

# 11

# Liquids and Intermolecular Forces

## Visualizing Concepts

In this chapter we will use the temperature units °C and K interchangeably when designating specific heats and *changes* in temperature.

11.1 The diagram best describes a liquid. In the diagram, the particles are close together, mostly touching but there is no regular arrangement or order. This rules out a gaseous sample, where the particles are far apart, and a crystalline solid, which has a regular repeating structure in all three directions.

11.2 (a) (i) Hydrogen bonding; H-F interactions qualify for this narrowly defined interaction.  
(ii) London dispersion forces, the only intermolecular forces between nonpolar F<sub>2</sub> molecules.  
(iii) Ion-dipole forces between Na<sup>+</sup> cation and the negative end of a polar covalent water molecule.  
(iv) Dipole-dipole forces between oppositely charged portions of two polar covalent SO<sub>2</sub> molecules.

(b) London dispersion forces in (ii) are probably the weakest.

11.3 The viscosity of glycerol will be greater than that of 1-propanol. Viscosity is the resistance of a substance to flow. The stronger the intermolecular forces in a liquid, the greater its viscosity. Hydrogen bonding is the predominant force for both molecules. Glycerol has three times as many O-H groups and many more H-bonding interactions than 1-propanol, so it experiences stronger intermolecular forces and greater viscosity. (Both molecules have the same carbon-chain length, so dispersion forces are similar.)

11.4 When heat is added to a liquid, the temperature of the liquid rises. If enough heat is added to reach the boiling point, any excess heat is used to vaporize the liquid. If heat is still available when all the liquid is converted to gas, the temperature of the gas rises.

Use the specific heat of CH<sub>4</sub>(l) to calculate the amount of heat required to raise the temperature of 32.0 g of CH<sub>4</sub>(l) from -170 °C to -161.5 °C. If this is less than 42 kJ, use ΔH<sub>vap</sub> to calculate the energy required to vaporize the liquid, and so on, until exactly 42.0 kJ has been used to increase the temperature and/or change the state of CH<sub>4</sub>.

Heat the liquid to its boiling point: ΔT = [-161.5 °C - (-170 °C)] = 8.5 °C = 8.5 K

$$\frac{3.48 \text{ J}}{\text{g} \cdot \text{K}} \times 32.0 \text{ g CH}_4 \times 8.5 \text{ °C} = 946.56 = 9.5 \times 10^2 \text{ J} = 0.95 \text{ kJ}$$

Heating  $\text{CH}_4(\text{l})$  to its boiling point requires only 0.95 kJ. We have added 42 kJ, so there is definitely enough heat to vaporize the liquid.  $\Delta H_{\text{vap}}$  for  $\text{CH}_4(\text{l})$  is 8.20 kJ/mol. The 32.0 g sample is 2.00 mol  $\text{CH}_4(\text{l})$ , so the energy required to vaporize the sample at  $-161.5^\circ\text{C}$  is  $(2 \times 8.20 \text{ kJ/mol}) = 16.4 \text{ kJ}$ . The energy used to heat the sample to  $-161.5^\circ\text{C}$  and vaporize it at this temperature is  $(0.947 \text{ kJ} + 16.4 \text{ kJ}) = 17.347 = 17.3 \text{ kJ}$ . We have  $(42.0 \text{ kJ} - 17.347 \text{ kJ}) = 24.653 = 24.7 \text{ kJ}$  left to heat the gas.

$$\Delta T = 24.65 \text{ kJ} \times \frac{\text{g} \cdot \text{K}}{2.22 \text{ J}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1}{32.0 \text{ g CH}_4} = 346.99 = 347^\circ\text{C}$$

The final temperature of the methane gas,  $\text{CH}_4(\text{g})$ , is then  $(-161.5^\circ\text{C} + 346.99^\circ\text{C}) = 185.49 = 185^\circ\text{C}$ .

- 11.5 (a) 385 mm Hg. Find  $30^\circ\text{C}$  on the horizontal axis, and follow a vertical line from this point to its intersection with the red vapor pressure curve. Follow a horizontal line from the intersection to the vertical axis and read the vapor pressure.
- (b)  $22^\circ\text{C}$ . Reverse the procedure outlined in part (a). Find 300 torr on the vertical axis, follow it to the curve and down to the value on the horizontal axis.
- (c)  $47^\circ\text{C}$ . The normal boiling point of a liquid is the temperature at which its vapor pressure is 1 atm, or 760 mm Hg. A vapor pressure of 1 atm is very near the top of this diagram, at approximately  $47^\circ\text{C}$ .
- 11.6 The stronger the intermolecular forces, the greater the average kinetic energy required to escape these forces, and the higher the boiling point. Propanol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , has hydrogen bonding, by virtue of its  $-\text{OH}$  group, so it has the higher boiling point. Van der Waals forces in the two liquids are similar because molar masses are the same for both molecules.
- 11.7 (a) 360 K, the normal boiling point; 260 K, normal freezing point. The left-most line is the freezing/melting curve, the right-most line is the condensation/boiling curve. The normal boiling and freezing points are the temperatures of boiling and freezing at 1 atm pressure.
- (b) The material is solid in the left-most green (or pale blue) zone, liquid in the blue zone, and gas in the tan zone. (i) gas (ii) solid (iii) liquid
- (c) The triple point, where all three phases are in equilibrium, is the point where the three lines on the phase diagram meet. For this substance, the triple point is approximately 185 K at 0.45 atm.
- 11.8 (a) The substance is in a liquid crystalline state at temperatures  $T_1$  and  $T_2$ . At  $T_1$ , the molecules are aligned in layers and the long molecular axes are perpendicular to the layer planes; this describes a smectic A phase. At  $T_2$ , the long molecular axes are aligned but the ends are not aligned; this describes a nematic phase.
- (b)  $T_3$  is the highest temperature. The molecular arrangement in this phase has the least order, so it represents the highest temperature. (The molecules are closely packed, but not aligned in any way; this describes an ordinary liquid phase.)

## Molecular Comparisons of Gases, Liquids, and Solids (section 11.1)

- 11.9 (a) solid < liquid < gas  
(b) gas < liquid < solid  
(c) Matter in the gaseous state is most easily compressed, because particles are far apart and there is much empty space.
- 11.10 (a) In solids, particles are in essentially fixed positions relative to each other, so the average energy of attraction is stronger than average kinetic energy. In liquids, particles are close together but moving relative to each other. The average attractive energy and average kinetic energy are approximately balanced. In gases, particles are far apart and in constant, random motion. Average kinetic energy is much greater than average energy of attraction.  
(b) As the temperature of a substance is increased, the average kinetic energy of the particles increases. In a collection of particles (molecules), the state is determined by the strength of interparticle forces relative to the average kinetic energy of the particles. As the average kinetic energy increases, more particles are able to overcome intermolecular attractive forces and move to a less ordered state, from solid to liquid to gas.  
(c) If a gas is placed under very high pressure, the particles undergo many collisions with the container and with each other. The large number of particle-particle collisions increases the likelihood that intermolecular attractions will cause the molecules to coalesce (liquefy).
- 11.11 By observation (or a quick WebElements© search), we know that Ar is a gas, CCl<sub>4</sub> is a liquid and Si is a solid at standard conditions. (Si is a substance in which the particles are held together by chemical bonds, like the ones listed in Table 11.2.) The order of increasing boiling point is then Ar < CCl<sub>4</sub> < Si.
- 11.12 By observation (or a quick WebElements© search), we know that Ne is a gas, Br<sub>2</sub> is a liquid and Ga is a solid at standard conditions. The order of increasing boiling point is then Ne < Br<sub>2</sub> < Ga.
- 11.13 (a) At standard temperature and pressure, the molar volumes of Cl<sub>2</sub> and NH<sub>3</sub> are nearly the same because they are both gases. In the gas phase, molecules are far apart and most of the volume occupied by the substance is empty space. Differences in molecular characteristics such as weight, shape and dipole moment have little bearing on the molar volume of a gas.  
The ideal gas law states that one mole of any gas at STP will occupy a fixed volume. The slight difference in molar volumes of the two gases is predicted by the van der Waals correction, which quantifies deviation from ideal behavior.  
(b) On cooling to 160 K, both compounds condense from the gas phase to the solid state. Condensation, as the word implies, eliminates most of the empty space between molecules, so we expect a significant decrease in the molar volume.  
(c) 
$$\frac{1 \text{ cm}^3}{2.02 \text{ g Cl}_2} \times \frac{70.096 \text{ g Cl}_2}{1 \text{ mol Cl}_2} = 35.1 \text{ cm}^3/\text{mol Cl}_2 = 0.0351 \text{ L/mol Cl}_2$$

$$\frac{1 \text{ cm}^3}{0.84 \text{ g NH}_3} \times \frac{17.031 \text{ g NH}_3}{1 \text{ mol NH}_3} = 20.3 \text{ cm}^3/\text{mol NH}_3 = 0.0203 \text{ L/mol NH}_3$$

- (d) Solid state molar volumes are not as similar as those in the gaseous state. In the solid state, most of the empty space is gone, so molecular characteristics do influence molar volumes.  $\text{Cl}_2$  is heavier than  $\text{NH}_3$  and the Cl-Cl bond distance is almost double the N-H bond distance (Figure 7.6). Intermolecular attractive forces among polar  $\text{NH}_3$  molecules bind them more tightly than forces among nonpolar  $\text{Cl}_2$  molecules. These factors all contribute to a molar volume for  $\text{Cl}_2(\text{s})$  that is almost twice that of  $\text{NH}_3(\text{s})$ .
- (e) Like solids, liquids are condensed phases. That is, there is little empty space between molecules in the liquid state. We expect the molar volumes of the liquids to be closer to those in the solid state than those in the gaseous state.
- 11.14 (a) The average distance between molecules is greater in the liquid state. Density is the ratio of the mass of a substance to the volume it occupies. For the same substance in different states, mass will be the same. The smaller the density, the greater the volume occupied, and the greater the distance between molecules. The liquid at  $130^\circ$  has the lower density ( $1.08 \text{ g/cm}^3$ ), so the average distance between molecules is greater.
- (b) As the temperature of a substance increases, the average kinetic energy and speed of the molecules increases. At the melting point the molecules, on average, have enough kinetic energy to break away from the very orderly array that was present in the solid. As the translational motion of the molecules increases, the occupied volume increases and the density decreases. Thus, the solid density,  $1.266 \text{ g/cm}^3$  at  $15^\circ\text{C}$ , is greater than the liquid density,  $1.08 \text{ g/cm}^3$  at  $130^\circ\text{C}$ .

