

CHAPTER 12

INTERMOLECULAR FORCES AND LIQUIDS AND SOLIDS

12.7 ICl has a dipole moment and Br₂ does not. The dipole moment increases the intermolecular attractions between ICl molecules and causes that substance to have a higher melting point than bromine.

12.8 **Strategy:** Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between *all* species.

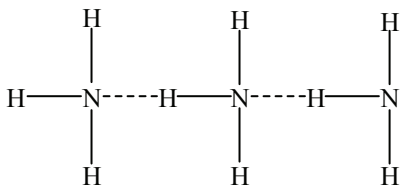
Solution: The three molecules are essentially nonpolar. There is little difference in electronegativity between carbon and hydrogen. Thus, the only type of intermolecular attraction in these molecules is dispersion forces. Other factors being equal, the molecule with the greater number of electrons will exert greater intermolecular attractions. By looking at the molecular formulas you can predict that the order of increasing boiling points will be CH₄ < C₃H₈ < C₄H₁₀.

On a very cold day, propane and butane would be liquids (boiling points -44.5°C and -0.5°C , respectively); only **methane** would still be a gas (boiling point -161.6°C).

12.9 All are tetrahedral (AB₄ type) and are nonpolar. Therefore, the only intermolecular forces possible are dispersion forces. Without worrying about what causes dispersion forces, you only need to know that the strength of the dispersion force increases with the number of electrons in the molecule (all other things being equal). As a consequence, the magnitude of the intermolecular attractions and of the boiling points should increase with increasing molar mass.

- 12.10 (a) Benzene (C₆H₆) molecules are nonpolar. Only dispersion forces will be present.
(b) Chloroform (CH₃Cl) molecules are polar (why?). Dispersion and dipole-dipole forces will be present.
(c) Phosphorus trifluoride (PF₃) molecules are polar. Dispersion and dipole-dipole forces will be present.
(d) Sodium chloride (NaCl) is an ionic compound. Ion-ion (and dispersion) forces will be present.
(e) Carbon disulfide (CS₂) molecules are nonpolar. Only dispersion forces will be present.

12.11 The center ammonia molecule is hydrogen-bonded to two other ammonia molecules.



12.12 In this problem you must identify the species capable of hydrogen bonding among themselves, not with water. In order for a molecule to be capable of hydrogen bonding with another molecule like itself, it must have at least one hydrogen atom bonded to N, O, or F. Of the choices, only (e) CH₃COOH (acetic acid) shows this structural feature. The others cannot form hydrogen bonds among themselves.

12.13 CO_2 is a nonpolar molecular compound. The only intermolecular force present is a relatively weak dispersion force (small molar mass). CO_2 will have the lowest boiling point.

CH_3Br is a polar molecule. Dispersion forces (present in all matter) and dipole–dipole forces will be present. This compound has the next highest boiling point.

CH_3OH is polar and can form hydrogen bonds, which are especially strong dipole-dipole attractions. Dispersion forces and hydrogen bonding are present to give this substance the next highest boiling point.

RbF is an ionic compound (Why?). Ion–ion attractions are much stronger than any intermolecular force. RbF has the highest boiling point.

12.14 Strategy: The molecule with the stronger intermolecular forces will have the higher boiling point. If a molecule contains an N–H, O–H, or F–H bond it can form intermolecular hydrogen bonds. A hydrogen bond is a particularly strong dipole-dipole intermolecular attraction.

Solution: 1-butanol has the higher boiling point because the molecules can form hydrogen bonds with each other (It contains an O–H bond). Diethyl ether molecules do contain both oxygen atoms and hydrogen atoms. However, all the hydrogen atoms are bonded to carbon, not oxygen. There is no hydrogen bonding in diethyl ether, because carbon is not electronegative enough.

12.15 (a) O_2 : it has more electrons than N_2 (both are nonpolar) and therefore has stronger dispersion forces.

(b) SO_2 : it is polar (most important) and also has more electrons than CO_2 (nonpolar). More electrons imply stronger dispersion forces.

(c) HF : although HI has more electrons and should therefore exert stronger dispersion forces, HF is capable of hydrogen bonding and HI is not. Hydrogen bonding is the stronger attractive force.

12.16 (a) Xe : it has more electrons and therefore stronger dispersion forces.

(b) CS_2 : it has more electrons (both molecules nonpolar) and therefore stronger dispersion forces.

(c) Cl_2 : it has more electrons (both molecules nonpolar) and therefore stronger dispersion forces.

(d) LiF : it is an ionic compound, and the ion-ion attractions are much stronger than the dispersion forces between F_2 molecules.

(e) NH_3 : it can form hydrogen bonds and PH_3 cannot.

12.17 (a) CH_4 has a lower boiling point because NH_3 is polar and can form hydrogen bonds; CH_4 is nonpolar and can only form weak attractions through dispersion forces.

(b) KCl is an ionic compound. Ion–ion forces are much stronger than any intermolecular forces. I_2 is a nonpolar molecular substance; only weak dispersion forces are possible.

12.18 Strategy: Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Also look for molecules that contain an N–H, O–H, or F–H bond, which are capable of forming intermolecular hydrogen bonds. Keep in mind that dispersion forces exist between *all* species.

Solution:

(a) Water has O–H bonds. Therefore, water molecules can form hydrogen bonds. The attractive forces that must be overcome are hydrogen bonding and dispersion forces.

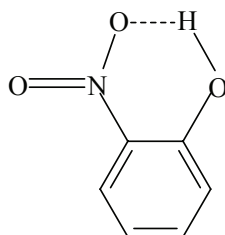
(b) Bromine (Br_2) molecules are nonpolar. Only dispersion forces must be overcome.

(c) Iodine (I_2) molecules are nonpolar. Only dispersion forces must be overcome.

(d) In this case, the F–F bond must be broken. This is an *intramolecular* force between two F atoms, not an *intermolecular* force between F₂ molecules. The attractive forces of the covalent bond must be overcome.

