

## CHAPTER 5

### LIQUIDS AND SOLIDS

- 5.2** (a) London forces, dipole-dipole, hydrogen bonding; (b) London forces, dipole-dipole; (c) London forces, dipole-dipole; (d) London forces
- 5.4** (b) and (d),  $O_2$  and  $CO_2$  do not have dipole moments.
- 5.6** Ionic solids are high melting because the energy to get the ions to move past each other is very strong, on the order of  $250 \text{ kJ} \cdot \text{mol}^{-1}$ . Dissolution in water, however, compensates for the energy required to separate the ions by hydrating those ions. The energy produced when the ions are hydrated offsets the energy required to separate the ions. In network solids the bonds are covalent. Because the atoms there are not in ionic form, there is no hydration energy (or solvation energy if other solvents are used) to offset the breaking of the covalent bonds. Also, covalent bonds such as C—C bonds are very strong, with an average value of  $318 \text{ kJ} \cdot \text{mol}^{-1}$  for a single bond. Comparisons between ionic solids and network solids are complicated by the fact that there is more than one interaction—i.e., an ion will bond to a number of ions in the solid state just as the atoms in a network solid form covalent bonds to a number of other atoms.
- 5.8** Only molecules with H attached to the electronegative atoms N, O, and F can hydrogen bond. Of the molecules given, only (b)  $CH_3COOH$  and

(c)  $\text{CH}_3\text{CH}_2\text{OH}$  have hydrogen attached to oxygen, so these are the only ones that can undergo hydrogen bonding.

**5.10** Arrangement III should possess the strongest intermolecular attractions because the molecules are oriented with hydrogen atoms directed toward the lone pairs on nitrogen atoms of neighboring molecules. This geometry allows hydrogen bonding to occur more readily than in arrangement I or II.

**5.12** (a)  $\text{H}_2\text{O}$  ( $100^\circ\text{C}$  vs.  $-60.3^\circ\text{C}$ ) because hydrogen bonding is important for  $\text{H}_2\text{O}$  but not for  $\text{H}_2\text{S}$ ; (b)  $\text{NH}_3$  ( $-33^\circ\text{C}$  vs.  $-78^\circ\text{C}$ ) because hydrogen bonding is important in ammonia but not phosphine; (c)  $\text{KBr}$  ( $1435^\circ\text{C}$  vs.  $3.6^\circ\text{C}$ ) because it is an ionic compound as opposed to a molecular compound; (d)  $\text{SiH}_4$  ( $-112^\circ\text{C}$  vs.  $-164^\circ\text{C}$ ) because it has more electrons with which to form stronger London forces.

**5.14** (a)  $\text{BF}_3$  is a trigonal planar molecule whereas  $\text{ClF}_3$  is T-shaped. The latter will be polar and should have the higher boiling point.  $\text{BF}_3$  boils at  $-99.9^\circ\text{C}$ ;  $\text{ClF}_3$  boils at  $11.3^\circ\text{C}$ . (b)  $\text{SF}_4$  is seesaw shaped whereas  $\text{CF}_4$  is tetrahedral. The former should be polar and have the higher boiling point. The greater number of electrons of  $\text{SF}_4$  also contribute to the higher boiling point.  $\text{SF}_4$  boils at  $-40^\circ\text{C}$ ;  $\text{CF}_4$  boils at  $-129^\circ\text{C}$ . (c) Both molecules are planar but the *cis* form will have a dipole moment and the *trans* form will not. This will give the *cis* form dipole-dipole interactions not present in the other molecule, giving it the higher boiling point. The *cis* compound boils at  $60.3^\circ\text{C}$  whereas the *trans* compound boils at  $47.5^\circ\text{C}$ .

- 5.16** The ionic radius of  $\text{Ca}^{2+}$  is 100 pm and that of  $\text{In}^{3+}$  is 72 pm. The ratio of energies will be given by

$$E_p \propto \frac{-|z|\mu}{d^2}$$

$$E_{p\text{Ca}^{2+}} \propto \frac{-|z|\times\mu}{d^2} = \frac{-|2|\mu}{(100)^2}$$

$$E_{p\text{In}^{3+}} \propto \frac{-|z|\mu}{d^2} = \frac{-|3|\mu}{(72)^2}$$

The electric dipole moment of the water molecule ( $\mu$ ) will cancel:

$$\text{ratio} \left( \frac{E_{p\text{Ca}^{2+}}}{E_{p\text{In}^{3+}}} \right) = \frac{-|2|\mu/(100)^2}{-|3|\mu/(72)^2} = \frac{2(72)^2}{3(100)^2} = 0.35$$

The attraction of the  $\text{Ca}^{2+}$  ion will be less than that of the  $\text{In}^{3+}$  ion because it has both a larger radius and a lower charge.

- 5.18** The ionic radius of  $\text{Na}^+$  is 102 pm and that of  $\text{K}^+$  is 138 pm. The ratio of energies will be given by

$$E_p \propto \frac{-|z|\mu}{d^2}$$

$$E_{p\text{Na}^+} \propto \frac{-|1|\mu}{(102 \text{ pm})^2}$$

$$E_{p\text{K}^+} \propto \frac{-|1|\mu}{(138 \text{ pm})^2}$$

The electric dipole moment of the water molecule ( $\mu$ ) will cancel:

$$\text{ratio} \left( \frac{E_{p\text{Na}^+}}{E_{p\text{K}^+}} \right) = \frac{\frac{-|1|\mu}{(102 \text{ pm})^2}}{\frac{-|1|\mu}{(138 \text{ pm})^2}} = \frac{(138 \text{ pm})^2}{(102 \text{ pm})^2} = 1.83$$

The water molecule will be more strongly attracted to the  $\text{Na}^+$  ion because of its smaller radius.

- 5.20** (a) network; (b) ionic; (c) molecular; (d) molecular;  
(e) network

**5.22** Yes, we would expect the energy of interaction between two rotating molecules to be temperature dependent. As the temperature is raised, the volume will increase, the molecules will be farther apart,  $r$  in the denominator of Eq. 4 will increase, and the potential energy of interaction will be reduced in magnitude. In addition, the rate of rotation will increase with the temperature so the time when the dipoles are aligned favorably is likely to be reduced.

**5.24** (a) Ethanol should have a greater viscosity than dimethyl ether because ethanol can hydrogen bond while dimethyl ether cannot. (b) Propanone (a.k.a. acetone) should be more viscous than butane because it is more polar than butane.

