CHAPTER 16

LIQUIDS AND SOLIDS

Intermolecular Forces and Physical Properties

11. Intermolecular forces are the relatively weak forces between molecules that hold the molecules together in the solid and liquid phases. Intramolecular forces are the forces within a molecule. These are the covalent bonds in a molecule. Intramolecular forces (covalent bonds) are much stronger than intermolecular forces.

Dipole forces are the forces that act between polar molecules. The electrostatic attraction between the partial positive end of one polar molecule and the partial negative end of another is the dipole force. Dipole forces are generally weaker than hydrogen bonding. Both of these forces are due to dipole moments in molecules. Hydrogen bonding is given a separate name from dipole forces because hydrogen bonding is a particularly strong dipole force. Any neutral molecule that has a hydrogen covalently bonded to N, O, or F exhibits the relatively strong hydrogen bonding intermolecular forces.

London dispersion forces are accidental-induced dipole forces. Like dipole forces, London dispersion forces are electrostatic in nature. Dipole forces are the electrostatic forces between molecules having a permanent dipole. London dispersion forces are the electrostatic forces between molecules having an accidental or induced dipole. All covalent molecules (polar and nonpolar) have London dispersion forces, but only polar molecules (those with permanent dipoles) exhibit dipole forces.


Yes, there is considerable overlap. Consider some of the examples in Exercise 16.20. Benzene (only LD forces) has a higher boiling point than acetone (dipole-dipole). Also, there is even more overlap of the stronger forces (metallic, covalent, and ionic).

13. Fusion refers to a solid converting to a liquid, and vaporization refers to a liquid converting to a gas. Only a fraction of the hydrogen bonds are broken in going from the solid phase to the liquid phase. Most of the hydrogen bonds are still present in the liquid phase and must be broken during the liquid to gas phase transition. Thus the enthalpy of vaporization is much larger than the enthalpy of fusion since more intermolecular forces are broken during the vaporization process.

14. Chalk is composed of the ionic compound calcium carbonate (CaCO₃). The electrostatic forces in ionic compounds are much stronger than the intermolecular forces in covalent compounds. Therefore, CaCO₃ should have a much higher boiling point than the covalent
compounds found in motor oil and in H₂O. Motor oil is composed of nonpolar C–C and C–H bonds. The intermolecular forces in motor oil are therefore London dispersion forces. We generally consider these forces to be weak. However, with compounds that have large molar masses, these London dispersion forces add up significantly and can overtake the relatively strong hydrogen-bonding interactions in water.

15. Ionic compounds have ionic forces. Covalent compounds all have London dispersion (LD) forces, whereas polar covalent compounds have dipole forces and/or hydrogen-bonding forces. For hydrogen bonding (H-bonding) forces, the covalent compound must have either a N–H, O–H, or F–H bond in the molecule.

16. a. OCS; OCS is polar and has dipole-dipole forces in addition to London dispersion (LD) forces. All polar molecules have dipole forces. CO₂ is nonpolar and only has LD forces. To predict polarity, draw the Lewis structure and deduce if the individual bond dipoles cancel.

17. a. H₂NCH₂CH₂NH₂; more extensive hydrogen bonding (H-bonding) is possible because two NH₂ groups are present.

18. As the strengths of the interparticle forces increase, boiling point, freezing point, viscosity, ΔHᵥap, and ΔHᵋᵤₙ increase while vapor pressure decreases.

a. HBr; HBr is polar, whereas Kr and Cl₂ are nonpolar. HBr has dipole forces unlike Kr and Cl₂.

b. NaCl; ionic forces are much stronger than the intermolecular forces for molecular solids.
c. I₂: All are nonpolar, so the largest molecule (I₂) will have the strongest LD forces and the lowest vapor pressure.

d. N₂: nonpolar and smallest, so it has weakest intermolecular forces.

e. H₂O₂: H–O–O–H structure produces stronger H-bonding interactions than H–F, so H₂O₂ has the greatest viscosity.

f. CH₃CH₂OH: can form H-bonding interactions unlike the other covalent compounds.

g. I₂: I₂ has only LD forces, whereas CsBr and CaO have much stronger ionic forces. I₂ has the weakest intermolecular forces, so it has the smallest ΔHfusion.

19. a. Neopentane is more compact than n-pentane. There is less surface-area contact among neopentane molecules. This leads to weaker LD forces and a lower boiling point.

b. HF is capable of H-bonding; HCl is not.

c. LiCl is ionic, and HCl is a molecular solid with only dipole forces and LD forces. Ionic forces are much stronger than the forces for molecular solids.

d. n-Hexane is a larger molecule, so it has stronger LD forces.

20. Benzene Naphthalene

\begin{align*}
\text{Benzene} & \quad \text{Naphthalene} \\
& \quad \text{LD forces only} \\
& \quad \text{LD forces only}
\end{align*}

*Note:* London dispersion forces in molecules such as benzene and naphthalene are fairly large. The molecules are flat, and there is efficient surface-area contact between molecules. Large surface-area contact leads to stronger London dispersion forces.

Carbon tetrachloride (CCl₄) has polar bonds but is a nonpolar molecule. CCl₄ only has LD forces.

In terms of size and shape: CCl₄ < C₆H₆ < C₁₀H₈
The strengths of the LD forces are proportional to size and are related to shape. Although the size of CCl$_4$ is fairly large, the overall spherical shape gives rise to relatively weak LD forces as compared to flat molecules such as benzene and naphthalene. The physical properties given in the problem are consistent with the order listed previously. Each of the physical properties will increase with an increase in intermolecular forces.

Acetone

LD, dipole

Acetic acid

LD, dipole, H-bonding

Benzoic acid

LD, dipole, H-bonding

We would predict the strength of interparticle forces of the last three molecules to be:

acetone < acetic acid < benzoic acid

polar H-bonding H-bonding, but large LD forces because of greater size and shape

This ordering is consistent with the values given for boiling point, melting point, and $\Delta H_{\text{vap}}$.

The overall order of the strengths of intermolecular forces based on physical properties are:

acetone $< \text{CCl}_4 < \text{C}_6\text{H}_6 < \text{acetic acid} < \text{naphthalene} < \text{benzoic acid}$

The order seems reasonable except for acetone and naphthalene. Because acetone is polar, we would not expect it to boil at the lowest temperature. However, in terms of size and shape, acetone is the smallest molecule and the LD forces in acetone must be very small compared to the other molecules. Naphthalene must have very strong LD forces because of its size and flat shape.

21. Ar exists as individual atoms that are held together in the condensed phases by London dispersion forces. The molecule that will have a boiling point closest to Ar will be a nonpolar substance with about the same molar mass as Ar (39.95 g/mol); this same size nonpolar substance will have about equivalent strength of London dispersion forces. Of the choices, only Cl$_2$ (70.90 g/mol) and F$_2$ (38.00 g/mol) are nonpolar. Because F$_2$ has a molar mass closest to that of Ar, one would expect the boiling point of F$_2$ to be close to that of Ar.
22. NaCl, MgCl₂, NaF, MgF₂, and AlF₃ all have very high melting points indicative of strong intermolecular forces. They are all ionic solids. SiCl₄, SiF₄, F₂, Cl₂, PF₅, and SF₆ are nonpolar covalent molecules. Only LD forces are present. PCl₃ and SCl₂ are polar molecules. LD forces and dipole forces are present. In these eight molecular substances the intermolecular forces are weak and the melting points low. AlCl₃ doesn't seem to fit in as well. From the melting point, there are much stronger forces present than in the nonmetal halides, but they aren't as strong as we would expect for an ionic solid. AlCl₃ illustrates a gradual transition from ionic to covalent bonding, from an ionic solid to discrete molecules.

23. Ethanol, C₂H₆O, has 2(4) + 6(1) + 6 = 20 valence electrons.

\[
\begin{align*}
\text{Exhibits H-bonding and London dispersion forces.}
\end{align*}
\]

Dimethyl ether, C₂H₆O, also has 20 valence electrons. It has a Lewis structure of:

\[
\begin{align*}
\text{Exhibits dipole and London dispersion forces but no hydrogen bonding since it has no H covalently bonded to the O.}
\end{align*}
\]

Propane, C₃H₈, has 3(4) + 8(1) = 20 valence electrons.

\[
\begin{align*}
\text{Propane only has relatively nonpolar bonds, so it is nonpolar. Propane exhibits only London dispersion forces.}
\end{align*}
\]

The three compounds have similar molar mass, so the strength of the London dispersion forces will be approximately equivalent. Because dimethyl ether has additional dipole forces, it will boil at a higher temperature than propane. The compound with the highest boiling point is ethanol since it exhibits relatively strong hydrogen-bonding forces. The correct matching of boiling points is:

- ethanol, 78.5°C
- dimethyl ether, −23°C
- propane, −42.1°C

24. As the electronegativity of the atoms covalently bonded to H increases, the strength of the hydrogen-bonding interaction increases.
25. A single hydrogen bond in H₂O has a strength of 21 kJ/mol. Each H₂O molecule forms two H-bonds. Thus it should take 42 kJ/mol of energy to break all of the H-bonds in water. Consider the phase transitions:

\[
\text{Solid} \rightarrow \text{liquid} \rightarrow \text{vapor}
\]

\[\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}\]

It takes a total of 46.7 kJ/mol to convert solid H₂O to vapor (ΔH_{\text{sub}}). This would be the amount of energy necessary to disrupt all of the intermolecular forces in ice. Thus \((42 ÷ 46.7) \times 100 = 90\%\) of the attraction in ice can be attributed to H-bonding.

**Properties of Liquids**

26. Solid: rigid; has fixed volume and shape; slightly compressible

Liquid: definite volume but no specific shape; assumes shape of the container; slightly compressible

Gas: no fixed volume or shape; easily compressible

27. a. Surface tension: the resistance of a liquid to an increase in its surface area.

b. Viscosity: the resistance of a liquid to flow.

c. Melting point: the temperature (at constant pressure) where a solid converts entirely to a liquid as long as heat is applied. A more detailed definition is the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is constant.

d. Boiling point: the temperature (at constant pressure) where a liquid converts entirely to a gas as long as heat is applied. The detailed definition is the temperature at which the vapor pressure of the liquid is exactly equal to the external pressure.

e. Vapor pressure: the pressure of the vapor over a liquid at equilibrium.

As the strengths of intermolecular forces increase, surface tension, viscosity, melting point, and boiling point increase, whereas vapor pressure decreases.

28. The attraction of H₂O for glass is stronger than the H₂O–H₂O attraction. The meniscus is concave to increase the area of contact between glass and H₂O. The Hg–Hg attraction is greater than the Hg–glass attraction. The meniscus is convex to minimize the Hg–glass contact.
29. Water is a polar substance, and wax is a nonpolar substance; they are not attracted to each other. A molecule at the surface of a drop of water is subject to attractions only by water molecules below it and to each side. The effect of this uneven pull on the surface water molecules tends to draw them into the body of the water and causes the droplet to assume the shape that has the minimum surface area, a sphere.

30. As the physical properties indicate, the intermolecular forces are slightly stronger in D$_2$O than in H$_2$O.

31. The structure of H$_2$O$_2$ is H – O – O – H, which produces greater hydrogen bonding than in water. Thus the intermolecular forces are stronger in H$_2$O$_2$ than in H$_2$O resulting in a higher normal boiling point for H$_2$O$_2$ and a lower vapor pressure.

32. CO$_2$ is a gas at room temperature. As melting point and boiling point increase, the strength of the intermolecular forces also increases. Therefore, the strength of forces is CO$_2$ < CS$_2$ < CSe$_2$. From a structural standpoint, this is expected. All three are linear, nonpolar molecules. Thus only London dispersion forces are present. Because the molecules increase in size from CO$_2$ < CS$_2$ < CSe$_2$, the strength of the intermolecular forces will increase in the same order.

**Structures and Properties of Solids**

33. a. Crystalline solid: Regular, repeating structure
   
   Amorphous solid: Irregular arrangement of atoms or molecules

b. Ionic solid: Made up of ions held together by ionic bonding.
   
   Molecular solid: Made up of discrete covalently bonded molecules held together in the solid phase by weaker forces (LD, dipole or hydrogen bonds).

c. Molecular solid: Discrete, individual molecules
   
   Covalent network solid: No discrete molecules; a covalent network solid is one large molecule; the interparticle forces are the covalent bonds between atoms.

d. Metallic solid: Completely delocalized electrons, conductor of electricity (ions in a sea of electrons)
   
   Covalent network solid: Localized electrons; insulator or semiconductor

34. Closest packing: The packing of atoms (uniform, hard spheres) in a manner that most efficiently uses the available space with the least amount of empty space. The two types of closest packing are hexagonal closest packing and cubic closest packing. In both closest packed arrangements, the atoms (spheres) are packed in layers. The difference between the two closest packed arrangements is the ordering of the layers. Hexagonal closest packing has the third layer directly over the first layer forming a repeating layer pattern of abab.... In
cubic closest packing the layer pattern is abcabc.... The unit cell for hexagonal closest packing is a hexagonal prism. See Figure 16.14 for an illustration of the hexagonal prism unit cell. The unit cell for cubic closest packing is the face-centered cubic unit cell.