12.19 The linear structure (n-butane) has a higher boiling point (–0.5°C) than the branched structure (2-methylpropane, boiling point –11.7°C) because the linear form can be stacked together more easily.

12.20 The lower melting compound (shown below) can form hydrogen bonds only with itself (*intramolecular* hydrogen bonds), as shown in the figure. Such bonds do not contribute to *intermolecular* attraction and do not help raise the melting point of the compound. The other compound can form *intermolecular* hydrogen bonds; therefore, it will take a higher temperature to provide molecules of the liquid with enough kinetic energy to overcome these attractive forces to escape into the gas phase.



12.31 Ethanol molecules can attract each other with strong hydrogen bonds; dimethyl ether molecules cannot (why?). The surface tension of ethanol is greater than that of dimethyl ether because of stronger intermolecular forces (the hydrogen bonds). Note that ethanol and dimethyl ether have identical molar masses and molecular formulas so attractions resulting from dispersion forces will be equal.

12.32 Ethylene glycol has two –OH groups, allowing it to exert strong intermolecular forces through hydrogen bonding. Its viscosity should fall between ethanol (1 OH group) and glycerol (3 OH groups).

12.35 See Table 12.4 of the text. Descriptions of each crystal type and examples of each are given in the table.

12.36 See Table 12.4 of the text. The properties listed are those of an **ionic solid**.

12.37 See Table 12.4 of the text. The properties listed are those of a **molecular solid**.

12.38 See Table 12.4 of the text. The properties listed are those of a **covalent solid**.

12.39 In a metal, the bonding electrons are spread (or delocalized) over the entire crystal. The mobility of the delocalized electrons makes metals good conductors of heat and electricity. At higher temperatures, there is increased motion (vibration) of the atoms in the metal. The pathway for electrons to move freely through the metal is diminished. Therefore, the ability of a metal to conduct electricity decreases with increasing temperature.

12.40 Li and Be are metallic crystals, B and C are covalent crystals, and N₂, O₂, F₂, and Ne are molecular crystals.

12.41 Na₂O, MgO, and Al₂O₃ are composed of a metal and a nonmetal. All three have high melting points. These are **ionic solids**. SiO₂ is composed of a metalloid and a nonmetal. It has a high melting point, so we would classify it as a **covalent solid**. The final three compounds, P₄O₁₀, SO₃ and Cl₂O₇, are **molecular solids**.

- 12.42** In a molecular crystal the lattice points are occupied by molecules. Of the solids listed, the ones that are composed of molecules are Se_8 , HBr , CO_2 , P_4O_6 , and SiH_4 . In covalent crystals, atoms are held together in an extensive three-dimensional network entirely by covalent bonds. Of the solids listed, the ones that are composed of atoms held together by covalent bonds are Si, C, and B.
- 12.43** (a) In a simple cubic structure each sphere touches **six** others on the $\pm x$, $\pm y$ and $\pm z$ axes (see Figure 12.16).
 (b) In a body-centered cubic lattice each sphere touches **eight** others. Visualize the body-center sphere touching the eight corner spheres (see Figure 12.17).
 (c) In a face-centered cubic lattice each sphere touches **twelve** others (see Section 12.4 of the text).
- 12.44** A corner sphere is shared equally among eight unit cells, so only one-eighth of each corner sphere "belongs" to any one unit cell. A face-centered sphere is divided equally between the two unit cells sharing the face. A body-centered sphere belongs entirely to its own unit cell.

In a *simple cubic cell* there are eight corner spheres. One-eighth of each belongs to the individual cell giving a total of **one** whole sphere per cell. In a *body-centered cubic cell*, there are eight corner spheres and one body-center sphere giving a total of **two** spheres per unit cell (one from the corners and one from the body-center). In a *face-center* sphere, there are eight corner spheres and six face-centered spheres (six faces). The total number of spheres would be **four**: one from the corners and three from the faces.

- 12.45** The mass of one cube of edge 287 pm can be found easily from the mass of one cube of edge 1.00 cm (7.87 g):

$$\frac{7.87 \text{ g Fe}}{1 \text{ cm}^3} \times \left(\frac{1 \text{ cm}}{0.01 \text{ m}}\right)^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}}\right)^3 \times (287 \text{ pm})^3 = 1.86 \times 10^{-22} \text{ g Fe/unit cell}$$

The mass of one iron atom can be found by dividing the molar mass of iron (55.85 g) by Avogadro's number:

$$\frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} \times \frac{1 \text{ mol Fe}}{6.022 \times 10^{23} \text{ Fe atoms}} = 9.27 \times 10^{-23} \text{ g Fe/atom}$$

The number of iron atoms in one cell is the quotient of these numbers:

$$\frac{1 \text{ atom Fe}}{9.27 \times 10^{-23} \text{ g Fe}} \times \frac{1.86 \times 10^{-22} \text{ g Fe}}{1 \text{ unit cell}} = 2.01 \approx \mathbf{2 \text{ atoms/unit cell}}$$

What type of cubic cell is this?