**5.26**  $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{C}_6\text{H}_6 < \text{H}_2\text{O} < \text{CH}_3\text{CH}_2\text{OH} < \text{CH}_2\text{OHCH}_2\text{OH} < \text{CH}_2\text{OHCHOHCH}_2\text{OH}$

In order to predict relative viscosities we need to consider both the strength of intermolecular forces and the tendency of the molecules to get tangled like spaghetti (see Figure 5.12). Since glycerol,  $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$ , can form several hydrogen bonds per molecule and it has a long chain structure, it has both strong intermolecular forces and the tendency to get tangled. Ethylene glycol,  $\text{CH}_2\text{OHCH}_2\text{OH}$ , is just one  $-\text{CH}-\text{OH}-$  unit smaller than glycerol, so we would expect it to be less viscous than glycerol but more viscous than ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ . The relative viscosities of ethanol, water, and benzene are given in Figure 5.11. Finally, since propane,  $\text{CH}_3\text{CH}_2\text{CH}_3$ , has the weakest intermolecular forces it would be expected to be the least viscous. Note that it is the only substance in the group that is a gas under normal ambient conditions.

**5.28** Molecules with stronger intermolecular forces tend to have higher surface tension. Using this principle along with the data given in Table 5.3 we can match the values with the substances as follows:  $\text{H}_2\text{O}$  72.75,

$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$  18.43,  $\text{C}_6\text{H}_6$  28.85,  $\text{CH}_3\text{CH}_2\text{OH}$  22.75,  $\text{CH}_3\text{COOH}$  27.80.

Note that units for surface tension are mN/m.

- 5.30** Just as molecules have polarity, surfaces of solids have polarity. By carrying out the silylation reaction, the surface of the glass will become less polar because the  $\text{Si}(\text{CH}_3)_3$  groups are nonpolar. Therefore, polar liquids will not adhere to the surface quite so readily.
- 5.32** Assuming that we can ignore any elliptical deformation of the cross-sectional area occupied by the liquid in the tube as it is tilted, and that the surface tension is a constant, all of the factors in the expression seem to be independent of the tip angle,  $\theta$ . However, we should note that when the tube is vertical, i.e.,  $\theta = 0^\circ$ ,

$$h = l \cos \theta = \frac{2\gamma}{gdr}$$

where  $l$  is the length of the tube occupied by liquid and  $\cos(0^\circ) = 1$ . As  $\theta$  gets larger,  $\cos \theta$  gets smaller. Since all of the factors on the right-hand side of the equation are constant, it appears that we can expect the height of the meniscus above the zero level,  $h$ , to remain the same while the length of the liquid in the tube,  $l$ , grows in counterbalance to the decrease in  $\cos \theta$ .

[Note that some physics textbooks represent the height to which a liquid will rise in a capillary tube in terms of a contact angle,  $\theta$ , between the liquid and the side of the tube. This angle reflects the difference between liquid-solid and liquid-vapor surface tensions. It is not the same as the tip angle called  $\theta$  in this problem.]

- 5.34** For a picture of the simple, a.k.a. primitive, cubic unit cell, see Figures 5.28 and 5.33a. (a) There are eight atoms at the eight corners of the unit cell. One-eighth of each of these atoms will lie in the unit cell for a total of

one atom per unit cell. (b) Each atom will be bonded to six atoms that form an octahedron. (c) The edge length of the unit cell for a primitive cubic cell will be twice the atomic radius of the atom or 334 pm in this case.

**5.36** (a)  $a$  = length of side for a unit cell; for an fcc unit cell,

$$a = \sqrt{8} r \text{ or } 2\sqrt{2} r = 354 \text{ pm}$$

$$V = a^3 = (354 \text{ pm} \times 10^{-12} \text{ m} \cdot \text{pm}^{-1})^3 = 4.42 \times 10^{-29} \text{ m}^3 = 4.42 \times 10^{-23} \text{ cm}^3$$

For an fcc unit cell there are 4 atoms per unit cell; therefore we have

$$\begin{aligned} \text{mass (g)} &= 4 \text{ Ni atoms} \times \frac{1 \text{ mol Ni atoms}}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \times \frac{58.71 \text{ g}}{\text{mol Ni atoms}} \\ &= 3.90 \times 10^{-22} \text{ g} \end{aligned}$$

$$d = \frac{3.90 \times 10^{-22} \text{ g}}{4.42 \times 10^{-23} \text{ cm}^3} = 8.82 \text{ g} \cdot \text{cm}^3$$

$$(b) \quad a = \frac{4r}{\sqrt{3}} = \frac{4 \times 250 \text{ pm}}{\sqrt{3}} = 577 \text{ pm}$$

$$V = (577 \times 10^{-12} \text{ m})^3 = 1.92 \times 10^{-28} \text{ m}^3 = 1.92 \times 10^{-22} \text{ cm}^3$$

Given 2 atoms per bcc unit cell:

$$\begin{aligned} \text{mass (g)} &= 2 \text{ Rb atoms} \times \frac{1 \text{ mol Rb atoms}}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \times \frac{85.47 \text{ g}}{\text{mol Rb atoms}} \\ &= 2.84 \times 10^{-22} \text{ g} \end{aligned}$$

$$d = \frac{2.84 \times 10^{-22} \text{ g}}{1.92 \times 10^{-22} \text{ cm}^3} = 1.5 \text{ g} \cdot \text{cm}^3$$

**5.38**  $a$  = length of unit cell edge

$$V = \frac{\text{mass of unit cell}}{d}$$

$$(a) \quad V = a^3 = \frac{(1 \text{ unit cell}) \left( \frac{107.87 \text{ g Ag}}{\text{mol Ag}} \right)}{10.500 \text{ g} \cdot \text{cm}^3} \times \frac{\left( \frac{1 \text{ mol Ag}}{6.0221 \times 10^{23} \text{ atoms Ag}} \right) \left( \frac{4 \text{ atoms}}{1 \text{ unit cell}} \right)}{10.500 \text{ g} \cdot \text{cm}^3}$$

$$a = 4.0864 \times 10^{-8} \text{ cm}$$

$$\text{For an fcc cell, } a = \sqrt{8} r, r = \frac{\sqrt{2} a}{4} = \frac{\sqrt{2} (4.0864 \times 10^{-8} \text{ cm})}{4} \\ = 1.4448 \times 10^{-8} \text{ cm or } 144.48 \text{ pm}$$

$$(b) \quad V = a^3 = \frac{(1 \text{ unit cell}) \left( \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} \right)}{7.190 \text{ g} \cdot \text{cm}^3} \times \frac{\left( \frac{1 \text{ mol Cr}}{6.022 \times 10^{23} \text{ atoms Cr}} \right) \left( \frac{2 \text{ atoms}}{1 \text{ unit cell}} \right)}{7.190 \text{ g} \cdot \text{cm}^3}$$

$$a = 2.885 \times 10^{-8} \text{ cm}$$

$$r = \frac{\sqrt{3} a}{4} = \frac{\sqrt{3} (2.885 \times 10^{-8} \text{ cm})}{4} = 1.249 \times 10^{-8} \text{ cm} = 124.9 \text{ pm}$$

