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Appendix 4

Answers to Selected Problems

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Chapter 1

1. a. "Synthesis and Processing" b. "Properties" c. "Properties" and "Performance" d. "Synthesis and Processing"

3. The re-entrant foam has a negative Poisson ratio as described in the text. If the re-entrant foam is compressed, the denominator of the Poisson ratio (the fractional increase in length) will be negative. As a result, the numerator of the Poisson ratio (the fractional decrease in width) must be positive in order to satisfy the condition that the ratio be negative. Thus, compressing the foam (decrease in length) results in a decrease in width. The size of the cross-section will decrease when the foam is compressed.

4. Pulling on re-entrant foam causes the foam to expand in cross-sectional area, and compressing it causes the foam to shrink in cross-sectional area (*see* problem 3). If re-entrant foam is inserted into a hole, compression of the foam during insertion causes its cross-section to shrink, assisting the process. If an object is hung on the foam, the foam resists being pulled out of the hole by its expanding cross-section.

5. In general, any common material can be researched and traced from the raw material stage to the waste disposal stage. However, only certain products are actually recycled or reused to complete the cycle. Other materials might be said to "spiral" rather than cycle in that they cannot be reused for their

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original purpose. (For example, a polystyrene food container cannot be recycled into anything that comes in contact with food, so such material might be made into “speed bumps”, plastic lumber, etc.) Waste disposal questions alone can also make for interesting library research projects. We have found that students are able to find a reasonable amount of information about the following:

petroleum
nuclear fuel
glass
mercury
polyethylene
rubber
nuclear weapons
water
steel
other plastics
paper
carbon
antifreeze
motor oil
aluminum
batteries
cotton
diapers

Good starting points for research include
- *Encyclopedia of Physical Science and Technology*
- *McGraw-Hill Encyclopedia of Science and Technology*
- *Kirk-Othmer Encyclopedia of Science and Technology*
- *Ullmann's Encyclopedia of Industrial Technology*
- *Concise Encyclopedia of Polymer Processing and Application*
- *Handbook of Polymer Science and Technology*

Local experts may also be willing to serve as resource people.

Chapter 2

1. The molar masses of tantalum and niobium are 180.95 g/mol and 92.91 g/mol respectively, a ratio of 1.95:1.00. With nearly identical unit cell sizes, the difference in mass results in solids with densities that differ by a factor of 1.94:1.00.

2. The diameter of a tungsten atom is (2)(137 pm) = 274 pm
$= 2.74 \times 10^{-10}$ m $= 2.74 \times 10^{-8}$ cm = 2.74 Å

3. molar heat capacity = (3)(R)(number of ions per ionic formula unit)
RbCl: molar heat capacity = (3)(8.31 J $\text{mol}^{-1}\,\text{K}^{-1}$)(2) = 50.0 J $\text{mol}^{-1}\,\text{K}^{-1}$
MgF_2: molar heat capacity = (3)(8.31 J $\text{mol}^{-1}\,\text{K}^{-1}$)(3) = 74.8 J $\text{mol}^{-1}\,\text{K}^{-1}$
AlF_3: molar heat capacity = (3)(8.31 J $\text{mol}^{-1}\,\text{K}^{-1}$)(4) = 99.8 J $\text{mol}^{-1}\,\text{K}^{-1}$
Al_2O_3: molar heat capacity = (3)(8.31 J $\text{mol}^{-1}\,\text{K}^{-1}$)(5) = 124 J $\text{mol}^{-1}\,\text{K}^{-1}$

4. For example, aluminum molar heat capacity = 24 J $\text{mol}^{-1}\,\text{K}^{-1}$
(24 J $\text{mol}^{-1}\text{K}^{-1}$)(1 mol Al/26.98 g) = 0.89 J $\text{g}^{-1}\,\text{K}^{-1}$

5. For example, aluminum:
molar heat capacity of Al = 24 J $\text{mol}^{-1}\,\text{K}^{-1}$
gram heat capacity of Al = 0.89 J $\text{g}^{-1}\text{K}^{-1}$ (*see* problem 4)
gram heat capacity of H_2O = 4.184 J $\text{g}^{-1}\text{K}^{-1}$
heat absorbed by water = heat released by Al
heat absorbed by water = (gram heat capacity H_2O)(mass of H_2O)(ΔT),
heat released by Al = (gram heat capacity Al)(mass of Al)(ΔT),
Al and H_2O will thermally equilibrate to the same final temperature.
T_f = 310 K or 37 °C.

6. Heat released by metal = (gram heat capacity of metal)(mass of metal)(ΔT),
Heat absorbed by water = (gram heat capacity H_2O)(mass of H_2O)(ΔT),
heat absorbed by water = heat released by metal

the gram heat capacity of metal is calculated to be 0.491 J g^{-1} K^{-1}

The gram heat capacity and molar heat capacity differ by a factor of molar mass. Assuming the molar heat capacity of this metal to be the theoretical value for the molar heat capacity of a metallic element (25 J mol^{-1} K^{-1}, as per Table 2.1), the molar mass of the metal is

$$25 \text{ J mol}^{-1} \text{ K}^{-1} = (0.491 \text{ J g}^{-1}\text{K}^{-1})(\text{molar mass})$$

$$\text{molar mass} = (25 \text{ J mol}^{-1}\text{K}^{-1})/(0.491 \text{ J g}^{-1} \text{ K}^{-1}) = 51 \text{ g mol}^{-1}$$

The metal is predicted to be vanadium.

7. As a result of sodium bromide's solubility in water, the heat capacity of NaBr cannot be measured in water, because the energetics of dissolution and solvation will be observed together with the simple transfer of thermal energy. The measurement can be performed in ethyl alcohol, as sodium bromide will not dissolve in ethyl alcohol. The procedure to be used follows:

   As a first step, measure the heat capacity of ethyl alcohol. This can be accomplished by heating a sample of aluminum of known mass to a known temperature. For example, place the aluminum sample into boiling water and allow the aluminum to achieve thermal equilibrium with the water. Place the hot piece of aluminum into a preweighed sample of ethyl alcohol of known temperature and measure the temperature change to obtain the heat capacity of ethyl alcohol.

   To measure the heat capacity of NaBr, heat a dry, preweighed sample of NaBr in an oven and place the sodium bromide in a sample of ethyl alcohol of known mass and temperature. The rise in temperature together with the heat capacity of ethyl alcohol allows calculation of the heat capacity of NaBr.

9. (400 Ni atoms)(2.48 Å/Ni atom) = 992 Å or 9.92×10^{-8} m

10. $PV = nRT$
    $n = PV/RT$ $\quad P = (1.0 \times 10^{-10}$ torr)(1 atm/760 torr) $= 1.3 \times 10^{-13}$ atm
    $n = (1.3 \times 10^{-13}$ atm)$(1.0 \times 10^{-3}$ L)/[(0.0821 L-atm/mol-K)(296 K)]
    $n = 5.3 \times 10^{-18}$ mol gas
    $(5.3 \times 10^{-18}$ mol)$(6.02 \times 10^{23}$ gas molcules/mol) $= 3.2 \times 10^{6}$ molcules

11. Because there are only two degrees of freedom in Flatland, a mol of monatomic gas atoms will have an average thermal energy of (2)(1/2 RT) = RT, and a molar heat capacity of R or approximately 8.3 J mol^{-1} K^{-1}.

12. (0.38 J g^{-1} K^{-1})(63.55 g Cu/1 mol Cu) = 24 J mol^{-1} K^{-1}
    (24 J $mol^{-1}K^{-1}$)(1 mol Ag/107.87 g) = 0.22 J g^{-1} K^{-1}

13. Bi: (0.120 J g^{-1} °C^{-1})(208.98 g/1 mol Bi) = 25.1 J mol^{-1} °C^{-1}
    Zn: (0.388 J g^{-1} °C^{-1})(65.37 g/1 mol Zn) = 25.4 J mol^{-1} °C^{-1}
    Fe: (0.460 J g^{-1} °C^{-1})(55.85 g/1 mol Fe) = 25.7 J mol^{-1} °C^{-1}
    S: (0.787 J g^{-1} °C^{-1})(32.06 g/1 mol S) = 25.2 J mol^{-1} °C^{-1}

    Note that these molar heat capacities are comparable and close to the theoretical value of 25 J mol^{-1} °C^{-1} as described in the text.

14. a. In the absence of an external magnetic field, the magnetic domains of iron remain randomly oriented; thus, there is little net magnetization and no attraction to the iron filings.

b. The magnet aligns or orients the domains with the applied external field, creating a large net magnetization in the nail. The nail then serves as the source of a magnetic field that orients the domains of the iron filings, attracting the filings.

15. The equation: molar heat capacity = $3Rp$ (where p is the number of atoms in a formula unit) predicts a molar heat capacity for elemental iron (Fe) of $3R$. Calcium oxide, a 1:1 ionic substance composed of Ca^{2+} and O^{2-} ions, has a predicted molar heat capacity of $6R$ as $p = 2$. Since the formula weights of calcium oxide and elemental iron are about the same, the gram heat capacity of CaO should be about twice that of Fe.

16. Vanadium in VO has a formal oxidation state of +2 and an odd number of electrons (3), making it paramagnetic. In contrast, V_2O_5 has a formal oxidation state of +5 and no unpaired electrons, making it diamagnetic. Thus, VO is more strongly attracted to a magnetic field.

17. Stored chemical energy, present in the foods we eat, is used to give us the energy needed to squeeze the trigger to cock a spring-loaded hammer in the lighter. The cocked spring contains potential energy, which is converted to kinetic energy as the hammer accelerates towards the piezoelectric crystal. When the hammer strikes the crystal, the energy is converted to heat and is also used to mechanically induce a momentary net dipole moment that will generate a change in the electric field of the crystal. This can cause sparking in the nearby combustible gas and ignite it. The combustion results from an exothermic reaction between the fuel and oxygen.

18. Exercise machines with a tunable resistance to motion is one possibility.

Chapter 3

1. As examples, we do problems a, c, and l.

a. CsCl

8 Cl^- corner-shared ions: $(8)(1/8) = 1\ Cl^-$
1 Cs^+ ion within the cell: $(1)(1) = 1\ Cs^+$
Thus the unit cell is composed of 1 Cs^+ and 1 Cl^- ion. The empirical formula is CsCl.

c. Cu_2AlMn

8 Mn corner-shared atoms: (8)(1/8) = 1 Mn
6 Mn face-shared atoms: (6)(1/2) = 3 Mn
12 Al edge-shared ions: (12)(1/4) = 3 Al
1 Al atom within the cell: (1)(1) = 1 Al
8 Cu atoms within the cell (8)(1) = 8 Cu
Thus the unit cell is composed of four Mn atoms, four Al atoms, and eight Cu atoms. The empirical formula for the solid is Cu_2AlMn

l. CaC_2

8 Ca^{2+} corner-shared ions: $(8)(1/8) = 1\ Ca^{2+}$
6 Ca^{2+} face-shared ions: $(6)(1/2) = 3\ Ca^{2+}$
8 C^- edge-shared ions: $(8)(1/4) = 2\ C^-$
8 C^- face-shared ions: $(8)(1/2) = 4\ C^-$
2 C^- ions within the cell: $(2)(1) = 2\ C^-$

Thus the unit cell is composed of four Ca^{2+} and eight C^{-} ions. The empirical formula for the solid is CaC_2.

2. As examples, we do problems a and b.

a. The formula of the compound that crystallizes in a cubic unit cell with a rubidium ion on each corner and a bromide ion in the center of the cell is RbBr:
8 Rb^{+} corner-shared ions: (8)(1/8) = 1 Rb^{+}
1 Br^{-} ion within the cell: (1)(1) = 1 Br^{-}
The empirical formula is therefore RbBr.

The percent composition of RbBr is calculated as follows:
Molar mass of RbBr = (85.47 g) + (79.91 g) = 165.38 g
%Rb = (85.47 g/165.38 g)(100) = 51.68 %
%Br = (79.91 g/165.38 g)(100) = 48.32 %

The masses of rubidium cations and bromide anions required to prepare 5.00 g of RbBr are
(5.00 g RbBr)(1 mol/165.38 g) = 3.02×10^{-2} mol RbBr
(3.02×10^{-2} mol RbBr)(1 mol Rb^{+}/mol RbBr) = 3.02×10^{-2} mol Rb^{+}.
(3.02×10^{-2} mol Rb^{+})(85.47 g Rb^{+}/1 mol) = 2.58 g Rb^{+}.
(3.02×10^{-2} mol RbBr)(1 mol Br^{-}/mol RbBr) = 3.02×10^{-2} mol Br^{-}.
(3.02×10^{-2} mol Br^{-})(79.91 g Br^{-}/1 mol) = 2.41 g Br^{-}.

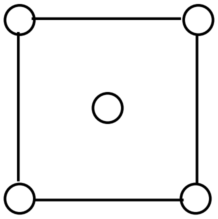
b. 8 Ni^{2+} corner-shared ions: (8)(1/8) = 1 Ni^{2+}
6 Ni^{2+} face-shared ions: (6)(1/2) = 3 Ni^{2+}
12 O^{2-} edge-shared ions: (12)(1/4) = 3 O^{2-}
1 O^{2-} ion within the cell: (1)(1) = 1 O^{2-}

The empirical formula is therefore NiO.

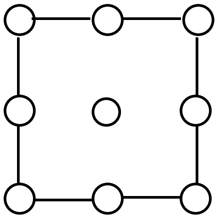
NiO is 78.58 % Ni and 21.42 % O

The masses of nickel cations and oxygen anions required to prepare 5.00 g of NiO are 3.93 g Ni^{2+} and 1.07 g of O^{2-}.