### Intermolecular Forces (section 11.2)

- 11.15 (a) London dispersion forces  
 (b) dipole-dipole and London dispersion forces  
 (c) dipole-dipole or in certain cases hydrogen bonding
- 11.16 Intermolecular forces are based on charge attraction and repulsion. Because substances must be electrically neutral overall, there are opposite charges (full or partial) in every substance. While repulsions occur, net forces are attractive because attractions lower the overall energy of the sample, and matter tends to exist in the lowest possible energy state.
- 11.17 (a)  $\text{SO}_2$  is a polar covalent molecule, so dipole-dipole and London dispersion forces must be overcome to convert the liquid to a gas.  
 (b)  $\text{CH}_3\text{COOH}$  is a polar covalent molecule that experiences London dispersion, dipole-dipole, and hydrogen-bonding (O-H bonds) forces. All of these forces must be overcome to convert the liquid to a gas.  
 (c)  $\text{H}_2\text{Se}$  is a polar covalent molecule that experiences London dispersion and dipole-dipole forces, so these must be overcome to change the liquid into a gas. (H-Se bonds do not lead to hydrogen-bonding interactions.)
- 11.18 (a)  $\text{CH}_3\text{OH}$  experiences hydrogen bonding, but  $\text{CH}_3\text{SH}$  does not.

- (b) Both gases are influenced by London dispersion forces. The heavier the gas particles, the stronger the London dispersion forces. The heavier Xe is a liquid at the specified conditions, while the lighter Ar is a gas.
- (c) Both gases are influenced by London dispersion forces. The larger, diatomic  $\text{Cl}_2$  molecules are more polarizable, experience stronger dispersion forces, and have the higher boiling point.
- (d) Acetone and 2-methylpropane are molecules with similar molar masses and London dispersion forces. Acetone also experiences dipole-dipole forces and has the higher boiling point.
- 11.19 (a) *Polarizability* is the ease with which the charge distribution (electron cloud) in a molecule can be distorted to produce an instantaneous dipole.
- (b) Sb is most polarizable because its valence electrons are farthest from the nucleus and least tightly held.
- (c) Polarizability increases as molecular size (and thus molecular weight) increases. In order of increasing polarizability:  $\text{CH}_4 < \text{SiH}_4 < \text{SiCl}_4 < \text{GeCl}_4 < \text{GeBr}_4$
- (d) The magnitude of London-dispersion forces and thus the boiling points of molecules increase as polarizability increases. The order of increasing boiling points is the order of increasing polarizability:  
 $\text{CH}_4 < \text{SiH}_4 < \text{SiCl}_4 < \text{GeCl}_4 < \text{GeBr}_4$
- 11.20 (a) True. A more polarizable molecule can develop a larger transient dipole, increasing the strength of electrostatic attractions and dispersion forces among molecules.
- (b) False. The noble gases are all monoatomic. Going down the family, the atomic radius and the size of the electron cloud increase. The larger the electron cloud, the more polarizable the atom, the stronger the London dispersion forces and the higher the boiling point. (In general, strength of forces and boiling point vary in the same direction, not opposite directions.)
- (c) False. Generally, dipole-dipole forces are stronger than dispersion forces for molecules of similar size and mass. The size of the molecule and the magnitude of its dipole moment (if there is one) determine the relative magnitudes of dispersion and dipole-dipole forces.
- (d) True. For molecules with similar molecular weights and elemental composition, linear molecules have the possibility for greater contact along and around their surfaces than spherical molecules. Their electron clouds are thus more polarizable, and dispersion forces are greater.
- 11.21 *Analyze/Plan.* For molecules with similar structures, the strength of dispersion forces increases with molecular size (molecular weight and number of electrons in the molecule).  
*Solve:* (a)  $\text{H}_2\text{S}$       (b)  $\text{CO}_2$       (c)  $\text{GeH}_4$
- 11.22 For molecules with similar structures, the strength of dispersion forces increases with molecular size (molecular weight and number of electrons in the molecule).
- (a)  $\text{Br}_2$

- (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$
- (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ . These two molecules have the same molecular formula and molecular weight ( $\text{C}_3\text{H}_7\text{Cl}$ , molecular weight = 78.5 amu), so the shapes of the molecules determine which has the stronger dispersion forces. According to Figure 11.6, the cylindrical (not branched) molecule will have stronger dispersion forces.
- 11.23 Both hydrocarbons experience dispersion forces. Rod-like butane molecules can contact each other over the length of the molecule, while spherical 2-methylpropane molecules can only touch tangentially. The larger contact surface of butane facilitates stronger forces and produces a higher boiling point.
- 11.24 Both molecules experience hydrogen bonding through their  $-\text{OH}$  groups and dispersion forces between their hydrocarbon portions. The position of the  $-\text{OH}$  group in isopropyl alcohol shields it somewhat from approach by other molecules and slightly decreases the extent of hydrogen bonding. Also, isopropyl alcohol is less rod-like (it has a shorter chain) than propyl alcohol, so dispersion forces are weaker. Since hydrogen bonding and dispersion forces are weaker in isopropyl alcohol, it has the lower boiling point.
- 11.25 (a) A molecule must contain H atoms bound to either N, O or F atoms in order to participate in hydrogen bonding with like molecules.
- (b)  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{OH}$  have N-H and O-H bonds, respectively; they will form hydrogen bonds with other molecules of the same kind. ( $\text{CH}_3\text{F}$  has C-F and C-H bonds, but no H-F bonds.)
- 11.26 (a) HF has the higher boiling point because hydrogen bonding is stronger than dipole-dipole forces.
- (b)  $\text{CHBr}_3$  has the higher boiling point because it has the higher molar mass, which leads to greater polarizability and stronger dispersion forces.
- (c) ICl has the higher boiling point because it is a polar molecule. For molecules with similar structures and molar masses, dipole-dipole forces are stronger than dispersion forces.
- 11.27 (a) Replacing a hydroxyl hydrogen with a  $\text{CH}_3$  group eliminates hydrogen bonding in that part of the molecule. This reduces the strength of intermolecular forces and leads to a (much) lower boiling point.
- (b)  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$  is a larger, more polarizable molecule with stronger London-dispersion forces and thus a higher boiling point.
- 11.28 (a)  $\text{C}_3\text{H}_8$ , dispersion;  $\text{C}_4\text{H}_{10}$ , dispersion.  $\text{C}_4\text{H}_{10}$  has the higher boiling point due to greater molar mass and similar strength of forces.
- (b)  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ , dipole-dipole, and dispersion;  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ , hydrogen bonding, dipole-dipole, and dispersion.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  has the higher boiling point due to the influence of hydrogen bonding.
- (c)  $\text{SO}_2$ , dipole-dipole and dispersion;  $\text{SO}_3$ , dispersion. This is a tough call;  $\text{SO}_2$  has dipole-dipole forces, but  $\text{SO}_3$  has a greater molecular weight. The relative strength of dispersion and dipole-dipole forces depends on the mass and shape

of the molecules.  $\text{SO}_3$  molecules have greater molecular weight and are planar, so alignment is facile and dispersion forces are strong;  $\text{SO}_3$  has the higher boiling point (confirmed by CRC *Handbook of Chemistry and Physics*).

- (d)  $\text{Cl}_2\text{CO}$ , dipole-dipole and dispersion;  $\text{H}_2\text{CO}$ , dipole-dipole and dispersion.  $\text{Cl}_2\text{CO}$  has the higher boiling point due to greater molecular weight and stronger dispersion forces. (Note that  $\text{H}_2\text{CO}$  does not have hydrogen bonding, because the H atoms are bound to C, not to O.)

