# Chemistry The Science in Context Volume I and II 5th Edition Gilbert Solutions Manual

Full Download: http://alibabadownload.com/product/chemistry-the-science-in-context-volume-i-and-ii-5th-edition-gilbert-solution

# CHAPTER 12 | Solids: Crystals, Alloys, and Polymers

## 12.1. Collect and Organize

From the drawings shown in Figure P12.1, we are to choose which represents a crystalline solid and which represents an amorphous solid.

#### Analyze

In crystalline solids, atoms or molecules arrange themselves in regular, repeating three-dimensional patterns. In an amorphous solid, the atoms or molecules are arranged randomly, with no defined repeating pattern.

# Solve

Drawings (b) and (d) are analogous to crystalline solids because they show a definite pattern, while (a) and (c) are amorphous.

#### Think About It

In drawings (b) and (d) there are two kinds of atoms; if the drawings represent metals, these two substances would be alloys. The regularity of (a) might also suggest that it is a lattice with an empty position.

# 12.2. Collect and Organize

For each of two patterns in Figure P12.2 we are to determine the unit cell and the numbers of light and dark squares within the unit cell.

#### Analyze

A unit cell is the smallest repeating pattern in a two- or three-dimensional pattern.

## Solve



(a) There are eight light squares and one dark square in this unit cell.

(b) There are two light squares  $(4 \times \frac{1}{2})$  and two dark squares  $(4 \times \frac{1}{4} + 1)$  in this unit cell.

#### **Think About It**

Both of these unit cells are based on a square.

# 12.3. Collect and Organize

Using Figure P12.3, we are to determine the unit cell and write the chemical formula for the compound where element A is represented as red spheres and element B is represented as blue spheres.

# Analyze

Once the unit cell is determined, the chemical formula can be deduced. Spheres on the corner are shared by eight unit cells and so are counted as one-eighth in the unit cell. Likewise, spheres on the edges are shared by four unit cells and are counted as one-fourth in the unit cell, and spheres on the faces of the unit cell are shared by two unit cells and are counted as one-half in the unit cell. Any atom completely inside a unit cell belongs entirely to it and counts as one.

# Solve



There are  $8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$  red spheres or 4 A atoms in the unit cell. There are  $12\left(\frac{1}{4}\right) + 1(1) = 4$  blue spheres or 4 B atoms in the unit cell. The chemical formula is A<sub>4</sub>B<sub>4</sub> or AB.

# Think About It

The empirical formula for this compound would be AB because that is the lowest whole-number ratio of elements in the substance.

# 12.4. Collect and Organize

Using Figure P12.4, we are to determine the number of A cations, B cations, and X anions in the portion of the unit cell shown.

# Analyze

Figure P12.4 shows eight A cations at the corners of the cube, six B cations at the faces, and one X anion in the center. Each corner ion is shared between eight unit cells, and each face ion is shared between two unit cells.

# Solve

Because eight A ions occupy the corners, and because the portion of the unit cell contains one-eighth of each corner ion, the number of A cations in the unit cell are

8 A cations  $\times \frac{1}{8} = 1$  A cation in the unit cell

Because six B ions occupy the faces, and because the portion of the unit cell contains one-half of each face ion, the number of B cations in the unit cell are

6 B cations  $\times \frac{1}{2} = 3$  B cations in the unit cell

Because one X ion occupies the center, and because the unit cell contains one of each center ion, the number of X anions in the unit cell is

1 X anion  $\times$  1 = 1 X anion in the unit cell

This gives a total of one anion and four cations per unit cell.

# Think About It

Based on the stoichiometry in the unit cell, the formula unit for this ionic solid must be AB<sub>3</sub>X.

## 12.5. Collect and Organize

We are to determine the formula of a compound in which A ions form an fcc unit cell and where half of the octahedral holes are occupied by B and one-eighth of the tetrahedral holes are occupied by C.

## Analyze

In a face-centered cubic (cubic closest-packed) array of A ions, there are eight tetrahedral holes and four octahedral holes.

#### Solve

The number of A ions in the fcc unit cell is

 $(8' \frac{1}{8}) + (6' \frac{1}{2}) = 4$ 

If one-half of the octahedral holes contain B ions, then there are two B ions in the unit cell. If one-eighth of the tetrahedral holes contain C ions, then there is one C ion in the unit cell. The chemical formula for this compound is  $A_4B_2C$ .

## Think About It

We may assume that the lattice is formed from an anion (the larger A spheres), and both species occupying the holes of the ccp lattice (the smaller B and C spheres) are cations.

## 12.6. Collect and Organize

We are to determine the formula of a copper–chloride compound in which the chloride ions form an fcc arrangement and the copper ions occupy half of the tetrahedral holes.

## Analyze

In an fcc arrangement, there are eight tetrahedral holes in the unit cell.

# Solve

The number of chloride ions in the unit cell is

 $(8' \frac{1}{8}) + (6' \frac{1}{2}) = 4$ 

The number of copper ions in the unit cell is

8 tetrahedral'  $\frac{1}{2} = 4$ 

The formula for the compound is CuCl.

# Think About It

There are equal numbers of copper and chloride atoms in the unit cell.

## 12.7. Collect and Organize

We are to determine the formula of a lithium-sulfur compound in which the sulfide ions form an fcc arrangement and the lithium ions occupy all of the tetrahedral holes.

#### Analyze

In an fcc arrangement, there are eight tetrahedral holes in the unit cell.

The number of sulfide anions in the unit cell is

 $(8' \frac{1}{8}) + (6' \frac{1}{2}) = 4$ 

The number of lithium cations in the unit cell is eight. The formula for the compound is Li<sub>2</sub>S.

## **Think About It**

This salt is neutral because the charge on two lithium ions (1+) in the formula balances the charge on one sulfide anion (2-).

## 12.8. Collect and Organize

From the unit cell of CsCl where the edge length is 412 pm, we are to calculate the radius of  $Cs^+$  ions knowing that the Cl<sup>-</sup> ion radius is 181 pm.

#### Analyze

CsCl forms a body-centered cubic unit cell where, although the Cl<sup>-</sup> ions at the corners are not touching, the ions along the body diagonal (Cl<sup>-</sup>–Cs<sup>+</sup>–Cl<sup>-</sup>) do touch. The length of the body diagonal of the bcc unit cell is  $\ell\sqrt{3}$ .

## Solve

Along the body diagonal we have  $2r_{C\Gamma} + 2r_{Cs^+}$  where *r* is the radius of the respective ions. Setting this equal to the length of the body diagonal and substituting in  $\ell$  (the unit cell edge length) and the radius of the Cl<sup>-</sup> ion gives

$$2r_{\rm CF} + 2r_{\rm Cs^+} = \ell\sqrt{3}$$
  
(2' 181 pm) +  $2r_{\rm Cs^+} = (412 \text{ pm})\sqrt{3}$   
 $2r_{\rm Cs^+} = 351.6 \text{ pm}$   
 $r_{\rm Cs^+} = 176 \text{ pm}$ 

#### Think About It

The  $Cs^+$  ion size in Figure 10.2 is 170 pm, which is close to the value calculated here. Remember that ionic size varies depending on how the ions pack in the crystals.

#### 12.9. Collect and Organize

We are to identify the elements highlighted in the periodic table in Figure P12.15 that do not adopt a rock salt structure for their chloride salt.

## Analyze

In the rock salt structure, the cations must fit into the octahedral holes between the closest-packed layers of Cl<sup>-</sup>. The radius ratio of cation to anion should be between 0.41 and 0.73. The radii of the cations of the highlighted elements from Figure 10.2 are Li<sup>+</sup> (76 pm), Na<sup>+</sup> (102 pm), K<sup>+</sup> (138 pm), Cs<sup>+</sup> (170 pm), and Sr<sup>2+</sup> (118 pm). The radius of Cl<sup>-</sup> is 181 pm.

For LiCl, the radius ratio is 
$$\frac{76 \text{ pm}}{181 \text{ pm}} = 0.42$$
  
For NaCl, the radius ratio is  $\frac{102 \text{ pm}}{181 \text{ pm}} = 0.564$   
For KCl, the radius ratio is  $\frac{138 \text{ pm}}{181 \text{ pm}} = 0.762$   
For CsCl, the radius ratio is  $\frac{170 \text{ pm}}{181 \text{ pm}} = 0.939$   
For SrCl<sub>2</sub>, the radius ratio is  $\frac{118 \text{ pm}}{181 \text{ pm}} = 0.652$ 

By the radius ratio rule, the rock salt structure is not probable for KCl ( $K^+$  would occupy cubic holes) nor for CsCl (Cs<sup>+</sup> would occupy cubic holes) or SrCl<sub>2</sub> (because it does not have a 1:1 cation-to-anion stoichiometry). LiCl is borderline. In nature, all of these adopt a rock salt structure except Cs (blue) and Sr (purple).

#### Think About It

In the hypothetical rock salt structure of  $SrCl_2$ ,  $Sr^{2+}$  would occupy one-half of the octahedral holes. In nature, this ionic compound instead adopts a fluorite structure.

# 12.10. Collect and Organize

We are to identify the elements highlighted in the periodic table in Figure P12.16 that do not adopt a fluorite  $(CaF_2)$  structure.

## Analyze

The radius ratio for the tetrahedral holes in fluorite is between 0.22 and 0.41. The radii of the highlighted cations are  $Cs^+$  (170 pm),  $Mg^{2^+}$  (72 pm),  $Ca^{2^+}$  (100 pm),  $Sr^{2^+}$  (118 pm), and  $Ba^{2^+}$  (135 pm). The radius of F<sup>-</sup> is 133 pm. Because the fluoride ions might occupy the tetrahedral holes in CsF, the appropriate radius ratio for that salt is

$$\frac{r_{\rm F}}{r_{\rm M^+}}$$

#### Solve

For CsF, the radius ratio is 
$$\frac{133}{170} = 0.782$$
  
For MgF<sub>2</sub>, the radius ratio is  $\frac{72}{133} = 0.54$   
For CaF<sub>2</sub>, the radius ratio is  $\frac{100}{133} = 0.752$   
For SrF<sub>2</sub>, the radius ratio is  $\frac{118}{133} = 0.887$   
For BaF<sub>2</sub>, the radius ratio is  $\frac{135}{133} = 1.02$ 

100

The fluorite structure is not possible for any of these salts as predicted by the radius ratio rule. However, both  $CaF_2$  and  $SrF_2$  adopt the fluorite structure. The elements Cs (red), Mg (orange), and Ba (purple) do not.

# Think About It

In order for  $CaF_2$  and  $SrF_2$  to adopt the fluorite structure, the fcc arrangement of  $F^-$  anions must be expanded to accommodate the relatively large  $Ca^{2+}$  and  $Sr^{2+}$  ions.

# 12.11. Collect and Organize

From Figure P12.11 showing the unit cell of magnesium boride, we are to determine its formula.

# Analyze

We are given that one B atom is inside the trigonal prismatic unit cell. Each corner of the unit cell has a Mg atom. Because the unit cell is trigonal prismatic, each corner atom is shared with 11 other unit cells and so has one-twelfth of its volume inside the unit cell.

## Solve

The number of B atoms in the unit cell is 1. The number of Mg atoms in the unit cell is  $6(\frac{1}{12}) = \frac{1}{2}$ . The formula from the unit cell is MgB<sub>2</sub> (in the lowest whole-number ratio).

# Think About It

It is tricky to see that the Mg atoms here are shared between 12 unit cells. Consider the center atom in the figure on the right-hand side. That atom is shared with 6 unit cells as shown, but there are also 6 more unit cells stacked on top of it that are not shown in the diagram.

# 12.12. Collect and Organize

From the diagram in Figure P12.12 showing the unit cell for a Y–Ba–Cu oxide, we are to determine the molecular formula and then consider which eight oxygens should be removed to give the unit cell for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. We are asked whether it makes a difference which oxygen atoms are removed.

# Analyze

Atoms on the corners of the unit cell contribute one-eighth of their volume to the unit cell. Atoms on the unit cell edges contribute one-fourth of their volume to the unit cell. Atoms on the face of a unit cell contribute one-half of their volume to the unit cell. Atoms inside the unit cell contribute all of their volume to the unit cell. When removing eight oxygen atoms from the figure to give  $YBa_2Cu_3O_7$ , we have to remove the atoms so as to maintain the stoichiometry of the superconductor.

## Solve

 $1(1 \text{ Y}) + 2(1 \text{ Ba}) + 8(\frac{1}{8} \text{ Cu}) + 8(\frac{1}{4} \text{ Cu}) + 20(\frac{1}{4} \text{ O}) + 8(\frac{1}{2} \text{ O}) \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_9$ 

It does matter which oxygen atoms are removed from the structure in Figure P12.12. To obtain a formula of  $YBa_2Cu_3O_7$  from  $YBa_2Cu_3O_9$  by removing eight oxygen atoms from the unit cell, we would have to remove the equivalent of two oxygen atoms. We could do this by removing eight edge O atoms. If we removed face atoms, we would only remove four O atoms. If we removed some edge atoms, we could remove four edge O atoms and two face O atoms to obtain the correct stoichiometry.

# Think About It

The actual unit cell of the superconductor (Figure 12.34) indeed shows that removal of eight edge O atoms gives  $YBa_2Cu_3O_7$ .

#### 12.13. Collect and Organize

For the three polymers shown in Figure P12.13, we can examine their molecular structures to determine which has the strongest intermolecular forces.

#### Analyze

As chlorine atoms are placed on the polymer backbone, the polarity of the backbone increases, so dipoledipole forces increase.

## Solve

(c) Poly(1,1-dichloroethylene) has the strongest intermolecular forces.

#### Think About It

Adding Cl atoms to the backbone also increases the strength of the weaker dispersion forces between the polymer chains.

#### 12.14. Collect and Organize

From the structure of dihydroxydimethylsilane (Figure P12.14) we are to draw the condensed structure for the repeating monomeric unit in Silly Putty.

## Analyze

The condensation reaction of dihydroxydimethylsilane combines the monomers of  $Si(CH_3)_2(OH)_2$  to create a larger molecule, losing water as a by-product. The –OH groups on the monomer will combine to produce the –O–Si–O– linkage for the polymer backbone.

## Solve

Continuing this reaction produces a long-chain polymer with the condensed structure



#### Think About It

These types of siloxane polymers have found uses in soft contact lenses, oils, and greases.

## 12.15. Collect and Organize

For the spider silk polymer shown in Figure P12.15, we are asked to identify the intermolecular forces present, and the functional groups on the monomer that reacted to form this condensation polymer.

#### Analyze

Intermolecular forces are present between the strands of the spider silk polymer, connecting H and O atoms on different polymer strands. The bond between the carbonyl carbon and the amine nitrogen atoms is an amide bond, which may be formed by a condensation reaction.

- (a) The intermolecular forces present are hydrogen bonds.
- (b) Each strand contains amide bonds, formed by the reaction of a primary amine and a carboxylic acid, as depicted below:



# Think About It

Polyamides like spider silk are polymers of amino acids. Many naturally occurring polymers are polyamides, with a structure similar to that depicted in Figure P12.15.

# 12.16. Collect and Organize

We are to answer questions about the given representations of solids, alloys, and polymers.

## Analyze

A body-centered cubic lattice has one-eighth of an atom on each corner of the cubic unit cell, and one atom wholly contained within the unit cell. A face-centered cubic lattice has one-eighth of an atom on each corner of the cubic unit cell, and one-half of an atom along each face of the unit cell. Ionic compounds are generally composed of cations contained in the holes of an anionic lattice. Interstitial alloys have nonhost metals contained in the holes of the host metal lattice, while in a substitutional alloy, one metal is substituted by another within the same lattice. Polymers are formed by an addition process when monomer units bond to form the polymer chain without the loss of any atoms or molecules. Polymers formed by a condensation process generate one molecule for each monomer added to the polymer chain. Strong cumulative intermolecular forces between polymer chains will lead to a rigid, hard material, while weak cumulative intermolecular forces will lead to soft, flexible materials.

## Solve

- (a) [B] depicts a body-centered cubic unit cell, while [H] depicts a face-centered cubic unit cell.
- (b) [E] is the ionic compound LiCl.
- (c) [F] is an interstitial alloy in which the black spheres are guests in the gray sphere lattice.
- (d) [C] and [G] are polymers prepared by an addition process, while [A] and [I] are polymers prepared by a condensation process.
- (e) [A] and [G] are rigid, hard materials.
- (f) [C] and [I] are flexible, stretchable, soft materials.

