) = 616.7 \text{ mm } (24.26 \text{ in.})$$

Hardness

6.46 (a) We are asked to compute the Brinell hardness for the given indentation. It is necessary to use the equation in Table 6.5 for HB, where P = 1000 kg, d = 2.50 mm, and D = 10 mm. Thus, the Brinell hardness is computed as

$$\mathrm{HB} = \frac{2P}{\pi D\left[D - \sqrt{D^2 - d^2}\right]}$$

$$= \frac{(2)(1000\ \text{kg})}{(\pi)(10\ \text{mm})\left[10\ \text{mm} - \sqrt{(10\ \text{mm})^2 - (2.50\ \text{mm})^2}\right]} = 200.5$$

(b) This part of the problem calls for us to determine the indentation diameter d which will yield a 300 HB when P = 500 kg. Solving for d from the equation in Table 6.5 gives

$$d = \sqrt{D^2 - \left[D - \frac{2P}{(\mathrm{HB})\pi D}\right]^2}$$

$$= \sqrt{(10\ \text{mm})^2 - \left[10\ \text{mm} - \frac{(2)(500\ \text{kg})}{(300)(\pi)(10\ \text{mm})}\right]^2} = 1.45\ \text{mm}$$

6.47 This problem calls for estimations of Brinell and Rockwell hardnesses.

(a) For the brass specimen, the stress-strain behavior for which is shown in Figure 6.12, the tensile strength is 450 MPa (65,000 psi). From Figure 6.19, the hardness for brass corresponding to this tensile strength is about 125 HB or 70 HRB.

(b) The steel alloy (Figure 6.21) has a tensile strength of about 1970 MPa (285,000 psi) [Problem 6.24(d)]. This corresponds to a hardness of about 560 HB or ~55 HRC from the line (extended) for steels in Figure 6.19.

6.48 This problem calls for us to specify expressions similar to Equations 6.20a and 6.20b for nodular cast iron and brass. These equations, for a straight line, are of the form

$$TS = C + (E)(\mathrm{HB})$$

where TS is the tensile strength, HB is the Brinell hardness, and C and E are constants, which need to be determined.

One way to solve for C and E is analytically--establishing two equations using TS and HB data points on the plot, as

$$(TS)_1 = C + (E)(\mathrm{BH})_1$$
$$(TS)_2 = C + (E)(\mathrm{BH})_2$$

Solving for E from these two expressions yields

$$E = \frac{(TS)_1 - (TS)_2}{(\mathrm{HB})_2 - (\mathrm{HB})_1}$$

For nodular cast iron, if we make the arbitrary choice of $(\mathrm{HB})_1$ and $(\mathrm{HB})_2$ as 200 and 300, respectively, then, from Figure 6.19, $(TS)_1$ and $(TS)_2$ take on values of 600 MPa (87,000 psi) and 1100 MPa (160,000 psi), respectively. Substituting these values into the above expression and solving for E gives

$$E = \frac{600\ \text{MPa} - 1100\ \text{MPa}}{200\ \text{HB} - 300\ \text{HB}} = 5.0\ \text{MPa/HB} \quad (730\ \text{psi/HB})$$

Now, solving for C yields

$$C = (TS)_1 - (E)(\mathrm{BH})_1$$

$$= 600\ \text{MPa} - (5.0\ \text{MPa/HB})(200\ \text{HB}) = -\,400\ \text{MPa}\ (-\,59{,}000\ \text{psi})$$

Thus, for nodular cast iron, these two equations take the form

$$TS(\text{MPa}) = -\,400 + 5.0 \times \text{HB}$$
$$TS(\text{psi}) = -\,59{,}000 + 730 \times \text{HB}$$

Now for brass, we take $(\mathrm{HB})_1$ and $(\mathrm{HB})_2$ as 100 and 200, respectively, then, from Figure 7.31, $(TS)_1$ and $(TS)_2$ take on values of 370 MPa (54,000 psi) and 660 MPa (95,000 psi), respectively. Substituting these values into the above expression and solving for E gives

$$E = \frac{370\ \text{MPa} - 660\ \text{MPa}}{100\ \ \text{HB} - 200\ \ \text{HB}} = 2.9\ \ \text{MPa/HB}\ \ (410\ \ \text{psi/HB})$$

Now, solving for C yields

$$C = (TS)_1 - (E)(\mathrm{BH})_1$$

$$= 370\ \text{MPa} - (2.9\ \text{MPa/HB})(100\ \text{HB}) = 80\ \text{MPa}\ \ (13{,}000\ \text{psi})$$

Thus, for brass these two equations take the form

$$TS(\text{MPa}) = 80 + 2.9\ \text{x HB}$$
$$TS(\text{psi}) = 13{,}000 + 410\ \text{x HB}$$

Variability of Material Properties

6.49 The five factors that lead to scatter in measured material properties are the following: (1) test method; (2) variation in specimen fabrication procedure; (3) operator bias; (4) apparatus calibration; and (5) material inhomogeneities and/or compositional differences.

6.50 The average of the given hardness values is calculated using Equation 6.21 as

$$\overline{\mathrm{HRG}} = \frac{\sum_{i=1}^{18} \mathrm{HRG}_i}{18}$$

$$= \frac{47.3 + 52.1 + 45.6 \ldots . + 49.7}{18} = 48.4$$

And we compute the standard deviation using Equation 6.22 as follows:

$$s = \sqrt{\frac{\sum_{i=1}^{18} \left(\mathrm{HRG}_i - \overline{\mathrm{HRG}}\right)^2}{18 - 1}}$$

$$= \left[\frac{(47.3 - 48.4)^2 + (52.1 - 48.4)^2 + \ldots . + (49.7 - 48.4)^2}{17}\right]^{1/2}$$

$$= \sqrt{\frac{64.95}{17}} = 1.95$$

Design/Safety Factors

6.51 The criteria upon which factors of safety are based are (1) consequences of failure, (2) previous experience, (3) accuracy of measurement of mechanical forces and/or material properties, and (4) economics.

6.52 The working stresses for the two alloys the stress-strain behaviors of which are shown in Figures 6.12 and 6.21 are calculated by dividing the yield strength by a factor of safety, which we will take to be 2. For the brass alloy (Figure 6.12), since σ_y = 250 MPa (36,000 psi), the working stress is 125 MPa (18,000 psi), whereas for the steel alloy (Figure 6.21), σ_y = 1570 MPa (228,000 psi), and, therefore, σ_w = 785 MPa (114,000 psi).

DESIGN PROBLEMS

6.D1 For this problem the working stress is computed using Equation 6.24 with $N = 2$, as

$$\sigma_w = \frac{\sigma_y}{2} = \frac{860\ \text{MPa}}{2} = 430\ \text{MPa}\ \ (62{,}500\ \text{psi})$$

Since the force is given, the area may be determined from Equation 6.1, and subsequently the original diameter d_0 may be calculated as

$$A_0 = \frac{F}{\sigma_w} = \pi\left(\frac{d_0}{2}\right)^2$$

And

$$d_0 = \sqrt{\frac{4F}{\pi\sigma_w}} = \sqrt{\frac{(4)(13{,}300\ \text{N})}{\pi\left(430\ \text{x}\ 10^6\ \text{N/m}^2\right)}}$$

$$= 6.3\ \text{x}\ 10^{-3}\ \text{m} = 6.3\ \text{mm}\ (0.25\ \text{in.})$$

6.D2 (a) This portion of the problem asks for us to compute the wall thickness of a thin-walled cylindrical Ni tube at 350°C through which hydrogen gas diffuses. The inside and outside pressures are, respectively, 0.658 and 0.0127 MPa, and the diffusion flux is to be no greater than 1.25 x 10^{-7} mol/m^2-s. This is a steady-state diffusion problem, which necessitates that we employ Equation 5.3. The concentrations at the inside and outside wall faces may be determined using Equation 6.28, and, furthermore, the diffusion coefficient is computed using Equation 6.29. Solving for Δx (using Equation 5.3)

$$\Delta x = -\frac{D\,\Delta C}{J}$$

$$= -\frac{1}{1.25 \times 10^{-7}\ \mathrm{mol/m^2-s}} \times$$

$$(4.76 \text{ x } 10^{-7})\exp\left(-\frac{39{,}560\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(350 + 273\ \mathrm{K})}\right) \times$$

$$(30.8)\exp\left(-\frac{12{,}300\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(350 + 273\ \mathrm{K})}\right)\left(\sqrt{0.0127\ \mathrm{MPa}} - \sqrt{0.658\ \mathrm{MPa}}\right)$$

$$= 0.00366 \text{ m} = 3.66 \text{ mm}$$

(b) Now we are asked to determine the circumferential stress:

$$\sigma = \frac{r\,\Delta p}{4\,\Delta x}$$

$$= \frac{(0.125\ \mathrm{m})(0.658\ \mathrm{MPa} - 0.0127\ \mathrm{MPa})}{(4)(0.00366\ \mathrm{m})}$$

$$= 5.50 \text{ MPa}$$

(c) Now we are to compare this value of stress to the yield strength of Ni at 350°C, from which it is possible to determine whether or not the 3.66 mm wall thickness is suitable. From the information given in the problem, we may write an equation for the dependence of yield strength (σ_y) on temperature (T) as follows:

$$\sigma_y = 100\text{ MPa} - \frac{5\text{ MPa}}{50°\text{C}}\left(T - T_r\right)$$

where T_r is room temperature and for temperature in degrees Celsius. Thus, at 350°C

$$\sigma_y = 100 \text{ MPa} - 0.1 \text{ MPa/°C} (350\text{°C} - 20\text{°C}) = 67 \text{ MPa}$$

Inasmuch as the circumferential stress (5.50 MPa) is much less than the yield strength (67 MPa), this thickness is entirely suitable.

(d) And, finally, this part of the problem asks that we specify how much this thickness may be reduced and still retain a safe design. Let us use a working stress by dividing the yield stress by a factor of safety, according to Equation 6.24. On the basis of our experience, let us use a value of 2.0 for *N*. Thus

$$\sigma_w = \frac{\sigma_y}{N} = \frac{67 \text{ MPa}}{2} = 33.5 \text{ MPa}$$

Using this value for σ_w and Equation 6.30, we now compute the tube thickness as

$$\Delta x = \frac{r\,\Delta p}{4\sigma_w}$$

$$= \frac{(0.125 \text{ m})(0.658 \text{ MPa} - 0.0127 \text{ MPa})}{4(33.5 \text{ MPa})}$$

$$= 0.00060 \text{ m} = 0.60 \text{ mm}$$

Substitution of this value into Fick's first law we calculate the diffusion flux as follows:

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -\left(4.76 \text{ x } 10^{-7}\right) \exp\left[-\frac{39{,}560 \text{ J/mol}}{(8.31 \text{ J/mol-K})(350 + 273 \text{ K})}\right] \times$$

$$\frac{(30.8)\exp\left[-\frac{12{,}300 \text{ J/mol}}{(8.31 \text{ J/mol-K})(350 + 273 \text{ K})}\right]\left(\sqrt{0.0127 \text{ MPa}} - \sqrt{0.658 \text{ MPa}}\right)}{0.0006 \text{ m}}$$

$$= 7.62 \text{ x } 10^{-7} \text{ mol/m}^2\text{-s}$$

Thus, the flux increases by approximately a factor of 6, from 1.25 x 10^{-7} to 7.62 x 10^{-7} mol/m^2-s with this reduction in thickness.

6.D3 This problem calls for the specification of a temperature and cylindrical tube wall thickness that will give a diffusion flux of 2.5 x 10^{-8} mol/m^2-s for the diffusion of hydrogen in nickel; the tube radius is 0.100 m and the inside and outside pressures are 1.015 and 0.01015 MPa, respectively. There are probably several different approaches that may be used; and, of course, there is not one unique solution. Let us employ the following procedure to solve this problem: (1) assume some wall thickness, and, then, using Fick's first law for diffusion (which also employs Equations 5.3 and 6.29), compute the temperature at which the diffusion flux is that required; (2) compute the yield strength of the nickel at this temperature using the dependence of yield strength on temperature as stated in Problem 6.D2; (3) calculate the circumferential stress on the tube walls using Equation 6.30; and (4) compare the yield strength and circumferential stress values--the yield strength should probably be at least twice the stress in order to make certain that no permanent deformation occurs. If this condition is not met then another iteration of the procedure should be conducted with a more educated choice of wall thickness.

As a starting point, let us arbitrarily choose a wall thickness of 2 mm (2 x 10^{-3} m). The steady-state diffusion equation, Equation 5.3, takes the form

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= 2.5 \text{ x } 10^{-8} \text{ mol/m}^2\text{-s}$$

$$= -\left(4.76 \text{ x } 10^{-7}\right)\exp\left[-\frac{39{,}560 \text{ J/mol}}{(8.31 \text{ J/mol-K})(T)}\right] \times$$

$$\frac{(30.8)\exp\left[-\dfrac{12{,}300 \text{ J/mol}}{(8.31 \text{ J/mol-K})(T)}\right]\left(\sqrt{0.01015 \text{ MPa}} - \sqrt{1.015 \text{ MPa}}\right)}{0.002 \text{ m}}$$

Solving this expression for the temperature T gives T = 500 K = 227°C; this value is satisfactory inasmuch as it is less than the maximum allowable value (300°C).

The next step is to compute the stress on the wall using Equation 6.30; thus

$$\sigma = \frac{r\,\Delta p}{4\,\Delta x}$$

$$= \frac{(0.100 \text{ m})(1.015 \text{ MPa} - 0.01015 \text{ MPa})}{(4)\left(2 \times 10^{-3} \text{ m}\right)}$$

$$= 12.6 \text{ MPa}$$

Now, the yield strength (σ_y) of Ni at this temperature may be computed using the expression

$$\sigma_y = 100 \text{ MPa} - \frac{5 \text{ MPa}}{50°\text{C}}\left(T - T_r\right)$$

where T_r is room temperature. Thus,

$$\sigma_y = 100 \text{ MPa} - 0.1 \text{ MPa/°C } (227°\text{C} - 20°\text{C}) = 79.3 \text{ MPa}$$

Inasmuch as this yield strength is greater than twice the circumferential stress, wall thickness and temperature values of 2 mm and 227°C are satisfactory design parameters.

CHAPTER 7

DISLOCATIONS AND STRENGTHENING MECHANISMS

PROBLEM SOLUTIONS

Basic Concepts of Dislocations

Characteristics of Dislocations

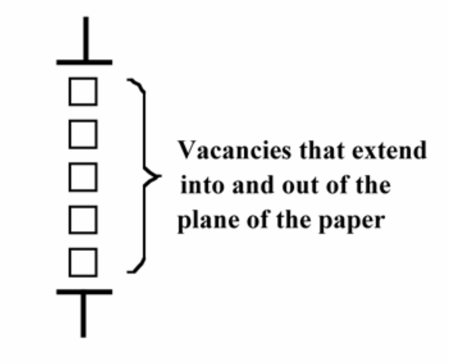
7.1 The dislocation density is just the total dislocation length per unit volume of material (in this case per cubic millimeters). Thus, the total length in 1000 mm^3 of material having a density of 10^5 mm^{-2} is just

$$(10^5\ \text{mm}^{-2})(1000\ \text{mm}^3) = 10^8\ \text{mm} = 10^5\ \text{m} = 62\ \text{mi}$$

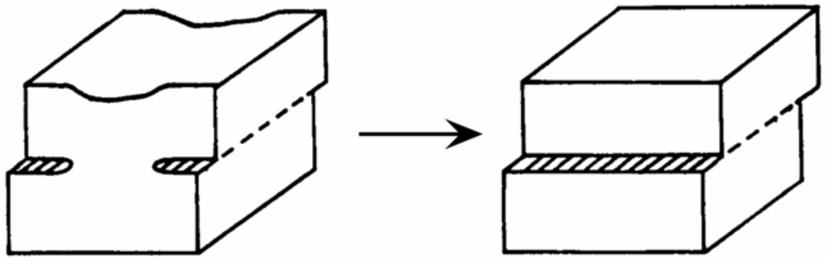
Similarly, for a dislocation density of 10^9 mm^{-2}, the total length is

$$(10^9\ \text{mm}^{-2})(1000\ \text{mm}^3) = 10^{12}\ \text{mm} = 10^9\ \text{m} = 6.2 \text{ x } 10^5\ \text{mi}$$

7.2 When the two edge dislocations become aligned, a planar region of vacancies will exist between the dislocations as:



7.3 It is possible for two screw dislocations of opposite sign to annihilate one another if their dislocation lines are parallel. This is demonstrated in the figure below.



7.4 For the various dislocation types, the relationships between the direction of the applied shear stress and the direction of dislocation line motion are as follows:

edge dislocation**--**parallel

screw dislocation**--**perpendicular

mixed dislocation**--**neither parallel nor perpendicular

Slip Systems

7.5 (a) A slip system is a crystallographic plane, and, within that plane, a direction along which dislocation motion (or slip) occurs.

(b) All metals do not have the same slip system. The reason for this is that for most metals, the slip system will consist of the most densely packed crystallographic plane, and within that plane the most closely packed direction. This plane and direction will vary from crystal structure to crystal structure.

7.6 (a) For the FCC crystal structure, the planar density for the (110) plane is given in Equation 3.11 as

$$\mathrm{PD}_{110}(\mathrm{FCC}) = \frac{1}{4R^2\sqrt{2}} = \frac{0.177}{R^2}$$

Furthermore, the planar densities of the (100) and (111) planes are calculated in Homework Problem 3.53, which are as follows:

$$\mathrm{PD}_{100}(\mathrm{FCC}) = \frac{1}{4R^2} = \frac{0.25}{R^2}$$

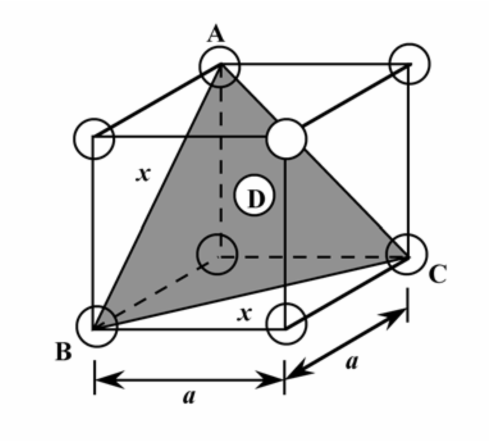
$$\mathrm{PD}_{111}(\mathrm{FCC}) = \frac{1}{2R^2\sqrt{3}} = \frac{0.29}{R^2}$$

(b) For the BCC crystal structure, the planar densities of the (100) and (110) planes were determined in Homework Problem 3.54, which are as follows:

$$\mathrm{PD}_{100}(\mathrm{BCC}) = \frac{3}{16R^2} = \frac{0.19}{R^2}$$

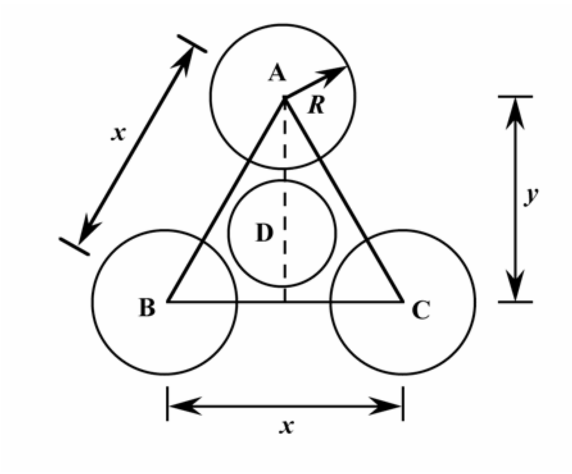
$$\mathrm{PD}_{110}(\mathrm{BCC}) = \frac{3}{8R^2\sqrt{2}} = \frac{0.27}{R^2}$$

Below is a BCC unit cell, within which is shown a (111) plane.



(*a*)

The centers of the three corner atoms, denoted by A, B, and C lie on this plane. Furthermore, the (111) plane does not pass through the center of atom D, which is located at the unit cell center. The atomic packing of this plane is presented in the following figure; the corresponding atom positions from the Figure (*a*) are also noted.



(*b*)

Inasmuch as this plane does not pass through the center of atom D, it is not included in the atom count. One sixth of each of the three atoms labeled A, B, and C is associated with this plane, which gives an equivalence of one-half atom.

In Figure (*b*) the triangle with A, B, and C at its corners is an equilateral triangle. And, from Figure (*b*), the area of this triangle is $\frac{xy}{2}$. The triangle edge length, x, is equal to the length of a face diagonal, as indicated in Figure (*a*). And its length is related to the unit cell edge length, a, as

$$x^2 = a^2 + a^2 = 2a^2$$

or

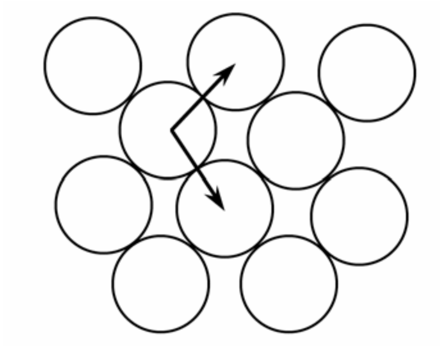
$$x = a\sqrt{2}$$

For BCC, $a = \frac{4R}{\sqrt{3}}$ (Equation 3.3), and, therefore,

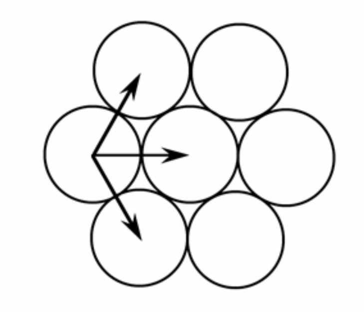
$$x = \frac{4R\sqrt{2}}{\sqrt{3}}$$

Also, from Figure (*b*), with respect to the length y we may write

7.7 Below is shown the atomic packing for a BCC {110}-type plane. The arrows indicate two different <111> type directions.



7.8 Below is shown the atomic packing for an HCP {0001}-type plane. The arrows indicate three different $< 11\overline{2}0 >$-type directions.



7.9 This problem asks that we compute the magnitudes of the Burgers vectors for copper and iron. For Cu, which has an FCC crystal structure, R = 0.1278 nm (Table 3.1) and $a = 2R\sqrt{2}$ = 0.3615 nm (Equation 3.1); also, from Equation 7.1a, the Burgers vector for FCC metals is

$$\mathbf{b} = \frac{a}{2}\langle 110\rangle$$

Therefore, the values for u, v, and w in Equation 7.10 are 1, 1, and 0, respectively. Hence, the magnitude of the Burgers vector for Cu is

$$|\mathbf{b}| = \frac{a}{2}\sqrt{u^2 + v^2 + w^2}$$

$$= \frac{0.3615 \text{ nm}}{2}\sqrt{(1)^2 + (1)^2 + (0)^2} = 0.2556 \text{ nm}$$

For Fe which has a BCC crystal structure, R = 0.1241 nm (Table 3.1) and $a = \frac{4R}{\sqrt{3}}$ = 0.2866 nm (Equation 3.3); also, from Equation 7.1b, the Burgers vector for BCC metals is

$$\mathbf{b} = \frac{a}{2}\langle 111\rangle$$

Therefore, the values for u, v, and w in Equation 7.10 are 1, 1, and 1, respectively. Hence, the magnitude of the Burgers vector for Fe is

$$|\mathbf{b}| = \frac{0.2866 \text{ nm}}{2}\sqrt{(1)^2 + (1)^2 + (1)^2} = 0.2482 \text{ nm}$$

7.10 (a) This part of the problem asks that we specify the Burgers vector for the simple cubic crystal structure (and suggests that we consult the answer to Concept Check 7.1). This Concept Check asks that we select the slip system for simple cubic from four possibilities. The correct answer is $\{100\}\langle 010\rangle$. Thus, the Burgers vector will lie in a $\langle 010\rangle$-type direction. Also, the unit slip distance is a (i.e., the unit cell edge length, Figures 4.3 and 7.1). Therefore, the Burgers vector for simple cubic is

$$\mathbf{b} = a\langle 010\rangle$$

Or, equivalently

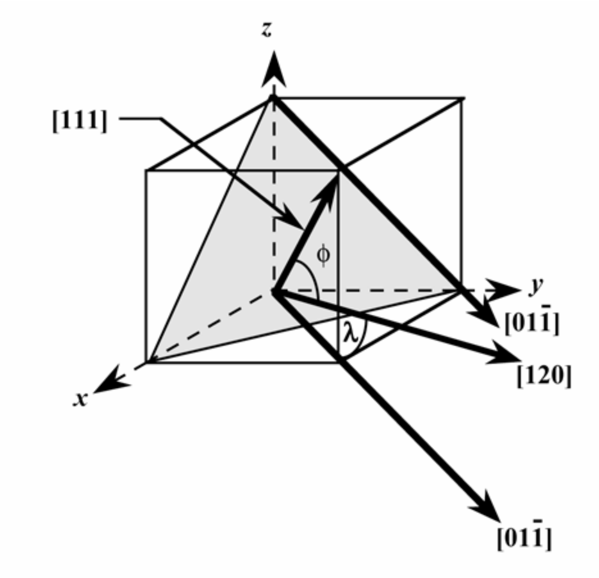
$$\mathbf{b} = a\langle 100\rangle$$

(b) The magnitude of the Burgers vector, $|\mathbf{b}|$, for simple cubic is

$$|\mathbf{b}| = a(1^2 + 0^2 + 0^2)^{1/2} = a$$

Slip in Single Crystals

7.11 We are asked to compute the *Schmid factor* for an FCC crystal oriented with its [120] direction parallel to the loading axis. With this scheme, slip may occur on the (111) plane and in the $[01\bar{1}]$ direction as noted in the figure below.



The angle between the [120] and $[01\bar{1}]$ directions, λ, may be determined using Equation 7.6

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [120]) $u_1 = 1$, $v_1 = 2$, $w_1 = 0$, and (for $[01\bar{1}]$) $u_2 = 0$, $v_2 = 1$, $w_2 = -1$. Therefore, λ is equal to

$$\lambda = \cos^{-1}\left[\frac{(1)(0) + (2)(1) + (0)(-1)}{\sqrt{\left[(1)^2 + (2)^2 + (0)^2\right]\left[(0)^2 + (1)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{10}}\right) = 50.8°$$

Now, the angle ϕ is equal to the angle between the normal to the (111) plane (which is the [111] direction), and the [120] direction. Again from Equation 7.6, and for $u_1 = 1$, $v_1 = 1$, $w_1 = 1$, $u_2 = 1$, $v_2 = 2$, and $w_2 = 0$, we have

$$\phi = \cos^{-1}\left[\frac{(1)(1) + (1)(2) + (1)(0)}{\sqrt{\left[(1)^2 + (1)^2 + (1)^2\right]\left[(1)^2 + (2)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{3}{\sqrt{15}}\right) = 39.2°$$

Therefore, the Schmid factor is equal to

$$\cos\lambda\cos\phi \;=\; \cos(50.8°)\cos(39.2°) \;=\; \left(\frac{2}{\sqrt{10}}\right)\left(\frac{3}{\sqrt{15}}\right) = 0.490$$

7.12 This problem calls for us to determine whether or not a metal single crystal having a specific orientation and of given critical resolved shear stress will yield. We are given that $\phi = 60°$, $\lambda = 35°$, and that the values of the critical resolved shear stress and applied tensile stress are 6.2 MPa (900 psi) and 12 MPa (1750 psi), respectively. From Equation 7.2

$$\tau_R = \sigma \cos\phi \cos\lambda = (12\text{ MPa})(\cos 60°)(\cos 35°) = 4.91\text{ MPa} \quad (717\text{ psi})$$

Since the resolved shear stress (4.91 MPa) is less that the critical resolved shear stress (6.2 MPa), the single crystal will not yield.

However, from Equation 7.4, the stress at which yielding occurs is

$$\sigma_y = \frac{\tau_{\text{crss}}}{\cos\phi \cos\lambda} = \frac{6.2\text{ MPa}}{(\cos 60°)(\cos 35°)} = 15.1\text{ MPa} \quad (2200\text{ psi})$$

7.13 We are asked to compute the critical resolved shear stress for Zn. As stipulated in the problem, ϕ = 65°, while possible values for λ are 30°, 48°, and 78°.

(a) Slip will occur along that direction for which ($\cos \phi \cos \lambda$) is a maximum, or, in this case, for the largest $\cos \lambda$. Cosines for the possible λ values are given below.

$$\cos(30°) = 0.87$$

$$\cos(48°) = 0.67$$

$$\cos(78°) = 0.21$$

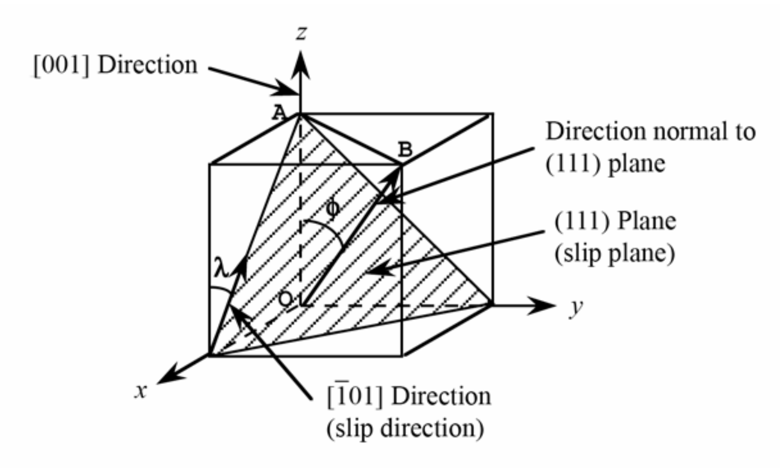
Thus, the slip direction is at an angle of 30° with the tensile axis.

(b) From Equation 7.4, the critical resolved shear stress is just

$$\tau_{\text{crss}} = \sigma_y (\cos \phi \cos \lambda)_{\text{max}}$$

$$= (2.5 \text{ MPa}) \left[\cos(65°) \cos(30°)\right] = 0.90 \text{ MPa} \quad (130 \text{ psi})$$

7.14 This problem asks that we compute the critical resolved shear stress for nickel. In order to do this, we must employ Equation 7.4, but first it is necessary to solve for the angles λ and ϕ which are shown in the sketch below.



The angle λ is the angle between the tensile axis—i.e., along the [001] direction—and the slip direction—i.e., [$\bar{1}$01]. The angle λ may be determined using Equation 7.6 as

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [001]) $u_1 = 0$, $v_1 = 0$, $w_1 = 1$, and (for [$\bar{1}$01]) $u_2 = -1$, $v_2 = 0$, $w_2 = 1$. Therefore, λ is equal to

$$\lambda = \cos^{-1}\left[\frac{(0)(-1) + (0)(0) + (1)(1)}{\sqrt{\left[(0)^2 + (0)^2 + (1)^2\right]\left[(-1)^2 + (0)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Furthermore, ϕ is the angle between the tensile axis—the [001] direction—and the normal to the slip plane—i.e., the (111) plane; for this case this normal is along a [111] direction. Therefore, again using Equation 7.6

$$\phi = \cos^{-1}\left[\frac{(0)(1) + (0)(1) + (1)(1)}{\sqrt{\left[(0)^2 + (0)^2 + (1)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

And, finally, using Equation 7.4, the critical resolved shear stress is equal to

$$\tau_{\text{crss}} = \sigma_y (\cos\phi \cos\lambda)$$

$$= (13.9\text{ MPa})\ \left[\cos(54.7°)\cos(45°)\right] = (13.9\text{ MPa})\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{2}}\right) = 5.68\text{ MPa}\quad(825\text{ psi})$$

7.15 This problem asks that, for a metal that has the FCC crystal structure, we compute the applied stress(s) that are required to cause slip to occur on a (111) plane in each of the $[1\bar{1}0]$, $[10\bar{1}]$, and $[0\bar{1}1]$ directions. In order to solve this problem it is necessary to employ Equation 7.4, but first we need to solve for the for λ and ϕ angles for the three slip systems.

For each of these three slip systems, the ϕ will be the same—i.e., the angle between the direction of the applied stress, [100] and the normal to the (111) plane, that is, the [111] direction. The angle ϕ may be determined using Equation 7.6 as

$$\phi = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [100]) $u_1 = 1$, $v_1 = 0$, $w_1 = 0$, and (for [111]) $u_2 = 1$, $v_2 = 1$, $w_2 = 1$. Therefore, ϕ is equal to

$$\phi = \cos^{-1}\left[\frac{(1)(1) + (0)(1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

Let us now determine λ for the $[1\bar{1}0]$ slip direction. Again, using Equation 7.6 where $u_1 = 1$, $v_1 = 0$, $w_1 = 0$ (for [100]), and $u_2 = 1$, $v_2 = -1$, $w_2 = 0$ (for $[1\bar{1}0]$. Therefore, λ is determined as

$$\lambda_{[100]-[1\bar{1}0]} = \cos^{-1}\left[\frac{(1)(1) + (0)(-1) + (0)(0)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (-1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Now, we solve for the yield strength for this (111)–$[1\bar{1}0]$ slip system using Equation 7.4 as

$$\sigma_y = \frac{\tau_{\text{crss}}}{(\cos\phi\ \cos\lambda)}$$

$$= \frac{0.5\ \text{MPa}}{\cos(54.7°)\ \cos(45°)} = \frac{0.5\ \text{MPa}}{(0.578)\,(0.707)} = 1.22\ \text{MPa}$$

Now, we must determine the value of λ for the (111)–$[10\bar{1}]$ slip system—that is, the angle between the [100] and $[10\bar{1}]$ directions. Again using Equation 7.6

$$\lambda_{[100]-[10\bar{1}]} = \cos^{-1}\left[\frac{(1)(1) + (0)(0) + (0)(-1)}{\sqrt{\Big[(1)^2 + (0)^2 + (0)^2\Big]\Big[(1)^2 + (0)^2 + (-1)^2\Big]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Thus, since the values of ϕ and λ for this (111)–$[10\bar{1}]$ slip system are the same as for (111)–$[1\bar{1}0]$, so also will σ_y be the same—viz 1.22 MPa.

And, finally, for the (111)–$[0\bar{1}1]$ slip system, λ is computed using Equation 7.6 as follows:

$$\lambda_{[100]-[0\bar{1}1]} = \cos^{-1}\left[\frac{(1)(0) + (0)(-1) + (0)(1)}{\sqrt{\Big[(1)^2 + (0)^2 + (0)^2\Big]\Big[(0)^2 + (-1)^2 + (1)^2\Big]}}\right]$$

$$= \cos^{-1}(0) = 90°$$

Thus, from Equation 7.4, the yield strength for this slip system is

$$\sigma_y = \frac{\tau_{\text{crss}}}{(\cos\phi\ \cos\lambda)}$$

$$= \frac{0.5\ \text{MPa}}{\cos(54.7°)\ \cos(90°)} = \frac{0.5\ \text{MPa}}{(0.578)\,(0)} = \infty$$

which means that slip will not occur on this (111)–$[0\bar{1}1]$ slip system.

7.16 (a) This part of the problem asks, for a BCC metal, that we compute the resolved shear stress in the $[1\bar{1}1]$ direction on each of the (110), (011), and $(10\bar{1})$ planes. In order to solve this problem it is necessary to employ Equation 7.2, which means that we first need to solve for the for angles λ and φ for the three slip systems.

For each of these three slip systems, the λ will be the same—i.e., the angle between the direction of the applied stress, [100] and the slip direction, $[1\bar{1}1]$. This angle λ may be determined using Equation 7.6

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [100]) $u_1 = 1$, $v_1 = 0$, $w_1 = 0$, and (for $[1\bar{1}1]$) $u_2 = 1$, $v_2 = -1$, $w_2 = 1$. Therefore, λ is determined as

$$\lambda = \cos^{-1}\left[\frac{(1)(1) + (0)(-1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (-1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

Let us now determine φ for the angle between the direction of the applied tensile stress—i.e., the [100] direction—and the normal to the (110) slip plane—i.e., the [110] direction. Again, using Equation 7.6 where $u_1 = 1$, $v_1 = 0$, $w_1 = 0$ (for [100]), and $u_2 = 1$, $v_2 = 1$, $w_2 = 0$ (for [110]), φ is equal to

$$\phi_{[100]-[110]} = \cos^{-1}\left[\frac{(1)(1) + (0)(1) + (0)(0)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Now, using Equation 7.2

$$\tau_R = \sigma \cos\phi \cos\lambda$$

we solve for the resolved shear stress for this slip system as

$$\tau_{R(110)-[1\bar{1}1]} = (4.0\ \text{MPa})\left[\cos(45°)\cos(54.7°)\right] = (4.0\ \text{MPa})(0.707)(0.578) = 1.63\ \text{MPa}$$

Now, we must determine the value of ϕ for the (011)–$[1\bar{1}1]$ slip system—that is, the angle between the direction of the applied stress, [100], and the normal to the (011) plane—i.e., the [011] direction. Again using Equation 7.6

$$\lambda_{[100]-[011]} = \cos^{-1}\left[\frac{(1)(0) + (0)(1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(0)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}(0) = 90°$$

Thus, the resolved shear stress for this (011)–$[1\bar{1}1]$ slip system is

$$\tau_{R(011)-[1\bar{1}1]} = = (4.0\ \text{MPa})\left[\cos(90°)\cos(54.7°)\right] = (4.0\ \text{MPa})(0)(0.578) = 0\ \text{MPa}$$

And, finally, it is necessary to determine the value of ϕ for the $(10\bar{1})-[1\bar{1}1]$ slip system —that is, the angle between the direction of the applied stress, [100], and the normal to the $(10\bar{1})$ plane—i.e., the $[10\bar{1}]$ direction. Again using Equation 7.6

$$\lambda_{[100]-[10\bar{1}]} = \cos^{-1}\left[\frac{(1)(1) + (0)(0) + (0)(-1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (0)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Here, as with the (110)–$[1\bar{1}1]$ slip system above, the value of ϕ is 45°, which again leads to

$$\tau_{R(10\bar{1})-[1\bar{1}1]} = (4.0\ \text{MPa})\left[\cos(45°)\cos(54.7°)\right] = (4.0\ \text{MPa})(0.707)(0.578) = 1.63\ \text{MPa}$$

(b) The most favored slip system(s) is (are) the one(s) that has (have) the largest τ_R value. Both (110)–$[1\bar{1}1]$ and $(10\bar{1})-[1\bar{1}1]$ slip systems are most favored since they have the same τ_R (1.63 MPa), which is greater than the τ_R value for $(011)-[1\bar{1}1]$ (viz., 0 MPa).

7.17 This problem asks for us to determine the tensile stress at which a BCC metal yields when the stress is applied along a [121] direction such that slip occurs on a (101) plane and in a $[\bar{1}11]$ direction; the critical resolved shear stress for this metal is 2.4 MPa. To solve this problem we use Equation 7.4; however it is first necessary to determine the values of ϕ and λ. These determinations are possible using Equation 7.6. Now, λ is the angle between [121] and $[\bar{1}11]$ directions. Therefore, relative to Equation 7.6 let us take $u_1 = 1$, $v_1 = 2$, and $w_1 = 1$, as well as $u_2 = -1$, $v_2 = 1$, and $w_2 = 1$. This leads to

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

$$= \cos^{-1}\left\{\frac{(1)(-1) + (2)(1) + (1)(1)}{\sqrt{\left[(1)^2 + (2)^2 + (1)^2\right]\left[(-1)^2 + (1)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{18}}\right) = 61.9°$$

Now for the determination of ϕ, the normal to the (101) slip plane is the [101] direction. Again using Equation 7.6, where we now take $u_1 = 1$, $v_1 = 2$, $w_1 = 1$ (for [121]), and $u_2 = 1$, $v_2 = 0$, $w_2 = 1$ (for [101]). Thus,

$$\phi = \cos^{-1}\left\{\frac{(1)(1) + (2)(0) + (1)(1)}{\sqrt{\left[(1)^2 + (2)^2 + (1)^2\right]\left[(1)^2 + (0)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{12}}\right) = 54.7°$$

It is now possible to compute the yield stress (using Equation 7.4) as

$$\sigma_y = \frac{\tau_{crss}}{\cos\phi\,\cos\lambda} = \frac{2.4\text{ MPa}}{\left(\frac{2}{\sqrt{12}}\right)\left(\frac{2}{\sqrt{18}}\right)} = 8.82\text{ MPa}$$

7.18 In order to determine the maximum possible yield strength for a single crystal of Cu pulled in tension, we simply employ Equation 7.5 as

$$\sigma_y = 2\tau_{\mathrm{crss}} = (2)(0.48\ \mathrm{MPa}) = 0.96\ \mathrm{MPa}\quad (140\ \mathrm{psi})$$

Deformation by Twinning

7.19 Four major differences between deformation by twinning and deformation by slip are as follows: (1) with slip deformation there is no crystallographic reorientation, whereas with twinning there is a reorientation; (2) for slip, the atomic displacements occur in atomic spacing multiples, whereas for twinning, these displacements may be other than by atomic spacing multiples; (3) slip occurs in metals having many slip systems, whereas twinning occurs in metals having relatively few slip systems; and (4) normally slip results in relatively large deformations, whereas only small deformations result for twinning.

Strengthening by Grain Size Reduction

7.20 Small-angle grain boundaries are not as effective in interfering with the slip process as are high-angle grain boundaries because there is not as much crystallographic misalignment in the grain boundary region for small-angle, and therefore not as much change in slip direction.

7.21 Hexagonal close packed metals are typically more brittle than FCC and BCC metals because there are fewer slip systems in HCP.

7.22 These three strengthening mechanisms are described in Sections 7.8, 7.9, and 7.10.

7.23 (a) Perhaps the easiest way to solve for σ_0 and k_y in Equation 7.7 is to pick two values each of σ_y and $d^{-1/2}$ from Figure 7.15, and then solve two simultaneous equations, which may be set up. For example

$d^{-1/2}$ (mm) $^{-1/2}$	σ_y (MPa)
4	75
12	175

The two equations are thus

$$75 = \sigma_0 + 4k_y$$

$$175 = \sigma_0 + 12k_y$$

Solution of these equations yield the values of

$$k_y = 12.5 \text{ MPa (mm)}^{1/2} \quad \left[1810 \text{ psi (mm)}^{1/2}\right]$$

$$\sigma_0 = 25 \text{ MPa (3630 psi)}$$

(b) When $d = 2.0 \times 10^{-3}$ mm, $d^{-1/2} = 22.4 \text{ mm}^{-1/2}$, and, using Equation 7.7,

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= (25 \text{ MPa}) + \left[12.5 \text{ MPa (mm)}^{1/2}\right]\left(22.4 \text{ mm}^{-1/2}\right) = 305 \text{ MPa} \quad (44,200 \text{ psi})$$

7.24 We are asked to determine the grain diameter for an iron which will give a yield strength of 310 MPa (45,000 psi). The best way to solve this problem is to first establish two simultaneous expressions of Equation 7.7, solve for σ_0 and k_y, and finally determine the value of d when σ_y = 310 MPa. The data pertaining to this problem may be tabulated as follows:

σ_y	d (mm)	$d^{-1/2}$ (mm)$^{-1/2}$
230 MPa	1×10^{-2}	10.0
275 MPa	6×10^{-3}	12.91

The two equations thus become

$$230 \text{ MPa} = \sigma_0 + (10.0)\, k_y$$

$$275 \text{ MPa} = \sigma_0 + (12.91)\, k_y$$

Which yield the values, σ_0 = 75.4 MPa and k_y = 15.46 MPa(mm)$^{1/2}$. At a yield strength of 310 MPa

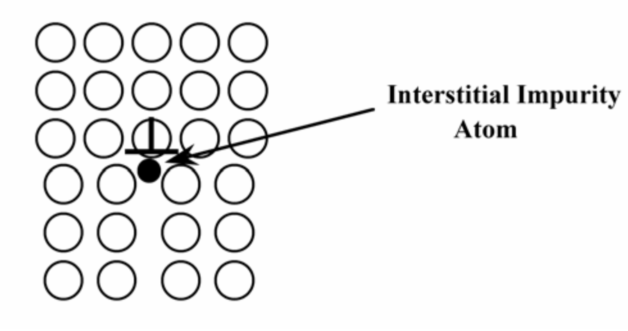
$$310 \text{ MPa} = 75.4 \text{ MPa} + \left[15.46 \text{ MPa (mm)}^{1/2}\right] d^{-1/2}$$

or $d^{-1/2}$ = 15.17 (mm)$^{-1/2}$, which gives $d = 4.34 \times 10^{-3}$ mm.

7.25 This problem asks that we determine the grain size of the brass for which is the subject of Figure 7.19. From Figure 7.19(a), the yield strength of brass at 0%CW is approximately 175 MPa (26,000 psi). This yield strength from Figure 7.15 corresponds to a $d^{-1/2}$ value of approximately 12.0 $(\mathrm{mm})^{-1/2}$. Thus, $d = 6.9 \times 10^{-3}$ mm.

Solid-Solution Strengthening

7.26 Below is shown an edge dislocation and where an interstitial impurity atom would be located. Compressive lattice strains are introduced by the impurity atom. There will be a net reduction in lattice strain energy when these lattice strains partially cancel tensile strains associated with the edge dislocation; such tensile strains exist just below the bottom of the extra half-plane of atoms (Figure 7.4).



Strain Hardening

7.27 (a) We are asked to show, for a tensile test, that

$$\%CW = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \text{ x } 100$$

From Equation 7.8

$$\%CW = \left[\frac{A_0 - A_d}{A_0}\right] \text{ x } 100 = \left[1 - \frac{A_d}{A_0}\right] \text{ x } 100$$

Which is also equal to

$$\left[1 - \frac{l_0}{l_d}\right] \text{ x } 100$$

since $A_d/A_0 = l_0/l_d$, the conservation of volume stipulation given in the problem statement. Now, from the definition of engineering strain (Equation 6.2)

$$\varepsilon = \frac{l_d - l_0}{l_0} = \frac{l_d}{l_0} - 1$$

Or,

$$\frac{l_0}{l_d} = \frac{1}{\varepsilon + 1}$$

Substitution for $l_0/\,l_d$ into the %CW expression above gives

$$\%CW = \left[1 - \frac{l_0}{l_d}\right] \text{ x } 100 = \left[1 - \frac{1}{\varepsilon + 1}\right] \text{ x } 100 = \left[\frac{\varepsilon}{\varepsilon + 1}\right] \text{ x } 100$$

(b) From Figure 6.12, a stress of 415 MPa (60,000 psi) corresponds to a strain of 0.16. Using the above expression

$$\%CW = \left[\frac{\varepsilon}{\varepsilon + 1}\right] \text{ x } 100 = \left[\frac{0.16}{0.16 + 1.00}\right] \text{ x } 100 = 13.8\%CW$$

7.28 In order for these two cylindrical specimens to have the same deformed hardness, they must be deformed to the same percent cold work. For the first specimen

$$\%\text{CW} = \frac{A_0 - A_d}{A_0} \text{ x } 100 = \frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2} \text{ x } 100$$

$$= \frac{\pi (15 \text{ mm})^2 - \pi (12 \text{ mm})^2}{\pi (15 \text{ mm})^2} \text{ x } 100 = 36\%\text{CW}$$

For the second specimen, the deformed radius is computed using the above equation and solving for r_d as

$$r_d = r_0 \sqrt{1 - \frac{\%\text{CW}}{100}}$$

$$= (11 \text{ mm}) \sqrt{1 - \frac{36\%\text{CW}}{100}} = 8.80 \text{ mm}$$

7.29 We are given the original and deformed cross-sectional dimensions for two specimens of the same metal, and are then asked to determine which is the hardest after deformation. The hardest specimen will be the one that has experienced the greatest degree of cold work. Therefore, all we need do is to compute the %CW for each specimen using Equation 7.8. For the circular one

$$\%\mathrm{CW} = \left[\frac{A_0 - A_d}{A_0}\right] \text{ x } 100$$

$$= \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right] \text{ x } 100$$

$$= \left[\frac{\pi\left(\frac{18.0\ \mathrm{mm}}{2}\right)^2 - \pi\left(\frac{15.9\ \mathrm{mm}}{2}\right)^2}{\pi\left(\frac{18.0\ \mathrm{mm}}{2}\right)^2}\right] \text{ x } 100 = 22.0\%\mathrm{CW}$$

For the rectangular one

$$\%\mathrm{CW} = \left[\frac{(20\ \mathrm{mm})(50\ \mathrm{mm}) - (13.7\ \mathrm{mm})(55.1\ \mathrm{mm})}{(20\ \mathrm{mm})(50\ \mathrm{mm})}\right] \text{ x } 100 = 24.5\%\mathrm{CW}$$

Therefore, the deformed rectangular specimen will be harder.

7.30 This problem calls for us to calculate the precold-worked radius of a cylindrical specimen of copper that has a cold-worked ductility of 15%EL. From Figure 7.19(c), copper that has a ductility of 15%EL will have experienced a deformation of about 20%CW. For a cylindrical specimen, Equation 7.8 becomes

$$\%\mathrm{CW} = \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right] \text{ x } 100$$

Since r_d = 6.4 mm (0.25 in.), solving for r_0 yields

$$r_0 = \frac{r_d}{\sqrt{1 - \frac{\%\mathrm{CW}}{100}}} = \frac{6.4 \text{ mm}}{\sqrt{1 - \frac{20.0}{100}}} = 7.2 \text{ mm} \quad (0.280 \text{ in.})$$

7.31 (a) We want to compute the ductility of a brass that has a yield strength of 345 MPa (50,000 psi). In order to solve this problem, it is necessary to consult Figures 7.19(a) and (c). From Figure 7.19(a), a yield strength of 345 MPa for brass corresponds to 20%CW. A brass that has been cold-worked 20% will have a ductility of about 24%EL [Figure 7.19(c)].

(b) This portion of the problem asks for the Brinell hardness of a 1040 steel having a yield strength of 620 MPa (90,000 psi). From Figure 7.19(a), a yield strength of 620 MPa for a 1040 steel corresponds to about 5%CW. A 1040 steel that has been cold worked 5% will have a tensile strength of about 750 MPa [Figure 7.19(b)]. Finally, using Equation 6.20a

$$\mathrm{HB} = \frac{TS\,(\mathrm{MPa})}{3.45} = \frac{750\ \ \mathrm{MPa}}{3.45} = 217$$

7.32 We are asked in this problem to compute the critical resolved shear stress at a dislocation density of 10^6 mm^{-2}. It is first necessary to compute the value of the constant *A* (in the equation provided in the problem statement) from the one set of data as

$$A = \frac{\tau_{\text{crss}} - \tau_0}{\sqrt{\rho_D}} = \frac{0.69 \text{ MPa} - 0.069 \text{ MPa}}{\sqrt{10^4 \text{ mm}^{-2}}} = 6.21 \text{ x } 10^{-3} \text{ MPa} - \text{mm} \;\; (0.90 \text{ psi} - \text{mm})$$

Now, the critical resolved shear stress may be determined at a dislocation density of 10^6 mm^{-2} as

$$\tau_{\text{crss}} = \tau_0 + A\sqrt{\rho_D}$$

$$= (0.069 \text{ MPa}) + \left(6.21 \text{ x } 10^{-3} \text{ MPa - mm}\right)\sqrt{10^6 \text{ mm}^{-2}} = 6.28 \text{ MPa} \;\; (910 \text{ psi})$$

CHAPTER 7

DISLOCATIONS AND STRENGTHENING MECHANISMS

PROBLEM SOLUTIONS

Basic Concepts of Dislocations
Characteristics of Dislocations

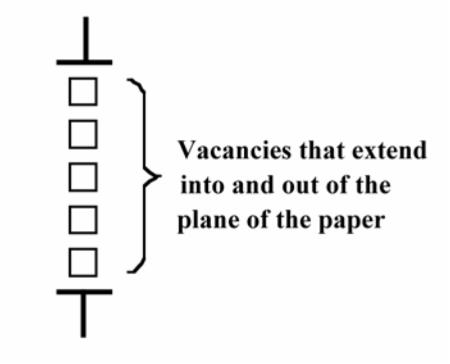
7.1 The dislocation density is just the total dislocation length per unit volume of material (in this case per cubic millimeters). Thus, the total length in 1000 mm^3 of material having a density of 10^5 mm^{-2} is just

$$\left(10^5 \text{ mm}^{-2}\right)\left(1000 \text{ mm}^3\right) = 10^8 \text{ mm} = 10^5 \text{ m} = 62 \text{ mi}$$

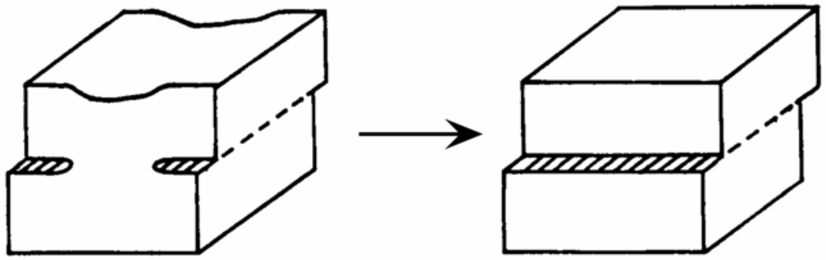
Similarly, for a dislocation density of 10^9 mm^{-2}, the total length is

$$\left(10^9 \text{ mm}^{-2}\right)\left(1000 \text{ mm}^3\right) = 10^{12} \text{ mm} = 10^9 \text{ m} = 6.2 \text{ x } 10^5 \text{ mi}$$

7.2 When the two edge dislocations become aligned, a planar region of vacancies will exist between the dislocations as:



7.3 It is possible for two screw dislocations of opposite sign to annihilate one another if their dislocation lines are parallel. This is demonstrated in the figure below.



7.4 For the various dislocation types, the relationships between the direction of the applied shear stress and the direction of dislocation line motion are as follows:

edge dislocation--parallel

screw dislocation--perpendicular

mixed dislocation--neither parallel nor perpendicular

Slip Systems

7.5 (a) A slip system is a crystallographic plane, and, within that plane, a direction along which dislocation motion (or slip) occurs.

(b) All metals do not have the same slip system. The reason for this is that for most metals, the slip system will consist of the most densely packed crystallographic plane, and within that plane the most closely packed direction. This plane and direction will vary from crystal structure to crystal structure.

7.6 (a) For the FCC crystal structure, the planar density for the (110) plane is given in Equation 3.11 as

$$\mathrm{PD}_{110}(\mathrm{FCC}) = \frac{1}{4R^2\sqrt{2}} = \frac{0.177}{R^2}$$

Furthermore, the planar densities of the (100) and (111) planes are calculated in Homework Problem 3.53, which are as follows:

$$\mathrm{PD}_{100}(\mathrm{FCC}) = \frac{1}{4R^2} = \frac{0.25}{R^2}$$

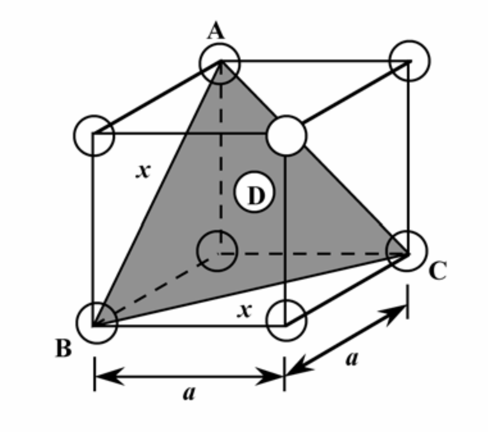
$$\mathrm{PD}_{111}(\mathrm{FCC}) = \frac{1}{2R^2\sqrt{3}} = \frac{0.29}{R^2}$$

(b) For the BCC crystal structure, the planar densities of the (100) and (110) planes were determined in Homework Problem 3.54, which are as follows:

$$\mathrm{PD}_{100}(\mathrm{BCC}) = \frac{3}{16R^2} = \frac{0.19}{R^2}$$

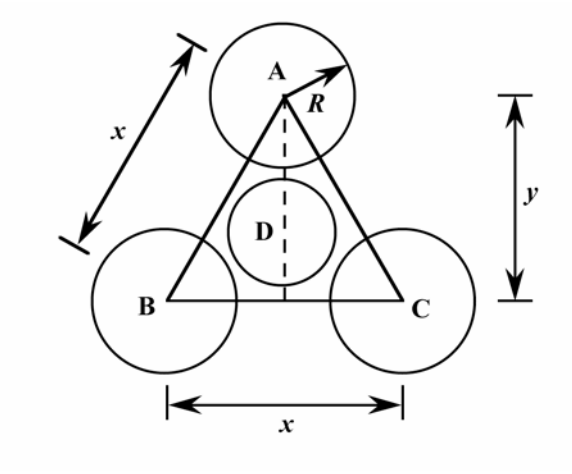
$$\mathrm{PD}_{110}(\mathrm{BCC}) = \frac{3}{8R^2\sqrt{2}} = \frac{0.27}{R^2}$$

Below is a BCC unit cell, within which is shown a (111) plane.



(*a*)

The centers of the three corner atoms, denoted by A, B, and C lie on this plane. Furthermore, the (111) plane does not pass through the center of atom D, which is located at the unit cell center. The atomic packing of this plane is presented in the following figure; the corresponding atom positions from the Figure (*a*) are also noted.



(*b*)

Inasmuch as this plane does not pass through the center of atom D, it is not included in the atom count. One sixth of each of the three atoms labeled A, B, and C is associated with this plane, which gives an equivalence of one-half atom.

In Figure (*b*) the triangle with A, B, and C at its corners is an equilateral triangle. And, from Figure (*b*), the area of this triangle is $\frac{xy}{2}$. The triangle edge length, *x*, is equal to the length of a face diagonal, as indicated in Figure (*a*). And its length is related to the unit cell edge length, *a*, as

$$x^2 = a^2 + a^2 = 2a^2$$

or

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

For BCC, $a = \frac{4R}{\sqrt{3}}$ (Equation 3.3), and, therefore,

$$x = \frac{4R\sqrt{2}}{\sqrt{3}}$$

Also, from Figure (*b*), with respect to the length *y* we may write

$$y^2 + \left(\frac{x}{2}\right)^2 = x^2$$

which leads to $y = \dfrac{x\sqrt{3}}{2}$. And, substitution for the above expression for ***x*** yields

$$y = \frac{x\sqrt{3}}{2} = \left(\frac{4R\sqrt{2}}{\sqrt{3}}\right)\left(\frac{\sqrt{3}}{2}\right) = \frac{4R\sqrt{2}}{2}$$

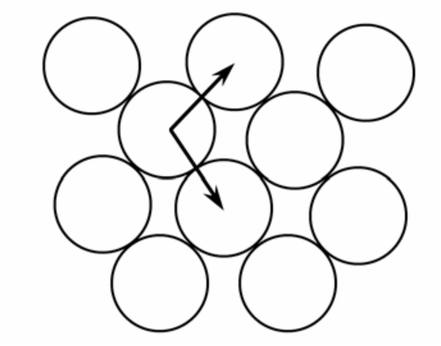
Thus, the area of this triangle is equal to

$$\text{AREA} = \frac{1}{2}\,x\,y = \left(\frac{1}{2}\right)\left(\frac{4R\sqrt{2}}{\sqrt{3}}\right)\left(\frac{4R\sqrt{2}}{2}\right) = \frac{8R^2}{\sqrt{3}}$$

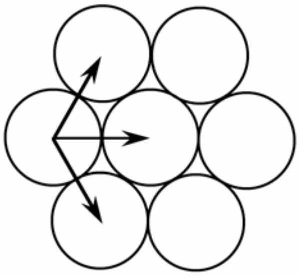
And, finally, the planar density for this (111) plane is

$$\text{PD}_{111}(\text{BCC}) = \frac{0.5\text{ atom}}{\dfrac{8R^2}{\sqrt{3}}} = \frac{\sqrt{3}}{16R^2} = \frac{0.11}{R^2}$$

7.7 Below is shown the atomic packing for a BCC {110}-type plane. The arrows indicate two different <111> type directions.



7.8 Below is shown the atomic packing for an HCP {0001}-type plane. The arrows indicate three different $<11\bar{2}0>$-type directions.



7.9 This problem asks that we compute the magnitudes of the Burgers vectors for copper and iron. For Cu, which has an FCC crystal structure, R = 0.1278 nm (Table 3.1) and $a = 2R\sqrt{2}$ = 0.3615 nm (Equation 3.1); also, from Equation 7.1a, the Burgers vector for FCC metals is

$$\mathbf{b} = \frac{a}{2}\langle 110\rangle$$

Therefore, the values for u, v, and w in Equation 7.10 are 1, 1, and 0, respectively. Hence, the magnitude of the Burgers vector for Cu is

$$|\mathbf{b}| = \frac{a}{2}\sqrt{u^2 + v^2 + w^2}$$

$$= \frac{0.3615 \text{ nm}}{2}\sqrt{(1)^2 + (1)^2 + (0)^2} = 0.2556 \text{ nm}$$

For Fe which has a BCC crystal structure, R = 0.1241 nm (Table 3.1) and $a = \frac{4R}{\sqrt{3}}$ = 0.2866 nm (Equation 3.3); also, from Equation 7.1b, the Burgers vector for BCC metals is

$$\mathbf{b} = \frac{a}{2}\langle 111\rangle$$

Therefore, the values for u, v, and w in Equation 7.10 are 1, 1, and 1, respectively. Hence, the magnitude of the Burgers vector for Fe is

$$|\mathbf{b}| = \frac{0.2866 \text{ nm}}{2}\sqrt{(1)^2 + (1)^2 + (1)^2} = 0.2482 \text{ nm}$$

7.10 (a) This part of the problem asks that we specify the Burgers vector for the simple cubic crystal structure (and suggests that we consult the answer to Concept Check 7.1). This Concept Check asks that we select the slip system for simple cubic from four possibilities. The correct answer is $\{100\}\langle 010\rangle$. Thus, the Burgers vector will lie in a $\langle 010\rangle$-type direction. Also, the unit slip distance is *a* (i.e., the unit cell edge length, Figures 4.3 and 7.1). Therefore, the Burgers vector for simple cubic is

$$\mathbf{b} = a\langle 010\rangle$$

Or, equivalently

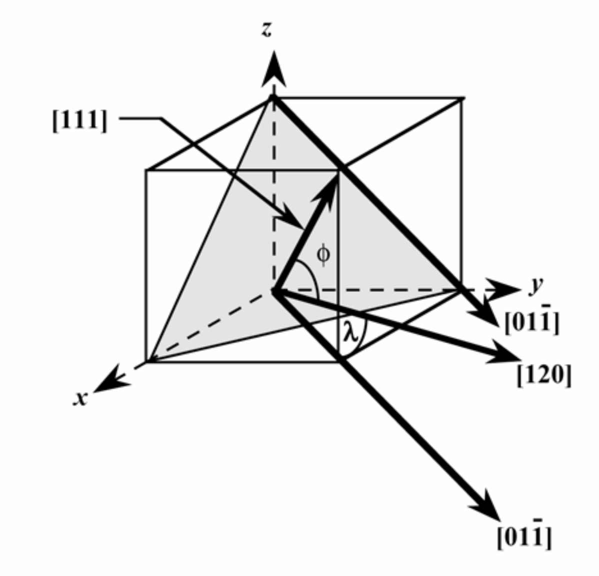
$$\mathbf{b} = a\langle 100\rangle$$

(b) The magnitude of the Burgers vector, |**b**|, for simple cubic is

$$|\mathbf{b}| = a(1^2 + 0^2 + 0^2)^{1/2} = a$$

Slip in Single Crystals

7.11 We are asked to compute the *Schmid factor* for an FCC crystal oriented with its [120] direction parallel to the loading axis. With this scheme, slip may occur on the (111) plane and in the $[01\bar{1}]$ direction as noted in the figure below.



The angle between the [120] and $[01\bar{1}]$ directions, λ, may be determined using Equation 7.6

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [120]) $u_1 = 1$, $v_1 = 2$, $w_1 = 0$, and (for $[01\bar{1}]$) $u_2 = 0$, $v_2 = 1$, $w_2 = -1$. Therefore, λ is equal to

$$\lambda = \cos^{-1}\left[\frac{(1)(0) + (2)(1) + (0)(-1)}{\sqrt{\left[(1)^2 + (2)^2 + (0)^2\right]\left[(0)^2 + (1)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{10}}\right) = 50.8°$$

Now, the angle ϕ is equal to the angle between the normal to the (111) plane (which is the [111] direction), and the [120] direction. Again from Equation 7.6, and for $u_1 = 1$, $v_1 = 1$, $w_1 = 1$, $u_2 = 1$, $v_2 = 2$, and $w_2 = 0$, we have

$$\phi = \cos^{-1}\left[\frac{(1)(1) + (1)(2) + (1)(0)}{\sqrt{\left[(1)^2 + (1)^2 + (1)^2\right]\left[(1)^2 + (2)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{3}{\sqrt{15}}\right) = 39.2°$$

Therefore, the Schmid factor is equal to

$$\cos\lambda\cos\phi \;=\; \cos(50.8°)\cos(39.2°) \;=\; \left(\frac{2}{\sqrt{10}}\right)\left(\frac{3}{\sqrt{15}}\right) = 0.490$$

7.12 This problem calls for us to determine whether or not a metal single crystal having a specific orientation and of given critical resolved shear stress will yield. We are given that $\phi = 60°$, $\lambda = 35°$, and that the values of the critical resolved shear stress and applied tensile stress are 6.2 MPa (900 psi) and 12 MPa (1750 psi), respectively. From Equation 7.2

$$\tau_R = \sigma \cos \phi \cos \lambda = (12\text{ MPa})(\cos 60°)(\cos 35°) = 4.91\text{ MPa} \quad (717\text{ psi})$$

Since the resolved shear stress (4.91 MPa) is less that the critical resolved shear stress (6.2 MPa), the single crystal will not yield.

However, from Equation 7.4, the stress at which yielding occurs is

$$\sigma_y = \frac{\tau_{\text{crss}}}{\cos \phi \cos \lambda} = \frac{6.2\text{ MPa}}{(\cos 60°)(\cos 35°)} = 15.1\text{ MPa} \quad (2200\text{ psi})$$

7.13 We are asked to compute the critical resolved shear stress for Zn. As stipulated in the problem, ϕ = 65°, while possible values for λ are 30°, 48°, and 78°.

(a) Slip will occur along that direction for which ($\cos \phi \cos \lambda$) is a maximum, or, in this case, for the largest $\cos \lambda$. Cosines for the possible λ values are given below.

$$\cos(30°) = 0.87$$

$$\cos(48°) = 0.67$$

$$\cos(78°) = 0.21$$

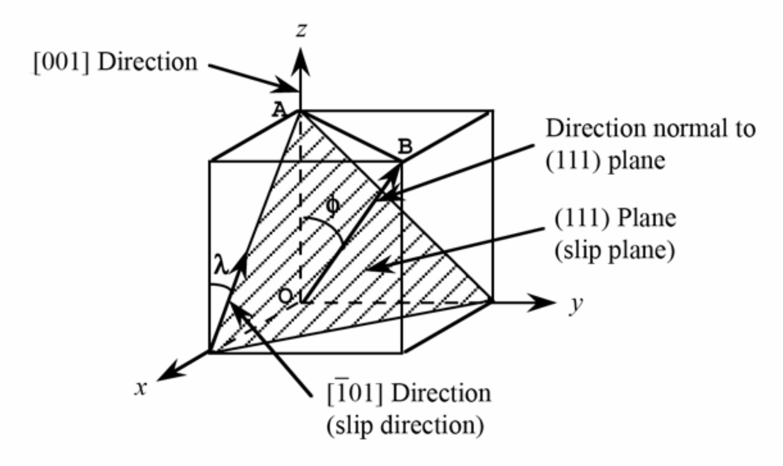
Thus, the slip direction is at an angle of 30° with the tensile axis.

(b) From Equation 7.4, the critical resolved shear stress is just

$$\tau_{\mathrm{crss}} = \sigma_y (\cos \phi \cos \lambda)_{\max}$$

$$= (2.5 \text{ MPa}) \left[\cos(65°) \cos(30°)\right] = 0.90 \text{ MPa} \quad (130 \text{ psi})$$

7.14 This problem asks that we compute the critical resolved shear stress for nickel. In order to do this, we must employ Equation 7.4, but first it is necessary to solve for the angles λ and ϕ which are shown in the sketch below.



The angle λ is the angle between the tensile axis—i.e., along the [001] direction—and the slip direction—i.e., [$\bar{1}$01]. The angle λ may be determined using Equation 7.6 as

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [001]) $u_1 = 0$, $v_1 = 0$, $w_1 = 1$, and (for [$\bar{1}$01]) $u_2 = -1$, $v_2 = 0$, $w_2 = 1$. Therefore, λ is equal to

$$\lambda = \cos^{-1}\left[\frac{(0)(-1) + (0)(0) + (1)(1)}{\sqrt{\left[(0)^2 + (0)^2 + (1)^2\right]\left[(-1)^2 + (0)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Furthermore, ϕ is the angle between the tensile axis—the [001] direction—and the normal to the slip plane—i.e., the (111) plane; for this case this normal is along a [111] direction. Therefore, again using Equation 7.6

$$\phi = \cos^{-1}\left[\frac{(0)(1) + (0)(1) + (1)(1)}{\sqrt{\left[(0)^2 + (0)^2 + (1)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

And, finally, using Equation 7.4, the critical resolved shear stress is equal to

$$\tau_{\text{crss}} = \sigma_y (\cos\phi \cos\lambda)$$

$$= (13.9\text{ MPa})\left[\cos(54.7°)\cos(45°)\right] = (13.9\text{ MPa})\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{2}}\right) = 5.68\text{ MPa} \quad (825\text{ psi})$$

7.15 This problem asks that, for a metal that has the FCC crystal structure, we compute the applied stress(s) that are required to cause slip to occur on a (111) plane in each of the $[1\bar{1}0]$, $[10\bar{1}]$, and $[0\bar{1}1]$ directions. In order to solve this problem it is necessary to employ Equation 7.4, but first we need to solve for the for λ and ϕ angles for the three slip systems.

For each of these three slip systems, the ϕ will be the same—i.e., the angle between the direction of the applied stress, [100] and the normal to the (111) plane, that is, the [111] direction. The angle ϕ may be determined using Equation 7.6 as

$$\phi = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [100]) $u_1 = 1$, $v_1 = 0$, $w_1 = 0$, and (for [111]) $u_2 = 1$, $v_2 = 1$, $w_2 = 1$. Therefore, ϕ is equal to

$$\phi = \cos^{-1}\left[\frac{(1)(1) + (0)(1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

Let us now determine λ for the $[1\bar{1}0]$ slip direction. Again, using Equation 7.6 where $u_1 = 1$, $v_1 = 0$, $w_1 = 0$ (for [100]), and $u_2 = 1$, $v_2 = -1$, $w_2 = 0$ (for $[1\bar{1}0]$. Therefore, λ is determined as

$$\lambda_{[100]-[1\bar{1}0]} = \cos^{-1}\left[\frac{(1)(1) + (0)(-1) + (0)(0)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (-1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Now, we solve for the yield strength for this (111)–$[1\bar{1}0]$ slip system using Equation 7.4 as

$$\sigma_y = \frac{\tau_{\text{crss}}}{(\cos\phi \, \cos\lambda)}$$

$$= \frac{0.5 \text{ MPa}}{\cos(54.7°)\ \cos(45°)} = \frac{0.5 \text{ MPa}}{(0.578)(0.707)} = 1.22 \text{ MPa}$$

Now, we must determine the value of λ for the (111)–$[10\bar{1}]$ slip system—that is, the angle between the [100] and $[10\bar{1}]$ directions. Again using Equation 7.6

$$\lambda_{[100]-[10\bar{1}]} = \cos^{-1}\left[\frac{(1)(1) + (0)(0) + (0)(-1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (0)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Thus, since the values of ϕ and λ for this (111)–$[10\bar{1}]$ slip system are the same as for (111)–$[1\bar{1}0]$, so also will σ_y be the same—viz 1.22 MPa.

And, finally, for the (111)–$[0\bar{1}1]$ slip system, λ is computed using Equation 7.6 as follows:

$$\lambda_{[100]-[0\bar{1}1]} = \cos^{-1}\left[\frac{(1)(0) + (0)(-1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(0)^2 + (-1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}(0) = 90°$$

Thus, from Equation 7.4, the yield strength for this slip system is

$$\sigma_y = \frac{\tau_{\text{crss}}}{(\cos\phi\ \cos\lambda)}$$

$$= \frac{0.5 \text{ MPa}}{\cos(54.7°)\ \cos(90°)} = \frac{0.5 \text{ MPa}}{(0.578)(0)} = \infty$$

which means that slip will not occur on this (111)–$[0\bar{1}1]$ slip system.

7.16 (a) This part of the problem asks, for a BCC metal, that we compute the resolved shear stress in the $[1\bar{1}1]$ direction on each of the (110), (011), and $(10\bar{1})$ planes. In order to solve this problem it is necessary to employ Equation 7.2, which means that we first need to solve for the for angles λ and ϕ for the three slip systems.

For each of these three slip systems, the λ will be the same—i.e., the angle between the direction of the applied stress, [100] and the slip direction, $[1\bar{1}1]$. This angle λ may be determined using Equation 7.6

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [100]) $u_1 = 1$, $v_1 = 0$, $w_1 = 0$, and (for $[1\bar{1}1]$) $u_2 = 1$, $v_2 = -1$, $w_2 = 1$. Therefore, λ is determined as

$$\lambda = \cos^{-1}\left[\frac{(1)(1) + (0)(-1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (-1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

Let us now determine ϕ for the angle between the direction of the applied tensile stress—i.e., the [100] direction—and the normal to the (110) slip plane—i.e., the [110] direction. Again, using Equation 7.6 where $u_1 = 1$, $v_1 = 0$, $w_1 = 0$ (for [100]), and $u_2 = 1$, $v_2 = 1$, $w_2 = 0$ (for [110]), ϕ is equal to

$$\phi_{[100]-[110]} = \cos^{-1}\left[\frac{(1)(1) + (0)(1) + (0)(0)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Now, using Equation 7.2

$$\tau_R = \sigma \cos\phi \cos\lambda$$

we solve for the resolved shear stress for this slip system as

$$\tau_{R(110)-[1\bar{1}1]} = (4.0\ \text{MPa})\left[\cos(45°)\cos(54.7°)\right] = (4.0\ \text{MPa})(0.707)(0.578) = 1.63\ \text{MPa}$$

Now, we must determine the value of ϕ for the (011)–[$1\bar{1}1$] slip system—that is, the angle between the direction of the applied stress, [100], and the normal to the (011) plane—i.e., the [011] direction. Again using Equation 7.6

$$\lambda_{[100]-[011]} = \cos^{-1}\left[\frac{(1)(0) + (0)(1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(0)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}(0) = 90°$$

Thus, the resolved shear stress for this (011)–[$1\bar{1}1$] slip system is

$$\tau_{R(011)-[1\bar{1}1]} = = (4.0\ \text{MPa})\left[\cos(90°)\cos(54.7°)\right] = (4.0\ \text{MPa})(0)(0.578) = 0\ \text{MPa}$$

And, finally, it is necessary to determine the value of ϕ for the $(10\bar{1})-[1\bar{1}1]$ slip system —that is, the angle between the direction of the applied stress, [100], and the normal to the $(10\bar{1})$ plane—i.e., the $[10\bar{1}]$ direction. Again using Equation 7.6

$$\lambda_{[100]-[10\bar{1}]} = \cos^{-1}\left[\frac{(1)(1) + (0)(0) + (0)(-1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (0)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Here, as with the (110)–[$1\bar{1}1$] slip system above, the value of ϕ is 45°, which again leads to

$$\tau_{R(10\bar{1})-[1\bar{1}1]} = (4.0\ \text{MPa})\left[\cos(45°)\cos(54.7°)\right] = (4.0\ \text{MPa})(0.707)(0.578) = 1.63\ \text{MPa}$$

(b) The most favored slip system(s) is (are) the one(s) that has (have) the largest τ_R value. Both (110)–[$1\bar{1}1$] and $(10\bar{1})-[1\bar{1}1]$ slip systems are most favored since they have the same τ_R (1.63 MPa), which is greater than the τ_R value for $(011)-[1\bar{1}1]$ (viz., 0 MPa).

7.17 This problem asks for us to determine the tensile stress at which a BCC metal yields when the stress is applied along a [121] direction such that slip occurs on a (101) plane and in a $[\bar{1}11]$ direction; the critical resolved shear stress for this metal is 2.4 MPa. To solve this problem we use Equation 7.4; however it is first necessary to determine the values of ϕ and λ. These determinations are possible using Equation 7.6. Now, λ is the angle between [121] and $[\bar{1}11]$ directions. Therefore, relative to Equation 7.6 let us take $u_1 = 1$, $v_1 = 2$, and $w_1 = 1$, as well as $u_2 = -1$, $v_2 = 1$, and $w_2 = 1$. This leads to

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

$$= \cos^{-1}\left\{\frac{(1)(-1) + (2)(1) + (1)(1)}{\sqrt{\left[(1)^2 + (2)^2 + (1)^2\right]\left[(-1)^2 + (1)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{18}}\right) = 61.9°$$

Now for the determination of ϕ, the normal to the (101) slip plane is the [101] direction. Again using Equation 7.6, where we now take $u_1 = 1$, $v_1 = 2$, $w_1 = 1$ (for [121]), and $u_2 = 1$, $v_2 = 0$, $w_2 = 1$ (for [101]). Thus,

$$\phi = \cos^{-1}\left\{\frac{(1)(1) + (2)(0) + (1)(1)}{\sqrt{\left[(1)^2 + (2)^2 + (1)^2\right]\left[(1)^2 + (0)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{12}}\right) = 54.7°$$

It is now possible to compute the yield stress (using Equation 7.4) as

$$\sigma_y = \frac{\tau_{\text{crss}}}{\cos\phi\,\cos\lambda} = \frac{2.4\text{ MPa}}{\left(\frac{2}{\sqrt{12}}\right)\left(\frac{2}{\sqrt{18}}\right)} = 8.82\text{ MPa}$$

7.18 In order to determine the maximum possible yield strength for a single crystal of Cu pulled in tension, we simply employ Equation 7.5 as

$$\sigma_y = 2\tau_{\text{crss}} = (2)(0.48 \text{ MPa}) = 0.96 \text{ MPa} \quad (140 \text{ psi})$$

Deformation by Twinning

7.19 Four major differences between deformation by twinning and deformation by slip are as follows: (1) with slip deformation there is no crystallographic reorientation, whereas with twinning there is a reorientation; (2) for slip, the atomic displacements occur in atomic spacing multiples, whereas for twinning, these displacements may be other than by atomic spacing multiples; (3) slip occurs in metals having many slip systems, whereas twinning occurs in metals having relatively few slip systems; and (4) normally slip results in relatively large deformations, whereas only small deformations result for twinning.

Strengthening by Grain Size Reduction

7.20 Small-angle grain boundaries are not as effective in interfering with the slip process as are high-angle grain boundaries because there is not as much crystallographic misalignment in the grain boundary region for small-angle, and therefore not as much change in slip direction.

7.21 Hexagonal close packed metals are typically more brittle than FCC and BCC metals because there are fewer slip systems in HCP.

7.22 These three strengthening mechanisms are described in Sections 7.8, 7.9, and 7.10.

7.23 (a) Perhaps the easiest way to solve for σ_0 and k_y in Equation 7.7 is to pick two values each of σ_y and $d^{-1/2}$ from Figure 7.15, and then solve two simultaneous equations, which may be set up. For example

$d^{-1/2}$ (mm) $^{-1/2}$	σ_y (MPa)
4	75
12	175

The two equations are thus

$$75 = \sigma_0 + 4k_y$$

$$175 = \sigma_0 + 12k_y$$

Solution of these equations yield the values of

$$k_y = 12.5 \text{ MPa (mm)}^{1/2} \quad \left[1810 \text{ psi (mm)}^{1/2}\right]$$

$$\sigma_0 = 25 \text{ MPa (3630 psi)}$$

(b) When d = 2.0 x 10^{-3} mm, $d^{-1/2}$ = 22.4 mm$^{-1/2}$, and, using Equation 7.7,

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= (25 \text{ MPa}) + \left[12.5 \text{ MPa (mm)}^{1/2}\right](22.4 \text{ mm}^{-1/2}) = 305 \text{ MPa } (44{,}200 \text{ psi})$$

7.24 We are asked to determine the grain diameter for an iron which will give a yield strength of 310 MPa (45,000 psi). The best way to solve this problem is to first establish two simultaneous expressions of Equation 7.7, solve for σ_0 and k_y, and finally determine the value of d when σ_y = 310 MPa. The data pertaining to this problem may be tabulated as follows:

σ_y	d (mm)	$d^{-1/2}$ (mm)$^{-1/2}$
230 MPa	1×10^{-2}	10.0
275 MPa	6×10^{-3}	12.91

The two equations thus become

$$230 \text{ MPa} = \sigma_0 + (10.0)\, k_y$$

$$275 \text{ MPa} = \sigma_0 + (12.91)\, k_y$$

Which yield the values, σ_0 = 75.4 MPa and k_y = 15.46 MPa(mm)$^{1/2}$. At a yield strength of 310 MPa

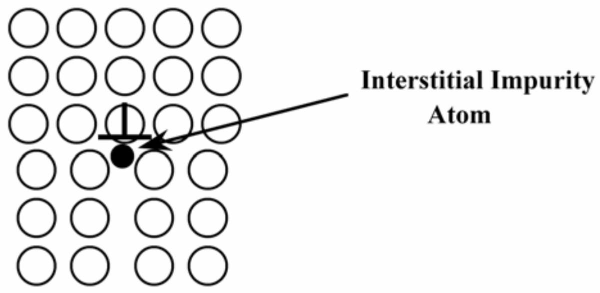
$$310 \text{ MPa} = 75.4 \text{ MPa} + \left[15.46 \text{ MPa (mm)}^{1/2}\right] d^{-1/2}$$

or $d^{-1/2}$ = 15.17 (mm)$^{-1/2}$, which gives $d = 4.34 \times 10^{-3}$ mm.

7.25 This problem asks that we determine the grain size of the brass for which is the subject of Figure 7.19. From Figure 7.19(a), the yield strength of brass at 0%CW is approximately 175 MPa (26,000 psi). This yield strength from Figure 7.15 corresponds to a $d^{-1/2}$ value of approximately 12.0 $(\text{mm})^{-1/2}$. Thus, $d = 6.9 \times 10^{-3}$ mm.

Solid-Solution Strengthening

7.26 Below is shown an edge dislocation and where an interstitial impurity atom would be located. Compressive lattice strains are introduced by the impurity atom. There will be a net reduction in lattice strain energy when these lattice strains partially cancel tensile strains associated with the edge dislocation; such tensile strains exist just below the bottom of the extra half-plane of atoms (Figure 7.4).



Strain Hardening

7.27 (a) We are asked to show, for a tensile test, that

$$\%\mathrm{CW} = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \mathrm{x}\ 100$$

From Equation 7.8

$$\%\mathrm{CW} = \left[\frac{A_0 - A_d}{A_0}\right] \mathrm{x}\ 100 = \left[1 - \frac{A_d}{A_0}\right] \mathrm{x}\ 100$$

Which is also equal to

$$\left[1 - \frac{l_0}{l_d}\right] \mathrm{x}\ 100$$

since $A_d/A_0 = l_0/l_d$, the conservation of volume stipulation given in the problem statement. Now, from the definition of engineering strain (Equation 6.2)

$$\varepsilon = \frac{l_d - l_0}{l_0} = \frac{l_d}{l_0} - 1$$

Or,

$$\frac{l_0}{l_d} = \frac{1}{\varepsilon + 1}$$

Substitution for $l_0/\,l_d$ into the %CW expression above gives

$$\%\mathrm{CW} = \left[1 - \frac{l_0}{l_d}\right] \mathrm{x}\ 100 = \left[1 - \frac{1}{\varepsilon + 1}\right] \mathrm{x}\ 100 = \left[\frac{\varepsilon}{\varepsilon + 1}\right] \mathrm{x}\ 100$$

(b) From Figure 6.12, a stress of 415 MPa (60,000 psi) corresponds to a strain of 0.16. Using the above expression

$$\%\mathrm{CW} = \left[\frac{\varepsilon}{\varepsilon + 1}\right] \mathrm{x}\ 100 = \left[\frac{0.16}{0.16 + 1.00}\right] \mathrm{x}\ 100 = 13.8\%\mathrm{CW}$$

7.28 In order for these two cylindrical specimens to have the same deformed hardness, they must be deformed to the same percent cold work. For the first specimen

$$\%\mathrm{CW} = \frac{A_0 - A_d}{A_0} \text{ x } 100 = \frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2} \text{ x } 100$$

$$= \frac{\pi (15 \text{ mm})^2 - \pi (12 \text{ mm})^2}{\pi (15 \text{ mm})^2} \text{ x } 100 = 36\%\mathrm{CW}$$

For the second specimen, the deformed radius is computed using the above equation and solving for r_d as

$$r_d = r_0 \sqrt{1 - \frac{\%\mathrm{CW}}{100}}$$

$$= (11 \text{ mm})\sqrt{1 - \frac{36\%\mathrm{CW}}{100}} = 8.80 \text{ mm}$$

7.29 We are given the original and deformed cross-sectional dimensions for two specimens of the same metal, and are then asked to determine which is the hardest after deformation. The hardest specimen will be the one that has experienced the greatest degree of cold work. Therefore, all we need do is to compute the %CW for each specimen using Equation 7.8. For the circular one

$$\%\mathrm{CW} = \left[\frac{A_0 - A_d}{A_0}\right] \text{ x } 100$$

$$= \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right] \text{ x } 100$$

$$= \left[\frac{\pi\left(\frac{18.0 \text{ mm}}{2}\right)^2 - \pi\left(\frac{15.9 \text{ mm}}{2}\right)^2}{\pi\left(\frac{18.0 \text{ mm}}{2}\right)^2}\right] \text{ x } 100 = 22.0\%\mathrm{CW}$$

For the rectangular one

$$\%\mathrm{CW} = \left[\frac{(20 \text{ mm})(50 \text{ mm}) - (13.7 \text{ mm})(55.1 \text{ mm})}{(20 \text{ mm})(50 \text{ mm})}\right] \text{ x } 100 = 24.5\%\mathrm{CW}$$

Therefore, the deformed rectangular specimen will be harder.

7.30 This problem calls for us to calculate the precold-worked radius of a cylindrical specimen of copper that has a cold-worked ductility of 15%EL. From Figure 7.19(c), copper that has a ductility of 15%EL will have experienced a deformation of about 20%CW. For a cylindrical specimen, Equation 7.8 becomes

$$\%\mathrm{CW} = \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right] \times 100$$

Since r_d = 6.4 mm (0.25 in.), solving for r_0 yields

$$r_0 = \frac{r_d}{\sqrt{1 - \frac{\%\mathrm{CW}}{100}}} = \frac{6.4 \text{ mm}}{\sqrt{1 - \frac{20.0}{100}}} = 7.2 \text{ mm} \quad (0.280 \text{ in.})$$

7.31 (a) We want to compute the ductility of a brass that has a yield strength of 345 MPa (50,000 psi). In order to solve this problem, it is necessary to consult Figures 7.19(a) and (c). From Figure 7.19(a), a yield strength of 345 MPa for brass corresponds to 20%CW. A brass that has been cold-worked 20% will have a ductility of about 24%EL [Figure 7.19(c)].

(b) This portion of the problem asks for the Brinell hardness of a 1040 steel having a yield strength of 620 MPa (90,000 psi). From Figure 7.19(a), a yield strength of 620 MPa for a 1040 steel corresponds to about 5%CW. A 1040 steel that has been cold worked 5% will have a tensile strength of about 750 MPa [Figure 7.19(b)]. Finally, using Equation 6.20a

$$\mathrm{HB} = \frac{TS\,(\mathrm{MPa})}{3.45} = \frac{750\ \ \mathrm{MPa}}{3.45} = 217$$

7.32 We are asked in this problem to compute the critical resolved shear stress at a dislocation density of 10^6 mm^{-2}. It is first necessary to compute the value of the constant *A* (in the equation provided in the problem statement) from the one set of data as

$$A = \frac{\tau_{\text{crss}} - \tau_0}{\sqrt{\rho_D}} = \frac{0.69 \text{ MPa} - 0.069 \text{ MPa}}{\sqrt{10^4 \text{ mm}^{-2}}} = 6.21 \text{ x } 10^{-3} \text{ MPa} - \text{mm} \;\; (0.90 \text{ psi} - \text{mm})$$

Now, the critical resolved shear stress may be determined at a dislocation density of 10^6 mm^{-2} as

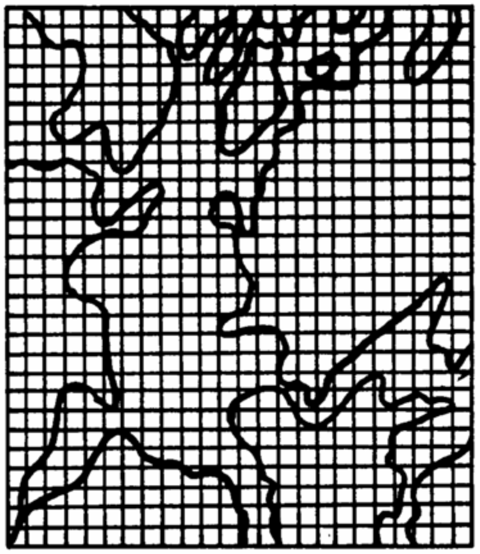
$$\tau_{\text{crss}} = \tau_0 + A\sqrt{\rho_D}$$

$$= (0.069 \text{ MPa}) + \left(6.21 \text{ x } 10^{-3} \text{ MPa - mm}\right)\sqrt{10^6 \text{ mm}^{-2}} = 6.28 \text{ MPa} \;\; (910 \text{ psi})$$

Recovery
Recrystallization
Grain Growth

7.33 For recovery, there is some relief of internal strain energy by dislocation motion; however, there are virtually no changes in either the grain structure or mechanical characteristics. During recrystallization, on the other hand, a new set of strain-free grains forms, and the material becomes softer and more ductile.

7.34 We are asked to estimate the fraction of recrystallization from the photomicrograph in Figure 7.21*c*. Below is shown a square grid onto which is superimposed the recrystallized regions from the micrograph. Approximately 400 squares lie within the recrystallized areas, and since there are 672 total squares, the specimen is about 60% recrystallized.



7.35 During cold-working, the grain structure of the metal has been distorted to accommodate the deformation. Recrystallization produces grains that are equiaxed and smaller than the parent grains.

7.36 (a) The driving force for recrystallization is the difference in internal energy between the strained and unstrained material.

(b) The driving force for grain growth is the reduction in grain boundary energy as the total grain boundary area decreases.

7.37 In this problem, we are asked for the length of time required for the average grain size of a brass material to increase a specified amount using Figure 7.25.

(a) At 600°C, the time necessary for the average grain diameter to grow to 0.03 is about 6 min; and the total time to grow to 0.3 mm is approximately 3000 min. Therefore, the time to grow from 0.03 to 0.3 mm is 3000 min - 6 min, or approximately 3000 min.

(b) At 700°C the time required for this same grain size increase is approximately 80 min.

7.38 (a) Using the data given and Equation 7.9 (taking $n = 2$), we may set up two simultaneous equations with d_0 and K as unknowns; thus

$$\left(5.6 \text{ x } 10^{-2} \text{ mm}\right)^2 - d_0^2 = (40 \text{ min})K$$

$$\left(8.0 \text{ x } 10^{-2} \text{ mm}\right)^2 - d_0^2 = (100 \text{ min})K$$

Solution of these expressions yields a value for d_0, the original grain diameter, of

$$d_0 = 0.031 \text{ mm},$$

and a value for K of 5.44 x 10^{-5} mm^2/min

(b) At 200 min, the diameter d is computed using a rearranged form of Equation 7.9 as

$$d = \sqrt{d_0^2 + Kt}$$

$$= \sqrt{(0.031 \text{ mm})^2 + \left(5.44 \text{ x } 10^{-5} \text{ mm}^2/\text{min}\right)(200 \text{ min})} = 0.109 \text{ mm}$$

7.39 Yes, it is possible to reduce the average grain diameter of an undeformed alloy specimen from 0.050 mm to 0.020 mm. In order to do this, plastically deform the material at room temperature (i.e., cold work it), and then anneal at an elevated temperature in order to allow recrystallization and some grain growth to occur until the average grain diameter is 0.020 mm.

7.40 (a) The temperature dependence of grain growth is incorporated into the constant *K* in Equation 7.9.

(b) The explicit expression for this temperature dependence is of the form

$$K = K_0 \exp\left(-\frac{Q}{RT}\right)$$

in which K_0 is a temperature-independent constant, the parameter *Q* is an activation energy, and *R* and *T* are the gas constant and absolute temperature, respectively.

7.41 This problem calls for us to calculate the yield strength of a brass specimen after it has been heated to an elevated temperature at which grain growth was allowed to occur; the yield strength (150 MPa) was given at a grain size of 0.01 mm. It is first necessary to calculate the constant k_y in Equation 7.7 as

$$k_y = \frac{\sigma_y - \sigma_0}{d^{-1/2}}$$

$$= \frac{150 \text{ MPa} - 25 \text{ MPa}}{(0.01 \text{ mm})^{-1/2}} = 12.5 \text{ MPa} - \text{mm}^{1/2}$$

Next, we must determine the average grain size after the heat treatment. From Figure 7.25 at 500°C after 1000 s (16.7 min) the average grain size of a brass material is about 0.016 mm. Therefore, calculating σ_y at this new grain size using Equation 7.7 we get

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= 25 \text{ MPa} + \left(12.5 \text{ MPa - mm}^{1/2}\right)(0.016 \text{ mm})^{-1/2} = 124 \text{ MPa} \quad (18{,}000 \text{ psi})$$

DESIGN PROBLEMS

Strain Hardening

Recrystallization

7.D1 This problem calls for us to determine whether or not it is possible to cold work steel so as to give a minimum Brinell hardness of 240 and a ductility of at least 15%EL. According to Figure 6.19, a Brinell hardness of 240 corresponds to a tensile strength of 800 MPa (116,000 psi). Furthermore, from Figure 7.19(b), in order to achieve a tensile strength of 800 MPa, deformation of at least 13%CW is necessary. Finally, if we cold work the steel to 13%CW, then the ductility is 15%EL from Figure 7.19(c). Therefore, it *is possible* to meet both of these criteria by plastically deforming the steel.

7.D2 We are asked to determine whether or not it is possible to cold work brass so as to give a minimum Brinell hardness of 150 and at the same time have a ductility of at least 20%EL. According to Figure 6.19, a Brinell hardness of 150 corresponds to a tensile strength of 500 MPa (72,000 psi.) Furthermore, from Figure 7.19(b), in order to achieve a tensile strength of 500 MPa, deformation of at least 36%CW is necessary. Finally, if we are to achieve a ductility of at least 20%EL, then a maximum deformation of 23%CW is possible from Figure 7.19(c). Therefore, it is *not possible* to meet both of these criteria by plastically deforming brass.

7.D3 (a) For this portion of the problem we are to determine the ductility of cold-worked steel that has a Brinell hardness of 240. From Figure 6.19, a Brinell hardness of 240 corresponds to a tensile strength of 820 MPa (120,000 psi), which, from Figure 7.19(b), requires a deformation of 17%CW. Furthermore, 17%CW yields a ductility of about 13%EL for steel, Figure 7.19(c).

(b) We are now asked to determine the radius after deformation if the uncold-worked radius is 10 mm (0.40 in.). From Equation 7.8 and for a cylindrical specimen

$$\%\mathrm{CW} = \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right] \times 100$$

Now, solving for r_d from this expression, we get

$$r_d = r_0\sqrt{1 - \frac{\%\mathrm{CW}}{100}}$$

$$= (10 \text{ mm})\sqrt{1 - \frac{17}{100}} = 9.11 \text{ mm} \quad (0.364 \text{ in.})$$

7.D4 This problem asks us to determine which of copper, brass, and a 1040 steel may be cold-worked so as to achieve a minimum yield strength of 310 MPa (45,000 psi) while maintaining a minimum ductility of 27%EL. For each of these alloys, the minimum cold work necessary to achieve the yield strength may be determined from Figure 7.19(a), while the maximum possible cold work for the ductility is found in Figure 7.19(c). These data are tabulated below.

	Yield Strength (> 310 MPa)	Ductility (> 27%EL)
Steel	Any %CW	Not possible
Brass	> 15%CW	< 18%CW
Copper	> 38%CW	< 10%CW

Thus, only brass is a possible candidate since for this alloy only there is an overlap of %CW's to give the required minimum yield strength and ductility values.

7.D5 This problem calls for us to explain the procedure by which a cylindrical rod of 1040 steel may be deformed so as to produce a given final diameter (8.9 mm), as well as a specific minimum tensile strength (825 MPa) and minimum ductility (12%EL). First let us calculate the percent cold work and attendant tensile strength and ductility if the drawing is carried out without interruption. From Equation 7.8

$$\%\mathrm{CW} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \text{ x } 100$$

$$= \frac{\pi\left(\frac{11.4 \text{ mm}}{2}\right)^2 - \pi\left(\frac{8.9 \text{ mm}}{2}\right)^2}{\pi\left(\frac{11.4 \text{ mm}}{2}\right)^2} \text{ x } 100 = 40\%\mathrm{CW}$$

At 40%CW, the steel will have a tensile strength on the order of 900 MPa (130,000 psi) [Figure 7.19(b)], which is adequate; however, the ductility will be less than 9%EL [Figure 7.19(c)], which is insufficient.

Instead of performing the drawing in a single operation, let us initially draw some fraction of the total deformation, then anneal to recrystallize, and, finally, cold-work the material a second time in order to achieve the final diameter, tensile strength, and ductility.

Reference to Figure 7.19(b) indicates that 17%CW is necessary to yield a tensile strength of 825 MPa (122,000 psi). Similarly, a maximum of 19%CW is possible for 12%EL [Figure 7.19(c)]. The average of these extremes is 18%CW. If the final diameter after the first drawing is d'_0, then

$$18\%\mathrm{CW} = \frac{\pi\left(\frac{d'_0}{2}\right)^2 - \pi\left(\frac{8.9 \text{ mm}}{2}\right)^2}{\pi\left(\frac{d'_0}{2}\right)^2} \text{ x } 100$$

And, solving for d'_0, yields

$$d'_0 = \frac{8.9 \text{ mm}}{\sqrt{1 - \frac{18\%\mathrm{CW}}{100}}} = 9.83 \text{ mm (0.387 in.)}$$

7.D6 Let us first calculate the percent cold work and attendant yield strength and ductility if the drawing is carried out without interruption. From Equation 7.8

$$\%\mathrm{CW} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \text{ x } 100$$

$$= \frac{\pi\left(\frac{10.2 \text{ mm}}{2}\right)^2 - \pi\left(\frac{7.6 \text{ mm}}{2}\right)^2}{\pi\left(\frac{10.2 \text{ mm}}{2}\right)^2} \text{ x } 100 = 44.5\%\mathrm{CW}$$

At 44.5%CW, the brass will have a yield strength on the order of 420 MPa (61,000 psi), Figure 7.19(a), which is adequate; however, the ductility will be about 5%EL, Figure 7.19(c), which is insufficient.

Instead of performing the drawing in a single operation, let us initially draw some fraction of the total deformation, then anneal to recrystallize, and, finally, cold work the material a second time in order to achieve the final diameter, yield strength, and ductility.

Reference to Figure 7.19(a) indicates that 27.5%CW is necessary to give a yield strength of 380 MPa. Similarly, a maximum of 27.5%CW is possible for 15%EL [Figure 7.19(c)]. Thus, to achieve both the specified yield strength and ductility, the brass must be deformed to 27.5 %CW. If the final diameter after the first drawing is d_0', then, using Equation 7.8

$$27.5\%\mathrm{CW} = \frac{\pi\left(\frac{d_0'}{2}\right)^2 - \pi\left(\frac{7.6 \text{ mm}}{2}\right)^2}{\pi\left(\frac{d_0'}{2}\right)^2} \text{ x } 100$$

And, solving for d_0' yields

$$d_0' = \frac{7.6 \text{ mm}}{\sqrt{1 - \frac{27.5\%\mathrm{CW}}{100}}} = 8.93 \text{ mm (0.351 in.)}$$

7.D7 This problem calls for us to cold work some brass stock that has been previously cold worked in order to achieve minimum tensile strength and ductility values of 450 MPa (65,000 psi) and 13%EL, respectively, while the final diameter must be 12.7 mm (0.50 in.). Furthermore, the material may not be deformed beyond 65%CW. Let us start by deciding what percent coldwork is necessary for the minimum tensile strength and ductility values, assuming that a recrystallization heat treatment is possible. From Figure 7.19(b), at least 27%CW is required for a tensile strength of 450 MPa. Furthermore, according to Figure 7.19(c), 13%EL corresponds a maximum of 30%CW. Let us take the average of these two values (i.e., 28.5%CW), and determine what previous specimen diameter is required to yield a final diameter of 12.7 mm. For cylindrical specimens, Equation 7.8 takes the form

$$\%\text{CW} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \text{ x } 100$$

Solving for the original diameter d_0 yields

$$d_0 = \frac{d_d}{\sqrt{1 - \frac{\%\text{CW}}{100}}} = \frac{12.7 \text{ mm}}{\sqrt{1 - 0.285}} = 15.0 \text{ mm} \quad (0.591 \text{ in.})$$

Now, let us determine its undeformed diameter realizing that a diameter of 19.0 mm corresponds to 35%CW. Again solving for d_0 using the above equation and assuming d_d = 19.0 mm yields

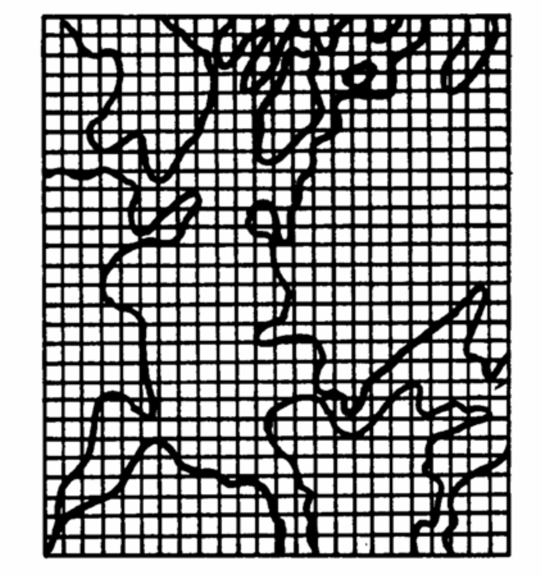
$$d_0 = \frac{d_d}{\sqrt{1 - \frac{\%\text{CW}}{100}}} = \frac{19.0 \text{ mm}}{\sqrt{1 - 0.35}} = 23.6 \text{ mm} \quad (0.930 \text{ in.})$$

At this point let us see if it is possible to deform the material from 23.6 mm to 15.0 mm without exceeding the 65%CW limit. Again employing Equation 7.8

$$\%\text{CW} = \frac{\pi\left(\frac{23.6 \text{ mm}}{2}\right)^2 - \pi\left(\frac{15.0 \text{ mm}}{2}\right)^2}{\pi\left(\frac{23.6 \text{ mm}}{2}\right)^2} \text{ x } 100 = 59.6\%\text{CW}$$

In summary, the procedure which can be used to produce the desired material would be as follows: cold work the as-received stock to 15.0 mm (0.591 in.), heat treat it to achieve complete recrystallization, and then cold work the material again to 12.7 mm (0.50 in.), which will give the desired tensile strength and ductility.

7.34 We are asked to estimate the fraction of recrystallization from the photomicrograph in Figure 7.21*c*. Below is shown a square grid onto which is superimposed the recrystallized regions from the micrograph. Approximately 400 squares lie within the recrystallized areas, and since there are 672 total squares, the specimen is about 60% recrystallized.



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(a) At 600°C, the time necessary for the average grain diameter to grow to 0.03 is about 6 min; and the total time to grow to 0.3 mm is approximately 3000 min. Therefore, the time to grow from 0.03 to 0.3 mm is 3000 min - 6 min, or approximately 3000 min.

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$$(5.6 \text{ x } 10^{-2} \text{ mm})^2 - d_0^2 = (40 \text{ min})K$$

$$(8.0 \text{ x } 10^{-2} \text{ mm})^2 - d_0^2 = (100 \text{ min})K$$

Solution of these expressions yields a value for d_0, the original grain diameter, of

$$d_0 = 0.031 \text{ mm},$$

and a value for K of 5.44 x 10^{-5} mm^2/min

(b) At 200 min, the diameter d is computed using a rearranged form of Equation 7.9 as

$$d = \sqrt{d_0^2 + Kt}$$

$$= \sqrt{(0.031 \text{ mm})^2 + (5.44 \text{ x } 10^{-5} \text{ mm}^2/\text{min})(200 \text{ min})} = 0.109 \text{ mm}$$

7.39 Yes, it is possible to reduce the average grain diameter of an undeformed alloy specimen from 0.050 mm to 0.020 mm. In order to do this, plastically deform the material at room temperature (i.e., cold work it), and then anneal at an elevated temperature in order to allow recrystallization and some grain growth to occur until the average grain diameter is 0.020 mm.