3.



bcc



fcc

4. As an example, we do the calculation for barium. Barium crystallizes in a cubic unit cell with an edge of length 5.025 Å. There is a barium atom on each of the corners of the unit cell and in the center of the unit cell.
Contents of a unit cell:
(8 corner Ba atoms)(1/8 occupancy) = 1 Ba atom
(1 Ba atom within the cell)(1 occupancy) = 1 Ba atom
There is a total of 2 Ba atoms per unit cell.

Mass of a unit cell:
(2 Ba atoms/unit cell)(1 mol Ba/6.022×10^{23} atoms)(137.33 g/mol Ba)
= 4.561×10^{-22} g per unit cell

Volume of a unit cell:
$(5.025\ \text{Å})^3(1 \times 10^{-8}\ \text{cm/Å})^3 = 1.269 \times 10^{-22}\ \text{cm}^3$

Density = mass/volume = 4.561×10^{-22} g/(1.269×10^{-22} cm^3) = 3.594 g/cm^3

5. Contents of unit cell:
(8 corner Al atoms)(1/8 occupancy) = 1 Al atom
(6 face-centered atoms)(1/2 occupancy) = 3 Al atoms
There are 4 Al atoms per cell

Mass of a unit cell:
(4 Al atoms)(1 mol Al/6.022×10^{23} atoms)(26.98 g/mol Al) = 1.792×10^{-22} g

Volume of a unit cell:
$(4.050\ \text{Å})^3(1 \times 10^{-8}\ \text{cm/Å})^3 = 6.643 \times 10^{-23}\ \text{cm}^3$

Density = mass/volume = 1.792×10^{-22} g/ 6.643×10^{-23} cm^3 = 2.698 g/cm^3

6. Contents of unit cell:
(8 corner Ca^{2+} ions)(1/8 occupancy) = 1 Ca^{2+} ion
(12 edge Ca^{2+} ions)(1/4 occupancy) = 3 Ca^{2+} ions
There is a total of 4 Ca^{2+} ions per cell
(8 internal F^- ions)(1 occupancy) = 8 F^- ions

Mass of a unit cell, in atomic mass units (amu):
(4 Ca^{2+} ions)(40.08 amu/Ca^{2+}) + (8 F^- ions))(19.00 amu/F^-) = 312.32 amu

Volume of unit cell:
$(5.46295\ \text{Å})^3(1 \times 10^{-8}\ \text{cm/Å})^3 = 1.63035 \times 10^{-22}\ \text{cm}^3$

Mass of a unit cell, in grams:
(1.63035×10^{-22} cm^3)(3.1805 g/cm^3) = 5.1853×10^{-22} g

Division of the amu mass by the gram mass gives Avagadro's number (*N*)
N = (312.32 amu)/(5.1853×10^{-22} g) = 6.0232×10^{23}

7. Yes, both represent CsCl. Both show the 1:1 ratio of ions and the correct cubic coordination (Chapter 5) of both cations and anions.

8. As examples, we do the Ga(P,As) solid solution system.
Maximum % Ga occurs in GaP (molar mass = 100.69 g/mol):
% Ga = (69.72 g/100.69 g/mol)(100) = 69.24%

Minimum % Ga occurs in GaAs (molar mass = 144.64 g/mol):
% Ga = (69.72 g/144.64 g/mol)(100) = 48.20%

9. Contents of top unit cell:
(8 corner Ti^{4+} ions)(1/8 occupancy) = 1 Ti^{4+} ion
(12 edge O^{2-} ions)(1/4 occupancy) = 3 O^{2-} ions
(1 internal Ca^{2+} ion)(1 occupancy) = 1 Ca^{2+} ion

Contents of bottom unit cell:
(8 corner Ca^{2+} ions)(1/8 occupancy) = 1 Ca^{2+} ions
(6 face-shared O^{2-} ions)(1/2 occupancy) = 3 O^{2-} ions

(1 internal Ti^{4+} ion)(1 occupancy) = 1 Ti^{4+} ion

Both representations lead to the empirical formula $CaTiO_3$ and the same spatial relationships of atoms. They represent identical structures.

10. The molar mass of $KCl_{0.30}Br_{0.70}$ is calculated as follows:
(1)(39.0983 g K/mol) + (0.30)(35.4527 g Cl/mol) + (0.70)(79.904 g Br/mol) = 105.667 g

The percent by mass of bromide ions in $KCl_{0.30}Br_{0.70}$ is given by
(56 g Br)(100)/(105.667 g $KCl_{0.30}Br_{0.70}$) = 53% Br

Therefore, the mass of Br in a 1.00-g sample of $KCl_{0.30}Br_{0.70}$ is
(1.00 g $KCl_{0.30}Br_{0.70}$) (53 g Br)/(100 g $KCl_{0.30}Br_{0.70}$) = 0.53 g Br

The amount of AgBr that can be produced from 0.53 g Br is calculated to be

(0.53 g Br)(1 mol Br/79.904 g Br) = 6.6×10^{-3} mol Br

$$(6.6 \times 10^{-3}\ \text{mol Br})\ \frac{1\ \text{mol AgBr}}{1\ \text{mol Br}}\ \frac{187.77\ \text{g AgBr}}{1\ \text{mol AgBr}} = 1.2\ \text{g AgBr}$$

11. a. volume of unit cell = $(4.29 \times 10^{-8}\ \text{cm})^3 = 7.90 \times 10^{-23}\ \text{cm}^3$
mass of unit cell = $(7.90 \times 10^{-23}\ \text{cm}^3)(5.66\ \text{g/cm}^3) = 4.47 \times 10^{-22}$ g

b. Let x = the number of oxygen atoms in a unit cell
Then $0.932x$ = the number of iron atoms in a unit cell
$(0.932x)(55.847\ \text{g/mol})/(6.022 \times 10^{23}$ ions per mol) +
$(x)(16.00\ \text{g/mol})/(6.022 \times 10^{23}$ ions per mol) = 4.47×10^{-22} g
$(1.13 \times 10^{-22}\ \text{g})(x) = 4.47 \times 10^{-22}$ g
$x = 3.96$ = number of oxygen atoms per unit cell
(0.932)(3.96) = 3.69 iron atoms per unit cell

c. (3.96/4.00)(100) = 99% of oxygen sites occupied
(3.69/4.00)(100) = 92% of iron sites occupied

12. Assuming 100 g TiO_x
(70.90 g Ti)(1 mol Ti/47.88 g) = 1.481 mol Ti
(29.10 g O)(1 mol O/16.00 g) = 1.819 mol O
Molar ratios: Ti: (1.481/1.481) = 1.000; O: (1.819/1.481) = 1.228
Empirical formula = $TiO_{1.228}$

13. We do isolation of Cd as an example: What mass of $Cd_{0.010}Zn_{0.99}S$ must be processed to isolate 1,000 kg of cadmium?
molar mass $Cd_{0.010}Zn_{0.99}S$ = 98 g/mol
$(1.000 \times 10^3$ kg Cd)(1,000 g/kg)(1 mol Cd/112.41 g) = 8.896×10^3 mol Cd

$$8.896 \times 10^3\ \text{mol Cd} \times \frac{1\ \text{mol}\ Cd_{0.010}Zn_{0.99}S}{0.010\ \text{mol Cd}} \times \frac{98\ \text{g}}{1\ \text{mol}\ Cd_{0.010}Zn_{0.99}S}$$

$= 8.7 \times 10^7$ g $Cd_{0.010}Zn_{0.99}S$

14. Molar mass of $CdS_{0.29}Se_{0.71}$ = $1\underline{7}8$ g
% Cd = 63%, % S = 5.2%, % Se = 32%

Molar mass of $Na_{0.24}WO_3$ = $2\underline{3}7.37$ g
% Na = 2.3%, % W = 77.5%, % O = 20.2%

15. $x = 0.54$ and $y = 0.63$

16. For example, if $x = 0.50$
$Ca_5(PO_4)_3OH + 0.50\ NaF \rightarrow Ca_5(PO_4)_3(OH)_{0.50}F_{0.50} + 0.50\ NaOH$
$(1.00\ g\ Ca_5(PO_4)_3OH)(1\ mol/\ 502.32\ g) = 1.99 \times 10^{-3}\ mol\ Ca_5(PO_4)_3OH$
$(1.99 \times 10^{-3}\ mol\ Ca_5(PO_4)_3OH)(0.50\ mol\ NaF/1\ mol\ Ca_5(PO_4)_3OH) =$
$9.\underline{9}5 \times 10^{-4}\ mol\ NaF$
$(9.\underline{9}5 \times 10^{-4}\ mol\ NaF)(41.99\ g/\ 1\ mol\ NaF) = 4.2 \times 10^{-2}\ g\ NaF$

17. For example, if $x = 0.50$
$Si_{0.50}Ge_{0.50} + O_2 \rightarrow 0.50\ SiO_2 + 0.50\ GeO_2$
$(0.5356\ g\ Si_{0.50}Ge_{0.50})(1\ mol/5\underline{0}.35\ g) = 1.\underline{0}64 \times 10^{-2}\ mol\ Si_{0.50}Ge_{0.50}$
$(1.\underline{0}64 \times 10^{-2}\ mol\ Si_{0.50}Ge_{0.50})(0.50\ mol\ SiO_2/1\ mol\ Si_{0.50}Ge_{0.50}) =$
$5.\underline{3}18 \times 10^{-3}\ mol\ SiO_2$
$(5.\underline{3}18 \times 10^{-3}\ mol\ SiO_2)(60.09\ g/1\ mol\ SiO_2) = 0.32\ g\ SiO_2$
$(1.\underline{0}64 \times 10^{-2}\ mol\ Si_{0.50}Ge_{0.50})(0.50\ mol\ GeO_2/1\ mol\ Si_{0.50}Ge_{0.50}) =$
$5.\underline{3}18 \times 10^{-3}\ mol\ GeO_2$
$(5.\underline{3}18 \times 10^{-3}\ mol\ GeO_2)(104.61\ g/1\ mol\ GeO_2) = 0.56\ g\ GeO_2$
Total mass of oxides = 0.88 g

18. For example, if $x = 0.50$
$2\ Ca_5(PO_4)_3(OH)_{0.50}F_{0.50} + 7H_2SO_4 \rightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 + H_2O + HF$
$(1.000 \times 10^3\ kg\ Ca_5(PO_4)_3(OH)_{0.50}F_{0.50})(1 \times 10^3\ g/kg)(1\ mol/5\underline{0}3.31\ g) =$
$1.\underline{9}87 \times 10^3\ mol\ Ca_5(PO_4)_3(OH)_{0.50}F_{0.50}$
$(1.\underline{9}87 \times 10^3\ mol\ Ca_5(PO_4)_3(OH)_{0.50}F_{0.50})\ x$
$(1\ mol\ HF/2\ mol\ Ca_5(PO_4)_3(OH)_{0.50}F_{0.50})(20.01\ g/mol\ HF) =$
$2.0 \times 10^4\ g\ HF$

19. For example, if $x= 0.50$
$CdS_{0.50}Se_{0.50} + 2\ HCl \rightarrow CdCl_2 + 0.50\ H_2S + 0.50\ H_2Se$
$(0.5356\ g\ CdS_{0.50}Se_{0.50})(1\ mol\ /1\underline{6}8\ g) = 3.\underline{1}9 \times 10^{-3}\ mol\ CdS_{0.50}Se_{0.50}$
$(3.\underline{1}9 \times 10^{-3}\ mol\ CdS_{0.50}Se_{0.50})(1\ mol\ CdCl_2/1\ mol\ CdS_{0.50}Se_{0.50}) =$
$3.\underline{1}9 \times 10^{-3}\ mol\ CdCl_2$
$(3.\underline{1}9 \times 10^{-3}\ mol\ CdCl_2)(183.3\ g/1\ mol) = 0.58\ g\ CdCl_2$

20. For example, if $x = 0.50$
$CdS_{0.50}Se_{0.50} + 2\ HCl \rightarrow CdCl_2 + 0.50\ H_2S + 0.50\ H_2Se$
$(0.5356\ g\ CdS_{0.50}Se_{0.50})(1\ mol\ /1\underline{6}8\ g) = 3.\underline{1}9 \times 10^{-3}\ mol\ CdS_{0.50}Se_{0.50}$
$(3.\underline{1}9 \times 10^{-3}\ mol\ CdS_{0.50}Se_{0.50})(0.50\ mol\ H_2S/1\ mol\ CdS_{0.50}Se_{0.50}) =$
$1.\underline{6}0 \times 10^{-3}\ mol\ H_2S$

$PV = nRT$
$V = nRT/P = (1.\underline{6}0 \times 10^{-3}\ mol\ H_2S)(0.0821\ L{\cdot}atm/mol{\cdot}K)(273\ K)/(1\ atm)$
$V = 0.036\ L$

21. liquid H_2: $(1\ cm^3)(0.070\ g/cm^3) = 0.070\ g\ H_2$

For LiH:
volume of unit cell = $(4.085\ \text{Å})^3(1 \times 10^{-8}\ cm/1\ \text{Å})^3 = 6.817 \times 10^{-23}\ cm^3$
cell contents: $(8\ corner\ Li^+\ ions)(1/8\ occupancy) = 1\ Li^+\ ion$
$(6\ face\text{-}centered\ Li^+\ ions)(1/2\ occupancy) = 3\ Li^+\ ions$
$(12\ H^-\ edge\text{-}shared\ ions)(1/4\ occupancy) = 3\ H^-\ ions$
$(1\ internal\ H^-\ ion)(1\ occupancy) = 1\ H^-\ ion$
mass of unit cell:

$$= (4\ H^-\ ions)\ \frac{1.008\ g}{mol\ H}\ \frac{1\ mol\ H^-}{6.022 \times 10^{23}\ ions} + (4\ Li^+\ ions)\ \frac{6.941\ g}{mol\ Li}\ \frac{1\ mol\ Li^+}{6.022 \times 10^{23}\ ions}$$

