CHAPTER 10

LIQUIDS AND SOLIDS

Questions

12. 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.

13. In the vapor phase, gas molecules are relatively far apart from each other, so far apart that gas molecules are assumed to exhibit no intermolecular forces.

14. Hydrogen bonding occurs when hydrogen atoms are covalently bonded to highly electronegative atoms such as oxygen, nitrogen, or fluorine. Because the electronegativity difference between hydrogen and these highly electronegative atoms is relatively large, the N–H, O–H, and F–H bonds are very polar covalent bonds. This leads to strong dipole forces. Also, the small size of the hydrogen atom allows the dipoles to approach each other more closely than can occur between most polar molecules. Both of these factors make hydrogen bonding a special type of dipole interaction.

15. Atoms have an approximately spherical shape (on average). It is impossible to pack spheres together without some empty space among the spheres.

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

Critical pressure: The pressure that must be applied to a substance at its critical temperature to produce a liquid.
The kinetic energy distribution changes as one raises the temperature ($T_4 > T_c > T_3 > T_2 > T_1$). At the critical temperature $T_c$, all molecules have kinetic energies greater than the intermolecular forces $F$, and a liquid can't form. *Note:* The various temperature distributions shown in the plot are not to scale. The area under each temperature distribution should be equal to each other (area = total number of molecules).

17. Evaporation takes place when some molecules at the surface of a liquid have enough energy to break the intermolecular forces holding them in the liquid phase. When a liquid evaporates, the molecules that escape have high kinetic energies. The average kinetic energy of the remaining molecules is lower; thus the temperature of the liquid is lower.

18. 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.

19. 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.

20. 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.

21. a. As the strength of 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.

22. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ = 44 \text{kJ/mol}$; heat must be absorbed by water in order to evaporate. This heat comes from the surroundings. Hence, as water evaporates, the surroundings (which includes earth) get cooler.

23. Sublimation will occur, allowing water to escape as $\text{H}_2\text{O}(g)$.

24. Water boils when the vapor pressure equals the external pressure. Because the external pressure is significantly lower at high altitudes, a lower temperature is required to equalize the vapor pressure of water to the external pressure. Thus food cooked in boiling water at high elevations cooks at a lower temperature, so it takes longer.

25. The strength of intermolecular forces determines relative boiling points. The types of intermolecular forces for covalent compounds are London dispersion forces, dipole forces, and hydrogen bonding. Because the three compounds are assumed to have similar molar mass and shape, the strength of the London dispersion forces will be about equal among the three compounds. One of the compounds will be nonpolar, so it only has London dispersion forces. The other two compounds will be polar, so they have additional dipole forces and will boil at
a higher temperature than the nonpolar compound. One of the polar compounds will have an H covalently bonded to either N, O, or F. This gives rise to the strongest type of covalent intermolecular forces, hydrogen bonding. The compound that hydrogen bonds will have the highest boiling point, whereas the polar compound with no hydrogen bonding will boil at a temperature in the middle of the other compounds.

26. 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 \( \pi \) 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.

27. 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) and for most solids, the molecules pack together as close as possible; hence solids are usually more dense than the liquid phase. H₂O is an
exception to this. Water molecules are particularly well suited for hydrogen bonding interaction with each other because each molecule has two polar O–H bonds and two lone pairs on the oxygen. This can lead to the association of four hydrogen atoms with each oxygen atom: two by covalent bonds and two by dipoles. To keep this 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.

28. Because silicon carbide is made from Group 4A elements, and because it is extremely hard, one would expect SiC to form a covalent network structure similar to diamond.

29. If TiO₂ conducts electricity as a liquid, then it is an ionic solid; if not, then TiO₂ is a network solid.

30. The interparticle forces in ionic solids (the ionic bonds) are much stronger than the interparticle forces in molecular solids (dipole forces, London forces, etc.). The difference in intermolecular forces is most clearly shown in the huge difference in melting points between ionic and molecular solids. Table salt and ordinary sugar are both crystalline solids at room temperature that look very similar to each other. However, sugar can be melted easily in a saucepan during the making of candy, whereas the full heat of a stove will not melt salt. When a substance melts, some interparticle forces must be broken. Ionic solids (salt) require a much larger amount of energy to break the interparticle forces as compared to the relatively weak forces in molecular solids (sugar).

31. 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_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.

32. 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 I₂ would look like this:
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.

Exercises

Intermolecular Forces and Physical Properties

33. 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.
   a. LD only  
   b. dipole, LD  
   c. H-bonding, LD  
   d. ionic  
   e. LD only (CH₄ is a nonpolar covalent compound.)  
   f. dipole, LD  
   g. ionic

34. 
   a. ionic  
   b. dipole, LD (LD = London dispersion)  
   c. LD only  
   d. LD only (For all practical purposes, a C–H bond can be considered as a nonpolar bond.)  
   e. ionic  
   f. LD only  
   g. H-bonding, LD

35. 
   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 whether the individual bond dipoles cancel.
   b. SeO₂; both SeO₂ and SO₂ are polar compounds, so they both have dipole forces as well as LD forces. However, SeO₂ is a larger molecule, so it would have stronger LD forces.
   c. H₂NCH₂CH₂NH₂; more extensive hydrogen bonding (H-bonding) is possible because two NH₂ groups are present.
d.  H₂CO; H₂CO is polar, whereas CH₃CH₃ is nonpolar. H₂CO has dipole forces in addition to LD forces. CH₃CH₃ only has LD forces.

e.  CH₃OH; CH₃OH can form relatively strong H-bonding interactions, unlike H₂CO.

36.  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 Cl₂ (70.90 g/mol) and F₂ (38.00 g/mol) are nonpolar. Because F₂ has a molar mass closest to that of Ar, one would expect the boiling point of F₂ to be close to that of Ar.

37.  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.

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

Exhibits H-bonding and London dispersion forces.

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

Exhibits dipole and London dispersion forces but no hydrogen bonding since it has no H covalently bonded to the O.

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

Propane only has relatively nonpolar bonds, so it is nonpolar. Propane exhibits only London dispersion forces.

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

39. Boiling points and freezing points are assumed directly related to the strength of the intermolecular forces, whereas vapor pressure is inversely related to the strength of the intermolecular forces.

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 substances.

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 the weakest intermolecular forces.

e. CH₄; smallest, nonpolar molecule, so it has the weakest LD forces.

f. HF; HF can form relatively strong H-bonding interactions, unlike the others.

g. CH₃CH₂CH₂OH; H-bonding, unlike the others, so it has strongest intermolecular forces.

40. a. CBr₄; largest of these nonpolar molecules, so it has strongest LD forces.

b. F₂; ionic forces in LiF are much stronger than the molecular forces in F₂ and HCl. HCl has dipole forces, whereas the nonpolar F₂ does not exhibit these. So F₂ has the weakest intermolecular forces and the lowest freezing point.

c. CH₂CH₂OH; can form H-bonding interactions, unlike the other covalent compounds.

d. H₂O₂; H–O–O–H structure produces stronger H-bonding interactions than HF, so it has the greatest viscosity.

e. H₂CO; H₂CO is polar, so it has dipole forces, unlike the other nonpolar covalent compounds.

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

Properties of Liquids

41. The attraction of H₂O for glass is stronger than the H₂O–H₂O attraction. The miniscus is concave to increase the area of contact between glass and H₂O. The Hg–Hg attraction is greater than the Hg–glass attraction. The miniscus is convex to minimize the Hg–glass contact.
42. 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.