# Think About It

The linear chains of polyethylene depicted in [G] will exhibit a large number of relatively weak London dispersion intermolecular forces. The longer the polymer strands, the greater the summed intermolecular forces will be, leading to strong interstrand attraction.

# 12.17. Collect and Organize

We are asked to differentiate between cubic closest-packed (ccp) and hexagonal closest-packed (hcp) structures.

# Analyze

Both structures contain layers of close-packed atoms and differ only in how the layers are stacked.

Cubic closest-packed structures have an *abcabc*... pattern, and hexagonal closest-packed structures have an *abab*... pattern.

## Think About It

The unit cell for ccp is face-centered cubic (Figure 12.11), and the unit cell for hcp is hexagonal (Figure 12.5).

## 12.18. Collect and Organize

We are asked to describe the defining features of simple cubic, body-centered cubic, and face-centered cubic crystal structures, and to rank these in order of decreasing packing efficiency.

## Analyze

Packing efficiency is a measure of the volume of the cube occupied by the atoms. The greater the volume of the cube occupied by atoms, the higher the packing efficiency.

# Solve

Simple cubic cells feature a repeating arrangement of square-packed layers directly over one another, in the pattern *aaa*... Overall, there is one particle contained in the volume of the unit cell, and the packing efficiency is 52%.

Body-centered cubic cells feature a repeating arrangement of square-packed layers offset with respect to each other, in the pattern *ababab*... Overall, there are two particles contained in the volume of the unit cell, and the packing efficiency is 68%.

Face-centered cubic cells feature a repeating arrangement of close-packed layers, staggered such that the repeating pattern is *abcabc*... Overall, there are four particles contained in the volume of the unit cell, and the packing efficiency is 74%.

The unit cells, in order of decreasing packing efficiency, are

face-centered cubic > body-centered cubic > simple cubic

# Think About It

Close-packed layers are much more efficient at packing than square-packed layers; as a result, the fcc and hcp structures have a higher packing efficiency than simple cubic and bcc.

## 12.19. Collect and Organize

We are asked which has the greater packing efficiency, the simple cubic or the body-centered cubic structure.

## Analyze

Packing efficiency is the fraction of space within a unit cell that is occupied by the atoms.

## Solve

We read in Section 12.2 of the textbook that the simple cubic cell has the lowest packing efficiency of all the unit cells, so the body-centered cubic structure has a greater packing efficiency than the simple cubic structure.

## **Think About It**

The packing efficiency of the unit cell structures can be calculated. For simple cubic, the packing efficiency is only 52%, whereas for body-centered cubic it is 68% and for face-centered and hexagonal it is 74%.

# 12.20. Collect and Organize

By looking at Figure 12.9 we are to predict which structure, body-centered cubic (bcc) or face-centered cubic (fcc), has the greater packing efficiency.

## Analyze

In the face-centered cubic unit cell, there are atoms located at each face of the unit cell as well as at each corner. This gives four atoms per unit cell. In the body-centered cubic unit cell, there is one atom in the center of the unit cell as well as atoms at the corners. This gives two atoms per unit.

# Solve

From Figure 12.9 we can see that the packing in the bcc unit cell is less dense (more open spaces) than in the fcc unit cell. Therefore, the fcc unit cell has greater packing efficiency.

## Think About It

The ccp and hcp structures, being closest packed, have the same packing efficiency, with 74% of the unit cell filled with atoms.

# 12.21. Collect and Organize

Iron can adapt either the bcc unit cell structure (at room temperature) or the fcc unit cell structure (at 1070°C). We are asked whether these two forms are allotropes.

## Analyze

Allotropes are defined as different molecular forms of an element.

## Solve

Iron is not molecular, and the bcc and fcc unit cell structures describe only a difference in atom packing in the metal. Therefore, these structural forms are not allotropes.

## Think About It

Elements that do have allotropes include phosphorus, sulfur, and carbon.

## 12.22. Collect and Organize

We are to explain why calcium is fcc at low temperatures and bcc at higher temperatures.

## Analyze

The fcc structure is more tightly packed than the bcc structure.

## Solve

At high temperatures there is greater atomic motion than at low temperatures, so the calcium atoms might adopt the less tightly packed bcc unit cell structure at high temperatures.

## **Think About It**

The change in structure at the atomic level means that there are changes at the macroscopic level. For example, we might expect that a sample of calcium would expand and become less dense when heated.

#### 12.23. Collect and Organize

Knowing that  $\ell = 240.6$  pm for the bcc structure of europium, we are to calculate the radius of one atom of europium.

#### Analyze

For the bcc structure, the body diagonal contains two atoms of europium, or 4*r*, and the body diagonal is equal to  $\ell\sqrt{3}$  where  $\ell$  is the unit cell edge length, 240.6 pm.

#### Solve

$$4r = \ell\sqrt{3}$$
  
 $r = \frac{\ell\sqrt{3}}{4} = \frac{240.6 \text{ pm}' \sqrt{3}}{4} = 104.2 \text{ pm}$ 

#### Think About It

If the structure of the unit cell were simple cubic, the radius of the europium atom would simply be

 $2r = \ell$ 

$$r = \frac{\ell}{2} = 120.0 \text{ pm}$$

#### 12.24. Collect and Organize

Using the fact that nickel crystallizes in an fcc unit cell with an edge length of 350.7 pm, we are to calculate the radius of the nickel atom.

#### Analyze

In an fcc unit cell, the edge length is  $\ell$  and the face diagonal is  $\ell\sqrt{2}$ . The face diagonal has the atoms touching and is equal to 4r where r is the radius of the touching atoms. To determine r for nickel, we can substitute  $\ell = 350.7$  pm into the face diagonal relationship  $\ell\sqrt{2} = 4r$ .

#### Solve

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

$$350.7 \text{ pm}\sqrt{2} = 4r$$

$$r = 124.0 \text{ pm}$$

#### **Think About It**

This calculated value is identical to the value of 124 pm listed in Appendix 3.

#### 12.25. Collect and Organize

We are to calculate the edge length of the unit cell of Ba knowing that it crystallizes in a bcc unit cell and that  $r_{Ba} = 222$  pm.

#### Analyze

The body diagonal of a bcc unit cell has the relationship  $\ell\sqrt{3} = 4r$ . An edge has the length  $\ell$ , so all we need to do is rearrange the body diagonal expression to solve for  $\ell$ :

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

$$\ell = \frac{4r}{\sqrt{3}} = \frac{4'\ 222\ \text{pm}}{\sqrt{3}} = 513\ \text{pm}$$

# **Think About It**

Be careful to not assume that the edge length of every unit cell is  $\ell = 2r$ , as in a simple cubic.

#### 12.26. Collect and Organize

We are to calculate the edge length of the unit cell of Al knowing that it crystallizes in an fcc unit cell and  $r_{Al} = 143$  pm.

## Analyze

The face diagonal of an fcc unit cell has the relationship  $\ell\sqrt{2} = 4r$ . An edge has the length  $\ell$ , so all we need to do is rearrange the face diagonal expression to solve for  $\ell$ :

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

Solve

$$\ell = \frac{4r}{\sqrt{2}} = \frac{4' \ 143 \ \text{pm}}{\sqrt{2}} = 404 \ \text{pm}$$

#### Think About It

Be careful to not assume that the edge length of every unit cell is  $\ell = 2r$ , as in a simple cubic.

# 12.27. Collect and Organize

We are to determine the type of unit cell for a form of copper using the density of the crystal ( $8.95 \text{ g/cm}^3$ ) and the radius of the Cu atom (127.8 pm).

## Analyze

For each type of unit cell (simple cubic, body-centered cubic, and face-centered cubic), we can compare the calculated density to that of the actual density given for the crystalline form of copper. Density is mass per volume. The mass of each unit cell is the mass of the copper atoms contained in each unit cell. To find this, we first have to determine the number of atoms of Cu in each unit cell based on its structure. Then, we multiply by the mass of one atom of Cu:

1 Cu atom' 
$$\frac{1 \text{ mol}}{6.022' \ 10^{23} \text{ atoms}}$$
,  $\frac{63.55 \text{ g}}{1 \text{ mol}} = 1.055' \ 10^{-22} \text{ g}$ 

The volume of each unit cell is  $\ell^3$ , which is related to r in a way that depends on the type of unit cell.

## Solve

For a simple cubic unit cell where all the Cu atoms are at the corners of the cube:

Number of Cu atoms =  $8 \times \frac{1}{8} = 1$  Cu atom

$$\ell = 2r = 2 \times 127.8 \text{ pm} = 255.6 \text{ pm}$$

Converting to centimeters for the calculation of density (g/cm<sup>3</sup>) gives

$$255.6 \text{ pm}' \quad \frac{1' \quad 10^{-10} \text{ cm}}{1 \text{ pm}} = 2.556' \quad 10^{-8} \text{ cm}$$
  
Volume =  $\ell^3 = (2.556 \times 10^{-8} \text{ cm})^3 = 1.670 \times 10^{-23} \text{ cm}^3$   
Density =  $\frac{1 \text{ Cu atom}' \quad 1.055' \quad 10^{-22} \text{ g/atom}}{1.670' \quad 10^{-23} \text{ cm}^3} = 6.32 \text{ g/cm}^3$ 

For a body-centered cubic unit cell where there is one Cu atom in the center of the unit cell and eight Cu atoms at the corners of the cube:

Number of Cu atoms = 
$$(8 \times \frac{1}{8}) + 1 = 2$$
 Cu atoms

From the body diagonal  $4r = \ell\sqrt{3}$  or  $\ell = 4r/\sqrt{3}$ :

$$\ell = \frac{4' \ 127.8 \ \text{pm}}{\sqrt{3}} = 295.1 \ \text{pm}$$

Converting to centimeters for calculation of density (g/cm<sup>3</sup>) gives

295.1 pm' 
$$\frac{1' \ 10^{-10} \ \text{cm}}{1 \ \text{pm}} = 2.951' \ 10^{-8} \ \text{cm}$$
  
Volume =  $\ell^3 = (2.951 \times 10^{-8} \ \text{cm})^3 = 2.570 \times 10^{-23} \ \text{cm}^3$   
Density =  $\frac{2 \ \text{Cu} \ \text{atoms'} \ 1.055' \ 10^{-22} \ \text{g/atom}}{2.570' \ 10^{-23} \ \text{cm}^3} = 8.21 \ \text{g/cm}^3$ 

For a face-centered cubic unit cell where there are eight Cu atoms at the corners of the unit cell and six on the faces:

Number of Cu atoms =  $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$  Cu atoms

From the face diagonal  $4r = \ell \sqrt{2}$  or  $\ell = 4r/\sqrt{2}$ :

$$\ell = \frac{4' \ 127.8 \ \text{pm}}{\sqrt{2}} = 361.5 \ \text{pm}$$

Converting to centimeters for calculation of density (g/cm<sup>3</sup>) gives

$$361.5 \text{ pm}' \frac{1' \ 10^{-10} \text{ cm}}{1 \text{ pm}} = 3.615' \ 10^{-8} \text{ cm}$$
$$\text{Volume} = \ell^3 = (3.615 \times 10^{-8} \text{ cm})^3 = 4.724 \times 10^{-23} \text{ cm}^3$$
$$\text{Density} = \frac{4 \text{ Cu atoms}' \ 1.055' \ 10^{-22} \text{ g/atom}}{4.724' \ 10^{-23} \text{ cm}^3} = 8.93 \text{ g/cm}^3$$

The fcc unit cell gives a density closest to the given density, so we predict that in this crystalline form of Cu the atoms pack in (c) an fcc unit cell.

#### Think About It

Notice that even though the fcc unit cell has the largest edge length, the unit cell contains more atoms, so it yields the densest structure.

#### 12.28. Collect and Organize

We are to determine the type of unit cell for a form of molybdenum using the density of the crystal  $(10.28 \text{ g/cm}^3)$  and the radius of the Mo atom (139 pm).

#### Analyze

For each type of unit cell (simple cubic, body-centered cubic, and face-centered cubic), we can compare the calculated density to that of the actual density given for the crystalline form of molybdenum. Density is mass per volume. The mass of each unit cell is the mass of the molybdenum atoms contained in each unit cell. To find this, we first have to determine the number of atoms of Mo in each unit cell based on its structure. Then, we multiply by the mass of one atom of Mo:

1 Mo atom' 
$$\frac{1 \text{ mol}}{6.022' \ 10^{23} \text{ atoms}}$$
,  $\frac{95.96 \text{ g}}{1 \text{ mol}} = 1.593' \ 10^{-22} \text{ g}$ 

The volume of each unit cell is  $\ell^3$ , which is related to r in a way that depends on the type of unit cell.

# Solve

For a simple cubic unit cell where all the Mo atoms are at the corners of the cube:

Number of Mo atoms =  $8 \times \frac{1}{8} = 1$  Mo atom

$$\ell = 2r = 2 \times 139 \text{ pm} = 278 \text{ pm}$$

Converting to centimeters for calculation of density (g/cm<sup>3</sup>) gives

278 pm' 
$$\frac{1' \ 10^{-10} \ \text{cm}}{1 \ \text{pm}} = 2.78' \ 10^{-8} \ \text{cm}$$
  
Volume =  $\ell^3 = (2.78 \times 10^{-8} \ \text{cm})^3 = 2.15 \times 10^{-23} \ \text{cm}^3$   
Density =  $\frac{1 \ \text{Mo atom'} \ 1.593' \ 10^{-22} \ \text{g/atom}}{2.15' \ 10^{-23} \ \text{cm}^3} = 7.41 \ \text{g/cm}^3$ 

For a body-centered cubic unit cell where there is one Mo atom in the center of the unit cell and eight Mo atoms at the corners of the cube:

Number of Mo atoms = 
$$(8 \times \frac{1}{8}) + 1 = 2$$
 Mo atoms

From the body diagonal  $4r = \ell \sqrt{3}$  or  $\ell = 4r/\sqrt{3}$ :

$$\ell = \frac{4' \ 139 \ \text{pm}}{\sqrt{3}} = 321 \ \text{pm}$$

Converting to centimeters for calculation of density (g/cm<sup>3</sup>) gives

$$321 \text{ pm}' \quad \frac{1' \quad 10^{-10} \text{ cm}}{1 \text{ pm}} = 3.21' \quad 10^{-8} \text{ cm}$$
$$\text{Volume} = \ell^3 = (3.21 \times 10^{-8} \text{ cm})^3 = 3.31 \times 10^{-23} \text{ cm}^3$$
$$\text{Density} = \frac{2 \text{ Mo atoms}' \quad 1.593' \quad 10^{-22} \text{ g/atom}}{3.31' \quad 10^{-23} \text{ cm}^3} = 9.63 \text{ g/cm}^3$$

For a face-centered cubic unit cell where there are eight Mo atoms at the corners of the unit cell and six on the faces:

Number of Mo atoms = 
$$(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$$
 Mo atoms

From the face diagonal  $4r = \ell \sqrt{2}$  or  $\ell = 4r/\sqrt{2}$ :

$$\ell = \frac{4' \ 139 \ \text{pm}}{\sqrt{2}} = 393 \ \text{pm}$$

Converting to centimeters for calculation of density (g/cm<sup>3</sup>) gives

$$393 \text{ pm}' \frac{1' \ 10^{-10} \text{ cm}}{1 \text{ pm}} = 3.93' \ 10^{-8} \text{ cm}$$
$$\text{Volume} = \ell^3 = (3.93 \times 10^{-8} \text{ cm})^3 = 6.07 \times 10^{-23} \text{ cm}^3$$
$$\text{Density} = \frac{4 \text{ Mo atoms}' \ 1.593' \ 10^{-22} \text{ g/atom}}{6.07' \ 10^{-23} \text{ cm}^3} = 10.5 \text{ g/cm}^3$$

The fcc unit cell for Mo gives a calculated density closest to the given density, so we predict that in this case Mo forms crystals packing in (c) an fcc arrangement.

## Think About It

Notice that even though the fcc unit cell has the largest edge length, the unit cell contains more atoms and so it yields the densest structure.

#### 12.29. Collect and Organize

We may use the radius and crystal structure of sodium to determine the density of Na under high pressures.

