CHAPTER 5

LIQUIDS AND SOLIDS

5.1 (a) London forces, dipole-dipole;   (b) London forces, dipole-dipole;
(c) London forces, dipole-dipole, hydrogen bonding;   (d) London forces

5.3 Only   (b) CH_3Cl,   (c) CH_2Cl_2, and   (d) $CHCl_3$ will have dipole-dipole interactions. The molecules CH_4 and CCl_4 do not have dipole moments.

5.5 The interaction energies can be ordered based on the relationship the energy has to the distance separating the interacting species. Thus ion-ion interactions are the strongest and are directly proportional to the distance separating the two interacting species. Ion-dipole energies are inversely proportional to d^2, whereas dipole-dipole for constrained molecules (i.e., solid state) is inversely proportional to d^3. Dipole-dipole interactions where the molecules are free to rotate become comparable to induced dipole-induced dipole interactions, which are both inversely related to d^6. The order thus derived is: (b) dipole-induced dipole $\cong$ (c) dipole-dipole in the gas phase < (e) dipole-dipole in the solid phase < (a) ion-dipole < (d) ion-ion.

5.7 Only molecules with H attached to the electronegative atoms F, N, and O can hydrogen bond. Additionally, there must be lone pairs available for the H's to bond to. This is true only of (c) H_2SO_3.

5.9   III because the dipoles are aligned with oppositely charged ends closest to each other thereby maximizing dipole-dipole attractions.

5.11   (a) NaCl $(801°C$ vs. $-114.8°C)$ because it is an ionic compound as opposed to a molecular compound;   (b) butanol $(-90°C$ vs. $-116°C)$ due to hydrogen bonding in butanol that is not possible in diethyl ether; (c) triiodomethane because it will have much stronger London dispersion forces $(-82.2°C$ for trifluoromethane vs. $219°C$ for triiodomethane);   (d) because the number of possible hydrogen bonds is greater than the number in methanol.

5.13   (a) PF_3 and PBr_3 are both trigonal pyramidal and should have similar intermolecular forces, but PBr_3 has the greater number of electrons and should have the higher boiling point. The boiling point of PF_3 is $-101.5°C$ and that of PBr_3 is   (b) SO_2 is bent and has a dipole moment whereas CO_2 is linear and will be nonpolar. SO_2 should have the higher boiling point. SO_2 boils at $-10°C$, whereas CO_2 sublimes at $-78°C$. (c) BF_3 and BCl_3 are both trigonal planar, so the choice of higher boiling point depends on the difference in total number of electrons. BCl_3 should have the higher boiling point $(12.5°C$ vs. $-99.9°C)$.   (d) AsF_3 is pyramidal and has a dipole moment, whereas AsF_5 is a trigonal bipyramid and is nonpolar. AsF_5, on the other hand, has more electrons, so the two effects oppose each other. The actual boiling points of ASF_3 and AsF_5 are $63°C$ and $-53°C$, respectively, so the effect of the polarity is greater than the effect of the increased mass, in this case.

5.15   The ionic radius of Al^{3+} is 53 pm and that of Be^{2+} is 27 pm. The ratio of energies will be given by

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

$$V_{Al^{3+}} \propto \frac{-|z|\mu}{d^2} = \frac{-|3|\mu}{(53)^2}$$

$$V_{Be^{2+}} \propto \frac{-|z|\mu}{d^2} = \frac{-|2|\mu}{(27)^2}$$

The electric dipole moment of the water molecule (μ) will cancel:

$$\text{ratio}\left(\frac{V_{Al^{3+}}}{V_{Be^{2+}}}\right) = \frac{-|3|\mu/(53)^2}{-|2|\mu/(27)^2} = \frac{3(27)^2}{2(53)^2} = 0.39$$

The attraction of the Be^{2+} ion will be greater than that of the Al^{3+} ion. Even though the Be^{2+} ion has a lower charge, its radius is much smaller than that of Al^{3+}, making the attraction greater.