43. 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.

44. 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**

45. \[ n \lambda = 2d \sin \theta, \quad d = \frac{n \lambda}{2 \sin \theta} = \frac{1 \times 154 \text{ pm}}{2 \times \sin 14.22^\circ} = 313 \text{ pm} = 3.13 \times 10^{-10} \text{ m} \]

46. \[ d = \frac{n \lambda}{2 \sin \theta} = \frac{2 \times 154 \text{ pm}}{2 \times \sin 22.20^\circ} = 408 \text{ pm} = 4.08 \times 10^{-10} \text{ m} \]

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

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

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

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

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

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:
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\[ l^2 + l^2 = (4r)^2 \]
\[ 2l^2 = 16r^2 \]
\[ l = r \sqrt{8} \]

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

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 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}

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

50. 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: \[ l = 3.85 \times 10^{-8} \text{ cm} = \text{cube edge length} \]

51. 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 = \(4 \text{ Pb atoms} \times \frac{1 \text{ mol Pb}}{6.022 \times 10^{23} \text{ atoms mol Pb}} \times \frac{207.2 \text{ g Pb}}{23} = 1.38 \times 10^{-21} \text{ g}\)

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 49, the relationship between the cube edge length \(l\) and the radius \(r\) of an atom in a face-centered unit cell is \(l = r \sqrt{2}\).

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

52. The volume of a unit cell is:
\[ V = l^3 = (383.3 \times 10^{-10} \text{ cm})^3 = 5.631 \times 10^{-23} \text{ cm}^3\]

There are four Ir 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:
\[ \text{mass} = 4 \text{ Ir atoms} \times \frac{1 \text{ mol Ir}}{6.022 \times 10^{23} \text{ atoms mol Ir}} \times \frac{192.2 \text{ g Ir}}{23 \text{ atoms}} = 1.277 \times 10^{-21} \text{ g}\]

Density = \(\frac{\text{mass}}{\text{volume}} = \frac{1.277 \times 10^{-21} \text{ g}}{5.631 \times 10^{-23} \text{ cm}^3} = 22.68 \text{ g/cm}^3\)

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

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

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

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

54. For a face-centered unit cell, the radius \(r\) of an atom is related to the length of a cube edge \(l\) by the equation \(l = r \sqrt{2}\) (see Exercise 49).

\[ \text{Radius} = r = \frac{l}{\sqrt{8}} = 392 \times 10^{-12} \text{ m} / \sqrt{8} = 1.39 \times 10^{-10} \text{ m} = 1.39 \times 10^{-8} \text{ cm}\]

The volume of a unit cell is \(l^3\), so the mass of the unknown metal \((X)\) in a unit cell is:
\[ \text{volume} \times \text{density} = (3.92 \times 10^{-8} \text{ cm})^3 \times \frac{21.45 \text{ g X}}{\text{cm}^3} = 1.29 \times 10^{-21} \text{ g X}\]
Because each face-centered unit cell contains four atoms of X:

\[
mol \text{ X in unit cell} = 4 \text{ atoms X} \times \frac{1 \text{ mol X}}{6.022 \times 10^{23} \text{ atoms X}} = 6.642 \times 10^{-24} \text{ mol X}
\]

Therefore, each unit cell contains \(1.29 \times 10^{-21}\) g X, which is equal to \(6.642 \times 10^{-24}\) mol X. The molar mass of X is:

\[
\frac{1.29 \times 10^{-21} \text{ g X}}{6.642 \times 10^{-24} \text{ mol X}} = 194 \text{ g/mol}
\]

From the periodic table, the best choice for the metal is platinum.

55. For a body-centered unit cell, \(8 \text{ corners } \times \frac{1/8 \text{ Ti}}{\text{ corner}} + \text{ Ti at body center} = 2 \text{ Ti atoms.}\)

All body-centered unit cells have two atoms per unit cell. For a unit cell where \(l = \text{ cube edge length:}\)

\[
\text{density} = 4.50 \text{ g/cm}^3 = \frac{2 \text{ atoms Ti} \times \frac{1 \text{ mol Ti}}{6.022 \times 10^{23} \text{ atoms}} \times 47.88 \text{ g Ti}}{l^3}
\]

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 = \(4 \times \text{ radius of atoms} = 4r.\)

The triangle we need to solve is:

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

\(r = 1.42 \times 10^{-8} \text{ cm} = 142 \text{ pm}\)

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

56. From Exercise 55:
In a body-centered cubit unit cell, there are two atoms per unit cell. For a unit cell:

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

57. If gold has a face-centered cubic structure, then there are four atoms per unit cell, and from Exercise 49:

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

If gold has a body-centered cubic structure, then there are two atoms per unit cell, and from Exercise 55:

\[
\text{Density} = \frac{2 \text{ atoms Au} \times \frac{1 \text{ mol Au}}{6.022 \times 10^{23} \text{ atoms}} \times 197.0 \text{ g Au}}{(3.33 \times 10^{-10} \text{ cm})^3} = 17.7 \text{ g/cm}^3
\]

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

\[ l = r \sqrt{8} = (137 \text{ pm}) \sqrt{8} = 387 \text{ pm} = 3.87 \times 10^{-8} \text{ cm} \]

\[
\text{density} = \frac{4 \text{ atoms W} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{183.9 \text{ g W}}{\text{mol}}}{(3.87 \times 10^{-8} \text{ cm})^3} = 21.1 \text{ g/cm}^3
\]

If body-centered cubic:

\[ l = \frac{4r}{\sqrt{3}} = \frac{4 \times 137 \text{ pm}}{\sqrt{3}} = 316 \text{ pm} = 3.16 \times 10^{-8} \text{ cm} \]

\[
\text{density} = \frac{2 \text{ atoms W} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{183.9 \text{ g W}}{\text{mol}}}{(3.16 \times 10^{-8} \text{ cm})^3} = 19.4 \text{ g/cm}^3
\]

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

59. In a face-centered unit cell (ccp structure), the atoms touch along the face diagonal:

\[ (4r)^2 = l^2 + l^2 \]
\[ l = r \sqrt{8} \]
\[ V_{\text{cube}} = l^3 = (r \sqrt{8})^3 = (22.63)r^3 \]

There are four atoms in a face-centered cubic cell (see Exercise 49). Each atom has a volume of \((4/3)\pi r^3 = \text{volume of a sphere}.
\[
V_{\text{atoms}} = 4 \times \frac{4}{3} \pi r^3 = (16.76)r^3
\]

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

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 × 1/8 atom per corner = 1 atom/unit cell). Each atom has an assumed volume of \((4/3)\pi r^3\) = volume of a sphere.

\[
V_{\text{atom}} = \frac{4}{3} \pi r^3 = (4.189)r^3
\]

So \[
\frac{V_{\text{atom}}}{V_{\text{cube}}} = \frac{(4.189)r^3}{8r^3} = 0.5236, \text{ or } 52.36\% \text{ of the volume of each unit cell is occupied by atoms.}
\]

A cubic closest packed structure (face-centered cubic unit cell) packs the atoms much more efficiently than a simple cubic structure.

60. From Exercise 55, a body-centered unit cell contains two net atoms, and 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 = \(l^3 = (4r/\sqrt{3})^3 = (12.32)r^3\)

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

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

To determine the radius of the Fe atoms, we need to determine the cube edge length \(l\).