$= 5.280 \times 10^{-23}\ g$

$$\text{density of LiH} = \text{mass/volume} = \frac{5.280 \times 10^{-23}\ \text{g}}{0.817 \times 10^{-23}\ \text{cm}^3} = 0.7745\ \text{g/cm}^3$$

mass of hydrogen in 1 cm^3 LiH
(1 cm^3 LiH)(0.7745 g/cm^3)(1.008 g H/7.949 g LiH) = 0.09821 g H

there is more hydrogen by mass in 1 cm^3 of LiH than in 1 cm^3 of H_2

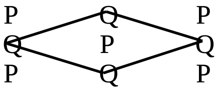
22. $KCl + RbCl \rightarrow 2\ K_{0.50}Rb_{0.50}Cl$
$(10.0\ \text{g}\ K_{0.50}Rb_{0.50}Cl)(1\ \text{mol}/9\underline{7}.7\ \text{g}) = 0.1\underline{0}2\ \text{mol}\ K_{0.50}Rb_{0.50}Cl$
$(0.1\underline{0}2\ \text{mol}\ K_{0.50}Rb_{0.50}Cl)\ \dfrac{1\ \text{mol KCl}}{2\ \text{mol}\ K_{0.50}Rb_{0.50}Cl} = 5.\underline{1}0 \times 10^{-2}\ \text{mol KCl}$
$(5.\underline{1}0 \times 10^{-2}\ \text{mol KCl})(74.55\ \text{g}/1\ \text{mol KCl}) = 3.8\ \text{g KCl}$
$(0.1\underline{0}2\ \text{mol}\ K_{0.50}Rb_{0.50}Cl)\ \dfrac{1\ \text{mol RbCl}}{2\ \text{mol}\ K_{0.50}Rb_{0.50}Cl} = 5.\underline{1}0 \times 10^{-2}\ \text{mol RbCl}$
$(5.\underline{1}0 \times 10^{-2}\ \text{mol RbCl})(120.92\ \text{g}/1\ \text{mol RbCl}) = 6.2\ \text{g RbCl}$

23. a. salt b. molcule c. alloy d. molcule e. salt

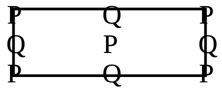
24. Ba and O; extended ionic solid
Cu and Ni; extended metallic solid
N and O; discrete molcule
Na and F; extended ionic solid

25. Ni and Cu have the same structure (fcc) and similar atomic radii. The same is true for Mo and V, which are bcc metals. These pairs are expected to most easily substitute for one another and form solid solutions, Ni_xCu_{1-x} and Mo_xV_{1-x}.

26. a.



b)



a.
P: (1)(1 occupancy) = 1 P
Q: (4)(1/4 occupancy) = 1 Q

PQ

b.
P: (4)(1/4 occupancy) = 1 P
(1)(1 occupancy) = 1 P
Q: (4)(1/2 occupancy) = 2 Q
P_2Q_2 = PQ

27. a. three in the unit cell, but nine others in neighboring cells also exist, giving a total of twelve.
b. only one in the unit cell, but seven more exist in neighboring cells, giving a total of eight.

28. six

29. Cs and Cl

30. $GaAs_{0.75}P_{0.25}$ molar mass = 133.65 g

31. $CdS_{0.10}Se_{0.90}$ molar mass = 187 g

32. Elemental analysis would not be able to distinguish between $Cu_{0.5}Ni_{0.5}$ and an equimolar homogeneous mixture of Cu and Ni. The magnetic properties of elemental Cu and Ni are quite different. Nickel is ferromagnetic (Chapter 2), and could be separated from a mixture with copper by the use of a magnet. The Cu and Ni in a $Cu_{0.5}Ni_{0.5}$ solid solution cannot be separated by a magnet. Thus magnetic properties could distinguish the two samples.

Chapter 4

1. $c = \nu\lambda$
   $(2.998 \times 10^8 \text{ m/s}) = (\nu)(1.54 \text{ Å})(1 \times 10^{-10} \text{ m/Å})$
   $\nu = 1.95 \times 10^{18} \text{ s}^{-1}$

2. a. $(2)(d)(\sin \theta) = n\lambda$
   $(2)(4.123 \text{ Å})(\sin \theta) = (2)(1.54 \text{ Å})$
   $\theta = 22.0°$
   b. $\theta = 15.8°$ c. $\theta = 27.4°$ d. $\theta = 21.0°$ e. $\theta = 25.9°$

3. $\sin \theta = n\lambda/(2d)$ For $n = 1$ and $\lambda = 1.54$ Å, $\sin \theta = 0.770 \text{ Å}/d$
   a. $\sin \theta = (0.77\text{Å}/1.79 \text{ Å}) = 0.430$ $\theta = 25.5°$
   b. $\theta = 15.9°$ c. $\theta = 17.2°$ d. $\theta = 20.9°$ e. $\theta = 18.1°$

4. $n = 1$ $\lambda = 1.54$ Å $d = (1)(1.54 \text{ Å})/[(2)(\sin \theta)] = 0.770 \text{ Å}/(\sin \theta)$
   a. $d = 1.79$ Å b. $d = 2.81$ Å c. $d = 2.60$ Å d. $d = 2.16$ Å e. $d = 2.47$ Å

5. $c = \nu\lambda$
   $(2.998 \times 10^8 \text{ m/s}) = (\nu)(670 \text{ nm})(1 \times 10^{-9} \text{ m/nm})$
   $\nu = 4.47 \times 10^{14} \text{ s}^{-1}$

7. a. vertical spots b. horizontal spots c. square pattern of spots

8. a. The smaller square array gives the larger square diffraction pattern.
   b. The pattern on the left gives a square pattern; the array on the right gives a rectangle with the long distance between spots in the horizontal direction.
   c. Both arrays give rectangular diffraction patterns. The array on the left will give a diffraction pattern with the longer edge of the rectangle in the vertical direction. The array on the right will produce a diffraction pattern with the longer edge of the rectangle in the horizontal direction.
   d. An array of lines gives a series of dots in the diffraction pattern. The horizontal pattern of lines will give a diffraction pattern consisting of a set of spots running in the vertical direction, and the vertical array of lines gives a diffraction pattern consisting of a set of spots in the horizontal direction.

9. a. The diffraction pattern with fewer spots is due to array b which has an extra dot in the middle of each square.
   b. Light diffracted by the added dots is out of phase with the light diffracted by the other dots of the array, creating destructive interference that removes every other spot from the diffraction pattern.
   c. The unit cell of Figure 9a can be considered to be a rectangle, with its longer sides in the vertical direction. Long distances in dot arrays become short in the diffraction pattern (reciprocal lattice effect) so the diffraction pattern will also be a rectangle, with the short edge in the vertical direction. The unit cell of Figure 9b can be viewed as a slightly squashed, tilted parallelogram. The repeat unit in the diffraction pattern will also be a tilted parallelogram.

10. Assume a d-spacing of 1.0×10^{-4} m (1.0×10^{6} Å) and compare φ values for first-order diffraction using the equation for Fraunhofer diffraction:

IR: $d \sin \varphi = n\lambda$	UV: $d \sin \varphi = n\lambda$
$(1.0 \times 10^{6}\ \text{Å}) \sin \varphi = (1)(8{,}000\ \text{Å})$	$(1.0 \times 10^{6}\ \text{Å}) \sin \varphi = (1)(3{,}000\ \text{Å})$
$\sin \varphi = 8.0 \times 10^{-3}$	$\sin \varphi = 3.0 \times 10^{-3}$
$\varphi = 0.46°$	$\varphi = 0.17°$

The angle and therefore the size of the diffraction pattern increases with the wavelength of light used. UV radiation would lead to a small diffraction pattern, and IR radiation would yield a large diffraction pattern.

11. In order for diffraction to occur, the wavelength of incident radiation must be approximately the same as the spacing of the atoms. Atomic separations are typically a few angstroms. X-rays, with wavelength of about 1 Å, are a far better match to interatomic spacings than visible light ($\lambda \sim 4{,}000$ Å to 7,000 Å).

12. The STM can only collect two-dimensional information. The penetrating nature of X-rays and subsequent diffraction off various planes of atoms adds information in the third dimension.

13. Referring to Figure 4.1, φ can be calculated from
$\tan \varphi = X/L = (3.8\ \text{cm}/6.0 \times 10^{2}\ \text{cm}) = 6.3 \times 10^{-3}$
$\varphi = 0.36°$ (compare this angle to those calculated in problem 4.10)
$(d)(\sin \varphi) = n\lambda$
$(d)(\sin 0.36°) = (1)(6.33 \times 10^{-7}\ \text{m})$ $d = 1.00 \times 10^{-4}$ m

14. For a given order of diffraction (n value), as d becomes smaller, sin θ must become larger to satisfy the Bragg equation: $2d(\sin \theta) = n\lambda$. Thus, as sin θ and θ increase, the observed spacing of the spots in a diffraction pattern increases.

15. a. In moving from sc to bcc, one half of the spots in the diffraction pattern disappear. This disappearance is due to complete destructive interference that occurs with some of the X-ray waves. The destructive interference is caused by the presence of the scattering center in the body of the bcc cell. In moving from bcc to fcc, one half of the spots again disappear, as a result of destructive interference that occurs from the scattering centers located on the faces of the cell.

b. We do CsCl. The diffraction pattern of CsCl should reflect both the positions of the ions in the cell, as well as their relative sizes. Because Cs ions and Cl ions are different, the destructive interference due to the Cs ion in the center of the cell is *incomplete*. The CsCl diffraction pattern is predicted to have spots at the same locations as the sc pattern of question 15a, but the intensities of half of the spots will be less than the corresponding spots in the sc diffraction pattern. The spots of reduced intensity will be at the same locations as the spots that completely disappeared in the diffraction pattern of the bcc structure of 15a.

Chapter 5

1. a. $V = (4/3)\pi r^3$ $V_{\text{atom}} = (4/3)(\pi)(0.50\ \text{Å})^3 = 0.52\ \text{Å}^3$
b. In a simple cubic structure, the corner atoms of the unit cell touch.

Therefore, the length of the unit cell will equal 2*r*. In this problem, the length of the cell = $2r = 1.00$ Å

c. $V_{\text{cell}} = (1.00 \text{ Å})^3 = 1.00 \text{ Å}^3$

d. Volume of atoms in cell:

(8 corner atoms)(1/8 occupancy) = volume of one atom = 0.52 Å^3.

Packing efficiency = volume of atoms in cell/V_{cell} = $\dfrac{0.52 \text{ Å}^3}{1.00 \text{ Å}^3} \times 100 = 52\%$

2. a. $V = (4/3)\pi r^3$ $V_{\text{atom}} = (4/3)(\pi)(0.50 \text{ Å})^3 = 0.52 \text{ Å}^3$

b. In a bcc structure, the corner atoms do not touch each other. The atoms touch along the body-diagonal; the body-diagonal has a length equal to 4*r* or 2*d*. If the bcc cell has an edge length of *a*, the face-diagonals have a length given by the Pythagorean theorem to be $(2)^{0.5}a$. The body-diagonal of the cell constitutes the hypotenuse of a right triangle; the face-diagonal and cell edge are the other two sides. Thus we have

$$[(2)^{0.5}a]^2 + a^2 = (2d)^2$$
$$3a^2 = 4d^2$$
$$a^2 = (4/3)d^2$$
$$a = 1.155d$$

c. $V = (a)^3 = [(1.155)(1.00 \text{ Å})]^3 = 1.54 \text{ Å}^3$

d. Atoms in unit cell:

(8 corner atoms)(1/8 occupancy) = 1 atom

(1 body-centered atom)(1 occupancy) = 1 atom

or a total of 2 atoms per unit cell.

Volume of atoms per unit cell = (2 atoms)(0.52 Å^3/atom) = 1.04 Å^3

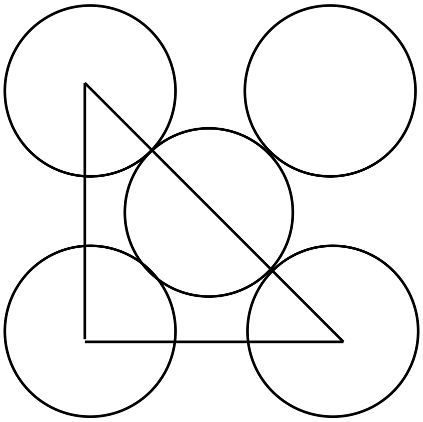
Volume of unit cell = 1.54 Å^3

Packing efficiency = $(100)(1.04 \text{ Å}^3)/1.54 \text{ Å}^3 = 68\%$

3. a. $V = (4/3)\pi r^3$

$V_{\text{atom}} = (4/3)(\pi)(0.500 \text{ Å})^3 = 0.524 \text{ Å}^3$

b.