5.17 The ionic radius of Al^{3+} is 53 pm and that of Ga^{3+} is 62 pm. The ratio of energies will be given by

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

$$V_{Al^{3+}} \propto \frac{-|3|\mu}{(53 \text{ pm})^2}$$

$$V_{Ga^{3+}} \propto \frac{-|3|\mu}{(62 \text{ pm})^2}$$

The electric dipole moment of water ($\cdot$) will cancel:

$$\text{ratio}\left(\frac{V_{Al^{3+}}}{V_{Ga^{3+}}}\right) = \frac{\dfrac{-|3|\mu}{(53 \text{ pm})^2}}{\dfrac{-|3|\mu}{(62 \text{ pm})^2}} = \frac{(62 \text{ pm})^2}{(53 \text{ pm})^2} = 1.4$$

The water molecule will be more strongly attracted to the Al^{3+} ion because of its smaller radius.

5.19 (a) Xenon is larger, with more electrons, giving rise to larger London forces that increase the melting point.   (b) Hydrogen bonding in water

causes the molecules to be held together more tightly than in diethyl ether.
(c) Both molecules have the same molar mass, but pentane is a linear molecule compared to dimethylpropane, which is a compact, spherical molecule. The compactness of the dimethylpropane gives it a lower surface area. That means that the intermolecular attractive forces, which are of the same type (London forces) for both molecules, will have a larger effect for pentane.

5.21 $F = \dfrac{-\mathrm{d}E_P}{\mathrm{d}r} = \dfrac{-\mathrm{d}}{\mathrm{d}r}\left(\dfrac{1}{r^6}\right) = -\left(\dfrac{-6}{r^7}\right) \propto \dfrac{1}{r^7}$

5.23 (a) *cis*-Dichloroethene is polar, whereas *trans*-dichloroethene, whose individual bond dipole moments cancel, is nonpolar. Therefore, *cis*-dichloroethene has the greater intermolecular forces and the greater surface tension. (b) Surface tension of liquids decreases with increasing temperature as a result of thermal motion as temperature rises. Increased thermal motion allows the molecules to more easily break away from each other, which manifests itself as decreased surface tension.

5.25 At 50°C all three compounds are liquids. C_6H_6 (nonpolar) $< C_6H_5SH$ (polar, but no hydrogen bonding) $< C_6H_5OH$ (polar and with hydrogen bonding). The viscosity will show the same ordering as the boiling points, which are 80°C for C_6H_6, 169°C for C_6H_5SH, 182° for C_6H_5OH.

5.27 CH_4, -162°C; CH_3CH_3, -88.5°C; $(CH_3)_2CHCH_2CH_3$, 28°C; $CH_3(CH_2)_3CH_3$, 36°C; CH_3OH, 64.5°C; CH_3CH_2OH, 78.3 °C; $CH_3CHOHCH_3$, 82.5°C; C_5H_9OH (cyclic, but not aromatic), 140°C; $C_6H_5CH_3OH$ (aromatic ring), 205°C; $OHCH_2CHOHCH_2OH$, 290°C

5.29 (a) hydrogen bonding; (b) London dispersion forces in crease

5.31 Using $h = \dfrac{2\gamma}{gdr}$ we can calculate the height. For water:

$$r = \frac{1}{2}\,diameter = \frac{1}{2}\,(0.15\ \text{mm})\left(\frac{1\ \text{m}}{1000\ \text{mm}}\right) = 7.5 \times 10^{-5}\ \text{m}$$

$$d = 0.997\ \text{g} \cdot \text{cm}^{-3}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)\left(\frac{10^6\ \text{cm}^3}{\text{m}^3}\right) = 9.97 \times 10^2\ \text{kg} \cdot \text{m}^{-3}$$

$$h = \frac{2(72.75 \times 10^{-3}\ \text{N} \cdot \text{m}^{-1})}{(9.81\ \text{m} \cdot \text{s}^{-1})(9.97 \times 10^2\ \text{kg} \cdot \text{m}^{-3})(7.5 \times 10^{-5}\ \text{m})} = 0.20\ \text{m or } 200\ \text{mm}$$

Remember that $1\ \text{N} = 1\ \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$

For ethanol:

$$d = 0.79\ \text{g} \cdot \text{cm}^{-3}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)\left(\frac{10^6\ \text{cm}^3}{\text{m}^3}\right) = 7.9 \times 10^2\ \text{kg} \cdot \text{m}^{-3}$$

$$h = \frac{2(22.8 \times 10^{-3}\ \text{N} \cdot \text{m}^{-1})}{(9.81\ \text{m} \cdot \text{s}^{-1})(7.9 \times 10^2\ \text{kg} \cdot \text{m}^{-3})(7.5 \times 10^{-5}\ \text{m})} = 0.078\ \text{m or } 78\ \text{mm}$$

Water will rise to a higher level than ethanol. There are two opposing effects to consider. While the greater density of water, as compared to ethanol, acts against it rising as high, it has a much higher surface tension.