## Analyze

Using the radius of a sodium atom, we may determine the edge length of the unit cell using the relationship  $r = 0.3536 \ell$  for a body-centered cubic structure. We may calculate the volume by cubing the edge length, and calculate the mass of the two atoms contained in the unit cell. By dividing this mass by the calculated volume, we can determine the density of Na. Under standard conditions, the density of Na is 0.971 g/cm<sup>3</sup>. The density should be similar under high pressure.

Solve

$$\ell = \frac{186 \text{ pm}}{0.3536}, \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}}, \frac{100 \text{ cm}}{1 \text{ m}} = 5.260' \ 10^{-8} \text{ cm}$$
Volume = (5.260' 10<sup>-8</sup> cm)<sup>3</sup> = 1.455' 10<sup>-22</sup> cm<sup>3</sup>  
4 Na atoms'  $\frac{1 \text{ mol Na}}{6.022' \ 10^{23} \text{ atoms Na}}, \frac{22.9898 \text{ g Na}}{1 \text{ mol Na}} = 1.527' \ 10^{-22} \text{ g}$ 

$$d = \frac{1.527' \ 10^{-22} \text{ g}}{1.455' \ 10^{-22} \text{ cm}^3} = 1.05 \text{ g/cm}^3$$

#### Think About It

The density is near our expected value. It is important to account for both Na atoms in the bcc unit cell.

#### 12.30. Collect and Organize

We may use the radius of calcium to calculate the density of the simple cubic phase of the metal under pressure. If we instead calculate the density of the fcc phase, then use that density for the simple cubic phase, we may calculate the radius of the calcium atoms in the simple cubic phase.

#### Analyze

Using the radius of calcium from the Appendix (197 pm), we may determine the edge length of the unit cell using the relationship  $r = 0.5 \ell$  for a simple cubic structure. We may calculate the volume by cubing the edge length, and calculate the mass of the one calcium atom contained in the unit cell. Dividing this mass by the calculated volume, we can determine the density of Ca.

We may calculate the density of the fcc phase in the same manner as in part (a) using the relationship  $r = 0.3536 \,\ell$  and recognizing that the fcc unit cell contains four Ca atoms. We may determine the volume of the sc phase by dividing the volume of the sc unit cell by the density calculated for the fcc phase. The cube root of this volume is the edge length of the sc unit cell, which is related to the radius by the equation  $r = 0.5 \,\ell$ . The radius of calcium should be slightly smaller than 197 pm.

# Solve

(a)

$$\ell = \frac{197 \text{ pm}}{0.5}, \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}}, \frac{100 \text{ cm}}{1 \text{ m}} = 3.94' \ 10^{-8} \text{ cm}$$
Volume =  $(3.94' \ 10^{-8} \text{ cm})^3 = 6.12' \ 10^{-23} \text{ cm}^3$ 
1 Ca atoms'  $\frac{1 \text{ mol Ca}}{6.022' \ 10^{23} \text{ atoms Ca}}, \frac{40.078 \text{ g Ca}}{1 \text{ mol Ca}} = 6.655' \ 10^{-23} \text{ g}$ 

$$d = \frac{6.655' \ 10^{-23} \text{ g}}{6.12' \ 10^{-23} \text{ cm}^3} = 1.09 \text{ g/cm}^3$$

(b) Calculating the density of the fcc phase:

$$\ell = \frac{197 \text{ pm}}{0.3536}, \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}}, \frac{100 \text{ cm}}{1 \text{ m}} = 5.571' \ 10^{-8} \text{ cm}$$
Volume = (5.571' 10<sup>-8</sup> cm)<sup>3</sup> = 1.729' 10<sup>-22</sup> cm<sup>3</sup>  
4 Ca atoms'  $\frac{1 \text{ mol Ca}}{6.022' \ 10^{23} \text{ atoms Ca}}, \frac{40.078 \text{ g Ca}}{1 \text{ mol Ca}} = 2.662' \ 10^{-22} \text{ g}$ 

$$d = \frac{2.662' \ 10^{-22} \text{ g}}{1.729' \ 10^{-22} \text{ cm}^3} = 1.54 \text{ g/cm}^3$$

Using the density of the fcc phase, calculating the radius of the Ca atom:

Volume = 
$$\frac{\text{m}}{d} = \frac{6.655' \ 10^{-23} \ \text{g}}{1.54 \ \text{g/cm}^3} = 4.322' \ 10^{-23} \ \text{cm}^3$$
  
 $\ell = \sqrt[3]{4.322' \ 10^{-23} \ \text{cm}^3} = 3.509' \ 10^{-8} \ \text{cm}' \ \frac{1 \ \text{m}}{100 \ \text{cm}}, \ \frac{1' \ 10^{12} \ \text{pm}}{1 \ \text{m}} = 350.9 \ \text{pm}$   
 $r = 0.5(350.9 \ \text{pm}) = 175 \ \text{pm}$ 

#### Think About It

The radius calculated in (b) is roughly 89% of the radius listed under standard conditions, which seems like a reasonable range. More accurate data could be obtained using X-ray crystallography.

#### 12.31. Collect and Organize

We can use the dimensions of the hexagonal unit cell to determine the density of titanium.

## Analyze

The volume of a hexagonal unit cell may be determined using the equation

$$V = \frac{3\sqrt{3}a^2h}{2}$$

where *a* is the side length of the hexagon (295 pm), and *h* is the height of the unit cell (469 pm). Converting the cell dimensions provided in Figure P12.31 from pm to cm will yield the volume of the unit cell in cm<sup>3</sup>. The mass of Ti in the hcp unit cell may be calculated by dividing the six Ti atoms in the unit cell by Avogadro's number and multiplying by the molar mass of titanium. The density is calculated by dividing the mass of Ti in the unit cell by the volume of the unit cell.

# Solve

$$a = 295 \text{ pm}' \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}}' \frac{100 \text{ cm}}{1 \text{ m}} = 2.95' \ 10^{-8} \text{ cm}$$

$$h = 469 \text{ pm}' \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}}' \frac{100 \text{ cm}}{1 \text{ m}} = 4.69' \ 10^{-8} \text{ cm}$$

$$Volume = \frac{3\sqrt{3} (2.95' \ 10^{-8} \text{ cm})^2 (4.69' \ 10^{-8} \text{ cm})}{2} = 1.06' \ 10^{-22} \text{ cm}^3$$

$$6 \text{ Ti atoms}' \frac{1 \text{ mol Ti}}{6.022' \ 10^{23} \text{ atoms Ti}}' \frac{47.867 \text{ g Ti}}{1 \text{ mol Ti}} = 4.769' \ 10^{-22} \text{ g}$$

$$d = \frac{4.769' \ 10^{-22} \text{ g}}{1.06' \ 10^{-22} \text{ cm}^3} = 4.50 \text{ g/cm}^3$$

## **Think About It**

Titanium is a relatively light and strong metal that is used for medical implants and other applications where a strong, light metal is required.

#### 12.32. Collect and Organize

We can use the dimensions of the hexagonal unit cell to determine the density of cobalt.

## Analyze

The volume of a hexagonal unit cell may be determined using the equation

$$V = \frac{3\sqrt{3a^2h}}{2}$$

where a is the side length of the hexagon (251 pm), and h is the height of the unit cell (407 pm).

Converting the cell dimensions provided in Figure P12.32 from pm to cm will yield the volume of the unit cell in cm<sup>3</sup>. The mass of Co in the hcp unit cell may be calculated by dividing the six Co atoms in the unit cell by Avogadro's number and multiplying by the molar mass of cobalt. The density is calculated by dividing the mass of Co in the unit cell by the volume of the unit cell. Since the cell dimensions are smaller than those of titanium, and the molar mass of cobalt is higher than that of titanium, it is reasonable to expect that the density of Co will also be greater than Ti.

#### Solve

$$a = 251 \text{ pm'} \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}}, \frac{100 \text{ cm}}{1 \text{ m}} = 2.51' \ 10^{-8} \text{ cm}$$

$$h = 407 \text{ pm'} \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}}, \frac{100 \text{ cm}}{1 \text{ m}} = 4.07' \ 10^{-8} \text{ cm}$$

$$Volume = \frac{3\sqrt{3} (2.51' \ 10^{-8} \text{ cm})^2 (4.07' \ 10^{-8} \text{ cm})}{2} = 6.66' \ 10^{-23} \text{ cm}^3$$

$$6 \text{ Co atoms'} \frac{1 \text{ mol Co}}{6.022' \ 10^{23} \text{ atoms Co}}, \frac{58.933 \text{ g Co}}{1 \text{ mol Co}} = 5.872' \ 10^{-22} \text{ g}$$

$$d = \frac{5.872' \ 10^{-22} \text{ g}}{6.66' \ 10^{-23} \text{ cm}^3} = 8.81 \text{ g/cm}^3$$

Cobalt is nearly twice as dense as titanium.

#### **Think About It**

Our prediction was reasonable. More mass in a smaller volume must lead to a greater density of matter.

#### 12.33. Collect and Organize

We are asked to describe the differences between substitutional and interstitial alloys and give an example of each.

#### Analyze

An alloy is a mixture of two or more metallic elements in solution with each other. The differences between substitutional and interstitial alloys involve the arrangement of atoms in the solution.

Substitutional alloys involve replacing atoms in a lattice with atoms of another element. An example of a substitutional alloy is bronze, an alloy composed of a copper lattice containing up to 30% tin. The tin atoms may be randomly distributed throughout the bronze, occupying any lattice position normally occupied by a copper atom in pure copper metal.

Interstitial alloys contain solutes in the spaces or "holes" left when the solvent lattice formed. An example of an interstitial alloy is austenite, an alloy containing carbon atoms in the octahedral holes of the iron fcc lattice.

# Think About It

Both interstitial alloys and substitutional alloys have a range of compositions rather than fixed ratios of components.

# 12.34. Collect and Organize

We can use the definitions of intermetallic compounds and homogeneous alloys to describe the similarities and differences between these terms.

# Analyze

An alloy is a mixture of two or more metallic elements in solution with each other. An intermetallic compound is an alloy with a reproducible stoichiometry.

# Solve

Both are homogeneous mixtures of solids. There is a subtle difference, however. An alloy is a mixture of two or more *metallic* elements, and an intermetallic compound is an alloy with a defined composition.

# Think About It

All alloys are solid solutions, but not all solid solutions are alloys.

# 12.35. Collect and Organize

We are asked what effect the substitution of one Ni atom at the center of the bcc Ti unit cell would have on the edge length of the crystal.

# Analyze

From the appendix, we find that Ni has a radius of 124 pm and Ti has a radius of 147 pm. In a bcc unit cell, atoms touch along the body diagonal, but not directly along an edge.

# Solve

Ni is smaller than Ti. By substituting a nickel atom for a titanium atom, the body diagonal will be shorter, and thus the unit cell will be smaller than that for pure titanium. The edge length for NiTi will be smaller than for Ti alone.



Atoms touch along body diagonal

# Think About It

Using the same logic, we could also predict that the unit cell for NiTi will be larger than that for pure Ni.

#### 12.36. Collect and Organize

Given that white gold is an alloy of Au and Ni, we are asked whether it is more malleable than pure Au.

## Analyze

When other metals are alloyed into a pure metal, the atomic structure of the metal is changed so that the atoms are not in as regular an arrangement as in the pure metal.

## Solve

The disruption of the gold lattice by the smaller Ni atoms in white gold restricts the gold atoms from slipping past each other as easily as in pure gold. Therefore, pure gold is more malleable.

#### Think About It

Pure gold is too soft to be used for jewelry, so it is alloyed with other metals such as nickel to make it more durable.

## 12.37. Collect and Organize

We are asked to decide if including hafnium atoms in place of magnesium atoms will generate an alloy with a greater or lesser density than pure magnesium.

#### Analyze

The size of the hafnium and magnesium atoms are nearly identical, so we can assume that there are no distortions to the unit cell when this substitution occurs. The atomic mass of magnesium is 24.3050 amu, and the atomic mass of hafnium is 178.49 amu.

#### Solve

The significant increase in mass when hafnium is substituted for magnesium will result in an alloy of greater density than that of pure magnesium.

#### Think About It

The density of the resulting alloy will be less than that of pure hafnium.

## 12.38. Collect and Organize

We consider here why alloys of transition metals with the second-row nonmetals B, N, and C are interstitial rather than substitutional alloys.

#### Analyze

Substitutional alloys generally have atomic radii of the alloying elements within 15% of each other. The sizes of the transition metals are in the range of 124–180 pm (Appendix 3), and the radii of B, C, and N are in the range of 75–88 pm (Appendix 3).

The radius ratio of these alloys fall in the range

$$\frac{75 \text{ pm}}{180 \text{ pm}} = 0.42 \text{ to } \frac{88 \text{ pm}}{124 \text{ pm}} = 0.71$$

These ratios are significantly smaller than the 0.85 or higher ratio for substitutional alloys. Therefore, the large difference in atomic sizes accounts for the alloying elements occupying interstitial rather than substitutional lattice sites.

## Think About It

According to the ratio range calculated above for these alloys, we predict that B, N, and C occupy octahedral holes in the closest-packed lattices of transition metals.

## 12.39. Collect and Organize

We are to compare the two unit cells in Figure P12.39 and decide if both are accurate depictions of NiTi.

#### Analyze

For a bcc unit cell, one-eighth of an atom is located in the cell at each corner, and an entire atom is located in the center. For the diagram to be accurate, the unit cells must each produce a 1:1 ratio of Ni:Ti.

# Solve

For 8 X atoms at the corners and 1 Y atoms in the center of the unit cell:

(a)  $\frac{1}{8}$  (8 Ti atoms) + 1(1 Ni atoms) = NiTi

(b)  $\frac{1}{8}$  (8 Ni atoms) + 1(1 Ti atoms) = NiTi

Both unit cells produce the same ratio of Ni to Ti, so both are valid.

# Think About It

This alloy structure is similar to the bcc unit cell of CsCl.

## 12.40. Collect and Organize

We are to compare the two unit cells in Figure P12.40 and decide if both are possible depictions of the same substitutional alloy.

#### Analyze

For an fcc unit cell, one-eighth of an atom is located in the cell at each corner, and one-half an atom is located on each face. If the ratio of atoms in the left and right diagrams are the same, the depictions are equivalent. We can assume the yellow spheres represent Au atoms and the bronze spheres represent Cu atoms.

## Solve

Left:  $\frac{1}{8}(8 \text{ Cu atoms}) + \frac{1}{2}(6 \text{ Au atoms}) = \text{CuAu}_3$ 

Right:  $\frac{1}{8}(8 \text{ Au atoms}) + \frac{1}{2}(6 \text{ Cu atoms}) = \text{Cu}_3\text{Au}$ 

The ratio of atoms does not match, so the two diagrams are not equivalent.

#### Think About It

The diagram on the left represents the rose gold substitutional alloy, with 25% copper content.

## 12.41. Collect and Organize

By substituting the radius of hydrogen into the radius ratio for the tetrahedral holes of an fcc unit cell, we may determine the range of metal hosts that could form an interstitial alloy with hydrogen. We are asked to determine if the interstitial alloy formed as a result of hydrogen present in the form of a hydride ion would more likely occupy octahedral or tetrahedral holes in the host metal.

## Analyze

For the fcc unit cell, the acceptable range of host and nonhost radii is

$$r_{\text{nonhost}}/r_{\text{host}} = 0.22 - 0.4$$

The radius of the hydrogen atom (the nonhost) is 37 pm. The ratio of 0.41 represents the smallest difference between hydrogen and the metal. This gives the minimum radius the metal could have for hydrogen to fit into tetrahedral holes of the fcc lattice.

## Solve

(a) The smallest metal host radius that would form such an alloy is

$$r_{\rm host} = \frac{37 \text{ pm}}{0.41} = 90 \text{ pm}$$

(b) The radius of the hydride ion (146 pm) is closer to that of most metals. The hydride ion is more likely to form a substitutional alloy.

## **Think About It**

Even if the hydride ion were to occupy the octahedral holes of a metal, the metal would have to have a radius of >200 pm!

## 12.42. Collect and Organize

We are to determine the minimum radius of an atom that can accommodate boron (88 pm) in octahedral holes. To answer this we can use the highest value of the ratio range for octahedral holes (Table 12.5). We are also asked to determine the molecular formula given an average occupancy of one boron atom per unit cell.