11.29

Physical Property	$\text{H}_2\text{O}$	$\text{H}_2\text{S}$
Normal Boiling Point, °C	100.00	-60.7
Normal Melting Point, °C	0.00	-85.5

- (a) Based on its much higher normal melting and boiling point,  $\text{H}_2\text{O}$  has stronger intermolecular forces.  $\text{H}_2\text{O}$ , with H bound to O, has hydrogen bonding.  $\text{H}_2\text{S}$ , with H bound to S, has dipole-dipole forces. (The electronegativities of H and S, 2.1 and 2.5, respectively, are similar. The H-S bond dipoles in  $\text{H}_2\text{S}$  are not large, but S does have two nonbonded electron pairs. The molecule has medium polarity.)
- (b)  $\text{H}_2\text{S}$  is probably a typical compound, where there is less empty space in the more ordered solid and the solid is denser than the liquid. For  $\text{H}_2\text{O}$ , maximizing the number of hydrogen bonds to each molecule in the solid requires more empty space than in the liquid. The solid is less dense than the liquid and ice floats.
- (c) Specific heat is the energy required to raise the temperature of one gram of the substance one degree Celsius. Raising the temperature of a substance increases average kinetic energy and molecular motion. Hydrogen bonding in water is such a strong attractive interaction that the energy required to disrupt it and increase molecular motion is large.

11.30

- (a) In the solid state,  $\text{NH}_3$  molecules are arranged so as to form the maximum number of hydrogen bonds. At the melting point, the average kinetic energy of the molecules is large enough so that they are free to move relative to each other. As they move, old hydrogen bonds break and new ones form, but the strict relative order required for maximum hydrogen bonding is no longer present.
- (b) In the liquid state, molecules are moving relative to one another while touching, which makes some hydrogen bonding possible. When molecules achieve enough kinetic energy to vaporize, the distance between them increases beyond the point where hydrogen bonds can form.

11.31

$\text{SO}_4^{2-}$  has a greater negative charge than  $\text{BF}_4^-$ , so ion-ion electrostatic attractions are greater in sulfate salts. These strong forces limit the ion mobility required for the formation of an ionic liquid. (This is called an electronic effect.)

11.32

The longer the alkyl side chain of the 1-alkyl-3-methylimidazolium cation, the more irregular the shape of the cation. Particles with irregular shapes are more difficult to pack into solids, so the melting point of the salt decreases as the length of the alkyl group and irregularity increases. (This is called a steric effect.)





corresponding increase in chain length, molecular weight, and strength of dispersion forces. The boiling points, surface tension, and viscosities all increase because the strength of dispersion forces increases.

- (b) Ethylene glycol has an  $-OH$  group at both ends of the molecule. This greatly increases the possibilities for hydrogen bonding, so the overall intermolecular attractive forces are greater and the viscosity of ethylene glycol is much greater.
- (c) Water has the highest surface tension but lowest viscosity because it is the smallest molecule in the series. Since water molecules are small, they approach each other closely and form many strong hydrogen bonds. There is no hydrocarbon chain to disrupt hydrogen bond formation or to inhibit their attraction to molecules in the interior of the drop. Water molecules at the surface of a drop are missing a few hydrogen bonds and are strongly pulled into the center of the drop, resulting in high surface tension. The absence of an alkyl chain also means the molecules can move around each other easily, resulting in the low viscosity.
- 11.38 (a) For molecules with similar shapes, viscosity usually decreases with decreasing molecular weight. Since *n*-pentane has one fewer carbon atom and a shorter chain than *n*-hexane, the molecules are slightly more free to move around each other and *n*-pentane will have the smaller viscosity.
- (b) At 270 K ( $-3\text{ }^{\circ}\text{C}$ ), both neopentane and *n*-pentane will be liquids. According to Figure 11.6, neopentane is roughly spherical, while *n*-pentane is cylindrical or rod-shaped. The spherical neopentane has weaker dispersion forces and the molecules are more free to tumble, so it will have the smaller viscosity.

### Phase Changes (Section 11.4)

- 11.39 (a) melting, endothermic  
(b) evaporation or vaporization, endothermic  
(c) deposition, exothermic  
(d) condensation, exothermic
- 11.40 (a) condensation, exothermic  
(b) sublimation, endothermic  
(c) vaporization (evaporation), endothermic  
(d) freezing, exothermic
- 11.41 The heat energy required to increase the kinetic energy of molecules enough to melt the solid does not produce a large separation of molecules. The specific order is disrupted, but the molecules remain close together. On the other hand, when a liquid is vaporized, the intermolecular forces which maintain close molecular contacts must be overcome. Because molecules are being separated, the energy requirement is higher than for melting.

- 11.42 (a) Liquid ethyl chloride at room temperature is far above its boiling point. When the liquid contacts the room temperature surface, heat sufficient to vaporize the liquid is transferred from the surface to the ethyl chloride, and the heat content of the molecules increases. At constant atmospheric pressure,  $\Delta H = q$ , so the heat content and the enthalpy content of  $C_2H_5Cl(g)$  is higher than that of  $C_2H_5Cl(l)$ . This indicates that the specific heat of the gas is less than that of the liquid, because the heat content of the gas starts at a higher level.
- (b) Liquid  $C_2H_5Cl$  is vaporized (boiled),  $C_2H_5Cl(g)$  is warmed to the final temperature, and the solid surface is cooled to the final temperature. The enthalpy of vaporization ( $\Delta H_{vap}$ ) of  $C_2H_5Cl(l)$ , the specific heat of  $C_2H_5Cl(g)$ , and the specific heat of the solid surface must be considered.

- 11.43 *Analyze.* The heat required to vaporize 60 g of  $H_2O$  equals the heat lost by the cooled water.

*Plan.* Using the enthalpy of vaporization, calculate the heat required to vaporize 60 g of  $H_2O$  in this temperature range. Using the specific heat capacity of water, calculate the mass of water that can be cooled  $15^\circ C$  if this much heat is lost.

*Solve.* Evaporation of 60 g of water requires:

$$60 \text{ g } H_2O \times \frac{2.4 \text{ kJ}}{1 \text{ g } H_2O} = 1.44 \times 10^2 \text{ kJ} = 1.4 \times 10^5 \text{ J}$$

Cooling a certain amount of water by  $15^\circ C$ :

$$1.44 \times 10^5 \text{ J} \times \frac{1 \text{ g} \cdot K}{4.184 \text{ J}} \times \frac{1}{15^\circ C} = 2294 = 2.3 \times 10^3 \text{ g } H_2O$$

*Check.* The units are correct. A surprisingly large mass of water ( $2300 \text{ g} \approx 2.3 \text{ L}$ ) can be cooled by this method.

- 11.44 Energy released when 200 g of  $H_2O$  is cooled from  $15^\circ C$  to  $0^\circ C$ :

$$\frac{4.184 \text{ J}}{\text{g} \cdot K} \times 200 \text{ g } H_2O \times 15^\circ C = 12.55 \times 10^3 \text{ J} = 13 \text{ kJ}$$

Energy released when 200 g of  $H_2O$  is frozen (there is no change in temperature during a change of state):

$$\frac{334 \text{ J}}{\text{g}} \times 200 \text{ g } H_2O = 6.68 \times 10^4 \text{ J} = 66.8 \text{ kJ}$$

Total energy released =  $12.55 \text{ kJ} + 66.8 \text{ kJ} = 79.35 = 79.4 \text{ kJ}$

Mass of freon that will absorb 79.4 kJ when vaporized:

$$79.35 \text{ kJ} \times \frac{1 \times 10^3 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ g } CCl_2F_2}{289 \text{ J}} = 275 \text{ g } CCl_2F_2$$

- 11.45 *Analyze/Plan.* Follow the logic in Sample Exercise 11.3. *Solve.* Physical data for ethanol,  $C_2H_5OH$ , is:  $mp = -114^\circ C$ ;  $\Delta H_{fus} = 5.02 \text{ kJ/mol}$ ;  $C_{s(solid)} = 0.97 \text{ J/g} \cdot K$ ;  $bp = 78^\circ C$ ;  $\Delta H_{vap} = 38.56 \text{ kJ/mol}$ ;  $C_{s(liquid)} = 2.3 \text{ J/g} \cdot K$ . *Solve.*

- (a) Heat the liquid from  $35^\circ C$  to  $78^\circ C$ ,  $\Delta T = 43^\circ C = 43 \text{ K}$ .

$$42.0 \text{ g } C_2H_5OH \times \frac{2.3 \text{ J}}{\text{g} \cdot K} \times 43 \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 4.1538 = 4.2 \text{ kJ}$$

Vaporize (boil) the liquid at 78 °C, using  $\Delta H_{\text{vap}}$ .

$$42.0 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g}} \times \frac{38.56 \text{ kJ}}{\text{mol}} = 35.1535 = 35.2 \text{ kJ}$$

Total energy required is  $4.1538 \text{ kJ} + 35.1535 \text{ kJ} = 39.3073 = 39.3 \text{ kJ}$ .