- 12.46 Strategy:** The problem gives a generous hint. First, we need to calculate the volume (in cm^3) occupied by 1 mole of Ba atoms. Next, we calculate the volume that a Ba atom occupies. Once we have these two pieces of information, we can multiply them together to end up with the number of Ba atoms per mole of Ba.

$$\frac{\text{number of Ba atoms}}{\text{cm}^3} \times \frac{\text{cm}^3}{1 \text{ mol Ba}} = \frac{\text{number of Ba atoms}}{1 \text{ mol Ba}}$$

Solution: The volume that contains one mole of barium atoms can be calculated from the density using the following strategy:

$$\frac{\text{volume}}{\text{mass of Ba}} \rightarrow \frac{\text{volume}}{\text{mol Ba}}$$

$$\frac{1 \text{ cm}^3}{3.50 \text{ g Ba}} \times \frac{137.3 \text{ g Ba}}{1 \text{ mol Ba}} = \frac{39.23 \text{ cm}^3}{1 \text{ mol Ba}}$$

We carry an extra significant figure in this calculation to limit rounding errors. Next, the volume that contains two barium atoms is the volume of the body-centered cubic unit cell. Some of this volume is empty space because packing is only 68.0 percent efficient. But, this will not affect our calculation.

$$V = a^3$$

Let's also convert to cm^3 .

$$V = (502 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \right)^3 \times \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right)^3 = \frac{1.265 \times 10^{-22} \text{ cm}^3}{2 \text{ Ba atoms}}$$

We can now calculate the number of barium atoms in one mole using the strategy presented above.

$$\frac{\text{number of Ba atoms}}{\text{cm}^3} \times \frac{\text{cm}^3}{1 \text{ mol Ba}} = \frac{\text{number of Ba atoms}}{1 \text{ mol Ba}}$$

$$\frac{2 \text{ Ba atoms}}{1.265 \times 10^{-22} \text{ cm}^3} \times \frac{39.23 \text{ cm}^3}{1 \text{ mol Ba}} = \mathbf{6.20 \times 10^{23} \text{ atoms/mol}}$$

This is close to Avogadro's number, 6.022×10^{23} particles/mol.

- 12.47** In a body-centered cubic cell, there is one sphere at the cubic center and one at each of the eight corners. Each corner sphere is shared among eight adjacent unit cells. We have:

$$1 \text{ center sphere} + \left(\frac{1}{8} \times 8 \text{ corner spheres} \right) = 2 \text{ spheres per cell}$$

There are **two** vanadium atoms per unit cell.

- 12.48** The mass of the unit cell is the mass in grams of two europium atoms.

$$m = \frac{2 \text{ Eu atoms}}{1 \text{ unit cell}} \times \frac{1 \text{ mol Eu}}{6.022 \times 10^{23} \text{ Eu atoms}} \times \frac{152.0 \text{ g Eu}}{1 \text{ mol Eu}} = 5.048 \times 10^{-22} \text{ g Eu/unit cell}$$

$$V = \frac{5.048 \times 10^{-22} \text{ g}}{1 \text{ unit cell}} \times \frac{1 \text{ cm}^3}{5.26 \text{ g}} = 9.60 \times 10^{-23} \text{ cm}^3/\text{unit cell}$$

The edge length (a) is:

$$a = V^{1/3} = (9.60 \times 10^{-23} \text{ cm}^3)^{1/3} = 4.58 \times 10^{-8} \text{ cm} = \mathbf{458 \text{ pm}}$$

- 12.49** The volume of the unit cell is:

$$V = a^3 = (543 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \right)^3 \times \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right)^3 = 1.60 \times 10^{-22} \text{ cm}^3$$

$$m = dV = \frac{2.33 \text{ g}}{1 \text{ cm}^3} \times (1.60 \times 10^{-22} \text{ cm}^3) = 3.73 \times 10^{-22} \text{ g}$$

The mass of one silicon atom is: $\frac{28.09 \text{ g Si}}{1 \text{ mol Si}} \times \frac{1 \text{ mol Si}}{6.022 \times 10^{23} \text{ atoms Si}} = 4.665 \times 10^{-23} \text{ g/atom}$

The number of silicon atoms in one unit cell is:

$$\frac{1 \text{ atom Si}}{4.665 \times 10^{-23} \text{ g Si}} \times \frac{3.73 \times 10^{-22} \text{ g Si}}{1 \text{ unit cell}} = \mathbf{8 \text{ atoms/unit cell}}$$

- 12.50 Strategy:** Recall that a corner atom is shared with 8 unit cells and therefore only 1/8 of corner atom is within a given unit cell. Also recall that a face atom is shared with 2 unit cells and therefore 1/2 of a face atom is within a given unit cell. See Figure 12.18 of the text.

Solution: In a face-centered cubic unit cell, there are atoms at each of the eight corners, and there is one atom in each of the six faces. Only one-half of each face-centered atom and one-eighth of each corner atom belongs to the unit cell.

$$X \text{ atoms/unit cell} = (8 \text{ corner atoms})(1/8 \text{ atom per corner}) = 1 X \text{ atom/unit cell}$$

$$Y \text{ atoms/unit cell} = (6 \text{ face-centered atoms})(1/2 \text{ atom per face}) = 3 Y \text{ atoms/unit cell}$$

The unit cell is the smallest repeating unit in the crystal; therefore, the empirical formula is **XY₃**.

- 12.51**
- (a) Carbon dioxide forms molecular crystals; it is a molecular compound and can only exert weak dispersion type intermolecular attractions because of its lack of polarity.
 - (b) Boron is a nonmetal with an extremely high melting point. It forms covalent crystals like carbon (diamond).
 - (c) Sulfur forms molecular crystals; it is a molecular substance (S₈) and can only exert weak dispersion type intermolecular attractions because of its lack of polarity.
 - (d) KBr forms ionic crystals because it is an ionic compound.
 - (e) Mg is a metal; it forms metallic crystals.
 - (f) SiO₂ (quartz) is a hard, high melting nonmetallic compound; it forms covalent crystals like boron and C (diamond).
 - (g) LiCl is an ionic compound; it forms ionic crystals.
 - (h) Cr (chromium) is a metal and forms metallic crystals.

- 12.52** In diamond, each carbon atom is covalently bonded to four other carbon atoms. Because these bonds are strong and uniform, diamond is a very hard substance. In graphite, the carbon atoms in each layer are linked by strong bonds, but the layers are bound by weak dispersion forces. As a result, graphite may be cleaved easily between layers and is not hard.