35. a. Both forms of carbon are network solids. In diamond, each carbon atom is surrounded by a tetrahedral arrangement of other carbon atoms to form a huge molecule. Each carbon atom is covalently bonded to four other carbon atoms.

The structure of graphite is based on layers of carbon atoms arranged in fused six-membered rings. Each carbon atom in a particular layer of graphite is surrounded by three other carbons in a trigonal planar arrangement. This requires sp² hybridization. Each carbon has an unhybridized p atomic orbital; all of these p orbitals in each six-membered ring overlap with each other to form a delocalized π electron system.

b. Silica is a network solid having an empirical formula of SiO₂. The silicon atoms are singly bonded to four oxygens. Each silicon atom is at the center of a tetrahedral arrangement of oxygen atoms that are shared with other silicon atoms. The structure of silica is based on a network of SiO₄ tetrahedra with shared oxygen atoms rather than discrete SiO₂ molecules.

Silicates closely resemble silica. The structure is based on interconnected SiO₄ tetrahedra. However, in contrast to silica, where the O/Si ratio is 2:1, silicates have O/Si ratios greater than 2:1 and contain silicon-oxygen anions. To form a neutral solid silicate, metal cations are needed to balance the charge. In other words, silicates are salts containing metal cations and polyatomic silicon-oxygen anions.

When silica is heated above its melting point and cooled rapidly, an amorphous (disordered) solid called glass results. Glass more closely resembles a very viscous solution than it does a crystalline solid. To affect the properties of glass, several different additives are thrown into the mixture. Some of these additives are Na₂CO₃, B₂O₃, and K₂O, with each compound serving a specific purpose relating to the properties of glass.

36. a. Both CO₂ and H₂O are molecular solids. Both have an ordered array of the individual molecules, with the molecular units occupying the lattice points. A difference within each solid lattice is the strength of the intermolecular forces. CO₂ is nonpolar and only exhibits London dispersion forces. H₂O exhibits the relatively strong hydrogen-bonding interactions. The differences in strength is evidenced by the solid-phase changes that occur at 1 atm. CO₂(s) sublimes at a relatively low temperature of −78°C. In sublimation, all of the intermolecular forces are broken. However, H₂O(s) doesn’t have a phase change until 0°C, and in this phase change from ice to water only a fraction of the intermolecular forces are broken. The higher temperature and the fact that only a portion of the intermolecular forces are broken are attributed to the strength of the intermolecular forces in H₂O(s) as compared to CO₂(s).

Related to the intermolecular forces are the relative densities of the solid and liquid phases for these two compounds. CO₂(s) is denser than CO₂(l) whereas H₂O(s) is less dense than H₂O(l). For CO₂(s), the molecules pack together as close as possible; hence solids are usually more dense than the liquid phase. For H₂O, each molecule has two lone pairs and two bonded hydrogen atoms. Because of the equal number of lone pairs and
O–H bonds, each H₂O molecule can form two hydrogen-bonding interactions to other H₂O molecules. To keep this symmetric arrangement (which maximizes the hydrogen-bonding interactions), the H₂O(s) molecules occupy positions that create empty space in the lattice. This translates into a smaller density for H₂O(s) as compared to H₂O(l).

b. Both NaCl and CsCl are ionic compounds with the anions at the lattice points of the unit cells and the cations occupying the empty spaces created by anions (called holes). In NaCl, the Cl⁻ anions occupy the lattice points of a face-centered unit cell, with the Na⁺ cations occupying the octahedral holes. Octahedral holes are the empty spaces created by six Cl⁻ ions. CsCl has the Cl⁻ ions at the lattice points of a simple cubic unit cell, with the Cs⁺ cations occupying the middle of the cube.

37. A crystalline solid will have the simpler diffraction pattern because a regular, repeating arrangement is necessary to produce planes of atoms that will diffract the X rays in regular patterns. An amorphous solid does not have a regular repeating arrangement and will produce a complicated diffraction pattern.

38. a. CO₂: molecular  b. SiO₂: covalent network  c. Si: atomic, covalent network  
d. CH₄: molecular  e. Ru: atomic, metallic  f. I₂: molecular  
g. KBr: ionic  h. H₂O: molecular  i. NaOH: ionic  
m. GaAs: covalent network  n. BaO: ionic  o. NO: molecular  
p. GeO₂: ionic

39. \[ \lambda = \frac{2 \sin \theta}{n} = \frac{2 \times 1.36 \times 10^{-10} \text{ m} \times \sin 15.0^\circ}{1} = 7.04 \times 10^{-11} \text{ m} = 0.704 \text{ Å} \]

40. \[ n\lambda = 2d \sin \theta, \quad d = \frac{n\lambda}{2 \sin \theta} = \frac{1 \times 2.63 \text{ Å}}{2 \times \sin 15.55^\circ} = 4.91 \text{ Å} = 4.91 \times 10^{-10} \text{ m} = 491 \text{ pm} \]

\[ \sin \theta = \frac{n\lambda}{2d} = \frac{2 \times 2.63 \text{ Å}}{2 \times 4.91 \text{ Å}} = 0.536, \quad \theta = 32.4^\circ \]

41. \[ n\lambda = 2d \sin \theta, \quad d = \frac{n\lambda}{2 \sin \theta} = \frac{1 \times 1.54 \text{ Å}}{2 \times \sin 14.22^\circ} = 3.13 \text{ Å} = 3.13 \times 10^{-10} \text{ m} = 313 \text{ pm} \]
42. In a face-centered cubic unit cell (ccp structure), the atoms touch along the face diagonal:

\[(4r)^2 = l^2 + l^2\]

\[l = r\sqrt{2}\]

\[V_{\text{cube}} = l^3 = (r\sqrt{2})^3 = 22.63 \text{ } r^3\]

There are four atoms in a face-centered cubic cell. Each atom has a volume of \(\frac{4}{3}\pi r^3\).

\[V_{\text{atoms}} = 4 \times \frac{4}{3}\pi r^3 = 16.76 \text{ } r^3\]

So \(\frac{V_{\text{atoms}}}{V_{\text{cube}}} = \frac{16.76 \text{ } r^3}{22.63 \text{ } r^3} = 0.7406\), or 74.06% of the volume of each unit cell is occupied by atoms.

A body-centered cubic unit cell contains two net atoms (8 corner atoms \(\times\) 1/8 atom per corner + 1 center atom = 2 atoms/unit cell). In a body-centered unit cell (see Figure 16.18), the atoms touch along the body diagonal of the unit cell. Therefore, body diagonal = \(4r = \sqrt{3}l\).

The length of a cube edge (\(l\)) is related to the radius of the atom (\(r\)) by the equation \(l = 4r/\sqrt{3}\).

Volume of unit cell = \(l^3 = (4r/\sqrt{3})^3 = 12.32 \text{ } r^3\)

Volume of atoms in unit cell = \(2 \times \frac{4}{3}\pi r^3 = 8.378 \text{ } r^3\)

So \(\frac{V_{\text{atoms}}}{V_{\text{cube}}} = \frac{8.378 \text{ } r^3}{12.32 \text{ } r^3} = 0.6800 = 68.00\% \text{ occupied.}\)

In a simple cubic unit cell, the atoms touch along the cube edge (\(l\)):

\[2(\text{radius}) = 2r = l\]

\[V_{\text{cube}} = l^3 = (2r)^3 = 8r^3\]

There is one atom per simple cubic cell (8 corner atoms \(\times\) 1/8 atom per corner = 1 atom/unit cell). Each atom has an assumed volume of \(\frac{4}{3}\pi r^3\) = volume of a sphere.
\[ V_{\text{atom}} = \frac{4}{3} \pi r^3 = 4.189 \, r^3 \]

So \( \frac{V_{\text{atom}}}{V_{\text{cube}}} = \frac{4.189 \, r^3}{8r^3} = 0.5236 \), or 52.36% occupied.

A cubic closest packed structure (face-centered cubic unit cell) packs the atoms more efficiently than a body-centered cubic unit cell, which is more efficient than a simple cubic unit cell.

43. A cubic closest packed structure has a face-centered cubic unit cell. In a face-centered cubic unit, there are:

\[
8 \text{ corners} \times \frac{1}{8} \text{ atom/corner} + 6 \text{ faces} \times \frac{1}{2} \text{ atom/face} = 4 \text{ atoms}
\]

The atoms in a face-centered cubic unit cell touch along the face diagonal of the cubic unit cell. Using the Pythagorean formula, where \( l \) = length of the face diagonal and \( r \) = radius of the atom:

\[
l^2 + l^2 = (4r)^2
\]

\[
2l^2 = 16r^2
\]

\[
l = r \sqrt{8}
\]

\[ l = r \sqrt{8} = 197 \times 10^{-12} \, \text{m} \times \sqrt{8} = 5.57 \times 10^{-10} \, \text{m} = 5.57 \times 10^{-8} \, \text{cm} \]

Volume of a unit cell = \( l^3 = (5.57 \times 10^{-8} \, \text{cm})^3 = 1.73 \times 10^{-22} \, \text{cm}^3 \)

Mass of a unit cell = \( 4 \, \text{Ca atoms} \times \frac{1 \, \text{mol Ca}}{6.022 \times 10^{23} \, \text{atoms}} \times \frac{40.08 \, \text{g Ca}}{\text{mol Ca}} = 2.662 \times 10^{-22} \, \text{g Ca} \)

Density = \( \frac{\text{mass}}{\text{volume}} = \frac{2.662 \times 10^{-22} \, \text{g}}{1.73 \times 10^{-22} \, \text{cm}^3} = 1.54 \, \text{g/cm}^3 \)

44. The unit cell for cubic closest packing is the face-centered unit cell. The volume of a unit cell is:

\[ V = l^3 = (492 \times 10^{-10} \, \text{cm})^3 = 1.19 \times 10^{-22} \, \text{cm}^3 \]

There are four Pb atoms in the unit cell, as is the case for all face-centered cubic unit cells. The mass of atoms in a unit cell is:
mass = 4 Pb atoms \times \frac{1 \text{ mol Pb}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{207.2 \text{ g Pb}}{\text{mol Pb}} = 1.38 \times 10^{-21} \text{ g}

Density = \frac{\text{mass}}{\text{volume}} = \frac{1.38 \times 10^{-21} \text{ g}}{1.19 \times 10^{-22} \text{ cm}^3} = 11.6 \text{ g/cm}^3

From Exercise 16.43, the relationship between the cube edge length $l$ and the radius of an atom in a face-centered unit cell is $l = r \sqrt{8}$.

$$r = \frac{l}{\sqrt{8}} = 492 \text{ pm}/\sqrt{8} = 174 \text{ pm} = 1.74 \times 10^{-10} \text{ m}$$

45. There are four Ni atoms in each unit cell: For a unit cell:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = 6.84 \text{ g/cm}^3 = \frac{4 \text{ Ni atoms} \times \frac{1 \text{ mol Ni}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{58.69 \text{ g Ni}}{\text{mol Ni}}}{l^3}$$

Solving: $l = 3.85 \times 10^{-8} \text{ cm} = \text{cube edge length}$

For a face centered cube:

$$(4r)^2 = l^2 + l^2 = 2l^2$$

$$r \sqrt{8} = l, \quad r = l/\sqrt{8}$$

$$r = 3.85 \times 10^{-8} \text{ cm}/\sqrt{8}$$

$$r = 1.36 \times 10^{-8} \text{ cm} = 136 \text{ pm}$$

46. A face-centered cubic unit cell contains four atoms. For a unit cell:

mass of X = volume $\times$ density = $(4.09 \times 10^{-8} \text{ cm})^3 \times 10.5 \text{ g/cm}^3 = 7.18 \times 10^{-22} \text{ g}$

$$\text{mol X} = 4 \text{ atoms} \times \frac{1 \text{ mol X}}{6.022 \times 10^{23} \text{ atoms}} = 6.642 \times 10^{-24} \text{ mol X}$$

Molar mass = $\frac{7.18 \times 10^{-22} \text{ g X}}{6.642 \times 10^{-24} \text{ mol X}} = 108 \text{ g/mol}; \text{ the metal is silver (Ag).}$

47. For a body-centered unit cell: 8 corners $\times \frac{1/8 \text{ Ti}}{\text{corner}} + 1 \text{ Ti at body center} = 2 \text{ Ti atoms}$

All body-centered unit cells have two atoms per unit cell. For a unit cell:
density = 4.50 g/cm³ = \( \frac{2 \text{ atoms Ti} \times \frac{1 \text{ mol Ti}}{6.022 \times 10^{23} \text{ atoms}} \times 47.88 \text{ g Ti}}{l^3} \), where \( l \) = cube edge length

Solving: \( l = \text{edge length of unit cell} = 3.28 \times 10^{-8} \text{ cm} = 328 \text{ pm} \)

Assume Ti atoms just touch along the body diagonal of the cube, so body diagonal = \( 4 \times \) radius of atoms = \( 4r \).

The triangle we need to solve is:

\[
(4r)^2 = (3.28 \times 10^{-8} \text{ cm})^2 + [(3.28 \times 10^{-8} \text{ cm}) \sqrt{2}]^2, \quad r = 1.42 \times 10^{-8} \text{ cm} = 142 \text{ pm}
\]

For a body-centered cubic unit cell, the radius of the atom is related to the cube edge length by \( 4r = l \sqrt{3} \) or \( l = 4r/\sqrt{3} \).