(b) Heat the solid from -155 °C to -114 °C,  $\Delta T = 41 \text{ °C} = 41 \text{ K}$ .

$$42.0 \text{ g C}_2\text{H}_5\text{OH} \times \frac{0.97 \text{ J}}{\text{g} \cdot \text{K}} \times 41 \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.6703 = 1.7 \text{ kJ}$$

Melt the solid at -114 °C, using  $\Delta H_{\text{fus}}$ .

$$42.0 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g}} \times \frac{5.02 \text{ kJ}}{\text{mol}} = 4.5765 = 4.58 \text{ kJ}$$

Heat the liquid from -114°C to 78°C,  $\Delta T = 192 \text{ °C} = 192 \text{ K}$ .

$$42.0 \text{ g C}_2\text{H}_5\text{OH} \times \frac{2.3 \text{ J}}{\text{g} \cdot \text{K}} \times 192 \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 18.5472 = 19 \text{ kJ}$$

From (a), vaporizing (boiling) 42.0 g of  $\text{C}_2\text{H}_5\text{OH}$  liquid at 78°C requires 35.1535 kJ = 35.2 kJ.

$$\begin{aligned} \text{Total energy required} &= 1.6703 \text{ kJ} + 4.5765 \text{ kJ} + 18.5472 \text{ kJ} + 35.1535 \text{ kJ} = 59.9476 \\ &= 60 \text{ kJ.} \end{aligned}$$

*Check.* The relative energies of the various steps are reasonable; vaporization is the largest. The sum has no decimal places because (19 kJ) has no decimal places.

11.46 Consider the process in steps, using the appropriate thermochemical constant.

Heat the liquid from 10.00°C to 47.6 °C,  $\Delta T = 37.6 \text{ °C} = 37.6 \text{ K}$ , using the specific heat of the liquid.

$$35.0 \text{ g C}_2\text{Cl}_3\text{F}_3 \times \frac{0.91 \text{ J}}{\text{g} \cdot \text{K}} \times 37.6 \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.1976 = 1.2 \text{ kJ}$$

Boil the liquid at 47.6 °C (320.6 K), using the enthalpy of vaporization.

$$35.0 \text{ g C}_2\text{Cl}_3\text{F}_3 \times \frac{1 \text{ mol C}_2\text{Cl}_3\text{F}_3}{187.4 \text{ g C}_2\text{Cl}_3\text{F}_3} \times \frac{27.49 \text{ kJ}}{\text{mol}} = 5.1342 = 5.13 \text{ kJ}$$

Heat the gas from 47.6 °C to 105.00 °C,  $\Delta T = 57.4 \text{ °C} = 57.4 \text{ K}$ , using the specific heat of the gas.

$$35.0 \text{ g C}_2\text{Cl}_3\text{F}_3 \times \frac{0.67 \text{ J}}{\text{g} \cdot \text{K}} \times 57.4 \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.3460 = 1.3 \text{ kJ}$$

The total energy required is  $1.1967 \text{ kJ} + 5.1342 \text{ kJ} + 1.3460 \text{ kJ} = 7.6778 = 7.7 \text{ kJ}$ .

- 11.47
- The critical pressure is the pressure required to cause liquefaction at the critical temperature.
  - The critical temperature is the highest temperature at which a gas can be liquefied, regardless of pressure. As the force of attraction between molecules increases, the critical temperature of the compound increases.
  - The temperature of  $\text{N}_2(\text{l})$  is 77 K. All of the gases in Table 11.5 have critical temperatures higher than 77 K, so all of them can be liquefied at this temperature, given sufficient pressure.

- 11.48 (a)  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$  and  $\text{CClF}_3$  are polar molecules that experience dipole-dipole and London dispersion forces with like molecules.  $\text{CF}_4$  is a nonpolar compound that experiences only dispersion forces.
- (b) According to Solution 11.47(b), the higher the critical temperature, the stronger the intermolecular attractive forces of a substance. Therefore, the strength of intermolecular attraction increases moving from right to left across the series and as molecular weight increases.  $\text{CF}_4 < \text{CClF}_3 < \text{CCl}_2\text{F}_2 < \text{CCl}_3\text{F}$ .
- (c) The increasing intermolecular attraction with increasing molecular weight indicates that the critical temperature and pressure of  $\text{CCl}_4$  will be greater than that of  $\text{CCl}_3\text{F}$ . Looking at the numerical values in the series, an increase of 88 K in critical temperature and 3.1 atm in critical pressure to the corresponding values for  $\text{CCl}_3\text{F}$  seem reasonable.

Physical Property	$\text{CCl}_3\text{F}$	$\text{CCl}_4$ (predicted)	$\text{CCl}_4$ (CRC)
Critical Temperature (K)	47.1	557	556.6
Critical Pressure (atm)	43.5	46.6	44.6

The predicted values for  $\text{CCl}_4$  are in very good agreement with literature values. The key concept is that dispersion, not dipole-dipole, forces dominate the physical properties in the series.

### Vapor Pressure (section 11.5)

- 11.49 (a) No effect.
- (b) No effect.
- (c) Vapor pressure decreases with increasing intermolecular attractive forces because fewer molecules have sufficient kinetic energy to overcome attractive forces and escape to the vapor phase.
- (d) Vapor pressure increases with increasing temperature because average kinetic energies of molecules increases.
- (e) Vapor pressure decreases with increasing density. Density, the ratio of mass to volume occupied, increases as molecular weight increases. The strength of attractive dispersion forces also increases, so fewer molecules have sufficient kinetic energy to escape to the vapor phase and vapor pressure decreases.
- 11.50 A normal boiling point of 56 °C places the liquid-vapor curve for acetone between the curves for diethyl ether and ethanol on Figure 11.25. Following a vertical line of increasing vapor pressure at 25 °C, we first cross the ethanol curve, then the (virtual) acetone curve. This means that, at 25 °C, the vapor pressure of acetone is higher than the vapor pressure of ethanol. (The lower boiling point of acetone is a strong indicator that it will have a higher vapor pressure than ethanol at a given temperature.)
- 11.51 (a) *Analyze/Plan.* Given the molecular formulae of several substances, determine the kind of intermolecular forces present, and rank the strength of these forces. The weaker the forces, the more volatile the substance. *Solve.*

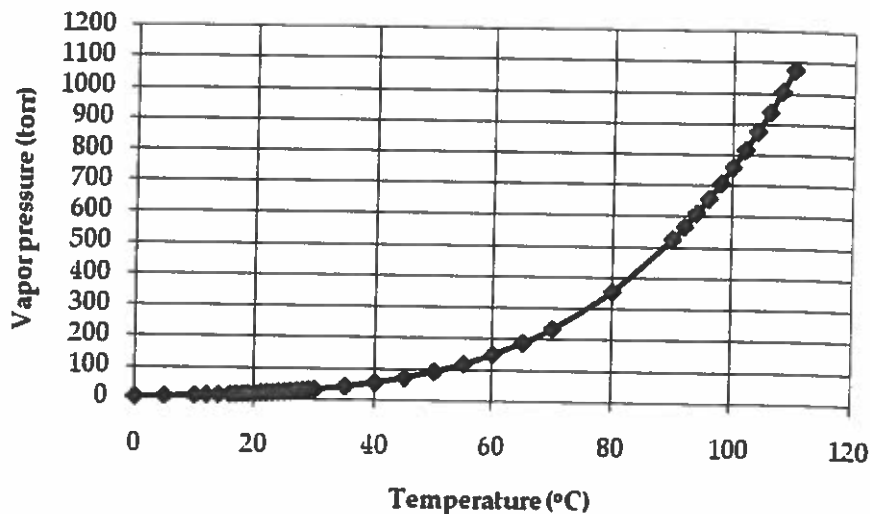


The weaker the intermolecular forces, the higher the vapor pressure, the more volatile the compound. The order of increasing volatility is the order of decreasing strength of intermolecular forces. By analogy to attractive forces in HCl (Section 11.2), the trend will be dominated by dispersion forces, even though four of the molecules ( $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$ ) are polar. Thus, the order of increasing volatility is the order of decreasing molar mass and decreasing strength of dispersion forces.

- (b)  $\text{CH}_4 < \text{CH}_3\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CH}_2\text{Br}_2 < \text{CHBr}_3 < \text{CBr}_4$
- Boiling point increases as the strength of intermolecular forces increases, so the order of boiling points is the order of increasing strength of forces. This is the order of decreasing volatility and the reverse of the order in part (a).
- 11.52 (a) False. The heavier (and larger)  $\text{CBr}_4$  has stronger dispersion forces, a higher boiling point, lower vapor pressure and is less volatile.
- (b) True.
- (c) False.
- (d) False.
- 11.53 (a) The water in the two pans is at the same temperature, the boiling point of water at the atmospheric pressure of the room. During a phase change, the temperature of a system is constant. All energy gained from the surroundings is used to accomplish the transition, in this case to vaporize the liquid water. The pan of water that is boiling vigorously is gaining more energy and the liquid is being vaporized more quickly than in the other pan, but the temperature of the phase change is the same.
- (b) Vapor pressure does not depend on either volume or surface area of the liquid. As long as the containers are at the same temperature, the vapor pressures of water in the two containers are the same.
- 11.54 (a) On a humid day, there are more gaseous water molecules in the air and more are recaptured by the surface of the liquid, making evaporation slower.
- (b) At high altitude, atmospheric pressure is lower and water boils at a lower temperature. This lower boiling temperature at high altitude means that cooking an egg takes longer.
- 11.55 *Analyze/Plan.* Follow the logic in Sample Exercise 11.4. The boiling point is the temperature at which the vapor pressure of a liquid equals atmospheric pressure. *Solve.*
- (a) The boiling point of ethanol at 200 torr is  $\sim 48^\circ\text{C}$ .
- (b) The vapor pressure of ethanol at  $60^\circ\text{C}$  is approximately 340 torr. Thus, at  $60^\circ\text{C}$  ethyl alcohol would boil at an external pressure of 340 torr.
- (c) The boiling point of diethyl ether at 400 torr is  $\sim 17^\circ\text{C}$ .
- (d)  $40^\circ\text{C}$  is above the normal boiling point of diethyl ether, so the pressure at which  $40^\circ\text{C}$  is the boiling point is greater than 760 torr. According to Figure 11.25, a

boiling point of 40 °C requires an external pressure of 1000 torr. (At these conditions, the vapor pressure of diethyl ether is 1000 torr.)