**5.40** (a) In the fcc geometry, the unit cell will contain four atoms of Kr. The density will be given by

$$\text{mass in unit cell} = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{83.80 \text{ g Kr}}{\text{mol Kr}} \times \frac{1 \text{ mol Kr}}{6.022 \times 10^{23} \text{ atoms}} \\ = 5.566 \times 10^{-22} \text{ g} \cdot \text{unit cell}^{-1}$$

$$\text{volume of unit cell} = \left( 559 \text{ pm} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}} \right)^3 \\ = 1.75 \times 10^{-22} \text{ cm}^3 \cdot \text{unit cell}^{-1}$$

$$\text{density} = \frac{\text{mass in unit cell}}{\text{volume of unit cell}} = \frac{5.566 \times 10^{-22} \text{ g} \cdot \text{unit cell}^{-1}}{1.75 \times 10^{-22} \text{ cm}^3 \cdot \text{unit cell}^{-1}} = 3.18 \text{ g} \cdot \text{cm}^3$$

(b) The face diagonal of the unit cell will equal four times the radius of the Kr atom:

$$\sqrt{2} a = 4 r$$

$$r = \frac{\sqrt{2} a}{4} = \frac{\sqrt{2} (559 \text{ pm})}{4} = 198 \text{ pm}$$

$$(c) \quad V = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (198 \text{ pm})^3 = 3.25 \times 10^7 \text{ pm}^3$$

(d) Volume occupied by the four Kr atoms in one unit cell

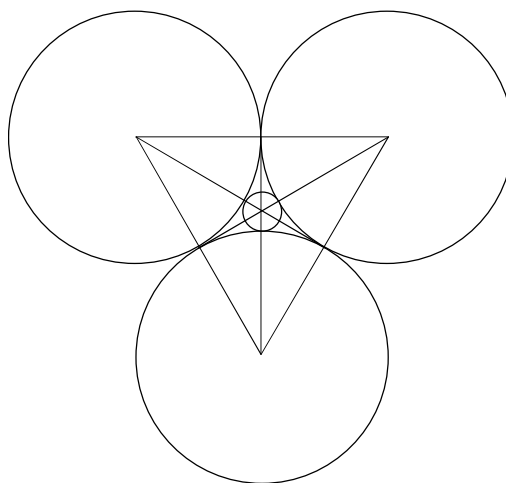
$$= 4(3.25 \times 10^7 \text{ pm}^3) = 1.30 \times 10^8 \text{ pm}^3 . \text{ The volume of the unit will be}$$

$$(559 \text{ pm})^3 = 1.75 \times 10^8 \text{ pm}^3 . \text{ The percent of occupied space will be given}$$

by

$$\frac{1.30 \times 10^8 \text{ pm}^3}{1.75 \times 10^8 \text{ pm}^3} \times 100 = 74.3\%$$

- 5.42** Recall from plane geometry that in an equilateral triangle, the altitudes, perpendicular bisectors of the sides, and angle bisectors coincide and divide each other in the ratio 2:1.



Since the vertical line in the sketch above is the altitude,  $a$ , of the equilateral triangle that connects the centers of the large circles, we can set  $a = 3x$ . Then two-thirds of its length is below the center of the small circle. From the sketch, we can see that  $2x = r_{\text{large}} + r_{\text{small}}$ .

We can use the Pythagorean Theorem to get  $x$  in terms of  $r_{\text{large}}$ .



$$(2r_{\text{large}})^2 = r_{\text{large}}^2 + a^2$$

$$a^2 = 3r_{\text{large}}^2$$

$$a = \sqrt{3}r_{\text{large}} = 3x$$

$$x = \frac{r_{\text{large}}}{\sqrt{3}}$$

Recall  $2x = r_{\text{large}} + r_{\text{small}}$ , so

$$2\left(\frac{r_{\text{large}}}{\sqrt{3}}\right) = r_{\text{large}} + r_{\text{small}}$$

$$r_{\text{small}} = 1.1547r_{\text{large}} - r_{\text{large}} = 0.1547r_{\text{large}}$$

In other words, the radius of the cavity is 15.5% as large as the radius of the large disks. A CD has a radius of  $61 \pm 1$  mm with a measured cavity radius between three close-packed disks of  $9 \pm 1$  mm. This experimental result is in good agreement with our geometrical treatment since  $0.155 \times 61 = 9.5$ .

**5.44** (a) anions:  $8 \text{ corners} \times \frac{1}{8} \text{ atom} \cdot \text{corner}^{-1} + 6 \text{ faces} \times \frac{1}{2} \text{ atom} \cdot \text{face}^{-1} = 4$

atoms; cations:  $12 \text{ edges} \times \frac{1}{4} \text{ atom} \cdot \text{edge}^{-1} + 1 \text{ atom in center} = 4$  atoms;

the cation to anion ratio is thus  $4 : 4$  or  $1 : 1$ .

(b) calcium ions at corners of cell and at face centers:

$8 \text{ corners} \times \frac{1}{8} \text{ atom} \cdot \text{corner}^{-1} + 6 \text{ faces} \times \frac{1}{2} \text{ atom} \cdot \text{face}^{-1} = 4$  atoms; fluoride ions:

8 atoms in tetrahedral sites within the face-centered cubic lattice of  $\text{Ca}^{2+}$  ions; these atoms lie completely within the unit cell.

ratio of  $\text{Ca} : \text{F} = 4 : 8$  or  $1 : 2$ , giving an empirical formula of  $\text{CaF}_2$

**5.46** Ti atoms at corners:  $8 \text{ corners} \times \frac{1}{8} \text{ atom} \cdot \text{corner}^{-1} = 1$  Ti

Ca atoms: 1 atom at center = 1 Ca

O atoms: 12 atoms, one on each edge gives  $12 \text{ edges} \times \frac{1}{4} \text{ atom} \cdot \text{edge}^{-1}$  or 3 atoms:

3 O

empirical formula =  $\text{CaTiO}_3$

**5.48** (a)  $\text{ratio} = \frac{138 \text{ pm}}{196 \text{ pm}} = 0.704$ , predict rock-salt structure with (6,6)

coordination;

(b)  $\text{ratio} = \frac{58 \text{ pm}}{196 \text{ pm}} = 0.29$ , predict zinc-blende structure with (4,4)

coordination; however, LiBr actually adopts the rock-salt structure.

(c)  $\text{ratio} = \frac{136 \text{ pm}}{140 \text{ pm}} = 0.971$ , predict cesium-chloride structure with (8,8)

coordination; however, BaO actually adopts the rock-salt structure.