7.40 (a) The temperature dependence of grain growth is incorporated into the constant K in Equation 7.9.

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7.41 This problem calls for us to calculate the yield strength of a brass specimen after it has been heated to an elevated temperature at which grain growth was allowed to occur; the yield strength (150 MPa) was given at a grain size of 0.01 mm. It is first necessary to calculate the constant k_y in Equation 7.7 as

$$k_y = \frac{\sigma_y - \sigma_0}{d^{-1/2}}$$

$$= \frac{150\ \text{MPa} - 25\ \text{MPa}}{(0.01\ \text{mm})^{-1/2}} = 12.5\ \text{MPa} - \text{mm}^{1/2}$$

Next, we must determine the average grain size after the heat treatment. From Figure 7.25 at 500°C after 1000 s (16.7 min) the average grain size of a brass material is about 0.016 mm. Therefore, calculating σ_y at this new grain size using Equation 7.7 we get

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= 25\ \text{MPa} + \left(12.5\ \text{MPa - mm}^{1/2}\right)(0.016\ \text{mm})^{-1/2} = 124\ \text{MPa}\ \ (18{,}000\ \text{psi})$$

DESIGN PROBLEMS

Strain Hardening
Recrystallization

7.D1 This problem calls for us to determine whether or not it is possible to cold work steel so as to give a minimum Brinell hardness of 240 and a ductility of at least 15%EL. According to Figure 6.19, a Brinell hardness of 240 corresponds to a tensile strength of 800 MPa (116,000 psi). Furthermore, from Figure 7.19(b), in order to achieve a tensile strength of 800 MPa, deformation of at least 13%CW is necessary. Finally, if we cold work the steel to 13%CW, then the ductility is 15%EL from Figure 7.19(c). Therefore, it *is possible* to meet both of these criteria by plastically deforming the steel.

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7.D3 (a) For this portion of the problem we are to determine the ductility of cold-worked steel that has a Brinell hardness of 240. From Figure 6.19, a Brinell hardness of 240 corresponds to a tensile strength of 820 MPa (120,000 psi), which, from Figure 7.19(b), requires a deformation of 17%CW. Furthermore, 17%CW yields a ductility of about 13%EL for steel, Figure 7.19(c).

(b) We are now asked to determine the radius after deformation if the uncold-worked radius is 10 mm (0.40 in.). From Equation 7.8 and for a cylindrical specimen

$$\%\text{CW} = \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right] \text{ x } 100$$

Now, solving for r_d from this expression, we get

$$r_d = r_0\sqrt{1 - \frac{\%\text{CW}}{100}}$$

$$= (10 \text{ mm})\sqrt{1 - \frac{17}{100}} = 9.11 \text{ mm} \quad (0.364 \text{ in.})$$

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Thus, only brass is a possible candidate since for this alloy only there is an overlap of %CW's to give the required minimum yield strength and ductility values.

7.D5 This problem calls for us to explain the procedure by which a cylindrical rod of 1040 steel may be deformed so as to produce a given final diameter (8.9 mm), as well as a specific minimum tensile strength (825 MPa) and minimum ductility (12%EL). First let us calculate the percent cold work and attendant tensile strength and ductility if the drawing is carried out without interruption. From Equation 7.8

$$\%\mathrm{CW} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \text{ x } 100$$

$$= \frac{\pi\left(\frac{11.4 \text{ mm}}{2}\right)^2 - \pi\left(\frac{8.9 \text{ mm}}{2}\right)^2}{\pi\left(\frac{11.4 \text{ mm}}{2}\right)^2} \text{ x } 100 = 40\%\mathrm{CW}$$

At 40%CW, the steel will have a tensile strength on the order of 900 MPa (130,000 psi) [Figure 7.19(b)], which is adequate; however, the ductility will be less than 9%EL [Figure 7.19(c)], which is insufficient.

Instead of performing the drawing in a single operation, let us initially draw some fraction of the total deformation, then anneal to recrystallize, and, finally, cold-work the material a second time in order to achieve the final diameter, tensile strength, and ductility.

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$$18\%\mathrm{CW} = \frac{\pi\left(\frac{d'_0}{2}\right)^2 - \pi\left(\frac{8.9 \text{ mm}}{2}\right)^2}{\pi\left(\frac{d'_0}{2}\right)^2} \text{ x } 100$$

And, solving for d'_0, yields

$$d'_0 = \frac{8.9 \text{ mm}}{\sqrt{1 - \frac{18\%\mathrm{CW}}{100}}} = 9.83 \text{ mm (0.387 in.)}$$

7.D6 Let us first calculate the percent cold work and attendant yield strength and ductility if the drawing is carried out without interruption. From Equation 7.8

$$\%\text{CW} = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \text{ x } 100$$

$$= \frac{\pi\left(\frac{10.2 \text{ mm}}{2}\right)^2 - \pi\left(\frac{7.6 \text{ mm}}{2}\right)^2}{\pi\left(\frac{10.2 \text{ mm}}{2}\right)^2} \text{ x } 100 = 44.5\%\text{CW}$$

At 44.5%CW, the brass will have a yield strength on the order of 420 MPa (61,000 psi), Figure 7.19(a), which is adequate; however, the ductility will be about 5%EL, Figure 7.19(c), which is insufficient.

Instead of performing the drawing in a single operation, let us initially draw some fraction of the total deformation, then anneal to recrystallize, and, finally, cold work the material a second time in order to achieve the final diameter, yield strength, and ductility.

Reference to Figure 7.19(a) indicates that 27.5%CW is necessary to give a yield strength of 380 MPa. Similarly, a maximum of 27.5%CW is possible for 15%EL [Figure 7.19(c)]. Thus, to achieve both the specified yield strength and ductility, the brass must be deformed to 27.5 %CW. If the final diameter after the first drawing is d'_0, then, using Equation 7.8

$$27.5\%\text{CW} = \frac{\pi\left(\frac{d'_0}{2}\right)^2 - \pi\left(\frac{7.6 \text{ mm}}{2}\right)^2}{\pi\left(\frac{d'_0}{2}\right)^2} \text{ x } 100$$

And, solving for d'_0 yields

$$d'_0 = \frac{7.6 \text{ mm}}{\sqrt{1 - \frac{27.5\%\text{CW}}{100}}} = 8.93 \text{ mm (0.351 in.)}$$

7.D7 This problem calls for us to cold work some brass stock that has been previously cold worked in order to achieve minimum tensile strength and ductility values of 450 MPa (65,000 psi) and 13%EL, respectively, while the final diameter must be 12.7 mm (0.50 in.). Furthermore, the material may not be deformed beyond 65%CW. Let us start by deciding what percent coldwork is necessary for the minimum tensile strength and ductility values, assuming that a recrystallization heat treatment is possible. From Figure 7.19(b), at least 27%CW is required for a tensile strength of 450 MPa. Furthermore, according to Figure 7.19(c), 13%EL corresponds a maximum of 30%CW. Let us take the average of these two values (i.e., 28.5%CW), and determine what previous specimen diameter is required to yield a final diameter of 12.7 mm. For cylindrical specimens, Equation 7.8 takes the form

$$\%\text{CW} = \frac{\pi\left(\dfrac{d_0}{2}\right)^2 - \pi\left(\dfrac{d_d}{2}\right)^2}{\pi\left(\dfrac{d_0}{2}\right)^2} \text{ x } 100$$

Solving for the original diameter d_0 yields

$$d_0 = \frac{d_d}{\sqrt{1 - \dfrac{\%\text{CW}}{100}}} = \frac{12.7 \text{ mm}}{\sqrt{1 - 0.285}} = 15.0 \text{ mm} \quad (0.591 \text{ in.})$$

Now, let us determine its undeformed diameter realizing that a diameter of 19.0 mm corresponds to 35%CW. Again solving for d_0 using the above equation and assuming d_d = 19.0 mm yields

$$d_0 = \frac{d_d}{\sqrt{1 - \dfrac{\%\text{CW}}{100}}} = \frac{19.0 \text{ mm}}{\sqrt{1 - 0.35}} = 23.6 \text{ mm} \quad (0.930 \text{ in.})$$

At this point let us see if it is possible to deform the material from 23.6 mm to 15.0 mm without exceeding the 65%CW limit. Again employing Equation 7.8

$$\%\text{CW} = \frac{\pi\left(\dfrac{23.6 \text{ mm}}{2}\right)^2 - \pi\left(\dfrac{15.0 \text{ mm}}{2}\right)^2}{\pi\left(\dfrac{23.6 \text{ mm}}{2}\right)^2} \text{ x } 100 = 59.6\%\text{CW}$$

In summary, the procedure which can be used to produce the desired material would be as follows: cold work the as-received stock to 15.0 mm (0.591 in.), heat treat it to achieve complete recrystallization, and then cold work the material again to 12.7 mm (0.50 in.), which will give the desired tensile strength and ductility.

CHAPTER 8

FAILURE

PROBLEM SOLUTIONS

Principles of Fracture Mechanics

8.1 This problem asks that we compute the magnitude of the maximum stress that exists at the tip of an internal crack. Equation 8.1 is employed to solve this problem, as

$$\sigma_m = 2\sigma_0 \left(\frac{a}{\rho_t}\right)^{1/2}$$

$$= (2)(140\ \text{MPa}) \left[\frac{\dfrac{3.8\ \text{x}\ 10^{-2}\ \text{mm}}{2}}{1.9\ \text{x}\ 10^{-4}\ \text{mm}}\right]^{1/2} = 2800\ \text{MPa} \quad (400{,}000\ \text{psi})$$

8.2 In order to estimate the theoretical fracture strength of this material it is necessary to calculate σ_m using Equation 8.1 given that σ_0 = 1035 MPa, *a* = 0.5 mm, and ρ_t = 5 x 10^{-3} mm. Thus,

$$\sigma_m = 2\sigma_0 \left(\frac{a}{\rho_t}\right)^{1/2}$$

$$= (2)(1035 \text{ MPa}) \left[\frac{0.5 \text{ mm}}{5 \text{ x } 10^{-3} \text{ mm}}\right]^{1/2} = 2.07 \text{ x } 10^4 \text{ MPa} = 207 \text{ GPa} \quad (3 \text{ x } 10^6 \text{ psi})$$

8.3 We may determine the critical stress required for the propagation of an internal crack in aluminum oxide using Equation 8.3; taking the value of 393 GPa (Table 12.5) as the modulus of elasticity, we get

$$\sigma_c = \left[\frac{2E\gamma_s}{\pi a}\right]^{1/2}$$

$$= \left[\frac{(2)\left(393 \ \text{x} \ 10^9 \ \text{N/m}^2\right)(0.90 \ \ \text{N/m})}{(\pi)\left(\dfrac{0.4 \ \text{x} \ 10^{-3} \ \text{m}}{2}\right)}\right]^{1/2} = 33.6 \ \text{x}10^6 \ \text{N/m}^2 = 33.6 \ \ \text{MPa}$$

8.4 The maximum allowable surface crack length for MgO may be determined using Equation 8.3; taking 225 GPa as the modulus of elasticity (Table 12.5), and solving for *a*, leads to

$$a = \frac{2E\gamma_s}{\pi\sigma_c^2} = \frac{(2)\left(225 \text{ x } 10^9 \text{ N/m}^2\right)(1.0 \text{ N/m})}{(\pi)\left(13.5 \text{ x } 10^6 \text{ N/m}^2\right)^2}$$

$$= 7.9 \text{ x } 10^{-4} \text{ m} = 0.79 \text{ mm (0.031 in.)}$$

8.5 This problem asks us to determine whether or not the 4340 steel alloy specimen will fracture when exposed to a stress of 1030 MPa, given the values of K_{Ic}, Y, and the largest value of a in the material. This requires that we solve for σ_c from Equation 8.6. Thus

$$\sigma_c = \frac{K_{Ic}}{Y\sqrt{\pi a}} = \frac{54.8 \text{ MPa}\sqrt{\text{m}}}{(1.0)\sqrt{(\pi)\left(0.5 \text{ x } 10^{-3} \text{ m}\right)}} = 1380 \text{ MPa} \quad (199{,}500 \text{ psi})$$

Therefore, fracture will *not* occur because this specimen will tolerate a stress of 1380 MPa (199,500 psi) before fracture, which is greater than the applied stress of 1030 MPa (150,000 psi).

8.6 We are asked to determine if an aircraft component will fracture for a given fracture toughness $\left(40\ \text{MPa}\sqrt{\text{m}}\right)$, stress level (260 MPa), and maximum internal crack length (6.0 mm), given that fracture occurs for the same component using the same alloy for another stress level and internal crack length. It first becomes necessary to solve for the parameter *Y*, using Equation 8.5, for the conditions under which fracture occurred (i.e., σ = 300 MPa and a = 4.0 mm). Therefore,

$$Y = \frac{K_{Ic}}{\sigma\sqrt{\pi a}} = \frac{40\ \text{MPa}\sqrt{\text{m}}}{(300\ \text{MPa})\sqrt{(\pi)\left(\dfrac{4\ \text{x}\ 10^{-3}\ \text{m}}{2}\right)}} = 1.68$$

Now we will solve for the product $Y\sigma\sqrt{\pi a}$ for the other set of conditions, so as to ascertain whether or not this value is greater than the K_{Ic} for the alloy. Thus,

$$Y\sigma\sqrt{\pi a} = (1.68)(260\ \text{MPa})\sqrt{(\pi)\left(\frac{6\ \text{x}\ 10^{-3}\ \text{m}}{2}\right)}$$

$$= 42.4\ \text{MPa}\sqrt{\text{m}} \qquad (39\ \text{ksi}\sqrt{\text{in.}})$$

Therefore, fracture *will* occur since this value $\left(42.4\ \text{MPa}\sqrt{\text{m}}\right)$ is greater than the K_{Ic} of the material, $40\ \text{MPa}\sqrt{\text{m}}$.

8.7 This problem asks us to determine the stress level at which an a wing component on an aircraft will fracture for a given fracture toughness $\left(26 \text{ MPa}\sqrt{\text{m}}\right)$ and maximum internal crack length (6.0 mm), given that fracture occurs for the same component using the same alloy at one stress level (112 MPa) and another internal crack length (8.6 mm). It first becomes necessary to solve for the parameter *Y* for the conditions under which fracture occurred using Equation 8.5. Therefore,

$$Y = \frac{K_{Ic}}{\sigma\sqrt{\pi a}} = \frac{26 \text{ MPa}\sqrt{\text{m}}}{(112 \text{ MPa})\sqrt{(\pi)\left(\dfrac{8.6 \text{ x } 10^{-3} \text{ m}}{2}\right)}} = 2.0$$

Now we will solve for σ_c using Equation 8.6 as

$$\sigma_c = \frac{K_{Ic}}{Y\sqrt{\pi a}} = \frac{26 \text{ MPa}\sqrt{\text{m}}}{(2.0)\sqrt{(\pi)\left(\dfrac{6 \text{ x } 10^{-3} \text{ m}}{2}\right)}} = 134 \text{ MPa} \quad (19{,}300 \text{ psi})$$

8.8 For this problem, we are given values of K_{Ic} $\left(82.4\ \text{MPa}\sqrt{\text{m}}\right)$, σ (345 MPa), and Y (1.0) for a large plate and are asked to determine the minimum length of a surface crack that will lead to fracture. All we need do is to solve for a_c using Equation 8.7; therefore

$$a_c = \frac{1}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2 = \frac{1}{\pi}\left[\frac{82.4\ \text{MPa}\sqrt{\text{m}}}{(1.0)(345\ \text{MPa})}\right]^2 = 0.0182\ \text{m} = 18.2\ \text{mm} \quad (0.72\ \text{in.})$$

8.9 This problem asks us to calculate the maximum internal crack length allowable for the Ti-6Al-4V titanium alloy in Table 8.1 given that it is loaded to a stress level equal to one-half of its yield strength. For this alloy, $K_{Ic} = 55\ \text{MPa}\sqrt{\text{m}}\ \left(50\ \text{ksi}\sqrt{\text{in.}}\right)$; also, $\sigma = \sigma_y/2$ = (910 MPa)/2 = 455 MPa (66,000 psi). Now solving for $2a_c$ using Equation 8.7 yields

$$2a_c = \frac{2}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2 = \frac{2}{\pi}\left[\frac{55\ \text{MPa}\sqrt{\text{m}}}{(1.5)(455\ \text{MPa})}\right]^2 = 0.0041\ \text{m} = 4.1\ \text{mm} \quad (0.16\ \text{in.})$$

8.10 This problem asks that we determine whether or not a critical flaw in a wide plate is subject to detection given the limit of the flaw detection apparatus (3.0 mm), the value of K_{Ic} $\left(98.9 \text{ MPa}\sqrt{\text{m}}\right)$, the design stress ($\sigma_y/2$ in which σ_y = 860 MPa), and Y = 1.0. We first need to compute the value of a_c using Equation 8.7; thus

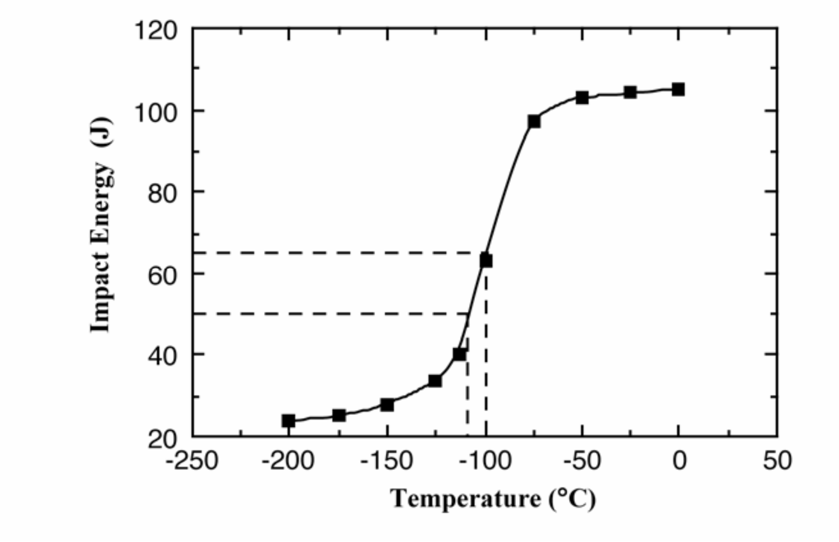
$$a_c = \frac{1}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2 = \frac{1}{\pi}\left[\frac{98.9 \text{ MPa}\sqrt{\text{m}}}{(1.0)\left(\dfrac{860 \text{ MPa}}{2}\right)}\right]^2 = 0.0168 \text{ m} = 16.8 \text{ mm} \quad (0.66 \text{ in.})$$

Therefore, the critical flaw is subject to detection since this value of a_c (16.8 mm) is greater than the 3.0 mm resolution limit.

8.11 The student should do this problem on his/her own.

Impact Fracture Testing

8.12 (a) The plot of impact energy versus temperature is shown below.



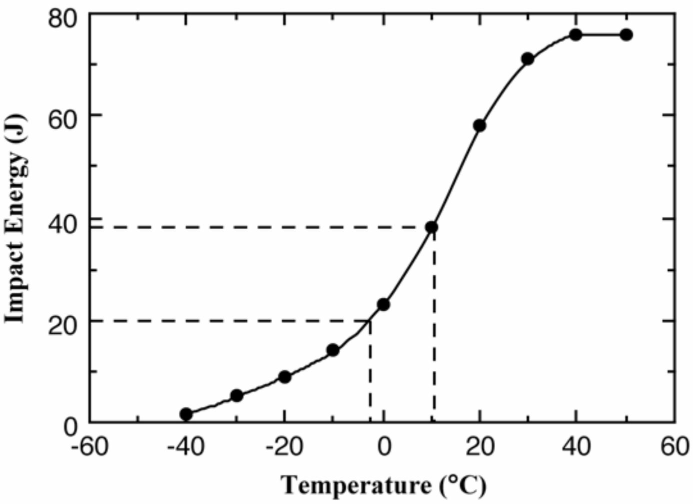
(b) The average of the maximum and minimum impact energies from the data is

$$\text{Average} = \frac{105\ \text{J} + 24\ \text{J}}{2} = 64.5\ \text{J}$$

As indicated on the plot by the one set of dashed lines, the ductile-to-brittle transition temperature according to this criterion is about –100°C.

(c) Also, as noted on the plot by the other set of dashed lines, the ductile-to-brittle transition temperature for an impact energy of 50 J is about –110°C.

8.13 The plot of impact energy versus temperature is shown below.



(b) The average of the maximum and minimum impact energies from the data is

$$\text{Average} = \frac{76 \text{ J} + 1.5 \text{ J}}{2} = 38.8 \text{ J}$$

As indicated on the plot by the one set of dashed lines, the ductile-to-brittle transition temperature according to this criterion is about 10°C.

(c) Also, as noted on the plot by the other set of dashed lines, the ductile-to-brittle transition temperature for an impact energy of 20 J is about –2°C.

Cyclic Stresses (Fatigue)

The *S-N* Curve

8.14 (a) Given the values of σ_m (70 MPa) and σ_a (210 MPa) we are asked to compute $\sigma_{\max}$ and $\sigma_{\min}$. From Equation 8.14

$$\sigma_m = \frac{\sigma_{\max} + \sigma_{\min}}{2} = 70 \text{ MPa}$$

Or,

$$\sigma_{\max} + \sigma_{\min} = 140 \text{ MPa}$$

Furthermore, utilization of Equation 8.16 yields

$$\sigma_a = \frac{\sigma_{\max} - \sigma_{\min}}{2} = 210 \text{ MPa}$$

Or,

$$\sigma_{\max} - \sigma_{\min} = 420 \text{ MPa}$$

Simultaneously solving these two expressions leads to

$$\sigma_{\max} = 280 \text{ MPa} \quad (40{,}000 \text{ psi})$$
$$\sigma_{\min} = -140 \text{ MPa} \quad (-20{,}000 \text{ psi})$$

(b) Using Equation 8.17 the stress ratio *R* is determined as follows:

$$R = \frac{\sigma_{\min}}{\sigma_{\max}} = \frac{-140 \text{ MPa}}{280 \text{ MPa}} = -0.50$$

(c) The magnitude of the stress range σ_r is determined using Equation 8.15 as

$$\sigma_r = \sigma_{\max} - \sigma_{\min} = 280 \text{ MPa} - (-140 \text{ MPa}) = 420 \text{ MPa} \quad (60{,}000 \text{ psi})$$

8.15 This problem asks that we determine the minimum allowable bar diameter to ensure that fatigue failure will not occur for a 1045 steel that is subjected to cyclic loading for a load amplitude of 66,700 N (15,000 $\mathrm{lb_f}$). From Figure 8.34, the fatigue limit stress amplitude for this alloy is 310 MPa (45,000 psi). Stress is defined in Equation 6.1 as $\sigma = \frac{F}{A_0}$. For a cylindrical bar

$$A_0 = \pi\left(\frac{d_0}{2}\right)^2$$

Substitution for A_0 into the Equation 6.1 leads to

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{4F}{\pi d_0^2}$$

We now solve for d_0, taking stress as the fatigue limit divided by the factor of safety. Thus

$$d_0 = \sqrt{\frac{4F}{\pi\left(\frac{\sigma}{N}\right)}}$$

$$= \sqrt{\frac{(4)(66{,}700\ \mathrm{N})}{(\pi)\left(\frac{310\ \times 10^6\ \mathrm{N/m^2}}{2}\right)}} = 23.4\ \times 10^{-3}\ \mathrm{m} = 23.4\ \mathrm{mm}\quad (0.92\ \mathrm{in.})$$

8.16 We are asked to determine the fatigue life for a cylindrical 2014-T6 aluminum rod given its diameter (6.4 mm) and the maximum tensile and compressive loads (+5340 N and –5340 N, respectively). The first thing that is necessary is to calculate values of σ_{max} and σ_{min} using Equation 6.1. Thus

$$\sigma_{\text{max}} = \frac{F_{\text{max}}}{A_0} = \frac{F_{\text{max}}}{\pi \left(\frac{d_0}{2}\right)^2}$$

$$= \frac{5340 \text{ N}}{(\pi)\left(\frac{6.4 \text{ x } 10^{-3} \text{ m}}{2}\right)^2} = 166 \text{ x } 10^6 \text{ N/m}^2 = 166 \text{ MPa} \quad (24{,}400 \text{ psi})$$

$$\sigma_{\text{min}} = \frac{F_{\text{min}}}{\pi \left(\frac{d_0}{2}\right)^2}$$

$$= \frac{-5340 \text{ N}}{(\pi)\left(\frac{6.4 \text{ x } 10^{-3} \text{ m}}{2}\right)^2} = -166 \text{ x } 10^6 \text{ N/m}^2 = -166 \text{ MPa} \quad (-24{,}400 \text{ psi})$$

Now it becomes necessary to compute the stress amplitude using Equation 8.16 as

$$\sigma_a = \frac{\sigma_{\text{max}} - \sigma_{\text{min}}}{2} = \frac{166 \text{ MPa} - (-166 \text{ MPa})}{2} = 166 \text{ MPa} \quad (24{,}400 \text{ psi})$$

From Figure 8.34, for the 2014-T6 aluminum, the number of cycles to failure at this stress amplitude is about 1 x 10^7 cycles.

8.17 This problem asks that we compute the maximum and minimum loads to which a 15.2 mm (0.60 in.) diameter 2014-T6 aluminum alloy specimen may be subjected in order to yield a fatigue life of 1.0 x 10^8 cycles; Figure 8.34 is to be used assuming that data were taken for a mean stress of 35 MPa (5,000 psi). Upon consultation of Figure 8.34, a fatigue life of 1.0 x 10^8 cycles corresponds to a stress amplitude of 140 MPa (20,000 psi). Or, from Equation 8.16

$$\sigma_{\text{max}} - \sigma_{\text{min}} = 2\sigma_a = (2)(140\ \text{MPa}) = 280\ \text{MPa}\ \ (40{,}000\ \text{psi})$$

Since σ_m = 35 MPa, then from Equation 8.14

$$\sigma_{\text{max}} + \sigma_{\text{min}} = 2\sigma_m = (2)(35\ \text{MPa}) = 70\ \text{MPa}\ \ (10{,}000\ \text{psi})$$

Simultaneous solution of these two expressions for σ_{max} and σ_{min} yields

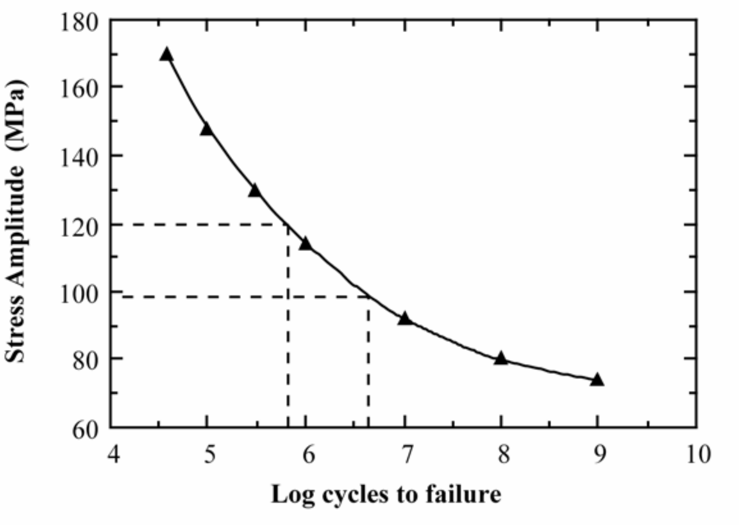
$$\sigma_{\text{max}} = +175\ \text{MPa}\ \ (+25{,}000\ \text{psi})$$
$$\sigma_{\text{min}} = -105\ \text{MPa}\ \ (-15{,}000\ \text{psi})$$

Now, inasmuch as $\sigma = \dfrac{F}{A_0}$ (Equation 6.1), and $A_0 = \pi\left(\dfrac{d_0}{2}\right)^2$ then

$$F_{\text{max}} = \frac{\sigma_{\text{max}}\pi d_0^2}{4} = \frac{(175\ \text{x}\ 10^6\ \text{N/m}^2)\,(\pi)(15.2\ \text{x}\ 10^{-3}\ \text{m})^2}{4} = 31{,}750\ \text{N}\ \ \ (7070\ \ \text{lb}_\text{f})$$

$$F_{\text{min}} = \frac{\sigma_{\text{min}}\pi d_0^2}{4} = \frac{(-105\ \text{x}\ 10^6\ \text{N/m}^2)\,(\pi)(15.2\ \text{x}\ 10^{-3}\ \text{m})^2}{4} = -19{,}000\ \text{N}\ \ \ (-4240\ \ \text{lb}_\text{f})$$

8.18 (a) The fatigue data for this alloy are plotted below.



(b) As indicated by one set of dashed lines on the plot, the fatigue strength at 4 x 10^6 cycles [log (4 x 10^6) = 6.6] is about 100 MPa.

(c) As noted by the other set of dashed lines, the fatigue life for 120 MPa is about 6 x 10^5 cycles (i.e., the log of the lifetime is about 5.8).

8.19 We are asked to compute the maximum torsional stress amplitude possible at each of several fatigue lifetimes for the brass alloy the fatigue behavior of which is given in Problem 8.18. For each lifetime, first compute the number of cycles, and then read the corresponding fatigue strength from the above plot.

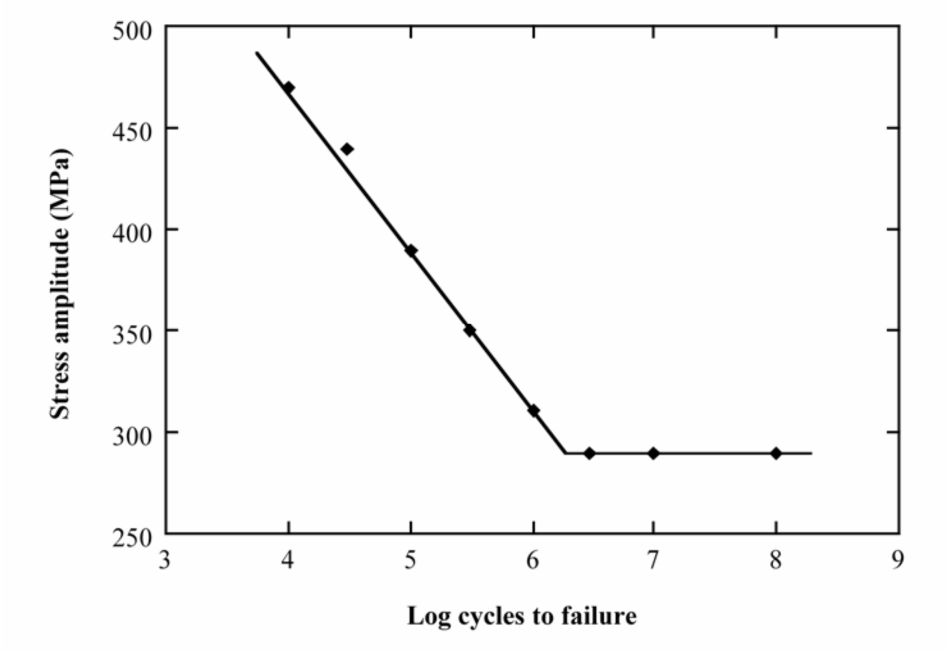
(a) Fatigue lifetime = (1 yr)(365 days/yr)(24 h/day)(60 min/h)(1800 cycles/min) = 9.5 x 10^8 cycles. The stress amplitude corresponding to this lifetime is about 74 MPa.

(b) Fatigue lifetime = (30 days)(24 h/day)(60 min/h)(1800 cycles/min) = 7.8 x 10^7 cycles. The stress amplitude corresponding to this lifetime is about 80 MPa.

(c) Fatigue lifetime = (24 h)(60 min/h)(1800 cycles/min) = 2.6 x 10^6 cycles. The stress amplitude corresponding to this lifetime is about 103 MPa.

(d) Fatigue lifetime = (60 min/h)(1800 cycles/min) = 108,000 cycles. The stress amplitude corresponding to this lifetime is about 145 MPa.

8.20 (a) The fatigue data for this alloy are plotted below.



(b) The fatigue limit is the stress level at which the curve becomes horizontal, which is 290 MPa (42,200 psi).

(c) From the plot, the fatigue lifetimes at a stress amplitude of 415 MPa (60,000 psi) is about 50,000 cycles (log N = 4.7). At 275 MPa (40,000 psi) the fatigue lifetime is essentially an infinite number of cycles since this stress amplitude is below the fatigue limit.

(d) Also from the plot, the fatigue strengths at 2 x 10^4 cycles (log N = 4.30) and 6 x 10^5 cycles (log N = 5.78) are 440 MPa (64,000 psi) and 325 MPa (47,500 psi), respectively.

8.21 This problem asks that we determine the maximum lifetimes of continuous driving that are possible at an average rotational velocity of 600 rpm for the alloy the fatigue data of which is provided in Problem 8.20 and at a variety of stress levels.

(a) For a stress level of 450 MPa (65,000 psi), the fatigue lifetime is approximately 18,000 cycles. This translates into (1.8 x 10^4 cycles)(1 min/600 cycles) = 30 min.

(b) For a stress level of 380 MPa (55,000 psi), the fatigue lifetime is approximately 1.5 x 10^5 cycles. This translates into (1.5 x 10^5 cycles)(1 min/600 cycles) = 250 min = 4.2 h.

(c) For a stress level of 310 MPa (45,000 psi), the fatigue lifetime is approximately 1 x 10^6 cycles. This translates into (1 x 10^6 cycles)(1 min/600 cycles) = 1667 min = 27.8 h.

(d) For a stress level of 275 MPa (40,000 psi), the fatigue lifetime is essentially infinite since we are below the fatigue limit.

8.22 For this problem we are given, for three identical fatigue specimens of the same material, $\sigma_{\max}$ and $\sigma_{\min}$ data, and are asked to rank the lifetimes from the longest to the shortest. In order to do this it is necessary to compute both the mean stress and stress amplitude for each specimen. Since from Equation 8.14

$$\sigma_m = \frac{\sigma_{\max} + \sigma_{\min}}{2}$$

$$\sigma_m(\mathrm{A}) = \frac{450 \text{ MPa} + (-150 \text{ MPa})}{2} = 150 \text{ MPa}$$

$$\sigma_m(\mathrm{B}) = \frac{300 \text{ MPa} + (-300 \text{ MPa})}{2} = 0 \text{ MPa}$$

$$\sigma_m(\mathrm{C}) = \frac{500 \text{ MPa} + (-200 \text{ MPa})}{2} = 150 \text{ MPa}$$

Furthermore, using Equation 8.16

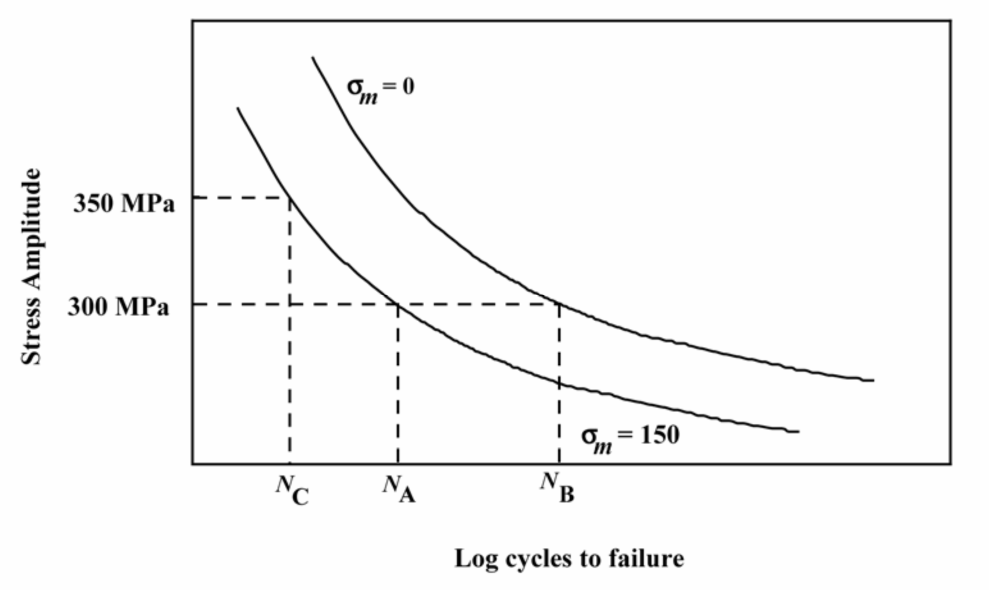
$$\sigma_a = \frac{\sigma_{\max} - \sigma_{\min}}{2}$$

$$\sigma_a(\mathrm{A}) = \frac{450 \text{ MPa} - (-150 \text{ MPa})}{2} = 300 \text{ MPa}$$

$$\sigma_a(\mathrm{B}) = \frac{300 \text{ MPa} - (-300 \text{ MPa})}{2} = 300 \text{ MPa}$$

$$\sigma_a(\mathrm{C}) = \frac{500 \text{ MPa} - (-200 \text{ MPa})}{2} = 350 \text{ MPa}$$

On the basis of these results, the fatigue lifetime for specimen B will be greater than specimen A which in turn will be greater than specimen C. This conclusion is based upon the following *S-N* plot on which curves are plotted for two σ_m values.


$\sigma_m = 0$
$\sigma_m = 150$
350 MPa
300 MPa
Stress Amplitude
N_C
N_A
N_B
Log cycles to failure

8.23 Five factors that lead to scatter in fatigue life data are (1) specimen fabrication and surface preparation, (2) metallurgical variables, (3) specimen alignment in the test apparatus, (4) variation in mean stress, and (5) variation in test cycle frequency.

Crack Initiation and Propagation

Factors That Affect Fatigue Life

8.24 (a) With regard to size, beachmarks are normally of macroscopic dimensions and may be observed with the naked eye; fatigue striations are of microscopic size and it is necessary to observe them using electron microscopy.

(b) With regard to origin, beachmarks result from interruptions in the stress cycles; each fatigue striation is corresponds to the advance of a fatigue crack during a single load cycle.

8.25 Four measures that may be taken to increase the fatigue resistance of a metal alloy are:

(1) Polish the surface to remove stress amplification sites.

(2) Reduce the number of internal defects (pores, etc.) by means of altering processing and fabrication techniques.

(3) Modify the design to eliminate notches and sudden contour changes.

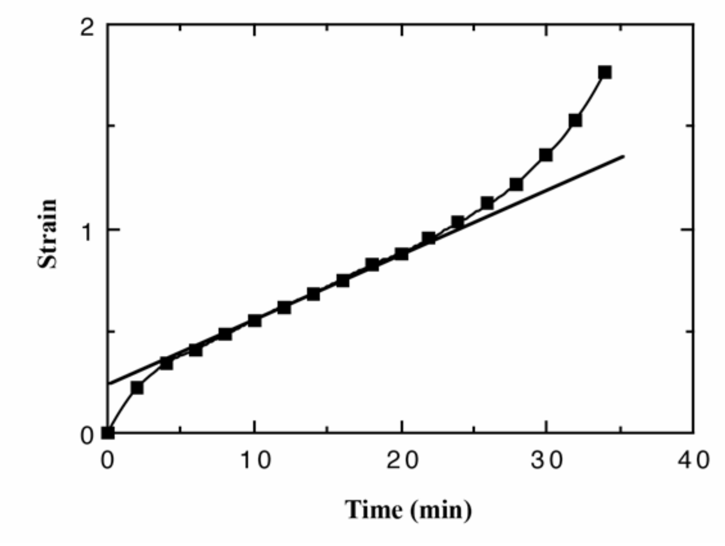
(4) Harden the outer surface of the structure by case hardening (carburizing, nitriding) or shot peening.

Generalized Creep Behavior

8.26 Creep becomes important at about $0.4T_m$, T_m being the absolute melting temperature of the metal. (The melting temperatures in degrees Celsius are found inside the front cover of the book.)

For Sn, $0.4T_m = (0.4)(232 + 273) = 202$ K or -71°C (-96°F)
For Mo, $0.4T_m = (0.4)(2617 + 273) = 1156$ K or 883°C (1621°F)
For Fe, $0.4T_m = (0.4)(1538 + 273) = 724$ K or 451°C (845°F)
For Au, $0.4T_m = (0.4)(1064 + 273) = 535$ K or 262°C (504°F)
For Zn, $0.4T_m = (0.4)(420 + 273) = 277$ K or 4°C (39°F)
For Cr, $0.4T_m = (0.4)(1875 + 273) = 859$ K or 586°C (1087°F)

8.27 These creep data are plotted below



The steady-state creep rate ($\Delta\varepsilon/\Delta t$) is the slope of the linear region (i.e., the straight line that has been superimposed on the curve) as

$$\frac{\Delta\varepsilon}{\Delta t} = \frac{1.20 - 0.25}{30 \text{ min} - 0 \text{ min}} = 3.2 \times 10^{-2} \text{ min}^{-1}$$

Stress and Temperature Effects

8.28 This problem asks that we determine the total elongation of a low carbon-nickel alloy that is exposed to a tensile stress of 70 MPa (10,000 psi) at 427°C for 10,000 h; the instantaneous and primary creep elongations are 1.3 mm (0.05 in.).

From the 427°C line in Figure 8.31, the steady state creep rate $\dot{\varepsilon}_s$ is about 4.7 x 10^{-7} h^{-1} at 70 MPa. The steady state creep strain, ε_s, therefore, is just the product of $\dot{\varepsilon}_s$ and time as

$$\varepsilon_s = \dot{\varepsilon}_s \text{ x (time)}$$

$$= (4.7 \text{ x } 10^{-7} \text{ h}^{-1})(10,000 \text{ h}) = 4.7 \text{ x} 10^{-3}$$

Strain and elongation are related as in Equation 6.2; solving for the steady state elongation, Δl_s, leads to

$$\Delta l_s = l_0 \varepsilon_s = (1015 \text{ mm})(4.7 \text{ x } 10^{-3}) = 4.8 \text{ mm} \quad (0.19 \text{ in.})$$

Finally, the total elongation is just the sum of this Δl_s and the total of both instantaneous and primary creep elongations [i.e., 1.3 mm (0.05 in.)]. Therefore, the total elongation is 4.8 mm + 1.3 mm = 6.1 mm (0.24 in.).

8.29 We are asked to determine the tensile load necessary to elongate a 635 mm long low carbon-nickel alloy specimen 6.44 mm after 5,000 h at 538°C. It is first necessary to calculate the steady state creep rate so that we may utilize Figure 8.31 in order to determine the tensile stress. The steady state elongation, Δl_s, is just the difference between the total elongation and the sum of the instantaneous and primary creep elongations; that is,

$$\Delta l_s = 6.44 \text{ mm} - 1.8 \text{ mm} = 4.64 \text{ mm} \quad (0.18 \text{ in.})$$

Now the steady state creep rate, $\dot{\varepsilon}_s$ is just

$$\dot{\varepsilon}_s = \frac{\Delta \varepsilon}{\Delta t} = \frac{\dfrac{\Delta l_s}{l_0}}{\Delta t} = \frac{\dfrac{4.64 \text{ mm}}{635 \text{ mm}}}{5{,}000 \text{ h}}$$

$$= 1.46 \times 10^{-6} \text{ h}^{-1}$$

Employing the 538°C line in Figure 8.31, a steady state creep rate of 1.46×10^{-6} h^{-1} corresponds to a stress σ of about 40 MPa (5,800 psi) [since $\log (1.46 \times 10^{-6}) = -5.836$]. From this we may compute the tensile load using Equation 6.1 as

$$F = \sigma A_0 = \sigma \pi \left(\frac{d_0}{2}\right)^2$$

$$= \left(40 \times 10^6 \text{ N/m}^2\right)(\pi)\left(\frac{19.0 \times 10^{-3} \text{ m}}{2}\right)^2 = 11{,}300 \text{ N} \quad (2560 \text{ lb}_\text{f})$$

8.30 This problem asks us to calculate the rupture lifetime of a component fabricated from a low carbon-nickel alloy exposed to a tensile stress of 31 MPa at 649°C. All that we need do is read from the 649°C line in Figure 8.30 the rupture lifetime at 31 MPa; this value is about 10,000 h.

8.31 We are asked in this problem to determine the maximum load that may be applied to a cylindrical low carbon-nickel alloy component that must survive 10,000 h at 538°C. From Figure 8.30, the stress corresponding to 10^4 h is about 70 MPa (10,000 psi). Since stress is defined in Equation 6.1 as $\sigma = F/A_0$, and for a cylindrical specimen, $A_0 = \pi\left(\frac{d_0}{2}\right)^2$, then

$$F = \sigma A_0 = \sigma\pi\left(\frac{d_0}{2}\right)^2$$

$$= \left(70 \text{ x } 10^6 \text{ N/m}^2\right)(\pi)\left(\frac{19.1 \text{ x } 10^{-3} \text{ m}}{2}\right)^2 = 20{,}000 \text{ N} \quad (4420 \text{ lb}_f)$$

8.32 The slope of the line from a log $\dot{\varepsilon}_s$ versus log σ plot yields the value of *n* in Equation 8.19; that is

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma}$$

We are asked to determine the values of *n* for the creep data at the three temperatures in Figure 8.31. This is accomplished by taking ratios of the differences between two log $\dot{\varepsilon}_s$ and log σ values. (Note: Figure 8.31 plots log σ versus log $\dot{\varepsilon}_s$; therefore, values of *n* are equal to the reciprocals of the slopes of the straight-line segments.)

Thus for 427°C

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log \left(10^{-6}\right) - \log \left(10^{-7}\right)}{\log\ (82\ \text{MPa}) - \log\ (54\ \text{MPa})} = 5.5$$

While for 538°C

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log \left(10^{-5}\right) - \log \left(10^{-7}\right)}{\log\ (59\ \text{MPa}) - \log\ (22\ \text{MPa})} = 4.7$$

And at 649°C

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log \left(10^{-5}\right) - \log \left(10^{-7}\right)}{\log\ (15\ \text{MPa}) - \log\ (8.3\ \text{MPa})} = 7.8$$

8.33 (a) We are asked to estimate the activation energy for creep for the low carbon-nickel alloy having the steady-state creep behavior shown in Figure 8.31, using data taken at σ = 55 MPa (8000 psi) and temperatures of 427°C and 538°C. Since σ is a constant, Equation 8.20 takes the form

$$\dot{\varepsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right) = K_2^{'} \exp\left(-\frac{Q_c}{RT}\right)$$

where $K_2^{'}$ is now a constant. (Note: the exponent n has about the same value at these two temperatures per Problem 8.32.) Taking natural logarithms of the above expression

$$\ln \dot{\varepsilon}_s = \ln K_2^{'} - \frac{Q_c}{RT}$$

For the case in which we have creep data at two temperatures (denoted as T_1 and T_2) and their corresponding steady-state creep rates ($\dot{\varepsilon}_{s_1}$ and $\dot{\varepsilon}_{s_2}$), it is possible to set up two simultaneous equations of the form as above, with two unknowns, namely $K_2^{'}$ and Q_c. Solving for Q_c yields

$$Q_c = -\frac{R\left(\ln \dot{\varepsilon}_{s_1} - \ln \dot{\varepsilon}_{s_2}\right)}{\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

Let us choose T_1 as 427°C (700 K) and T_2 as 538°C (811 K); then from Figure 8.31, at σ = 55 MPa, $\dot{\varepsilon}_{s_1} = 10^{-7}$ h^{-1} and $\dot{\varepsilon}_{s_2} = 8 \times 10^{-6}$ h^{-1}. Substitution of these values into the above equation leads to

$$Q_c = -\frac{(8.31\ \text{J/mol-K})\left[\ln\left(10^{-7}\right) - \ln\left(8 \times 10^{-6}\right)\right]}{\left[\frac{1}{700\ \text{K}} - \frac{1}{811\ \text{K}}\right]}$$

$$= 186{,}200\ \text{J/mol}$$

(b) We are now asked to estimate $\dot{\varepsilon}_s$ at 649°C (922 K). It is first necessary to determine the value of $K_2^{'}$, which is accomplished using the first expression above, the value of Q_c, and one value each of $\dot{\varepsilon}_s$ and T (say $\dot{\varepsilon}_{s_1}$ and T_1). Thus,

$$K_2' = \dot{\varepsilon}_{s_1} \exp\left(\frac{Q_c}{RT_1}\right)$$

$$= \left(10^{-7}\ \text{h}^{-1}\right) \exp\left[\frac{186{,}200\ \text{J/mol}}{(8.31\ \text{J/mol-K})(700\ \text{K})}\right] = 8.0\ \text{x}\ 10^{6}\ \text{h}^{-1}$$

Now it is possible to calculate $\dot{\varepsilon}_s$ at 649°C (922 K) as follows:

$$\dot{\varepsilon}_s = K_2' \exp\left(-\frac{Q_c}{RT}\right)$$

$$= \left(8.0\ \text{x}\ 10^{-6}\ \text{h}^{-1}\right) \exp\left[\frac{186{,}200\ \text{J/mol}}{(8.31\ \text{J/mol-K})(922\ \text{K})}\right]$$

$$= 2.23\ \text{x}\ 10^{-4}\ \text{h}^{-1}$$

8.34 This problem gives $\dot{\varepsilon}_s$ values at two different stress levels and 200°C, and the activation energy for creep, and asks that we determine the steady-state creep rate at 250°C and 48 MPa (7000 psi).

Taking natural logarithms of both sides of Equation 8.20 yields

$$\ln \dot{\varepsilon}_s = \ln K_2 + n \ln \sigma - \frac{Q_c}{RT}$$

With the given data there are two unknowns in this equation--namely K_2 and n. Using the data provided in the problem statement we can set up two independent equations as follows:

$$\ln\left(2.5 \text{ x } 10^{-3} \text{ h}^{-1}\right) = \ln K_2 + n \ln(55 \text{ MPa}) - \frac{140{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(473 \text{ K})}$$

$$\ln\left(2.4 \text{ x } 10^{-2} \text{ h}^{-1}\right) = \ln K_2 + n \ln(69 \text{ MPa}) - \frac{140{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(473 \text{ K})}$$

Now, solving simultaneously for n and K_2 leads to $n = 9.97$ and $K_2 = 3.27 \text{ x } 10^{-5} \text{ h}^{-1}$. Thus it is now possible to solve for $\dot{\varepsilon}_s$ at 48 MPa and 523 K using Equation 8.20 as

$$\dot{\varepsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right)$$

$$= \left(3.27 \text{ x } 10^{-5} \text{ h}^{-1}\right)(48 \text{ MPa})^{9.97} \exp\left[-\frac{140{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(523 \text{ K})}\right]$$

$$1.94 \text{ x } 10^{-2} \text{ h}^{-1}$$

8.35 This problem gives $\dot{\epsilon}_s$ values at two different temperatures and 140 MPa (20,000 psi), and the value of the stress exponent n = 8.5, and asks that we determine the steady-state creep rate at a stress of 83 MPa (12,000 psi) and 1300 K.

Taking natural logarithms of both sides of Equation 8.20 yields

$$\ln \dot{\epsilon}_s = \ln K_2 + n \ln \sigma - \frac{Q_c}{RT}$$

With the given data there are two unknowns in this equation--namely K_2 and Q_c. Using the data provided in the problem statement we can set up two independent equations as follows:

$$\ln\left(6.6 \text{ x } 10^{-4} \text{ h}^{-1}\right) = \ln K_2 + (8.5) \ln(140 \text{ MPa}) - \frac{Q_c}{(8.31 \text{ J/mol-K})(1090 \text{ K})}$$

$$\ln\left(8.8 \text{ x } 10^{-2} \text{ h}^{-1}\right) = \ln K_2 + (8.5) \ln(140 \text{ MPa}) - \frac{Q_c}{(8.31 \text{ J/mol-K})(1200 \text{ K})}$$

Now, solving simultaneously for K_2 and Q_c leads to K_2 = 57.5 h^{-1} and Q_c = 483,500 J/mol. Thus, it is now possible to solve for $\dot{\epsilon}_s$ at 83 MPa and 1300 K using Equation 8.20 as

$$\dot{\epsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right)$$

$$= \left(57.5 \text{ h}^{-1}\right)(83 \text{ MPa})^{8.5} \exp\left[-\frac{483{,}500 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1300 \text{ K})}\right]$$

4.31 x 10^{-2} h^{-1}

Alloys for High-Temperature Use

8.36 Three metallurgical/processing techniques that are employed to enhance the creep resistance of metal alloys are (1) solid solution alloying, (2) dispersion strengthening by using an insoluble second phase, and (3) increasing the grain size or producing a grain structure with a preferred orientation.

DESIGN PROBLEMS

8.D1 Each student or group of students is to submit their own report on a failure analysis investigation that was conducted.

Principles of Fracture Mechanics

8.D2 (a) This portion of the problem calls for us to rank four polymers relative to critical crack length in the wall of a spherical pressure vessel. In the development of Design Example 8.1, it was noted that critical crack length is proportional to the square of the K_{Ic}–σ_y ratio. Values of K_{Ic} and σ_y as taken from Tables B.4 and B.5 are tabulated below. (Note: when a range of σ_y or K_{Ic} values is given, the average value is used.)

Material	K_{Ic} $(\mathrm{MPa}\sqrt{\mathrm{m}})$	σ_y (MPa)
Nylon 6,6	2.75	51.7
Polycarbonate	2.2	62.1
Poly(ethylene terephthlate)	5.0	59.3
Poly(methyl methacrylate)	1.2	63.5

On the basis of these values, the five polymers are ranked per the squares of the K_{Ic}–σ_y ratios as follows:

Material	$\left(\frac{K_{Ic}}{\sigma_y}\right)^2$ (mm)
PET	7.11
Nylon 6,6	2.83
PC	1.26
PMMA	0.36

These values are smaller than those for the metal alloys given in Table 8.3, which range from 0.93 to 43.1 mm.

(b) Relative to the leak-before-break criterion, the $K_{Ic}^2 - \sigma_y$ ratio is used. The five polymers are ranked according to values of this ratio as follows:

Material	$\frac{K_{Ic}^2}{\sigma_y}$ (MPa - m)
PET	0.422
Nylon 6,6	0.146
PC	0.078
PMMA	0.023

These values are all smaller than those for the metal alloys given in Table 8.4, which values range from 1.2 to 11.2 MPa-m.

Data Extrapolation Methods

8.D3 This problem asks that we compute the maximum allowable stress level to give a rupture lifetime of 20 days for an S-590 iron component at 923 K. It is first necessary to compute the value of the Larson-Miller parameter as follows:

$$T\left(20 + \log t_r\right) = (923\ \text{K})\left\{20 + \log\left[(20\ \text{days})(24\ \text{h/day})\right]\right\}$$

$$= 20.9 \times 10^3$$

From the curve in Figure 8.32, this value of the Larson-Miller parameter corresponds to a stress level of about 280 MPa (40,000 psi).

8.D4 We are asked in this problem to calculate the temperature at which the rupture lifetime is 200 h when an S-590 iron component is subjected to a stress of 55 MPa (8000 psi). From the curve shown in Figure 8.32, at 55 MPa, the value of the Larson-Miller parameter is 26.7 x 10^3 (K-h). Thus,

$$26.7 \text{ x } 10^3 \text{ (K - h)} = T\left(20 + \log t_r\right)$$

$$= T\left[20 + \log(200 \text{ h})\right]$$

Or, solving for T yields T = 1197 K (924°C).

8.D5 This problem asks that we determine, for an 18-8 Mo stainless steel, the time to rupture for a component that is subjected to a stress of 100 MPa (14,500 psi) at 600°C (873 K). From Figure 8.35, the value of the Larson-Miller parameter at 100 MPa is about 22.4 x 10^3, for T in K and t_r in h. Therefore,

$$22.4 \times 10^3 = T(20 + \log t_r)$$

$$= 873(20 + \log t_r)$$

And, solving for t_r

$$25.66 = 20 + \log t_r$$

which leads to t_r = 4.6 x 10^5 h = 52 yr.

8.D6 We are asked in this problem to calculate the stress levels at which the rupture lifetime will be 1 year and 15 years when an 18-8 Mo stainless steel component is subjected to a temperature of 650°C (923 K). It first becomes necessary to calculate the value of the Larson-Miller parameter for each time. The values of t_r corresponding to 1 and 15 years are 8.76 x 10^3 h and 1.31 x 10^5 h, respectively. Hence, for a lifetime of 1 year

$$T(20 + \log t_r) = 923\left[20 + \log\left(8.76 \text{ x } 10^3\right)\right] = 22.10 \text{ x } 10^3$$

And for t_r = 15 years

$$T(20 + \log t_r) = 923\left[20 + \log\left(1.31 \text{ x } 10^5\right)\right] = 23.18 \text{ x } 10^3$$

Using the curve shown in Figure 8.35, the stress values corresponding to the one- and fifteen-year lifetimes are approximately 110 MPa (16,000 psi) and 80 MPa (11,600 psi), respectively.

CHAPTER 9

PHASE DIAGRAMS

PROBLEM SOLUTIONS

Solubility Limit

9.1 (a) We are asked to determine how much sugar will dissolve in 1000 g of water at 80°C. From the solubility limit curve in Figure 9.1, at 80°C the maximum concentration of sugar in the syrup is about 74 wt%. It is now possible to calculate the mass of sugar using Equation 4.3 as

$$C_{\text{sugar}}(\text{wt\%}) = \frac{m_{\text{sugar}}}{m_{\text{sugar}} + m_{\text{water}}} \times 100$$

$$74 \text{ wt\%} = \frac{m_{\text{sugar}}}{m_{\text{sugar}} + 1000 \text{ g}} \times 100$$

Solving for m_{sugar} yields $m_{\text{sugar}} = 2846$ g

(b) Again using this same plot, at 20°C the solubility limit (or the concentration of the saturated solution) is about 64 wt% sugar.

(c) The mass of sugar in this saturated solution at 20°C (m'_{sugar}) may also be calculated using Equation 4.3 as follows:

$$64 \text{ wt\%} = \frac{m'_{\text{sugar}}}{m'_{\text{sugar}} + 1000 \text{ g}} \times 100$$

which yields a value for m'_{sugar} of 1778 g. Subtracting the latter from the former of these sugar concentrations yields the amount of sugar that precipitated out of the solution upon cooling m''_{sugar}; that is

$$m''_{\text{sugar}} = m_{\text{sugar}} - m'_{\text{sugar}} = 2846 \text{ g} - 1778 \text{ g} = 1068 \text{ g}$$

9.2 (a) From Figure 9.8, the maximum solubility of Pb in Sn at 100°C corresponds to the position of the β–(α + β) phase boundary at this temperature, or to about 2 wt% Pb.

(b) From this same figure, the maximum solubility of Sn in Pb corresponds to the position of the α–(α + β) phase boundary at this temperature, or about 5 wt% Sn.

Microstructure

9.3 Three variables that determine the microstructure of an alloy are (1) the alloying elements present, (2) the concentrations of these alloying elements, and (3) the heat treatment of the alloy.

Phase Equilibria

9.4 In order for a system to exist in a state of equilibrium the free energy must be a minimum for some specified combination of temperature, pressure, and composition.

One-Component (or Unary) Phase Diagrams

9.5 This problem asks us to consider a specimen of ice that is at –15°C and 10 atm pressure.

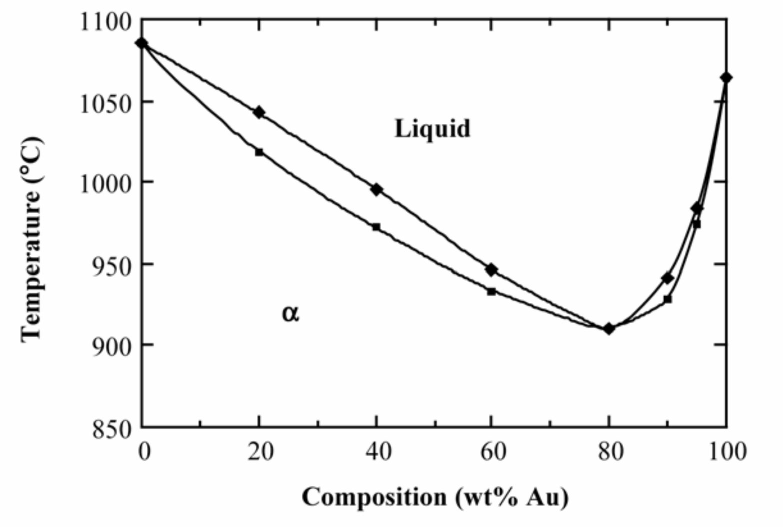
(a) Melting occurs, (by changing pressure) as, moving vertically (upward) at this temperature, we cross the Ice-Liquid phase boundary of Figure 9.2. This occurs at approximately 1,000 atm; thus, the pressure of the specimen must be raised from 10 to 1,000 atm.

(b) In order to determine the pressure at which sublimation occurs at this temperature, we move vertically downward from 10 atm until we cross the Ice-Vapor phase boundary of Figure 9.2. This intersection occurs at approximately 0.003 atm.

9.6 The melting and boiling temperatures for ice at a pressure of 0.1 atm may be determined by moving horizontally across the pressure-temperature diagram of Figure 9.2 at this pressure. The temperature corresponding to the intersection of the Ice-Liquid phase boundary is the melting temperature, which is approximately 2°C. On the other hand, the boiling temperature is at the intersection of the horizontal line with the Liquid-Vapor phase boundary--approximately 70°C.

Binary Isomorphous Systems

9.7 The copper-gold phase diagram is constructed below.



Interpretation of Phase Diagrams

9.8 This problem asks that we cite the phase or phases present for several alloys at specified temperatures.

(a) For an alloy composed of 15 wt% Sn-85 wt% Pb and at 100°C, from Figure 9.8, α and β phases are present, and

$$C_\alpha = 5 \text{ wt\% Sn-95 wt\% Pb}$$
$$C_\beta = 98 \text{ wt\% Sn-2 wt\% Pb}$$

(b) For an alloy composed of 25 wt% Pb-75 wt% Mg and at 425°C, from Figure 9.20, only the α phase is present; its composition is 25 wt% Pb-75 wt% Mg.

(c) For an alloy composed of 85 wt% Ag-15 wt% Cu and at 800°C, from Figure 9.7, β and liquid phases are present, and

$$C_\beta = 92 \text{ wt\% Ag-8 wt\% Cu}$$
$$C_L = 77 \text{ wt\% Ag-23 wt\% Cu}$$

(d) For an alloy composed of 55 wt% Zn-45 wt% Cu and at 600°C, from Figure 9.19, β and γ phases are present, and

$$C_\beta = 51 \text{ wt\% Zn-49 wt\% Cu}$$
$$C_\gamma = 58 \text{ wt\% Zn-42 wt\% Cu}$$

(e) For an alloy composed of 1.25 kg Sn and 14 kg Pb and at 200°C, we must first determine the Sn and Pb concentrations (using Equation 4.3), as

$$C_{\text{Sn}} = \frac{1.25 \text{ kg}}{1.25 \text{ kg} + 14 \text{ kg}} \times 100 = 8.2 \text{ wt\%}$$

$$C_{\text{Pb}} = \frac{14 \text{ kg}}{1.25 \text{ kg} + 14 \text{ kg}} \times 100 = 91.8 \text{ wt\%}$$

From Figure 9.8, only the α phase is present; its composition is 8.2 wt% Sn-91.8 wt% Pb.

(f) For an alloy composed of 7.6 lb_m Cu and 144.4 lb_m Zn and at 600°C, we must first determine the Cu and Zn concentrations (using Equation 4.3), as

$$C_{\text{Cu}} = \frac{7.6 \text{ lb}_\text{m}}{7.6 \text{ lb}_\text{m} + 144.4 \text{ lb}_\text{m}} \times 100 = 5.0 \text{ wt\%}$$

$$C_{\text{Zn}} = \frac{144.4 \text{ lb}_\text{m}}{7.6 \text{ lb}_\text{m} + 144.4 \text{ lb}_\text{m}} \times 100 = 95.0 \text{ wt\%}$$

From Figure 9.19, only the *L* phase is present; its composition is 95.0 wt% Zn-5.0 wt% Cu

(g) For an alloy composed of 21.7 mol Mg and 35.4 mol Pb and at 350°C, it is necessary to determine the Mg and Pb concentrations in weight percent. However, we must first compute the masses of Mg and Pb (in grams) using a rearranged form of Equation 4.4:

$$m'_{\text{Pb}} = n_{m_{\text{Pb}}} A_{\text{Pb}} = (35.4 \text{ mol})(207.2 \text{ g/mol}) = 7335 \text{ g}$$

$$m'_{\text{Mg}} = n_{m_{\text{Mg}}} A_{\text{Mg}} = (21.7 \text{ mol})(24.3 \text{ g/mol}) = 527 \text{ g}$$

Now, using Equation 4.3, concentrations of Pb and Mg are determined as follows:

$$C_{\text{Pb}} = \frac{7335 \text{ g}}{7335 \text{ g} + 527 \text{ g}} \times 100 = 93 \text{ wt\%}$$

$$C_{\text{Mg}} = \frac{527 \text{ g}}{7335 \text{ g} + 527 \text{ g}} \times 100 = 7 \text{ wt\%}$$

From Figure 9.20, *L* and Mg_2Pb phases are present, and

$$C_L = 94 \text{ wt\% Pb} - 6 \text{ wt\% Mg}$$

$$C_{\text{Mg}_2\text{Pb}} = 81 \text{ wt\% Pb} - 19 \text{ wt\% Mg}$$

(h) For an alloy composed of 4.2 mol Cu and 1.1 mol Ag and at 900°C, it is necessary to determine the Cu and Ag concentrations in weight percent. However, we must first compute the masses of Cu and Ag (in grams) using a rearranged form of Equation 4.4:

$$m'_{\mathrm{Cu}} = n_{m_{\mathrm{Cu}}} A_{\mathrm{Cu}} = (4.2 \text{ mol})(63.55 \text{ g/mol}) = 266.9 \text{ g}$$

$$m'_{\mathrm{Ag}} = n_{m_{\mathrm{Ag}}} A_{\mathrm{Ag}} = (1.1 \text{ mol})(107.87 \text{ g/mol}) = 118.7 \text{ g}$$

Now, using Equation 4.3, concentrations of Cu and Ag are determined as follows:

$$C_{\mathrm{Cu}} = \frac{266.9 \text{ g}}{266.9 \text{ g} + 118.7 \text{ g}} \times 100 = 69.2 \text{ wt\%}$$

$$C_{\mathrm{Ag}} = \frac{118.7 \text{ g}}{266.9 \text{ g} + 118.7 \text{ g}} \times 100 = 30.8 \text{ wt\%}$$

From Figure 9.7, α and liquid phases are present; and

$$C_\alpha = 8 \text{ wt\% Ag-92 w\% Cu}$$
$$C_L = 45 \text{ wt\% Ag-55 wt\% Cu}$$

9.9 It *is possible* to have a Cu-Ag alloy, which at equilibrium consists of a β phase of composition 92 wt% Ag-8 wt% Cu and a liquid phase of composition 77 wt% Ag-23 wt% Cu. From Figure 9.7 a horizontal tie line can be constructed across the β + *L* phase region at about 800°C which intersects the *L*–(β + *L*) phase boundary at 76 wt% Ag, and also the (β + *L*)–β phase boundary at 92 wt% Ag.

9.10 It *is possible* to have a Cu-Ag alloy, which at equilibrium consists of an α phase of composition 4 wt% Ag-96 wt% Cu and a β phase of composition 95 wt% Ag-5 wt% Cu. From Figure 9.7 a horizontal tie can be constructed across the α + β region at 690°C which intersects the α–(α + β) phase boundary at 4 wt% Ag, and also the (α + β)–β phase boundary at 95 wt% Ag.

9.11 Upon heating a lead-tin alloy of composition 30 wt% Sn-70 wt% Pb from 150°C and utilizing Figure 9.8:

(a) The first liquid forms at the temperature at which a vertical line at this composition intersects the eutectic isotherm--i.e., at 183°C.

(b) The composition of this liquid phase corresponds to the intersection with the (α + L)–L phase boundary, of a tie line constructed across the α + L phase region just above this eutectic isotherm--i.e., C_L = 61.9 wt% Sn.

(c) Complete melting of the alloy occurs at the intersection of this same vertical line at 30 wt% Sn with the (α + L)–L phase boundary--i.e., at about 260°C.

(d) The composition of the last solid remaining prior to complete melting corresponds to the intersection with α–(α + L) phase boundary, of the tie line constructed across the α + L phase region at 260°C--i.e., C_α is about 13 wt% Sn.

9.12 Upon cooling a 50 wt% Ni-50 wt% Cu alloy from 1400°C and utilizing Figure 9.3a:

(a) The first solid phase forms at the temperature at which a vertical line at this composition intersects the L–($\alpha + L$) phase boundary--i.e., at about 1320°C.

(b) The composition of this solid phase corresponds to the intersection with the L–($\alpha + L$) phase boundary, of a tie line constructed across the $\alpha + L$ phase region at 1320°C--i.e., C_α = 62 wt% Ni-38 wt% Cu.

(c) Complete solidification of the alloy occurs at the intersection of this same vertical line at 50 wt% Ni with the ($\alpha + L$)–α phase boundary--i.e., at about 1270°C.

(d) The composition of the last liquid phase remaining prior to complete solidification corresponds to the intersection with the L–($\alpha + L$) boundary, of the tie line constructed across the $\alpha + L$ phase region at 1270°C--i.e., C_L is about 37 wt% Ni-63 wt% Cu.

9.13 This problem asks us to determine the phases present and their concentrations at several temperatures, as an alloy of composition 52 wt% Zn-48 wt% Cu is cooled. From Figure 9.19:

At 1000°C, a liquid phase is present; $W_L = 1.0$

At 800°C, the β phase is present, and $W_\beta = 1.0$

At 500°C, β and γ phases are present, and

$$W_\gamma = \frac{C_0 - C_\beta}{C_\gamma - C_\beta} = \frac{52 - 49}{58 - 49} = 0.33$$

$$W_\beta = 1.00 - 0.33 = 0.67$$

At 300°C, the β' and γ phases are present, and

$$W_{\beta'} = \frac{C_\gamma - C_0}{C_\gamma - C_{\beta'}} = \frac{59 - 52}{59 - 50} = 0.78$$

$$W_\gamma = 1.00 - 0.78 = 0.22$$

9.14 This problem asks that we determine the phase mass fractions for the alloys and temperatures in Problem 9.8.

(a)

$$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{98 - 15}{98 - 5} = 0.89$$

$$W_\beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{15 - 5}{98 - 5} = 0.11$$

(b) $W_\alpha = 1.0$

(c)

$$W_\beta = \frac{C_0 - C_L}{C_\beta - C_L} = \frac{85 - 77}{92 - 77} = 0.53$$

$$W_L = \frac{C_\beta - C_0}{C_\beta - C_L} = \frac{92 - 85}{92 - 77} = 0.47$$

(d)

$$W_\beta = \frac{C_\gamma - C_0}{C_\gamma - C_\beta} = \frac{58 - 55}{58 - 51} = 0.43$$

$$W_\gamma = \frac{C_0 - C_\beta}{C_\gamma - C_\beta} = \frac{55 - 51}{58 - 51} = 0.57$$

(e) $W_\alpha = 1.0$

(f) $W_L = 1.0$

(g)

$$W_{\mathrm{Mg_2Pb}} = \frac{C_{\mathrm{L}} - C_0}{C_L - C_{\mathrm{Mg_2Pb}}} = \frac{94 - 93}{94 - 81} = 0.08$$

$$W_L = \frac{C_0 - C_{\mathrm{Mg_2Pb}}}{C_L - C_{\mathrm{Mg_2Pb}}} = \frac{93 - 81}{94 - 81} = 0.92$$

(h)

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{45 - 30.8}{45 - 8} = 0.38$$

$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{30.8 - 8}{45 - 8} = 0.62$$

9.15 (a) This part of the problem calls for us to cite the temperature to which a 85 wt% Pb-15 wt% Sn alloy must be heated in order to have 50% liquid. Probably the easiest way to solve this problem is by trial and error--that is, on the Pb-Sn phase diagram (Figure 9.8), moving vertically at the given composition, through the α + *L* region until the tie-line lengths on both sides of the given composition are the same. This occurs at approximately 280°C (535°F).

(b) We can also produce a 50% liquid solution at 200°C, by adding Sn to the alloy. At 200°C and within the α + *L* phase region

$$C_\alpha = 17 \text{ wt\% Sn-83 wt\% Pb}$$
$$C_L = 57 \text{ wt\% Sn-43 wt\% Pb}$$

Let C_0 be the new alloy composition to give $W_\alpha = W_L = 0.5$. Then,

$$W_\alpha = 0.5 = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{57 - C_0}{57 - 17}$$

And solving for C_0 gives 37 wt% Sn. Now, let m_{Sn} be the mass of Sn added to the alloy to achieve this new composition. The amount of Sn in the original alloy is

$$(0.15)(2.0 \text{ kg}) = 0.30 \text{ kg}$$

Then, using a modified form of Equation 4.3

$$\left[\frac{0.30 \text{ kg} + m_{\text{Sn}}}{2.0 \text{ kg} + m_{\text{Sn}}}\right] \times 100 = 37$$

And, solving for m_{Sn} (the mass of tin to be added), yields $m_{\text{Sn}} = 0.698$ kg.

9.16 (a) This portion of the problem asks that we calculate, for a Pb-Mg alloy, the mass of lead in 7.5 kg of the solid α phase at 300°C just below the solubility limit. From Figure 9.20, the solubility limit for the α phase at 300°C corresponds to the position (composition) of the α-α + Mg_2Pb phase boundary at this temperature, which is about 17 wt% Pb. Therefore, the mass of Pb in the alloy is just (0.17)(7.5 kg) = 1.3 kg.

(b) At 400°C, the solubility limit of the α phase increases to approximately 32 wt% Pb. In order to determine the additional amount of Pb that may be added ($m_{Pb'}$), we utilize a modified form of Equation 4.3 as

$$C_{Pb} = 32 \text{ wt\%} = \frac{1.3 \text{ kg} + m_{Pb'}}{7.5 \text{ kg} + m_{Pb'}} \times 100$$

Solving for $m_{Pb'}$ yields $m_{Pb'}$ = 1.62 kg.

9.17 (a) In order to determine the temperature of a 65 wt% Ni-35 wt% Cu alloy for which α and liquid phases are present with the α phase of composition 70 wt% Ni, we need to construct a tie line across the $\alpha + L$ phase region of Figure 10.3a that intersects the solidus line at 70 wt% Ni; this is possible at about 1340°C.

(b) The composition of the liquid phase at this temperature is determined from the intersection of this same tie line with liquidus line, which corresponds to about 59 wt% Ni.

(c) The mass fractions of the two phases are determined using the lever rule, Equations 9.1 and 9.2 with C_0 = 65 wt% Ni, C_L = 59 wt% Ni, and C_α = 70 wt% Ni, as

$$W_\alpha = \frac{C_0 - C_L}{C_\alpha - C_L} = \frac{65 - 59}{70 - 59} = 0.55$$

$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L} = \frac{70 - 65}{70 - 59} = 0.45$$

9.18 (a) We are given that the mass fractions of α and liquid phases are both 0.5 for a 40 wt% Pb-60 wt% Mg alloy and are asked to estimate the temperature of the alloy. Using the appropriate phase diagram, Figure 9.20, by trial and error with a ruler, a tie line within the $\alpha + L$ phase region that is divided in half for an alloy of this composition exists at about 540°C.

(b) We are now asked to determine the compositions of the two phases. This is accomplished by noting the intersections of this tie line with both the solidus and liquidus lines. From these intersections, C_α = 26 wt% Pb, and C_L = 54 wt% Pb.

9.19 The problem is to solve for compositions at the phase boundaries for both α and β phases (i.e., C_α and C_β). We may set up two independent lever rule expressions, one for each composition, in terms of C_α and C_β as follows:

$$W_{\alpha 1} = 0.78 = \frac{C_\beta - C_{01}}{C_\beta - C_\alpha} = \frac{C_\beta - 70}{C_\beta - C_\alpha}$$

$$W_{\alpha 2} = 0.36 = \frac{C_\beta - C_{02}}{C_\beta - C_\alpha} = \frac{C_\beta - 35}{C_\beta - C_\alpha}$$

In these expressions, compositions are given in wt% of A. Solving for C_α and C_β from these equations, yield

$$C_\alpha = 88.3 \text{ (or 88.3 wt\% A-11.7 wt\% B)}$$

$$C_\beta = 5.0 \text{ (or 5.0 wt\% A-95.0 wt\% B)}$$

9.20 For this problem, we are asked to determine the composition of the β phase given that

$$C_0 = 40 \text{ (or 40 wt\% B-60 wt\% A)}$$

$$C_\alpha = 13 \text{ (or 13 wt\% B-87 wt\% A)}$$

$$W_\alpha = 0.66$$

$$W_\beta = 0.34$$

If we set up the lever rule for W_α

$$W_\alpha = 0.66 = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{C_\beta - 40}{C_\beta - 13}$$

And solving for C_β

$$C_\beta = 92.4 \text{ (or 92.4 wt\% B-7.6 wt\% A)}$$

9.21 Yes, it is possible to have a Cu-Ag alloy of composition 20 wt% Ag-80 wt% Cu which consists of mass fractions $W_\alpha = 0.80$ and $W_L = 0.20$. Using the appropriate phase diagram, Figure 9.7, by trial and error with a ruler, the tie-line segments within the $\alpha + L$ phase region are proportioned such that

$$W_\alpha = 0.8 = \frac{C_L - C_0}{C_L - C_\alpha}$$

for $C_0 = 20$ wt% Ag. This occurs at about 800°C.

9.22 It is *not possible* to have a 50 wt% Pb-50 wt% Mg alloy that has masses of 5.13 kg and 0.57 kg for the α and Mg_2Pb phases, respectively. In order to demonstrate this, it is first necessary to determine the mass fraction of each phase as:

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_{Mg_2Pb}} = \frac{5.13 \text{ kg}}{5.13 \text{ kg} + 0.57 \text{ kg}} = 0.90$$

$$W_{Mg_2Pb} = 1.00 - 0.90 = 0.10$$

Now, if we apply the lever rule expression for W_α

$$W_\alpha = \frac{C_{Mg_2Pb} - C_0}{C_{Mg_2Pb} - C_\alpha}$$

Since the Mg_2Pb phase exists only at 81 wt% Pb, and C_0 = 50 wt% Pb

$$W_\alpha = 0.90 = \frac{81 - 50}{81 - C_\alpha}$$

Solving for C_α from this expression yields C_α = 46.6 wt% Pb. From Figure 9.20, the maximum concentration of Pb in the α phase in the α + Mg_2Pb phase field is about 42 wt% Pb. Therefore, this alloy is not possible.

9.23 This portion of the problem asks that we derive Equation 9.6a, which is used to convert from phase weight fraction to phase volume fraction. Volume fraction of phase α, V_α, is defined by Equation 9.5 as

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta} \tag{9.S1}$$

where v_α and v_β are the volumes of the respective phases in the alloy. Furthermore, the density of each phase is equal to the ratio of its mass and volume, or upon rearrangement

$$v_\alpha = \frac{m_\alpha}{\rho_\alpha} \tag{9.S2a}$$

$$v_\beta = \frac{m_\beta}{\rho_\beta} \tag{9.S2b}$$

Substitution of these expressions into Equation 9.S1 leads to

$$V_\alpha = \frac{\dfrac{m_\alpha}{\rho_\alpha}}{\dfrac{m_\alpha}{\rho_\alpha} + \dfrac{m_\beta}{\rho_\beta}} \tag{9.S3}$$

in which m's and ρ's denote masses and densities, respectively. Now, the mass fractions of the α and β phases (i.e., W_α and W_β) are defined in terms of the phase masses as

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_\beta} \tag{9.S4a}$$

$$W_\beta = \frac{m_\beta}{m_\alpha + m_\beta} \tag{9.S4b}$$

Which, upon rearrangement yield

$$m_\alpha = W_\alpha (m_\alpha + m_\beta) \tag{9.S5a}$$

$$m_\beta = W_\beta (m_\alpha + m_\beta) \tag{9.S5b}$$

Incorporation of these relationships into Equation 9.S3 leads to

$$V_\alpha = \frac{\dfrac{W_\alpha (m_\alpha + m_\beta)}{\rho_\alpha}}{\dfrac{W_\alpha (m_\alpha + m_\beta)}{\rho_\alpha} + \dfrac{W_\beta (m_\alpha + m_\beta)}{\rho_\beta}}$$

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}} \tag{9.S6}$$

which is the desired equation.

For this portion of the problem we are asked to derive Equation 9.7a, which is used to convert from phase volume fraction to mass fraction. Mass fraction of the α phase is defined as

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_\beta} \tag{9.S7}$$

From Equations 9.S2a and 9.S2b

$$m_\alpha = v_\alpha \rho_\alpha \tag{9.S8a}$$

$$m_\beta = v_\beta \rho_\beta \tag{9.S8b}$$

Substitution of these expressions into Equation 9.S7 yields

$$W_\alpha = \frac{v_\alpha \rho_\alpha}{v_\alpha \rho_\alpha + v_\beta \rho_\beta} \tag{9.S9}$$

From Equation 9.5 and its equivalent for V_β the following may be written:

$$v_\alpha = V_\alpha (v_\alpha + v_\beta) \tag{9.S10a}$$

$$v_\beta = \mathrm{V}_\beta(v_\alpha + v_\beta) \tag{9.S10b}$$

Substitution of Equations 9.S10a and 9.S10b into Equation 9.S9 yields

$$W_\alpha = \frac{V_\alpha(v_\alpha + v_\beta)\rho_\alpha}{V_\alpha(v_\alpha + v_\beta)\rho_\alpha + \mathrm{V}_\beta(v_\alpha + v_\beta)\rho_\beta}$$

$$W_\alpha = \frac{V_\alpha \rho_\alpha}{V_\alpha \rho_\alpha + V_\beta \rho_\beta} \tag{9.S11}$$

which is the desired expression.

9.24 This problem asks that we determine the phase volume fractions for the alloys and temperatures in Problems 9.8a, b, and d. This is accomplished by using the technique illustrated in Example Problem 9.3, and also the results of Problems 9.8 and 9.14.

(a) This is a Sn-Pb alloy at 100°C, wherein

C_α = 5 wt% Sn-95 wt% Pb
C_β = 98 wt% Sn-2 wt% Pb
$W_\alpha = 0.89$
$W_\beta = 0.11$
$\rho_{Sn} = 7.29$ g/cm^3
$\rho_{Pb} = 11.27$ g/cm^3

Using these data it is first necessary to compute the densities of the α and β phases using Equation 4.10a. Thus

$$\rho_\alpha = \frac{100}{\dfrac{C_{Sn(\alpha)}}{\rho_{Sn}} + \dfrac{C_{Pb(\alpha)}}{\rho_{Pb}}}$$

$$= \frac{100}{\dfrac{5}{7.29\ \text{g/cm}^3} + \dfrac{95}{11.27\ \text{g/cm}^3}} = 10.97\ \text{g/cm}^3$$

$$\rho_\beta = \frac{100}{\dfrac{C_{Sn(\beta)}}{\rho_{Sn}} + \dfrac{C_{Pb(\beta)}}{\rho_{Pb}}}$$

$$= \frac{100}{\dfrac{98}{7.29\ \text{g/cm}^3} + \dfrac{2}{11.27\ \text{g/cm}^3}} = 7.34\ \text{g/cm}^3$$

Now we may determine the V_α and V_β values using Equation 9.6. Thus,

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}}$$

$$= \frac{\dfrac{0.89}{10.97\ \text{g/cm}^3}}{\dfrac{0.89}{10.97\ \text{g/cm}^3} + \dfrac{0.11}{7.34\ \text{g/cm}^3}} = 0.84$$

$$V_\beta = \frac{\dfrac{W_\beta}{\rho_\beta}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}}$$

$$= \frac{\dfrac{0.11}{7.34\ \text{g/cm}^3}}{\dfrac{0.89}{10.97\ \text{g/cm}^3} + \dfrac{0.11}{7.34\ \text{g/cm}^3}} = 0.16$$

(b) This is a Pb-Mg alloy at 425°C, wherein only the α phase is present. Therefore, $V_\alpha = 1.0$.

(d) This is a Zn-Cu alloy at 600°C, wherein

C_β = 51 wt% Zn-49 wt% Cu
C_γ = 58 wt% Zn-42 wt% Cu
$W_\beta = 0.43$
$W_\gamma = 0.57$
$\rho_{Zn} = 6.67\ \text{g/cm}^3$
$\rho_{Cu} = 8.68\ \text{g/cm}^3$

Using these data it is first necessary to compute the densities of the β and γ phases using Equation 4.10a. Thus

$$\rho_\beta = \frac{100}{\dfrac{C_{Zn(\beta)}}{\rho_{Zn}} + \dfrac{C_{Cu(\beta)}}{\rho_{Cu}}}$$

$$= \frac{100}{\dfrac{51}{6.67\ \text{g/cm}^3} + \dfrac{49}{8.68\ \text{g/cm}^3}} = 7.52\ \text{g/cm}^3$$

$$\rho_\gamma = \frac{100}{\dfrac{C_{\text{Zn}(\gamma)}}{\rho_{\text{Zn}}} + \dfrac{C_{\text{Cu}(\gamma)}}{\rho_{\text{Cu}}}}$$

$$= \frac{100}{\dfrac{58}{6.67\ \text{g/cm}^3} + \dfrac{42}{8.68\ \text{g/cm}^3}} = 7.39\ \text{g/cm}^3$$

Now we may determine the V_β and V_γ values using Equation 9.6. Thus,

$$V_\beta = \frac{\dfrac{W_\beta}{\rho_\beta}}{\dfrac{W_\beta}{\rho_\beta} + \dfrac{W_\gamma}{\rho_\gamma}}$$

$$= \frac{\dfrac{0.43}{7.52\ \text{g/cm}^3}}{\dfrac{0.43}{7.52\ \text{g/cm}^3} + \dfrac{0.57}{7.39\ \text{g/cm}^3}} = 0.43$$

$$V_\gamma = \frac{\dfrac{W_\gamma}{\rho_\gamma}}{\dfrac{W_\beta}{\rho_\beta} + \dfrac{W_\gamma}{\rho_\gamma}}$$

$$= \frac{\dfrac{0.57}{7.39\ \text{g/cm}^3}}{\dfrac{0.43}{7.52\ \text{g/cm}^3} + \dfrac{0.57}{7.39\ \text{g/cm}^3}} = 0.57$$

Development of Microstructure in Isomorphous Alloys

9.25 (a) Coring is the phenomenon whereby concentration gradients exist across grains in polycrystalline alloys, with higher concentrations of the component having the lower melting temperature at the grain boundaries. It occurs, during solidification, as a consequence of cooling rates that are too rapid to allow for the maintenance of the equilibrium composition of the solid phase.

(b) One undesirable consequence of a cored structure is that, upon heating, the grain boundary regions will melt first and at a temperature below the equilibrium phase boundary from the phase diagram; this melting results in a loss in mechanical integrity of the alloy.

Mechanical Properties of Isomorphous Alloys

9.26 This problem asks if a noncold-worked Cu-Ni solid solution alloy is possible having a minimum tensile strength of 380 MPa (55,000 psi) and also a ductility of at least 45%EL. From Figure 9.6a, a tensile strength greater than 380 MPa is possible for compositions between about 32 and 90 wt% Ni. On the other hand, according to Figure 9.6b, ductilities greater than 45%EL exist for compositions less than about 13 wt% and greater than about 94 wt% Ni. Therefore, such an alloy is *not possible* inasmuch, that in order to meet the stipulated criteria:

For a TS > 380 MPa	32 wt% < C_{Ni} < 90 wt%
For %EL > 45%	C_{Ni} < 13 wt% or C_{Ni} > 94 wt%

Binary Eutectic Systems

9.27 We are asked to determine the approximate temperature from which a 60 wt% Pb-40 wt% Mg alloy was quenched, given the mass fractions of α and Mg_2Pb phases. We can write a lever-rule expression for the mass fraction of the α phase as

$$W_\alpha = 0.42 = \frac{C_{\mathrm{Mg_2Pb}} - C_0}{C_{\mathrm{Mg_2Pb}} - C_\alpha}$$

The value of C_0 is stated as 60 wt% Pb-40 wt% Mg, and $C_{\mathrm{Mg_2Pb}}$ is 81 wt% Pb-19 wt% Mg, which is independent of temperature (Figure 9.20); thus,

$$0.42 = \frac{81 - 60}{81 - C_\alpha}$$

which yields

$$C_\alpha = 31.0 \text{ wt\% Pb}$$

The temperature at which the α–(α + Mg_2Pb) phase boundary (Figure 9.20) has a value of 31.0 wt% Pb is about 400°C (750°F).

Development of Microstructure in Eutectic Alloys

9.28 Upon solidification, an alloy of eutectic composition forms a microstructure consisting of alternating layers of the two solid phases because during the solidification atomic diffusion must occur, and with this layered configuration the diffusion path length for the atoms is a minimum.

9.29 A “phase” is a homogeneous portion of the system having uniform physical and chemical characteristics, whereas a “microconstituent” is an identifiable element of the microstructure (that may consist of more than one phase).

9.30 This problem asks if it is possible to have a Mg-Pb alloy for which the mass fractions of primary α and total α are 0.60 and 0.85, respectively, at 460°C. In order to make this determination we need to set up the appropriate lever rule expression for each of these quantities. From Figure 9.20 and at 460°C, C_{α} = 41 wt% Pb, $C_{\mathrm{Mg_2Pb}}$ = 81 wt% Pb, and C_{eutectic} = 67 wt% Pb.

For primary α

$$W_{\alpha'} = \frac{C_{\mathrm{eutectic}} - C_0}{C_{\mathrm{eutectic}} - C_{\alpha}} = \frac{67 - C_0}{67 - 41} = 0.60$$

Solving for C_0 gives C_0 = 51.4 wt% Pb.

Now the analogous expression for total α

$$W_{\alpha} = \frac{C_{\mathrm{Mg_2Pb}} - C_0}{C_{\mathrm{Mg_2Pb}} - C_{\alpha}} = \frac{81 - C_0}{81 - 41} = 0.85$$

which yields a value of 47 wt% Pb for C_0. Therefore, since these two C_0 values are different, this alloy is *not* possible.

9.31 This problem asks if it is possible to have a Pb-Sn alloy for which the masses of primary β and total β are 2.21 and 2.53 kg, respectively in 2.8 kg total of the alloy at 180°C. In order to make this determination we first need to convert these masses to mass fractions. Thus,

$$W_{\beta'} = \frac{2.21\ \text{kg}}{2.8\ \text{kg}} = 0.789$$

$$W_{\beta} = \frac{2.53\ \text{kg}}{2.8\ \text{kg}} = 0.904$$

Next it is necessary to set up the appropriate lever rule expression for each of these quantities. From Figure 9.8 and at 180°C, C_α = 18.3 wt% Sn, C_β = 97.8 wt% Sn, and C_{eutectic} = 61.9 wt% Sn.

For primary β

$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_\beta - C_{\text{eutectic}}} = \frac{C_0 - 61.9}{97.8 - 61.9} = 0.789$$

And solving for C_0 gives C_0 = 90.2 wt% Sn.

Now the analogous expression for total β

$$W_{\beta} = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{C_0 - 18.3}{97.8 - 18.3} = 0.904$$

And this value of C_0 is also 90.2 wt% Sn. Therefore, since these two C_0 values are identical, this alloy *is possible*.

9.32 (a) This portion of the problem asks that we determine the mass fractions of α and β phases for an 80 wt% Sn-20 wt% Pb alloy (at 180°C). In order to do this it is necessary to employ the lever rule using a tie line that extends entirely across the α + β phase field. From Figure 9.8 and at 180°C, C_α = 18.3 wt% Sn, C_β = 97.8 wt% Sn, and C_{eutectic} = 61.9 wt% Sn. Therefore, the two lever-rule expressions are as follows:

$$W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{97.8 - 80}{97.8 - 18.3} = 0.224$$

$$W_\beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{80 - 18.3}{97.8 - 18.3} = 0.776$$

(b) Now it is necessary to determine the mass fractions of primary β and eutectic microconstituents for this same alloy. This requires that we utilize the lever rule and a tie line that extends from the maximum solubility of Pb in the β phase at 180°C (i.e., 97.8 wt% Sn) to the eutectic composition (61.9 wt% Sn). Thus

$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_\beta - C_{\text{eutectic}}} = \frac{80.0 - 61.9}{97.8 - 61.9} = 0.504$$

$$W_{\text{e}} = \frac{C_\beta - C_0}{C_\beta - C_{\text{eutectic}}} = \frac{97.8 - 80.0}{97.8 - 61.9} = 0.496$$

(c) And, finally, we are asked to compute the mass fraction of eutectic β, $W_{e\beta}$. This quantity is simply the difference between the mass fractions of total β and primary β as

$$W_{e\beta} = W_\beta - W_{\beta'} = 0.776 - 0.504 = 0.272$$

9.33 This problem asks that we determine the composition of a Cu-Ag alloy at 775°C given that $W_{\alpha'}$ = 0.73 and W_{eutectic} = 0.27. Since there is a primary α microconstituent present, we know that the alloy composition, C_0 is between 8.0 and 71.9 wt% Ag (Figure 9.7). Furthermore, this figure also indicates that C_α = 8.0 wt% Ag and C_{eutectic} = 71.9 wt% Ag. Applying the appropriate lever rule expression for $W_{\alpha'}$

$$W_{\alpha'} = \frac{C_{\text{eutectic}} - C_0}{C_{\text{eutectic}} - C_\alpha} = \frac{71.9 - C_0}{71.9 - 8.0} = 0.73$$

and solving for C_0 yields C_0 = 25.2 wt% Ag.

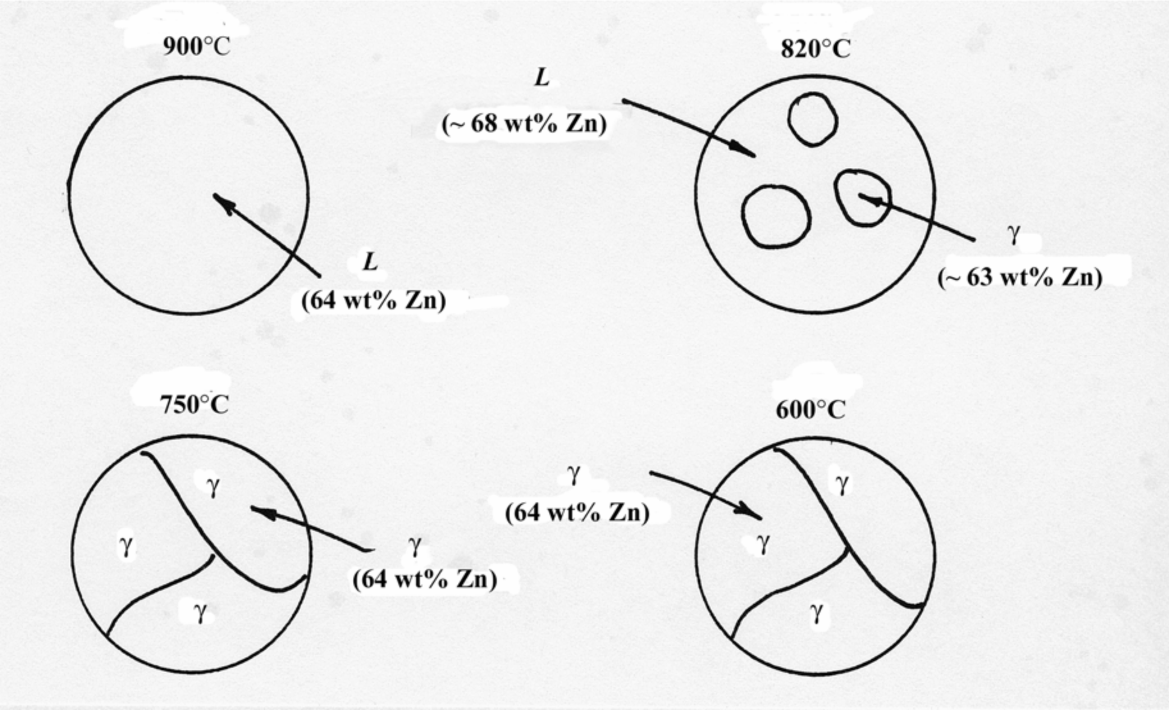
9.34 We are given a hypothetical eutectic phase diagram for which C_{eutectic} = 64 wt% B, C_α = 12 wt% B at the eutectic temperature, and also that $W_{\beta'}$ = 0.367 and W_β = 0.768; from this we are asked to determine the composition of the alloy. Let us write lever rule expressions for $W_{\beta'}$ and W_β

$$W_\beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{C_0 - 12}{\mathrm{C}_\beta - 12} = 0.768$$

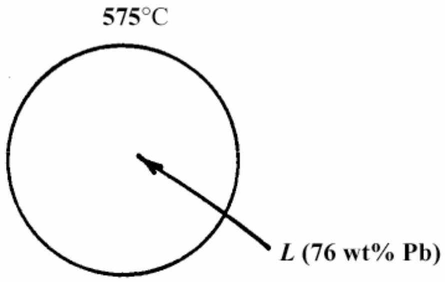
$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_\beta - C_{\text{eutectic}}} = \frac{C_0 - 64}{\mathrm{C}_\beta - 64} = 0.367$$

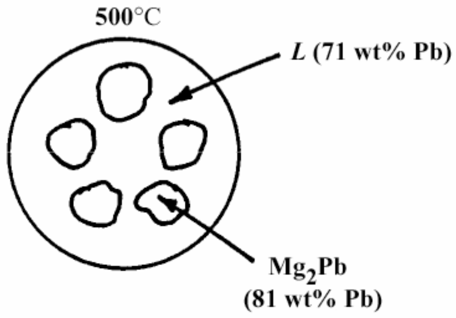
Thus, we have two simultaneous equations with C_0 and C_β as unknowns. Solving them for C_0 gives C_0 = 75 wt% B.

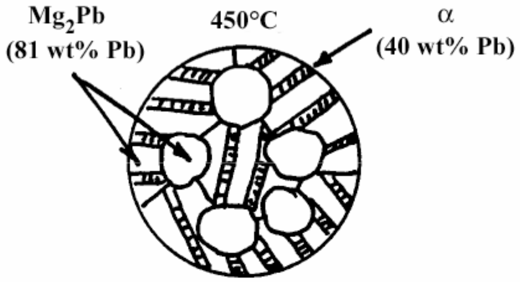
9.35 Schematic sketches of the microstructures that would be observed for an 64 wt% Zn-36 wt% Cu alloy at temperatures of 900°C, 820°C, 750°C, and 600°C are shown below. The phase compositions are also indicated. (*Note:* it was necessary to use the Cu-Zn phase diagram, Figure 9.19, in constructing these sketches.)

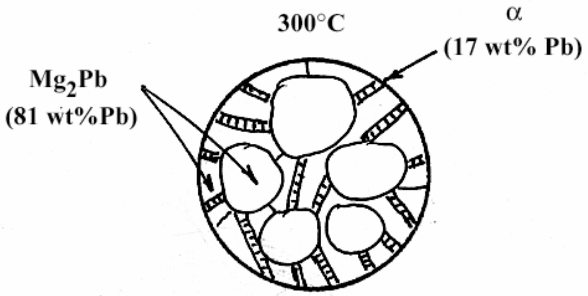


9.36 Schematic sketches of the microstructures that would be observed for a 76 wt% Pb-24 wt% Mg alloy at temperatures of 575°C, 500°C, 450°C, and 300°C are shown below. The phase compositions are also indicated. (*Note:* it was necessary to use the Mg-Pb phase diagram, Figure 9.20, in constructing these sketches.)

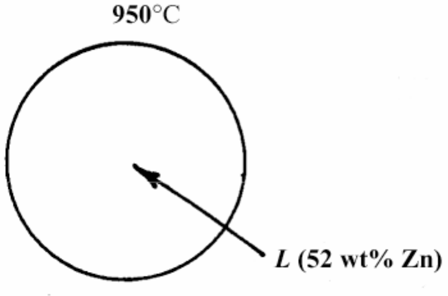


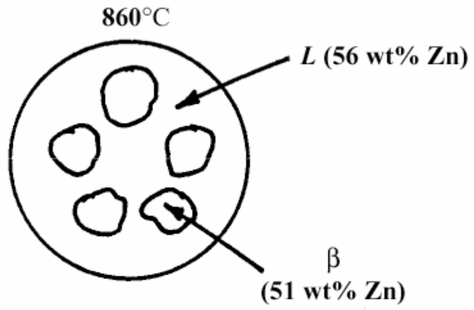


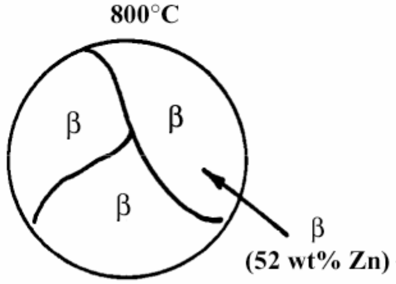


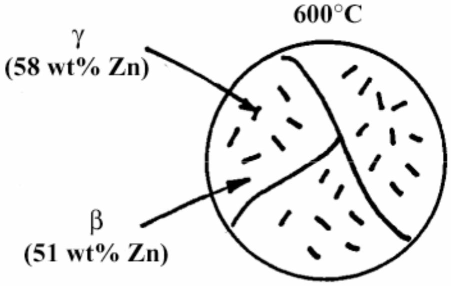


9.37 Schematic sketches of the microstructures that would be observed for a 52 wt% Zn-48 wt% Cu alloy at temperatures of 950°C, 860°C, 800°C, and 600°C are shown below. The phase compositions are also indicated. (*Note:* it was necessary to use the Cu-Zn phase diagram, Figure 9.19, in constructing these sketches.)

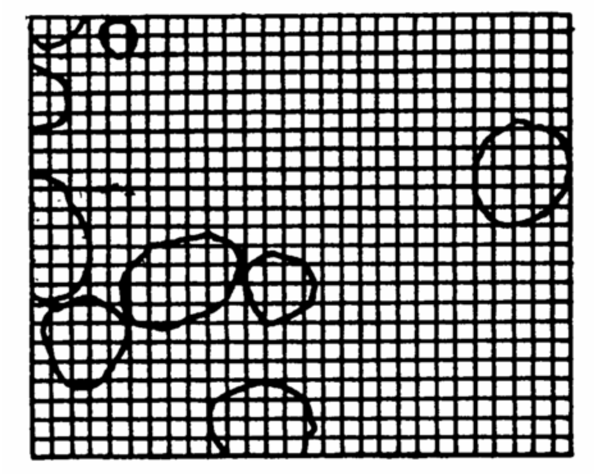








9.38 We are asked in this problem to estimate the composition of the Pb-Sn alloy which microstructure is shown in Figure 9.17. Primary α and eutectic microconstituents are present in the photomicrograph, and it is given that their densities are 11.2 and 8.7 g/cm^3, respectively. Below is shown a square grid network onto which is superimposed outlines of the primary α phase areas.



The area fraction of this primary α phase may be determined by counting squares. There are a total of 644 squares, and of these, approximately 104 lie within the primary α phase particles. Thus, the area fraction of primary α is 104/644 = 0.16, which is also assumed to be the volume fraction.

We now want to convert the volume fractions into mass fractions in order to employ the lever rule to the Pb-Sn phase diagram. To do this, it is necessary to utilize Equations 9.7a and 9.7b as follows:

$$W_{\alpha'} = \frac{V_{\alpha'}\,\rho_{\alpha'}}{V_{\alpha'}\,\rho_{\alpha'} + V_{\text{eutectic}}\,\rho_{\text{eutectic}}}$$

$$= \frac{(0.16)\left(11.2\ \text{g/cm}^3\right)}{(0.16)\left(11.2\ \text{g/cm}^3\right) + (0.84)\left(8.7\ \text{g/cm}^3\right)} = 0.197$$

$$W_{\text{eutectic}} = \frac{V_{\text{eutectic}}\,\rho_{\text{eutectic}}}{V_{\alpha\tilde{O}}\rho_{\alpha\tilde{O}} + V_{\text{eutectic}}\,\rho_{\text{eutectic}}}$$

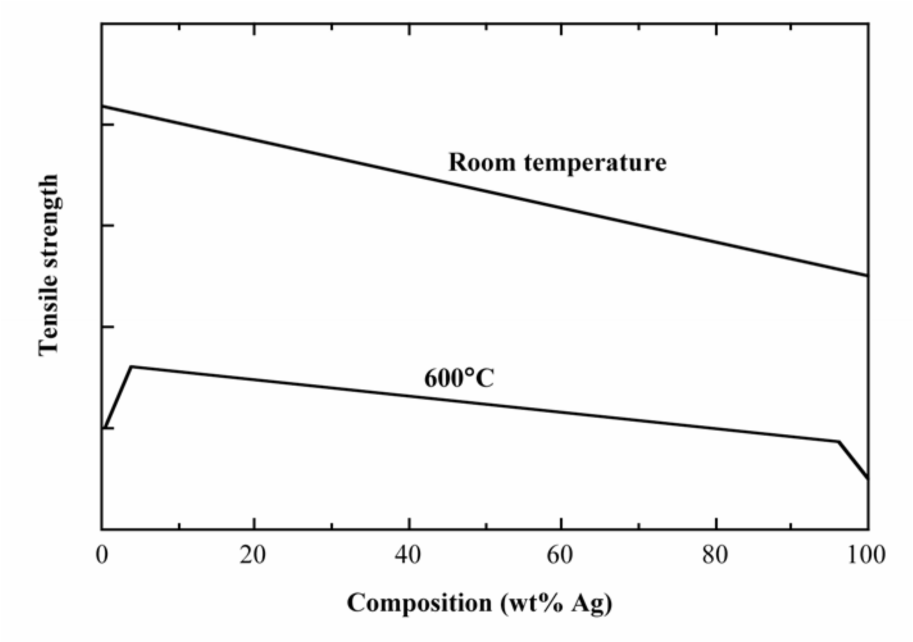
$$= \frac{(0.84)\left(8.7\ \text{g/cm}^3\right)}{(0.16)\left(11.2\ \text{g/cm}^3\right) + (0.84)\left(8.7\ \text{g/cm}^3\right)} = 0.803$$

From Figure 9.8, we want to use the lever rule and a tie-line that extends from the eutectic composition (61.9 wt% Sn) to the α–(α + β) phase boundary at 180°C (about 18.3 wt% Sn). Accordingly

$$W_{\alpha'} = 0.197 = \frac{61.9 - C_0}{61.9 - 18.3}$$

wherein C_0 is the alloy composition (in wt% Sn). Solving for C_0 yields C_0 = 53.3 wt% Sn. This value is in good agreement with the actual composition—viz. 50 wt% Sn.