Volume of unit cell = \(2 \text{ Fe atoms} \times \frac{1 \text{ mol Fe}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{55.85 \text{ g Fe}}{7.86 \text{ g}} \times \frac{1 \text{ cm}^3}{2.36 \times 10^{-23} \text{ cm}^3} = 2.36 \times 10^{-23} \text{ cm}^3\)

\[
l = 4r/\sqrt{3}, \quad r = l\sqrt{3}/4 = 2.87 \times 10^{-8} \text{ cm} \times \sqrt{3}/4 = 1.24 \times 10^{-8} \text{ cm}
\]

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

62. 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.
63. In has fewer valence electrons than Se. Thus Se doped with In would be a p-type semiconductor.

64. 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 an n-type GaAs semiconductor, dope with an excess Group 5A element or dope with a Group 6A element such as sulfur.

65. \[ E_{\text{gap}} = 2.5 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV} = 4.0 \times 10^{-19} \text{ J}; \] we want \( E_{\text{gap}} = E_{\text{light}} = \frac{hc}{\lambda} \), so:

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

66. \[ E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s})}{730. \times 10^{-9} \text{ m}} = 2.72 \times 10^{-19} \text{ J} = \text{energy of band gap}
\]

67. Sodium chloride structure: 8 corners \( \times \frac{1/8 \text{ Cl}}{\text{corner}} + 6 \text{ faces} \times \frac{1/2 \text{ Cl}}{\text{face}} = 4 \text{ Cl ions} \)

12 edges \( \times \frac{1/4 \text{ Na}}{\text{edge}} + 1 \text{ Na at body center} = 4 \text{ Na ions}; \text{NaCl is the formula.} \)

Cesium chloride structure: 1 Cs ion at body center; 8 corners \( \times \frac{1/8 \text{ Cl}}{\text{corner}} = 1 \text{ Cl ion}; \text{CsCl is the formula.} \)

Zinc sulfide structure: There are four Zn ions inside the cube.

8 corners \( \times \frac{1/8 \text{ S}}{\text{corner}} + 6 \text{ faces} \times \frac{1/2 \text{ S}}{\text{face}} = 4 \text{ S ions}; \text{ZnS is the formula.} \)

Titanium oxide structure: 8 corners \( \times \frac{1/8 \text{ Ti}}{\text{corner}} + 1 \text{ Ti at body center} = 2 \text{ Ti ions} \)

4 faces \( \times \frac{1/2 \text{ O}}{\text{face}} + 2 \text{ O inside cube} = 4 \text{ O ions}; \text{TiO}_2 \text{ is the formula.} \)

68. Both As ions are inside the unit cell. 8 corners \( \times \frac{1/8 \text{ Ni}}{\text{corner}} + 4 \text{ edges} \times \frac{1/4 \text{ Ni}}{\text{edge}} = 2 \text{ Ni ions} \)

The unit cell contains 2 ions of Ni and 2 ions of As, which gives a formula of NiAs.

69. 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\(_2\).
70. There are two tetrahedral holes per closest packed anion. Let \( f \) = fraction of tetrahedral holes filled by the cations.

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

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

\[
\text{ZrI}_4: \quad \text{Cation-to-anion ratio} = \frac{1}{4} = \frac{2f}{1}, \quad f = \frac{1}{8}; \quad \text{one-eighth the tetrahedral holes are filled by Zr}^{4+} \text{ cations.}
\]

71. In a cubic closest packed array of anions, there are twice the number of tetrahedral holes as anions present, and an equal number of octahedral holes as anions present. A cubic closest packed array of sulfide ions will have four \( \text{S}^{2-} \) ions, eight tetrahedral holes, and four octahedral holes. In this structure we have \( 1/8(8) = 1 \) \( \text{Zn}^{2+} \) ion and \( 1/2(4) = 2 \) \( \text{Al}^{3+} \) ions present, along with the 4 \( \text{S}^{2-} \) ions. The formula is \( \text{ZnAl}_2\text{S}_4 \).

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

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 \( 1/4 \times 4 = 1 \) net cation from the corners. Each repeating square has two cations and four anions. The empirical formula is \( \text{MA}_2 \).

73. 8 \( \text{F}^- \) ions at corners \( \times \frac{1}{8} \text{F}^- \text{/corner} = 1 \text{F}^- \text{ ion per unit cell; Because there is one cubic hole per cubic unit cell, there is a 2:1 ratio of F}^- \text{ ions to metal ions in the crystal if only half of the body centers are filled with the metal ions. The formula is MF}_2, \text{ where M}^{2+} \text{ is the metal ion.}

74. \( \text{Mn} \) ions at 8 corners: \( 8 \times \frac{1}{8} = 1 \text{ Mn ion; F ions at 12 edges: } 12 \times \frac{1}{4} = 3 \text{ F ions; the formula is MnF}_3 \). Assuming fluoride is \(-1\) charged, then the charge on Mn is \(+3\).

75. From Figure 10.37, MgO has the NaCl structure containing 4 \( \text{Mg}^{2+} \) ions and 4 \( \text{O}^{2-} \) 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 O\(^{2-}\) 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 O\(^{2-}\) anions and the diameter of the Mg\(^{2+}\) cation, so:

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

76. Assuming K\(^+\) and Cl\(^-\) just touch along the cube edge \(l\):

\[
l = 2(314 \text{ pm}) = 628 \text{ pm} = 6.28 \times 10^{-8} \text{ cm}
\]

Volume of unit cell = \(l^3\).

The unit cell contains four K\(^+\) and four Cl\(^-\) ions. For a unit cell:

\[
density = \frac{4 \text{ KCl formula units} \times \frac{1 \text{ mol KCl}}{6.022 \times 10^{23} \text{ formula units}} \times \frac{74.55 \text{ g KCl}}{\text{mol KCl}}}{(6.28 \times 10^{-8} \text{ cm})^3}
\]

\[= 2.00 \text{ g/cm}^3\]

77. 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\(^-\) ions touch along the body diagonal.

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

In each unit cell:

\[
\text{mass} = 1 \text{ CsCl formula unit} \times \frac{1 \text{ mol CsCl}}{6.022 \times 10^{23} \text{ formula units}} \times \frac{168.4 \text{ g CsCl}}{\text{mol CsCl}}
\]

\[= 2.796 \times 10^{-22} \text{ g}\]

\[
\text{volume} = l^3 = 2.796 \times 10^{-22} \text{ g CsCl} \times \frac{1 \text{ cm}^3}{3.97 \text{ g CsCl}} = 7.04 \times 10^{-23} \text{ cm}^3
\]

\[l^3 = 7.04 \times 10^{-23} \text{ cm}^3, \quad l = 4.13 \times 10^{-8} \text{ cm} = 413 \text{ pm} = \text{length of cube edge}\]
\[2r_{\text{Cs}^+} + 2r_{\text{Cl}^-} = \sqrt{3} l = \sqrt{3}(413 \text{ pm}) = 715 \text{ pm}\]

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

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

The distance calculated from the density is 8 pm (2.3%) greater than that calculated from tables of ionic radii.

78. 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.