5.33 (a) At center: 1 center $\times$ 1 atom $\cdot$ center^{-1} = 1 atom; at 8 corners, 8 corners $\times$ $\frac{1}{8}$ atom $\cdot$ corner^{-1} = 1 atom; total = 2 atoms;   (b) There are eight nearest neighbors, hence a coordination number of 8;   (c) The direction along which atoms touch each other is the body diagonal of the unit cell. This body diagonal will be composed of four times the radius of the atom. In terms of the unit cell edge length a, the body diagonal will be $\sqrt{3}\,a$. The unit cell edge length will, therefore, be given by

$$4r = \sqrt{3}\,a \text{ or } a = \frac{4r}{\sqrt{3}} = \frac{4 \cdot (124\ \text{pm})}{\sqrt{3}} = 286\ \text{pm}$$

5.35 (a) a = length of side for a unit cell; for an fcc unit

cell, $a = \sqrt{8}\ r$ or $2\sqrt{2}\ r = 404$ pm.

$V = a^3 = (404 \text{ pm} \times 10^{-12} \text{ m} \cdot \text{pm}^{-1})^3 = 6.59 \times 10^{-29} \text{ m}^3 = 6.59 \times 10^{-23} \text{ cm}^3$.

Because for a fcc unit cell there are 4 atoms per unit cell, we have

$$\text{mass(g)} = 4 \text{ Al atoms} \times \frac{1 \text{ mol Al atoms}}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \times \frac{26.98 \text{ g}}{\text{mol Al atoms}}$$

$$= 1.79 \times 10^{-22} \text{ g}$$

$$d = \frac{1.79 \times 10^{-22} \text{ g}}{6.59 \times 10^{-23} \text{ cm}^3} = 2.72 \text{ g} \cdot \text{cm}^{-3}$$

(b) $a = \dfrac{4r}{\sqrt{3}} = \dfrac{4 \times 235 \text{ pm}}{\sqrt{3}} = 543$ pm

$V = (543 \times 10^{-12} \text{ m})^3 = 1.60 \times 10^{-28} \text{ m}^3 = 1.60 \times 10^{-22} \text{ cm}^3$

There are 2 atoms per bcc unit cell:

$$\text{mass(g)} = 2 \text{ K atoms} \times \frac{1 \text{ mol K atoms}}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \times \frac{39.10 \text{ g}}{\text{mol K atoms}}$$

$$= 1.30 \times 10^{-22} \text{ g}$$

$$d = \frac{1.30 \times 10^{-22} \text{ g}}{1.60 \times 10^{-22} \text{ cm}^3} = 0.813 \text{ g} \cdot \text{cm}^{-3}$$

5.37 a = length of unit cell edge

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

(a)

$$V = a^3 = \frac{(1 \text{ unit cell})\left(\dfrac{195.09 \text{ g Pt}}{\text{mol Pt}}\right)\left(\dfrac{1 \text{ mol Pt}}{6.022 \times 10^{23} \text{ atoms Pt}}\right)\left(\dfrac{4 \text{ atoms}}{1 \text{ unit cell}}\right)}{21.450 \text{ g} \cdot \text{cm}^3}$$

$a = 3.92 \times 10^{-8}$ cm

Because for an fcc cell, $a = \sqrt{8}\ r, r = \dfrac{\sqrt{2}\ a}{4} = \dfrac{\sqrt{2}\ (3.92 \times 10^{-8} \text{ cm})}{4}$

$$= 1.39 \times 10^{-8} \text{ cm} = 139 \text{ pm}$$

(b) $V = a^3$

$$= \frac{(1 \text{ unit cell}) \left(\dfrac{180.95 \text{ g Ta}}{1 \text{ mol Ta}} \right) \left(\dfrac{1 \text{ mol Ta}}{6.022 \times 10^{23} \text{ atoms Ta}} \right) \left(\dfrac{2 \text{ atoms}}{1 \text{ unit cell}} \right)}{16.654 \text{ g} \cdot \text{cm}^3}$$

$$= 3.61 \times 10^{-23} \text{ cm}^3$$

$$a = 3.30 \times 10^{-8} \text{ cm}$$

$$r = \frac{\sqrt{3}\, a}{4} = \frac{\sqrt{3} \left(3.30 \times 10^{-8} \text{ cm} \right)}{4} = 1.43 \times 10^{-8} \text{ cm} = 143 \text{ pm}$$

