IB

11 Intermolecular Forces, Liquids and Solids

Visualizing Concepts

11.2 (a) Hydrogen bonding; H–F interactions qualify for this narrowly defined interaction.

(b) London dispersion forces, the only intermolecular forces between nonpolar F_2 molecules.

(c) Ion-dipole forces between Na^+ cation and the negative end of a polar covalent water molecule.

(d) Dipole-dipole forces between oppositely charged portions of two polar covalent SO_2 molecules.

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.)

11.5 The stronger the intermolecular forces, the greater the average kinetic energy required to escape these forces, and the higher the boiling point. $CH_3CH_2CH_2OH$ has hydrogen bonding, by virtue of its -OH group, so it has the higher boiling point. Dispersion forces are similar because molar masses are the same for both molecules.

11.6 (a) 360 K, the normal boiling point; 265 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 white zone, liquid in the blue zone, and gas in the yellow zone. (i) gas (ii) solid (iii) liquid

11.8 (a) Clearly, the structure is close-packed. The question is: cubic or hexagonal? Without looking deeper into the layers of oranges, one cannot distinguish whether the layer structure is cubic (ABCABC) or hexagonal (ABABAB) close-packed.

(b) CN = 12, regardless of whether the structure is hexagonal or cubic close packed.

(c) Molecular. There are no strong bonds between particles.

Kinetic-Molecular Theory

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) At constant temperature, the average kinetic energy of a collection of particles is constant. Compression brings particles closer together and increases the number of particle-particle collisions. With more collisions, the likelihood of intermolecular attractions causing the particles to coalesce (liquefy) is greater.

11.12 (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° has the lower density (1.08 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 g/cm^3 at 15°C, is greater than the liquid density, 1.08 g/cm^3 at 130°C.

Intermolecular Forces

11.14 (a) London-dispersion forces

(b) dipole-dipole and London-dispersion forces

(c) hydrogen bonding (dominates properties of these small molecules) and London-dispersion forces (less significant)

11.16 (a) CH_3OH experiences hydrogen bonding, but CH_3SH 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.

(b) sublimation, endothermic

(c) vaporization (evaporation), endothermic

(d) freezing, exothermic

11.36 (a) Liquid ethyl chloride at room temperature is far above its boiling point. When the liquid contacts the metal surface, heat sufficient to vaporize the liquid is transferred from the metal to the ethyl chloride, and the heat content of the molecules increases. At constant atmospheric pressure, ΔH = q, so the heat content and the enthalpy content of $C_2H_5Cl(g)$ is higher than that of $C_2H_5Cl(l)$.

(b) Attractive intermolecular forces hold the C_2H_5Cl molecules in close contact in the liquid phase. In order to overcome these attractive forces and maintain separation in the gas phase, the enthalpy content of the C_2H_5Cl molecules must increase when they change from the liquid to the gaseous state.

11.38 Energy released when 100 g of H_2O is cooled from 18°C to 0°C:

$$\frac{4.184\ \text{J}}{\text{g} \bullet \text{K}} \times 100\ \text{g H}_2\text{O} \times 18^{\circ}\text{C} = 7.53 \times 10^3\ \text{J} = 7.5\ \text{kJ}$$

Energy released when 100 g of H_2O is frozen (there is no change in temperature during a change of state):

$$\frac{334\ \text{J}}{\text{g}} \times 100\ \text{g H}_2\text{O} = 3.34 \times 10^4\ \text{J} = 33.4\ \text{kJ}$$

Total energy released = 7.53 kJ + 33.4 kJ = 40.93 = 40.9 kJ

Mass of freon that will absorb 40.9 kJ when vaporized:

$$40.93\ \text{kJ} \times \frac{1 \times 10^3\ \text{J}}{1\ \text{kJ}} \times \frac{1\ \text{g CCl}_2\text{F}_2}{289\ \text{J}} = 142\ \text{g CCl}_2\text{F}_2$$

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

Heat the liquid from 5.00°C to 47.6°C (278.00 K to 320.6 K), using the specific heat of the liquid.

$$25.0\ \text{g C}_2\text{Cl}_3\text{F}_3 \times \frac{0.91\ \text{J}}{\text{g} \bullet \text{K}} \times 42.6\ \text{K} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = 0.969 = 0.97\ \text{kJ}$$

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

$$25.0\ \text{g C}_2\text{Cl}_3\text{F}_3 \times \frac{1\ \text{mol C}_2\text{Cl}_3\text{F}_3}{187.4\ \text{g C}_2\text{Cl}_3\text{F}_3} \times \frac{27.49\ \text{kJ}}{\text{mol}} = 3.667 = 3.67\ \text{kJ}$$

Heat the gas from 47.6°C to 82.00°C (320.6 K to 355.00 K), using the specific heat of the gas.

$$25.0\ \text{g C}_2\text{Cl}_3\text{F}_3 \times \frac{0.67\ \text{J}}{\text{g} \bullet \text{K}} \times 34.4\ \text{K} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = 0.576 = 0.58\ \text{kJ}$$

The total energy required is 0.969 kJ + 3.667 kJ + 0.576 kJ = 5.21 kJ.