## Analyze

To fit in an octahedral hole, the radius of boron divided by the atom's radius must be between 0.41 and 0.73. The ratio of 0.41 represents the largest difference between boron and the atom. The ratio of 0.73 represents the smallest difference between boron and the atom. This gives the minimum radius the atom could have for boron to fit into octahedral holes of the closest-packed atoms. The fcc unit cell contains four octahedral holes and four metal atoms per unit cell.

## Solve

(a)

$$\frac{\text{radius of boron atom}}{\text{radius of closest-packed atom}} = 0.73$$

Radius of atom = 
$$\frac{\text{radius of boron}}{0.73} = \frac{88 \text{ pm}}{0.73} = 121 \text{ pm}$$

(b) If one octahedral hole is occupied per unit cell, the ratio of metal to boron will be  $M_4B_1$ , or  $MB_{0.25}$ .

## **Think About It**

The maximum radius that would hold boron in an octahedral hole would use 0.41 in the calculation. Using that value, the radius of the atom would be 215 pm.

## 12.43. Collect and Organize

By calculating the radius ratio of Sn to Ag, we can determine whether dental alloys of Sn and Ag are substitutional or interstitial alloys.

## Analyze

It would be possible for an alloy to be both interstitial and substitutional as long as the voids within the lattice are about the same size as the metal atom. In particular, if the host metal has a simple cubic structure, the alloying metal may fit in a cubic void (radius ratio > 0.73) as well as substitute for the host metal in the lattice structure.

## Solve

$$\frac{r_{\rm Sn}}{r_{\rm Ag}} = \frac{140 \text{ pm}}{144 \text{ pm}} = 0.972$$

Because these radii are within 15% of each other, an alloy of silver and tin is a substitutional alloy.

## **Think About It**

Remember that it is also important for the metals in substitutional alloys to crystallize in the same closestpacked (hcp, ccp, simple cubic, bcc) structures.

## 12.44. Collect and Organize

We can compare the difference in atomic size for  $Sn_3Hg$  and for bronze made of Cu and Sn to determine which alloy has a smaller mismatch.

## Analyze

We can use the ratios of the atomic radii to answer this question. We are given the radii for tin (140 pm) and mercury (151 pm). The radius of the copper atom is listed in Appendix 3 as 128 pm.

## Solve

For Sn<sub>3</sub>Hg:

$$\frac{r_{\text{Sn}}}{r_{\text{Hg}}} = \frac{140 \text{ pm}}{151 \text{ pm}}$$
, 100 = 92.7% or a 7.3% difference

For bronze:

 $\frac{r_{\rm Cu}}{r_{\rm Sn}} = \frac{128 \text{ pm}}{140 \text{ pm}}$ , 100 = 91.4% or an 8.6% difference

Sn<sub>3</sub>Hg has a smaller mismatch in atomic size.

# Think About It

Both alloys are substitutional because the elements' radii are within 15% of each other.

# 12.45. Collect and Organize

We are to predict the formula of vanadium carbide if the vanadium lattice is ccp (fcc) and two octahedral holes are occupied by carbon atoms.

## Analyze

The fcc arrangement of V atoms has four atoms of V in the unit cell. This fcc unit cell also contains four octahedral holes and eight tetrahedral holes.

## Solve

If only two of the four octahedral holes are occupied, the ratio of atoms in this lattice is  $V_4C_2$ , or  $V_2C$ .

# Think About It

If all of the octahedral holes were filled, the formula of the alloy would be VC.

#### 12.46. Collect and Organize

We are to predict the formula of manganese nitride if the manganese lattice is ccp (fcc) and one tetrahedral hole is occupied by a nitrogen atom.

## Analyze

The fcc arrangement of Mn atoms has four atoms of Mn in the unit cell. This fcc unit cell also contains four octahedral holes and eight tetrahedral holes.



## Solve

If only one of the eight tetrahedral holes is occupied, the ratio of atoms in this lattice is Mn<sub>4</sub>N.

#### Think About It

If all of the tetrahedral holes were filled, the formula of the alloy would be  $MnN_2$ .

## 12.47. Collect and Organize

We can use the radii of Ni and Ti to calculate the density of the nitinol alloy.

#### Analyze

Nitinol is an alloy composed of one Ni atom and one Ti atom per bcc unit cell. The radii of Ni (124 pm) and Ti (147 pm) may be used to calculate the body diagonal for the bcc unit cell:

Body diagonal = 
$$2(r_{Ni}) + 2(r_{Ti})$$

We may then use the relationship below to determine the edge length of the unit cell:

Body diagonal = 
$$\sqrt{(\text{edge length})^2 + (\text{face diagonal})^2} = \sqrt{\ell^2 + (\ell\sqrt{2})^2}$$

Cubing the edge length yields the volume of the unit cell. We may determine the mass of the unit cell by multiplying the number of each atom by its molar mass and dividing by Avogadro's number. The density is obtained by dividing this mass by the volume of the unit cell determined above.

#### Solve

Calculating the volume of the unit cell:

Body diagonal = 2(124 pm)+ 2(147 pm)= 542 pm' 
$$\frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}}$$
,  $\frac{100 \text{ cm}}{1 \text{ m}}$  = 5.42' 10<sup>-8</sup> cm  
 $\ell^2 + (\ell\sqrt{2})^2 = (5.42' \ 10^{-8} \text{ cm})^2$   
 $3\ell^2 = 2.938' \ 10^{-15} \text{ cm}^2$   
 $\ell = 3.129' \ 10^{-8} \text{ cm}$   
Volume =  $(3.129' \ 10^{-8} \text{ cm})^3 = 3.064' \ 10^{-23} \text{ cm}^3$ 

The mass of the unit cell is

1 Ti atom' 
$$\frac{1 \text{ mol Ti}}{6.022' \ 10^{23} \text{ atoms Ti}}$$
,  $\frac{47.867 \text{ g Ti}}{1 \text{ mol Ti}} = 7.949' \ 10^{-23} \text{ g Ti}$   
1 Ni atom'  $\frac{1 \text{ mol Ni}}{6.022' \ 10^{23} \text{ atoms Ni}}$ ,  $\frac{58.6934 \text{ g Ni}}{1 \text{ mol Ni}} = 9.746' \ 10^{-23} \text{ g Ni}$ 

Mass = 
$$7.949' \ 10^{-23} \text{ g Ti} + 9.746' \ 10^{-23} \text{ g Ni} = 1.770' \ 10^{-22} \text{ g}$$

The density of nitinol is

$$d = \frac{1.770' \ 10^{-22} \ g}{3.064' \ 10^{-23} \ \text{cm}^3} = 5.78 \ \text{g/cm}^3$$

#### **Think About It**

The calculated density for nitinol is reasonable for this alloy of two first-row transition metals.

#### 12.48. Collect and Organize

We can use the radii of Cu and Au to calculate the density of the rose gold alloy.

## Analyze

We can use a weighted average of the radii for Au (144 pm, 75%) and Cu (128 pm, 25%) to calculate the edge length of the fcc unit cell using the relationship  $r = 0.3536 \ell$ . The fcc unit cell contains four atoms, which equates to three Au atoms for every one Cu atom. By adding the masses of these atoms, we may determine the mass of the unit cell. The density of rose gold is obtained by dividing the mass of the unit cell by the volume calculated.

# Solve

Calculating the volume of the unit cell:

Average 
$$r = 0.25(128 \text{ pm}) + 0.75(144 \text{ pm}) = 140 \text{ pm}' \frac{1 \text{ m}}{1' \cdot 10^{12} \text{ pm}}' \frac{100 \text{ cm}}{1 \text{ m}} = 1.40' \cdot 10^{-8} \text{ cm}$$
  
 $\ell = \frac{1.40' \cdot 10^{-8} \text{ cm}}{0.3536} = 3.959' \cdot 10^{-8} \text{ cm}$   
Volume =  $(3.959' \cdot 10^{-8} \text{ cm})^3 = 6.205' \cdot 10^{-23} \text{ cm}^3$ 

The mass of the unit cell is

3 Au atoms' 
$$\frac{1 \text{ mol Au}}{6.022' \ 10^{23} \text{ atoms Au}}$$
,  $\frac{196.9666 \text{ g Au}}{1 \text{ mol Au}} = 9.812' \ 10^{-22} \text{ g Au}$   
1 Cu atom'  $\frac{1 \text{ mol Cu}}{6.022' \ 10^{23} \text{ atoms Cu}}$ ,  $\frac{63.546 \text{ g Cu}}{1 \text{ mol Cu}} = 1.055' \ 10^{-22} \text{ g Cu}$   
Mass = 9.812' \ 10^{-22} \text{ g Au} + 1.055' \ 10^{-22} \text{ g Cu} = 1.0867' \ 10^{-21} \text{ g}

$$d = \frac{1.0867' \ 10^{-21} \ g}{6.205' \ 10^{-23} \ \text{cm}^3} = 17.5 \ \text{g/cm}^3$$

#### **Think About It**

The density of rose gold is much higher than that calculated for nitinol in Problem 12.47. This makes sense because gold is much heavier than the first-row elements Ni and Ti.

## 12.49. Collect and Organize

We are asked to determine the type of structure depicted in Figure P12.49 and the relative proportions of each element present in the unit cell.

## Analyze

Figure P12.45 depicts a body-centered cubic unit cell with opposite corners occupied by Cu atoms and the remainder of the lattice positions occupied by Zn atoms. For a bcc unit cell, at each corner, one-eighth of an atom is located in the cell, and an entire atom is located in the center.

## Solve

- (a) The unit cell depicted in Figure P12.49 is a bcc unit cell. The alloy is a substitutional alloy, in which some of the lattice positions of the Zn unit cell are occupied by Cu atoms.
- (b) The proportions of Cu and Zn in this lattice are



The ratio of atoms is  $Cu_{0.5}Zn_{1.5}$ , or  $CuZn_3$ .

## **Think About It**

Though rose gold and the CuZn alloy described in this problem have the same ratio of component elements, they adopt different unit cells.

## 12.50. Collect and Organize

We are asked to determine if the alloy depicted in Figure P12.50 is a substitutional or an interstitial alloy. We can determine the composition of the alloy by analyzing the ratio of atoms in this lattice.

## Analyze

Figure P12.50 depicts a repeating bcc lattice of gray atoms, with four green atoms substituted for the central gray atoms. From Figure 12.6, we see that Al adopts an fcc lattice, and Fe adopts a bcc lattice. For a bcc unit cell, one-eighth of an atom is located at each corner in the cell, and an entire atom is located in the center.

#### Solve

- (a) The alloy depicted in Figure P12.50 is a substitutional alloy, in which the half of the central gray atoms have been replaced by green atoms.
- (b) By matching the unit cell to that predicted for the pure elements, we may assume that the gray atoms are Fe, and the green atoms are Al. Over the eight adjoining unit cells, the occupancy is



The ratio of atoms is  $4(1.5 \text{ Fe atoms}) + 4(1.5 \text{ Fe atoms} + 1 \text{ Al atom}) = \text{Fe}_{12}\text{Al}_4$ , or Fe<sub>3</sub>Al.

## **Think About It**

The repeating unit of this alloy is a group of eight adjacent bcc unit cells.

# 12.51. Collect and Organize

Given that the unit cell edge length for an alloy of Cu and Sn is the same as that for pure Cu, we are to determine whether the alloy would be more dense than pure Cu.

## Analyze

Density is mass per volume. If the unit cell edge length is the same for both the alloy and pure copper, then the volumes of the unit cells of both substances are the same. The density would be greater only if the mass of the unit cell alloy is greater than for the pure copper.

## Solve

Because tin has a greater molar mass than copper, the mass of the unit cell in the alloy would be greater and therefore, yes, the density of the alloy would be greater than the density of pure copper.

## Think About It

The unit cell volume does not change much for substitutional alloys because the alloying atoms are close in size (within 15%) to the atoms being replaced.

## 12.52. Collect and Organize

Assuming the unit cell edge length does not change, we are to predict whether the alloy has a greater density if carbon is placed into the interstices of the vanadium lattice.

## Analyze

Density is mass per volume. If the unit cell edge length is the same for both the alloy and pure vanadium, then the volumes of the unit cells of both substances are the same. The density would be greater only if the mass of the unit cell alloy is greater than for the pure vanadium.

## Solve

Because carbon is being added to the interstices in the closest-packed vanadium structure, the mass of the unit cell increases. Therefore, yes, the density of the alloy is greater than that of pure vanadium.

# Think About It

Interstitial alloys have small atoms as alloying elements so as to fit into the octahedral or tetrahedral holes of the closest-packed layer of larger metal atoms.

## 12.53. Collect and Organize

We are to explain why the  $Cl^-$  ions in the rock salt structure of LiCl touch in the unit cell, but those in KCl do not.

#### Analyze

In the fcc rock salt lattice, the alkali metal,  $Li^+$  or  $K^+$ , is placed into the octahedral holes of the unit cell. From the radius ratio rule applied to LiCl and KCl (ionic radii are given in Figure 10.2),

$$\frac{r_{\rm Li^+}}{r_{\rm CI}} = \frac{76 \text{ pm}}{181 \text{ pm}} = 0.42 \qquad \frac{r_{\rm K^+}}{r_{\rm CI}} = \frac{138 \text{ pm}}{181 \text{ pm}} = 0.76$$

# Solve

The radius ratios show that  $K^+$  is large and so does not fit well into the octahedral holes (radius ratio between 0.41 and 0.73). Therefore, the rock salt structure for KCl has Cl<sup>-</sup> ions that may not touch in order to accommodate the large K<sup>+</sup> ions in the fcc lattice.

# Think About It

The radius ratio rule is simply a guide to predicting in which type of hole cations will fit within the anion lattice. You will find that sometimes we would predict an octahedral hole for a cation when the actual crystal places the cation into a cubic hole, for example.

#### 12.54. Collect and Organize

We are asked if the size of the octahedral holes changes as we consider the lattices of the halogens from fluorine to iodide (i.e., down the group).

#### Analyze

As we descend the halogens, the principal quantum number increases, leading to an increase in atomic radius. To help envision the alterations to the structure that occur when we increase the atomic radius, imagine an fcc lattice composed of baseballs, compared to the same lattice composed of basketballs.

#### Solve

While the ratio of volume occupied by atoms and holes is unaltered, the absolute size of the holes increases with increasing radius. The iodide lattice will contain larger holes.

## **Think About It**

We also see this trend when considering the ratio of host and nonhost radii in Table 12.5. Though the radius ratio will remain the same for a given lattice, the size of the guest may increase with increasing host atom radius.

#### 12.55. Collect and Organize

We are to describe how CsCl could be viewed as both a simple cubic and a body-centered cubic structure.

#### Analyze

A simple cubic structure consists of atoms located only at the corners of a cube. A body-centered cubic structure consists of an atom inside a cube of atoms.

The radius of  $Cl^-$  is 181 pm and the radius of  $Cs^+$  is 170 pm, so their radii are very similar. The  $Cs^+$  ion at the center of Figure P12.55 occupies the center of the cubic cell, so CsCl could be viewed as a body-centered cubic structure when taking into account the ions' slight difference in size. However, if we look at the ions as roughly equal in size, the unit cell becomes two interpenetrating simple cubic unit cells.

## Think About It

In the body-centered cubic unit cell, the cubic hole in the simple cubic unit cell is filled.

#### 12.56. Collect and Organize

We are asked to consider what changes to the lattice of ZnS would occur if some of the  $S^{2^-}$  ions were replaced with  $Se^{2^-}$  ions.

#### Analyze

The radii of  $S^{2^-}$  and  $Se^{2^-}$  are 184 pm and 198 pm, respectively, and the radius of  $Zn^{2^+}$  is 74 pm. The structure of ZnS is an fcc lattice of  $S^{2^-}$  ions with  $Zn^{2^+}$  ions in four of the eight tetrahedral holes. The acceptable ratio of radii for an ion occupying a tetrahedral hole in an fcc unit cell is

$$\frac{r_{\text{nonhost}}}{r_{\text{host}}} = 0.22 - 0.41$$

Comparing the radius ratio for the extreme cases (ZnS and ZnSe) will reveal whether the structure must change to accommodate the change in ion size.