9.39 The (a) and (b) portions of the problem ask that we make schematic plots on the same graph for the tensile strength versus composition for copper-silver alloys at both room temperature and 600°C; such a graph is shown below.



(c) Upon consultation of the Cu-Ag phase diagram (Figure 9.7) we note that silver is virtually insoluble in copper (i.e., there is no α-phase region at the left extremity of the phase diagram); the same may be said the solubility of copper in silver and for the β phase. Thus, only the α and β phase will exist for all compositions at room temperature; in other words, there will be no solid-solution strengthening effects at room temperature. All other things being equal, the tensile strength will depend (approximately) on the tensile strengths of each of the α and β phases as well as their phase fractions in a manner described by Equation 9.24 for the elastic modulus (Problem 9.64). That is, for this problem

$$(TS)_{\text{alloy}} \cong (TS)_\alpha V_\alpha + (TS)_\beta V_\beta$$

in which TS and V denote tensile strength and volume fraction, respectively, and the subscripts represent the alloy/phases. Also, mass fractions of the α and β phases change linearly with changing composition (according to the lever rule). Furthermore, inasmuch as the densities of both Cu and Ag are similar, weight and volume fractions of the α and β phases will also be similar (see Equation 9.6). In summary, the previous discussion explains the linear dependence of the room temperature tensile strength on composition as represented in the above plot given that the TS of pure copper is greater than for pure silver (as stipulated in the problem statement).

At 600°C, the curve will be shifted to significantly lower tensile strengths inasmuch as tensile strength diminishes with increasing temperature (Section 6.6, Figure 6.14). In addition, according to Figure 9.7, about 4 wt% of silver will dissolve in copper (i.e., in the α phase), and about 4 wt% of copper will dissolve in silver (i.e., in the β phase). Therefore, solid-solution strengthening will occur over these compositions ranges, as noted in the graph shown above. Furthermore, between 4% Ag and 96% Ag, the curve will be approximately linear for the same reasons noted in the previous paragraph.

Equilibrium Diagrams Having Intermediate Phases or Compounds

9.40 This problem gives us the compositions in weight percent for the two intermetallic compounds A_3B and AB_3, and then asks us to identify element B if element A is zirconium. Probably the easiest way to solve this problem is to first compute the ratio of the atomic weights of these two elements using Equation 4.6a; then, since we know the atomic weight of zirconium (91.22 g/mol), it is possible to determine the atomic weight of element B, from which an identification may be made.

First of all, consider the A_3B intermetallic compound; inasmuch as it contains three times the number of A atoms than and B atoms, its composition in atomic percent is 75 at% A-25 at% B. Equation 4.6a may be written in the form:

$$C_B' = 25 \text{ at\%} = \frac{C_B A_A}{C_A A_B + C_B A_A} \times 100$$

where A_A and A_B are the atomic weights for elements A and B, and C_A and C_B are their compositions in weight percent. For this A_3B compound, and making the appropriate substitutions in the above equation leads to

$$25 \text{ at\% B} = \frac{(9.0 \text{ wt\% B})(A_A)}{(91.0 \text{ wt\% A})(A_B) + (9.0 \text{ wt\% B})(A_A)} \times 100$$

Now, solving this expression yields,

$$A_B = 0.297\, A_A$$

Since zirconium is element A and it has an atomic weight of 91.22 g/mol, the atomic weight of element B is just

$$A_B = (0.297)(91.22 \text{ g/mol}) = 27.09 \text{ g/mol}$$

Upon consultation of the period table of the elements (Figure 2.6) we note the element that has an atomic weight closest to this value is aluminum (26.98 g/mol). Therefore, element B is aluminum, and the two intermetallic compounds are Zr_3Al and $ZrAl_3$.

Congruent Phase Transformations

Eutectoid and Peritectic Reactions

9.41 The principal difference between congruent and incongruent phase transformations is that for congruent no compositional changes occur with any of the phases that are involved in the transformation. For incongruent there will be compositional alterations of the phases.

9.42 In this problem we are asked to specify temperature-composition points for all eutectics, eutectoids, peritectics, and congruent phase transformations for the tin-gold system (Figure 9.36).

There are two eutectics on this phase diagram. One exists at 10 wt% Au-90 wt% Sn and 217°C. The reaction upon cooling is

$$L \rightarrow \alpha + \beta$$

The other eutectic exists at 80 wt% Au-20 wt% Sn and 280°C. This reaction upon cooling is

$$L \rightarrow \delta + \zeta$$

There are three peritectics. One exists at 30 wt% Au-70 wt% Sn and 252°C. Its reaction upon cooling is as follows:

$$L + \gamma \rightarrow \beta$$

The second peritectic exists at 45 wt% Au-55 wt% Sn and 309°C. This reaction upon cooling is

$$L + \delta \rightarrow \gamma$$

The third peritectic exists at 92 wt% Au-8 wt% Sn and 490°C. This reaction upon cooling is

$$L + \eta \rightarrow \zeta$$

There is one congruent melting point at 62.5 wt% Au-37.5 wt% Sn and 418°C. Its reaction upon cooling is

$$L \rightarrow \delta$$

No eutectoids are present.

9.43 In this problem we are asked to specify temperature-composition points for all eutectics, eutectoids, peritectics, and congruent phase transformations for a portion of the aluminum-copper phase diagram (Figure 9.37).

There is one eutectic on this phase diagram, which exists at 8.3 wt% Al-91.7 wt% Cu and 1036°C. Its reaction upon cooling is

$$L \rightarrow \alpha + \beta$$

There are four eutectoids for this system. One exists at 11.8 wt% Al-88.2 wt% Cu and 565°C. This reaction upon cooling is

$$\beta \rightarrow \alpha + \gamma_2$$

Another eutectoid exists at 15.4 wt% Al-84.6 wt% Cu and 964°C. For cooling the reaction is

$$\chi \rightarrow \beta + \gamma_1$$

A third eutectoid exists at 15.5 wt% Al-84.5 wt% Cu and 786°C. For cooling the reaction is

$$\gamma_1 \rightarrow \beta + \gamma_2$$

The other eutectoid exists at 23.5 wt% Al-76.5 wt% Cu and 560°C. For cooling the reaction is

$$\varepsilon_2 \rightarrow \delta + \zeta_1$$

There are four peritectics on this phase diagram. One exists at 15.3 wt% Al-84.7 wt% Cu and 1037°C. The reaction upon cooling is

$$\beta + L \rightarrow \chi$$

Another peritectic exists at 17 wt% Al-83 wt% Cu and 1021°C. It's cooling reaction is

$$\chi + L \rightarrow \gamma_1$$

Another peritectic exists at 20.5 wt% Al-79.5 wt% Cu and 961°C. The reaction upon cooling is

$$\gamma_1 + L \rightarrow \varepsilon_1$$

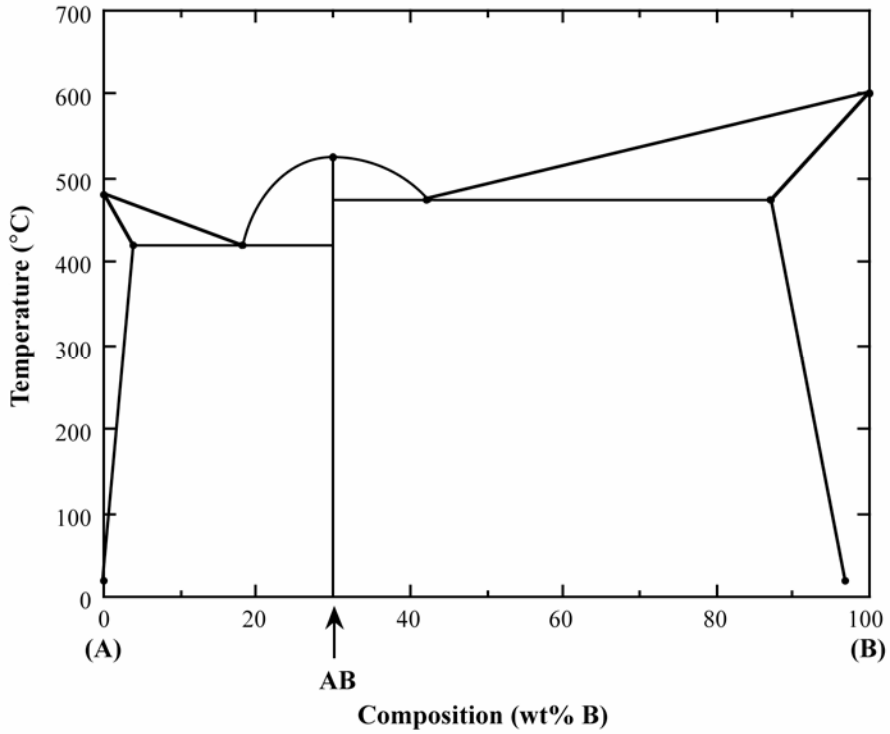
Another peritectic exists at 28.4 wt% Al-71.6 wt% Cu and 626°C. The reaction upon cooling is

$$\varepsilon_2 + L \rightarrow \eta_1$$

There is a single congruent melting point that exists at 12.5 wt% Al-87.5 wt% Cu and 1049°C. The reaction upon cooling is

$$L \rightarrow \beta$$

9.44 Below is shown the phase diagram for these two A and B metals.



The Gibbs Phase Rule

9.45 We are asked to specify the value of F for Gibbs phase rule at points A, B, and C on the pressure-temperature diagram for H_2O (Figure 9.38). Gibbs phase rule in general form is

$$P + F = C + N$$

For this system, the number of components, C, is 1, whereas N, the number of noncompositional variables, is 2--viz. temperature and pressure. Thus, the phase rule now becomes

$$P + F = 1 + 2 = 3$$

Or

$$F = 3 - P$$

where P is the number of phases present at equilibrium.

At point A, only a single (liquid) phase is present (i.e., $P = 1$), or

$$F = 3 - P = 3 - 1 = 2$$

which means that both temperature and pressure are necessary to define the system.

At point B which is on the phase boundary between liquid and vapor phases, two phases are in equilibrium ($P = 2$); hence

$$F = 3 - P = 3 - 2 = 1$$

Or that we need to specify the value of either temperature or pressure, which determines the value of the other (pressure or temperature).

And, finally, at point C, three phases are present—viz. ice I, vapor, and liquid—and the number of degrees of freedom is zero since

$$F = 3 - P = 3 - 3 = 0$$

Thus, point C is an invariant point (in this case a triple point), and we have no choice in the selection of externally controllable variables in order to define the system.

The Iron-Iron Carbide (Fe-Fe_3C) Phase Diagram

Development of Microstructure in Iron-Carbon Alloys

9.46 This problem asks that we compute the mass fractions of α ferrite and cementite in pearlite. The lever-rule expression for ferrite is

$$W_\alpha = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha}$$

and, since C_{Fe_3C} = 6.70 wt% C, C_0 = 0.76 wt% C, and C_α = 0.022 wt% C

$$W_\alpha = \frac{6.70 - 0.76}{6.70 - 0.022} = 0.89$$

Similarly, for cementite

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{0.76 - 0.022}{6.70 - 0.022} = 0.11$$

9.47 (a) A “hypoeutectoid” steel has a carbon concentration less than the eutectoid; on the other hand, a “hypereutectoid” steel has a carbon content greater than the eutectoid.

(b) For a hypoeutectoid steel, the proeutectoid ferrite is a microconstituent that formed above the eutectoid temperature. The eutectoid ferrite is one of the constituents of pearlite that formed at a temperature below the eutectoid. The carbon concentration for both ferrites is 0.022 wt% C.

9.48 This problem asks that we compute the carbon concentration of an iron-carbon alloy for which the fraction of total cementite is 0.10. Application of the lever rule (of the form of Equation 9.12) yields

$$W_\alpha = 0.10 = \frac{C_0' - C_\alpha}{C_{\mathrm{Fe_3C}} - C_\alpha} = \frac{C_0' - 0.022}{6.70 - 0.022}$$

and solving for C_0'

$$C_0' = 0.69 \text{ wt\% C}$$

9.49 In this problem we are given values of W_α and $W_{\mathrm{Fe_3C}}$ (0.86 and 0.14, respectively) for an iron-carbon alloy and then are asked to specify the proeutectoid phase. Employment of the lever rule for total α leads to

$$W_\alpha = 0.86 = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_\alpha} = \frac{6.70 - C_0}{6.70 - 0.022}$$

Now, solving for C_0, the alloy composition, leads to C_0 = 0.96 wt% C. Therefore, the proeutectoid phase is $\mathrm{Fe_3C}$ since C_0 is greater than 0.76 wt% C.

9.50 This problem asks us to consider various aspects of 3.5 kg of austenite containing 0.95 wt% C that is cooled to below the eutectoid.

(a) The proeutectoid phase will be Fe_3C since 0.95 wt% C is greater than the eutectoid composition (0.76 wt% C).

(b) For this portion of the problem, we are asked to determine how much total ferrite and cementite form. Application of the appropriate lever rule expression yields

$$W_\alpha = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha} = \frac{6.70 - 0.95}{6.70 - 0.022} = 0.86$$

which, when multiplied by the total mass of the alloy, gives (0.86)(3.5 kg) = 3.01 kg of total ferrite.

Similarly, for total cementite,

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{0.95 - 0.022}{6.70 - 0.022} = 0.14$$

And the mass of total cementite that forms is (0.14)(3.5 kg) = 0.49 kg.

(c) Now we are asked to calculate how much pearlite and the proeutectoid phase (cementite) form. Applying Equation 9.22, in which $C_1' = 0.95$ wt% C

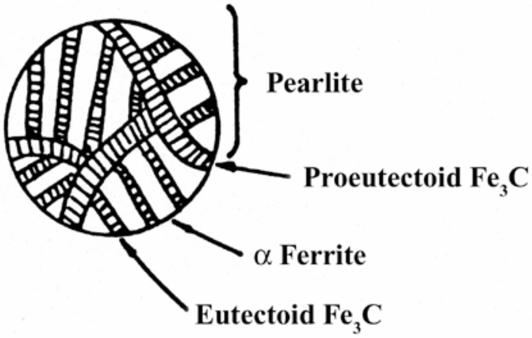
$$W_p = \frac{6.70 - C_1'}{6.70 - 0.76} = \frac{6.70 - 0.95}{6.70 - 0.76} = 0.97$$

which corresponds to a mass of (0.97)(3.5 kg) = 3.4 kg. Likewise, from Equation 9.23

$$W_{Fe_3C'} = \frac{C_1' - 0.76}{5.94} = \frac{0.95 - 0.76}{5.94} = 0.03$$

which is equivalent to (0.03)(3.5 kg) = 0.11 kg of the total 3.5 kg mass.

(d) Schematically, the microstructure would appear as:


Pearlite
Proeutectoid Fe_3C
α Ferrite
Eutectoid Fe_3C

9.51 We are called upon to consider various aspects of 6.0 kg of austenite containing 0.45 wt% C, that is cooled to below the eutectoid.

(a) Ferrite is the proeutectoid phase since 0.45 wt% C is less than 0.76 wt% C.

(b) For this portion of the problem, we are asked to determine how much total ferrite and cementite form. For ferrite, application of the appropriate lever rule expression yields

$$W_\alpha = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_\alpha} = \frac{6.70 - 0.45}{6.70 - 0.022} = 0.94$$

which corresponds to (0.94)(6.0 kg) = 5.64 kg of total ferrite.

Similarly, for total cementite,

$$W_{\mathrm{Fe_3C}} = \frac{C_0 - C_\alpha}{C_{\mathrm{Fe_3C}} - C_\alpha} = \frac{0.45 - 0.022}{6.70 - 0.022} = 0.06$$

Or (0.06)(6.0 kg) = 0.36 kg of total cementite form.

(c) Now consider the amounts of pearlite and proeutectoid ferrite. Using Equation 9.20

$$W_\mathrm{p} = \frac{C_0' - 0.022}{0.74} = \frac{0.45 - 0.022}{0.74} = 0.58$$

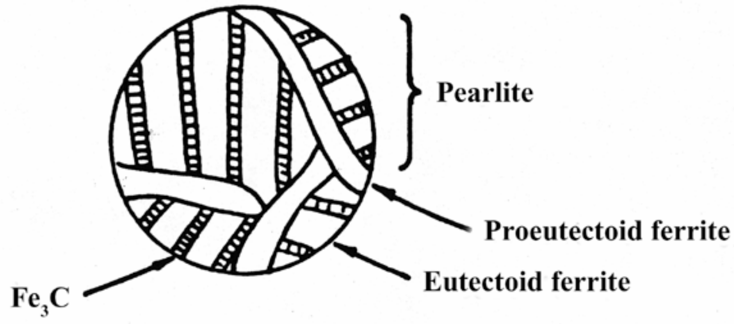
This corresponds to (0.58)(6.0 kg) = 3.48 kg of pearlite.

Also, from Equation 9.21,

$$W_{\alpha'} = \frac{0.76 - 0.45}{0.74} = 0.42$$

Or, there are (0.42)(6.0 kg) = 2.52 kg of proeutectoid ferrite.

(d) Schematically, the microstructure would appear as:


Pearlite
Proeutectoid ferrite
Eutectoid ferrite
Fe$_3$C

9.52 The mass fractions of proeutectoid ferrite and pearlite that form in a 0.35 wt% C iron-carbon alloy are considered in this problem. From Equation 9.20

$$W_p = \frac{C_0' - 0.022}{0.74} = \frac{0.35 - 0.022}{0.74} = 0.44$$

And, from Equation 9.21 (for proeutectoid ferrite)

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.35}{0.74} = 0.56$$

9.53 This problem asks that we determine the carbon concentration in an iron-carbon alloy, given the mass fractions of proeutectoid ferrite and pearlite. From Equation 9.20

$$W_\text{p} = 0.826 = \frac{C_0' - 0.022}{0.74}$$

which yields C_0' = 0.63 wt% C.

9.54 In this problem we are given values of W_α and $W_{\text{Fe}_3\text{C}}$ for an iron-carbon alloy (0.91 and 0.09, respectively), and then are asked to specify whether the alloy is hypoeutectoid or hypereutectoid. Employment of the lever rule for total α leads to

$$W_\alpha = 0.91 = \frac{C_{\text{Fe}_3\text{C}} - C_0}{C_{\text{Fe}_3\text{C}} - C_\alpha} = \frac{6.70 - C_0}{6.70 - 0.022}$$

Now, solving for C_0, the alloy composition, leads to C_0 = 0.62 wt% C. Therefore, the alloy is hypoeutectoid since C_0 is less than 0.76 wt% C.

9.55 We are asked in this problem to determine the concentration of carbon in an alloy for which $W_{Fe_3C'}$ = 0.11 and W_p = 0.89. If we let $C_1^{'}$ equal the carbon concentration in the alloy, employment of the appropriate lever rule expression, Equation 9.22, leads to

$$W_p = \frac{6.7 - C_1^{'}}{6.7 - 0.76} = 0.89$$

Solving for $C_1^{'}$ yields $C_1^{'}$ = 1.41 wt% C.

9.56 In this problem we are asked to consider 1.5 kg of a 99.7 wt% Fe-0.3 wt% C alloy that is cooled to a temperature below the eutectoid.

(a) Equation 9.21 must be used in computing the amount of proeutectoid ferrite that forms. Thus,

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.30}{0.74} = 0.622$$

Or, (0.622)(1.5 kg) = 0.933 kg of proeutectoid ferrite forms.

(b) In order to determine the amount of eutectoid ferrite, it first becomes necessary to compute the amount of total ferrite using the lever rule applied entirely across the $\alpha + Fe_3C$ phase field, as

$$W_{\alpha} = \frac{C_{Fe_3C} - C_0'}{C_{Fe_3C} - C_{\alpha}} = \frac{6.70 - 0.30}{6.70 - 0.022} = 0.958$$

which corresponds to (0.958)(1.5 kg) = 1.437 kg. Now, the amount of eutectoid ferrite is just the difference between total and proeutectoid ferrites, or

$$1.437 \text{ kg} - 0.933 \text{ kg} = 0.504 \text{ kg}$$

(c) With regard to the amount of cementite that forms, again application of the lever rule across the entirety of the $\alpha + Fe_3C$ phase field, leads to

$$W_{Fe_3C} = \frac{C_0' - C_{\alpha}}{C_{Fe_3C} - C_{\alpha}} = \frac{0.30 - 0.022}{6.70 - 0.022} = 0.042$$

which amounts to (0.042)(1.5 kg) = 0.063 kg cementite in the alloy.

9.57 This problem asks that we compute the maximum mass fraction of proeutectoid cementite possible for a hypereutectoid iron-carbon alloy. This requires that we utilize Equation 9.23 with $C_1^{'}$ = 2.14 wt% C, the maximum solubility of carbon in austenite. Thus,

$$W_{\mathrm{Fe_3C'}} = \frac{C_1^{'} - 0.76}{5.94} = \frac{2.14 - 0.76}{5.94} = 0.232$$

9.58 This problem asks if it is possible to have an iron-carbon alloy for which W_{Fe_3C} = 0.057 and $W_{\alpha'}$ = 0.36. In order to make this determination, it is necessary to set up lever rule expressions for these two mass fractions in terms of the alloy composition, then to solve for the alloy composition of each; if both alloy composition values are equal, then such an alloy is possible. The lever-rule expression for the mass fraction of total cementite is

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{C_0 - 0.022}{6.70 - 0.022} = 0.057$$

Solving for this C_0 yields C_0 = 0.40 wt% C. Now for $W_{\alpha'}$ we utilize Equation 9.21 as

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = 0.36$$

This expression leads to C_0' = 0.49 wt% C. And, since C_0 and C_0' are different this alloy is *not* possible.

9.59 This problem asks if it is possible to have an iron-carbon alloy for which W_α = 0.860 and W_p = 0.969. In order to make this determination, it is necessary to set up lever rule expressions for these two mass fractions in terms of the alloy composition, then to solve for the alloy composition of each; if both alloy composition values are equal, then such an alloy is possible. The lever-rule expression for the mass fraction of total ferrite is

$$W_\alpha = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha} = \frac{6.70 - C_0}{6.70 - 0.022} = 0.860$$

Solving for this C_0 yields C_0 = 0.95 wt% C. Therefore, this alloy is hypereutectoid since C_0 is greater than the eutectoid composition (0.76 wt%). Thus, it is necessary to use Equation 9.22 for W_p as

$$W_p = \frac{6.70 - C_1'}{5.94} = 0.969$$

This expression leads to C_1' = 0.95 wt% C. Since $C_0 = C_1'$, this alloy *is* possible.

9.60 This problem asks that we compute the mass fraction of eutectoid cementite in an iron-carbon alloy that contains 1.00 wt% C. In order to solve this problem it is necessary to compute mass fractions of total and proeutectoid cementites, and then to subtract the latter from the former. To calculate the mass fraction of total cementite, it is necessary to use the lever rule and a tie line that extends across the entire α + Fe_3C phase field as

$$W_{\mathrm{Fe_3C}} = \frac{C_0 - C_\alpha}{C_{\mathrm{Fe_3C}} - C_\alpha} = \frac{1.00 - 0.022}{6.70 - 0.022} = 0.146$$

Now, for the mass fraction of proeutectoid cementite we use Equation 9.23

$$W_{\mathrm{Fe_3C'}} = \frac{C_1' - 0.76}{5.94} = \frac{1.00 - 0.76}{5.94} = 0.040$$

And, finally, the mass fraction of eutectoid cementite $W_{\mathrm{Fe_3C''}}$ is just

$$W_{\mathrm{Fe_3C''}} = W_{\mathrm{Fe_3C}} - W_{\mathrm{Fe_3C'}} = 0.146 - 0.040 = 0.106$$

9.61 This problem asks whether or not it is possible to determine the composition of an iron-carbon alloy for which the mass fraction of eutectoid cementite is 0.109; and if so, to calculate the composition. Yes, it is possible to determine the alloy composition; and, in fact, there are two possible answers. For the first, the eutectoid cementite exists in addition to proeutectoid cementite. For this case the mass fraction of eutectoid cementite ($W_{Fe_3C''}$) is just the difference between total cementite and proeutectoid cementite mass fractions; that is

$$W_{Fe_3C''} = W_{Fe_3C} - W_{Fe_3C'}$$

Now, it is possible to write expressions for W_{Fe_3C} (of the form of Equation 9.12) and $W_{Fe_3C'}$ (Equation 9.23) in terms of C_0, the alloy composition. Thus,

$$W_{Fe_3C''} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} - \frac{C_0 - 0.76}{5.94}$$

$$= \frac{C_0 - 0.022}{6.70 - 0.022} - \frac{C_0 - 0.76}{5.94} = 0.109$$

And, solving for C_0 yields C_0 = 0.84 wt% C.

For the second possibility, we have a hypoeutectoid alloy wherein all of the cementite is eutectoid cementite. Thus, it is necessary to set up a lever rule expression wherein the mass fraction of total cementite is 0.109. Therefore,

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{C_0 - 0.022}{6.70 - 0.022} = 0.109$$

And, solving for C_0 yields C_0 = 0.75 wt% C.

9.62 This problem asks whether or not it is possible to determine the composition of an iron-carbon alloy for which the mass fraction of eutectoid ferrite is 0.71; and if so, to calculate the composition. Yes, it is possible to determine the alloy composition; and, in fact, there are two possible answers. For the first, the eutectoid ferrite exists in addition to proeutectoid ferrite (for a hypoeutectoid alloy). For this case the mass fraction of eutectoid ferrite ($W_{\alpha''}$) is just the difference between total ferrite and proeutectoid ferrite mass fractions; that is

$$W_{\alpha''} = W_{\alpha} - W_{\alpha'}$$

Now, it is possible to write expressions for W_{α} (of the form of Equation 9.12) and $W_{\alpha'}$ (Equation 9.21) in terms of C_0, the alloy composition. Thus,

$$\mathrm{W}_{\alpha''} = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_{\alpha}} - \frac{0.76 - C_0}{0.74}$$

$$= \frac{6.70 - C_0}{6.70 - 0.022} - \frac{0.76 - C_0}{0.74} = 0.71$$

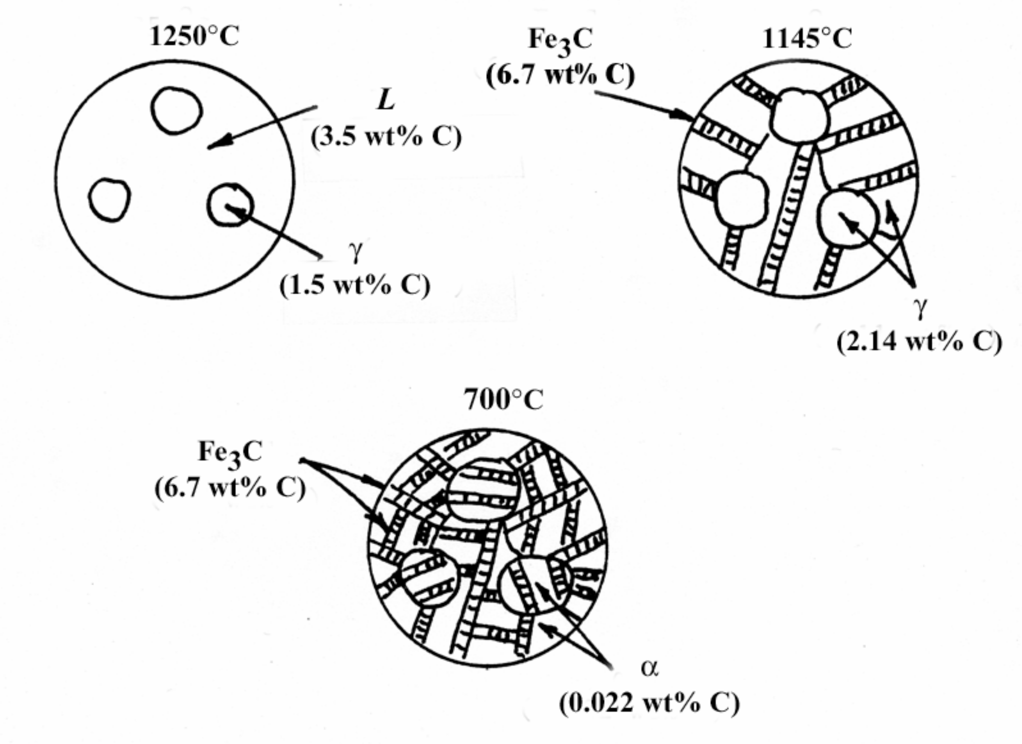
And, solving for C_0 yields C_0 = 0.61 wt% C.

For the second possibility, we have a hypereutectoid alloy wherein all of the ferrite is eutectoid ferrite. Thus, it is necessary to set up a lever rule expression wherein the mass fraction of total ferrite is 0.71. Therefore,

$$W_{\alpha} = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022} = 0.71$$

And, solving for C_0 yields C_0 = 1.96 wt% C.

9.63 Schematic microstructures for the iron-carbon alloy of composition 3 wt% C-97 wt% Fe and at temperatures of 1250°C, 1145°C, and 700°C are shown below; approximate phase compositions are also indicated. (*Note:* it was necessary to use the Fe-Fe_3C phase diagram, Figure 9.24, in constructing these sketches.)



9.64 This problem asks that we determine the approximate Brinell hardness of a 99.75 wt% Fe-0.25 wt% C alloy, using a relationship similar to Equation 9.24. First, we compute the mass fractions of pearlite and proeutectoid ferrite using Equations 9.20 and 9.21, as

$$W_p = \frac{C_0' - 0.022}{0.74} = \frac{0.25 - 0.022}{0.74} = 0.308$$

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.25}{0.74} = 0.689$$

Now, we compute the Brinell hardness of the alloy using a modified form of Equation 9.24 as

$$\mathrm{HB}_{\mathrm{alloy}} = \mathrm{HB}_{\alpha'} W_{\alpha'} + \mathrm{HB}_p W_p$$

$$= (80)(0.689) + (280)(0.308) = 141$$

The Influence of Other Alloying Elements

9.65 This problem asks us to consider an alloy of composition 95.7 wt% Fe, 4.0 wt% W, and 0.3 wt% C.

(a) From Figure 9.34, the eutectoid temperature for 4.0 wt% W is approximately 900°C.

(b) From Figure 9.35, the eutectoid composition is approximately 0.21 wt% C.

(c) Since the carbon concentration of the alloy (0.3 wt%) is greater than the eutectoid (0.21 wt% C), cementite is the proeutectoid phase.

9.66 We are asked to consider a steel alloy of composition 93.65 wt% Fe, 6.0 wt% Mn, and 0.35 wt% C.

(a) From Figure 9.34, the eutectoid temperature for 6.0 wt% Mn is approximately 700°C (1290°F).

(b) From Figure 9.35, the eutectoid composition is approximately 0.44 wt% C. Since the carbon concentration in the alloy (0.35 wt%) is less than the eutectoid (0.44 wt% C), the proeutectoid phase is ferrite.

(c) Assume that the α–(α + Fe_3C) phase boundary is at a negligible carbon concentration. Modifying Equation 9.21 leads to

$$W_{\alpha'} = \frac{0.44 - C_0'}{0.44 - 0} = \frac{0.44 - 0.35}{0.44} = 0.20$$

Likewise, using a modified Equation 9.20

$$W_p = \frac{C_0' - 0}{0.44 - 0} = \frac{0.35}{0.44} = 0.80$$

CHAPTER 10

PHASE TRANSFORMATIONS IN METALS

PROBLEM SOLUTIONS

The Kinetics of Phase Transformations

10.1 The two stages involved in the formation of particles of a new phase are *nucleation* and *growth*. The nucleation process involves the formation of normally very small particles of the new phase(s) which are stable and capable of continued growth. The growth stage is simply the increase in size of the new phase particles.

10.2 (a) This problem first asks that we rewrite the expression for the total free energy change for nucleation (analogous to Equation 10.1) for the case of a cubic nucleus of edge length a. The volume of such a cubic radius is a^3, whereas the total surface area is $6a^2$ (since there are six faces each of which has an area of a^2). Thus, the expression for ΔG is as follows:

$$\Delta G = a^3 \Delta G_v + 6a^2 \gamma$$

Differentiation of this expression with respect to a is as

$$\frac{d\,\Delta G}{da} = \frac{d\left(a^3 \Delta G_v\right)}{da} + \frac{d\left(6a^2 \gamma\right)}{da}$$

$$= 3a^2 \Delta G_v + 12a\gamma$$

If we set this expression equal to zero as

$$3a^2 \Delta G_v + 12a\gamma = 0$$

and then solve for a (= a^*), we have

$$a^* = -\frac{4\gamma}{\Delta G_v}$$

Substitution of this expression for a in the above expression for ΔG yields an equation for ΔG^* as

$$\Delta G^* = (a^*)^3 \Delta G_v + 6(a^*)^2 \gamma$$

$$= \left(-\frac{4\gamma}{\Delta G_v}\right)^3 \Delta G_v + 6\gamma\left(-\frac{4\gamma}{\Delta G_v}\right)^2$$

$$= \frac{32\gamma^3}{(\Delta G_v)^2}$$

(b) ΔG_v for a cube—i.e., $(32)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right]$—is greater that for a sphere—i.e., $\left(\frac{16\pi}{3}\right)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right]$ = $(16.8)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right]$. The reason for this is that surface-to-volume ratio of a cube is greater than for a sphere.

10.3 This problem states that ice homogeneously nucleates at –40°C, and that we are to calculate the critical radius given the latent heat of fusion (–3.1 x 10^8 J/m^3) and the surface free energy (25 x 10^{-3} J/m^2). Solution to this problem requires the utilization of Equation 10.6 as

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)\left(25 \text{ x } 10^{-3} \text{ J/m}^2\right)(273 \text{ K})}{-3.1 \text{ x } 10^{8} \text{ J/m}^3}\right]\left(\frac{1}{40 \text{ K}}\right)$$

$$= 1.10 \text{ x } 10^{-9} \text{ m} = 1.10 \text{ nm}$$

10.4 (a) This portion of the problem asks that we compute $r*$ and $\Delta G*$ for the homogeneous nucleation of the solidification of Ni. First of all, Equation 10.6 is used to compute the critical radius. The melting temperature for nickel, found inside the front cover is 1455°C; also values of ΔH_f (-2.53×10^9 J/m^3) and γ (0.255 J/m^2) are given in the problem statement, and the supercooling value found in Table 10.1 is 319°C (or 319 K). Thus, from Equation 10.6 we have

$$r* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)\left(0.255 \text{ J/m}^2\right)(1455 + 273 \text{ K})}{-2.53 \text{ x } 10^9 \text{ J/m}^3}\right]\left(\frac{1}{319 \text{ K}}\right)$$

$$= 1.09 \text{ x } 10^{-9} \text{ m} = 1.09 \text{ nm}$$

For computation of the activation free energy, Equation 10.7 is employed. Thus

$$\Delta G* = \left(\frac{16\,\pi\,\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2}$$

$$= \left[\frac{(16)(\pi)\left(0.255 \text{ J/m}^2\right)^3 (1455 + 273 \text{ K})^2}{(3)\left(-2.53 \text{ x } 10^9 \text{ J/m}^3\right)^2}\right]\left[\frac{1}{(319 \text{ K})^2}\right]$$

$$= 1.27 \text{ x } 10^{-18} \text{ J}$$

(b) In order to compute the number of atoms in a nucleus of critical size (assuming a spherical nucleus of radius $r*$), it is first necessary to determine the number of unit cells, which we then multiply by the number of atoms per unit cell. The number of unit cells found in this critical nucleus is just the ratio of critical nucleus and unit cell volumes. Inasmuch as nickel has the FCC crystal structure, its unit cell volume is just a^3 where a is the unit cell length (i.e., the lattice parameter); this value is 0.360 nm, as cited in the problem statement. Therefore, the number of unit cells found in a radius of critical size is just

$$\# \text{ unit cells/particle} = \frac{\frac{4}{3}\pi r*^3}{a^3}$$

$$= \frac{\left(\frac{4}{3}\right)(\pi)(1.09\ \text{nm})^3}{(0.360\ \text{nm})^3} = 116\ \text{unit cells}$$

Inasmuch as 4 atoms are associated with each FCC unit cell, the total number of atoms per critical nucleus is just

$$(116\ \text{unit cells/critical nucleus})(4\ \text{atoms/unit cell}) = 464\ \text{atoms/critical nucleus}$$

10.5 (a) For this part of the problem we are asked to calculate the critical radius for the solidification of nickel (per Problem 10.4), for 200 K and 300 K degrees of supercooling, and assuming that the there are 10^6 nuclei per meter cubed for homogeneous nucleation. In order to calculate the critical radii, we replace the $T_m - T$ term in Equation 10.6 by the degree of supercooling (denoted as ΔT) cited in the problem.

For 200 K supercooling,

$$r^*_{200} = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{\Delta T}\right)$$

$$= \left[-\frac{(2)\left(0.255\ \mathrm{J/m^2}\right)(1455 + 273\ \mathrm{K})}{-2.53 \times 10^{9}\ \mathrm{J/m^3}}\right]\left(\frac{1}{200\ \mathrm{K}}\right)$$

$$= 1.74 \times 10^{-9}\ \mathrm{m} = 1.74\ \mathrm{nm}$$

For 300 K supercooling,

$$r^*_{300} = \left[-\frac{(2)\left(0.255\ \mathrm{J/m^2}\right)(1455 + 273\ \mathrm{K})}{-2.53 \times 10^{9}\ \mathrm{J/m^3}}\right]\left(\frac{1}{300\ \mathrm{K}}\right)$$

$$= 1.16 \times 10^{-9}\ \mathrm{m} = 1.16\ \mathrm{nm}$$

In order to compute the number of stable nuclei that exist at 200 K and 300 K degrees of supercooling, it is necessary to use Equation 10.8. However, we must first determine the value of K_1 in Equation 10.8, which in turn requires that we calculate ΔG^* at the homogeneous nucleation temperature using Equation 10.7; this was done in Problem 10.4, and yielded a value of $\Delta G^* = 1.27 \times 10^{-18}$ J. Now for the computation of K_1, using the value of n^* for at the homogenous nucleation temperature (10^6 nuclei/m^3):

$$K_1 = \frac{n^*}{\exp\left(-\frac{\Delta G^*}{kT}\right)}$$

$$= \frac{10^6\ \mathrm{nuclei/m^3}}{\exp\left[-\frac{1.27 \times 10^{-18}\ \mathrm{J}}{\left(1.38 \times 10^{-23}\ \mathrm{J/atom-K}\right)(1455\ \mathrm{K} - 319\ \mathrm{K})}\right]}$$

$$= 1.52 \times 10^{41}\ \mathrm{nuclei/m^3}$$

Now for 200 K supercooling, it is first necessary to recalculate the value Δ*G** of using Equation 10.7, where, again, the $T_m - T$ term is replaced by the number of degrees of supercooling, denoted as Δ*T*, which in this case is 200 K. Thus

$$\Delta G^*_{200} = \left(\frac{16\,\pi\,\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(\Delta T)^2}$$

$$= \left[\frac{(16)(\pi)\left(0.255 \text{ J/m}^2\right)^3 (1455 + 273 \text{ K})^2}{(3)\left(-2.53 \text{ x } 10^9 \text{ J/m}^3\right)^2}\right]\left[\frac{1}{(200 \text{ K})^2}\right]$$

$$= 3.24 \text{ x } 10^{-18} \text{ J}$$

And, from Equation 10.8, the value of *n** is

$$n^*_{200} = K_1 \exp\left(-\frac{\Delta G^*_{200}}{kT}\right)$$

$$= \left(1.52 \text{ x } 10^{41} \text{ nuclei/m}^3\right) \exp\left[-\frac{3.24 \text{ x} 10^{-18} \text{ J}}{\left(1.38 \text{ x } 10^{-23} \text{ J/atom-K}\right)(1455 \text{ K} - 200 \text{ K})}\right]$$

$$= 8.60 \text{ x } 10^{-41} \text{ stable nuclei}$$

Now, for 300 K supercooling the value of Δ*G** is equal to

$$\Delta G^*_{300} = \left[\frac{(16)(\pi)\left(0.255 \text{ J/m}^2\right)^3 (1455 + 273 \text{ K})^2}{(3)\left(-2.53 \text{ x } 10^9 \text{ J/m}^3\right)^2}\right]\left[\frac{1}{(300 \text{ K})^2}\right]$$

$$= 1.44 \text{ x } 10^{-18} \text{ J}$$

from which we compute the number of stable nuclei at 300 K of supercooling as

$$n^*_{300} = K_1 \exp\left(-\frac{\Delta G^*_{300}}{kT}\right)$$

$$n^* = \left(1.52 \text{ x } 10^{41} \text{ nuclei/m}^3\right) \exp\left[-\frac{1.44 \text{ x} 10^{-18} \text{ J}}{\left(1.38 \text{ x } 10^{-23} \text{ J/atom}-\text{K}\right)(1455 \text{ K} - 300 \text{ K})}\right]$$

= 88 stable nuclei

(b) Relative to critical radius, *r** for 300 K supercooling is slightly smaller that for 200 K (1.16 nm versus 1.74 nm). [From Problem 10.4, the value of *r** at the homogeneous nucleation temperature (319 K) was 1.09 nm.] More significant, however, are the values of *n** at these two degrees of supercooling, which are dramatically different—8.60 x 10^{-41} stable nuclei at ΔT = 200 K, versus 88 stable nuclei at ΔT = 300 K!

10.6 This problem calls for us to compute the length of time required for a reaction to go to 90% completion. It first becomes necessary to solve for the parameter k in Equation 10.17. It is first necessary to manipulate this equation such that k is the dependent variable. We first rearrange Equation 10.17 as

$$\exp\left(-kt^{n}\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^{n} = \ln(1 - y)$$

Now solving for k gives

$$k = -\frac{\ln(1 - y)}{t^{n}}$$

And, from the problem statement, for $y = 0.25$ when $t = 125$ s and given that $n = 1.5$, the value of k is equal to

$$k = -\frac{\ln(1 - 0.25)}{(125 \text{ s})^{1.5}} = 2.06 \text{ x } 10^{-4}$$

We now want to manipulate Equation 10.17 such that t is the dependent variable. The above equation may be written in the form:

$$t^{n} = -\frac{\ln(1 - y)}{k}$$

And solving this expression for t leads to

$$t = \left[-\frac{\ln(1 - y)}{k}\right]^{1/n}$$

Now, using this equation and the value of k determined above, the time to 90% transformation completion is equal to

$$t = \left[-\frac{\ln(1 - 0.90)}{2.06 \text{ x } 10^{-4}}\right]^{1/1.5} = 500 \text{ s}$$

10.7 This problem asks that we compute the rate of some reaction given the values of *n* and *k* in Equation 10.17. Since the reaction rate is defined by Equation 10.18, it is first necessary to determine $t_{0.5}$, or the time necessary for the reaction to reach $y = 0.5$. We must first manipulate Equation 10.17 such that *t* is the dependent variable. We first rearrange Equation 10.17 as

$$\exp\left(-kt^n\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^n = \ln(1 - y)$$

which my be rearranged so as to read

$$t^n = -\frac{\ln\,(1 - y)}{k}$$

Now, solving for *t* from this expression leads to

$$t = \left[-\frac{\ln\,(1 - y)}{k}\right]^{1/n}$$

For $t_{0.5}$ this equation takes the form

$$t_{0.5} = \left[-\frac{\ln\,(1 - 0.5)}{k}\right]^{1/n}$$

And, incorporation of values for *n* and *k* given in the problem statement (2.0 and 5 x 10^{-4}, respectively), then

$$t_{0.5} = \left[-\frac{\ln\,(1 - 0.5)}{5 \text{ x } 10^{-4}}\right]^{1/2} = 37.23 \text{ s}$$

Now, the rate is computed using Equation 10.18 as

$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{37.23 \text{ s}} = 2.69 \text{ x } 10^{-2} \text{ s}^{-1}$$

10.8 This problem gives us the value of y (0.30) at some time t (100 min), and also the value of n (5.0) for the recrystallization of an alloy at some temperature, and then asks that we determine the rate of recrystallization at this same temperature. It is first necessary to calculate the value of k. We first rearrange Equation 10.17 as

$$\exp\left(-kt^n\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^n = \ln(1 - y)$$

Now solving for k gives

$$k = -\frac{\ln\,(1 - y)}{t^n}$$

which, using the values cited above for y, n, and t yields

$$k = -\frac{\ln\,(1 - 0.30)}{(100\ \text{min})^5} = 3.57 \times 10^{-11}$$

At this point we want to compute $t_{0.5}$, the value of t for $y = 0.5$, which means that it is necessary to establish a form of Equation 10.17 in which t is the dependent variable. From one of the above equations

$$t^n = -\frac{\ln\,(1 - y)}{k}$$

And solving this expression for t leads to

$$t = \left[-\frac{\ln\,(1 - y)}{k}\right]^{1/n}$$

For $t_{0.5}$, this equation takes the form

$$t_{0.5} = \left[-\frac{\ln\,(1 - 0.5)}{k}\right]^{1/n}$$

and incorporation of the value of k determined above, as well as the value of n cited in the problem statement (5.0), then $t_{0.5}$ is equal to

$$t_{0.5} = \left[-\frac{\ln\ (1\ -\ 0.5)}{3.57\ \ \mathrm{x}\ 10^{-11}} \right]^{1/5} = 114.2\ \ \mathrm{min}$$

Therefore, from Equation 10.18, the rate is just

$$\mathrm{rate} = \frac{1}{t_{0.5}} = \frac{1}{114.2\ \ \mathrm{min}} = 8.76\ \ \mathrm{x}\ 10^{-3}\ (\mathrm{min})^{-1}$$

10.9 For this problem, we are given, for the austenite-to-pearlite transformation, two values of y and two values of the corresponding times, and are asked to determine the time required for 95% of the austenite to transform to pearlite.

The first thing necessary is to set up two expressions of the form of Equation 10.17, and then to solve simultaneously for the values of n and k. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln\,(1 - y) = -kt^n$$

Or

$$-\ln\,(1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln\,k + n\,\ln t$$

which is the form of the equation that we will now use. Using values cited in the problem statement, the two equations are thus

$$\ln\left\{\ln\left[\frac{1}{1 - 0.2}\right]\right\} = \ln\,k + n\ln(280\text{ s})$$

$$\ln\left\{\ln\left[\frac{1}{1 - 0.6}\right]\right\} = \ln\,k + n\ln(425\text{ s})$$

Solving these two expressions simultaneously for n and k yields n = 3.385 and $k = 1.162 \times 10^{-9}$.

Now it becomes necessary to solve for the value of t at which y = 0.95. One of the above equations—viz

$$-\ln (1 - y) = kt^n$$

may be rewritten as

$$t^n = -\frac{\ln (1 - y)}{k}$$

And solving for t leads to

$$t = \left[-\frac{\ln (1 - y)}{k}\right]^{1/n}$$

Now incorporating into this expression values for n and k determined above, the time required for 95% austenite transformation is equal to

$$t = \left[-\frac{\ln (1 - 0.95)}{1.162 \times 10^{-9}}\right]^{1/3.385} = 603 \text{ s}$$

10.10 For this problem, we are given, for the recrystallization of aluminum, two values of y and two values of the corresponding times, and are asked to determine the fraction recrystallized after a total time of 116.8 min.

The first thing necessary is to set up two expressions of the form of Equation 10.17, and then to solve simultaneously for the values of n and k. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln\,(1 - y) = -kt^n$$

Or

$$-\ln\,(1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. The two equations are thus

$$\ln\left\{\ln\left[\frac{1}{1 - 0.30}\right]\right\} = \ln k + n \ln(95.2 \text{ min})$$

$$\ln\left\{\ln\left[\frac{1}{1 - 0.80}\right]\right\} = \ln k + n \ln(126.6 \text{ min})$$

Solving these two expressions simultaneously for n and k yields n = 5.286 and k = 1.239 x 10^{-11}.

Now it becomes necessary to solve for y when t = 116.8 min. Application of Equation 10.17 leads to

$$y = 1 - \exp\left(-kt^{n}\right)$$

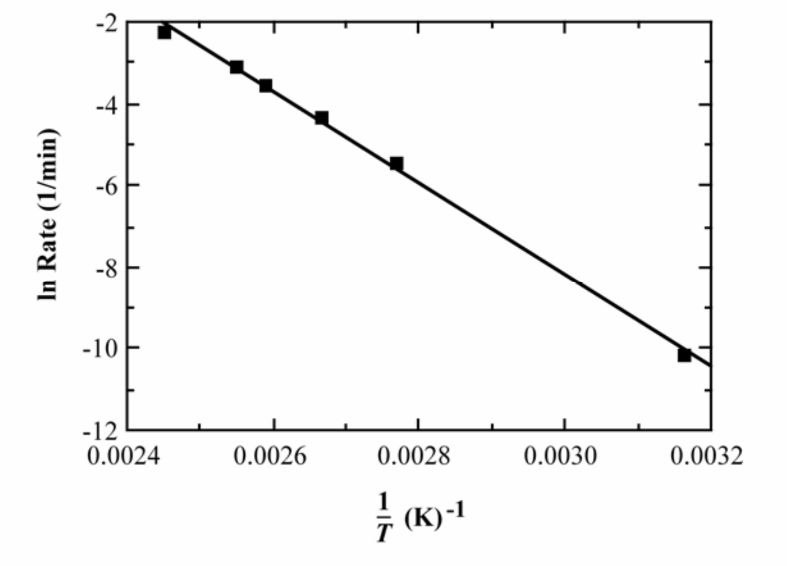
$$= 1 - \exp\left[-\left(1.239 \text{ x } 10^{-11}\right)\left(116.8 \text{ min}\right)^{5.286}\right] = 0.65$$

10.11 This problem asks us to consider the percent recrystallized versus logarithm of time curves for copper shown in Figure 10.11.

(a) The rates at the different temperatures are determined using Equation 10.18, which rates are tabulated below:

Temperature (°C)	Rate $(\text{min})^{-1}$
135	0.105
119	4.4×10^{-2}
113	2.9×10^{-2}
102	1.25×10^{-2}
88	4.2×10^{-3}
43	3.8×10^{-5}

(b) These data are plotted below.



The activation energy, Q, is related to the slope of the line drawn through the data points as

$$Q = -\text{Slope}\ (R)$$

where R is the gas constant. The slope of this line is equal to

$$\text{Slope} = \frac{\Delta \ln \text{rate}}{\Delta\left(\dfrac{1}{T}\right)} = \frac{\ln \text{ rate}_1 - \ln \text{ rate}_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

Let us take $1/T_1 = 0.0025\ \text{K}^{-1}$ and $1/T_2 = 0.0031\ \text{K}^{-1}$; the corresponding ln rate values are ln $\text{rate}_1 = -2.6$ and ln $\text{rate}_2 = -9.4$. Thus, using these values, the slope is equal to

$$\text{Slope} = \frac{-2.6 - (-9.4)}{0.0025\ \text{K}^{-1} - 0.0031\ \text{K}^{-1}} = -1.133 \text{ x } 10^4\ \text{K}$$

And, finally the activation energy is

$$Q = -\ (\text{Slope})(R) = -\left(-1.133 \text{ x } 10^4\ \text{K}^{-1}\right)(8.31\ \text{J/mol - K})$$

$$= 94{,}150 \text{ J/mol}$$

(c) At room temperature (20°C), $1/T = 1/(20 + 273\ \text{K}) = 3.41 \text{ x } 10^{-3}\ \text{K}^{-1}$. Extrapolation of the data in the plot to this $1/T$ value gives

$$\ln (\text{rate}) \cong -12.8$$

which leads to

$$\text{rate} \cong \exp(-12.8) = 2.76 \text{ x } 10^{-6}\ (\text{min})^{-1}$$

But since

$$\text{rate} = \frac{1}{t_{0.5}}$$

$$t_{0.5} = \frac{1}{\text{rate}} = \frac{1}{2.76 \text{ x } 10^{-6}\ (\text{min})^{-1}}$$

$$= 3.62 \text{ x } 10^5 \text{ min} = 250 \text{ days}$$

10.12 In this problem we are asked to determine, from Figure 10.11, the values of the constants *n* and *k* (Equation 10.17) for the recrystallization of copper at 119°C. One way to solve this problem is to take two values of percent recrystallization (which is just 100*y*, Equation 10.17) and their corresponding time values, then set up two simultaneous equations, from which *n* and *k* may be determined. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln\,(1 - y) = -kt^n$$

Or

$$-\ln\,(1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. From the 119°C curve of Figure 10.11, let us arbitrarily choose two percent recrystallized values, 20% and 80% (i.e., y_1 = 0.20 and y_2 = 0.80). Their corresponding time values are t_1 = 16.1 min and t_2 = 30.4 min (realizing that the time axis is scaled logarithmically). Thus, our two simultaneous equations become

$$\ln\left[\ln\left(\frac{1}{1 - 0.2}\right)\right] = \ln k + n \ln\,(16.1)$$

$$\ln\left[\ln\left(\frac{1}{1-0.8}\right)\right] = \ln k + n \ln (30.4)$$

from which we obtain the values $n = 3.11$ and $k = 3.9 \times 10^{-5}$.

Metastable Versus Equilibrium States

10.13 Two limitations of the iron-iron carbide phase diagram are:

(1) The nonequilibrium martensite does not appear on the diagram; and

(2) The diagram provides no indication as to the time-temperature relationships for the formation of pearlite, bainite, and spheroidite, all of which are composed of the equilibrium ferrite and cementite phases.

10.14 (a) Superheating and supercooling correspond, respectively, to heating or cooling above or below a phase transition temperature without the occurrence of the transformation.

(b) These phenomena occur because right at the phase transition temperature, the driving force is not sufficient to cause the transformation to occur. The driving force is enhanced during superheating or supercooling.

Isothermal Transformation Diagrams

10.15 We are called upon to consider the isothermal transformation of an iron-carbon alloy of eutectoid composition.

(a) From Figure 10.22, a horizontal line at 675°C intersects the 50% and reaction completion curves at about 80 and 300 seconds, respectively; these are the times asked for in the problem statement.

(b) The pearlite formed will be coarse pearlite. From Figure 10.30(a), the hardness of an alloy of composition 0.76 wt% C that consists of coarse pearlite is about 205 HB (93 HRB).

10.16 The microstructures of pearlite, bainite, and spheroidite all consist of α-ferrite and cementite phases. For pearlite, the two phases exist as layers which alternate with one another. Bainite consists of very fine and parallel needle-shaped particles of cementite that are surrounded an α-ferrite matrix. For spheroidite, the matrix is ferrite, and the cementite phase is in the shape of sphere-shaped particles.

Bainite is harder and stronger than pearlite, which, in turn, is harder and stronger than spheroidite.

10.17 The driving force for the formation of spheroidite is the net reduction in ferrite-cementite phase boundary area.

10.18 This problem asks us to determine the nature of the final microstructure of an iron-carbon alloy of eutectoid composition, that has been subjected to various isothermal heat treatments. Figure 10.22 is used in these determinations.

(a) 100% bainite

(b) 50% medium pearlite and 50% martensite

(c) 50% fine pearlite, 25% bainite, and 25% martensite

(d) 100% spheroidite

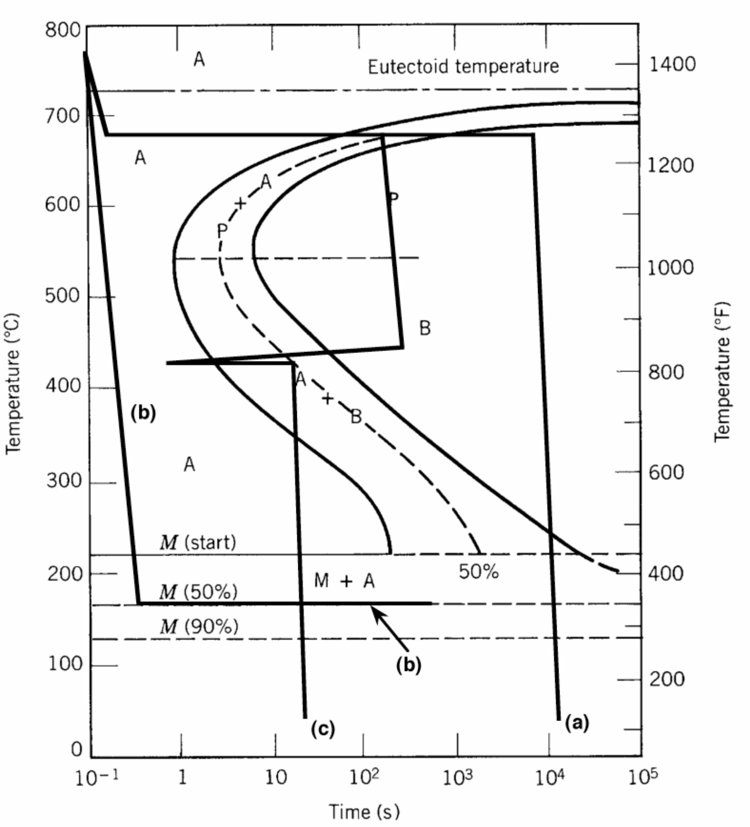
(e) 100% tempered martensite

(f) 100% coarse pearlite

(g) 100% fine pearlite

(h) 50% bainite and 50% martensite

10.19 Below is shown the isothermal transformation diagram for a eutectoid iron-carbon alloy, with time-temperature paths that will yield (a) 100% coarse pearlite; (b) 50% martensite and 50% austenite; and (c) 50% coarse pearlite, 25% bainite, and 25% martensite.



10.20 We are asked to determine which microconstituents are present in a 1.13 wt% C iron-carbon alloy that has been subjected to various isothermal heat treatments. These microconstituents are as follows:

(a) Martensite

(b) Proeutectoid cementite and martensite

(c) Bainite

(d) Spheroidite

(e) Cementite, medium pearlite, bainite, and martensite

(f) Bainite and martensite

(g) Proeutectoid cementite, pearlite, and martensite

(h) Proeutectoid cementite and fine pearlite

10.21 This problem asks us to determine the approximate percentages of the microconstituents that form for five of the heat treatments described in Problem 10.20.

(a) 100% martensite

(c) 100% bainite

(d) 100% spheroidite

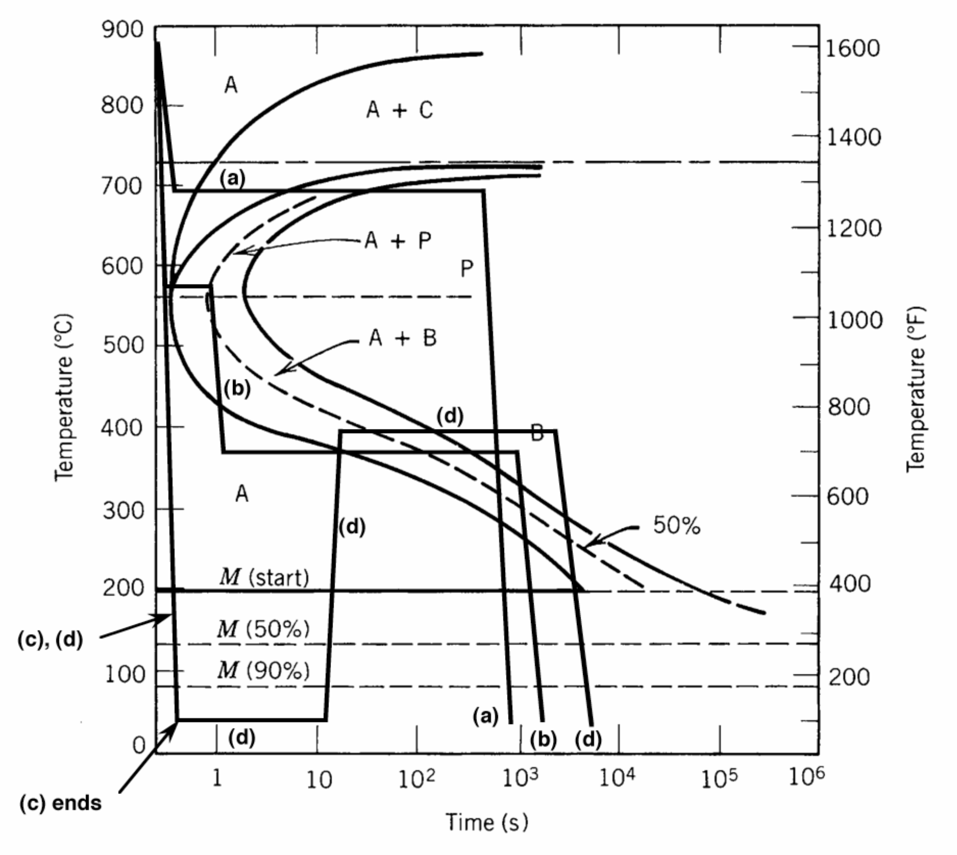
(f) 60% bainite and 40% martensite

(h) After holding for 7 s at 600°C, the specimen has completely transformed to proeutectoid cementite and fine pearlite; no further reaction will occur at 450°C. Therefore, we can calculate the mass fractions using the appropriate lever rule expressions, Equations 9.22 and 9.23, as follows:

$$W_{\mathrm{Fe_3C'}} = \frac{C_1' - 0.76}{5.94} = \frac{1.13 - 0.76}{5.94} = 0.062 \text{ or } 6.2\%$$

$$W_{\mathrm{p}} = \frac{6.70 - C_1'}{5.94} = \frac{6.70 - 1.13}{5.94} = 0.938 \text{ or } 93.8\%$$

10.22 Below is shown an isothermal transformation diagram for a 1.13 wt% C iron-carbon alloy, with time-temperature paths that will produce (a) 6.2% proeutectoid cementite and 93.8% coarse pearlite; (b) 50% fine pearlite and 50% bainite; (c) 100% martensite; and (d) 100% tempered martensite.



Continuous Cooling Transformation Diagrams

10.23 We are called upon to name the microstructural products that form for specimens of an iron-carbon alloy of eutectoid composition that are continuously cooled to room temperature at a variety of rates. Figure 10.27 is used in these determinations.

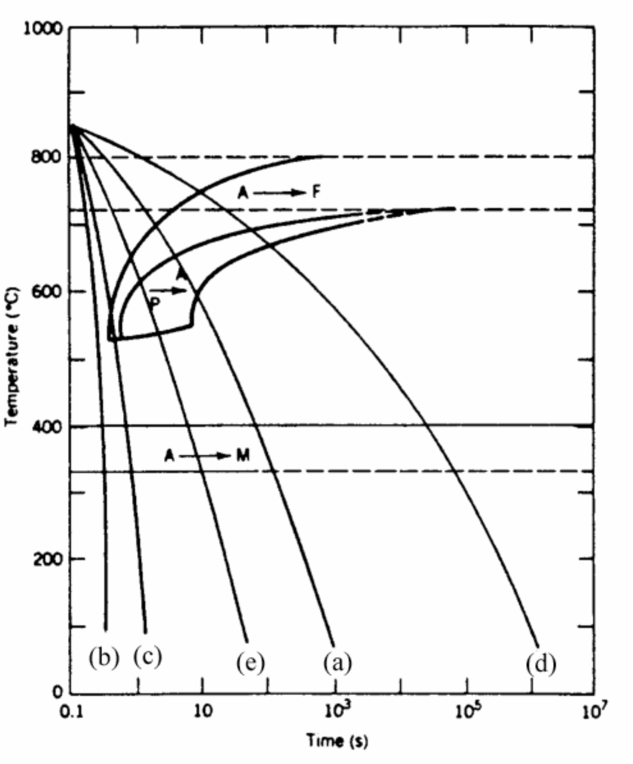
(a) At a rate of 1°C/s, coarse pearlite forms.

(b) At a rate of 20°C/s, fine pearlite forms.

(c) At a rate of 50°C/s, fine pearlite and martensite form.

(d) At a rate of 175ºC/s, martensite forms.

10.24 Below is shown a continuous cooling transformation diagram for a 0.35 wt% C iron-carbon alloy, with continuous cooling paths that will produce (a) fine pearlite and proeutectoid ferrite; (b) martensite; (c) martensite and proeutectoid ferrite; (d) coarse pearlite and proeutectoid ferrite; and (e) martensite, fine pearlite, and proeutectoid ferrite.



10.25 Two important differences between continuous cooling transformation diagrams for plain carbon and alloy steels are: (1) for an alloy steel, a bainite nose will be present, which nose will be absent for plain carbon alloys; and (2) the pearlite-proeutectoid noses for plain carbon steel alloys are positioned at shorter times than for the alloy steels.

CHAPTER 11

APPLICATIONS AND PROCESSING OF METAL ALLOYS

PROBLEM SOLUTIONS

Ferrous Alloys

11.1 This question asks that we list four classifications of steels, and, for each, to describe properties and cite typical applications.

Low Carbon Steels

Properties: nonresponsive to heat treatments; relatively soft and weak; machinable and weldable.

Typical applications: automobile bodies, structural shapes, pipelines, buildings, bridges, and tin cans.

Medium Carbon Steels

Properties: heat treatable, relatively large combinations of mechanical characteristics.

Typical applications: railway wheels and tracks, gears, crankshafts, and machine parts.

High Carbon Steels

Properties: hard, strong, and relatively brittle.

Typical applications: chisels, hammers, knives, and hacksaw blades.

High Alloy Steels (Stainless and Tool)

Properties: hard and wear resistant; resistant to corrosion in a large variety of environments.

Typical applications: cutting tools, drills, cutlery, food processing, and surgical tools.

11.2 (a) Ferrous alloys are used extensively because:

(1) Iron ores exist in abundant quantities.

(2) Economical extraction, refining, and fabrication techniques are available.

(3) The alloys may be tailored to have a wide range of properties.

(b) Disadvantages of ferrous alloys are:

(1) They are susceptible to corrosion.

(2) They have a relatively high density.

(3) They have relatively low electrical conductivities.

11.3 The alloying elements in tool steels (e.g., Cr, V, W, and Mo) combine with the carbon to form very hard and wear-resistant carbide compounds.

11.4 We are asked to compute the volume percent graphite in a 2.5 wt% C cast iron. It first becomes necessary to compute mass fractions using the lever rule. From the iron-carbon phase diagram (Figure 11.2), the tie-line in the α and graphite phase field extends from essentially 0 wt% C to 100 wt% C. Thus, for a 2.5 wt% C cast iron

$$W_\alpha = \frac{C_{\mathrm{Gr}} - C_0}{C_{\mathrm{Gr}} - C_\alpha} = \frac{100 - 2.5}{100 - 0} = 0.975$$

$$W_{\mathrm{Gr}} = \frac{C_0 - C_\alpha}{C_{\mathrm{Gr}} - C_\alpha} = \frac{2.5 - 0}{100 - 0} = 0.025$$

Conversion from weight fraction to volume fraction of graphite is possible using Equation 9.6a as

$$V_{\mathrm{Gr}} = \frac{\dfrac{W_{\mathrm{Gr}}}{\rho_{\mathrm{Gr}}}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_{\mathrm{Gr}}}{\rho_{\mathrm{Gr}}}}$$

$$= \frac{\dfrac{0.025}{2.3\ \mathrm{g/cm^3}}}{\dfrac{0.975}{7.9\ \mathrm{g/cm^3}} + \dfrac{0.025}{2.3\ \mathrm{g/cm^3}}}$$

$$= 0.081 \text{ or } 8.1 \text{ vol\%}$$

11.5 Gray iron is weak and brittle in tension because the tips of the graphite flakes act as points of stress concentration.

11.6 This question asks us to compare various aspects of gray and malleable cast irons.

(a) With respect to composition and heat treatment:

Gray iron--2.5 to 4.0 wt% C and 1.0 to 3.0 wt% Si. For most gray irons there is no heat treatment after solidification.

Malleable iron--2.5 to 4.0 wt% C and less than 1.0 wt% Si. White iron is heated in a nonoxidizing atmosphere and at a temperature between 800 and 900°C for an extended time period.

(b) With respect to microstructure:

Gray iron--Graphite flakes are embedded in a ferrite or pearlite matrix.

Malleable iron--Graphite clusters are embedded in a ferrite or pearlite matrix.

(c) With respect to mechanical characteristics:

Gray iron--Relatively weak and brittle in tension; good capacity for damping vibrations.

Malleable iron--Moderate strength and ductility.

11.7 This question asks us to compare white and nodular cast irons.

(a) With regard to composition and heat treatment:

White iron--2.5 to 4.0 wt% C and less than 1.0 wt% Si. No heat treatment; however, cooling is rapid during solidification.

Nodular cast iron--2.5 to 4.0 wt% C, 1.0 to 3.0 wt% Si, and a small amount of Mg or Ce. A heat treatment at about 700°C may be necessary to produce a ferritic matrix.

(b) With regard to microstructure:

White iron--There are regions of cementite interspersed within pearlite.

Nodular cast iron--Nodules of graphite are embedded in a ferrite or pearlite matrix.

(c) With respect to mechanical characteristics:

White iron--Extremely hard and brittle.

Nodular cast iron--Moderate strength and ductility.

11.8 It is *not possible* to produce malleable iron in pieces having large cross-sectional dimensions. White cast iron is the precursor of malleable iron, and a rapid cooling rate is necessary for the formation of white iron, which may not be accomplished at interior regions of thick cross-sections.

Nonferrous Alloys

11.9 The principal difference between wrought and cast alloys is as follows: wrought alloys are ductile enough so as to be hot or cold worked during fabrication, whereas cast alloys are brittle to the degree that shaping by deformation is not possible and they must be fabricated by casting.

11.10 Rivets of a 2017 aluminum alloy must be refrigerated before they are used because, after being solution heat treated, they precipitation harden at room temperature. Once precipitation hardened, they are too strong and brittle to be driven.

11.11 The chief difference between heat-treatable and nonheat-treatable alloys is that heat-treatable alloys may be strengthened by a heat treatment wherein a precipitate phase is formed (precipitation hardening) or a martensitic transformation occurs. Nonheat-treatable alloys are not amenable to strengthening by such treatments.

11.12 This question asks us for the distinctive features, limitations, and applications of several alloy groups.

Titanium Alloys

Distinctive features: relatively low density, high melting temperatures, and high strengths are possible.

Limitation: because of chemical reactivity with other materials at elevated temperatures, these alloys are expensive to refine.

Applications: aircraft structures, space vehicles, and in chemical and petroleum industries.

Refractory Metals

Distinctive features: extremely high melting temperatures; large elastic moduli, hardnesses, and strengths.

Limitation: some experience rapid oxidation at elevated temperatures.

Applications: extrusion dies, structural parts in space vehicles, incandescent light filaments, x-ray tubes, and welding electrodes.

Superalloys

Distinctive features: able to withstand high temperatures and oxidizing atmospheres for long time periods.

Applications: aircraft turbines, nuclear reactors, and petrochemical equipment.

Noble Metals

Distinctive features: highly resistant to oxidation, especially at elevated temperatures; soft and ductile.

Limitation: expensive.

Applications: jewelry, dental restoration materials, coins, catalysts, and thermocouples.

Forming Operations

11.13 The advantages of cold working are:

(1) A high quality surface finish.
(2) The mechanical properties may be varied.
(3) Close dimensional tolerances.

The disadvantages of cold working are:

(1) High deformation energy requirements.
(2) Large deformations must be accomplished in steps, which may be expensive.
(3) A loss of ductility.

The advantages of hot working are:

(1) Large deformations are possible, which may be repeated.
(2) Deformation energy requirements are relatively low.

The disadvantages of hot working are:

(1) A poor surface finish.
(2) A variety of mechanical properties is not possible.

11.14 (a) The advantages of extrusion as opposed to rolling are as follows:

(1) Pieces having more complicated cross-sectional geometries may be formed.

(2) Seamless tubing may be produced.

(b) The disadvantages of extrusion over rolling are as follows:

(1) Nonuniform deformation over the cross-section.

(2) A variation in properties may result over a cross-section of an extruded piece.

Casting

11.15 Four situations in which casting is the preferred fabrication technique are:

(1) For large pieces and/or complicated shapes.

(2) When mechanical strength is not an important consideration.

(3) For alloys having low ductilities.

(4) When it is the most economical fabrication technique.

11.16 This question asks us to compare sand, die, investment, lost foam, and continuous casting techniques.

For *sand casting*, sand is the mold material, a two-piece mold is used, ordinarily the surface finish is not an important consideration, the sand may be reused (but the mold may not), casting rates are low, and large pieces are usually cast.

For *die casting*, a permanent mold is used, casting rates are high, the molten metal is forced into the mold under pressure, a two-piece mold is used, and small pieces are normally cast.

For *investment casting*, a single-piece mold is used, which is not reusable; it results in high dimensional accuracy, good reproduction of detail, and a fine surface finish; and casting rates are low.

For *lost foam casting*, the pattern is polystyrene foam, whereas the mold material is sand. Complex geometries and tight tolerances are possible. Casting rates are higher than for investment, and there are few environmental wastes.

For *continuous casting*, at the conclusion of the extraction process, the molten metal is cast into a continuous strand having either a rectangular or circular cross-section; these shapes are desirable for subsequent secondary metal-forming operations. The chemical composition and mechanical properties are relatively uniform throughout the cross-section.

Miscellaneous Techniques

11.17 This problem asks that we specify and compare the microstructures and mechanical properties in the heat-affected weld zones for 1080 and 4340 alloys assuming that the average cooling rate is 10°C/s. Figure 10.27 shows the continuous cooling transformation diagram for an iron-carbon alloy of eutectoid composition (1080), and, in addition, cooling curves that delineate changes in microstructure. For a cooling rate of 10°C/s (which is less than 35°C/s) the resulting microstructure will be totally pearlite--probably a reasonably fine pearlite. On the other hand, in Figure 10.28 is shown the CCT diagram for a 4340 steel. From this diagram it may be noted that a cooling rate of 10°C/s produces a totally martensitic structure. Pearlite is softer and more ductile than martensite, and, therefore, is most likely more desirable.

11.18 If a steel weld is cooled very rapidly, martensite may form, which is very brittle. In some situations, cracks may form in the weld region as it cools.

Annealing Processes

11.19 Full annealing--Heat to about 50°C above the A_3 line, Figure 11.10 (if the concentration of carbon is less than the eutectoid) or above the A_1 line (if the concentration of carbon is greater than the eutectoid) until the alloy comes to equilibrium; then furnace cool to room temperature. The final microstructure is coarse pearlite.

Normalizing--Heat to at least 55°C above the A_3 line Figure 11.10 (if the concentration of carbon is less than the eutectoid) or above the A_{cm} line (if the concentration of carbon is greater than the eutectoid) until the alloy completely transforms to austenite, then cool in air. The final microstructure is fine pearlite.

Quenching--Heat to a temperature within the austenite phase region and allow the specimen to fully austenitize, then quench to room temperature in oil or water. The final microstructure is martensite.

Tempering--Heat a quenched (martensitic) specimen, to a temperature between 450 and 650°C, for the time necessary to achieve the desired hardness. The final microstructure is tempered martensite.

11.20 Three sources of residual stresses in metal components are plastic deformation processes, nonuniform cooling of a piece that was cooled from an elevated temperature, and a phase transformation in which parent and product phases have different densities.

Two adverse consequences of these stresses are distortion (or warpage) and fracture.

11.21 This question asks that we cite the approximate minimum temperature at which it is desirable to austenitize several iron-carbon alloys during a normalizing heat treatment.

(a) For 0.15 wt% C, heat to at least 915°C (1680°F) since the A_3 temperature is 860°C (1580°F).

(b) For 0.50 wt% C, heat to at least 825°C (1520°F) since the A_3 temperature is 770°C (1420°F).

(c) For 1.10 wt% C, heat to at least 900°C (1655°F) since the A_{cm} temperature is 845°C (1555°F).

11.22 We are asked for the approximate temperature at which several iron-carbon alloys should be austenitized during a full-anneal heat treatment.

(a) For 0.20 wt% C, heat to about 890°C (1635°F) since the A_3 temperature is 840°C (1545°F).

(b) For 0.60 wt% C, heat to about 800°C (1470°F) since the A_3 temperature is 750°C (1380°F).

(c) For 0.76 wt% C, heat to about 777°C (1430°F) since the A_1 temperature is 727°C (1340°F).

(d) For 0.95 wt% C, heat to about 777°C (1430°F) since the A_1 temperature is 727°C (1340°F).

11.23 The purpose of a spheroidizing heat treatment is to produce a very soft and ductile steel alloy having a spheroiditic microstructure. It is normally used on medium- and high-carbon steels, which, by virtue of carbon content, are relatively hard and strong.

Heat Treatment of Steels

11.24 Hardness is a measure of a material's resistance to localized surface deformation, whereas hardenability is a measure of the depth to which a ferrous alloy may be hardened by the formation of martensite. Hardenability is determined from hardness tests.

11.25 The presence of alloying elements (other than carbon) causes a much more gradual decrease in hardness with position from the quenched end for a hardenability curve. The reason for this effect is that alloying elements retard the formation of pearlitic and bainitic structures which are not as hard as martensite.

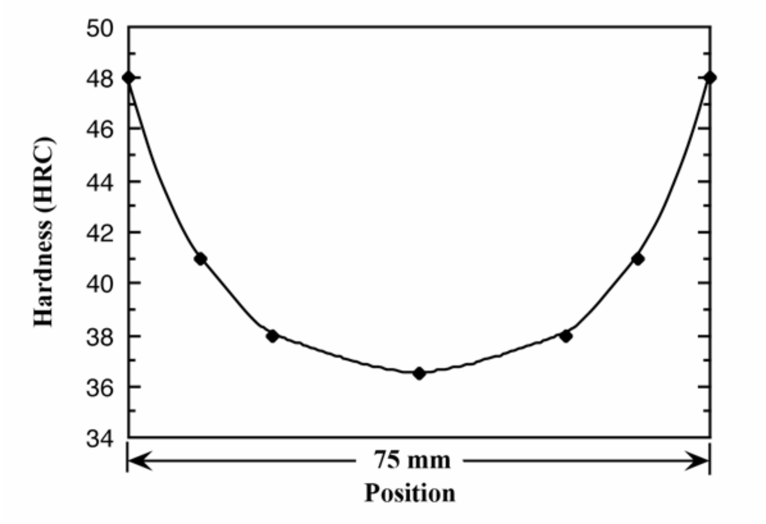
11.26 A decrease of austenite grain size will decrease the hardenability. Pearlite normally nucleates at grain boundaries, and the smaller the grain size, the greater the grain boundary area, and, consequently, the easier it is for pearlite to form.

11.27 The two thermal properties of a liquid medium that influence its quenching effectiveness are thermal conductivity and heat capacity.

11.28 (a) This part of the problem calls for us to construct a radial hardness profile for a 75 mm (3 in.) diameter cylindrical specimen of an 8640 steel that has been quenched in moderately agitated oil. In the manner of Example Problem 11.1, the equivalent distances and hardnesses tabulated below were determined from Figures 11.14 and 11.17(b).

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	13	48
3/4 *R*	18	41
Midradius	22	38
Center	26	36

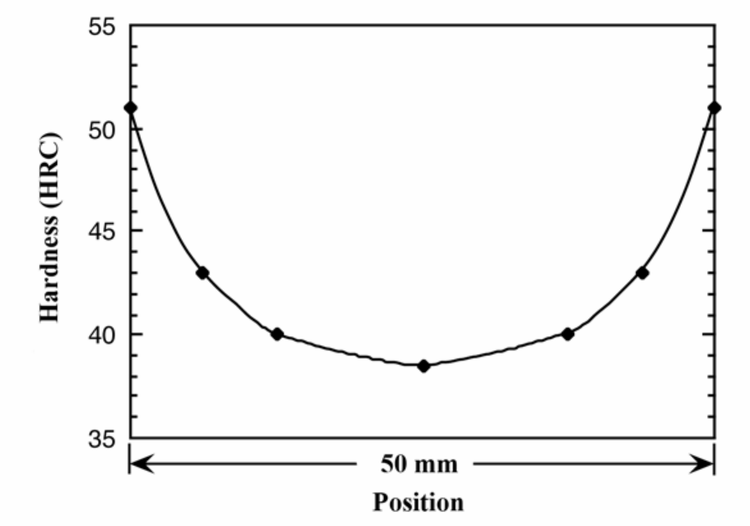
The resulting hardness profile is plotted below.



(b) The radial hardness profile for a 50 mm (2 in.) diameter specimen of a 5140 steel that has been quenched in moderately agitated oil is desired. The equivalent distances and hardnesses tabulated below were determined using Figures 11.14 and 11.17(b).

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	7	51
3/4 *R*	12	43
Midradius	14	40
Center	16	38.5

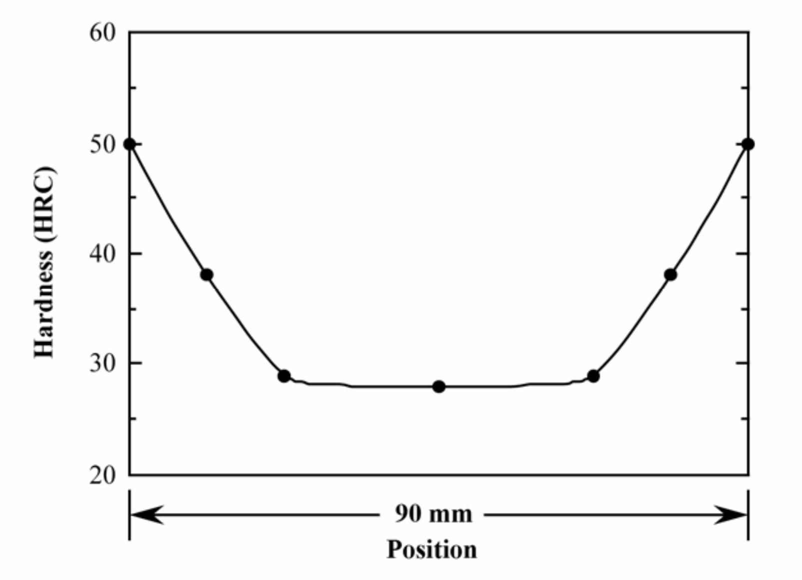
The resulting hardness profile is plotted below.



(c) The radial hardness profile for a 90-mm (3-1/2 in.) diameter specimen of an 8630 steel that has been quenched in moderately agitated water is desired. The equivalent distances and hardnesses for the various radial positions, as determined using Figures 11.15 and 11.17(a) are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	3	50
3/4 *R*	10	38
Midradius	17	29
Center	22	27

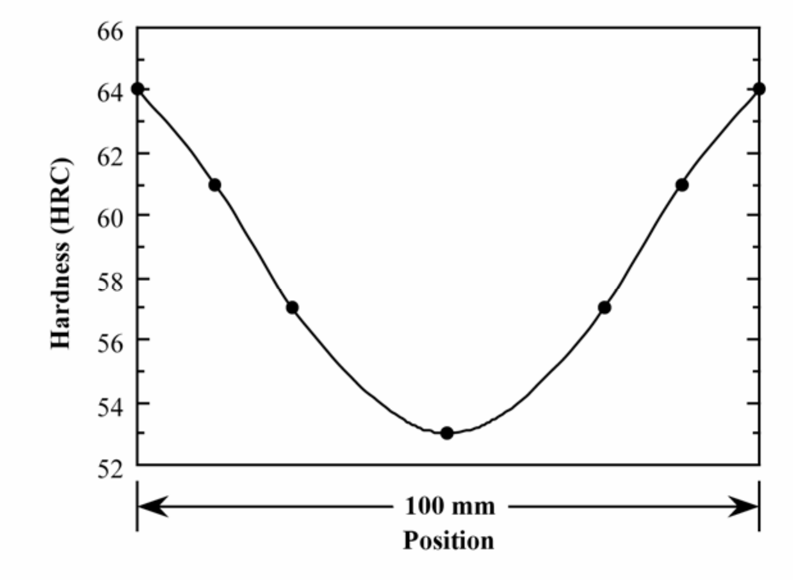
The resulting hardness profile is plotted here.



(d) The radial hardness profile for a 100-mm (4-in.) diameter specimen of a 8660 steel that has been quenched in moderately agitated water is desired. The equivalent distances and hardnesses for the various radial positions, as determined using Figures 11.15 and 11.17(a), are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	3	64
3/4 *R*	11	61
Midradius	20	57
Center	26	53

The resulting hardness profile is plotted here.


66
64
62
60
58
56
54
52
Hardness (HRC)
100 mm
Position

11.29 We are asked to compare the effectiveness of quenching in moderately agitated water and oil by graphing, on a single plot, the hardness profiles for 75-mm (3-in.) diameter cylindrical specimens of an 8640 steel that had been quenched in both media.

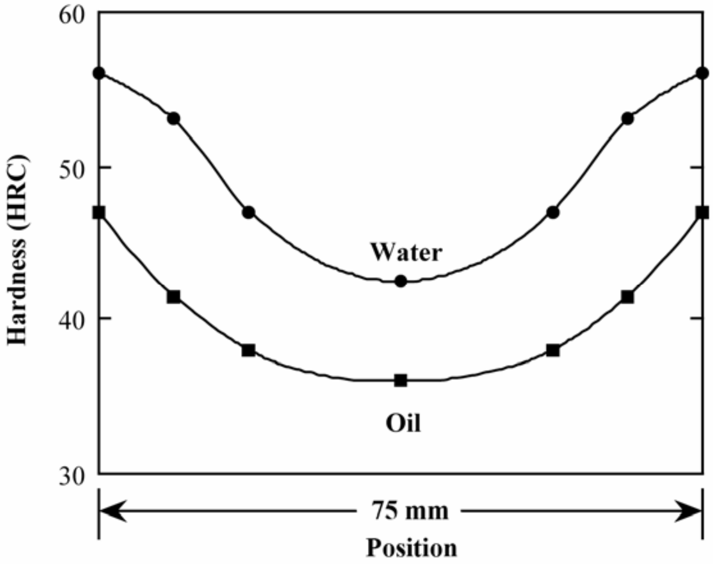
For moderately agitated water, the equivalent distances and hardnesses for the several radial positions [Figures 11.17(a) and 11.15] are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	3	56
3/4 *R*	8	53
Midradius	13	47
Center	17	42.5

While for moderately agitated oil, the equivalent distances and hardnesses for the several radial positions [Figures 11.17(b) and 11.15] are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	13	47
3/4 *R*	19	41.5
Midradius	22	38
Center	25	36

These data are plotted here.



Precipitation Hardening

11.30 This problem asks us to compare various aspects of precipitation hardening, and the quenching and tempering of steel.

(a) With regard to the total heat treatment procedure, the steps for the *hardening of steel* are as follows:

(1) Austenitize above the upper critical temperature.
(2) Quench to a relatively low temperature.
(3) Temper at a temperature below the eutectoid.
(4) Cool to room temperature.

With regard to *precipitation hardening*, the steps are as follows:

(1) Solution heat treat by heating into the solid solution phase region.
(2) Quench to a relatively low temperature.
(3) Precipitation harden by heating to a temperature that is within the solid two-phase region.
(4) Cool to room temperature.

(b) For the *hardening of steel*, the microstructures that form at the various heat treating stages in part (a) are:

(1) Austenite
(2) Martensite
(3) Tempered martensite
(4) Tempered martensite

For *precipitation hardening*, the microstructures that form at the various heat treating stages in part (a) are:

(1) Single phase
(2) Single phase--supersaturated
(3) Small plate-like particles of a new phase within a matrix of the original phase.
(4) Same as (3)

(c) For the *hardening of steel*, the mechanical characteristics for the various steps in part (a) are as follows:

(1) Not important
(2) The steel becomes hard and brittle upon quenching.
(3) During tempering, the alloy softens slightly and becomes more ductile.
(4) No significant changes upon cooling to or maintaining at room temperature.

For *precipitation hardening*, the mechanical characteristics for the various steps in part (a) are as follows:

(1) Not important
(2) The alloy is relatively soft.
(3) The alloy hardens with increasing time (initially), and becomes more brittle; it may soften with overaging.

(4) The alloy may continue to harden or overage at room temperature.

11.31 For precipitation hardening, natural aging is allowing the precipitation process to occur at the ambient temperature; artificial aging is carried out at an elevated temperature.

DESIGN PROBLEMS

Ferrous Alloys

Nonferrous Alloys

11.D1 This problem calls for us to select, from a list of alloys, the best alloy for each of several applications and then to justify each choice.

(a) Gray cast iron would be the best choice for an engine block because it is relatively easy to cast, is wear resistant, has good vibration damping characteristics, and is relatively inexpensive.

(b) Stainless steel would be the best choice for a heat exchanger to condense steam because it is corrosion resistant to the steam and condensate.

(c) Titanium alloys are the best choice for high-speed aircraft jet engine turbofan blades because they are light weight, strong, and easily fabricated very resistant to corrosion. However, one drawback is their cost.

(d) A tool steel would be the best choice for a drill bit because it is very hard retains its hardness at high temperature and is wear resistant, and, thus, will retain a sharp cutting edge.

(e) For a cryogenic (low-temperature) container, an aluminum alloy would be the best choice; aluminum alloys have an FCC crystal structure, and therefore, are ductile at very low temperatures.

(f) As a pyrotechnic in flares and fireworks, magnesium is the best choice because it ignites easily and burns readily in air with a very bright flame.

(g) Platinum is the best choice for high-temperature furnace elements to be used in oxidizing atmospheres because it is very ductile, has a relatively very high melting temperature, and is highly resistant to oxidation.

11.D2 (a) Compositionally, the metallic glass materials are rather complex; several compositions are as follows: $Fe_{80}B_{20}$, $Fe_{72}Cr_8P_{13}C_7$, $Fe_{67}Co_{18}B_{14}Si$, $Pd_{77.5}Cu_{6.0}Si_{16.5}$, and $Fe_{40}Ni_{38}Mo_4B_{18}$.

(b) These materials are exceptionally strong and tough, extremely corrosion resistant, and are easily magnetized.

(c) Principal drawbacks for these materials are 1) complicated and exotic fabrication techniques are required; and 2) inasmuch as very rapid cooling rates are required, at least one dimension of the material must be small--i.e., they are normally produced in ribbon form.

(d) Potential uses include transformer cores, magnetic amplifiers, heads for magnetic tape players, reinforcements for pressure vessels and tires, shields for electromagnetic interference, security tapes for library books.

(e) Production techniques include centrifuge melt spinning, planar-flow casting, rapid pressure application, arc melt spinning.

11.D3 This question provides us with a list of several metal alloys, and then asks us to pick those that may be strengthened by heat treatment, by cold work, or both. Those alloys that may be heat treated are either those noted as "heat treatable" (Tables 11.6 through 11.9), or as martensitic stainless steels (Table 11.4). Alloys that may be strengthened by cold working must not be exceptionally brittle (which may be the case for cast irons, Table 11.5), and, furthermore, must have recrystallization temperatures above room temperature (which immediately eliminates zinc). The alloys that fall within the three classifications are as follows:

Heat Treatable	Cold Workable	Both
410 stainless steel	410 stainless steel	410 stainless steel
4340 steel	4340 steel	4340 steel
ZK60A magnesium	ZK60A magnesium	ZK60A magnesium
356.0 aluminum	C26000 cartridge brass	
	R56400 Ti	
	1100 aluminum	

11.D4 This problem asks us to rank four alloys (brass, steel, titanium, and aluminum), from least to greatest weight for a structural member to support a 44,400 N (10,000 $\mathrm{lb_f}$) load without experiencing plastic deformation. From Equation 6.1, the cross-sectional area (A_0) must necessarily carry the load (F) without exceeding the yield strength (σ_y), as

$$A_0 = \frac{F}{\sigma_y}$$

Now, given the length l, the volume of material required (V) is just

$$V = lA_0 = \frac{lF}{\sigma_y}$$

Finally, the mass of the member (m) is

$$m = V\rho = \frac{\rho l F}{\sigma_y}$$

Here ρ is the density. Using the values given for these alloys

$$m(\text{brass}) = \frac{(8.5\ \text{g/cm}^3)(25\ \text{cm})(44,400\ \text{N})}{(345\ \text{x}\ 10^6\ \text{N/m}^2)\left(\dfrac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 273\ \text{g}$$

$$m(\text{steel}) = \frac{(7.9\ \text{g/cm}^3)(25\ \text{cm})(44,400\ \text{N})}{(690\ \text{x}\ 10^6\ \text{N/m}^2)\left(\dfrac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 127\ \text{g}$$

$$m(\text{aluminum}) = \frac{(2.7\ \text{g/cm}^3)(25\ \text{cm})(44,400\ \text{N})}{(275\ \text{x}\ 10^6\ \text{N/m}^2)\left(\dfrac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 109\ \text{g}$$

$$m(\text{titanium}) = \frac{(4.5\ \text{g/cm}^3)(25\ \text{cm})(44,400\ \text{N})}{(480\ \text{x}\ 10^6\ \text{N/m}^2)\left(\dfrac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 104\ \text{g}$$

Thus, titanium would have the minimum weight (or mass), followed by aluminum, steel, and brass.

11.D5 This question asks for us to decide whether or not it would be advisable to hot-work or cold-work several metals and alloys.

Platinum is one of the noble metals. Even though it has a high melting temperature and good resistance to oxidation, at room temperature it is relatively soft and ductile, and is amenable to cold working.

Molybdenum, one of the refractory metals, is hard and strong at room temperature, has a high recrystallization temperature, and experiences oxidation at elevated temperatures. Cold-working is difficult because of its strength, and hot-working is not practical because of oxidation problems. Most molybdenum articles are fabricated by powder metallurgy, or by using cold-working followed by annealing cycles.

Lead would almost always be hot-worked. Even deformation at room temperature would be considered hot-working inasmuch as its recrystallization temperature is below room temperature (Table 7.2).

304 stainless steel is relatively resistant to oxidation. However, it is very ductile and has a moderate yield strength (Table 11.4), therefore, it may be cold-worked, but hot-working is also a possibility.

Copper is relatively soft and very ductile and ductile at room temperature (see, for example, C11000 copper in Table 11.6); therefore, it may be cold-worked.

Heat Treatment of Steels

11.D6 A 38-mm (1-1/2 in.) diameter steel specimen is to be quenched in moderately agitated oil. We are to decide which of five different steels will have surface and center hardnesses of at least 50 and 40 HRC, respectively.

In moderately agitated oil, the equivalent distances from the quenched end for a 38 mm diameter bar for surface and center positions are 5 mm (3/16 in.) and 12 mm (15/32 in.), respectively [Figure 11.17(b)]. The hardnesses at these two positions for the alloys cited (as determined using Figure 11.14) are given below.

Alloy	Surface Hardness (HRC)	Center Hardness (HRC)
1040	40	24
5140	53	42
4340	57	55
4140	56	53
8640	55	48

Thus, alloys 4340, 4140, 8640, and 5140 will satisfy the criteria for both surface and center hardnesses.

11.D7 (a) This problem calls for us to decide which of 8660, 8640, 8630, and 8620 alloys may be fabricated into a cylindrical piece 57 mm (2-1/4 in.) in diameter which, when quenched in mildly agitated water, will produce a minimum hardness of 45 HRC throughout the entire piece.

The center of the steel cylinder will cool the slowest and therefore will be the softest. In moderately agitated water the equivalent distance from the quenched end for a 57 mm diameter bar for the center position is about 11 mm (7/16 in.) [Figure 11.17(a)]. The hardnesses at this position for the alloys cited (Figure 11.15) are given below.

Alloy	Center Hardness (HRC)
8660	61
8640	49
8630	36
8620	25

Therefore, only 8660 and 8640 alloys will have a minimum of 45 HRC at the center, and therefore, throughout the entire cylinder.

(b) This part of the problem asks us to do the same thing for moderately agitated oil. In moderately agitated oil the equivalent distance from the quenched end for a 57 mm diameter bar at the center position is about 17.5 mm (11.16 in.) [Figure 11.17(b)]. The hardnesses at this position for the alloys cited (Figure 11.15) are given below.

Alloy	Center Hardness (HRC)
8660	59
8640	42
8630	30
8620	21

Therefore, only the 8660 alloy will have a minimum of 45 HRC at the center, and therefore, throughout the entire cylinder.

11.D8 A forty-four millimeter (one and three-quarter inch) diameter cylindrical steel specimen is to be heat treated such that the microstructure throughout will be at least 50% martensite. We are to decide which of several alloys will satisfy this criterion if the quenching medium is moderately agitated (a) oil, and (b) water.

(a) Since the cooling rate is lowest at the center, we want a minimum of 50% martensite at the center position. From Figure 11.17(b), the cooling rate is equal to an equivalent distance from the quenched end of 13 mm (9/16 in.). According to Figure 11.14, the hardness corresponding to 50% martensite for these alloys is 42 HRC. Thus, all we need do is to determine which of the alloys have a 42 HRC hardness at an equivalent distance from the quenched end of 13 mm (9/16 in.). At an equivalent distance of 13 mm, the following hardnesses are determined from Figure 11.14 for the various alloys.

Alloy	Hardness (HRC)
4340	55
4140	52
8640	47
5140	41
1040	23

Thus, only alloys 4340, 4140 and 8640 will qualify.

(b) For moderately agitated water, the cooling rate at the center of a 44 mm (1-3/4 in.) diameter specimen is 9 mm (11/32 in.) equivalent distance from the quenched end [Figure 11.17(a)]. At this position, the following hardnesses are determined from Figure 11.14 for the several alloys.

Alloy	Hardness (HRC)
4340	57
4140	55
8640	53
5140	48
1040	30

It is still necessary to have a hardness of 42 HRC or greater at the center; thus, alloys 4340, 4140, 8640, and 5140 qualify.

11.D9 A fifty-millimeter (two-inch) diameter cylindrical steel specimen is to be quenched in moderately agitated water. We are to decide which of eight different steels will have surface and center hardnesses of at least 50 and 40 HRC, respectively.

In moderately agitated water, the equivalent distances from the quenched end for a 50-mm diameter bar for surface and center positions are 2 mm (1/16 in.) and 10 mm (3/8 in.), respectively [Figure 11.17(a)]. The hardnesses at these two positions for the alloys cited are given below (as determined from Figures 11.14 and 11.15).

Alloy	Surface Hardness (HRC)	Center Hardness (HRC)
1040	50	27
5140	56	45
4340	57	56
4140	57	54
8620	42	27
8630	51	38
8640	57	51
8660	64	64

Thus, alloys 5140, 4340, 4140, 8640, and 8660 will satisfy the criteria for both surface hardness (minimum 50 HRC) and center hardness (minimum 40 HRC).

11.D10 We are asked to determine the maximum diameter possible for a cylindrical piece of 4140 steel that is to be quenched in moderately agitated oil such that the microstructure will consist of at least 80% martensite throughout the entire piece. From Figure 11.14, the equivalent distance from the quenched end of a 4140 steel to give 80% martensite (or a 50 HRC hardness) is 16 mm (5/8 in.). Thus, the quenching rate at the center of the specimen should correspond to this equivalent distance. Using Figure 11.17(b), the center specimen curve takes on a value of 16 mm (5/8 in.) equivalent distance at a diameter of about 50 mm (2 in.).

11.D11 We are to determine, for a cylindrical piece of 8660 steel, the maximum allowable diameter possible in order yield a surface hardness of 58 HRC, when the quenching is carried out in moderately agitated oil.

From Figure 11.15, the equivalent distance from the quenched end of an 8660 steel to give a hardness of 58 HRC is about 18 mm (3/4 in.). Thus, the quenching rate at the surface of the specimen should correspond to this equivalent distance. Using Figure 11.17(b), the surface specimen curve takes on a value of 18 mm equivalent distance at a diameter of about 95 mm (3.75 in.).

11.D12 This problem asks if it is possible to temper an oil-quenched 4140 steel cylindrical shaft 25 mm (1 in.) in diameter so as to give a minimum yield strength of 950 MPa (140,000 psi) and a minimum ductility of 17%EL. In order to solve this problem it is necessary to use Figures 11.20(b) and 11.20(c), which plot, respectively, yield strength and ductility versus tempering temperature. For the 25 mm diameter line of Figure 11.20(b), tempering temperatures less than about 575°C are required to give a yield strength of at least 950 MPa. Furthermore, from Figure 11.20(c), for the 25 mm diameter line, tempering temperatures greater than about 550°C will give ductilities greater than 17%EL. Hence, it *is possible* to temper this alloy to produce the stipulated minimum yield strength and ductility; the tempering temperature will lie between 550°C and 575°C.

11.D13 This problem asks if it is possible to temper an oil-quenched 4140 steel cylindrical shaft 50 mm (2 in.) in diameter so as to give a minimum tensile strength of 900 MPa (130,000 psi) and a minimum ductility of 20%EL. In order to solve this problem it is necessary to use Figures 11.20(a) and 11.20(c), which plot, respectively, tensile strength and ductility versus tempering temperature. For the 50 mm diameter line of Figure 11.20(a), tempering temperatures less than about 590°C are required to give a tensile strength of at least 900 MPa. Furthermore, from Figure 11.20(c), for the 50 mm diameter line, tempering temperatures greater than about 600°C will give ductilities greater than 20%EL. Hence, it *is not possible* to temper this alloy to produce the stipulated minimum tensile strength and ductility. To meet the tensile strength minimum, T(tempering) < 590°C, whereas for ductility minimum, T(tempering) > 600°C; thus, there is no overlap of these tempering temperature ranges.

Precipitation Hardening

11.D14 This problem is concerned with the precipitation-hardening of copper-rich Cu-Be alloys. It is necessary for us to use the Cu-Be phase diagram (Figure 11.28).

(a) The range of compositions over which these alloys may be precipitation hardened is between approximately 0.2 wt% Be (the maximum solubility of Be in Cu at about 300°C) and 2.7 wt% Be (the maximum solubility of Be in Cu at 866°C).

(b) The heat treatment procedure, of course, will depend on the composition chosen. First of all, the solution heat treatment must be carried out at a temperature within the α phase region, after which, the specimen is quenched to room temperature. Finally, the precipitation heat treatment is conducted at a temperature within the $\alpha + \gamma_2$ phase region.

For example, for a 1.5 wt% Be-98.5 wt% Cu alloy, the solution heat treating temperature must be between about 600°C (1110°F) and 900°C (1650°F), while the precipitation heat treatment would be below 600°C (1110°F), and probably above 300°C (570°F). Below 300°C, diffusion rates are low, and heat treatment times would be relatively long.

11.D15 We are asked to specify a practical heat treatment for a 2014 aluminum alloy that will produce a minimum yield strength of 345 MPa (50,000 psi), and a minimum ductility of 12%EL. From Figure 11.27(a), the following heat treating temperatures and time ranges are possible to the give the required yield strength.

Temperature (°C)	Time Range (h)
260	not possible
204	0.3-15
149	10-700
121	300-?

With regard to temperatures and times to give the desired ductility [Figure 11.27(b)]:

Temperature (°C)	Time Range (h)
260	<0.02, >10
204	<0.4, >350
149	<20
121	<1000

From these tabulations, the following may be concluded:

It is not possible to heat treat this alloy at 260°C so as to produce the desired set of properties—attainment of a yield strength of 345 MPa is not possible at this temperature.

At 204°C, the heat treating time would need to be about 0.4 h, which is practical.

At 149°C, the time range is between 10 and 20 h, which is a little on the long side.

Finally, at 121°C, the time range is unpractically long (300 to 1000 h).

11.D16 This problem inquires as to the possibility of producing a precipitation-hardened 2014 aluminum alloy having a minimum yield strength of 380 MPa (55,000 psi) and a ductility of at least 15%EL. In order to solve this problem it is necessary to consult Figures 11.27(a) and 11.27(b). Below are tabulated the times required at the various temperatures to achieve the stipulated yield strength.

Temperature (°C)	Time Range (h)
260	not possible
204	0.5-7
149	10-250
121	500-2500

With regard to temperatures and times to give the desired ductility:

Temperature (°C)	Time Range (h)
260	<0.005
204	<0.13
149	<10
121	<500

Therefore, an alloy having this combination of yield strength and ductility is marginally possible. A heat treatment at 149°C for 10 h would probably just achieve the stipulated ductility and yield strength.