11.42 (a) According to Solution 11.41(b), the higher the critical temperature, the stronger the intermolecular forces of a substance. Therefore, the strength of intermolecular forces decreases moving from left to right across the series and as molecular weight decreases.

(b) The molecules in this series experience London-dispersion forces and, except for CF_4, dipole-dipole forces. We expect the strength of dispersion forces to increase with increasing molecular weight, which agrees with the trends in critical temperature and pressure.

Vapor Pressure and Boiling Point

11.44 (a) The pressure difference on the manometer is 130 mm Hg and the gas in the vessel is essentially 100% molecules of the substance in the vapor phase. When the vessel is evacuated, virtually all air is removed. As the frozen liquid warms, it establishes a vapor pressure of 130 mm Hg. This is the pressure difference on the manometer.

(b) The pressure difference is 1 atm. The gas is 130 mm Hg of the molecular vapor and the rest is air. The liquid vaporizes in contact with the atmosphere, so atmospheric pressure is maintained above the liquid, but the equilibrium gas composition reflects the amount of vapor necessary to maintain 130 mm pressure, plus enough air to maintain a total pressure of 1 atm.

(c) The pressure difference is 890 mm Hg (1 atm + 130 mm Hg) and the gas is a mixture of 130 mm vapor and 1 atm air. The initial air pressure in the flask is 1 atm and no air is allowed to escape. The gas in the flask is not in equilibrium with the atmosphere and the final pressure in the flask does not equal atmospheric pressure. After a most of the liquid vaporizes, the total gas pressure is the result of 130 mm vapor and 1 atm air.

11.46 Both molecules are pyramidal, with a nonbonding electron pair on the central atom. Even though the molecules are polar covalent, differences in their intermolecular forces and physical properties are likely to be dominated by differences in dispersion forces.

(a) PCl_3

(b) $AsCl_3$

(c) At the same temperature, the average kinetic energy of molecules of the two substances is equal.

(d) The strength of dispersion forces increases with increasing molecular weight, so $AsCl_3$ will experience stronger intermolecular forces. This is the basis of predictions in parts (a) and (b) above.

11.48 (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. The eggs must be cooked longer at the lower temperature.

(b) We expect Se^{2-} to have a larger ionic radius than S^{2-}, since Se is below S in the chalcogen family and both ions have the same charge. Thus, HgSe will occupy a larger volume and the unit cell edge will be longer.

(c) For HgSe:

$$\text{density} = \frac{4\ \text{HgSe units}}{(6.085\ \text{Å})^3} \times \frac{279.55\ \text{g HgSe}}{6.022 \times 10^{23}\ \text{HgSe units}} \times \left(\frac{1\ \text{Å}}{1 \times 10^{-8}\ \text{cm}}\right)^3 = 8.241\ \text{g/cm}^3$$

Even though HgSe has a larger unit cell volume than HgS, it also has a larger molar mass. The mass of Se is more than twice that of S, while the radius of Se^{2-} is only slightly larger than that of S (Figure 7.7). The greater mass of Se accounts for the greater density of HgSe.

Bonding in Solids

11.72 (a) ionic (b) metallic

(c) ionic (somewhat borderline, could be modeled as ionic with some covalent character to the bonds, in keeping with the high oxidation state of Zr, or as a network solid with ionic character to the bonding, in keeping with the electronegativity difference between Zr and O.)

(d) molecular (e) molecular (f) molecular

11.74 (a) metallic

(b) molecular or metallic (physical properties of metals vary widely)

(c) covalent-network or ionic (d) covalent-network (e) ionic

11.76 According to Table 11.7, the solid could be either ionic with low water solubility or network covalent. Due to the extremely high sublimation temperature, it is probably covalent-network.

11.78 (a) HF – hydrogen bonding versus dipole-dipole for HCl

(b) C(graphite) – covalent-network bonding versus London dispersion forces for CH_4

(c) KBr – ionic versus dispersion forces for nonpolar Br_2

(d) MgF_2 – higher charge on Mg^{2+} than Li^+

Additional Exercises

11.80 (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.

11.81 (a) The *cis* isomer has stronger dipole-dipole forces; the *trans* isomer is nonpolar. The higher boiling point of the *cis* isomer supports this conclusion.