- 5.50** (a) In the rock-salt structure, the unit cell edge length is equal to two times the distance between centers of the oppositely charged ions. Thus for NaI,  $a = 644 \text{ pm}$ . The volume of the unit cell will be given by converting to  $\text{cm}^3$ :

$$V = \left( 644 \text{ pm} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}} \right)^3 = 2.67 \times 10^{-22} \text{ cm}^3$$

There are four formula units in the unit cell (see Exercise 5.44) so the mass in the unit cell will be given by

$$\text{mass in unit cell} = \frac{\left( \frac{4 \text{ formula units}}{1 \text{ unit cell}} \right) \times \left( \frac{149.89 \text{ g NaI}}{1 \text{ mol NaI}} \right)}{6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1}} = 9.96 \times 10^{-22} \text{ g}$$

The density will be given by the mass in the unit cell divided by the volume of the unit cell:

$$d = \frac{9.96 \times 10^{-22} \text{ g}}{2.67 \times 10^{-22} \text{ cm}^3} = 3.73 \text{ g} \cdot \text{cm}^3$$

- (b) For the cesium-chloride structure, it is the body diagonal that represents two times the distance between the cation and anion centers. Thus the body diagonal is equal to 712 pm.

For a cubic cell, the body diagonal  $= \sqrt{3} a = 712 \text{ pm}$   
 $a = 411 \text{ pm}$

$$a^3 = V = \left( 411 \text{ pm} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}} \right)^3 = 6.94 \times 10^{-23} \text{ cm}^3$$

There is one formula unit of CsCl in the unit cell, so the mass in the unit cell will be given by

$$\text{mass in unit cell} = \frac{\left( \frac{1 \text{ formula unit}}{1 \text{ unit cell}} \right) \left( \frac{168.36 \text{ g CsCl}}{1 \text{ mol CsCl}} \right)}{6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1}} = 2.796 \times 10^{-22} \text{ g}$$

$$d = \frac{2.796 \times 10^{-22} \text{ g}}{6.94 \times 10^{-23} \text{ cm}^3} = 4.03 \text{ g} \cdot \text{cm}^3$$

- 5.52** (a) Solid methane is held together only by London forces, whereas chloromethane is held in solid form by both London forces and dipole-dipole forces. Methanol will exhibit both London forces and dipole-dipole interactions, in addition to hydrogen bonding. (b) The melting points should increase in the order  
 $\text{CH}_4 (-183^\circ\text{C}) < \text{CH}_3\text{Cl} (-97^\circ\text{C}) < \text{CH}_3\text{COOH} (16^\circ\text{C})$ .

**5.54** boron, carbon, phosphorus, silicon

- 5.56** (a) The alloy is substitutional—the phosphorus atoms are similar in size to the silicon atoms and can replace them in the crystal lattice.  
 (b) Because phosphorus has one more valence electron than silicon, the added electron will be forced into the conduction band (see Chapter 3) making it easier for this electron to move through the solid. The conductivity of the doped silicon is thus higher than the pure material.

- 5.58** The formula of zinc oxide is ZnO with one zinc atom per oxygen atom. After heating in a vacuum, some of the oxygen atoms are able to leave the

lattice as  $\text{O}_2(\text{g})$ . Because the oxidation state of oxygen in zinc oxide is  $-2$  and in  $\text{O}_2$  it is  $0$ , some of the zinc atoms must have been reduced from  $\text{Zn}^{2+}$  to  $\text{Zn}^0$ . Because this process is reversible, the lattice must remain mostly intact. The result is that the  $\text{ZnO}_x (x < 1)$  will have more electrons that can move into the conduction band, enhancing the electrical conductivity of the semiconductor. Regaining these electrons reverses this process and lowers the electrical conductivity to the starting value.

- 5.60** (a) The residual composition of Wood's metal is Bi; this constitutes 51% of the alloy by mass. The number of moles per 100 g of alloy is: 0.105 mol Sn, 0.111 mol Cd, 0.11 mol Pb, and 0.24 mol Bi. The atom ratio is 2.3 Bi : 1.1 Cd : 1.1 Pb : 1 Sn.

(b) Of 100 g of steel, there are 1.75 g C and 98.25 g iron.

$$\text{mol C} = \frac{1.75 \text{ g}}{12.01 \text{ g} \cdot \text{mol}^{-1}}$$

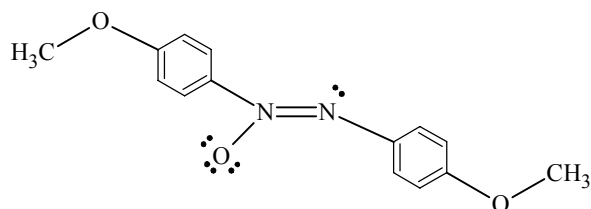
$$\text{mol C} = 0.146 \text{ mol}$$

$$\text{mol Fe} = \frac{98.25 \text{ g}}{55.85 \text{ g} \cdot \text{mol}^{-1}}$$

$$\text{mol Fe} = 1.759 \text{ mol}$$

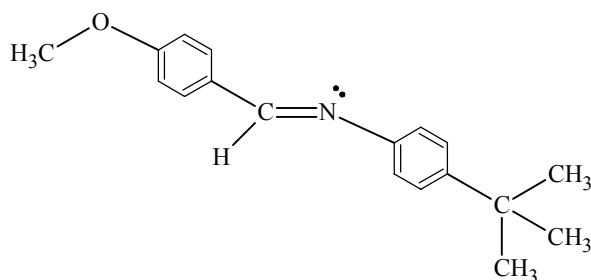
$$\text{Ratio Fe : C} = 1.759 \text{ mol} \div 0.146 \text{ mol} = 12.0 : 1$$

- 5.62** (a) The N atoms fit the pattern for a trigonal planar arrangement of three objects—two bonds and one lone pair for one nitrogen atom, and three bonds for the other. This corresponds to  $\text{sp}^2$  hybridization. The bond angles are all close to  $120^\circ$ .



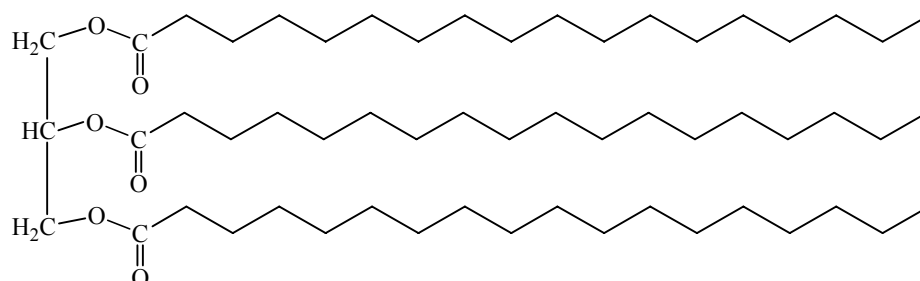
(b) The multiple bond structure of this molecule gives rise to the rigid rod-like nature of the molecule. The alternating double bonds that allow electrons to be delocalized extend from one ring across the bridging N atoms to the other ring. To maintain the delocalization, the phenyl rings do not rotate about the O—N axis. Thus, the entire molecule is like a stiff, flat rod. Only the CH<sub>3</sub> groups rotate. Another feature that enhances the tendency to form liquid crystalline materials is the inclusion of the aromatic rings. The  $\pi$ -bonds in aromatic rings show a strong tendency to stack one upon another; this helps orient the molecules in the liquid crystalline array. (c) There is an infinite number of answers here. Basically, any molecule that has a fairly rigid backbone structure without too many dangling appendages to interfere with the packing will be a possible liquid crystalline material.

