CHAPTER 10
LIQUIDS, SOLIDS, AND CHANGES OF STATE

Chapter Learning Goals

Section 10.1 Calculate percent ionic character from a dipole moment. Using only VSEPR geometries and electronegativity trends, determine whether a molecule is expected to be polar and have a dipole moment. Give the direction of a dipole moment.

Section 10.2 Identify the major type of intermolecular forces present in substances, and determine which of two substances exhibits the stronger intermolecular force. Relate relative strengths of intermolecular forces to physical properties of molecules.

Section 10.3 Describe viscosity and surface tension, and relate these properties to intermolecular forces.

Section 10.4 Describe fusion, freezing, vaporization, condensation, sublimation, and deposition. For a phase change, determine whether enthalpy is increasing or decreasing and whether entropy is increasing or decreasing. Use the $\Delta G = \Delta H - T\Delta S$ equation to calculate the entropy change for a phase change or the temperature (boiling point, melting point, sublimation point) at which the phase change occurs.

Section 10.5 Use the Clausius-Clapeyron equation to calculate vapor pressure or heat of vaporization.

Section 10.6 Classify solids as ionic, molecular, covalent network, or metallic, and give the major forces of attraction of each.

Section 10.7 Use the Bragg equation to calculate the distance between layers of atoms in a crystal.

Section 10.8 Identify unit cells. For metals crystallizing in one of the three cubic unit cells, determine the number of atoms, mass, volume, density, atomic radius, and packing efficiency.

Section 10.9 From unit cell information for ionic solids, determine the types and numbers of ions, the oxidation state and geometry around each ion, and the formula or the ionic compound.

Section 10.10 Describe structure of the allotropes of carbon and SiO_2.

Section 10.11 Sketch a phase diagram, labeling the axes and each of the regions, and locate the triple point, critical point, normal melting point, and the normal boiling point. Use phase diagrams to describe physical changes.

Lecture Outline

10.1 Polar Covalent Bonds and Dipole Moments

A. Bond dipole – A bond is polar if the atoms joined have different electronegativities
   1. A bond with partial positive (δ+) and partial negative (δ–) ends
   2. Due to in electronegativity difference of the atoms in the bond
   3. Represented by $\rightarrow$; indicates direction of electron displacement
      a. Point of arrow represents δ– end of dipole
      b. Crossed end represents δ+ end of dipole

B. Polar molecules – due to the net sum of individual bond polarities and lone-pair contributions in the molecule
   1. Molecular dipoles – A molecule is polar if the bond polarities are not arranged symmetrically .
      a. Center of mass of positive charge (nuclei) doesn't coincide with the center of mass of negative charge (electrons).
      b. An uneven distribution of charges results in a net dipole moment.
   2. Lone pairs of electrons make substantial contributions to net molecular polarity.
   3. Individual bond polarities cancel in symmetrical molecules.

C. Dipole moment (μ)
   1. Magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges
   2. $\mu = Q \times r$

10.2. Intermolecular Forces

A. Intermolecular forces – relatively weak forces of attraction between 2 molecules. **Note:** Not to be confused with intramolecular forces, which are relatively strong bonding forces that hold atoms together in molecules.
   1. Attractive forces between molecules that hold them together in certain temperatures ranges.
   2. Often called van der Waals forces
   3. Divided into categories
      a. Ion-dipole
      b. Dipole-dipole
      c. London dispersion forces
      d. Hydrogen bonding
   4. Electrical in nature

B. Ion-dipole forces
   1. Result of electrical interactions between an ion and partial charges on a polar molecule
   2. Favored orientation
      a. δ+ end of molecule near the anion
      b. δ– end of molecule near the cation
   3. Important in aqueous solutions of ionic substances, where dipolar water molecules surround the ions

C. Dipole-dipole force
   1. Result from electrical interactions among dipoles on neighboring molecules
   2. Generally weak – strength depends on sizes of the dipole moments involved
   3. Significant only when molecules in close contact
   4. Correlation between dipole moment and boiling point
      a. High dipole moment corresponds to strong intermolecular forces
      b. Substance must overcome intermolecular forces to boil
      c. Stronger intermolecular forces require higher boiling points

D. London dispersion forces
   1. Result from motion of electrons around atoms
      a. Due to instantaneous unsymmetrical electron distribution
      b. Creates a short-lived dipole moment (instantaneous dipole)
   2. Instantaneous dipole induces a temporary dipole on neighboring atoms
   3. Weak attractive forces
   4. Polarizability – ease of molecule's electron cloud distorted by a nearby electric field
      a. Smaller molecules and lighter atoms with fewer electrons

i. Relatively nonpolarizable
ii. Smaller dispersion forces
b. Larger molecules and heavier atoms with more electrons
i. More polarizable
ii. Larger dispersion forces
c. Molecules with more spread-out shapes
i. Maximize molecular surface area
ii. Greater contact between molecules
iii. Have higher dispersion forces