In graphite, carbon atoms are arranged in six-membered rings (see Figure 12.22 of the text). The carbon atoms are all sp^2 hybridized, and the remaining $2p$ orbital is used in pi bonding. Each layer of graphite has a delocalized molecular orbital, in which electrons are free to move around making graphite a good conductor of electricity in directions along the planes of carbon atoms. In diamond, all the carbon atoms are sp^3 hybridized and no pi bonding exists. Electrons are not free to move, and diamond is a poor conductor of electricity.

- 12.71** The molar heat of vaporization of water is 40.79 kJ/mol. One must find the number of moles of water in the sample:

$$\text{Moles H}_2\text{O} = 74.6 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 4.14 \text{ mol H}_2\text{O}$$

We can then calculate the amount of heat.

$$q = 4.14 \text{ mol H}_2\text{O} \times \frac{40.79 \text{ kJ}}{1 \text{ mol H}_2\text{O}} = \mathbf{169 \text{ kJ}}$$

12.72 Step 1: Warming ice to the melting point.

$$q_1 = ms\Delta t = (866 \text{ g H}_2\text{O})(2.03 \text{ J/g}^\circ\text{C})[0 - (-10)^\circ\text{C}] = 17.6 \text{ kJ}$$

Step 2: Converting ice at the melting point to liquid water at 0°C . (See Table 12.7 of the text for the heat of fusion of water.)

$$q_2 = 866 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g H}_2\text{O}} \times \frac{6.01 \text{ kJ}}{1 \text{ mol}} = 289 \text{ kJ}$$

Step 3: Heating water from 0°C to 100°C .

$$q_3 = ms\Delta t = (866 \text{ g H}_2\text{O})(4.184 \text{ J/g}^\circ\text{C})[(100 - 0)^\circ\text{C}] = 362 \text{ kJ}$$

Step 4: Converting water at 100°C to steam at 100°C . (See Table 12.5 of the text for the heat of vaporization of water.)

$$q_4 = 866 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g H}_2\text{O}} \times \frac{40.79 \text{ kJ}}{1 \text{ mol}} = 1.96 \times 10^3 \text{ kJ}$$

Step 5: Heating steam from 100°C to 126°C .

$$q_5 = ms\Delta t = (866 \text{ g H}_2\text{O})(1.99 \text{ J/g}^\circ\text{C})[(126 - 100)^\circ\text{C}] = 44.8 \text{ kJ}$$

$$q_{\text{total}} = q_1 + q_2 + q_3 + q_4 + q_5 = \mathbf{2.67 \times 10^3 \text{ kJ}}$$

How would you set up and work this problem if you were computing the heat lost in cooling steam from 126°C to ice at -10°C ?

- 12.73** (a) Other factors being equal, liquids evaporate faster at higher temperatures.
 (b) The greater the surface area, the greater the rate of evaporation.
 (c) Weak intermolecular forces imply a high vapor pressure and rapid evaporation.

12.74 $\Delta H_{\text{vap}} = \Delta H_{\text{sub}} - \Delta H_{\text{fus}} = 62.30 \text{ kJ/mol} - 15.27 \text{ kJ/mol} = \mathbf{47.03 \text{ kJ/mol}}$

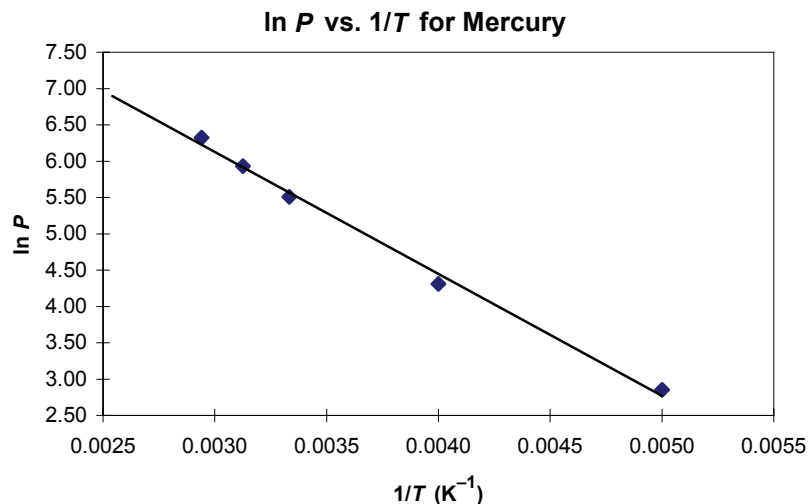
12.75 The substance with the lowest boiling point will have the highest vapor pressure at some particular temperature. Thus, butane will have the highest vapor pressure at -10°C and toluene the lowest.

12.76 Two phase changes occur in this process. First, the liquid is turned to solid (freezing), then the solid ice is turned to gas (sublimation).

12.77 The solid ice turns to gas (sublimation). The temperature is too low for melting to occur.

12.78 When steam condenses to liquid water at 100°C , it releases a large amount of heat equal to the enthalpy of vaporization. Thus steam at 100°C exposes one to more heat than an equal amount of water at 100°C .

12.79 The graph is shown below:



Using the first and last points to determine the slope, we have:

$$\text{Slope} = \frac{\ln P_i - \ln P_f}{\frac{1}{T_i} - \frac{1}{T_f}} = \frac{6.32 - 2.85}{(1.63 \times 10^{-3} - 2.11 \times 10^{-3})\text{K}^{-1}} = -7230 \text{ K}$$

$$-7230 \text{ K} = \frac{-\Delta H_{\text{vap}}}{R} = \frac{-\Delta H_{\text{vap}}}{8.314 \text{ J/K} \cdot \text{mol}}$$

$$\Delta H_{\text{vap}} = \mathbf{60.1 \text{ kJ/mol}}$$

12.80 We can use a modified form of the Clausius-Clapeyron equation to solve this problem. See Equation (12.4) in the text.