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

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

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

\[l = 4.47 \times 10^{-8} \text{ cm} = 2r_{\text{Mn}^{2+}} + 2(1.40 \times 10^{-8} \text{ cm}), \text{ } r_{\text{Mn}^{2+}} = 8.35 \times 10^{-8} \text{ cm} = 84 \text{ pm}\]

79. a. \(\text{CO}_2\): molecular  b. \(\text{SiO}_2\): network  c. \(\text{Si}\): atomic, network
d. \(\text{CH}_4\): molecular  e. \(\text{Ru}\): atomic, metallic  f. \(\text{I}_2\): molecular
g. \(\text{KBr}\): ionic  h. \(\text{H}_2\text{O}\): molecular  i. \(\text{NaOH}\): ionic
j. \(\text{U}\): atomic, metallic  k. \(\text{CaCO}_3\): ionic  l. \(\text{PH}_3\): molecular

80. a. \(\text{diamond}\): atomic, network  b. \(\text{PH}_3\): molecular  c. \(\text{H}_2\): molecular
d. \(\text{Mg}\): atomic, metallic  e. \(\text{KCl}\): ionic  f. \(\text{quartz}\): network
g. \(\text{NH}_4\text{NO}_3\): ionic  h. \(\text{SF}_2\): molecular  i. \(\text{Ar}\): atomic, group 8A
j. \(\text{Cu}\): atomic, metallic  k. \(\text{C}_6\text{H}_{12}\text{O}_6\): molecular

81. 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 = NiTi

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

82. Al: $8 \text{ corners} \times \frac{1}{8} \text{Al}_{\text{corner}} = 1 \text{Al}$; Ni: $6 \text{ face centers} \times \frac{1}{2} \text{Ni}_{\text{face center}} = 3 \text{Ni}$

The composition of the specific phase of the superalloy is AlNi₃.

83. Structure 1                      Structure 2

$8 \text{ corners} \times \frac{1}{8} \text{Ca}_{\text{corner}} = 1 \text{Ca atom}$                     $8 \text{ corners} \times \frac{1}{8} \text{Ti}_{\text{corner}} = 1 \text{Ti atom}$

$6 \text{ faces} \times \frac{1}{2} \text{O}_{\text{face}} = 3 \text{O atoms}$                     $12 \text{ edges} \times \frac{1}{4} \text{O}_{\text{corner}} = 3 \text{O atoms}$

1 Ti at body center. Formula = CaTiO₃                                      1 Ca at body center. Formula = CaTiO₃

In the extended lattice of both structures, each Ti atom is surrounded by six O atoms.

84. With a cubic closest packed array of oxygen ions, we have 4 $O^{2-}$ ions per unit cell. We need to balance the total $-8$ charge of the anions with a $+8$ charge from the Al$^{3+}$ and Mg$^{2+}$ cations. The only combination of ions that gives a $+8$ charge is 2 Al$^{3+}$ ions and 1 Mg$^{2+}$ ion. The formula is Al₂MgO₄.

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 Al$^{3+}$ and 1 Mg$^{2+}$ per unit cell. Hence one-half of the octahedral holes are filled with Al$^{3+}$ ions, and one-eighth of the tetrahedral holes are filled with Mg$^{2+}$ ions.

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

Cu: $8 \text{ corners} \times \frac{1}{8} \text{Cu}_{\text{corner}} = 1 \text{Cu}, 8 \text{ edges} \times \frac{1}{4} \text{Cu}_{\text{edge}} = 2 \text{Cu}$, total = 3 Cu atoms

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

Formula: YBa₂Cu₃O₉

b. The structure of this superconductor material follows the second perovskite structure described in Exercise 83. The YBa₂Cu₃O₉ 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.
Superconductor formula is $\text{YBa}_2\text{Cu}_3\text{O}_7$.

86. a. Structure (a):

$\text{Ba}: \text{2 Ba inside unit cell}; \text{Tl}: \text{8 corners } \times \frac{1/8 \text{Tl}}{\text{corner}} = 1 \text{Tl}$

$\text{Cu}: \text{4 edges } \times \frac{1/4 \text{Cu}}{\text{edge}} = 1 \text{Cu}$

$\text{O}: \text{6 faces } \times \frac{1/2 \text{O}}{\text{face}} + \text{8 edges } \times \frac{1/4 \text{O}}{\text{edge}} = 7 \text{O}; \text{ Formula } = \text{TlBa}_2\text{CuO}_5$.

Structure (b):

$\text{Tl}$ and $\text{Ba}$ are the same as in structure (a).

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

$\text{O}: \text{10 faces } \times \frac{1/2 \text{O}}{\text{face}} + \text{8 edges } \times \frac{1/4 \text{O}}{\text{edge}} = 7 \text{O}; \text{ Formula } = \text{TlBa}_2\text{CaCu}_2\text{O}_7$.

Structure (c):

$\text{Tl}$ and $\text{Ba}$ are the same, and two $\text{Ca}$ are located inside the unit cell.

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

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. $\text{TlBa}_2\text{CuO}_5$: $3 + 2(2) + x + 5(-2) = 0, x = +3$

Only $\text{Cu}^{3+}$ is present in each formula unit.

$\text{TlBa}_2\text{CaCu}_2\text{O}_7$: $3 + 2(2) + 2 + 2(x) + 7(-2) = 0, x = +5/2$

Each formula unit contains 1 $\text{Cu}^{2+}$ and 1 $\text{Cu}^{3+}$.

$\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$: $3 + 2(2) + 2(2) + 3(x) + 9(-2) = 0, x = +7/3$

Each formula unit contains 2 $\text{Cu}^{2+}$ and 1 $\text{Cu}^{3+}$.

$\text{TlBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11}$: $3 + 2(2) + 3(2) + 4(x) + 11(-2) = 0, x = +9/4$

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 are discussed in part c. The superconductor material in Exercise 85 achieves variable copper oxidation states by omitting oxygen at various sites in the lattice.

Phase Changes and Phase Diagrams

87. 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>
</tr>
</thead>
<tbody>
<tr>
<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</td>
<td>8.598 $\times 10^{-4}$</td>
<td>1013</td>
<td>9.872 $\times 10^{-4}$</td>
</tr>
<tr>
<td>100.</td>
<td>4.61</td>
<td>1353</td>
<td>7.391 $\times 10^{-4}$</td>
<td>1173</td>
<td>8.525 $\times 10^{-4}$</td>
</tr>
<tr>
<td>400.</td>
<td>5.99</td>
<td>1513</td>
<td>6.609 $\times 10^{-4}$</td>
<td>1313</td>
<td>7.616 $\times 10^{-4}$</td>
</tr>
<tr>
<td>760.</td>
<td>6.63</td>
<td>1583</td>
<td>6.317 $\times 10^{-4}$</td>
<td>1383</td>
<td>7.231 $\times 10^{-4}$</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

Slope $= -\Delta H_{\text{vap}}/R$, $\Delta H_{\text{vap}} = -$ slope $\times R = 1.90 \times 10^4$ K $\times 8.3145$ J/K$\cdot$mol

$\Delta H_{\text{vap}} = 1.58 \times 10^5$ J/mol $= 158$ kJ/mol
For Mg:

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

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

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

The bonding is stronger in Li because \( \Delta H_{\text{vap}} \) is larger for Li.

We graph \( \ln P_{\text{vap}} \) vs \( 1/T \). 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>

Slope = \( \frac{6.6 - 2.5}{(2.80 \times 10^{-3} - 3.70 \times 10^{-3}) \text{ K}^{-1}} = -4600 \text{ K} \)

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

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).