5.39 (a) The volume of the unit cell is

$$V_{\text{unit cell}} = \left(543 \text{ pm} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}} \right)^3 = 1.601 \times 10^{-22} \text{ cm}^3$$

mass in unit cell $= (1.601 \times 10^{-22} \text{ cm}^3) \times (2.33 \text{ g} \cdot \text{cm}^{-3}) = 3.73 \times 10^{-22} \text{ g}$

(b) The mass of a Si atom is

$28.09 \text{ g} \cdot \text{mol}^{-1} \div (6.022 \times 10^{23}) \text{ atoms} \cdot \text{mol}^{-1} = 4.665 \times 10^{-23} \text{ g} \cdot \text{atom}^{-1}$

Therefore, there are $3.73 \times 10^{-22} \text{ g} \div 4.665 \times 10^{-23} \text{ g} \cdot \text{atom}^{-1} = 8$ atoms per unit cell.

5.41 volume of a cylinder = base area x length = $\pi r^2 l$

volume of a triangular prism = base area x length = $(bhl)/2 = \sqrt{3} r^2 l$ for a triangle inscribed in the centers of three touching cylinder bases

Each of the inscribed triangle's 60° angles accounts for 1/6 of the volume of each of the three touching cylinders, or a total cylinder volume of (3/6) $\pi r^2 l$. So the percent of the space occupied by the cylinders is (0.5) $\pi r^2 l$ *100/ $\sqrt{3} r^2 l = 0.5\pi/\sqrt{3} = 90.7\%$

5.43 (a) There are eight chloride ions at the eight corners, giving a total of

$8 \text{ corners} \times \frac{1}{8} \text{ atom} \cdot \text{corner}^{-1} = 1 \text{ Cl}^- \text{ ion}$

There is one Cs^+ that lies at the center of the unit cell. All of this ion belongs to the unit cell. The ratio is thus 1 : 1 for an empirical formula of CsCl, with one formula unit per unit cell.

(b) The titanium atoms lie at the corners of the unit cell and at the body center: 8 corners $\times \frac{1}{8}$ atom $\cdot$ corner^{-1} +1 at body center = 2 atoms per unit cell

Four Oxygen atoms lie on the faces of the unit cell and two lie completely within the unit cell, giving:

4 atoms in faces $\times \frac{1}{2}$ atom $\cdot$ face^{-1} + 2 atoms wholly within cell = 4 atoms

The ratio is thus two Ti per four O, or an empirical formula of TiO_2 with two formula units per unit cell (c) The Ti atoms are 6-coordinate and the O atoms are 3-coordinate.

5.45   Y: 8 atoms $\times \frac{1}{8}$ atom $\cdot$ corner^{-1} = 1 Y atom

Ba: 8 atoms $\times \frac{1}{4}$ atom $\cdot$ edge^{-1} = 2 Ba atoms

Cu: 3 Cu atoms completely inside unit cell = 3 Cu atoms

O: 10 atoms on faces $\times \frac{1}{2}$ atom $\cdot$ face^{-1} + 2 atoms completely inside unit cell = 7 O atoms

Formula = $YBa_2Cu_3O_7$

5.47   (a) ratio $= \dfrac{149 \text{ pm}}{133 \text{ pm}} = 1.12$, predict cesium-chloride structure with (8,8) coordination; however, rubidium fluoride actually adopts the rock-salt structure

(b) ratio $= \dfrac{72 \text{ pm}}{140 \text{ pm}} = 0.51$, predict rock-salt structure with (6,6) coordination

(c) ratio $= \dfrac{102 \text{ pm}}{196 \text{ pm}} = 0.520$, predict rock-salt structure with (6,6) coordination

5.49 (a) In the rock-salt structure, the unit cell edge length is equal to two times the radius of the cation plus two times the radius of the anion. Thus for CaO, $a = 2(100 \text{ pm}) + 2(140 \text{ pm}) = 480 \text{ pm}$. The volume of the unit cell will be given by (converting to cm^3 because density is normally given in terms of $g \cdot cm^{-3}$)

$$V = \left(480 \text{ pm} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}}\right)^3 = 1.11 \times 10^{-22} \text{ cm}^3$$