CHAPTER 12

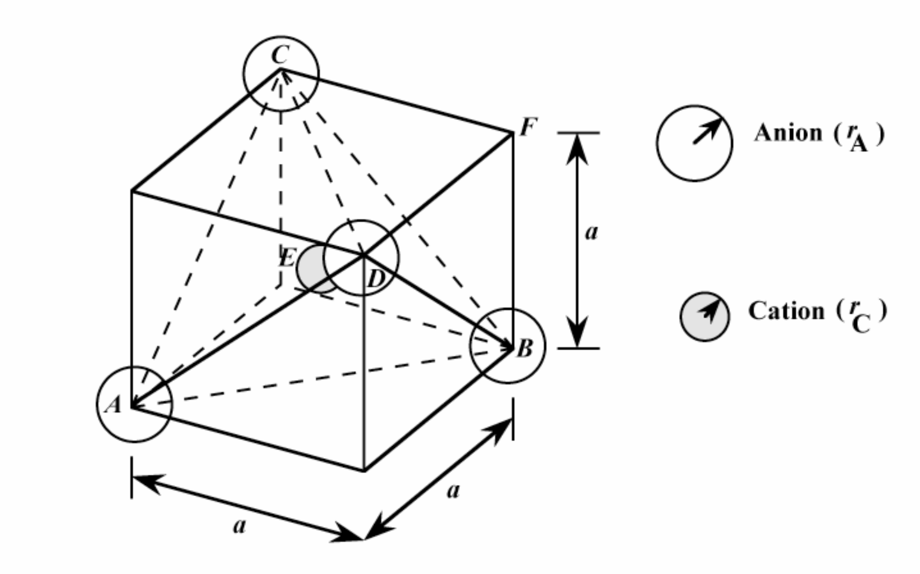
STRUCTURES AND PROPERTIES OF CERAMICS

PROBLEM SOLUTIONS

Crystal Structures

12.1 The two characteristics of component ions that determine the crystal structure of a ceramic compound are: 1) the magnitude of the electrical charge on each ion, and 2) the relative sizes of the cations and anions.

12.2 In this problem we are asked to show that the minimum cation-to-anion radius ratio for a coordination number of four is 0.225. If lines are drawn from the centers of the anions, then a tetrahedron is formed. The tetrahedron may be inscribed within a cube as shown below.



The spheres at the apexes of the tetrahedron are drawn at the corners of the cube, and designated as positions *A*, *B*, *C*, and *D*. (These are reduced in size for the sake of clarity.) The cation resides at the center of the cube, which is designated as point *E*. Let us now express the cation and anion radii in terms of the cube edge length, designated as *a*. The spheres located at positions *A* and *B* touch each other along the bottom face diagonal. Thus,

$$\overline{AB} = 2r_A$$

But

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

or

$$\overline{AB} = a\sqrt{2} = 2r_A$$

And

$$a = \frac{2r_A}{\sqrt{2}}$$

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 ionic radii as

$$\overline{AEF} = 2(r_A + r_C)$$

(The line *AEF* has not been drawn to avoid confusion.) From the triangle *ABF*

$$(\overline{AB})^2 + (\overline{FB})^2 = (\overline{AEF})^2$$

But,

$$\overline{FB} = a = \frac{2r_A}{\sqrt{2}}$$

and

$$\overline{AB} = 2r_A$$

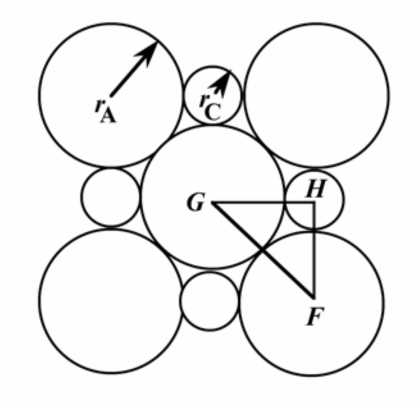
from above. Thus,

$$(2r_A)^2 + \left(\frac{2r_A}{\sqrt{2}}\right)^2 = \left[2(r_A + r_C)\right]^2$$

Solving for the r_C/r_A ratio leads to

$$\frac{r_C}{r_A} = \frac{\sqrt{6} - 2}{2} = 0.225$$

12.3 This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414 (using the rock salt crystal structure). Below is shown one of the faces of the rock salt crystal structure in which anions and cations just touch along the edges, and also the face diagonals.



From triangle *FGH*,

$$\overline{GF} = 2r_A$$

and

$$\overline{FH} = \overline{GH} = r_A + r_C$$

Since *FGH* is a right triangle

$$(\overline{GH})^2 + (\overline{FH})^2 = (\overline{FG})^2$$

or

$$(r_A + r_C)^2 + (r_A + r_C)^2 = (2r_A)^2$$

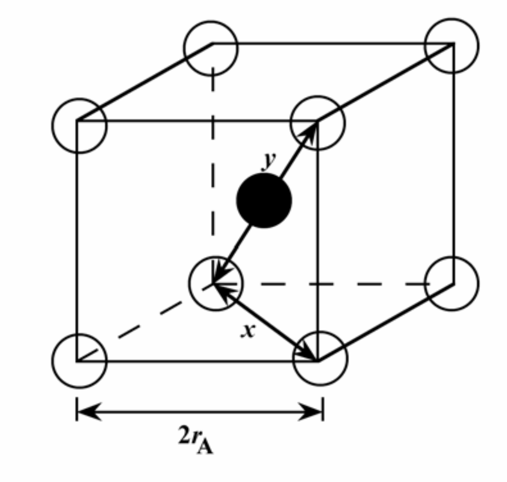
which leads to

$$r_A + r_C = \frac{2r_A}{\sqrt{2}}$$

Or, solving for r_C/r_A

$$\frac{r_C}{r_A} = \left(\frac{2}{\sqrt{2}} - 1\right) = 0.414$$

12.4 This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732. From the cubic unit cell shown below



the unit cell edge length is $2r_A$, and from the base of the unit cell

$$x^2 = (2r_A)^2 + (2r_A)^2 = 8r_A^2$$

Or

$$x = 2r_A\sqrt{2}$$

Now from the triangle that involves x, y, and the unit cell edge

$$x^2 + (2r_A)^2 = y^2 = (2r_A + 2r_C)^2$$

$$(2r_A\sqrt{2})^2 + 4r_A^2 = (2r_A + 2r_C)^2$$

Which reduces to

$$2r_A(\sqrt{3} - 1) = 2r_C$$

Or

$$\frac{r_C}{r_A} = \sqrt{3} - 1 = 0.732$$

12.5 This problem calls for us to predict crystal structures for several ceramic materials on the basis of ionic charge and ionic radii.

(a) For CaO, using data from Table 12.3

$$\frac{r_{\mathrm{Ca}^{2+}}}{r_{\mathrm{O}^{2-}}} = \frac{0.100 \text{ nm}}{0.140 \text{ nm}} = 0.714$$

Now, from Table 12.2, the coordination number for each cation (Ca^{2+}) is six, and, using Table 12.4, the predicted crystal structure is sodium chloride.

(b) For MnS, using data from Table 12.3

$$\frac{r_{\mathrm{Mn}^{2+}}}{r_{\mathrm{S}^{2-}}} = \frac{0.067 \text{ nm}}{0.184 \text{ nm}} = 0.364$$

The coordination number is four (Table 12.2), and the predicted crystal structure is zinc blende (Table 12.4).

(c) For KBr, using data from Table 12.3

$$\frac{r_{\mathrm{K}^{+}}}{r_{\mathrm{Br}^{-}}} = \frac{0.138 \text{ nm}}{0.196 \text{ nm}} = 0.704$$

The coordination number is six (Table 12.2), and the predicted crystal structure is sodium chloride (Table 12.4).

(d) For CsBr, using data from Table 12.3

$$\frac{r_{\mathrm{Cs}^{+}}}{r_{\mathrm{Br}^{-}}} = \frac{0.170 \text{ nm}}{0.196 \text{ nm}} = 0.867$$

The coordination number is eight (Table 12.2), and the predicted crystal structure is cesium chloride (Table 12.4).

12.6 We are asked to cite the cations in Table 12.3 which would form fluorides having the cesium chloride crystal structure. First of all, the possibilities would include only the monovalent cations Cs^+, K^+, and Na^+. Furthermore, the coordination number for each cation must be 8, which means that $0.732 < r_C/r_A < 1.0$ (Table 12.2). From Table 12.3 the r_C/r_A ratios for these three cations and the F^- ion are as follows:

$$\frac{r_{Cs^+}}{r_{F^-}} = \frac{0.170 \text{ nm}}{0.133 \text{ nm}} = 1.28$$

$$\frac{r_{K^+}}{r_{F^-}} = \frac{0.138 \text{ nm}}{0.133 \text{ nm}} = 1.04$$

$$\frac{r_{Na^+}}{r_{F^-}} = \frac{0.102 \text{ nm}}{0.133 \text{ nm}} = 0.77$$

Thus, only sodium will form the CsCl crystal structure with fluorine.

12.7 This problem asks that we compute the atomic packing factor for the rock salt crystal structure when $r_C/r_A = 0.414$. From Equation 3.2

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

With regard to the sphere volume, V_S, there are four cation and four anion spheres per unit cell. Thus,

$$V_S = (4)\left(\frac{4}{3}\pi r_A^3\right) + (4)\left(\frac{4}{3}\pi r_C^3\right)$$

But, since $r_C/r_A = 0.414$

$$V_S = \frac{16}{3}\pi r_A^3 \left[1 + (0.414)^3\right] = (17.94)\ r_A^3$$

Now, for $r_C/r_A = 0.414$ the corner anions in Table 12.2 just touch one another along the cubic unit cell edges such that

$$V_C = a^3 = \left[2(r_A + r_C)\right]^3$$

$$= \left[2(r_A + 0.414 r_A)\right]^3 = (22.62) r_A^3$$

Thus

$$\text{APF} = \frac{V_S}{V_C} = \frac{(17.94)\ r_A^3}{(22.62)\ r_A^3} = 0.79$$

12.8 This question is concerned with the zinc blende crystal structure in terms of close-packed planes of anions.

(a) The stacking sequence of close-packed planes of anions for the zinc blende crystal structure will be the same as FCC (and not HCP) because the anion packing is FCC (Table 12.4).

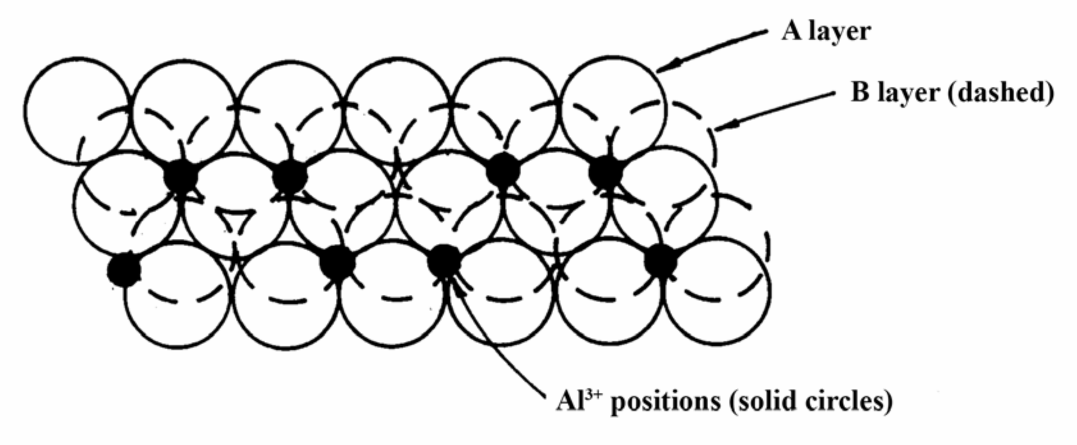
(b) The cations will fill tetrahedral positions since the coordination number for cations is four (Table 12.4).

(c) Only one-half of the tetrahedral positions will be occupied because there are two tetrahedral sites per anion, and yet only one cation per anion.

12.9 This question is concerned with the corundum crystal structure in terms of close-packed planes of anions.

(a) For this crystal structure, two-thirds of the octahedral positions will be filled with Al^{3+} ions since there is one octahedral site per O^{2-} ion, and the ratio of Al^{3+} to O^{2-} ions is two-to-three.

(b) Two close-packed O^{2-} planes and the octahedral positions between these planes that will be filled with Al^{3+} ions are sketched below.



12.10 (a) This portion of the problem asks that we specify which type of interstitial site the Be^{2+} ions will occupy in BeO if the ionic radius of Be^{2+} is 0.035 nm and the O^{2-} ions form an HCP arrangement. Since, from Table 12.3, $r_{O^{2-}}$ = 0.140 nm, then

$$\frac{r_{Be^{2+}}}{r_{O^{2-}}} = \frac{0.035 \text{ nm}}{0.140 \text{ nm}} = 0.250$$

Inasmuch as r_C/r_A is between 0.225 and 0.414, the coordination number for Be^{2+} is 4 (Table 12.2); therefore, tetrahedral interstitial positions are occupied.

(b) We are now asked what fraction of these available interstitial sites are occupied by Be^{2+} ions. Since there are two tetrahedral sites per O^{2-} ion, and the ratio of Be^{2+} to O^{2-} is 1:1, one-half of these sites are occupied with Be^{2+} ions.

12.11 (a) We are first of all asked to cite, for $FeTiO_3$, which type of interstitial site the Fe^{2+} ions will occupy. From Table 12.3, the cation-anion radius ratio is

$$\frac{r_{Fe^{2+}}}{r_{O^{2-}}} = \frac{0.077 \text{ nm}}{0.140 \text{ nm}} = 0.550$$

Since this ratio is between 0.414 and 0.732, the Fe^{2+} ions will occupy octahedral sites (Table 12.2).

(b) Similarly, for the Ti^{4+} ions

$$\frac{r_{Ti^{4+}}}{r_{O^{2-}}} = \frac{0.061 \text{ nm}}{0.140 \text{ nm}} = 0.436$$

Since this ratio is between 0.414 and 0.732, the Ti^{4+} ions will also occupy octahedral sites.

(c) Since both Fe^{2+} and Ti^{4+} ions occupy octahedral sites, no tetrahedral sites will be occupied.

(d) For every $FeTiO_3$ formula unit, there are three O^{2-} ions, and, therefore, three octahedral sites; since there is one ion each of Fe^{2+} and Ti^{4+}, two-thirds of these octahedral sites will be occupied.

12.12 First of all, open the "Molecular 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 types, colors for the spheres (atoms/ions), and specify atom/ion sizes. Let us enter "Pb" as the name for the lead ions (since "Pb" the symbol for lead), and "O" as the name for the oxygen ions. Next it is necessary to choose a color for each ion type from the selections that appear in the pull-down menu—for example, "LtBlue" (light blue) for Pb and LtRed (light red) for O. In the "Atom Size" window, it is necessary to enter an atom/ion size. In the instructions for this step, it is suggested that the atom/ion diameter in nanometers be used. From the table found inside the front cover of the textbook, the ionic radii for lead and oxygen are 0.120 nm and 0.140 nm, respectively, and, therefore, their ionic diameters are twice these values (i.e., 0.240 nm and 0.280 nm); therefore, we enter the values "0.240" and "0.280" for the two atom types. Now click on the "Register" button, followed by clicking on the "Go to Step 2" button.

In the "Step 2" window we specify positions for all of the ions within the unit cell; their point coordinates are specified in the problem statement. Now we must enter a name in the box provided for each of the ions in the unit cell. For example, for oxygen let us name the first ion "O1". Its point coordinates are 000, and, therefore, we enter a "0" (zero) in each of the "x", "y", and "z" atom position boxes. Next, in the "Atom Type" pull-down menu we select "O", the name we specified in Step 1. For the next oxygen ion, which has point coordinates of 100, let us name it "O2"; since it is located a distance of *a* units along the *x*-axis the value of "0.397" is entered in the "x" atom position box (since this is the value of *a* given in the problem statement); zeros are entered in each of the "y" and "z" position boxes. We next click on the "Register" button. This same procedure is repeated for all 10 the point coordinates for the oxygen ions, as well as the four coordinates for lead ions; these values are specified in the problem statement. For the oxygen ion having point coordinates of "111" respective values of "0.397", "0.397", and "0.502" 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* (0.397) and *c* (0.502 nm), respectively. For fractional point coordinates, the appropriate *a* or *c* value is multiplied by the fraction. For example, for oxygen ions, the last point coordinate set in the left-hand column, $\frac{1}{2}\frac{1}{2}0$, the x, y, and z atom positions are $\frac{1}{2}(0.397) = 0.1985$, $\frac{1}{2}(0.397) = 0.1985$, and 0, respectively. The x, y, and z position entries for the 10 sets of point coordinates for the oxygen ions are as follows:

0, 0, and 0
0.397, 0, and 0
0, 0.397, and 0
0.397, 0.397, and 0
0.1985, 0.1985, and 0

0, 0, and 0.502
0.397, 0, and 0.502
0, 0.397, and 0.502
0.397, 0.397, and 0.502
0.1985, 0.1985, and 0.502

Likewise, for the lead ions, x, y, and z position entries for the four sets of points coordinates are the following:

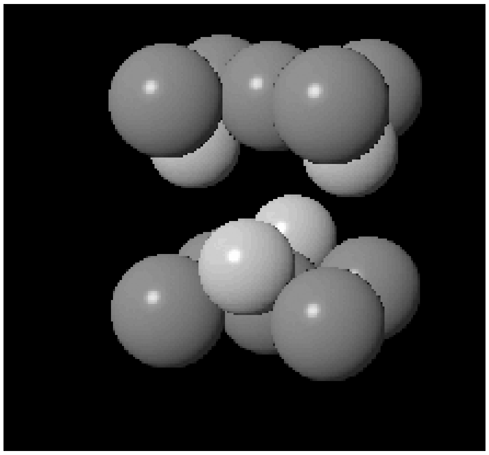
0.1985, 0, and 0.383
0.1985, 0.397, and 0.383

0, 0.1985, and 0.1190
0.397, 0.1985, and 0.1190

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 solid, single dashed, double, and triple are possibilities), or we may elect to not represent any bonds at all (in which case we click on the "Go to Step 4" button). If it is decided to show bonds, probably the best thing to do is to represent unit cell edges as bonds.

The window in Step 4 presents all the data that have been entered; you may review these data for accuracy. If any changes are required, it is necessary to close out all windows back to the one in which corrections are to be made, and then reenter data in succeeding windows. When you are fully satisfied with your data, click on the "Generate" button, and the image that you have defined will be displayed. The image may then be rotated by using mouse click-and-drag.

Your image should appear as follows:



Here the darker spheres represent oxygen ions, while lead ions are depicted by the lighter balls.

[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.]

12.13 We are asked to calculate the theoretical density of NiO. This density may be computed using Equation (12.1) as

$$\rho = \frac{n'(A_{\mathrm{Ni}} + A_{\mathrm{O}})}{V_C N_{\mathrm{A}}}$$

Since the crystal structure is rock salt, $n' = 4$ formula units per unit cell. Using the ionic radii for Ni^{2+} and O^{2-} from Table 12.3, the unit cell volume is computed as follows:

$$V_C = a^3 = \left(2r_{\mathrm{Ni}^{2+}} + 2r_{\mathrm{O}^{2-}}\right)^3 = \left[2(0.069 \text{ nm}) + 2(0.140 \text{ nm})\right]^3$$

$$= 0.0730 \ \frac{\text{nm}^3}{\text{unit cell}} = 7.30 \times 10^{-23} \ \frac{\text{cm}^3}{\text{unit cell}}$$

Thus,

$$\rho = \frac{(4 \text{ formula units/unit cell})(58.69 \text{ g/mol} + 16.00 \text{ g/mol})}{\left(7.30 \times 10^{-23} \text{ cm}^3\text{/unit cell}\right)\left(6.023 \times 10^{23} \text{ formula units/mol}\right)}$$

$$= 6.79 \text{ g/cm}^3$$

12.14 (a) This part of the problem calls for us to determine the unit cell edge length for FeO. The density of FeO is 5.70 g/cm^3 and the crystal structure is rock salt. From Equation 12.1

$$\rho = \frac{n'(A_{\mathrm{Fe}} + A_{\mathrm{O}})}{V_C N_{\mathrm{A}}} = \frac{n'(A_{\mathrm{Fe}} + A_{\mathrm{O}})}{a^3 N_{\mathrm{A}}}$$

Or, solving for *a*

$$a = \left[\frac{n'(A_{\mathrm{Fe}} + A_{\mathrm{O}})}{\rho N_{\mathrm{A}}}\right]^{1/3}$$

$$= \left[\frac{(4 \text{ formula units/unit cell})(55.85 \text{ g/mol} + 16.00 \text{ g/mol})}{(5.70 \text{ g/cm}^3)(6.023 \times 10^{23} \text{ formula units/mol})}\right]^{1/3}$$

$$= 4.37 \times 10^{-8} \text{ cm} = 0.437 \text{ nm}$$

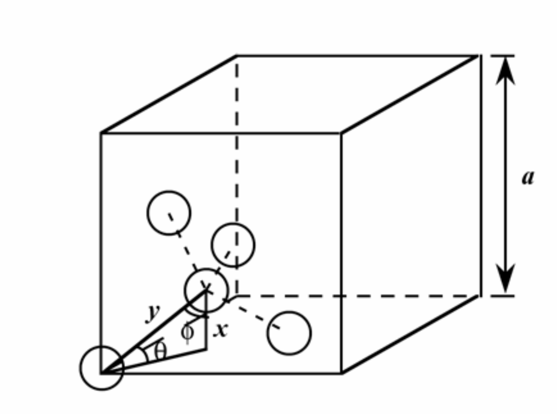
(b) The edge length is determined from the Fe^{2+} and O^{2-} radii for this portion of the problem. Now

$$a = 2r_{\mathrm{Fe}^{2+}} + 2r_{\mathrm{O}^{2-}}$$

From Table 12.3

$$a = 2(0.077 \text{ nm}) + 2(0.140 \text{ nm}) = 0.434 \text{ nm}$$

12.15 This problem asks that we compute the theoretical density of diamond given that the C—C distance and bond angle are 0.154 nm and 109.5°, respectively. The first thing we need do is to determine the unit cell edge length from the given C—C distance. The drawing below shows the cubic unit cell with those carbon atoms that bond to one another in one-quarter of the unit cell.



From this figure, ϕ is one-half of the bond angle or $\phi = 109.5°/2 = 54.75°$, which means that

$$\theta = 90° - 54.75° = 35.25°$$

since the triangle shown is a right triangle. Also, $y = 0.154$ nm, the carbon-carbon bond distance. Furthermore, $x = a/4$, and therefore,

$$x = \frac{a}{4} = y \sin \theta$$

Or

$$a = 4y \sin \theta = (4)(0.154 \text{ nm})(\sin 35.25°) = 0.356 \text{ nm}$$

$$= 3.56 \times 10^{-8} \text{ cm}$$

The unit cell volume, V_C is just a^3, that is

$$V_C = a^3 = (3.56 \times 10^{-8} \text{ cm})^3 = 4.51 \times 10^{-23} \text{cm}^3$$

We must now utilize a modified Equation 12.1 since there is only one atom type. There are 8 equivalent atoms per unit cell, and therefore

$$\rho = \frac{n' A_C}{V_C N_A}$$

$$= \frac{(8 \text{ atoms/unit cell})(12.01 \text{ g/g-atom})}{\left(4.51 \times 10^{-23} \text{ cm}^3\text{/unit cell}\right)\left(6.023 \times 10^{23} \text{ atoms/g-atom}\right)}$$

$$= 3.54 \text{ g/cm}^3$$

The measured density is 3.51 g/cm^3.

12.16 This problem asks that we compute the theoretical density of ZnS given that the Zn—S distance and bond angle are 0.234 nm and 109.5°, respectively. The first thing we need do is to determine the unit cell volume from the given Zn—S distance. From the previous problem, the unit cell volume V_C is just a^3, a being the unit cell edge length, and

$$V_C = (4y \sin\theta)^3 = [(4)(0.234\text{ nm})(\sin 35.25°)]^3$$

$$= 0.1576\text{ nm}^3 = 1.576 \times 10^{-22}\text{ cm}^3$$

Now we must utilize Equation 12.1 with $n' = 4$ formula units, and A_{Zn} and A_{S} being 65.39 and 32.06 g/mol, respectively. Thus

$$\rho = \frac{n'(A_{\text{Zn}} + A_{\text{S}})}{V_C N_{\text{A}}}$$

$$= \frac{(4\text{ formula units/unit cell})(65.39\text{ g/mol} + 32.06\text{ g/mol})}{(1.576 \times 10^{-22}\text{ cm}^3\text{/unit cell})(6.023 \times 10^{23}\text{ formula units/mol})}$$

$$= 4.11\text{ g/cm}^3$$

The measured value of the density is 4.10 g/cm^3.

12.17 We are asked to determine the number of Si^{4+} and O^{2-} ions per unit cell for a crystalline form of silica (SiO_2). For this material, $a = 0.700$ nm and $\rho = 2.32$ g/cm^3. Solving for n' from Equation 12.1, we get

$$n' = \frac{\rho V_C N_A}{A_{Si} + 2A_O} = \frac{\rho a^3 N_A}{A_{Si} + 2A_O}$$

$$= \frac{(2.32 \text{ g/cm}^3)(7.00 \text{ x } 10^{-8} \text{ cm})^3 (6.023 \text{ x } 10^{23} \text{ formula units/mol})}{(28.09 \text{ g/mol} + 2[16.00] \text{ g/mol})}$$

$$= 7.98 \text{ or almost } 8$$

Therefore, there are eight Si^{4+} and sixteen O^{2-} per unit cell.

12.18 (a) We are asked to compute the density of CsCl. Modifying the result of Problem 3.3, we get

$$a = \frac{2r_{\mathrm{Cs}^+} + 2r_{\mathrm{Cl}^-}}{\sqrt{3}} = \frac{2(0.170 \text{ nm}) + 2(0.181 \text{ nm})}{\sqrt{3}}$$

$$= 0.405 \text{ nm} = 4.05 \text{ x } 10^{-8} \text{ cm}$$

From Equation 12.1

$$\rho = \frac{n'(A_{\mathrm{Cs}} + A_{\mathrm{Cl}})}{V_C N_\mathrm{A}} = \frac{n'(A_{\mathrm{Cs}} + A_{\mathrm{Cl}})}{a^3 N_\mathrm{A}}$$

For the CsCl crystal structure, n' = 1 formula unit/unit cell, and thus

$$\rho = \frac{(1 \text{ formula unit/unit cell})(132.91 \text{ g/mol} + 35.45 \text{ g/mol})}{(4.05 \text{ x } 10^{-8} \text{ cm})^3/\text{unit cell}\,(6.023 \text{ x } 10^{23} \text{ formula units/mol})}$$

$$= 4.20 \text{ g/cm}^3$$

(b) This value of the density is greater than the measured density (3.99 g/cm^3). The reason for this discrepancy is that the ionic radii in Table 12.3, used for this computation, were for a coordination number of six, when, in fact, the coordination number of both Cs$^+$ and Cl$^-$ is eight. The ionic radii should be slightly greater, leading to a larger V_C value, and a lower density.

12.19 This problem asks that we compute the density of CaF_2. A unit cell of the fluorite structure is shown in Figure 12.5. It may be seen that there are four CaF_2 units per unit cell (i.e., $n' = 4$ formula units/unit cell). Assume that for each of the eight small cubes in the unit cell

$$a = \frac{2r_{\mathrm{Ca}^{2+}} + 2r_{\mathrm{F}^-}}{\sqrt{3}}$$

and, from Table 12.3

$$a = \frac{2(0.100 \text{ nm}) + 2(0.133 \text{ nm})}{\sqrt{3}} = 0.269 \text{ nm} = 2.69 \times 10^{-8} \text{ cm}$$

The volume of the unit cell is just

$$V_C = (2a)^3 = \left[(2)\left(2.69 \times 10^{-3} \text{ cm}\right)\right]^3 = 1.56 \times 10^{-22} \text{ cm}^3$$

Thus, from Equation 12.1

$$\rho = \frac{n'\left(A_{\mathrm{Ca}} + 2A_{\mathrm{F}}\right)}{V_C N_{\mathrm{A}}}$$

$$= \frac{(4 \text{ formula units/unit cell})\left[40.08 \text{ g/mol} + (2)(19.00 \text{ g/mol})\right]}{\left(1.56 \times 10^{-22} \text{ cm}^3\text{/unit cell}\right)\left(6.023 \times 10^{23} \text{ formula units/mol}\right)}$$

$$= 3.33 \text{ g/cm}^3$$

The measured density is 3.18 g/cm^3.

12.20 We are asked to specify possible crystal structures for an AX type of ceramic material given its density (2.10 g/cm^3), that the unit cell has cubic symmetry with edge length of 0.57 nm, and the atomic weights of the A and X elements (28.5 and 30.0 g/mol, respectively). Using Equation 12.1 and solving for n' yields

$$n' = \frac{\rho V_C N_A}{\sum A_C + \sum A_A}$$

$$= \frac{(2.10\ \text{g/cm}^3)\left[(5.70 \times 10^{-8}\ \text{cm})^3/\text{unit cell}\right](6.023 \times 10^{23}\ \text{formula units/mol})}{(30.0\ +\ 28.5)\ \text{g/mol}}$$

$$= 4.00\ \text{formula units/unit cell}$$

Of the three possible crystal structures, only sodium chloride and zinc blende have four formula units per unit cell, and therefore, are possibilities.

12.21 This problem asks us to compute the atomic packing factor for Fe_3O_4 given its density and unit cell edge length. It is first necessary to determine the number of formula units in the unit cell in order to calculate the sphere volume. Solving for *n'* from Equation 12.1 leads to

$$n' = \frac{\rho V_C N_\mathrm{A}}{\sum A_\mathrm{C} + \sum A_\mathrm{A}}$$

$$= \frac{(5.24\ \mathrm{g/cm^3})\left[(8.39 \times 10^{-8}\ \mathrm{cm})^3/\mathrm{unit\ cell}\right](6.023 \times 10^{23}\ \mathrm{formula\ units/mol})}{(3)(55.85\ \mathrm{g/mol}) + (4)(16.00\ \mathrm{g/mol})}$$

$$= 8.0\ \mathrm{formula\ units/unit\ cell}$$

Thus, in each unit cell there are 8 Fe^{2+}, 16 Fe^{3+}, and 32 O^{2-} ions. From Table 12.3, $r_{\mathrm{Fe}^{2+}} = 0.077$ nm, $r_{\mathrm{Fe}^{3+}} = 0.069$ nm, and $r_{\mathrm{O}^{2-}} = 0.140$ nm. Thus, the total sphere volume in Equation 3.2 (which we denote as V_S), is just

$$V_S = (8)\left(\frac{4}{3}\pi\right)(7.7 \times 10^{-9}\mathrm{cm})^3 + (16)\left(\frac{4}{3}\pi\right)(6.9 \times 10^{-9}\mathrm{cm})^3$$

$$+ (32)\left(\frac{4}{3}\pi\right)(1.40 \times 10^{-8}\ \mathrm{cm})^3$$

$$= 4.05 \times 10^{-22}\ \mathrm{cm^3}$$

Now, the unit cell volume (V_C) is just

$$V_C = a^3 = (8.39 \times 10^{-8}\ \mathrm{cm})^3 = 5.90 \times 10^{-22}\ \mathrm{cm^3}$$

Finally, the atomic packing factor (APF) from Equation 3.2 is just

$$\mathrm{APF} = \frac{V_S}{V_C} = \frac{4.05 \times 10^{-22}\ \mathrm{cm^3}}{5.90 \times 10^{-22}\ \mathrm{cm^3}} = 0.686$$

12.22 This problem asks for us to calculate the atomic packing factor for aluminum oxide given values for the *a* and *c* lattice parameters, and the density. It first becomes necessary to determine the value of *n'* in Equation 12.1. This necessitates that we calculate the value of V_C, the unit cell volume. In Problem 3.6 it was shown that the area of the hexagonal base (AREA) is related to *a* as

$$\text{AREA} = 6\left(\frac{a}{2}\right)^2 \sqrt{3} = 1.5a^2\sqrt{3}$$

$$= (1.5)(4.759 \text{ x } 10^{-8} \text{ cm})^2(\sqrt{3}) = 5.88 \text{ x } 10^{-15} \text{ cm}^2$$

The unit cell volume now is just

$$V_C = (\text{AREA})(c) = (5.88 \text{ x } 10^{-15} \text{ cm}^2)(1.2989 \text{ x } 10^{-7} \text{ cm})$$

$$= 7.64 \text{ x } 10^{-22} \text{ cm}^3$$

Now, solving for *n'* (Equation 12.1) yields

$$n' = \frac{\rho N_A V_C}{\sum A_C + \sum A_A}$$

$$= \frac{(3.99 \text{ g/cm}^3)(6.023 \text{ x } 10^{23} \text{ formula units/mol})(7.64 \text{ x } 10^{-22} \text{ cm}^3\text{/unit cell})}{(2)(26.98 \text{ g/mol}) + (3)(16.00\text{g/mol})}$$

$$= 18.0 \text{ formula units/unit cell}$$

Or, there are 18 Al_2O_3 units per unit cell, or 36 Al^{3+} ions and 54 O^{2-} ions. From Table 12.3, the radii of these two ion types are 0.053 and 0.140 nm, respectively. Thus, the total sphere volume in Equation 3.2 (which we denote as V_S), is just

$$V_S = (36)\left(\frac{4}{3}\pi\right)(5.3 \text{ x } 10^{-9}\text{cm})^3 + (54)\left(\frac{4}{3}\pi\right)(1.4 \text{ x } 10^{-8}\text{cm})^3$$

$$= 6.43 \text{ x } 10^{-22} \text{ cm}^3$$

Finally, the APF is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{6.43 \text{ x } 10^{-22} \text{ cm}^3}{7.64 \text{ x } 10^{-22} \text{ cm}^3} = 0.842$$

12.23 We are asked in this problem to compute the atomic packing factor for the diamond cubic crystal structure, given that the angle between adjacent bonds is 109.5°. The first thing that we must do is to determine the unit cell volume V_C in terms of the atomic radius r. From Problem 12.15 the following relationship was developed

$$a = 4y \sin \theta$$

in which $y = 2r$ and $\theta = 35.25°$. Furthermore, since the unit cell is cubic, $V_C = a^3$; therefore

$$V_C = (4y \sin \theta)^3 = [(4)(2r)(\sin 35.25°)]^3 = 98.43\, r^3$$

Now, it is necessary to determine the sphere volume in the unit cell, V_S, in terms of r. For this unit cell (Figure 12.15) there are 4 interior atoms, 6 face atoms, and 8 corner atoms. The entirety of the interior atoms, one-half of each face atom, and one-eighth of each corner atom belong to the unit cell. Therefore, there are 8 equivalent atoms per unit cell; hence

$$V_S = (8)\left(\frac{4}{3}\pi r^3\right) = 33.51\ r^3$$

Finally, the atomic packing factor is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{33.51\ r^3}{98.43\ r^3} = 0.340$$

12.24 We are asked in this problem to compute the atomic packing factor for the CsCl crystal structure. This requires that we take the ratio of the sphere volume within the unit cell and the total unit cell volume. From Figure 12.3 there is the equivalence of one Cs and one Cl ion per unit cell; the ionic radii of these two ions are 0.170 nm and 0.181 nm, respectively (Table 12.3). Thus, the sphere volume, V_S, is just

$$V_S = \frac{4}{3}(\pi)\left[(0.170\text{ nm})^3 + (0.181\text{ nm})^3\right] = 0.0454\ \text{nm}^3$$

For CsCl the unit cell edge length, a, in terms of the atomic radii is just

$$a = \frac{2r_{\text{Cs}^+} + 2r_{\text{Cl}^-}}{\sqrt{3}} = \frac{2(0.170\text{ nm}) + 2(0.181\text{ nm})}{\sqrt{3}}$$

$$= 0.405\text{ nm}$$

Since $V_C = a^3$

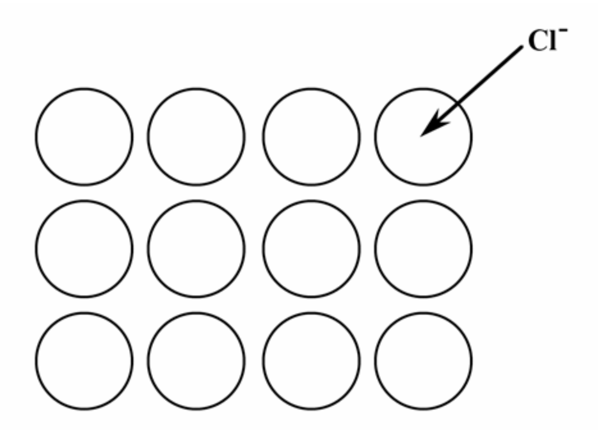
$$V_C = (0.405\text{ nm})^3 = 0.0664\text{ nm}^3$$

And, finally the atomic packing factor is just

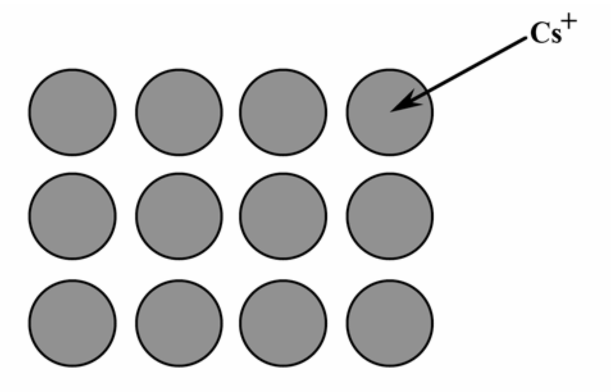
$$\text{APF} = \frac{V_S}{V_C} = \frac{0.0454\text{ nm}^3}{0.0664\text{ nm}^3} = 0.684$$

12.25 This problem asks that we represent specific crystallographic planes for various ceramic crystal structures.

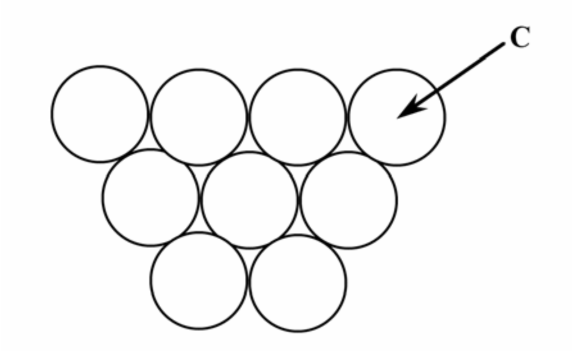
(a) A (100) plane for the cesium chloride crystal structure would appear as



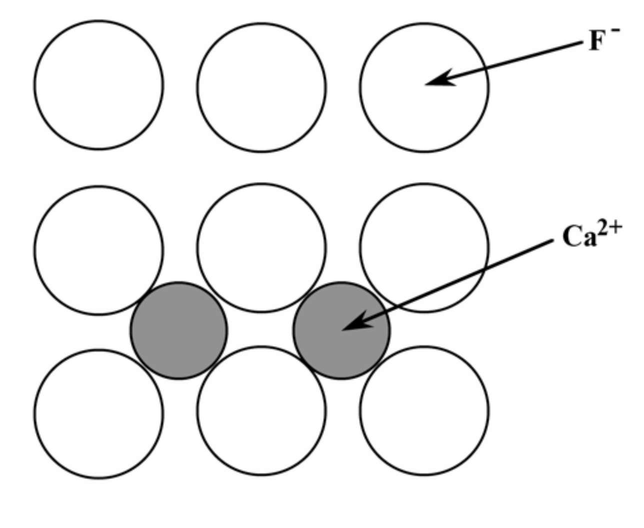
(b) A (200) plane for the cesium chloride crystal structure would appear as



(c) A (111) plane for the diamond cubic crystal structure would appear as



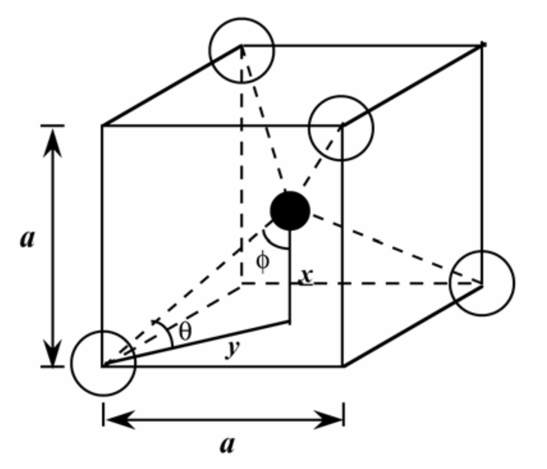
(d) A (110) plane for the fluorite crystal structure would appear as



Silicate Ceramics

12.26 The silicate materials have relatively low densities because the atomic bonds are primarily covalent in nature (Table 12.1), and, therefore, directional. This limits the packing efficiency of the atoms, and therefore, the magnitude of the density.

12.27 This problem asks for us to determine the angle between covalent bonds in the SiO_4^{4-} tetrahedron. Below is shown one such tetrahedron situated within a cube.



Now if we extend the base diagonal from one corner to the other, it is the case that

$$(2y)^2 = a^2 + a^2 = 2a^2$$

or

$$y = \frac{a\sqrt{2}}{2}$$

Furthermore, $x = a/2$, and

$$\tan\theta = \frac{x}{y} = \frac{a/2}{a\sqrt{2}/2} = \frac{1}{\sqrt{2}}$$

From which

$$\theta = \tan^{-1}\left(\frac{1}{\sqrt{2}}\right) = 35.26°$$

Now, solving for the angle ϕ

$$\phi = 180° - 90° - 35.26° = 54.74°$$

Finally, the bond angle is just 2ϕ, or $2\phi = (2)(54.74°) = 109.48°$.

Imperfections in Ceramics

12.28 Frenkel defects for anions would not exist in appreciable concentrations because the anion is quite large and is highly unlikely to exist as an interstitial.

12.29 We are asked in this problem to calculate the fraction of lattice sites that are Schottky defects for CsCl at its melting temperature (645°C), assuming that the energy for defect formation is 1.86 eV. In order to solve this problem it is necessary to use Equation 12.3 and solve for the N_s/N ratio. Rearrangement of this expression and substituting values for the several parameters leads to

$$\frac{N_s}{N} = \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \exp\left[-\frac{1.86 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(645 + 273 \text{ K})}\right]$$

$$= 7.87 \text{ x } 10^{-6}$$

12.30 This problem asks that we compute the number of Frenkel defects per cubic meter in silver chloride at 350°C. Solution of this problem is possible using Equation 12.2. However, we must first determine the value of *N*, the number of lattice sites per cubic meter, which is possible using a modified form of Equation 4.2; thus

$$N = \frac{N_\mathrm{A}\rho}{A_\mathrm{Ag} + A_\mathrm{Cl}}$$

$$= \frac{(6.023 \times 10^{23}\ \mathrm{atoms/mol})(5.50\ \mathrm{g/cm^3})(10^6\ \mathrm{cm^3/m^3})}{107.87\ \mathrm{g/mol} + 35.45\ \mathrm{g/mol}}$$

$$= 2.31 \times 10^{28}\ \text{lattice sites/m}^3$$

And, finally the value of N_{fr} is computed using Equation 12.2 as

$$N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right)$$

$$= (2.31 \times 10^{28}\ \text{lattice sites/m}^3)\exp\left[-\frac{1.1\ \mathrm{eV}}{(2)(8.62 \times 10^{-5}\ \mathrm{eV/K})(350 + 273\ \mathrm{K})}\right]$$

$$= 8.24 \times 10^{23}\ \text{defects/m}^3$$

12.31 This problem provides for some oxide ceramic, at temperatures of 750°C and 1500°C, values for density and the number of Schottky defects per cubic meter. The (a) portion of the problem asks that we compute the energy for defect formation. To begin, let us combine a modified form of Equation 4.2 and Equation 12.3 as

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \left(\frac{N_A \rho}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT}\right)$$

Inasmuch as this is a hypothetical oxide material, we don't know the atomic weight of metal M, nor the value of Q_s in the above equation. Therefore, let us write equations of the above form for two temperatures, T_1 and T_2. These are as follows:

$$N_{s1} = \left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right) \tag{12.S1a}$$

$$N_{s2} = \left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right) \tag{12.S1b}$$

Dividing the first of these equations by the second leads to

$$\frac{N_{s1}}{N_{s2}} = \frac{\left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right)}{\left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right)}$$

which, after some algebraic manipulation, reduces to the form

$$\frac{N_{s1}}{N_{s2}} = \frac{\rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{12.S2}$$

Now, taking natural logarithms of both sides of this equation gives

$$\ln\left(\frac{N_{s1}}{N_{s2}}\right) = \ln\left(\frac{\rho_1}{\rho_2}\right) - \frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and solving for Q_s leads to the expression

$$Q_s = \frac{-2k\left[\ln\left(\frac{N_{s1}}{N_{s2}}\right) - \ln\left(\frac{\rho_1}{\rho_2}\right)\right]}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Let us take T_1 = 750°C and T_2 = 1500°C, and we may compute the value of Q_s as

$$Q_s = \frac{-(2)(8.62 \times 10^{-5}\ \text{eV/K})\left[\ln\left(\frac{5.7 \times 10^{9}\ \text{m}^{-3}}{5.8 \times 10^{17}\ \text{m}^{-3}}\right) - \ln\left(\frac{3.50\ \text{g/cm}^3}{3.40\ \text{g/cm}^3}\right)\right]}{\frac{1}{750 + 273\ \text{K}} - \frac{1}{1500 + 273\ \text{K}}}$$

$$= 7.70\ \text{eV}$$

(b) It is now possible to solve for N_s at 1000°C using Equation 12.S2 above. This time let's take T_1 = 1000°C and T_2 = 750°C. Thus, solving for N_{s1}, substituting values provided in the problem statement and Q_s determined above yields

$$N_{s1} = \frac{N_{s2}\,\rho_1}{\rho_2}\exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$= \frac{(5.7 \times 10^{9}\ \text{m}^{-3})(3.45\ \text{g/cm}^3)}{3.50\ \text{g/cm}^3}\exp\left[-\frac{7.70\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})}\left(\frac{1}{1000 + 273\ \text{K}} - \frac{1}{750 + 273\ \text{K}}\right)\right]$$

$$= 3.0 \text{ x } 10^{13}\ \text{m}^{-3}$$

(c) And, finally, we want to determine the identity of metal M. This is possible by computing the atomic weight of M (A_M) from Equation 12.S1a. Rearrangement of this expression leads to

$$\left(\frac{N_\text{A}\rho_1}{A_\text{M} + A_\text{O}}\right) = N_{s1}\exp\left(\frac{Q_s}{2kT_1}\right)$$

And, after further algebraic manipulation

$$\left[\frac{N_A \rho_1}{N_{s1} \exp\left(\dfrac{Q_s}{2kT_1}\right)}\right] = A_M + A_O$$

And, solving this expression for A_M gives

$$A_M = \left[\frac{N_A \rho_1}{N_{s1} \exp\left(\dfrac{Q_s}{2kT_1}\right)}\right] - A_O$$

Now, assuming that T_1 = 750°C, the value of A_M is

$$A_M = \left\{\frac{(6.023 \times 10^{23}\ \text{ions/mol})(3.50\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{(5.7 \times 10^9\ \text{ions/m}^3)\exp\left[\dfrac{7.7\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(750 + 273\ \text{K})}\right]}\right\} - 16.00\ \text{g/mol}$$

$$= 24.45\ \text{g/mol}$$

Upon consultation of the periodic table in Figure 2.6, the divalent metal (i.e., that forms M^{2+} ions) that has an atomic weight closest to 24.45 g/mol is magnesium. Thus, this metal oxide is MgO.

12.32 Stoichiometric means having exactly the ratio of anions to cations as specified by the chemical formula for the compound.

12.33 (a) For a $Cu^{2+}O^{2-}$ compound in which a small fraction of the copper ions exist as Cu^{+}, for each Cu^{+} formed there is one less positive charge introduced (or one more negative charge). In order to maintain charge neutrality, we must either add an additional positive charge or subtract a negative charge. This may be accomplished be either creating Cu^{2+} interstitials or O^{2-} vacancies.

(b) There will be two Cu^{+} ions required for each of these defects.

(c) The chemical formula for this nonstoichiometric material is $Cu_{1+x}O$ or CuO_{1-x}, where x is some small fraction.

12.34 (a) For Ca^{2+} substituting for Li^+ in Li_2O, lithium vacancies would be created. For each Ca^{2+} substituting for Li^+, one positive charge is added; in order to maintain charge neutrality, a single positive charge may be removed. Positive charges are eliminated by creating lithium vacancies, and for every Ca^{2+} ion added, a single lithium vacancy is formed.

(b) For O^{2-} substituting for Cl^- in $CaCl_2$, chlorine vacancies would be created. For each O^{2-} substituting for a Cl^-, one negative charge is added; negative charges are eliminated by creating chlorine vacancies. In order to maintain charge neutrality, one O^{2-} ion will lead to the formation of one chlorine vacancy.

Ceramic Phase Diagrams

12.35 There is only one eutectic for the portion of the ZrO_2-CaO system shown in Figure 12.26, which, upon cooling, is

$$\text{Liquid} \rightarrow \text{cubic } ZrO_2 + CaZrO_3$$

There are two eutectoids, which reactions are as follows:

$$\text{tetragonal} \rightarrow \text{monoclinic } ZrO_2 + \text{cubic } ZrO_2$$

$$\text{cubic} \rightarrow \text{monoclinic } ZrO_2 + CaZr_4O_9$$

12.36 (a) For this portion of the problem we are to determine the type of vacancy defect that is produced on the Al_2O_3-rich side of the spinel phase field (Figure 12.25) and the percentage of these vacancies at the maximum nonstoichiometry (82 mol% Al_2O_3). On the alumina-rich side of this phase field, there is an excess of Al^{3+} ions, which means that some of the Al^{3+} ions substitute for Mg^{2+} ions. In order to maintain charge neutrality, Mg^{2+} vacancies are formed, and for every Mg^{2+} vacancy formed, two Al^{3+} ions substitute for three Mg^{2+} ions.

Now, we will calculate the percentage of Mg^{2+} vacancies that exist at 82 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material, which consists of 50 Mg^{2+} ions and 100 Al^{3+} ions. Furthermore, let us designate the number of Mg^{2+} vacancies as x, which means that $2x$ Al^{3+} ions have been added and $3x$ Mg^{2+} ions have been removed (two of which are filled with Al^{3+} ions). Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is $(100 + 2x)/2$; similarly the number of moles of MgO is $(50 – 3x)$. Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 + 2x}{2}}{\dfrac{100 + 2x}{2} + (50 - 3x)}\right] \times 100$$

If we solve for x when the mol% of Al_2O_3 = 82, then x = 12.1. Thus, adding $2x$ or (2)(12.1) = 24.2 Al^{3+} ions to the original material consisting of 100 Al^{3+} and 50 Mg^{2+} ions will produce 12.1 Mg^{2+} vacancies. Therefore, the percentage of vacancies is just

$$\text{\% vacancies} = \frac{12.1}{100 + 50} \times 100 = 8.1\%$$

(b) Now, we are asked to make the same determinations for the MgO-rich side of the spinel phase field, for 39 mol% Al_2O_3. In this case, Mg^{2+} ions are substituting for Al^{3+} ions. Since the Mg^{2+} ion has a lower charge than the Al^{3+} ion, in order to maintain charge neutrality, negative charges must be eliminated, which may be accomplished by introducing O^{2-} vacancies. For every 2 Mg^{2+} ions that substitute for 2 Al^{3+} ions, one O^{2-} vacancy is formed.

Now, we will calculate the percentage of O^{2-} vacancies that exist at 39 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material which consists of 50 Mg^{2+} ions 100 Al^{3+} ions. Furthermore, let us designate the number of O^{2-} vacancies as y, which means that $2y$ Mg^{2+} ions have been added and $2y$ Al^{3+} ions have been removed. Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is $(100 – 2y)/2$; similarly the number of moles of MgO is $(50 + 2y)$. Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 - 2y}{2}}{\dfrac{100 - 2y}{2} + (50 + 2y)}\right] \times 100$$

If we solve for y when the mol% of Al_2O_3 = 39, then $y = 7.91$. Thus, 7.91 O^{2-} vacancies are produced in the original material that had 200 O^{2-} ions. Therefore, the percentage of vacancies is just

$$\text{\% vacancies} = \frac{7.91}{200} \times 100 = 3.96\%$$

12.37 (a) The chemical formula for kaolinite clay may also be written as Al_2O_3–$2SiO_2$-$2H_2O$. Thus, if we remove the chemical water, the formula becomes Al_2O_3–$2SiO_2$. The formula weight for Al_2O_3 is just (2)(26.98 g/mol) + (3)(16.00 g/mol) = 101.96 g/mol; and for SiO_2 the formula weight is 28.09 g/mol + (2)(16.00 g/mol) = 60.09 g/mol. Thus, the composition of this product, in terms of the concentration of Al_2O_3, $C_{Al_2O_3}$, in weight percent is just

$$C_{Al_2O_3} = \frac{101.96 \text{ g/mol}}{101.96 \text{ g/mol} + (2)(60.09 \text{ g/mol})} \times 100 = 45.9 \text{ wt\%}$$

(b) The liquidus and solidus temperatures for this material as determined from the SiO_2–Al_2O_3 phase diagram, Figure 12.27, are 1825°C and 1587°C, respectively.

Brittle Fracture of Ceramics

12.38 (a) There may be significant scatter in the fracture strength for some given ceramic material because the fracture strength depends on the probability of the existence of a flaw that is capable of initiating a crack; this probability varies from specimen to specimen of the same material.

(b) The fracture strength increases with decreasing specimen size because as specimen size decreases, the probably of the existence of a flaw of that is capable of initiating a crack diminishes.

12.39 We are asked for the critical crack tip radius for a glass. From Equation 8.1

$$\sigma_m = 2\sigma_0 \left(\frac{a}{\rho_t}\right)^{1/2}$$

Fracture will occur when σ_m reaches the fracture strength of the material, which is given as $E/10$; thus

$$\frac{E}{10} = 2\sigma_0 \left(\frac{a}{\rho_t}\right)^{1/2}$$

Or, solving for ρ_t

$$\rho_t = \frac{400\ a\sigma_0^2}{E^2}$$

From Table 12.5, E = 69 GPa, and thus,

$$\rho_t = \frac{(400)\left(1 \text{ x } 10^{-2} \text{ mm}\right)(70 \text{ MPa})^2}{\left(69 \text{ x } 10^3 \text{ MPa}\right)^2}$$

$$= 4.1 \text{ x } 10^{-6} \text{ mm} = 4.1 \text{ nm}$$

12.40 This problem asks that we compute the crack tip radius ratio before and after etching. Let

$$\rho_t = \text{ original crack tip radius, and}$$
$$\rho_t' = \text{etched crack tip radius}$$

Also,

$$\sigma_f' = \sigma_f$$

$$a' = \frac{a}{2}$$

$$\sigma_0' = 4\sigma_0$$

Solving for $\dfrac{\rho_t'}{\rho_t}$ from the following

$$\sigma_f = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2} = \sigma_f' = 2\sigma_0'\left(\frac{a'}{\rho_t'}\right)^{1/2}$$

yields

$$\frac{\rho_t'}{\rho_t} = \left(\frac{\sigma_0'}{\sigma_0}\right)^2\left(\frac{a'}{a}\right) = \left(\frac{4\sigma_0}{\sigma_0}\right)^2\left(\frac{a/2}{a}\right) = 8$$

Stress-Strain Behavior

12.41 (a) For this portion of the problem we are asked to compute the flexural strength for a spinel specimen that is subjected to a three-point bending test. The flexural strength (Equation 12.7a) is just

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

for a rectangular cross-section. Using the values given in the problem statement,

$$\sigma_{fs} = \frac{(3)(350\ \text{N})\left(25\ \text{x}\ 10^{-3}\,\text{m}\right)}{(2)\left(9.0\ \text{x}\ 10^{-3}\,\text{m}\right)\left(3.8\ \text{x}\ 10^{-3}\,\text{m}\right)^2} = 101\ \text{MPa}\quad (15{,}200\ \text{psi})$$

(b) We are now asked to compute the maximum deflection. From Table 12.5, the elastic modulus (*E*) for spinel is 260 GPa (38 x 10^6 psi). Also, the moment of inertia for a rectangular cross section (Figure 12.32) is just

$$I = \frac{bd^3}{12}$$

Thus,

$$\Delta y = \frac{FL^3}{48E\left(\dfrac{bd^3}{12}\right)} = \frac{FL^3}{4Ebd^3}$$

$$= \frac{(310\ \text{N})\left(25\ \text{x}\ 10^{-3}\,\text{m}\right)^3}{(4)\left(260\ \text{x}\ 10^{9}\,\text{N/m}^2\right)\left(9.0\ \text{x}\ 10^{-3}\,\text{m}\right)\left(3.8\ \text{x}\ 10^{-3}\,\text{m}\right)^3}$$

$$= 9.4\ \text{x}\ 10^{-6}\ \text{m} = 9.4\ \text{x}\ 10^{-3}\ \text{mm}\ \left(3.9\ \text{x}\ 10^{-4}\ \text{in.}\right)$$

12.42 We are asked to calculate the maximum radius of a circular specimen of MgO that is loaded using three-point bending. Solving for R from Equation 12.7b

$$R = \left[\frac{F_f L}{\sigma_{fs}\pi}\right]^{1/3}$$

which, when substituting the parameters stipulated in the problem statement, yields

$$R = \left[\frac{(5560\ \text{N})(45\ \text{x}\ 10^{-3}\,\text{m})}{(105\ \text{x}\ 10^{6}\,\text{N/m}^2)(\pi)}\right]^{1/3}$$

$$= 9.1\ \text{x}\ 10^{-3}\ \text{m} = 9.1\ \text{mm}\ \ (0.36\ \text{in.})$$

12.43 For this problem, the load is given at which a circular specimen of aluminum oxide fractures when subjected to a three-point bending test; we are then are asked to determine the load at which a specimen of the same material having a square cross-section fractures. It is first necessary to compute the flexural strength of the aluminum oxide, Equation 12.7b, and then, using this value, we may calculate the value of F_f in Equation 12.7a. From Equation 12.7b

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$

$$= \frac{(3000 \text{ N})\left(40 \text{ x } 10^{-3} \text{ m}\right)}{(\pi)\left(5.0 \text{ x } 10^{-3} \text{ m}\right)^3} = 306 \text{ x } 10^6 \text{ N/m}^2 = 306 \text{ MPa} \quad (42{,}970 \text{ psi})$$

Now, solving for F_f from Equation 12.7a, realizing that $b = d = 12$ mm, yields

$$F_f = \frac{2\sigma_{fs} d^3}{3L}$$

$$= \frac{(2)\left(306 \text{ x } 10^6 \text{ N/m}^2\right)\left(15 \text{ x } 10^{-3} \text{m}\right)^3}{(3)\left(40 \text{ x } 10^{-3} \text{m}\right)} = 17{,}200 \text{ N} \quad (3870 \text{ lb}_\text{f})$$

12.44 (a) This portion of the problem asks that we determine whether or not a cylindrical specimen of aluminum oxide having a flexural strength of 300 MPa (43,500 psi) and a radius of 5 mm will fracture when subjected to a load of 7500 N in a three-point bending test; the support point separation is given as 15 mm. Using Equation 12.7b we will calculate the value of σ; if this value is greater than σ_{fs} (300 MPa), then fracture is expected to occur. Employment of Equation 12.7b yields

$$\sigma = \frac{FL}{\pi R^3} = \frac{(7500 \text{ N})(15 \text{ x } 10^{-3} \text{ m})}{(\pi)(5 \text{ x } 10^{-3} \text{ m})^3} = 286.5 \text{ x } 10^6 \text{ N/m}^2 = 286.5 \text{ MPa} \quad (40{,}300 \text{ psi})$$

Since this value is less than the given value of σ_{fs} (300 MPa), then fracture is not predicted.

(b) The certainty of this prediction is not 100% because there is always some variability in the flexural strength for ceramic materials, and since this value of σ is relatively close to σ_{fs} then there is some chance that fracture will occur.

Mechanisms of Plastic Deformation

12.45 Crystalline ceramics are harder yet more brittle than metals because they (ceramics) have fewer slip systems, and, therefore, dislocation motion is highly restricted.

Miscellaneous Mechanical Considerations

12.46 (a) This portion of the problem requests that we compute the modulus of elasticity for nonporous spinel given that E = 240 GPa for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0, using P = 0.05, which gives

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{240 \text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 265 \text{ GPa} \quad \left(38.6 \text{ x } 10^6 \text{ psi}\right)$$

(b) Now we are asked to determine the value of E at P = 15 vol% (i.e., 0.15). Using Equation 12.9 we get

$$E = E_0\left(1 - 1.9P + 0.9P^2\right)$$

$$= (265 \text{ GPa})\left[1 - (1.9)(0.15) + (0.09)(0.15)^2\right] = 195 \text{ GPa} \quad \left(28.4 \text{ x } 10^6 \text{ psi}\right)$$

12.47 (a) This portion of the problem requests that we compute the modulus of elasticity for nonporous TiC given that E = 310 GPa (45 x 10^6 psi) for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0, using P = 0.05, which gives

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{310 \text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 342 \text{ GPa} \quad (49.6 \text{ x } 10^6 \text{ psi})$$

(b) Now we are asked to compute the volume percent porosity at which the elastic modulus of TiC is 240 MPa (35 x 10^6 psi). Since from part (a), E_0 = 342 GPa, and using Equation 12.9 we get

$$\frac{E}{E_0} = \frac{240 \text{ MPa}}{342 \text{ MPa}} = 0.702 = 1 - 1.9P + 0.9P^2$$

Or

$$0.9P^2 - 1.9P + 0.298 = 0$$

Now, solving for the value of P using the quadratic equation solution yields

$$P = \frac{1.9 \pm \sqrt{(-1.9)^2 - (4)(0.9)(0.298)}}{(2)(0.9)}$$

The positive and negative roots are

$$P^+ = 1.94$$

$$P^- = 0.171$$

Obviously, only the negative root is physically meaningful, and therefore the value of the porosity to give the desired modulus of elasticity is 17.1 vol%.

12.48 (a) This part of the problem asks us to determine the flexural strength of nonporous MgO assuming that the value of n in Equation 12.10 is 3.75. Taking natural logarithms of both sides of Equation 12.10 yields

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

In Table 12.5 it is noted that for $P = 0.05$, $\sigma_{fs} = 105$ MPa. For the nonporous material $P = 0$ and, $\ln \sigma_0 = \ln \sigma_{fs}$. Solving for $\ln \sigma_0$ from the above equation and using these data gives

$$\ln \sigma_0 = \ln \sigma_{fs} + nP$$

$$= \ln (105 \text{ MPa}) + (3.75)(0.05) = 4.841$$

or $\sigma_0 = e^{4.841} = 127$ MPa (18,100 psi)

(b) Now we are asked to compute the volume percent porosity to yield a σ_{fs} of 74 MPa (10,700 psi). Taking the natural logarithm of Equation 12.10 and solving for P leads to

$$P = \frac{\ln \sigma_0 - \ln \sigma_{fs}}{n}$$

$$= \frac{\ln (127 \text{ MPa}) - \ln (74 \text{ MPa})}{3.75}$$

$$= 0.144 \text{ or } 14.4 \text{ vol\%}$$

12.49 (a) Given the flexural strengths at two different volume fraction porosities, we are asked to determine the flexural strength for a nonporous material. If the natural logarithm is taken of both sides of Equation 12.10, then

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

Using the data provided in the problem statement, two simultaneous equations may be written as

$$\ln (70 \text{ MPa}) = \ln \sigma_0 - (0.10)\, n$$

$$\ln (60 \text{ MPa}) = \ln \sigma_0 - (0.15)\, n$$

Solving for n and σ_0 leads to $n = 3.08$ and $\sigma_0 = 95.3$ MPa. For the nonporous material, $P = 0$, and, from Equation 12.10, $\sigma_0 = \sigma_{fs}$. Thus, σ_{fs} for $P = 0$ is 95.3 MPa.

(b) Now, we are asked for σ_{fs} at $P = 0.20$ for this same material. Utilizing Equation 12.10 yields

$$\sigma_{fs} = \sigma_0 \exp(-nP)$$

$$= (95.3 \text{ MPa}) \exp\left[-(3.08)(0.20)\right]$$

$$= 51.5 \text{ MPa}$$

DESIGN PROBLEMS

Crystal Structures

12.D1 This problem asks that we determine the concentration (in weight percent) of InAs that must be added to GaAs to yield a unit cell edge length of 0.5820 nm. The densities of GaAs and InAs were given in the problem statement as 5.316 and 5.668 g/cm^3, respectively. To begin, it is necessary to employ Equation 12.1, and solve for the unit cell volume, V_C, for the InAs-GaAs alloy as

$$V_C = \frac{n' A_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

where A_{ave} and ρ_{ave} are the atomic weight and density, respectively, of the InAs-GaAs alloy. Inasmuch as both of these materials have the zinc blende crystal structure, which has cubic symmetry, V_C is just the cube of the unit cell length, a. That is

$$V_C = a^3 = (0.5820 \text{ nm})^3$$

$$= \left(5.820 \times 10^{-8} \text{ cm}\right)^3 = 1.971 \times 10^{-22} \text{ cm}^3$$

It is now necessary to construct expressions for A_{ave} and ρ_{ave} in terms of the concentration of indium arsenide, C_{InAs} using Equations 4.11a and 4.10a. For A_{ave} we have

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{A_{\text{InAs}}} + \dfrac{\left(100 - C_{\text{InAs}}\right)}{A_{\text{GaAs}}}}$$

$$= \frac{100}{\dfrac{C_{\text{InAs}}}{189.74 \text{ g/mol}} + \dfrac{\left(100 - C_{\text{InAs}}\right)}{144.64 \text{ g/mol}}}$$

whereas for ρ_{ave}

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{\rho_{\text{InAs}}} + \dfrac{\left(100 - C_{\text{InAs}}\right)}{\rho_{\text{GaAs}}}}$$

$$= \frac{100}{\dfrac{C_{\text{InAs}}}{5.668\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{InAs}})}{5.316\ \text{g/cm}^3}}$$

Within the zinc blende unit cell there are four formula units, and thus, the value of *n'* in Equation 12.1 is 4; hence, this expression may be written in terms of the concentration of InAs in weight percent as follows:

$$V_C = 1.971 \text{ x } 10^{-22} \text{ cm}^3$$

$$= \frac{n' A_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= \frac{(4\ \text{fu/unit cell})\left[\dfrac{100}{\dfrac{C_{\text{InAs}}}{189.74\ \text{g/mol}} + \dfrac{(100 - C_{\text{InAs}})}{144.64\ \text{g/mol}}}\right]}{\left[\dfrac{100}{\dfrac{C_{\text{InAs}}}{5.668\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{InAs}})}{5.316\ \text{g/cm}^3}}\right](6.023 \text{ x } 10^{23}\ \text{fu/mol})}$$

And solving this expression for C_{InAs} leads to C_{InAs} = 46.1 wt%.

Stress-Strain Behavior

12.D2 This problem asks for us to determine which of the ceramic materials in Table 12.5, when fabricated into cylindrical specimens and stressed in three-point loading, will not fracture when a load of 445 N (100 lb_f) is applied, and also will not experience a center-point deflection of more than 0.021 mm (8.5 x 10^{-4} in.). The first of these criteria is met by those materials that have flexural strengths greater than the stress calculated using Equation 12.7b. According to this expression

$$\sigma_{fs} = \frac{FL}{\pi R^3}$$

$$= \frac{(445\text{ N})(50.8 \text{ x } 10^{-3}\text{ m})}{(\pi)(3.8 \text{ x } 10^{-3}\text{ m})^3} = 131 \text{ x } 10^6 \text{ N/m}^2 = 131 \text{ MPa } (18{,}900 \text{ psi})$$

Of the materials in Table 12.5, the following have flexural strengths greater than this value: Si_3N_4, ZrO_2, SiC, Al_2O_3, glass-ceramic, mullite, and spinel.

For the second criterion we must solve for the magnitude of the modulus of elasticity, *E*, from the equation given in Problem 12.41 where the expression for the cross-sectional moment of inertia appears in Figure 12.32; that is, for a circular cross-section $I = \frac{\pi R^4}{4}$. Solving for *E* from these two expressions

$$E = \frac{FL^3}{12\pi R^4 \Delta y}$$

$$= \frac{(445\text{ N})(50.8 \text{ x } 10^{-3}\text{ m})^3}{(12)(\pi)(3.8 \text{ x } 10^{-3}\text{ m})^4 (0.021 \text{ x } 10^{-3}\text{ m})}$$

$$= 353 \text{ x } 10^9 \text{ N/m}^2 = 353 \text{ GPa } (49.3 \text{ x } 10^6 \text{ psi})$$

Of those materials that satisfy the first criterion, only Al_2O_3 has a modulus of elasticity greater than this value (Table 12.5), and, therefore, is a possible candidate.

CHAPTER 13

APPLICATIONS AND PROCESSING OF CERAMICS

PROBLEM SOLUTIONS

Glasses

Glass-Ceramics

13.1 Two desirable characteristics of glasses are optical transparency and ease of fabrication.

13.2 (a) Crystallization is the process whereby a glass material is caused to transform to a crystalline solid, usually by a heat treatment.

(b) Two properties that may be improved by crystallization are (1) a lower coefficient of thermal expansion, and (2) higher strengths.

Refractories

13.3 For refractory ceramic materials, three characteristics that improve with increasing porosity are (1) decreased thermal expansion and contraction upon thermal cycling, (2) improved thermal insulation, and (3) improved resistance to thermal shock. Two characteristics that are adversely affected are (1) load-bearing capacity and (2) resistance to attack by corrosive materials.

13.4 (a) From Figure 12.25, for a spinel-bonded magnesia material (88.5 wt%MgO-11.5 wt% Al_2O_3), the maximum temperature without a liquid phase corresponds to the temperature at the MgO(ss)-[MgO(ss) + Liquid] boundary at this composition, which is approximately 2220°C (4030°F).

(b) The maximum temperature without the formation of a liquid phase for a magnesia-alumina spinel (25 wt%MgO-75 wt% Al_2O_3) lies at the phase boundary between $MgAl_2O_4$(ss)-($MgAl_2O_4$ + Liquid) phase fields (just slightly to the right of the congruent melting point at which the two phase boundaries become tangent); this temperature is approximately 2070°C (3760°F).

13.5 For each section of this problem two SiO_2-Al_2O_3 compositions are given; we are to decide, on the basis of the SiO_2-Al_2O_3 phase diagram (Figure 12.27), which is the more desirable refractory and then justify the choice.

(a) The 99.8 wt% SiO_2-0.2 wt% Al_2O_3 will be more desirable because the liquidus temperature will be greater for this composition; therefore, at any temperature within the cristobalite + liquid region on the phase diagram, there will be a lower fraction of the liquid phase present than for the 99.0 wt% SiO_2-1.0 wt% Al_2O_3 composition, and, thus, the mechanical integrity will be greater.

(b) The 74 wt% Al_2O_3-26 wt% SiO_2 composition will be more desirable because, for this composition, a liquid phase does not form until about 1750°C [i.e., the temperature at which a vertical line at 74 wt% Al_2O_3 crosses the boundary between the mullite and (mullite + liquid) phase regions]; for the 70 wt% Al_2O_3-30 wt% SiO_2 material, a liquid phase forms at a much lower temperature--1587°C.

(c) The 95 wt% Al_2O_3-5 wt% SiO_2 composition will be more desirable because the liquidus temperature will be greater for this composition. Therefore, at any temperature within the alumina + liquid region on the phase diagram, there will be a lower fraction of the liquid phase present than for the 90 wt% Al_2O_3-10 wt% SiO_2 composition, and, thus, the mechanical integrity of the 95 wt% Al_2O_3-5 wt% SiO_2 material will be greater.

13.6 This problem calls for us to compute the mass fractions of liquid for two fireclay refractory materials at 1600°C. In order to solve this problem it is necessary that we use the SiO_2-Al_2O_3 phase diagram (Figure 12.27). The mass fraction of liquid, W_L, as determined using the lever rule and tie line at 1600°C, is just

$$W_L = \frac{C_{\text{mullite}} - C_0}{C_{\text{mullite}} - C_L}$$

where C_{mullite} = 72 wt% Al_2O_3 and C_L = 8 wt% Al_2O_3, as determined using the tie-line; also, C_0 is the composition (in weight percent Al_2O_3) of the refractory material.

(a) For the 25 wt% Al_2O_3-75 wt% SiO_2 composition, C_0 = 25 wt% Al_2O_3, and

$$W_L = \frac{72 - 25}{72 - 8} = 0.73$$

(b) For the 45 wt% Al_2O_3-55 wt% SiO_2 composition, C_0 = 45 wt% Al_2O_3, and

$$W_L = \frac{72 - 45}{72 - 8} = 0.42$$

13.7 This problem asks that we specify, for the MgO-Al_2O_3 system, Figure 12.25, the maximum temperature without the formation of a liquid phase; it is approximately 2800°C which is possible for pure MgO.

Cements

13.8 For clay-based aggregates, a liquid phase forms during firing, which infiltrates the pores between the unmelted particles; upon cooling, this liquid becomes a glass, that serves as the bonding phase.

With cements, the bonding process is a chemical, hydration reaction between the water that has been added and the various cement constituents. The cement particles are bonded together by reactions that occur at the particle surfaces.

Fabrication and Processing of Glasses and Glass-Ceramics

13.9 We are asked to compute the weight of soda ash and limestone that must be added to 125 lb_m of SiO_2 to yield a glass composition of 78 wt% SiO_2, 17 wt% Na_2O, and 5 wt% CaO. Let x = the weight of Na_2O and y = the weight of CaO. Then, employment of a modified form Equation 4.3, we may write the following expressions for the concentrations of Na_2O (C_{Na_2O}) and CaO (C_{CaO}):

$$C_{Na_2O} = 17\text{ wt\%} = \frac{x}{125 + x + y} \times 100$$

$$C_{CaO} = 5\text{ wt\%} = \frac{y}{125 + x + y} \times 100$$

Solving for x and y from these two expressions yields x = 27.2 lb_m Na_2O and y = 8.0 lb_m CaO.

Now, in order to compute the weights of Na_2CO_3 and $CaCO_3$, we must employ molecular weights. The molecular weights of Na_2CO_3 $(MW_{Na_2CO_3})$ and Na_2O (MW_{Na_2O}) are as follows:

$$MW_{Na_2CO_3} = 2(A_{Na}) + A_C + 3(A_O)$$

$$= 2(22.99\text{ g/mol}) + 12.01\text{ g/mol} + 3(16.00\text{g/mol}) = 105.99\text{ g/mol}$$

$$MW_{Na_2O} = 2(A_{Na}) + A_O$$

$$= 2(22.99\text{ g/mol}) + 16.00\text{ g/mol} = 61.98\text{ g/mol}$$

And, finally, the mass of Na_2CO_3 $(m_{Na_2CO_3})$ is equal to

$$m_{Na_2CO_3} = (27.2\ lb_m)\left(\frac{MW_{Na_2CO_3}}{MW_{Na_2O}}\right)$$

$$= (27.2\ lb_m)\left(\frac{105.99\text{ g/mol}}{61.98\text{ g/mol}}\right) = 46.5\ lb_m$$

Likewise, the molecular weights of $CaCO_3$ (MW_{CaCO_3}) and CaO (MW_{CaO}) are as follows:

$$MW_{CaCO_3} = A_{Ca} + A_C + 3(A_O)$$

$$= 40.08 \text{ g/mol} + 12.01 \text{ g/mol} + (3)(16.00 \text{ g/mol}) = 100.09 \text{ g/mol}$$

$$MW_{CaO} = A_{Ca} + A_O$$

$$= 40.08 \text{ g/mol} + 16.00 \text{ g/mol} = 56.08 \text{ g/mol}$$

Such that the mass of $CaCO_3$ (m_{CaCO_3}) is equal to

$$m_{CaCO_3} = (8.0 \text{ lb}_m)\left(\frac{MW_{CaCO_3}}{MW_{CaO}}\right)$$

$$= (8.0 \text{ lb}_m)\left(\frac{100.09 \text{ g/mol}}{56.08 \text{ g/mol}}\right) = 14.3 \text{ lb}_m$$

13.10 The glass transition temperature is, for a noncrystalline ceramic, that temperature at which there is a change of slope for the specific volume versus temperature curve (Figure 13.6).

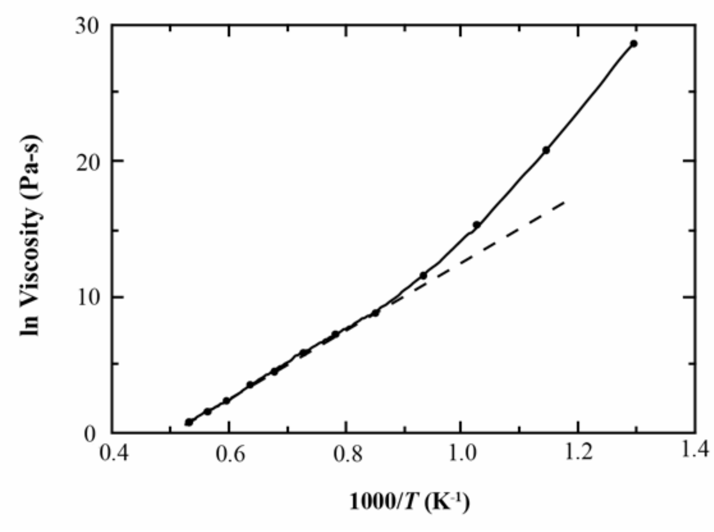
The melting temperature is, for a crystalline material, that temperature at which there is a sudden and discontinuous decrease in the specific-volume-versus-temperature curve.

13.11 The annealing point is that temperature at which the viscosity of the glass is 10^{12} Pa-s (10^{13} P). From Figure 13.7, these temperatures for the several glasses are as follows:

Glass	Annealing Temperature
Soda-lime	500°C (930°F)
Borosilicate	570°C (1060°F)
96% Silica	930°C (1705°F)
Fused silica	1170°C (2140°F)

13.12 The softening point of a glass is that temperature at which the viscosity is 4 x 10^6 Pa-s; from Figure 13.7, these temperatures for the 96% silica, borosilicate, and soda-lime glasses are 1540°C (2800°F), 830°C (1525°F), and 700°C (1290°F), respectively.

13.13 (a) Below is shown the logarithm viscosity versus reciprocal of temperature plot for the soda-lime glass, using the data in Figure 13.7. The dashed line has been drawn through the data points corresponding to temperatures between 900 and 1600ºC (as stipulated in the problem statement).



(b) The activation energy, Q_{vis}, may be computed according to

$$Q_{\text{vis}} = R\left[\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}\right] = R\left(\frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}\right)$$

where R is the gas constant, and $\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}$ is the slope of the dashed line that has been constructed. Taking $1/T_1$ and $1/T_2$ as 0.6×10^{-3} and 1.10×10^{-3} K^{-1}, respectively, then the corresponding values of $\ln \eta_1$ and $\ln \eta_2$ are 2.5 and 15.0. Therefore,

$$Q_{\text{vis}} = R\left(\frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}\right) = (8.31 \text{ J/mol} - \text{K})\left(\frac{2.5 - 15.0}{0.6 \times 10^{-3} \text{ K}^{-1} - 1.10 \times 10^{-3} \text{ K}^{-1}}\right)$$

$$= 208{,}000 \text{ J/mol}$$

13.14 This problem calls for us to determine the maximum temperature to which a cylindrical specimen of borosilicate glass may be heated in order that its deformation be less than 2.5 mm over a week's time. According to Equation 6.1

$$\sigma = \frac{F}{A_0} = \frac{2\ \text{N}}{\pi\left(\dfrac{4\ \text{x}\ 10^{-3}\ \text{m}}{2}\right)^2} = 1.59\ \text{x}\ 10^5\ \text{Pa}$$

Also,

$$\frac{d\varepsilon}{dt} = \frac{d\left(\dfrac{\Delta l}{l_0}\right)}{dt}$$

$$= \frac{2.5\ \text{mm}/125\ \text{mm}}{(1\ \text{wk})(7\ \text{days}/\text{week})(24\ \text{h}/\text{day})(3600\ \text{s}/\text{h})} = 3.31\ \text{x}\ 10^{-8}\ \text{s}^{-1}$$

Thus,

$$\eta = \frac{\sigma}{d\varepsilon/dt} = \frac{1.59\ \text{x}\ 10^5\ \text{Pa}}{3.31\ \text{x}\ 10^{-8}\ \text{s}^{-1}} = 4.8\ \text{x}\ 10^{12}\ \text{Pa - s}$$

From Figure 13.7, the temperature at which the viscosity of the borosilicate glass is 4.8 x 10^{12} Pa-s is about 540°C (1005°F).

13.15 (a) Residual thermal stresses are introduced into a glass piece when it is cooled because surface and interior regions cool at different rates, and, therefore, contract different amounts; since the material will experience very little, if any deformation, stresses are established.

(b) Yes, thermal stresses will be introduced because of thermal expansion upon heating for the same reason as for thermal contraction upon cooling.

13.16 Borosilicate glasses and fused silica are resistant to thermal shock because they have relatively low coefficients of thermal expansion; therefore, upon heating or cooling, the difference in the degree of expansion or contraction across a cross-section of a ware that is constructed from these materials will be relatively low.

13.17 Thermal tempering of glasses is described in Section 13.9.

13.18 Chemical tempering will be accomplished by substitution, for Na^+, another monovalent cation with a slightly larger diameter. From Table 12.3, both K^+ and Cs^+ fill these criteria, having ionic radii of 0.138 and 0.170 nm, respectively, which are larger than the ionic radius of Na^+ (0.102 nm). In fact, soda-lime glasses are tempered by a K^+-Na^+ ion exchange.

Fabrication and Processing of Clay Products

13.19 Two desirable characteristics of clay minerals relative to fabrication processes are (1) they become hydroplastic (and therefore formable) when mixed with water; and (2) during firing, clays melt over a range of temperatures, which allows some fusion and bonding of the ware without complete melting and a loss of mechanical integrity and shape.

13.20 Clays become hydroplastic when water is added because the water molecules occupy regions between the layered molecular sheets; these water molecules essentially eliminate the secondary molecular bonds between adjacent sheets, and also form a thin film around the clay particles. The net result is that the clay particles are relatively free to move past one another, which is manifested as the hydroplasticity phenomenon.

13.21 (a) The three components of a whiteware ceramic are clay, quartz, and a flux.

(b) With regard to the role that each component plays:

Quartz acts as a filler material.

Clay facilitates the forming operation since, when mixed with water, the mass may be made to become either hydroplastic or form a slip. Also, since clays melt over a range of temperatures, the shape of the piece being fired will be maintained.

The flux facilitates the formation of a glass having a relatively low melting temperature.

13.22 (a) It is important to control the rate of drying inasmuch as if the rate of drying is too rapid, there will be nonuniform shrinkage between surface and interior regions, such that warping and/or cracking of the ceramic ware may result.

(b) Three factors that affect the rate of drying are temperature, humidity, and rate of air flow. The rate of drying is enhanced by increasing both the temperature and rate of air flow, and by decreasing the humidity of the air.

13.23 The reason that drying shrinkage is greater for products having smaller clay particles is because there is more particle surface area, and, consequently, more water will surround a given volume of particles. The drying shrinkage will thus be greater as this water is removed, and as the interparticle separation decreases.

13.24 (a) Three factors that influence the degree to which vitrification occurs in clay-based ceramic wares are: (1) composition (especially the concentration of flux present); (2) the temperature of firing; and (3) the time at the firing temperature.

(b) Density will increase with degree of vitrification since the total remaining pore volume decreases.

Firing distortion will increase with degree of vitrification since more liquid phase will be present at the firing temperature.

Strength will also increase with degree of vitrification inasmuch as more of the liquid phase forms, which fills in a greater fraction of pore volume. Upon cooling, the liquid forms a glass matrix of relatively high strength.

Corrosion resistance normally increases also, especially at service temperatures below that at which the glass phase begins to soften. The rate of corrosion is dependent on the amount of surface area exposed to the corrosive medium; hence, decreasing the total surface area by filling in some of the surface pores, diminishes the corrosion rate.

Thermal conductivity will increase with degree of vitrification. The glass phase has a higher conductivity than the pores that it has filled.

Powder Pressing

13.25 The principal disadvantage of hot-isostatic pressing is that it is expensive. The pressure is applied on a pre-formed green piece by a gas. Thus, the process is slow, and the equipment required to supply the gas and withstand the elevated temperature and pressure is costly.

DESIGN PROBLEM

13.D1 (a) Important characteristics that are required of a ceramic material to be used for kitchen cookware are: (1) it must have a high resistance to thermal shock (Section 19.5) in order to withstand relatively rapid changes in temperature; (2) it must have a relatively high thermal conductivity; 3) it must be relatively strong and tough in order to endure normal kitchen use; and 4) it must be nontoxic.

(b) Possible materials worth considering are a common soda-lime glass, a borosilicate (Pyrex) glass, and a glass ceramic. These materials and some of their characteristics are discussed in this chapter. Using Equation 17.9 a comparison of the resistance to thermal shock may be made. The student will need to obtain cost information.

(c) It is left to the student to make this determination and justify the decision.

CHAPTER 14

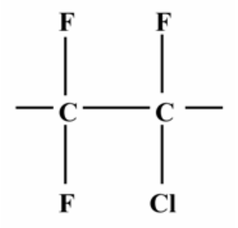
POLYMER STRUCTURES

PROBLEM SOLUTIONS

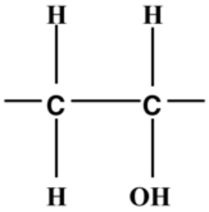
Hydrocarbon Molecules
Polymer Molecules
The Chemistry of Polymer Molecules

14.1 The repeat unit structures called for are sketched below.

(a) Polychlorotrifluoroethylene



(b) Poly(vinyl alcohol)



Molecular Weight

14.2 Repeat unit weights for several polymers are asked for in this problem.

(a) For polytetrafluoroethylene, each repeat unit consists of two carbons and four fluorines (Table 14.3). If A_C and A_F represent the atomic weights of carbon and fluorine, respectively, then

$$m = 2(A_C) + 4(A_F)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

(b) For poly(methyl methacrylate), from Table 14.3, each repeat unit has five carbons, eight hydrogens, and two oxygens. Thus,

$$m = 5(A_C) + 8(A_H) + 2(A_O)$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) + (2)(16.00 \text{ g/mol}) = 100.11 \text{ g/mol}$$

(c) For nylon 6,6, from Table 14.3, each repeat unit has twelve carbons, twenty-two hydrogens, two nitrogens, and two oxygens. Thus,

$$m = 12(A_C) + 22(A_H) + 2(A_N) + 2(A_O)$$

$$= (12)(12.01 \text{ g/mol}) + (22)(1.008 \text{ g/mol}) + (2)(14.01 \text{ g/mol}) + (2)(16.00 \text{ g/mol})$$

$$= 226.32 \text{ g/mol}$$

(d) For poly(ethylene terephthalate), from Table 14.3, each repeat unit has ten carbons, eight hydrogens, and four oxygens. Thus,

$$m = 10(A_C) + 8(A_H) + 4(A_O)$$

$$= (10)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) + (4)(16.00 \text{ g/mol}) = 192.16 \text{ g/mol}$$

14.3 We are asked to compute the degree of polymerization for polystyrene, given that the number-average molecular weight is 500,000 g/mol. The repeat unit molecular weight of polystyrene is just

$$m = 8(A_\mathrm{C}) + 8(A_\mathrm{H})$$

$$= (8)(12.01\ \mathrm{g/mol}) + (8)(1.008\ \mathrm{g/mol}) = 104.14\ \mathrm{g/mol}$$

Now it is possible to compute the degree of polymerization using Equation 14.6 as

$$DP = \frac{\overline{M}_n}{m} = \frac{500{,}000\ \mathrm{g/mol}}{104.14\ \mathrm{g/mol}} = 4800$$

14.4 (a) The repeat unit molecular weight of polypropylene is called for in this portion of the problem. For polypropylene, from Table 14.3, each repeat unit has three carbons and six hydrogens. Thus,

$$m = 3(A_{\mathrm{C}}) + 6(A_{\mathrm{H}})$$

$$= (3)(12.01\text{ g/mol}) + (6)(1.008\text{ g/mol}) = 42.08\text{ g/mol}$$

(b) We are now asked to compute the number-average molecular weight. Since the degree of polymerization is 15,000, using Equation 14.6

$$\overline{M}_n = (DP)m = (15{,}000)(42.08\text{ g/mol}) = 631{,}000\text{ g/mol}$$

14.5 (a) From the tabulated data, we are asked to compute $\overline{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt Range	Mean M_i	x_i	x_iM_i
10,000-20,000	15,000	0.03	450
20,000-30,000	25,000	0.09	2250
30,000-40,000	35,000	0.15	5250
40,000-50,000	45,000	0.25	11,250
50,000-60,000	55,000	0.22	12,100
60,000-70,000	65,000	0.14	9100
70,000-80,000	75,000	0.08	6000
80,000-90,000	85,000	0.04	3400

$$\overline{M}_n = \sum x_i M_i = 49,800 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\overline{M}_w$, the weight-average molecular weight.

Molecular wt. Range	Mean M_i	w_i	w_iM_i
10,000-20,000	15,000	0.01	150
20,000-30,000	25,000	0.04	1000
30,000-40,000	35,000	0.11	3850
40,000-50,000	45,000	0.23	10,350
50,000-60,000	55,000	0.24	13,200
60,000-70,000	65,000	0.18	11,700
70,000-80,000	75,000	0.12	9000
80,000-90,000	85,000	0.07	5950

$$\overline{M}_w = \sum w_i M_i = 55,200 \text{ g/mol}$$

(c) Now we are asked to compute the degree of polymerization, which is possible using Equation 14.6. For polytetrafluoroethylene, the repeat unit molecular weight is just

$$m = 2(A_{\text{C}}) + 4(A_{\text{F}})$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

And

$$DP = \frac{\overline{M}_n}{m} = \frac{49{,}800 \text{ g/mol}}{100.02 \text{ g/mol}} = 498$$

14.6 (a) From the tabulated data, we are asked to compute $\overline{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt. Range	Mean M_i	x_i	$x_i M_i$
8,000-20,000	14,000	0.05	700
20,000-32,000	26,000	0.15	3900
32,000-44,000	38,000	0.21	7980
44,000-56,000	50,000	0.28	14,000
56,000-68,000	62,000	0.18	11,160
68,000-80,000	74,000	0.10	7400
80,000-92,000	86,000	0.03	2580

$$\overline{M}_n = \sum x_i M_i = 47{,}720 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\overline{M}_w$, the weight-average molecular weight. This determination is performed as follows:

Molecular wt. Range	Mean M_i	w_i	$w_i M_i$
8,000-20,000	14,000	0.02	280
20,000-32,000	26,000	0.08	2080
32,000-44,000	38,000	0.17	6460
44,000-56,000	50,000	0.29	14,500
56,000-68,000	62,000	0.23	14,260
68,000-80,000	74,000	0.16	11,840
80,000-92,000	86,000	0.05	4300

$$\overline{M}_w = \sum w_i M_i = 53{,}720 \text{ g/mol}$$

(c) We are now asked if the degree of polymerization is 477, which of the polymers in Table 14.3 is this material? It is necessary to compute m in Equation 14.6 as

$$m = \frac{\overline{M}_n}{DP} = \frac{47{,}720 \text{ g/mol}}{477} = 100.04 \text{ g/mol}$$

The repeat unit molecular weights of the polymers listed in Table 14.3 are as follows:

Polyethylene--28.05 g/mol
Poly(vinyl chloride)--62.49 g/mol
Polytetrafluoroethylene--100.02 g/mol
Polypropylene--42.08 g/mol
Polystyrene--104.14 g/mol
Poly(methyl methacrylate)--100.11 g/mol
Phenol-formaldehyde--133.16 g/mol
Nylon 6,6--226.32 g/mol
PET--192.16 g/mol
Polycarbonate--254.27 g/mol

Therefore, polytetrafluoroethylene is the material since its repeat unit molecular weight is closest to that calculated above.

14.7 This problem asks if it is possible to have a poly(vinyl chloride) homopolymer with the given molecular weight data and a degree of polymerization of 1120. The appropriate data are given below along with a computation of the number-average molecular weight.

Molecular wt. Range	Mean M_i	x_i	x_iM_i
8,000-20,000	14,000	0.05	700
20,000-32,000	26,000	0.15	3900
32,000-44,000	38,000	0.21	7980
44,000-56,000	50,000	0.28	14,000
56,000-68,000	62,000	0.18	11,160
68,000-80,000	74,000	0.10	7440
80,000-92,000	86,000	0.03	2580

$$\overline{M}_w = \sum x_i M_i = 47{,}720 \text{ g/mol}$$

For PVC, from Table 14.3, each repeat unit has two carbons, three hydrogens, and one chlorine. Thus,

$$m = 2(A_{\mathrm{C}}) + 3(A_{\mathrm{H}}) + (A_{\mathrm{Cl}})$$

$$= (2)(12.01 \text{ g/mol}) + (3)(1.008 \text{ g/mol}) + (35.45 \text{ g/mol}) = 62.49 \text{ g/mol}$$

Now, we will compute the degree of polymerization using Equation 14.6 as

$$DP = \frac{\overline{M}_n}{m} = \frac{47{,}720 \text{ g/mol}}{62.49 \text{ g/mol}} = 764$$

Thus, such a homopolymer is *not possible* since the calculated degree of polymerization is 764 not 1120.

14.8 (a) For chlorinated polyethylene, we are asked to determine the weight percent of chlorine added for 8% Cl substitution of all original hydrogen atoms. Consider 50 carbon atoms; there are 100 possible side-bonding sites. Ninety-two are occupied by hydrogen and eight are occupied by Cl. Thus, the mass of these 50 carbon atoms, m_C, is just

$$m_C = 50(A_C) = (50)(12.01 \text{ g/mol}) = 600.5 \text{ g}$$

Likewise, for hydrogen and chlorine,

$$m_H = 92(A_H) = (92)(1.008 \text{ g/mol}) = 92.74 \text{ g}$$

$$m_{Cl} = 8(A_{Cl}) = (8)(35.45 \text{ g/mol}) = 283.60 \text{ g}$$

Thus, the concentration of chlorine, C_{Cl}, is determined using a modified form of Equation 4.3 as

$$C_{Cl} = \frac{m_{Cl}}{m_C + m_H + m_{Cl}} \times 100$$

$$= \frac{283.60 \text{ g}}{600.5 \text{ g} + 92.74 \text{ g} + 283.60 \text{ g}} \times 100 = 29.0 \text{ wt\%}$$

(b) Chlorinated polyethylene differs from poly(vinyl chloride), in that, for PVC, (1) 25% of the side-bonding sites are substituted with Cl, and (2) the substitution is probably much less random.

Molecular Shape

14.9 This problem first of all asks for us to calculate, using Equation 14.11, the average total chain length, *L*, for a linear polyethylene polymer having a number-average molecular weight of 300,000 g/mol. It is necessary to calculate the number-average degree of polymerization, *DP*, using Equation 14.6. For polyethylene, from Table 14.3, each repeat unit has two carbons and four hydrogens. Thus,

$$m = 2(A_\mathrm{C}) + 4(A_\mathrm{H})$$

$$= (2)(12.01 \text{ g/mol}) + (4)(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$$

and

$$DP = \frac{\overline{M}_n}{m} = \frac{300{,}000 \text{ g/mol}}{28.05 \text{ g/mol}} = 10{,}695$$

which is the number of repeat units along an average chain. Since there are two carbon atoms per repeat unit, there are two C—C chain bonds per repeat unit, which means that the total number of chain bonds in the molecule, *N*, is just (2)(10,695) = 21,390 bonds. Furthermore, assume that for single carbon-carbon bonds, $d = 0.154$ nm and $\theta = 109°$ (Section 14.4); therefore, from Equation 14.11

$$L = Nd \sin\left(\frac{\theta}{2}\right)$$

$$= (21{,}390)(0.154 \text{ nm})\left[\sin\left(\frac{109°}{2}\right)\right] = 2682 \text{ nm}$$

It is now possible to calculate the average chain end-to-end distance, *r*, using Equation 14.12 as

$$r = d\sqrt{N} = (0.154 \text{ nm})\sqrt{21{,}390} = 22.5 \text{ nm}$$

14.10 (a) This portion of the problem asks for us to calculate the number-average molecular weight for a linear polytetrafluoroethylene for which *L* in Equation 14.11 is 2000 nm. It is first necessary to compute the value of *N* using this equation, where, for the C—C chain bond, $d = 0.154$ nm, and $\theta = 109°$. Thus

$$N = \frac{L}{d \sin\left(\frac{\theta}{2}\right)}$$

$$= \frac{2000 \text{ nm}}{(0.154 \text{ nm}) \sin\left(\frac{109°}{2}\right)} = 15,900$$

Since there are two C—C bonds per PTFE repeat unit, there is an average of $N/2$ or 15,900/2 = 7950 repeat units per chain, which is also the degree of polymerization, *DP*. In order to compute the value of $\overline{M}_n$ using Equation 14.6, we must first determine *m* for PTFE. Each PTFE repeat unit consists of two carbon and four fluorine atoms, thus

$$m = 2(A_\text{C}) + 4(A_\text{F})$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

Therefore

$$\overline{M}_n = (DP)m = (7950)(100.02 \text{ g/mol}) = 795,000 \text{ g/mol}$$

(b) Next, we are to determine the number-average molecular weight for $r = 15$ nm. Solving for *N* from Equation 14.12 leads to

$$N = \frac{r^2}{d^2} = \frac{(15 \text{ nm})^2}{(0.154 \text{ nm})^2} = 9490$$

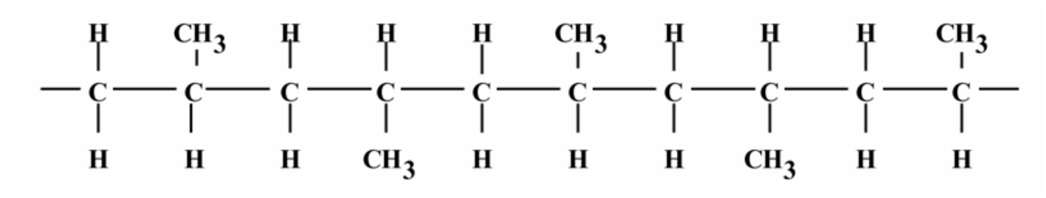
which is the total number of bonds per average molecule. Since there are two C—C bonds per repeat unit, then $DP = N/2 = 9490/2 = 4745$. Now, from Equation 14.6

$$\overline{M}_n = (DP)m = (4745)(100.02 \text{ g/mol}) = 474,600 \text{ g/mol}$$

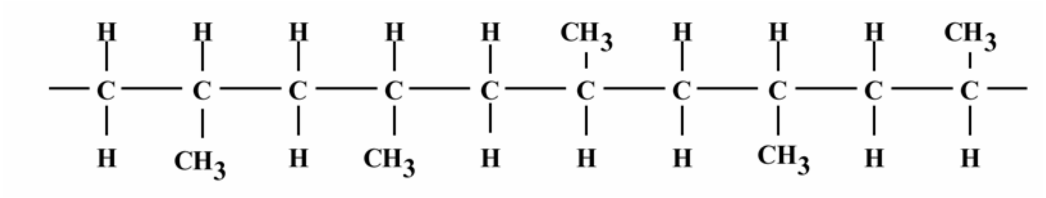
Molecular Configurations

14.11 We are asked to sketch portions of a linear polypropylene molecule for different configurations (using two-dimensional schematic sketches).

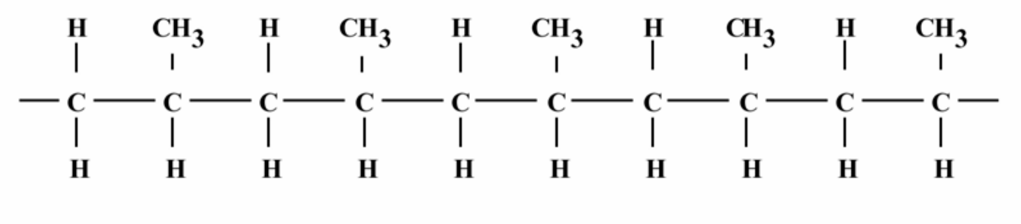
(a) Syndiotactic polypropylene



(b) Atactic polypropylene

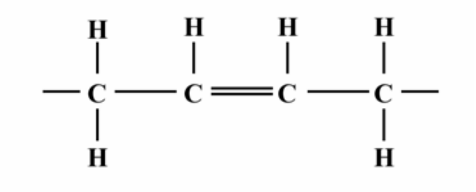


(c) Isotactic polypropylene

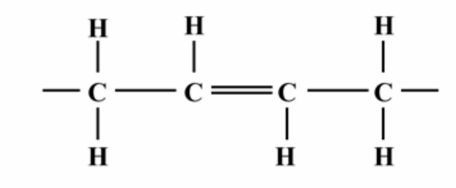


14.12 This problem asks for us to sketch cis and trans structures for butadiene and chloroprene.

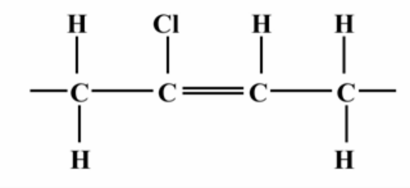
(a) The structure for *cis* polybutadiene (Table 14.5) is



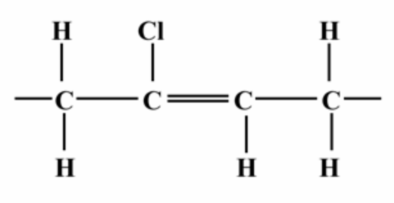
The structure of *trans* butadiene is



(b) The structure of *cis* chloroprene (Table 14.5) is



The structure of *trans* chloroprene is



Thermoplastic and Thermosetting Polymers

14.13 This question asks for comparisons of thermoplastic and thermosetting polymers.

(a) Thermoplastic polymers soften when heated and harden when cooled, whereas thermosetting polymers, harden upon heating, while further heating will not lead to softening.

(b) Thermoplastic polymers have linear and branched structures, while for thermosetting polymers, the structures will normally be network or crosslinked.

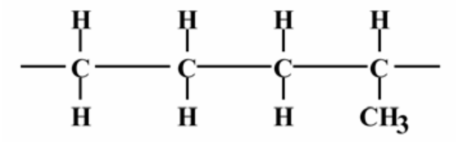
14.14 (a) It is *not possible* to grind up and reuse phenol-formaldehyde because it is a network thermoset polymer and, therefore, is not amenable to remolding.

(b) Yes, it is *possible* to grind up and reuse polypropylene since it is a thermoplastic polymer, will soften when reheated, and, thus, may be remolded.

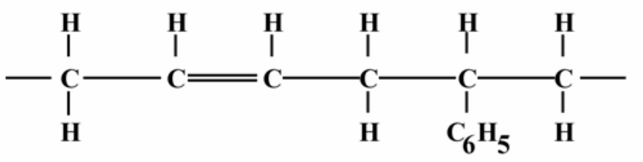
Copolymers

14.15 This problem asks for sketches of the repeat unit structures for several alternating copolymers.

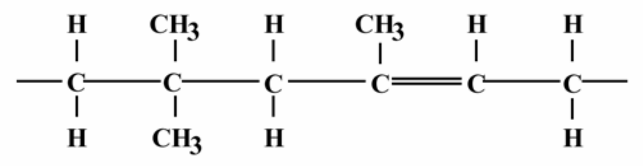
(a) For poly(ethylene-propylene)



(b) For poly(butadiene-styrene)



(c) For poly(isobutylene-isoprene)



14.16 For a poly(acrylonitrile-butadiene) alternating copolymer with a number-average molecular weight of 1,000,000 g/mol, we are asked to determine the average number of acrylonitrile and butadiene repeat units per molecule.

Since it is an alternating copolymer, the number of both types of repeat units will be the same. Therefore, consider them as a single repeat unit, and determine the number-average degree of polymerization. For the acrylonitrile repeat unit, there are three carbon atoms, three hydrogen atoms, and one nitrogen atom, while the butadiene repeat consists of four carbon atoms and six hydrogen atoms. Therefore, the acrylonitrile-butadiene combined repeat unit weight is just

$$m = 7(A_{\text{C}}) + 9(A_{\text{H}}) \; + \; 1(A_{\text{N}})$$

$$= (7)(12.01 \text{ g/mol}) + (9)(1.008 \text{ g/mol}) \; + \; (14.01 \text{ g/mol}) = 107.15 \text{ g/mol}$$

From Equation 14.6, the degree of polymerization is just

$$DP \; = \; \frac{\overline{M}_n}{m} \; = \; \frac{1{,}000{,}000 \text{ g/mol}}{107.15 \text{ g/mol}} \; = \; 9333$$

Thus, there is an average of 9333 of both repeat unit types per molecule.