#### Solve

For ZnS, the radius ratio is

$$\frac{r_{\text{nonhost}}}{r_{\text{host}}} = \frac{74 \text{ pm}}{184 \text{ pm}} = 0.40$$

For ZnSe, the radius ratio is

$$\frac{r_{\text{nonhost}}}{r_{\text{host}}} = \frac{74 \text{ pm}}{198 \text{ pm}} = 0.37$$

Both of these lie within the acceptable range for  $Zn^{2^+}$  occupying the tetrahedral holes of an fcc host lattice. Yes, the Se<sup>2-</sup> ions should occupy the same sites at the S<sup>2-</sup> ions.

#### Think About It

The difference in the ratio of S and Se is approximately 8%, which is within the acceptable tolerance of 15%.

#### 12.57. Collect and Organize

We can use the radius ratio rule and the formula for the salt to determine whether  $CaCl_2$  could have a rock salt structure.

## Analyze

From Figure 11.1, the radius of Cl<sup>-</sup> is 181 pm and the radius of Ca<sup>2+</sup> is 100 pm. The radius ratio is therefore

$$\frac{r_{\rm Ca^{2+}}}{r_{\rm CF}} = \frac{100 \text{ pm}}{181 \text{ pm}} = 0.552$$

## Solve

The radius ratio of  $Ca^{2+}$  and  $Cl^{-}$  shows that the  $Ca^{2+}$  ions would fit into the octahedral holes of an fcc lattice of  $Cl^{-}$  anions. However, this structure would not be like NaCl, where all the octahedral holes are filled in the fcc lattice. To balance charge, only half of the octahedral holes are filled in CaCl<sub>2</sub>.

# Think About It

 $CaCl_2$  does not have a structure like  $CaF_2$ , in which the  $Ca^{2+}$  ions form an fcc array into which the F<sup>-</sup> ions fill all the octahedral holes. Instead it adopts a rutile, TiO<sub>2</sub>, structure.

## 12.58. Collect and Organize and Analyze

We are asked to account for the different structures of NaF and CaF<sub>2</sub>.

## Solve

NaF has a 1:1 ratio of ions, and  $CaF_2$  has a 1:2 ratio of ions. The same unit cell cannot accommodate both of these ion ratios.

#### **Think About It**

The ratio of atoms or ions in the unit cell must match the ratio of atoms or ions in the bulk compound.

#### 12.59. Collect and Organize

We are to predict the effect on density of an ionic compound of rock salt structure as the cation-anion radius ratio increases.

#### Analyze

When the cation–anion ratio increases, the cation is increasing, relatively, in size. If the anions remain in the rock salt structure, they might have to expand the fcc structure to accommodate larger cations.

#### Solve

As the cation–anion radius ratio increases, the closest-packed anions would expand so as to maintain the cations in the octahedral holes of the fcc lattice. The cell volume, therefore, increases, and the calculated density would be less than the measured density.

#### **Think About It**

Another factor in density is the molar mass of the ions of the structure.

#### 12.60. Collect and Organize

We are to predict the effect on the unit cell edge length for an ionic compound with the rock salt structure as the cation–anion radius ratio increases.

#### Analyze

As the cation-anion radius ratio increases, the closest-packed anions may have to expand to accommodate the larger cations in the octahedral holes of the fcc structure.

## Solve

As the cation–anion radius ratio increases, the expansion of the unit cell to accommodate the larger cations means that the calculated edge length ( $\ell$ ) from the fcc unit cell ( $4r = \ell \sqrt{2}$  along the body diagonal) will be less than the observed edge length because larger cations in the octahedral holes cause the anions along the face diagonal to no longer touch.

## **Think About It**

In more advanced texts, several radii are provided in tables for cation size. Often radii are listed for the cation in tetrahedral, octahedral, and cubic holes. Sometimes the size differences between the same ions, but different holes, are substantial.

#### 12.61. Collect and Organize

For a ccp array of  $O^{2^-}$  ions with one-fourth of the octahedral holes containing Fe<sup>3+</sup>, one-eighth of the tetrahedral holes containing Fe<sup>3+</sup>, and one-fourth of the octahedral holes containing Mg<sup>2+</sup>, we are asked to write the formula of the ionic compound.

# Analyze

In a ccp array of ions, there are four octahedral holes and eight tetrahedral holes. The ccp array has an fcc unit cell, which has four closest-packed anions.

# Solve

The unit cell will have the following:

4 O<sup>2-</sup> anions in the fcc unit cell
1 Fe<sup>3+</sup> in octahedral holes
1 Fe<sup>3+</sup> in tetrahedral holes
1 Mg<sup>2+</sup> in octahedral holes

The formula is MgFe<sub>2</sub>O<sub>4</sub>.

## **Think About It**

The salt has charge balance as well:  $4 \text{ O}^{2-}$  gives a charge of 8–, which is balanced by 2 Fe<sup>3+</sup> plus 1 Mg<sup>2+</sup> or a charge of 8+.

## 12.62. Collect and Organize

We are to deduce the formula of the compound in which  $Ba^{2+}$  occupies half of the cubic holes in a simple cubic arrangement of  $F^-$  anions.

## Analyze

The number of cubic holes in the simple cubic unit cell is one. The number of  $F^-$  anions in the unit cell is also one.

## Solve

Because the  $Ba^{2^+}$  occupies half of the cubic holes in the structure, it is helpful to consider two unit cells. Two unit cells have two F<sup>-</sup> anions and two cubic holes, one of which is occupied by the  $Ba^{2^+}$  cation. Therefore, the formula of the compound is  $BaF_2$ .

## **Think About It**

 $Ba^{2+}$  occupies only half of the cubic holes in the structure of this compound in order to maintain charge balance.

# 12.63. Collect and Organize

We consider the structure of anatase, a form of  $TiO_2$ , found on a map of Vinland believed to date from the 1400s.

#### Analyze

We can predict the type of hole Ti<sup>4+</sup> is likely to occupy by calculating the radius ratio  $r_{\text{Ti}^{4+}}/r_{\text{O}^2}$ . The radius ratios for tetrahedral, octahedral, and cubic holes are 0.22–0.41, 0.41–0.73, and 0.73–1.00, respectively (Table 12.4). In the ccp structure the unit cell is fcc. This unit cell contains four octahedral and eight tetrahedral holes.

#### Solve

(a) From the radius ratio,

$$\frac{r_{\rm Ti^{4+}}}{r_{\rm O^{2-}}} = \frac{60.5 \text{ pm}}{140 \text{ pm}} = 0.432$$

Ti<sup>4+</sup> is expected to occupy octahedral holes.

(b) To give charge balance, there is one Ti<sup>4+</sup> ion for every two O<sup>2-</sup> ions in the lattice. Because the unit cell contains four O<sup>2-</sup> ions, there must be two Ti<sup>4+</sup> ions in the unit cell. Since there are four octahedral holes in the unit cell, this must mean that half of the octahedral holes in the unit cell are occupied.

## Think About It

If the Ti<sup>4+</sup> were small enough to fit into the tetrahedral holes, then one-fourth of the tetrahedral holes would be occupied.

#### 12.64. Collect and Organize

Given the ccp structure of the  $O^{2^-}$  anions in olivine (M<sub>2</sub>SiO<sub>4</sub>) and the fact that Si<sup>4+</sup> cations occupy the tetrahedral holes and M<sup>2+</sup> cations occupy the octahedral holes in the structure, we are to calculate the fraction of tetrahedral and octahedral holes that are occupied and consider why the unit cell volumes differ between Mg<sub>2</sub>SiO<sub>4</sub> and Fe<sub>2</sub>SiO<sub>4</sub>.

#### Analyze

The ccp structure has an fcc unit cell. This cell contains four  $O^{2^-}$  ions with four octahedral holes and eight tetrahedral holes. Because the unit cell contains four  $O^{2^-}$  ions, the same as the formula for olivine, we need only look at one unit cell.

#### Solve

- (a) Because there is one  $Si^{4+}$  ion in the formula, there is one of these ions in one of the tetrahedral holes in the unit cell. The fraction of tetrahedral holes occupied, therefore, is one-eighth. There are two  $M^{2+}$  ions in the unit cell distributed among four octahedral holes. The fraction of octahedral holes that are occupied, therefore, is 2/4, or one-half.
- (b) The Fe<sup>2+</sup> cation is larger than Mg<sup>2+</sup>. Even though they both fit in octahedral holes in the structure, the larger Fe<sup>2+</sup> ions expand the lattice of  $O^{2-}$  ions slightly, giving Fe<sub>2</sub>SiO<sub>4</sub> a larger unit cell volume.

# Think About It

If the  $Si^{4+}$  ions were located in the octahedral holes, then one-fourth of the octahedral holes would be occupied. The  $M^{2+}$  ions would then occupy one-fourth of the tetrahedral holes.

## 12.65. Collect and Organize

We are asked to identify the differences between the rock salt and cesium chloride structures and explain how both structures are a suitable match for MgSe.

#### Analyze

In the rock salt structure, the  $Se^{2^-}$  ions would be in an fcc array, with  $Mg^{2^+}$  occupying all of the octahedral holes. In the cesium chloride structure, the  $Se^{2^-}$  ions are in a simple cubic array, with  $Mg^{2^+}$  ions occupying the cubic holes.

#### Solve

- (a) The rock salt and cesium chloride lattices have the same ratio of ions, but the relative arrangements differ. In the rock salt structure, the Se<sup>2-</sup> ions would be in an fcc array, with Mg<sup>2+</sup> occupying all of the octahedral holes. In the cesium chloride structure, the Se<sup>2-</sup> ions are in a simple cubic array, with Mg<sup>2+</sup> ions occupying the cubic holes.
- (b) Both structures have the same ratio of Mg to Se.
- For the rock salt structure, the ratio is Mg<sub>4</sub>Se<sub>4</sub>, or MgSe:

$$\frac{1}{4} (12 \text{ Mg}^{2+}) + 1 \text{ Mg}^{2+} = 4 \text{ Mg}^{2+}$$
$$\frac{1}{8} (8 \text{ Se}^{2-}) + \frac{1}{2} (6 \text{ Se}^{2-}) = 4 \text{ Se}^{2-}$$

For the cesium chloride structure, the ratio is MgSe:

$$1 \text{ Mg}^{2+} = 1 \text{ Mg}^{2+}$$
$$\frac{1}{8} (8 \text{ Se}^{2-}) = 1 \text{ Se}^{2-}$$

#### **Think About It**

We can also imagine the rock salt structure as two interpenetrating fcc lattices, and the cesium chloride structure as two interpenetrating simple cubic lattices.

## 12.66. Collect and Organize

We are asked to identify the differences between the rock salt form of ZnS and the sphalerite form and explain how both structures are consistent with the stoichiometry of ZnS.

#### Analyze

Both the rock salt and sphalerite forms of ZnS have an fcc unit cell of  $S^{2-}$  ions. They differ only in which holes are occupied in the unit cell, namely, octahedral or tetrahedral, respectively. We can compare the ratio of ions in each structure.

## Solve

- (a) The rock salt ( $\alpha$ ) form of ZnS has an fcc arrangement of S<sup>2-</sup> ions with *all* of the four *octahedral* holes in the unit cell occupied by Zn<sup>2+</sup>. The sphalerite ( $\beta$ ) form of ZnS also has an fcc arrangement of S<sup>2-</sup> ions, but with half of the eight *tetrahedral* holes in the unit cell occupied by Zn<sup>2+</sup>.
- (b) Both structures support the same ratio of Zn to S.
- For the rock salt structure, the ratio is  $Zn_4S_4$ , or ZnS:

$$\frac{1}{4} (12 \ Zn^{2+}) + 1 \ Zn^{2+} = 4 \ Zn^{2+}$$
$$\frac{1}{8} (8 \ S^{2-}) + \frac{1}{2} (6 \ S^{2-}) = 4 \ S^{2-}$$

For the sphalerite structure, the ratio is  $Zn_4S_4$ , or ZnS:

$$4 \operatorname{Zn}^{2+} = 4 \operatorname{Zn}^{2+}$$
$$\frac{1}{8} \left( 8 \operatorname{S}^{2-} \right) + \frac{1}{2} \left( 6 \operatorname{S}^{2-} \right) = 4 \operatorname{S}^{2-}$$

## Think About It

The  $Zn^{2+}$  ions move from the tetrahedral holes to the larger octahedral holes under high pressure.

#### 12.67. Collect and Organize

Knowing the structure of the unit cell of  $\text{ReO}_3$  and the radii of Re and O atoms (given as 137 pm and 73 pm, respectively), we are asked to calculate the density of  $\text{ReO}_3$ .

#### Analyze

Given that there are Re atoms at each corner of the cubic unit cell, there is  $(8' \frac{1}{8})$ , or 1 Re atom, in the unit cell. Likewise, given that there are 12 edge O atoms, there are  $(12' \frac{1}{4}) = 3$  O atoms in the unit cell. We are told that the atoms touch (Re–O–Re) along an edge of the unit cell, so the cell edge length is

To calculate the density of ReO<sub>3</sub> we use

$$d = \frac{\text{mass of atoms in unit cell}}{\text{volume of unit cell}}$$

The mass, m, of atoms in a unit cell of ReO<sub>3</sub> is

$$m = \frac{1 \operatorname{Re atom'} \frac{186.21 \text{ g}}{\text{mol}} + 3 \text{ O atoms'} \frac{15.999 \text{ g}}{\text{mol}}}{6.022' \text{ 10}^{23} \text{ atoms/mol}} = 3.889' \text{ 10}^{-22} \text{ g}$$

The volume, V, of the unit cell (in cm<sup>3</sup>) is

$$V = \overset{\text{av}}{\underbrace{\text{b}}} 420 \text{ pm}' \frac{1' \ 10^{-10} \text{ cm}}{1 \text{ pm}} \overset{\text{o}}{\frac{1}{5}} = 7.409' \ 10^{-23} \text{ cm}^3$$

The density, d, of the solid is then

$$d = \frac{3.889' \ 10^{-22} \ g}{7.409' \ 10^{-23} \ \text{cm}^3} = 5.25 \ \text{g/cm}^3$$

#### Think About It

Remember that this is a calculated, or theoretical, density. The actual density, even if the structure is correctly described, may differ slightly from the theoretical value.

# 12.68. Collect and Organize

CsCl crystallizes in a bcc unit cell with an edge length of 412 pm (Figure P12.55). Knowing this along with the molar mass of CsCl, we can calculate the density of the CsCl crystal.

#### Analyze

Density is mass per volume. The volume of the unit cell is the cube of the edge length  $(\ell^3)$ . This we should express in units of cubic centimeters for writing the density (in g/cm<sup>3</sup>). The mass of the atoms in the unit cell is the mass of one Cs<sup>+</sup> ion and one Cl<sup>-</sup> ion. We have to express mass in terms of grams per atom, converting from grams per mole.

## Solve

Volume of a unit cell = 
$$\underbrace{\tilde{g}}_{4}^{2}$$
 412 pm'  $\frac{1' \ 10^{-10} \ \text{cm}}{1 \ \text{pm}} \frac{\tilde{g}}{\frac{1}{3}}^{2}$  = 6.993'  $10^{-23} \ \text{cm}^{3}$   
Mass of a unit cell =  $\underbrace{\tilde{g}}_{4}^{2} \frac{32.905 \ \text{g Cs}}{1 \ \text{mol}}$  +  $\frac{35.453 \ \text{g Cl}\ddot{g}}{1 \ \text{mol}} \frac{1 \ \text{mol}}{\frac{1}{3}}$  = 2.7957'  $10^{-22} \ \text{g}$   
Density =  $\frac{2.7957' \ 10^{-22} \ \text{g}}{6.993' \ 10^{-23} \ \text{cm}^{3}}$  = 4.00 g/cm<sup>3</sup>

#### Think About It

Remember that a body-centered cubic structure contains a total of two atoms. For CsCl, the unit cell contains just one  $Cl^-$  and one  $Cs^+$ .

#### 12.69. Collect and Organize

Given the structure (rock salt) and density (3.60 g/cm<sup>3</sup>) of MgO, we are asked to calculate the length of the edge of the unit cell ( $\ell$ ).