$$P_1 = 40.1 \text{ mmHg}$$

$$P_2 = ?$$

$$T_1 = 7.6^\circ\text{C} = 280.6 \text{ K}$$

$$T_2 = 60.6^\circ\text{C} = 333.6 \text{ K}$$

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

$$\ln \frac{40.1}{P_2} = \frac{31000 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left(\frac{1}{333.6 \text{ K}} - \frac{1}{280.6 \text{ K}} \right)$$

$$\ln \frac{40.1}{P_2} = -2.11$$

Taking the antilog of both sides, we have:

$$\frac{40.1}{P_2} = 0.121$$

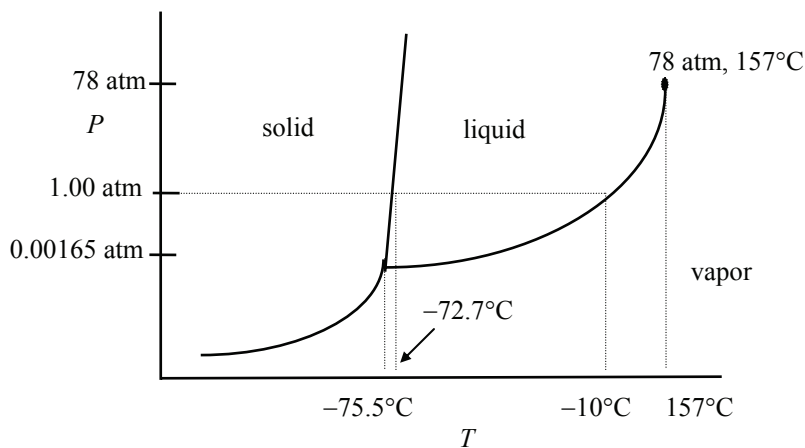
$$P_2 = \mathbf{331 \text{ mmHg}}$$

- 12.81** Application of the Clausius-Clapeyron, Equation (12.4) of the text, predicts that the more the vapor pressure rises over a temperature range, the smaller the heat of vaporization will be. Considering the equation below, if the vapor pressure change is greater, then $\frac{P_1}{P_2}$ is a smaller number and therefore ΔH is smaller. Thus, the molar heat of vaporization of $X < Y$.

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

- 12.84** The pressure exerted by the blades on the ice lowers the melting point of the ice. A film of liquid water between the blades and the solid ice provides lubrication for the motion of the skater. The main mechanism for ice skating, however, is due to friction.
- 12.85** Initially, the ice melts because of the increase in pressure. As the wire sinks into the ice, the water above the wire refreezes. Eventually the wire actually moves completely through the ice block without cutting it in half.
- 12.86** Region labels: The region containing point A is the solid region. The region containing point B is the liquid region. The region containing point C is the gas region.
- Raising the temperature at constant pressure beginning at A implies starting with solid ice and warming until melting occurs. If the warming continued, the liquid water would eventually boil and change to steam. Further warming would increase the temperature of the steam.
 - At point C water is in the gas phase. Cooling without changing the pressure would eventually result in the formation of solid ice. Liquid water would never form.
 - At B the water is in the liquid phase. Lowering the pressure without changing the temperature would eventually result in boiling and conversion to water in the gas phase.

12.87



- 12.88**
- Boiling liquid ammonia requires breaking hydrogen bonds between molecules. Dispersion forces must also be overcome.
 - P_4 is a nonpolar molecule, so the only intermolecular forces are of the dispersion type.
 - CsI is an ionic solid. To dissolve in any solvent, ion-ion interparticle forces must be overcome. Also, hydrogen bonds and dispersion forces must be overcome to break the attractions between some of the HF molecules.
 - Metallic bonds must be broken.

- 12.89** (a) A low surface tension means the attraction between molecules making up the surface is weak. Water has a high surface tension; water bugs could not "walk" on the surface of a liquid with a low surface tension.
- (b) A low critical temperature means a gas is very difficult to liquefy by cooling. This is the result of weak intermolecular attractions. Helium has the lowest known critical temperature (5.3 K).
- (c) A low boiling point means weak intermolecular attractions. It takes little energy to separate the particles. All ionic compounds have extremely high boiling points.
- (d) A low vapor pressure means it is difficult to remove molecules from the liquid phase because of high intermolecular attractions. Substances with low vapor pressures have high boiling points (why?).

Thus, only choice **(d)** indicates strong intermolecular forces in a liquid. The other choices indicate weak intermolecular forces in a liquid.

- 12.90** The HF molecules are held together by strong intermolecular hydrogen bonds. Therefore, liquid HF has a lower vapor pressure than liquid HI. (The HI molecules do not form hydrogen bonds with each other.)
- 12.91** The properties of hardness, high melting point, poor conductivity, etc. could place boron in either the ionic or covalent categories. However, boron atoms will not alternately form positive and negative ions to achieve an ionic crystal. The structure is covalent because the units are single boron atoms.
- 12.92** Reading directly from the graph: **(a)** solid; **(b)** vapor.
- 12.93** Only 1/8 of a corner atom, all of a body-centered atom, and 1/2 of a face atom are within a given unit cell. In a given unit cell there would be 8 corner atoms, 1 body-centered atom, and 6 face atoms. The empirical formula is XYZ_3 .
- 12.94** Because the critical temperature of CO_2 is only 31°C , the liquid CO_2 in the fire extinguisher vaporizes above this temperature, no matter the applied pressure inside the extinguisher. 31°C is approximately 88°F , so on a hot summer day, no liquid CO_2 will exist inside the extinguisher, and hence no sloshing sound would be heard.
- 12.95** The vapor pressure of mercury (as well as all other substances) is 760 mmHg at its normal boiling point.
- 12.96** As the vacuum pump is turned on and the pressure is reduced, the liquid will begin to boil because the vapor pressure of the liquid is greater than the external pressure (approximately zero). The heat of vaporization is supplied by the water, and thus the water cools. Soon the water loses sufficient heat to drop the temperature below the freezing point. Finally the ice sublimates under reduced pressure.
- 12.97** It has reached the critical point; the point of critical temperature (T_c) and critical pressure (P_c).
- 12.98** (a) Two triple points: Diamond/graphite/liquid and graphite/liquid/vapor.
- (b) Diamond.
- (c) Apply high pressure at high temperature.