14.17 This problem asks for us to calculate the number-average molecular weight of a random poly(isobutylene-isoprene) copolymer. For the isobutylene repeat unit there are four carbon and eight hydrogen atoms. Thus, its repeat unit molecular weight is

$$m_{\mathrm{Ib}} = 4(A_{\mathrm{C}}) + 8(A_{\mathrm{H}})$$

$$= (4)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 56.10 \text{ g/mol}$$

The isoprene repeat unit is composed of five carbon and eight hydrogen atoms. Thus, its repeat unit molecular weight is

$$m_{\mathrm{Ip}} = 5(A_{\mathrm{C}}) + 8(A_{\mathrm{H}})$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 68.11 \text{ g/mol}$$

From Equation 14.7, the average repeat unit molecular weight is just

$$\overline{m} = f_{\mathrm{Ib}} m_{\mathrm{Ib}} + f_{\mathrm{Ip}} m_{\mathrm{Ip}}$$

$$= (0.25)(56.10 \text{ g/mol}) + (0.75)(68.11 \text{ g/mol}) = 65.11 \text{ g/mol}$$

Since DP = 1500 (as stated in the problem), $\overline{M}_n$ may be computed using Equation 14.6 as

$$\overline{M}_n = \overline{m}\,(DP) = (65.11 \text{ g/mol})(1500) = 97{,}700 \text{ g/mol}$$

14.18 For an alternating copolymer that has a number-average molecular weight of 100,000 g/mol and a degree of polymerization of 2210, we are to determine one of the repeat unit types if the other type is ethylene. It is first necessary to calculate $\overline{m}$ using Equation 14.6 as

$$\overline{m} \;=\; \frac{\overline{M}_n}{DP} \;=\; \frac{100{,}000\text{ g/mol}}{2210} \;=\; 42.25\text{ g/mol}$$

Since this is an alternating copolymer we know that chain fraction of each repeat unit type is 0.5; that is $f_e = f_x = 0.5$, f_e and f_x being, respectively, the chain fractions of the ethylene and unknown repeat units. Also, the repeat unit molecular weight for ethylene is

$$m_s = 2(A_{\text{C}}) + 4(A_{\text{H}})$$

$$= 2(12.01\text{ g/mol}) + 4(1.008\text{ g/mol}) = 28.05\text{ g/mol}$$

Now, using Equation 14.7, it is possible to calculate the repeat unit weight of the unknown repeat unit type, m_x. Thus

$$m_x \;=\; \frac{\overline{m} - f_e m_e}{f_x}$$

$$= \;\frac{45.25\text{ g/mol} \;-\; (0.5)(28.05\text{ g/mol})}{0.5} \;=\; 62.45\text{ g/mol}$$

Finally, it is necessary to calculate the repeat unit molecular weights for each of the possible other repeat unit types. These are calculated below:

$m_{\text{styrene}} = 8(A_{\text{C}}) + 8(A_{\text{H}}) = 8(12.01\text{ g/mol}) + 8(1.008\text{ g/mol}) = 104.16\text{ g/mol}$

$m_{\text{propylene}} = 3(A_{\text{C}}) + 6(A_{\text{H}}) = 3(12.01\text{ g/mol}) + 6(1.008\text{ g/mol}) = 42.08\text{ g/mol}$

$m_{\text{TFE}} = 2(A_{\text{C}}) + 4(A_{\text{F}}) = 2(12.01\text{ g/mol}) + 4(19.00\text{ g/mol}) = 100.02\text{ g/mol}$

$m_{\text{VC}} = 2(A_{\text{C}}) + 3(A_{\text{H}}) + (A_{\text{Cl}}) = 2(12.01\text{ g/mol}) + 3(1.008\text{ g/mol}) + 35.45\text{ g/mol} = 62.49\text{ g/mol}$

Therefore, vinyl chloride is the other repeat unit type since its m value is almost the same as the calculated m_x.

14.19 (a) This portion of the problem asks us to determine the ratio of butadiene to acrylonitrile repeat units in a copolymer having a weight-average molecular weight of 250,000 g/mol and a degree of polymerization of 4640. It first becomes necessary to calculate the average repeat unit molecular weight of the copolymer, $\overline{m}$, using Equation 14.6 as

$$\overline{m} = \frac{\overline{M}_n}{DP} = \frac{250{,}000 \text{ g/mol}}{4640} = 53.88 \text{ g/mol}$$

If we designate f_b as the chain fraction of butadiene repeat units, since the copolymer consists of only two repeat unit types, the chain fraction of acrylontrile repeat units f_a is just $1 - f_b$. Now, Equation 14.7 for this copolymer may be written in the form

$$\overline{m} = f_b m_b + f_a m_a = f_b m_b + (1 - f_b) m_a$$

in which m_b and m_a are the repeat unit molecular weights for butadiene and acrylontrile, respectively. These values are calculated as follows:

$$m_b = 4(A_\text{C}) + 6(A_\text{H}) = 4(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

$$m_a = 3(A_\text{C}) + 3(A_\text{H}) + (A_\text{N}) = 3(12.01 \text{ g/mol}) + 3(1.008 \text{ g/mol}) + (14.01 \text{ g/mol})$$

$$= 53.06 \text{ g/mol.}$$

Solving for f_b in the above expression yields

$$f_b = \frac{\overline{m} - m_a}{m_b - m_a} = \frac{53.88 \text{ g/mol} - 53.06 \text{ g/mol}}{54.09 \text{ g/mol} - 53.06 \text{ g/mol}} = 0.80$$

Furthermore, $f_a = 1 - f_b = 1 - 0.80 = 0.20$; or the ratio is just

$$\frac{f_b}{f_a} = \frac{0.80}{0.20} = 4.0$$

(b) Of the possible copolymers, the only one for which there is a restriction on the ratio of repeat unit types is alternating; the ratio must be 1:1. Therefore, on the basis of the result in part (a), the possibilities for this copolymer are random, graft, and block.

14.20 For a copolymer consisting of 35 wt% ethylene and 65 wt% propylene, we are asked to determine the fraction of both repeat unit types.

In 100 g of this material, there are 35 g of ethylene and 65 g of propylene. The ethylene (C_2H_4) molecular weight is

$$m(\text{ethylene}) = 2(A_\text{C}) + 4(A_\text{H})$$

$$= (2)(12.01 \text{ g/mol}) + (4)(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$$

The propylene (C_3H_6) molecular weight is

$$m(\text{propylene}) = 3(A_\text{C}) + 6(A_\text{H})$$

$$= (3)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 42.08 \text{ g/mol}$$

Therefore, in 100 g of this material, there are

$$\frac{35 \text{ g}}{28.05 \text{ g/mol}} = 1.25 \text{ mol of ethylene}$$

and

$$\frac{65 \text{ g}}{42.08 \text{ g/mol}} = 1.54 \text{ mol of propylene}$$

Thus, the fraction of the ethylene repeat unit, f(ethylene), is just

$$f(\text{ethylene}) = \frac{1.25 \text{ mol}}{1.25 \text{ mol} + 1.54 \text{ mol}} = 0.45$$

Likewise,

$$f(\text{propylene}) = \frac{1.54 \text{ mol}}{1.25 \text{ mol} + 1.54 \text{ mol}} = 0.55$$

14.21 For a random poly(styrene-butadiene) copolymer in which $\overline{M}_n$ = 350,000 g/mol and *DP* = 5000, we are asked to compute the fractions of styrene and butadiene repeat units.

From Table 14.5, the styrene repeat unit has eight carbon and eight hydrogen atoms. Thus,

$$m_{st} = (8)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 104.14 \text{ g/mol}$$

Also, from Table 14.5, the butadiene repeat unit has four carbon and six hydrogen atoms, and

$$m_{bu} = (4)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

From Equation 14.7

$$\overline{m} = f_{st}m_{st} + f_{bu}m_{bu}$$

Now, let $x = f_{st}$, such that

$$\overline{m} = 104.14x + (54.09)(1 - x)$$

since $f_{st} + f_{bu} = 1$. Also, from Equation 14.6

$$DP = \frac{\overline{M}_n}{\overline{m}}$$

Or

$$5000 = \frac{350{,}000 \text{ g/mol}}{[104.14x + 54.09(1 - x)] \text{ g/mol}}$$

Solving for x leads to $x = f_{st} = f(\text{styrene}) = 0.32$. Also,

$$f(\text{butadiene}) = 1 - x = 1 - 0.32 = 0.68$$

Polymer Crystallinity

14.22 The tendency of a polymer to crystallize decreases with increasing molecular weight because as the chains become longer it is more difficult for all regions along adjacent chains to align so as to produce the ordered atomic array.

14.23 For each of four pairs of polymers, we are asked to (1) state whether it is possible to decide which is more likely to crystallize; (2) if so, which is more likely and why; and (3) it is not possible to decide then why.

(a) No, it is not possible to decide for these two polymers. On the basis of tacticity, the isotactic PP is more likely to crystallize than the atactic PVC. On the other hand, with regard to side-group bulkiness, the PVC is more likely to crystallize.

(b) Yes, it is possible to decide for these two copolymers. The linear and syndiotactic polypropylene is more likely to crystallize than crosslinked cis-isoprene since linear polymers are more likely to crystallize than crosslinked ones.

(c) Yes, it is possible to decide for these two polymers. The linear and isotactic polystyrene is more likely to crystallize than network phenol-formaldehyde; network polymers rarely crystallize, whereas isotactic ones crystallize relatively easily.

(d) Yes, it is possible to decide for these two copolymers. The block poly(acrylonitrile-isoprene) copolymer is more likely to crystallize than the graft poly(chloroprene-isobutylene) copolymer. Block copolymers crystallize more easily than graft ones.

14.24 For this problem we are given the density of nylon 6,6 (1.213 g/cm^3), an expression for the volume of its unit cell, and the lattice parameters, and are asked to determine the number of repeat units per unit cell. This computation necessitates the use of Equation 3.5, in which we solve for *n*. Before this can be carried out we must first calculate V_C, the unit cell volume, and *A* the repeat unit molecular weight. For V_C

$$V_C = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

$$= (0.497)(0.547)(1.729)\sqrt{1 - 0.441 - 0.054 - 0.213 + 2(0.664)(0.232)(0.462)}$$

$$= 0.3098 \text{ nm}^3 = 3.098 \times 10^{-22} \text{ cm}^3$$

The repeat unit for nylon 6,6 is shown in Table 14.3, from which the value of *A* may be determined as follows:

$$A = 12(A_\text{C}) + 22(A_\text{H}) + 2(A_\text{O}) + 2(A_\text{N})$$

$$= 12(12.01 \text{ g/mol}) + 22(1.008 \text{ g/mol}) + 2(16.00 \text{ g/mol}) + 2(14.01 \text{ g/mol})$$

$$= 226.32 \text{ g/mol}$$

Finally, solving for *n* from Equation 3.5 leads to

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

$$= \frac{(1.213 \text{ g/cm}^3)(3.098 \times 10^{-22} \text{ cm}^3\text{/unit cell})(6.023 \times 10^{23} \text{ repeat units/mol})}{226.32 \text{ g/mol}}$$

$$= 1 \text{ repeat unit/unit cell}$$

14.25 (a) We are asked to compute the densities of totally crystalline and totally amorphous poly(ethylene terephthalate) (ρ_c and ρ_a from Equation 14.8). From Equation 14.8 let $C = \frac{\text{\% crystallinity}}{100}$, such that

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$$

Rearrangement of this expression leads to

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are specified in the problem statement, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which ρ_{s1} = 1.408 g/cm^3, ρ_{s2} = 1.343 g/cm^3, C_1 = 0.743, and C_2 = 0.312. Solving the above two equations for ρ_a and ρ_c leads to

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

$$= \frac{(1.408 \text{ g/cm}^3)(1.343 \text{ g/cm}^3)(0.743 - 0.312)}{(0.743)(1.408 \text{ g/cm}^3) - (0.312)(1.343 \text{ g/cm}^3)} = 1.300 \text{ g/cm}^3$$

And

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)}$$

$$= \frac{(1.408 \text{ g/cm}^3)(1.343 \text{ g/cm}^3)(0.312 - 0.743)}{(1.343 \text{ g/cm}^3)(0.312 - 1.0) - (1.408 \text{ g/cm}^3)(0.743 - 1.0)} = 1.450 \text{ g/cm}^3$$

(b) Now we are to determine the % crystallinity for ρ_s = 1.382 g/cm^3. Again, using Equation 14.8

$$\%\ \text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

$$= \frac{(1.450\ \text{g/cm}^3)(1.382\ \text{g/cm}^3 - 1.300\ \text{g/cm}^3)}{(1.382\ \text{g/cm}^3)(1.450\ \text{g/cm}^3 - 1.300\ \text{g/cm}^3)} \times 100$$

$$= 57.4\%$$

14.26 (a) We are asked to compute the densities of totally crystalline and totally amorphous polypropylene (ρ_c and ρ_a from Equation 14.8). From Equation 14.8 let $C = \frac{\text{\% crystallinity}}{100}$, such that

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$$

Rearrangement of this expression leads to

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are specified in the problem, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which ρ_{s1} = 0.904 g/cm^3, ρ_{s2} = 0.895 g/cm^3, C_1 = 0.628, and C_2 = 0.544. Solving the above two equations for ρ_a and ρ_c leads to

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

$$= \frac{(0.904 \text{ g/cm}^3)(0.895 \text{ g/cm}^3)(0.628 - 0.544)}{(0.628)(0.904 \text{ g/cm}^3) - (0.544)(0.895 \text{ g/cm}^3)} = 0.841 \text{ g/cm}^3$$

And

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)}$$

$$= \frac{(0.904 \text{ g/cm}^3)(0.895 \text{ g/cm}^3)(0.544 - 0.628)}{(0.895 \text{ g/cm}^3)(0.544 - 1.0) - (0.904 \text{ g/cm}^3)(0.628 - 1.0)} = 0.946 \text{ g/cm}^3$$

(b) Now we are asked to determine the density of a specimen having 74.6% crystallinity. Solving for ρ_s from Equation 14.8 and substitution for ρ_a and ρ_c which were computed in part (a) yields

$$\rho_s = \frac{-\rho_c \rho_a}{C(\rho_c - \rho_a) - \rho_c}$$

$$= \frac{-(0.946 \text{ g/cm}^3)(0.841 \text{ g/cm}^3)}{(0.746)(0.946 \text{ g/cm}^3 - 0.841 \text{ g/cm}^3) - 0.946 \text{ g/cm}^3}$$

$$= 0.917 \text{ g/cm}^3$$

Diffusion in Polymeric Materials

14.27 This is a permeability problem in which we are asked to compute the diffusion flux of oxygen through a 15-mm thick sheet of low density polyethylene. In order to solve this problem it is necessary to employ Equation 14.9. The permeability coefficient of O_2 through LDPE is given in Table 14.6 as 2.2 x 10^{-13} (cm^3 STP)-cm/cm^2-s-Pa. Thus, from Equation 14.9

$$J = P_M \frac{\Delta P}{\Delta x} = P_M \frac{P_2 - P_1}{\Delta x}$$

and taking P_1 = 150 kPa (150,000 Pa) and P_2 = 2000 kPa (2,000,000 Pa) we get

$$= \left\lfloor 2.2 \text{ x } 10^{-13} \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{\text{cm}^2 \text{ - s - Pa}} \right\rfloor \left(\frac{2{,}000{,}000 \text{ Pa } - 150{,}000 \text{ Pa}}{1.5 \text{ cm}} \right)$$

$$= 2.7 \text{ x } 10^{-6} \frac{(\text{cm}^3 \text{ STP})}{\text{cm}^2 \text{ - s}}$$

14.28 This problem asks us to compute the permeability coefficient for carbon dioxide through high density polyethylene at 325 K given a steady-state permeability situation. It is necessary for us to Equation 14.9 in order to solve this problem. Rearranging this expression and solving for the permeability coefficient gives

$$P_M = \frac{J\,\Delta x}{\Delta P} = \frac{J\,\Delta x}{P_2 - P_1}$$

Taking P_1 = 2500 kPa (2,500,000 Pa) and P_1 = 4000 kPa (4,000,000 Pa), the permeability coefficient of CO_2 through HDPE is equal to

$$P_M = \frac{\left[2.2 \text{ x } 10^{-8} \ \frac{(\text{cm}^3 \text{ STP})}{\text{cm}^2 \text{ - s}}\right](5 \text{ cm})}{(4{,}000{,}000 \text{ Pa } - \ 2{,}500{,}000 \text{ Pa})}$$

$$= 0.73 \text{ x } 10^{-13} \ \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{\text{cm}^2 \text{ - s - Pa}}$$

14.29 This problem asks that we compute the diffusion flux at 350 K for water in polystyrene. It is first necessary to compute the value of the permeability coefficient at 350 K. The temperature dependence of P_M is given in the problem statement, as follows:

$$P_M = P_{M_0} \exp\left(-\frac{Q_p}{RT}\right)$$

And, incorporating values provided for the constants P_{M_0} and Q_p, we get

$$P_M = \left[9.0 \text{ x } 10^{-5} \ \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{\text{cm}^2\text{ - s - Pa}}\right] \exp\left[-\frac{42{,}300 \ \text{J/mol}}{(8.314 \ \text{J/mol - K})(350 \ \text{K})}\right]$$

$$= 4.4 \text{ x } 10^{-11} \ \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{\text{cm}^2\text{ - s - Pa}}$$

And, using Equation 14.9, the diffusion flux is equal to

$$J = P_M \frac{\Delta P}{\Delta x} = P_M \frac{P_2 - P_1}{\Delta x}$$

$$= 4.4 \text{ x } 10^{-11} \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{\text{cm}^2\text{ - s - Pa}} \left(\frac{20{,}000 \text{ Pa } - 1{,}000 \text{ Pa}}{3.0 \text{ cm}}\right)$$

$$= 2.8 \text{ x } 10^{-7} \ \frac{(\text{cm}^3 \text{ STP})}{\text{cm}^2\text{ - s}}$$

CHAPTER 15

CHARACTERISTICS, APPLICATIONS, AND PROCESSING OF POLYMERS

PROBLEM SOLUTIONS

Stress-Strain Behavior

15.1 From Figure 15.3, the elastic modulus is the slope in the elastic linear region of the 20°C curve, which is

$$E = \frac{\Delta\,(\text{stress})}{\Delta\,(\text{strain})} = \frac{30 \text{ MPa} - 0 \text{ MPa}}{9 \text{ x } 10^{-3} - 0} = 3.3 \text{ GPa} \quad (483{,}000 \text{ psi})$$

The value range cited in Table 15.1 is 2.24 to 3.24 GPa (325,000 to 470,000 psi). Thus, the plotted value is a little on the high side.

The tensile strength corresponds to the stress at which the curve ends, which is 52 MPa (7500 psi). This value lies within the range cited in Table 15.1—48.3 to 72.4 MPa (7000 to 10,500 psi).

Viscoelastic Deformation

15.2 The explanation of viscoelasticity is given in Section 15.4.

15.3 This problem asks for a determination of the relaxation modulus of a viscoelastic material, which behavior is according to Equation 15.10--i.e.,

$$\sigma(t) = \sigma(0)\exp\left(-\frac{t}{\tau}\right)$$

We want to determine σ(10), but it is first necessary to compute τ from the data provided in the problem statement. Thus, solving for τ from the above expression,

$$\tau = \frac{-t}{\ln\left[\dfrac{\sigma(t)}{\sigma(0)}\right]} = \frac{-30\ \text{s}}{\ln\left[\dfrac{0.5\ \text{MPa}}{3.5\ \text{MPa}}\right]} = 15.4\ \text{s}$$

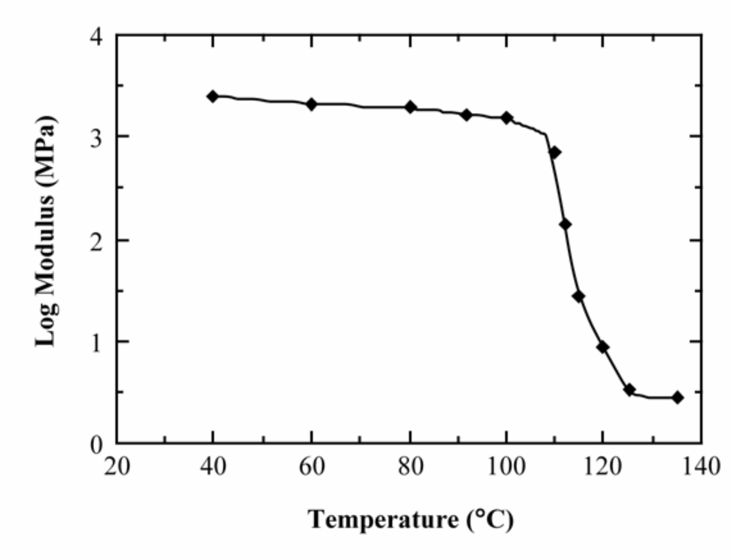
Therefore,

$$\sigma(10) = (3.5\ \text{MPa})\exp\left(-\frac{10\ \text{s}}{15.4\ \text{s}}\right) = 1.83\ \text{MPa}$$

Now, using Equation 15.1

$$E_r(10) = \frac{\sigma(10)}{\varepsilon_0} = \frac{1.83\ \text{MPa}}{0.5} = 3.66\ \text{MPa}\ \ (522\ \text{psi})$$

15.4 Below is plotted the logarithm of $E_r(10)$ versus temperature.



The glass-transition temperature is that temperature corresponding to the abrupt decrease in log $E_r(10)$, which for this PMMA material is about 115°C.

15.5 We are asked to make schematic strain-time plots for various polystyrene materials and at several temperatures.

(a) Crystalline polystyrene at 70°C behaves in a glassy manner (Figure 15.8, curve *A*); therefore, the strain-time behavior would be as Figure 15.5(b).

(b) Amorphous polystyrene at 180°C behaves as a viscous liquid (Figure 15.8, curve *C*); therefore, the strain-time behavior will be as Figure 15.5(d).

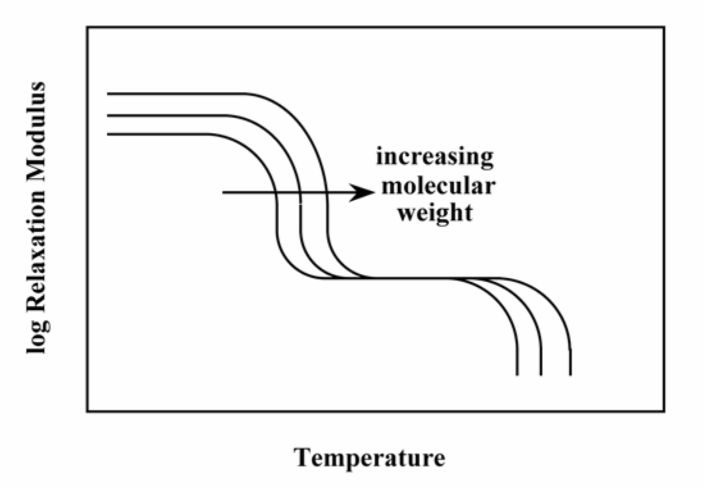
(c) Crosslinked polystyrene at 180°C behaves as a rubbery material (Figure 15.8, curve *B*); therefore, the strain-time behavior will be as Figure 15.5(c).

(d) Amorphous polystyrene at 100°C behaves as a leathery material (Figure 15.7); therefore, the strain-time behavior will be as Figure 15.5(c).

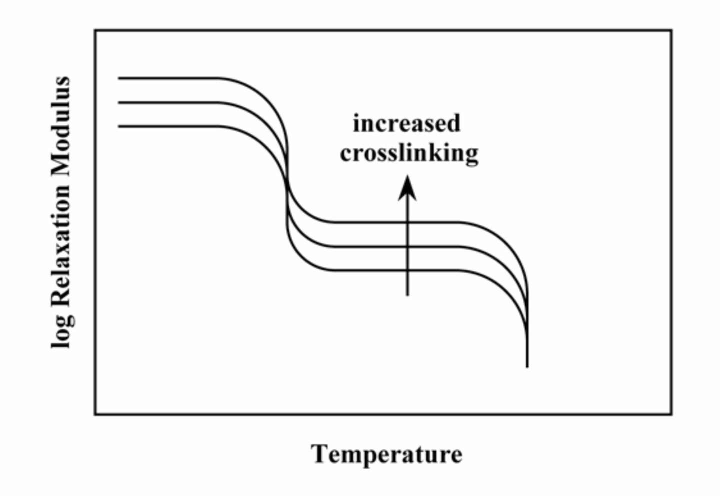
15.6 (a) Stress relaxation tests are conducted by rapidly straining the material elastically in tension, holding the strain level constant, and then measuring the stress as a function of time. For viscoelastic creep tests, a stress (usually tensile) is applied instantaneously and maintained constant while strain is measured as a function of time.

(b) The experimental parameters of interest from the stress relaxation and viscoelastic creep tests are the relaxation modulus and creep modulus (or creep compliance), respectively. The relaxation modulus is the ratio of stress measured after 10 s and strain (Equation 15.1); creep modulus is the ratio of stress and strain taken at a specific time (Equation 15.2).

15.7 (a) This portion of the problem calls for a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased molecular weight. Such a plot is given below. Increasing molecular weight increases both glass-transition and melting temperatures.



(b) We are now called upon to make a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased crosslinking. Such a plot is given below. Increasing the degree of crosslinking will increase the modulus in both glassy and rubbery regions.



Fracture of Polymers

Miscellaneous Mechanical Considerations

15.8 For thermoplastic polymers, five factors that favor brittle fracture are as follows: (1) a reduction in temperature, (2) an increase in strain rate, (3) the presence of a sharp notch, (4) increased specimen thickness, and (5) modifications of the polymer structure.

15.9 (a) The fatigue limits for PMMA and the steel alloy are 10 MPa (1450 psi) and 290 MPa (42,200 psi), respectively.

(b) At 10^6 cycles, the fatigue strengths for nylon 6 and 2014-T6 aluminum are 11 MPa (1600 psi) and 200 MPa (30,000 psi), respectively.

Deformation of Semicrystalline Polymers

15.10 (a) and (b) The mechanisms by which semicrystalline polymers elastically and plastically deform are described in Section 15.7.

(c) The explanation of the mechanism by which elastomers elastically deform is provided in Section 15.9.

Factors That Influence the Mechanical Properties of Semicrystalline Polymers

Deformation of Elastomers

15.11 (a) The tensile modulus is not directly influenced by a polymer's molecular weight.

(b) Tensile modulus increases with increasing degree of crystallinity for semicrystalline polymers. This is due to enhanced secondary interchain bonding which results from adjacent aligned chain segments as percent crystallinity increases. This enhanced interchain bonding inhibits relative interchain motion.

(c) Deformation by drawing also increases the tensile modulus. The reason for this is that drawing produces a highly oriented molecular structure, and a relatively high degree of interchain secondary bonding.

(d) When an undeformed semicrystalline polymer is annealed below its melting temperature, the tensile modulus increases.

(e) A drawn semicrystalline polymer that is annealed experiences a decrease in tensile modulus as a result of a reduction in chain-induced crystallinity, and a reduction in interchain bonding forces.

15.12 (a) The tensile strength of a semicrystalline polymer increases with increasing molecular weight. This effect is explained by increased chain entanglements at higher molecular weights.

(b) Increasing the degree of crystallinity of a semicrystalline polymer leads to an enhancement of the tensile strength. Again, this is due to enhanced interchain bonding and forces; in response to applied stresses, interchain motions are thus inhibited.

(c) Deformation by drawing increases the tensile strength of a semicrystalline polymer. This effect is due to the highly oriented chain structure that is produced by drawing, which gives rise to higher interchain secondary bonding forces.

(d) Annealing an undeformed semicrystalline polymer produces an increase in its tensile strength.

15.13 Normal butane has a higher melting temperature as a result of its molecular structure (Section 14.2). There is more of an opportunity for van der Waals bonds to form between two molecules in close proximity to one another than for isobutane because of the linear nature of each normal butane molecule.

15.14 This problem gives us the tensile strengths and associated number-average molecular weights for two poly(methyl methacrylate) materials and then asks that we estimate the tensile strength for $\overline{M}_n$ = 40,000 g/mol. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$50 \text{ MPa} = TS_\infty - \frac{A}{30{,}000 \text{ g/mol}}$$

$$150 \text{ MPa} = TS_\infty - \frac{A}{50{,}000 \text{ g/mol}}$$

Thus, the values of the two constants are: TS_∞ = 300 MPa and A = 7.50 x 10^6 MPa-g/mol. Substituting these values into Equation 15.3 for $\overline{M}_n$ = 40,000 g/mol leads to

$$TS = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

$$= 300 \text{ MPa} - \frac{7.50 \text{ x } 10^6 \text{ MPa - g/mol}}{40{,}000 \text{ g/mol}}$$

$$= 112.5 \text{ MPa}$$

15.15 This problem gives us the tensile strengths and associated number-average molecular weights for two polyethylene materials and then asks that we estimate the $\overline{M}_n$ that is required for a tensile strength of 140 MPa. Equation 15.3 cites the dependence of the tensile strength on $\overline{M}_n$. Thus, using the data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$90 \text{ MPa} = TS_\infty - \frac{A}{20{,}000 \text{ g/mol}}$$

$$180 \text{ MPa} = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

Thus, the values of the two constants are: TS_∞ = 270 MPa and $A = 3.6 \times 10^6$ MPa-g/mol. Solving for $\overline{M}_n$ in Equation 15.3 and substituting TS = 140 MPa as well as the above values for TS_∞ and A leads to

$$\overline{M}_n = \frac{A}{TS_\infty - TS}$$

$$= \frac{3.6 \times 10^6 \text{ MPa - g/mol}}{270 \text{ MPa} - 140 \text{ MPa}} = 27{,}700 \text{ g/mol}$$

15.16 For each of four pairs of polymers, we are to do the following: (1) determine whether or not it is possible to decide which has the higher tensile modulus; (2) if so, note which has the higher tensile modulus and then state the reasons for this choice; and (3) if it is not possible to decide, then state why.

(a) Yes, it is possible. The linear and isotactic poly(vinyl chloride) will display a greater tensile modulus. Linear polymers are more likely to crystallize that branched ones. In addition, polymers having isotactic structures will normally have a higher degree of crystallinity that those having atactic structures. Increasing a polymer's crystallinity leads to an increase in its tensile modulus. In addition, tensile modulus is independent of molecular weight--the atactic/branched material has the higher molecular weight.

(b) Yes, it is possible. The block styrene-butadiene copolymer with 10% of possible sites crosslinked will have the higher modulus. Block copolymers normally have higher degrees of crystallinity than random copolymers of the same material. A higher degree of crystallinity favors larger moduli. In addition, the block copolymer also has a higher degree of crosslinking; increasing the amount of crosslinking also enhances the tensile modulus.

(c) No, it is not possible. Branched polyethylene will tend to have a low degree of crystallinity since branched polymers don't normally crystallize. The atactic polypropylene probably also has a relatively low degree of crystallinity; atactic structures also don't tend to crystallize, and polypropylene has a more complex repeat unit structure than does polyethylene. Tensile modulus increases with degree of crystallinity, and it is not possible to determine which polymer is more crystalline. Furthermore, tensile modulus is independent of molecular weight.

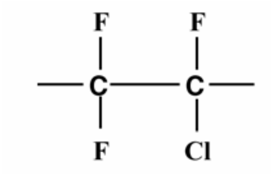
15.17 For each of four pairs of polymers, we are to do the following: (1) determine whether or not it is possible to decide which has the higher tensile strength; (2) if it is possible, then note which has the higher tensile strength and then state the reasons for this choice; and (3) if it is not possible to decide, to state why.

(a) Yes, it is possible. The linear and isotactic material will have the higher tensile strength. Both linearity and isotacticity favor a higher degree of crystallinity than do branching and atacticity; and tensile strength increases with increasing degree of crystallinity. Furthermore, the molecular weight of the linear/isotactic material is higher (100,000 g/mol versus 75,000 g/mol), and tensile strength increases with increasing molecular weight.

(b) No, it is not possible. Alternating copolymers tend to be more crystalline than graft copolymers, and tensile strength increases with degree of crystallinity. However, the graft material has a higher degree of crosslinking, and tensile strength increases with the percentage of crosslinks.

(c) Yes, it is possible. The network polyester will display a greater tensile strength. Relative chain motion is much more restricted than for the lightly branched polytetrafluoroethylene since there are many more of the strong covalent bonds for the network structure.

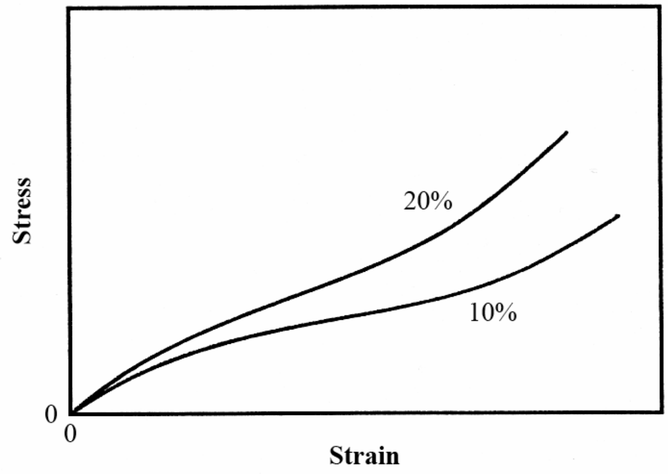
15.18 The strength of a polychlorotrifluoroethylene having the repeat unit structure



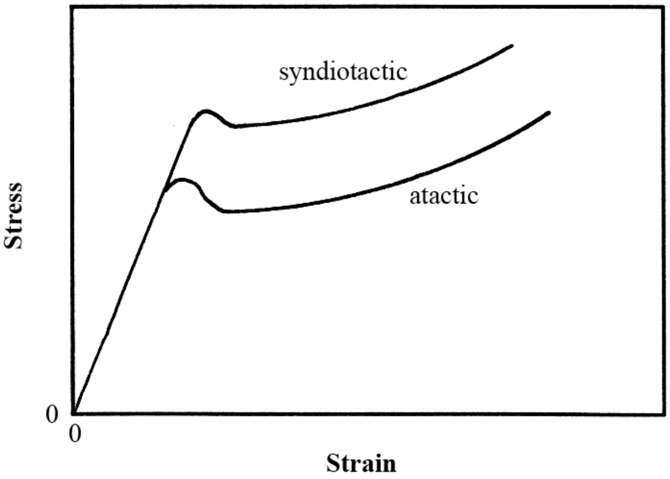
$$-\overset{\displaystyle F}{\underset{\displaystyle F}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle F}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}-$$

will be greater than for a polytetrafluoroethylene having the same molecular weight and degree of crystallinity. The replacement of one fluorine atom within the PTFE repeat unit with a chlorine atom leads to a higher interchain attraction, and, thus, a stronger polymer. Furthermore, poly(vinyl chloride) is stronger than polyethylene (Table 15.1) for the same reason.

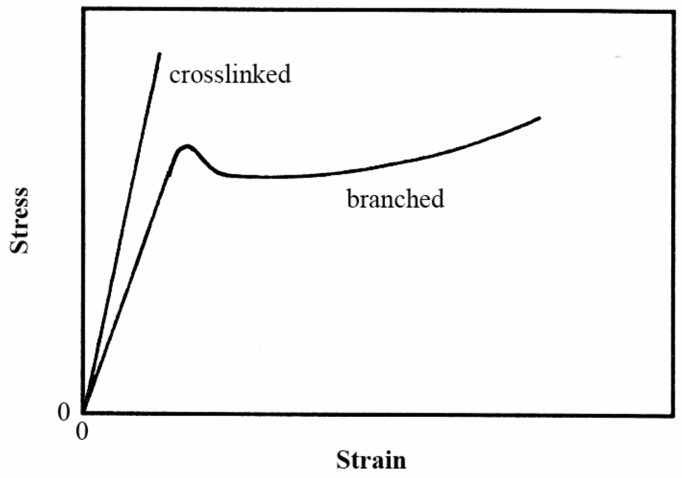
15.19 (a) Shown below are the stress-strain curves for the two polyisoprene materials, both of which have a molecular weight of 100,000 g/mol. These two materials are elastomers and will have curves similar to curve *C* in Figure 15.1. However, the curve for the material having the greater number of crosslinks (20%) will have a higher elastic modulus at all strains.



(b) Shown below are the stress-strain curves for the two polypropylene materials. These materials will most probably display the stress-strain behavior of a normal plastic, curve *B* in Figure 15.1. However, the syndiotactic polypropylene has a higher molecular weight and will also undoubtedly have a higher degree of crystallinity; therefore, it will have a higher strength.



(c) Shown below are the stress-strain curves for the two polyethylene materials. The branched polyethylene will display the behavior of a normal plastic, curve *B* in Figure 15.1. On the other hand, the heavily crosslinked polyethylene will be stiffer, stronger, and more brittle (curve *A* of Figure 15.1).



15.20 Two molecular characteristics essential for elastomers are: (1) they must be amorphous, having chains that are extensively coiled and kinked in the unstressed state; and (2) there must be some crosslinking.

15.21 This question asks us to choose from a list of materials those which would be expected to be elastomers and those which would be thermosetting polymers.

(a) Linear and crystalline polyethylene would be neither an elastomer nor a thermoset since it is a linear polymer.

(b) Phenol-formaldehyde having a network structure would be a thermosetting polymer since it has a network structure. It would not be an elastomer since it does not have a crosslinked chain structure.

(c) Heavily crosslinked polyisoprene having a glass transition temperature of 50°C would be a thermosetting polymer because it is heavily crosslinked. It would not be an elastomer since it is heavily crosslinked and room temperature is below its T_g.

(d) Lightly crosslinked polyisoprene having a glass transition temperature of –60°C is both an elastomer and a thermoset. It is an elastomer because it is lightly crosslinked and has a T_g below room temperature. It is a thermoset because it is crosslinked.

(e) Linear and partially amorphous poly(vinyl chloride) is neither an elastomer nor a thermoset. In order to be either it must have some crosslinking.

15.22 This problem asks that we compute the fraction of possible crosslink sites in 15 kg of polychloroprene when 5.2 kg of S is added, assuming that, on the average, 5.5 sulfur atoms participate in each crosslink bond. Given the butadiene repeat unit in Table 14.5, we may calculate its molecular weight as follows:

$$A(\text{chloroprene}) = 4(A_{\text{C}}) + 5(A_{\text{H}}) + A_{\text{Cl}}$$

$$= (4)(12.01 \text{ g/mol}) + 5(1.008 \text{ g/mol}) + 35.45 \text{ g/mol} = 88.53 \text{ g/mol}$$

Which means that in 15 kg of chloroprene there are $\dfrac{15{,}000 \text{ g}}{88.53 \text{ g/mol}} = 169.4 \text{ mol} = n_{\text{chloro}}$.

For the vulcanization of polychloroprene, there are two possible crosslink sites per repeat unit—one for each of the two carbon atoms that are doubly bonded. Furthermore, each of these crosslinks forms a bridge between two repeat units. Therefore, we can say that there is the equivalent of one crosslink per repeat unit. Let us now calculate the number of moles of sulfur (n_{sulfur}) that react with the chloroprene, by taking the mole ratio of sulfur to chloroprene, and then dividing this ratio by 5.5 atoms per crosslink; this yields the fraction of possible sites that are crosslinked. Thus

$$n_{\text{sulfur}} = \frac{5200 \text{ g}}{32.06 \text{ g/mol}} = 162.2 \text{ mol}$$

And

$$\text{fraction sites crosslinked} = \frac{\dfrac{n_{\text{sulfur}}}{n_{\text{chloro}}}}{5.5} = \frac{\dfrac{162.2 \text{ mol}}{169.4 \text{ mol}}}{5.5} = 0.174$$

15.23 For an alternating acrylonitrile-butadiene copolymer, we are asked to compute the weight percent sulfur necessary for complete crosslinking, assuming that, on the average, four sulfur atoms participate in each crosslink. The acrylonitrile and butadiene repeat units are shown in Table 14.5, from which it may be noted that there are two possible crosslink sites on each butadiene repeat unit (one site at each of the two carbon atoms that are doubly bonded), and no possible sites for acrylonitrile; also, since it is an alternating copolymer, the ratio of butadiene to acrylonitrile repeat units is 1:1. Thus, for each pair of combined butadiene-acrylonitrile repeat units which crosslink, eight sulfur atoms are required, or, for complete crosslinking, the sulfur-to-(acrylonitrile-butadiene) ratio is 4:1.

Now, let us consider as our basis, one mole of the combined acrylonitrile-butadiene repeat units. In order for complete crosslinking, four moles of sulfur are required. Thus, for us to convert this composition to weight percent, it is necessary to convert moles to mass. The acrylonitrile repeat unit consists of three carbon atoms, three hydrogen atoms, and one nitrogen atom; the butadiene repeat unit is composed of four carbons and six hydrogens. This gives a molecular weight for the combined repeat unit of

$$m(\text{acrylonitrile-butadiene}) = 3(A_\text{C}) + 3(A_\text{H}) + A_\text{N} + 4(A_\text{C}) + 6(A_\text{H})$$

$$= 7(12.01 \text{ g/mol}) + 9(1.008 \text{ g/mol}) + 14.007 \text{ g/mol} = 107.15 \text{ g/mol}$$

Or, in one mole of this combined repeat unit, there are 107.15 g. Furthermore, for complete crosslinking 4.0 mol of sulfur is required, which amounts to (4.0 mol)(32.06 g/mol) = 128.24 g. Thus, the concentration of S in weight percent C_S (using Equation 4.3) is just

$$C_\text{S} = \frac{128.24 \text{ g}}{128.24 \text{ g} + 107.15 \text{ g}} \times 100 = 54.5 \text{ wt\%}$$

15.24 This problem asks for us to determine how many crosslinks form per isoprene repeat unit when 45.3 wt% sulfur is added, assuming that, on the average, five sulfur atoms participate in each crosslink. If we arbitrarily consider 100 g of the vulcanized material, 45.3 g will be sulfur and 54.7 g will be polyisoprene. Next, let us find how many moles of sulfur and isoprene correspond to these masses. The atomic weight of sulfur is 32.06 g/mol, and thus,

$$\#\ \text{moles S} = \frac{45.3\ \text{g}}{32.06\ \text{g/mol}} = 1.41\ \text{mol}$$

Now, in each isoprene repeat unit there are five carbon atoms and eight hydrogen atoms. Thus, the molecular weight of a mole of isoprene units is

$$(5)(12.01\ \text{g/mol}) + (8)(1.008\ \text{g/mol}) = 68.11\ \text{g/mol}$$

Or, in 54.7 g of polyisoprene, the number of moles is equal to

$$\#\ \text{moles isoprene} = \frac{54.7\ \text{g}}{68.11\ \text{g/mol}} = 0.793\ \text{mol}$$

Therefore, the ratio of moles of S to the number of moles of polyisoprene is

$$\frac{1.41\ \text{mol}}{0.793\ \text{mol}} : 1 \ = \ 1.78 : 1$$

When all possible sites are crosslinked, the ratio of the number of moles of sulfur to the number of moles of isoprene is 5:1; this is because there are two crosslink sites per repeat unit and each crosslink is shared between repeat units on adjacent chains, and there are 5 sulfur atoms per crosslink. Finally, to determine the fraction of sites that are crosslinked, we just divide the actual crosslinked sulfur/isoprene ratio by the completely crosslinked ratio. Or,

$$\text{fraction of repeat unit sites crosslinked} = \frac{1.78/1}{5/1} \ = \ 0.356$$

15.25 We are asked what weight percent of sulfur must be added to polyisoprene in order to ensure that 10% of possible sites are crosslinked, assuming that, on the average, 3.5 sulfur atoms are associated with each crosslink. Table 14.5 shows the chemical repeat unit for isoprene. For each of these units there are two possible crosslink sites; one site is associated with each of the two carbon atoms that are involved in the chain double bond. Since 10% of the possible sites are crosslinked, for each 100 isoprene repeat units 10 of them are crosslinked; actually there are two crosslink sites per repeat unit, but each crosslink is shared by two chains. Furthermore, on the average we assume that each crosslink is composed of 3.5 sulfur atoms; thus, there must be 3.5 x 10 or 35 sulfur atoms added for every 100 isoprene repeat units. In terms of moles, it is necessary to add 35 moles of sulfur to 100 moles of isoprene. The atomic weight of sulfur is 32.06 g/mol, while the molecular weight of isoprene is

$$A(\text{isoprene}) = 5(A_\text{C}) + 8(A_\text{H})$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 68.11 \text{ g/mol}$$

The mass of sulfur added (m_S) is

$$m_\text{S} = (35 \text{ mol})(32.06 \text{ g/mol}) = 1122 \text{ g}$$

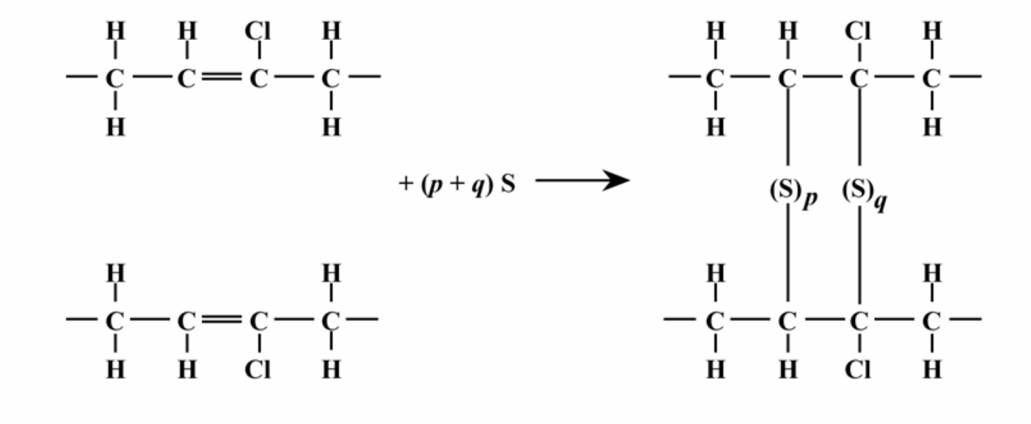
While for isoprene

$$m_\text{ip} = (100 \text{ mol})(68.11 \text{ g/mol}) = 6811 \text{ g}$$

Or, the concentration of sulfur in weight percent (Equation 4.3) is just

$$C_\text{S} = \frac{m_\text{S}}{m_\text{S} + m_\text{ip}} \times 100 = \frac{1122 \text{ g}}{1122 \text{ g} + 6811 \text{ g}} \times 100 = 14.1 \text{ wt\%}$$

15.26 The reaction by which a chloroprene rubber may become vulcanized is as follows:



Crystallization

15.27 In this problem we are asked to determine the values of the constants n and k (Equation 10.17) for the crystallization of polypropylene at 150°C (Figure 15.17). One way to solve this problem is to take two values of percent recrystallization (which is just 100y, Equation 10.17) and their corresponding time values, then set up two simultaneous equations, from which n and k may be determined. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln\,(1 - y) = -kt^n$$

Or

$$-\ln\,(1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k \; + \; n \ln t$$

which is the form of the equation that we will now use. From the 150°C curve of Figure 15.17, let us arbitrarily choose two percent crystallized values of 20% and 80% (i.e., y_1 = 0.20 and y_2 = 0.80). The corresponding time values are t_1 = 220 min and t_2 = 460 min (realizing that the time axis is scaled logarithmically). Thus, our two simultaneous equations become

$$\ln\left[\ln\left(\frac{1}{1 - 0.20}\right)\right] = \ln k \; + \; n \ln\,(220)$$

$$\ln\left[\ln\left(\frac{1}{1 - 0.80}\right)\right] = \ln k + n \ln (460)$$

from which we obtain the values $n = 2.68$ and $k = 1.2 \times 10^{-7}$.

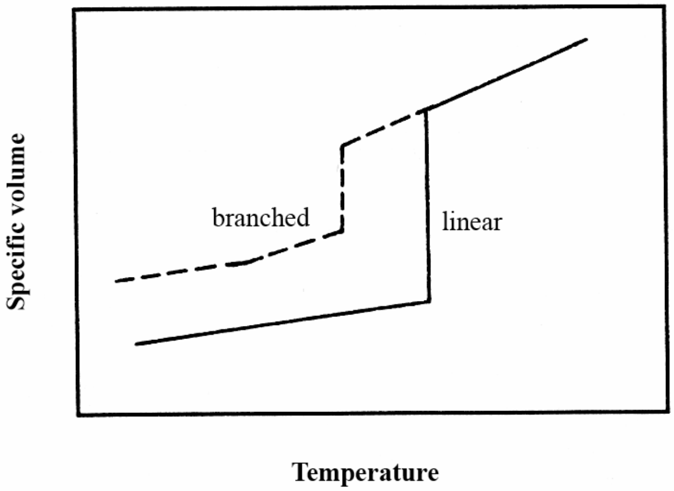
Melting and Glass Transition Temperatures

15.28 This question asks us to name which, of several polymers, would be suitable for the fabrication of cups to contain hot coffee. At its glass transition temperature, an amorphous polymer begins to soften. The maximum temperature of hot coffee is probably slightly below 100°C (212°F). Of the polymers listed, only polystyrene and polycarbonate have glass transition temperatures of 100°C or above (Table 15.2), and would be suitable for this application.

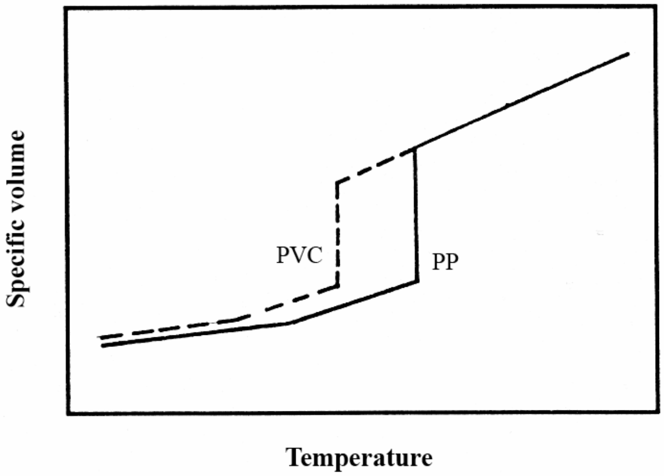
15.29 In order for a polymer to be suited for use as an ice cube tray it must have a glass-transition temperature below 0°C. Of those polymers listed in Table 15.2 only low-density and high-density polyethylene, PTFE, and polypropylene satisfy this criterion.

Factors That Influence Melting and Glass Transition Temperatures

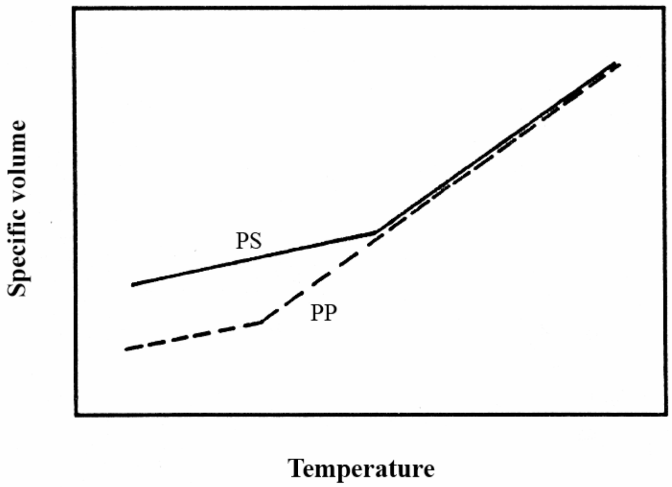
15.30 (a) Shown below are specific volume-versus-temperature curves for the two polyethylene materials. The linear polyethylene will be highly crystalline, and, therefore, will exhibit behavior similar to curve *C* in Figure 15.18. The branched polyethylene will be semicrystalline, and, therefore its curve will appear as curve *B* in this same figure. Furthermore, since the linear polyethylene has the greater molecular weight, it will also have the higher melting temperature.



(b) Shown below are specific volume-versus-temperature curves for the poly(vinyl chloride) and polypropylene materials. Since both are 50% crystalline, they will exhibit behavior similar to curve *B* in Figure 15.18. However, since the polypropylene has the greater molecular weight it will have the higher melting temperature. Furthermore, polypropylene will also have the higher glass-transition temperature inasmuch as its CH_3 side group is bulkier than the Cl for PVC.



(c) Shown below are specific volume-versus-temperature curves for the polystyrene and polypropylene materials. Since both are totally amorphous, they will exhibit the behavior similar to curve *A* in Figure 15.18. However, since the polystyrene repeat unit has a bulkier side group than polypropylene (Table 14.3), its chain flexibility will be lower, and, thus, its glass-transition temperature will be higher.



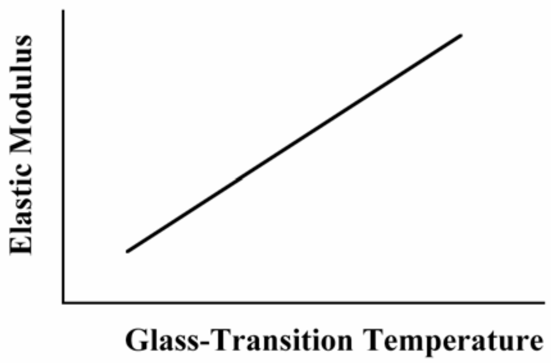
15.31 (a) Yes, it is possible to determine which polymer has the higher melting temperature. The linear polyethylene will most likely have a higher percent crystallinity, and, therefore, a higher melting temperature than the branched polyethylene. The molecular weights of both materials are the same and, thus, molecular weight is not a consideration.

(b) Yes, it is possible to determine which polymer has the higher melting temperature. Of these two polytetrafluoroethylene polymers, the PTFE with the higher density (2.20 g/cm^3) will have the higher percent crystallinity, and, therefore, a higher melting temperature than the lower density PTFE. The molecular weights of both materials are the same and, thus, molecular weight is not a consideration.

(c) Yes, it is possible to determine which polymer has the higher melting temperature. The linear polyethylene will have the greater melting temperature inasmuch as it will have a higher degree of crystallinity; polymers having a syndiotactic structure do not crystallize as easily as those polymers having identical single-atom side groups. With regard to molecular weight, or rather, degree of polymerization, it is about the same for both materials (8000), and therefore, is not a consideration.

(d) No, it is not possible to determine which of the two polymers has the higher melting temperature. The syndiotactic polypropylene will have a higher degree of crystallinity than the atactic material. On the basis of this effect alone, the syndiotactic PP should have the greater T_m, since melting temperature increases with degree of crystallinity. However, the molecular weight for the syndiotactic polypropylene (500,000 g/mol) is less than for the atactic material (750,000 g/mol); and this factor leads to a lowering of the melting temperature

15.32 For an amorphous polymer, the elastic modulus may be enhanced by increasing the number of crosslinks (while maintaining the molecular weight constant); this will also enhance the glass transition temperature. Thus, the modulus-glass transition temperature behavior would appear as



Elastomers

Fibers

Miscellaneous Applications

15.33 The backbone chain of most polymers consists of carbon atoms that are linked together. For the silicone polymers, this backbone chain is composed of silicon and oxygen atoms that alternate positions.

15.34 Two important characteristics for polymers that are to be used in fiber applications are: (1) they must have high molecular weights, and (2) they must have chain configurations/structures that will allow for a high degrees of crystallinity.

15.35 Five important characteristics for polymers that are to be used in thin-film applications are: (1) low density; (2) high flexibility; (3) high tensile and tear strengths; (4) resistance to moisture/chemical attack; and (5) low gas permeability.

Polymerization

15.36 For addition polymerization, the reactant species have the same chemical composition as the monomer species in the molecular chain. This is not the case for condensation polymerization, wherein there is a chemical reaction between two or more monomer species, producing the repeating unit. There is often a low molecular weight by-product for condensation polymerization; such is not found for addition polymerization.

15.37 (a) This problem asks that we determine how much ethylene glycol must be added to 20.0 kg of terephthalic acid to produce a linear chain structure of poly(ethylene terephthalate) according to Equation 15.9. Since the chemical formulas are provided in this equation we may calculate the molecular weights of each of these materials as follows:

$$MW(\text{ethylene glycol}) = 2(A_{\text{C}}) + 6(A_{\text{H}}) + 2(A_{\text{O}})$$

$$= 2(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) + 2(16.00 \text{ g/mol}) = 62.07 \text{ g/mol}$$

$$MW(\text{terephthalic acid}) = 8(A_{\text{C}}) + 6(A_{\text{H}}) + 4(A_{\text{O}})$$

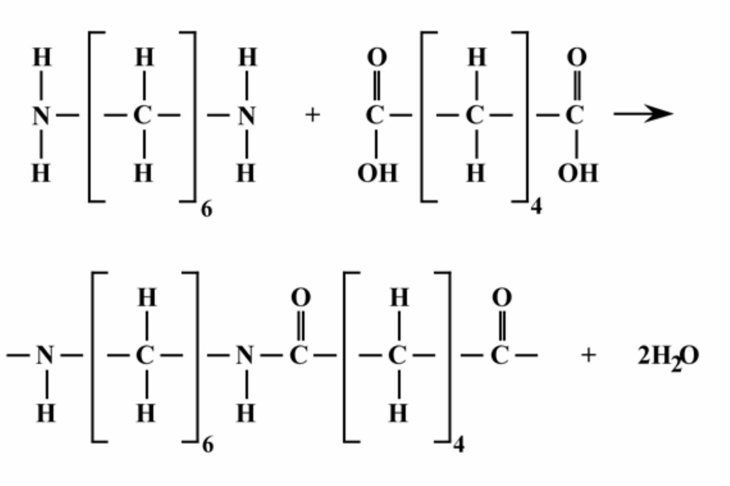
$$= 8\,(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) + 4(16.00 \text{ g/mol}) = 166.13 \text{ g/mol}$$

The 20.0 kg mass of terephthalic acid equals 20,000 g or $\dfrac{20{,}000 \text{ g}}{166.13 \text{ g/mol}} = 120.39$ mol. Since, according to Equation 15.9, each mole of terephthalic acid used requires one mole of ethylene glycol, which is equivalent to (120.39 mol)(62.07 g/mol) = 7473 g = 7.473 kg.

(b) Now we are asked for the mass of the resulting polymer. Inasmuch as one mole of water is given off for every repeat unit produced, this corresponds to 120.39 moles or (120.39 mol)(18.02 g/mol) = 2169 g or 2.169 kg since the molecular weight of water is 18.02 g/mol. The mass of poly(ethylene terephthalate) is just the sum of the masses of the two reactant materials [as computed in part (a)] minus the mass of water released, or

$$\text{mass [poly(ethylene terephthalate)]} = 20.0 \text{ kg} + 7.473 \text{ kg} - 2.169 \text{ kg} = 25.304 \text{ kg}$$

15.38 This problem asks for us to calculate the masses of hexamethylene diamine and adipic acid necessary to yield 20 kg of completely linear nylon 6,6. The chemical equation for this reaction is the answer to Concept Check 15.12, which is as follows:



From this equation we may calculate the molecular weights of these molecules.

$$MW(\text{adipic}) = 6(A_{\text{C}}) + 10(A_{\text{H}}) + 4(A_{\text{O}})$$

$$= 6(12.01\text{ g/mol}) + 10(1.008\text{ g/mol}) + 4(16.00\text{ g/mol}) = 146.14\text{ g/mol}$$

$$MW(\text{hexamethylene}) = 6(A_{\text{C}}) + 16(A_{\text{H}}) + 2(A_{\text{N}})$$

$$= 6(12.01\text{ g/mol}) + 16(1.008\text{ g/mol}) + 2(14.01\text{ g/mol}) = 116.21\text{ g/mol}$$

$$MW(\text{nylon}) = 12(A_{\text{C}}) + 22(A_{\text{H}}) + 2(A_{\text{N}}) + 2(A_{\text{O}})$$

$$= 12(12.01\text{ g/mol}) + 22(1.008\text{ g/mol}) + 2(14.01\text{ g/mol}) + 2(16.00\text{ g/mol})$$

$$= 226.32\text{ g/mol}$$

The mass of 20 kg of nylon 6,6 equals 20,000 g or

$$m(\text{nylon}) = \frac{20{,}000 \text{ g}}{226.32 \text{ g/mol}} = 88.37 \text{ mol}$$

Since, according to the chemical equation given above, each mole of nylon 6,6 that is produced requires one mole each of adipic acid and hexamethylene diamine, with two moles of water as the by-product. The masses corresponding to 88.37 moles of adipic acid and hexamethylene diamine are as follows:

$$m(\text{adipic}) = (88.37 \text{ mol})(146.14 \text{ g/mol}) = 12{,}914 \text{ g} = 12.914 \text{ kg}$$

$$m(\text{hexamethylene}) = (88.37 \text{ mol})(116.21 \text{ g/mol}) = 10{,}269 \text{ g} = 10.269 \text{ kg}$$

Polymer Additives

15.39 The distinction between dye and pigment colorants is that a dye dissolves within and becomes a part of the polymer structure, whereas a pigment does not dissolve, but remains as a separate phase.

Forming Techniques for Plastics

15.40 Four factors that determine what fabrication technique is used to form polymeric materials are: (1) whether the polymer is thermoplastic or thermosetting; (2) if thermoplastic, the softening temperature; (3) atmospheric stability; and (4) the geometry and size of the finished product.

15.41 This question requests that we compare polymer molding techniques. For compression molding, both heat and pressure are applied after the polymer and necessary additives are situated between the mold members. For transfer molding, the solid materials (normally thermosetting in nature) are first melted in the transfer chamber prior to being forced into the die. And, for injection molding (normally used for thermoplastic materials), the raw materials are impelled by a ram through a heating chamber, and finally into the die cavity.

Fabrication of Fibers and Films

15.42 Fiber materials that are melt spun must be thermoplastic because: (1) In order to be melt spun, they must be capable of forming a viscous liquid when heated, which is not possible for thermosets. (2) During drawing, mechanical elongation must be possible; inasmuch as thermosetting materials are, in general, hard and relatively brittle, they are not easily elongated.

15.43 Of the two polymers cited, the one that was formed by extrusion and then rolled would have the higher strength. Both blown and extruded materials would have roughly comparable strengths; however the rolling operation would further serve to enhance the strength of the extruded material.

DESIGN QUESTIONS

15.D1 (a) Several advantages of using transparent polymeric materials for eyeglass lenses are: they have relatively low densities, and, therefore, are light in weight; they are relatively easy to grind to have the desired contours; they are less likely to shatter than are glass lenses; wraparound lenses for protection during sports activities are possible; and they filter out more ultraviolet radiation than do glass lenses.

The principal disadvantage of these types of lenses is that some are relatively soft and are easily scratched (although antiscratch coatings may be applied). Plastic lenses are not as mechanically stable as glass, and, therefore, are not as precise optically.

(b) Some of the properties that are important for polymer lens materials are: they should be relatively hard in order to resist scratching; they must be impact resistant; they should be shatter resistant; they must have a relatively high index of refraction such that thin lenses may be ground for very nearsighted people; and they should absorb significant proportions of all types of ultraviolet radiation, which radiation can do damage to the eye tissues.

(c) Of those polymers discussed in this chapter and Chapter 4, likely lens candidates are polystyrene, poly(methyl methacrylate), and polycarbonate; these three materials are not easily crystallized, and, therefore, are normally transparent. Upon consultation of their fracture toughnesses (Table B.5 in Appendix B), polycarbonate is the most superior of the three.

Commercially, the two plastic lens materials of choice are polycarbonate and allyl diglycol carbonate (having the trade name CR-39). Polycarbonate is very impact resistant, but not as hard as CR-39. Furthermore, PC comes in both normal and high refractive-index grades.

15.D2 There are three primary requirements for polymeric materials that are utilized in the packaging of food products and drinks; these are: (1) sufficient strength, to include tensile, tear, and impact strengths; (2) barrier protection--that is, being resistant to permeation by oxygen, water vapor, and carbon dioxide; and (3) being nonreactive with the food/drink contents--such reactions can compromise the integrity of the packaging material, or they can produce toxic by-products.

With regard to strength, poly(ethylene terephthalate) (PET or PETE) and oriented polypropylene (OPP) have high tensile strengths, linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) have high tear strengths, while those polymers having the best impact strengths are PET and poly(vinyl chloride) (PVC). Relative to barrier characteristics, ethylene vinyl alcohol (EVOH) and poly(vinylidene chloride) (PVDC) copolymers are relatively impermeable to oxygen and carbon dioxide, whereas high-density polyethylene (HDPE), PVDC, polypropylene, and LDPE are impervious to water vapor.

Most common polymers are relatively nonreactive with food products, and are considered safe; exceptions are acrylonitrile and plasticizers used in PVC materials.

The aesthetics of packaging polymers are also important in the marketing of food and drink products. Some will be colored, many are adorned with printing, others need to be transparent and clear, and many need to be resistant to scuffing.

On the basis of the preceding discussion, examples of polymers that are used for specific applications are as follows:

PET(E) for soda pop containers;
PVC for beer containers;
LDPE and HDPE films for packaging bread and bakery products.

15.D3 The primary reasons that the automotive industry has replaced metallic automobile components with polymer and composite materials are: polymers/composites (1) have lower densities, and afford higher fuel efficiencies; (2) may be produced at lower costs but with comparable mechanical characteristics; (3) are in many environments more corrosion resistant; (4) reduce noise, and (5) are thermally insulating and thus reduce the transference of heat.

These replacements are many and varied. Several are as follows:

Bumper fascia are molded from an elastomer-modified polypropylene.

Overhead consoles are made of poly(phenylene oxide) and recycled polycarbonate.

Rocker arm covers are injection molded of a glass- and mineral-reinforced nylon 6,6 composite.

Torque converter reactors, water outlets, pulleys, and brake pistons, are made from phenolic thermoset composites that are reinforced with glass fibers.

Air intake manifolds are made of a glass-reinforced nylon 6,6.

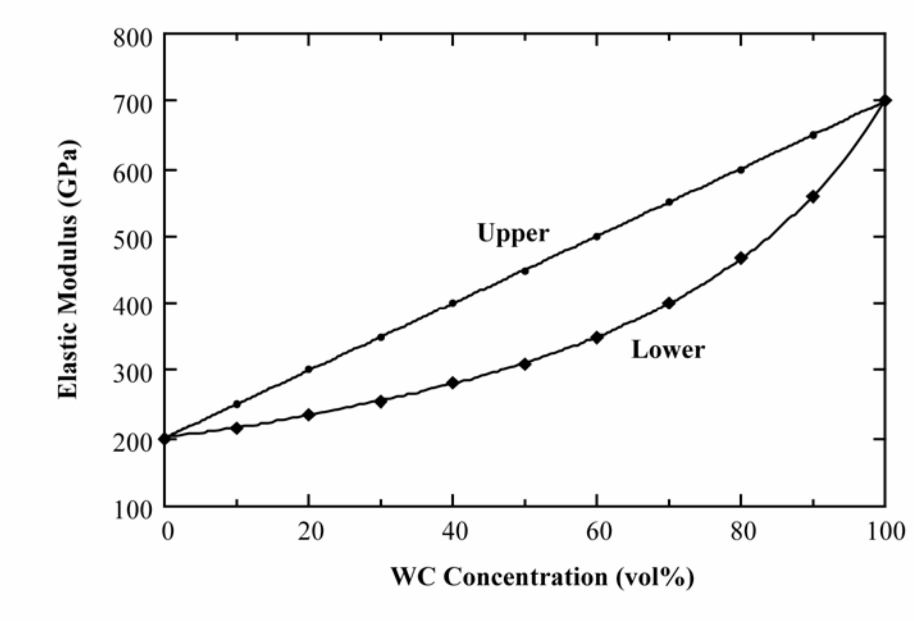
CHAPTER 16

COMPOSITES

PROBLEM SOLUTIONS

Large-Particle Composites

16.1 The elastic modulus versus volume percent of WC is shown below, on which is included both upper and lower bound curves; these curves were generated using Equations 16.1 and 16.2, respectively, as well as the moduli of elasticity for cobalt and WC given in the problem statement.



16.2 This problem asks for the maximum and minimum thermal conductivity values for a TiC-Ni cermet. Using a modified form of Equation 16.1 the maximum thermal conductivity k_{max} is calculated as

$$k_{\text{max}} = k_m V_m + k_p V_p = k_{\text{Ni}} V_{\text{Ni}} + k_{\text{TiC}} V_{\text{TiC}}$$

$$= (67 \text{ W/m-K})(0.10) + (27 \text{ W/m-K})(0.90) = 31.0 \text{ W/m-K}$$

Using a modified form of Equation 16.2, the minimum thermal conductivity k_{min} will be

$$k_{\text{min}} = \frac{k_{\text{Ni}} k_{\text{TiC}}}{V_{\text{Ni}} k_{\text{TiC}} + V_{\text{TiC}} k_{\text{Ni}}}$$

$$= \frac{(67 \text{ W/m-K})(27 \text{ W/m-K})}{(0.10)(27 \text{ W/m-K}) + (0.90)(67 \text{ W/m-K})}$$

$$= 28.7 \text{ W/m-K}$$

16.3 Given the elastic moduli and specific gravities for copper and tungsten we are asked to estimate the upper limit for specific stiffness when the volume fractions of tungsten and copper are 0.70 and 0.30, respectively. There are two approaches that may be applied to solve this problem. The first is to estimate both the upper limits of elastic modulus [$E_c(u)$] and specific gravity (ρ_c) for the composite, using expressions of the form of Equation 16.1, and then take their ratio. Using this approach

$$E_c(u) = E_{\mathrm{Cu}}V_{\mathrm{Cu}} + E_{\mathrm{W}}V_{\mathrm{W}}$$

$$= (110 \text{ GPa})(0.30) + (407 \text{ GPa})(0.70)$$

$$= 318 \text{ GPa}$$

And

$$\rho_c = \rho_{\mathrm{Cu}}V_{\mathrm{Cu}} + \rho_{\mathrm{W}}V_{\mathrm{W}}$$

$$= (8.9)(0.30) + (19.3)(0.70) = 16.18$$

Therefore

$$\text{Specific Stiffness} = \frac{E_c(u)}{\rho_c} = \frac{318 \text{ GPa}}{16.18} = 19.65 \text{ GPa}$$

With the alternate approach, the specific stiffness is calculated, again employing a modification of Equation 16.1, but using the specific stiffness-volume fraction product for both metals, as follows:

$$\text{Specific Stiffness} = \frac{E_{\mathrm{Cu}}}{\rho_{\mathrm{Cu}}}V_{\mathrm{Cu}} + \frac{E_{\mathrm{W}}}{\rho_{\mathrm{W}}}V_{\mathrm{W}}$$

$$= \frac{110 \text{ GPa}}{8.9}(0.30) + \frac{407 \text{ GPa}}{19.3}(0.70) = 18.47 \text{ GPa}$$

16.4 (a) Concrete consists of an aggregate of particles that are bonded together by a cement.

(b) Three limitations of concrete are: (1) it is a relatively weak and brittle material; (2) it experiences relatively large thermal expansions (contractions) with changes in temperature; and (3) it may crack when exposed to freeze-thaw cycles.

(c) Three reinforcement strengthening techniques are: (1) reinforcement with steel wires, rods, etc.; (2) reinforcement with fine fibers of a high modulus material; and (3) introduction of residual compressive stresses by prestressing or posttensioning.

Dispersion-Strengthened Composites

16.5 The similarity between precipitation hardening and dispersion strengthening is the strengthening mechanism--i.e., the precipitates/particles effectively hinder dislocation motion.

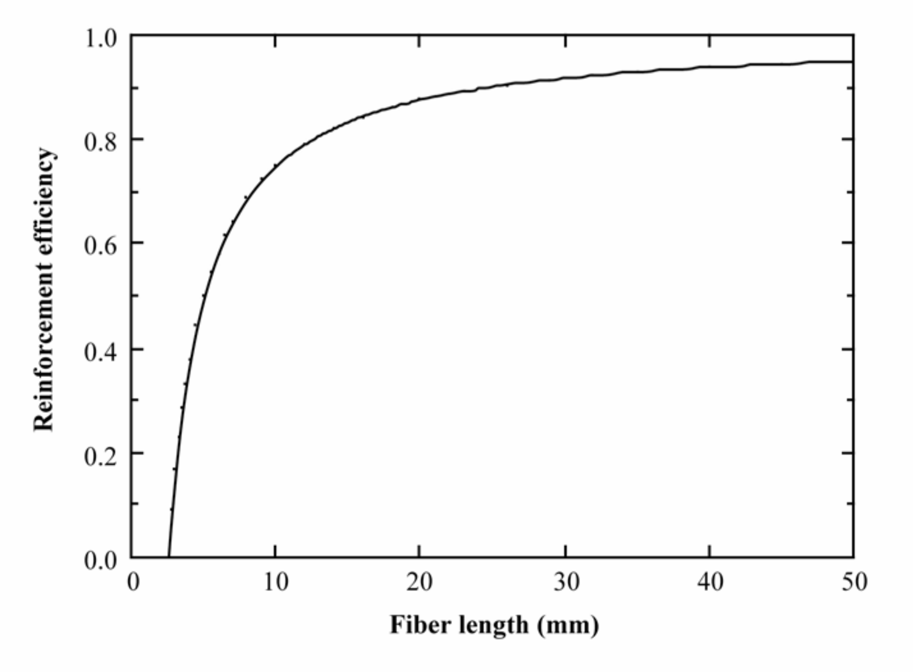
The two differences are: (1) the hardening/strengthening effect is not retained at elevated temperatures for precipitation hardening--however, it is retained for dispersion strengthening; and (2) the strength is developed by a heat treatment for precipitation hardening--such is not the case for dispersion strengthening.

Influence of Fiber Length

16.6 This problem asks that, for a glass fiber-epoxy matrix combination, to determine the fiber-matrix bond strength if the critical fiber length-fiber diameter ratio is 40. Thus, we are to solve for τ_c in Equation 16.3. Since we are given that σ_f^* = 3.45 GPa from Table 16.4, and that $\frac{l_c}{d}$ = 40, then

$$\tau_c = \sigma_f^* \left(\frac{d}{2\,l_c}\right) = \left(3.45 \text{ x } 10^3 \text{ MPa}\right) \frac{1}{(2)(40)} = 43.1 \text{ MPa}$$

16.7 (a) The plot of reinforcement efficiency versus fiber length is given below.



(b) This portion of the problem asks for the length required for a 0.90 efficiency of reinforcement. Solving for *l* from the given expression

$$l = \frac{2x}{1 - \eta}$$

Or, when x = 1.25 mm (0.05 in.) and η = 0.90, then

$$l = \frac{(2)(1.25 \text{ mm})}{1 - 0.90} = 25 \text{ mm} \ \ (1.0 \text{ in.})$$

Influence of Fiber Orientation and Concentration

16.8 This problem calls for us to compute the longitudinal tensile strength and elastic modulus of an aramid fiber-reinforced polycarbonate composite.

(a) The longitudinal tensile strength is determined using Equation 16.17 as

$$\sigma_{cl}^* = \sigma'_m (1 - V_f) + \sigma_f^* V_f$$

$$= (35 \text{ MPa})(0.55) + (3600)(0.45)$$

$$= 1640 \text{ MPa} \ (238{,}000 \text{ psi})$$

(b) The longitudinal elastic modulus is computed using Equation 16.10a as

$$E_{cl} = E_m V_m + E_f V_f$$

$$= (2.4 \text{ GPa})(0.55) + (131 \text{ GPa})(0.45)$$

$$= 60.3 \text{ GPa} \ (8.74 \times 10^6 \text{ psi})$$

16.9 This problem asks for us to determine if it is possible to produce a continuous and oriented aramid fiber-epoxy matrix composite having longitudinal and transverse moduli of elasticity of 35 GPa and 5.17 GPa, respectively, given that the modulus of elasticity for the epoxy is 3.4 GPa. Also, from Table 16.4 the value of *E* for aramid fibers is 131 GPa. The approach to solving this problem is to calculate values of V_f for both longitudinal and transverse cases using the data and Equations 16.10b and 16.16; if the two V_f values are the same then this composite is possible.

For the longitudinal modulus E_{cl} (using Equation 16.10b),

$$E_{cl} = E_m(1 - V_{fl}) + E_f V_{fl}$$

$$35 \text{ GPa} = (3.4 \text{ GPa})(1 - V_{fl}) + (131 \text{ GPa})V_{fl}$$

Solving this expression for V_{fl} (i.e., the volume fraction of fibers for the longitudinal case) yields $V_{fl} = 0.248$.

Now, repeating this procedure for the transverse modulus E_{ct} (using Equation 16.16)

$$E_{ct} = \frac{E_m E_f}{(1 - V_{ft})E_f + V_{ft}E_m}$$

$$5.17 \text{ GPa} = \frac{(3.4 \text{ GPa})(131 \text{ GPa})}{(1 - V_{ft})(131 \text{ GPa}) + V_{ft}(3.4 \text{ GPa})}$$

Solving this expression for V_{ft} (i.e., the volume fraction of fibers for the transverse case), leads to $V_{ft} = 0.351$. Thus, since V_{fl} and V_{ft} are not equal, the proposed composite is *not possible*.

16.10 This problem asks for us to compute the elastic moduli of fiber and matrix phases for a continuous and oriented fiber-reinforced composite. We can write expressions for the longitudinal and transverse elastic moduli using Equations 16.10b and 16.16, as

$$E_{cl} = E_m\left(1 - V_f\right) + E_f V_f$$

$$33.1 \text{ GPa} = E_m(1 - 0.30) + E_f(0.30)$$

And

$$E_{ct} = \frac{E_m E_f}{\left(1 - V_f\right)E_f + V_f E_m}$$

$$3.66 \text{ GPa} = \frac{E_m E_f}{(1 - 0.30)E_f + 0.30E_m}$$

Solving these two expressions simultaneously for E_m and E_f leads to

$$E_m = 2.6 \text{ GPa} \quad (3.77 \text{ x } 10^5 \text{ psi})$$

$$E_f = 104 \text{ GPa} \quad (15 \text{ x } 10^6 \text{ psi})$$

16.11 (a) In order to show that the relationship in Equation 16.11 is valid, we begin with Equation 16.4—i.e.,

$$F_c = F_m + F_f$$

which may be manipulated to the form

$$\frac{F_c}{F_m} = 1 + \frac{F_f}{F_m}$$

or

$$\frac{F_f}{F_m} = \frac{F_c}{F_m} - 1$$

For elastic deformation, combining Equations 6.1 and 6.5

$$\sigma = \frac{F}{A} = \varepsilon E$$

or

$$F = A\varepsilon E$$

We may write expressions for F_c and F_m of the above form as

$$F_c = A_c \varepsilon E_c$$

$$F_m = A_m \varepsilon E_m$$

which, when substituted into the above expression for F_f/F_m, gives

$$\frac{F_f}{F_m} = \frac{A_c \varepsilon E_c}{A_m \varepsilon E_m} - 1$$

But, $V_m = A_m/A_c$, which, upon rearrangement gives

$$\frac{A_c}{A_m} = \frac{1}{V_m}$$

which, when substituted into the previous expression leads to

$$\frac{F_f}{F_m} = \frac{E_c}{E_m V_m} - 1$$

Also, from Equation 16.10a, $E_c = E_m V_m + E_f V_f$, which, when substituted for E_c into the previous expression, yields

$$\frac{F_f}{F_m} = \frac{E_m V_m + E_f V_f}{E_m V_m} - 1$$

$$= \frac{E_m V_m + E_f V_f - E_m V_m}{E_m V_m} = \frac{E_f V_f}{E_m V_m}$$

the desired result.

(b) This portion of the problem asks that we establish an expression for F_f/F_c. We determine this ratio in a similar manner. Now $F_c = F_f + F_m$ (Equation 16.4), or division by F_c leads to

$$1 = \frac{F_f}{F_c} + \frac{F_m}{F_c}$$

which, upon rearrangement, gives

$$\frac{F_f}{F_c} = 1 - \frac{F_m}{F_c}$$

Now, substitution of the expressions in part (a) for F_m and F_c that resulted from combining Equations 6.1 and 6.5 results in

$$\frac{F_f}{F_c} = 1 - \frac{A_m \varepsilon E_m}{A_c \varepsilon E_c} = 1 - \frac{A_m E_m}{A_c E_c}$$

Since the volume fraction of fibers is equal to $V_m = A_m/A_c$, then the above equation may be written in the form

$$\frac{F_f}{F_c} = 1 - \frac{V_m E_m}{E_c}$$

And, finally substitution of Equation 16.10(a) for E_c into the above equation leads to the desired result as follows:

$$\frac{F_f}{F_c} = 1 - \frac{V_m E_m}{V_m E_m + V_f E_f}$$

$$= \frac{V_m E_m + V_f E_f - V_m E_m}{V_m E_m + V_f E_f}$$

$$= \frac{V_f E_f}{V_m E_m + V_f E_f}$$

$$= \frac{V_f E_f}{(1 - V_f) E_m + V_f E_f}$$

16.12 (a) Given some data for an aligned and continuous carbon-fiber-reinforced nylon 6,6 composite, we are asked to compute the volume fraction of fibers that are required such that the fibers carry 97% of a load applied in the longitudinal direction. From Equation 16.11

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m} = \frac{E_f V_f}{E_m \left(1 - V_f\right)}$$

Now, using values for F_f and F_m from the problem statement

$$\frac{F_f}{F_m} = \frac{0.97}{0.03} = 32.3$$

And when we substitute the given values for E_f and E_m into the first equation leads to

$$\frac{F_f}{F_m} = 32.3 = \frac{(260 \text{ GPa})V_f}{(2.8 \text{ GPa})\left(1 - V_f\right)}$$

And, solving for V_f yields, $V_f = 0.258$.

(b) We are now asked for the tensile strength of this composite. From Equation 16.17,

$$\sigma_{cl}^* = \sigma'_m\left(1 - V_f\right) + \sigma_f^* V_f$$

$$= (50 \text{ MPa})(1 - 0.258) + (4000 \text{ MPa})(0.258)$$

$$= 1070 \text{ MPa} \quad (155{,}000 \text{ psi})$$

since values for σ_f^* (4000 MPa) and σ'_m (50 MPa) are given in the problem statement.

16.13 The problem stipulates that the cross-sectional area of a composite, A_c, is 480 mm^2 (0.75 in.^{2}), and the longitudinal load, F_c, is 53,400 N (12,000 lb$_f$) for the composite described in Problem 16.8.

(a) First, we are asked to calculate the F_f/F_m ratio. According to Equation 16.11

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m} = \frac{(131\ \text{GPa})(0.45)}{(2.4\ \text{GPa})(0.55)} = 44.7$$

Or, $F_f = 44.7F_m$

(b) Now, the actual loads carried by both phases are called for. From Equation 16.4

$$F_f + F_m = F_c = 53{,}400\ \text{N}$$

$$44.7F_m + F_m = 53{,}400\ \text{N}$$

which leads to

$$F_m = 1168\ \text{N}\ \ (263\ \text{lb}_\text{f})$$

$$F_f = F_c - F_m = 53{,}400\ \text{N} - 1168\ \text{N} = 52{,}232\ \text{N}\ \ (11{,}737\ \text{lb}_\text{f})$$

(c) To compute the stress on each of the phases, it is first necessary to know the cross-sectional areas of both fiber and matrix. These are determined as

$$A_f = V_f A_c = (0.45)(480\ \text{mm}^2) = 216\ \text{mm}^2\ \ (0.34\ \text{in.}^2)$$

$$A_m = V_m A_c = (0.55)(480\ \text{mm}^2) = 264\ \text{mm}^2\ \ (0.41\ \text{in.}^2)$$

Now, the stresses are determined using Equation 6.1 as

$$\sigma_f = \frac{F_f}{A_f} = \frac{52{,}232\ \text{N}}{(216\ \text{mm}^2)(1\ \text{m}/1000\ \text{mm})^2} = 242 \times 10^6\ \text{N/m}^2 = 242\ \text{MPa}\ \ (34{,}520\ \text{psi})$$

$$\sigma_m = \frac{F_m}{A_m} = \frac{1168\ \text{N}}{(264\ \text{mm}^2)(1\ \text{m}/1000\ \text{mm})^2} = 4.4 \times 10^6\ \text{N/m}^2 = 4.4\ \text{MPa}\ \ (641\ \text{psi})$$

(d) The strain on the composite is the same as the strain on each of the matrix and fiber phases; applying Equation 6.5 to both matrix and fiber phases leads to

$$\varepsilon_m = \frac{\sigma_m}{E_m} = \frac{4.4 \text{ MPa}}{2.4 \text{ x } 10^3 \text{ MPa}} = 1.83 \text{ x } 10^{-3}$$

$$\varepsilon_f = \frac{\sigma_f}{E_f} = \frac{242 \text{ MPa}}{131 \text{ x } 10^3 \text{ MPa}} = 1.84 \text{ x } 10^{-3}$$

16.14 For a continuous and aligned fibrous composite, we are given its cross-sectional area (970 mm^2), the stresses sustained by the fiber and matrix phases (215 and 5.38 MPa), the force sustained by the fiber phase (76,800 N), and the total longitudinal strain (1.56 x 10^{-3}).

(a) For this portion of the problem we are asked to calculate the force sustained by the matrix phase. It is first necessary to compute the volume fraction of the matrix phase, V_m. This may be accomplished by first determining V_f and then V_m from $V_m = 1 - V_f$. The value of V_f may be calculated since, from the definition of stress (Equation 6.1), and realizing $V_f = A_f/A_c$ as

$$\sigma_f = \frac{F_f}{A_f} = \frac{F_f}{V_f A_c}$$

Or, solving for V_f

$$V_f = \frac{F_f}{\sigma_f A_c} = \frac{76{,}800 \text{ N}}{\left(215 \text{ x } 10^6 \text{ N/m}^2\right)(970 \text{ mm}^2)(1 \text{ m}/1000 \text{ mm})^2} = 0.369$$

Also

$$V_m = 1 - V_f = 1 - 0.369 = 0.631$$

And, an expression for σ_m analogous to the one for σ_f above is

$$\sigma_m = \frac{F_m}{A_m} = \frac{F_m}{V_m A_c}$$

From which

$$F_m = V_m \sigma_m A_c = (0.631)\left(5.38 \text{ x } 10^6 \text{ N/m}^2\right)\left(0.970 \text{ x } 10^{-3} \text{ m}^2\right) = 3290 \text{ N} \quad (738 \text{ lb}_\text{f})$$

(b) We are now asked to calculate the modulus of elasticity in the longitudinal direction. This is possible realizing that $E_c = \dfrac{\sigma_c}{\varepsilon}$ (from Equation 6.5) and that $\sigma_c = \dfrac{F_m + F_f}{A_c}$ (from Equation 6.1). Thus

$$E_c = \frac{\sigma_c}{\varepsilon} = \frac{\dfrac{F_m + F_f}{A_c}}{\varepsilon} = \frac{F_m + F_f}{\varepsilon A_c}$$

$$= \frac{3290\ \text{N} + 76{,}800\ \text{N}}{\left(1.56\ \text{x}\ 10^{-3}\right)\left(970\ \text{mm}^2\right)(1\ \text{m}/1000\ \text{mm})^2} = 52.9 \times 10^9\ \text{N/m}^2 = 52.9\ \text{GPa} \quad (7.69\ \text{x}\ 10^6\ \text{psi})$$

(c) Finally, it is necessary to determine the moduli of elasticity for the fiber and matrix phases. This is possible assuming Equation 6.5 for the matrix phase—i.e.,

$$E_m = \frac{\sigma_m}{\varepsilon_m}$$

and, since this is an isostrain state, $\varepsilon_m = \varepsilon_c = 1.56\ \text{x}\ 10^{-3}$. Thus

$$E_m = \frac{\sigma_m}{\varepsilon_c} = \frac{5.38\ \text{x}\ 10^6\ \text{N/m}^2}{1.56\ \text{x}\ 10^{-3}} = 3.45\ \text{x}\ 10^9\ \text{N/m}^2$$

$$= 3.45\ \text{GPa} \quad (5.0\ \text{x}\ 10^5\ \text{psi})$$

The elastic modulus for the fiber phase may be computed in an analogous manner:

$$E_f = \frac{\sigma_f}{\varepsilon_f} = \frac{\sigma_f}{\varepsilon_c} = \frac{215\ \text{x}\ 10^6\ \text{N/m}^2}{1.56\ \text{x}\ 10^{-3}} = 1.38\ \text{x}\ 10^{11}\ \text{N/m}^2$$

$$= 138\ \text{GPa} \quad (20\ \text{x}\ 10^6\ \text{psi})$$

16.15 In this problem, for an aligned carbon fiber-epoxy matrix composite, we are given the volume fraction of fibers (0.20), the average fiber diameter (6 x 10^{-3} mm), the average fiber length (8.0 mm), the fiber fracture strength (4.5 GPa), the fiber-matrix bond strength (75 MPa), the matrix stress at composite failure (6.0 MPa), and the matrix tensile strength (60 MPa); and we are asked to compute the longitudinal strength. It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine the longitudinal strength using Equation 16.17, otherwise, use of either Equation 16.18 or Equation 16.19 is necessary. Thus, from Equation 16.3

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(4.5 \text{ x } 10^3 \text{ MPa})(6 \text{ x } 10^{-3} \text{ mm})}{2(75 \text{ MPa})} = 0.18 \text{ mm}$$

Inasmuch as $l >> l_c$ (8.0 mm >> 0.18 mm), then use of Equation 16.17 is appropriate. Therefore,

$$\sigma_{cl}^* = \sigma'_m(1 - V_f) + \sigma_f^* V_f$$

$$= (6 \text{ MPa})(1 - 0.20) + (4.5 \text{ x } 10^3 \text{ MPa})(0.20)$$

$$= 905 \text{ MPa} \ \ (130{,}700 \text{ psi})$$

16.16 In this problem, for an aligned carbon fiber-epoxy matrix composite, we are given the desired longitudinal tensile strength (500 MPa), the average fiber diameter (1.0 x 10^{-2} mm), the average fiber length (0.5 mm), the fiber fracture strength (4 GPa), the fiber-matrix bond strength (25 MPa), and the matrix stress at composite failure (7.0 MPa); and we are asked to compute the volume fraction of fibers that is required. It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine V_f using Equation 16.17, otherwise, use of either Equation 16.18 or Equation 16.19 is necessary. Thus,

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(4 \text{ x } 10^3 \text{ MPa})(1.0 \text{ x } 10^{-2} \text{ mm})}{2(25 \text{ MPa})} = 0.80 \text{ mm}$$

Inasmuch as $l < l_c$ (0.50 mm < 0.80 mm), then use of Equation 16.19 is required. Therefore,

$$\sigma_{cd'}^* = \frac{l\tau_c}{d} V_f + \sigma_m'(1 - V_f)$$

$$500 \text{ MPa} = \frac{(0.5 \text{ x } 10^{-3} \text{ m})(25 \text{ MPa})}{0.01 \text{ x } 10^{-3} \text{ m}}(V_f) + (7 \text{ MPa})(1 - V_f)$$

Solving this expression for V_f leads to $V_f = 0.397$.

16.17 In this problem, for an aligned glass fiber-epoxy matrix composite, we are asked to compute the longitudinal tensile strength given the following: the average fiber diameter (0.015 mm), the average fiber length (2.0 mm), the volume fraction of fibers (0.25), the fiber fracture strength (3500 MPa), the fiber-matrix bond strength (100 MPa), and the matrix stress at composite failure (5.5 MPa). It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine σ_{cl}^* using Equation 16.17, otherwise, use of either Equations 16.18 or 16.19 is necessary. Thus,

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(3500 \text{ MPa})(0.015 \text{ mm})}{2(100 \text{ MPa})} = 0.263 \text{ mm} \quad (0.010 \text{ in.})$$

Inasmuch as $l > l_c$ (2.0 mm > 0.263 mm), but since l is not much greater than l_c, then use of Equation 16.18 is necessary. Therefore,

$$\sigma_{cd}^* = \sigma_f^* V_f \left(1 - \frac{l_c}{2l}\right) + \sigma'_m (1 - V_f)$$

$$= (3500 \text{ MPa})(0.25)\left[1 - \frac{0.263 \text{ mm}}{(2)(2.0 \text{ mm})}\right] + (5.5 \text{ MPa})(1 - 0.25)$$

$$= 822 \text{ MPa} \quad (117{,}800 \text{ psi})$$

16.18 (a) This portion of the problem calls for computation of values of the fiber efficiency parameter. From Equation 16.20

$$E_{cd} = KE_f V_f + E_m V_m$$

Solving this expression for K yields

$$K = \frac{E_{cd} - E_m V_m}{E_f V_f} = \frac{E_{cd} - E_m(1 - V_f)}{E_f V_f}$$

For glass fibers, E_f = 72.5 GPa (Table 16.4); using the data in Table 16.2, and taking an average of the extreme E_m values given, E_m = 2.29 GPa (0.333 x 10^6 psi). And, for V_f = 0.20

$$K = \frac{5.93 \text{ GPa} - (2.29 \text{ GPa})(1 - 0.2)}{(72.5 \text{ GPa})(0.2)} = 0.283$$

For V_f = 0.3

$$K = \frac{8.62 \text{ GPa} - (2.29 \text{ GPa})(1 - 0.3)}{(72.5 \text{ GPa})(0.3)} = 0.323$$

And, for V_f = 0.4

$$K = \frac{11.6 \text{ GPa} - (2.29 \text{ GPa})(1 - 0.4)}{(72.5 \text{ GPa})(0.4)} = 0.353$$

(b) For 50 vol% fibers (V_f = 0.50), we must assume a value for K. Since it is increasing with V_f, let us estimate it to increase by the same amount as going from 0.3 to 0.4—that is, by a value of 0.03. Therefore, let us assume a value for K of 0.383. Now, from Equation 16.20

$$E_{cd} = KE_f V_f + E_m V_m$$

$$= (0.383)(72.5 \text{ GPa})(0.5) + (2.29 \text{ GPa})(0.5)$$

$$= 15.0 \text{ GPa} \quad (2.18 \text{ x } 10^6 \text{ psi})$$

The Fiber Phase

The Matrix Phase

16.19 (a) For polymer-matrix fiber-reinforced composites, three functions of the polymer-matrix phase are: (1) to bind the fibers together so that the applied stress is distributed among the fibers; (2) to protect the surface of the fibers from being damaged; and (3) to separate the fibers and inhibit crack propagation.

(b) The matrix phase must be ductile and is usually relatively soft, whereas the fiber phase must be stiff and strong.

(c) There must be a strong interfacial bond between fiber and matrix in order to: (1) maximize the stress transmittance between matrix and fiber phases; and (2) minimize fiber pull-out, and the probability of failure.

16.20 (a) The matrix phase is a continuous phase that surrounds the noncontinuous dispersed phase.

(b) In general, the matrix phase is relatively weak, has a low elastic modulus, but is quite ductile. On the other hand, the fiber phase is normally quite strong, stiff, and brittle.

Polymer-Matrix Composites

16.21 (a) This portion of the problem calls for us to calculate the specific longitudinal strengths of glass-fiber, carbon-fiber, and aramid-fiber reinforced epoxy composites, and then to compare these values with the specific strengths of several metal alloys.

The longitudinal specific strength of the glass-reinforced epoxy material ($V_f = 0.60$) in Table 16.5 is just the ratio of the longitudinal tensile strength and specific gravity as

$$\frac{1020 \text{ MPa}}{2.1} = 486 \text{ MPa}$$

For the carbon-fiber reinforced epoxy

$$\frac{1240 \text{ MPa}}{1.6} = 775 \text{ MPa}$$

And, for the aramid-fiber reinforced epoxy

$$\frac{1380 \text{ MPa}}{1.4} = 986 \text{ MPa}$$

Now, for the metal alloys we use data found in Tables B.1 and B.4 in Appendix B (using the density values from Table B.1 for the specific gravities). For the cold-rolled 7-7PH stainless steel

$$\frac{1380 \text{ MPa}}{7.65} = 180 \text{ MPa}$$

For the normalized 1040 plain carbon steel, the ratio is

$$\frac{590 \text{ MPa}}{7.85} = 75 \text{ MPa}$$

For the 7075-T6 aluminum alloy

$$\frac{572 \text{ MPa}}{2.80} = 204 \text{ MPa}$$

For the C26000 brass (cold worked)

$$\frac{525 \text{ MPa}}{8.53} = 62 \text{ MPa}$$

For the AZ31B (extruded) magnesium alloy

$$\frac{262 \text{ MPa}}{1.77} = 148 \text{ MPa}$$

For the annealed Ti-5Al-2.5Sn titanium alloy

$$\frac{790 \text{ MPa}}{4.48} = 176 \text{ MPa}$$

(b) The longitudinal specific modulus is just the longitudinal tensile modulus-specific gravity ratio. For the glass-fiber reinforced epoxy, this ratio is

$$\frac{45 \text{ GPa}}{2.1} = 21.4 \text{ GPa}$$

For the carbon-fiber reinforced epoxy

$$\frac{145 \text{ GPa}}{1.6} = 90.6 \text{ GPa}$$

And, for the aramid-fiber reinforced epoxy

$$\frac{76 \text{ GPa}}{1.4} = 54.3 \text{ GPa}$$

The specific moduli for the metal alloys (Tables B.1 and B.2) are as follows:

For the cold rolled 17-7PH stainless steel

$$\frac{204 \text{ GPa}}{7.65} = 26.7 \text{ GPa}$$

For the normalized 1040 plain-carbon steel

$$\frac{207 \text{ GPa}}{7.85} = 26.4 \text{ GPa}$$

For the 7075-T6 aluminum alloy

$$\frac{71\ \text{GPa}}{2.80} = 25.4\ \text{GPa}$$

For the cold worked C26000 brass

$$\frac{110\ \text{GPa}}{8.53} = 12.9\ \text{GPa}$$

For the extruded AZ31B magnesium alloy

$$\frac{45\ \text{GPa}}{1.77} = 25.4\ \text{GPa}$$

For the Ti-5Al-2.5Sn titanium alloy

$$\frac{110\ \text{GPa}}{4.48} = 24.6\ \text{GPa}$$

16.22 (a) The four reasons why glass fibers are most commonly used for reinforcement are listed at the beginning of Section 16.8 under "Glass Fiber-Reinforced Polymer (GFRP) Composites."

(b) The surface perfection of glass fibers is important because surface flaws or cracks act as points of stress concentration, which will dramatically reduce the tensile strength of the material.

(c) Care must be taken not to rub or abrade the surface after the fibers are drawn. As a surface protection, newly drawn fibers are coated with a protective surface film.

16.23 "Graphite" is crystalline carbon having the structure shown in Figure 12.17, whereas "carbon" will consist of some noncrystalline material as well as areas of crystal misalignment.

16.24 (a) Reasons why fiberglass-reinforced composites are utilized extensively are: (1) glass fibers are very inexpensive to produce; (2) these composites have relatively high specific strengths; and (3) they are chemically inert in a wide variety of environments.

(b) Several limitations of these composites are: (1) care must be exercised in handling the fibers inasmuch as they are susceptible to surface damage; (2) they are lacking in stiffness in comparison to other fibrous composites; and (3) they are limited as to maximum temperature use.

Hybrid Composites

16.25 (a) A hybrid composite is a composite that is reinforced with two or more different fiber materials in a single matrix.

(b) Two advantages of hybrid composites are: (1) better overall property combinations, and (2) failure is not as catastrophic as with single-fiber composites.

16.26 (a) For a hybrid composite having all fibers aligned in the same direction

$$E_{cl} = E_m V_m + E_{f1} V_{f1} + E_{f2} V_{f2}$$

in which the subscripts *f*1 and *f*2 refer to the two types of fibers.

(b) Now we are asked to compute the longitudinal elastic modulus for a glass- and aramid-fiber hybrid composite. From Table 16.4, the elastic moduli of aramid and glass fibers are, respectively, 131 GPa (19 x 10^6 psi) and 72.5 GPa (10.5 x 10^6 psi). Thus, from the previous expression

$$E_{cl} = (4\text{ GPa})(1.0 - 0.25 - 0.35) + (131\text{ GPa})(0.25) + (72.5\text{ GPa})(0.35)$$

$$= 59.7\text{ GPa} \quad (8.67 \text{ x } 10^6 \text{ psi})$$

16.27 This problem asks that we derive a generalized expression analogous to Equation 16.16 for the transverse modulus of elasticity of an aligned hybrid composite consisting of two types of continuous fibers. Let us denote the subscripts *f*1 and *f*2 for the two fiber types, and *m* , *c*, and *t* subscripts for the matrix, composite, and transverse direction, respectively. For the isostress state, the expressions analogous to Equations 16.12 and 16.13 are

$$\sigma_c = \sigma_m = \sigma_{f1} = \sigma_{f2}$$

And

$$\varepsilon_c = \varepsilon_m V_m + \varepsilon_{f1} V_{f1} + \varepsilon_{f2} V_{f2}$$

Since $\varepsilon = \sigma/E$ (Equation 6.5), making substitutions of the form of this equation into the previous expression yields

$$\frac{\sigma}{E_{ct}} = \frac{\sigma}{E_m} V_m + \frac{\sigma}{E_{f1}} V_{f1} + \frac{\sigma}{E_{f2}} V_{f2}$$

Thus

$$\frac{1}{E_{ct}} = \frac{V_m}{E_m} + \frac{V_{f1}}{E_{f1}} + \frac{V_{f2}}{E_{f2}}$$

$$= \frac{V_m E_{f1} E_{f2} + V_{f1} E_m E_{f2} + V_{f2} E_m E_{f1}}{E_m E_{f1} E_{f2}}$$

And, finally, taking the reciprocal of this equation leads to

$$E_{ct} = \frac{E_m E_{f1} E_{f2}}{V_m E_{f1} E_{f2} + V_{f1} E_m E_{f2} + V_{f2} E_m E_{f1}}$$

Processing of Fiber-Reinforced Composites

16.28 Pultrusion, filament winding, and prepreg fabrication processes are described in Section 16.13.

For pultrusion, the advantages are: the process may be automated, production rates are relatively high, a wide variety of shapes having constant cross-sections are possible, and very long pieces may be produced. The chief disadvantage is that shapes are limited to those having a constant cross-section.

For filament winding, the advantages are: the process may be automated, a variety of winding patterns are possible, and a high degree of control over winding uniformity and orientation is afforded. The chief disadvantage is that the variety of shapes is somewhat limited.

For prepreg production, the advantages are: resin does not need to be added to the prepreg, the lay-up arrangement relative to the orientation of individual plies is variable, and the lay-up process may be automated. The chief disadvantages of this technique are that final curing is necessary after fabrication, and thermoset prepregs must be stored at subambient temperatures to prevent complete curing.

Laminar Composites

Sandwich Panels

16.29 Laminar composites are a series of sheets or panels, each of which has a preferred high-strength direction. These sheets are stacked and then cemented together such that the orientation of the high-strength direction varies from layer to layer.

These composites are constructed in order to have a relatively high strength in virtually all directions within the plane of the laminate.

16.30 (a) Sandwich panels consist of two outer face sheets of a high-strength material that are separated by a layer of a less-dense and lower-strength core material.

(b) The prime reason for fabricating these composites is to produce structures having high in-plane strengths, high shear rigidities, and low densities.

(c) The faces function so as to bear the majority of in-plane tensile and compressive stresses. On the other hand, the core separates and provides continuous support for the faces, and also resists shear deformations perpendicular to the faces.

DESIGN PROBLEMS

16.D1 Inasmuch as there are a number of different sports implements that employ composite materials, no attempt will be made to provide a complete answer for this question. However, a list of this type of sporting equipment would include skis and ski poles, fishing rods, vaulting poles, golf clubs, hockey sticks, baseball and softball bats, surfboards and boats, oars and paddles, bicycle components (frames, wheels, handlebars), canoes, and tennis and racquetball rackets.

Influence of Fiber Orientation and Concentration

16.D2 In order to solve this problem, we want to make longitudinal elastic modulus and tensile strength computations assuming 40 vol% fibers for all three fiber materials, in order to see which meet the stipulated criteria [i.e., a minimum elastic modulus of 55 GPa (8 x 10^6 psi), and a minimum tensile strength of 1200 MPa (175,000 psi)]. Thus, it becomes necessary to use Equations 16.10b and 16.17 with V_m = 0.6 and V_f = 0.4, E_m = 3.1 GPa, and σ_m^* = 69 MPa.

For glass, E_f = 72.5 GPa and σ_f^* = 3450 MPa. Therefore,

$$E_{cl} = E_m(1 - V_f) + E_f V_f$$

$$= (3.1 \text{ GPa})(1 - 0.4) + (72.5 \text{ GPa})(0.4) = 30.9 \text{ GPa} \quad (4.48 \text{ x } 10^6 \text{ psi})$$

Since this is less than the specified minimum (i.e., 55 GPa), glass is not an acceptable candidate.