## Analyze

The volume of the unit cell is simply  $\ell^3$ . From the density we can calculate the volume, V, as

$$V = \frac{\text{mass of unit cell}}{1}$$

density

From the volume of the cubic unit cell, where the lengths of all the edges are equal, we can calculate the edge length:

Edge length = 
$$\sqrt[3]{volume}$$

In the fcc unit cell there are four Mg atoms and four O atoms to give a mass, m, of

$$m = \frac{4 \text{ Mg atoms'}}{\frac{24.305 \text{ g}}{\text{mol}} + 4 \text{ O atoms'}} \frac{15.999 \text{ g}}{\text{mol}}}{\frac{15.999 \text{ g}}{\text{mol}}} = 2.677' \text{ 10}^{-22} \text{ g}$$

Solve

Volume = 
$$\frac{2.677' \ 10^{-22} \ g}{3.60 \ g/cm^3}$$
 = 7.436'  $10^{-23} \ cm^3$   
 $\ell = \sqrt[3]{\text{volume}} = \sqrt[3]{7.436' \ 10^{-23} \ cm^3}$  = 4.21'  $10^{-8} \ cm \text{ or } 421 \ pm$ 

#### Think About It

This value seems reasonable. The radius of an oxygen atom is 73 pm, and that of a manganese atom is 127 pm (Appendix 3). Assuming that the O–Mn–O atoms touch along the fcc unit edge length (a good first approximation), the edge length would be

$$73 + 127 + 127 + 73 = 400 \text{ pm}$$

## 12.70. Collect and Organize

Given the crystalline structure of KBr (rock salt, which is fcc in  $Cl^-$  with Na<sup>+</sup> in all of the octahedral holes) and its density (2.75 g/cm<sup>3</sup>), we can calculate the length of an edge of the unit cell.

## Analyze

The rock salt structure for KBr means that there are four  $Br^-$  ions and four  $K^+$  ions in the unit cell. From the density and the mass of the atoms in the unit cell, we can calculate the volume of the unit cell:

Volume = 
$$\frac{\text{mass}}{\text{density}}$$

From the volume of the cubic unit cell, where the lengths of all the edges are equal, we can calculate the edge length:

Edge length =  $\sqrt[3]{\text{volume}}$ 

The edge length should be expressed in picometers.

## Solve

Mass of the unit cell = 
$$\oint_{\mathbf{e}} 4'$$
  $\frac{39.098 \text{ g}}{\text{mol}} \frac{\ddot{\mathbf{p}}}{\ddot{\mathbf{p}}} + \oint_{\mathbf{e}} 4'$   $\frac{79.904 \text{ g}}{\text{mol}} \frac{\ddot{\mathbf{p}}}{\ddot{\mathbf{p}}} + \frac{1 \text{ mol}}{6.022' \cdot 10^{23}} = 7.9045' \cdot 10^{-22} \text{ g}$   
Volume =  $\frac{7.9045' \cdot 10^{-22} \text{ g}}{2.75 \text{ g/cm}^3} = 2.8743' \cdot 10^{-22} \text{ cm}^3$   
Edge length =  $\sqrt[3]{2.8743' \cdot 10^{-22} \text{ cm}^3} = 6.60' \cdot 10^{-8} \text{ cm}$   
Edge length in picometers =  $6.60' \cdot 10^{-8} \text{ cm}' \cdot \frac{1 \text{ pm}}{1' \cdot 10^{-10} \text{ cm}} = 660 \text{ pm}$ 

# Think About It

We can calculate the Br<sup>-</sup> radius from this now. For an fcc crystal,  $4r = \ell\sqrt{2} = 660$  pm  $\sqrt{2} = 933$  pm. The radius of Br<sup>-</sup> in this crystal is then 933 pm/4 = 233 pm.

## 12.71. Collect and Organize

To answer why black phosphorus has puckered rings when graphite has planar rings, we need to consider the hybridization of the phosphorus and carbon atoms that make up these two substances.

## Analyze

In both substances, the atoms are each bound to two other atoms. The phosphorus atom brings five valence electrons to its structure, but carbon brings only four to its structure.

## Solve

The hybridization of the phosphorus atom in black phosphorus is  $sp^3$  with bond angles of 102° to give a puckered ring. In graphite, the carbon atoms are  $sp^2$  hybridized with bond angles of 120°, which gives graphite a flat geometry.

## **Think About It**

Graphite carbon atoms also  $\pi$ -bond to each other since they each have an electron in the unhybridized p orbital.

## 12.72. Collect and Organize

We are to consider whether the structure of the molecule that would result if the C atoms in graphite were replaced by alternating B and N atoms would be planar or puckered (refer to Figure P12.71).

## Analyze

Boron has three valence electrons and nitrogen has five. Boron and nitrogen are each replacing carbon atoms in graphite (Figure P12.71). Each carbon atom had brought four valence electrons to the original structure.

## Solve

In order to pucker the ring, lone pairs would have to be introduced onto the atoms in the structure. Because B and N with eight total valence electrons replace two C atoms, also with eight valence electrons, the ring of BN atoms remains flat.

# **Think About It**

BN is boron nitride, a very tough, hard, high-temperature ceramic material.

## 12.73. Collect and Organize

We can use the edge length of the fcc lattice of  $C_{60}$  to calculate the density of buckminsterfullerene and the radius of a  $C_{60}$  molecule.

## Analyze

The mass of the unit cell may be calculated by multiplying the molar mass of C<sub>60</sub> (720.66 g/mol) by the four atoms in an fcc unit cell and dividing by Avogadro's number. We may determine the volume of the unit cell by cubing the edge length (1410 pm). The density is equal to the mass divided by the volume of the unit cell. Using the relationship  $r = 0.3536 \ell$ , we may calculate the radius of the C<sub>60</sub> molecule.

$$4 C_{60} \text{ molecules'} \frac{1 \text{ mol } C_{60}}{6.022' \ 10^{23} \text{ } C_{60} \text{ molecules'}} \frac{720.66 \text{ g } \text{ } C_{60}}{1 \text{ mol } \text{ } C_{60}} = 4.7868' \ 10^{-21} \text{ g}$$

$$\text{Volume} = \bigotimes_{e}^{\infty} 1410 \text{ pm'} \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm}} \frac{100 \text{ cm}}{1 \text{ m}} \frac{\overset{3}{2}}{\overset{3}{\cancel{6}}} = 2.8032' \ 10^{-21} \text{ cm}^{3}$$

$$d = \frac{4.7868' \ 10^{-21} \text{ g}}{2.8032' \ 10^{-21} \text{ cm}^{3}} = 1.708 \text{ g/cm}^{3}$$

(b) The radius of the  $C_{60}$  molecules is r = 0.3536(1410 pm) = 498.6 pm.

## Think About It

The  $C_{60}$  molecule has a radius that is roughly five to six times that of most ions or atoms, though the density is similar to that observed for the other allotropes of carbon, graphite and diamond.

## 12.74. Collect and Organize

We can use the radii of  $C_{60}$  and  $K^+$  to determine the type of hole the  $K^+$  ions are likely to occupy in  $K_3C_{60}$ . We can also calculate the density of  $K_6C_{60}$ , which occupies an fcc lattice.

## Analyze

- (a) The ratio of nonhost (K<sup>+</sup>, 138 pm) to host (C<sub>60</sub>, 498.6 pm) radii may be calculated to determine if K<sup>+</sup> will occupy a tetrahedral ( $r_{nonhost}/r_{host} = 0.22 0.41$ ) or an octahedral hole ( $r_{nonhost}/r_{host} = 0.41 0.73$ ). The fcc lattice contains four octahedral holes and eight tetrahedral holes, three of which are occupied in K<sub>3</sub>C<sub>60</sub>.
- (b) The mass of the unit cell may be calculated by multiplying the molar mass of  $C_{60}$  (720.66 g/mol) by the two atoms in a bcc unit cell, dividing by Avogadro's number, then adding the mass of the six K<sup>+</sup> ions. The edge length of the unit cell may be determined using the relationship  $r = 0.4330 \ \ell$ . We may determine the volume of the unit cell by cubing the edge length. The density is equal to the mass divided by the volume of the unit cell.

#### Solve

(a) The radius ratio for  $K_3C_{60}$  is

$$\frac{r_{\rm nonhost}}{r_{\rm host}} = \frac{138 \text{ pm}}{498.6 \text{ pm}} = 0.28$$

This ratio fits nicely in the range expected for a guest occupying tetrahedral holes. Three of the eight tetrahedral holes are occupied by  $K^+$  ions.

(b)

$$2 C_{60} \text{ molecules'} \frac{1 \text{ mol } C_{60}}{6.022' 10^{23} \text{ C}_{60} \text{ molecules'}} \frac{720.66 \text{ g } \text{ C}_{60}}{1 \text{ mol } \text{ C}_{60}} = 2.3934' 10^{-21} \text{ g}$$

$$12 \text{ K}^{+} \text{ ions'} \frac{1 \text{ mol } \text{ K}^{+}}{6.022' 10^{23} \text{ K}^{+} \text{ ions'}} \frac{39.0983 \text{ g } \text{ K}^{+}}{1 \text{ mol } \text{ K}^{+}} = 7.791' 10^{-22} \text{ g}$$

$$m = 2.3934' 10^{-21} \text{ g} + 7.791' 10^{-22} \text{ g} = 3.1725' 10^{-21} \text{ g}$$

$$\ell = \frac{498.6 \text{ pm}}{0.4330} = 1151.5 \text{ pm'} \frac{1 \text{ m}}{1' 10^{12} \text{ pm'}} \frac{100 \text{ cm}}{1 \text{ m}} = 1.1515' 10^{-21} \text{ cm}$$

$$Volume = (1.1515' 10^{-21} \text{ cm})^{3} = 1.5268' 10^{-21} \text{ cm}^{3}$$

$$d = \frac{3.1725' 10^{-21} \text{ g}}{1.5268' 10^{-21} \text{ cm}^{3}} = 2.078 \text{ g/cm}^{3}$$

## **Think About It**

The density of  $K_6C_{60}$  is higher than that of  $C_{60}$  (calculated in Problem 12.73), as we would expect after adding a metal ion.

#### 12.75. Collect and Organize

Knowing the distance between the phosphorus atoms in its cubic form, we are to calculate the density.

#### Analyze

Density is mass per unit volume. The mass of phosphorus in one unit cell will be the number of atoms of P in one unit cell multiplied by the molar mass of P and divided by Avogadro's number. The volume of the unit cell is the cube of the length of the side of the unit cell. Density is usually expressed as grams per cubic centimeter ( $g/cm^3$ ), so we have to convert picometers to centimeters.

#### Solve

Mass of phosphorus in one unit cell:

$$8(\frac{1}{8} \text{ atoms})' \frac{1 \text{ mol}}{6.022' \ 10^{23} \text{ atoms}}' \frac{30.97 \text{ g}}{1 \text{ mol}} = 5.143' \ 10^{-23} \text{ g}$$

Volume of the unit cell:

$$\overset{\text{a}}{\underbrace{\$}}_{2}^{2} 38 \text{ pm}' \frac{1' \ 10^{-10} \text{ cm}}{1 \text{ pm}} \frac{\overset{\text{b}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}}}}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}{\overset{\text{c}}}}} = 1.35' \ 10^{-23} \text{ cm}^{3}$$

Density of cubic phosphorus:

$$\frac{5.143' \ 10^{-23} \ g}{1.35' \ 10^{-23} \ cm^3} = 3.81 \ g/cm^3$$

#### **Think About It**

The density of phosphorus in another form would be different. If we measure the density of a crystal of known composition, we may be able to determine what its unit cell looks like.

## 12.76. Collect and Organize

For the imaginary form of ice nine where the O atoms are ccp, we are to determine which holes the H atoms would occupy.

#### Analyze

The ccp (fcc) structure of O atoms will give four atoms per unit cell. This fcc arrangement contains eight tetrahedral holes and four octahedral holes.

## Solve

The ratio of O to H in the ice is 1:2, so the unit cell must contain eight H atoms along with four O atoms. The H atoms must then be small enough to fit into at least some of the tetrahedral holes. If H occupies all of the tetrahedral holes, the 1:2 ratio of O to H is preserved for ice.

#### Think About It

By the radius ratio rule

 $\frac{r_{\rm H}}{r_{\rm O}} = \frac{37 \text{ pm}}{73 \text{ pm}} = 0.51$ 

we expect the octahedral holes to be occupied. However, without also placing H into tetrahedral holes, the 1:2 ratio of O to H for the ice could not be preserved.

# 12.77. Collect and Organize

We are asked whether it is possible to make a polymer that consists of more than one type of monomer.

## Analyze

Polymers are generated when monomers react, typically in an addition or condensation process. Monomers must have appropriate functional groups to react with one another in a polymerization reaction, such as the double bond of an olefin required to generate a polyolefin:



# Solve

A different monomer with the same functional group (the alkene) but a different substituent (the black or white circles) may be employed to form a polymer.



# Think About It

The polymer depicted above is known as a block copolymer. Other architectures are possible, such as random arrangements of different monomers or several discrete blocks.

## 12.78. Collect and Organize

We are to compare a polyethylene chain with the saturated hydrocarbon with the chemical formula  $C_{24}H_{50}$ .

## Analyze

Polyethylene is generated by the addition of ethylene monomer units to form a saturated hydrocarbon chain with the repeating formula  $[C_2H_4]_n$ . The hydrocarbon  $C_{24}H_{50}$  would contain approximately 12 monomer units. The predominant intermolecular forces for a hydrocarbon are London dispersion forces.

## Solve

Both the polymer and  $C_{24}H_{50}$  are saturated hydrocarbons that would be expected to exhibit London dispersion forces. While the  $C_{24}H_{50}$  chain is quite small (~12 monomer units), most polyethylene chains would be hundreds or thousands of monomer units in length. While each polymer chain is likely to have a slightly different molecular weight, a pure sample of  $C_{24}H_{50}$  would all have the same molecular weight.

## **Think About It**

The statements above will still be true regardless of the molecular weight or degree of branching of the polyethylene polymer. These things would change the melting temperature and material properties of the polymer, but not the fundamental differences between a polymer and a discrete molecular compound.

#### 12.79. Collect and Organize

We are asked to determine how many  $C_2H_4$  monomer units are contained in a polyethylene polymer with an average molecular weight of 100,000 g/mol.

#### Analyze

Each  $C_2H_4$  monomer has a molecular weight of 28.06 g/mol. Assuming each polymer strand has a molecular weight of 100,000 g/mol, the ratio of these two molecular weights should tell us the number of monomer units:

number of monomer units = 
$$\frac{MW_{polymer}}{MW_{monomer}}$$

Solve

$$\frac{100,000 \text{ g/mol}}{28.06 \text{ g/mol}} = 3564 \text{ monomer units}$$

#### Think About It

Another way to describe the mathematical relationship between monomer and polymer molecular weights is  $MW_{polymer} = number of monomer units' MW_{monomer}$ 

# 12.80. Collect and Organize

We are asked to determine how many  $C_4H_6$  monomer units are contained in a polyethylene polymer with an average molecular weight of 100,000 g/mol.

#### Analyze

Each  $C_4H_6$  monomer has a molecular weight of 54.10 g/mol. Assuming each polymer strand has a molecular weight of 100,000 g/mol, the ratio of these two molecular weights should tell us the number of monomer units.

number of monomer units = 
$$\frac{MW_{polymer}}{MW_{monomer}}$$

Solve

$$\frac{100,000 \text{ g/mol}}{54.10 \text{ g/mol}} = 1848 \text{ monomer units}$$

## **Think About It**

It is difficult to estimate our certainty in the number of monomer units given an average molecular weight for the polymer of 100,000. This figure could have six significant figures (i.e.,  $1.00000 \times 10^5$  g/mol), though one or two significant figures (i.e.,  $1. \times 10^5$  g/mol or  $1.0 \times 10^5$  g/mol) is more likely. Our answer should have the same number of significant figures as the polymer molecular weight.

#### 12.81. Collect and Organize

From the carbon-skeleton structure of vinyl acetate (Figure P12.81), we are to draw the structure of poly(vinyl acetate).

#### Analyze

Poly(vinyl acetate) is an addition polymer in which the C = C double bonds link together to form the polymer backbone. In this polymer the acetate group is a side chain off the polymer chain.



# Think About It

Because of its flexibility, poly(vinyl acetate), or PVA, is used in bookbinding and, as an emulsion in water, as an adhesive for wood, paper, and cloth.

# 12.82. Collect and Organize

For the polymer of acetylene, HC==CH, we are asked to draw the molecular structure of three monomeric units of this addition polymer and describe the two stereoisomeric forms of the polymer.