There are four formula units in the unit cell, so the mass in the unit cell will be given by

$$\text{mass in unit cell} = \frac{\left(\dfrac{4 \text{ formula units}}{1 \text{ unit cell}}\right) \times \left(\dfrac{56.08 \text{ g CaO}}{1 \text{ mol CaO}}\right)}{6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1}} = 3.725 \times 10^{-22} \text{ g}$$

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

$$d = \frac{3.725 \times 10^{-22} \text{ g}}{1.11 \times 10^{-22} \text{ cm}^3} = 3.37 \text{ g} \cdot \text{cm}^{-3}$$

(b) For a cesium chloride-like structure, it is the body diagonal that represents two times the radius of the cation and plus two times the radius of the anion. Thus the body diagonal for CsBr is equal to $2(170 \text{ pm}) + 2(196) = 732 \text{ pm}$.

For a cubic cell, the body diagonal $= \sqrt{3}\, a = 732 \text{ pm}$
$$a = 423 \text{ pm}$$

$$a^3 = V = \left(423 \text{ pm} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}}\right)^3 = 7.57 \times 10^{-23} \text{ cm}^3$$

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

$$\text{mass in unit cell} = \frac{\left(\dfrac{1 \text{ formula units}}{1 \text{ unit cell}}\right)\left(\dfrac{212.82 \text{ g CsBr}}{1 \text{ mol CsBr}}\right)}{6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1}} = 3.534 \times 10^{-22} \text{ g}$$

$$d = \frac{3.534 \times 10^{-22} \text{ g}}{7.57 \times 10^{-23} \text{ cm}^3} = 4.67 \text{ g} \cdot \text{cm}^3$$

5.51 Glucose will be held in the solid by London forces, dipole-dipole interactions, and hydrogen bonds; benzophenone will be held in the solid by dipole-dipole interactions and London forces; methane will be held together by London forces only. London forces are strongest in benzophenone, but glucose can experience hydrogen bonding, which is a strong interaction and dominates intermolecular forces. Methane has few electrons so experiences only weak London forces. We would expect the melting points to increase in the order CH_4 (m.p. $= -182°C$)

< benzophenone (m.p. $= 48°C$) < glucose (m.p. $= 148 - 155°C$).

5.53 one form of boron nitride, silicon dioxide, plus many others

5.55 (a) The alloy is undoubtedly interstitial, because the atomic radius of nitrogen is much smaller (74 pm vs. 124 pm) than that of iron. The rule of thumb is that the solute atom be less than 60% the solvent atom in radius, in order for an interstitial alloy to form. That criterion is met here.   (b) We expect that nitriding will make iron harder and stronger, with a lower electrical conductivity.

5.57 Graphite is a metallic conductor parallel to the planes; the electrons are quite free to move within them. Between planes, however, there is an energy barrier to conduction, though this barrier can be partially overcome by raising the temperature. Thus, graphite is a semiconductor perpendicular to the planes and a conductor parallel to the planes.

5.59 (a) These problems are most easily solved by assuming 100 g of substance. In 100 g of Ni-Cu alloy there will be 25 g Ni and 75 g Cu,

corresponding to 0.43 mol Ni and 1.2 mol Cu. The atom ratio will be the same as the mole ratio:

$$\frac{1.2 \text{ mol Cu}}{0.43 \text{ mol Ni}} = 2.8 \text{ Cu per Ni}$$

(b) Pewter, which is 7% Sb, 3% Cu, and 90% Sn, will contain 7 g Sb, 3 g Cu, and 90 g Sn per 100 g of alloy. This will correspond to 0.06 mol Sb, 0.05 mol Cu, and 0.76 mol Sn per 100 g. The atom ratio will be 15 Sn : 1.2 Sb : 1 Cu.

5.61 There are too many ways that these molecules can rotate and twist so that they do not remain rod-like. The molecular backbone when the molecule is stretched out is rod-like, but the molecules tend to curl up on themselves, destroying any possibility of long range order with neighboring molecules. This is partly due to the fact that the molecules have only single bonds that allow rotation about the bonds, so that each molecule can adopt many configurations. If multiple bonds are present, the bonding is more rigid.

5.63 Use of a nonpolar solvent such as hexane or benzene (etc.) in place of water should give rise to the formation of inverse micelles.