For carbon (PAN standard-modulus), E_f = 230 GPa and σ_f^* = 4000 MPa (the average of the range of values in Table B.4), thus, from Equation 16.10b

$$E_{cl} = (3.1 \text{ GPa})(0.6) + (230 \text{ GPa})(0.4) = 93.9 \text{ GPa} \quad (13.6 \text{ x } 10^6 \text{ psi})$$

which is greater than the specified minimum. In addition, from Equation 16.17

$$\sigma_{cl}^* = \sigma_m'(1 - V_f) + \sigma_f^* V_f$$

$$= (30 \text{ MPa})(0.6) + (4000 \text{ MPa})(0.4) = 1620 \text{ MPa} \quad (234,600 \text{ psi})$$

which is also greater than the minimum (1200 MPa). Thus, carbon (PAN standard-modulus) is a candidate.

For aramid, E_f = 131 GPa and σ_f^* = 3850 MPa (the average of the range of values in Table B.4), thus (Equation 16.10b)

$$E_{cl} = (3.1 \text{ GPa})(0.6) + (131 \text{ GPa})(0.4) = 54.3 \text{ GPa} \quad (7.87 \text{ x } 10^6 \text{ psi})$$

which value is also less than the minimum. Therefore, aramid also not a candidate, which means that only the carbon (PAN standard-modulus) fiber-reinforced epoxy composite meets the minimum criteria.

16.D3 This problem asks us to determine whether or not it is possible to produce a continuous and oriented carbon fiber-reinforced epoxy having a modulus of elasticity of at least 69 GPa in the direction of fiber alignment, and a maximum specific gravity of 1.40. We will first calculate the minimum volume fraction of fibers to give the stipulated elastic modulus, and then the maximum volume fraction of fibers possible to yield the maximum permissible specific gravity; if there is an overlap of these two fiber volume fractions then such a composite is possible.

With regard to the elastic modulus, from Equation 16.10b

$$E_{cl} = E_m(1 - V_f) + E_f V_f$$

$$69 \text{ GPa} = (2.4 \text{ GPa})(1 - V_f) + (260 \text{ GPa})(V_f)$$

Solving for V_f yields $V_f = 0.26$. Therefore, $V_f > 0.26$ to give the minimum desired elastic modulus.

Now, upon consideration of the specific gravity (or density), ρ, we employ the following modified form of Equation 16.10b

$$\rho_c = \rho_m(1 - V_f) + \rho_f V_f$$

$$1.40 = 1.25(1 - V_f) + 1.80(V_f)$$

And, solving for V_f from this expression gives $V_f = 0.27$. Therefore, it is necessary for $V_f < 0.27$ in order to have a composite specific gravity less than 1.40.

Hence, such a composite *is possible* if $0.26 < V_f < 0.27$

16.D4 This problem asks us to determine whether or not it is possible to produce a continuous and oriented glass fiber-reinforced polyester having a tensile strength of at least 1250 MPa in the longitudinal direction, and a maximum specific gravity of 1.80. We will first calculate the minimum volume fraction of fibers to give the stipulated tensile strength, and then the maximum volume fraction of fibers possible to yield the maximum permissible specific gravity; if there is an overlap of these two fiber volume fractions then such a composite is possible.

With regard to tensile strength, from Equation 16.17

$$\sigma_{cl}^* = \sigma'_m(1 - V_f) + \sigma_f^* V_f$$

$$1250 \text{ MPa} = (20 \text{ MPa})(1 - V_f) + (3500 \text{ MPa})(V_f)$$

Solving for V_f yields $V_f = 0.353$. Therefore, $V_f > 0.353$ to give the minimum desired tensile strength.

Now, upon consideration of the specific gravity (or density), ρ, we employ the following modified form of Equation 16.10b:

$$\rho_c = \rho_m(1 - V_f) + \rho_f V_f$$

$$1.80 = 1.35(1 - V_f) + 2.50(V_f)$$

And, solving for V_f from this expression gives $V_f = 0.391$. Therefore, it is necessary for $V_f < 0.391$ in order to have a composite specific gravity less than 1.80.

Hence, such a composite *is possible* if $0.353 < V_f < 0.391$.

16.D5 In this problem, for an aligned and discontinuous glass fiber-epoxy matrix composite having a longitudinal tensile strength of 1200 MPa, we are asked to compute the required fiber fracture strength, given the following: the average fiber diameter (0.015 mm), the average fiber length (5.0 mm), the volume fraction of fibers (0.35), the fiber-matrix bond strength (80 MPa), and the matrix stress at fiber failure (6.55 MPa).

To begin, since the value of σ_f^* is unknown, calculation of the value of l_c in Equation 16.3 is not possible, and, therefore, we are not able to decide which of Equations 16.18 and 16.19 to use. Thus, it is necessary to substitute for l_c in Equation 16.3 into Equation 16.18, solve for the value of σ_f^*, then, using this value, solve for l_c from Equation 16.3. If $l > l_c$, we use Equation 16.18, otherwise Equation 16.19 must be used. *Note:* the σ_f^* parameters in Equations 16.18 and 16.3 are the same. Realizing this, and substituting for l_c in Equation 16.3 into Equation 16.18 leads to

$$\sigma_{cd}^* = \sigma_f^* V_f \left[1 - \frac{\sigma_f^* d}{4\tau_c l}\right] + \sigma_m'(1 - V_f)$$

$$= \sigma_f^* V_f - \frac{\sigma_f^{*2} V_f d}{4\tau_c l} + \sigma_m' - \sigma_m' V_f$$

This expression is a quadratic equation in which σ_f^* is the unknown. Rearrangement into a more convenient form leads to

$$\sigma_f^{*2}\left[\frac{V_f d}{4\tau_c l}\right] - \sigma_f^*(V_f) + \left[\sigma_{cd}^* - \sigma_m'(1 - V_f)\right] = 0$$

Or

$$a\sigma_f^{*2} + b\sigma_f^* + c = 0$$

where

$$a = \frac{V_f d}{4\tau_c l}$$

$$= \frac{(0.35)\left(0.015 \text{ x } 10^{-3} \text{ m}\right)}{(4)(80 \text{ MPa})\left(5 \text{ x } 10^{-3} \text{ m}\right)} = 3.28 \text{ x } 10^{-6} \text{ (MPa)}^{-1} \quad \left[2.23 \text{ x } 10^{-8} \text{ (psi)}^{-1}\right]$$

Furthermore,

$$b = -V_f = -0.35$$

And

$$c = \sigma^*_{cd} - \sigma'_m\left(1 - V_f\right)$$

$$= 1200 \text{ MPa} - (6.55 \text{ MPa})(1 - 0.35) = 1195.74 \text{ MPa} \quad (174{,}383 \text{ psi})$$

Now solving the above quadratic equation for σ^*_f yields

$$\sigma^*_f = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-(-0.35) \pm \sqrt{(-0.35)^2 - (4)\left[3.28 \text{ x } 10^{-6} \text{ (MPa)}^{-1}\right](1195.74 \text{ MPa})}}{(2)\left[3.28 \text{ x } 10^{-6} \text{ (MPa)}^{-1}\right]}$$

$$= \frac{0.3500 \pm 0.3268}{6.56 \text{ x } 10^{-6}} \text{ MPa} \quad \left[\frac{0.3500 \pm 0.3270}{4.46 \text{ x } 10^{-8}} \text{ psi}\right]$$

This yields the two possible roots as

$$\sigma^*_f(+) = \frac{0.3500 + 0.3268}{6.56 \text{ x } 10^{-6}} \text{ MPa} = 103{,}200 \text{ MPa} \quad (15.2 \text{ x } 10^6 \text{ psi})$$

$$\sigma^*_f(-) = \frac{0.3500 - 0.3268}{6.56 \text{ x } 10^{-6}} \text{ MPa} = 3537 \text{ MPa} \quad (515{,}700 \text{ psi})$$

Upon consultation of the magnitudes of σ^*_f for various fibers and whiskers in Table 16.4, only $\sigma^*_f(-)$ is reasonable. Now, using this value, let us calculate the value of l_c using Equation 16.3 in order to ascertain if use of Equation 16.18 in the previous treatment was appropriate. Thus

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(3537\ \text{MPa})(0.015\ \text{mm})}{(2)(80\ \text{MPa})} = 0.33\ \text{mm}\ \ (0.0131\ \text{in.})$$

Since $l > l_c$ (5.0 mm > 0.33 mm), our choice of Equation 16.18 was indeed appropriate, and σ_f^* = 3537 MPa (515,700 psi).

16.D6 (a) This portion of the problem calls for a determination of which of the four fiber types is suitable for a tubular shaft, given that the fibers are to be continuous and oriented with a volume fraction of 0.40. Using Equation 16.10 it is possible to solve for the elastic modulus of the shaft for each of the fiber types. For example, for glass (using moduli data in Table 16.6)

$$E_{cs} = E_m(1 - V_f) + E_f V_f$$

$$= (2.4 \text{ GPa})(1.00 - 0.40) + (72.5 \text{ GPa})(0.40) = 30.4 \text{ GPa}$$

This value for E_{cs} as well as those computed in a like manner for the three carbon fibers are listed in Table 16.D1.

Table 16.D1 Composite Elastic Modulus for Each of Glass and Three Carbon Fiber Types for $V_f = 0.40$

Fiber Type	E_{cs} (GPa)
Glass	30.4
Carbon—standard modulus	93.4
Carbon—intermediate modulus	115
Carbon—high modulus	161

It now becomes necessary to determine, for each fiber type, the inside diameter d_i. Rearrangement of Equation 16.23 such that d_i is the dependent variable leads to

$$d_i = \left[d_0^4 - \frac{4FL^3}{3\pi E\Delta y}\right]^{1/4}$$

The d_i values may be computed by substitution into this expression for E the E_{cs} data in Table 16.D1 and the following

$F = 1700$ N
$L = 1.25$ m
$\Delta y = 0.20$ mm

d_0 = 100 mm

These d_i data are tabulated in the second column of Table 16.D2. No entry is included for glass. The elastic modulus for glass fibers is so low that it is not possible to use them for a tube that meets the stipulated criteria; mathematically, the term within brackets in the above equation for d_i is negative, and no real root exists. Thus, only the three carbon types are candidate fiber materials.

Table 16.D2 Inside Tube Diameter, Total Volume, and Fiber, Matrix, and Total Costs for Three Carbon-Fiber Epoxy-Matrix Composites

Fiber Type	Inside Diameter (mm)	Total Volume (cm^3)	Fiber Cost ($)	Matrix Cost ($)	Total Cost ($)
Glass	–	–	–	–	–
Carbon--standard modulus	70.4	3324	83.76	20.46	104.22
Carbon--intermediate modulus	78.9	2407	121.31	14.82	136.13
Carbon--high modulus	86.6	1584	199.58	9.75	209.33

(b) Also included in Table 16.D2 is the total volume of material required for the tubular shaft for each carbon fiber type; Equation 16.24 was utilized for these computations. Since V_f = 0.40, 40% this volume is fiber and the other 60% is epoxy matrix. In the manner of Design Example 16.1, the masses and costs of fiber and matrix materials were determined, as well as the total composite cost. These data are also included in Table 16.D2. Here it may be noted that the carbon standard-modulus fiber yields the least expensive composite, followed by the intermediate- and high-modulus materials.

CHAPTER 17

CORROSION AND DEGRADATION OF MATERIALS

PROBLEM SOLUTIONS

Electrochemical Considerations

17.1 (a) Oxidation is the process by which an atom gives up an electron (or electrons) to become a cation. Reduction is the process by which an atom acquires an extra electron (or electrons) and becomes an anion.

(b) Oxidation occurs at the anode; reduction at the cathode.

17.2 (a) This problem asks that we write possible oxidation and reduction half-reactions for magnesium in various solutions.

(i) In HCl, possible reactions are

$$Mg \rightarrow Mg^{2+} + 2e^- \quad \text{(oxidation)}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(reduction)}$$

(ii) In an HCl solution containing dissolved oxygen, possible reactions are

$$Mg \rightarrow Mg^{2+} + 2e^- \quad \text{(oxidation)}$$

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad \text{(reduction)}$$

(iii) In an HCl solution containing dissolved oxygen and Fe^{2+} ions, possible reactions are

$$Mg \rightarrow Mg^{2+} + 2e^- \quad \text{(oxidation)}$$

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad \text{(reduction)}$$

$$Fe^{2+} + 2e^- \rightarrow Fe \quad \text{(reduction)}$$

(b) The magnesium would probably oxidize most rapidly in the HCl solution containing dissolved oxygen and Fe^{2+} ions because there are two reduction reactions that will consume electrons from the oxidation of magnesium.

17.3 (a) The Faraday constant (represented here as "*F*") is just the product of the charge per electron and Avogadro's number; that is

$$F = eN_A = \left(1.602 \text{ x } 10^{-19} \text{ C/electron}\right)\left(6.023 \text{ x } 10^{23} \text{ electrons/mol}\right)$$

$$= 96{,}488 \text{ C/mol}$$

(b) At 25°C (298 K),

$$\frac{RT}{nF}\ln(x) = \frac{(8.31 \text{ J/mol - K})(298 \text{ K})}{(n)(96{,}500 \text{ C/mol})}(2.303) \log(x)$$

$$= \frac{0.0592}{n} \log(x)$$

This gives units in volts since a volt is a J/C.

17.4 (a) We are asked to compute the voltage of a nonstandard Pb-Sn electrochemical cell. Since tin is lower in the standard emf series (Table 17.1), we will begin by assuming that tin is oxidized and lead is reduced, as

$$\mathrm{Sn} + \mathrm{Pb}^{2+} \rightarrow \mathrm{Sn}^{2+} + \mathrm{Pb}$$

and Equation 17.20 takes the form

$$\Delta V = (V^{\circ}_{\mathrm{Pb}} - V^{\circ}_{\mathrm{Sn}}) - \frac{0.0592}{2} \log \frac{[\mathrm{Sn}^{2+}]}{[\mathrm{Pb}^{2+}]}$$

$$= \left[-0.126 \text{ V} - (-0.136 \text{ V})\right] - \frac{0.0592}{2} \log \left[\frac{0.25}{5 \times 10^{-2}}\right]$$

$$= -0.011 \text{ V}$$

since, from Table 17.1, the standard potentials for Pb and Sn are –0.126 and –0.136, respectively.

(b) Since the ΔV is negative, the spontaneous cell direction is just the reverse of that above, or

$$\mathrm{Sn}^{2+} + \mathrm{Pb} \rightarrow \mathrm{Sn} + \mathrm{Pb}^{2+}$$

17.5 This problem calls for us to determine whether or not a voltage is generated in a Fe/Fe^{2+} concentration cell, and, if so, its magnitude. Let us label the Fe cell having a 0.5 *M* Fe^{2+} solution as cell 1, and the other as cell 2. Furthermore, assume that oxidation occurs within cell 2, wherein $[\mathrm{Fe}_2^{2+}]$ = 2 x 10^{-2} *M*. Hence,

$$\mathrm{Fe}_2 \ + \ \mathrm{Fe}_1^{2+} \rightarrow \mathrm{Fe}_2^{2+} \ + \ \mathrm{Fe}_1$$

and, employing Equation 17.20 leads to

$$\Delta V \ = \ - \ \frac{0.0592}{2} \log \frac{\left[\mathrm{Fe}_2^{2+}\right]}{\left[\mathrm{Fe}_1^{2+}\right]}$$

$$= \ - \ \frac{0.0592}{2} \log \left[\frac{2 \text{ x } 10^{-2}\ M}{0.5\,M}\right] \ = +\,0.0414 \text{ V}$$

Therefore, a voltage of 0.0414 V is generated when oxidation occurs in the cell 2, the one having a Fe^{2+} concentration of 2 x 10^{-2} *M*.

17.6 We are asked to calculate the concentration of Cu^{2+} ions in a copper-cadmium electrochemical cell. The electrochemical reaction that occurs within this cell is just

$$\mathrm{Cd} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Cd}^{2+} + \mathrm{Cu}$$

while ΔV = 0.775 V and $[\mathrm{Cd}^{2+}] = 6.5 \times 10^{-2}$ *M*. Thus, Equation 17.20 is written in the form

$$\Delta V = \left(V_{\mathrm{Cu}}^{\circ} - V_{\mathrm{Cd}}^{\circ}\right) - \frac{0.0592}{2} \log \frac{[\mathrm{Cd}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

This equation may be rewritten as

$$-\frac{\Delta V - \left(V_{\mathrm{Cu}}^{\circ} - V_{\mathrm{Cd}}^{\circ}\right)}{0.0296} = \log \frac{[\mathrm{Cd}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

Solving this expression for $[\mathrm{Cu}^{2+}]$ gives

$$[\mathrm{Cu}^{2+}] = [\mathrm{Cd}^{2+}] \exp + \left[(2.303) \frac{\Delta V - \left(V_{\mathrm{Cu}}^{\circ} - V_{\mathrm{Pb}}^{\circ}\right)}{0.0296}\right]$$

The standard potentials from Table 17.1 are V_{Cu}° = +0.340 V and V_{Cd}° = – 0.403 V. Therefore,

$$[\mathrm{Cu}^{2+}] = (6.5 \times 10^{-2}\ M) \exp + \left[(2.303)\ \frac{0.775\ \mathrm{V} - \{0.340\ \mathrm{V} - (-0.403\ \mathrm{V})\}}{0.0296}\right]$$

$$= 0.784\ M$$

17.7 This problem asks for us to calculate the temperature for a zinc-lead electrochemical cell when the potential between the Zn and Pb electrodes is +0.568 V. On the basis of their relative positions in the standard emf series (Table 17.1), assume that Zn is oxidized and Pb is reduced. Thus, the electrochemical reaction that occurs within this cell is just

$$\mathrm{Pb}^{2+} + \mathrm{Zn} \rightarrow \mathrm{Pb} + \mathrm{Zn}^{2+}$$

Thus, Equation 17.20 is written in the form

$$\Delta V = \left(V^{\circ}_{\mathrm{Pb}} - V^{\circ}_{\mathrm{Zn}}\right) - \frac{RT}{nF}\ln\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Pb}^{2+}]}$$

Solving this expression for *T* gives

$$T = -\frac{nF}{R}\left[\frac{\Delta V - \left(V^{\circ}_{\mathrm{Pb}} - V^{\circ}_{\mathrm{Zn}}\right)}{\ln\dfrac{[\mathrm{Zn}^{2+}]}{[\mathrm{Pb}^{2+}]}}\right]$$

The standard potentials from Table 17.1 are $V^{\circ}_{\mathrm{Zn}} = -\,0.763$ V and $V^{\circ}_{\mathrm{Pb}} = -\,0.126$ V. Therefore,

$$T = -\frac{(2)(96{,}500\ \mathrm{C/mol})}{8.31\ \mathrm{J/mol\text{-}K}}\left[\frac{0.568\ \mathrm{V} - \left\{-0.126\ \mathrm{V} - (-0.763\ \mathrm{V})\right\}}{\ln\left(\dfrac{10^{-2}\ M}{10^{-4}\ M}\right)}\right]$$

$$= 348\ \mathrm{K} = 75^{\circ}\mathrm{C}$$

17.8 This problem asks, for several pairs of alloys that are immersed in seawater, to predict whether or not corrosion is possible, and if it is possible, to note which alloy will corrode. In order to make these predictions it is necessary to use the galvanic series, Table 17.2. If both of the alloys in the pair reside within the same set of brackets in this table, then galvanic corrosion is unlikely. However, if the two alloys do not lie within the same set of brackets, then that alloy appearing lower in the table will experience corrosion.

(a) For the aluminum-cast iron couple, corrosion is possible, and aluminum will corrode.

(b) For the Inconel-nickel couple, corrosion is unlikely inasmuch as both alloys appear within the same set of brackets (in both active and passive states).

(c) For the cadmium-zinc couple, corrosion is possible, and zinc will corrode.

(d) For the brass-titanium pair, corrosion is possible, and brass will corrode.

(e) For the low-carbon steel-copper couple, corrosion is possible, and the low-carbon steel will corrode.

17.9 (a) The following metals and alloys may be used to galvanically protect cast iron: aluminum/aluminum alloys, cadmium, zinc, magnesium/magnesium alloys. These metals/alloys appear below cast iron in the galvanic series. Table 17.2.

(b) The following metals/alloys could be used to protect a nickel-steel galvanic couple: aluminum/aluminum alloys, cadmium, zinc, magnesium/magnesium alloys; all these metal/alloys are anodic to steel in the galvanic series.

Corrosion Rates

17.10 This problem is just an exercise in unit conversions. The parameter K in Equation 17.23 must convert the units of W, ρ, A, and t, into the unit scheme for the CPR.

For CPR in mpy (mil/yr)

$$K = \frac{W(\mathrm{mg})(1\ \mathrm{g}/1000\ \mathrm{mg})}{\rho\left(\dfrac{\mathrm{g}}{\mathrm{cm}^3}\right)\left(\dfrac{2.54\ \mathrm{cm}}{\mathrm{in.}}\right)^3\left[A(\mathrm{in.}^2)\right]\left(\dfrac{1\ \mathrm{in.}}{1000\ \mathrm{mil}}\right)[t(\mathrm{h})]\left(\dfrac{1\ \mathrm{day}}{24\ \mathrm{h}}\right)\left(\dfrac{1\ \mathrm{yr}}{365\ \mathrm{days}}\right)}$$

$$= 534.6$$

For CPR in mm/yr

$$K = \frac{W(\mathrm{mg})(1\ \mathrm{g}/1000\ \mathrm{mg})}{\rho\left(\dfrac{\mathrm{g}}{\mathrm{cm}^3}\right)\left(\dfrac{1\ \mathrm{cm}}{10\ \mathrm{mm}}\right)^3\left[A(\mathrm{cm}^2)\right]\left(\dfrac{10\ \mathrm{mm}}{\mathrm{cm}}\right)^2[t(\mathrm{h})]\left(\dfrac{1\ \mathrm{day}}{24\ \mathrm{h}}\right)\left(\dfrac{1\ \mathrm{yr}}{365\ \mathrm{days}}\right)}$$

$$= 87.6$$

17.11 This problem calls for us to compute the time of submersion of a metal plate. In order to solve this problem, we must first rearrange Equation 17.23, as

$$t = \frac{KW}{\rho A\,(\mathrm{CPR})}$$

Thus, using values for the various parameters given in the problem statement

$$t = \frac{(87.6)\left(7.6 \text{ x } 10^{6} \text{ mg}\right)}{\left(4.5 \text{ g/cm}^{3}\right)\left(800 \text{ in.}^{2}\right)(4 \text{ mm/yr})}$$

$$= 4.62 \text{ x } 10^{4} \text{ h} = 5.27 \text{ yr}$$

17.12 This problem asks for us to calculate the CPR in both mpy and mm/yr for a thick steel sheet of area 100 in.^{2} which experiences a weight loss of 485 g after one year. Employment of Equation 17.23 leads to

$$\mathrm{CPR(mm/yr)} = \frac{KW}{\rho A t}$$

$$= \frac{(87.6)(485\ \mathrm{g})(10^3\ \mathrm{mg/g})}{(7.9\ \mathrm{g/cm^3})(100\ \mathrm{in.^2})(2.54\ \mathrm{cm/in.})^2(24\ \mathrm{h/day})(365\ \mathrm{day/yr})(1\ \mathrm{yr})}$$

$$= 0.952\ \mathrm{mm/yr}$$

Also

$$\mathrm{CPR(mpy)} = \frac{(534)(485\ \mathrm{g})(10^3\ \mathrm{mg/g})}{(7.9\ \mathrm{g/cm^3})(100\ \mathrm{in.^2})(24\ \mathrm{h/day})(365\ \mathrm{day/yr})(1\ \mathrm{yr})}$$

$$= 37.4\ \mathrm{mpy}$$

17.13 (a) We are to demonstrate that the CPR is related to the corrosion current density, *i*, in A/cm^2 through the expression

$$\text{CPR} = \frac{KAi}{n\rho}$$

in which *K* is a constant, *A* is the atomic weight, *n* is the number of electrons ionized per metal atom, and ρ is the density of the metal. Possibly the best way to make this demonstration is by using a unit dimensional analysis. The corrosion rate, *r*, in Equation 17.24 has the units (SI)

$$r = \frac{i}{nF} = \frac{\text{C/m}^2\text{-s}}{(\text{unitless})(\text{C/mol})} = \frac{\text{mol}}{\text{m}^2\text{-s}}$$

The units of CPR in Equation 17.23 are length/time, or in the SI scheme, m/s. In order to convert the above expression to the units of m/s it is necessary to multiply *r* by the atomic weight *A* and divide by the density ρ as

$$\frac{rA}{\rho} = \frac{(\text{mol/m}^2\text{-s})(\text{g/mol})}{\text{g/m}^3} = \text{m/s}$$

Thus, the CPR is proportional to *r*, and substituting for *r* from Equation 17.24 into the above expression leads to

$$\text{CPR} = K''r = \frac{K'Ai}{nF\rho}$$

in which *K'* and *K"* are constants which will give the appropriate units for CPR. Also, since *F* (i.e., Faraday’s constant) is also a constant, this expression will take the form

$$\text{CPR} = \frac{KAi}{n\rho}$$

in which *K* = *K'*/*F*.

(b) Now we will calculate the value of *K* in order to give the CPR in mpy for *i* in μA/cm^2 (10^{-6} A/cm^2). It should be noted that the units of A (in μA/cm^2) are amperes or C/s. Substitution of the units normally used into the former CPR expression above leads to

$$\text{CPR} = K'\frac{Ai}{nF\rho}$$

$$= K' \ \frac{(\mathrm{g/mol})(\mathrm{C/s\text{-}cm^2})}{(\mathrm{unitless})(\mathrm{C/mol})(\mathrm{g/cm^3})} = \ \mathrm{cm/s}$$

Since we want the CPR in mpy and i is given in μA/cm^2, and realizing that $K = K'/F$ leads to

$$K \ = \ \left(\frac{1}{96{,}500 \ \ \mathrm{C/mol}}\right)\left(\frac{10^{-6} \ \mathrm{C}}{\mu\mathrm{C}}\right)\left(\frac{1 \ \ \mathrm{in.}}{2.54 \ \ \mathrm{cm}}\right)\left(\frac{10^{3} \ \mathrm{mil}}{\mathrm{in.}}\right)\left(\frac{3.1536 \ \ \mathrm{x} \ 10^{7} \ \ \mathrm{s}}{\mathrm{yr}}\right)$$

$$= 0.129$$

17.14 We are asked to compute the CPR in mpy for the corrosion of Fe for a corrosion current density of 8 x 10^{-5} A/cm^2 (80 μA/cm^2). From Problem 17.13, the value of *K* in Equation 17.38 is 0.129, and therefore

$$\text{CPR} = \frac{KAi}{n\rho}$$

$$= \frac{(0.129)(55.85\ \text{g/mol})(80\ \mu\text{A/cm}^2)}{(2)(7.9\ \text{g/cm}^3)} = 36.5\ \text{mpy}$$

Prediction of Corrosion Rates

17.15 (a) Activation polarization is the condition wherein a reaction rate is controlled by one step in a series of steps that takes place at the slowest rate. For corrosion, activation polarization is possible for both oxidation and reduction reactions. Concentration polarization occurs when a reaction rate is limited by diffusion in a solution. For corrosion, concentration polarization is possible only for reduction reactions.

(b) Activation polarization is rate controlling when the reaction rate is low and/or the concentration of active species in the liquid solution is high.

(c) Concentration polarization is rate controlling when the reaction rate is high and/or the concentration of active species in the liquid solution is low.

17.16 (a) The phenomenon of dynamic equilibrium is the state wherein oxidation and reduction reactions are occurring at the same rate such that there is no net observable reaction.

(b) The exchange current density is just the current density which is related to both the rates of oxidation and reduction (which are equal) according to Equation 17.26 for the dynamic equilibrium state.

17.17 (a) This portion of the problem asks that we compute the rate of oxidation for Ni given that both the oxidation and reduction reactions are controlled by activation polarization, and also given the polarization data for both nickel oxidation and hydrogen reduction. The first thing necessary is to establish relationships of the form of Equation 17.25 for the potentials of both oxidation and reduction reactions. Next we will set these expressions equal to one another, and then solve for the value of *i* which is really the corrosion current density, i_c. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows:

For hydrogen reduction

$$V_H = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{0_H}}\right)$$

And for Ni oxidation

$$V_{Ni} = V_{(Ni/Ni^{2+})} + \beta_{Ni} \log\left(\frac{i}{i_{0_{Ni}}}\right)$$

Setting $V_H = V_{\mathbf{Ni}}$ and solving for log *i* (log i_c) leads to

$$\log i_c = \left(\frac{1}{\beta_{Ni} - \beta_H}\right)\left[V_{(H^+/H_2)} - V_{(Ni/Ni^{2+})} - \beta_H \log i_{0_H} + \beta_{Ni} \log i_{0_{Ni}}\right]$$

And, incorporating values for the various parameters provided in the problem statement leads to

$$\log i_c = \left[\frac{1}{0.12 - (-0.10)}\right]\Big[0 - (-0.25) - (-0.10)\left\{\log(6 \text{ x } 10^{-7})\right\} + (0.12)\left\{\log(10^{-8})\right\}\Big]$$

$$= -6.055$$

Or

$$i_c = 10^{-6.055} = 8.81 \text{ x } 10^{-7} \text{ A/cm}^2$$

And from Equation 17.24

$$r = \frac{i_c}{nF}$$

$$= \frac{8.81 \ \text{x} \ 10^{-7} \ \text{C/s-cm}^2}{(2)(96{,}500 \ \text{C/mol})} = 4.56 \ \text{x} \ 10^{-12} \ \text{mol/cm}^2\text{-s}$$

(b) Now it becomes necessary to compute the value of the corrosion potential, V_c. This is possible by using either of the above equations for V_H or V_{Ni} and substituting for i the value determined above for i_c. Thus

$$V_c = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i_c}{i_{0_H}}\right)$$

$$= 0 + (-0.10 \ \text{V}) \log\left(\frac{8.81 \ \text{x} \ 10^{-7} \ \text{A/cm}^2}{6 \ \text{x} \ 10^{-7} \ \text{A/cm}^2}\right) = -0.0167 \ \text{V}$$

17.18 (a) This portion of the problem asks that we compute the rate of oxidation for a divalent metal M given that both the oxidation and reduction reactions are controlled by activation polarization, and also given the polarization data for both M oxidation and hydrogen reduction. The first thing necessary is to establish relationships of the form of Equation 17.25 for the potentials of both oxidation and reduction reactions. Next we will set these expressions equal to one another, and then solve for the value of *i* which is really the corrosion current density, i_c. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows:

For hydrogen reduction

$$V_{\mathrm{H}} = V_{(\mathrm{H}^+/\mathrm{H}_2)} + \beta_{\mathrm{H}} \log\left(\frac{i}{i_{0_{\mathrm{H}}}}\right)$$

And for M oxidation

$$V_{\mathrm{M}} = V_{(\mathrm{M}/\mathrm{M}^{2+})} + \beta_{\mathrm{M}} \log\left(\frac{i}{i_{0_{\mathrm{M}}}}\right)$$

Setting $V_{\mathrm{H}} = V_{\mathrm{M}}$ and solving for log *i* (log i_c) leads to

$$\log i_c = \left(\frac{1}{\beta_{\mathrm{M}} - \beta_{\mathrm{H}}}\right)\left[V_{(\mathrm{H}^+/\mathrm{H}_2)} - V_{(\mathrm{M}/\mathrm{M}^{2+})} - \beta_{\mathrm{H}} \log i_{0_{\mathrm{H}}} + \beta_{\mathrm{M}} \log i_{0_{\mathrm{M}}}\right]$$

And, incorporating values for the various parameters provided in the problem statement leads to

$$\log i_c = \left[\frac{1}{0.10 - (-0.15)}\right]\left[0 - (-0.90) - (-0.15)\left\{\log\left(10^{-10}\right)\right\} + (0.10)\left\{\log\left(10^{-12}\right)\right\}\right]$$

$$= -7.20$$

Or

$$i_c = 10^{-7.20} = 6.31 \times 10^{-8} \text{ A/cm}^2$$

And from Equation 17.24

$$r = \frac{i_c}{nF}$$

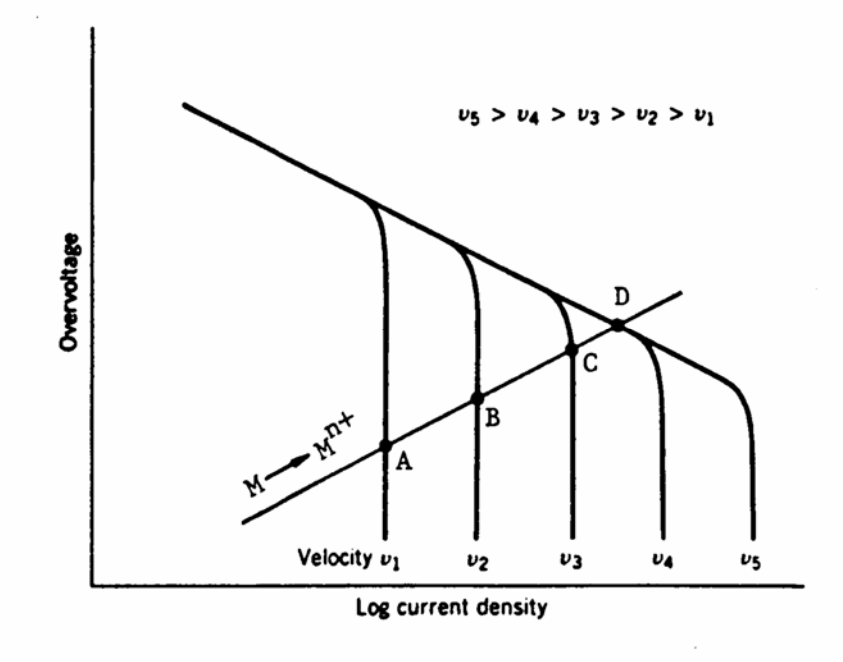
$$= \frac{6.31 \text{ x } 10^{-8} \text{ C/s-cm}^2}{(2)(96{,}500 \text{ C/mol})} = 3.27 \text{ x } 10^{-13} \text{ mol/cm}^2\text{ - s}$$

(b) Now it becomes necessary to compute the value of the corrosion potential, V_c. This is possible by using either of the above equations for V_H or V_M and substituting for i the value determined above for i_c. Thus

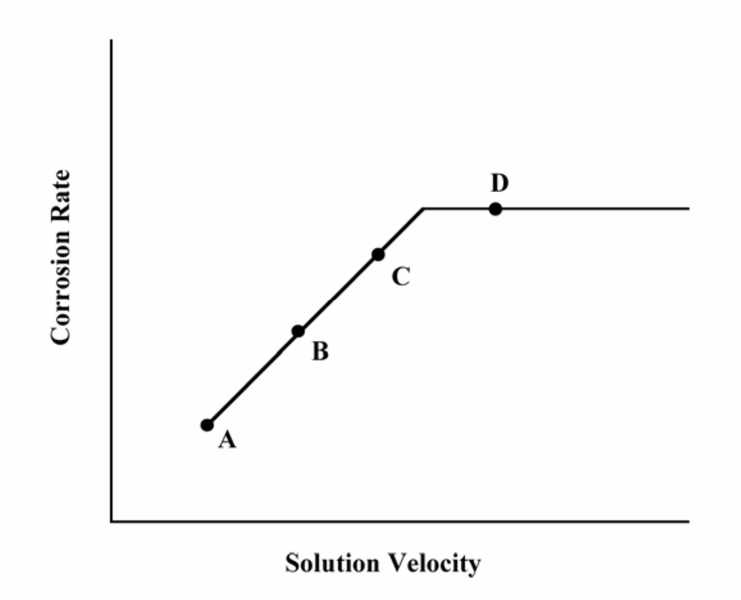
$$V_c = \text{V}_{(\text{H}^+/\text{H}_2)} + \beta_\text{H} \log \left(\frac{i_c}{i_{0_\text{H}}}\right)$$

$$= 0 + (-0.15 \text{ V}) \log \left(\frac{6.31 \text{ x } 10^{-8} \text{ A/cm}^2}{10^{-10} \text{ A/cm}^2}\right) = -0.420 \text{ V}$$

17.19 This problem asks that we make a schematic plot of corrosion rate versus solution velocity. The reduction reaction is controlled by combined activation-concentration polarization for which the overvoltage versus logarithm current density is shown in Figure 17.26. The oxidation of the metal is controlled by activation polarization, such that the electrode kinetic behavior for the combined reactions would appear schematically as shown below.



Thus, the plot of corrosion rate versus solution velocity would be as



The corrosion rate initially increases with increasing solution velocity (for velocities v_1, v_2, and v_3), corresponding to intersections in the concentration polarization regions for the reduction reaction. However, for the higher solution velocities (v_4 and v_5), the metal oxidation line intersects the reduction reaction curve in the linear activation polarization region, and, thus, the reaction becomes independent of solution velocity.

Passivity

17.20 Passivity is the loss of chemical reactivity, under particular environmental conditions, of normally active metals and alloys. Stainless steels and aluminum alloys often passivate.

17.21 The chromium in stainless steels causes a very thin and highly adherent surface coating to form over the surface of the alloy, which protects it from further corrosion. For plain carbon steels, rust, instead of this adherent coating, forms.

Forms of Corrosion

17.22 For each of the forms of corrosion, the conditions under which it occurs, and measures that may be taken to prevent or control it are outlined in Section 17.7.

17.23 Cold-worked metals are more susceptible to corrosion than noncold-worked metals because of the increased dislocation density for the latter. The region in the vicinity of a dislocation that intersects the surface is at a higher energy state, and, therefore, is more readily attacked by a corrosive solution.

17.24 For a small anode-to-cathode area ratio, the corrosion rate will be higher than for a large ratio. The reason for this is that for some given current flow associated with the corrosion reaction, for a small area ratio the current density at the anode will be greater than for a large ratio. The corrosion rate is proportional to the current density (i) according to Equation 17.24.

17.25 For a concentration cell, corrosion occurs at that region having the lower concentration. In order to explain this phenomenon let us consider an electrochemical cell consisting of two divalent metal M electrodes each of which is immersed in a solution containing a different concentration of its M^{2+} ion; let us designate the low and high concentrations of M^{2+} as $[M_L^{2+}]$ and $[M_H^{2+}]$, respectively. Now assuming that reduction and oxidation reactions occur in the high- and low-concentration solutions, respectively, let us determine the cell potential in terms of the two $[M^{2+}]$'s; if this potential is positive then we have chosen the solutions in which the reduction and oxidation reactions appropriately.

Thus, the two half-reactions in the form of Equations 17.16 are

$$M_H^{2+} + 2e^- \rightarrow M \qquad V_M^\circ$$

$$M \rightarrow M_L^{2+} + 2e^- \qquad -V_M^\circ$$

Whereas the overall cell reaction is

$$M_H^{2+} + M \rightarrow M + M_L^{2+}$$

From Equation 17.19, this yields a cell potential of

$$\Delta V = V_M^\circ - V_M^\circ - \frac{RT}{nF}\ln\left(\frac{[M_L^{2+}]}{[M_H^{2+}]}\right)$$

$$= -\frac{RT}{nF}\ln\left(\frac{[M_L^{2+}]}{[M_H^{2+}]}\right)$$

Inasmuch as $[M_L^{2+}] < [M_H^{2+}]$ then the natural logarithm of the $[M^{2+}]$ ratio is negative, which yields a positive value for ΔV. This means that the electrochemical reaction is spontaneous as written, or that oxidation occurs at the electrode having the lower M^{2+} concentration.

Corrosion Prevention

17.26 (a) Inhibitors are substances that, when added to a corrosive environment in relatively low concentrations, decrease the environment's corrosiveness.

(b) Possible mechanisms that account for the effectiveness of inhibitors are: (1) elimination of a chemically active species in the solution; (2) attachment of inhibitor molecules to the corroding surface so as to interfere with either the oxidation or reduction reaction; and (3) the formation of a very thin and protective coating on the corroding surface.

17.27 Descriptions of the two techniques used for galvanic protection are as follows:

(1) A sacrificial anode is electrically coupled to the metal piece to be protected, which anode is also situated in the corrosion environment. The sacrificial anode is a metal or alloy that is chemically more reactive in the particular environment. It (the anode) preferentially oxidizes, and, upon giving up electrons to the other metal, protects it from electrochemical corrosion.

(2) An impressed current from an external dc power source provides excess electrons to the metallic structure to be protected.

Oxidation

17.28 With this problem we are given, for three metals, their densities, oxide chemical formulas, and oxide densities, and are asked to compute the Pilling-Bedworth ratios, and then to specify whether or not the oxide scales that form will be protective. The general form of the equation used to calculate this ratio is Equation 17.32 (or Equation 17.33). For magnesium, oxidation occurs by the reaction

$$\mathrm{Mg} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{MgO}$$

and therefore, from Equation 17.32

$$\mathrm{P-B\ ratio} = \frac{A_{\mathrm{MgO}}\,\rho_{\mathrm{Mg}}}{A_{\mathrm{Mg}}\,\rho_{\mathrm{MgO}}}$$

$$= \frac{(40.31\ \mathrm{g/mol})(1.74\ \mathrm{g/cm^3})}{(24.31\ \mathrm{g/mol})(3.58\ \mathrm{g/cm^3})} = 0.81$$

Thus, this would probably be a nonprotective oxide film since the P-B ratio is less than unity; to be protective, this ratio should be between one and two.

The oxidation reaction for V is just

$$2\mathrm{V} + \frac{5}{2}\mathrm{O_2} \rightarrow \mathrm{V_2O_5}$$

and the P-B ratio is (Equation 17.33)

$$\mathrm{P-B\ ratio} = \frac{A_{\mathrm{V_2O_5}}\,\rho_{\mathrm{V}}}{(2)A_{\mathrm{V}}\,\rho_{\mathrm{V_2O_5}}}$$

$$= \frac{(181.88\ \mathrm{g/mol})(6.11\ \mathrm{g/cm^3})}{(2)(50.94\ \mathrm{g/mol})(3.36\ \mathrm{g/cm^3})} = 3.25$$

Hence, the film would be nonprotective since the ratio does not lie between one and two.

Now for Zn, the reaction for its oxidation is analogous to that for Mg above. Therefore,

$$\text{P} - \text{B ratio} \;=\; \frac{A_{\text{ZnO}}\,\rho_{\text{Zn}}}{A_{\text{Zn}}\,\rho_{\text{ZnO}}}$$

$$= \;\frac{(81.39\ \ \text{g/mol})(7.13\ \ \text{g/cm}^3)}{(65.39\ \ \text{g/mol})(5.61\ \ \text{g/cm}^3)} \;=\; 1.58$$

Thus, the ZnO film would probably be protective since the ratio is between one and two.

17.29 Silver does not oxidize appreciably at room temperature and in air even though, according to Table 17.3, the oxide coating should be nonprotective. The reason for this is that the oxidation of silver in air is not thermodynamically favorable; therefore, the lack of a reaction is independent of whether or not a protective scale forms.

17.30 For this problem we are given weight gain-time data for the oxidation of Ni at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a parabolic, linear, or logarithmic rate expression, which expressions are represented by Equations 17.34, 17.35, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the parabolic relationship is valid; that is from Equation 17.34

$$W^2 = K_1 t + K_2$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then using two combinations of two pairs of equations, solve for K_1 and K_2; if K_1 and K_2 have the same values for both solutions, then the kinetics are parabolic. If the values are not identical then the other kinetic relationships need to be explored. Thus, the three equations are

$$\begin{aligned}(0.527)^2 &= 0.278 = 10K_1 + K_2\\(0.857)^2 &= 0.734 = 30K_1 + K_2\\(1.526)^2 &= 2.329 = 100K_1 + K_2\end{aligned}$$

From the first two equations $K_1 = 0.0228$ and $K_2 = 0.050$; these same two values are obtained using the last two equations. Hence, the oxidation rate law is parabolic.

(b) Since a parabolic relationship is valid, this portion of the problem calls for us to determine W after a total time of 600 min. Again, using Equation 17.34 and the values of K_1 and K_2

$$W^2 = K_1 t + K_2$$

$$= (0.0228)(600 \text{ min}) + 0.05 = 13.37$$

Or $W = \sqrt{13.73} = 3.70 \text{ mg/cm}^2$.

17.31 For this problem we are given weight gain-time data for the oxidation of some metal at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression, which expressions are described by Equations 17.35, 17.34, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the rate expression is parabolic, that is from Equation 17.34

$$W^2 = K_1 t + K_2$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then using two combinations of two pairs of equations, solve for K_1 and K_2; if K_1 and K_2 have the same values for both solutions, then the rate law is parabolic. If the values are not the same then the other kinetic relationships need to be explored. Thus, the three equations are

$$(6.16)^2 = 37.95 = 100K_1 + K_2$$

$$(8.59)^2 = 73.79 = 250K_1 + K_2$$

$$(12.72)^2 = 161.8 = 1000K_1 + K_2$$

From the first two equations $K_1 = 0.238$ and $K_2 = 14.2$; while from the second and third equations $K_1 = 0.117$ and $K_2 = 44.5$. Thus, a parabolic rate expression is not obeyed by this reaction.

Let us now investigate linear kinetics in the same manner, using Equation 17.35, $W = K_3 t$. The three equations are thus

$$6.16 = 100K_3$$

$$8.59 = 250K_3$$

$$12.72 = 1000K_3$$

And the three K_3 values may be computed (one for each equation) which are 6.16×10^{-2}, 3.44×10^{-2}, and 1.272×10^{-2}. Since these K_3 values are all different, a linear rate law is not a possibility, and, by process of elimination, a logarithmic expression is obeyed.

(b) In order to determine the value of W after 5000 min, it is first necessary that we solve for the K_4, K_5, and K_6 constants of Equation 17.36. One way this may be accomplished is to use an equation solver In some instances it is desirable to express Equation 17.36 in exponential form, as

$$K_5 + K_6 = 10^{W/K_4}$$

For some solvers, using the above expression, the following instructions can be used:

```
K5 *t1 + K6 = 10^(W1/K4)
K5 *t2 + K6 = 10^(W2/K4)
K5 *t3 + K6 = 10^(W3/K4)

t1 = 100;        W1 = 6.16
t2 = 250;        W2 = 8.59
t3 = 1000;       W3 = 12.72
```

The resulting solutions—i.e., values for the *K* parameters—are

$K_4 = 7.305$
$K_5 = 0.0535$
$K_6 = 1.622$

Now solving Equation 17.36 for *W* at a time of 5000 min

$$W = K_4 \log \left(K_5 t + K_6\right)$$

$$= 7.305 \log \left[(0.0535)(5000 \text{ min}) + 1.622\right]$$

$$= 17.75 \text{ mg/cm}^2$$

17.32 For this problem we are given weight gain-time data for the oxidation of some metal at an elevated temperature.

(a) We are first asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression, which expressions are described by Equations 17.35, 17.34, and 17.36, respectively. One way to make this determination is by trial and error. Let us assume that the rate expression is linear, that is from Equation 17.35

$$W = K_3 t$$

which means that we may establish three simultaneous equations using the three sets of given W and t values, then solve for K_3 for each; if K_3 is the same for all three cases, then the rate law is linear. If the values are not the same then the other kinetic relationships need to be explored. Thus, the three equations are

$$1.54 = 10K_3$$

$$23.24 = 150K_3$$

$$95.37 = 620K_3$$

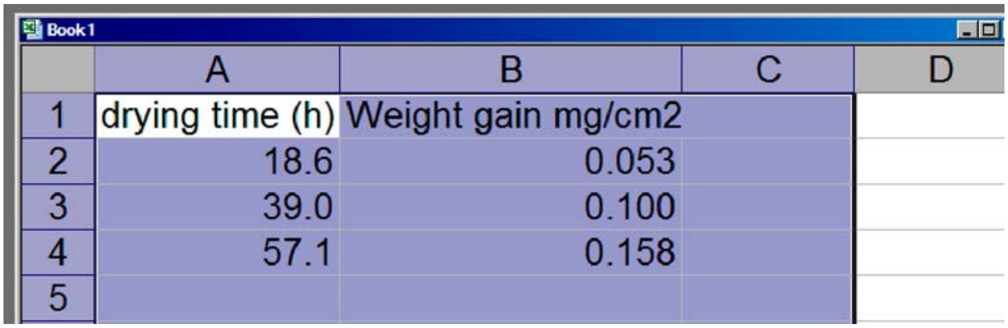
In all three instances the value of K_3 is about equal to 0.154, which means the oxidation rate obeys a linear expression.

(b) Now we are to calculate W after a time of 1200 min; thus

$$W = K_3 t = (0.154)(1200 \text{ min}) = 184.80 \text{ mg/cm}^2$$

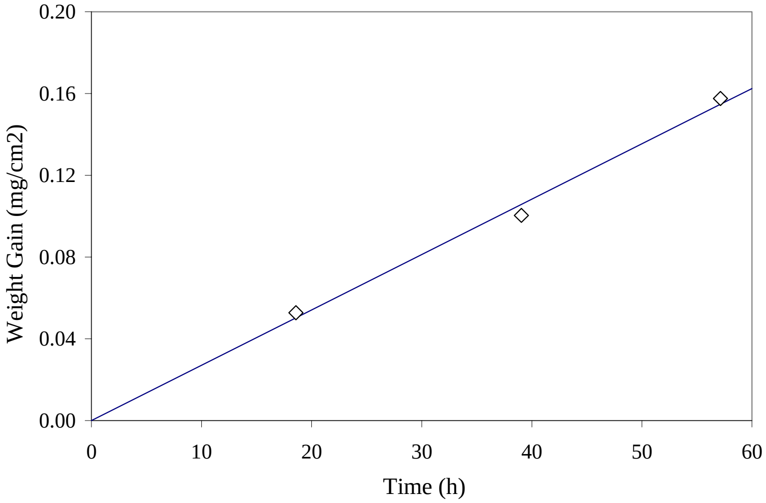
Bond Rupture

17.33 One way to solve this problem is to use the Excel spreadsheet software. We can begin by plotting the data provided in the problem statement. This will at least tell us whether or not the oxidation kinetics are linear. The data may be entered in the spreadsheet as follows:



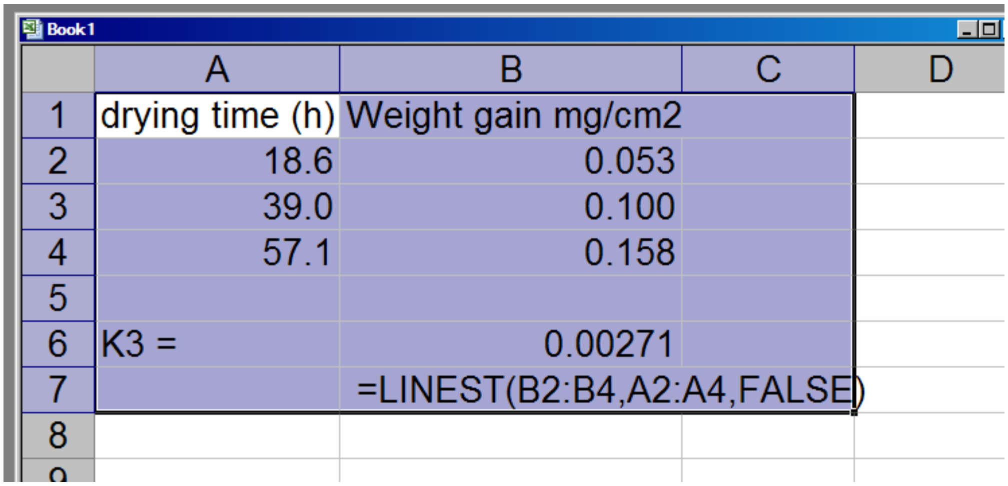
	A	B	C	D
1	drying time (h)	Weight gain mg/cm2		
2	18.6	0.053		
3	39.0	0.100		
4	57.1	0.158		
5				

And, when these data is plotted, the following graph results:



From this plot it is obvious that the oxidation kinetics do indeed obey a linear relationship.

It next becomes necessary to solve for the constant K_3 of Equation 17.35. This is possible using the function LINEST(*known_y's*,*known_x's*,*const*) in Excel. Additional entries are made in the worksheet as follows:



	A	B	C
1	drying time (h)	Weight gain mg/cm2	
2	18.6	0.053	
3	39.0	0.100	
4	57.1	0.158	
5			
6	K3 =	0.00271	
7		=LINEST(B2:B4,A2:A4,FALSE)	
8			

Here values for *known_y's* are in cells B2, B3, and B4 which is abbreviated in Excel as B2:B4. The values for *known_x's* are in cells A2, A3, and A4 which is abbreviated as A2:A4. The value of *const* determines whether or not the linear equation will be fit with a *y*-intercept as shown below.

	y-intercept	no y-intercept
Equation Form	y = mx + b	y = mx
Value of *const*	*const* = TRUE	*const* = FALSE

Since Equation 17.35 has no *y*-intercept, we enter the equation

= LINEST(B2:B4,A2:A4,FALSE)

into cell B6 which gives us the result that the slope K_3 = 0.00271 mg/cm^2-h.

(b) The time to reach W = 0.120 mg/cm^2 is calculated by rearranging Equation 17.35 to give

$$t = \frac{W}{K_3} = \frac{0.120 \text{ mg/cm}^2}{0.00271 \text{ mg/cm}^2 \text{ - h}} = 44.3 \text{ h}$$

DESIGN PROBLEMS

17.D1 Possible methods that may be used to reduce corrosion of the heat exchanger by the brine solution are as follows:

(1) Reduce the temperature of the brine; normally, the rate of a corrosion reaction increases with increasing temperature.

(2) Change the composition of the brine; the corrosion rate is often quite dependent on the composition of the corrosion environment.

(3) Remove as much dissolved oxygen as possible. Under some circumstances, the dissolved oxygen may form bubbles, which can lead to erosion-corrosion damage.

(4) Minimize the number of bends and/or changes in pipe contours in order to minimize erosion-corrosion.

(5) Add inhibitors.

(6) Avoid connections between different metal alloys.

17.D2 This question asks that we suggest appropriate materials, and if necessary, recommend corrosion prevention measures that should be taken for several specific applications. These are as follows:

(a) Laboratory bottles to contain relatively dilute solutions of nitric acid. Probably the best material for this application would be polytetrafluoroethylene (PTFE). The reasons for this are: (1) it is flexible and will not easily break if dropped; and (2) PTFE is resistant to this type of acid, as noted in Table 17.4.

(b) Barrels to contain benzene. Poly(ethylene terephthalate) (PET) would be suited for this application, since it is resistant to degradation by benzene (Table 17.4), and is less expensive than the other two materials listed in Table 17.4 (see Appendix C).

(c) Pipe to transport hot alkaline (basic) solutions. The best material for this application would probably be a nickel alloy (Section 13.3). Polymeric materials listed in Table 17.4 would not be suitable inasmuch as the solutions are hot.

(d) Underground tanks to store large quantities of high-purity water. The outside of the tanks should probably be some type of low-carbon steel that is cathodically protected (Sections 17.8 and 17.9). Inside the steel shell should be coated with an inert polymeric material; polytetrafluoroethylene or some other fluorocarbon would probably be the material of choice (Table 17.4).

(e) Architectural trim for high-rise buildings. The most likely candidate for this application would probably be an aluminum alloy. Aluminum and its alloys are relatively corrosion resistant in normal atmospheres (Section 16.8), retain their lustrous appearance, and are relatively inexpensive (Appendix C).

17.D3 Each student or group of students is to submit their own report on a corrosion problem investigation that was conducted.

CHAPTER 18

ELECTRICAL PROPERTIES

PROBLEM SOLUTIONS

Ohm's Law
Electrical Conductivity

18.1 This problem calls for us to compute the electrical conductivity and resistance of a silicon specimen.

(a) We use Equations 18.3 and 18.4 for the conductivity, as

$$\sigma = \frac{1}{\rho} = \frac{Il}{VA} = \frac{Il}{V\pi\left(\frac{d}{2}\right)^2}$$

And, incorporating values for the several parameters provided in the problem statement, leads to

$$\sigma = \frac{(0.25\ \text{A})\left(45\ \text{x}\ 10^{-3}\ \text{m}\right)}{(24\ \text{V})(\pi)\left(\frac{7.0\ \text{x}\ 10^{-3}\ \text{m}}{2}\right)^2} = 12.2\ (\Omega\text{ - m})^{-1}$$

(b) The resistance, *R*, may be computed using Equations 18.2 and 18.4, as

$$R = \frac{l}{\sigma A} = \frac{l}{\sigma\pi\left(\frac{d}{2}\right)^2}$$

$$= \frac{57\ \text{x}\ 10^{-3}\ \text{m}}{\left[12.2\ (\Omega - \text{m})^{-1}\right](\pi)\left(\frac{7.0\ \text{x}\ 10^{-3}\ \text{m}}{2}\right)^2} = 121.4\ \Omega$$

18.2 For this problem, given that an aluminum wire 10 m long must experience a voltage drop of less than 1.0 V when a current of 5 A passes through it, we are to compute the minimum diameter of the wire. Combining Equations 18.3 and 18.4 and solving for the cross-sectional area A leads to

$$A = \frac{Il}{V\sigma}$$

From Table 18.1, for aluminum $\sigma = 3.8 \times 10^{7}\ (\Omega\text{-m})^{-1}$. Furthermore, inasmuch as $A = \pi\left(\frac{d}{2}\right)^2$ for a cylindrical wire, then

$$\pi\left(\frac{d}{2}\right)^2 = \frac{Il}{V\sigma}$$

or

$$d = \sqrt{\frac{4Il}{\pi V\sigma}}$$

When values for the several parameters given in the problem statement are incorporated into this expression, we get

$$d = \sqrt{\frac{(4)(5\text{ A})(10\text{ m})}{(\pi)(1.0\text{ V})\left[3.8 \times 10^{7}\ (\Omega - \text{m})^{-1}\right]}}$$

$$= 1.3 \times 10^{-3}\text{ m} = 1.3\text{ mm}$$

18.3 This problem asks that we compute, for a plain carbon steel wire 3 mm in diameter, the maximum length such that the resistance will not exceed 20 Ω. From Table 18.1 for a plain carbon steel $\sigma = 0.6 \text{ x } 10^7 \ (\Omega\text{-m})^{-1}$. If *d* is the diameter then, combining Equations 18.2 and 18.4 leads to

$$l = R\sigma A = R\sigma\pi\left(\frac{d}{2}\right)^2$$

$$= (20\ \Omega)\left[0.6 \text{ x } 10^7\ (\Omega - \text{m})^{-1}\right](\pi)\left(\frac{3 \text{ x } 10^{-3}\ \text{m}}{2}\right)^2 = 848\ \text{ m}$$

18.4 Let us demonstrate, by appropriate substitution and algebraic manipulation, that Equation 18.5 may be made to take the form of Equation 18.1. Now, Equation 18.5 is just

$$J = \sigma E$$

(In this equation we represent the electric field with an "*E*".) But, by definition, *J* is just the current density, the current per unit cross-sectional area, or $J = \frac{I}{A}$. Also, the electric field is defined by $E = \frac{V}{l}$. And, substituting these expressions into Equation 18.5 leads to

$$\frac{I}{A} = \sigma \frac{V}{l}$$

But, from Equations 18.2 and 18.4

$$\sigma = \frac{l}{RA}$$

and

$$\frac{I}{A} = \left(\frac{l}{RA}\right)\left(\frac{V}{l}\right)$$

Solving for *V* from this expression gives $V = IR$, which is just Equation 18.1.

18.5 (a) In order to compute the resistance of this aluminum wire it is necessary to employ Equations 18.2 and 18.4. Solving for the resistance in terms of the conductivity,

$$R = \frac{\rho l}{A} = \frac{l}{\sigma A} = \frac{l}{\sigma\pi\left(\frac{d}{2}\right)^2}$$

From Table 18.1, the conductivity of aluminum is 3.8 x 10^7 (Ω-m)$^{-1}$, and

$$R = \frac{l}{\sigma\pi\left(\frac{d}{2}\right)^2} = \frac{5 \text{ m}}{\left[3.8 \text{ x } 10^7 \ (\Omega-\text{m})^{-1}\right](\pi)\left(\frac{5 \text{ x } 10^{-3} \text{ m}}{2}\right)^2}$$

$$= 6.7 \text{ x } 10^{-3}\ \Omega$$

(b) If V = 0.04 V then, from Equation 18.1

$$I = \frac{V}{R} = \frac{0.04 \text{ V}}{6.7 \text{ x } 10^{-3}\ \Omega} = 6.0 \text{ A}$$

(c) The current density is just

$$J = \frac{I}{A} = \frac{I}{\pi\left(\frac{d}{2}\right)^2} = \frac{6.0 \text{ A}}{\pi\left(\frac{5 \text{ x } 10^{-3} \text{ m}}{2}\right)^2} = 3.06 \text{ x } 10^5 \text{ A/m}^2$$

(d) The electric field is just

$$E = \frac{V}{l} = \frac{0.04 \text{ V}}{5 \text{ m}} = 8.0 \text{ x } 10^{-3} \text{ V/m}$$

Electronic and Ionic Conduction

18.6 When a current arises from a flow of electrons, the conduction is termed *electronic*; for *ionic conduction*, the current results from the net motion of charged ions.

Energy Band Structures in Solids

18.7 For an isolated atom, there exist discrete electron energy states (arranged into shells and subshells); each state may be occupied by, at most, two electrons, which must have opposite spins. On the other hand, an electron band structure is found for solid materials; within each band exist closely spaced yet discrete electron states, each of which may be occupied by, at most, two electrons, having opposite spins. The number of electron states in each band will equal the total number of corresponding states contributed by all of the atoms in the solid.

Conduction in Terms of Band and Atomic Bonding Models

18.8 This question asks that we explain the difference in electrical conductivity of metals, semiconductors, and insulators in terms of their electron energy band structures.

For metallic materials, there are vacant electron energy states adjacent to the highest filled state; thus, very little energy is required to excite large numbers of electrons into conducting states. These electrons are those that participate in the conduction process, and, because there are so many of them, metals are good electrical conductors.

There are no empty electron states adjacent to and above filled states for semiconductors and insulators, but rather, an energy band gap across which electrons must be excited in order to participate in the conduction process. Thermal excitation of electrons will occur, and the number of electrons excited will be less than for metals, and will depend on the band gap energy. For semiconductors, the band gap is narrower than for insulators; consequently, at a specific temperature more electrons will be excited for semiconductors, giving rise to higher conductivities.

Electron Mobility

18.9 The drift velocity of a free electron is the average electron velocity in the direction of the force imposed by an electric field.

The mobility is the proportionality constant between the drift velocity and the electric field. It is also a measure of the frequency of scattering events (and is inversely proportional to the frequency of scattering).

18.10 (a) The drift velocity of electrons in Si may be determined using Equation 18.7. Since the room temperature mobility of electrons is 0.14 m^2/V-s (Table 18.3), and the electric field is 500 V/m (as stipulated in the problem statement),

$$v_d = \mu_e E$$

$$= (0.14\ \text{m}^2/\text{V-s})(500\ \text{V/m}) = 70\ \text{m/s}$$

(b) The time, *t*, required to traverse a given length, *l* (= 25 mm), is just

$$t = \frac{l}{v_d} = \frac{25\ \text{x}\ 10^{-3}\,\text{m}}{70\ \text{m/s}} = 3.6\ \text{x}\ 10^{-4}\ \text{s}$$

18.11 (a) The number of free electrons per cubic meter for aluminum at room temperature may be computed using Equation 18.8 as

$$n = \frac{\sigma}{|e|\,\mu_e}$$

$$= \frac{3.8 \text{ x } 10^7 \, (\Omega - \text{m})^{-1}}{\left(1.602 \text{ x } 10^{-19} \text{ C}\right)\left(0.0012 \text{ m}^2/\text{V - s}\right)}$$

$$= 1.98 \text{ x } 10^{29} \text{ m}^{-3}$$

(b) In order to calculate the number of free electrons per aluminum atom, we must first determine the number of copper atoms per cubic meter, N_{Al}. From Equation 4.2 (and using the atomic weight and density values for Al found inside the front cover—viz. 26.98 g/mol and 2.71 g/cm^3)

$$N_{\text{Al}} = \frac{N_{\text{A}}\,\rho'}{A_{\text{Al}}}$$

$$= \frac{\left(6.023 \text{ x } 10^{23} \text{ atoms/mol}\right)\left(2.71 \text{ g/cm}^3\right)\left(10^6 \text{ cm}^3/\text{m}^3\right)}{26.98 \text{ g/mol}}$$

$$= 6.03 \text{ x } 10^{28} \text{ m}^{-3}$$

(*Note*: in the above expression, density is represented by ρ' in order to avoid confusion with resistivity which is designated by ρ.) And, finally, the number of free electrons per aluminum atom is just n/N_{Al}

$$\frac{n}{N_{\text{Al}}} = \frac{1.98 \text{ x } 10^{29} \text{ m}^{-3}}{6.03 \text{ x } 10^{28} \text{ m}^{-3}} = 3.28$$

18.12 (a) This portion of the problem asks that we calculate, for silver, the number of free electrons per cubic meter (n) given that there are 1.3 free electrons per silver atom, that the electrical conductivity is 6.8 x 10^7 (Ω-m)$^{-1}$, and that the density (ρ'_{Ag}) is 10.5 g/cm^3. (Note: in this discussion, the density of silver is represented by ρ'_{Ag} in order to avoid confusion with resistivity which is designated by ρ.) Since $n = 1.3N_{\mathrm{Ag}}$, and N_{Ag} is defined in Equation 4.2 (and using the atomic weight of Ag found inside the front cover—viz 107.87 g/mol), then

$$n = 1.3N_{\mathrm{Ag}} = 1.3\left[\frac{\rho'_{\mathrm{Ag}}N_{\mathrm{A}}}{A_{\mathrm{Ag}}}\right]$$

$$= 1.3\left[\frac{(10.5 \text{ g/cm}^3)(6.023 \text{ x } 10^{23} \text{ atoms/mol})}{107.87 \text{ g/mol}}\right]$$

$$= 7.62 \text{ x } 10^{22} \text{ cm}^{-3} = 7.62 \text{ x } 10^{28} \text{ m}^{-3}$$

(b) Now we are asked to compute the electron mobility, μ_e. Using Equation 18.8

$$\mu_e = \frac{\sigma}{n\,|e|}$$

$$= \frac{6.8 \text{ x } 10^7 \ (\Omega-\text{m})^{-1}}{(7.62 \text{ x } 10^{28}\,\text{m}^{-3})(1.602 \text{ x } 10^{-19}\,\text{C})} = 5.57 \text{ x } 10^{-3} \text{ m}^2/\text{V-s}$$

Electrical Resistivity of Metals

18.13 We want to solve for the parameter A in Equation 18.11 using the data in Figure 18.37. From Equation 18.11

$$A = \frac{\rho_i}{c_i (1 - c_i)}$$

However, the data plotted in Figure 18.37 is the total resistivity, ρ_{total}, and includes both impurity (ρ_i) and thermal (ρ_t) contributions (Equation 18.9). The value of ρ_t is taken as the resistivity at $c_i = 0$ in Figure 18.37, which has a value of 1.7×10^{-8} (Ω-m); this must be subtracted out. Below are tabulated values of A determined at $c_i = 0.10$, 0.20, and 0.30, including other data that were used in the computations. (*Note:* the c_i values were taken from the upper horizontal axis of Figure 18.37, since it is graduated in atom percent zinc.)

c_i	$1 - c_i$	ρ_{total} (Ω-m)	ρ_i (Ω-m)	A (Ω-m)
0.10	0.90	4.0×10^{-8}	2.3×10^{-8}	2.56×10^{-7}
0.20	0.80	5.4×10^{-8}	3.7×10^{-8}	2.31×10^{-7}
0.30	0.70	6.15×10^{-8}	4.45×10^{-8}	2.12×10^{-7}

So, there is a slight decrease of A with increasing c_i.

18.14 (a) Perhaps the easiest way to determine the values of ρ_0 and a in Equation 18.10 for pure copper in Figure 18.8, is to set up two simultaneous equations using two resistivity values (labeled ρ_{t1} and ρ_{t2}) taken at two corresponding temperatures (T_1 and T_2). Thus,

$$\rho_{t1} = \rho_0 + aT_1$$

$$\rho_{t2} = \rho_0 + aT_2$$

And solving these equations simultaneously lead to the following expressions for a and ρ_0:

$$a = \frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}$$

$$\rho_0 = \rho_{t1} - T_1\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right]$$

$$= \rho_{t2} - T_2\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right]$$

From Figure 18.8, let us take T_1 = –150°C, T_2 = –50°C, which gives $\rho_{t1} = 0.6 \text{ x } 10^{-8}$ (Ω-m), and $\rho_{t2} = 1.25 \text{ x } 10^{-8}$ (Ω-m). Therefore

$$a = \frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}$$

$$= \frac{\left[(0.6 \text{ x } 10^{-8}) - (1.25 \text{ x } 10^{-8})\right](\Omega\text{ - m})}{-150°\text{C} - (-50°\text{C})}$$

$$6.5 \text{ x } 10^{-11} \ (\Omega\text{-m})/°\text{C}$$

and

$$\rho_0 = \rho_{t1} - T_1\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right]$$

$$= \left(0.6 \text{ x } 10^{-8}\right) - (-150)\ \frac{\left[\left(0.6 \text{ x } 10^{-8}\right) - \left(1.25 \text{ x } 10^{-8}\right)\right](\Omega\text{ - m})}{-150°\text{C} - (-50°\text{C})}$$

$$= 1.58 \text{ x } 10^{-8}\ (\Omega\text{-m})$$

(b) For this part of the problem, we want to calculate *A* from Equation 18.11

$$\rho_i = Ac_i\,(1 - c_i)$$

In Figure 18.8, curves are plotted for three c_i values (0.0112, 0.0216, and 0.0332). Let us find *A* for each of these c_i's by taking a ρ_{total} from each curve at some temperature (say 0°C) and then subtracting out ρ_i for pure copper at this same temperature (which is 1.7 x 10^{-8} Ω-m). Below is tabulated values of *A* determined from these three c_i values, and other data that were used in the computations.

c_i	$1 - c_i$	ρ_{total} (Ω-m)	ρ_i (Ω-m)	*A* (Ω-m)
0.0112	0.989	3.0 x 10^{-8}	1.3 x 10^{-8}	1.17 x 10^{-6}
0.0216	0.978	4.2 x 10^{-8}	2.5 x 10^{-8}	1.18 x 10^{-6}
0.0332	0.967	5.5 x 10^{-8}	3.8 x 10^{-8}	1.18 x 10^{-6}

The average of these three *A* values is 1.18 x 10^{-6} (Ω-m).

(c) We use the results of parts (a) and (b) to estimate the electrical resistivity of copper containing 2.50 at% Ni (c_i = 0.025) at120°C. The total resistivity is just

$$\rho_{\text{total}} = \rho_t + \rho_i$$

Or incorporating the expressions for ρ_t and ρ_i from Equations 18.10 and 18.11, and the values of ρ_0, *a*, and *A* determined above, leads to

$$\rho_{\text{total}} = (\rho_0 + aT) + Ac_i\,(1 - c_i)$$

$$= \left\{1.58 \text{ x } 10^{-8}\ (\Omega\text{ - m}) + \left[6.5 \text{ x } 10^{-11}\ (\Omega\text{ - m})/°\text{C}\right](120°\text{C})\right\}$$

$$+ \left\{\left[1.18 \text{ x } 10^{-6}\ (\Omega\text{ - m})\right](0.0250)\,(1 - 0.0250)\right\}$$

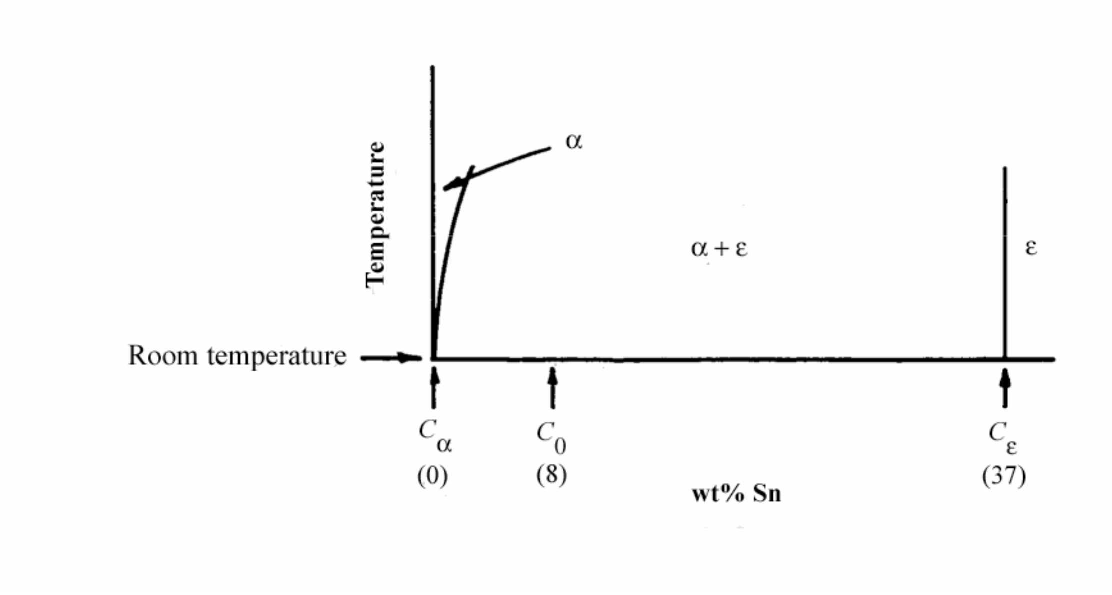
$$= 5.24 \text{ x } 10^{-8}\ (\Omega\text{-m})$$

18.15 We are asked to determine the electrical conductivity of a Cu-Ni alloy that has a tensile strength of 275 MPa. From Figure 7.16(a), the composition of an alloy having this tensile strength is about 8 wt% Ni. For this composition, the resistivity is about 14×10^{-8} Ω-m (Figure 18.9). And since the conductivity is the reciprocal of the resistivity, Equation 18.4, we have

$$\sigma = \frac{1}{\rho} = \frac{1}{14 \ \mathrm{x}\ 10^{-8}\ \Omega - \mathrm{m}} = 7.1 \ \mathrm{x}\ 10^{6}\ (\Omega\text{ - m})^{-1}$$

18.16 This problem asks for us to compute the room-temperature conductivity of a two-phase Cu-Sn alloy which composition is 89 wt% Cu-11 wt% Sn. It is first necessary for us to determine the volume fractions of the α and ε phases, after which the resistivity (and subsequently, the conductivity) may be calculated using Equation 18.12. Weight fractions of the two phases are first calculated using the phase diagram information provided in the problem.

We may represent a portion of the phase diagram near room temperature as follows:



Applying the lever rule to this situation

$$W_\alpha = \frac{C_\varepsilon - C_0}{C_\varepsilon - C_\alpha} = \frac{37 - 11}{37 - 0} = 0.703$$

$$W_\varepsilon = \frac{C_0 - C_\alpha}{C_\varepsilon - C_\alpha} = \frac{11 - 0}{37 - 0} = 0.297$$

We must now convert these mass fractions into volume fractions using the phase densities given in the problem statement. (*Note:* in the following expressions, density is represented by ρ' in order to avoid confusion with resistivity which is designated by ρ.) Utilization of Equations 9.6a and 9.6b leads to

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho'_\alpha}}{\dfrac{W_\alpha}{\rho'_\alpha} + \dfrac{W_\varepsilon}{\rho'_\varepsilon}}$$

$$= \frac{\dfrac{0.703}{8.94\ \text{g/cm}^3}}{\dfrac{0.703}{8.94\ \text{g/cm}^3} + \dfrac{0.297}{8.25\ \text{g/cm}^3}}$$

$$= 0.686$$

$$V_\varepsilon = \frac{\dfrac{W_\varepsilon}{\rho'_\varepsilon}}{\dfrac{W_\alpha}{\rho'_\alpha} + \dfrac{W_\varepsilon}{\rho'_\varepsilon}}$$

$$= \frac{\dfrac{0.297}{8.25\ \text{g/cm}^3}}{\dfrac{0.703}{8.94\ \text{g/cm}^3} + \dfrac{0.297}{8.25\ \text{g/cm}^3}}$$

$$= 0.314$$

Now, using Equation 18.12

$$\rho = \rho_\alpha V_\alpha + \rho_\varepsilon V_\varepsilon$$

$$= \left(1.88 \text{ x } 10^{-8}\ \Omega\text{-m}\right)(0.686) + \left(5.32 \text{ x } 10^{-7}\ \Omega\text{-m}\right)(0.314)$$

$$= 1.80 \text{ x } 10^{-7}\ \Omega\text{-m}$$

Finally, for the conductivity (Equation 18.4)

$$\sigma = \frac{1}{\rho} = \frac{1}{1.80 \text{ x } 10^{-7}\ \Omega-\text{m}} = 5.56 \text{ x} 10^6\ (\Omega\text{-m})^{-1}$$

18.17 We are asked to select which of several metals may be used for a 3 mm diameter wire to carry 12 A, and have a voltage drop less than 0.01 V per foot (300 mm). Using Equations 18.3 and 18.4, let us determine the minimum conductivity required, and then select from Table 18.1, those metals that have conductivities greater than this value. Combining Equations 18.3 and 18.4, the minimum conductivity is just

$$\sigma = \frac{Il}{VA} = \frac{Il}{V\pi\left(\frac{d}{2}\right)^2}$$

$$= \frac{(12\ \text{A})(300\ \text{x}\ 10^{-3}\ \text{m})}{(0.01\ \text{V})\ (\pi)\left(\frac{3\ \text{x}\ 10^{-3}\ \text{m}}{2}\right)^2} = 5.1\ \text{x}\ 10^7\ (\Omega\text{ - m})^{-1}$$

Thus, from Table 18.1, only copper, and silver are candidates.

Intrinsic Semiconduction

18.18 (a) For this part of the problem, we first read, from Figure 18.16, the number of free electrons (i.e., the intrinsic carrier concentration) at room temperature (298 K). These values are n_i(Ge) = 5 x 10^{19} m^{-3} and n_i(Si) = 7 x 10^{16} m^{-3}.

Now, the number of atoms per cubic meter for Ge and Si (N_{Ge} and N_{Si}, respectively) may be determined using Equation 4.2 which involves the densities (ρ'_{Ge} and ρ'_{Si}) and atomic weights (A_{Ge} and A_{Si}). (*Note:* here we use ρ' to represent density in order to avoid confusion with resistivity, which is designated by ρ. Also, the atomic weights for Ge and Si, 72.59 and 28.09 g/mol, respectively, are found inside the front cover.) Therefore,

$$N_{\text{Ge}} = \frac{N_{\text{A}}\rho'_{\text{Ge}}}{A_{\text{Ge}}}$$

$$= \frac{(6.023 \text{ x } 10^{23} \text{ atoms/mol})(5.32 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{72.59 \text{ g/mol}}$$

$$= 4.4 \text{ x } 10^{28} \text{ atoms/m}^3$$

Similarly, for Si

$$N_{\text{Si}} = \frac{N_{\text{A}}\rho'_{\text{Si}}}{A_{\text{Si}}}$$

$$= \frac{(6.023 \text{ x } 10^{23} \text{ atoms/mol})(2.33 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{28.09 \text{ g/mol}}$$

$$= 5.00 \text{ x } 10^{28} \text{ atoms/m}^3$$

Finally, the ratio of the number of free electrons per atom is calculated by dividing n_i by N. For Ge

$$\frac{n_i(\text{Ge})}{N_{\text{Ge}}} = \frac{5 \text{ x } 10^{19} \text{ electrons/m}^3}{4.4 \text{ x } 10^{28} \text{ atoms/m}^3}$$

$$1.1 \text{ x } 10^{-9} \text{ electron/atom}$$

And, for Si

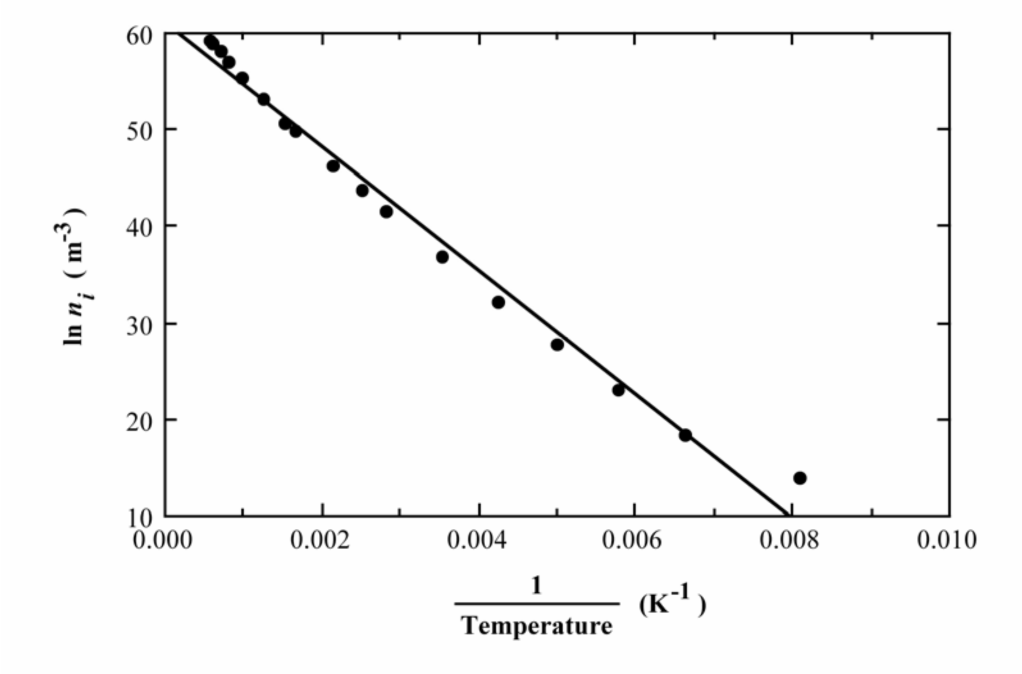
$$\frac{n_i\,(\mathrm{Si})}{N_{\mathrm{Si}}} = \frac{7 \;\; \mathrm{x}\; 10^{16}\ \mathrm{electrons/m^3}}{5.00 \;\; \mathrm{x}\; 10^{28}\ \mathrm{atoms/m^3}}$$

$$= 1.4\ \mathrm{x}\ 10^{-12}\ \mathrm{electron/atom}$$

(b) The difference is due to the magnitudes of the band gap energies (Table 18.3). The band gap energy at room temperature for Si (1.11 eV) is larger than for Ge (0.67 eV), and, consequently, the probability of excitation across the band gap for a valence electron is much smaller for Si.

18.19 This problem asks that we make plots of ln n_i versus reciprocal temperature for both Si and Ge, using the data presented in Figure 18.16, and then determine the band gap energy for each material realizing that the slope of the resulting line is equal to $-E_g/2k$.

Below is shown such a plot for Si.



The slope of the line is equal to

$$\text{Slope} = \frac{\Delta \ln \eta_i}{\Delta\left(\frac{1}{T}\right)} = \frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Let us take $1/T_1 = 0.001$ and $1/T_2 = 0.007$; their corresponding ln η values are $\ln \eta_1 = 54.80$ and $\ln \eta_2 = 16.00$. Incorporating these values into the above expression leads to a slope of

$$\text{Slope} = \frac{54.80 - 16.00}{0.001 - 0.007} = -6470$$

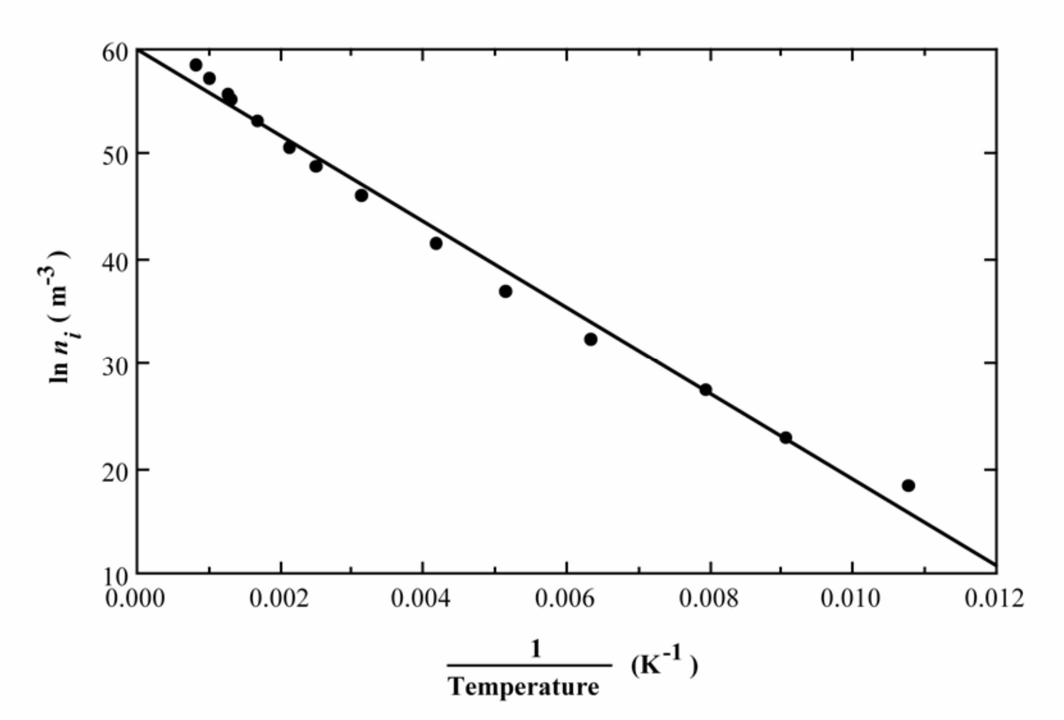
This slope leads to an E_g value of

$$E_g = -2k\,(\text{Slope})$$

$$= -2\left(8.62 \text{ x } 10^{-5} \text{ eV/K}\right)(-6470) = 1.115 \text{ eV}$$

The value cited in Table 18.3 is 1.11 eV.

Now for Ge, an analogous plot is shown below.



We calculate the slope and band gap energy values in the manner outlined above. Let us take $1/T_1 = 0.001$ and $1/T_2 = 0.011$; their corresponding ln η values are $\ln \eta_1 = 55.56$ and $\ln \eta_2 = 14.80$. Incorporating these values into the above expression leads to a slope of

$$\text{Slope} = \frac{55.56 - 14.80}{0.001 - 0.011} = -4076$$

This slope leads to an E_g value of

$$E_g = -2k\,(\text{Slope})$$

$$= -2\left(8.62 \text{ x } 10^{-5} \text{ eV/K}\right)(-4076) = 0.70 \text{ eV}$$

This value is in good agreement with the 0.67 eV cited in Table 18.3.

18.20 The factor 2 in Equation 18.35a takes into account the creation of two charge carriers (an electron and a hole) for each valence-band-to-conduction-band intrinsic excitation; both charge carriers may participate in the conduction process.

18.21 In this problem we are asked to compute the intrinsic carrier concentration for PbS at room temperature. Since the conductivity and both electron and hole mobilities are provided in the problem statement, all we need do is solve for *n* and *p* (i.e., n_i) using Equation 18.15. Thus,

$$n_i = \frac{\sigma}{|e|(\mu_e + \mu_h)}$$

$$= \frac{25\ (\Omega\text{ - m})^{-1}}{(1.602\ \text{x}\ 10^{-19}\ \text{C})(0.06\ +\ 0.02)\ \ \text{m}^2/\text{V - s}}$$

$$= 1.95\ \text{x}\ 10^{21}\ \text{m}^{-3}$$

18.22 Yes, compound semiconductors can exhibit intrinsic behavior. They will be intrinsic even though they are composed of two different elements as long as the electrical behavior is not influenced by the presence of other elements.

18.23 This problem calls for us to decide for each of several pairs of semiconductors, which will have the smaller band gap energy and then cite a reason for the choice.

(a) Germanium will have a smaller band gap energy than C (diamond) since Ge is lower in row IVA of the periodic table (Figure 2.6) than is C. In moving from top to bottom of the periodic table, E_g decreases.

(b) Indium antimonide will have a smaller band gap energy than aluminum phosphide. Both of these semiconductors are III-V compounds, and the positions of both In and Sb are lower vertically in the periodic table (Figure 2.6) than Al and P.

(c) Gallium arsenide will have a smaller band gap energy than zinc selenide. All four of these elements are in the same row of the periodic table, but Zn and Se are more widely separated horizontally than Ga and As; as the distance of separation increases, so does the band gap.

(d) Cadmium telluride will have a smaller band gap energy than zinc selenide. Both are II-VI compounds, and Cd and Te are both lower vertically in the periodic table than Zn and Se.

(e) Cadmium sulfide will have a smaller band gap energy than sodium chloride since Na and Cl are much more widely separated horizontally in the periodic table than are Cd and S.

Extrinsic Semiconduction

18.24 These semiconductor terms are defined in the Glossary. Examples are as follows: intrinsic--high purity (undoped) Si, GaAs, CdS, etc.; extrinsic--P-doped Ge, B-doped Si, S-doped GaP, etc.; compound--GaAs, InP, CdS, etc.; elemental--Ge and Si.

18.25 For this problem we are to determine the electrical conductivity of and n-type semiconductor, given that $n = 5 \text{ x } 10^{17}\ \text{m}^{-3}$ and the electron drift velocity is 350 m/s in an electric field of 1000 V/m. The conductivity of this material may be computed using Equation 18.16. But before this is possible, it is necessary to calculate the value of μ_e from Equation 18.7. Thus, the electron mobility is equal to

$$\mu_e = \frac{v_d}{E}$$

$$= \frac{350 \text{ m/s}}{1000 \text{ V/m}} = 0.35 \text{ m}^2/\text{V}-\text{s}$$

Thus, from Equation 18.16, the conductivity is

$$\sigma = n|e|\mu_e$$

$$= (5 \text{ x } 10^{17}\ \text{m}^{-3})(1.602 \text{ x } 10^{-19}\ \text{C})(0.35 \text{ m}^2/\text{V}-\text{s})$$

$$= 0.028\ (\Omega\text{-m})^{-1}$$

18.26 The explanations called for are found in Section 18.11.

18.27 (a) No hole is generated by an electron excitation involving a donor impurity atom because the excitation comes from a level within the band gap, and thus, no missing electron is created within the normally filled valence band.

(b) No free electron is generated by an electron excitation involving an acceptor impurity atom because the electron is excited from the valence band into the impurity level within the band gap; no free electron is introduced into the conduction band.

18.28 Nitrogen will act as a donor in Si. Since it (N) is from group VA of the periodic table (Figure 2.6), and an N atom has one more valence electron than an Si atom.

Boron will act as an acceptor in Ge. Since it (B) is from group IIIA of the periodic table, a B atom has one less valence electron than a Ge atom.

Sulfur will act as a donor in InSb. Since S is from group VIA of the periodic table, it will substitute for Sb; also, an S atom has one more valence electron than an Sb atom.

Indium will act as a donor in CdS. Since In is from group IIIA of the periodic table, it will substitute for Cd; and, an In atom has one more valence electron than a Cd atom.

Arsenic will act as an acceptor in ZnTe. Since As is from group VA of the periodic table, it will substitute for Te; furthermore, an As atom has one less valence electron than a Te atom.

18.29 (a) In this problem, for a Si specimen, we are given values for *p* $(2.0 \times 10^{22}\ \text{m}^{-3})$ and σ $[500\ (\Omega\text{-m})^{-1}]$, while values for μ_h and μ_e (0.05 and 0.14 m^2/V-s, respectively) are found in Table 18.3. In order to solve for *n* we must use Equation 18.13, which, after rearrangement, leads to

$$n = \frac{\sigma - p|e|\mu_h}{|e|\mu_e}$$

$$= \frac{500\ (\Omega-\text{m})^{-1} - (2.0\ \times 10^{22}\ \text{m}^{-3})(1.602\ \times 10^{-19}\ \text{C})(0.05\ \text{m}^2/\text{V-s})}{(1.602\ \times 10^{-19}\ \text{C})(0.14\ \text{m}^2/\text{V-s})}$$

$$= 2.97 \times 10^{20}\ \text{m}^{-3}$$

(b) This material is *p*-type extrinsic since *p* $(2.0 \times 10^{22}\ \text{m}^{-3})$ is greater than *n* $(2.97 \times 10^{20}\ \text{m}^{-3})$.

18.30 (a) This germanium material to which has been added 10^{24} m^{-3} As atoms is *n*-type since As is a donor in Ge. (Arsenic is from group VA of the periodic table--Ge is from group IVA.)

(b) Since this material is *n*-type extrinsic, Equation 18.16 is valid. Furthermore, each As atom will donate a single electron, or the electron concentration is equal to the As concentration since all of the As atoms are ionized at room temperature; that is $n = 10^{24}$ m^{-3}, and, as given in the problem statement, $\mu_e = 0.1$ m^2/V-s. Thus

$$\sigma = n|e|\mu_e$$

$$= (10^{24} \text{ m}^{-3})(1.602 \text{ x } 10^{-19} \text{ C})(0.1 \text{ m}^2/\text{V-s})$$

$$= 1.6 \text{ x } 10^{4} \ (\Omega\text{-m})^{-1}$$

18.31 In order to solve for the electron and hole mobilities for GaSb, we must write conductivity expressions for the two materials, of the form of Equation 18.13—i.e.,

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

For the intrinsic material

$$8.9 \text{ x } 10^4 \ (\Omega\text{ - m})^{-1} = \left(8.7 \text{ x } 10^{23} \text{ m}^{-3}\right)\left(1.602 \text{ x } 10^{-19} \text{ C}\right)\mu_e$$
$$+ \left(8.7 \text{ x } 10^{23} \text{ m}^{-3}\right)\left(1.602 \text{ x } 10^{-19} \text{ C}\right)\mu_h$$

which reduces to

$$0.639 = \mu_e + \mu_h$$

Whereas, for the extrinsic GaSb

$$2.3 \text{ x } 10^5 \ (\Omega\text{ - m})^{-1} = \left(7.6 \text{ x } 10^{22} \text{ m}^{-3}\right)\left(1.602 \text{ x } 10^{-19} \text{ C}\right)\mu_e$$
$$+ \left(1.0 \text{ x } 10^{25} \text{ m}^{-3}\right)\left(1.602 \text{ x } 10^{-19} \text{ C}\right)\mu_h$$

which may be simplified to

$$0.1436 = 7.6 \text{ x } 10^{-3}\mu_e + \mu_h$$

Thus, we have two independent expressions with two unknown mobilities. Upon solving these equations simultaneously, we get μ_e = 0.50 m^2/V-s and μ_h = 0.14 m^2/V-s.

The Temperature Dependence of Carrier Concentration

18.32 In order to estimate the electrical conductivity of intrinsic silicon at 80°C, we must employ Equation 18.15. However, before this is possible, it is necessary to determine values for n_i, μ_e, and μ_h. According to Figure 18.16, at 80°C (353 K), $n_i = 1.5 \times 10^{18}$ m^{-3}, whereas from the "<10^{20} m^{-3}" curves of Figures 18.19a and 18.19b, at 80ºC (353 K), $\mu_e = 0.10$ m^2/V-s and $\mu_h = 0.035$ m^2/V-s (realizing that the mobility axes of these two plot are scaled logarithmically). Thus, the conductivity at 80°C is

$$\sigma = n_i\,|e|\,(\mu_e + \mu_h)$$

$$\sigma = (1.5 \text{ x } 10^{18} \text{ m}^{-3})(1.602 \text{ x } 10^{-19} \text{ C})(0.10 \text{ m}^2/\text{V-s} + 0.035 \text{ m}^2/\text{V}-\text{s})$$

$$= 0.032\ (\Omega\text{-m})^{-1}$$

18.33 This problem asks for us to assume that electron and hole mobilities for intrinsic Ge are temperature-dependent, and proportional to $T^{-3/2}$ for temperature in K. It first becomes necessary to solve for C in Equation 18.36 using the room-temperature (298 K) conductivity [2.2 $(\Omega\text{-m})^{-1}$] (Table 18.3). This is accomplished by taking natural logarithms of both sides of Equation 18.36 as

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

and after rearranging and substitution of values for E_g (0.67 eV, Table 18.3), and the room-temperature conductivity, we get

$$\ln C = \ln \sigma + \frac{3}{2}\ln T + \frac{E_g}{2kT}$$

$$= \ln (2.2) + \frac{3}{2}\ln (298) + \frac{0.67 \text{ eV}}{(2)(8.62 \text{ x } 10^{-5} \text{ eV/K})(298 \text{ K})}$$

$$= 22.38$$

Now, again using Equation 18.36, we are able to compute the conductivity at 448 K (175°C)

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

$$= 22.38 - \frac{3}{2}\ln (448 \text{ K}) - \frac{0.67 \text{ eV}}{(2)(8.62 \text{ x } 10^{-5} \text{ eV/K})(448 \text{ K})}$$

$$= 4.548$$

which leads to

$$\sigma = e^{4.548} = 94.4\ (\Omega\text{-m})^{-1}.$$

18.34 This problem asks that we determine the temperature at which the electrical conductivity of intrinsic Ge is 40 (Ω-m)$^{-1}$, using Equation 18.36 and the results of Problem 18.33. First of all, taking logarithms of Equation 18.36

$$\ln \sigma = \ln C - \frac{3}{2} \ln T - \frac{E_g}{2kT}$$

And, from Problem 18.33 the value of ln C was determined to be 22.38. Using this and σ = 40 (Ω-m)$^{-1}$, the above equation takes the form

$$\ln 40 = 22.38 - \frac{3}{2} \ln T - \frac{0.67 \text{ eV}}{(2)\left(8.62 \text{ x } 10^{-5} \text{ eV/K}\right)(T)}$$

In order to solve for T from the above expression it is necessary to use an equation solver. For some solvers, the following set of instructions may be used:

```
ln(40) = 22.38 –1.5*ln(T) – 0.67/(2*8.62*10^-5*T)
```

The resulting solution is T = 400, which value is the temperature in K; this corresponds to T(ºC) = 400 – 273 = 127°C.

18.35 This problem asks that we estimate the temperature at which GaAs has an electrical conductivity of 1.6 x 10^{-3} (Ω-m)$^{-1}$ assuming that the conductivity has a temperature dependence as shown in Equation 18.36. From the room temperature (298 K) conductivity [10^{-6} (Ω-m)$^{-1}$] and band gap energy (1.42 eV) of Table 18.3 we determine the value of C (Equation 18.36) by taking natural logarithms of both sides of the equation, and after rearrangement as follows:

$$\ln C = \ln \sigma + \frac{3}{2}\ln T + \frac{E_g}{2kT}$$

$$= \ln \left[10^{-6}\ (\Omega - \mathrm{m})^{-1}\right] + \frac{3}{2}\ln (298\ \mathrm{K}) + \frac{1.42\ \mathrm{eV}}{(2)(8.62\ \mathrm{x}\ 10^{-5}\ \mathrm{eV/K})(298\ \mathrm{K})}$$

$$= 22.37$$

Now we substitute this value into Equation 18.36 in order to determine the value of T for which σ = 1.6 x 10^{-3} (Ω-m)$^{-1}$, thus

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

$$\ln \left[1.6\ \mathrm{x}\ 10^{-3}\ (\Omega - \mathrm{m})^{-1}\right] = 22.37 - \frac{3}{2}\ln T - \frac{1.42\ \mathrm{eV}}{(2)(8.62 \times 10^{-5}\ \mathrm{eV/K})(T)}$$

This equation may be solved for T using an equation solver. For some solvers, the following set of instructions may be used:

```
ln(1.6*10^–3) = 22.37 – 1.5*ln(T) – 1.42/(2*8.62*10^–5*T)
```

The resulting solution is T = 417; this value is the temperature in K which corresponds to T(ºC) = 417 K – 273 = 144°C.

18.36 This question asks that we compare and then explain the difference in temperature dependence of the electrical conductivity for metals and intrinsic semiconductors.

For metals, the temperature dependence is described by Equation 18.10 (and converting from resistivity to conductivity using Equation 18.4), as

$$\sigma = \frac{1}{\rho_0 + aT}$$

That is, the electrical conductivity decreases with increasing temperature.

Alternatively, from Equation 18.8, the conductivity of metals is equal to

$$\sigma = n|e|\mu_e$$

As the temperature rises, n will remain virtually constant, whereas the mobility (μ_e) will decrease, because the thermal scattering of free electrons will become more efficient. Since $|e|$ is independent of temperature, the net result will be diminishment in the magnitude of σ.

For intrinsic semiconductors, the temperature-dependence of conductivity is just the opposite of that for metals—i.e, conductivity increases with rising temperature. One explanation is as follows: Equation 18.15 describes the conductivity; i.e.,

$$\sigma = n|e|(\mu_e + \mu_h) = p|e|(\mu_e + \mu_h)$$
$$= n_i|e|(\mu_e + \mu_h)$$

Both n and p increase dramatically with rising temperature (Figure 18.16), since more thermal energy becomes available for valence band-conduction band electron excitations. The magnitudes of μ_e and μ_h will diminish somewhat with increasing temperature (per the upper curves of Figures 18.19a and 18.19b), as a consequence of the thermal scattering of electrons and holes. However, this reduction of μ_e and μ_h will be overwhelmed by the increase in n and p, with the net result is that σ increases with temperature.

An alternative explanation is as follows: for an intrinsic semiconductor the temperature dependence is represented by an equation of the form of Equation 18.36. This expression contains two terms that involve temperature—a preexponential one (in this case $T^{-3/2}$) and the other in the exponential. With rising temperature the preexponential term decreases, while the exp ($-E_g/2kT$) parameter increases. With regard to relative magnitudes, the exponential term increases much more rapidly than the preexponential one, such that the electrical conductivity of an intrinsic semiconductor increases with rising temperature.

Factors That Affect Carrier Mobility

18.37 This problems asks that we determine the room-temperature electrical conductivity of silicon that has been doped with 10^{23} m^{-3} of arsenic atoms. Inasmuch as As is a group VA element in the periodic table (Figure 2.6) it acts as a donor in silicon. Thus, this material is *n*-type extrinsic, and it is necessary to use Equation 18.16), with $n = 10^{23}$ m^{-3} since at room temperature all of the As donor impurities are ionized. The electron mobility, from Figure 18.18 at an impurity concentration of 10^{23} m^{-3}, is 0.065 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = n\,|e|\,\mu_e = \left(10^{23}\ \mathrm{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \mathrm{C}\right)\left(0.065\ \mathrm{m}^2/\mathrm{V-s}\right) = 1040\ (\Omega - \mathrm{m})^{-1}$$

18.38 Here we are asked to calculate the room-temperature electrical conductivity of silicon that has been doped with 2 x 10^{24} m^{-3} of boron atoms. Inasmuch as B is a group IIIA element in the periodic table (Figure 2.6) it acts as an acceptor in silicon. Thus, this material is *p*-type extrinsic, and it is necessary to use Equation 18.17, with p = 2 x 10^{24} m^{-3} since at room temperature all of the B acceptor impurities are ionized. The hole mobility, from Figure 18.18 at an impurity concentration of 2 x 10^{24} m^{-3}, is 0.0065 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = p\,|e|\,\mu_e = \left(2 \times 10^{24}\ \mathrm{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \mathrm{C}\right)\left(0.0065\ \mathrm{m}^2/\mathrm{V-s}\right) = 2080\ (\Omega - \mathrm{m})^{-1}$$

18.39 In this problem we are to estimate the electrical conductivity, at 75°C, of silicon that has been doped with 10^{22} m^{-3} of phosphorous atoms. Inasmuch as P is a group VA element in the periodic table (Figure 2.6) it acts as a donor in silicon. Thus, this material is *n*-type extrinsic, and it is necessary to use Equation 18.16; *n* in this expression is 10^{22} m^{-3} since at 75°C all of the P donor impurities are ionized. The electron mobility is determined using Figure 18.19a. From the 10^{22} m^{-3} impurity concentration curve and at 75°C (348 K), μ_e = 0.08 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = n\,|e|\,\mu_e = \left(10^{22}\ \mathrm{m}^{-3}\right)\left(1.602 \text{ x } 10^{-19}\ \mathrm{C}\right)\left(0.08\ \mathrm{m}^2/\mathrm{V-s}\right) = 128\ (\Omega - \mathrm{m})^{-1}$$

18.40 In this problem we are to estimate the electrical conductivity, at 135°C, of silicon that has been doped with 10^{24} m^{-3} of aluminum atoms. Inasmuch as Al is a group IIIA element in the periodic table (Figure 2.6) it acts as an acceptor in silicon. Thus, this material is *p*-type extrinsic, and it is necessary to use Equation 18.17; *p* in this expression is 10^{24} m^{-3} since at 135°C all of the Al acceptor impurities are ionized. The hole mobility is determined using Figure 18.19b. From the 10^{24} m^{-3} impurity concentration curve and at 135°C (408 K,) $\mu_h = 0.007$ m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = p\,|e|\,\mu_h = \left(10^{24}\ \mathrm{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \mathrm{C}\right)\left(0.007\ \mathrm{m}^2/\mathrm{V-s}\right) = 1120\ \ (\Omega-\mathrm{m})^{-1}$$

The Hall Effect

18.41 (a) This portion of the problem calls for us to determine the electron mobility for some hypothetical metal using the Hall effect. This metal has an electrical resistivity of 3.3 x 10^{-8} (Ω-m), while the specimen thickness is 15 mm, I_x = 25 A and B_z = 0.95 tesla; under these circumstances a Hall voltage of –2.4 x 10^{-7} V is measured. It is first necessary to convert resistivity to conductivity (Equation 18.4). Thus

$$\sigma = \frac{1}{\rho} = \frac{1}{3.3 \text{ x} 10^{-8} \ (\Omega - \text{m})} = 3.0 \text{ x } 10^{7} \ (\Omega\text{ - m})^{-1}$$

The electron mobility may be determined using Equation 18.20b; and upon incorporation of Equation 18.18, we have

$$\mu_e = |R_\text{H}|\sigma$$

$$= \frac{|V_\text{H}| d\sigma}{I_x B_z}$$

$$= \frac{\left(\left|-2.4 \text{ x } 10^{-7} \text{ V}\right|\right)(15 \text{ x } 10^{-3} \text{ m})\left[3.0 \text{ x } 10^{7} \ (\Omega - \text{m})^{-1}\right]}{(25 \text{ A})(0.95 \text{ tesla})}$$

$$= 0.0045 \ \text{m}^2/\text{V - s}$$

(b) Now we are to calculate the number of free electrons per cubic meter. From Equation 18.8 we have

$$n = \frac{\sigma}{|e|\,\mu_e}$$

$$= \frac{3.0 \text{ x } 10^{7} \ (\Omega\text{ - m})^{-1}}{(1.602 \text{ x } 10^{-19} \text{ C})(0.0045 \ \text{m}^2/\text{V - s})}$$

$$= 4.17 \text{ x } 10^{28} \ \text{m}^{-3}$$

18.42 In this problem we are asked to determine the magnetic field required to produce a Hall voltage of -3.5×10^{-7} V, given that $\sigma = 1.2 \times 10^{7}$ $(\Omega\text{-m})^{-1}$, $\mu_e = 0.0050$ m^2/V-s, $I_x = 40$ A, and $d = 35$ mm. Combining Equations 18.18 and 18.20b, and after solving for B_z, we get

$$B_z = \frac{|V_{\mathrm{H}}|\sigma d}{I_x \mu_e}$$

$$= \frac{\left(\left|-3.5 \text{ x } 10^{-7} \text{ V}\right|\right)\left[1.2 \text{ x } 10^{7} \ (\Omega - \text{m})^{-1}\right]\left(35 \text{ x } 10^{-3} \text{ m}\right)}{(40 \text{ A})\left(0.0050 \ \text{m}^2/\text{V - s}\right)}$$

$$= 0.74 \text{ tesla}$$

Semiconducting Devices

18.43 The explanations called for are found in Section 18.15.

18.44 The energy generated by the electron-hole annihilation reaction, Equation 18.21, is dissipated as heat.

18.45 In an electronic circuit, a transistor may be used to (1) amplify an electrical signal, and (2) act as a switching device in computers.