# Analyze

We are given that polyacetylene is an addition polymer. In the text we saw that ethylene forms polyethylene through the addition reaction

$$n \operatorname{H}_2 \operatorname{C}=\operatorname{CH}_2 \longrightarrow - \operatorname{CH}_2 - \operatorname{CH}_2 \xrightarrow{]_n}$$

We can use this reaction to model the monomeric units of polyacetylene. Because polyacetylene has double bonds in its structure, cis-trans isomerism is possible along the polymer chain.

## Solve

(a) Three monomeric units of polyacetylene would be

$$-\left[CH=CH-CH=CH-CH=CH\right]_{n}$$

(b) The cis form of polyacetylene is

The trans form of polyacetylene is



# **Think About It**

As prepared, a film of polyacetylene is nonconductive, but when oxidized with  $I_2$ , polyacetylene can conduct electricity as well as silver metal.

# 12.83. Collect and Organize

Given the structure of a glyceride, we can draw the structures of the alcohol and fatty acids that may be obtained by saponification in the presence of a base.

# Analyze

Saponification cleaves the ester bond, forming an alcohol and an acid with the same number of carbon atoms and functional groups.



Saponification will generate three equivalents of dodecanoic acid and one equivalent of glycerol.

#### Think About It

Glycerol is also a by-product of biodiesel formation, which is also generated in the presence of a strong base such as NaOH.

#### 12.84. Collect and Organize

For each of the polymers shown in Figure P12.84, which were synthesized through the condensation reaction of  $H_2N(CH_2)_6NH_2$  with  $HO_2C(CH_2)_nCO_2H$ , we are asked to determine the number of carbon atoms in the chain (*n*) of the dicarboxylic acids used.

#### Analyze

The number of carbon atoms in the chain equals the value of n, which is the number of  $-(CH_2)$ - units in the chain of the dicarboxylic acid.

#### Solve

(a) 4

- (b) 6
- (c) 8

#### **Think About It**

Because *n* is defined in the problem as the number of carbon atoms in the dicarboxylic acid formula  $HO_2C(CH_2)_nCO_2H$ , we do not count the carboxylic acid carbon atoms.

## 12.85. Collect and Organize

For the two polymers shown in Figure P12.85, we are to write the formulas of the monomers that would react to form each and then consider how the physical properties of the two polymers might differ.

#### Analyze

- (a) Both polymers can be produced in a condensation reaction between a difunctional carboxylic acid and a difunctional amine.
- (b) The difference between the two polymers lies in the lengths of the polymer chains between the two N—H bonds or the two C==O bonds along the chain.

#### Solve

(a) Polymer I monomers are

Polymer II monomers are  

$$H_2N(CH_2)_8NH_2$$
 and  $HOC(CH_2)_8COH$   
 $H_2N(CH_2)_6NH_2$  and  $HOC(CH_2)_{10}COH$ 

(b) Because of the longer chain length between C=O bonds in Polymer II, we might expect that this polymer would be more flexible along that portion of the polymer chain.

# Think About It

Water is produced in the condensation reactions to form these polymers.

# 12.86. Collect and Organize

Given the reaction between dimethyl terephthalate and 1,4-di(hydroxymethyl)cyclohexane to form Kodel (Figure P12.86), we are asked to classify the reaction as either a condensation or addition reaction, give the other product of the reaction, and compare the properties of Kodel to those of Dacron, which is prepared using ethylene glycol.

# Analyze

- (a) In addition polymerization reactions, the atoms are joined in the monomers to form the polymeric backbone without loss of atoms. In condensation polymerization reactions, the two monomers react to form the polymeric backbone and a small molecule, like water.
- (b) The structure of ethylene glycol is



# Solve

- (a) Kodel is a condensation polymer. Methanol (CH<sub>3</sub>OH) is the by-product of the polymerization reaction.
- (b) Kodel has a carbon six-membered ring in its backbone, not a straight chain as in Dacron. Therefore, Kodel might be better able to accept organic dyes, which are nonpolar.

# Think About It

Kodel, being fairly polar because of the saturated six-membered carbon ring, is fairly resistant to water and has been used to make clothing.

# 12.87. Collect and Organize

From the reaction shown in Figure P12.87 for the formation of Lexan, we are to determine the other reaction product and describe why Lexan is called a polycarbonate.

# Analyze

The reaction to form Lexan looks like a condensation reaction, so we expect that a small molecule was eliminated in the reaction. A carbonate group is  $CO_3^{2^-}$ .

# Solve

- (a) Because HCl is eliminated in the reaction, the -OCOO- linkage in the polymer is obtained.
- (b) The CO<sub>3</sub> or –OCOO– linkage gives the term *polycarbonate* to Lexan.

# Think About It

Polycarbonates are a group of thermoplastics, which have found uses in signs, computer casings, and compact discs.

# 12.88. Collect and Organize

We are asked about the structure and biodegradability of poly(caprolactone), PCL.

# Analyze

Solubility follows the "like dissolves like" rule, in which compounds with similar intermolecular forces will form a solution. Both PCL and levonorgestrel are polar, and levonorgestrel contains an OH group capable of hydrogen bonding. A condensation polymer is formed when monomer units bond and release a molecule, while an addition polymer is formed without the release of any atoms or molecules. Reaction of a condensation polymer with water would regenerate the monomer, degrading the polymer.

- (a) Levonorgestrel is capable of forming a hydrogen bond between the OH group and the carbonyl group of poly(caprolactone). This strong attraction makes levonorgestrel soluble in PCL.
- (b) Hydrolysis of the ester in PCL generates 6-hydroxyhexanoic acid:



(c) As the name suggests, PCL is formed when caprolactone, a cyclic ester monomer, reacts with a growing polymer chain. PCL is thus an addition polymer.



#### Think About It

Though it is possible to imagine PCL formation by condensation of 6-hydroxyhexanoic acid, this reaction is quite slow and produces PCL of low molecular weight and poor quality.

#### 12.89. Collect and Organize

For a unit cell with X at the eight corners of the cubic unit cell, Y at the center of the cube, and Z at the center of each face, we are to write the formula of the compound.

#### Analyze

Each atom at the corner of a cube counts as one-eighth in the unit cell. Each atom on a face counts as one-half in the unit cell. Each atom in the center of the unit cell counts as one.

## Solve

Element X =  $\frac{1}{8} \times 8 = 1$  X Element Y = 1 × 1 = 1 Y Element Z = 6 ×  $\frac{1}{2}$  = 3 Z

The formula for the compound is XYZ<sub>3</sub>.

## Think About It

An example of this kind of structure is perovskite, CaTiO<sub>3</sub>.

## 12.90. Collect and Organize

Given that a uranium oxide packs into a ccp structure and the oxide ions are located in all of the tetrahedral holes, we are to write the formula for this  $U_x O_y$  salt.

## Analyze

The unit cell for the ccp structure is the face-centered cube. This unit cell would contain four uranium atoms with eight tetrahedral holes.

If all of the tetrahedral holes are filled, then there are eight  $O^{2^-}$  ions in the unit cells. This gives four U and eight O atoms in the unit cell for a formula of  $UO_2$ .

# Think About It

The oxidation number of uranium in this oxide is +4.

## 12.91. Collect and Organize

Given the phase diagram for titanium, we can identify the predominant phase under specific conditions and track phase changes as the pressure increases at a constant temperature.

## Analyze

- (a) We may identify the phase at 1500 K and 6 GPa by drawing lines from these points along the x and y axes and observing the phase where the lines intersect.
- (b) We may track phase changes at a temperature of 725°C (998 K) by drawing a vertical line from this point along the *x*-axis and observing how many phase boundary lines it crosses.



# Solve

- (a) At 1500 K and 6 GPa, titanium is present in the bcc ( $\beta$ ) phase.
- (b) Titanium undergoes two phase changes as we increase pressure. The transitions are hcp ( $\alpha$ )  $\rightarrow$  bcc ( $\beta$ ) around 6 GPa, and bcc ( $\beta$ )  $\rightarrow$  hex (3,  $\omega$ ) around 11 GPa.

## Think About It

Don't forget to check the units on your temperature. If you had looked for phase transitions as we increase the pressure at 725 K, you would have discovered only one.

## 12.92. Collect and Organize

Given the phase diagram for thallium, we may determine the temperature and pressure where all three solid phases (fcc, bcc, and hcp) are present and determine whether the melting point increases, decreases, or stays constant as pressure increases.

#### Analyze

The phase boundaries will all intersect where all three solid phases of thallium are present. Drawing horizontal and vertical lines from this point to the axes will allow us to read the temperature and pressure at which these phases are all present. The behavior of the melting point may be determined by following the phase boundary line separating the bcc and liquid phases.



#### Solve

- (a) All three solid phases of thallium are present at approximately 390 K and 3.8 GPa.
- (b) The melting point will increase as the pressure increases (slope is positive).

#### Think About It

The positive slope of the solid/liquid phase boundary line indicates that, like most species, the density of solid thallium is greater than that of the liquid phase.

#### 12.93. Collect and Organize

We consider cubic nanoparticles of Ag (25 nm on each side) and are asked to calculate the number of unit cells in a particle, the number of Ag atoms in a particle, and the number of silver atoms present in 1360  $\mu$ g of silver nanoparticles.

#### Analyze

- (a) We are given that the unit cells are face-centered cubic. In this arrangement the unit-cell edge length (ℓ) is 4r/√2 where r is the radius of the silver atom. From Appendix 3, the radius of a silver atom is 144 pm. Dividing the side length of a nanoparticle by the edge length of the unit cell, we may determine the number of unit cells along an edge of the nanoparticle; we may determine the number of unit cells per particle by cubing this value.
- (b) The number of atoms in the nanoparticle may be found by multiplying the number of unit cells per particle, determined in (a), by four Ag particles per bcc unit cell.
- (c) Converting the mass of silver to grams, dividing by the molar mass of Ag (107.8682 g/mol), multiplying by Avogadro's number, and dividing by the ratio of silver atoms per nanoparticle determined in (b) will furnish the number of nanoparticles in a sock.

#### Solve

(a) The edge length of a silver unit cell is

$$\ell = \frac{144 \text{ pm}}{0.3536}, \frac{1 \text{ nm}}{1000 \text{ pm}} = 0.4072 \text{ nm}$$

The number of unit cells in a nanoparticle edge is

$$\frac{25 \text{ nm}}{0.4072 \text{ nm}} = 61.4 \text{ unit cells per edge}$$

(b) An edge may not contain a fraction of a unit cell, so we must round down. Cubing this edge length gives  $(61)^3 = 2.3 \times 10^5$  unit cells per particle. The number of Ag atoms in a nanoparticle is

$$\frac{2.3' \ 10^5 \ unit \ cells}{nanoparticle}, \ \frac{4 \ Ag \ atoms}{1 \ unit \ cell} = 9.1' \ 10^5 \ Ag \ atoms$$

(c) The number of nanoparticles in one sock is

1360 µg Ag' 
$$\frac{1 \text{ g Ag}}{1' 10^6 \text{ µg Ag}}$$
,  $\frac{1 \text{ mol Ag}}{107.8682 \text{ g Ag}}$ ,  $\frac{6.022' 10^{23} \text{ atoms Ag}}{1 \text{ mol Ag}}$ ,  $\frac{1 \text{ nanoparticle}}{9.1' 10^5 \text{ Ag atoms}} = 8.4' 10^{12} \text{ nanoparticles}$ 

#### **Think About It**

Even though nanoparticles are very small, they still contain thousands of Ag atoms.

#### 12.94. Collect and Organize

Given the dimensions of a gold "nanorod" (a cylinder), we may determine the number of gold atoms in a nanorod, the number of unit cells in a nanorod, and the mass of a nanorod.

#### Analyze

Gold crystallizes in an fcc unit cell.



(a) and (b) We may determine the volume of the cylinder  $(V = \pi r^2 h)$  given the diameter (32 nm) and height (67 nm). The volume of the unit cell may be determined using the radius of the gold atom (144 pm) and the relationship  $r = 0.3536 \ell$ . By cubing the edge length, we may determine the volume of the gold unit cell. Dividing the volume of the nanorod by the volume of the unit cell, we may determine the number of unit cells in a nanorod. In an fcc lattice, there are four atoms in a unit cell, so the number of gold atoms in a nanorod is four times the number of unit cells in a nanorod.

(c) The mass of each nanorod is equal to the number of gold atoms in a nanorod as determined in (a), divided by Avogadro's number, and multiplied by the molar mass of gold (196.9666 g/mol).

#### Solve

(a) Volume of the nanorod:

$$V = \pi \underbrace{\frac{\overset{\circ}{8}}{\overset{\circ}{8}} 32 \text{ nm}'}_{\overset{\circ}{8}} \frac{100 \text{ cm}}{1' \text{ 10}^9 \text{ nm}} \underbrace{\overset{\circ}{\overset{\circ}{3}}}{\overset{\circ}{3}}_{\overset{\circ}{3}} \underset{\overset{\circ}{8}}{\overset{\circ}{8}} 67 \text{ nm}' \frac{100 \text{ cm}}{1' \text{ 10}^9 \text{ nm}} \underbrace{\overset{\circ}{\overset{\circ}{3}}}{\overset{\circ}{3}}_{\overset{\circ}{3}} = 5.388' \text{ 10}^{-17} \text{ cm}^3$$

Volume of the unit cell:

$$r = 144 \text{ pm'} \frac{1 \text{ m}}{1' \ 10^{12} \text{ pm'}} \frac{100 \text{ cm}}{1 \text{ m}} = 1.44' \ 10^{-8} \text{ cm}$$
$$\ell = \frac{1.44' \ 10^{-8} \text{ cm}}{0.3536} = 4.072' \ 10^{-8} \text{ cm}$$
$$V = (4.072' \ 10^{-8} \text{ cm})^3 = 6.754' \ 10^{-23} \text{ cm}^3$$

The number of unit cells in a nanorod is

$$\frac{V_{\text{nanorod}}}{V_{\text{unit cell}}} = \frac{5.388' \ 10^{-17} \ \text{cm}^3}{6.754' \ 10^{-23} \ \text{cm}^3} = 7.98' \ 10^5 \ \text{unit cells/nanorod}$$

The number of gold atoms in a nanorod is

$$\frac{7.98' \ 10^5 \ \text{unit cells}}{\text{nanorod}}, \ \frac{4 \ \text{Au atoms}}{1 \ \text{unit cell}} = 3.2' \ 10^6 \ \text{Au atoms}$$

- (b) There are  $7.9 \times 10^5$  unit cells in a gold nanorod.
- (c) The mass of each nanorod is

$$\frac{3.2' \ 10^{6} \ \text{Au atoms}}{\text{nanorod}}, \ \frac{196.9666 \ \text{Au atoms}}{1 \ \text{mol Au}}, \ \frac{1 \ \text{mol Au}}{6.022' \ 10^{23} \ \text{Au atoms}} = 1.0' \ 10^{-15} \ \text{g}$$

## **Think About It**

Although each nanorod is quite small, each one contains nearly one million unit cells!

## 12.95. Collect and Organize

We consider different possible crystal structures of Fe (radius 126 pm) and compare the densities of bcc and hcp iron and calculate the density of a crystal of 96% Fe and 4% Si.

#### Analyze

For each structure, the density is the mass of atoms in the unit cell divided by the volume of the cubic unit cell. For the bcc unit cell, there are two atoms per unit cell, and the edge length is  $\ell = 4r/\sqrt{3}$ . For the hcp unit cell, there are two atoms per unit cell.