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

\[ -8.6 \times 10^{-4} + 3.66 \times 10^{-3} = 1/T_2 = 2.80 \times 10^{-3}, T_2 = 357 \text{ K} = \text{normal boiling point} \]

89. At 100.°C (373 K), the vapor pressure of H\(_2\)O is 1.00 atm = 760. torr. For water, \( \Delta H_{\text{vap}} = 40.7 \text{ kJ/mol} \).

\[ \ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \text{ or } \ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]
\[
\ln\left(\frac{520. \text{torr}}{760. \text{torr}}\right) = \frac{40.7 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right), \quad -7.75 \times 10^{-5} = \left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right)
\]

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

90. At 100.°C (373 K), the vapor pressure of H\textsubscript{2}O is 1.00 atm. For water, \(\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}\).

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

\[
\ln\left(\frac{P_2}{1.00 \text{ atm}}\right) = \frac{40.7 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left(\frac{1}{373 \text{ K}} - \frac{1}{388 \text{ K}}\right), \quad \ln P_2 = 0.51, \quad P_2 = e^{0.51} = 1.7 \text{ atm}
\]

\[
\ln\left(\frac{3.50}{1.00}\right) = \frac{40.7 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right), \quad 2.56 \times 10^{-4} = \left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right)
\]

\[2.56 \times 10^{-4} = 2.68 \times 10^{-3} - \frac{1}{T_2}, \quad \frac{1}{T_2} = 2.42 \times 10^{-3}, \quad T_2 = \frac{1}{2.42 \times 10^{-3}} = 413 \text{ K} \text{ or } 140.\text{°C}\]

91. \[
\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right), \quad \ln\left(\frac{836 \text{ torr}}{213 \text{ torr}}\right) = \frac{\Delta H_{\text{vap}}}{8.3145 \text{ J/K} \cdot \text{mol}} \left(\frac{1}{313 \text{ K}} - \frac{1}{353 \text{ K}}\right)
\]

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

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

\[T_1 = 350. \text{K} = 77^\circ \text{C}; \text{ the normal boiling point of CCl}_4 \text{ is } 77^\circ \text{C}.
\]

92. \[
\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\]

\[P_1 = 760. \text{torr}, \quad T_1 = 56.5^\circ \text{C} + 273.2 = 329.7 \text{ K}; \quad P_2 = 630. \text{torr}, \quad T_2 = ?
\]

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

\[\frac{1}{T_2} - 3.033 \times 10^{-3} = 4.88 \times 10^{-5}, \quad \frac{1}{T_2} = 3.082 \times 10^{-3}, \quad T_2 = 324.5 \text{ K} = 51.3^\circ \text{C}\]
\[ \ln \left( \frac{630 \text{ torr}}{P_2} \right) = \frac{32.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{298.2} - \frac{1}{324.5} \right), \ln 630 - \ln P_2 = 1.05 \]

\[ \ln P_2 = 5.40, \quad P_2 = e^{5.40} = 221 \text{ torr} \]

93.

94. \( X(g, 100.\degree C) \rightarrow X(g, 75\degree C), \Delta T = -25\degree C \)

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

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

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

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

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

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

95. a. Many more intermolecular forces must be broken to convert a liquid to a gas as compared with converting a solid to a liquid. Because more intermolecular forces must be broken, much more energy is required to vaporize a liquid than is required to melt a solid. Therefore, \( \Delta H_{\text{vap}} \) is much larger than \( \Delta H_{\text{fus}} \).

b. \( 1.00 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g}} \times \frac{2.60 \text{ kJ}}{\text{mol Na}} = 0.113 \text{ kJ} = 113 \text{ J} \) to melt 1.00 g Na
c. \[ 1.00 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g}} \times \frac{97.0 \text{ kJ}}{1 \text{ mol Na}} = 4.22 \text{ kJ} = 4220 \text{ J} \] to vaporize 1.00 g Na.

d. This is the reverse process of that described in part c, so the energy change is the same quantity but opposite in sign. Therefore, \( q = -4220 \text{ J; i.e., 4220 J of heat will be released.} \)

96. Melt: \[ 8.25 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g}} \times \frac{9.92 \text{ kJ}}{1 \text{ mol C}_6\text{H}_6} = 1.05 \text{ kJ} \]

Vaporize: \[ 8.25 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol C}_6\text{H}_6}{78.11 \text{ g}} \times \frac{30.7 \text{ kJ}}{1 \text{ mol C}_6\text{H}_6} = 3.24 \text{ kJ} \]

As is typical, the energy required to vaporize a certain quantity of substance is much larger than the energy required to melt the same quantity of substance. A lot more intermolecular forces must be broken to vaporize a substance as compared to melting a substance.

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

\( \text{H}_2\text{O}(s, -20.0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, 0^\circ\text{C}), \Delta T = 20.0^\circ\text{C} \)

\[ q_1 = s_{\text{ice}} \times m \times \Delta T = \frac{2.03 \text{ J}}{\text{g} \cdot \text{g}^\circ\text{C}} \times 5.00 \times 10^2 \text{ g} \times 20.0^\circ\text{C} = 2.0 \times 10^4 \text{ J} = 20. \text{ kJ} \]

\( \text{H}_2\text{O}(s, 0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(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{6.02 \text{ kJ}}{1 \text{ mol}} = 167 \text{ kJ} \]

\( \text{H}_2\text{O}(l, 0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 100.0^\circ\text{C}), q_3 = \frac{4.2 \text{ J}}{\text{g} \cdot \text{g}^\circ\text{C}} \times 5.00 \times 10^2 \text{ g} \times 100.0^\circ\text{C} = 2.1 \times 10^5 \text{ J} = 210 \text{ kJ} \]

\( \text{H}_2\text{O}(l, 100.0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(g, 100.0^\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}}{1 \text{ mol}} = 1130 \text{ kJ} \]

\( \text{H}_2\text{O}(g, 100.0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(g, 250.0^\circ\text{C}), q_5 = \frac{2.0 \text{ J}}{\text{g} \cdot \text{g}^\circ\text{C}} \times 5.00 \times 10^2 \text{ g} \times 150.0^\circ\text{C} = 1.5 \times 10^5 \text{ J} \]

\[ q_{\text{total}} = q_1 + q_2 + q_3 + q_4 + q_5 = 20. + 167 + 210 + 1130 + 150 = 1680 \text{ kJ} \]

98. \( \text{H}_2\text{O}(g, 125^\circ\text{C}) \rightarrow \text{H}_2\text{O}(g, 100.0^\circ\text{C}), q_1 = 2.0 \text{ J/g} \cdot \text{g}^\circ\text{C} \times 75.0 \text{ g} \times (-25.0^\circ\text{C}) = -3800 \text{ J} = -3.8 \text{ kJ} \)

\( \text{H}_2\text{O}(g, 100.0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 100.0^\circ\text{C}), q_2 = 75.0 \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} \times \frac{-40.7 \text{ kJ}}{1 \text{ mol}} = -169 \text{ kJ} \)

\( \text{H}_2\text{O}(l, 100.0^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 0^\circ\text{C}), q_3 = 4.2 \text{ J/g} \cdot \text{g}^\circ\text{C} \times 75.0 \text{ g} \times (-100.0^\circ\text{C}) = -32,000 \text{ J} = -32 \text{ kJ} \)

To convert \( \text{H}_2\text{O}(g) \) at 125°C to \( \text{H}_2\text{O}(l) \) at 0°C requires \((-3.8 \text{ kJ} - 169 \text{ kJ} - 32 \text{ kJ}) = -205 \text{ kJ} \) of heat removed. To convert from \( \text{H}_2\text{O}(l) \) at 0°C to \( \text{H}_2\text{O}(s) \) at 0°C requires:
\[ q_i = 75.0 \text{g} \times \frac{1 \text{mol}}{18.02 \text{g}} \times \frac{-6.02 \text{kJ}}{\text{mol}} = -25.1 \text{kJ} \]

This amount of energy puts us over the \(-215 \text{kJ}\) limit \((-205 \text{kJ} - 25.1 \text{kJ} = -230 \text{kJ})\). Therefore, a mixture of \(\text{H}_2\text{O(s)}\) and \(\text{H}_2\text{O(l)}\) will be present at \(0^\circ\text{C}\) when \(215 \text{kJ}\) of heat is removed from the gas sample.