5.65 (a) Pentane and 2,2-dimethylpropane are isomers; both have the chemical formula C_5H_{12}. We will assume that 2,2-dimethylpropane is roughly spherical and that all the hydrogen atoms lie on this sphere. The surface area of a sphere is given by $A = 4\pi r^2$. For this particular sphere, $A = 4\pi(254 \text{ pm})^2 = 8.11 \times 10^5 \text{ pm}^2$.
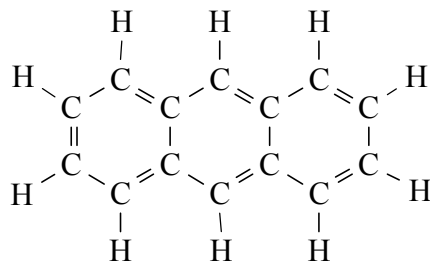
(b) For pentane, the surface area of rectangular prism is

$2(295 \text{ pm} \times 766 \text{ pm}) +$

$2(295 \text{ pm} \times 254 \text{ pm}) + 2(254 \text{ pm} \times 766 \text{ pm}) = 9.91 \times 10^5 \text{ pm}^2$.
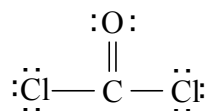
(c) The pentane should have the higher boiling point. It has a significantly larger surface area and should have stronger intermolecular forces between the molecules.

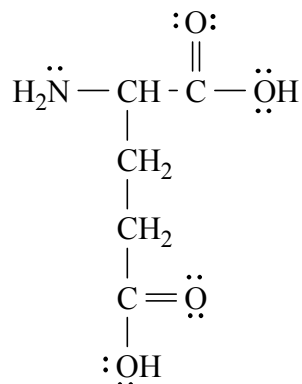**5.67** (a) anthracene, $C_{14}H_{10}$

London forces

(b) phosgene, $COCl_2$

Dipole-dipole forces, London forces

(c) glutamic acid, $C_5H_9NO_4$

Hydrogen bonding, dipole-dipole forces, London forces

5.69 (a) tetrachloromethane; (b) water

5.71 The unit cell for a cubic close-packed lattice is the fcc unit cell. For this cell, the relation between the radius of the atom r and the unit cell edge length a is

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

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

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

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

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

or

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

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

For the different gases we calculate the results given in the following table:

Gas	Density $(\gamma \cdot \psi\mu^{\times})$	Molar mass $(\gamma \cdot \mu o\lambda^{-+})$	Radius (pm)
Neon	1.20	20.18	170
Argon	1.40	39.95	203
Krypton	2.16	83.80	225
Xenon	2.83	131.30	239
Radon	4.4	222	246

5.73 There are two approaches to this problem. The information given does not specify the radius of the tungsten atom. This value can be looked up in Appendix 2D. We can calculate an answer, however, based simply upon the fact that the density is $19.3 \text{ g} \cdot \text{cm}^{-3}$ for the bcc cell, by taking the ratio between the expected densities, based upon the assumption that the atomic radius of tungsten will be the same for both. The unit cell for a cubic close-packed lattice is the fcc unit cell. For this cell, the relation between the radius of the atom r and the unit cell edge length a is

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

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

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 is 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 is given by

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

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

or

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

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

Likewise, for a body-centered cubic lattice there will be two atoms per unit cell. For this cell, the relationship 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 4 times the radius of the atom. The body diagonal is found from the Pythagorean theorem to be equal to the $\sqrt{3}\,a$.

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

The volume of the unit cell is given by

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

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

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

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

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

The density will be given by

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

$$= \frac{\left(\dfrac{2 \text{ atoms}}{\text{unit cell}}\right)\left(\dfrac{M}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}}\right)}{(2.309 \times 10^{-10}\, r)^3}$$

$$= \frac{(2.698 \times 10^5)M}{r^3}$$

or

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

Setting these two expressions equal 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 of tungsten M is the same for both ratios 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

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

$$= 1.088\, d_{\text{bcc}}$$

For W, $d_{\text{fcc}} = 1.088 \times 19.6 \text{ g} \cdot \text{cm}^3$

$$= 21.3 \text{ g} \cdot \text{cm}^{-3}$$

5.75 (a) The oxidation state of the titanium atoms must balance the charge on the oxide ions, O^{2-}. The presence of 1.18 O^{2-} ions means that the Ti present must have a charge to compensate the -2.36 charge on the oxide ions. The average oxidation state of Ti is thus $+2.36$.   (b) This is most easily solved by setting up a set of two equations in two unknowns. We

know that the total charge on the titanium atoms present must equal 2.36, so if we multiply the charge on each type of titanium by the fraction of titanium present in that oxidation state and sum the values, we should get 2.36:

let x = fraction of Ti^{2+}, y = fraction of Ti^{3+}, then
2x + 3y = 2.36

Also, because we are assuming all the titanium is either +2 or +3, the fractions of each present must add up to 1:

x + y = 1

Solving these two equations simultaneously, we obtain y = 0.36, x = 0.64.