- 5.64** The strategy employed here is simply to modify the attached groups with a view toward disrupting some of the London interactions that the molecule will have with its neighbors, thus allowing the molecules more freedom to move with respect to each other—if the intermolecular forces are too strong, the material will be held in the solid state longer. One must be careful, because too much disruption of these forces will also destroy the liquid crystal order as well. This is still a matter of trial and error in many cases. For example, the molecule



is very similar to *p*-azoxyanisole but has a liquid crystal range of 21°C–47°C. It would be expected that the bulky *t*-butyl group (–C(CH<sub>3</sub>)<sub>3</sub>) would help to disrupt the orderly packing of the molecule.

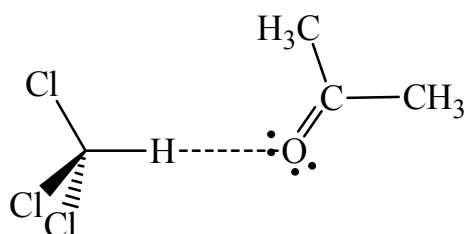
- 5.66** (a) Note that each kink in the long chains represents one  $-\text{CH}_2-$  group while the terminus of each chain is a  $-\text{CH}_3$  group.



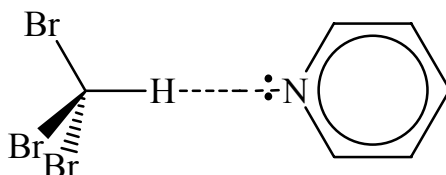
- (b) London forces are very important here. Notice that the long chains are aligned parallel to each other, as may be expected because they each have a large surface area that can interact with the other chains.
- (c) Although this molecule does have some oxygen atoms with lone pairs, the long hydrocarbon chains are very nonpolar. Given that stearic acid itself is only slightly soluble in water, one would expect this molecule to be insoluble, which is indeed the case.

- 5.68** (a)

(i)



(ii)



- (b) The hydrogen atom that has low electron density in both cases is attached to carbon on the trihalomethane molecule. The hydrogen bonds formed by these pairs of molecules are referred to as weak hydrogen

bonds. The hydrogen atoms are not as electropositive as they would be if they were bound directly to O, N, or F. But electronegative atoms attached to a neighboring carbon atom draw enough electron density away from the H through the bonds to allow it to participate in hydrogen bonding with a lone pair on an electronegative atom in another molecule.

- 5.70** (a) A body-centered cubic lattice has two atoms per unit cell. For this cell, the relation between the radius of the atom  $r$  and the unit cell edge length  $a$  is derived from the body diagonal of the cell, which is equal to four times the radius of the atom. The body diagonal is found from the Pythagorean theorem to be equal to

$$\sqrt{3} a.$$

$$4 r = \sqrt{3} a$$

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

The volume of the unit cell is given by

$$V = a^3 = \left( \frac{4 r}{\sqrt{3}} \right)^3$$

If  $r$  is given in pm, then a conversion factor to cm is required:

$$V = a^3 = \left( \frac{4 r}{\sqrt{3}} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{10 \text{ cm}}{\text{m}} \right)^3$$

Because there are two atoms per bcc unit cell, the mass in the unit cell will be given by

$$\text{mass} = \left( \frac{2 \text{ atoms}}{\text{unit cell}} \right) \left( \frac{M}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \right)$$

The density will be given by

$$\begin{aligned}
 d &= \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{\left(\frac{2 \text{ atoms}}{\text{unit cell}}\right) \left(\frac{M}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}}\right)}{\left(\frac{4r}{\sqrt{3}} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}}\right)^3} \\
 &= \frac{\left(\frac{2 \text{ atoms}}{\text{unit cell}}\right) \left(\frac{M}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}}\right)}{(2.309 \times 10^{-10} r)^3} \\
 &= \frac{(2.698 \times 10^5) M}{r^3}
 \end{aligned}$$

or

$$r = \sqrt[3]{\frac{(2.698 \times 10^5) M}{\text{density}}}$$

where  $M$  is the molar mass in  $\text{g} \cdot \text{mol}^{-1}$  and  $r$  is the radius in pm.

For the fcc unit cell, the relation between the radius of the atom  $r$  and the unit cell edge length  $a$  is

$$\begin{aligned}
 4r &= \sqrt{2} a \\
 a &= \frac{4r}{\sqrt{2}}
 \end{aligned}$$

The volume of the unit cell is given by

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

If  $r$  is given in pm, then a conversion factor to cm is required:

$$V = a^3 = \left(\frac{4r}{\sqrt{2}} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}}\right)^3$$

Because there are four atoms per fcc unit cell, the mass in the unit cell will be given by

$$\text{mass} = \left(\frac{4 \text{ atoms}}{\text{unit cell}}\right) \left(\frac{M}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}}\right)$$

The density will be given by



$$d = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{\left(\frac{4 \text{ atoms}}{\text{unit cell}}\right) \left(\frac{M}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}}\right)}{\left(\frac{4r}{\sqrt{2}} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}}\right)^3}$$

$$= \frac{(2.936 \times 10^5)M}{r^3}$$

or

$$r = \sqrt[3]{\frac{(2.936 \times 10^5)M}{d}}$$

where  $M$  is the molar mass in  $\text{g} \cdot \text{mol}^{-1}$  and  $r$  is the radius in pm.

Setting these bcc and fcc equations equal to each other (because both are equal to  $r$ ) and cubing both sides, we obtain

$$\frac{(2.936 \times 10^5)M}{d_{\text{fcc}}} = \frac{(2.698 \times 10^5)M}{d_{\text{bcc}}}$$

The molar mass  $M$  is the same and will cancel from the equation.

$$\frac{(2.936 \times 10^5)}{d_{\text{fcc}}} = \frac{(2.698 \times 10^5)}{d_{\text{bcc}}}$$

Rearranging, we get

$$\begin{aligned} d_{\text{fcc}} &= \frac{(2.936 \times 10^5)}{(2.698 \times 10^5)} d_{\text{bcc}} \\ &= 1.088 d_{\text{bcc}} \\ &= 1.088 \times 19.6 \text{ g} \cdot \text{cm}^3 \\ &= 21.0 \text{ g} \cdot \text{cm}^3 \end{aligned}$$

(c) For the different alkali metals, we calculate the results given in the following table:

Gas	Density bcc (g · cm <sup>3</sup> )	Density fcc (g · cm <sup>3</sup> )	Molar mass (g · mol <sup>-1</sup> )	Radius (pm)
Li	0.53	0.58	6.94	152
Na	0.97	1.0	22.99	186
K	0.86	0.94	39.10	231
Rb	1.53	1.66	85.47	247
Cs	1.87	2.03	132.91	268

(d) Li, Na, and K all have densities less than that of water and should float, but not for long, as they all react violently with water to form MOH(aq) and H<sub>2</sub>(g).