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

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{6.02 \times 10^3 \text{J}}{\text{mol}} \times 30.0 \text{mol} \right) + \left( \frac{2.03 \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} + 1.81 \times 10^5 \text{J} + 5.5 \times 10^3 \text{J} = 2.36 \times 10^5 \text{J} \\
2.36 \times 10^5 \text{J} \times \frac{1 \text{g} \text{CF}_2\text{Cl}_2}{158 \text{J}} = 1.49 \times 10^3 \text{g} \text{CF}_2\text{Cl}_2 \text{ must be vaporized.} \\

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

To melt 50.0 \text{g} \text{ice requires: } 50.0 \text{g} \text{ice} \times \frac{1 \text{mol} \text{H}_2\text{O}}{18.02 \text{g}} \times \frac{6.02 \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 \(0^\circ\text{C}.\)

101. 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 line equilibrium has a positive slope, the solid phase is denser than the liquid phase.
102. 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 monoclinic solid phase is stable at T = 100.0°C and P = 1 atm.

d. Normal melting point = 115.21°C; normal boiling point = 444.6°C; the normal melting and boiling points occur at P = 1.0 atm.

e. Rhombic is the densest phase because the rhombic-monoclinic equilibrium line has a positive slope, and because the solid-liquid equilibrium lines also have positive slopes.

f. No; P = 1.0 × 10^5 atm is at a pressure somewhere between the 95.31 and 115.18°C triple points. At this pressure, the rhombic and gas phases are never in equilibrium with each other, so rhombic sulfur cannot sublime at P = 1.0 × 10^5 atm. However, monoclinic sulfur can sublime at this pressure.

g. From the phase diagram, we would start off with gaseous sulfur. At 100.0°C and ~1 × 10^5 atm, S(g) would convert to the solid monoclinic form of sulfur. Finally at 100.0°C and some large pressure less than 1420 atm, S(s, monoclinic) would convert to the solid rhombic form of sulfur. Summarizing, the phase changes are S(g) → S(monoclinic) → S(rhombic).

103. 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.

104. The following sketch of the Br2 phase diagram is not to scale. Because the triple point of Br2 is at a temperature below the freezing point of Br2, the slope of the solid-liquid line is positive.
The positive slopes of all the lines indicate that \( \text{Br}_2(\text{s}) \) is more dense than \( \text{Br}_2(\text{l}) \), which is more dense than \( \text{Br}_2(\text{g}) \). At room temperature (\( \sim 22^\circ\text{C} \)) and 1 atm, \( \text{Br}_2(\text{l}) \) is the stable phase. \( \text{Br}_2(\text{l}) \) cannot exist at a temperature below the triple-point temperature of \( -7.3^\circ\text{C} \) or 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 \( \rightarrow \) liquid \( \rightarrow \) gas.

105. 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 \( \text{H}_2\text{O} \)). 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.

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

**Connecting to Biochemistry**

107. The structures of the two \( \text{C}_2\text{H}_4\text{O} \) compounds (20 valence e\(^-\)) are:
exhibits relatively strong hydrogen bonding

does not exhibit hydrogen bonding

The liquid will have the stronger intermolecular forces. Therefore, the first compound above (ethanol) is the liquid, whereas the second compound (dimethyl ether) with the weaker intermolecular forces is the gas.

108. Benzene          Naphthalene

LD forces only        LD forces only

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 CCl₄ 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 above. Each of the physical properties will increase with an increase in intermolecular forces.
We would predict the strength of interparticle forces of the last three molecules to be:

\[
\text{acetone} < \text{acetic acid} < \text{benzoic acid}
\]

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:

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

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.

109. Both molecules are capable of H-bonding. However, in oil of wintergreen the hydrogen bonding is \textit{intramolecular} (within each molecule):

In methyl-4-hydroxybenzoate, the H-bonding is \textit{intermolecular} (between molecules), resulting in stronger forces between molecules and a higher melting point.

110. With the charged ends, this tripeptide exhibits ionic forces. Between the charged ends, there are nonpolar \( \text{CH}_3 \) groups, polar \( \text{C}=\text{O} \) groups, and polar \( \text{N}−\text{H} \) groups. The nonpolar \( \text{CH}_3 \) groups will interact with \( \text{CH}_3 \) groups on other tripeptides through London dispersion forces. The polar \( \text{C}=\text{O} \) group allows the tripeptides to interact with each other through dipole forces. And finally, the \( \text{N}−\text{H} \) bonds allow for hydrogen-bonding interactions with other tripeptides.
111. $\text{C}_2\text{H}_5\text{OH}(l) \rightarrow \text{C}_2\text{H}_5\text{OH}(g)$ 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.

112. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ = 44 \text{ kJ/mol}$; the vaporization of water is an endothermic process. In order to evaporate, water must absorb heat from the surroundings. In this case, part of the surroundings is our body. So, as water evaporates, our body supplies heat, and as a result, our body temperature can cool down. From Le Chatelier’s principle, the less water vapor in the air, the more favorable the evaporation process. Thus the less humid the surroundings, the more favorably water converts into vapor, and the more heat that is lost by our bodies.

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

114. 
\[
\ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right), \quad \ln \left( \frac{760 \text{ torr}}{400. \text{ torr}} \right) = \frac{\Delta H_{\text{vap}}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{291.1 \text{ K}} - \frac{1}{307.8 \text{ K}} \right)
\]

Solving: $\Delta H_{\text{vap}} = 2.83 \times 10^4 \text{ J/mol} = 28.3 \text{ kJ/mol}$

**Additional Exercises**

115. As the physical properties indicate, the intermolecular forces are slightly stronger in $\text{D}_2\text{O}$ than in $\text{H}_2\text{O}$.

116. $\text{CH}_3\text{CO}_2\text{H}$: H-bonding + dipole forces + LD forces

$\text{CH}_2\text{ClCO}_2\text{H}$: H-bonding + larger electronegative atom replacing H (greater dipole) + LD forces

$\text{CH}_3\text{CO}_2\text{CH}_3$: Dipole forces (no H-bonding) + LD forces

From the intermolecular forces listed above, we predict $\text{CH}_3\text{CO}_2\text{CH}_3$ to have the weakest intermolecular forces and $\text{CH}_2\text{ClCO}_2\text{H}$ to have the strongest. The boiling points are consistent with this view.

117. 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.

$\text{NH}_3$ can form hydrogen-bonding interactions, whereas the others cannot. Substance C is $\text{NH}_3$. The other two are nonpolar compounds with only London dispersion forces. Because $\text{CH}_4$ is smaller than $\text{SiH}_4$, $\text{CH}_4$ will have weaker LD forces and is substance A. Therefore, substance B is $\text{SiH}_4$. 
118. As the electronegativity of the atoms covalently bonded to H increases, the strength of the hydrogen-bonding interaction increases.

\[
\begin{align*}
N \cdots H \cdots N < N \cdots H \cdots O < O \cdots H \cdots O < O \cdots H \cdots F < F \cdots H \cdots F
\end{align*}
\]

weakest strongest

119. 8 corners × \(1/8\) Xe corner + 1 Xe inside cell = 2 Xe; 8 edges × \(1/4\) F edge + 2 F inside cell = 4 F

Empirical formula is XeF₂. This is also the molecular formula.