11.56 (a)



- A plot of vapor pressure vs. temperature data for H<sub>2</sub>O from Appendix B is shown above. The vapor pressure of water at body temperature, 37 °C, is approximately 50 torr.
- (b) The data point at 760.0 torr, 100 °C is the normal boiling point of H<sub>2</sub>O. This is the temperature at which the vapor pressure of H<sub>2</sub>O is equal to a pressure of 1 atm or 760 torr.
- (c) At an external (atmospheric) pressure of 633 torr, the boiling point of H<sub>2</sub>O is approximately 96 °C.
- (d) At an external pressure of 774 torr, the boiling point of water is approximately 100.5 °C.
- (e) Follow the logic in Sample Exercise 10.14 to calculate rms speeds at the two temperatures. The rms speed is one way to represent the "average" speed of a large collection of particles.

$$u = (3RT/MM)^{1/2}. \quad MM = 18.0 \text{ g/mol} = 18.0 \times 10^{-3} \text{ kg/mol}$$

$$R = 8.314 \text{ kg} \cdot \text{m}^2/\text{s}^2 \cdot \text{mol} \cdot \text{K}. \quad \text{At } T = 96^\circ\text{C} = 369 \text{ K},$$

$$u = \left( \frac{3(8.314 \text{ kg} \cdot \text{m}^2/\text{s}^2 \cdot \text{mol} \cdot \text{K}) 369 \text{ K}}{18.0 \times 10^{-3} \text{ kg/mol}} \right)^{1/2} = 715 \text{ m/s}$$

$$\text{At } T = 100.5^\circ\text{C} = 373.6 \text{ K},$$

$$u = \left( \frac{3(8.314 \text{ kg} \cdot \text{m}^2/\text{s}^2 \cdot \text{mol} \cdot \text{K}) 373.6 \text{ K}}{18.0 \times 10^{-3} \text{ kg/mol}} \right)^{1/2} = 719.50 = 720 \text{ m/s}$$

The difference in the two rms speeds is less than 1% of the average of the two values. Given the precision of estimating boiling temperatures from the plot, the two rms speeds are essentially equal.

## Phase Diagrams (section 11.6)

- 11.57 (a) The *critical point* is the temperature and pressure beyond which the gas and liquid phases are indistinguishable.
- (b) The gas/liquid line ends at the critical point because at conditions beyond the critical temperature and pressure, there is no distinction between gas and liquid. In experimental terms, a gas cannot be liquefied at temperatures higher than the critical temperature, regardless of pressure.
- 11.58 (a) The *triple point* on a phase diagram represents the temperature and pressure at which the gas, liquid, and solid phases are in equilibrium.
- (b) No. A phase diagram represents a closed system, one where no matter can escape and no substance other than the one under consideration is present; air cannot be present in the system. Even if air is excluded, at 1 atm of external pressure, the triple point of water is inaccessible, regardless of temperature [see Figure 11.28].
- 11.59 (a) The water vapor would deposit to form a solid at a pressure of around 4 torr. At higher pressure, perhaps 5 atm or so, the solid would melt to form liquid water. This occurs because the melting point of ice, which is 0 °C at 1 atm, decreases with increasing pressure.
- (b) In thinking about this exercise, keep in mind that the total pressure is being maintained at a constant 0.50 atm. That pressure is composed of water vapor pressure and some other pressure, which could come from an inert gas. At 100 °C and 0.50 atm, water is in the vapor phase. As it cools, the water vapor will condense to the liquid at the temperature where the vapor pressure of liquid water is 0.50 atm. From Appendix B, we see that condensation occurs at approximately 82 °C. Further cooling of the liquid water results in freezing to the solid at approximately 0 °C. The freezing point of water increases with decreasing pressure, so at 0.50 atm, the freezing temperature is very slightly above 0 °C.
- 11.60 (a) Solid CO<sub>2</sub> sublimates to form CO<sub>2</sub>(g) at a temperature of about -60 °C.
- (b) Solid CO<sub>2</sub> melts to form CO<sub>2</sub>(l) at a temperature of about -55 °C. The CO<sub>2</sub>(l) boils when the temperature reaches approximately -45 °C.
- 11.61 *Analyze/Plan.* Follow the logic in Sample Exercise 11.5, using the phase diagram for neon. *Solve.*
- (a) The normal melting point is the temperature where solid becomes liquid at 1 atm pressure. Following a horizontal line at 1 atm to the solid-liquid line, the normal melting point is approximately 24 K.
- (b) Neon sublimates, changes directly from solid to gas, at pressures less than the triple point pressure, 0.43 atm.
- (c) Room temperature is 298 K, in the region where neon is a supercritical fluid. Neon cannot be liquefied at any temperature above the critical temperature, 44 K, regardless of pressure.

- 11.62 (a) The normal boiling point is the temperature where liquid becomes gas at 1 atm pressure. Moving vertically down from 1 atm on the liquid-gas line to the temperature axis, the normal boiling point is approximately 27 to 28 K, or  $-246\text{ }^{\circ}\text{C}$  to  $-245\text{ }^{\circ}\text{C}$ .
- (b) The much higher critical temperature and pressure of Ar (150.9 K, 48 atm) compared with those of Ne (25 K, 0.43 atm), indicate that Ar experiences much stronger intermolecular forces than Ne.
- 11.63 *Analyze/Plan.* Follow the logic in Sample Exercise 11.5, using the phase diagram for methane in Figure 11.30. *Solve.*
- (a) According to Sample Exercise 11.5, the triple point of methane ( $\text{CH}_4$ ) is approximately  $(-180\text{ }^{\circ}\text{C}, 0.1\text{ atm})$ . The solid-liquid line in the phase diagram is essentially vertical in the pressure range 0.1-100 atm. This means that conditions at the surface of Titan ( $-178\text{ }^{\circ}\text{C}, 1.6\text{ atm}$ ) are very close to the solid-liquid line. Methane on the surface of Titan is likely to exist in both solid and liquid forms.
- (b) Methane is a liquid at  $-178\text{ }^{\circ}\text{C}$  and 1.6 atm. Moving upward through Titan's atmosphere at a constant temperature of  $-178\text{ }^{\circ}\text{C}$ , pressure decreases. At a pressure slightly greater than 0.1 atm, we expect to see vaporization to gaseous methane. If we begin with solid methane at 1.6 atm and a temperature slightly below  $-180\text{ }^{\circ}\text{C}$ , we expect sublimation to gaseous methane at a pressure slightly less than 0.1 atm.
- 11.64 The density of Ga(s),  $5.91\text{ g/cm}^3$ , is less than the density of Ga(l),  $6.1\text{ g/cm}^3$ , just above the melting temperature. "Typically" the density of a solid is greater than the density of its liquid. Gallium is then an atypical substance, like water, where the solid state is denser and more compact than the liquid. This results in a backward sloping solid-liquid line on the phase diagram for water, and we also expect to see this unusual feature on the diagram for gallium.

### Liquid Crystals (section 11.7)

- 11.65 In a nematic liquid crystalline phase, molecules are aligned along their long axes, but the molecular ends are not aligned. In an ordinary liquid, molecules have no orderly arrangement; they are randomly oriented. Both an ordinary liquid and a nematic liquid crystal phase are fluids; molecules are free to move relative to one another. In an ordinary liquid, molecules can move in any direction. In a nematic phase, molecules are free to translate in all dimensions. Molecules cannot tumble or rotate out of the molecular plane, or the order of the nematic phase is lost and the sample becomes an ordinary liquid.
- 11.66 Reinitzer observed that cholesteryl benzoate has a phase that exhibits properties intermediate between those of the solid and liquid phases. This "liquid-crystalline" phase, formed by melting at  $145\text{ }^{\circ}\text{C}$ , is viscous and opaque; its viscosity decreases on heating and it becomes clear at  $179\text{ }^{\circ}\text{C}$ .
- 11.67 The presence of polar groups or nonbonded electron pairs leads to relatively strong dipole-dipole interactions between molecules. These are a significant part of the orienting forces necessary for liquid crystal formation.