E. Hydrogen bonds – attractive interaction between a hydrogen atom bonded to an electronegative O, N, or F atom and an unshared electron pair on another nearby electronegative atom
1. Quite strong
2. Responsible for water's remarkable properties
3. Results in higher boiling points than might be expected
4. Contributing factors
a. Extraordinary electronegativity and small sizes of F, O, and N: H–F, H–O, H–N bonds are highly polar
b. Small size of hydrogen

10.3. Some Properties of Liquids

A. Viscosity
1. Measure of a liquid's resistance to flow
2. SI unit: $N \cdot s/m^2$
3. Ease with which molecules move around in the liquid
4. Related to intermolecular forces – stronger the forces, higher the viscosity

B. Surface tension
1. Resistance of a liquid to spreading out and increasing its surface area
2. Due to difference in intermolecular forces felt by liquid surface molecules and liquid interior molecules
3. Related to intermolecular forces – stronger the forces, greater the surface tension

C. Properties temperature dependent
1. Increase in temperature corresponds to increase in kinetic energy
2. Molecules with high kinetic energies more easily overcome intermolecular forces

10.4. Phase Changes

A. Phase changes (changes of state)
1. Physical form but not chemical identity of a substance changes
2. Matter in any one state can change into either of the other two
3. Sublimation – solid changes directly into a gas
4. Temperature remains constant during all phase changes.
5. Some metals can exist in more than one solid phase, such as the metallic and nonmetallic forms of tin.

B. Phase change associated with free-energy change, ΔG
1. $\Delta G = \Delta H - T\Delta S$
2. Enthalpy part – energy change associated with making or breaking intermolecular attractions holding liquids and solids together
3. Entropy part – associated with change in disorder between various states
4. Solid $\rightarrow$ liquid, solid $\rightarrow$ gas, liquid $\rightarrow$ gas: ΔH and ΔS both positive
5. Gas $\rightarrow$ liquid, gas $\rightarrow$ solid, liquid $\rightarrow$ solid: ΔH and ΔS both negative
6. Knowing ΔH and ΔS for a phase transition can calculate temperature at which two phases are in equilibrium.
a. At equilibrium, $\Delta G = 0$
b. $T = \Delta H/\Delta S$

C. Heating curve – graphical display of results of adding heat to a sample (See textbook Figure 10.10.)
1. Melting point
a. Temperature at which solid and liquid coexist in equilibrium as molecules break free from their position in the crystal and enter the liquid phase

b. Heat of fusion (ΔH_{fusion}) – amount of energy required to overcome enough intermolecular forces to convert solid into liquid

2. Boiling point

a. Temperature at which liquid and vapor coexist in equilibrium as molecules break free from the surface of the liquid and enter the gas phase

b. Heat of vaporization (ΔH_{vap}) – amount of energy necessary to convert liquid into gas

3. $\Delta H_{vap} >> \Delta H_{fusion}$

a. For vaporization, must overcome all intermolecular forces in compound

b. For fusion, must overcome fewer intermolecular forces

10.5. Evaporation, Vapor Pressure, and Boiling Point

A. Evaporation – escape of molecules from a liquid surface

B. Vapor pressure – pressure exerted by vapor molecules over a liquid in a closed container

1. Dynamic equilibrium
2. Number of molecules escaping liquid = number of molecules returning to liquid
3. Constant total number of molecules in both liquid and vapor phases
4. Individual molecules constantly passing back and forth from one phase to another

C. Explained by kinetic molecular theory – increase in temperature results in higher fraction of molecules with sufficient kinetic energy to overcome surface tension and escape into the vapor

D. Value of vapor pressure

1. Related to intermolecular forces and temperature
2. Smaller the intermolecular forces, higher the vapor pressure – molecules loosely held in liquid and easily escape
3. Higher the temperature, higher the kinetic energy – molecules have sufficient kinetic energy to escape the liquid

E. Clausius-Clapeyron equation

1. Relates vapor pressure of a liquid to inverse of its temperature

$$\ln\left(P_{vap}\right)=\left(\frac{-\Delta H_{vap}}{RT}\right)+\ \text{C, where C = a constant characteristic of each substance}$$

2. Plot ln (P_{vap}) versus 1/T

a. Straight line

b. Slope = $-\Delta H_{vap}/R$

3. Knowing vapor pressure at several temperatures, can calculate ΔH_{vap} of a liquid from

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

F. Boiling point

1. Temperature at which vapor pressure of a liquid equals the external pressure pushing on the surface, and all of the liquid can change into the vapor phase
2. Normal boiling point – external pressure = 1 atm
3. External pressure < 1 atm – liquid boils at a lower temperature
4. External pressure > 1 atm – liquid boils at a higher temperature

10.6. Kinds of Solids

A. Crystalline solids

1. Solids with atoms, ions, or molecules in an ordered, long-range arrangement
2. Macroscopically – observe flat faces and sharp angles
3. Types of crystalline solids – textbook Table 10.9

a. Ionic solids

i. Constituent particles are ions

ii. Example: NaCl

iii. Ordered into a 3-D arrangement held together by ionic bonds

b. Molecular solids

i. Constituent particles are molecules held together by intermolecular forces
ii. Examples: sucrose and ice
c. Covalent network solids
i. Atoms linked together by covalent bonds into a giant 3-D array
ii. Examples: diamond and quartz
d. Metallic solids
i. Comparable to network solids but consist of metal atoms
ii. Examples: Ag and Fe
iii. Have metallic properties
B. Amorphous solids
1. Constituent particles randomly arranged
2. No ordered long-range structure