48. From Exercise 16.47:

\[
16r^2 = \bar{l}^2 + 2\bar{l}^2
\]

\[
l = 4r/\sqrt{3} = 2.309 \text{ r}
\]

\[
l = 2.309(222 \text{ pm}) = 513 \text{ pm} = 5.13 \times 10^{-8} \text{ cm}
\]

In a body-centered cubic unit cell, there are two atoms per unit cell. For a unit cell:

\[
density = \frac{\text{mass}}{\text{volume}} = \frac{2 \text{ atoms Ba} \times \frac{1 \text{ mol Ba}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{137.3 \text{ g Ba}}{\text{mol Ba}}}{(5.13 \times 10^{-8} \text{ cm})^3} = \frac{3.38 \text{ g}}{\text{cm}^3}
\]

49. If gold has a face-centered cubic structure, then there are four atoms per unit cell, and from Exercise 16.43:
2r^2 = 16r^2

l = r\sqrt{8} = (144 \text{ pm})\sqrt{8} = 407 \text{ pm}

l = 407 \times 10^{-12} \text{ m} = 4.07 \times 10^{-8} \text{ cm}

\begin{align*}
\text{Density} &= \frac{4 \text{ atoms Au} \times \frac{1 \text{ mol Au}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{197.0 \text{ g Au}}{\text{mol Au}}}{(4.07 \times 10^{-8} \text{ cm})^3} \\
&= 19.4 \text{ g/cm}^3
\end{align*}

If gold has a body-centered cubic structure, then there are two atoms per unit cell, and from Exercise 16.47:

\begin{align*}
16r^2 &= l^2 + 2r^2 \\
l &= \frac{4r}{\sqrt{3}} = 333 \text{ pm} = 333 \times 10^{-12} \text{ m}
\end{align*}

\begin{align*}
l &= 333 \times 10^{-10} \text{ cm} = 3.33 \times 10^{-8} \text{ cm}
\end{align*}

\begin{align*}
\text{Density} &= \frac{2 \text{ atoms Au} \times \frac{1 \text{ mol Au}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{197.0 \text{ g Au}}{\text{mol Au}}}{(3.33 \times 10^{-8} \text{ cm})^3} \\
&= 17.7 \text{ g/cm}^3
\end{align*}

The measured density of gold is consistent with a face-centered cubic unit cell.

50. If face-centered cubic:

\begin{align*}
l &= r\sqrt{8} = (137 \text{ pm})\sqrt{8} = 387 \text{ pm} = 3.87 \times 10^{-8} \text{ cm}
\end{align*}

\begin{align*}
\text{Density} &= \frac{4 \text{ atoms W} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{183.9 \text{ g W}}{\text{mol}}}{(3.87 \times 10^{-8} \text{ cm})^3} \\
&= 21.1 \text{ g/cm}^3
\end{align*}

If body-centered cubic:

\begin{align*}
l &= \frac{4r}{\sqrt{3}} = \frac{4 \times 137 \text{ pm}}{\sqrt{3}} = 316 \text{ pm} = 3.16 \times 10^{-8} \text{ cm}
\end{align*}
Density = \frac{2 \text{ atoms W} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms mol}^{-1}} \times 183.9 \text{ g W}}{(3.16 \times 10^{-8} \text{ cm})^3} = 19.4 \text{ g/cm}^3

The measured density of tungsten is consistent with a body-centered unit cell.

51. Conductor: The energy difference between the filled and unfilled molecular orbitals is minimal. We call this energy difference the band gap. Because the band gap is minimal, electrons can easily move into the conduction bands (the unfilled molecular orbitals).

Insulator: Large band gap; electrons do not move from the filled molecular orbitals to the conduction bands since the energy difference is large.

Semiconductor: Small band gap; the energy difference between the filled and unfilled molecular orbitals is smaller than in insulators, so some electrons can jump into the conduction bands. The band gap, however, is not as small as with conductors, so semiconductors have intermediate conductivity.

a. As the temperature is increased, more electrons in the filled molecular orbitals have sufficient kinetic energy to jump into the conduction bands (the unfilled molecular orbitals).

b. A photon of light is absorbed by an electron that then has sufficient energy to jump into the conduction bands.

c. An impurity either adds electrons at an energy near that of the conduction bands (n-type) or creates holes (unfilled energy levels) at energies in the previously filled molecular orbitals (p-type). Both n-type and p-type semiconductors increase conductivity by creating an easier path for electrons to jump from filled to unfilled energy levels.

In conductors, electrical conductivity is inversely proportional to temperature. Increases in temperature increase the motions of the atoms, which gives rise to increased resistance (decreased conductivity). In a semiconductor, electrical conductivity is directly proportional to temperature. An increase in temperature provides more electrons with enough kinetic energy to jump from the filled molecular orbitals to the conduction bands, increasing conductivity.

52. To produce an n-type semiconductor, dope Ge with a substance that has more than four valence electrons, e.g., a Group 5A element. Phosphorus or arsenic are two substances that will produce n-type semiconductors when they are doped into germanium. To produce a p-type semiconductor, dope Ge with a substance that has fewer than four valence electrons, e.g., a Group 3A element. Gallium or indium are two substances that will produce p-type semiconductors when they are doped into germanium.

Doping germanium with phosphorus (or arsenic) produces an n-type semiconductor. The phosphorus adds electrons at energies near the conduction band of germanium. Electrons do not need as much energy to move from filled to unfilled energy levels, so conduction increases. Doping germanium with gallium (or indium) produces a p-type semiconductor.
Because gallium has fewer valence electrons than germanium, holes (unfilled energy levels) at energies in the previously filled molecular orbitals are created, which induces greater electron movement (greater conductivity).

53. A rectifier is a device that produces a current that flows in one direction from an alternating current that flows in both directions. In a p-n junction, a p-type and an n-type semiconductor are connected. The natural flow of electrons in a p-n junction is for the excess electrons in the n-type semiconductor to move to the empty energy levels (holes) of the p-type semiconductor. Only when an external electric potential is connected so that electrons flow in this natural direction will the current flow easily (forward bias). If the external electric potential is connected in reverse of the natural flow of electrons, no current flows through the system (reverse bias). A p-n junction only transmits a current under forward bias, thus converting the alternating current to direct current.

54. An alloy is a substance that contains a mixture of elements and has metallic properties. In a substitutional alloy, some of the host metal atoms are replaced by other metal atoms of similar size, e.g., brass, pewter, plumber’s solder. An interstitial alloy is formed when some of the interstices (holes) in the closest packed metal structure are occupied by smaller atoms, e.g., carbon steels.

55. In has fewer valence electrons than Se. Thus Se doped with In would be a p-type semiconductor.

56. To make a p-type semiconductor, we need to dope the material with atoms that have fewer valence electrons. The average number of valence electrons is four when 50-50 mixtures of Group 3A and Group 5A elements are considered. We could dope with more of the Group 3A element or with atoms of Zn or Cd. Cadmium is the most common impurity used to produce p-type GaAs semiconductors. To make a n-type GaAs semiconductor, dope with an excess Group 5A element or dope with a Group 6A element such as sulfur.

57. \[ E_{\text{gap}} = 2.5 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV} = 4.0 \times 10^{-19} \text{ J} \] we want \( E_{\text{gap}} = E_{\text{light}} \).

\[
E_{\text{light}} = \frac{hc}{\lambda} = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})}{4.0 \times 10^{-19} \text{ J}} = 5.0 \times 10^{-7} \text{ m} = 5.0 \times 10^2 \text{ nm}
\]

58. \[
E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.298 \times 10^8 \text{ m/s})}{730 \times 10^{-9} \text{ m}} = 2.72 \times 10^{-19} \text{ J} = \text{energy of band gap}
\]

59. The structures of most binary ionic solids can be explained by the closest packing of spheres. Typically, the larger ions, usually the anions, are packed in one of the closest packing arrangements, and the smaller cations fit into holes among the closest packed anions. There are different types of holes within the closest packed anions that are determined by the number of spheres that form them. Which of the three types of holes are filled usually depends on the relative size of the cation to the anion. Ionic solids will always try to maximize electrostatic attractions among oppositely charged ions and minimize the repulsions among ions with like charges.
The structure of sodium chloride can be described in terms of a cubic closest packed array of Cl\(^-\) ions with Na\(^+\) ions in all of the octahedral holes. An octahedral hole is formed between six Cl\(^-\) anions. The number of octahedral holes is the same as the number of packed ions. So in the face-centered unit cell of sodium chloride, there are four net Cl\(^-\) ions and four net octahedral holes. Because the stoichiometry dictates a 1:1 ratio between the number of Cl\(^-\) anions and Na\(^+\) cations, all of the octahedral holes must be filled with Na\(^+\) ions.

In zinc sulfide, the sulfide anions also occupy the lattice points of a cubic closest packing arrangement. But instead of having the cations in octahedral holes, the Zn\(^{2+}\) cations occupy tetrahedral holes. A tetrahedral hole is the empty space created when four spheres are packed together. There are twice as many tetrahedral holes as packed anions in the closest packed structure. Therefore, each face-centered unit cell of sulfide anions contains four net S\(^2-\) ions and eight net tetrahedral holes. For the 1:1 stoichiometry to work out, only one-half of the tetrahedral holes are filled with Zn\(^{2+}\) ions. This gives four S\(^2-\) ions and four Zn\(^{2+}\) ions per unit cell for an empirical formula of ZnS.

60. A repeating pattern in the two-dimensional structure is:

```
  A
  B
  A
  B
```

Assuming the anions A are the larger circles, there are four anions completely in this repeating square. The corner cations (smaller circles) are shared by four different repeating squares. Therefore, there is one cation in the middle of the square plus 1/4 (4) = 1 net cation from the corners. Each repeating square has two cations and four anions. The empirical formula is MA\(_2\).

61. There is one octahedral hole per closest packed anion in a closest packed structure. If one-half of the octahedral holes are filled, then there is a 2:1 ratio of fluoride ions to cobalt ions in the crystal. The formula is CoF\(_2\).

62. There are two tetrahedral holes per closest packed anion. Let \( f \) = fraction of tetrahedral holes filled by the cations.

\[
\text{Na}_2\text{O}: \text{cation-to-anion ratio} = \frac{2}{1} = \frac{2f}{1}, \quad f = 1; \quad \text{all the tetrahedral holes are filled by Na}^+ \text{ cations.}
\]

\[
\text{CdS}: \text{cation-to-anion ratio} = \frac{1}{1} = \frac{2f}{1}, \quad f = \frac{1}{2}; \quad \text{one-half the tetrahedral holes are filled by Cd}^{2+} \text{ cations.}
\]

\[
\text{ZrI}_4: \text{cation-to-anion ratio} = \frac{1}{4} = \frac{2f}{1}, \quad f = \frac{1}{8}; \quad \text{one-eighth the tetrahedral holes are filled by Zr}^{4+} \text{ cations.}
\]
63. Mn ions at 8 corners: 8(1/8) = 1 Mn ion; F ions at 12 edges: 12(1/4) = 3 F ions; the formula is MnF₃. Assuming fluoride is −1 charged, then the charge on Mn is +3.

64. From Figure 16.42, MgO has the NaCl structure containing 4 Mg²⁺ ions and 4 O²⁻ ions per face-centered unit cell.

\[
4 \text{ MgO formula units} \times \frac{1 \text{ mol MgO}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{40.31 \text{ g MgO}}{1 \text{ mol MgO}} = 2.678 \times 10^{-22} \text{ g MgO}
\]

Volume of unit cell = \(2.678 \times 10^{-22} \text{ g MgO} \times \frac{1 \text{ cm}^3}{3.58 \text{ g}} = 7.48 \times 10^{-23} \text{ cm}^3\)

Volume of unit cell = \(l^3\), \(l =\) cube edge length; \(l = (7.48 \times 10^{-23} \text{ cm}^3)^{1/3} = 4.21 \times 10^{-8} \text{ cm}\)

For a face-centered unit cell, the O²⁻ ions touch along the face diagonal:

\[
\sqrt{2} l = 4r_{O^{2-}}, \quad r_{O^{2-}} = \frac{\sqrt{2} \times 4.21 \times 10^{-8} \text{ cm}}{4} = 1.49 \times 10^{-8} \text{ cm}\]

The cube edge length goes through two radii of the O²⁻ anions and the diameter of the Mg²⁺ cation. So:

\[l = 2r_{O^{2-}} + 2r_{Mg^{2+}}, \quad 4.21 \times 10^{-8} \text{ cm} = 2(1.49 \times 10^{-8} \text{ cm}) + 2r_{Mg^{2+}}, \quad r_{Mg^{2+}} = 6.15 \times 10^{-9} \text{ cm}\]

65. CsCl is a simple cubic array of Cl⁻ ions with Cs⁺ in the middle of each unit cell. There is one Cs⁺ and one Cl⁻ ion in each unit cell. Cs⁺ and Cl⁻ touch along the body diagonal.