12.99 Using Equation (12.4) of the text:

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

$$\ln \left(\frac{1}{2} \right) = \left(\frac{\Delta H_{\text{vap}}}{8.314 \text{ J/K} \cdot \text{mol}} \right) \left(\frac{1}{368 \text{ K}} - \frac{1}{358 \text{ K}} \right) = \Delta H_{\text{vap}} \left(\frac{-7.59 \times 10^{-5}}{8.314 \text{ J/mol}} \right)$$

$$\Delta H_{\text{vap}} = 7.59 \times 10^4 \text{ J/mol} = \mathbf{75.9 \text{ kJ/mol}}$$

12.100 W must be a reasonably non-reactive metal. It conducts electricity and is malleable, but doesn't react with nitric acid. Of the choices, it must be gold.

X is nonconducting (and therefore isn't a metal), is brittle, is high melting, and reacts with nitric acid. Of the choices, it must be lead sulfide.

Y doesn't conduct and is soft (and therefore is a nonmetal). It melts at a low temperature with sublimation. Of the choices, it must be iodine.

Z doesn't conduct, is chemically inert, and is high melting (network solid). Of the choices, it must be mica (SiO_2).

Would the colors of the species have been any help in determining their identity?

- 12.101** (a) False. Permanent dipoles are usually much stronger than temporary dipoles.
 (b) False. The hydrogen atom must be bonded to N, O, or F.
 (c) True.
 (d) False. The magnitude of the attraction depends on both the ion charge and the polarizability of the neutral atom or molecule.

12.102 Sublimation temperature is -78°C or 195 K at a pressure of 1 atm.

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

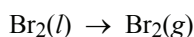
$$\ln \frac{P_1}{1} = \frac{25.9 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{195 \text{ K}} - \frac{1}{150 \text{ K}} \right)$$

$$\ln \frac{P_1}{1} = -4.79$$

Taking the antilog of both sides gives:

$$P_1 = \mathbf{8.3 \times 10^{-3} \text{ atm}}$$

12.103 The standard enthalpy change for the formation of gaseous bromine from liquid bromine is simply the difference between the standard enthalpies of formation of the products and the reactants in the equation:



$$\Delta H^\circ = \Delta H_f^\circ[\text{Br}_2(g)] - \Delta H_f^\circ[\text{Br}_2(l)] = (1)(30.7 \text{ kJ/mol}) - 0 = \mathbf{30.7 \text{ kJ/mol}}$$

12.104 Smaller ions have more concentrated charges (charge densities) and are more effective in ion-dipole interaction. The greater the ion-dipole interaction, the larger is the heat of hydration.

12.105 (a) Decreases (b) no change (c) no change

12.106 $3\text{Hg}(l) + \text{O}_3(g) \rightarrow 3\text{HgO}(s)$

Conversion to solid HgO changes its surface tension.

12.107 The pressure inside the cooker increases and so does the boiling point of water.

12.108 The moles of water vapor can be calculated using the ideal gas equation.

$$n = \frac{PV}{RT} = \frac{\left(187.5 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(5.00 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(338 \text{ K})} = 0.0445 \text{ mol}$$

$$\text{mass of water vapor} = 0.0445 \text{ mol} \times 18.02 \text{ g/mol} = 0.802 \text{ g}$$

Now, we can calculate the percentage of the 1.20 g sample of water that is vapor.

$$\% \text{ of H}_2\text{O vaporized} = \frac{0.802 \text{ g}}{1.20 \text{ g}} \times 100\% = \mathbf{66.8\%}$$

12.109 Ethanol mixes well with water. The mixture has a lower surface tension and readily flows out of the ear channel.

12.110 For a face-centered cubic unit cell, the length of an edge (a) is given by:

$$a = \sqrt{8}r$$

$$a = \sqrt{8}(191 \text{ pm}) = 5.40 \times 10^2 \text{ pm}$$

The volume of a cube equals the edge length cubed (a^3).

$$V = a^3 = (5.40 \times 10^2 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}}\right)^3 \times \left(\frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}}\right)^3 = 1.57 \times 10^{-22} \text{ cm}^3$$

Now that we have the volume of the unit cell, we need to calculate the mass of the unit cell in order to calculate the density of Ar. The number of atoms in one face centered cubic unit cell is four.

$$m = \frac{4 \text{ atoms}}{1 \text{ unit cell}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{39.95 \text{ g}}{1 \text{ mol}} = \frac{2.65 \times 10^{-22} \text{ g}}{1 \text{ unit cell}}$$

$$d = \frac{m}{V} = \frac{2.65 \times 10^{-22} \text{ g}}{1.57 \times 10^{-22} \text{ cm}^3} = \mathbf{1.69 \text{ g/cm}^3}$$

12.111 The cane is made of many molecules held together by intermolecular forces. The forces are strong and the molecules are packed tightly. Thus, when the handle is raised, all the molecules are raised because they are held together.

12.112 The two main reasons for spraying the trees with water are:

- 1) As water freezes, heat is released.

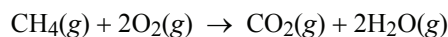


The heat released protects the fruit. Of course, spraying the trees with warm water is even more helpful.

- 2) The ice forms an insulating layer to protect the fruit.

12.113 When the tungsten filament inside the bulb is heated to a high temperature (about 3000°C), the tungsten sublimates (solid \rightarrow gas phase transition) and then it condenses on the inside walls of the bulb. The inert, pressurized Ar gas retards sublimation and oxidation of the tungsten filament.

12.114 The fuel source for the Bunsen burner is most likely methane gas. When methane burns in air, carbon dioxide and water are produced.