The diagram represents one face of a fcc system. As shown, a right triangle can be drawn with a hypotenuse of length 4*r* or 2.00 Å, and the other sides equal in length to that of the cell edge, *a*. This information allows calculation of the cell edge length by the Pythagorean theorem:

$$a^2 + a^2 = (4r)^2 = (2.00 \text{ Å})^2$$
$$2a^2 = 4.00 \text{ Å}^2$$
$$a = 1.41 \text{ Å}$$

c. $V_{\text{cell}} = (1.41\ \text{Å})^3 = 2.80\ \text{Å}^3$

d. Atoms in unit cell:
(8 corner atoms)(1/8 occupancy) = 1 atom
(6 face-shared atoms)(1/2 occupancy) = 3 atoms
or a total of 4 atoms per unit cell.

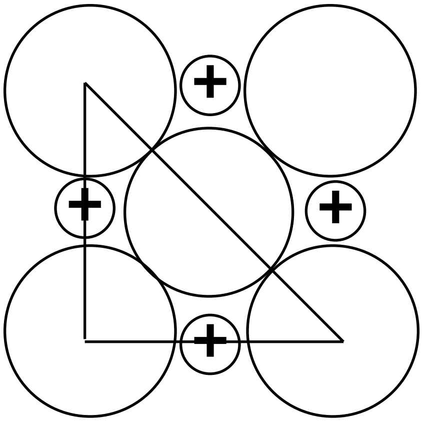
$V_{\text{atoms}} = (0.524\ \text{Å}^3/\text{atom})(4\ \text{atoms}) = 2.08\ \text{Å}^3$

Packing efficiency = $(2.08\ \text{Å}^3)(100)/(2.80\ \text{Å}^3) = 74.3\%$

4. d.

5. The solid may be described as two interpenetrating sc arrays of ions. Thus, both figures accurately describe the CsCl structure.

6. LiH adopts the NaCl structure with a cell edge length of 4.085 Å. A generalized view of one face of the NaCl structure is



A right triangle can be drawn on the cell face with a hypotenuse of length 4*r*, and the other sides equal in length *a* to that of the cell edge (4.085 Å). This information allows calculation of the ionic radius of H^-:

$$(4r)^2 = (4.085\ \text{Å})^2 + (4.085\ \text{Å})^2$$
$$r = 1.443\ \text{Å}$$

7. For example, Ba (bcc) cell length = 5.025 Å.
$V_{\text{cell}} = (5.025\ \text{Å})^3(1 \times 10^{-8}\ \text{cm}/1\ \text{Å})^3 = 1.269 \times 10^{-22}\ \text{cm}^3$

The bcc structure contains the following Ba atoms:
(8 corner atoms)(1/8 occupancy) = 1 atom
(1 atom within cell)(1 occupancy) = 1 atom
or a total of 2 atoms per unit cell.

(2 Ba atoms)(1 mol Ba/6.022×10^{23} atoms)(137.33 g/mol Ba) = 4.561×10^{-22} g

Density = mass/volume = $(4.561 \times 10^{-22}\ \text{g})/(1.269 \times 10^{-22}\ \text{cm}^3) = 3.594\ \text{g/cm}^3$

8. Two tetrahedral holes exist per ccp sulfur atom and half of them are full. Therefore there is one zinc atom per sulfur atom, so the empirical formula of the compound is ZnS.

9. Two tetrahedral holes exist per ccp sulfide ion, and each of them contains a lithium ion. Therefore the empirical formula is Li_2S.

10. One octahedral hole exists per ccp chloride ion and all of the octahedral holes contain silver ions. The empirical formula of the compound is AgCl.

11. There is one cubic hole per iodide ion in a simple cubic array of iodide ions. All of the cubic holes contain a thallium ion. The empirical formula is TlI.

12. The cubic array of F^- yields
(8 corner ions)(1/8 occupancy) = 1 F^- ion
One cubic hole exists per unit cell. Half of the cubic holes are filled with Ba^{2+} ions and the other half are empty. Therefore, on average, there is one half Ba^{2+} ion per unit cell. There is one F^- ion per unit cell. The formula of the compound is $Ba_{0.5}F$ or BaF_2.

14. For example, aluminum adopts the fcc structure with a cell edge length of 4.050 Å. The diagram presented in the solution to problem 3 of this chapter represents one face of the fcc array of aluminum atoms. A right triangle can be drawn on the cell face with a hypotenuse of length $4r$, and the other sides equal in length to that of the cell edge (4.050 Å). This information allows calculation of the atomic radius of Al:

$$(4r)^2 = (4.050)^2 + (4.050)^2$$
$$16r^2 = 32.805 \text{ Å}^2$$
$$r = 1.432 \text{ Å}$$

15. For example, carbon. Diamond has a unit cell edge length of 3.5668 Å. If the unit cell is subdivided into eight smaller cubes of equal volume, each edge of the small cubic cells has a length of (3.5668 Å)/2 = 1.7834 Å. The length x of the face-diagonal of the mini-cell is then given by

$$(1.7834 \text{ Å})^2 + (1.7834 \text{ Å})^2 = x^2 \qquad x = 2.5221 \text{ Å}$$

The length y of the body-diagonal of the small cubic cell is calculated to be

$$(1.7834 \text{ Å})^2 + (2.5221 \text{ Å})^2 = y^2 \qquad y = 3.0889 \text{ Å}$$

The body-diagonal has a length equal to $4r$. Thus, $r = 0.77223$ Å.

16. For example, CaO. Cell edge length = 4.8105 Å. A generalized view of one face of the NaCl structure is shown in problem 6 of this chapter.

A right triangle can be drawn on the cell face with a hypotenuse of length (4)(oxide radius), and the other sides equal in length to that of the cell edge (4.8105 Å). This information allows calculation of the ionic radius of O^{2-}:

$$(4r)^2 = (4.8105 \text{ Å})^2 + (4.8105 \text{ Å})^2$$
$$16r^2 = 46.281 \text{ Å}^2$$
$$r = 1.7008 \text{ Å}$$

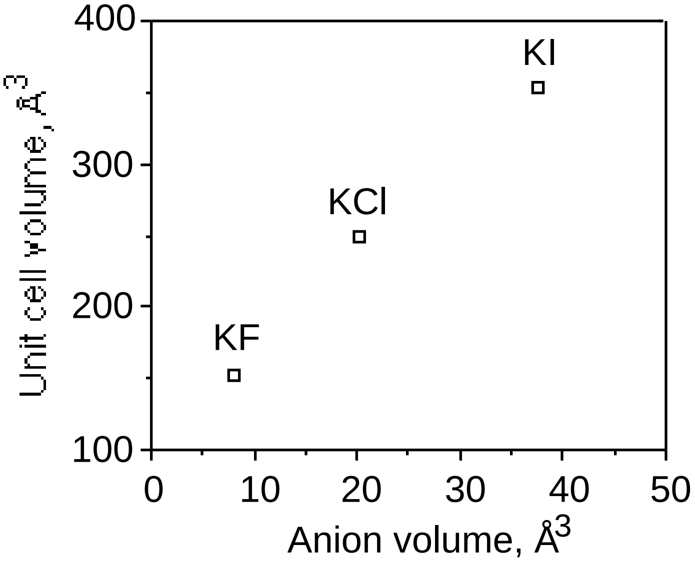
The length of the CaO cell edge is the sum of two oxide radii plus two calcium ion radii:

$$4.8105 \text{ Å} = (2)(O^{2-} \text{ radius}) + (2)(Ca^{2+} \text{ radius})$$
$$4.8105 \text{ Å} = (2)(1.7008 \text{ Å}) + (2)(Ca^{2+} \text{ radius})$$
$$Ca^{2+} \text{ radius} = 0.70445 \text{ Å}$$

17. The plot of unit cell volume versus anion volume was prepared from the following data:

Anion	Anion radius (Å)	Anion volume ($Å^3$), $V = (4/3)\,\pi r^3$
F^-	1.19	7.06
Cl^-	1.67	19.5
I^-	2.06	36.6

Salt	Cell Length (Å)	Cell Volume ($Å^3$)
KF	5.347	152.9
KCl	6.2929	249.20
KBr	6.6000	287.50
KI	7.0656	352.73



The volume of KBr (287.50 $Å^3$) and this plot allow one to estimate the volume of the Br^- anion (31 $Å^3$), and to calculate an ionic radius for Br^- of 1.9 Å.

18. undistorted cubic holes: Po
undistorted octahedral holes: Al, Co, Pb
undistorted tetrahedral holes: Al, Co, Pb

19.

Type	Anisotropic	Isotropic
Ionic	CdI_2	NaCl
Covalent	graphite	diamond

20. Aluminum adopts an efficiently packed fcc structure, but silicon adopts the less efficiently packed diamond structure: The aluminum atoms pack with far less empty space between atoms than silicon, overcoming the difference in size and atomic weight.

21. Although the two-dimensional arrangement of atoms in individual planes of hcp and ccp structures are identical, the stacking pattern or three-dimensional sequencing of layers is different, and therefore the structures are different.

22. The radius ratio rule may be used to predict the coordination number and type of holes favored by ionic compounds, but not of solids with strong directional covalent bonding like diamond and graphite.

23. Ratio = 1.00; radius ratio rule predicts 8-coordinate. See No. 22.

24. The cell shown in Figure 5.15 cannot account for the stoichiometry of $CdCl_2$:
(8 corner chloride ions)(1/8 occupancy) = 1 chloride ion
(6 face-centered chloride ions)(1/2 occupancy) = 3 chloride ions
(6 edge-shared cadmium ions)(1/4 occupancy) = 1.5 cadmium ions
= $Cd_{1.5}Cl_4$ or Cd_3Cl_8

25. a. Referring to the *z*-level diagram of Figure 5.16:
(8 corner arsenic ions)(1/8 occupancy) = 1 arsenic ion
(1 arsenic ion within cell)(1 occupancy) = 1 arsenic ion
(2 nickel ions within cell)(1 occupancy) = 2 nickel ions
= Ni_2As_2 or NiAs

b. (8 corner chloride ions)(1/8 occupancy) = 1 chloride ion
(6 face-centered chloride ions)(1/2 occupancy) = 3 chloride ions
(12 edge-shared sodium ions)(1/4 occupancy) = 3 sodium ions
(1 sodium ion within cell)(1 occupancy) = 1 sodium ion
= Na_4Cl_4 or NaCl

c. Referring to the *z*-level diagram of Figure 5.17A:
(8 corner iodide ions)(1/8 occupancy) = 1 iodide ion
(1 iodide ion within cell)(1 occupancy) = 1 iodide ion
(1 cadmium ion within cell)(1 occupancy) = 1 cadmium ion
= CdI_2

d. Referring to the *z*-level diagram of Figure 5.19:
(8 corner oxide ions)(1/8 occupancy) = 1 oxide ion
(6 face-centered oxide ions)(1/2 occupancy) = 3 oxide ions
(8 lithium ions within cell)(1 occupancy) = 8 lithium ions
= Li_8O_4 or Li_2O

e. .Referring to the *z*-level diagram of Figure 5.20:
(8 corner fluoride ions)(1/8 occupancy) = 1 fluoride ion
(6 face-centered fluoride ions)(1/2 occupancy) = 3 fluoride ions
(12 edge-shared fluoride ions)(1/4 occupancy) = 3 fluoride ions
(1 fluoride ion within cell)(1 occupancy) = 1 fluoride ion
(4 calcium ions within cell)(1 occupancy) = 4 calcium ions
= Ca_4F_8 or CaF_2

26. As shown in Figure 5.17B, a single crystal of CdI_2 is expected to cleave easily between adjacent layers of iodide ions. Along this plane there is no electrostatic attraction between Cd^{2+} and I^- ions.

27. The *z*-level diagram of Figure 5.23B represents the placement of holes for a unit cell containing two hexagonal close packed atoms:
$z = 0$ and 1.0: (8 corner atoms)(1/8 occupancy) = 1 atom
$z = 0.5$: (1 atom within cell)(1 occupancy) = 1 atom

This cell contains four T_d holes (or two holes per close packed atom):
$z = 0.125$ and 0.875: (8 T_d holes)(1/4 occupancy) = 2 T_d holes
$z = 0.375$ and 0.625: (2 T_d holes within cell)(1 occupancy) = 2 T_d holes

The cell also contains two O_h holes (or one hole per close packed atom):
z = 0.25 and 0.75: (2 O_h holes within cell)(1 occupancy) = 2 O_h holes

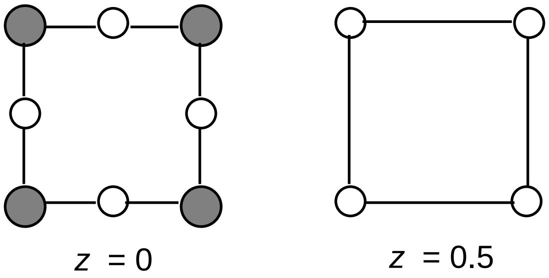
In summary, a unit cell containing two hcp atoms contains four T_d holes and two O_h holes. Thus, for every atom there is one O_h hole and two T_d holes.

28. Figure 5.13A shows a ccp array of four chloride ions:
(8 corner chloride ions)(1/8 occupancy) = 1 chloride ion
(6 face-centered chloride ions)(1/2 occupancy) = 3 chloride ions
The sodium cations are located in the octahedral holes of the lattice:
(12 edge-shared sodium ions)(1/4 occupancy) = 3 sodium ions
(1 sodium ion within cell)(1 occupancy) = 1 sodium ion
for a total of four octahedral holes (one per close-packed ion).

The unit cell shown in Figure 5.19 may also be described as a combination of eight small cubes. Each of these eight small cubes has four oxide ions that form a tetrahedral hole. Each of the tetrahedral holes is fully contained within the unit cell, which has a total of four oxide ions. Thus there are eight tetrahedral holes in the unit cell, or two per close-packed oxide ion.