#### Solve

(a) The edge length of a bcc unit cell is

$$\ell = \frac{4r}{\sqrt{3}} = \frac{4'\ 126\ \text{pm}}{\sqrt{3}} = 291.0\ \text{pm or } 2.91'\ 10^{-8}\ \text{cm}$$

The volume of the unit cell is

$$V = (291.0' \ 10^{-8} \ \text{cm})^3 = 2.464' \ 10^{-23} \ \text{cm}^3$$

The mass of the unit cell is

2 atoms Fe' 
$$\frac{55.85 \text{ g}}{\text{mol}}$$
,  $\frac{1 \text{ mol}}{6.022' \text{ 10}^{23} \text{ atoms}} = 1.855' \text{ 10}^{-22} \text{ g}$ 

The density is

$$d = \frac{1.855' \ 10^{-22} \ g}{2.464' \ 10^{-23} \ cm^3} = 7.53 \ g/cm^3$$

(b) In the hcp unit cell there are also two atoms in the unit cell. We are given that the volume of the unit cell is  $5.414 \times 10^{-23}$  cm<sup>3</sup>, so the density is

$$d = \frac{1.855' \ 10^{-22} \ g}{5.414' \ 10^{-23} \ cm^3} = 3.42 \ g/cm^3$$

(c) If 4% of the mass is due to Si replacing Fe, the molar mass of the alloy would be

$$0.04' \frac{28.09 \text{ g}}{\text{mol}} + 0.96' \frac{55.85 \text{ g}}{\text{mol}} = 54.74 \text{ g/mol}$$

The mass of two atoms in the unit cell would be

2 atoms' 
$$\frac{54.74 \text{ g}}{\text{mol}}$$
,  $\frac{1 \text{ mol}}{6.022' \text{ 10}^{23} \text{ atoms}} = 1.818' \text{ 10}^{-22} \text{ g}$ 

The density is

$$d = \frac{1.818' \ 10^{-22} \ g}{5.414' \ 10^{-23} \ \text{cm}^3} = 3.36 \ \text{g/cm}^3$$

#### Think About It

Replacing Fe with an element of lower molar mass (silicon) gives a lower-density alloy.

## 12.96. Collect and Organize

For MgSr, which crystallizes in the CsCl bcc structure, we are to calculate the density using the known value of the unit-cell edge length (390 pm).

#### Analyze

The bcc structure of MgSr contains one Mg atom and one Sr atom in the unit cell. From that information we can calculate the mass of the unit cell. For the volume of the unit cell, we need only to cube the given edge length.

## Solve

Mass of unit cell:

$$m = \underbrace{\overset{2}{\mathbf{g}}}_{\mathbf{mol}} \underbrace{\frac{24.305 \text{ g}}{\text{mol}}}_{\mathbf{mol}} + \frac{\underline{87.62 \text{ g}}}{\underline{6}} \underbrace{\frac{3}{6}}_{\mathbf{mol}} \underbrace{\frac{1 \text{ mol}}{6.022' \text{ 10}^{23}}}_{\mathbf{mol}} = 1.859' \text{ 10}^{-22} \text{ g}$$

Density:

$$d = \frac{1.859' \ 10^{-22} \ g}{\frac{a}{8}390 \ \text{pm}'} \frac{1' \ 10^{-10} \ \text{cm}}{\frac{\ddot{0}}{\dot{g}}} = 3.13 \ \text{g/cm}^3$$

## **Think About It**

The radii of Mg (160 pm) and Sr (215 pm) are close enough that it is reasonable to think that the Mg atoms would fit well into cubic holes in a lattice of Sr atoms (radius ratio = 0.744, which is just beyond the high end of the octahedral radius ratio range).

## 12.97. Collect and Organize

For the same crystalline structure of AuZn with  $\ell = 319$  and AgZn with  $\ell = 316$  pm, we can use the different molar masses of gold and silver and the length of the unit-cell edges to calculate the densities and predict which alloy is more dense.

#### Analyze

Because gold has a much higher molar mass than silver, we can easily predict that the density of the AuZn alloy would be greater than that of the AgZn alloy, despite the slightly smaller unit-cell edge length and therefore smaller volume.

For AuZn:

$$d = \frac{\left(262.38 \text{ g/mol}' \text{ 1 mol}/6.022' \text{ 10}^{23}\right)}{\left(3.19' \text{ 10}^{-8} \text{ cm}\right)^3} = 13.4 \text{ g/cm}^3$$

For AgZn:

$$d = \frac{(173.28 \text{ g/mol}' 1 \text{ mol}/6.022' 10^{23})}{(3.16' 10^{-8} \text{ cm})^3} = 9.12 \text{ g/cm}^3$$

The AuZn alloy is more dense than the AgZn alloy.

# Think About It

Indeed, the prediction was correct, and AuZn is substantially more dense than AgZn.

## 12.98. Collect and Organize

By consulting Figure P12.98, we are asked to determine the coordination number of the holes between close-packed layers and to determine if there are other types of holes in this structure.

## Analyze

The close-packed layers are stacked directly on top of one another, creating *aaaa*... layers. It is difficult to see the holes in Figure P12.98, but if we expand the view, separating the layers, it is easier to observe the number of nearest neighbors for each hole.



Holes are related in similar fashion to the atoms in a unit cell.

## Solve

From the figure, we see that each hole is directly adjacent to six spheres, so each has a coordination number of 6. All spheres in the unit cell are equivalent, so all holes are equivalent as well.

## Think About It

This is an unusual arrangement of close-packed layers. It is more common to find close-packed layers in an *ababab*... or *abcabc*... repeating pattern.

## 12.99. Collect and Organize

We are asked how Mn would incorporate into an iron lattice, either in the holes or as a substitute for iron.

#### Analyze

To occupy holes in the structure, Mn would have to have a distinctly smaller radius than the Fe radius. From Appendix 3, we find that the Mn radius is 127 pm and the Fe radius is 126 pm.

## Solve

The radii of these metals are very similar, so Mn likely forms a substitutional alloy with iron.

#### Think About It

The radius of carbon (77 pm) is small enough to fit into the interstices of the iron–manganese lattice. The radius ratio of carbon to iron (77/126) gives a value of 0.61. This indicates that carbon would fit into the octahedral holes of the iron lattice.

## 12.100. Collect and Organize

In considering alloys with aluminum, we are to decide whether the sizes of the atoms in each alloy indicate that the alloy would be substitutional, not interstitial. Additionally, we are to calculate the density of LiAl if it has a bcc structure.

#### Analyze

- (a) For an alloy to be substitutional, the two metals should crystallize in the same structures, and the sizes of the metal atoms should be within 15% of each other. For each of the alloys, we need to calculate the size ratio of the small atom in the alloy to the large atom in the alloy. If this ratio is 0.85 or greater, then the alloy would be predicted to be substitutional. We are given the radii of the atoms: AI = 143 pm, Li = 152 pm, Au = 144 pm, and Ti = 147 pm.
- (b) To calculate the density of the bcc LiAl alloy, we need to determine first the volume of the cube using the body diagonal to calculate the length of an edge of the unit cell:  $4r = \ell \sqrt{3}$  where

 $4r = 2 \times r_{\text{Li}}$  (at the center of the cube)  $+ 2 \times r_{\text{Al}}$  atom (at the corners of the cube)

The volume of the unit cell is  $\ell^3$ . Next we need to calculate the mass of the unit cell. The bcc unit cell contains one atom of Li and one atom of Al. Using the molar masses of Li and Al and Avogadro's number, we can calculate the mass of the unit cell. Density is mass per volume, usually expressed as grams per cubic centimeter.

#### Solve

(a) The alloy ratios are

For AlLi: 
$$\frac{143 \text{ pm}}{152 \text{ pm}} = 0.941$$
  
For AuAl<sub>2</sub>:  $\frac{143 \text{ pm}}{144 \text{ pm}} = 0.993$   
For Al<sub>3</sub>Ti:  $\frac{143 \text{ pm}}{147 \text{ pm}} = 0.973$ 

All of these alloys have atoms within the required 15% size difference of each other, so we certainly would predict that these would be substitutional alloys.

(b) Rearranging the body diagonal equation to solve for  $\ell$  gives

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

$$4r = (2' 152 \text{ pm}) + (2' 143 \text{ pm}) = 590 \text{ pm or } 5.90' 10^{-8} \text{ cm}$$

$$\ell = \frac{5.90' \ 10^{-8} \ \text{cm}}{\sqrt{3}} = 3.41' \ 10^{-8} \ \text{cm}$$

Volume of the unit cell =  $(3.41' \ 10^{-8} \ \text{cm})^3 = 3.965' \ 10^{-23} \ \text{cm}^3$ 

Mass of unit cell = 
$$\frac{36.941 \text{ g Li}}{96} + \frac{26.982 \text{ g Al}\ddot{9}}{\text{mol}} + \frac{1 \text{ mol}}{6.022' \text{ l}^{23}} = 5.633' \text{ l}^{-23} \text{ g}$$
  
Density =  $\frac{5.633' \text{ l}^{-23} \text{ g}}{3.965' \text{ l}^{-23} \text{ cm}^3} = 1.42 \text{ g/cm}^3$ 

## Think About It

Aluminum alloys are important for their strength at low temperatures, resistance to corrosion, high electrical conductivity, and ease of being cast into any shape.

## 12.101. Collect and Organize

From the formula  $Cu_3Al$  for an alloy with a bcc structure, we are to determine how the copper and aluminum atoms are distributed between the unit cells.

#### Analyze

The bcc unit cell contains two atoms. The radii of Al and Cu are 143 and 128, respectively. The radius ratio is 0.895.

# Solve

The radius ratio indicates that Cu atoms fit into the cubic holes of the Al lattice. Another way to look at this is as a simple cubic arrangement of Cu atoms with an Al atom in the center of the unit cell. To be consistent with the formula ( $Cu_3Al$ ), we would have to consider three unit cells, one of which would have one Al atom in the center.

#### Think About It

It is probably also possible to have an alloy of formula Al<sub>3</sub>Cu since their atomic radii are so similar.

#### 12.102. Collect and Organize

We consider the structure of AIP as both an ionic compound and as a covalent compound.

#### Analyze

For both types of possible bonding for AlP, we can use the radius ratio rule to determine whether the ionic and covalent radii are consistent with the sphalerite structure of AlP. The sphalerite structure has an fcc arrangement of  $P^{3-}$ , with  $Al^{3+}$  occupying half of the eight tetrahedral holes. The radius ratio range for tetrahedral holes is 0.22–0.41.

# Solve

(a)  $\frac{r_{\rm Al^{3+}}}{r_{\rm P^{3-}}} = \frac{54 \text{ pm}}{212 \text{ pm}} = 0.25$ 

This radius ratio is below 0.41. Yes, the  $Al^{3+}$  would fit into tetrahedral holes to give a sphalerite structure.

(b) The atomic radii from Appendix 3 are 143 pm for Al and 110 pm for P. For a lattice of P atoms,

$$\frac{r_{\rm Al}}{r_{\rm P}} = \frac{143 \text{ pm}}{110 \text{ pm}} = 1.30$$

If we consider the P atoms in a lattice of Al atoms,

$$\frac{r_{\rm P}}{r_{\rm Al}} = \frac{110 \text{ pm}}{143 \text{ pm}} = 0.769$$

Both of these ratios are inconsistent with the size requirements of atoms in a molecular sphalerite structure. No, AIP would not adopt a lattice that corresponds to a covalent compound.

# Think About It

From our calculations, we can say that the bonding in AlP is mostly ionic given that it has a sphalerite structure.

## 12.103. Collect and Organize

We are asked to identify the monomers that would generate the polymers depicted in Figure P12.103.

## Analyze

Polymers are composed of repeating monomer units linked together in a chain. The polymer depicted in (a) is a polyamide (arising from the formation of an amide bond between an acid and a primary amine), and (b) is a polyester (arising from the formation of an ester linkage between an acid and an alcohol).

#### Solve

The monomer units are



#### **Think About It**

The monomer unit may be difficult to identify from depictions such as those in Figure P12.103. By extending the polymer through several repeating units, amide or ester linkages may be more easily identified.

#### 12.104. Collect and Organize

From the structure of nylon we can identify functional groups that make the polymer hydrophilic.

#### Analyze

Hydrophilic means "water loving." The polar functional groups on nylon are hydrophilic. The structure of nylon is shown in Figure 12.42.

The amide groups [-C(=O)NH-] in nylon are hydrophilic.

# Think About It

The alkyl chain  $-(CH_2)_6-$  on the polymer backbone of nylon is hydrophobic, "water avoiding."

#### 12.105. Collect and Organize

We are to draw the carbon-skeleton structure of the condensation polymer of  $H_2N(CH_2)_6COOH$  and compare that structure to nylon-6.

#### Analyze

In a condensation polymerization reaction, a small molecule is formed. When the reaction is between an amine and a carboxylic acid, that small molecule is water. In the condensation of  $H_2N(CH_2)_6COOH$  with itself, the polymer has a repeating unit of just this monomer.

# Solve

The condensation reaction and the line structure of the polymer are



In this polymer there is one monomeric repeating unit with seven carbon atoms because it is prepared from the difunctional  $H_2N(CH_2)_6COOH$  monomer. In nylon-6 the polymer also has a single monomeric unit but with six carbon atoms.

#### Think About It

We can make different nylons with different properties by changing the monomers used in the condensation reaction.

#### 12.106. Collect and Organize

We are to draw all the possible trimers possible from the condensation reaction of putrescine  $[H_2N(CH_2)_4NH_2]$  with adipic acid and terephthalic acid (Figure P12.106). In addition we are asked what ratio of monomers would be necessary to prepare a polymer with a 1:1 ratio of the two carboxylic acids in the polymer chain.

#### Analyze

In the condensation reaction, the difunctional amine can react with two carboxylic acid molecules to form a trimer.

# Solve (a)



(b) 1 mole adipic acid to 1 mole terephthalic acid to 2 moles putrescine.

# Think About It

The polymer from part (b) would have the backbone structure.



## 12.107. Collect and Organize

We consider the effects of cross-linking of a polymer on its physical properties. We are asked to predict how the properties of a styrene–divinylbenzene copolymer might differ from those of 100% polystyrene.

## Analyze

Cross-linking "ties" together individual polymer strands with covalent bonds.

# Solve

Cross-linking increases the strength, hardness, melting (softening) point, and the chemical resistance of a polymer.

#### Think About It

Synthetic rubber for tires is a cross-linked polymer. The cross-linking renders the rubber tougher and more elastic.

# 12.108. Collect and Organize

Using the given structures of maleic anhydride and styrene (Figure P12.108), we are to draw two structural repeating units of the polymer formed from these two monomers. By comparing the structure to that of polystyrene, we can predict how the two polymers' properties might differ.

## Analyze

Solve (a)

Both polystyrene and the polymer formed from maleic anhydride and styrene are addition polymers. The structure of polystyrene is





(b) The polymer made from maleic anhydride and styrene is expected to be more hydrophilic, because of the presence of the oxygen atoms, and less rigid.

#### Think About It

This type of polymer, which is derived from two different monomers, is a *copolymer*.

## 12.109. Collect and Organize

For the polymerization of methyl 2-cyanoacrylate (Figure P12.109), we are to draw the structure of two of the repeating units for the polymer.

## Analyze

The polymerization of methyl 2-cyanoacrylate is through addition polymerization (as in the formation of polystyrene).

# Solve



# Chemistry The Science in Context Volume I and II 5th Edition Gilbert Solutions Manual

Full Download: http://alibabadownload.com/product/chemistry-the-science-in-context-volume-i-and-ii-5th-edition-gilbert-solution 56 | *Chapter 12* 

#### **Think About It**

The presence of water, -OH, or -NHR functioning as OH<sup>-</sup> and RNH<sup>-</sup> (Nu:<sup>-</sup>) groups serves to start the polymerization reaction.



## 12.110. Collect and Organize

Considering the synthesis and properties of silicones  $[R_2SiO]_n$  (Figure P12.110), we are to write two balanced equations for the reactions and explain why silicones are hydrophobic.

#### Analyze

- (a) The two equations are (1) the reaction of R<sub>2</sub>SiCl<sub>2</sub> with water to give a new monomer, whose formula is R<sub>2</sub>SiCl(OH), and HCl and (2) the reaction of two R<sub>2</sub>SiCl(OH) molecules eliminating water to give ClR<sub>2</sub>Si–O–SiR<sub>2</sub>Cl.
- (b) Water-repellent polymers are nonpolar.

#### Solve

- (a)  $R_2SiCl_2(aq) + H_2O(\ell) \rightarrow R_2SiCl(OH)(aq) + HCl(aq)$  $R_2SiCl(OH)(aq) + (HO)SiClR_2(aq) \rightarrow R_2ClSi-O-SiClR_2(aq) + H_2O(\ell)$
- (b) Silicones repel water because the side chains (R groups) are nonpolar.

#### Think About It

Silicones have many applications, including cookware (because they are nonstick and heat resistant), contact lenses (because of their oxygen permeability), and lubricants (because of their clean application).