The water vapor produced during the combustion condenses to liquid water when it comes in contact with the outside of the cold beaker.

12.115 The packing efficiency is: $\frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}} \times 100\%$

An atom is assumed to be spherical, so the volume of an atom is $(4/3)\pi r^3$. The volume of a cubic unit cell is a^3 (a is the length of the cube edge). The packing efficiencies are calculated below:

(a) Simple cubic cell: cell edge (a) = $2r$

$$\text{Packing efficiency} = \frac{\left(\frac{4\pi r^3}{3}\right) \times 100\%}{(2r)^3} = \frac{4\pi r^3 \times 100\%}{24r^3} = \frac{\pi}{6} \times 100\% = \mathbf{52.4\%}$$

Remember, there is one atom per simple cubic unit cell.

(b) Body-centered cubic cell: cell edge = $\frac{4r}{\sqrt{3}}$

$$\text{Packing efficiency} = \frac{2 \times \left(\frac{4\pi r^3}{3}\right) \times 100\%}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{2 \times \left(\frac{4\pi r^3}{3}\right) \times 100\%}{\left(\frac{64r^3}{3\sqrt{3}}\right)} = \frac{2\pi\sqrt{3}}{16} \times 100\% = \mathbf{68.0\%}$$

Remember, there are two atoms per body-centered cubic unit cell.

(c) Face-centered cubic cell: cell edge = $\sqrt{8}r$

$$\text{Packing efficiency} = \frac{4 \times \left(\frac{4\pi r^3}{3}\right) \times 100\%}{(\sqrt{8}r)^3} = \frac{\left(\frac{16\pi r^3}{3}\right) \times 100\%}{8r^3\sqrt{8}} = \frac{2\pi}{3\sqrt{8}} \times 100\% = \mathbf{74.0\%}$$

Remember, there are four atoms per face-centered cubic unit cell.

12.116 The ice condenses the water vapor inside. Since the water is still hot, it will begin to boil at reduced pressure. (Be sure to drive out as much air in the beginning as possible.)

12.117 (a) To calculate the boiling point of trichlorosilane, we rearrange Equation (12.4) of the text to get:

$$\frac{1}{T_2} = \frac{R}{\Delta H_{\text{vap}}} \ln \frac{P_1}{P_2} + \frac{1}{T_1}$$

where T_2 is the normal boiling point of trichlorosilane. Setting $P_1 = 0.258$ atm, $T_1 = (-2 + 273)\text{K} = 271$ K, $P_2 = 1.00$ atm, we write:

$$\frac{1}{T_2} = \frac{8.314 \text{ J/K} \cdot \text{mol}}{28.8 \times 10^3 \text{ J/mol}} \ln \frac{0.258}{1.00} + \frac{1}{271 \text{ K}}$$

$$T_2 = 303 \text{ K} = 30^\circ\text{C}$$

The Si atom is sp^3 -hybridized and the SiCl_3H molecule has a tetrahedral geometry and a dipole moment. Thus, trichlorosilane is polar and the predominant forces among its molecules are dipole-dipole forces. Since dipole-dipole forces are normally fairly weak, we expect trichlorosilane to have a low boiling point, which is consistent with the calculated value of 30°C .

(b) From Section 12.5 of the text, we see that SiO_2 forms a covalent crystal. Silicon, like carbon in Group 4A, also forms a covalent crystal. The strong covalent bonds between Si atoms (in silicon) and between Si and O atoms (in quartz) account for their high melting points and boiling points.

(c) To test the 10^{-9} purity requirement, we need to calculate the number of Si atoms in 1 cm^3 . We can arrive at the answer by carrying out the following three steps: (1) Determine the volume of an Si unit cell in cubic centimeters, (2) determine the number of Si unit cells in 1 cm^3 , and (3) multiply the number of unit cells in 1 cm^3 by 8, the number of Si atoms in a unit cell.

Step 1: The volume of the unit cell, V , is

$$V = a^3$$

$$V = (543 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \times \frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}} \right)^3$$

$$V = 1.60 \times 10^{-22} \text{ cm}^3$$

Step 2: The number of cells per cubic centimeter is given by:

$$\text{number of unit cells} = 1 \text{ cm}^3 \times \frac{1 \text{ unit cell}}{1.60 \times 10^{-22} \text{ cm}^3} = 6.25 \times 10^{21} \text{ unit cells}$$

Step 3: Since there are 8 Si atoms per unit cell, the total number of Si atoms is:

$$\text{number of Si atoms} = \frac{8 \text{ Si atoms}}{1 \text{ unit cell}} \times (6.25 \times 10^{21} \text{ unit cells}) = 5.00 \times 10^{22} \text{ Si atoms}$$

Finally, to calculate the purity of the Si crystal, we write:

$$\frac{\text{B atoms}}{\text{Si atoms}} = \frac{1.0 \times 10^{13} \text{ B atoms}}{5.00 \times 10^{22} \text{ Si atoms}} = 2.0 \times 10^{-10}$$

Since this number is smaller than 10^{-9} , the purity requirement is satisfied.