5.77   (a) true. If this is not the case, the unit cell will not match with other unit cells of the same type when stacked to form the entire lattice.

(b) false. Unit cells do not have to have atoms at the corners.

(c) true. In order for the unit cell to repeat properly, opposite faces must have the same composition.

(d) false. If one face is centered, the opposing face must be centered, but the other faces do not necessarily have to be centered.

5.79   There are several ways to draw unit cells that will repeat to generate the entire lattice. Some examples are shown below. 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).
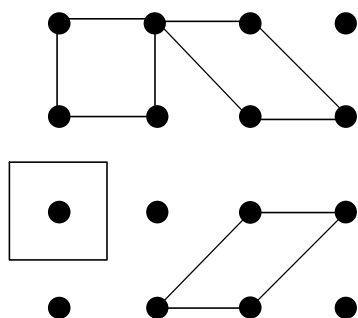
(a)   (b)
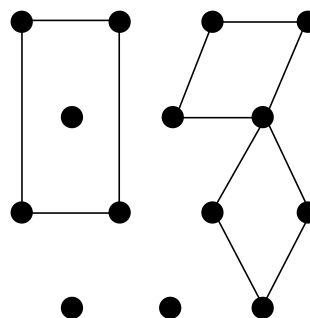
5.81   In a salt such as sodium chloride or sodium bromide, all the interactions
will be ionic. In sodium acetate or sodium methoxide, however, the
organic anions CH_3COO^- and CH_3O^- will have the negative charges
localized largely on the oxygen atoms, which are the most electronegative
atoms. The carbon part of the molecule will interact with other parts of the
crystal lattice via London forces rather than ionic interactions. In general,
solid organic salts will not be as hard as purely ionic substances and will
also have lower melting points.

5.83   Fused silica, also known as fused quartz, is predominantly SiO_2 with very
few impurities. This glass is the most refractory, which means it can be
used at the highest temperatures. Quartz vessels are routinely used for
reactions that must be carried out at temperatures up to 1000°C. Vycor,
which is 96% SiO_2, can be used at up to ca. 900°C, and normal
borosilicate glasses at up to approximately 550°C. This is due to the fact
that the glasses melt at lower temperatures, as the amount of materials
other than SiO_2 increases. The borosilicate glasses (Pyrex or Kimax) are
commonly used because the lower softening points allow them to be more
easily molded and shaped into different types of glass objects, such as
reaction flasks, beakers, and other types of laboratory and technical
glassware.

5.85 For a bcc unit cell (see Example 5.3), $d = 3^{3/2}$ (55.85

g/mol)/32(6.022x10^{23}/mole)x(1.24x10^{-8}cm)^3 = 7.90 g/cm^3

$(1.5 \text{ cm})^3$ x 7.90 g/cm^3 x (1 mole/55.85 g) =0.477 mole Fe

(1.00 atm x15.5 L) / (0.08206 L atm /K mol) (298K) = 0.634 mol O_2

Fe is LR, so (0.5)(0.477 mole)(159.70 g/mole) = 38.1 g Fe_2O_3 is

theoretical yield, or maximum mass that can be produced.

5.87 For M, there is total of one atom in the unit cell from the corners;

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

anions: $8 \text{ tetrahedral holes} \times 1 \text{ atom} \cdot \text{tetrahedral hole}^{-1} = 8 \text{ atoms}$

The cation to anion ratio is thus 4 : 8 or 1 : 2; the empirical formula is

MA_2.