18.46 The differences in operation and application for junction transistors and MOSFETs are described in Section 18.15.

Conduction in Ionic Materials

18.47 We are asked in this problem to determine the electrical conductivity for the nonstoichiometric $Fe_{(1-x)}O$, given $x = 0.040$ and that the hole mobility is 1.0×10^{-5} m^2/V-s. It is first necessary to compute the number of vacancies per cubic meter for this material. For this determination let us use as our basis 10 unit cells. For the sodium chloride crystal structure there are four cations and four anions per unit cell. Thus, in ten unit cells of FeO there will normally be forty O^{2-} and forty Fe^{2+} ions. However, when $x = 0.04$, (0.04)(40) = 1.6 of the Fe^{2+} sites will be vacant. (Furthermore, there will be 3.2 Fe^{3+} ions in these ten unit cells inasmuch as two Fe^{3+} ions are created for every vacancy). Therefore, each unit cell will, on the average contain 0.16 vacancies. Now, the number of vacancies per cubic meter is just the number of vacancies per unit cell divided by the unit cell volume; this volume is just the unit cell edge length (0.437 nm) cubed. Thus

$$\frac{\#\text{ vacancies}}{\text{m}^3} = \frac{0.16 \text{ vacancies/unit cell}}{(0.437 \times 10^{-9} \text{ m})^3}$$

$$= 1.92 \times 10^{27} \text{ vacancies/m}^3$$

Inasmuch as it is assumed that the vacancies are saturated, the number of holes (p) is also 1.92×10^{27} m^{-3}. It is now possible, using Equation 18.17, to compute the electrical conductivity of this material as

$$\sigma = p|e|\mu_h$$

$$= (1.92 \times 10^{27} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})(1.0 \times 10^{-5} \text{ m}^2/\text{V-s}) = 3076 \ (\Omega\text{-m})^{-1}$$

18.48 For this problem, we are given, for NaCl, the activation energy (173,000 J/mol) and preexponential ($4.0 \text{ x } 10^{-4}$ m^2/s) for the diffusion coefficient of Na$^+$ and are asked to compute the mobility for a Na$^+$ ion at 873 K. The mobility, μ_{Na^+}, may be computed using Equation 18.23; however, this expression also includes the diffusion coefficient D_{Na^+}, which is determined using Equation 5.8 as

$$D_{\text{Na}^+} = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= \left(4.0 \text{ x } 10^{-4} \text{ m}^2/\text{s}\right) \exp\left[-\frac{173{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(873 \text{ K})}\right]$$

$$= 1.76 \text{ x } 10^{-14} \text{ m}^2/\text{s}$$

Now solving for μ_{Na^+} yields

$$\mu_{\text{Na}^+} = \frac{n_{\text{Na}^+} e D_{\text{Na}^+}}{kT}$$

$$= \frac{(1)\left(1.602 \text{ x } 10^{-19} \text{ C/atom}\right)\left(1.76 \text{ x } 10^{-14} \text{ m}^2/\text{s}\right)}{\left(1.38 \text{ x } 10^{-23} \text{ J/atom-K}\right)(873 \text{ K})}$$

$$= 2.34 \text{ x } 10^{-13} \text{ m}^2/\text{V-s}$$

(Note: the value of n_{Na^+} is unity, since the valence for sodium is one.)

Capacitance

18.49 We want to compute the plate spacing of a parallel-plate capacitor as the dielectric constant is increased form 2.2 to 3.7, while maintaining the capacitance constant. Combining Equations 18.26 and 18.27 yields

$$C = \frac{\varepsilon_r \varepsilon_0 A}{l}$$

Now, let us use the subscripts 1 and 2 to denote the initial and final states, respectively. Since $C_1 = C_2$, then

$$\frac{\varepsilon_{r1} \varepsilon_0 A}{l_1} = \frac{\varepsilon_{r2} \varepsilon_0 A}{l_2}$$

And, solving for l_2

$$l_2 = \frac{\varepsilon_{r2} l_1}{\varepsilon_{r1}} = \frac{(3.7)(2 \text{ mm})}{2.2} = 3.36 \text{ mm}$$

18.50 This problem asks for us to ascertain which of the materials listed in Table 18.5 are candidates for a parallel-plate capacitor that has dimensions of 38 mm by 65 mm, a plate separation of 1.3 mm so as to have a minimum capacitance of 7 x 10^{-11} F, when an ac potential of 1000 V is applied at 1 MHz. Upon combining Equations 18.26 and 18.27 and solving for the dielectric constant ε_r we get

$$\varepsilon_r = \frac{lC}{\varepsilon_0 A}$$

$$= \frac{(1.3 \text{ x } 10^{-3}\,\text{m})(7 \text{ x } 10^{-11}\,\text{F})}{(8.85 \text{ x } 10^{-12}\,\text{F/m})(38 \text{ x } 10^{-3}\,\text{m})(65 \text{ x } 10^{-3}\,\text{m})}$$

$$= 4.16$$

Thus, the minimum value of ε_r to achieve the desired capacitance is 4.16 at 1 MHz. Of those materials listed in the table, titanate ceramics, mica, steatite, soda-lime glass, porcelain, and phenol-formaldehyde are candidates.

18.51 In this problem we are given, for a parallel-plate capacitor, its area (3225 mm^2), the plate separation (1 mm), and that a material having an ε_r of 3.5 is positioned between the plates.

(a) We are first asked to compute the capacitance. Combining Equations 18.26 and 18.27, and solving for *C* yields

$$C = \frac{\varepsilon_r \varepsilon_0 A}{l}$$

$$= \frac{(3.5)\left(8.85 \text{ x } 10^{-12} \text{ F/m}\right)\left(3225 \text{ mm}^2\right)\left(1 \text{ m}^2/10^6 \text{ mm}^2\right)}{10^{-3} \text{ m}}$$

$$= 10^{-10} \text{ F} = 100 \text{ pF}$$

(b) Now we are asked to compute the electric field that must be applied in order that 2 x 10^{-8} C be stored on each plate. First we need to solve for *V* in Equation 18.24 as

$$V = \frac{Q}{C} = \frac{2 \text{ x } 10^{-8} \text{ C}}{10^{-10} \text{ F}} = 200 \text{ V}$$

The electric field *E* may now be determined using Equation 18.6; thus

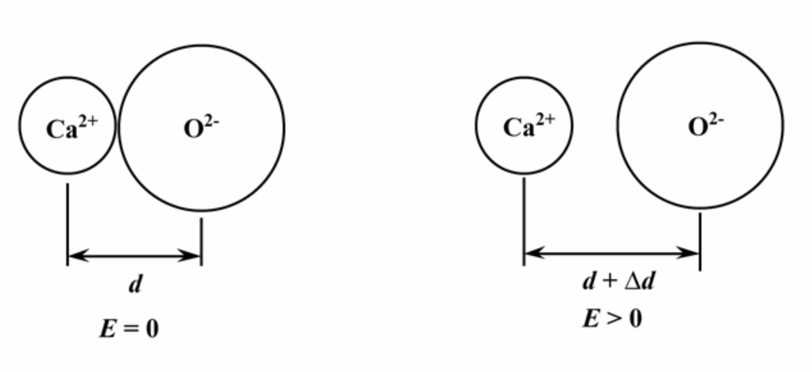
$$E = \frac{V}{l} = \frac{200 \text{ V}}{10^{-3} \text{ m}} = 2.0 \text{ x } 10^5 \text{ V/m}$$

18.52 This explanation is found in Section 18.19.

Field Vectors and Polarization

Types of Polarization

18.53 Shown below are the relative positions of Ca^{2+} and O^{2-} ions, without and with an electric field present.



Now,

$$d = r_{Ca^{2+}} + r_{O^{2-}} = 0.100 \text{ nm} + 0.140 \text{ nm} = 0.240 \text{ nm}$$

and

$$\Delta d = 0.05\, d = (0.05)(0.240 \text{ nm}) = 0.0120 \text{ nm} = 1.20 \times 10^{-11} \text{ m}$$

From Equation 18.28, the dipole moment, p, is just

$$p = q\,\Delta d$$

$$= (1.602 \times 10^{-19} \text{ C})(1.20 \times 10^{-11} \text{ m})$$

$$= 1.92 \times 10^{-30} \text{ C-m}$$

18.54 (a) In order to solve for the dielectric constant in this problem, we must employ Equation 18.32, in which the polarization and the electric field are given. Solving for ε_r from this expression gives

$$\varepsilon_r = \frac{P}{\varepsilon_0 E} + 1$$

$$= \frac{4.0 \text{ x } 10^{-6} \text{ C/m}^2}{(8.85 \text{ x } 10^{-12} \text{ F/m})(1 \text{ x } 10^5 \text{ V/m})} + 1$$

$$= 5.52$$

(b) The dielectric displacement may be determined using Equation 18.31, as

$$D = \varepsilon_0 E + P$$

$$= (8.85 \text{ x } 10^{-12} \text{ F/m})(1 \text{ x } 10^5 \text{ V/m}) + 4.0 \text{ x } 10^{-6} \text{ C/m}^2$$

$$= 4.89 \text{ x } 10^{-6} \text{ C/m}^2$$

18.55 (a) We want to solve for the voltage when $Q = 2.0 \text{ x } 10^{-10}$ C, $A = 650 \text{ mm}^2$, $l = 4.0$ mm, and $\varepsilon_r = 3.5$. Combining Equations 18.24, 18.26, and 18.27 yields

$$C = \frac{Q}{V} = \varepsilon\frac{A}{l} = \varepsilon_r\varepsilon_0\frac{A}{l}$$

Or

$$\frac{Q}{V} = \varepsilon_r\varepsilon_0\frac{A}{l}$$

And, solving for *V*, and incorporating values provided in the problem statement, leads to

$$V = \frac{Ql}{\varepsilon_r\varepsilon_0 A}$$

$$= \frac{(2.0 \text{ x } 10^{-10}\text{ C})(4.0 \text{ x } 10^{-3}\text{ m})}{(3.5)(8.85 \text{ x } 10^{-12}\text{ F/m})(650 \text{ mm}^2)(1 \text{ m}^2/10^6 \text{ mm}^2)}$$

$$= 39.7 \text{ V}$$

(b) For this same capacitor, if a vacuum is used

$$V = \frac{Ql}{\varepsilon_0 A}$$

$$= \frac{(2.0 \text{ x } 10^{-10}\text{ C})(4.0 \text{ x } 10^{-3}\text{ m})}{(8.85 \text{ x } 10^{-12}\text{ F/m})(650 \text{ x } 10^{-6}\text{ m}^2)}$$

$$= 139 \text{ V}$$

(c) The capacitance for part (a) is just

$$C = \frac{Q}{V} = \frac{2.0 \text{ x } 10^{-10}\text{ C}}{39.7 \text{ V}} = 5.04 \text{ x } 10^{-12}\text{ F}$$

While for part (b)

$$C = \frac{Q}{V} = \frac{2.0 \text{ x } 10^{-10}\text{ C}}{139 \text{ V}} = 1.44 \text{ x } 10^{-12}\text{ F}$$

(d) The dielectric displacement may be computed by combining Equations 18.31, 18.32 and 18.6, as

$$D = \varepsilon_0 E + P = \varepsilon_0 E + \varepsilon_0(\varepsilon_r - 1)E = \varepsilon_0 \varepsilon_r E = \frac{\varepsilon_0 \varepsilon_r V}{l}$$

And incorporating values for ε_r and l provided in the problem statement, as well as the value of V computed in part (a)

$$D = \frac{(8.85 \text{ x } 10^{-12}\text{ F/m})(3.5)(39.7 \text{ V})}{4.0 \text{ x } 10^{-3}\text{ m}}$$

$$= 3.07 \text{ x } 10^{-7}\text{ C/m}^2$$

(e) The polarization is determined using Equations 18.32 and 18.6 as

$$P = \varepsilon_0(\varepsilon_r - 1)E = \varepsilon_0(\varepsilon_r - 1)\frac{V}{l}$$

$$= \frac{(8.85 \text{ x } 10^{-12}\text{ F/m})(3.5 - 1)(39.7 \text{ V})}{4.0 \text{ x } 10^{-3}\text{ m}}$$

$$= 2.20 \text{ x } 10^{-7}\text{ C/m}^2$$

18.56 (a) For electronic polarization, the electric field causes a net displacement of the center of the negatively charged electron cloud relative to the positive nucleus. With ionic polarization, the cations and anions are displaced in opposite directions as a result of the application of an electric field. Orientation polarization is found in substances that possess permanent dipole moments; these dipole moments become aligned in the direction of the electric field.

(b) Only electronic polarization is to be found in gaseous argon; being an inert gas, its atoms will not be ionized nor possess permanent dipole moments.

Both electronic and ionic polarizations will be found in solid LiF, since it is strongly ionic. In all probability, no permanent dipole moments will be found in this material.

Both electronic and orientation polarizations are found in liquid H_2O. The H_2O molecules have permanent dipole moments that are easily oriented in the liquid state.

Only electronic polarization is to be found in solid Si; this material does not have molecules with permanent dipole moments, nor is it an ionic material.

18.57 (a) This portion of the problem asks that we compute the magnitude of the dipole moment associated with each unit cell of $BaTiO_3$, which is illustrated in Figure 18.35. The dipole moment *p* is defined by Equation 18.28 as $p = qd$ in which *q* is the magnitude of each dipole charge, and *d* is the distance of separation between the charges. Each Ti^{4+} ion has four units of charge associated with it, and thus $q = (4)(1.602 \times 10^{-19}\ \text{C}) = 6.41 \times 10^{-19}\ \text{C}$. Furthermore, *d* is the distance the Ti^{4+} ion has been displaced from the center of the unit cell, which is just 0.006 nm + 0.006 nm = 0.012 nm [Figure 18.35(b)]. Hence

$$p = qd = \left(6.41 \times 10^{-19}\ \text{C}\right)\left(0.012 \times 10^{-9}\ \text{m}\right)$$

$$= 7.69 \times 10^{-30}\ \text{C-m}$$

(b) Now it becomes necessary to compute the maximum polarization that is possible for this material. The maximum polarization will exist when the dipole moments of all unit cells are aligned in the same direction. Furthermore, it is computed by dividing the above value of *p* by the volume of each unit cell, which is equal to the product of three unit cell edge lengths, as shown in Figure 18.35. Thus

$$P = \frac{p}{V_C}$$

$$= \frac{7.69 \times 10^{-30}\ \text{C}-\text{m}}{\left(0.403 \times 10^{-9}\ \text{m}\right)\left(0.398 \times 10^{-9}\ \text{m}\right)\left(0.398 \times 10^{-9}\ \text{m}\right)}$$

$$= 0.121\ \text{C/m}^2$$

Frequency Dependence of the Dielectric Constant

18.58 For this soda-lime glass, in order to compute the fraction of the dielectric constant at low frequencies that is attributed to ionic polarization, we must determine the ε_r within this low-frequency regime; such is tabulated in Table 18.5, and at 1 MHz its value is 6.9. Thus, this fraction is just

$$\text{fraction} = \frac{\varepsilon_r(\text{low}) - \varepsilon_r(\text{high})}{\varepsilon_r(\text{low})}$$

$$= \frac{6.9 - 2.3}{6.9} = 0.67$$

Ferroelectricity

18.59 The ferroelectric behavior of $BaTiO_3$ ceases above its ferroelectric Curie temperature because the unit cell transforms from tetragonal geometry to cubic; thus, the Ti^{4+} is situated at the center of the cubic unit cell, there is no charge separation, and no net dipole moment.

DESIGN PROBLEMS

Electrical Resistivity of Metals

18.D1 This problem asks that we calculate the composition of a copper-nickel alloy that has a room temperature resistivity of 2.5 x 10^{-7} Ω-m. The first thing to do is, using the 90 Cu-10 Ni resistivity data, determine the impurity contribution, and, from this result, calculate the constant A in Equation 18.11. Thus,

$$\rho_{\text{total}} = 1.90 \text{ x } 10^{-7} \ (\Omega\text{ - m}) = \rho_i + \rho_t$$

From Table 18.1, for pure copper, and using Equation 18.4

$$\rho_t = \frac{1}{\sigma} = \frac{1}{6.0 \text{ x } 10^7 \ (\Omega - \text{m})^{-1}} = 1.67 \text{ x } 10^{-8} \ (\Omega\text{ - m})$$

Thus, for the 90 Cu-10 Ni alloy

$$\rho_i = \rho_{\text{total}} - \rho_t = 1.90 \text{ x } 10^{-7} - 1.67 \text{ x } 10^{-8}$$

$$= 1.73 \text{ x } 10^{-7} \ (\Omega\text{-m})$$

In the problem statement, the impurity (i.e., nickel) concentration is expressed in weight percent. However, Equation 18.11 calls for concentration in atom fraction (i.e., atom percent divided by 100). Consequently, conversion from weight percent to atom fraction is necessary. (Note: we now choose to denote the atom fraction of nickel as c'_{Ni}, and the weight percents of Ni and Cu by C_{Ni} and C_{Cu}, respectively.) Using these notations, this conversion may be accomplished by using a modified form of Equation 4.6a as

$$c'_{\text{Ni}} = \frac{C'_{\text{Ni}}}{100} = \frac{C_{\text{Ni}} A_{\text{Cu}}}{C_{\text{Ni}} A_{\text{Cu}} + C_{\text{Cu}} A_{\text{Ni}}}$$

Here A_{Ni} and A_{Cu} denote the atomic weights of nickel and copper (which values are 58.69 and 63.55 g/mol, respectively). Thus

$$c'_{\text{Ni}} = \frac{(10 \text{ wt\%})(63.55 \text{ g/mol})}{(10 \text{ wt\%})(63.55 \text{ g/mol}) + (90 \text{ wt\%})(58.69 \text{ g/mol})}$$

$$= 0.107$$

Now, solving for A in Equation 18.11

$$A = \frac{\rho_i}{c'_{\mathrm{Ni}}\left(1 - c'_{\mathrm{Ni}}\right)}$$

$$= \frac{1.73 \text{ x } 10^{-7}\,(\Omega - \mathrm{m})}{(0.107)(1 - 0.107)} = 1.81 \text{ x } 10^{-6}\ (\Omega - \mathrm{m})$$

Now it is possible to compute the c'_{Ni} to give a room temperature resistivity of 2.5 x 10^{-7} Ω-m. Again, we must determine ρ_i as

$$\rho_i = \rho_{\text{total}} - \rho_t$$

$$= 2.5 \text{ x } 10^{-7} - 1.67 \text{ x } 10^{-8} = 2.33 \text{ x } 10^{-7}\ (\Omega - \mathrm{m})$$

If Equation 18.11 is expanded, then

$$\rho_i = A c'_{\mathrm{Ni}} - A c'^{2}_{\mathrm{Ni}}$$

Or, rearranging this equation, we have

$$A c'^{2}_{\mathrm{Ni}} - A c'_{\mathrm{Ni}} + \rho_i = 0$$

Now, solving for c'_{Ni} (using the quadratic equation solution)

$$c'_{\mathrm{Ni}} = \frac{A \pm \sqrt{A^2 - 4A\rho_i}}{2A}$$

Again, from the above

$A = 1.81 \text{ x } 10^{-6}$ (Ω-m)
$\rho_i = 2.33 \text{ x } 10^{-7}$ (Ω-m)

which leads to

$$c'_{\mathrm{Ni}} = \frac{1.81 \text{ x } 10^{-6} \pm \sqrt{(1.81 \text{ x } 10^{-6})^2 - (4)(1.81 \text{ x } 10^{-6})(2.33 \text{ x } 10^{-7})}}{(2)(1.81 \text{ x } 10^{-6})}$$

And, taking the negative root,

$$c'_{\mathrm{Ni}} = 0.152$$

Or, in terms of atom percent,

$$C'_{\mathrm{Ni}} = 100c'_{\mathrm{Ni}} = (100)(0.152) = 15.2 \text{ at\%}$$

While the concentration of copper is

$$C'_{\mathrm{Cu}} = 100 - C'_{\mathrm{Ni}} = 100 - 15.2 = 84.8 \text{ at\%}$$

Now, converting this composition to weight percent Ni, requires that we use Equation 4.7a as

$$C_{\mathrm{Ni}} = \frac{C'_{\mathrm{Ni}} A_{\mathrm{Ni}}}{C'_{\mathrm{Ni}} A_{\mathrm{Ni}} + C'_{\mathrm{Cu}} A_{\mathrm{Cu}}} \text{ x } 100$$

$$= \frac{(15.2 \text{ at\%})(58.69 \text{ g/mol})}{(15.2 \text{ at\%})(58.69 \text{ g/mol}) + (84.8 \text{ at\%})(63.55 \text{ g/mol})} \text{ x } 100$$

$$= 14.2 \text{ wt\%}$$

18.D2 This problem asks that we determine the electrical conductivity of an 85 wt% Cu-15 wt% Zn alloy at –100°C using information contained in Figures 18.8 and 18.37. In order to solve this problem it is necessary to employ Equation 18.9 which is of the form

$$\rho_{\text{total}} = \rho_t + \rho_i$$

since it is assumed that the alloy is undeformed. Let us first determine the value of ρ_i at room temperature (25°C) which value will be independent of temperature. From Figure 18.8, at 25°C and for pure Cu, $\rho_t(25) = 1.75 \times 10^{-8}$ Ω-m. Now, since it is assumed that the curve in Figure 18.37 was generated also at room temperature, we may take ρ as $\rho_{\text{total}}(25)$ at 85 wt% Cu-15 wt% Zn which has a value of 4.7×10^{-8} Ω-m. Thus

$$\rho_i = \rho_{\text{total}}(25) - \rho_t(25)$$

$$= 4.7 \times 10^{-8}\ \Omega\text{-m} - 1.75 \times 10^{-8}\ \Omega\text{-m} = 2.95 \times 10^{-8}\ \Omega\text{-m}$$

Finally, we may determine the resistivity at –100°C, $\rho_{\text{total}}(-100)$, by taking the resistivity of pure Cu at –100°C from Figure 18.8, which gives us $\rho_t(-100) = 0.90 \times 10^{-8}$ Ω-m. Therefore

$$\rho_{\text{total}}(-100) = \rho_i + \rho_t(-100)$$

$$= 2.95 \times 10^{-8}\ \Omega\text{-m} + 0.90 \times 10^{-8}\ \Omega\text{-m} = 3.85 \times 10^{-8}\ \Omega\text{-m}$$

And, using Equation 18.4 the conductivity is calculated as

$$\sigma = \frac{1}{\rho} = \frac{1}{3.85 \times 10^{-8}\ \Omega - \text{m}} = 2.60 \times 10^{7}\ (\Omega\text{-m})^{-1}$$

18.D3 To solve this problem, we want to consult Figures 7.16(b) and 18.9 in order to determine the Ni concentration ranges over which the yield strength is greater than 130 MPa (19,000 psi) and the conductivity exceeds 4.0 x 10^6 (Ω-m)$^{-1}$.

From Figure 7.16(b), a Ni concentration greater than about 23 wt% is necessary for a yield strength in excess of 130 MPa. In Figure 18.9 is plotted the resistivity versus the Ni content. Since conductivity is the reciprocal of resistivity, the resistivity must be less than 25 x 10^{-8} Ω-m--i.e., $\frac{1}{4.0 \text{ x } 10^6 \ (\Omega - \text{m})^{-1}}$. According to the figure, this will be the case for Ni concentrations less than 17 wt%.

Hence, it is *not* possible to prepare an alloy meeting the criteria; for the stipulated yield strength the required Ni content must be greater than 23 wt%, whereas for the required conductivity, less than 17 wt% Ni is necessary.

Extrinsic Semiconduction
Factors That Affect Carrier Mobility

18.D4 First of all, those elements which, when added to silicon render it *n*-type, lie one group to the right of silicon in the periodic table; these include the group VA elements (Figure 2.6)--i.e., nitrogen, phosphorus, arsenic, and antimony.

Since this material is extrinsic and *n*-type, $n >> p$, and the electrical conductivity is a function of the hole concentration according to Equation 18.16. Also, the number of free electrons is about equal to the number of donor impurities, N_d. That is

$$n \sim N_d$$

From Equation 18.16, the conductivity is a function of both the electron concentration (n) and the electron mobility (μ_e). Furthermore, the room-temperature electron mobility is dependent on impurity concentration (Figure 18.18). One way to solve this problem is to use an iterative approach—i.e., assume some donor impurity concentration (which will also equal the value of n), then determine a "calculated" electron mobility from Equation 18.16—i.e.,

$$\mu_e = \frac{\sigma}{n\,|e|}$$

and, finally, compare this mobility with the "measured" value from Figure 18.18, taken at the assumed n (i.e., N_d) value.

Let us begin by assuming that $N_d = 10^{22}$ m^{-3}. Thus, the "calculated" mobility value is

$$\mu_e = \frac{\sigma}{n|e|} = \frac{200\ (\Omega - \text{m})^{-1}}{(10^{22}\ \text{m}^{-3})(1.602 \text{ x } 10^{-19}\ \text{C})} = 0.125\ \text{m}^2/\text{V} - \text{s}$$

From Figure 18.18, at an impurity concentration of 10^{22} m^{-3} the "measured" electron mobility is 0.10 m^2/V-s, which is slightly lower than the "calculated" value.

For our next choice, let us assume a higher impurity concentration, say 10^{23} m^{-3}. At this higher concentration there will be a reduction of both "calculated" and "measured" electron mobilities. The "calculated" value is just

$$\mu_e = \frac{\sigma}{n\,|e|} = \frac{200\ (\Omega - \text{m})^{-1}}{(10^{23}\ \text{m}^{-3})(1.602 \text{ x } 10^{-19}\ \text{C})} = 0.0125\ \text{m}^2/\text{V} - \text{s}$$

Whereas, Figure 18.18 yields a "measured" μ_e of 0.06 m^2/V-s, which is higher than the "calculated" value. Therefore, the correct impurity concentration will lie somewhere between 10^{22} and 10^{23} m^{-3} probably closer to the lower of these two values. At 1.3 x 10^{22} m^{-3}, both "measured" and "calculated" μ_e values are about equal (0.095 m^2/V-s).

It next becomes necessary to calculate the concentration of donor impurities in atom percent. This computation first requires the determination of the number of silicon atoms per cubic meter, N_{Si}, using Equation 4.2, which is as follows

$$N_{\text{Si}} = \frac{N_{\text{A}}\rho'_{\text{Si}}}{A_{\text{Si}}}$$

$$= \frac{(6.023 \text{ x } 10^{23} \text{ atoms/mol})(2.33 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{28.09 \text{ g/mol}}$$

$$= 5 \text{ x } 10^{28} \text{ m}^{-3}$$

(Note: in the above discussion, the density of silicon is represented by ρ'_{Si} in order to avoid confusion with resistivity, which is designated by ρ.)

The concentration of donor impurities in atom percent (C'_d) is just the ratio of N_d and (N_d + N_{Si}) multiplied by 100 as

$$C'_d = \frac{N_d}{N_d + N_{\text{Si}}} \text{ x } 100$$

$$= \frac{1.3 \text{ x } 10^{22} \text{ m}^{-3}}{(1.3 \text{ x } 10^{22} \text{ m}^{-3}) + (5 \text{ x } 10^{28} \text{ m}^{-3})} \text{ x } 100 = 2.6 \text{ x } 10^{-5} \text{ at\%}$$

Now, conversion to weight percent (C_d) is possible using Equation 4.7a as

$$C_d = \frac{C'_d A_d}{C'_d A_d + C'_{\text{Si}} A_{\text{Si}}} \text{ x } 100$$

where A_d and A_{Si} are the atomic weights of the donor and silicon, respectively. Thus, the concentration in weight percent will depend on the particular donor type. For example, for nitrogen

$$C_N = \frac{C'_N A_N}{C'_N A_N + C'_{Si} A_{Si}} \times 100$$

$$= \frac{(2.6 \ \text{x} \ 10^{-5} \text{at\%})(14.01 \ \text{g/mol})}{(2.6 \ \text{x} \ 10^{-5} \text{at\%})(14.01 \ \text{g/mol}) + (99.999974 \ \text{at\%})(28.09 \ \text{g/mol})} \times 100$$

$$= 1.3 \ \text{x} \ 10^{-5} \ \text{wt\%}$$

Similar calculations may be carried out for the other possible donor impurities which yield

$$C_P = 2.87 \ \text{x} \ 10^{-5} \ \text{wt\%}$$

$$C_{As} = 6.93 \ \text{x} \ 10^{-5} \ \text{wt\%}$$

$$C_{Sb} = 1.127 \ \text{x} \ 10^{-4} \ \text{wt\%}$$

18.D5 This problem asks for us to determine the temperature at which boron is to be diffused into high-purity silicon in order to achieve a room-temperature electrical conductivity of 1000 (Ω-m)$^{-1}$ at a distance 0.2 μm from the surface if the B concentration at the surface is maintained at 1.0 x 10^{25} m^{-3}. It is first necessary for us to compute the hole concentration (since B is an acceptor in Si) at this 0.2 μm location.

From Equation 18.17, the conductivity is a function of both the hole concentration (p) and the hole mobility (μ_h). Furthermore, the room-temperature hole mobility is dependent on impurity concentration (Figure 18.18). One way to solve this problem is to use an iterative approach—i.e., assume some boron concentration, N_B (which will also equal the value of p), then determine a "calculated" hole mobility from Equation 18.17—i.e.,

$$\mu_h = \frac{\sigma}{p|e|}$$

and then compare this mobility with the "measured" value from Figure 18.18, taken at the assumed p (i.e., N_B).

Let us begin by assuming that $N_B = 10^{24}$ m^{-3}. Thus, the "calculated" mobility value is

$$\mu_h = \frac{\sigma}{p|e|} = \frac{1000\ (\Omega - \mathrm{m})^{-1}}{(10^{24}\ \mathrm{m}^{-3})(1.602\ \mathrm{x}\ 10^{-19}\ \mathrm{C})} = 0.0062\ \mathrm{m}^2/\mathrm{V-s}$$

From Figure 18.18, at an impurity concentration of 10^{24} m^{-3} the "measured" hole mobility is 0.01 m^2/V-s, which is higher than the "calculated" value.

For our next choice, let us assume a lower boron concentration, say 10^{23} m^{-3}. At this lower concentration there will be an increase of both "calculated" and "measured" hole mobilities. The "calculated" value is just

$$\mu_h = \frac{\sigma}{p|e|} = \frac{1000\ (\Omega - \mathrm{m})^{-1}}{(10^{23}\ \mathrm{m}^{-3})(1.602\ \mathrm{x}\ 10^{-19}\ \mathrm{C})} = 0.062\ \mathrm{m}^2/\mathrm{V-s}$$

Whereas, Figure 18.18 yields a "measured" μ_h of 0.024 m^2/V-s, which is lower than the "calculated" value. Therefore, the correct impurity concentration will lie somewhere between 10^{23} and 10^{24} m^{-3}. At 4.0 x 10^{23} m^{-3}, "measured" and "calculated" values are about equal (0.015 m^2/V-s).

With regard to diffusion, the problem is one involving the nonsteady-state diffusion of B into the Si, wherein we have to solve for temperature. Temperature is incorporated into the diffusion coefficient expression given in the problem. But we must first employ the solution to Fick's second law for constant surface composition boundary conditions, Equation 5.5; in this expression C_0 is taken to be zero inasmuch as the problem stipulates that the initial boron concentration may be neglected. Thus,

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

$$\frac{4.0 \text{ x } 10^{23}\,\text{m}^{-3} - 0}{1.0 \text{ x } 10^{25}\,\text{m}^{-3} - 0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

which reduces to

$$0.9600 = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

In order to solve this expression for a value $\frac{x}{2\sqrt{Dt}}$ of it is necessary to interpolate using data in Table 5.1. Thus

z	erf(z)
1.4	0.9523
z	0.9600
1.5	0.9661

$$\frac{z - 1.4}{1.5 - 1.4} = \frac{0.9600 - 0.9523}{0.9661 - 0.9523}$$

From which, $z = 1.4558$; which is to say

$$1.4558 = \frac{x}{2\sqrt{Dt}}$$

Inasmuch as there are 3600 s/h (= t) and $x = 0.2$ μm (= $2 \text{ x } 10^{-7}$ m) the above equation becomes

$$1.4558 = \frac{2 \text{ x } 10^{-7}\text{ m}}{2\sqrt{(D)(3600 \text{ s})}}$$

which, when solving for the value of D, leads to

$$D = \frac{1}{3600 \text{ s}}\left[\frac{2 \times 10^{-7}\text{ m}}{(2)(1.4558)}\right]^2 = 1.31 \times 10^{-18}\ \text{m}^2/\text{s}$$

Now, equating this value to the expression for D given in the problem gives

$$D = 1.31 \text{ x } 10^{-18} \text{ m}^2\text{/s} = \left(2.4 \text{ x } 10^{-4}\right) \exp\left[-\frac{347{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(T)}\right]$$

To solve for T, let us take the natural logarithms of both sides of the above equation; this leads to

$$\ln\left(1.31 \text{ x } 10^{-18}\right) = \ln\left(2.4 \text{ x } 10^{-4}\right) - \frac{347{,}000}{8.31T}$$

$$-41.176 = -8.335 - \frac{4.176 \text{ x } 10^4}{T}$$

which yields a value for T of 1271 K (998°C).

Conduction in Ionic Materials

18.D6 This problem asks, for the nonstoichiometric $Fe_{(1-x)}O$, given the electrical conductivity [1200 $(\Omega\text{-m})^{-1}$] and hole mobility (1.0 x 10^{-5} m^2/V-s) that we determine the value of *x*. It is first necessary to compute the number of holes per unit volume (*p*) using Equation 18.17. Thus

$$p = \frac{\sigma}{|e|\mu_h}$$

$$= \frac{1200\ (\Omega - \mathrm{m})^{-1}}{\left(1.602\ \times 10^{-19}\ \mathrm{C}\right)\left(1.0\ \times 10^{-5}\ \mathrm{m}^2/\mathrm{V\text{-}s}\right)} = 7.49\ \times\ 10^{26}\ \mathrm{holes/m^3}$$

Inasmuch as it is assumed that the acceptor states are saturated, the number of vacancies is also 7.49 x 10^{26} m^{-3}. Next, it is possible to compute the number of vacancies per unit cell by taking the product of the number of vacancies per cubic meter times the volume of a unit cell. This volume is just the unit cell edge length (0.437 nm) cubed:

$$\frac{\#\ \text{vacancies}}{\text{unit cell}} = \left(7.49\ \times 10^{26}\ \mathrm{m}^{-3}\right)\left(0.437\ \ \mathrm{x}\ 10^{-9}\mathrm{m}\right)^3 = 0.0625$$

A unit cell for the sodium chloride structure contains the equivalence of four cations and four anions. Thus, if we take as a basis for this problem 10 unit cells, there will be 0.625 vacancies, 40 O^{2-} ions, and 39.375 iron ions (since 0.625 of the iron sites is vacant). (It should also be noted that since two Fe^{3+} ions are created for each vacancy, that of the 39.375 iron ions, 38.125 of them are Fe^{2+} and 1.25 of them are Fe^{3+}). In order to find the value of $(1 - x)$ in the chemical formula, we just take the ratio of the number of total Fe ions (39.375) and the number of total Fe ion sites (40). Thus

$$(1 - x) = \frac{39.375}{40} = 0.984$$

Or the formula for this nonstoichiometric material is $Fe_{0.984}O$.

Semiconductor Devices

18.D7 (a) In this portion of the problem we are asked to determine the time required to grow a layer of SiO_2 that is 100 nm (i.e., 0.100 μm) thick on the surface of a silicon chip at 1000°C, in an atmosphere of O_2 (oxygen pressure = 1 atm). Thus, using Equation 18.37, it is necessary to solve for the time *t*. However, before this is possible, we must calculate the value of *B* from Equation 18.38a as follows:

$$B = 800 \exp\left(-\frac{1.24 \text{ eV}}{kT}\right) = (800) \exp\left[-\frac{1.24 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(1000 + 273 \text{ K})}\right]$$

$$= 0.00990 \ \mu\text{m}^2/\text{h}$$

Now, solving for *t* from Equation 18.37 using the above value for *B* and that $x = 0.100$ μm, we have

$$t = \frac{x^2}{B} = \frac{(0.100 \ \mu\text{m})^2}{0.00990 \ \mu\text{m}^2/\text{h}}$$

$$= 1.01 \text{ h}$$

Repeating the computation for *B* at 700°C:

$$B = (800) \exp\left[-\frac{1.24 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(700 + 273 \text{ K})}\right]$$

$$= 3.04 \times 10^{-4} \ \mu\text{m}^2/\text{h}$$

And solving for the oxidation time as above

$$t = \frac{(0.100 \ \mu\text{m})^2}{3.04 \times 10^{-4} \ \mu\text{m}^2/\text{h}} = 32.9 \text{ h}$$

(b) This part of the problem asks for us to compute the heating times to form an oxide layer 100 nm thick at the same two temperatures (1000°C and 700°C) when the atmosphere is water vapor (1 atm pressure). At 1000°C, the value of *B* is determined using Equation 18.38b, as follows:

$$B = 215 \exp\left(-\frac{0.70\ \text{eV}}{kT}\right) = (215) \exp\left[-\frac{0.70\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1000 + 273\ \text{K})}\right]$$

$$= 0.365\ \mu\text{m}^2/\text{h}$$

And computation of the time *t* from the rearranged form of Equation 18.37, leads to

$$t = \frac{x^2}{B} = \frac{(0.100\ \mu\text{m})^2}{0.365\ \mu\text{m}^2/\text{h}}$$

$$= 0.0274\ \text{h} = 98.6\ \text{s}$$

And at 700°C, the value of *B* is

$$B = (215) \exp\left[-\frac{0.70\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(700 + 273\ \text{K})}\right] = 0.0510\ \mu\text{m}^2/\text{h}$$

Whereas the time required to grow the 100 nm oxide layer is

$$t = \frac{x^2}{B} = \frac{(0.100\ \mu\text{m})^2}{0.0510\ \mu\text{m}^2/\text{h}}$$

$$= 0.196\ \text{h} = 706\ \text{s}$$

From the above computations, it is very apparent (1) that the 100 nm oxide layer forms more rapidly at 1000°C (than at 700°C) in both O_2 and H_2O gaseous atmospheres, and (2) that the oxide layer formation is more rapid in water vapor than in oxygen.

18.D8 We are asked to compare silicon and gallium arsenide semiconductors relative to properties and applications.

The following are the characteristics and applications for Si: (1) being an elemental semiconductor, it is cheaper to grow in single-crystalline form; (2) because of its electron band structure, it is best used in transistors; (3) electronic processes are relatively slow due to the low mobilities for electrons and holes (Table 18.3).

For GaAs: (1) it is much more expensive to produce inasmuch as it is a compound semiconductor; (2) because of its electron band structure it is best used in light-emitting diodes and semiconducting lasers; (3) its band gap may be altered by alloying; (4) electronic processes are more rapid than in Si due to the greater mobilities for electrons and holes; (5) absorption of electromagnetic radiation is greater in GaAs, and therefore, thinner layers are required for solar cells.

CHAPTER 19

THERMAL PROPERTIES

PROBLEM SOLUTIONS

Heat Capacity

19.1 The energy, E, required to raise the temperature of a given mass of material, m, is the product of the specific heat, the mass of material, and the temperature change, ΔT, as

$$E = c_p m \Delta T$$

The ΔT in this problem is equal to 150°C – 20°C = 130°C (= 130 K), while the mass is 5 kg, and the specific heats are presented in Table 19.1. Thus,

$$E(\text{aluminum}) = (900\ \text{J/kg-K})(5\ \text{kg})(130\ \text{K}) = 5.85 \times 10^5\ \text{J}$$

$$E(\text{brass}) = (375\ \text{J/kg-K})(5\ \text{kg})(130\ \text{K}) = 2.44 \times 10^5\ \text{J}$$

$$E(\text{alumina}) = (775\ \text{J/kg-K})(5\ \text{kg})(130\ \text{K}) = 5.04 \times 10^5\ \text{J}$$

$$E(\text{polypropylene}) = (1925\ \text{J/kg-K})(5\ \text{kg})(130\ \text{K}) = 1.25 \times 10^6\ \text{J}$$

19.2 We are asked to determine the temperature to which 10 lb_m of brass initially at 25°C would be raised if 65 Btu of heat is supplied. This is accomplished by utilization of a modified form of Equation 19.1 as

$$\Delta T = \frac{\Delta Q}{m c_p}$$

in which ΔQ is the amount of heat supplied, m is the mass of the specimen, and c_p is the specific heat. From Table 19.1, c_p = 375 J/kg-K for brass, which in Customary U.S. units is just

$$c_p = (375 \text{ J/kg-K})\left(\frac{2.39 \text{ x } 10^{-4} \text{ Btu/lb}_\text{m}\text{-°F}}{1 \text{ J/kg-K}}\right) = 0.090 \text{ Btu/lb}_\text{m}\text{-°F}$$

Thus

$$\Delta T = \frac{65 \text{ Btu}}{(10 \text{ lb}_\text{m})(0.090 \text{ Btu/lb}_\text{m}\text{-°F})} = 72.2\text{°F}$$

and

$$T_f = T_0 + \Delta T = 77\text{°F} + 72.2\text{°F} = 149.2\text{°F} \ \ (65.1\text{°C})$$

19.3 (a) This problem asks that we determine the room-temperature heat capacities at constant pressure, C_p, for copper, iron, gold, and nickel. All we need do is multiply the c_p values in Table 19.1 by the atomic weights (values are found inside the front cover), taking into account the conversion from grams to kilograms (for the atomic weights). Thus, for Cu

$$C_p \; = \; (386 \text{ J/kg-K})(1 \text{ kg}/1000 \text{ g})(63.55 \text{ g/mol}) \; = \; 24.5 \text{ J/mol-K}$$

For Fe

$$C_p \; = \; (448 \text{ J/kg-K})(1 \text{ kg}/1000 \text{ g})(55.85 \text{ g/mol}) \; = \; 25.0 \text{ J/mol-K}$$

For Au

$$C_p \; = \; (128 \text{ J/kg-K})(1 \text{ kg}/1000 \text{ g})(196.97 \text{ g/mol}) \; = \; 25.2 \text{ J/mol-K}$$

For Ni

$$C_p \; = \; (443 \text{ J/kg-K})(1 \text{ kg}/1000 \text{ g})(58.69 \text{ g/mol}) \; = \; 26.0 \text{ J/mol-K}$$

(b) These values of C_p are very close to one another because room temperature is considerably above the Debye temperature for these metals; therefore, the values of C_p should be about equal to $3R$ [(3)(8.31 J/mol-K) = 24.9 J/mol-K], which is indeed the case for all four of these metals.

19.4 (a) For copper, C_v at 20 K may be approximated by Equation 19.2, since this temperature is significantly below the Debye temperature (340 K). The value of C_v at 20 K is given, and thus, we may compute the constant *A* as

$$A = \frac{C_v}{T^3} = \frac{0.38 \text{ J/mol-K}}{(20 \text{ K})^3} = 4.75 \text{ x } 10^{-5} \text{ J/mol-K}^4$$

Therefore, at 40 K

$$C_v = AT^3 = \left(4.75 \text{ x } 10^{-5} \text{ J/mol-K}^4\right)(40 \text{ K})^3 = 3.04 \text{ J/mol-K}$$

and

$$c_v = (3.04 \text{ J/mol-K})(1 \text{ mol/63.55 g})(1000 \text{ g/kg}) = 47.8 \text{ J/kg-K}$$

(b) Since 400 K is above the Debye temperature, a good approximation for C_v is

$$C_v = 3R$$

$$= (3)(8.31 \text{ J/mol-K}) = 24.9 \text{ J/mol-K}$$

And, converting this to specific heat

$$c_v = (24.9 \text{ J/mol-K})(1 \text{ mol/63.55 g})(1000 \text{ g/kg}) = 392 \text{ J/kg-K}$$

19.5 For aluminum, we want to compute the Debye temperature, θ_D, given the expression for A in Equation 19.2 and the heat capacity at 15 K. First of all, let us determine the magnitude of A, as

$$A = \frac{C_v}{T^3}$$

$$= \frac{(4.60\ \text{J/mol-K})(1\ \text{kg}/1000\ \text{g})(26.98\ \text{g/mol})}{(15\ \text{K})^3}$$

$$= 3.68 \text{ x } 10^{-5}\ \text{J/mol-K}^4$$

As stipulated in the problem statement

$$A = \frac{12\pi^4 R}{5\theta_D^3}$$

Or, solving for θ_D

$$\theta_D = \left(\frac{12\pi^4 R}{5A}\right)^{1/3}$$

$$= \left[\frac{(12)(\pi)^4(8.31\ \text{J/mol-K})}{(5)\left(3.68 \text{ x } 10^{-5}\ \text{J/mol-K}^4\right)}\right]^{1/3} = 375\ \text{K}$$

19.6 (a) The reason that C_v rises with increasing temperature at temperatures near 0 K is because, in this temperature range, the allowed vibrational energy levels of the lattice waves are far apart relative to the available thermal energy, and only a portion of the lattice waves may be excited. As temperature increases, more of the lattice waves may be excited by the available thermal energy, and, hence, the ability of the solid to absorb energy (i.e., the magnitude of the heat capacity) increases.

(b) At temperatures far removed from 0 K, C_v becomes independent of temperature because all of the lattice waves have been excited and the energy required to produce an incremental temperature change is nearly constant.

Thermal Expansion

19.7 The two metals from which a bimetallic strip is constructed have different coefficients of thermal expansion. Consequently, a change in temperature will cause the strip to bend. For a thermostat that operates a furnace, as the temperature drops below a lower limit, the bimetallic strip bends so as to make an electrical contact, thus, turning on the furnace. With rising temperature, the strip bends in the opposite direction, breaking the contact (and turning the furnace off) when an upper-limit temperature is exceeded.

19.8 In order to determine the change in length of the copper wire, we must employ a rearranged form of Equation 19.3b and using the value of α_l taken from Table 19.1 [17.0×10^{-6} (°C)$^{-1}$] as

$$\Delta l = l_0 \alpha_l \Delta T = l_0 \alpha_l (T_f - T_0)$$

$$= (15 \text{ m}) \left[17.0 \times 10^{-6} (^\circ\text{C})^{-1}\right] (-9^\circ\text{C} - 40^\circ\text{C})$$

$$= -1.25 \times 10^{-2} \text{ m} = -12.5 \text{ mm} \quad (-0.49 \text{ in.})$$

19.9 The linear coefficient of thermal expansion for this material may be determined using a rearranged form of Equation 19.3b as

$$\alpha_l = \frac{\Delta l}{l_0 \Delta T} = \frac{\Delta l}{l_0 (T_f - T_0)} = \frac{0.48 \text{ x } 10^{-3} \text{ m}}{(0.4 \text{ m})(100°\text{C} - 20°\text{C})}$$

$$= 15.0 \text{ x } 10^{-6} \ (°\text{C})^{-1}$$

19.10 The phenomenon of thermal expansion using the potential energy-versus-interatomic spacing curve is explained in Section 19.3.

19.11 In this problem we are asked to determine the density of iron at 700°C. Let us use as the basis for this determination 1 cm^3 of material at 20°C, which has a mass of 7.870 g; it is assumed that this mass will remain constant upon heating to 700°C. Let us compute the volume expansion of this cubic centimeter of iron as it is heated to 700°C. A volume expansion expression is given in Equation 19.4—viz.,

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T$$

or

$$\Delta V = V_0 \alpha_v \Delta T$$

Also, $\alpha_v = 3\alpha_l$, as stipulated in the problem. The value of α_l given in Table 19.1 for iron is 11.8 x 10^{-6} $(°\text{C})^{-1}$. Therefore, the volume, V, of this specimen of Fe at 700°C is just

$$V = V_0 + \Delta V = V_0\left(1 + \alpha_v \Delta T\right) = V_0\left(1 + 3\alpha_l \Delta T\right)$$

$$= \left(1 \text{ cm}^3\right)\left\{1 + (3)\left[11.8 \text{ x } 10^{-6} \ (°\text{C})^{-1}\right](700°\text{C} - 20°\text{C})\right\}$$

$$= 1.02471 \text{ cm}^3$$

Thus, the density is just the 7.870 g divided by this new volume—i.e.,

$$\rho = \frac{7.870 \text{ g}}{1.02471 \text{ cm}^3} = 7.680 \text{ g/cm}^3$$

19.12 (a) In this portion of the problem we are asked to determine the density of gold at 800°C on the basis of thermal expansion considerations. The basis for this determination will be 1 cm^3 of material at 20°C; this volume of gold has a mass of 19.320 g, which mass is assumed to remain constant upon heating to the 800°C. Let us first compute the volume expansion of this cubic centimeter of copper as it is heated to 800°C. According to Equation 19.4 volume expansion is equal to

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T$$

where α_v, the volume coefficient of thermal expansion, as stipulated in the problem statement, is equal to $3\alpha_l$. The value of α_l given in Table 19.1 for gold is $14.2 \times 10^{-6}\ (°\text{C})^{-1}$. Therefore, the volume of this specimen of Au at 800°C (V) is equal to

$$V = V_0 + \Delta V = V_0 + V_0 \alpha_v \Delta T = V_0 (1 + \alpha_v \Delta T)$$

$$= V_0 (1 + 3\alpha_l \Delta T) = V_0 \left[1 + 3\alpha_l (T_f - T_0)\right]$$

$$= (1\ \text{cm}^3)\left\{1 + (3)\left[14.2 \times 10^{-6}\ (°\text{C})^{-1}\right](800°\text{C} - 20°\text{C})\right\}$$

$$= 1.03323\ \text{cm}^3$$

Thus, the density is just the 19.320 g divided by this new volume—i.e.,

$$\rho = \frac{19.320\ \text{g}}{1.03323\ \text{cm}^3} = 18.699\ \text{g/cm}^3$$

(b) Now we are asked to compute the density at 800°C taking into consideration the creation of vacancies which will further lower the density. To begin, this determination requires that we calculate the number of vacancies using Equation 4.1. But it first becomes necessary to compute the number of Au atoms per cubic centimeter (N_{Au}) at 800°C using Equation 4.2. Thus,

$$N_{\text{Au}} = \frac{N_{\text{A}}\, \rho_{\text{Au}}}{A_{\text{Au}}}$$

$$= \frac{(6.023 \times 10^{23}\ \text{atoms/mol})(18.699\ \text{g/cm}^3)}{196.97\ \text{g/mol}}$$

$$= 5.72 \text{ x } 10^{22} \text{ atoms/cm}^3$$

Now, from Equation 4.1, the total number of vacancies, N_v, is computed as

$$N_v = N_{\text{Au}} \exp\left(-\frac{Q_v}{kT}\right)$$

$$= \left(5.72 \times 10^{22} \text{ atoms/cm}^3\right) \exp\left[-\frac{0.98 \text{ eV/atom}}{\left(8.62 \times 10^{-5} \text{ eV/K}\right)(800 + 273 \text{ K})}\right]$$

$$= 1.432 \times 10^{18} \text{ vacancies/cm}^3$$

We now want to determine the number of vacancies per unit cell, which is possible if the unit cell volume is multiplied by N_v. The unit cell volume (V_C) may be calculated using Equation 3.5 taking $n = 4$ inasmuch as Au has the FCC crystal structure. Thus, from a rearranged form of Equation 3.5

$$V_C = \frac{nA_{\text{Au}}}{\rho_{\text{Au}} N_{\text{A}}}$$

$$= \frac{(4 \text{ atoms/unit cell})(196.97 \text{ g/mol})}{\left(18.699 \text{ g/cm}^3\right)\left(6.023 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 6.996 \times 10^{-23} \text{ cm}^3\text{/unit cell}$$

Now, the number of vacancies per unit cell, n_v, is just

$$n_v = N_v V_C$$

$$= \left(1.432 \times 10^{18} \text{ vacancies/cm}^3\right)\left(6.996 \times 10^{-23} \text{ cm}^3\text{/unit cell}\right)$$

$$= 0.0001002 \text{ vacancies/unit cell}$$

What this means is that instead of there being 4.0000 atoms per unit cell, there are only 4.0000 – 0.0001002 = 3.9998998 atoms per unit cell. And, finally, the density may be computed using Equation 3.5 taking $n = 3.9998998$; thus

$$\rho_{\mathrm{Au}} = \frac{nA_{\mathrm{Au}}}{V_C\,N_{\mathrm{A}}}$$

$$= \frac{(3.9998998\ \text{atoms/unit cell})(196.97\ \text{g/mol})}{\left(6.996 \times 10^{-23}\ \text{cm}^3/\text{unit cell}\right)\left(6.023\ \text{x}\ 10^{23}\ \text{atoms/mol}\right)}$$

$$= 18.698\ \text{g/cm}^3$$

Thus, the influence of the vacancies is almost insignificant--their presence reduces the density by only 0.001 g/cm^3 (from 18.699 g/cm^3 to 18.698 g/cm^3).

19.13 This problem asks that we calculate the values of c_v for aluminum and iron at room temperature using Equation 19.10, the data in Table 19.1, given that $\alpha_v = 3\alpha_l$, and also values of the compressibility. From Equation 19.10

$$c_v = c_p - \frac{\alpha_v^2 v_0 T}{\beta}$$

And, from Table 19.1 and the problem statement

$c_p(\text{Al}) = 900$ J/kg-K
$c_p(\text{Fe}) = 448$ J/kg-K
$\alpha_v(\text{Al}) = (3)[23.6 \text{ x } 10^{-6}\ (°\text{C})^{-1}] = 7.08 \text{ x } 10^{-5}\ (°\text{C})^{-1}$
$\alpha_v(\text{Fe}) = (3)[(11.8 \text{ x } 10^{-6}\ (°\text{C})^{-1}] = 3.54 \text{ x } 10^{-5}\ (°\text{C})^{-1}$
$\beta(\text{Al}) = 1.77 \text{ x } 10^{-11}\ (\text{Pa})^{-1}$
$\beta(\text{Fe}) = 2.65 \text{ x } 10^{-12}\ (\text{Pa})^{-1}$

The specific volume is just the reciprocal of the density; thus, in units of m^3/kg

$$v_0(\text{Al}) = \frac{1}{\rho} = \left(\frac{1}{2.71 \text{ g/cm}^3}\right)\left(\frac{1000 \text{ g}}{\text{kg}}\right)\left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 = 3.69 \text{ x } 10^{-4} \text{ m}^3/\text{kg}$$

$$v_0(\text{Fe}) = \left(\frac{1}{7.87 \text{ g/cm}^3}\right)\left(\frac{1000 \text{ g}}{\text{kg}}\right)\left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 = 1.27 \text{ x } 10^{-4} \text{ m}^3/\text{kg}$$

Therefore, for aluminum

$$c_v(\text{Al}) = c_p(\text{Al}) - \frac{\alpha_v^2(\text{Al})\ v_0(\text{Al})T}{\beta(\text{Al})}$$

$$= 900 \text{ J/kg-K} - \frac{\left[7.08 \text{ x } 10^{-5}\ (°\text{C})^{-1}\right]^2 (3.69 \text{ x}10^{-4} \text{ m}^3/\text{kg})(293 \text{ K})}{1.77 \text{ x } 10^{-11}\ (\text{N/m}^2)^{-1}}$$

$$= 869 \text{ J/kg-K}$$

And, also for iron

$$c_v(\text{Fe}) = 448 \text{ J/kg-K} - \frac{\left[3.54 \text{ x } 10^{-5} \ (^\circ\text{C})^{-1}\right]^2 \left(1.27 \text{ x } 10^{-4} \text{ m}^3/\text{kg}\right)(293 \text{ K})}{2.65 \text{ x } 10^{-12} \left(\text{N/m}^2\right)^{-1}}$$

$$= 430 \text{ J/kg-K}$$

19.14 This problem asks for us to determine the temperature to which a cylindrical rod of tungsten 15.025 mm in diameter must be heated in order for it of just fit into a 15.000 mm diameter circular hole in a plate of 1025 steel (which, of course, is also heated), assuming that the initial temperature is 25°C. This requires the use of Equation 19.3a, which is applied to the diameters of both the rod and hole. That is

$$\frac{d_f - d_0}{d_0} = \alpha_l (T_f - T_0)$$

Solving this expression for d_f yields

$$d_f = d_0 \left[1 + \alpha_l (T_f - T_0) \right]$$

Now all we need do is to establish expressions for d_f(steel) and d_f (W), set them equal to one another, and solve for T_f. According to Table 19.1, α_l(steel) = 12.0 x 10^{-6} $(°\mathrm{C})^{-1}$ and α_l (W) = 4.5 x 10^{-6} $(°\mathrm{C})^{-1}$. Thus

$$d_f\,(\text{steel}) = d_f\,(\text{W})$$

$$(15.000 \text{ mm}) \Big[1 + \left\{ 12.0 \text{ x } 10^{-6} (°\mathrm{C})^{-1} \right\} (T_f - 25°\mathrm{C}) \Big]$$

$$= (15.025 \text{ mm}) \Big[1 + \left\{ 4.5 \text{ x } 10^{-6} (°\mathrm{C})^{-1} \right\} (T_f - 25°\mathrm{C}) \Big]$$

Now solving for T_f gives T_f = 222.4°C

Thermal Conductivity

19.15 (a) The steady-state heat flux through the plate may be computed using Equation 19.5; the thermal conductivity for brass, found in Table 19.1, is 120 W/m-K. Therefore,

$$q = -k\frac{\Delta T}{\Delta x}$$

$$= -(120\ \text{W/m-K})\left[\frac{(50 + 273\ \text{K}) - (150 + 273\ \text{K})}{7.5\ \text{x}\ 10^{-3}\,\text{m}}\right]$$

$$= 1.60\ \text{x}\ 10^{6}\ \text{W/m}^{2}$$

(b) Let *dQ*/*dt* represent the total heat loss such that

$$\frac{dQ}{dt} = qAt$$

where *A* and *t* are the cross-sectional area and time, respectively. Thus,

$$\frac{dQ}{dt} = \left(1.60\ \text{x}\ 10^{6}\ \text{J/s-m}^{2}\right)\left(0.5\ \text{m}^{2}\right)(60\ \text{s/min})(60\ \text{min/h})$$

$$= 2.88\ \text{x}\ 10^{9}\ \text{J/h}\quad (2.73\ \text{x}\ 10^{6}\ \text{Btu/h})$$

(c) If soda-lime glass is used (*k* = 1.7 W/m-K, Table 19.1),

$$\frac{dQ}{dt} = -\,k\,A\,t\frac{\Delta T}{\Delta x}$$

$$= -\ (1.7\ \text{J/s-m-K})\left(0.5\ \text{m}^{2}\right)(3600\ \text{s/h})\left(\frac{-100\ \ \text{K}}{7.5\ \ \text{x}\ 10^{-3}\ \text{m}}\right)$$

$$= 4.08\ \text{x}\ 10^{7}\ \text{J/h}\quad (3.9\ \text{x}\ 10^{4}\ \text{Btu/h})$$

(d) If the thickness of the brass is increased to 15 mm, then

$$\frac{dQ}{dt} = -\,k\,A\,t\,\frac{\Delta T}{\Delta x} = -\,(120\ \text{W/m-K})\left(0.5\ \text{m}^2\right)(3600\ \text{s/h})\left(\frac{-\,100\ \text{K}}{15\ \text{x}\ 10^{-3}\ \text{m}}\right)$$

$$= \ 1.44\ \text{x}\ 10^9\ \text{J/h} \quad (1.36\ \text{x}\ 10^6\ \text{Btu/h})$$

19.16 (a) Equation 19.7 is not valid for ceramic and polymeric materials since, in the development of this expression, it is assumed that free electrons are responsible for both electrical and thermal conduction. Such is the case for most metals. For ceramics and polymers, free electrons are the primary contributors to the electrical conductivity. However, free electrons do not contribute significantly to the thermal conductivity. For ceramics, thermal conduction is primarily by means of phonons; for polymers, the energy transfer is made by chain vibrations, translations, and rotations.

(b) Estimated room-temperature values of *L*, in Ω-W/(K)^2, for the several materials are determined below. Electrical conductivity values were determined by taking reciprocals of the electrical resistivities given in Table B.9, Appendix B; thermal conductivities are taken from Table B.7 in the same appendix. (*Note:* when a range of values is given in these tables, an average value is used in the computation.)

For zirconia (3 mol% Y_2O_3)

$$L = \frac{k}{\sigma T} = \frac{2.65 \text{ W/m-K}}{\left[\dfrac{1}{10^{10}\ (\Omega-\text{m})}\right](293 \text{ K})} = 9.0 \times 10^{7} \ \Omega\text{-W/K}^2$$

For synthetic diamond

$$L = \frac{3150 \text{ W/m-K}}{\left[\dfrac{1}{1.5 \times 10^{-2}\ (\Omega-\text{m})}\right](293 \text{ K})} = 0.161 \ \Omega\text{-W/K}^2$$

For intrinsic gallium arsenide

$$L = \frac{45.5 \text{ W/m-K}}{\left[\dfrac{1}{10^{6}\ (\Omega-\text{m})}\right](293 \text{ K})} = 1.55 \times 10^{5} \ \Omega\text{-W/K}^2$$

For poly(ethylene terephthalate) (PET)

$$L = \frac{0.15 \text{ W/m-K}}{\left[\dfrac{1}{10^{12}\ (\Omega-\text{m})}\right](293 \text{ K})} = 5.12 \times 10^{8} \ \Omega\text{-W/K}^2$$

For silicone

$$L = \frac{0.23 \text{ W/m-K}}{\left[\dfrac{1}{10^{13} \, (\Omega - \text{m})}\right](293 \text{ K})} = 7.8 \text{ x } 10^{9} \ \ \Omega \text{ - W/K}^{2}$$

19.17 Thermal conductivities are higher for crystalline than for noncrystalline ceramics because, for noncrystalline, phonon scattering, and thus the resistance to heat transport, is much more effective due to the highly disordered and irregular atomic structure.

19.18 Metals are typically better thermal conductors than are ceramic materials because, for metals, most of the heat is transported by free electrons (of which there are relatively large numbers). In ceramic materials, the primary mode of thermal conduction is via phonons, and phonons are more easily scattered than are free electrons.

19.19 (a) Porosity decreases the thermal conductivity of ceramic and polymeric materials because the thermal conductivity of a gas phase that occupies pore space is extremely small relative to that of the solid material. Furthermore, contributions from gaseous convection are generally insignificant.

(b) Increasing the degree of crystallinity of a semicrystalline polymer enhances its thermal conductivity; the vibrations, rotations, etc. of the molecular chains are more effective modes of thermal transport when a crystalline structure prevails.

19.20 For some ceramic materials, the thermal conductivity first decreases with rising temperature because the scattering of lattice vibrations increases with temperature. At higher temperatures, the thermal conductivity will increase for some ceramics that are porous because radiant heat transfer across pores may become important, which process increases with rising temperature.

19.21 This question asks for us to decide, for each of several pairs of materials, which has the larger thermal conductivity and why.

(a) Pure silver will have a larger conductivity than sterling silver because the impurity atoms in the latter will lead to a greater degree of free electron scattering.

(b) Polycrystalline silica will have a larger conductivity than fused silica because fused silica is noncrystalline and lattice vibrations are more effectively scattered in noncrystalline materials.

(c) The poly(vinyl chloride) will have the larger conductivity than the polystyrene because the former will have the higher degree of crystallinity. Both polymers are syndiotactic and have the same degree of polymerization. However, with regard to side-group bulkiness, the PVC is more likely to crystallize. Since heat transfer is accomplished by molecular chain vibrations, and the coordination of these vibrations increases with percent crystallinity, the higher the crystallinity, the greater the thermal conductivity.

(d) The isotactic polypropylene will have a larger thermal conductivity than the atactic polypropylene because isotactic polymers have a higher degree of crystallinity. The influence of crystallinity on conductivity is explained in part (c).

19.22 This problem asks that we treat a porous material as a composite wherein one of the phases is a pore phase, and that we estimate upper and lower limits for the room-temperature thermal conductivity of an aluminum oxide material having a 0.25 volume fraction of pores. The upper limit of k (k_{upper}) may be determined using Equation 16.1 with thermal conductivity substituted for the elastic modulus, E. From Table 19.1, the value of k for Al_2O_3 is 39 W/m-K, while for still air in the pore phase, k = 0.02 W/m-K (Section 19.4). Thus

$$k_{\text{upper}} = V_{\text{p}} k_{\text{air}} + V_{\text{Al}_2\text{O}_3} k_{\text{Al}_2\text{O}_3}$$

$$= (0.25)(0.02\ \text{W/m-K}) + (0.75)(39\ \text{W/m-K}) = 29.3\ \text{W/m-K}$$

For the lower limit we employ a modification of Equation 16.2 as

$$k_{\text{lower}} = \frac{k_{\text{air}} k_{\text{Al}_2\text{O}_3}}{V_{\text{p}} k_{\text{Al}_2\text{O}_3} + V_{\text{Al}_2\text{O}_3} k_{\text{air}}}$$

$$= \frac{(0.02\ \text{W/m-K})(39\ \text{W/m-K})}{(0.25)(39\ \text{W/m-K}) + (0.75)(0.02\ \text{W/m-K})} = 0.080\ \text{W/m-K}$$

19.23 (a) The units of D_T are

$$D_T = \frac{k\,(\mathrm{J/s\text{-}m\text{-}K})}{\rho(\mathrm{kg/m^3})\,c_p(\mathrm{J/kg\text{-}K})} = \mathrm{m^2/s}$$

(b) The values of D_T for the several materials are given below. (Note: values for k and c_p are taken from Table 19.1; density values are from Table B.1, Appendix B, and converted to units of kilograms per meter cubed):

For copper

$$D_T = \frac{k}{\rho c_p} = \frac{398\ \mathrm{W/m\text{-}K}}{(8.94\ \mathrm{x}\ 10^3\,\mathrm{kg/m^3})(386\ \mathrm{J/kg\text{-}K})} = 1.15\ \mathrm{x}\ 10^{-4}\ \mathrm{m^2/s}$$

For brass

$$D_T = \frac{120\ \mathrm{W/m\text{-}K}}{(8.53\ \mathrm{x}\ 10^3\ \mathrm{kg/m^3})(375\ \mathrm{J/kg\text{-}K})} = 3.75\ \mathrm{x}\ 10^{-5}\ \mathrm{m^2/s}$$

For magnesia

$$D_T = \frac{37.7\ \mathrm{W/m\text{-}K}}{(3.58\ \mathrm{x}\ 10^3\ \mathrm{kg/m^3})(940\ \mathrm{J/kg\text{-}K})} = 1.12\ \mathrm{x}\ 10^{-5}\ \mathrm{m^2/s}$$

For fused silica

$$D_T = \frac{1.4\ \mathrm{W/m\text{-}K}}{(2.2\ \mathrm{x}\ 10^3\ \mathrm{kg/m^3})(740\ \mathrm{J/kg\text{-}K})} = 8.6\ \mathrm{x}\ 10^{-7}\ \mathrm{m^2/s}$$

For polystyrene

$$D_T = \frac{0.13\ \mathrm{W/m\text{-}K}}{(1.05\ \mathrm{x}\ 10^3\ \mathrm{kg/m^3})(1170\ \mathrm{J/kg\text{-}K})} = 1.06\ \mathrm{x}\ 10^{-7}\ \mathrm{m^2/s}$$

For polypropylene

$$D_T = \frac{0.12\ \mathrm{W/m\text{-}K}}{(0.91\ \mathrm{x}\ 10^3\ \mathrm{kg/m^3})(1925\ \mathrm{J/kg\text{-}K})} = 6.9\ \mathrm{x}\ 10^{-8}\ \mathrm{m^2/s}$$

Thermal Stresses

19.24 We want to show that Equation 19.8 is valid beginning with Equation 19.3. Upon examination of Equation 19.3b,

$$\frac{\Delta l}{l_0} = \alpha_l \Delta T$$

it may be noted that the term on the left-hand side is the same expression as that for the definition of engineering strain (Equation 6.2); that is

$$\varepsilon = \frac{\Delta l}{l_0}$$

Furthermore, elastic stress and strain are related through Hooke's law, Equation 6.5:

$$\sigma = E\varepsilon$$

Making appropriate substitutions and algebraic manipulations gives

$$\frac{\Delta l}{l_0} = \varepsilon = \frac{\sigma}{E} = \alpha_l \Delta T$$

Or, solving for σ

$$\sigma = E\alpha_l \Delta T$$

which is the form of Equation 19.8.

19.25 (a) Thermal stresses may be introduced into a structure by rapid heating or cooling because temperature gradients will be established across the cross section due to more rapid temperature changes at the surface than within the interior; thus, the surface will expand or contract at a different rate than the interior and since this surface expansion or contraction will be restrained by the interior, stresses will be introduced.

(b) For cooling, the surface stresses will be tensile in nature since the interior contracts to a lesser degree than the cooler surface.

(c) For heating, the surface stresses will be compressive in nature since the interior expands to a lesser degree than the hotter surface.

19.26 (a) We are asked to compute the magnitude of the stress within a brass rod that is heated while its ends are maintained rigid. To do this we employ Equation 19.8, using a value of 97 GPa for the modulus of elasticity of brass (Table 6.1), and a value of 20.0 x 10^{-6} (°C)$^{-1}$ for α_l (Table 19.1). Therefore

$$\sigma = E\alpha_l(T_0 - T_f)$$

$$= (97 \text{ x } 10^3 \text{ MPa})\left[20.0 \text{ x } 10^{-6} (°\text{C})^{-1}\right](15°\text{C} - 85°\text{C})$$

$$= -136 \text{ MPa} \quad (-20{,}000 \text{ psi})$$

The stress will be compressive since its sign is negative.

(b) The stress will be the same [–136 MPa (–20,000 psi)], since stress is independent of bar length.

(c) Upon cooling the indicated amount, the stress becomes

$$\sigma = E\alpha_l(T_0 - T_f)$$

$$= (97 \text{ x } 10^3 \text{ MPa})\left[20.0 \text{ x } 10^{-6} (°\text{C})^{-1}\right]\left[(15°\text{C} - (-15°\text{C})\right]$$

$$= +58 \text{ MPa} \quad (+8400 \text{ psi})$$

This stress will be tensile since its sign is positive.

19.27 We want to heat the steel wire in order to reduce the stress level from 70 MPa to 17 MPa; in doing so, we reduce the stress in the wire by 70 MPa – 17 MPa = 53 MPa, which stress will be a compressive one (i.e., σ = –53 MPa). Solving for T_f from Equation 19.8 [and using values for *E* and α_l of 207 GPa (Table 6.1) and 12.0 x 10^{-6} $(°\text{C})^{-1}$ (Table 19.1), respectively] yields

$$T_f = T_0 - \frac{\sigma}{E\alpha_l}$$

$$= 20°\text{C} - \frac{-53 \text{ MPa}}{(207 \text{ x } 10^3 \text{ MPa})\left[12.0 \text{ x } 10^{-6} \, (°\text{C})^{-1}\right]}$$

$$= 20°\text{C} + 21.3°\text{C} = 41.3°\text{C} \;\; (106°\text{F})$$

19.28 This problem asks for us to determine the change in diameter of a cylindrical brass rod 150.00 mm long and 10.000 mm in diameter when it is heated from 20°C to 160°C while its ends are maintained rigid. There will be two contributions to the diameter increase of the rod; the first is due to thermal expansion (which will be denoted as Δd_1), while the second is from Poisson's lateral expansion as a result of elastic deformation from stresses that are established from the inability of the rod to elongate as it is heated (denoted as Δd_2). The magnitude of Δd_1 may be computed using a modified form of Equation 19.3 as

$$\Delta d_1 = d_0 \alpha_l (T_f - T_0)$$

From Table 19.1 the value of α_l for brass is 20.0 x 10^{-6} $(°\mathrm{C})^{-1}$. Thus,

$$\Delta d_1 = (10.000 \text{ mm}) \left[20.0 \text{ x } 10^{-6} \ (°\mathrm{C})^{-1}\right](160°\mathrm{C} - 20°\mathrm{C})$$

$$= 0.0280 \text{ mm}$$

Now, Δd_2 is related to the transverse strain (ε_x) according to a modified form of Equation 6.2 as

$$\frac{\Delta d_2}{d_0} = \varepsilon_x$$

Also, transverse strain and longitudinal strain (ε_z) are related according to Equation 6.8:

$$\varepsilon_x = -\nu\varepsilon_z$$

where ν is Poisson’s ratio. Substitution of this expression for ε_x into the first equation above leads to

$$\frac{\Delta d_2}{d_0} = -\nu\varepsilon_z$$

Furthermore, the longitudinal strain is related to the modulus of elasticity through Equation 6.5—i.e.,

$$\varepsilon_z = \frac{\sigma}{E}$$

And, therefore,

$$\frac{\Delta d_2}{d_0} = -\nu \frac{\sigma}{E}$$

Now, from Equation 19.8 stress is equal to

$$\sigma = E\alpha_l(T_0 - T_f)$$

which, when substituted into the preceding equation leads to

$$\frac{\Delta d_2}{d_0} = -\frac{\nu E\alpha_l(T_0 - T_f)}{E} = -\nu\alpha_l(T_0 - T_f)$$

Solving for Δd_2 and realizing that, for brass, $\nu = 0.34$ (Table 6.1) yields

$$\Delta d_2 = -d_0\nu\alpha_l(T_0 - T_f)$$

$$= -(10.000 \text{ mm})(0.34)\left[20.0 \text{ x } 10^{-6} \ (°\text{C})^{-1}\right](20°\text{C} - 160°\text{C})$$

$$= 0.0095 \text{ mm}$$

Finally, the total Δd is just $\Delta d_1 + \Delta d_2 = 0.0280 \text{ mm} + 0.0095 \text{ mm} = 0.0375 \text{ mm}$.

19.29 This problem asks for us to determine to what temperature a cylindrical rod of nickel 120.00 mm long and 12.000 mm in diameter must be cooled from 70°C in order to have a 0.023-mm reduction in diameter if the rod ends are maintained rigid. There will be two contributions to the diameter decrease of the rod; the first is due to thermal contraction (which will be denoted as Δd_1), while the second is from Poisson's lateral contraction as a result of elastic deformation from stresses that are established from the inability of the rod to contract as it is cooled (denoted as Δd_2). The magnitude of Δd_1 may be computed using a modified form of Equation 19.3b as

$$\Delta d_1 = d_0 \alpha_l (T_f - T_0)$$

Now, Δd_2 is related to the transverse strain (ε_x) according to a modified form of Equation 6.2 as

$$\frac{\Delta d_2}{d_0} = \varepsilon_x$$

Also, transverse strain and longitudinal strain (ε_z) are related according to Equation 6.8:

$$\varepsilon_x = - \nu \varepsilon_z$$

where ν is Poisson’s ratio. Substitution of this expression for ε_x into the first equation above leads to

$$\frac{\Delta d_2}{d_0} = - \nu \varepsilon_z$$

Furthermore, the longitudinal strain is related to the modulus of elasticity through Equation 6.5—i.e.,

$$\varepsilon_z = \frac{\sigma}{E}$$

And, therefore,

$$\frac{\Delta d_2}{d_0} = - \nu \frac{\sigma}{E}$$

Now, from Equation 19.8 stress is equal to

$$\sigma = E\alpha_l (T_0 - T_f)$$

which, when substituted into the preceding equation leads to

$$\frac{\Delta d_2}{d_0} = -\frac{\nu E \alpha_l (T_0 - T_f)}{E} = -\nu \alpha_l (T_0 - T_f)$$

And, solving for Δd_2 from this expression

$$\Delta d_2 = -d_0 \nu \alpha_l (T_0 - T_f)$$

The total Δd is just $\Delta d = \Delta d_1 + \Delta d_2$, and

$$\Delta d = d_0 \alpha_l (T_f - T_0) + d_0 \nu \alpha_l (T_f - T_0) = d_0 \alpha_l (T_f - T_0)(1 + \nu)$$

The values of ν and α_l for nickel are 0.31 and 13.3 x 10^{-6} $(°\mathrm{C})^{-1}$, respectively (Tables 6.1 and 19.1). Incorporating, into the above equation, these values, as well as those for Δd, d_0, and T_0 cited in the problem statement gives

$$-(0.023\text{ mm}) = (12.000\text{ mm})\left[13.3 \text{ x } 10^{-6}\ (°\mathrm{C})^{-1}\right](T_f - 70°\mathrm{C})(1 + 0.31)$$

And, finally, solving the above expression for T_f yields $T_f = -40°\mathrm{C}$.

19.30 According to Equation 19.9, the thermal shock resistance of a ceramic piece may be enhanced by increasing the fracture strength and thermal conductivity, and by decreasing the elastic modulus and linear coefficient of thermal expansion. Of these parameters, σ_f and α_l are most amenable to alteration, usually be changing the composition and/or the microstructure.

DESIGN PROBLEMS

Thermal Expansion

19.D1 For these railroad tracks, each end is allowed to expand one-half of the joint space distance, or the track may expand a total of this distance (5.4 mm). Equation 19.3a is used to solve for T_f, where the value α_l for the 1025 steel [12.0×10^{-6} $(°\mathrm{C})^{-1}$] is found in Table 19.1. Thus, solving for T_f from Equation 19.3a leads to

$$T_f = \frac{\Delta l}{\alpha_l l_0} + T_0$$

$$= \frac{5.4 \times 10^{-3} \text{ m}}{\left[12.0 \times 10^{-6} \, (°\mathrm{C})^{-1}\right](11.9 \text{ m})} + 4°\mathrm{C}$$

$$= 37.8°\mathrm{C} + 4°\mathrm{C} = 41.8°\mathrm{C} \ \ (107.3°\mathrm{F})$$

Thermal Stresses

19.D2 This is a materials selection problem wherein we must decide for which of the five metals listed, the stress in the rod will not exceed 138 MPa (20,000 psi), when it is heated while its ends are mounted between rigid supports. Upon examination of Equation 19.8, it may be noted that all we need do is to compute the $E\alpha_l\Delta T$ product for each of the candidate materials, and then note for which of them the stress is less than the stipulated maximum. [The value of ΔT is $T_0 - T_f = 20°\text{C} - (-60°\text{C}) = 80°\text{C}$.] These parameters and their product for each of the alloys are tabulated below. (Modulus of elasticity values were taken from Table 6.1, while the α_l values came from Table 19.1.)

Alloy	α_l (°C)$^{-1}$	E (MPa)	$\alpha_l E\Delta T$ (MPa)
Aluminum	23.6×10^{-6}	69×10^3	130
Copper	17.0×10^{-6}	110×10^3	150
Brass	20.0×10^{-6}	97×10^3	155
1025 Steel	12.0×10^{-6}	207×10^3	200
Tungsten	4.5×10^{-6}	407×10^3	145

Thus, aluminum is the only suitable candidate.

19.D3 (a) This portion of the problem asks that we cite the units for the thermal shock resistance parameter (*TSR*). From Equation 19.9

$$TSR = \frac{\sigma_f \left(\mathrm{N/m^2}\right) k\,(\mathrm{W/m\text{-}K})}{E\left(\mathrm{N/m^2}\right) \alpha_l (°\mathrm{C})^{-1}} = \mathrm{W/m}$$

(Note: in reducing units in the above expression, we have assumed that units of temperature in K and °C are equivalent)

(b) Now we are asked to rank soda-lime glass, fused silica, and silicon as to their thermal shock resistance. Thus, all we need do is calculate, for each, the value of *TSR* using Equation 19.9. Values of *E*, σ_f, α_l, and *k* are found, respectively, in Tables B.2, B.4, B.6, and B.7, Appendix B. (Note: whenever a range for a property value in these tables is cited, the average of the extremes is used.)

For soda-lime glass

$$TSR = \frac{\sigma_f\, k}{E \alpha_l}$$

$$= \frac{(69 \text{ MPa})(1.7 \text{ W/m-K})}{\left(69 \text{ x } 10^3 \text{ MPa}\right)\left[9.0 \text{ x } 10^{-6}\,(°\mathrm{C})^{-1}\right]} = 189 \text{ W/m}$$

For fused silica

$$TSR = \frac{(104 \text{ MPa})(1.4 \text{ W/m-K})}{\left(73 \text{ x } 10^3 \text{ MPa}\right)\left[0.4 \text{ x } 10^{-6}\,(°\mathrm{C})^{-1}\right]} = 4986 \text{ W/m}$$

And, for silicon

$$TSR = \frac{(130 \text{ MPa})(141 \text{ W/m-K})}{\left(129 \text{ x } 10^3 \text{ MPa}\right)\left[2.5 \text{ x } 10^{-6}\,(°\mathrm{C})^{-1}\right]} = 56{,}800 \text{ W/m}$$

Thus, these materials may be ranked according to their thermal shock resistance from the greatest to the least as follows: silicon, fused silica, and soda-lime glass.

19.D4 We want to compute the maximum temperature change allowable without thermal shock for these several ceramic materials, which temperature change is a function of the fracture strength, elastic modulus, and linear coefficient of thermal expansion. These data and the ΔT_f's are tabulated below. (Values for E, σ_f, and α_l are taken from Tables B.2, B.4, B.6 in Appendix B.)

Material	σ_f (MPa)	E (MPa)	α_l (°C)$^{-1}$	ΔT_f (°C)
Soda-lime glass	69	69×10^3	9.0×10^{-6}	111
Borosilicate glass	69	70×10^3	3.3×10^{-6}	300
Aluminum oxide (96%)	358	303×10^3	7.4×10^{-6}	160
Gallium arsenide	57	85×10^3	5.9×10^{-6}	114

CHAPTER 20

MAGNETIC PROPERTIES

PROBLEM SOLUTIONS

Basic Concepts

20.1 (a) We may calculate the magnetic field strength generated by this coil using Equation 20.1 as

$$H = \frac{NI}{l}$$

$$= \frac{(400 \text{ turns})(15 \text{ A})}{0.25 \text{ m}} = 24{,}000 \text{ A - turns/m}$$

(b) In a vacuum, the flux density is determined from Equation 20.3. Thus,

$$B_0 = \mu_0 H$$

$$= (1.257 \text{ x } 10^{-6} \text{ H/m})(24{,}000 \text{ A - turns/m}) = 3.0168 \text{ x } 10^{-2} \text{ tesla}$$

(c) When a bar of chromium is positioned within the coil, we must use an expression that is a combination of Equations 20.5 and 20.6 in order to compute the flux density given the magnetic susceptibility. Inasmuch as χ_m = 3.13 x 10^{-4} (Table 20.2), then

$$B = \mu_0 H + \mu_0 M = \mu_0 H + \mu_0 \chi_m H = \mu_0 H(1 + \chi_m)$$

$$= (1.257 \text{ x } 10^{-6} \text{ H/m})(24{,}000 \text{ A - turns/m})(1 + 3.13 \text{ x } 10^{-4})$$

$$= 3.0177 \text{ x } 10^{-2} \text{ tesla}$$

which is essentially the same result as part (b). This is to say that the influence of the chromium bar within the coil makes an imperceptible difference in the magnitude of the *B* field.

(d) The magnetization is computed from Equation 20.6:

$$M = \chi_m H = (3.13 \text{ x } 10^{-4})(24{,}000 \text{ A - turns/m}) = 7.51 \text{ A/m}$$

20.2 This problem asks us to show that χ_m and μ_r are related according to $\chi_m = \mu_r - 1$. We begin with Equation 20.5 and substitute for M using Equation 20.6. Thus,

$$B = \mu_0 H + \mu_0 M = \mu_0 H + \mu_0 \chi_m H$$

But B is also defined in Equation 20.2 as

$$B = \mu H$$

When the above two expressions are set equal to one another as

$$\mu H = \mu_0 H + \mu_0 \chi_m H$$

This leads to

$$\mu = \mu_0 (1 + \chi_m)$$

If we divide both sides of this expression by μ_0, and from the definition of μ_r (Equation 20.4), then

$$\frac{\mu}{\mu_0} = \mu_r = 1 + \chi_m$$

or, upon rearrangement

$$\chi_m = \mu_r - 1$$

which is the desired result.

20.3 For this problem, we want to convert the volume susceptibility of copper $\left(\text{i.e., } -0.96 \text{ x } 10^{-5}\right)$ into other systems of units.

For the mass susceptibility

$$\chi_m(\mathrm{kg}) = \frac{\chi_m}{\rho\,(\mathrm{kg/m^3})}$$

$$= \frac{-0.96 \text{ x } 10^{-5}}{8.96 \text{ x } 10^3 \text{ kg/m}^3} = -1.07 \text{ x } 10^{-9}$$

For the atomic susceptibility

$$\chi_m(\mathrm{a}) = \chi_m(\mathrm{kg}) \text{ x } \left[\text{atomic weight (in kg)}\right]$$

$$= \left(-1.07 \text{ x } 10^{-9}\right)(0.06355 \text{ kg/mol}) = -6.81 \text{ x } 10^{-11}$$

For the cgs-emu susceptibilities,

$$\chi'_m = \frac{\chi_m}{4\pi} = \frac{-0.96 \text{ x } 10^{-5}}{4\pi} = -7.64 \text{ x } 10^{-7}$$

$$\chi'_m(\mathrm{g}) = \frac{\chi'_m}{\rho(\mathrm{g/cm^3})} = \frac{-7.64 \text{ x } 10^{-7}}{8.96 \text{ g/cm}^3} = -8.53 \text{ x } 10^{-8}$$

$$\chi_m^{\tilde{O}}(\mathrm{a}) = \chi_m^{\tilde{O}}(\mathrm{g}) \text{ x } \left[\text{atomic weight (in g)}\right]$$

$$= \left(-8.53 \text{ x } 10^{-8}\right)(63.55 \text{ g/mol}) = -5.42 \text{ x } 10^{-6}$$

20.4 (a) The two sources of magnetic moments for electrons are the electron's orbital motion around the nucleus, and also, its spin.

(b) Each electron will have a net magnetic moment from spin, and possibly, orbital contributions, which do not cancel for an isolated atom.

(c) All atoms do not have a net magnetic moment. If an atom has completely filled electron shells or subshells, there will be a cancellation of both orbital and spin magnetic moments.

Diamagnetism and Paramagnetism

Ferromagnetism

20.5 (a) The magnetic permeability of this material may be determined according to Equation 20.2 as

$$\mu = \frac{B}{H} = \frac{0.630 \text{ tesla}}{5 \text{ x } 10^5 \text{ A/m}} = 1.26 \text{ x } 10^{-6} \text{ H/m}$$

(b) The magnetic susceptibility is calculated using a combined form of Equations 20.4 and 20.7 as

$$\chi_m = \mu_r - 1 = \frac{\mu}{\mu_0} - 1$$

$$= \frac{1.26 \text{ x } 10^{-6} \text{ H/m}}{1.257 \text{ x } 10^{-6} \text{ H/m}} - 1 = 2.39 \text{ x } 10^{-3}$$

(c) This material would display both diamagnetic and paramagnetic behavior. All materials are diamagnetic, and since χ_m is positive and on the order of 10^{-3}, there would also be a paramagnetic contribution.

20.6 (a) This portion of the problem calls for us to compute the magnetic susceptibility within a bar of some metal alloy when $M = 1.2 \times 10^6$ A/m and H =200 A/m. This requires that we solve for χ_m from Equation 20.6 as

$$\chi_m = \frac{M}{H} = \frac{1.2 \times 10^6 \text{ A/m}}{200 \text{ A/m}} = 6000$$

(b) In order to calculate the permeability we must employ a combined form of Equations 20.4 and 20.7 as follows:

$$\mu = \mu_r \mu_0 = (\chi_m + 1)\mu_0$$

$$= (6000 + 1)(1.257 \times 10^{-6} \text{ H/m}) = 7.54 \times 10^{-3} \text{ H/m}$$

(c) The magnetic flux density may be determined using Equation 20.2 as

$$B = \mu H = (7.54 \times 10^{-3} \text{ H/m})(200 \text{ A/m}) = 1.51 \text{ tesla}$$

(d) This metal alloy would exhibit ferromagnetic behavior on the basis of the magnitude of its χ_m (6000), which is considerably larger than the χ_m values for diamagnetic and paramagnetic materials listed in Table 20.2.

20.7 (a) The saturation magnetization for Fe may be determined in the same manner as was done for Ni in Example Problem 20.1. Thus, using a modified form of Equation 20.9

$$M_s = 2.2 \mu_B N$$

in which μ_B is the Bohr magneton and N is the number of Fe atoms per cubic meter. Also, there are 2.2 Bohr magnetons per Fe atom. Now, N (the number of iron atoms per cubic meter) is related to the density and atomic weight of Fe, and Avogadro's number according to Equation 20.10 as

$$N = \frac{\rho_{\text{Fe}} N_{\text{A}}}{A_{\text{Fe}}}$$

$$= \frac{(7.87 \text{ x } 10^6 \text{ g/m}^3)(6.023 \text{ x } 10^{23} \text{atoms/mol})}{55.85 \text{ g/mol}}$$

$$= 8.49 \text{ x } 10^{28} \text{ atoms/m}^3$$

Therefore,

$$M_s = 2.2\ \mu_B N = (2.2 \text{ BM/atom})(9.27 \text{ x } 10^{-24} \text{ A - m}^2\text{/BM})(8.49 \text{ x } 10^{28} \text{ atoms/m}^3)$$

$$= 1.73 \text{ x } 10^6 \text{ A/m}$$

(b) The saturation flux density is determined according to Equation 20.8. Thus

$$B_s = \mu_0 M_s$$

$$= (1.257 \text{ x } 10^{-6} \text{ H/m})(1.73 \text{ x } 10^6 \text{ A/m}) = 2.18 \text{ tesla}$$

20.8 We want to confirm that there are 1.72 Bohr magnetons associated with each cobalt atom. Therefore, let n'_B be the number of Bohr magnetons per atom, which we will calculate. This is possible using a modified and rearranged form of Equation 20.9—that is

$$n'_B = \frac{M_s}{\mu_B N}$$

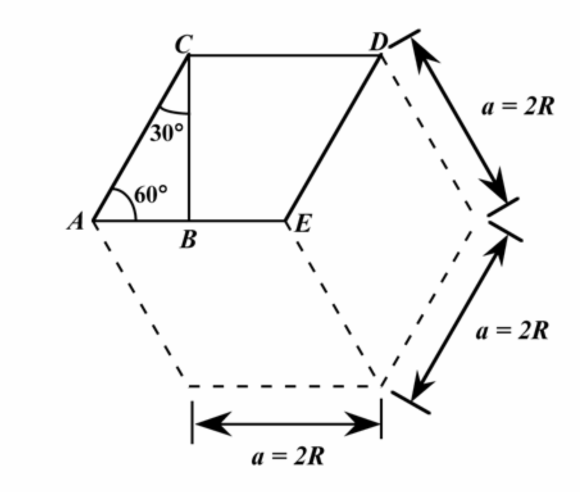
Now, N is just the number of atoms per cubic meter, which is the number of atoms per unit cell (six for HCP, Section 3.4) divided by the unit cell volume-- that is,

$$N = \frac{6}{V_C}$$

which, when substituted into the first equation gives

$$n'_B = \frac{M_s V_C}{6\mu_B}$$

Now, the unit cell volume is just the product of the base area times the cell height, c. This base area is just three times the area of the parallelepiped *ACDE* shown below.



The area of *ACDE* is just the length of $\overline{CD}$ times the height $\overline{BC}$. But $\overline{CD}$ is just a, the unit cell edge length, and

$$\overline{BC} = a \cos (30°) = \frac{a\sqrt{3}}{2}$$

Thus, the base area is just

$$\text{AREA} = (3)(\overline{CD})(\overline{BC}) = (3)(a)\left(\frac{a\sqrt{3}}{2}\right) = \frac{3a^2}{2}\sqrt{3}$$

and since $c = 1.623a$

$$V_C = (\text{AREA})(c) = \frac{3a^2 c}{2}\sqrt{3} = \frac{3a^2(1.623)a}{2}\sqrt{3} = \frac{3a^3(1.623)}{2}\sqrt{3}$$

Thus, substitution of this equation with the one above for

$$n'_{\text{B}} = \frac{M_s V_C}{6\mu_{\text{B}}} = \frac{M_s}{6\mu_{\text{B}}}\left[\frac{3(1.623)\sqrt{3}a^3}{2}\right]$$

and, since $a = 0.2506$ nm, the value of n'_{B} is calculated as

$$n'_{\text{B}} = \frac{(1.45 \times 10^6 \text{ A/m})}{(6 \text{ atoms/unit cell})(9.27 \times 10^{-24} \text{ A-m}^2/\text{Bohr magneton})}\left[\frac{3(1.623)\sqrt{3}(0.2506 \times 10^{-9} \text{ m})^3/\text{unit cell}}{2}\right]$$

$$= 1.73 \text{ Bohr magnetons/atom}$$

20.9 We are to determine the number of Bohr magnetons per atom for a hypothetical metal that has a simple cubic crystal structure, an atomic radius of 0.125 nm, and a saturation flux density of 0.85 tesla. It becomes necessary to employ Equation 20.8 and a modified form of Equation 20.9 as follows:

$$n_\mathrm{B} = \frac{M_s}{\mu_\mathrm{B} N} = \frac{\dfrac{B_s}{\mu_0}}{\mu_\mathrm{B} N} = \frac{B_s}{\mu_0 \mu_\mathrm{B} N}$$

Here n_B is the number of Bohr magnetons per atom, and N is just the number of atoms per cubic meter, which is the number of atoms per unit cell [one for simple cubic (Figure 3.23)] divided by the unit cell volume—that is,

$$N = \frac{1}{V_C}$$

which, when substituted into the above equation gives

$$n_\mathrm{B} = \frac{B_s V_C}{\mu_0 \mu_\mathrm{B}}$$

For the simple cubic crystal structure (Figure 3.23), $a = 2r$, where r is the atomic radius, and $V_C = a^3 = (2r)^3$. Substituting this relationship into the above equation yields

$$n_\mathrm{B} = \frac{B_s\,(2r)^3}{\mu_0\,\mu_\mathrm{B}}$$

$$= \frac{(0.85\ \text{tesla})(8)\left(0.125\ \text{x}\ 10^{-9}\ \text{m}\right)^3}{\left(1.257\ \text{x}\ 10^{-6}\ \text{H/m}\right)\left(9.27\ \text{x}\ 10^{-24}\ \text{A-m}^2/\text{BM}\right)} = 1.14\ \text{Bohr magnetons/atom}$$

20.10 Ferromagnetic materials may be permanently magnetized (whereas paramagnetic ones may not) because of the ability of net spin magnetic moments of adjacent atoms to align with one another. This mutual magnetic moment alignment in the same direction exists within small volume regions--domains. When a magnetic field is applied, favorably oriented domains grow at the expense of unfavorably oriented ones, by the motion of domain walls. When the magnetic field is removed, there remains a net magnetization by virtue of the resistance to movement of domain walls; even after total removal of the magnetic field, the magnetization of some net domain volume will be aligned near the direction that the external field was oriented.

For paramagnetic materials, there is no magnetic dipole coupling, and, consequently, domains do not form. When a magnetic field is removed, the atomic dipoles assume random orientations, and no magnetic moment remains.

Antiferromagnetism and Ferrimagnetism

20.11 Hund's rule states that the spins of the electrons of a shell will add together in such a way as to yield the maximum magnetic moment. This means that as electrons fill a shell the spins of the electrons that fill the first half of the shell are all oriented in the same direction; furthermore, the spins of the electrons that fill the last half of this same shell will all be aligned and oriented in the opposite direction. For example, consider the iron ions in Table 20.4; from Table 2.2, the electron configuration for the outermost shell for the Fe atom is $3d^6 4s^2$. For the Fe^{3+} ion the outermost shell configuration is $3d^5$, which means that five of the ten possible 3*d* states are filled with electrons. According to Hund's rule the spins of all of these electrons are aligned, there will be no cancellation, and therefore, there are five Bohr magnetons associated with each Fe^{3+} ion, as noted in the table. For Fe^{2+} the configuration of the outermost shell is $3d^6$, which means that the spins of five electrons are aligned in one direction, and the spin of a single electron is aligned in the opposite direction, which cancels the magnetic moment of one of the other five; thus, this yields a net moment of four Bohr magnetons.

For Mn^{2+} the electron configuration is $3d^5$, the same as Fe^{3+}, and, therefore it will have the same number of Bohr magnetons (i.e., five).

For Co^{2+} the electron configuration is $3d^7$, which means that the spins of five electrons are in one direction, and two are in the opposite direction, which gives rise to a net moment of three Bohr magnetons.

For Ni^{2+} the electron configuration is $3d^8$ which means that the spins of five electrons are in one direction, and three are in the opposite direction, which gives rise to a net moment of two Bohr magnetons.

For Cu^{2+} the electron configuration is $3d^9$ which means that the spins of five electrons are in one direction, and four are in the opposite direction, which gives rise to a net moment of one Bohr magneton.

20.12 (a) The saturation magnetization of cobalt ferrite is computed in the same manner as Example Problem 20.2; from Equation 20.13

$$M_s = \frac{n_B \mu_B}{a^3}$$

Now, n_B is just the number of Bohr magnetons per unit cell. The net magnetic moment arises from the Co^{2+} ions, of which there are eight per unit cell, each of which has a net magnetic moment of three Bohr magnetons (Table 20.4). Thus, n_B is twenty-four. Therefore, from the above equation

$$M_s = \frac{(24 \text{ BM/unit cell})(9.27 \text{ x } 10^{-24} \text{ A - m}^2/\text{BM})}{(0.838 \text{ x } 10^{-9} \text{ m})^3/\text{unit cell}}$$

$$= 3.78 \text{ x } 10^5 \text{ A/m}$$

(b) This portion of the problem calls for us to compute the saturation flux density. From Equation 20.8

$$B_s = \mu_0 M_s$$

$$= (1.257 \text{ x } 10^{-6} \text{ H/m})(3.78 \text{ x } 10^5 \text{ A/m}) = 0.475 \text{ tesla}$$

20.13 We want to compute the number of Bohr magnetons per Cu^{2+} ion in $(CuFe_2O_4)_8$. Let n_B represent the number of Bohr magnetons per Cu^{2+} ion; then, using Equation 20.9, we have

$$M_s = n_B \mu_B N$$

in which N is the number of Cu^{2+} ions per cubic meter of material. But, from Equation 20.10

$$N = \frac{\rho N_A}{A}$$

Here A is the molecular weight of $CuFe_2O_4$ (239.25 g/mol). Thus, combining the previous two equations

$$M_s = \frac{n_B \mu_B \rho N_A}{A}$$

or, upon rearrangement (and expressing the density in units of grams per meter cubed),

$$n_B = \frac{M_s A}{\mu_B \rho N_A}$$

$$= \frac{(1.35 \text{ x } 10^5 \text{ A/m})(239.25 \text{ g/mol})}{(9.27 \text{ x } 10^{-24} \text{ A-m}^2\text{/BM})(5.40 \text{ x } 10^6 \text{ g/m}^3)(6.023 \text{ x } 10^{23} \text{ ions/mol})}$$

$$= 1.07 \text{ Bohr magnetons/Cu}^{2+} \text{ ion}$$

20.14 For this problem we are given that samarium iron garnet may be written in the form $\mathrm{Sm}_3^c\mathrm{Fe}_2^a\mathrm{Fe}_3^d\mathrm{O}_{12}$ where the superscripts *a*, *c*, and *d* represent different sites on which the Sm^{3+} and Fe^{3+} ions are located, and that the spin magnetic moments for the ions on *a* and *c* sites are oriented parallel to one another and antiparallel to the Fe^{3+} ions on the *d* sites. We are to determine the number of Bohr magnetons associated with each Sm^{3+} ion given that each unit cell consists of eight formula units, the unit cell is cubic with an edge length of 1.2529 nm, the saturation magnetization for the material is 1.35 x 10^5 A/m, and that there are 5 Bohr magnetons for each Fe^{3+} ion.

The first thing to do is to calculate the number of Bohr magnetons per unit cell, which we will denote n_B. Solving for n_B using Equation 20.13, we get

$$n_\mathrm{B} = \frac{M_s a^3}{\mu_\mathrm{B}}$$

$$= \frac{(1.35 \times 10^5 \mathrm{A/m})(1.2529 \text{ x } 10^{-9} \mathrm{m})^3}{9.27 \text{ x } 10^{-24} \mathrm{A\text{-}m^2/BM}} = 28.64 \text{ Bohr magnetons/unit cell}$$

Now, there are 8 formula units per unit cell or $\frac{28.64}{8} = 3.58$ Bohr magnetons per formula unit. Furthermore, for each formula unit there are two Fe^{3+} ions on *a* sites and three Fe^{3+} on *d* sites which magnetic moments are aligned antiparallel. Since there are 5 Bohr magnetons associated with each Fe^{3+} ion, the net magnetic moment contribution per formula unit from the Fe^{3+} ions is 5 Bohr magnetons. This contribution is antiparallel to the contribution from the Sm^{3+} ions, and since there are three Sm^{3+} ions per formula unit, then

$$\text{No. of Bohr magnetons/Sm}^{3+} = \frac{3.58 \text{ BM} + 5 \text{ BM}}{3} = 2.86 \text{ BM}$$

The Influence of Temperature on Magnetic Behavior

20.15 For ferromagnetic materials, the saturation magnetization decreases with increasing temperature because the atomic thermal vibrational motions counteract the coupling forces between the adjacent atomic dipole moments, causing some magnetic dipole misalignment. Ferromagnetic behavior ceases above the Curie temperature because the atomic thermal vibrations are sufficiently violent so as to completely destroy the mutual spin coupling forces.

Domains and Hysteresis

20.16 The phenomenon of magnetic hysteresis and an explanation as to why it occurs for ferromagnetic and ferrimagnetic materials is given in Section 20.7.

20.17 (a) This portion of the problem asks that we compute the flux density in a coil of wire 0.5 m long, having 20 turns, and carrying a current of 1.0 A, and that is situated in a vacuum. Combining Equations 20.1 and 20.3, and solving for *B* yields

$$B_0 = \mu_0 H = \frac{\mu_0 N I}{l}$$

$$= \frac{(1.257 \text{ x } 10^{-6} \text{ H/m})(20 \text{ turns})(1.0 \text{ A})}{0.5 \text{ m}} = 5.03 \text{ x } 10^{-5} \text{ tesla}$$

(b) Now we are to compute the flux density with a bar of the iron-silicon alloy, the *B*-*H* behavior for which is shown in Figure 20.29. It is necessary to determine the value of *H* using Equation 20.1 as

$$H = \frac{NI}{l} = \frac{(20 \text{ turns})(1.0 \text{ A})}{0.5 \text{ m}} = 40 \text{ A - turns/m}$$

Using the curve in Figure 20.29, B = 1.30 tesla at H = 40 A-turns/m.

