CHAPTER TEN

LIQUIDS AND SOLIDS

For Review

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

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

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

As the size of a molecule increases, the strength of the London dispersion forces increases. This is because, as the electron cloud about a molecule gets larger, it is easier for the electrons to be drawn away from the nucleus. The molecule is said to be more polarizable.

London dispersion (LD) < dipole-dipole < H bonding < metallic bonding, covalent network, ionic.

Yes, there is considerable overlap. Consider some of the examples in Exercise 10.98. Benzene (only LD forces) has a higher boiling point than acetone (dipole-dipole forces). Also, there is even more overlap among the stronger forces (metallic, covalent, and ionic).

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

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

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

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

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

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

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

Gas: no fixed volume or shape; easily compressible

4. a. Crystalline solid: Regular, repeating structure

   Amorphous solid: Irregular arrangement of atoms or molecules

b. Ionic solid: Made up of ions held together by ionic bonding

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

c. Molecular solid: Discrete, individual molecules

   Network solid: No discrete molecules; A network solid is one large molecule. The forces holding the atoms together are the covalent bonds between atoms.

d. Metallic solid: Completely delocalized electrons, conductor of electricity (cations in a sea of electrons)

   Network solid: Localized electrons; Insulator or semiconductor

5. Lattice: a three-dimensional system of points designating the positions of the centers of the components of a solid (atoms, ions, or molecules)

Unit cell: the smallest repeating unit of a lattice

A simple cubic unit cell has an atom, ion or molecule located at the eight corners of a cube. There is one net atom per simple cubic unit cell. Because the atoms in the cubic unit cell are assumed to touch along the cube edge, cube edge = \( P = 2r \) where \( r \) = radius of the atom. A body-centered cubic unit cell has an atom, ion or molecule at the eight corners of a cube and one atom, ion, or molecule located at the center of the cube. There are two net atoms per body-centered cubic unit cell. Because the atoms in the cubic unit cell are assumed to touch along the body diagonal of the cube, body diagonal = \( \sqrt{3} P = 4r \) where \( P \) = cube edge and \( r \) = radius of atom. A face-centered cubic unit cell has an atom, ion, or molecule at the eight
corners of a cube and an atom, ion, or molecule located at the six faces of the cube. There are
four net atoms per face-centered unit cell. Because the atoms in the cubic unit cell are
assumed to touch along the face diagonal of the cube, face diagonal = \( \sqrt{2} \) \( a \) = 4r.

6. Closest packing: the packing of atoms (uniform, hard spheres) in a manner that most
efficiently uses the available space with the least amount of empty space. The two types of
closest packing are hexagonal closest packing and cubic closest packing. In both closest
packed arrangements, the atoms (spheres) are packed in layers. The difference between the
two closest packed arrangements is the ordering of the layers. Hexagonal closest packing has
the third layer directly over the first layer forming a repeating layer pattern of abab… In
cubic closest packing the layer pattern is abcabc… The unit cell for hexagonal closest
packing is a hexagonal prism. See Fig. 10.14 for an illustration of the hexagonal prism unit
cell. The unit cell for cubic closest packing is the face-centered cubic unit cell.

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

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

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

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

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

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

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

To produce an n-type semiconductor, dope Ge with a substance that has more than 4 valence
electrons, e.g., a group 5A element. Phosphorus or arsenic are two substances which will
produce n-type semiconductors when they are doped into germanium. To produce a p-type
semiconductor, dope Ge with a substance that has fewer than 4 valence electrons, e.g., a
group 3A element. Gallium or indium are two substances which will produce p-type semiconductors when they are doped into germanium.

8. The structures of most binary ionic solids can be explained by the closest packing of spheres. Typically, the larger ions, usually the anions, are packed in one of the closest packing arrangements, and the smaller cations fit into holes among the closest packed anions. There are different types of holes within the closest packed anions which are determined by the number of spheres that form them. Which of the three types of holes are filled usually depends on the relative size of the cation to the anion. Ionic solids will always try to maximize electrostatic attractions among oppositely charged ions and minimize the repulsions among ions with like charges.

The structure of sodium chloride can be described in terms of a cubic closest packed array of Cl\(^-\) ions with Na\(^+\) ions in all of the octahedral holes. An octahedral hole is formed between 6 Cl\(^-\) anions. The number of octahedral holes is the same as the number of packed ions. So in the face-centered unit cell of sodium chloride, there are 4 net Cl\(^-\) ions and 4 net octahedral holes. Because the stoichiometry dictates a 1:1 ratio between the number of Cl\(^-\) anions and Na\(^+\) cations, all of the octahedral holes must be filled with Na\(^+\) ions.