Body diagonal = \(2r_{Cs^+} + 2r_{Cl^-} = \sqrt{3} l\), \(l =\) length of cube edge

In each unit cell:

mass = 1 CsCl unit(1 mol/6.022 \times 10^{23} \text{ units})(168.4 g/mol) = 2.796 \times 10^{-22} \text{ g}

volume = \(l^3 = \text{mass/density} = 2.796 \times 10^{-22} \text{ g}/3.97 \text{ g cm}^{-3} = 7.04 \times 10^{-23} \text{ cm}^3\)

\[l^3 = 7.04 \times 10^{-23} \text{ cm}^3, \quad l = 4.13 \times 10^{-8} \text{ cm} = 413 \text{ pm} = \text{length of cube edge}\]

\[2r_{Cs^+} + 2r_{Cl^-} = \sqrt{3} l = \sqrt{3} (413 \text{ pm}) = 715 \text{ pm}\]

The distance between ion centers = \(r_{Cs^+} + r_{Cl^-} = 715 \text{ pm}/2 = 358 \text{ pm}\).

From ionic radius: \(r_{Cs^+} = 169 \text{ pm} \) and \(r_{Cl^-} = 181 \text{ pm}; \quad r_{Cs^+} + r_{Cl^-} = 169 + 181 = 350 \text{ pm}\)

The distance calculated from the density is 8 pm (2.3%) greater than that calculated from tables of ionic radii.
66. Total charge of all iron ions present in a formula unit is +2 to balance the −2 charge from the one O atom. The sum of iron ions in a formula unit is 0.950. Let \( x = \) fraction Fe\(^{2+}\) ions in a formula unit and \( y = \) fraction of Fe\(^{3+}\) ions present in a formula unit.

Setting up two equations: \( x + y = 0.950 \) and \( 2x + 3y = 2.000 \)

Solving: \( 2x + 3(0.950 - x) = 2.000 \), \( x = 0.85 \) and \( y = 0.10 \)

\[
\frac{0.10}{0.95} = 0.11 = \text{fraction of iron as Fe}^{3+} \text{ ions}
\]

If all Fe\(^{2+}\), then 1.000 Fe\(^{2+}\) ion/O\(^{2−}\) ion; 1.000 − 0.950 = 0.050 = vacant sites. 5.0% of the Fe\(^{2+}\) sites are vacant.

67. For a cubic hole to be filled, the cation to anion radius ratio is between \( 0.732 < \frac{r_+}{r_−} < 1.00 \).

CsBr: Cs\(^+\) radius = 169 pm, Br\(^−\) radius = 195 pm; \( \frac{r_+}{r_−} = \frac{169}{195} = 0.867 \)

From the radius ratio, Cs\(^+\) should occupy cubic holes. The structure should be the CsCl structure. The actual structure is the CsCl structure.

KF: K\(^+\) radius = 133 pm, F\(^−\) radius = 136 pm; \( \frac{r_+}{r_−} = \frac{133}{136} = 0.978 \)

Again, we would predict a structure similar to CsCl, i.e., cations in the middle of a simple cubic array of anions. The actual structure is the NaCl structure.

The radius ratio rules fail for KF. Exceptions are common for crystal structures.

68. a. The NaCl unit cell has a face-centered cubic arrangement of the anions with cations in the octahedral holes. There are four NaCl formula units per unit cell, and since there is a 1:1 ratio of cations to anions in MnO, then there would be four MnO formula units per unit cell assuming an NaCl-type structure. The CsCl unit cell has a simple cubic structure of anions with the cations in the cubic holes. There is one CsCl formula unit per unit cell, so there would be one MnO formula unit per unit cell if a CsCl structure is observed.

\[
\text{Formula units of MnO per unit cell} = \frac{(4.47 \times 10^{-8} \text{ cm})^3 \times 5.28 \text{ g MnO}}{\text{cm}^3} \times \frac{1 \text{ mol MnO}}{70.94 \text{ g MnO}} 
\times \frac{6.022 \times 10^{23} \text{ formula units MnO}}{\text{mol MnO}_4} = 4.00 \text{ formula units MnO}
\]

From the calculation, MnO crystallizes in the NaCl type structure.

b. From the NaCl structure and assuming the ions touch each other, then \( l = \) cube edge length = \( 2r_{Mn^{2+}} + 2r_{O^{2−}} \).

\[
l = 4.47 \times 10^{-8} \text{ cm} = 2r_{Mn^{2+}} + 2(1.40 \times 10^{-8} \text{ cm}), \quad r_{Mn^{2+}} = 8.35 \times 10^{-8} \text{ cm} = 84 \text{ pm}
\]
c. \( \frac{r_{\text{Mn}^{2+}}}{r_{\text{O}^{2-}}} = \frac{84 \text{ pm}}{140. \text{ pm}} = 0.60 \)

From Table 16.6 of the text, octahedral holes should be filled when \( 0.414 < r_+/r_- < 0.732 \). Because the calculated radius ratio falls within the prescribed limits, we would expect \( \text{Mn}^{2+} \) to occupy the octahedral holes formed by the cubic closest packed array of \( \text{O}^{2-} \) ions (as predicted in part a).

69. a. \( 8 \) corners \( \times \frac{1}{8} \text{ Xe} \) corner + 1 Xe inside cell = 2 Xe; \( 8 \) edges \( \times \frac{1}{4} \text{ F} \) edge + 2 F inside cell = 4 F

Empirical formula is \( \text{XeF}_2 \). This is also the molecular formula.

b. For a unit cell:

\[
\text{mass} = 2 \times \frac{1 \text{ mol XeF}_2}{6.022 \times 10^{23} \text{ molecules}} \times \frac{169.3 \text{ g XeF}_2}{\text{ mol XeF}_2} = 5.62 \times 10^{-22} \text{ g}
\]

\[
\text{volume} = (7.02 \times 10^{-8} \text{ cm})(4.32 \times 10^{-8} \text{ cm})(4.32 \times 10^{-8} \text{ cm}) = 1.31 \times 10^{-22} \text{ cm}^3
\]

\[
\text{density} = d = \frac{\text{mass}}{\text{volume}} = \frac{5.62 \times 10^{-22} \text{ g}}{1.31 \times 10^{-22} \text{ cm}^3} = 4.29 \text{ g/cm}^3
\]

70. a. The unit cell consists of Ni at the cube corners and Ti at the body center or Ti at the cube corners and Ni at the body center.

b. \( 8 \times \frac{1}{8} = 1 \) atom from corners + 1 atom at body center; empirical formula = \( \text{NiTi} \)

c. Both have coordination numbers of 8 (both are surrounded by 8 atoms).

71. With a cubic closest packed array of oxygen ions, we have 4 \( \text{O}^{2-} \) ions per unit cell. We need to balance the total \(-8\) charge of the anions with a \(+8\) charge from the \( \text{Al}^{3+} \) and \( \text{Mg}^{2+} \) cations. The only combination of ions that gives a \(+8\) charge is 2 \( \text{Al}^{3+} \) ions and 1 \( \text{Mg}^{2+} \) ion. The formula is \( \text{Al}_2\text{MgO}_4 \).

There are an equal number of octahedral holes as anions (4) in a cubic closest packed array and twice the number of tetrahedral holes as anions in a cubic closest packed array. For the stoichiometry to work out, we need 2 \( \text{Al}^{3+} \) and 1 \( \text{Mg}^{2+} \) per unit cell. Hence one-half the octahedral holes are filled with \( \text{Al}^{3+} \) ions, and one-eighth the tetrahedral holes are filled with \( \text{Mg}^{2+} \) ions.

72. a. For the unit with Ti in the center of the cube:

\[
\text{1 Ti at body center; 8 corners} \times \frac{1/8 \text{ Ca}}{\text{corner}} = 1 \text{ Ca atom}
\]

\[
6 \text{ face centers} \times \frac{1/2 \text{ oxygen}}{\text{face center}} = 3 \text{ O atoms}; \text{ formula} = \text{CaTiO}_3
\]
b. The Ti atoms are at the corners of each unit cell and the oxygen atoms are at the center of each edge in the unit cell.

Because each of the 12 cube edges is shared by 4 unit cells:

\[
12 \times \frac{1}{4} = 3 \text{ O atoms}; \quad 8 \times \frac{1}{8} = 1 \text{ Ti atom}; \quad 1 \text{ Ca at center}; \quad \text{formula} = \text{CaTiO}_3
\]

c. Six oxygen atoms surround each Ti atom in the extended lattice of both representations.

73. a. Y: 1 Y in center; Ba: 2 Ba in center

\[
\text{Cu}: \quad 8 \text{ corners} \times \frac{1/8 \text{ Cu}}{\text{corner}} = 1 \text{ Cu}, \quad 8 \text{ edges} \times \frac{1/4 \text{ Cu}}{\text{edge}} = 2 \text{ Cu}, \quad \text{total} = 3 \text{ Cu atoms}
\]

\[
\text{O}: \quad 20 \text{ edges} \times \frac{1/4 \text{ O}}{\text{edge}} = 5 \text{ oxygen}, \quad 8 \text{ faces} \times \frac{1/2 \text{ O}}{\text{face}} = 4 \text{ oxygen}, \quad \text{total} = 9 \text{ O atoms}
\]

Formula: YBa_2Cu_3O_9

b. The structure of this superconductor material follows the alternative perovskite structure described in Exercise 16.72b. The YBa_2Cu_3O_9 structure is three of these cubic perovskite unit cells stacked on top of each other. The oxygen atoms are in the same places, Cu takes the place of Ti, two of the calcium atoms are replaced by two barium atoms, and one Ca is replaced by Y.

c. Y, Ba, and Cu are the same. Some oxygen atoms are missing.

\[
12 \text{ edges} \times \frac{1/4 \text{ O}}{\text{edge}} = 3 \text{ O}, \quad 8 \text{ faces} \times \frac{1/2 \text{ O}}{\text{face}} = 4 \text{ O}, \quad \text{total} = 7 \text{ O atoms}
\]

Superconductor formula is YBa_2Cu_3O_7.

Phase Changes and Phase Diagrams

74. a. Evaporation: process where liquid molecules escape the liquid’s surface to form a gas.

b. Condensation: process where gas molecules hit the surface of a liquid and convert to a liquid.

c. Sublimation: process where a solid converts directly to a gas without passing through the liquid state.

d. Boiling: the temperature and pressure at which a liquid completely converts to a gas as long as heat is applied.

e. Melting: temperature and pressure at which a solid completely converts to a liquid as long as heat is applied.
f. Enthalpy of vaporization ($\Delta H_{\text{vap}}$): the enthalpy change that occurs at the boiling point when a liquid converts into a gas.

g. Enthalpy of fusion ($\Delta H_{\text{fus}}$): the enthalpy change that occurs at the melting point when a solid converts into a liquid.

h. Heating curve: a plot of temperature versus time as heat is applied at a constant rate to some substance.

75. A volatile liquid is one that evaporates relatively easily. Volatile liquids have large vapor pressures because the intermolecular forces that prevent evaporation are relatively weak.

76. Equilibrium: There is no change in composition; the vapor pressure is constant. Dynamic: Two processes, vapor $\rightarrow$ liquid and liquid $\rightarrow$ vapor, are both occurring but with equal rates, so the composition of the vapor is constant.

77. a. As the intermolecular forces increase, the rate of evaporation decreases.

b. As temperature increases, the rate of evaporation increases.

c. As surface area increases, the rate of evaporation increases.

78. At any temperature the plot tells us that substance A has a higher vapor pressure than substance B, with substance C having the lowest vapor pressure. Therefore, the substance with the weakest intermolecular forces is A, and the substance with the strongest intermolecular forces is C.

NH$_3$ can form hydrogen-bonding interactions, whereas the others cannot. Substance C is NH$_3$. The other two are nonpolar compounds with only London dispersion forces. Because CH$_4$ is smaller than SiH$_4$, CH$_4$ will have weaker LD forces and is substance A. Therefore, substance B is SiH$_4$.

79. C$_2$H$_5$OH(l) $\rightarrow$ C$_2$H$_5$OH(g) is an endothermic process. Heat is absorbed when liquid ethanol vaporizes; the internal heat from the body provides this heat, which results in the cooling of the body.

80. The phase change H$_2$O(g) $\rightarrow$ H$_2$O(l) releases heat that can cause additional damage. Also, steam can be at a temperature greater than 100°C.