- 12.118** First, we need to calculate the volume (in cm^3) occupied by 1 mole of Fe atoms. Next, we calculate the volume that a Fe atom occupies. Once we have these two pieces of information, we can multiply them together to end up with the number of Fe atoms per mole of Fe.

$$\frac{\text{number of Fe atoms}}{\text{cm}^3} \times \frac{\text{cm}^3}{1 \text{ mol Fe}} = \frac{\text{number of Fe atoms}}{1 \text{ mol Fe}}$$

The volume that contains one mole of iron atoms can be calculated from the density using the following strategy:

$$\begin{aligned} \frac{\text{volume}}{\text{mass of Fe}} &\rightarrow \frac{\text{volume}}{\text{mol Fe}} \\ \frac{1 \text{ cm}^3}{7.874 \text{ g Fe}} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} &= \frac{7.093 \text{ cm}^3}{1 \text{ mol Fe}} \end{aligned}$$

Next, the volume that contains two iron atoms is the volume of the body-centered cubic unit cell. Some of this volume is empty space because packing is only 68.0 percent efficient. But, this will not affect our calculation.

$$V = a^3$$

Let's also convert to cm^3 .

$$V = (286.7 \text{ pm})^3 \times \left(\frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} \right)^3 \times \left(\frac{1 \text{ cm}}{0.01 \text{ m}} \right)^3 = \frac{2.357 \times 10^{-23} \text{ cm}^3}{2 \text{ Fe atoms}}$$

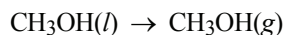
We can now calculate the number of iron atoms in one mole using the strategy presented above.

$$\begin{aligned} \frac{\text{number of Fe atoms}}{\text{cm}^3} \times \frac{\text{cm}^3}{1 \text{ mol Fe}} &= \frac{\text{number of Fe atoms}}{1 \text{ mol Fe}} \\ \frac{2 \text{ Fe atoms}}{2.357 \times 10^{-23} \text{ cm}^3} \times \frac{7.093 \text{ cm}^3}{1 \text{ mol Fe}} &= \mathbf{6.019 \times 10^{23} \text{ Fe atoms/mol}} \end{aligned}$$

The small difference between the above number and 6.022×10^{23} is the result of rounding off and using rounded values for density and other constants.

- 12.119** If we know the values of ΔH_{vap} and P of a liquid at one temperature, we can use the Clausius-Clapeyron equation, Equation (12.4) of the text, to calculate the vapor pressure at a different temperature. At 65.0°C , we can calculate ΔH_{vap} of methanol. Because this is the boiling point, the vapor pressure will be 1 atm (760 mmHg).

First, we calculate ΔH_{vap} . From Appendix 2 of the text, $\Delta H_f^\circ [\text{CH}_3\text{OH}(l)] = -238.7 \text{ kJ/mol}$



$$\Delta H_{\text{vap}} = \Delta H_f^\circ [\text{CH}_3\text{OH}(g)] - \Delta H_f^\circ [\text{CH}_3\text{OH}(l)]$$

$$\Delta H_{\text{vap}} = -201.2 \text{ kJ/mol} - (-238.7 \text{ kJ/mol}) = 37.5 \text{ kJ/mol}$$

Next, we substitute into Equation (12.4) of the text to solve for the vapor pressure of methanol at 25°C .

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

$$\ln \frac{P_1}{760} = \frac{37.5 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{338 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\ln \frac{P_1}{760} = -1.79$$

Taking the antilog of both sides gives:

$$P_1 = 127 \text{ mmHg}$$

- 12.120** All alkali metals have a body-centered cubic structure. Figure 12.19 of the text gives the equation for the radius of a body-centered cubic unit cell.

$$r = \frac{\sqrt{3}a}{4}, \text{ where } a \text{ is the edge length.}$$

Because $V = a^3$, if we can determine the volume of the unit cell (V), then we can calculate a and r .

Using the ideal gas equation, we can determine the moles of metal in the sample.

$$n = \frac{PV}{RT} = \frac{\left(19.2 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \right) (0.843 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (1235 \text{ K})} = 2.10 \times 10^{-4} \text{ mol}$$

Next, we calculate the volume of the cube, and then convert to the volume of one unit cell.

$$\text{Vol. of cube} = (0.171 \text{ cm})^3 = 5.00 \times 10^{-3} \text{ cm}^3$$

This is the volume of 2.10×10^{-4} mole. We convert from volume/mole to volume/unit cell.

$$\text{Vol. of unit cell} = \frac{5.00 \times 10^{-3} \text{ cm}^3}{2.10 \times 10^{-4} \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{2 \text{ atoms}}{1 \text{ unit cell}} = 7.91 \times 10^{-23} \text{ cm}^3/\text{unit cell}$$

Recall that there are 2 atoms in a body-centered cubic unit cell.

Next, we can calculate the edge length (a) from the volume of the unit cell.

$$a = \sqrt[3]{V} = \sqrt[3]{7.91 \times 10^{-23} \text{ cm}^3} = 4.29 \times 10^{-8} \text{ cm}$$

Finally, we can calculate the radius of the alkali metal.

$$r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}(4.29 \times 10^{-8} \text{ cm})}{4} = 1.86 \times 10^{-8} \text{ cm} = 186 \text{ pm}$$

Checking Figure 8.4 of the text, we conclude that the metal is **sodium, Na**.

To calculate the density of the metal, we need the mass and volume of the unit cell. The volume of the unit cell has been calculated ($7.91 \times 10^{-23} \text{ cm}^3/\text{unit cell}$). The mass of the unit cell is

$$2 \text{ Na atoms} \times \frac{22.99 \text{ amu}}{1 \text{ Na atom}} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} = 7.635 \times 10^{-23} \text{ g}$$

$$d = \frac{m}{V} = \frac{7.635 \times 10^{-23} \text{ g}}{7.91 \times 10^{-23} \text{ cm}^3} = \mathbf{0.965 \text{ g/cm}^3}$$

The density value also matches that of sodium.

- 12.121** The original diagram shows that as heat is supplied to the water, its temperature rises. At the boiling point (represented by the horizontal line), water is converted to steam. Beyond this point the temperature of the steam rises above 100°C.

Choice (a) is eliminated because it shows no change from the original diagram even though the mass of water is doubled.

Choice (b) is eliminated because the rate of heating is greater than that for the original system. Also, it shows water boiling at a higher temperature, which is not possible.

Choice (c) is eliminated because it shows that water now boils at a temperature below 100°C, which is not possible.

Choice (d) therefore represents what actually happens. The heat supplied is enough to bring the water to its boiling point, but not raise the temperature of the steam.