29. There are two tetrahedral holes and one octahedral hole per C_{60} unit in the fcc structure (*see* problem 28). If these holes are all filled with potassium ions, the formula of the salt will be K_3C_{60}.

30.



31. (8 corner copper ions)(1/8 occupancy) = 1 copper ion
(8 edge-shared copper ions)(1/4 occupancy) = 2 copper ions
(12 edge-shared oxide ions)(1/4 occupancy) = 3 oxide ions
(8 face-shared oxide ions)(1/2 occupancy) = 4 oxide ions
(2 barium ions within cell)(1 occupancy) = 2 barium ions
(1 yttrium ion within cell)(1 occupancy) = 1 yttrium ion
= $YBa_2Cu_3O_7$

32. For example, Figure 5.31D:
(2 silicon atoms within cell)(1 occupancy) = 2 silicon atoms
(5 oxygen atoms within cell)(1 occupancy) = 5 oxygen atoms
(2 corner-shared oxygen atoms)(1/2 occupancy) = 1 oxygen atom
= $Si_2O_6^{4-}$ or SiO_3^{2-}

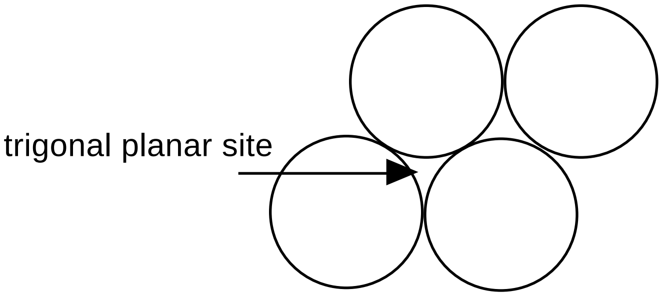
Figure 5.32:
(2 silicon atoms within cell)(1 occupancy) = 2 silicon atoms
(4 face-shared silicon atoms)(1/2 occupancy) = 2 silicon atoms
(8 oxygen atoms within cell)(1 occupancy) = 8 oxygen atoms
(6 face-shared oxygen atoms)(1/2 occupancy) = 3 oxygen atom
= $Si_4O_{11}^{6-}$

Figure 5.33:
(1 silicon atom within cell)(1 occupancy) = 1 silicon atom
(4 edge-shared silicon atoms)(1/4 occupancy) = 1 silicon atom
(4 oxygen atoms within cell)(1 occupancy) = 4 oxygen atoms
(4 edge-shared oxygen atoms)(1/4 occupancy) = 1 oxygen atom
= $Si_2O_5^{2-}$

33. a. $Si_4O_{11}^{6-} \rightarrow AlSi_3O_{11}^{7-}$
b. $Si_4O_{11}^{6-} \rightarrow Al_2Si_2O_{11}^{8-}$

34. a. six
b. $[Fe^{3+}]_4[Fe(CN)_6^{4-}]_3$
c. The salt does not have a 1:1 cation:anion stoichiometry and therefore cannot have a perfect NaCl structure. Rather, it exists with a NaCl-like structure with periodic anion vacancies.

35.



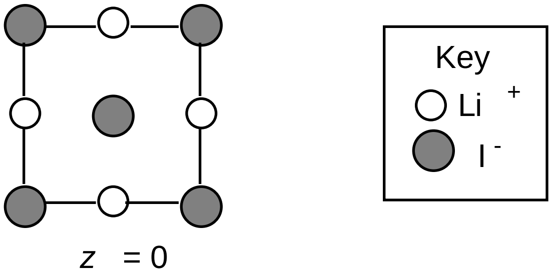
36. Two-thirds of the octahedral holes are filled with aluminum ions, and one octahedral hole exists per O^{2-} ion. Therefore, the formula of the compound is $Al_{2/3}O$ or Al_2O_3.

37. One-fourth of the tetrahedral holes are filled with mercury ions, and there are two tetrahedral holes per iodide ion. Therefore the formula of the compound is $Hg_{1/2}I$ or HgI_2.

38. One-eighth of the tetrahedral holes are filled with tin ions, and there are two tetrahedral holes per iodide ion. Therefore the formula of the compound is $Sn_{1/4}I$ or SnI_4.

39. One-third of the tetrahedral holes are filled with aluminum ions, and there are two tetrahedral holes per selenium ion. Therefore the formula of the compound is $Al_{2/3}Se$ or Al_2Se_3.

40. a. LiI adopts the NaCl structure:



b. The LiI cell edge length = 6.000 Å. A generalized, space-filling view of one face of the LiI structure is shown in the solution to problem 6 of this chapter.

A right triangle can be inscribed on the cell face with a hypotenuse of length (4)(I radius), and the other sides equal the length of the cell edge (6.000 Å). This information allows calculation of the ionic radius r of I^-:

$$(4r)^2 = (6.000\ \text{Å})^2 + (6.000\ \text{Å})^2$$
$$16r^2 = 72.000\ \text{Å}^2$$
$$r = 2.121\ \text{Å}$$

c. The length of the LiI cell edge is the sum of two iodide radii plus two lithium ion radii:

6.000 Å = (2)(I^- radius) + (2)(Li^+ radius)
6.000 Å = (2)(2.121 Å) + (2)(Li^+ radius)
Li^+ radius = 0.8790 Å

d. For example, LiCl also adopts the NaCl structure with cell edge length = 5.12954 Å. The chloride ionic radius can be calculated as in part c as follows:

5.12954 Å = (2)(Cl^- radius) + (2)(Li^+ radius)
5.12954 Å = (2)(Cl^- radius) + (2)(0.8790 Å)
Cl^- radius = 1.686 Å

Other results calculated in this manner are tabulated as follows:

Ion	Ionic Radius (Å)	Ion	Ionic Radius (Å)
Li^+	0.879	F^-	1.130
Na^+	1.134	Cl^-	1.686
K^+	1.460	Br^-	1.872
		I^-	2.121

41. Layers A and B of MoS_2 in Figure 5.26 will slip relative to one another because of the weak van der Waals forces that hold these layers together.

42. The sheets of sp^2-hybridized carbon atoms of graphite will slip relative to one another because of the weak van der Waals forces that hold these layers together.

43. a. The cation positions are the same. The centers of the C_2^{2-} units of CaC_2 match the Cl^- positions of NaCl.
b. The arsenic atoms in MgAgAs and the sulfur atoms in ZnS both pack in fcc structures. The Mg (or Ag) atoms in MgAgAs and the Zn atoms in ZnS fill half of the tetrahedral holes. In the MgAgAs structure the Ag atoms (or Mg atoms) occupy the remaining tetrahedral hole positions.

c. Both CdI_2 and NiAs are based on hcp anions. The cations in these solids are located in O_h holes formed by the anions. In the CdI_2 structure, alternating planes of cations are vacant.

44. A bcc metal has eight nearest neighbors, and a fcc metal has twelve.

Chapter 6

2. Iron is body-centered cubic with cell edge length = 2.8606 Å, and unit cell volume of $(2.8606\ \text{Å})^3(1 \times 10^{-8}\ \text{cm/Å})^3 = 2.3408 \times 10^{-23}\ \text{cm}^3$. Each unit cell contains (8 corner atoms)(1/8 occupancy) = 1 iron atom
(1 body-centered atom)(1 occupancy) = 1 iron atom
= two iron atoms per unit cell.

The mass of the two atoms is
$(2\ \text{Fe atoms})(1\ \text{mol Fe}/6.022 \times 10^{23}\ \text{atoms})(55.85\ \text{g/mol Fe}) = 1.855 \times 10^{-22}\ \text{g}$

$\text{Density} = \text{mass/volume} = (1.855 \times 10^{-22}\ \text{g})/(2.3408 \times 10^{-23}\ \text{cm}^3) = 7.925\ \text{g/cm}^3$

If 0.10% of the iron sites were vacant, the mass of the unit cell would equal
$(0.999)(1.855 \times 10^{-22}\ \text{g}) = 1.8\underline{5}3 \times 10^{-22}\ \text{g}$

$\text{density of the iron} = \text{mass/volume} = \dfrac{1.8\underline{5}3 \times 0^{-22}\ \text{g}}{2.3408 \times 0^{-23}\ \text{cm}^3} = 7.92\ \text{g/cm}^3$

1 cm^3 of defect free iron would weigh: $(1\ \text{cm}^3)(7.925\ \text{g/cm}^3) = 7.925$ g
1 cm^3 of iron with 0.10% vacancies would weigh essentially the same amount:
$(1\ \text{cm}^3)(7.92\ \text{g/cm}^3) = 7.92$ g

3. STM images the surface of a sample, and defects are frequently observed at grain boundaries like those at the surface of a solid. In addition, STM provides atom-by-atom images that might indicate the presence of a point defect. X-ray crystallography is a technique that cannot distinguish a single atom, but rather examines the bulk of a sample. The diffraction phenomenon depends on many planes of repeating atoms and yields averaged data based on a large number of these atoms.

4. $(1.00 \times 10^{-3}\ \text{g NaCl})\ (1\ \text{mol NaCl}/58.44\ \text{g}) = 1.71 \times 10^{-5}\ \text{mol NaCl}$
$(1.71 \times 10^{-5}\ \text{mol NaCl})(6.022 \times 10^{23}\ \text{NaCl formula units/mol NaCl})$
$= 1.03 \times 10^{19}$ NaCl formula units
$(1.03 \times 10^{19}\ \text{NaCl formula units})(1\ \text{defect}/1 \times 10^{15}\ \text{NaCl formula units})$
$= 1.03 \times 10^{4}$ defects (or missing pairs of ions)

5. Figure 6.17 and lattice information from Appendix 5.6 can be used to generate the following approximations:

Compound	Edge Length (Å)	λ_{max} (nm)
NaI	6.4728	~ 600
LiI	6.000	~ 500

7. Each substitution of a Na^+ ion by a Mg^{2+} ion places one unit of positive charge in excess of electrical neutrality in the solid. Answers a–c all maintain or exacerbate the charge imbalance imposed by the dopant. Only d offers a method of establishing charge balance by removing Na^+ ions equal in number to those substituted for the dopant.

8. Rather than dragging its entire body over a surface, a caterpillar moves by displacing only a portion of its body at any given instant. This is similar to the movement of a dislocation, seen in Figure 6.10A.

9. Aisles fill in the gaps that would naturally occur between columns of seats as you move away from the stage or field.

10. Refer to Figure 6.17 for the necessary data.

Compound	Unit Cell Length (Å)	F-center Abs. Max. (nm)
KCl	6.3	560
RbCl	6.6	620

As indicated in the text of this chapter, F-centers in $K_{1-x}Rb_xCl$ solid solutions have absorption maxima that lie between pure KCl and pure RbCl. In a $K_{0.5}Rb_{0.5}Cl$ solid solution, the expected parameters would be approximately 6.4 Å and 590 nm.

11. In the solid solution only one absorption peak would be expected, at about 590 nm (*see* problem 10). In the two-component physical mixture you would expect two peaks, at about 560 and 620 nm.

12. In an hcp metal there is only one set of slip planes; the slip planes are located between the ABAB... stacking planes. This feature can be contrasted to ccp metals in which close-packed slip planes exist in four different sets.

Chapter 7

1. a. $x = 0.75$ and $y = 0.40$.

2. c. Referring to Figure 7.16, complementary AZ pairs are indicated. Cadmium (Group 12) and tellurium (group 16) can form cadmium telluride, a solid that is structurally similar to α-Sn with the same number of valence electrons.

3. a. A substance with a band gap in the infrared region of the electromagnetic spectrum will absorb light throughout the visible portion of the electromagnetic spectrum and appear black.

4. d.

5. d. When the reducing agent fills the lower energy band with electrons, the sample will become an insulator with a large band gap.

6. b. Metals are characterized by increasing resistivity with increasing temperature; or alternatively, by increasing conductivity with decreasing temperature.

7. b.

8. One liter of 1.0 M NaOH will contain 2.0 mols of carriers (ions).
$(2.0 \text{ mols carriers})(6.022 \times 10^{23} \text{ carriers/mol}) = 1.2 \times 10^{24} \text{ carriers}$
$\text{carrier conc.} = 1.2 \times 10^{24} \text{ carriers}/1.0 \times 10^{3} \text{ cm}^3 = 1.2 \times 10^{21} \text{ carriers/cm}^3$

9. a. $R = \rho L/A$
   $A = \rho L/R$
   $A = [(1.67 \times 10^{-6}\ \text{ohm-cm})(150\ \text{m})(100\ \text{cm/m})]/(150\ \text{ohm})$
   $A = 1.67 \times 10^{-4}\ \text{cm}^2$

   b. $A = \pi r^2$ $r = 7.29 \times 10^{-3}$ cm, $d = 1.46 \times 10^{-2}$ cm

10. Referring to Figure 7.18, a band gap energy of 2.4 eV will give the material a yellow or yellow–orange color.

11. If red light is to be transmitted (not absorbed), then the material should begin to absorb in the orange region, at about 2.1 eV.

12. The color emitted from an LED when a voltage is applied depends on the magnitude of the band gap. Approximate values for band-gap energies and corresponding emission colors are given in the first column of Figure 7.18. Referring to Figure 7.19 then allows determination of approximate values for x in GaP_xAs_{1-x}.

Color	Band Gap Energy (eV)	x
Red	1.9	0.5
Orange	2.1	0.7
Yellow	2.2	0.9
Blue	2.8	—

A blue LED cannot be made from this family, because none of these solids has a band gap large enough to correspond to blue light.