81. The mathematical equation that relates the vapor pressure of a substance to temperature is:

$$\ln P_{\text{vap}} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} \right) + C$$

As shown above, this equation is in the form of the straight-line equation. If one plots $\ln P_{\text{vap}}$ versus $1/T$ with temperature in Kelvin, the slope of the straight line is $-\Delta H_{\text{vap}}/R$. Because $\Delta H_{\text{vap}}$ is always positive, the slope of the straight line will be negative.
82. At 100.°C (373 K), the vapor pressure of H2O is 1.00 atm = 760. torr. For water, \( \Delta H_{\text{vap}} = 40.7 \text{ kJ/mol} \).

\[
\ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{or} \quad \ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

\[
\ln \left( \frac{520. \text{ torr}}{760. \text{ torr}} \right) = \frac{40.7 \times 10^3 \text{ J/mol}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{373 \text{ K}} - \frac{1}{T_2} \right) - 7.75 \times 10^{-5} = \left( \frac{1}{373 \text{ K}} - \frac{1}{T_2} \right)
\]

\(-7.75 \times 10^{-5} = 2.68 \times 10^{-3} - \frac{1}{T_2}, \quad \frac{1}{T_2} = 2.76 \times 10^{-3}, \quad T_2 = \frac{1}{2.76 \times 10^{-3}} = 362 \text{ K or 89°C} \)

\[
\ln \left( \frac{P_2}{1.00} \right) = \frac{40.7 \times 10^3 \text{ J/mol}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{373 \text{ K}} - \frac{1}{623 \text{ K}} \right), \quad P_2 = 5.27, \quad P_2 = e^{5.27} = 194 \text{ atm}
\]

83. \[
\ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right), \quad \ln \left( \frac{836 \text{ torr}}{213 \text{ torr}} \right) = \frac{\Delta H_{\text{vap}}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{313 \text{ K}} - \frac{1}{353 \text{ K}} \right)
\]

Solving: \( \Delta H_{\text{vap}} = 3.1 \times 10^4 \text{ J/mol} \); for the normal boiling point, \( P = 1.00 \text{ atm} = 760. \text{ torr} \).

\[
\ln \left( \frac{760. \text{ torr}}{213 \text{ torr}} \right) = \frac{3.1 \times 10^4 \text{ J/mol}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{313 \text{ K}} - \frac{1}{T_1} \right), \quad \frac{1}{313} - \frac{1}{T_1} = 3.4 \times 10^{-4}
\]

\( T_1 = 350. \text{ K} = 77°C \); the normal boiling point of CCl₄ is 77°C.

84. \[
\ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\( P_1 = 760. \text{ torr}, \quad T_1 = 56.5°C + 273.2 = 329.7 \text{ K}; \quad P_2 = 630. \text{ torr}, \quad T_2 = ? \)

\[
\ln \left( \frac{760.}{630.} \right) = \frac{32.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{329.7 \text{ K}} - \frac{1}{329.7 \text{ K}} \right), \quad 0.188 = 3.85 \times 10^3 \left( \frac{1}{T_2} - 3.033 \times 10^{-3} \right)
\]

\[
\frac{1}{T_2} - 3.033 \times 10^{-3} = 4.88 \times 10^{-5}, \quad \frac{1}{T_2} = 3.082 \times 10^{-3}, \quad T_2 = 324.5 \text{ K} = 51.3°C
\]

\[
\ln \left( \frac{630. \text{ torr}}{P_2} \right) = \frac{32.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{298.2 \text{ K}} - \frac{1}{324.5} \right), \quad \ln 630. - \ln P_2 = 1.05
\]

\( \ln P_2 = 5.40, \quad P_2 = e^{5.40} = 221 \text{ torr} \)
85. If we graph \( \ln P_{\text{vap}} \) versus \( 1/T \) with temperature in Kelvin, the slope of the resulting straight line will be \(-\Delta H_{\text{vap}}/R\).

<table>
<thead>
<tr>
<th>( P_{\text{vap}} )</th>
<th>( \ln P_{\text{vap}} )</th>
<th>( T ) (Li)</th>
<th>( 1/T )</th>
<th>( T ) (Mg)</th>
<th>( 1/T )</th>
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</thead>
<tbody>
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<td>1 torr</td>
<td>0</td>
<td>1023 K</td>
<td>9.775 ( \times 10^{-4} ) K(^{-1} )</td>
<td>893 K</td>
<td>11.2 ( \times 10^{-4} ) K(^{-1} )</td>
</tr>
<tr>
<td>10.</td>
<td>2.3</td>
<td>1163 K</td>
<td>8.598 ( \times 10^{-4} ) K(^{-1} )</td>
<td>1013 K</td>
<td>9.872 ( \times 10^{-4} ) K(^{-1} )</td>
</tr>
<tr>
<td>100.</td>
<td>4.61</td>
<td>1353 K</td>
<td>7.391 ( \times 10^{-4} ) K(^{-1} )</td>
<td>1173 K</td>
<td>8.525 ( \times 10^{-4} ) K(^{-1} )</td>
</tr>
<tr>
<td>400.</td>
<td>5.99</td>
<td>1513 K</td>
<td>6.609 ( \times 10^{-4} ) K(^{-1} )</td>
<td>1313 K</td>
<td>7.616 ( \times 10^{-4} ) K(^{-1} )</td>
</tr>
<tr>
<td>760.</td>
<td>6.63</td>
<td>1583 K</td>
<td>6.317 ( \times 10^{-4} ) K(^{-1} )</td>
<td>1383 K</td>
<td>7.231 ( \times 10^{-4} ) K(^{-1} )</td>
</tr>
</tbody>
</table>

For Li:

We get the slope by taking two points \((x, y)\) that are on the line we draw. For a line, slope = \( \Delta y/\Delta x \); or we can determine the straight-line equation using a calculator. The general straight-line equation is \( y = mx + b \) where \( m \) = slope and \( b \) = \( y \) intercept.

The equation of the Li line is: \( \ln P_{\text{vap}} = -1.90 \times 10^4(1/T) + 18.6 \), slope = \(-1.90 \times 10^4 \) K

\[ \Delta H_{\text{vap}} = -\text{slope} \times R = 1.90 \times 10^4 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta H_{\text{vap}} = 1.58 \times 10^5 \text{ J/mol} = 158 \text{ kJ/mol} \]

For Mg:

The equation of the line is: \( \ln P_{\text{vap}} = -1.67 \times 10^4(1/T) + 18.7 \), slope = \(-1.67 \times 10^4 \) K

\[ \Delta H_{\text{vap}} = -\text{slope} \times R = 1.67 \times 10^4 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta H_{\text{vap}} = 1.39 \times 10^5 \text{ J/mol} = 139 \text{ kJ/mol} \]

The bonding is stronger in Li because \( \Delta H_{\text{vap}} \) is larger for Li.
86. Again, we graph \( \ln P_{\text{vap}} \) versus \( 1/T \). The slope of the line equals \( -\Delta H_{\text{vap}}/R \).

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( 10^3/T ) (K(^{-1}))</th>
<th>( P_{\text{vap}} ) (torr)</th>
<th>( \ln P_{\text{vap}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>3.66</td>
<td>14.4</td>
<td>2.67</td>
</tr>
<tr>
<td>283</td>
<td>3.53</td>
<td>26.6</td>
<td>3.28</td>
</tr>
<tr>
<td>293</td>
<td>3.41</td>
<td>47.9</td>
<td>3.87</td>
</tr>
<tr>
<td>303</td>
<td>3.30</td>
<td>81.3</td>
<td>4.40</td>
</tr>
<tr>
<td>313</td>
<td>3.19</td>
<td>133</td>
<td>4.89</td>
</tr>
<tr>
<td>323</td>
<td>3.10</td>
<td>208</td>
<td>5.34</td>
</tr>
<tr>
<td>353</td>
<td>2.83</td>
<td>670</td>
<td>6.51</td>
</tr>
</tbody>
</table>

The slope of the line is \(-4600 \text{ K}\).

\[ -4600 \text{ K} = -\frac{\Delta H_{\text{vap}}}{R} = \frac{-\Delta H_{\text{vap}}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}, \quad \Delta H_{\text{vap}} = 38,000 \text{ J/mol} = 38 \text{ kJ/mol} \]

To determine the normal boiling point, we can use the following formula:

\[ \ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

At the normal boiling point, the vapor pressure equals 1.00 atm, or 760 torr. At 273 K, the vapor pressure is 14.4 torr (from data in the problem).

\[ \ln \left( \frac{14.4}{760} \right) = \frac{38,000}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{T_2} - \frac{1}{273 \text{ K}} \right), \quad -3.97 = 4.6 \times 10^3 \left( 1/T_2 - 3.66 \times 10^{-3} \right) \]

\[ -8.6 \times 10^{-3} + 3.66 \times 10^{-3} = 1/T_2 = 2.80 \times 10^{-3}, \quad T_2 = 357 \text{ K} = \text{ normal boiling point} \]

87.
88. \( X(\text{g, } 100.\, ^\circ\text{C}) \rightarrow X(\text{g, } 75^\circ\text{C}) \), \( \Delta T = -25^\circ\text{C} \)

\[ q_1 = s_{\text{gas}} \times m \times \Delta T = \frac{1.0 \, \text{J}}{\text{g} \cdot ^\circ\text{C}} \times 250. \, \text{g} \times (-25^\circ\text{C}) = -6300 \, \text{J} = -6.3 \, \text{kJ} \]

\( X(\text{g, } 75^\circ\text{C}) \rightarrow X(\text{l, } 75^\circ\text{C}) \), \( q_2 = 250. \, \text{g} \times \frac{1 \, \text{mol}}{75.0 \, \text{g}} \times \frac{-20. \, \text{kJ}}{\text{mol}} = -67 \, \text{kJ} \)

\( X(\text{l, } 75^\circ\text{C}) \rightarrow X(\text{l, } -15^\circ\text{C}) \), \( q_3 = \frac{2.5 \, \text{J}}{\text{g} \cdot ^\circ\text{C}} \times 250. \, \text{g} \times (-90^\circ\text{C}) = -56,000 \, \text{J} = -56 \, \text{kJ} \)

\( X(\text{l, } -15^\circ\text{C}) \rightarrow X(\text{s, } -15^\circ\text{C}) \), \( q_4 = 250. \, \text{g} \times \frac{1 \, \text{mol}}{75.0 \, \text{g}} \times \frac{-5.0 \, \text{kJ}}{\text{mol}} = -17 \, \text{kJ} \)

\( X(\text{s, } -15^\circ\text{C}) \rightarrow X(\text{s, } -50^\circ\text{C}) \), \( q_5 = \frac{3.0 \, \text{J}}{\text{g} \cdot ^\circ\text{C}} \times 250. \, \text{g} \times (-35^\circ\text{C}) = -26,000 \, \text{J} = -26 \, \text{kJ} \)

\( q_{\text{total}} = q_1 + q_2 + q_3 + q_4 + q_5 = -6.3 - 67 - 56 - 17 - 26 = -172 \, \text{kJ} \)

89. To calculate \( q_{\text{total}} \), break up the heating process into five steps.

\( \text{H}_2\text{O}(\text{s, } -20.\, ^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{s, } 0^\circ\text{C}) \), \( \Delta T = 20^\circ\text{C} \)

\[ q_1 = s_{\text{ice}} \times m \times \Delta T = \frac{2.1 \, \text{J}}{\text{g} \cdot ^\circ\text{C}} \times 5.00 \times 10^2 \, \text{g} \times 20^\circ\text{C} = 2.1 \times 10^4 \, \text{J} = 21 \, \text{kJ} \]

\( \text{H}_2\text{O}(\text{s, } 0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{l, } 0^\circ\text{C}) \), \( q_2 = 5.00 \times 10^2 \, \text{g} \, \text{H}_2\text{O} \times \frac{1 \, \text{mol}}{18.02 \, \text{g}} \times \frac{6.01 \, \text{kJ}}{\text{mol}} = 167 \, \text{kJ} \)

\( \text{H}_2\text{O}(\text{l, } 0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{l, } 100^\circ\text{C}) \), \( q_3 = \frac{4.2 \, \text{J}}{\text{g} \cdot ^\circ\text{C}} \times 5.00 \times 10^2 \, \text{g} \times 100^\circ\text{C} = 2.1 \times 10^5 \, \text{J} = 210 \, \text{kJ} \)

\( \text{H}_2\text{O}(\text{l, } 100^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{g, } 100^\circ\text{C}) \), \( q_4 = 5.00 \times 10^2 \, \text{g} \times \frac{1 \, \text{mol}}{18.02 \, \text{g}} \times \frac{40.7 \, \text{kJ}}{\text{mol}} = 1130 \, \text{kJ} \)

\( \text{H}_2\text{O}(\text{g, } 100^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{g, } 250^\circ\text{C}) \), \( q_5 = \frac{2.0 \, \text{J}}{\text{g} \cdot ^\circ\text{C}} \times 5.00 \times 10^2 \, \text{g} \times 150^\circ\text{C} = 1.5 \times 10^5 \, \text{J} \)

\[ q_{\text{total}} = q_1 + q_2 + q_3 + q_4 + q_5 = 21 + 167 + 210 + 1130 + 150 = 1680 \, \text{kJ} \]

90. \( \text{H}_2\text{O}(\text{g, } 125^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{g, } 100^\circ\text{C}) \), \( q_1 = 2.0 \, \text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1} \times 75.0 \, \text{g} \times (-25^\circ\text{C}) = -3800 \, \text{J} \)

\[ = -3.8 \, \text{kJ} \]

\( \text{H}_2\text{O}(\text{g, } 100^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{l, } 100^\circ\text{C}) \), \( q_2 = 75.0 \, \text{g} \times \frac{1 \, \text{mol}}{18.02 \, \text{g}} \times \frac{-40.7 \, \text{kJ}}{\text{mol}} = -169 \, \text{kJ} \)
H$_2$O(l, 100.°C) → H$_2$O(l, 0°C), \( q_3 = 4.2 \, \text{J} \, ^\circ\text{C}^{-1} \, \text{g}^{-1} \times 75.0 \, \text{g} \times (-100.\, ^\circ\text{C}) = -32,000 \, \text{J} = -32 \, \text{kJ} \)

To convert H$_2$O(g) at 125°C to H$_2$O(l) at 0°C requires \((-3.8 \, \text{kJ} - 169 \, \text{kJ} - 32 \, \text{kJ} =)\) \(-205 \, \text{kJ}\) of heat removed. To convert from H$_2$O(l) at 0°C to H$_2$O(s) at 0°C requires:

\[
q_4 = 75.0 \, \text{g} \times \frac{1 \, \text{mol}}{18.02 \, \text{g}} \times \frac{-6.01 \, \text{kJ}}{\text{mol}} = -25.0 \, \text{kJ}
\]

This amount of energy puts us over the \(-215 \, \text{kJ}\) limit \(-205 \, \text{kJ} - 25.0 \, \text{kJ} = -230. \, \text{kJ}\). Therefore, a mixture of H$_2$O(s) and H$_2$O(l) will be present at 0°C when 215 kJ of heat are removed from the gas sample.