(c) Finally, we are to assume that a bar of Mo is situated within the coil, and to calculate the current that is necessary to produce the same *B* field as when the iron-silicon alloy in part (b) was used. Molybdenum is a paramagnetic material having a χ_m of 1.19 x 10^{-4} (Table 20.2). Combining Equations 20.2, 20.4, and 20.7 we solve for *H*

$$H = \frac{B}{\mu} = \frac{B}{\mu_0 \, \mu_r} = \frac{B}{\mu_0 (1 + \chi_m)}$$

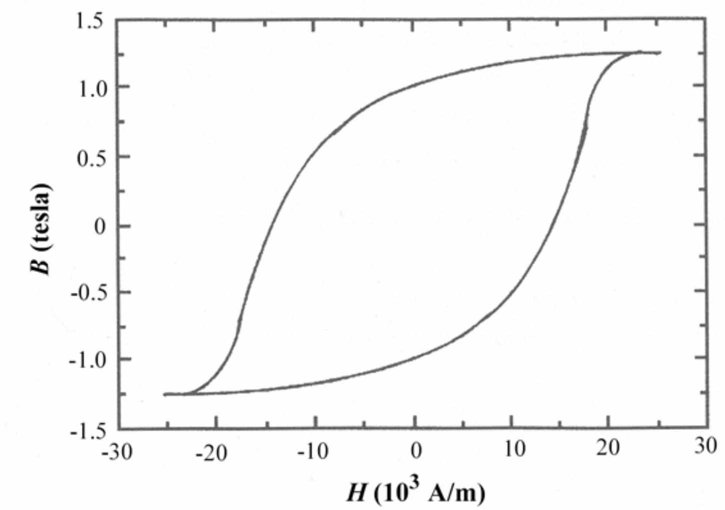
And when Mo is positioned within the coil, then, from the above equation

$$H = \frac{1.30 \text{ tesla}}{(1.257 \text{ x } 10^{-6} \text{ H/m})(1 + 1.19 \text{ x } 10^{-4})} = 1.034 \text{ x } 10^6 \text{ A - turns/m}$$

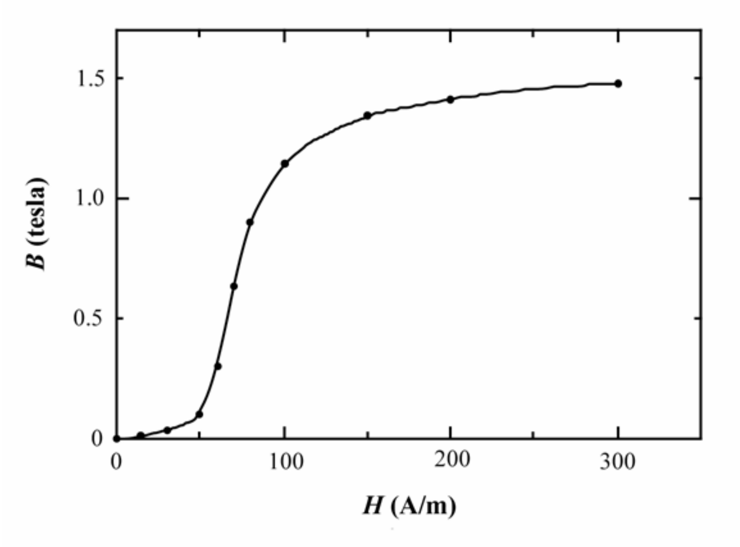
Now, the current may be determined using Equation 20.1:

$$I = \frac{Hl}{N} = \frac{(1.034 \text{ x } 10^6 \text{ A - turns/m})(0.5 \text{ m})}{20 \text{ turns}} = 25{,}850 \text{ A}$$

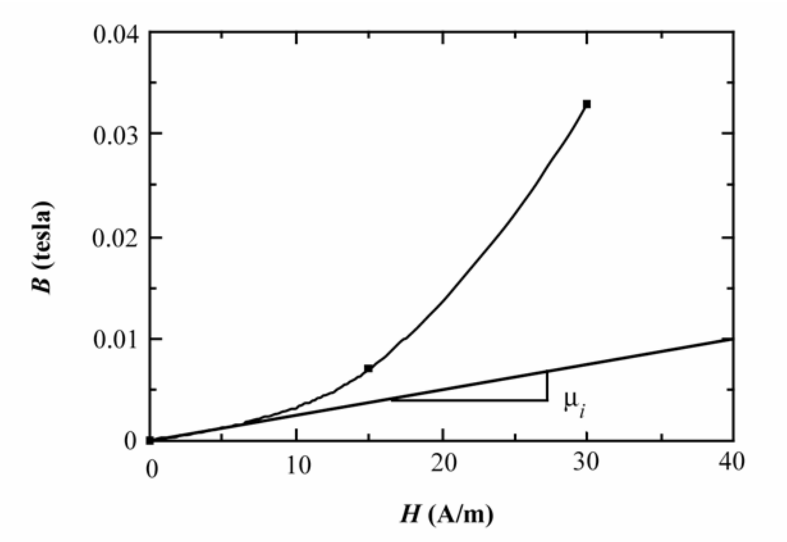
20.18 The *B* versus *H* curve for this material is shown below.



20.19 (a) The *B-H* data for the plain carbon steel provided in the problem statement are plotted below.



(b) The first three data points are plotted below.



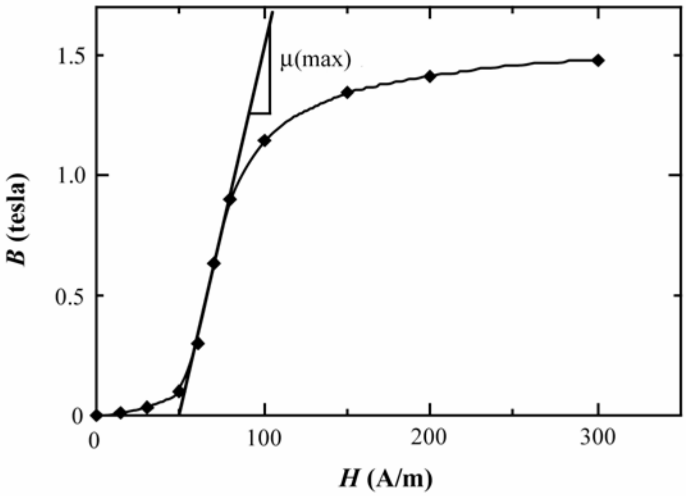
The slope of the initial portion of the curve is μ_i (as shown), is

$$\mu_i = \frac{\Delta B}{\Delta H} = \frac{(0.01 - 0)\ \text{tesla}}{(40 - 0)\ \text{A/m}} = 2.5 \text{ x } 10^{-4}\ \text{H/m}$$

Also, the initial relative permeability, μ_{ri}, (Equation 20.4) is just

$$\mu_{ri} = \frac{\mu_i}{\mu_0} = \frac{2.5 \text{ x } 10^{-4}\ \text{H/m}}{1.257 \text{ x } 10^{-6}\ \text{H/m}} = 200$$

(c) The maximum permeability is the tangent to the *B*-*H* curve having the greatest slope; it is drawn on the plot below, and designated as μ(max).



The value of μ(max) is (modifying Equation 20.2)

$$\mu(\text{max}) = \frac{\Delta B}{\Delta H} = \frac{(1.5 - 0)\ \text{tesla}}{(100 - 50)\ \text{A - m}} = 3.0 \text{ x } 10^{-2}\ \text{H/m}$$

(d) The *H* field at which μ(max) occurs is approximately 70 A/m [as taken from the plot shown in part (c)].

(e) We are asked for the maximum susceptibility, χ(max). Combining modified forms of Equations 20.7 and 20.4 yields

$$\chi(\text{max}) = \mu_r(\text{max}) - 1 = \frac{\mu(\text{max})}{\mu_0} - 1$$

$$= \frac{3.0 \text{ x } 10^{-2}\ \text{H/m}}{1.257 \text{ x } 10^{-6}\ \text{H/m}} - 1 = 23{,}865$$

20.20 In order to demagnetize a magnet having a coercivity of 7000 A/m, an *H* field of 7000 A/m must be applied in a direction opposite to that of magnetization. According to Equation 20.1

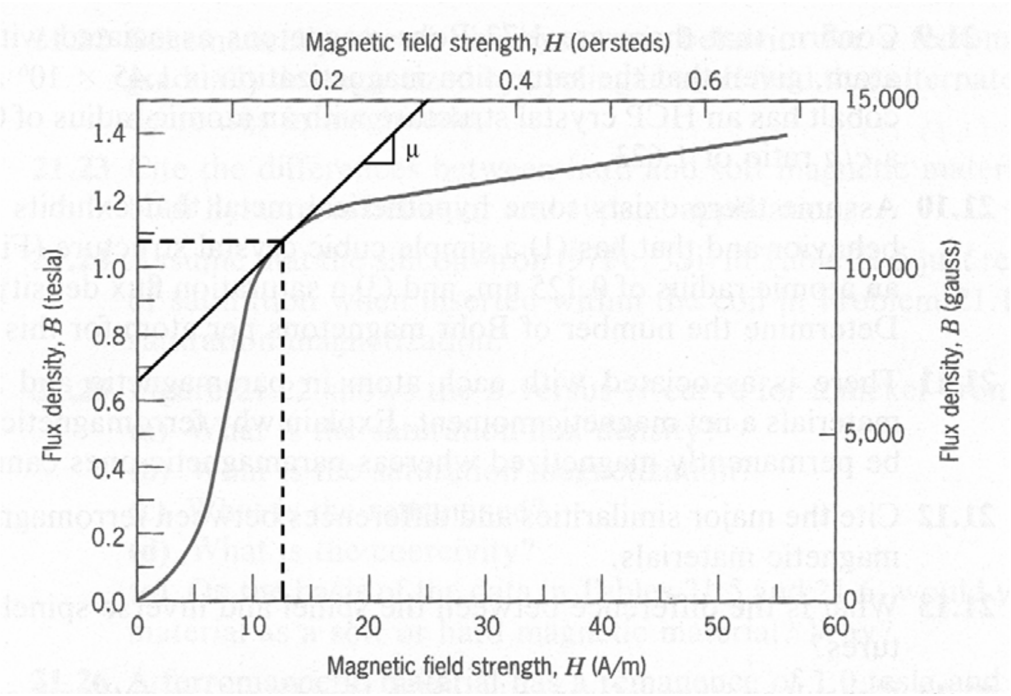
$$I = \frac{Hl}{N}$$

$$= \frac{(7000 \text{ A/m})(0.25 \text{ m})}{150 \text{ turns}} = 11.7 \text{ A}$$

20.21 (a) We want to determine the magnitude of the *B* field within an iron-silicon alloy, the *B*-*H* behavior for which is shown in Figure 20.29, when $l = 0.40$ m, $N = 50$ turns, and $I = 0.1$ A. Applying Equation 20.1

$$H = \frac{NI}{l} = \frac{(50 \text{ turns})(0.1 \text{ A})}{0.40 \text{ m}} = 12.5 \text{ A/m}$$

Below is shown the *B*-versus-*H* plot for this material. The *B* value from the curve corresponding to $H = 12.5$ A/m is about 1.07 tesla.



(b)

(i) The permeability at this field is just $\Delta B/\Delta H$ of the tangent of the *B*-*H* curve at $H = 12.5$ A/m. The slope of this line as drawn in the above figure is

$$\mu = \frac{\Delta B}{\Delta H} = \frac{(1.50 - 0.66) \text{ tesla}}{(25 - 0) \text{ A/m}} = 3.36 \times 10^{-2} \text{ H/m}$$

(ii) From Equation 20.4, the relative permeability is

$$\mu_r = \frac{\mu}{\mu_0} = \frac{3.36 \times 10^{-2} \text{ H/m}}{1.257 \times 10^{-6} \text{ H/m}} = 26,730$$

(iii) Using Equation 20.7, the susceptibility is

$$\chi_m = \mu_r - 1 = 26{,}730 - 1 = 26{,}729$$

(iv) The magnetization is determined from Equation 20.6 as

$$M = \chi_m H = (26{,}729)(12.5\ \text{A/m}) = 3.34 \text{ x } 10^5\ \text{A/m}$$

Magnetic Anisotropy

20.22 This problem asks for us to estimate saturation values of *H* for single crystal nickel in the [100], [110], and [111] directions. All we need do is read values of *H* at points A, B, and C on the curves shown in Figure 20.17. Saturation in the [111] direction (point A) is approximately 3000 A/m. Corresponding values in [110] and [111] directions are approximately 15,000 and 17,500 A/m, respectively.

20.23 In this problem we are asked to estimate the energy required to magnetize single crystals of iron in [100], [110], and [111] directions. These energies correspond to the products of μ_0 and the areas between the vertical axis of Figure 20.17 and the three curves for single crystal iron taken to the saturation magnetization. For the [100] direction this area is about 6.8 x 10^8 A^2/m^2. When this value is multiplied by the value of μ_0 (1.257 x 10^{-6} H/m), we get a value of about 850 J/m^3. The corresponding approximate areas for [110] and [111] directions are 9 x 10^9 A^2/m^2 and 1.2 x 10^{10} A^2/m^2, respectively; when multiplied by μ_0 the respective energies for [110] and [111] directions are 1.1 x 10^4 and 1.5 x 10^4 J/m^3.

Soft Magnetic Materials

Hard Magnetic Materials

20.24 Relative to hysteresis behavior, a hard magnetic material has a high remanence, a high coercivity, a high saturation flux density, high hysteresis energy losses, and a low initial permeability; a soft magnetic material, on the other hand, has a high initial permeability, a low coercivity, and low hysteresis energy losses.

With regard to applications, hard magnetic materials are utilized for permanent magnets; soft magnetic materials are used in devices that are subjected to alternating magnetic fields such as transformer cores, generators, motors, and magnetic amplifier devices.

20.25 We want to determine the saturation magnetization of the silicon-iron (97 Fe-3 Si) in Table 20.5, if it just reaches saturation when inserted within the coil described in Problem 20.1—i.e., *l* = 0.25 m, *N* = 400 turns, and *A* = 15 A.. It is first necessary to compute the *H* field within this coil using Equation 20.1 as

$$H_s = \frac{NI}{l} = \frac{(400 \text{ turns})(15 \text{ A})}{0.25 \text{ m}} = 24{,}000 \text{ A - turns/m}$$

Now, the saturation magnetization may be determined from a rearranged form of Equation 20.5 as

$$M_s = \frac{B_s - \mu_0 H_s}{\mu_0}$$

The value of B_s in Table 20.5 is 2.01 tesla; thus,

$$M_s = \frac{(2.01 \text{ tesla}) - \left(1.257 \text{ x } 10^{-6} \text{ H/m}\right)\left(24{,}000 \text{ A/m}\right)}{1.257 \text{ x } 10^{-6} \text{ H/m}}$$

$$= 1.58 \text{ x } 10^{6} \text{ A/m}$$

20.26 (a) The saturation flux density for the nickel-iron, the *B-H* behavior for which is shown in Figure 20.30, is 1.5 tesla, the maximum *B* value shown on the plot.

(b) The saturation magnetization is computed from Equation 20.8 as

$$M_s = \frac{B_s}{\mu_0}$$

$$= \frac{1.5 \text{ tesla}}{1.257 \text{ x } 10^{-6} \text{ H/m}} = 1.19 \text{ x } 10^6 \text{ A/m}$$

(c) The remanence, B_r, is read from this plot as from the hysteresis loop shown in Figure 20.14; its value is about 1.47 tesla.

(d) The coercivity, H_c, is read from this plot as from Figure 20.14; the value is about 17 A/m.

(e) On the basis of Tables 20.5 and 20.6, this is most likely a soft magnetic material. The saturation flux density (1.5 tesla) lies within the range of values cited for soft materials, and the remanence (1.47 tesla) is close to the values given in Table 20.6 for hard magnetic materials. However, the H_c (17 A/m) is significantly lower than for hard magnetic materials. Also, if we estimate the area within the hysteresis curve, we get a value of approximately 100 J/m^3, which is in line with the hysteresis loss per cycle for soft magnetic materials.

Magnetic Storage

20.27 The manner in which information is stored magnetically is discussed in Section 20.11.

Superconductivity

20.28 (a) Given Equation 20.14 and the data in Table 20.7, we are asked to calculate the critical magnetic fields for lead at 2.5 and 5.0 K. From the table, for Pb, T_C = 7.19 K and $B_C(0)$ = 0.0803 tesla. Thus, from Equation 20.2

$$H_C(0) = \frac{B_C(0)}{\mu_0}$$

$$= \frac{0.0803 \text{ tesla}}{1.257 \text{ x } 10^{-6} \text{ H/m}} = 6.39 \text{ x } 10^4 \text{ A/m}$$

Now, solving for $H_C(2.5)$ and $H_C(5.0)$ using Equation 20.14 yields

$$H_C(T) = H_C(0)\left[1 - \frac{T^2}{T_C^2}\right]$$

$$H_C(2.5) = (6.39 \text{ x } 10^4 \text{ A/m})\left[1 - \frac{(2.5 \text{ K})^2}{(7.19 \text{ K})^2}\right] = 5.62 \text{ x } 10^4 \text{ A/m}$$

$$H_C(5.0) = (6.39 \text{ x } 10^4 \text{ A/m})\left[1 - \frac{(5.0 \text{ K})^2}{(7.19 \text{ K})^2}\right] = 3.30 \text{ x } 10^4 \text{ A/m}$$

(b) Now we are to determine the temperature to which lead must be cooled in a magnetic field of 15,000 A/m in order for it to be superconductive. All we need do is to solve for T from Equation 20.14—i.e.,

$$T = T_C\sqrt{1 - \frac{H_C(T)}{H_C(0)}}$$

And, since the value of $H_C(0)$ was computed in part (a), then

$$T = (7.19 \text{ K})\sqrt{1 - \frac{15{,}000 \text{ A/m}}{63{,}900 \text{ A/m}}} = 6.29 \text{ K}$$

20.29 We are asked to determine which of the superconducting elements in Table 20.7 are superconducting at 2 K and in a magnetic field of 40,000 A/m. First of all, in order to be superconductive at 2 K within any magnetic field, the critical temperature must be greater than 2 K. Thus, aluminum, titanium, and tungsten may be eliminated upon inspection. Now, for each of lead, mercury, and tin it is necessary, using Equation 20.14, to compute the value of $H_C(2)$—also substituting for $H_C(0)$ from Equation 20.3; if $H_C(2)$ is greater than 40,000 A/m then the element will be superconductive. Hence, for Pb

$$H_C(2) = H_C(0)\left[1 - \frac{T^2}{T_C^2}\right] = \frac{B_C(0)}{\mu_0}\left[1 - \frac{T^2}{T_C^2}\right]$$

$$= \frac{0.0803 \text{ tesla}}{1.257 \text{ x } 10^{-6} \text{ H/m}}\left[1 - \frac{(2.0 \text{ K})^2}{(7.19 \text{ K})^2}\right] = 5.89 \text{ x } 10^4 \text{ A/m}$$

Since this value is greater than 40,000 A/m, Pb will be superconductive.

Similarly for Hg

$$H_C(2) = \frac{0.0411 \text{ tesla}}{1.257 \text{ x } 10^{-6} \text{ H/m}}\left[1 - \frac{(2.0 \text{ K})^2}{(4.15 \text{ K})^2}\right] = 2.51 \text{ x } 10^4 \text{ A/m}$$

Inasmuch as this value is less than 40,000 A/m, Hg will not be superconductive.

As for Sn

$$H_C(2) = \frac{0.0305 \text{ tesla}}{1.257 \text{ x } 10^{-6} \text{ H/m}}\left[1 - \frac{(2.0 \text{ K})^2}{(3.72 \text{ K})^2}\right] = 1.73 \text{ x } 10^3 \text{ A/m}$$

Therefore, Sn is not superconductive.

20.30 For type I superconductors, with increasing magnetic field the material is completely diamagnetic and superconductive below H_C, while at H_C conduction becomes normal and complete magnetic flux penetration takes place. On the other hand, for type II superconductors upon increasing the magnitude of the magnetic field, the transition from the superconducting to normal conducting states is gradual between lower-critical and upper-critical fields; so also is magnetic flux penetration gradual. Furthermore, type II generally have higher critical temperatures and critical magnetic fields.

20.31 The Meissner effect is a phenomenon found in superconductors wherein, in the superconducting state, the material is diamagnetic and completely excludes any external magnetic field from its interior. In the normal conducting state complete magnetic flux penetration of the material occurs.

20.32 The primary limitation of the new superconducting materials that have relatively high critical temperatures is that, being ceramics, they are inherently brittle.

DESIGN PROBLEMS

Ferromagnetism

20.D1 For this problem we are asked to determine the composition of a Co-Fe alloy that will yield a saturation magnetization of 1.47 x 10^6 A/m. To begin, let us compute the number of Bohr magnetons per unit cell n_B for this alloy from an expression that results from combining Equations 20.11 and 20.12. That is

$$n_B = \frac{M_s V_C}{\mu_B}$$

in which M_s is the saturation magnetization, V_C is the unit cell volume, and μ_B is the magnitude of the Bohr magneton. In Problem 20.8 it was demonstrated that, for HCP

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

Furthermore, for HCP, the unit cell edge length, *a*, and the atomic radius, *R* are related as *a* = 2*R*; also, as stipulated in the problem statement, *c* = 1.623*a*. Making these substitutions into the above equation leads to the following:

$$V_C = \frac{(3)(1.623)(2R)^3}{2}\sqrt{3}$$

From the inside of the front cover of the book, the value of *R* for Co is given as 0.125 nm (1.25 x 10^{-10} m). Therefore,

$$V_C = \frac{(3)(1.623)\left[(2)(1.25 \text{ x } 10^{-10} \text{ m})\right]^3(\sqrt{3})}{2}$$

$$= 6.59 \text{ x } 10^{-29} \text{ m}^3$$

And, now solving for n_B from the first equation above, yields

$$n_B = \; = \frac{M_s V_C}{\mu_B} = \frac{(1.47 \times 10^6 \text{ A/m})(6.59 \times 10^{-29} \text{ m}^3/\text{unit cell})}{\dfrac{9.27 \times 10^{-24} \text{ A - m}^2}{\text{Bohr magneton}}}$$

$$= \frac{10.45 \text{ Bohr magneton}}{\text{unit cell}}$$

Inasmuch as there are 1.72 and 2.22 Bohr magnetons for each of Co and Fe (Section 20.4), and, for HCP, there are 6 equivalent atoms per unit cell (Section 3.4), if we represent the fraction of Fe atoms by *x*, then

$$n_B = 10.45 \text{ Bohr magnetons/unit cell}$$

$$= \left(\frac{2.22 \text{ Bohr magnetons}}{\text{Fe atom}}\right)\left(\frac{6x \text{ Fe atoms}}{\text{unit cell}}\right) + \left(\frac{1.72 \text{ Bohr magnetons}}{\text{Co atom}}\right)\left[\frac{(6)(1 - x) \text{ Co atoms}}{\text{unit cell}}\right]$$

And solving for *x*, the fraction of Fe atoms , *x* = 0.0433, of 4.33 at% Fe.

In order to convert this composition to weight percent, we employ Equation 4.7 as

$$C_{Fe} = \frac{C'_{Fe}A_{Fe}}{C'_{Fe}A_{Fe} + C'_{Co}A_{Co}} \times 100$$

$$= \frac{(4.33 \text{ at\%})(55.85 \text{ g/mol})}{(4.33 \text{ at\%})(55.85 \text{ g/mol}) + (95.67 \text{ at\%})(58.93 \text{ g/mol})} \times 100$$

$$= 4.11 \text{ wt\%}$$

Ferrimagnetism

20.D2 This problem asks that we design a cubic mixed-ferrite magnetic material that has a saturation magnetization of 4.25 x 10^5 A/m. From Example Problem 20.2 the saturation magnetization for Fe_3O_4 is 5.0 x 10^5 A/m. In order to decrease the magnitude of M_s it is necessary to replace some fraction of the Fe^{2+} with another divalent metal ion that has a smaller magnetic moment. From Table 20.4 it may be noted that Co^{2+}, Ni^{2+}, and Cu^{2+}, with 3, 2, and 1 Bohr magnetons per ion, respectively, have fewer than the 4 Bohr magnetons/Fe^{2+} ion. Let us first consider Ni^{2+} (with 2 Bohr magnetons per ion) and employ Equation 20.13 to compute the number of Bohr magnetons per unit cell (n_B), assuming that the Ni^{2+} addition does not change the unit cell edge length (0.839 nm, Example Problem 20.2). Thus,

$$n_B = \frac{M_s a^3}{\mu_B}$$

$$= \frac{(4.25 \text{ x } 10^5 \text{ A/m})(0.839 \text{ x } 10^{-9} \text{ m})^3/\text{unit cell}}{9.27 \text{ x } 10^{-24} \text{ A-m}^2/\text{Bohr magneton}}$$

$$= 27.08 \text{ Bohr magnetons/unit cell}$$

If we let x represent the fraction of Ni^{2+} that have substituted for Fe^{2+}, then the remaining unsubstituted Fe^{2+} fraction is equal to $1 - x$. Furthermore, inasmuch as there are 8 divalent ions per unit cell, we may write the following expression:

$$n_B = 8[2x + 4(1 - x)] = 27.08$$

which leads to $x = 0.308$. Thus, if 30.8 at% of the Fe^{2+} in Fe_3O_4 are replaced with Ni^{2+}, the saturation magnetization will be decreased to 4.25 x 10^5 A/m.

Upon going through this same procedure for Co and Cu, we find that $x_{Co} = 0.615$ (or 61.5 at%) and $x_{Cu} = 0.205$ (20.5 at%) will yield the 4.25 x 10^5 A/m saturation magnetization.

CHAPTER 21

OPTICAL PROPERTIES

Electromagnetic Radiation

21.1 In order to compute the frequency of a photon of green light, we must use Equation 21.2 as

$$\nu = \frac{c}{\lambda} = \frac{3 \text{ x } 10^{8} \text{ m/s}}{5 \text{ x } 10^{-7} \text{ m}} = 6 \text{ x } 10^{14} \text{ s}^{-1}$$

Now, for the energy computation, we employ Equation 21.3 as follows:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \text{ x } 10^{-34} \text{ J-s})(3 \text{ x } 10^{8} \text{ m/s})}{5 \text{ x } 10^{-7} \text{ m}}$$

$$= 3.98 \text{ x } 10^{-19} \text{ J} \quad (2.48 \text{ eV})$$

Light Interactions with Solids

21.2 Opaque materials are impervious to light transmission; it is not possible to see through them.

Light is transmitted diffusely through translucent materials (there is some internal light scattering). Objects are not clearly distinguishable when viewed through a translucent material.

Virtually all of the incident light is transmitted through transparent materials, and one can see clearly through them.

Atomic and Electronic Interactions

21.3 (a) The phenomenon of electronic polarization by electromagnetic radiation is described in Section 21.4.

(b) Two consequences of electronic polarization in transparent materials are absorption and refraction.

Optical Properties of Metals

21.4 The electron band structures of metals are such that empty and available electron states are adjacent to filled states. Electron excitations from filled to empty states are possible with the absorption of electromagnetic radiation having frequencies within the visible spectrum, according to Equation 21.6. The light energy is totally absorbed or reflected, and, since none is transmitted, the material is opaque.

Refraction

21.5 In ionic materials, the larger the size of the component ions the greater the degree of electronic polarization.

21.6 In order for a material to have an index of refraction less than unity, the velocity of light in the material (*v*) would necessarily have to be greater than the velocity of light in a vacuum (Equation 21.7). This is not possible.

21.7 We want to compute the velocity of light in diamond given that ε_r = 5.5 and χ_m = -2.17 x 10^{-5}. The velocity is determined using Equation 21.8; but first, we must calculate the values of ε and μ for diamond. According to Equation 18.27

$$\varepsilon = \varepsilon_r \varepsilon_0 = (5.5)(8.85 \text{ x } 10^{-12} \text{ F/m}) = 4.87 \text{ x } 10^{-11} \text{ F/m}$$

Now, combining Equations 20.4 and 20.7

$$\mu = \mu_0 \mu_r = \mu_0 (\chi_m + 1)$$

$$= (1.257 \text{ x } 10^{-6} \text{ H/m})(1 - 2.17 \text{ x } 10^{-5}) = 1.257 \text{ x } 10^{-6} \text{ H/m}$$

And, finally, from Equation 21.8

$$v = \frac{1}{\sqrt{\varepsilon\mu}}$$

$$= \frac{1}{\sqrt{(4.87 \text{ x } 10^{-11} \text{ F/m})(1.257 \text{ x } 10^{-6} \text{ H/m})}}$$

$$= 1.28 \text{ x } 10^{8} \text{ m/s}$$

21.8 The frequencies of visible radiation are on the order of 10^{15} Hz (Figure 21.2). At these frequencies only electronic polarization is operable (Figure 18.34). Thus, ε_r from Equation 21.10 is the electronic contribution to ε_r; let us designate it as ε_r'. Or, in other words

$$\varepsilon_r' = n^2$$

For fused silica

$$\varepsilon_r'(\text{silica}) = (1.458)^2 = 2.13$$

And, for polystyrene (PS)

$$\varepsilon_r'(\text{PS}) = (1.60)^2 = 2.56$$

The fraction of the electronic contribution is just the ratio of ε_r' and ε_r, where ε_r values are taken from Table 18.5 (4.0 and 2.6 for fused silica and polystyrene, respectively). Thus

$$\frac{\varepsilon_r'(\text{silica})}{\varepsilon_r(60\ \text{Hz})} = \frac{2.13}{4.0} = 0.53$$

and

$$\frac{\varepsilon_r\tilde{Q}(\text{PS})}{\varepsilon_r(60\ \text{Hz})} = \frac{2.56}{2.60} = 0.98$$

21.9 This problem asks for us, using data in Table 21.1, to estimate the dielectric constants for silica glass, soda-lime glass, PTFE, polyethylene, and polystyrene, and then to compare these values with those cited in Table 18.5 and briefly explain any discrepancies. From Equation 21.10

$$\varepsilon_r = n^2$$

Thus, for fused silica, since $n = 1.458$

$$\varepsilon_r = (1.458)^2 = 2.13$$

Similarly, for soda-lime glass

$$\varepsilon_r = (1.51)^2 = 2.28$$

And, for PTFE

$$\varepsilon_r = (1.35)^2 = 1.82$$

For polyethylene

$$\varepsilon_r = (1.51)^2 = 2.28$$

For polystyrene

$$\varepsilon_r = (1.60)^2 = 2.56$$

When we compare the values of ε_r for the polymers with those in Table 18.5 at frequencies of 1 MHz, there is reasonable agreement (i.e., 1.82 versus 2.1 for PTFE, 2.28 versus 2.3 for polyethylene, and 2.56 versus 2.6 for polystyrene). However, for fused silica and soda-lime glass there are some significant discrepancies (i.e., 2.13 versus 3.8 for the fused silica, and 2.28 versus 6.9 for the soda-lime glass). The reason for these discrepancies is that for these two materials an ionic component to the dielectric constant is present at 1 MHz, but is absent at frequencies within the visible electromagnetic spectrum, which frequencies are on the order 10^9 MHz (10^{15} Hz). These effects may be noted in Figure 18.34.

21.10 Dispersion in a transparent medium is the phenomenon wherein the index of refraction varies slightly with the wavelength of the electromagnetic radiation.

Reflection

21.11 For this problem we want to compute the maximum value of n_s in Equation 21.13 that will give R = 0.050. Then we are to consult Table 21.1 in order to ascertain which of the materials listed have indices of refraction less than this maximum value. From Equation 21.13

$$0.050 = \frac{(n_s - 1)^2}{(n_s + 1)^2} = \frac{n_s^2 - 2n_s + 1}{n_s^2 + 2n_s + 1}$$

or, upon rearrangement

$$0.95\, n_s^2 - 2.10\, n_s + 0.95 = 0$$

The value of n_s is determined by using the quadratic equation solution as follows:

$$n_s = \frac{-(-2.10) \pm \sqrt{(-2.10)^2 - (4)(0.95)(0.95)}}{(2)(0.95)}$$

$$= \frac{2.10 \pm 0.894}{1.90}$$

The two solutions are: $n_s(+) = 1.576$ and $n_s(-) = 0.634$. The $n_s(+)$ solution is the one that is physically reasonable. Thus, of the materials listed, soda-lime glass, Pyrex glass, and polypropylene have indices of refraction less than 1.576, and would be suitable for this application.

21.12 The thickness and dielectric constant of a thin surface coating are selected such that there is destructive interference between the light beam that is reflected from the lens-coating interface and the light beam that is reflected from the coating-air interface; thus, the net intensity of the total reflected beam is very low.

21.13 This problem calls for a calculation of the reflectivity between two quartz grains having different orientations and indices of refraction (1.544 and 1.553) in the direction of light propagation, when the light is at normal incidence to the grain boundary. We must employ Equation 21.12 since the beam is normal to the grain boundary. Thus,

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

$$= \frac{(1.553 - 1.544)^2}{(1.553 + 1.544)^2} = 8.45 \text{ x } 10^{-6}$$

Absorption

21.14 This problem asks us to determine the range of visible light wavelengths over which ZnSe (E_g = 2.58 eV) is transparent. Only photons having energies of 2.58 eV or greater are absorbed by valence-band-to-conduction-band electron transitions. Thus, photons having energies less than 2.58 eV are not absorbed; the minimum photon energy for visible light is 1.8 eV (Equation 21.16b), which corresponds to a wavelength of 0.7 μm. From Equation 21.3, the wavelength of a photon having an energy of 2.58 eV (i.e., the band-gap energy) is just

$$\lambda = \frac{hc}{E} = \frac{\left(4.13 \text{ x } 10^{-15} \text{ eV-s}\right)\left(3 \text{ x } 10^{8} \text{ m/s}\right)}{2.58 \text{ eV}}$$

$$= 4.80 \text{ x } 10^{-7} \text{ m} = 0.48 \ \mu\text{m}$$

Thus, pure ZnSe is transparent to visible light having wavelengths between 0.48 and 0.7 μm.

21.15 The magnitude of the absorption coefficient (β in Equation 21.18) depends on the radiation wavelength for intrinsic insulators and semiconducting materials. This is because, for photons having energies less than the band-gap energy (or in terms of wavelength, when $\lambda > \frac{hc}{E_g}$), photon absorption due to valence-band-to-conduction-band electron transitions are not possible, and, therefore, the value of β will be relatively small. On the other hand, when photons having energies equal to or greater than the band gap energy (i.e., when $\lambda \leq \frac{hc}{E_g}$) these electron transitions by the absorption of photons will occur with the result that the magnitude of β will be relatively large.

In addition, there may be impurity levels that lie within the band gap (Section 21.7) from or to which electron excitations may occur with the absorption of light radiation at specific wavelengths.

21.16 In this problem we are asked to calculate the fraction of nonreflected light transmitted through a 12-mm thickness of transparent material, given that the fraction transmitted through a 5-mm thickness is 0.95. From Equation 21.18, the fraction of nonreflected light transmitted is just $I_T^{'}/I_0^{'}$. Using this expression we must first determine the value of β**;** this is possible by algebraic manipulation of Equation 21.18. Dividing both sides of the equation by $I_0^{'}$, and then taking natural logarithms leads to

$$\ln\left(\frac{I_T^{'}}{I_0^{'}}\right) = -\beta x$$

Now solving for β and also incorporating values for $I_T^{'}/I_0^{'}$ and x provided in the problem statement gives

$$\beta = -\frac{1}{x}\ln\left(\frac{I_T^{'}}{I_0^{'}}\right)$$

$$= -\left(\frac{1}{5\ \text{mm}}\right)\ln(0.95) = 1.026 \text{ x } 10^{-2}\ \text{mm}^{-1}$$

And computation of $I_T^{'}/I_0^{'}$ when x = 12 mm (Equation 21.18) is as follows:

$$\frac{I_T^{'}}{I_0^{'}} = \exp(-\beta x)$$

$$= \exp\left[-(1.026 \text{ x } 10^{-2}\ \text{mm}^{-1})(12\ \text{mm})\right] = 0.884$$

Transmission

21.17 The problem asks that we derive Equation 21.19, which is

$$I_T = I_0(1 - R)^2\, e^{-\beta l}$$

If we examine Figure 21.7, at the front (or left) interface, some of the incident beam having intensity I_0 is reflected. Since $I_R = I_0 R$ at this surface, then

$$I_T' = I_0 - I_0 R = I_0(1 - R)$$

in which I_T' is the intensity of the nonreflected beam at the front surface that is transmitted.

Now there will be absorption of this transmitted beam as it passes through the solid and transparent medium according to Equation 21.18. Just inside the back (or right) interface, the beam has passed through a thickness l of this material ($x = l$) and, therefore, the intensity of the transmitted beam at this point (I_T'') is just

$$I_T'' = I_0(1 - R)\, e^{-\beta l}$$

Finally, a second reflection will occur at the back interface as the beam passes out of the medium. The intensity of the reflected beam (I_R'') is just

$$I_R'' = I_T'' R = I_0 R(1 - R)\, e^{-\beta l}$$

And the intensity of the final transmitted beam (I_T) becomes

$$I_T = I_T'' - I_R''$$

$$= I_0(1 - R)\, e^{-\beta l} - I_0 R(1 - R)\, e^{-\beta l}$$

$$= I_0(1 - R)^2\, e^{-\beta l}$$

which is Equation 21.19, the desired expression.

21.18 We are asked to compute the thickness of material to yield a transmissivity of 0.70 given that *T* is 0.80 when l = 15 mm, n = 1.5, and for normally incident radiation. The first requirement is that we calculate the value of β for this material using Equations 21.13 and 21.19. The value of *R* is determined using Equation 21.13 as

$$R = \frac{(n_s - 1)^2}{(n_s + 1)^2}$$

$$= \frac{(1.5 - 1)^2}{(1.5 + 1)^2} = 4.0 \text{ x } 10^{-2}$$

Now, it is necessary to compute the value of β using Equation 21.19. Dividing both sides of Equation 21.19 by $I_0(1 - R)^2$ leads to

$$\frac{I_T}{I_0(1 - R)^2} = e^{-\beta l}$$

And taking the natural logarithms of both sides of this expression gives

$$\ln\left[\frac{I_T}{I_0(1 - R)^2}\right] = -\beta l$$

and solving for β we get

$$\beta = -\frac{1}{l}\ln\left[\frac{I_T}{I_0(1 - R)^2}\right]$$

Since the transmissivity is *T* is equal to I_T/I_0, then the above equation takes the form

$$\beta = -\frac{1}{l}\ln\left[\frac{T}{(1 - R)^2}\right]$$

Using values for l and *T* provided in the problem statement, as well as the value of *R* determined above, we solve for β as

$$\beta = -\left(\frac{1}{15 \text{ mm}}\right)\ln\left[\frac{0.80}{\left(1 - 4.0 \text{ x } 10^{-2}\right)^2}\right] = 9.43 \text{ x } 10^{-3} \text{ mm}^{-1}$$

Now, solving for l when T = 0.70 using the rearranged form of Equation 21.19 above

$$l = -\frac{1}{\beta}\ln\left[\frac{T}{(1-R)^2}\right]$$

$$= -\frac{1}{9.43 \text{ x } 10^{-3} \text{ mm}^{-1}}\ln\left[\frac{0.70}{(1-4.0 \text{ x } 10^{-2})^2}\right]$$

$$= 29.2 \text{ mm}$$

Color

21.19 (a) The characteristic color of a metal is determined by the distribution of wavelengths of the nonabsorbed light radiation that is reflected.

(b) The characteristic color of a transparent nonmetal is determined by the distribution of wavelengths of the nonabsorbed light radiation that is transmitted through the material.

21.20 For a transparent material that appears colorless, any absorption within its interior is the same for all visible wavelengths. On the other hand, if there is any selective absorption of visible light (usually by electron excitations), the material will appear colored, its color being dependent on the frequency distribution of the transmitted light beam.

Opacity and Translucency in Insulators

21.21 The three absorption mechanisms in nonmetallic materials involve electronic polarization, electron transitions, and scattering. Electronic polarization is described in Section 21.4; absorption by electron transitions is discussed in Sections 21.4 and 21.7; and scattering is discussed in Section 21.10.

21.22 Amorphous polymers are normally transparent because there is no scattering of a light beam within the material. However, for semicrystalline polymers, visible light will be scattered at boundaries between amorphous and crystalline regions since they have different indices of refraction. This leads to translucency or, for extensive scattering, opacity, except for semicrystalline polymers having very small crystallites.

Luminescence
Photoconductivity
Lasers

21.23 (a) The phenomenon of luminescence is described in Section 21.11.

(b) The feature that distinguishes fluorescence from phosphorescence is the magnitude of the time interval between photon absorption and reemission events. Fluorescence is for delay times less than a second; phosphorescence occurs for longer times.

21.24 The phenomenon of photoconductivity is explained in Section 21.12.

21.25 A photographic light meter is used to measure the intensity of incident light radiation. Each photon of incident light induces a valence-band-to-conduction band electron transition in which both electrons and holes are produced, as depicted in Figure 21.5(a). The magnitude of the photoinduced current resulting from these transitions is registered, which is proportional to the numbers of electrons and holes, and thus, the number of incident photons, or, equivalently, the intensity of the incident light radiation.

21.26 Section 21.13 contains a description of the operation of a ruby laser.

21.27 This problem asks for the difference in energy between metastable and ground electron states for a ruby laser. The wavelength of the radiation emitted by an electron transition from the metastable to ground state is cited as 0.6943 μm. The difference in energy between these states, ΔE, may be determined from a combined form of Equations 21.6 and 21.2, as

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$= \frac{(4.13 \text{ x } 10^{-15} \text{ eV-s})(3 \text{ x } 10^{8} \text{ m/s})}{6.943 \text{ x } 10^{-7} \text{ m}}$$

$$= 1.78 \text{ eV}$$

Optical Fibers in Communications

21.28 This problem asks for us to determine the value of the absorption coefficient for optical fiber glass given that β for window glass is 10^{-4} mm^{-1}; furthermore, the intensity of nonabsorbed light transmitted through a 25-mm thickness of window glass is equivalent to the nonabsorbed light transmitted through a 16-km length of the optical fiber material. Using Equation 21.18, it is first necessary to compute the fraction of light transmitted through the window glass—i.e., $\frac{I_T'}{I_0'}$. Thus

$$\frac{I_T'}{I_0'} = e^{-\beta x}$$

$$= \quad e^{-\,(10^{-4}\,\text{mm}^{-1})(25.4\,\text{mm})} = 0.9975$$

Now, solving for β from Equation 21.18 leads to

$$\beta = -\frac{1}{x}\ln\left(\frac{I_T'}{I_0'}\right)$$

And substitution into this expression the above value for $\frac{I_T'}{I_0'}$ (0.9975) and x = 16 km = 16 x 10^3 m = 16 x 10^6 mm yields

$$\beta = -\frac{1}{16\ \text{x}10^6\ \text{mm}}\ \ln\ (0.9975) = 1.56\ \text{x}\ 10^{-10}\ \text{mm}^{-1}$$

DESIGN PROBLEM

Atomic and Electronic Interactions

21.D1 This problem stipulates that GaAs and GaP have room-temperature band gap energies of 1.42 and 2.25 eV, respectively, that they form solid solutions in all proportions, that alloys of these two semiconductors are used for light-emitting diodes wherein light is generated by conduction band-to-valence band electron transitions, and that the band gap of a GaAs-GaP alloy increases approximately linearly with GaP additions (in mol%). We are asked to determine the composition of an alloy that will emit red light having a wavelength of 0.68 μm. It first becomes necessary to compute the band-gap energy corresponding to this wavelength of light using Equation 21.3 as

$$E_g = \frac{hc}{\lambda}$$

$$= \frac{(4.13 \text{ x } 10^{-15} \text{ eV-s})(3 \text{ x } 10^{8} \text{ m/s})}{0.68 \text{ x } 10^{-6} \text{ m}} = 1.82 \text{ eV}$$

Realizing that at 0 mol% GaP, E_g = 1.42 eV, while at 100 mol% GaP, E_g = 2.25 eV, it is possible to set up the relationship

$$\frac{100 \text{ mol\%} - C_{\text{GaP}}}{100 \text{ mol\%} - 0 \text{ mol\%}} = \frac{2.25 \text{ eV} - 1.82 \text{ eV}}{2.25 \text{ eV} - 1.42 \text{ eV}}$$

Solving for C_{GaP}, the composition of GaP, we get C_{GaP} = 48.2 mol%.

CHAPTER 22

MATERIALS SELECTION AND DESIGN CONSIDERATIONS

PROBLEM SOLUTIONS

Materials Selection Using Performance Indices

22.D1 (a) This portion of the problem asks for us to determine which of the materials listed in the database of Appendix B have torsional strength performance indices greater than 10.0 (for τ_f and ρ in units of MPa and g/cm^3, respectively) and, in addition, shear strengths greater that 350 MPa. To begin, it is noted in Section 22.2 that the shear yield strength, $\tau_f = 0.6\sigma_y$. On this basis, and given that $P = \tau_f^{2/3}/\rho$ (Equation 22.9), it follows that

$$P = \frac{(0.6\sigma_y)^{2/3}}{\rho}$$

It is possible to expedite the materials selection process for this criterion using the "Engineering Material Properties" component of *VMSE* as follows:

1. Click on "Engineering Material Properties" at the bottom of the opening window.
2. In the window that appears, click on the "Show Combination/Ratio/Product" box.
3. In the next window that appears click on the "Ratio" box.
4. Click on the "Select property:" pull-down menu, and select "σ_y (Yield Strength)" item. Then click on the "Add display of selected property" box. Yield strength values of all materials will displayed in the database portion of the window.
5. Next, from the "Select property" pull-down menu select "ρ (Density)", and then click on the "Add display of selected property" box. Density values of all materials will displayed in the second column database portion of the window.
6. There are two "Power for" boxes at the bottom of the top portion window—default values in these boxes are "1.0". The in the left-most box enter "0.667" (the decimal equivalent for 2/3rds), which is the exponent to which the first column entries (i.e., the yield strength values) will be taken. Leave the default "1.0" in the right-most box, since the exponent to which the density is to be taken is "1.0".
7. Now click on the "Take Ratio" button. The $\sigma_y^{2/3}/\rho$ ratio is then displayed in the third database column.
8. Values that appear in this column may be sorted from highest to lowest value by clicking on the "Ratio" heading at the top of this column.

9. We want all metal alloys with $(0.6\sigma_y)^{2/3}/\rho$ ratios greater than 10.0. This means that we want to select from the values tabulated those metals with $\sigma_y^{2/3}/\rho$ values greater than $\dfrac{10.0}{(0.6)^{2/3}} = 14.06$.

Sixteen metal alloys are found to satisfy this criterion; these are listed along with their $(0.6\sigma_y)^{2/3}$ and σ_y values in the table below.

Alloy	Condition	$\dfrac{(0.6\sigma_y)^{2/3}}{\rho}$	σ_y
Ti-6Al-4V	Aged	17.14	1103
7075 Al	T6	16.11	505
7075 Al	T651	16.11	505
AZ31B Mg	Rolled	14.65	220
Ti-6Al-4V	Annealed	14.18	830
AZ31B Mg	Extruded	13.75	200
Ti-5Al-2.5Sn	Annealed	13.22	760
440A Stainless	Q/T, 315°C	12.73	1650
2024 Al	T3	12.63	345
4340 Steel	Q/T, 315°C	12.50	1620
4140 Steel	Q/T, 315ºC	12.24	1570
2024 Al	T351	12.13	325
6061 Al	T6	11.16	276
6061 Al	T651	11.16	276
17-7PH Stainless	PH, 510ºC	11.13	1310
17-7PH	Cold rolled	10.55	1210

Now, the second criterion calls for the material to have a shear strength greater than 350 MPa. Again, since $\sigma_y = \tau_f/0.6$, the minimum yield strength required is σ_y = 350 MPa/0.6, or σ_y = 583 MPa. Values of σ_y from the database are also given in this table. It is noted that the all aluminum and magnesium alloys are eliminated on the basis of this second criterion.

(b) This portion of the problem calls for us to conduct a cost analysis for these eight remaining alloys. Below is given a tabulation of values for $\rho/(0.6\sigma_y)^{2/3}$, relative cost $\bar{c}$ (as taken from Appendix C), and the product of these two parameters. (It should be noted that no values of $\bar{c}$ are given for five of these materials.) The three remaining materials are ranked on the basis of cost, from least to most expensive.

Alloy	Condition	$\dfrac{\rho}{(0.6\sigma_y)^{2/3}}$	$\bar{c}$	$(\bar{c})\dfrac{\rho}{(0.6\sigma_y)^{2/3}}$
17-7PH Stain.	Cold rolled	0.0948	12	1.14
Ti-6Al-4V	Annealed	0.0705	132	9.31
Ti-5Al-2.5Sn	Annealed	0.0756	157	11.87

Thus, the 17-7PH stainless steel is the overwhelming choice of the three materials for which cost data are given since it has the lowest value for the $(\bar{c})\dfrac{\rho}{(0.6\sigma_y)^{2/3}}$ product.

It is up to the student to select the best metal alloy to be used for this solid cylindrical shaft (and then to justify this selection).

22.D2 This problem asks that we conduct a stiffness-to-mass performance analysis on a solid cylindrical shaft that is subjected to a torsional stress. The stiffness performance index P_s is given as Equation 22.11 in the textbook:

$$P_s = \frac{\sqrt{G}}{\rho}$$

in which G is the shear modulus and ρ is the density. Densities for the five materials are tabulated in Table 22.1. Shear moduli for the glass and carbon fiber-reinforced composites were stipulated in the problem (8.6 and 9.2 GPa, respectively). For the three metal alloys, values of the shear modulus may be computed using Equation 6.9 and the values of the modulus of elasticity and Poisson's ratio given in Tables B.2 and B.3 in Appendix B. For example, for the 2024-T6 aluminum alloy

$$G = \frac{E}{2\,(1 + \nu)}$$

$$= \frac{72.4 \text{ GPa}}{2\ (1\ +\ 0.33)} = 27.2 \text{ GPa}$$

Values of G for the titanium alloy and 4340 steel (determined in a similar manner) are, respectively, 42.5 and 79.6 GPa.

Below are tabulated the density, shear modulus, and stiffness performance index for each of these five materials.

Material	ρ (Mg/m^3)	G (GPa)	$\frac{\sqrt{G}}{\rho}$ $\left[(\text{GPa})^{1/2}\text{m}^3/\text{Mg}\right]$
Carbon fiber-reinforced composite	1.5	9.2	2.02
Aluminum alloy (2024-T6)	2.8	27.2	1.86
Titanium alloy (Ti-6Al-4V)	4.4	42.5	1.48
Glass fiber-reinforced composite	2.0	8.6	1.47
4340 Steel (oil-quenched and tempered)	7.8	79.6	1.14

Thus, the carbon fiber-reinforced composite has the highest stiffness performance index, and the tempered steel the least.

The table shown below contains the reciprocal of the performance index in the first column, the relative cost $(\bar{c})$, and the product of these two factors, which provides a comparison of the relative costs of the materials to be used for this torsional shaft, when stiffness is an important consideration.

Material	$\frac{\rho}{\sqrt{G}}$ $\left[\mathrm{Mg/(GPa)^{1/2}\,m^3}\right]$	$\bar{c}$ (\$/\$)	$\bar{c}\left(\frac{\rho}{\sqrt{G}}\right)$ $\left[(\$/\$)\left\{\mathrm{Mg/(GPa)^{1/2}\,m^3}\right\}\right]$
4340 Steel (oil-quenched and tempered)	0.877	5	4.39
Aluminum alloy (2024-T6)	0.538	15	8.06
Glass fiber-reinforced composite	0.680	40	27.2
Carbon fiber-reinforced composite	0.495	80	39.6
Titanium alloy (Ti-4Al-6V)	0.676	110	74.4

Thus, a shaft constructed of the tempered steel would be the least expensive, whereas the most costly shaft would employ the titanium alloy.

22.D3 (a) This portion of the problem asks that we derive a performance index expression for strength analogous to Equation 22.9 for a cylindrical cantilever beam that is stressed in the manner shown in the accompanying figure. The stress on the unfixed end, σ, for an imposed force, F, is given by Equation 22.30:

$$\sigma = \frac{FLr}{I} \tag{22.D1}$$

where L and r are the rod length and radius, respectively, and I is the moment of inertia; for a cylinder the expression for I is provided in Figure 12.32:

$$I = \frac{\pi r^4}{4} \tag{22.D2}$$

Substitution of this expression for I into Equation 22.D1 leads to

$$\sigma = \frac{4FL}{\pi r^3} \tag{22.D3}$$

Now, the mass m of some given quantity of material is the product of its density (ρ) and volume. Inasmuch as the volume of a cylinder is just $\pi r^2 L$, then

$$m = \pi r^2 L \rho \tag{22.D4}$$

From this expression, the radius is just

$$r = \sqrt{\frac{m}{\pi L \rho}} \tag{22.D5}$$

Inclusion of Equation 22.D5 into Equation 22.D3 yields

$$\sigma = \frac{4F\,\pi^{1/2} L^{5/2} \rho^{3/2}}{m^{3/2}} \tag{22.D6}$$

And solving for the mass gives

$$m = \left(16\pi F^2 L^5\right)^{1/3} \frac{\rho}{\sigma^{2/3}} \tag{22.D7}$$

To ensure that the beam will not fail, we replace stress in Equation 22.D7 with the yield strength (σ_y) divided by a factor of safety (N) as

$$m = \left(16\pi F^2 L^5 N^2\right)^{1/3} \frac{\rho}{\sigma_y^{2/3}} \tag{22.D8}$$

Thus, the best materials to be used for this cylindrical cantilever beam when strength is a consideration are those having low $\frac{\rho}{\sigma_y^{2/3}}$ ratios. Furthermore, the strength performance index, P, is just the reciprocal of this ratio, or

$$P = \frac{\sigma_y^{2/3}}{\rho} \tag{22.D9}$$

The second portion of the problem asks for an expression for the stiffness performance index. Let us begin by consideration of Equation 22.31 which relates δ, the elastic deflection at the unfixed end, to the force (F), beam length (L), the modulus of elasticity (E), and moment of inertia (I) as

$$\delta = \frac{FL^3}{3EI} \tag{22.31}$$

Again, Equation 22.D2 gives an expression for I for a cylinder, which when substituted into Equation 22.31 yields

$$\delta = \frac{4FL^3}{3\pi E r^4} \tag{22.D10}$$

And, substitution of the expression for r (Equation 22.D5) into Equation 22.D10, leads to

$$\delta = \frac{4FL^3}{3\pi E\left(\sqrt{\dfrac{m}{\pi L\rho}}\right)^4}$$

$$= \frac{4FL^5\pi\rho^2}{3E\,m^2} \tag{22.D11}$$

Now solving this expression for the mass m yields

$$m = \left(\frac{4FL^5\pi}{3\delta}\right)^{1/2} \frac{\rho}{\sqrt{E}} \qquad (22.D12)$$

Or, for this cantilever situation, the mass of material experiencing a given deflection produced by a specific force is proportional to the $\frac{\rho}{\sqrt{E}}$ ratio for that material. And, finally, the stiffness performance index, *P*, is just the reciprocal of this ratio, or

$$P = \frac{\sqrt{E}}{\rho} \qquad (22.D13)$$

(b) Here we are asked to select those metal alloys in the database that have stiffness performance indices greater than 3.0 (for E and ρ in units of GPa and g/cm^3, respectively). It is possible to expedite the materials selection process for this criterion using the "Engineering Material Properties" component of *VMSE* as follows:

1. Click on "Engineering Material Properties" at the bottom of the opening window.
2. In the window that appears, click on the "Show Combination/Ratio/Product" box.
3. In the next window that appears click on the "Ratio" box.
4. Click on the "Select property:" pull-down menu, and select "*E* (Modulus of Elasticity)" item. Then click on the "Add display of selected property" box. Modulus of elasticity values of all materials will displayed in the database portion of the window.
5. Next, from the "Select property" pull-down menu select "ρ (Density)", and then click on the "Add display of selected property" box. Density values of all materials will displayed in the second column database portion of the window.
6. There are two "Power for" boxes at the bottom of the top portion window—default values in these boxes are "1.0". The in the left-most box enter "0.5" (the decimal equivalent for 1/2), which is the exponent to which the first column entries (i.e., the modulus of elasticity values) will be taken. Leave the default "1.0" in the right-most box, since the exponent to which the density is to be taken is "1.0".
7. Now click on the "Take Ratio" button. The $E^{1/2}/\rho$ ratio is then displayed in the third database column.
8. Values that appear in this column may be sorted from highest to lowest value by clicking on the "Ratio" heading at the top of this column.

Seventeen metal alloys satisfy this criterion; they and their $\frac{\sqrt{E}}{\rho}$ values are listed below, and ranked from highest to lowest value.

Alloy	Condition	$\frac{\sqrt{E}}{\rho}$
AZ31B Mg	Rolled	3.79
AZ31B Mg	Extruded	3.79
AZ91D Mg	As cast	3.71
356.0 Al	As cast, high production	3.16
356.0 Al	As cast, custom	3.16
356.0 Al	T6	3.16
6061 Al	O	3.08
6061 Al	T6	3.08
6061 Al	T651	3.08
2024 Al	O	3.07
2024 Al	T3	3.07
2024 Al	T351	3.07
1100 Al	O	3.07
1100 Al	H14	3.07
7075 Al	O	3.01
7075 Al	T6	3.01
7075 Al	T651	3.01

(c) We are now asked to do a cost analysis on the above alloys. This process may again be expedited using the “Engineering Materials Properties” database portion of *VMSE*. Repeat the procedure outlined above, except call for a display of the density in the first column, and the modulus of elasticity in the second column. Also enter into the right-most “Power for” box the value of “0.5”. Next click the “Take Ratio” button, and then sort (rank) values from lowest to highest values by clicking twice on the “Ratio” heading at the top of the third column. Next from the “Select property” pull-down menu, select “Relative cost”, and click on “Add display of selected property” button; relative cost of materials will now be displayed in the fourth column. Next click on the “Product” button, and the product of the entries in the last two columns (i.e., the $\rho/E^{1/2}$ ratio and relative cost) will be displayed in the fifth column.

Below are tabulated the $\frac{\rho}{\sqrt{E}}$ ratio, the relative material cost $(\bar{c})$, and the product of these two parameters; also those alloys for which cost data are provided are ranked, from least to most expensive.

Alloy	Condition	$\frac{\rho}{\sqrt{E}}$	$\bar{c}$	$(\bar{c})\left(\frac{\rho}{\sqrt{E}}\right)$
AZ91D Mg	As cast	0.264	5.4	1.43
6061 Al	T6	0.325	7.6	2.47
356.0 Al	As cast, high production	0.316	7.9	2.50
6061 Al	T651	0.325	8.7	2.83
AZ31B Mg	Extruded	0.264	12.6	3.33
1100 Al	O	0.326	12.3	4.01
AZ31B Mg	Rolled	0.264	15.7	4.14
7075 Al	T6	0.332	13.4	4.45
2024 Al	T3	0.325	14.1	4.59
356.0 Al	As cast, custom	0.316	15.7	4.96
356.0 Al	T6	0.316	16.6	5.25
2024 Al	T351	0.326	16.2	5.27
1100 Al	H14	0.326	--	--
2024 Al	O	0.326	--	--
6061 Al	O	0.325	--	--
7075 Al	O	0.332	--	--
7075 Al	T651	0.332	--	--

It is up to the student to select the best metal alloy to be used for this cantilever beam on a stiffness-per-mass basis, including the element of cost, and other relevant considerations.

(d) We are now asked to select those metal alloys in the database that have strength performance indices greater than 14.0 (for σ_y and ρ in units of MPa and g/cm^3, respectively). This process may be expedited using a procedure analogous to the one outlined in part (b).

Sixteen alloys satisfy this criterion; they and their $\frac{\sigma_y^{2/3}}{\rho}$ ratios (Equation 22.D9) are listed below; here they are ranked from highest to lowest ratio value.

Alloy	Condition	$\dfrac{\rho}{\sqrt{E}}$	$\bar{c}$	$(\bar{c})\left(\dfrac{\rho}{\sqrt{E}}\right)$
AZ91D Mg	As cast	0.264	5.4	1.43
6061 Al	T6	0.325	7.6	2.47
356.0 Al	As cast, high production	0.316	7.9	2.50
6061 Al	T651	0.325	8.7	2.83
AZ31B Mg	Extruded	0.264	12.6	3.33
1100 Al	O	0.326	12.3	4.01
AZ31B Mg	Rolled	0.264	15.7	4.14
7075 Al	T6	0.332	13.4	4.45
2024 Al	T3	0.325	14.1	4.59
356.0 Al	As cast, custom	0.316	15.7	4.96
356.0 Al	T6	0.316	16.6	5.25
2024 Al	T351	0.326	16.2	5.27
1100 Al	H14	0.326	--	--
2024 Al	O	0.326	--	--
6061 Al	O	0.325	--	--
7075 Al	O	0.332	--	--
7075 Al	T651	0.332	--	--

It is up to the student to select the best metal alloy to be used for this cantilever beam on a stiffness-per-mass basis, including the element of cost, and other relevant considerations.

(d) We are now asked to select those metal alloys in the database that have strength performance indices greater than 14.0 (for σ_y and ρ in units of MPa and g/cm^3, respectively). This process may be expedited using a procedure analogous to the one outlined in part (b).

Sixteen alloys satisfy this criterion; they and their $\dfrac{\sigma_y^{2/3}}{\rho}$ ratios (Equation 22.D9) are listed below; here they are ranked from highest to lowest ratio value.

AZ31B Mg	Rolled	4.86	15.7	0.763
2024 Al	T3	5.63	14.1	0.794
17-7PH Stain.	Cold rolled	6.74	12.0	0.809
Ti-6Al-4V	Soln. treated/aged	4.15	132	5.48
Ti-6Al-4V	Annealed	5.02	132	6.63
Ti-5Al-2.5Sn	Annealed	5.38	157	8.45
7075 Al	T651	4.42	--	--
440A Stain.	Q/T, 315ºC	5.59	--	--
4340 Steel	Q/T, 315ºC	5.69	--	--
4140 Steel	Q/T, 315ºC	5.81	--	--
2024 Al	T351	5.86	--	--
17-7PH Stain.	Pptn. Hardened	6.39	--	--

It is up to the student to select the best metal alloy to be used for this cantilever beam on a stiffness-per-mass basis, including the element of cost and any other relevant considerations.

(f) The student should use his or her own discretion in the selection the material to be used for this application when stiffness- and strength-per-mass, as well as cost are to be considered. Furthermore, the student should be able to justify the decision.

22.D4 (a) This portion of the problem asks that we compute values for and then rank several polymeric materials according to the stiffness performance index developed in Problem 22.D3(a); these values are then to be compared with those determined for metallic materials in this same problem. The stiffness performance index is given in Equation 22.D13, as follows:

$$P = \frac{\sqrt{E}}{\rho}$$

In the table below are listed the performance indices for these various polymers. (Note: as stipulated in the problem statement, averages are used for modulus values when ranges are provided in Appendix B.)

Material	$\frac{\sqrt{E}}{\rho}$
Polystyrene	1.59
Nylon 6,6	1.44
Poly(methyl methacrylate)	1.39
Poly(ethylene terephthalate)	1.38
Polycarbonate	1.29
Polypropylene	1.28
Poly(vinyl chloride)	1.26
High-density polyethylene	1.08
Polytetrafluoroethylene	0.32

These stiffness performance values are significantly lower than those for metals that were determined in Problem 22.D3(a); values for the metals range between about 3.0 and 3.8.

(b) We are now to conduct a cost analysis in the manner described in Section 22.2. Below are tabulated the $\frac{\rho}{\sqrt{E}}$ ratio, the relative material cost $(\bar{c})$, and the product of these two parameters for each of these polymers; also those polymers for which cost data are provided are ranked, from least to most expensive.

Polymer	$\frac{\rho}{\sqrt{E}}$	$\bar{c}$	$(\bar{c})\left(\frac{\rho}{\sqrt{E}}\right)$
Polystyrene	0.629	1.5	0.94
Polypropylene	0.781	1.8	1.41
High-density polyethylene	0.926	1.9	1.76
Poly(ethylene terephthalate)	0.725	2.9	2.10
Poly(vinyl chloride)	0.794	3.0	2.38
Poly(methyl methacrylate)	0.719	3.4	2.44
Nylon 6,6	0.694	7.4	5.14
Polycarbonate	0.775	7.3	5.66
Polytetrafluoroethylene	3.13	33.2	104

(c) And, finally, we are asked to determine the strength performance indices [per Problem 22.D3(a)] for these same polymeric materials. The strength performance index is given in Equation 22.D9, as follows:

$$P = \frac{\sigma_y^{2/3}}{\rho}$$

In the table below are listed the strength performance indices for these several polymers.

Material	$\frac{\sigma_y^{2/3}}{\rho}$
Poly(methyl methacrylate)	13.4
Polycarbonate	13.1
Nylon 6,6 (50% RH)	12.2
Polypropylene	11.6
Poly(ethylene terephthalate)	11.3
High-density polyethylene	10.0
Poly(vinyl chloride)	8.5
Polystyrene	--
Polytetrafluoroethylene	--

Note: no values of yield strength are listed for polystyrene and polytetrafluoroethylene in Table B.4 of Appendix B. Also, when ranges for σ_y were given, average values were used for the computation of the performance indices.

22.D5 (a) This portion of the problem asks that we derive strength and stiffness performance index expressions analogous to Equations 22.9 and 22.11 for a bar specimen having a square cross-section that is pulled in uniaxial tension along it longitudinal axis.

For stiffness, we begin by consideration of the elongation, Δl, in Equation 6.2 where the initial length l_0 is replaced by L. Thus, Equation 6.2 may now be written as

$$\Delta l = L\varepsilon \tag{22.D14}$$

in which ε is the engineering strain. Furthermore, assuming that the deformation is entirely elastic, Hooke's law, Equation 6.5, is obeyed by this material (i.e., $\sigma = E\varepsilon$), where σ is the engineering stress. Thus, combining Equation 22.D14 and the Hooke's law expression, leads to

$$\Delta l = L\varepsilon = \frac{L\sigma}{E} \tag{22.D15}$$

And, since σ is defined by Equation 6.1 as

$$\sigma = \frac{F}{A_0} \tag{6.1}$$

A_0 being the original cross-sectional area; in this case $A_0 = c^2$. Thus, incorporation of these relationships into Equation 22.D15 leads to an expression for Δl as

$$\Delta l = \frac{LF}{Ec^2} \tag{22.D16}$$

Now, the mass of material, m, is just the product of the density, ρ, and the volume of the beam, which volume is just Lc^2; that is

$$m = \rho L c^2 \tag{22.D17}$$

Or, solving for c^2

$$c^2 = \frac{m}{\rho L} \tag{22.D18}$$

Substitution the above expression for c^2 into Equation 22.D16 yields

$$\Delta l = \frac{L^2 F \rho}{E m} \tag{22.D19}$$

And solving for the mass

$$m = \left(\frac{L^2 F}{\Delta l}\right)\frac{\rho}{E} \tag{22.D20}$$

Thus, the best materials to be used for a light bar that is pulled in tension when stiffness is a consideration are those having low ρ/E ratios. The stiffness performance index, P_s, is the reciprocal of this ratio, or

$$P_s = \frac{E}{\rho} \tag{22.D21}$$

Now we will consider rod strength. The stress σ imposed on this beam by F may be determined using Equation 6.1; that is

$$\sigma = \frac{F}{A_0} = \frac{F}{c^2} \tag{22.D22}$$

In the stiffness treatment (Equation 22.D18) it was shown that $c^2 = m/\rho L$; making this substitution into Equation 22.D22 gives

$$\sigma = \frac{FL\rho}{m} \tag{22.D23}$$

Now, solving for the mass, m, leads to

$$m = (FL)\,\frac{\rho}{\sigma} \tag{22.D24}$$

And replacement of stress with yield strength, σ_y, divided by a factor of safety, N

$$m = (FLN)\frac{\rho}{\sigma_y} \tag{22.D25}$$

Hence, the best materials to be used for a light bar that is pulled in tension when strength is a consideration are those having low ρ/σ_y ratios; and the strength performance index, *P*, is just the reciprocal of this ratio, or

$$P = \frac{\sigma_y}{\rho} \tag{22.D26}$$

(b) Here we are asked to select those metal alloys in the database that have stiffness performance indices (i.e., E/ρ ratios, Equation 22.D21) greater than 26.0 (for E and ρ in units of GPa and g/cm^3, respectively). It is possible to expedite the materials selection process for this criterion using the "Engineering Material Properties" component of *VMSE* as follows:

1. Click on "Engineering Material Properties" at the bottom of the opening window.
2. In the window that appears, click on the "Show Combination/Ratio/Product" box.
3. In the next window that appears click on the "Ratio" box.
4. Click on the "Select property:" pull-down menu, and select "*E* (Modulus of Elasticity)" item. Then click on the "Add display of selected property" box. Modulus of elasticity values of all materials will displayed in the database portion of the window.
5. Next, from the "Select property" pull-down menu select "ρ (Density)", and then click on the "Add display of selected property" box. Density values of all materials will displayed in the second column database portion of the window.
6. There are two "Power for" boxes at the bottom of the top portion window—default values in these boxes are "1.0". Leave the default "1.0" in both boxes, since the exponents to which both the modulus of elasticity and density is to be taken are both "1.0".
7. Now click on the "Take Ratio" button. The E/ρ ratio is then displayed in the third database column.
8. Values that appear in this column may be sorted from highest to lowest value by clicking on the "Ratio" heading at the top of this column.

Thirty metal alloys satisfy this criterion. All of the twenty-one plain carbon and low alloy steels contained in the database fall into this group, and, in addition several other alloys. These and their E/ρ ratios are listed below, and are ranked from highest to lowest value. (All of these twenty one steel alloys have the same E/ρ ratio, and therefore are entered as a single item in the table.) These materials are ranked from highest to lowest ratio.

Alloy(s)	Condition	$\frac{E}{\rho}$
Molybdenum	Sheet/rod	31.3
356.0 Al	As cast, high production	26.9

356.0 Al	As cast, custom	26.9
356.0 Al	T6	26.9
17-7PH stainless	Plate, CR	26.6
17-7PH stainless	Pptn. hardened	26.6
Plain carbon/low alloy steels	Various	26.3
2024 Al	O	26.1
2024 Al	T3	26.1
2024 Al	T351	26.1

(c) We are now asked to do a cost analysis on the above alloys. This process may again be expedited using the "Engineering Materials Properties" database portion of *VMSE.* Repeat the procedure outlined above, except call for a display of the density in the first column, and the modulus of elasticity in the second column. Again, leave the values in the "Power for" boxes "1.0". Next click the "Take Ratio" button, and then sort (rank) values from lowest to highest values by clicking twice on the "Ratio" heading at the top of the third column. Next from the "Select property" pull-down menu, select "Relative cost", and click on "Add display of selected property" button; relative cost of materials will now be displayed in the fourth column. Next click on the "Product" button, and the product of the entries in the last two columns (i.e., the ρ/E ratio and relative cost) will be displayed in the fifth column.

Below are tabulated, for each alloy, the ρ/E ratio, the relative material cost $(\bar{c})$, and the product of these two parameters; only those alloys in the previous table for which cost data are given are included in the table; these are ranked, from least to most expensive.

Alloy	Condition	$10^{-2}\ \dfrac{\rho}{E}$	$\bar{c}$	$10^{-2}\ (\bar{c})\left(\dfrac{\rho}{E}\right)$
1020 steel	Plate, HR	3.79	0.8	3.03
A36 steel	Plate, HR	3.79	1.0	3.79
1040 steel	Plate, HR	3.79	1.1	4.17
A36 steel	Angle bar, HR	3.79	1.6	6.06
1020 steel	Plate, CR	3.79	1.6	6.06
1040 steel	Plate, CR	3.79	1.9	7.20
4140 steel	Bar, normalized	3.79	2.6	9.85
4340 steel	Bar, annealed	3.79	3.5	13.3

4140H steel	Round, normalized	3.79	4.2	15.9
4340 steel	Bar, normalized	3.79	4.7	17.8
356.0 Al	Cast, high prod.	3.72	7.9	29.4
17-7PH SS	Plate, CR	3.75	12	45.0
2024 Al	T3	3.83	14.1	54.0
356.0 Al	Cast, custom	3.72	15.7	58.4
356.0 Al	T6	3.72	16.6	61.8
2024 Al	T351	3.83	16.2	62.0
Molybdenum	Sheet/rod	3.19	143	456

It is up to the student to select the best metal alloy to be used for this bar pulled in tension on a stiffness-per-mass basis, including the element of cost and other relevant considerations.

(d) We are now asked to select those metal alloys in the database that have strength performance indices greater than 120 (for σ_y and ρ in units of MPa and g/cm^3, respectively). This process may be expedited using a procedure analogous to the one outlined in part (b).

Thirteen alloys satisfy this criterion; they and their σ_y/ρ ratios (per Equation 22.D26) are listed below; here the ranking is from highest to lowest ratio value.

Alloy	Condition	$\frac{\sigma_y}{\rho}$
Ti-6Al-4V	Soln. treated/aged	249
440A stainless	Q/T, 315°C	212
4340 steel	Q/T, 315°C	206
4140 steel	Q/T, 315°C	200
Ti-6Al-4V	Annealed	187
7075 Al	T6	180
7075 Al	T651	180
17-7PH stainless	Pptn. hardened	171
Ti-5Al-2.5Sn	Annealed	170
17-7PH stainless	Plate, CR	158
C17200 Cu	Soln. treated/aged	132
2024 Al	T3	125
AZ31B Mg	Sheet, rolled	124

(e) We are now asked to do a cost analysis on the above alloys. Again, we may expedite this process by utilizing the procedure outlined in part (c).

Below are tabulated, for each of the above alloys, the ρ/σ_y value, the relative material cost $(\overline{c})$, and the product of these two parameters; also those alloys for which cost data are provided are ranked, from least to most expensive.

Alloy	Condition	$10^{-3}\ \dfrac{\rho}{\sigma_y}$	$\overline{c}$	$10^{-2}\ (\overline{c})\left(\dfrac{\rho}{\sigma_y}\right)$
7075 Al	T6	5.56	13.4	7.5
17-7PH SS	Plate, CR	6.33	12.0	7.6
2024 Al	T3	8.00	14.1	11.3
AZ31B Mg	Sheet, rolled	8.06	15.7	12.7
C17200 Cu	Soln. treated/aged	7.58	51.4	39.0
Ti-6Al-4V	Soln. treated/aged	4.02	132	53.1
Ti-6Al-4V	Annealed	5.35	132	70.6
Ti-5Al-2.5Sn	Annealed	5.88	157	92.3
440A SS	Q/T, 315°C	4.72	--	--
4340 steel	Q/T, 315°C	4.85	--	--
4140 steel	Q/T, 315°C	5.00	--	--
7075 Al	T651	5.56	--	--
17-7PH SS	Pptn. hardened	5.85	--	--

It is up to the student to select the best metal alloy to be used for this bar pulled in tension on a strength-per-mass basis, including the element of cost and other relevant considerations.

(f) The student should use his or her own discretion in the selection the material to be used for this application when stiffness- and strength-per-mass, as well as cost are to be considered. Furthermore, the student should be able to justify the decision.

22.D6 (a) The first portion of this problem asks that we derive a performance index expression for the strength of a plate that is supported at its ends and subjected to a force that is uniformly distributed over the upper face. Equation 22.32 in the textbook is an expression for the deflection δ of the underside of the plate at $L/2$ in terms of the force F, the modulus of elasticity E, as well as the plate dimensions as shown in the accompanying figure. This equation is as follows:

$$\delta = \frac{5FL^3}{32\,Ewt^3} \tag{22.D27}$$

Now, the mass of the plate, m, is the product of its density (ρ) and volume. Inasmuch as the volume of the plate is Lwt, then

$$m = Lw\,t\rho \tag{22.D28}$$

From this expression, the thickness t is just

$$t = \frac{m}{Lw\rho} \tag{22.D29}$$

Substitution of this expression for t into Equation 22.D27 yields

$$\delta = \frac{5FL^6w^2\rho^3}{32\,Em^3} \tag{22.D30}$$

And solving for the mass gives

$$m = \left(\frac{5FL^6w^2}{32\delta}\right)^{1/3}\frac{\rho}{E^{1/3}} \tag{22.D31}$$

Now, the stiffness performance index P_1 is just the reciprocal of the $\frac{\rho}{E^{1/3}}$ term of this expression, or

$$P_1 = \frac{E^{1/3}}{\rho} \tag{22.D32}$$

For determination of the strength performance index, we substitute the expression for t (Equation 22.D29) into Equation 22.33 in the textbook, which yields

$$\sigma = \frac{3FL}{4wt^2} = \frac{3FL^3 w \rho^2}{4m^2} \tag{22.D33}$$

Now, as in the previous problems, in order to insure that the plate will not fail, we replace stress in the previous expression with the yield strength (σ_y) divided by a factor of safety (N) as

$$\frac{\sigma_y}{N} = \frac{3FL^3 w \rho^2}{4m^2} \tag{22.D34}$$

Now solving Equation 22.D34 for the mass

$$m = \left(\frac{3\,NFL^3 w}{4}\right)^{1/2} \frac{\rho}{\sigma_y^{1/2}} \tag{22.D35}$$

And, finally, the stiffness performance index P_2 is the reciprocal of the $\dfrac{\rho}{\sigma_y^{1/2}}$ ratio as

$$P_2 = \frac{\sigma_y^{1/2}}{\rho} \tag{22.D36}$$

(b) Here we are asked to select those metal alloys in the database that have stiffness performance indices (i.e., $E^{1/3}/\rho$ ratios, Equation 22.D32) greater than 1.40 (for E and ρ in units of GPa and g/cm^3, respectively). It is possible to expedite the materials selection process for this criterion using the "Engineering Material Properties" component of *VMSE* as follows:

1. Click on "Engineering Material Properties" at the bottom of the opening window.
2. In the window that appears, click on the "Show Combination/Ratio/Product" box.
3. In the next window that appears click on the "Ratio" box.
4. Click on the "Select property:" pull-down menu, and select "E (Modulus of Elasticity)" item. Then click on the "Add display of selected property" box. Modulus of elasticity values of all materials will displayed in the database portion of the window.
5. Next, from the "Select property" pull-down menu select "ρ (Density)", and then click on the "Add display of selected property" box. Density values of all materials will displayed in the second column database portion of the window.
6. There are two "Power for" boxes at the bottom of the top portion window—default values in these boxes are "1.0". The in the left-most box enter "0.333" (the decimal equivalent for 1/3), which is the exponent to

which the first column entries (i.e., the modulus of elasticity values) will be taken. Leave the default “1.0” in the right-most box, since the exponent to which the density is to be taken is “1.0”.

7. Now click on the “Take Ratio” button. The $E^{1/3}/\rho$ ratio is then displayed in the third database column.

8. Values that appear in this column may be sorted from highest to lowest value by clicking on the “Ratio” heading at the top of this column.

Seventeen metal alloys satisfy this criterion. They and their $E^{1/3}/\rho$ ratios are listed below. Furthermore, these materials are ranked from highest to lowest ratio.

Alloy	Condition	$\frac{E^{1/3}}{\rho}$
AZ31B Mg	Rolled	2.01
AZ31B Mg	Extruded	2.01
AZ91B Mg	As cast	1.96
356.0 Al	Cast, high production	1.55
356.0 Al	As cast, custom	1.55
356.0 Al	T6	1.55
6061 Al	O	1.52
6061 Al	T6	1.52
6061 Al	T651	1.52
1100 Al	O	1.51
1100 Al	H14	1.51
2024 Al	O	1.50
2024 Al	T3	1.50
2024 Al	T351	1.50
7075 Al	O	1.48
7075 Al	T6	1.48
7075 Al	T651	1.48

(c) We are now asked to do a cost analysis on the above alloys. This process may again be expedited using the “Engineering Materials Properties” database portion of *VMSE.* Repeat the procedure outlined above, except call for a display of the density in the first column, and the modulus of elasticity in the second column. Also enter into the right-most “Power for” box the value of “0.33”. Next click the “Take Ratio” button, and then sort (rank) values from lowest to highest values by clicking twice on the “Ratio” heading at the top of the third column.

Next from the “Select property” pull-down menu, select “Relative cost”, and click on “Add display of selected property” button; relative cost of materials will now be displayed in the fourth column. Next click on the “Product” button, and the product of the entries in the last two columns (i.e., the $\rho/E^{1/3}$ ratio and relative cost) will be displayed in the fifth column.

Below are tabulated, for each alloy, its $\rho/E^{1/3}$ ratio, the relative material cost $(\overline{c})$, and the product of these two parameters; these alloys are ranked, from least to most expensive.

Alloy	Condition	$\dfrac{\rho}{E^{1/3}}$	$\overline{c}$	$(\overline{c})\left(\dfrac{\rho}{E^{1/3}}\right)$
AZ91B Mg	As cast	0.509	5.4	2.75
6061 Al	T6	0.658	7.6	5.00
356.0 Al	Cast, high production	0.645	7.9	5.10
6061 Al	T651	0.658	8.7	5.72
AZ31B Mg	Extruded	0.498	12.6	6.27
AZ31B Mg	Rolled	0.498	15.7	7.82
1100 Al	O	0.661	12.3	8.13
7075 Al	T6	0.676	13.4	9.06
2024 Al	T3	0.665	14.1	9.38
356.0 Al	Cast, custom	0.645	15.7	10.13
356.0 Al	T6	0.645	16.6	10.71
2024 Al	T351	0.665	16.2	10.77
1100 Al	H14	0.661	--	--
2024 Al	O	0.665	--	--
6061 Al	O	0.658	--	--
7075 Al	O	0.676	--	--
7075 Al	T651	0.676	--	--

It is up to the student to select the best metal alloy to be used for this plate on a stiffness-per-mass basis, including the element of cost, as well as other relevant considerations.

(d) We are now asked to select those metal alloys in the database that have strength performance indices greater than 5.0 (for σ_y and ρ in units of MPa and g/cm^3, respectively). This process may be expedited using a procedure analogous to the one outlined in part (b).

Next from the “Select property” pull-down menu, select “Relative cost”, and click on “Add display of selected property” button; relative cost of materials will now be displayed in the fourth column. Next click on the “Product” button, and the product of the entries in the last two columns (i.e., the $\rho/E^{1/3}$ ratio and relative cost) will be displayed in the fifth column.

Below are tabulated, for each alloy, its $\rho/E^{1/3}$ ratio, the relative material cost $(\bar{c})$, and the product of these two parameters; these alloys are ranked, from least to most expensive.

Alloy	Condition	$\frac{\rho}{E^{1/3}}$	$\bar{c}$	$(\bar{c})\left(\frac{\rho}{E^{1/3}}\right)$
AZ91B Mg	As cast	0.509	5.4	2.75
6061 Al	T6	0.658	7.6	5.00
356.0 Al	Cast, high production	0.645	7.9	5.10
6061 Al	T651	0.658	8.7	5.72
AZ31B Mg	Extruded	0.498	12.6	6.27
AZ31B Mg	Rolled	0.498	15.7	7.82
1100 Al	O	0.661	12.3	8.13
7075 Al	T6	0.676	13.4	9.06
2024 Al	T3	0.665	14.1	9.38
356.0 Al	Cast, custom	0.645	15.7	10.13
356.0 Al	T6	0.645	16.6	10.71
2024 Al	T351	0.665	16.2	10.77
1100 Al	H14	0.661	--	--
2024 Al	O	0.665	--	--
6061 Al	O	0.658	--	--
7075 Al	O	0.676	--	--
7075 Al	T651	0.676	--	--

It is up to the student to select the best metal alloy to be used for this plate on a stiffness-per-mass basis, including the element of cost, as well as other relevant considerations.

(d) We are now asked to select those metal alloys in the database that have strength performance indices greater than 5.0 (for σ_y and ρ in units of MPa and g/cm^3, respectively). This process may be expedited using a procedure analogous to the one outlined in part (b).

Fifteen alloys satisfy this criterion; they and their $\frac{\sigma_y^{1/2}}{\rho}$ ratios (per Equation 22.D36) are listed below; here the ranking is from highest to lowest ratio value.

Alloy	Condition	$\frac{\sigma_y^{1/2}}{\rho}$
AZ31B Mg	Sheet, rolled	8.38
AZ31B Mg	Sheet, extruded	8.38
7075 Al	T6	8.03
7075 Al	T651	8.03
Ti-6Al-4V	Soln. treated/aged	7.50
2024 Al	T3	6.71
2024 Al	T351	6.51
Ti-6Al-4V	Annealed	6.50
Ti-5Al-2.5Sn	Annealed	6.15
6061 Al	T6	6.15
6061 Al	T651	6.15
AZ91D Mg	As cast	6.10
Stainless 440A	Q/T @ 315ºC	5.21
4340 Steel	Q/T @ 315ºC	5.13
4140 Steel	Q/T @ 315ºC	5.05

(e) We are now asked to do a cost analysis on the above alloys. Again, we may expedite this process by utilizing the procedure outlined in part (c).

Below are tabulated, for each alloy, its $\frac{\rho}{\sigma_y^{1/2}}$ value, the relative material cost $(\overline{c})$, and the product of these two parameters; also those alloys for which cost data are provided are ranked, from least to most expensive.

Alloy	Condition	$\frac{\rho}{\sigma_y^{1/2}}$	$\bar{c}$	$(\bar{c})\left(\frac{\rho}{\sigma_y^{1/2}}\right)$
AZ91D Mg	As cast	0.1639	5.4	0.885
6061 Al	T6	0.1625	7.6	1.24
6061 Al	T651	0.1625	8.7	1.41
AZ31B Mg	Sheet, extruded	0.1193	12.6	1.50
7075 Al	T6	0.1246	13.4	1.67
AZ31B Mg	Sheet, rolled	0.1193	15.7	1.87
2024 Al	T3	0.1491	14.1	2.10
2024 Al	T351	0.1537	16.2	2.49
Ti-6Al-4V	Soln. treated/aged	0.1334	132	17.61
Ti-6Al-4V	Annealed	0.1538	132	20.30
Ti-5Al-2.5Sn	Annealed	0.1625	157	25.51
7075 Al	T651	0.1246	--	--
Stainless 440A	Q/T @ 315ºC	0.1920	--	--
4340 Steel	Q/T @ 315ºC	0.1950	--	--
4140 Steel	Q/T @ 315ºC	0.1980	--	--

It is up to the student to select the best metal alloy to be used for this plate on a strength-per-mass basis, including the element of cost, as well as other relevant considerations.

(f) The student should use his or her own discretion in the selection the material to be used for this application when stiffness- and strength-per-mass, as well as cost are to be considered. Furthermore, the student should be able to justify the decision.

Design and Materials Selection for Springs

22.D7 (a) This portion of the problem asks that we compute the maximum tensile load that may be applied to a spring constructed of a cold-drawn and annealed 316 stainless steel such that the total deflection is less than 6.5 mm; there are eight coils in the spring, whereas, its center-to-center diameter is 20 mm, and the wire diameter is 2.5 mm. The total spring deflection δ_s may be determined by combining Equations 22.14 and 22.15; solving for the load *F* from the combined equation leads to

$$F = \frac{\delta_s d^4 G}{8 N_c D^3}$$

However, it becomes necessary to determine the value of the shear modulus *G*. This is possible using Equation 6.9 and values of the modulus of elasticity (193 GPa) and Poisson's ratio (0.30) as taken from Tables B.2 and B.3 in Appendix B. Thus

$$G = \frac{E}{2(1 + \nu)}$$

$$= \frac{193 \text{ GPa}}{2(1 + 0.30)} = 74.2 \text{ GPa}$$

Substitution of this value and values of the other parameters given in the problem statement into the above equation for *F* leads to

$$F = \frac{\delta_s d^4 G}{8 N_c D^3} = \frac{(6.5 \times 10^{-3} \text{ m})(2.5 \times 10^{-3} \text{ m})^4 (74.2 \times 10^9 \text{ N/m}^2)}{(8)(8 \text{ coils})(20 \times 10^{-3} \text{ m})^3}$$

$$= 36.8 \text{ N} \ \ (8.6 \text{ lb}_\text{f})$$

(b) We are now asked to compute the maximum tensile load that may be applied without any permanent deformation of the spring wire. This requires that we combine Equations 22.12 and 22.13 as

$$\tau = \frac{8FD}{\pi d^3} K_w = \frac{8FD}{\pi d^3}\left[1.60\left(\frac{D}{d}\right)\right]^{-0.140}$$

Solving this expression for *F* gives

$$F = \frac{\tau \pi d^3}{8D\left[1.60\left(\frac{D}{d}\right)^{-0.140}\right]}$$

Now, it is necessary to calculate the shear yield strength and substitute it for τ into the above equation. The problem statement stipulates that $\tau_y = 0.6\sigma_y$. From Table B.4 in Appendix B, we note that the tensile yield strength for this alloy in the cold-drawn and annealed state is 310 MPa; thus τ_y = (0.6)(310 MPa) = 186 MPa. Using this value, as well as the values of other parameters given in the problem statement, the value of *F* is equal to

$$F = \frac{\tau_y \pi d^3}{8D\left[1.60\left(\frac{D}{d}\right)^{-0.140}\right]}$$

$$= \frac{(186 \times 10^6 \text{ N/m}^2)\,\pi\,(2.5 \times 10^{-3} \text{ m})^3}{(8)(20 \times 10^{-3} \text{ m})\left[(1.60)\left(\frac{20 \times 10^{-3} \text{ m}}{2.5 \times 10^{-3} \text{ m}}\right)^{-0.140}\right]}$$

$$= 47.7 \text{ N} \;\; (11.1 \text{ lb}_\text{f})$$

22.D8 (a) In this portion of the problem we are asked to select candidate materials for a spring that consists of ten coils and which is not to plastically deform nor experience a deflection of more that 12 mm when a tensile force of 35 N is applied. The coil-to-coil diameter and wire diameter are 15 mm and 2.0 mm, respectively. In addition, we are to assume that $\tau_y = 0.6\sigma_y$ and that $G = 0.4E$. Let us first determine the minimum modulus of elasticity that is required such that the total deflection δ_s is less than 12 mm. This requires that we begin by computation of the deflection per coil δ_c using Equation 22.15 as

$$\delta_c = \frac{\delta_s}{N} = \frac{12 \text{ mm}}{10 \text{ coils}} = 1.2 \text{ mm/coil}$$

Now, upon rearrangement of Equation 22.14 and solving for E, realizing that $G = 0.4E$, we have

$$E = \frac{8FD^3}{(0.4)\delta_c d^4}$$

$$= \frac{(8)(35 \text{ N})(15 \times 10^{-3} \text{ m})^3}{(0.4)(1.2 \times 10^{-3} \text{ m})(2.0 \times 10^{-3} \text{ m})^4}$$

$$= 123 \times 10^9 \text{ N/m}^2 = 123 \text{ GPa}$$

Next, we will calculate the minimum required tensile yield strength by employing Equations 22.18 and 22.13. Solving for σ_y, and since $\tau_y = 0.6\sigma_y$ the following may be written

$$\sigma_y = \frac{\delta_c (0.4E)d}{(0.6)\pi D^2} K_w$$

$$= \frac{\delta_c (0.4E)d}{(0.6)\pi D^2}\left[1.60\left(\frac{D}{d}\right)^{-0.140}\right]$$

Incorporation into this expression the values of δ_c and E determined above, as well as values for other parameters given in the problem statement, σ_y is equal to

$$\sigma_y = \frac{(1.2 \times 10^{-3} \text{ m})(0.4)(123 \times 10^9 \text{ N/m}^2)(2.0 \times 10^{-3} \text{ m})}{(0.6)(\pi)(15 \times 10^{-3} \text{ m})^2}\left[1.60\left(\frac{15 \text{ mm}}{2.0 \text{ mm}}\right)^{-0.140}\right]$$

$$= 336 \text{ x } 10^6 \text{ N/m}^2 = 336 \text{ MPa}$$

After perusing Appendix B in the textbook, it is observed that 26 materials satisfy the two criteria that were determined above (viz. E = 123 GPa and σ_y = 336 MPa). These materials are listed below, along with their values of E, σ_y, %EL (which correlates to ease of formability), and relative cost, $\bar{c}$.

Material	Condition	E (GPa)	σ_y (MPa)	%EL	$\bar{c}$ (\$/\$)
1020 steel	Plate, CR	207	350	15	1.6
1040 steel	Plate, CR	207	490	12	1.9
1040 steel	Annealed	207	355	30.2	--
1040 steel	Normalized	207	375	28	--
4140 steel	Annealed	207	417	25.7	--
4140 steel	Bar, normalized	207	655	17.7	2.6
4140 steel	Q/T @ 315°C	207	1570	11.5	--
4340 steel	Bar, annealed	207	472	22	3.5
4340 steel	Bar, normalized	207	862	12.2	4.7
4340 steel	Q/T @ 315°C	207	1620	12	--
304 SS	CW, 1/4 hard	193	515	10	4.0
440A SS	Plate, annealed	200	415	20	6.7
440A SS	Q/T @ 315°C	200	1650	5	--
17-7PH SS	Plate, CR	204	1210	1	12.0
17-7PH SS	Ptn. hardened	204	1310	3.5	--
Ductile Iron (80-55-06)	As cast, high production	168	379	6	2.4
Ductile Iron (80-55-06)	As cast, low production	168	379	6	5.9
Ductile Iron (120-90-02)	Q/T, high production	164	621	2	2.4
Ductile Iron (120-90-02)	Q/T, low production	164	621	2	5.9
C17200 Cu	Soln. treated/aged	128	905-1205	4-10	51.4
C71500 Cu	CW, H80	150	545	3	12.9
Molybdenum	Sheet/rod	320	500	25	143
Tungsten	Sheet	400	760	2	111
Tungsten	Rod	400	760	2	166

Inconel 625	Annealed	207	517	42.5	35.0
Haynes 25	--	236	445	62	135

The student should make his or her own decision as to which material would be most desirable for this application. Consideration should be given to the magnitude of both the elastic modulus and yield strength, in that they should be somewhat greater than the required minima, yet not excessively greater than the minima. Furthermore, the alloy will have to be drawn into a wire, and, thus, the ductility in percent elongation is also a parameter to be considered. And, of course cost is important, as well as the corrosion resistance of the material; corrosion resistant issues for these various alloys are discussed in Chapter 17. And, as called for in the problem statement, the student should justify his or her decision.

22.D9 This problem involves a spring having 7 coils, a coil-to-coil diameter of 0.5 in., which is to deflect no more than 0.60 in. when a tensile load of 15 $\mathrm{lb_f}$ is applied. We are asked to calculate the minimum diameter to which a cold-drawn steel wire may be drawn such that plastic deformation of the spring wire will not occur. The spring will plastically deform when the right-hand side of Equation 22.18 equals the shear yield strength of the cold-drawn wire. Furthermore, the shear yield strength is a function of wire diameter according to Equation 22.34. When we set this expression equal to the right-hand side of Equation 22.18, the only unknown is the wire diameter, *d*, since, from Equation 22.15

$$\delta_c = \frac{\delta_s}{N} = \frac{0.60 \text{ in.}}{7 \text{ coils}}$$

$$= 0.086 \text{ in./coil}$$

Therefore,

$$\tau_y = \frac{63{,}000}{d^{0.2}} = \frac{\delta_c G d}{\pi D^2} K_w = \frac{\delta_c G d}{\pi D^2}\left[1.60\left(\frac{D}{d}\right)^{-0.140}\right]$$

Here the expression in Equation 22.13 for K_w has been included. Now, upon substitution of the value of δ_c (determined above) as well as values of parameters specified in the problem statement, the above expression becomes

$$\frac{63{,}000}{d^{0.2}} = \frac{(0.086 \text{ in./coil})(11.5 \text{ x } 10^6 \text{ psi})(d)}{\pi(0.50 \text{ in.})^2}\left[1.60\left(\frac{0.50 \text{ in.}}{d}\right)^{-0.140}\right]$$

which reduces to the following form:

$$\frac{63{,}000}{d^{0.2}} = 2.22 \times 10^6 (d)^{1.14}$$

And, upon further reduction we have

$$2.84 \times 10^{-2} = (d)^{1.34}$$

Finally, solving for *d* leads to

$$d = (2.84 \times 10^{-2})^{1/1.34} = 0.070 \text{ in.}$$

22.D10 This problem involves a spring that is to be constructed from a 4340 steel wire 3.0 mm in diameter; the design also calls for 5 coils, a coil-to-coil diameter of 12 mm, and the spring deflection is to be no more than 5.0 mm. We are asked to specify the heat treatment for this 4340 alloy such that plastic deformation of the spring wire will not occur. The spring will plastically deform when the right-hand side of Equation 22.18 equals the shear yield strength of wire. However, we must first determine the value of δ_c using Equation 22.15. Thus,

$$\delta_c = \frac{\delta_s}{N} = \frac{5.0 \text{ mm}}{5 \text{ coils}}$$

$$= 1.0 \text{ mm/coil}$$

Now, solving for τ_y when the expression for K_w (Equation 22.13) is substituted into Equation 22.18, and incorporating values for the various parameters, we have

$$\tau_y = \frac{\delta_c G d}{\pi D^2} K_w = \frac{\delta_c G d}{\pi D^2}\left[1.60\left(\frac{D}{d}\right)^{-0.140}\right]$$

$$= \frac{(1.0 \times 10^{-3} \text{ m})(80 \times 10^9 \text{ N/m}^2)(3.0 \times 10^{-3} \text{ m})}{(\pi)(12 \times 10^{-3} \text{ m})^2}\left[1.60\left(\frac{12 \text{ mm}}{3.0 \text{ mm}}\right)^{-0.140}\right]$$

$$= 700 \times 10^6 \text{ N/m}^2 = 700 \text{ MPa}$$

It is now possible to solve for the tensile yield strength σ_y as

$$\sigma_y = \frac{\tau_y}{0.6} = \frac{700 \text{ MPa}}{0.6} = 1170 \text{ MPa}$$

Thus, it is necessary to heat treat this 4340 steel in order to have a tensile yield strength of 1170 MPa. One way this could be accomplished is by first austenitizing the steel, quenching it in oil, and then tempering it (Section 10.8). In Figure 10.34 is shown the yield strength as a function of tempering temperature for a 4340 alloy that has been oil quenched. From this plot, in order to achieve a yield strength of 1170 MPa, tempering (for 1 h) at approximately 505°C is required.

Materials for Integrated Circuit Packages

22.D11 (a) This portion of the problem calls for us to search for possible materials to be used for a leadframe plate in an integrated circuit package. The requirements are (1) that the material be highly electrically conductive--i.e., an electrical conductivity of greater that 10 x 10^6 (Ω-m)$^{-1}$ [or, alternatively, an electrical resistivity of less than 1.0 x 10^{-7} (Ω-m)]; (2) that it have a coefficient of thermal expansion between 2 x 10^{-6} and 10 x 10^{-6} (°C)$^{-1}$; and (3) it must also be a thermal conductor having a thermal conductivity of at least 100 W/m-K. This problem may be solved using the "Engineering Materials Properties" component of *VMSE*, using the following procedure:

1. Click on "Engineering Material Properties" at the bottom of the opening window.

2. In the window that appears, click on the "Show Combination/Ratio/Product" box.

3. In the next window that appears click on the "Combination" box.

4. Three pull-down menus appear each of which has the label "<NONE>". From the first of these menus select "ρ_e(Electrical Resistivity)". At this time two windows appear below this menu box, which are labeled "Min:" and "Max:". Now we are dealing with electrical conductivity which is the reciprocal of electrical resistivity. Therefore, in "Max:" box enter the value of 1e-7; then in the "Min:" box enter some value a couple of orders of magnitude lower—say 1e-9.

5. In the middle "<NONE>" pull-down menu, select "α_l (Coeff. of Thermal Exp); in the "Min:" box enter "2e-6" and in the "Max:" box enter "10e-6".

6. Similarly for the right-most "<NONE>" pull-down menu, select "*k* (Thermal Conductivity)", and then enter a minimum value of "100" and a maximum value much higher, say "1000".

7. Finally, click on the "Extract Combination" button. This will allow a display of all materials that meet the three criteria that have been entered.

No materials were found that simultaneous meet these three conditions.

(b) Now we are asked to search for insulating materials to be used for the leadframe plate . The requirements are as follows: (1) an electrical conductivity less than 10^{-10} (Ω-m)$^{-1}$ [equivalently, an electrical resistivity greater than 10^{10} (Ω-m)]; a coefficient of thermal expansion between 2 x 10^{-6} and 10 x 10^{-6} (°C)$^{-1}$; and (3) a thermal conductivity greater than 30 W/m-K. A search may be conducted using *VMSE* as detailed in part (a). And no materials were found to simultaneously satisfy these criteria.

Design Questions

22.D12 Relatively high densities of digital information may be stored on the compact disc or CD. For example, sound (i.e., music) may be stored and subsequently reproduced virtually free of any interference. In essence, the CD is a laser-optical data-storage system, wherein a continuous laser beam functions as the playback element. The input signal is stored digitally (as optical read-only memory or OROM) in the form of very small, microscopic surface pits that have been embedded into the disc during the manufacturing process. The incident laser beam is reflected from the surface of the disc, and modulation (i.e., variation of the phase) of this read or reflected beam is achieved by optical interference that results from the depth of the pits.

These read-only discs consist of a substrate into which the datum pits have been replicated. This substrate must be protected, which is accomplished by applying a thin and reflective layer of aluminum, on top of which is coated an ultraviolet curable lacquer. Since the substrate is the key component of the optical path, its properties are extremely important. Some of the substrate characteristics that are critical are as follows: (1) it must be highly transparent; (2) it must be possible to economically produce discs that are uniformly thick and extremely flat; (3) water absorption must be low so as to avoid distortion; (4) high mechanical stability, good impact resistance, and high heat distortion resistance; (5) good flow properties (while in a molten state) so as to avoid the establishment of thermal stresses and subsequent optical nonuniformities (i.e., nonuniform birefringence); (6) the material must be clean and defect-free in order to ensure error-free scanning; and (7) it must have a long lifetime (on the order of 10 years).

The current material-of-choice for audio CDs is a relatively low molecular weight polycarbonate since it is the most economical material that best satisfies the above requirements.

22.D13 The mechanism by which the VCR head records and plays back audio/video signals is essentially the same as the manner by which the head on a computer storage device reads and writes, as described in Section 20.11.

Heads should be made from soft magnetic materials inasmuch as they are repeatedly magnetized and demagnetized. Some of the requisite properties for these materials are as follows: (1) a relatively high saturation flux density (a B_s of at least 0.5 tesla); (2) a relatively high initial permeability (at least 8000); (3) a relatively small hysteresis loop in order to keep energy losses small; (4) a low remanence; (5) a relatively high mechanical hardness in order to resist surface wear (a minimum Vickers hardness of 120); and (6) a moderate electrical resistivity (at least 0.6×10^{-6} Ω-m).

It is up to the student to supply three appropriate candidate materials having properties consistent with the above requirements.

22.D14 (a) Advantages of delivering drugs into the body using transdermal patches (as opposed to oral administration) are: (1) Drugs that are taken orally must pass through the digestive system and, consequently, may cause digestive discomfort. (2) Orally delivered drugs will ultimately pass through the liver which function is to filter out of the blood unnatural substances, including some drugs; thus, drug concentrations in the blood are diluted. (3) It is much easier to maintain a constant level of delivery over relatively long time periods using transdermal patches.

(b) In order for transdermal delivery, the skin must be permeable to the drug, or delivery agents must be available that can carry the drug through the skin.

(c) Characteristics that are required for transdermal patch materials are the following: they must be flexible; they must adhere to the skin; they must not cause skin irritation; they must be permeable to the drug; and they must not interact with the drug over long storage periods.

CHAPTER 23

ECONOMIC, EINVIRONMENTAL, AND SOCIETAL ISSUES IN MATERIALS SCIENCE AND ENGINEERING

QUESTION ANSWER

23.D1 The three materials that are used for beverage containers are glass, aluminum, and the polymer poly(ethylene terephthalate) (designated as PET or sometimes PETE). Currently, the most commonly used of these three materials is the PET. Its optical clarity is excellent, it is significantly lighter than glass, PET has high burst and impact strengths and is shatter-proof, it is inexpensive to produce, has high gas permeation resistance, is easily fabricated (by blow-molding), and PET containers are safer (there is no breakage as with glass and no cuts result from pull-tabs as with the Al cans). There are virtually no incineration and landfill problems with PET, although, PET is relatively nondegradable. On the down side, PET containers are nonrefillable, but even so, they require less energy to produce per filled unit volume than either aluminum or glass. Also, they can be recycled.

Glass containers are refillable and recyclable, are very impermeable to the passage of gases and liquids, and are more expensive to produce and fabricate into bottles than is PET. However, glass bottles are nonbiodegradable and can be dangerous when they break.

Aluminum beverage containers are nonrefillable and nonbiodegradable, but recyclable, and are also light in weight. Again, they are more expensive to produce than are PET bottles.