13. $x = 0.6$; $y = 0.3$ The gallium and indium atoms occupy positions equivalent to zinc in zinc blende; the arsenic and phosphorus atoms occupy positions equivalent to sulfur in zinc blende. The 1:1 stoichiometry of Zn:S dictates that the sum of the Ga and In atoms must equal the sum of the As and P atoms present in the solid. The As/P atoms form a fcc lattice with Ga/In atoms in half the tetrahedral holes. Fractional stoichiometries correspond to probabilities for finding a particular atom at a site (*see* Chapter 3).

14. The 2-eV solar cell should be on top as this material absorbs higher energy light but transmits low energy light to be absorbed by the 1-eV cell. Any high energy light passing through the first cell will also be absorbed by the 1-eV cell.

15. a. The solid should be a metallic conductor based on the partially filled higher energy band.
    b. The solid will become an insulator (large band gap) or semiconductor (small band gap) if an oxidizing agent is used to remove all the electrons from the higher energy band.

16. First, calculate the frequency and energy that corresponds to 7000 Å:
    $\nu = (3.00 \times 10^{8}\ \text{m s}^{-1})/(7000 \times 10^{-10}\ \text{m}) = 4.29 \times 10^{14}\ \text{s}^{-1}$
    $E = (4.29 \times 10^{14}\ \text{s}^{-1})(6.6262 \times 10^{-34}\ \text{J s}) = 2.84 \times 10^{-19}\ \text{J}$
    $E = (2.84 \times 10^{-19}\ \text{J})(1\ \text{eV}/1.6022 \times 10^{-19}\ \text{J}) = 1.77\ \text{eV}$

    Second, calculate the value of x in GaP_xAs_{1-x}. The problem states that the band gap increases linearly with x, when $0 \le x \le 0.45$. When $x = 0$, the band gap is 1.4 eV; when $x = 0.45$, the band gap is 2.0 eV. The slope m of the line is determined by these two points:

$$m = (2.0 - 1.4)/(0.45 - 0) = 1.33$$

The equation of the line determined by the two data points in the problem is

$$y = 1.33x + 1.4$$

The desired band gap is 1.77 eV. Substituting this value into the equation for the line gives a value for x:

$$1.77 = 1.33x + 1.4$$
$$x = 0.28$$

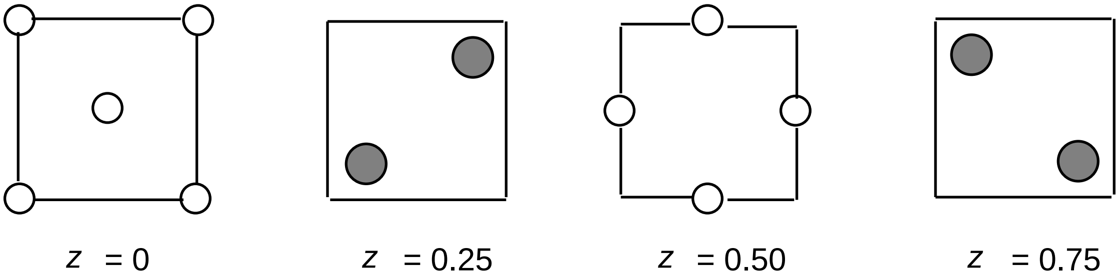
Thus, the solid solution that is predicted to give 7000 Å is $GaP_{0.28}As_{0.72}$. This problem can also be solved graphically, of course.

17. InSb and CdTe are isoelectronic with α-Sn. α-Sn is metallic with a small band gap (less than 0.1 eV). Ionic character increases with the difference in electronegativity between atoms A and Z. As ionic character increases, so does E_g. The expected trend in band-gap energies is Sn < InSb < CdTe.

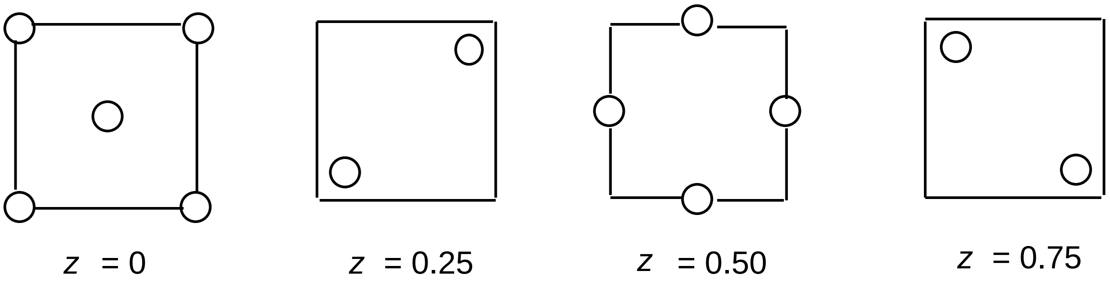
18. BN is isoelectronic with diamond and is also extremely hard.

19. Phosphorus is isovalent with arsenic, so substitution of As with P does not change the valence count. Cadmium has one less valence electron than gallium, but tin has one additional electron than gallium. Substituting one half of the Ga atoms with Cd and the other half with Sn leads to the same valence count. We therefore have $Cd_{0.5}Sn_{0.5}P$, or $CdSnP_2$.

20. GaP = zinc blende structure:



Si = diamond structure:



21. The partially filled valence band in sodium is exactly half filled because each sodium atom contributes a half-filled 3s atomic orbital to the formation of the valence band.

22. The conductivity of a semiconductor depends on its carrier concentration. At higher temperatures more thermal energy is available, and more electrons can be promoted across the band gap into the conduction band, where they contribute to electrical conductivity.

23. Metals are good electrical conductors at room temperature, but semiconductors generally are not. At liquid helium temperature, metals are excellent conductors (or superconductors), and semiconductors are insulators due to the lack of thermal energy necessary to promote electrons across the band gap.

24. Mg: Mg serves as an example of a metal. The Mg 3s band is filled but overlaps the Mg 3p band to create a partially filled band.

    Si: Si serves as an example of a semiconductor. At relatively low temperatures few electrons would be in the conduction band, whereas at higher temperatures a greater fraction of the electrons are promoted from the valence band to the conduction band; thus partially filled bands are generated.

    NaCl: NaCl serves as an example of an ionic insulator. Because of the large band gap in NaCl (*see* Table 7.4), this insulator contains bands that are either full or empty of electrons.

25. Oxidation of graphite removes electrons from the previously full valence band, leaving it partially filled and thereby giving it metallic properties. Bromine and sodium react to yield NaBr, an ionic insulator with a large band gap.

26. b. sp^2, three electrons per carbon are used to form sigma bonds.
    c. a nonhybridized 2p orbital; one electron per carbon
    d. half-full, metal
    e. polyacetylene would either be a semiconductor or an insulator, depending on the magnitude of the band gap. In fact, polyacetylene has a band gap of 1.9 eV, which makes it a semiconductor. It has a small electrical conductivity, similar to other common semiconductors, in the range of 10^{-9} $\text{ohm}^{-1}\ \text{cm}^{-1}$ (cis form) to 10^{-5} $\text{ohm}^{-1}\ \text{cm}^{-1}$ (trans form).
    f. Reaction with an oxidizing agent such as Br_2 causes electrons to be removed from the valence band, thereby giving a partially filled band. This greatly increases the conductivity of polyacetylene. If polyacetylene reacts with a reducing agent such as Li, electrons would be added to the conduction band, again giving a partially filled band. This also greatly increases polyacetylene's conductivity. In fact, by reacting *trans*-polyacetylene with either an oxidizing agent or a reducing agent, conductivities as high as 10^3 $\text{ohm}^{-1}\ \text{cm}^{-1}$ have been recorded, which are similar to the conductivities of many metals.

27. a. (8 corner Se atoms)(1/8 corner atom per cell) = 1 Se atom
    (10 face-centered Se atoms)(1/2 face atom per cell) = 5 Se atoms
    (1 Se atom within structure)(1 atom/cell) = 1 Se atom
    (4 edge-shared Se atoms)(1/4 atom/cell) = 1 Se atom
    Total Se atoms shown in structure = 8

    (4 Cu atoms within structure)(1 atom/cell) = 4 Cu atoms
    (4 In atoms within structure)(1 atom/cell) = 4 In atoms

Formula of compound: $Cu_4In_4Se_8$ or $CuInSe_2$

b. Comparison of the chalcopyrite structure to that of zinc blende (*see* Figure 5.21) shows that chalcopyrite has the same structure as zinc blende, with In atoms replacing half of the Zn atoms and Cu atoms replacing the other half of the zinc atoms. The unit cell of the chalcopyrite structure contains more planes of atoms along the *z* axis than does the zinc blende structure, because of the alternating positions occupied by the In and Cu atoms in the structure.

c. An indium atom has one additional valence electron compared to a zinc atom, and a copper atom contains one less valence electron than a zinc atom. Selenium is isovalent with sulfur. In the formula ZnS we therefore can replace every Zn atom with one half of an atom of In and one half of an atom of Cu, giving $Cu_{0.5}In_{0.5}Se$, or $CuInSe_2$.

28. Absorption begins at the band-gap energy. For the physical mixture, expect absorption at the band gap of GaAs. For the solid solution expect the onset of absorption midway between the band gaps of GaAs and GaP. For emission, expect two bands from the physical mixture at the two band-gap energies. In the solid solution expect emission at its band gap energy, midway between these two energies.

29. The most bonding orbital occurs with p orbitals overlapping with no sign changes (no nodes between orbitals). The most antibonding orbital occurs with sign mismatch at each overlap.

30. See Demonstration 7.11 and pursuant discussion.

31. The band shifts from about 840 to 800 nm, or by ~ 0.074 eV.

Chapter 8

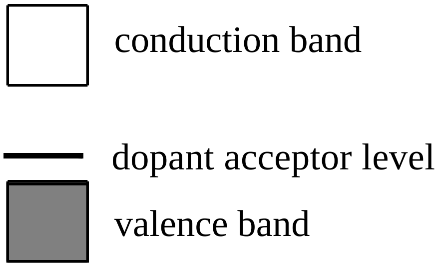
1. Ge has a smaller band gap (0.68 eV) than Si (1.11 eV); thus, a sample of Ge will have more electron–hole pairs at room temperature, as more electrons are able to be promoted across the smaller band gap. Similarly, Si (1.11 eV) will have more electron–hole pairs than GaAs (1.43 eV).

2. a. The value of p for Si is approximately $10^{16}\ cm^{-3}$ from the figure;
therefore, $p = n = 10^{16}\ cm^{-3}$
$K = pn = (10^{16}\ cm^{-3})^2 = 10^{32}\ cm^{-6}$

b. The negative slope of all data in Figure 8.5 indicates that autoionization is endothermic.

c. Figure 8.5 shows that at 20 °C, water has about 10^{14} H^+ ions/cm^3. Gallium arsenide has a hole concentration of about 10^6 h^+/cm^3 at 20 °C. Comparison of these values indicates that there are roughly 10^8 times more positively charged carriers in pure water than in undoped gallium arsenide.

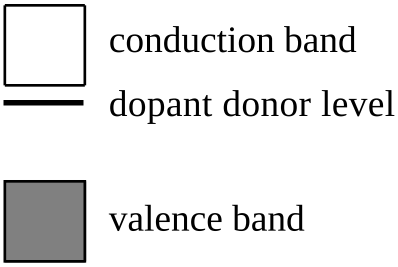
3. a. Indium-doped silicon is a p-type semiconductor with the following band diagram (*see* Figure 8.9C):



The Fermi level of In-doped silicon will initially be near the valence band, and will move toward the conduction band as P is added to the solid. This increase in energy results from mobile electrons (the result of P doping) neutralizing free holes generated by the original In dopants (*see* Figure s 8.9 and 8.11).

When the added P is about the same concentration as the original In dopant concentration, the Fermi level is near the center of the band gap (*see* Figure 8.9B). Addition of still more P causes the Fermi level to move progressively closer to the conduction band and yields a n-type semiconductor (*see* Figure 8.9D).

b. Antimony-doped silicon is a n-type semiconductor with the following band diagram (*see* Figure 8.9D):



The Fermi level of Sb-doped silicon will be near the conduction band, and will move toward the valence band as Al is added to the solid. This behavior results from mobile holes (the result of Al doping) neutralizing free electrons generated by the original Sb dopants (see Figure 8.11). When the added Al is about the same concentration as the original Sb concentration, the Fermi level is near the center of the band gap. Addition of still more Al causes the Fermi level to move progressively closer to the valence band and yields a p-type semiconductor.