91. Heat released = 0.250 g Na × \( \frac{1 \, \text{mol}}{22.99 \, \text{g}} \times \frac{368 \, \text{kJ}}{2 \, \text{mol}} = 2.00 \, \text{kJ} \)

To melt 50.0 g of ice requires: 50.0 g ice × \( \frac{1 \, \text{mol} \, \text{H}_2\text{O}}{18.02 \, \text{g}} \times \frac{6.01 \, \text{kJ}}{\text{mol}} = 16.7 \, \text{kJ} \)

The reaction doesn't release enough heat to melt all of the ice. The temperature will remain at 0°C.

92. In order to set up an equation, we need to know what phase exists at the final temperature. To heat 20.0 g of ice from -10.0°C to 0.0°C requires:

\[
q = \frac{2.08 \, \text{J}}{\text{g} \, ^\circ\text{C}} \times 20.0 \, \text{g} \times 10.0 \, ^\circ\text{C} = 416 \, \text{J}
\]

To convert ice to water at 0.0°C requires:

\[
q = 20.0 \, \text{g} \times \frac{1 \, \text{mol}}{18.02 \, \text{g}} \times \frac{6.01 \, \text{kJ}}{\text{mol}} = 6.67 \, \text{kJ} = 6670 \, \text{J}
\]

To chill 100.0 g of water from 80.0°C to 0.0°C requires:

\[
q = \frac{4.18 \, \text{J}}{\text{g} \, ^\circ\text{C}} \times 100.0 \, \text{g} \times 80.0 \, ^\circ\text{C} = 33,400 \, \text{J}
\]

From the heat values above, the liquid phase exists once the final temperature is reached (a lot more heat is lost when the 80.0 g of water is cooled to 0.0°C than heat is required to convert the ice into water). To calculate the final temperature, we will equate the heat gain by the ice to the heat loss by the water. We will keep all quantities positive in order to avoid sign errors. The heat gain by ice will be the 416 J required to convert the ice to 0.0°C plus the 6670 J required to convert ice at 0.0°C into water at 0.0°C plus the heat required to raise the temperature from 0.0°C to the final temperature.

Heat gain by ice = 416 J + 6670 J + \( \frac{4.18 \, \text{J}}{\text{g} \, ^\circ\text{C}} \times 20.0 \, \text{g} \times (T_f - 0.0 \, ^\circ\text{C}) = 7.09 \times 10^3 + (83.6)T_f \)
Heat loss by water = \( \frac{4.18 \text{ J}}{\text{g} \cdot ^\circ \text{C}} \times 100.0 \text{ g} \times (80.0^\circ \text{C} - T_f) = 3.34 \times 10^4 - 418T_f \)

Solving for the final temperature:

\[ 7.09 \times 10^3 + (83.6)T_f = 3.34 \times 10^4 - 418T_f, \quad 502T_f = 2.63 \times 10^4, \quad T_f = 52.4^\circ \text{C} \]

Total mass \( \text{H}_2\text{O} = 18 \text{ cubes} \times \frac{30.0 \text{ g}}{\text{cube}} = 540. \text{ g}; \quad 540. \text{ g} \text{ H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g}} = 30.0 \text{ mol H}_2\text{O} \)

Heat removed to produce ice at \(-5.0^\circ \text{C}\):

\[
\left( \frac{4.18 \text{ J}}{\text{g} \cdot ^\circ \text{C}} \times 540. \text{ g} \times 22.0^\circ \text{C} \right) + \left( \frac{6.01 \times 10^3 \text{ J}}{\text{mol}} \times 30.0 \text{ mol} \right) + \left( \frac{2.08 \text{ J}}{\text{g} \cdot ^\circ \text{C}} \times 540. \text{ g} \times 5.0^\circ \text{C} \right)
\]

\[ = 4.97 \times 10^4 \text{ J} + 1.80 \times 10^5 \text{ J} + 5.6 \times 10^3 \text{ J} = 2.35 \times 10^5 \text{ J} \]

\[ 2.35 \times 10^5 \text{ J} \times \frac{1 \text{ g CF}_2\text{Cl}_2}{158 \text{ J}} = 1.49 \times 10^3 \text{ g CF}_2\text{Cl}_2 \text{ must be vaporized.} \]

1.00 lb \( \times \frac{454 \text{ g}}{\text{lb}} = 454 \text{ g} \text{ H}_2\text{O}; \) a change of 1.00°F is equal to a change of 5/9°C.

The amount of heat in J in 1 Btu is: \( \frac{4.18 \text{ J}}{\text{g} \cdot ^\circ \text{C}} \times 454 \text{ g} \times \frac{5}{9}^\circ \text{C} = 1.05 \times 10^3 \text{ J}, \) or 1.05 kJ

It takes 40.7 kJ to vaporize 1 mol H\(_2\)O (\( \Delta H_{\text{vap}} \)). Combining these:

\[
\frac{1.00 \times 10^4 \text{ Btu}}{\text{h}} \times \frac{1.05 \text{ kJ}}{\text{Btu}} \times \frac{1 \text{ mol H}_2\text{O}}{40.7 \text{ kJ}} = 258 \text{ mol/h}; \quad \text{or}
\]

\[
\frac{258 \text{ mol}}{\text{h}} \times \frac{18.02 \text{ g H}_2\text{O}}{\text{mol}} = 4650 \text{ g/h} = 4.65 \text{ kg/h}
\]

See Figures 16.55 and 16.58 for the phase diagrams of H\(_2\)O and CO\(_2\). Most substances exhibit only three different phases: solid, liquid, and gas. This is true for H\(_2\)O and CO\(_2\). Also typical of phase diagrams is the positive slopes for both the liquid-gas equilibrium line and the solid-gas equilibrium line. This is also true for both H\(_2\)O and CO\(_2\). The solid-liquid equilibrium line also generally has a positive slope. This is true for CO\(_2\) but not for H\(_2\)O. In the H\(_2\)O phase diagram, the slope of the solid-liquid line is negative. The determining factor for the slope of the solid-liquid line is the relative densities of the solid and liquid phases. The solid phase is denser than the liquid phase in most substances; for these substances, the slope of the solid-liquid equilibrium line is positive. For water, the liquid phase is denser than the solid phase, which corresponds to a negative-sloping solid-liquid equilibrium line. Another difference between H\(_2\)O and CO\(_2\) is the normal melting points and normal boiling points. The term
normal just dictates a pressure of 1 atm. H₂O has a normal melting point (0°C) and a normal boiling point (100°C), but CO₂ does not. At 1 atm pressure, CO₂ only sublimes (goes from the solid phase directly to the gas phase). There are no temperatures at 1 atm for CO₂ where the solid and liquid phases are in equilibrium or where the liquid and gas phases are in equilibrium. There are other differences, but those discussed above are the major ones.

The relationship between melting points and pressure is determined by the slope of the solid-liquid equilibrium line. For most substances (CO₂ included), the positive slope of the solid-liquid line shows a direct relationship between the melting point and pressure. As pressure increases, the melting point increases. Water is just the opposite since the slope of the solid-liquid line in water is negative. Here, the melting point of water is inversely related to the pressure.

For boiling points, the positive slope of the liquid-gas equilibrium line indicates a direct relationship between the boiling point and pressure. This direct relationship is true for all substances, including H₂O and CO₂.

The critical temperature for a substance is defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied. The critical temperature, like the boiling-point temperature, is directly related to the strength of the intermolecular forces. Since H₂O exhibits relatively strong hydrogen bonding interactions and CO₂ only exhibits London dispersion forces, one would expect a higher critical temperature for H₂O than for CO₂.

96. Critical temperature: The temperature above which a liquid cannot exist, i.e., the gas cannot be liquefied by increased pressure.

Critical pressure: The pressure that must be applied to a substance at its critical temperature to produce a liquid.

97. The critical temperature is the temperature above which the vapor cannot be liquefied no matter what pressure is applied. Since N₂ has a critical temperature below room temperature (~22°C), it cannot be liquefied at room temperature. NH₃, with a critical temperature above room temperature, can be liquefied at room temperature.
98. The following sketch of the Br_2 phase diagram is not to scale. Because the triple point of Br_2 is at a temperature below the freezing point of Br_2, the slope of the solid-liquid line is positive.

![Phase Diagram](image)

The positive slopes of all the lines indicate that Br_2(s) is more dense than Br_2(l), which is more dense than Br_2(g). At room temperature (~22°C) and 1 atm, Br_2(l) is the stable phase. Br_2(l) cannot exist at a temperature below the triple-point temperature of −7.3°C and at a temperature above the critical-point temperature of 320°C. The phase changes that occur as temperature is increased at 0.10 atm are solid → liquid → gas.

99. A: solid; B: liquid; C: vapor
D: solid + vapor; E: solid + liquid + vapor
F: liquid + vapor; G: liquid + vapor; H: vapor

triple point: E; critical point: G

Normal freezing point: temperature at which solid-liquid line is at 1.0 atm (see following plot).

Normal boiling point: temperature at which liquid-vapor line is at 1.0 atm (see following plot).

Because the solid-liquid equilibrium line has a positive slope, the solid phase is denser than the liquid phase.
100.  
   
   a.  3
   
   b. Triple point at 95.31°C: rhombic, monoclinic, gas
      Triple point at 115.18°C: monoclinic, liquid, gas
      Triple point at 153°C: rhombic, monoclinic, liquid
   
   c. From the phase diagram, the rhombic phase is stable at $T \approx 20°C$ and $P = 1.0$ atm.
   
   d. Yes, monoclinic sulfur and vapor (gas) share a common boundary line in the phase diagram.
   
   e. Normal melting point = 115.21°C; normal boiling point = 444.6°C; the normal melting and boiling points occur at $P = 1.0$ atm.
   
   f. Rhombic, because the rhombic-monoclinic equilibrium line has a positive slope.

101.  
   
   a. two
   
   b. Higher-pressure triple point: graphite, diamond, and liquid; lower-pressure triple point: graphite, liquid, and vapor
   
   c. It is converted to diamond (the more dense solid form).
   
   d. Diamond is more dense, which is why graphite can be converted to diamond by applying pressure.

102. The typical phase diagram for a substance shows three phases and has a positive-sloping solid-liquid equilibrium line (water is atypical). A sketch of the phase diagram for I$_2$ would look like this:

   ![Phase Diagram](image)

   Statements a and e are true. For statement a, the liquid phase is always more dense than the gaseous phase (gases are mostly empty space). For statement e, because the triple point is at 90 torr, the liquid phase cannot exist at any pressure less than 90 torr, no matter what the temperature. For statements b, c, and d, examine the phase diagram to prove to yourself that they are false.

103. Because the density of the liquid phase is greater than the density of the solid phase, the slope of the solid-liquid boundary line is negative (as in H$_2$O). With a negative slope, the melting
points increase with a decrease in pressure, so the normal melting point of X should be greater than 225°C.

104. The following sketch of the phase diagram for Xe is not to scale.

From the three points given, the slope of the solid-liquid boundary line is positive, so Xe(s) is more dense than Xe(l). Also, the positive slope of this line tells us that the melting point of Xe increases as pressure increases. The same direct relationship exists for the boiling point of Xe because the liquid-gas boundary line also has a positive slope.

105. As P is lowered, we go from a to b on the phase diagram. The water boils. The evaporation of the water is endothermic, and the water is cooled (b \(\rightarrow\) c), forming some ice. If the pump is left on, the ice will sublime until none is left. This is the basis of freeze drying.

Additional Exercises

106. One B atom and one N atom together have the same number of electrons as two C atoms. The description of physical properties sounds a lot like the properties of graphite and diamond, the two solid forms of carbon. The two forms of BN have structures similar to graphite and diamond.

107. If TiO\(_2\) conducts electricity as a liquid, then it is an ionic solid; if not, then TiO\(_2\) is a network solid.
108. Sublimation will occur, allowing water to escape as H₂O(g).

109. B₂H₆: This compound contains only nonmetals, so it is probably a molecular solid with covalent bonding. The low boiling point confirms this.

SiO₂: This is the empirical formula for quartz, which is a network solid.

CsI: This is a metal bonded to a nonmetal, which generally form ionic solids. The electrical conductivity in aqueous solution confirms this.

W: Tungsten is a metallic solid as the conductivity data confirms.

110. If we extend the liquid-vapor line of the water phase diagram to below the freezing point, we find that supercooled water will have a higher vapor pressure than ice at -10°C (see Figure 16.51 of the text). To achieve equilibrium, there must be a constant vapor pressure. Over time, supercooled water will be transformed through the vapor into ice in an attempt to equilibrate the vapor pressure. Eventually there will only be ice at -10°C, and its vapor at the vapor pressure given by the solid-vapor line in the phase diagram.