120. 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.

121. 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 confirm.

122. 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.

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

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

123. \(24.7 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol}}{78.11 \text{ g}} = 0.316 \text{ mol C}_6\text{H}_6\)

\[
\frac{nRT}{V} = \frac{0.316 \text{ mol} \times \frac{0.08206 \text{ L atm}}{\text{K mol}} \times 293.2 \text{ K}}{100.0 \text{ L}} = 0.0760 \text{ atm, or 57.8 torr}
\]

124. 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 to 0.0°C requires:

\[
q = \frac{2.03 \text{ J}}{\text{g} \cdot \text{°C}} \times 20.0 \text{ g} \times 10.0 \text{°C} = 406 \text{ J}
\]
To convert ice to water at 0.0°C requires:

\[ q = 20.0 \text{ g} \times \frac{1 \text{ mol}}{18.02} \times \frac{6.02 \text{ kJ}}{\text{mol}} = 6.68 \text{ kJ} = 6680 \text{ J} \]

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

\[ q = \frac{4.18 \text{ J}}{\text{g} \cdot \text{°C}} \times 100.0 \text{ g} \times 80.0\text{°C} = 33,400 \text{ J} \text{ of heat removed} \]

From the heat values above, the liquid phase exists once the final temperature is reached (a lot more heat is lost when the 100.0 g of water is cooled to 0.0°C than the heat 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 the ice will be the 406 J required to convert the ice to 0.0°C plus the 6680 J required to convert the 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 = 406 J + 6680 J + \[ \frac{4.18 \text{ J}}{\text{g} \cdot \text{°C}} \times 20.0 \text{ g} \times (T_f - 0.0\text{°C}) = 7.09 \times 10^3 + (83.6)T_f \]

Heat loss by water = \[ \frac{4.18 \text{ J}}{\text{g} \cdot \text{°C}} \times 100.0 \text{ g} \times (80.0\text{°C} - T_f) = 3.34 \times 10^4 - 418T_f \]

Solving for the final temperature:

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

125. 1.00 lb \times \frac{454 \text{ g}}{\text{lb}} = 454 \text{ g} \text{ H}_2\text{O}; \text{ a change of } 1.00\text{°F} \text{ is equal to a change of } 5/9\text{°C}. \text{ The amount of heat in J in 1 Btu is } \frac{4.18 \text{ J}}{\text{g} \cdot \text{°C}} \times 454 \text{ g} \times \frac{5}{9} \text{°C} = 1.05 \times 10^3 \text{ J} = 1.05 \text{ kJ}. \text{ It takes } 40.7 \text{ kJ} \text{ to vaporize 1 mol H}_2\text{O (ΔH}_{\text{vap}}\text{). Combining these:}

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

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

126. The critical temperature is the temperature above which the vapor cannot be liquefied no matter what pressure is applied. Since N\textsubscript{2} has a critical temperature below room temperature (~22°C), it cannot be liquefied at room temperature. NH\textsubscript{3}, with a critical temperature above room temperature, can be liquefied at room temperature.
Challenge Problems

127. \[ \Delta H = q_p = 30.79 \text{ kJ}; \quad \Delta E = q_p + w, \quad w = -P\Delta V \]

\[ w = -P\Delta V = -1.00 \text{ atm}(28.90 \text{ L}) = -28.9 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{ L atm}} = -2930 \text{ J} \]

\[ \Delta E = 30.79 \text{ kJ} + (-2.93 \text{ kJ}) = 27.86 \text{ kJ} \]

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

These 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.

129. A single hydrogen bond in \( \text{H}_2\text{O} \) has a strength of 21 kJ/mol. Each \( \text{H}_2\text{O} \) 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:

\[ \text{Solid} \rightarrow \text{liquid} \rightarrow \text{vapor} \quad \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \]

\[ \Delta H_{\text{sub}} = 6.0 \text{ kJ/mol} + 40.7 \text{ kJ/mol} = 46.7 \text{ kJ/mol} \]

It takes a total of 46.7 kJ/mol to convert solid \( \text{H}_2\text{O} \) to vapor. This would be the amount of energy necessary to disrupt all of the intermolecular forces in ice. Thus \( (42 \div 46.7) \times 100 = 90\% \) of the attraction in ice can be attributed to H bonding.

130. \( 1 \text{ gal} \times \frac{3785 \text{ mL}}{\text{gal}} \times \frac{0.998 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g}} = 210. \text{ mol H}_2\text{O} \)

From Table 10.8, the vapor pressure of \( \text{H}_2\text{O} \) 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 \text{ ft.}

131. NaCl, MgCl$_2$, NaF, MgF$_2$, and AlF$_3$ all have very high melting points indicative of strong intermolecular forces. They are all ionic solids. SiCl$_4$, SiF$_4$, F$_2$, Cl$_2$, PF$_5$, and SF$_6$ are nonpolar covalent molecules. Only LD forces are present. PCl$_3$ and SCl$_2$ 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. AlCl$_3$ 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. AlCl$_3$ illustrates a gradual transition from ionic to covalent bonding, from an ionic solid to discrete molecules.

132. 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 $x = \text{fraction Fe}^{2+}$ ions in a formula unit and $y = \text{fraction of Fe}^{3+}$ ions present in a formula unit.

Setting up two equations:

$x + y = 0.950$ and $2x + 3y = 2.000$

Solving:

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

$\frac{0.10}{0.95} = 0.11 = \text{fraction of iron as Fe}^{3+}$ 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.

133. Assuming 100.00 g:

$28.31 \text{ g O} \times \frac{1 \text{ mol}}{16.00 \text{ g}} = 1.769 \text{ mol O}; \quad 71.69 \text{ g Ti} \times \frac{1 \text{ mol}}{47.88 \text{ g}} = 1.497 \text{ mol Ti}$

$\frac{1.769}{1.497} = 1.182; \quad \frac{1.497}{1.769} = 0.8462; \quad \text{the formula is TiO}_{1.182} \text{ or TiO}_{0.8462}.$

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:

$x + y = 0.8462$ (mass balance) and $2x + 3y = 2$ (charge balance)

$2x + 3(0.8462 - x) = 2, \quad x = 0.539 \text{ mol Ti}^{2+}/\text{mol O}^{2-} \text{ and } y = 0.307 \text{ mol Ti}^{3+}/\text{mol O}^{2-}$

$\frac{0.539}{0.8462} \times 100 = 63.7\% \text{ of the titanium ions are Ti}^{2+} \text{ and 36.3\% are Ti}^{3+} \text{ (a 1.75 : 1 ion ratio).}$
First, we need to get the empirical formula of spinel. Assume 100.0 g of spinel:

\[
37.9 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 1.40 \text{ mol Al}
\]

The mole ratios are 2 : 1 : 4.

\[
17.1 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} = 0.703 \text{ mol Mg}
\]

Empirical formula = Al$_2$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 $24.31 + 2(26.98) + 4(16.00) = 142.27 \text{ g/mol}$.

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

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.