4. a. Half cell reactions and standard potentials for the cell in Figure 8.12 are as follows:

cathode: $2\ H^+_{(aq)} + 2\ e^- \rightleftarrows H_{2(g)}$; $E° = 0.00$ V

anode: $H_{2(g)} + 2\ OH^-_{(aq)} \rightleftarrows 2\ H_2O_{(l)} + 2\ e^-$; $E° = 0.83$ V

overall: $2H^+_{(aq)} + 2\ OH^-_{(aq)} \rightleftarrows 2\ H_2O_{(l)}$

$E_{cell} = (0.00\text{ V}) + 0.83\text{ V} = 0.83\text{ V}$

b. $[H^+]$ in base compartment:

$[H^+][OH^-] = 1.0 \times 10^{-14}$

$[H^+](1.0\text{ M}) = 1.0 \times 10^{-14}$

$[H^+] = 1.0 \times 10^{-14}$ M

As given by equation 8.14;

$E_{cell} = -\{(2.3)(RT)/(F)\} \log\{[H^+_{base}]/[H^+_{acid}]\}$

$$E_{cell} = -\frac{(2.3)(8.314\ J/K)(298\ K)}{(9.65 \times 10^4\ C)} \log\{\frac{1.0 \times 10^{-14}\ M}{1.0\ M}\}$$

$E_{cell} = 0.83$ V

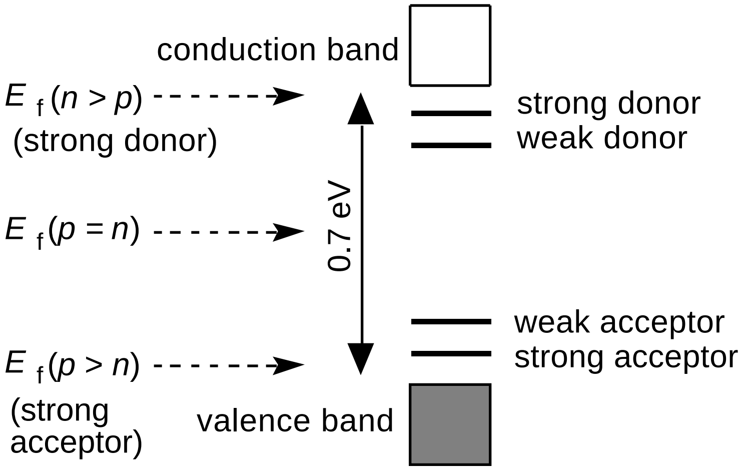
5. a. A silver atom contains one less valence electron than a cadmium atom. The valence-band hole concentration is increased in the solid, making the sample a p-type semiconductor.

   b. A bromine atom contains one more valence electron than a sulfur atom. The conduction-band electron concentration is increased in the solid, making the sample an n-type semiconductor.

6. a. $K = pn = 6 \times 10^{26}\ cm^{-6}$
   $p = n = K^{1/2} = (6 \times 10^{26}\ cm^{-6})^{1/2} = 2 \times 10^{13}\ cm^{-3}$
   Germanium doped with Group 13 elements like aluminum will be p-type with $p > n$. Germanium doped with Group 15 elements like phosphorus will be n-type with $n > p$.

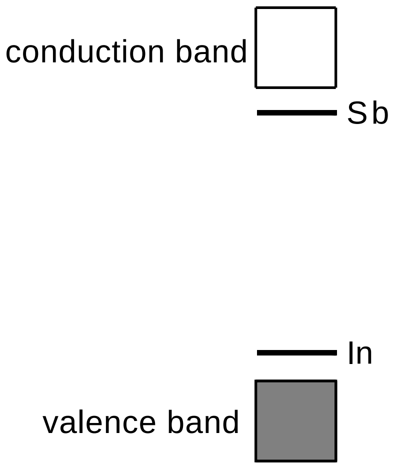
   b. $K = pn$ $\quad 6 \times 10^{26}\ cm^{-6} = p(3 \times 10^{18}\ cm^{-3})$ $\quad p = 2 \times 10^8\ cm^{-3}$

   c.



   d. The smaller K value for Si $(2 \times 10^{20}\ cm^{-6})$ relative to that for Ge $(6 \times 10^{26}\ cm^{-6})$ reflects the larger band gap of Si (1.11 eV) versus Ge (0.68 eV). The trend in band gaps is discussed in Chapter 7.

   e. The band diagram for a germanium semiconductor doped with indium or antimony is given as



Indium has one fewer valence electron than germanium. When doped into Ge, In acts as an acceptor of Ge valence-band electrons, creating localized In^- ions and additional valence band mobile holes:

$$In \rightarrow In^- + h^+$$

Antimony has one more valence electron than germanium. When doped into Ge, Sb acts as a donor of electrons to the Ge conduction band, creating localized Sb cations and additional mobile conduction band electrons:

$$Sb \rightarrow Sb^+ + e^-$$

f. The Fermi level for In-doped Ge will initially be near the valence band, as In is an acceptor and the semiconductor is p-type. Addition of Sb (a donor) to In-doped Ge will cause the Fermi level to move toward the conduction band. When the concentration of Sb is equal to the concentration of In, the Fermi level will be near the center of the band gap. As the concentration of Sb exceeds that of In, the Fermi level will continue to rise and approach the conduction band.

This process is similar to a neutralization reaction in aqueous solution.

g. Gold is a weak acceptor (ionization energy = 0.2 eV) and should be placed about midway between the top of the valence band and the middle of the band gap (0.2 eV above the valence band edge).

7. a. Gallium arsenide exhibits negligible absorbance of light below approximately 1.4 eV, its band-gap energy. Light higher in energy than 1.4 eV is strongly absorbed by GaAs, and corresponds to transitions between filled valence-band orbitals and unfilled conduction-band orbitals.

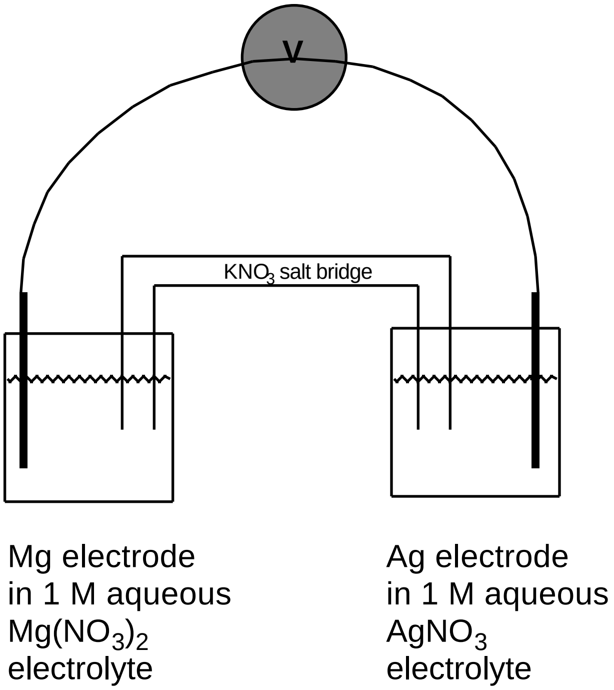
b. Substitution of Se for As generates mobile conduction-band electrons and immobile Se^+, forming the n-type portion of the junction. Substitution of Zn for Ga generates mobile valence-band holes and immobile Zn^-, forming the p-type portion of the junction. The p–n junction is defined in this case by the diffusion of Zn into the n-type solid, as described in the chapter. Gallium arsenide is isoelectronic with germanium.

c. For example, consider photons with energies of 1.0, 1.5, and 2.0 eV. Only photons with energy equal to or greater than the band-gap energy will be absorbed to produce valence holes and conduction band electrons. The 1.0-eV photon will not be absorbed by the solar cell and does not produce electricity. Both the 1.5- and 2.0-eV photons will be absorbed, and both will promote one valence electron into the conduction band leading to a contribution to the electric current. However, the energetic cost of these two events differs by 0.5 eV. The 1.5-eV photon was more efficient because it successfully promoted a valence band electron at a lower energetic cost than the 2.0-eV photon. The remainder of the energy of the 2.0-eV photon produces heat.

d. The solar spectrum shows that the sun has substantial output in the 1.5–2.1-eV range. These are energies that can be absorbed by GaAs with a band gap of 1.4 eV.

8. The semiconductivity of pure Si relies on an absorption of energy from an external source to promote electrons from the valence band to the conduction band. At low temperatures fewer electrons are promoted to the conduction band and conductivity drops dramatically. Doped Si can create conducting holes and electrons in the manner described for pure Si, but also by the promotion of electrons into or out of the dopant energy levels, which lie near the band edges for strong donors and acceptors. Less energy is needed for this process than for promotion of electrons across the band gap, and the semiconductivity of doped Si is thus much less temperature-dependent than it is for pure Si.

9. a.



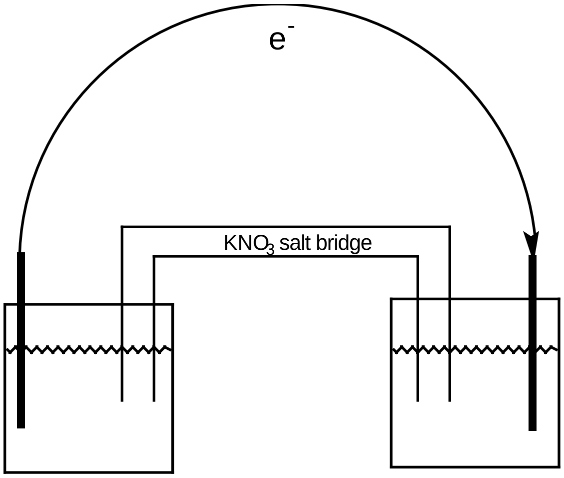
b. cathode: $2\ Ag^{+}_{(aq)} + 2\ e^{-} \rightleftarrows 2\ Ag_{(s)}$ $E° = 0.80\ V$

anode: $Mg_{(s)} \rightleftarrows Mg^{2+}_{(aq)} + 2\ e^{-}$ $E° = 2.37\ V$

overall: $2\ Ag^{+}_{(aq)} + Mg_{(s)} \rightleftarrows 2\ Ag_{(s)} + Mg^{2+}_{(aq)}$

$E_{cell} = 0.80\ V + 2.37\ V = 3.17\ V$

c.



$Mg_{(s)} \leftrightarrows Mg^{2+}_{(aq)} + 2e^-$
(anode reaction)

$Ag^+_{(aq)} + e^- \leftrightarrows Ag_{(s)}$
(cathode reaction)

d. The LED will glow only when forward biased; thus, the electrodes must be attached properly. Attach the LED to the electrochemical cell with the n-type portion connected to the anode (Mg electrode), and p-type portion connected to the cathode (Ag electrode), the direction of current flow.

e. InP may be doped with Group 12 acceptors like Cd or Ag to form the p-type region, as these atoms contain fewer valence electrons than In. Donors such as S and Se from Group 16 can be used to create the n-type region, as these atoms contain more valence electrons than P.

f. InP will emit light close to its band-gap energy which is the threshold energy for light absorption by a semiconductor. The absorption spectrum of InP shows the onset of absorbance at approximately 1.3 eV, and this is approximately where the emitted light is found.

g. The LED will remain lit so long as the electrochemical cell delivers a sufficient voltage to maintain the forward bias. The potential delivered by the cell will decrease over time in accord with the Nernst equation.

10. The ionization reaction $D \rightarrow D^+ + e^-$, where D is a weak donor, is analogous to writing

$$H_2O + NH_3 \leftrightarrows NH_4^+ + OH^-$$

for the weak base NH_3.
The ionization reaction $D + h^+ \rightarrow D^+$ is analogous to writing

$$NH_3 + H^+ \leftrightarrows NH_4^+$$

The former is an Arrhenius-like formulation of the basicity of NH_3 (NH_3 increases the OH^- concentration), whereas the latter is a Brφnsted-like formulation (NH_3 is a proton acceptor that reduces the concentration of H^+).

11. The energy associated with a given transition corresponds to the difference in energy between the two quantized levels involved in the process, or

$$\Delta E = \div E_{n_2} - E_{n_1} \div$$

The energies of the quantized levels of the hydrogen atom can be calculated using equation 7 of Chapter 8. If a value of 12 is used for the relative dielectric constant, ε_r, and a value of $0.3m_e$ is used for the effective mass of the electron, the equation can be used to approximate the energies of the quantized levels of phosphorus-doped silicon.

The energy levels are calculated as follows:

$E_{\text{joules}} = (-e^4)(0.3\ m)/(8\varepsilon_o{}^2\varepsilon_r{}^2h^2n^2)$, where
$e = 1.602 \times 10^{-19}$ C $\quad m = 9.109 \times 10^{-31}$ kg $\quad \varepsilon_o = 8.85 \times 10^{-12}\ \mathrm{C^2\ N^{-1}\ m^{-2}}$
$\varepsilon_r = 12 \quad h = 6.626 \times 10^{-34}\ \mathrm{kg\ m^2\ s^{-1}}$

This reduces to $E_{\text{joules}} = -4.54 \times 10^{-21}\ \mathrm{kg\ m^2\ s^{-2}/n^2}$, or $-4.54 \times 10^{-21}\ \mathrm{J/n^2}$
For $n = 1$, $E = -4.54 \times 10^{-21}$ J $\qquad$ For $n = 2$, $E = -1.14 \times 10^{-21}$ J
For $n = 3$, $E = -5.05 \times 10^{-22}$ J $\qquad$ For $n = 4$, $E = -2.84 \times 10^{-22}$ J

a. $n = 4$ to $n = 3$, $E = 2.21 \times 10^{-22}$ J
b. $n = 4$ to $n = 1$, $E = 4.26 \times 10^{-21}$ J
c. $n = 3$ to $n = 2$, $E = 6.35 \times 10^{-22}$ J

These energies correspond to wavenumber values of
a. 11.1 $\mathrm{cm^{-1}}$ $\qquad$ b. 214 $\mathrm{cm^{-1}}$ $\qquad$ c. 31.9 $\mathrm{cm^{-1}}$

These transitions occur in the far-IR or microwave portion of the electromagnetic spectrum.

d. The ambient thermal energy is given by kT. At 4.2 K this corresponds to 5.8×10^{-23} J or 3.6×10^{-4} eV.

12. b. 13.
d. 14. A zinc atom contains two fewer valence electrons than a germanium atom. Substitution of Zn for Ge generates mobile valence-band holes and immobile $\mathrm{Zn^{2-}}$. There are two energy levels within the band gap, one corresponding to $\mathrm{Zn \rightarrow Zn^- + h^+}$ and one to $\mathrm{Zn^- \rightarrow h^+ + Zn^{2-}}$. This is analogous to a diprotic acid.