In zinc sulfide, the sulfide anions also occupy the lattice points of a cubic closest packing arrangement. But instead of having the cations in octahedral holes, the Zn\(^{2+}\) cations occupy tetrahedral holes. A tetrahedral hole is the empty space created when four spheres are packed together. There are twice as many tetrahedral holes as packed anions in the closest packed structure. Therefore, each face-centered unit cell of sulfide anions contains 4 net S\(^{2-}\) ions and 8 net tetrahedral holes. For the 1:1 stoichiometry to work out, only one-half of the tetrahedral holes are filled with Zn\(^{2+}\) ions. This gives 4 S\(^{2-}\) ions and 4 Zn\(^{2+}\) ions per unit cell for an empirical formula of ZnS.

9. a. Evaporation: process where liquid molecules escape the liquid’s surface to form a gas.
   
b. Condensation: process where gas molecules hit the surface of a liquid and convert to a liquid.
   
c. Sublimation: process where a solid converts directly to a gas without passing through the liquid state.
   
d. Boiling: the temperature and pressure at which a liquid completely converts to a gas as long as heat is applied.
   
e. Melting: temperature and pressure at which a solid completely converts to a liquid as long as heat is applied.
   
f. Enthalpy of vaporization (\(\Delta H_{\text{vap}}\)): the enthalpy change that occurs at the boiling point when a liquid converts into a gas.
   
g. Enthalpy of fusion (\(\Delta H_{\text{fus}}\)): the enthalpy change that occurs at the melting point when a solid converts into a liquid.
h. Heating curve: a plot of temperature versus time as heat is applied at a constant rate to some substance.

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

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

10. See Fig. 10.49 and 10.52 for the phase diagrams of $\text{H}_2\text{O}$ and $\text{CO}_2$. Most substances exhibit only three different phases: solid, liquid, and gas. This is true for $\text{H}_2\text{O}$ and $\text{CO}_2$. Also typical of phase diagrams is the positive slopes for both the liquid-gas equilibrium line and the solid-gas equilibrium line. This is also true for both $\text{H}_2\text{O}$ and $\text{CO}_2$. The solid-liquid equilibrium line also generally has a positive slope. This is true for $\text{CO}_2$, but not for $\text{H}_2\text{O}$. In the $\text{H}_2\text{O}$ phase diagram, the slope of the solid-liquid line is negative. The determining factor for the slope of the solid-liquid line is the relative densities of the solid and liquid phases. The solid phase is denser than the liquid phase in most substances; for these substances, the slope of the solid-liquid equilibrium line is positive. For water, the liquid phase is denser than the solid phase which corresponds to a negative sloping solid-liquid equilibrium line. Another difference between $\text{H}_2\text{O}$ and $\text{CO}_2$ is the normal melting points and normal boiling points. The term normal just dictates a pressure of 1 atm. $\text{H}_2\text{O}$ has a normal melting point (0°C) and a normal boiling point (100°C), but $\text{CO}_2$ does not. At 1 atm pressure, $\text{CO}_2$ only sublimes (goes from the solid phase directly to the gas phase). There are no temperatures at 1 atm for $\text{CO}_2$ where the solid and liquid phases are in equilibrium or where the liquid and gas phases are in equilibrium. There are other differences, but those discussed above are the major ones.

The relationship between melting points and pressure is determined by the slope of the solid-liquid equilibrium line. For most substances (CO$_2$ included), the positive slope of the solid-liquid line shows a direct relationship between the melting point and pressure. As pressure increases, the melting point increases. Water is just the opposite since the slope of the solid-liquid line in water is negative. Here the melting point of water is inversely related to the pressure.

For boiling points, the positive slope of the liquid-gas equilibrium line indicates a direct relationship between the boiling point and pressure. This direct relationship is true for all substances including $\text{H}_2\text{O}$ and $\text{CO}_2$.

The critical temperature for a substance is defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied. The critical temperature, like the boiling point temperature, is directly related to the strength of the intermolecular forces. Since $\text{H}_2\text{O}$ exhibits relatively strong hydrogen bonding interactions and $\text{CO}_2$ only exhibits London dispersion forces, one would expect a higher critical temperature for $\text{H}_2\text{O}$ than for $\text{CO}_2$. 