The type of cubic cell formed is not important; only that Cu and Mn crystallize 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 since each unit cell must contain the same number of Mn and Cu atoms. Solving:

\[
\frac{\text{density}_{\text{Mn}}}{\text{density}_{\text{Cu}}} = \frac{\text{mass}_{\text{Mn}} \times \text{volume}_{\text{Cu}}}{\text{volume}_{\text{Mn}} \times \text{mass}_{\text{Cu}}} = \frac{\text{mass}_{\text{Mn}}}{\text{mass}_{\text{Cu}}} \times \frac{\text{volume}_{\text{Cu}}}{\text{volume}_{\text{Mn}}} = \frac{54.94 \text{ g/mol}}{63.55 \text{ g/mol}} \times \frac{(r_{\text{Cu}})^3}{(1.056 r_{\text{Cu}})^3}
\]

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

\[
\text{density}_{\text{Mn}} = 0.7341 \times \text{density}_{\text{Cu}} = 0.7341 \times 8.96 \text{ g/cm}^3 = 6.58 \text{ g/cm}^3
\]
136. a. The arrangement of the layers is:

A total of 20 cannon balls will be needed.

b. The layering alternates \textit{abcabc}, which is cubic closest packing.

c. tetrahedron

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

138. \[ w = -P\Delta V; \quad \text{assume a constant } P \text{ of 1.00 atm.} \]

\[ V_{373} = \frac{nRT}{P} = \frac{1.00(0.8206)(373)}{1.00} = 30.6 \text{ L for 1 mol of water vapor} \]

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

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

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

\[ \Delta E = q + w = 40.7 \text{ kJ} - 3.10 \text{ kJ} = 37.6 \text{ kJ} \]

\[ \frac{37.6}{40.7} \times 100 = 92.4\% \text{ of the energy goes to increase the internal energy of the water.} \]

The remainder of the energy (7.6\%) goes to do work against the atmosphere.
139. For a cube: \((\text{body diagonal})^2 = (\text{face diagonal})^2 + (\text{cube edge length})^2\)

In a simple cubic structure, the atoms touch on cube edge, so the cube edge = 2r, where r = radius of sphere.

\[
\text{Face diagonal} = \sqrt{(2r)^2 + (2r)^2} = \sqrt{4r^2 + 4r^2} = r\sqrt{8} = 2\sqrt{2}r
\]

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

The diameter of the hole = body diagonal − 2(radius of atoms at corners).

\[
\text{Diameter} = 2\sqrt{3}r - 2r; \ \text{thus the radius of the hole is:} \ \frac{2\sqrt{3}r - 2r}{2} = (\sqrt{3} - 1)r
\]

The volume of the hole is \(\frac{4}{3}\pi [(\sqrt{3} - 1)r]^3\).

140. Using the ionic radii values given in the question, let’s calculate the density of the two structures.

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

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

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

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

\(2r_+ + 2r_0 = 658 \text{ pm} = \text{body diagonal} = l\sqrt{3}, \ l = 658 \text{ pm}/\sqrt{3} = 380. \text{ pm}\)

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

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.
Integrative Problems

141. Molar mass of XY = \( \frac{19.0 \text{ g}}{0.132 \text{ mol}} = 144 \text{ g/mol} \)

X: [Kr] 5s\(^2\)4d\(^{10}\); this is cadmium, Cd.

Molar mass Y = 144 – 112.4 = 32 g/mol; Y is sulfur, S.

The semiconductor is CdS. The dopant has the electron configuration of bromine, Br. Because Br has one more valence electron than S, doping with Br will produce an n-type semiconductor.

142. Assuming 100.00 g of 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 g – 23.72 g = 76.28 g M; 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 = \( 4r = 2 \times 269.0 \times 10^{-12} \text{ m} = 5.380 \times 10^{-10} \text{ m} \)

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

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

143. \[ \ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right); \Delta H_{\text{vap}} = \frac{296 \text{ J}}{g} \times \frac{200.6 \text{ g}}{\text{mol}} = 5.94 \times 10^4 \text{ J/mol Hg} \]

\[ \ln \left( \frac{2.56 \times 10^{-3} \text{ torr}}{P_2} \right) = \frac{5.94 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{573 \text{ K}} - \frac{1}{298.2 \text{ K}} \right) \]
\[
\ln \left( \frac{2.56 \times 10^{-3} \text{ torr}}{P_2} \right) = -11.5, \quad P_2 = 2.56 \times 10^{-3} \text{ torr} e^{-11.5} = 253 \text{ torr}
\]

\[
n = \frac{PV}{RT} = \frac{253 \text{ torr} \times 1 \text{ atm}}{760 \text{ torr}} \times 15.0 \text{ L} \times \frac{0.08206 \text{ L atm}}{K \text{ mol}} \times 573 \text{ K} = 0.106 \text{ mol Hg}
\]

\[
0.106 \text{ mol Hg} \times \frac{6.022 \times 10^{23} \text{ atoms Hg}}{\text{mol Hg}} = 6.38 \times 10^{22} \text{ atoms Hg}
\]

**Marathon Problem**

144. \( q = s \times m \times \Delta T; \) heat loss by metal = heat gain by calorimeter. The change in temperature for the calorimeter is \( \Delta T = 25.2^\circ C \pm 0.2^\circ C - 25.0^\circ C \pm 0.2^\circ C. \) Including the error limits, \( \Delta T \) can range from 0.0 to 0.4°C. Because the temperature change can be 0.0°C, there is no way that the calculated heat capacity has any meaning.

The density experiment is also not conclusive.

\[
d = \frac{4 \text{ g}}{0.42 \text{ cm}^3} = 10 \text{ g/cm}^3 \text{ (1 significant figure)}
\]

\[
d_{\text{high}} = \frac{5 \text{ g}}{0.40 \text{ cm}^3} = 12.5 \text{ g/cm}^3 = 10 \text{ g/cm}^3 \text{ to 1 sig fig}
\]

\[
d_{\text{low}} = \frac{3 \text{ g}}{0.44 \text{ cm}^3} = 7 \text{ g/cm}^3
\]

From Table 1.5, the density of copper is 8.96 g/cm³. The results from this experiment cannot be used to distinguish between a density of 8.96 g/cm³ and 9.2 g/cm³.

The crystal structure determination is more conclusive. Assuming the metal is copper:

\[
\text{volume of unit cell} = (600. \text{ pm})^3 \left( \frac{1 \times 10^{-10} \text{ cm}}{1 \text{ pm}} \right)^3 = 2.16 \times 10^{-22} \text{ cm}^3
\]

\[
\text{Cu mass in unit cell} = 4 \text{ atoms } \times \frac{1 \text{ mol Cu}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{63.55 \text{ g Cu}}{\text{mol Cu}} = 4.221 \times 10^{-22} \text{ g Cu}
\]

\[
d = \frac{\text{mass}}{\text{volume}} = \frac{4.221 \times 10^{-22} \text{ g}}{2.16 \times 10^{-22} \text{ cm}^3} = 1.95 \text{ g/cm}^3
\]
Because the density of $\text{Cu}$ is 8.96 g/cm$^3$, then one can assume this metal is not copper. If the metal is not Cu, then it must be kryptonite (as the question reads). Because we don’t know the molar mass of kryptonite, we cannot confirm that the calculated density would be close to 9.2 g/cm$^3$.

To improve the heat capacity experiment, a more precise balance is a must and a more precise temperature reading is needed. Also, a larger piece of the metal should be used so that $\Delta T$ of the calorimeter has more significant figures. For the density experiment, we would need a more precise balance and a more precise way to determine the volume. Again, a larger piece of metal would help in order to ensure more significant figures in the volume.