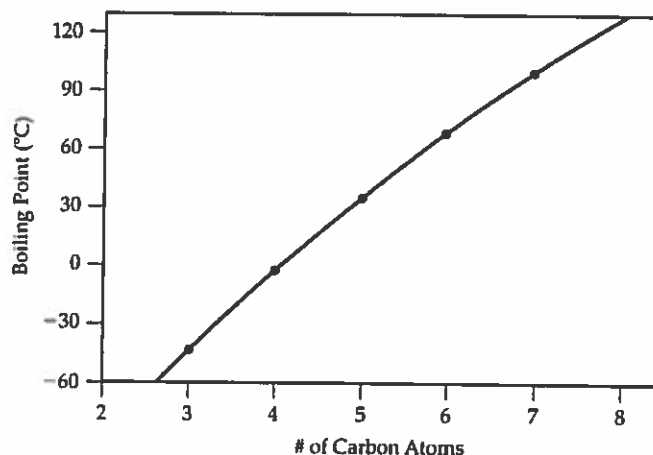


- 11.68 (a) The molecule has one double bond (and one triple bond).  
(b) The "LCD molecule" is long relative to its thickness. It has one C=C and one C≡N group that promote rigidity and polarizability along the length of the molecule. The C≡N group also provides dipole-dipole interactions that encourage alignment. Unlike the molecules in Figure 11.33, which contain planar phenyl rings, the LCD molecule contains nonaromatic, nonplanar six-membered rings. These rings are subject to substantial London dispersion effects. They probably contribute to specific physical properties such as the liquid crystal temperature range that make this molecule particularly functional in LCD displays.
- 11.69 Because order is maintained in at least one dimension, the molecules in a liquid-crystalline phase are not totally free to change orientation. This makes the liquid-crystalline phase more resistant to flow, more viscous, than the isotropic liquid.
- 11.70 A nematic phase is composed of sheets of molecules aligned along their lengths, but with no additional order within the sheet or between sheets. A cholesteric phase also contains this kind of sheet, but with some ordering between sheets. In a cholesteric phase, there is a characteristic angle between molecules in one sheet and those in an adjacent sheet. That is, one sheet of molecules is twisted at some characteristic angle relative to the next, producing a "screw" axis perpendicular to the sheets.
- 11.71 As the temperature of a substance increases, the average kinetic energy of the molecules increases. More molecules have sufficient kinetic energy to overcome intermolecular attractive forces, so overall ordering of the molecules decreases as temperature increases. Melting provides kinetic energy sufficient to disrupt alignment in one dimension in the solid, producing a smectic phase with ordering in two dimensions. Additional heating of the smectic phase provides kinetic energy sufficient to disrupt alignment in another dimension, producing a nematic phase with one-dimensional order.
- 11.72 In the nematic phase, molecules are aligned in one dimension, the long dimension of the molecule. In a smectic phase (A or C), molecules are aligned in two dimensions. Not only are the long directions of the molecules aligned, but the ends are also aligned. The molecules are organized into layers; the height of the layer is related to the length of the molecule.

### Additional Exercises

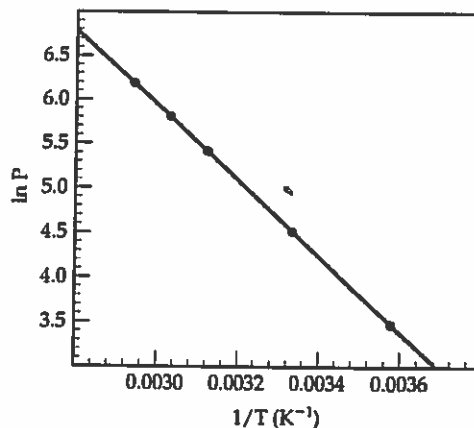
- 11.73 (a) decrease      (b) increase      (c) increase      (d) increase  
(e) increase      (f) increase      (g) increase
- 11.74 (a) Correct.  
(b) The lower boiling liquid must experience less total intermolecular forces.  
(c) If both liquids are structurally similar nonpolar molecules, the lower boiling liquid has a lower molecular weight than the higher boiling liquid.  
(d) Correct.  
(e) At their boiling points, both liquids have vapor pressures of 760 mm Hg.

- 11.75 (a) The *cis* isomer has stronger dipole-dipole forces; the *trans* isomer is nonpolar. (Since both molecules have the same molecular weight, we can say that the dipole-dipole and dispersion forces of the *cis* isomer are stronger than the dispersion-only forces of the *trans* isomer.)
- (b) The molecule with the stronger intermolecular interactions will have the higher boiling point. The *cis* isomer boils at 60.3 °C and the *trans* isomer boils at 47.5 °C.
- 11.76 (a) In dibromomethane,  $\text{CH}_2\text{Br}_2$ , the dispersion force contribution will be larger than for  $\text{CH}_2\text{Cl}_2$ , because bromine is more polarizable than the lighter element chlorine. At the same time, the dipole-dipole contribution for  $\text{CH}_2\text{Cl}_2$  is greater than for  $\text{CH}_2\text{Br}_2$  because  $\text{CH}_2\text{Cl}_2$  has a larger dipole moment.
- (b) Just the opposite comparisons apply to  $\text{CH}_2\text{F}_2$ , which is less polarizable and has a higher dipole moment than  $\text{CH}_2\text{Cl}_2$ .
- 11.77 When a halogen atom (Cl or Br) is substituted for H in benzene, the molecule becomes polar. These molecules experience dispersion forces similar to those in benzene plus dipole-dipole forces, so they have higher boiling points than benzene.  $\text{C}_6\text{H}_5\text{Br}$  has a higher molar mass and is more polarizable than  $\text{C}_6\text{H}_5\text{Cl}$ , so it has the higher boiling point.  $\text{C}_6\text{H}_5\text{OH}$  experiences hydrogen bonding, the strongest force between neutral molecules, so it has the highest boiling point.
- 11.78 The GC base pair, with more hydrogen bonds, is more stable to heating. In order to break up a base pair by heating, sufficient thermal energy must be added to break the existing hydrogen bonds. With 50% more hydrogen bonds, the GC pair is definitely more stable (harder to break apart) than the AT pair.
- 11.79 The two O-H groups in ethylene glycol are involved in many hydrogen bonding interactions, leading to its high boiling point and viscosity, relative to pentane, which experiences only dispersion forces.
- 11.80 The more carbon atoms in the hydrocarbon, the longer the chain, the more polarizable the electron cloud, the higher the boiling point. A plot of the number of carbon atoms versus boiling point is shown below. For 8 C atoms,  $\text{C}_8\text{H}_{18}$ , the boiling point is approximately 130°C.



- 11.81 Ionic liquids are the liquid phase of ionic compounds. Upon melting, the ions are free to move relative to one another. The ion-ion interparticle attractive forces at work in an ionic liquid are extremely strong relative to dispersion, dipole-dipole and even hydrogen bonding forces operating in most molecular solvents. These powerful ion-ion forces must be broken in order for an ion to escape to the vapor phase. In the distribution of particle energies at room temperature, very few ions have sufficient kinetic energy to escape these interactions and move to the vapor phase. With few particles in the vapor phase, the vapor pressures of ionic liquids are extremely low.
- 11.82 (a) Sweat, or salt water, on the surface of the body vaporizes to establish its typical vapor pressure at atmospheric pressure. Since the atmosphere is a totally open system, typical vapor pressure is never reached, and the sweat evaporates continuously. Evaporation is an endothermic process. The heat required to vaporized sweat is absorbed from your body, helping to keep it cool.
- (b) The vacuum pump reduces the pressure of the atmosphere (air + water vapor) above the water. Eventually, atmospheric pressure equals the vapor pressure of water and the water boils. Boiling is an endothermic process, and the temperature drops if the system is not able to absorb heat from the surroundings fast enough. As the temperature of the water decreases, the water freezes. (On a molecular level, the evaporation of water removes the molecules with the highest kinetic energies from the liquid. This decrease in average kinetic energy is what we experience as a temperature decrease.)
- 11.83 (a) If the Clausius-Clapeyron equation is obeyed, a graph of  $\ln P$  vs  $1/T(K)$  should be linear. Here are the data in a form for graphing.

<u>T(K)</u>	<u>1/T</u>	<u>P(torr)</u>	<u>ln P</u>
280.0	$3.571 \times 10^{-3}$	32.42	3.479
300.0	$3.333 \times 10^{-3}$	92.47	4.527
320.0	$3.125 \times 10^{-3}$	225.1	5.417
330.0	$3.030 \times 10^{-3}$	334.4	5.812
340.0	$2.941 \times 10^{-3}$	482.9	6.180



According to the graph, the Clausius-Clapeyron equation is obeyed, to a first approximation.

$$\Delta H_{\text{vap}} = -\text{slope} \times R; \text{slope} = \frac{3.479 - 6.180}{(3.571 - 2.941) \times 10^{-3}} = -\frac{2.701}{0.630 \times 10^{-3}} = -4.29 \times 10^3$$

$$\Delta H_{\text{vap}} = -(-4.29 \times 10^3) \times 8.314 \text{ J/K} \cdot \text{mol} = 35.7 \text{ kJ/mol}$$

- (b) The normal boiling point is the temperature at which the vapor pressure of the liquid equals atmospheric pressure, 760 torr. From the graph,

$$\ln 760 = 6.63, 1/T \text{ for this vapor pressure} = 2.828 \times 10^{-3}; T = 353.6 \text{ K}$$

11.84 (a) The Clausius-Clapeyron equation is  $\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + C$ .