111. For a right-angle triangle (opposite side not drawn in):

\[
\cos 30° = \frac{\text{adjacent}}{\text{hypotenuse}} = \frac{R}{R + r}, \quad 0.866 = \frac{R}{R + r}
\]

\[
(0.866)r = R - (0.866)R, \quad r = \left( \frac{0.134}{0.866} \right) \times R = (0.155)R
\]

The cation must have a radius that is 0.155 times the radius of the spheres to just fit into the trigonal hole.

112. The unit cell is a parallelepiped. There are three parallelepiped unit cells in a hexagon. In each parallelepiped there are atoms at each of the eight corners (shared by eight unit cells) plus one atom inside the unit cell: 2/3 of one atom plus 1/6 from each of two others. Thus there are two atoms in the unit cell. See next page for an illustration.
113. Ar is cubic closest packed. There are four Ar atoms per unit cell and with a face-centered
unit cell, the atoms touch along the face diagonal. Let \( l \) = length of cube edge.

\[
\text{Face diagonal} = 4r = l\sqrt{2}, \quad l = 4(190. \text{ pm})/\sqrt{2} = 537 \text{ pm} = 5.37 \times 10^{-8} \text{ cm}
\]

\[
\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{4 \text{ atoms} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{39.95 \text{ g}}{\text{mol}}}{(5.37 \times 10^{-8} \text{ cm})^3} = 1.71 \text{ g/cm}^3
\]

114. The ionic radius is 148 pm for Rb\(^+\) and 181 pm for Cl\(^-\). Using these values, let’s calculate the
density of the two structures.

Normal pressure: Rb\(^+\) and Cl\(^-\) touch along cube edge (form NaCl structure).

\[
\text{Cube edge} = l = 2(148 + 181) = 658 \text{ pm} = 6.58 \times 10^{-8} \text{ cm}; \text{ there are four RbCl units per unit cell.}
\]

\[
\text{Density} = d = \frac{4(85.47) + 4(35.45)}{6.022 \times 10^{23}(6.58 \times 10^{-8} \text{ cm})^3} = 2.82 \text{ g/cm}^3
\]

High pressure: Rb\(^+\) and Cl\(^-\) touch along body diagonal (form CsCl structure).

\[
2r_+ + 2r_- = 658 \text{ pm} = \text{body diagonal} = l\sqrt{3}, \quad l = 658 \text{ pm}/\sqrt{3} = 380. \text{ pm}
\]

Each unit cell contains 1 RbCl unit: \( d = \frac{85.47 + 35.45}{6.022 \times 10^{23}(3.80 \times 10^{-8} \text{ cm})^3} = 3.66 \text{ g/cm}^3
\]

The high-pressure form has the higher density. The density ratio is 3.66/2.82 = 1.30. We
would expect this because the effect of pressure is to push things closer together and thus
increase density.

115. Assuming 100.00 g: 28.31 g O \( \times \) \( \frac{1 \text{ mol}}{15.999 \text{ g}} \) = 1.769 mol O; 71.69 g Ti \( \times \) \( \frac{1 \text{ mol}}{47.88 \text{ g}} \) = 1.497 mol Ti

Dividing one mole quantity by the other, gives formulas of TiO\(_{1.182}\) or Ti\(_{0.8462}\)O.
For Ti$_{0.8462}$O, let $x = \text{Ti}^{2+}$ per mol O$^{2-}$ and $y = \text{Ti}^{3+}$ per mol O$^{2-}$. Setting up two equations and solving:

$$x + y = 0.8462 \quad \text{and} \quad 2x + 3y = 2; \quad 2x + 3(0.8462 - x) = 2$$

$$x = 0.539 \text{ mol Ti}^{2+}/\text{mol O}^{2-} \quad \text{and} \quad y = 0.307 \text{ mol Ti}^{3+}/\text{mol O}^{2-}$$

$$\frac{0.539}{0.8462} \times 100 = 63.7\% \text{ of the titanium is Ti}^{2+} \text{ and } 36.3\% \text{ is Ti}^{3+}.$$  

116. First, we need to get the empirical formula of spinel. Assume 100.0 g of spinel:

$$37.9 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 1.40 \text{ mol Al} \quad \text{The mole ratios are 2:1:4.}$$

$$17.1 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} = 0.703 \text{ mol Mg} \quad \text{Empirical formula = Al}_2\text{MgO}_4$$

$$45.0 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.81 \text{ mol O}$$

Assume each unit cell contains an integral value ($x$) of Al$_2$MgO$_4$ formula units. Each Al$_2$MgO$_4$ formula unit has a mass of $24.31 + 2(26.98) + 4(16.00) = 142.27$ g/mol.

Density = \(\frac{x \text{ formula units}}{6.022 \times 10^{23} \text{ formula units}} \times \frac{1 \text{ mol}}{8.09 \times 10^{-8} \text{ cm}^3} \times \frac{142.27 \text{ g}}{\text{mol}} = 3.57 \text{ g/cm}^3\)

Solving: $x = 8.00$

Each unit cell has 8 formula units of Al$_2$MgO$_4$ or 16 Al, 8 Mg, and 32 O atoms.

117. $24.7 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol}}{78.11 \text{ g}} = 0.316 \text{ mol C}_6\text{H}_6$

$$P_{C_6H_6} = \frac{nRT}{V} = \frac{0.316 \text{ mol} \times 0.08296 \text{ L atm/K mol} \times 293.2 \text{ K}}{100.0 \text{ L}} = 0.0760 \text{ atm, or 57.8 torr}\$$

118. $100.0 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.014 \text{ g N}_2} = 3.570 \text{ mol N}_2; \quad P_{H_2O} = \chi_{H_2O}P_{\text{total}}, \quad \chi_{H_2O} = \frac{23.8 \text{ torr}}{700. \text{ torr}} = 0.0340$

$$\chi_{H_2O} = 0.0340 = \frac{n_{H_2O}}{n_{N_2} + n_{H_2O}} = \frac{n_{H_2O}}{3.570 + n_{H_2O}}, \quad n_{H_2O} = 0.121 + (0.0340)n_{H_2O}$$

$$n_{H_2O} = 0.125 \text{ mol}; \quad 0.125 \text{ mol} \times 18.02 \text{ g/mol} = 2.25 \text{ g H}_2\text{O}$$
119. \( w = -P \Delta V; \) assume constant \( P \) of 1.00 atm.

\[
V_{373} = \frac{nRT}{P} = \frac{1.00 \times 0.08206 \times 373}{1.00} = 30.6 \text{ L for 1 mol of water vapor}
\]

Because the density of H\(_2\)O(l) is 1.00 g/cm\(^3\), 1.00 mol of H\(_2\)O(l) occupies 18.0 cm\(^3\) or 0.0180 L.

\[
w = -1.00 \text{ atm} (30.6 \text{ L} - 0.0180 \text{ L}) = -30.6 \text{ L atm}
\]

\[
w = -30.6 \text{ L atm} \times 101.3 \text{ J L}^{-1} \text{ atm}^{-1} = -3.10 \times 10^3 \text{ J} = -3.10 \text{ kJ}
\]

\[
\Delta E = q + w = 41.16 \text{ kJ} - 3.10 \text{ kJ} = 38.06 \text{ kJ}
\]

\[
\frac{38.06 \times 100}{41.16} = 92.47\% \text{ of the energy goes to increase the internal energy of the water.}
\]

The remainder of the energy (7.53\%) goes to do work against the atmosphere.

120. 

a. The arrangement of the layers is:

```
Layer 1

Layer 2

Layer 3

Layer 4
```

A total of 20 cannon balls will be needed.

b. The layering alternates abcabc, which is cubic closest packing.

c. tetrahedron

121. The three sheets of B's form a cube. In this cubic unit cell there are B atoms at every face, B atoms at every edge, B atoms at every corner, and one B atom in the center. A representation of this cube is:
Each unit cell of B atoms contains four A atoms. The number of B atoms in each unit cell is:

$$(8 \text{ corners} \times \frac{1}{8}) + (6 \text{ faces} \times \frac{1}{2}) + (12 \text{ edges} \times \frac{1}{4}) + (1 \text{ middle B}) = 8 \text{ B atoms}$$

The empirical formula is $\text{AB}_2$.

Each A atom is in a cubic hole of B atoms, so eight B atoms surround each A atom. This will also be true in the extended lattice. The structure of B atoms in the unit cell is a cubic arrangement with B atoms at every face, edge, corner, and center of the cube.

The type of cubic cell formed is not important; only that Cu and Mn crystallizes in the same type of cubic unit cell is important. Each cubic unit cell has a specific relationship between the cube edge length $l$ and the radius $r$. In all cases $l \propto r$. Therefore, $V \propto l^3 \propto r^3$. For the mass ratio, we can use the molar masses of Mn and Cu because each unit cell must contain the same number of Mn and Cu atoms. Solving:

$$\frac{\text{Density}_\text{Mn}}{\text{Density}_\text{Cu}} = \frac{\text{mass}_\text{Mn} \times \text{volume}_\text{Cu}}{\text{volume}_\text{Mn} \times \text{mass}_\text{Cu}} = \frac{\text{mass}_\text{Mn}}{\text{mass}_\text{Cu}} \times \frac{\text{volume}_\text{Cu}}{\text{volume}_\text{Mn}}$$

$$\frac{\text{Density}_\text{Mn}}{\text{Density}_\text{Cu}} = 0.8645 \times \left(\frac{1}{1.056}\right)^3 = 0.7341$$

$$\text{Density}_\text{Mn} = 0.7341 \times \text{Density}_\text{Cu} = 0.7341 \times 8.96 \text{ g/cm}^3 = 6.58 \text{ g/cm}^3$$
**Challenge Problems**

123. \[ E = \frac{\hbar^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2} \]
   \[ E_{111} = \frac{3\hbar^2}{8mL^2}; \quad E_{112} = \frac{6\hbar^2}{8mL^2}; \quad \Delta E = E_{112} - E_{111} = \frac{3\hbar^2}{8mL^2} \]

\[ \Delta E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s})}{9.50 \times 10^{-9} \text{ m}} = 2.09 \times 10^{-17} \text{ J} \]

\[ L^2 = \frac{3\hbar^2}{8m\Delta E}, \quad L = \left( \frac{3\hbar^2}{8m\Delta E} \right)^{1/2} = \left[ \frac{3(6.626 \times 10^{-34} \text{ J s})^2}{8(9.109 \times 10^{-31} \text{ kg})(2.09 \times 10^{-17} \text{ J})} \right]^{1/2} \]

\[ L = 9.30 \times 10^{-11} \text{ m} = 93.0 \text{ pm} \]

The sphere that fits in this cube will touch the cube at the center of each face. The diameter of the sphere will equal the length of the cube. So:

\[ 2r = L, \quad r = 93.0/2 = 46.5 \text{ pm} \]

124. \( \text{XeCl}_2\text{F}_2, 8 + 2(7) + 2(7) = 36 \text{ e}^- \)

There are two possible square planar molecular structures for \( \text{XeCl}_2\text{F}_2 \). One structure has the Cl atoms 90° apart, the other has the Cl atoms 180° apart. The structure with the Cl atoms 90° apart is polar; the other structure is nonpolar. The polar structure will have additional dipole forces, so it has the stronger intermolecular forces and is the liquid. The gas form of \( \text{XeCl}_2\text{F}_2 \) is the nonpolar form having the Cl atoms 180° apart.

125. Assuming 100.00 g of \( \text{MO}_2 \):

\[ 23.72 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.483 \text{ mol O} \]

\[ 1.483 \text{ mol O} \times \frac{1 \text{ mol M}}{2 \text{ mol O}} = 0.7415 \text{ mol M} \]

\[ 100.00 \text{ g} - 23.72 \text{ g} = 76.28 \text{ g M}; \quad \text{molar mass M} = \frac{76.28 \text{ g}}{0.7415 \text{ mol}} = 102.9 \text{ g/mol} \]

From the periodic table, element M is rhodium (Rh).
The unit cell for cubic closest packing is face-centered cubic (4 atoms/unit cell). The atoms for a face-centered cubic unit cell are assumed to touch along the face diagonal of the cube, so the face diagonal = 4r. The distance between the centers of touching Rh atoms will be the distance of 2r where r = radius of Rh atom.

Face diagonal = \( \sqrt{2} \ l \), where \( l = \) cube edge.