**5.72** (a) The ion-ion potential energy ratio will be given by

$$V \propto \frac{z_1 z_2}{d}$$

$$V_{\text{LiCl}} \propto \frac{z_1 z_2}{d_{\text{Li-Cl}}}$$

$$V_{\text{KCl}} \propto \frac{z_1 z_2}{d_{\text{K-Cl}}}$$

$$\text{ratio} \left( \frac{V_{\text{Li}^+}}{V_{\text{K}^+}} \right) = \frac{\frac{z_1 z_2}{d_{\text{Li-Cl}}}}{\frac{z_1 z_2}{d_{\text{K-Cl}}}} = \frac{1}{\frac{d_{\text{Li-Cl}}}{d_{\text{K-Cl}}}} = \frac{d_{\text{K-Cl}}}{d_{\text{Li-Cl}}}$$

From the ionic radii in Figure 1.41 we can calculate the LiCl and KCl distances to be

$$d_{\text{Li-Cl}} = 58 \text{ pm} + 181 \text{ pm} = 239 \text{ pm}$$

$$d_{\text{K-Cl}} = 138 \text{ pm} + 181 \text{ pm} = 319 \text{ pm}$$

$$\text{ratio} = \frac{319 \text{ pm}}{239 \text{ pm}} = 1.33$$

(b) The ratio for the ion-dipole interaction is derived as follows:

$$V \propto \frac{-|z|\mu}{d^2}$$

$$V_{\text{Li}^+} \propto \frac{-|z|\mu}{d^2} = \frac{-|1|\mu}{(58)^2}$$

$$V_{\text{K}^+} \propto \frac{-|z|\mu}{d^2} = \frac{-|1|\mu}{(138)^2}$$

The electric dipole moment of the water molecule ( $\mu$ ) will cancel:

$$\text{ratio} \left( \frac{V_{\text{Li}^+}}{V_{\text{K}^+}} \right) = \frac{-|1|\mu/(58)^2}{-|1|\mu/(138)^2} = \frac{(138)^2}{(58)^2} = 5.66$$

(c) Because the ion-dipole interactions are proportional to  $d^2$  and the ion-ion interactions directly proportional to  $d$ , the relative importance of hydration will be much larger for the smaller lithium ion.

**5.74** The number of oxide ions is equal to  $12 \text{ edges} \times \frac{1}{4} \text{ oxide ion in the unit cell per edge}$ , for a total of three. For the niobium atoms, there will be six faces with  $\frac{1}{2}$  of the niobium atom per face inside the cell, also for a total of three. The empirical formula will be NbO, with three formula units in the unit cell.

**5.76** (a) The oxidation state on uranium must balance the charge due to the oxide ions. If 2.17 oxide ions are present with a charge of  $-2$  per oxide ion, then the uranium must have an average oxidation state of  $+4.34$ .  
 (b) This is most easily solved by setting up two equations in two unknowns. We know that the total charge on the uranium atoms present must equal  $+4.34$ , so if we multiply the charge on each type of uranium by the fraction of uranium present in that oxidation state and sum the values, we should get  $4.34$ .

Let  $x$  = fraction of  $\text{U}^{4+}$ ,  $y$  = fraction of  $\text{U}^{5+}$ , then

$$4x + 5y = 4.34$$

Also, because we are assuming that all the uranium is either  $+4$  or  $+5$ , the fractions of each present must add up to 1:

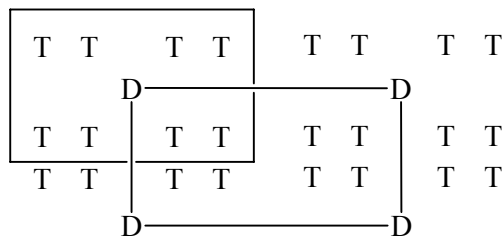
$$x + y = 1$$

Solving these two equations simultaneously, we obtain  $y = 0.34$ ,  $x = 0.66$ .

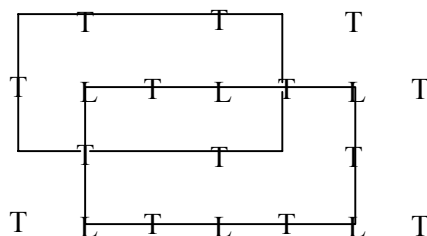
- 5.78** (a) False. In order for the unit cell to be considered body centered, the atom at the center must be identical to the atoms at the corners of the unit cell. (b) True. The properties of the unit cell in general must match the properties of the bulk material. (c) True. This is the basis for Bragg's law. (d) False. The angles that define the values of the unit cell can have any value, the only restriction being that opposing faces of the unit cell must be parallel.

- 5.80** There are several ways to draw unit cells that will repeat to generate the entire lattice. Some examples are shown below where T represents a tree, D a dog, and L a leaf. The choice of unit cell is determined by conventions that are beyond the scope of this text (the smallest unit cell that indicates all of the symmetry present in the lattice is typically the one of choice).

(a)



(b)



<b>5.82</b>	(a)	Molecule	Molar mass ( $\text{g} \cdot \text{mol}^{-1}$ )	Boiling point ( $^{\circ}\text{C}$ )
	(1)	$\text{CH}_4$	16.04	-164
	(2)	$\text{C}_2\text{H}_6$	30.07	-88.6
	(3)	$\text{CH}_3\text{CH}_2\text{CH}_3$	44.11	-42.1
	(4)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	58.13	-0.5
	(5)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	72.15	36.1
	(6)	$(\text{CH}_3)_3\text{CH}$	58.13	-11.7
	(7)	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$	72.15	27.8
	(8)	$\text{C}(\text{CH}_3)_4$	72.15	9.5

(b) The easiest comparison to make is among those compounds that are all straight chain compounds (those which do not have carbon atoms attached to more than two other carbon atoms). This includes [1] methane, [2] ethane, [3] propane, [4] butane, and [5] pentane. From the data it is clear that the boiling point increases regularly with an increase in molar mass. The increase in boiling point arises because the bigger molecules have more surface area and more electrons with which to interact with other molecules (i.e., the effect of the London forces will be greater if there is more surface area to interact via instantaneous dipoles).

(c) The molecular shape issue is best examined by comparing molecules of the same molar mass. The best comparisons are, therefore, between butane and 2-methylpropane (isobutane [6]), and between pentane, 2-methylbutane (isopentane [7]) and 2,2-dimethylpropane (neopentane [8]). What is clear is that the boiling point decreases as the number of side groups increases. If one constructs models of these compounds, one can see that the more branched a molecule is, the more spherical and compact it becomes. More spherical molecules have less surface area (which is exposed to other molecules for the formation of London forces).