5.89 The cesium chloride lattice is a simple cubic lattice of Cl^- ions with a

Cs^+ at the center of the unit cell (See 5.43). In the unit cell, there is a total

of one Cl^- ion and one Cs^+ ion. If the density is $3.988 \text{ g} \cdot \text{cm}^{-3}$, then we

can determine the volume and unit cell edge length. The molar mass of

CsCl is $168.36 \text{ g} \cdot \text{mol}^{-1}$.

$$3.988 \text{ g} \cdot \text{cm}^{-3} = \frac{\left(\dfrac{168.36 \text{ g} \cdot \text{mol}^{-1}}{6.022 \times 10^{23} \text{ formula units} \cdot \text{mol}^{-1}} \right)}{a^3}$$

$$a^3 = \frac{\left(\dfrac{168.36 \text{ g} \cdot \text{mol}^{-1}}{6.022 \times 10^{23} \text{ formula units} \cdot \text{mol}^{-1}} \right)}{3.988 \text{ g} \cdot \text{cm}^{-3}}$$

$a = 4.12 \times 10^{-8}$ cm

$\quad = 412$ pm

The volume of the unit cell is $(412 \text{ pm})^3 = 6.99 \times 10^7 \text{ pm}^3$.

We will determine the size of the Cs^+ and Cl^- ions from ionic radii given

in Appendix 2D, but we can check these values against the unit cell

dimensions. For this type of unit cell, the body diagonal will be equal to

$2\,r(\text{Cs}^+) + 2\,r(\text{Cl}^-) = a\sqrt{3} = 714$ pm. The sum of the ionic radii gives us

$2\,(170$ pm$) + 2\,(181$ pm$) = 702$ pm, which is in very good agreement. Note that we cannot calculate the size of these ions independently from the unit cell data without more information, because this lattice is not close-packed. We will assume that the ions are spherical. The volume occupied in the unit cell will be

$$V_{\text{Cs}^+} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(170 \text{ pm})^3 = 2.06 \times 10^7 \text{ pm}^3$$

$$V_{\text{Cl}^-} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(181 \text{ pm})^3 = 2.48 \times 10^7 \text{ pm}^3$$

The total occupied volume in the cell is

2.06×10^7 pm^3 $+ 2.48 \times 10^7$ pm^3 $= 4.54 \times 10^7$ pm^3. The empty space is

6.99×10^7 pm^3 $- 4.54 \times 10^7$ pm^3 $= 2.45 \times 10^7$ pm^3. The percent empty

space is 2.45×10^7 pm^3 $\div 6.99 \times 10^7$ pm^3 $\times 100 = 35\%$.

5.91 (a) In a simple cubic unit cell there is a total of one atom. The volume of the atom is given by $\frac{4}{3}\pi r^3$. The volume of the unit cell is given by a^3 and $a = 2r$, so the volume of the unit cell is $8r^3$. The fraction of occupied space in the unit cell is given by

$$\frac{\frac{4}{3}\pi r^3}{8r^3} = \frac{\frac{4}{3}\pi}{8} = 0.52$$

52% of the space is occupied, so 48% of this unit cell would be empty.

(b) The percentage of empty space in an fcc unit cell is 26%, so the fcc cell is much more efficient at occupying the space available.

5.93 The lattice layers from which constructive x-ray diffraction occurs are parallel. First draw perpendicular lines from the point of intersection of the top x-ray with the lattice plane to the lower x-ray for both the incident and diffracted rays. The x-rays are in phase and parallel at point A. If we want them to be still in phase and parallel when they exit the crystal, then they

must still be in phase when they reach point C. In order for this to be true, the extra distance that the second beam travels with respect to the first must be equal to some integral number of wave-lengths. The total extra distance traveled, $A \to B \to C$, is equal to $2x$. From the diagram, we can see that the angle A-D-B must also be equal to θ. The angles θ and α sum to $90°$, as do the angles α and A-D-B. We can then write $\sin \theta = \dfrac{x}{d}$ and $x = d \sin \theta$. The total distance traveled is $2x = 2d \sin \theta$. So, for the two x-rays to be in phase as they exit the crystal, $2d \sin \theta$ must be equal to an integral number of wave-lengths.

5.95   The answer to this problem is obtained from Bragg's law: $\lambda = 2d \sin \theta$ where λ is the wavelength of radiation, d is the interplanar spacing, and θ is the angle of incidence of the x-ray beam. Here $d = 401.8$ pm and $\lambda = 71.037$ pm.

$71.07 \text{ pm} = 2(401.8 \text{ pm})\sin \theta$
$\theta = 5.074°$

5.97 $3/2 \, kT = 1/2 \, mv^2$ $\lambda = h/mv$ $3kT = h^2/m\lambda^2$ $T = 633$ K