Face diagonal = 4r = 2 × 269.0 × 10⁻¹² m = 5.380 × 10⁻¹⁰ m

\[ \sqrt{2} \ l = 4r = 5.38 \times 10^{-10} \ m, \ l = \frac{5.38 \times 10^{-10} \ m}{\sqrt{2}} = 3.804 \times 10^{-10} \ m = 3.804 \times 10^{-8} \ cm \]

Density = \[ \frac{4 \text{ atoms Rh} \times \frac{1 \text{ mol Rh}}{6.0221 \times 10^{23} \text{ atoms}} \times \frac{102.9 \text{ g Rh}}{\text{mol Rh}}}{(3.804 \times 10^{-8} \ cm)^3} \] = 12.42 g/cm³

126. \( 1 \ \text{gal} \times \frac{3785 \ \text{mL}}{\text{gal}} \times \frac{0.998 \ \text{g}}{\text{mL}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \ \text{g}} = 210. \ \text{mol H}_2\text{O} \)

From Table 16.7, the vapor pressure of H₂O at 25°C is 23.756 torr. The water will evaporate until this partial pressure is reached.

\[ V = \frac{nRT}{P} = \frac{210. \text{ mol} \times \frac{0.08206 \ \text{L atm}}{\text{K mol}} \times 298 \ \text{K}}{23.756 \ \text{torr} \times \frac{1 \ \text{atm}}{760 \ \text{torr}}} = 1.64 \times 10^5 \ \text{L} \]

Dimension of cube = (1.64 \times 10^5 \ \text{L} \times 1 \ \text{dm}^3/\text{L})^{1/3} = 54.7 \ \text{dm}

54.7 \ \text{dm} \times \frac{1 \ \text{m}}{10 \ \text{dm}} \times \frac{1.094 \ \text{yards}}{\text{m}} \times \frac{3 \ \text{ft}}{\text{yard}} = 18.0 \ \text{ft}

The cube has dimensions of 18.0 ft \times 18.0 \times 18.0 ft.

127. For water vapor at 30.0°C and 31.824 torr:

\[ \text{density} = \frac{P(\text{molar mass})}{RT} = \frac{\left( \frac{31.824 \ \text{atm}}{760} \right) \left( \frac{18.015 \ \text{g}}{\text{mol}} \right)}{\frac{0.08206 \ \text{L atm}}{\text{K mol}} \times 303.2 \ \text{K}} = 0.03032 \ \text{g/L} \]

The volume of one molecule is proportional to \( d^3 \), where \( d \) is the average distance between molecules. For a large sample of molecules, the volume is still proportional to \( d^3 \). So:
\[ \frac{V_{\text{gas}}}{V_{\text{liq}}} = \frac{d_{\text{gas}}^3}{d_{\text{liq}}^3} \]

If we have 0.99567 g H\(_2\)O, then \( V_{\text{liq}} = 1.0000 \) cm\(^3\) = 1.0000 \( \times 10^{-3} \) L.

\[ V_{\text{gas}} = 0.99567 \text{ g} \times 1 \text{ L/0.03032 g} = 32.84 \text{ L} \]

\[ \frac{d_{\text{gas}}^3}{d_{\text{liq}}^3} = \frac{32.84 \text{ L}}{1.0000 \times 10^{-3} \text{ L}} = 3.284 \times 10^4, \quad \frac{d_{\text{gas}}}{d_{\text{liq}}} = (3.284 \times 10^4)^{1/3} = 32.02, \quad \frac{d_{\text{liq}}}{d_{\text{gas}}} = 0.03123 \]

128. \((\text{Body diagonal})^2 = (\text{face diagonal})^2 + (\text{cube edge length})^2\)

In a simple cubic structure, the atoms touch on cube edge so the cube edge = 2R.

Face diagonal = \( \sqrt{(2R)^2 + (2R)^2} = \sqrt{4R^2 + 4R^2} = R\sqrt{8} = 2\sqrt{2} \) R

\[ \text{Body diagonal} = \sqrt{(2\sqrt{2} R)^2 + (2R)^2} = \sqrt{12R^2} = 2\sqrt{3} \text{ R} \]

The diameter of the hole = body diagonal \(-\) 2 radius of atoms at corners = \( 2\sqrt{3} \text{ R} - 2R. \)

Thus the radius of the hole is: \( \frac{2\sqrt{3} \text{ R} - 2R}{2} = \left( \frac{2\sqrt{3} - 2}{2} \right) \text{R} = (\sqrt{3} - 1)\text{R} \)

The volume of the hole is: \( \frac{4}{3}\pi(\sqrt{3} - 1)\text{R}^3 \)

129. a. Structure a:

Ba: 2 Ba inside unit cell; Tl: 8 corners \(\times\) \( \frac{1/8 \text{ Tl}}{\text{corner}} = 1 \text{ Tl} \); Cu: 4 edges \(\times\) \( \frac{1/4 \text{ Cu}}{\text{edge}} = 1 \text{ Cu} \)

O: 6 faces \(\times\) \( \frac{1/2 \text{ O}}{\text{face}} + 8 \) edges \(\times\) \( \frac{1/4 \text{ O}}{\text{edge}} = 5 \text{ O} \)

Formula = TlBa\(_2\)CuO\(_5\).
Structure b:

Tl and Ba are the same as in structure a.

Ca: 1 Ca inside unit cell; Cu: 8 edges \( \times \frac{1/4 \text{ Cu}}{\text{edge}} = 2 \text{ Cu} \)

O: 10 faces \( \times \frac{1/2 \text{ O}}{\text{face}} + 8 \text{ edges} \times \frac{1/4 \text{ O}}{\text{edge}} = 7 \text{ O} \)

Formula = \( \text{TlBa}_2\text{CaCu}_2\text{O}_7 \).

Structure c:

Tl and Ba are the same and two Ca atoms are located inside the unit cell.

Cu: 12 edges \( \times \frac{1/4 \text{ Cu}}{\text{edge}} = 3 \text{ Cu} \); O: 14 faces \( \times \frac{1/2 \text{ O}}{\text{face}} + 8 \text{ edges} \times \frac{1/4 \text{ O}}{\text{edge}} = 9 \text{ O} \)

Formula = \( \text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9 \).

Structure d: Following similar calculations, formula = \( \text{TlBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11} \).

b. Structure a has one planar sheet of Cu and O atoms and the number increases by one for each of the remaining structures. The order of superconductivity temperature from lowest to highest temperature is \( a < b < c < d \).

c. \( \text{TlBa}_2\text{Cu}_x\text{O}_y: \ 3 + 2(2) + x + 5(-2) = 0, \ x = +3 \)
   Only \( \text{Cu}^{3+} \) is present in each formula unit.

\( \text{TlBa}_2\text{CaCu}_x\text{O}_y: \ 3 + 2(2) + 2 + 2(x) + 7(-2) = 0, \ x = +5/2 \)
Each formula unit contains 1 \( \text{Cu}^{2+} \) and 1 \( \text{Cu}^{3+} \).

\( \text{TlBa}_2\text{Ca}_2\text{Cu}_x\text{O}_y: \ 3 + 2(2) + 2(2) + 3(x) + 9(-2) = 0, \ x = +7/3 \)
Each formula unit contains 2 \( \text{Cu}^{2+} \) and 1 \( \text{Cu}^{3+} \).

\( \text{TlBa}_2\text{Ca}_3\text{Cu}_x\text{O}_{11}: \ 3 + 2(2) + 3(2) + 4(x) + 11(-2) = 0, \ x = +9/4 \)
Each formula unit contains 3 \( \text{Cu}^{2+} \) and 1 \( \text{Cu}^{3+} \).

d. This superconductor material achieves variable copper oxidation states by varying the numbers of Ca, Cu, and O in each unit cell. The mixtures of copper oxidation states is discussed in part c. The superconductor material in Exercise 16.73 achieves variable copper oxidation states by omitting oxygen at various sites in the lattice.
130. The liquid compound has the stronger intermolecular forces. The structures of the two C$_2$H$_6$O compounds (20 valence e$^-$) are:

- H\(\overset{\cdot}{C}\)C\(\overset{\cdot}{O}\)H exhibits relatively strong hydrogen bonding
- H\(\overset{\cdot}{C}\)\(\overset{\cdot}{O}\)C\(\overset{\cdot}{C}\)H does not exhibit hydrogen bonding

The first compound above (ethanol) is a liquid, whereas the second (dimethyl ether) is a gas.

131. For an octahedral hole, the geometry is:

From the diagram: \(\cos 45^\circ = \frac{\text{adjacent}}{\text{hypotenuse}} = \frac{2R}{2R + 2r} = \frac{R}{R + r}, \quad 0.707 = \frac{R}{R + r}\)

\(R = 0.707(R + r), \quad r = (0.414)R\)

LiCl unit cell:

- length of cube edge = \(2R + 2r = 514\) pm
- \(2R + 2(0.414 R) = 514\) pm, \(R = 182\) pm = Cl$^-$ radius
- \(2(182\) pm\) + 2\(r = 514\) pm, \(r = 75\) pm = Li$^+$ radius

From Figure 13.8, the Li$^+$ radius is 60 pm, and the Cl$^-$ radius is 181 pm. The Li$^+$ ion is much smaller than calculated. This probably means that the ions are not actually in contact with each other. The octahedral holes are larger than the Li$^+$ ion.
Marathon Problem

132. Use radius ratios and the information in Table 16.6 of the text to determine the type of structure. In the NaCl-type cubic unit cell, the cations occupy octahedral holes; in the CsCl-type cubic unit cell, the cations occupy cubic holes; in the ZnS-type cubic unit cell, the cations occupy the tetra-hedral holes. To determine the fraction of holes filled, the stoichiometry given in the formula will determine this. And finally, to determine the density, use the geometry relationships unique to each structure to determine the edge length (assuming the cations and anions touch); then go on to estimate the density.

For SnO₂:

\[ \frac{r_+}{r_-} = \frac{71 \text{ pm}}{140. \text{ pm}} = 0.51 \]

Radius ratios predict that octahedral holes will be filled. Therefore, we predict the NaCl-type unit cell for SnO₂. Because there is one octahedral hole per closest packed anion (O²⁻), one-half the octahedral holes will be filled by the Sn⁴⁺ cations. This is required by the 1:2 mole ratio of cations to anions in the SnO₂ formula.

To estimate the density in an NaCl-type unit cell, the cations and anions are assumed to touch along the cube edge. Since the unit cell contains four O²⁻ ions, two SnO₂ formula units are contained per unit cell.

\[ l = \text{cube edge length} = 2r_{\text{Sn}^4^+} + 2r_{\text{O}^2^-} = 2(71 \text{ pm}) + 2(140. \text{ pm}) = 422 \text{ pm} \]

\[ \text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{2 \text{ SnO}_2 \text{ units} \times \frac{1 \text{ mol SnO}_2}{6.022 \times 10^{23} \text{ units}} \times \frac{150.7 \text{ g SnO}_2}{\text{mol SnO}_2}}{(4.22 \times 10^{-8} \text{ cm})^3} = 6.66 \text{ g/cm}^3 \]

For AlP:

\[ \frac{r_+}{r_-} = \frac{50. \text{ pm}}{212 \text{ pm}} = 0.24 \]

Radius ratios predict tetrahedral holes for the Al³⁺ cations, which occurs in a ZnS-type unit cell. Because there are two tetrahedral holes per closest packed anion (P³⁻), Al³⁺ ions occupy one-half the tetrahedral holes. This is required to give the 1:1 formula stoichiometry in AlP.

In a ZnS-type unit cell, it is the body diagonal of the unit cell that allows determination of the cube edge length (\(l\)). From Figures 16.38 and 16.39 of the text, the body diagonal of a cube that encloses each tetrahedral hole has a length equal to \(2r_+ + 2r_-\). From Figure 16.41a, each AlP unit cell consists of eight of these smaller cubes. The length of the body diagonal of the unit cell is equal to \(4r_+ + 4r_-\). This relationship, along with realizing that each unit cell contains four P³⁻ ions so that four AlP formula units are contained per unit cell, allows determination of the density.

\[ \text{Body diagonal} = \sqrt{3} \ l = 4r_{\text{Al}^3^+} + 4r_{\text{P}^3^-}, \ l = \frac{4(50. \text{ pm}) + 4(212 \text{ pm})}{\sqrt{3}} = 605 \text{ pm} \]
Density = \( \frac{mass}{volume} \) = \( \frac{4 \text{ AlP units} \times \frac{1 \text{ mol AlP}}{6.022 \times 10^{23} \text{ units}} \times \frac{57.95 \text{ g AlP}}{1 \text{ mol AlP}}}{(6.05 \times 10^{-8} \text{ cm})^{3}} \) = 1.74 g/cm³

For BaO: \( \frac{r_{+}}{r_{-}} = \frac{135 \text{ pm}}{140. \text{ pm}} = 0.964 \)

Radius ratios predicts that Ba^{2+} ions occupy cubic holes. This is seen in CsCl-type unit cells. Because there is one cubic hole per simple cubic packing of anions (O^{2-}), all the cubic holes will be filled by Ba^{2+} ions. This is required to give the required 1:1 formula stoichiometry in BaO.

To estimate the density, the ions in a CsCl-type unit cell are assumed to just touch along the body diagonal of the unit cell so that body diagonal = \( 2r_{+} + 2r_{-} \). Because the unit cell contains one O^{2-} ion, one BaO formula unit is contained per unit cell.

Body diagonal = \( \sqrt{3} l = 2r_{\text{Ba}^{2+}} + 2r_{\text{O}^{2-}} \), \( l = \frac{2(135 \text{ pm}) + 2(140. \text{ pm})}{\sqrt{3}} = 318 \text{ pm} \)

Density = \( \frac{mass}{volume} \) = \( \frac{1 \text{ BaO unit} \times \frac{1 \text{ mol BaO}}{6.022 \times 10^{23} \text{ units}} \times \frac{153.3 \text{ g BaO}}{1 \text{ mol BaO}}}{(3.18 \times 10^{-8} \text{ cm})^{3}} \) = 7.92 g/cm³