- 5.84** Hydrogen ions can “migrate” through a solution much faster than other ions because they essentially do not really have to move at all. The hydrogen bonding network readily allows the shifting of hydrogen bonds, so that a proton can become available in solution almost instantaneously anywhere without any specific individual proton actually having to move any great distance. It amounts to the migration of a unit of positive charge through the network of hydrogen-bonded water molecules. Any other molecule or ion would have to migrate through the solution normally, as an intact unit.
- 5.86** (a) The gases with the larger van der Waals’  $a$  parameter are: (i) Ne; (ii) O<sub>2</sub>; (iii) CO<sub>2</sub>; (iv) H<sub>2</sub>CO; (v) CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>. (b) The gases with the larger van der Waals’  $b$  parameter are: (i) Br<sub>2</sub>; (ii) F<sub>2</sub>; (iii) CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>; (iv) Kr; (v) SO<sub>2</sub>.
- 5.88** (a) The octahedral hole is considerably bigger than the tetrahedral hole and can accommodate an ion with a radius about 3.7 times that of the tetrahedral hole.
- (b) If the anions are close packed in a cubic close-packed array, the unit cell will be a fcc unit cell. The octahedral sites will lie at the body center of the cell and at the center of each edge. If the unit cell is divided into octants, then there will be a tetrahedral site at the center of each octant. In the cubic close-packed geometry, the face diagonal of the unit cell will represent four times the radius of the anion:
- $$4 r_{\text{Anion}} = a \sqrt{2}$$
- If a cation occupies the octahedral site along the unit cell edge (a cation at the very center of the cell will be identical), then the maximum size it can have if the anions are close-packed will be when  $2 r_{\text{Anion}} + 2 r_{\text{Cation}} = a$ .
- Combining these two relationships, we see that the radius of the cation will be

$$2 r_{\text{Cation, octahedral}} = a - 2 r_{\text{Anion}} = a - 2 \left( \frac{a \sqrt{2}}{4} \right) = a - \frac{a \sqrt{2}}{2} = a \left( \frac{2 - \sqrt{2}}{2} \right)$$

The distance between the cation and the anion in a tetrahedral site will be given by  $\frac{1}{4}$  the body diagonal of the cell, which will correspond to

$$r_{\text{Cation, tetrahedral}} + r_{\text{Anion}}$$

$$r_{\text{Cation, tetrahedral}} + r_{\text{Anion}} = \frac{a \sqrt{3}}{4}$$

$$r_{\text{Cation, tetrahedral}} = \frac{a \sqrt{3}}{4} - r_{\text{Anion}} = \frac{a \sqrt{3}}{4} - \frac{a \sqrt{2}}{4} = \frac{a (\sqrt{3} - \sqrt{2})}{4}$$

The ratio of  $r_{\text{Cation, octahedral}}$  to  $r_{\text{Cation, tetrahedral}}$  will thus be given by

$$\text{ratio} = \frac{a \left( \frac{2 - \sqrt{2}}{2} \right)}{a (\sqrt{3} - \sqrt{2})/4} = \frac{\left( \frac{2 - \sqrt{2}}{2} \right)}{(\sqrt{3} - \sqrt{2})/4} = 3.7$$

Notice that the value of  $a$  will cancel in the calculation, so that the ratio is independent of the actual edge length.

(c) If half the tetrahedral holes are filled, there will be four cations in the unit cell. The fcc cell will have a total of four anions from contributions of atoms at the corners and face centers, so the empirical formula will be MA.

**5.90** The calcium fluoride lattice is based upon a face-centered cubic unit cell with the  $\text{Ca}^{2+}$  ions occupying the corners and face centers. The  $\text{F}^{-}$  ions are located in the centers of the eight tetrahedral cavities found within the face-centered cell. In the unit cell there are four formula units of  $\text{CaF}_2$ . Using this information and the density given in Ex. 5.79, we can calculate the volume of the unit cell.

$$V = \frac{\left( \frac{78.08 \text{ g} \cdot \text{mol}^{-1}}{6.022 \times 10^{23} \text{ formula units} \cdot \text{mol}^{-1}} \right) (4 \text{ formula units} \cdot \text{unit cell}^{-1})}{3.180 \text{ g} \cdot \text{cm}^{-3}}$$

$$V = 1.631 \times 10^{-22} \text{ cm}^3 = 1.631 \times 10^8 \text{ pm}^3$$

The occupied volume is calculated from the size of the ions using their ionic radii [ $r(\text{Ca}^{2+}) = 100 \text{ pm}$ ;  $r(\text{F}^-) = 133 \text{ pm}$ ].

$$V_{\text{Ca}^{2+}} = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (100 \text{ pm})^3 = 4.19 \times 10^6 \text{ pm}^3$$

$$V_{\text{F}^-} = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (133 \text{ pm})^3 = 9.85 \times 10^6 \text{ pm}^3$$

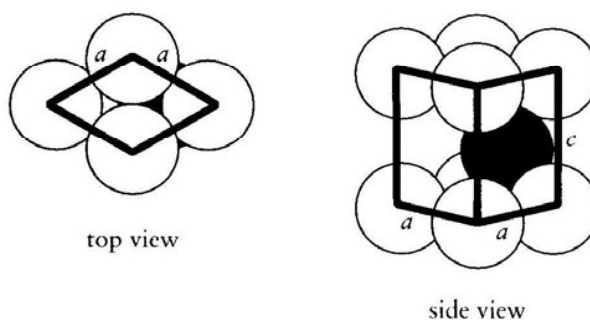
The total volume occupied is

$4(4.19 \times 10^6 \text{ pm}^3) + 8(9.85 \times 10^6 \text{ pm}^3) = 9.56 \times 10^7 \text{ pm}^3$ . The percent of empty space will be given by

$$\frac{(1.631 \times 10^8 \text{ pm}^3 - 9.56 \times 10^7 \text{ pm}^3)}{1.631 \times 10^8 \text{ pm}^3} \times 100 = 41.4\%$$

41.4% of the space is empty.

- 5.92** The difficulty with this problem is choosing a proper unit cell for the hexagonal lattice. This cell is represented below:

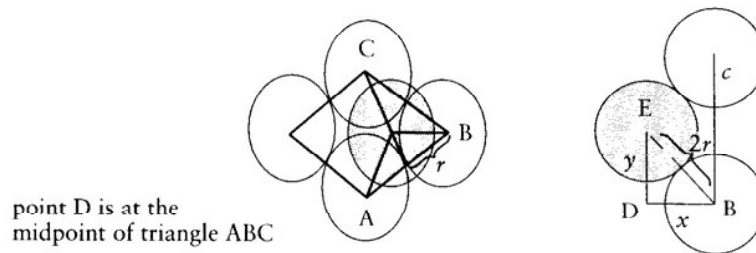


The unit cell has the hexagonal shape where there are two edges with the same length  $a$  and a third that is different from  $a$ , which is labeled  $c$ . In this unit cell there are a total of two atoms. One is present from the sum of the parts of the atoms on the corners; the second is the atom that is completely enclosed (see side view). All the atoms are equivalent, but the one inside the unit cell is shaded for easy reference.