For two vapor pressures,  $P_1$  and  $P_2$ , measured at corresponding temperatures  $T_1$  and  $T_2$ , the relationship is

$$\ln P_1 - \ln P_2 = \left( \frac{-\Delta H_{\text{vap}}}{RT_1} + C \right) - \left( \frac{-\Delta H_{\text{vap}}}{RT_2} + C \right)$$

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

(b)  $P_1 = 13.95$  torr,  $T_1 = 298$  K;  $P_2 = 144.78$  torr,  $T_2 = 348$  K

$$\ln \frac{13.95}{144.78} = \frac{-\Delta H_{\text{vap}}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{298} - \frac{1}{348} \right)$$

$$-2.33974 (8.314 \text{ J/mol} \cdot \text{K}) = -\Delta H_{\text{vap}} (4.821 \times 10^{-4} / \text{K})$$

$$\Delta H_{\text{vap}} = 4.035 \times 10^4 = 4.0 \times 10^4 \text{ J/mol} = 40 \text{ kJ/mol}$$

$[(1/T_1) - (1/T_2)]$  has 2 sig figs and so does the result.

(c) The normal boiling point of a liquid is the temperature at which the vapor pressure of the liquid is 760 torr.

$P_1 = 144.78$  torr,  $T_1 = 348$  K;  $P_2 = 760$  torr,  $T_2 = \text{b.p. of octane}$

$$\ln \left( \frac{144.78}{760.0} \right) = \frac{-4.035 \times 10^4 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{348 \text{ K}} - \frac{1}{T_2} \right)$$

$$\frac{-1.6581}{-4.8533 \times 10^{-3}} = 2.874 \times 10^{-3} - \frac{1}{T_2}; \frac{1}{T_2} = 2.874 \times 10^{-3} - 3.416 \times 10^{-4}$$

$$\frac{1}{T_2} = 2.532 \times 10^{-3} = 2.53 \times 10^{-3}; T_2 = 395 \text{ K} (122^\circ \text{C})$$

From the plot of boiling point versus number of carbon atoms in Exercise 11.80, we read an approximate boiling point for octane of  $130^\circ \text{C}$ . These two temperatures are close, but do differ by more than 5%. Considering experimental uncertainties in the vapor pressure data, and the empirical nature of the plot, the two values are surprisingly close. The literature boiling point of octane,  $126^\circ \text{C}$ , is exactly midway between our two estimates.

(d)  $P_1 = \text{vp of octane at } -30^\circ \text{C}$ ,  $T_1 = 243$  K;  $P_2 = 144.78$  torr,  $T_2 = 348$  K

$$\ln \frac{P_1}{144.78 \text{ torr}} = \frac{-4.035 \times 10^4 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{243} - \frac{1}{348} \right)$$

$$\ln \frac{P_1}{144.78 \text{ torr}} = \frac{-4.035 \times 10^4 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \times 1.242 \times 10^{-3} = -6.026 = -6.03$$

$$\frac{P_1}{144.78 \text{ torr}} = e^{-6.026}; P_1 = 0.002415(144.78) = 0.3496 = 0.35 \text{ torr}$$

[This result has 2 sig figs because  $(\ln = -6.03)$  has 2 decimal places. In a ln or log, the places left of the decimal show order of magnitude, and places right of the decimal show sig figs in the real number.] The result, 0.35 torr at  $-30^\circ \text{C}$ , is reasonable, since we expect vapor pressure to decrease as temperature decreases, and we are approaching the freezing point of octane,  $-57^\circ \text{C}$ .

11.85 Physical data for the two compounds from the *Handbook of Chemistry and Physics*:

	<u>MM</u>	<u>dipole moment</u>	<u>boiling point</u>
CH <sub>2</sub> Cl <sub>2</sub>	85 g/mol	1.60 D	40.0°C
CH <sub>3</sub> I	142 g/mol	1.62 D	42.4°C

- (a) The two substances have very similar molecular structures; each is an unsymmetrical tetrahedron with a single central carbon atom and no hydrogen bonding. Since the structures are very similar, the magnitudes of the dipole-dipole forces should be similar. This is verified by their very similar dipole moments. The heavier compound, CH<sub>3</sub>I, will have slightly stronger London dispersion forces. Since the nature and magnitude of the intermolecular forces in the two compounds are nearly the same, it is very difficult to predict which will be more volatile [or which will have the higher boiling point as in part (b)].
- (b) Given the structural similarities discussed in part (a), one would expect the boiling points to be very similar, and they are. Based on its larger molar mass (and dipole-dipole forces being essentially equal) one might predict that CH<sub>3</sub>I would have a slightly higher boiling point; this is verified by the known boiling points.

- (c) According to Equation 11.1,  $\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + C$

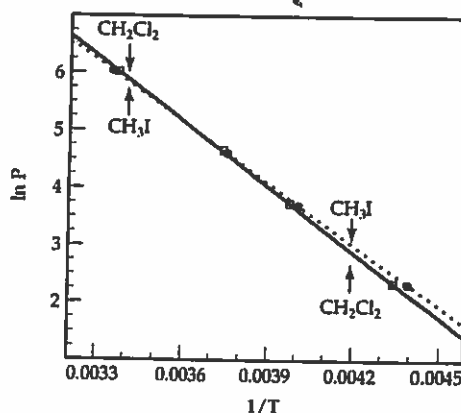
A plot of  $\ln P$  vs.  $1/T$  for each compound is linear. Since the order of volatility changes with temperature for the two compounds, the two lines must cross at some temperature; the slopes of the two lines,  $\Delta H_{\text{vap}}$  for the two compounds, and the y-intercepts,  $C$ , must be different.

(d)

CH <sub>2</sub> Cl <sub>2</sub>		
<u>ln P</u>	<u>T(K)</u>	<u>1/T</u>
2.303	229.9	$4.351 \times 10^{-3}$
3.689	250.9	$3.986 \times 10^{-3}$
4.605	266.9	$3.747 \times 10^{-3}$
5.991	297.3	$3.364 \times 10^{-3}$

CH <sub>3</sub> I		
<u>ln P</u>	<u>T(K)</u>	<u>1/T</u>
2.303	227.4	$4.398 \times 10^{-3}$
3.689	249.0	$4.016 \times 10^{-3}$
4.605	266.2	$3.757 \times 10^{-3}$
5.991	298.5	$3.350 \times 10^{-3}$



$$\begin{aligned} \text{For CH}_2\text{Cl}_2, -\Delta H_{\text{vap}}/R = \text{slope} &= \frac{(5.991 - 2.303)}{(3.364 \times 10^{-3} - 4.350 \times 10^{-3})} = \frac{-3.688}{0.987 \times 10^{-3}} \\ &= -3.74 \times 10^3 = -\Delta H_{\text{vap}}/R \end{aligned}$$

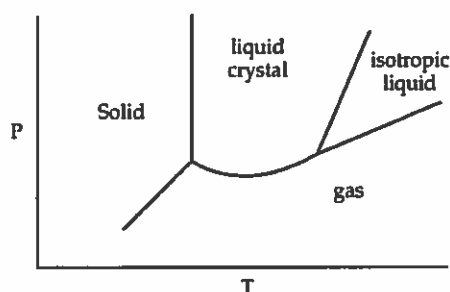
$$\Delta H_{\text{vap}} = 8.314 (3.74 \times 10^3) = 3.107 \times 10^4 \text{ J/mol} = 31.1 \text{ kJ/mol}$$

$$\begin{aligned} \text{For CH}_3\text{I}, -\Delta H_{\text{vap}}/R = \text{slope} &= \frac{(5.991 - 2.303)}{(3.350 \times 10^{-3} - 4.398 \times 10^{-3})} = \frac{-3.688}{1.048 \times 10^{-3}} = -3.519 \times 10^3 \\ &= -\Delta H_{\text{vap}}/R \end{aligned}$$

$$\Delta H_{\text{vap}} = 8.314 (3.519 \times 10^3) = 2.926 \times 10^4 \text{ J/mol} = 29.3 \text{ kJ/mol}$$

- 11.86 In a liquid crystal display (Figure 11.36), the molecules must be oriented to rotate polarized light by  $90^\circ$ . Light is then reflected back through both horizontal and vertical polarizers, producing a bright display. When voltage is applied, the molecules align with the voltage and light cannot pass through the horizontal polarizer, producing a dark spot on the display. At low Antarctic temperatures, the liquid crystalline phase is closer to its freezing point. The molecules have less kinetic energy due to temperature and the applied voltage may not be sufficient to overcome orienting forces among the molecules. If some or all of the molecules do not rotate when the voltage is applied, the display will not function properly.

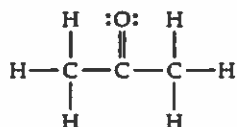
11.87



### Integrative Exercises

- 11.88 (a) In Table 11.4, viscosity increases as the length of the carbon chain increases. Longer molecular chains become increasingly entangled, increasing resistance to flow.
- (b) Whereas viscosity depends on molecular chain length in a critical way, surface tension depends on the strengths of intermolecular interactions between molecules. These dispersion forces do not increase as rapidly with increasing chain length and molecular weight as viscosity does.
- (c) The  $-\text{OH}$  group in *n*-octyl alcohol gives rise to hydrogen bonding among molecules, which increases molecular entanglement and leads to greater viscosity and higher boiling point.

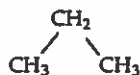
- 11.89 (a) 24 valence
- $e^-$
- , 12
- $e^-$
- pairs



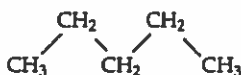
The geometry around the central C atom is trigonal planar, and around the two terminal C atoms, tetrahedral.