15. Referring to equation 17 in this chapter, the voltage that could be obtained from the p–n junction can be determined as follows:

E (in volts) $= -(2.3RT/F)[\log([\mathrm{e^-}]_{\text{p-type side}}/[\mathrm{e\text{-}}]_{\text{n-type side}})]$
$K = pn$
$[\mathrm{e^-}]_{\text{p-type side}} = K/p = 10^{20}\ \mathrm{cm^{-6}}/10^{17}\ \mathrm{cm^{-3}} = 10^3\ \mathrm{cm^{-3}}$

$$E = -\frac{(2.3)(8.314\ \mathrm{J/K})(298\ \mathrm{K})}{(9.65 \times 10^4\mathrm{C})}\ \log\left\{\frac{10^3\ \mathrm{cm^{-3}}}{10^{17}\ \mathrm{cm^{-3}}}\right\}$$

$E = 0.83$ V

16. a. The energy of one photon of 670-nm radiation is given by

$$E = hc/\lambda = \frac{(6.626 \times 10^{-34}\ \mathrm{J\ s})(3.00 \times 10^8\ \mathrm{m\ s^{-1}})}{(670 \times 0^{-9}\ \mathrm{m})} = 2.96 \times 10^{-19}\ \text{J/photon}$$

The energy of 1 mol of 670-nm photons therefore is

$(2.96 \times 10^{-19}$ J/photon$)(6.02 \times 10^{23}$ photons/mol photons$) =$
$= 1.79 \times 10^{5}$ J/mol photons

5 mW corresponds to 5×10^{-3} J/s.
$(5 \times 10^{-3}$ J/s$)/(1.79 \times 10^{5}$ J/mol photons$) = 3 \times 10^{-8}$ mols photons/s.

b. $(3 \times 10^{-8}$ mols photons/s)(1 mol e^-/1 mol photons)(96,500C/mol e^-) =
$= 3 \times 10^{-3}$ C s^{-1} = 3 mA

Chapter 9

1. d. 2. d. 3. d.

4. a. Assuming idealized oxygen stoichiometry, one method of preparation is
$Y_2O_{3(s)} + 4\ BaCO_{3(s)} + 6\ CuO_{(s)} + 0.5\ O_{2(g)} \rightarrow 2\ YBa_2Cu_3O_{7(s)} + 4\ CO_{2(g)}$
b. (12 g $YBa_2Cu_3O_7$)(1 mol /666.19 g) = 1.8×10^{-2} mol $YBa_2Cu_3O_7$
$(1.8 \times 10^{-2}$ mol $YBa_2Cu_3O_7$)(1 mol Y_2O_3/(2 mol $YBa_2Cu_3O_7$) =
9.0×10^{-3} mol Y_2O_3
$(9.0 \times 10^{-3}$ mol Y_2O_3)(225.81 g/1 mol Y_2O_3) = 2.03 g Y_2O_3
$(1.8 \times 10^{-2}$ mol $YBa_2Cu_3O_7$)(4 mol $BaCO_3$/2 mol $YBa_2Cu_3O_7$) =
3.6×10^{-2} mol $BaCO_3$ = 7.1 g $BaCO_3$
$(1.8 \times 10^{-2}$ mol $YBa_2Cu_3O_7$)(3 mol CuO/1 mol $YBa_2Cu_3O_7$) =
5.4×10^{-2} mol CuO = 4.3 g CuO

5. Compounds like Cu_2HgI_4 could be incorporated into the design of control circuits of refrigerators. When the interior of the refrigerator is cold, the insulating form of the compound would be present; this form would prevent the compressor from functioning. When the temperature inside the refrigerator rises, Cu_2HgI_4 (or a similar material) becomes conducting, and turns on the refrigeration unit, which will run until the compound cools and becomes an insulator again.

6. Thermochromic compounds could be incorporated into simple warning devices for tools such as drill bits that can fail under stresses of high temperature and pressure. At normal or safe operating temperatures the warning device is one particular color; when the temperature rises to an unsafe or undesirable temperature, a color change occurs, warning the operator of a potential safety problem.

7. I^-: (8 corner iodide ions)(1/8 occupancy) = 1 iodide ion
(10 face-shared iodide ions)(1/2 occupancy) = 5 iodide ions
(1 iodide ion within cell)(1 occupancy) = 1 iodide ion
(4 edge-shared iodide ions)(1/4 occupancy) = 1 iodide ion
Cu^+: (4 cuprous ions within cell)(1 occupancy) = 4 cuprous ions
Hg^{2+}: (2 mercuric ions within cell)(1 occupancy) = 2 mercuric ions
= $Cu_4Hg_2I_8$ or Cu_2HgI_4

8. a. white tin $\leftrightarrows$ gray tin
ΔG° = (1 mol)(ΔG°_f gray tin) - (1 mol)(ΔG°_f white tin)
ΔG° = (1 mol)(0.13 kJ/mol) - (1 mol)(0 kJ/mol) = 0.13 kJ
The reaction is spontaneous right to left at 298 K.
b. $\Delta G = \Delta H - T\Delta S$
$0 = [(1\text{ mol})(-2.09\text{ kJ/mol}) - (1\text{ mol})(0\text{ kJ/mol})] -$
$(T)[(1\text{ mol})(0.044\text{ kJ/mol·K}) - (1\text{ mol})(0.052\text{ kJ/mol·K})]$

(T)[(1 mol)(0.044 kJ/mol·K) - (1 mol)(0.052 kJ/mol·K)] = -2.09 kJ
T = 260 K

9. Vaporization of water requires the disruption of strong intermolcular forces (hydrogen bonding) and therefore requires a great deal of energy in order to convert the condensed, liquid phase to the disordered gaseous phase. A solid-state phase change like that exhibited by NiTi involves only slight shifts in atomic positions.

10. The hcp and ccp structures both have a 74% packing efficiency (Table 5.1). Application of pressure would not be expected to convert one form to the other.

11. If a pellet of 1-2-3 is cooled to below its critical temperature (easily done with liquid nitrogen), the superconducting sample can be placed over a magnet to levitate the superconductor. Use tongs, tweezers, or gloves to handle the cold 1-2-3 sample.

12. The interaction between the paramagnetic or ferromagnetic solid and the magnet depicted in Figure 2.10 demonstrates that paramagnetic and ferromagnetic materials are attracted towards magnetic fields; the result is that the balance measures a lower apparent weight for the sample. The superconductor, in contrast, will repel an external magnetic field (Meissner effect). The 1-2-3 sample should have an increased apparent weight as a result.

13. Two samples of 1-2-3 superconductor, cooled below their critical temperatures, could form the “bread” of a sandwich that has a magnet suspended in between. (*see* Jacob, A. T.; Pechmann, C. I.; Ellis, A. B. *J. Chem. Educ.* **1988**, *65*, 1094.)

14. The stoichiometry determination follows the procedure worked in the solution to exercise 7. In the Cu_2HgI_4 unit cell, the vacancies and divalent cations (Hg^{2+}) occupy the same planes (z = 0.37 and 0.87), whereas in the Ag_2HgI_4 unit cell the vacancies and the monovalent cations (Ag^+) occupy the same planes (z = 0.13 and 0.63).

15. Iodine: 5p orbitals; mercury: 6s

16. The yellow color of the low-temperature phase corresponds to a higher energy band gap than the orange color of the high-temperature phase (Figure 7.18). If a change in band widths is the reason for the smaller band gap at higher temperature, then the bands must have widened at higher temperature so as to shrink the energetic separation between the two band edges. A similar color shift and explanation can be invoked for the Cu_2HgI_4 with the red (low-temperature) to red–brown (high-temperature) color change also consistent with larger band widths and a smaller band gap at higher temperature.

17. Because the same disordered cubic structures occur for the high-temperature phases of Ag_2HgI_4 and Cu_2HgI_4, it might be possible to prepare solid solutions of composition $Ag_{2x}Cu_{2-2x}HgI_4$. However, because of the large difference in ionic radii for the two monovalent cations, only limited substitution of one monovalent cation for the other might be possible.

18. For example, for $Bi_2Ca_2Sr_2Cu_3O_{10}$, the oxidation number of Cu is +2.

19. Electricity can be used to resistively heat the sculpture, thereby transforming the memory metal from its low-temperature to its high-temperature shape.

20. From Figure 9.10, at 0 ˚C, a sample of Ni_xTi_{1-x} with $x = 0.51$ would be in the high-temperature phase, whereas a sample with $x = 0.49$ would be in the low-temperature phase.

21. The consistent applied stress over this processing cycle favors a particular orientation of variants in the low-temperature phase. *See* Wayman, C. M. *MRS Bull.* **!993**, *XVIII*, 49–56.

22. This is an exothermic reaction, the heat from which can be used to drive the martensite-to-austenite conversion of the unreacted NiTi. One of the reaction products is nickel bromide. Further details can be found in Gisser, K. R. C.; Philipp, D. M.; Ellis, A. B. *Chem. Mater.* **1992**, *4*, 700.

23. A sample could be prepared that is coiled or spring-shaped in the hig-temperature form and linear in the low-temperature form. Insert the cold linear sample into the artery, and when it warms to body temperature it assumes the coiled shape that can help keep the artery opened.

24. The rock salt structure has the lower density or the greater molar volume.

Chapter 10

1. In solution, Pb^{2+} and I^- ions can easily diffuse together to produce PbI_2. In the solid, this diffusion is far slower.

2. Grind the mixture, then heat it.

3. Co will oxidize to Co_3O_4 in air. Thus no Co will be available to reduce the Co_3O_4 initially present.

4. a. $Ti_2O_3(s) + V_2O_5(s) \rightarrow 2\ TiVO_4(s)$
   b. $Pb(s) + PbO(s) + Nb_2O_5(s) \rightarrow 2\ PbNbO_3(s)$
   c. $Ti(s) + 2S(s) \rightarrow TiS_2(s)$
   d. $2CrCl_3(s) + H_2(g) \rightarrow 2\ CrCl_2(s) + 2\ HCl(g)$
   e. $MnCl_2(aq) + 2\ NaOH(aq) \rightarrow Mn(OH)_2(s) + 2NaCl(aq)$
   $Mn(OH)_2(s) \rightarrow MnO(s) + H_2O(g)$
   f. $SiCl_4(l) + 4H_2O \rightarrow Si(OH)_4(s) + 4HCl$
   $Si(OH)_4\ (s) \rightarrow SiO_2(s) + 2H_2O$

5. V^{5+} is a weak oxidizing agent and will not oxidize chloride ion. Iodide ion is easier to oxidize.

6. The Li^+ is small enough to diffuse into the V_2O_5 structure with little or no change in the structure. The Cs^+ is rather large.

7. Decomposition of $La[Fe(C_2O_4)_3]$ produces an oxide with the La^{3+} and Fe^{3+} ions mixed on an atomic scale. Such mixing is not present in a mixture of $La_2(CO_3)_3$ and Fe_2O_3.

8. All three samples would give the same elemental analysis, because they all have the same relative numbers of Al, Ga, and As atoms. However, they would have distinguishable X-ray diffraction patterns: The physical mixture would have two sets of peaks corresponding to pure AlAs and pure GaAs.

The solid solution would have one set of peaks corresponding to pure $Al_{0.5}Ga_{0.5}As$. The layered solid grown by CVD methods would have a diffraction pattern that reflects the periodic arrangement of 20 atomic layers (10 layers of AlAs followed by 10 layers of GaAs).

9. There are countless possibilities. Structures like the following layer sequences would all correspond to 1:1 A:Z stoichiometry:

AAAAAAAAAA	AAAAAAAAAA	AAAAAAAAAA
ZZZZZZZZZZ	AAAAAAAAAA	AAAAAAAAAA
AAAAAAAAAA	ZZZZZZZZZZ	AAAAAAAAAA
ZZZZZZZZZZ	ZZZZZZZZZZ	ZZZZZZZZZZ
		ZZZZZZZZZZ
		ZZZZZZZZZZ

All of these structures would have different unit cells (different repeat distances) and thus different X-ray diffraction signatures.

10. One-eighth of the tetrahedral holes are occupied by Mg^{2+} ions and one-half of the octahedral holes are occupied by Al^{3+} ions.

11. a. The large band-gap material is A and thus corresponds to $Al_{0.3}Ga_{0.7}As$; the smaller band-gap material is B and is GaAs.

b. Both conduction band electrons and valence band holes will be at lower energy if they are at the band edge in region B (recall, Chapter 8, that holes “rise” to reach lower energy).

c. i. absorption in region B (photon energy is between the band-gap energies of the two materials).

ii. absorption in neither region (photon energy is below the band-gap energies of the two materials).

iii. absorption in both regions (photon energy is above the band-gap energies of both materials).

12. *See* the polymer sketch in Experiment 15 on silica gel. Because Ge is isovalent with Si, it could replace it in the structure. Fluorine might replace oxygen in the structure, in which case its tendency to form only a single bond may terminate the growth of the polymer at that position.

13. a. $0.5\ \mathrm{Ni(s)} + 0.5\ \mathrm{Al(s)} \rightarrow \mathrm{Ni_{0.5}Al_{0.5}(s)}$
b. Dividing the enthalpy of formation by the specific heat capacity gives an estimated temperature increase of nearly 2400 °C.

14. For example, platinum and palladium have nearly identical unit cell dimensions and would be good candidates for epitaxial growth.

15. Isoelectronic semiconductors like GaAs and ZnSe with nearly identical unit cell dimensions are good candidates for epitaxial growth as are Ge and GaAs.