The distance  $a$  is equal to twice the radius of the atom, but  $c$  must be calculated using geometry and trigonometry. It too is related to the radius of the atom for a close-packed lattice of a single element. Upon examining



the geometry in order to set up the calculation, what we note is that the totally enclosed atom forms a regular tetrahedron with three atoms in the face. The center of this tetrahedron lies exactly in the face of the unit cell. The distance from this point to the center of the enclosed atom is equal to  $\frac{1}{2}c$ , so if we can calculate that distance, we will be able easily to find the lattice parameter  $c$ . This is illustrated in the diagrams below.



The distance labeled  $y$  is  $\frac{1}{2}c$ . The distance labeled  $x$  in the figure on the right is the same as the line segment BD in the figure on the left. The triangle ABC is an equilateral triangle with all sides equal to  $a$  or  $2r$ . A line drawn from C perpendicular to line segment AB will bisect that segment. The angle ABC is  $60^\circ$  so that the angle ABD is equal to  $30^\circ$ . We can then write

$$\cos 30^\circ = \frac{r}{x}$$

$$x = \frac{r}{\cos 30^\circ}$$

$$x = \frac{2}{\sqrt{3}} r$$

To calculate  $y$ , we use the Pythagorean theorem:

$$y^2 + x^2 = (2r)^2$$

$$y^2 = 4r^2 - \left( \frac{2}{\sqrt{3}} r \right)^2$$

$$y^2 = 4r^2 - \frac{4}{3} r^2$$

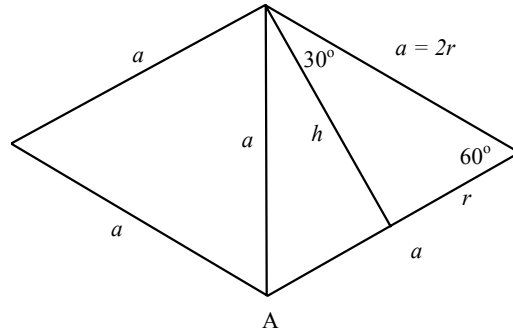
$$y^2 = \frac{8}{3} r^2$$

$$y = \frac{2\sqrt{2}}{\sqrt{3}} r$$

$$c = 2y = \frac{4\sqrt{2}}{\sqrt{3}} r$$

The volume of the unit cell is determined by multiplying  $c$  by the area of the unit cell face. This area is found by noting that the face is a parallelogram whose area will equal base  $\times$  height ( $b \times h$ ), where  $b = 2r$ .

We can obtain  $h$  from



$$\sin 60^\circ = \frac{h}{2r}$$

$$h = 2r \sin 60^\circ$$

$$h = \frac{2\sqrt{3}}{2} r = r \sqrt{3}$$

The area of the face is then

$$\text{face area} = 2r \times r \sqrt{3} = 2\sqrt{3} r^2$$

The volume of the unit cell is then

$$V = 2\sqrt{3} r^2 \times \frac{4\sqrt{2}}{\sqrt{3}} r$$

$$= 8\sqrt{2} r^3$$

The volume of an individual atom will be given by

$$V_{\text{atom}} = \frac{4}{3} \pi r^3$$

The total volume occupied by the atoms in the unit cell will, therefore, be

$$V_{\text{total}} = \frac{8}{3} \pi r^3$$

The fraction of occupied space will be given by

$$\frac{\left(\frac{8\pi r^3}{3}\right)}{(8\sqrt{2} r^3)} = \frac{\pi}{3\sqrt{2}} = 0.74$$

We can see that this is exactly equal to the fraction of occupied space for the face-centered cubic lattice as derived in the book (see section 5.9).

- 5.94** To solve this problem, we refer to Bragg's law:  $\lambda = 2 d \sin \theta$  where  $\lambda$  is the wavelength of radiation,  $d$  is the interplanar spacing, and  $\theta$  is the angle of incidence of the x-ray beam.

$$154 \text{ pm} = 2 d \sin 7.42^\circ$$

$$d = 596 \text{ pm}$$

- 5.96**  $1 \text{ eV} = 1 \text{ e}^-$  through a potential of 1 V

$$? \text{ eV} = \frac{1}{2} m_e v^2 \text{ when } \lambda = 100 \text{ pm} = \frac{h}{mv}$$

$$= \frac{1}{2} \left( \frac{h}{\lambda} \right) \left( \frac{h}{m\lambda} \right) = \frac{1}{2} \cdot \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(9.109 \times 10^{-31} \text{ kg})(1 \times 10^{-10} \text{ m})^2}$$

$$= 2.41 \times 10^{-17} \text{ J} \left( \frac{1 \text{ eV}}{1.6022 \times 10^{-19} \text{ J}} \right) = 150 \text{ eV}$$

Therefore, electrons must be accelerated through a potential of 150 V in order for them to have a wavelength of 100 pm. Under these conditions, electrons can be used in diffraction studies.

**5.98** The Coulomb potential energy of interaction for the point charge with the dipole can be represented by the sum of the repulsive and attractive terms as given by equation 1, page 162,  $E_p = \frac{q_1 q_2}{4\pi\epsilon_0 r}$ . To avoid confusion, we will call the point charge  $z$  since each end of the dipole is  $q$  or  $-q$ . The distance to one end of the dipole is  $r + \frac{l}{2}$  and the distance to the oppositely charged end is  $r - \frac{l}{2}$ . So the potential energy at the point charge is

$$E_p = |z| \left( \frac{kq}{r + \frac{l}{2}} - \frac{kq}{r - \frac{l}{2}} \right) = |z| \frac{kq}{r} \left( \frac{1}{1 + \frac{l}{2r}} - \frac{1}{1 - \frac{l}{2r}} \right)$$

where  $k = \frac{1}{4\pi\epsilon_0}$  and  $z$  is the magnitude of the point charge.

Since  $l \ll r$ , it is also true that  $\frac{l}{2r} \ll 1$ . Using the expansion given in

the problem,  $\frac{1}{(1+x)} = 1 - x + \dots$ , with  $x = \frac{l}{2r}$ , gives

$$\frac{1}{1 + \frac{l}{2r}} \approx 1 - \frac{l}{2r} \quad \text{and} \quad \frac{1}{1 - \frac{l}{2r}} \approx 1 + \frac{l}{2r}.$$

Then the expression for the potential energy becomes

$$E_p = |z| \frac{kq}{r} \left( 1 - \frac{l}{2r} - 1 - \frac{l}{2r} \right) = |z| \frac{kq}{r} \left( -\frac{2l}{2r} \right) = |z| \frac{-kql}{r^2}$$

Substituting  $k = \frac{1}{4\pi\epsilon_0}$  and  $\mu = ql$

$$E_p = -\frac{|z|\mu}{4\pi\epsilon_0 r^2}$$

Note that this expression agrees with equation 2, page 163.