- (b) Polar. The C=O bond is quite polar and the dipoles in the trigonal plane around the central C atom do not cancel.
- (c) Dipole-dipole and London-dispersion forces
- (d) Since the molecular weights of acetone and 1-propanol are similar, the strength of the London-dispersion forces in the two compounds is also similar. The big difference is that 1-propanol has hydrogen bonding, while acetone does not. These relatively strong attractive forces lead to the higher boiling point for 1-propanol.

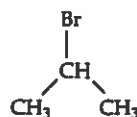
11.90



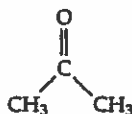
(i) MM = 44



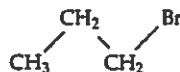
(ii) MM = 72



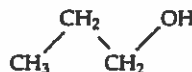
(iii) MM = 123



(iv) MM = 58



(v) MM = 123



(vi) MM = 60

It is useful to draw the structural formulas because intermolecular forces are determined by the size and shape (structure) of molecules.

- (a) *Molar mass*: compounds (i) and (ii) have similar rod-like structures; (ii) has a longer rod. The longer chain leads to greater molar mass, stronger London-dispersion forces and higher heat of vaporization.
- (b) *Molecular shape*: compounds (iii) and (v) have the same chemical formula and molar mass but different molecular shapes (they are structural isomers). The more rod-like shape of (v) leads to more contact between molecules, stronger dispersion forces and higher heat of vaporization.
- (c) *Molecular polarity*: rod-like hydrocarbons (i) and (ii) are essentially nonpolar, owing to free rotation about C-C  $\sigma$  bonds, while (iv) is quite polar, owing to the C=O group. (iv) has a smaller molar mass than (ii) but a larger heat of vaporization, which must be due to the presence of dipole-dipole forces in (iv). [Note that (iii) and (iv), with similar shape and molecular polarity, have very similar heats of vaporization.]
- (d) *Hydrogen-bonding interactions*: molecules (v) and (vi) have similar structures, but (vi) has hydrogen bonding and (v) does not. Even though molar mass and thus dispersion forces are larger for (v), (vi) has the higher heat of vaporization. This must be due to hydrogen bonding interactions.

- 11.91 (a) In order for butane to be stored as a liquid at temperatures above its boiling point ( $-5^{\circ}\text{C}$ ), the pressure in the tank must be greater than atmospheric pressure. In terms of the phase diagram of butane, the pressure must be high enough so that, at tank conditions, the butane is "above" the gas-liquid line and in the liquid region of the diagram.

The pressure of a gas is described by the ideal gas law as  $P = nRT/V$ ; pressure is directly proportional to moles of gas. The more moles of gas present in the tank the greater the pressure, until sufficient pressure is achieved for the gas to liquify. At the point where liquid and gas are in equilibrium and temperature is constant, liquid will vaporize or condense to maintain the equilibrium vapor pressure. That is, as long as some liquid is present, the gas pressure in the tank will be constant.

- (b) If butane gas escapes the tank, butane liquid will vaporize (evaporate) to maintain the equilibrium vapor pressure. Vaporization is an endothermic process, so the butane will absorb heat from the surroundings. The temperature of the tank and the liquid butane will decrease.

$$(c) \quad 250 \text{ g C}_4\text{H}_{10} \times \frac{1 \text{ mol C}_4\text{H}_{10}}{58.12 \text{ g C}_4\text{H}_{10}} \times \frac{21.3 \text{ kJ}}{\text{mol}} = 91.6 \text{ kJ}$$

$$V = \frac{nRT}{P} = 250 \text{ g} \times \frac{1 \text{ mol}}{58.12 \text{ g}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{308 \text{ K}}{755 \text{ torr}} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 109.44 = 109 \text{ L}$$

11.92 *Plan.*

- (i) Using thermochemical data from Appendix B, calculate the energy (enthalpy) required to melt and heat the  $\text{H}_2\text{O}$ .
- (ii) Using Hess's Law, calculate the enthalpy of combustion,  $\Delta H_{\text{comb}}$  for  $\text{C}_3\text{H}_8$ .
- (iii) Solve the stoichiometry problem.

*Solve.*

$$(i) \quad \text{Heat H}_2\text{O}(s) \text{ from } -20^{\circ}\text{C} \text{ to } 0.0^{\circ}\text{C}; 5.50 \times 10^3 \text{ g H}_2\text{O} \times \frac{2.092 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}} \times 20^{\circ}\text{C} = 2.301 \times 10^2 \text{ kJ}$$

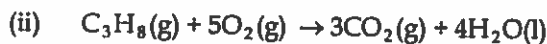
$$\text{Melt H}_2\text{O}(s); 5.50 \times 10^3 \text{ g H}_2\text{O} \times \frac{6.008 \text{ kJ}}{\text{mol H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 1834 = 1.83 \times 10^3 \text{ kJ}$$

$$= 2.3 \times 10^2 \text{ kJ}$$

$$\text{Heat H}_2\text{O}(l) \text{ from } 0^{\circ}\text{C} \text{ to } 75^{\circ}\text{C}; 5.50 \times 10^3 \text{ g H}_2\text{O} \times \frac{4.184 \text{ J}}{\text{g} \cdot ^{\circ}\text{C}} \times 75^{\circ}\text{C} = 1726 = 1.7 \times 10^3 \text{ kJ}$$

$$\text{Total energy} = 230.1 \text{ kJ} + 1834 \text{ kJ} + 1726 \text{ kJ} = 3790 = 3.8 \times 10^3 \text{ kJ}$$

(The result is significant to 100 kJ, limited by  $1.7 \times 10^3 \text{ kJ}$ )



Assume that one product is  $\text{H}_2\text{O}(\text{l})$ , since this leads to a more negative  $\Delta H_{\text{comb}}$  and fewer grams of  $\text{C}_3\text{H}_8(\text{g})$  required.

$$\Delta H_{\text{comb}} = 3\Delta H_f^{\circ} \text{CO}_2(\text{g}) + 4\Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_f^{\circ} \text{C}_3\text{H}_8(\text{g}) - 5\Delta H_f^{\circ} \text{O}_2(\text{g})$$

$$= 3(-393.5 \text{ kJ}) + 4(-285.83 \text{ kJ}) - (-103.85 \text{ kJ}) - 5(0) = -2219.97 = -2220 \text{ kJ}$$



$$(iii) \quad 3.790 \times 10^3 \text{ kJ required} \times \frac{1 \text{ mol C}_3\text{H}_8}{2219.97 \text{ kJ}} \times \frac{44.096 \text{ g C}_3\text{H}_8}{1 \text{ mol C}_3\text{H}_8} = 75 \text{ g C}_3\text{H}_8$$

( $3.8 \times 10^3$  kJ required has 2 sig figs and so does the result)

$$11.93 \quad P = \frac{nRT}{V} = \frac{g RT}{MV}; \quad T = 273.15 + 26.0 \text{ }^\circ\text{C} = 299.15 = 299.2 \text{ K}; \quad V = 5.00 \text{ L}$$

$$g \text{ C}_6\text{H}_6(\text{g}) = 7.2146 - 5.1493 = 2.0653 \text{ g C}_6\text{H}_6(\text{g})$$

$$P(\text{vapor}) = \frac{2.0653 \text{ g}}{78.11 \text{ g/mol}} \times \frac{299.15 \text{ K}}{5.00 \text{ L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 98.660 = 98.7 \text{ torr}$$

11.94 *Plan.* Relative humidity and v.p. of  $\text{H}_2\text{O}$  at given  $T \rightarrow P_{\text{H}_2\text{O}} \rightarrow$  ideal-gas law  $\rightarrow$  mol  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}$  molecules. Change  $^\circ\text{F} \rightarrow ^\circ\text{C}$ , volume of room from  $\text{ft}^3 \rightarrow \text{L}$ .

$$\text{Solve. } ^\circ\text{C} = 5/9 (^\circ\text{F} - 32); \quad ^\circ\text{C} = 5/9 (68 ^\circ\text{F} - 32) = 20 \text{ }^\circ\text{C};$$

$$\text{r.h.} = (P_{\text{H}_2\text{O}} \text{ in air} / \text{v.p. of H}_2\text{O}) \times 100$$

$$\text{From Appendix B, v.p. of H}_2\text{O at } 20 \text{ }^\circ\text{C} = 17.54 \text{ torr}$$

$$P_{\text{H}_2\text{O}} \text{ in air} = \text{r.h.} \times \text{v.p. of H}_2\text{O}/100 = 58 \times 17.54 \text{ torr}/100 = 10.173 = 10 \text{ torr}$$

$$V = 12 \text{ ft} \times 10 \text{ ft} \times 8 \text{ ft} \times \frac{12^3 \text{ in}^3}{\text{ft}^3} \times \frac{2.54^3 \text{ cm}^3}{\text{in}^3} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 2.718 \times 10^4 = 3 \times 10^4 \text{ L}$$

(The result has 1 sig fig, as does the measurement 8 ft.)

$$PV = nRT; \quad n = PV/RT$$

$$n = 10.173 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{\text{mol} \cdot \text{K}}{0.08206 \text{ L} \cdot \text{atm}} \times \frac{2.718 \times 10^4 \text{ L}}{293 \text{ K}} = 15.13 = 2 \times 10^1 \text{ mol H}_2\text{O}$$

$$15.13 \text{ mol H}_2\text{O} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = 9.112 \times 10^{24} = 9 \times 10^{24} \text{ H}_2\text{O molecules}$$