10.7. Probing the Structure of Solids: X–Ray Crystallography

A. Diffraction
1. Beam of electromagnetic radiation scattered by an object containing regularly spaced lines or points (e.g., atoms in a crystal)
2. Spacing must be comparable to the λ of the radiation
3. Interference between two λ's passing through the same region of space at the same time
a. Constructive interference
i. Waves in-phase (peak-to-peak and trough-to-trough)
ii. Increases intensity of wave
b. Destructive interference
i. Waves out-of-phase
ii. Waves cancel
B. Bragg analysis
1. X-rays diffracted by different layers of atoms in the crystal undergo constructive and destructive interference
2. Bragg equation: $n\lambda = 2\mathrm{d} \times \sin\theta$; $\mathrm{d} = \dfrac{n\lambda}{2\sin\theta}$
a. λ = known
b. Sin θ = angle at which incoming rays are reflected (can be measured)
c. *n* = the order of diffraction; an integer (usually 1)

10.8. Unit Cells and the Packing of Spheres in Crystalline Solids

A. Particles pack together in crystals so that they can be as close together as possible to maximize intermolecular attractions.
B. Simple cubic packing – spheres in one layer sit directly on top of those in the previous layer
1. All layers identical
2. Primitive-cubic unit cell
3. Coordination number = 6: sphere touches four neighbors in the same layer, one above and one below
4. Uses only 52% of available volume
C. Body–centered cubic packing – spheres in alternate layers in an *a*-*b*-*a*-*b* arrangement where spheres in *b* layers fit into small depressions between spheres in neighboring *a* layers
1. Body-centered cubic cell
2. Coordination number = 8; four neighbors above and four neighbors below
3. Occupies 68% of available volume
D. Hexagonal closest-packed – noncubic unit cell with two alternating layers (*a*-*b*-*a*-*b*)
1. Hexagonal arrangement of touching spheres
2. Spheres in *b* layer fit into small triangular depressions between spheres in *a* layer.
3. Coordination number = 12: six neighbors in the same layer, three above and three below
E. Cubic closest-packed – face-centered cubic unit cell with three alternating layers, *a*-*b*-*c*-*a*-*b*-*c*
1. *a*-*b* layers identical to hexagonal closest-packed
2. Third layer offset from both *a* and *b*
3. Coordination number = 12
F. Unit cells – small repeating units found in crystals

1. Symmetrical geometries
2. Stack to minimize space
3. Fourteen different geometries
    a. Parallelepipeds (six-sided geometric solids whose faces are parallelograms)
    b. Differ in lengths of cell edges and angles between edges

G. Cubic cells – all edges equal in length, and all angles 90°
1. Primitive-cubic unit cell for metals
    a. An atom at each of the eight corners
    b. Each atom shared with seven other neighboring cubes that come together at the same point.
    c. One-eighth of each corner atom belongs to a single cube
2. Body-centered cubic unit cell – additional atom in the center of the cube
3. Face-centered cubic unit cell – additional atom on each of the six cube faces
    a. Shared with one other neighboring cube
    b. One-half of each face atom belongs to a single cube

10.9. Structure of Some Ionic Solids

A. Spheres not all the same size – anions larger than cations
B. Ratio of anions to cations in a unit cell consistent with empirical formula.
C. Adopt a variety of different unit cells depending on ion sizes and charges
1. Face-centered cubic – NaCl, KCl.
2. Other common ionic unit cells – textbook Figure 10.25

10.10. Structure of Some Covalent Network Solids

A. Carbon
1. Allotropes
    a. Different structural forms of the same element
    b. Differ in physical and chemical properties
2. More than 40 amorphous forms of carbon
3. Diamond
    a. Each carbon atom sp^3 hybridized
    b. Covalently bonded with tetrahedral geometries
4. Graphite
    a. Two-dimensional sheets of fused six-membered rings
    b. Each carbon sp^2- hybridized
5. Fullerene
    a. Spherical C_{60} molecule
    b. Shape of a soccer ball

B. Silica (SiO_2)
1. Four single bonds between silicon and four oxygens in a covalent network structure
2. Quartz glass – result of heating silica above 1600°C then cooling the viscous liquid
    a. Si–O bonds reform in a random arrangement
    b. Amorphous solid
    c. Mix in additives – prepare a wide variety of glass
        i. Window glass – add $CaCO_3$ and Na_2CO_3
        ii. Colored glass – add transition metal ions
        iii. Borosilicate glass (Pyrex) – add B_2O_3; resistant to thermal shock because it doesn't expand much on heating

10.11. Phase Diagrams

A. Change any one state of matter spontaneously into either of the other two, depending on temperature and pressure
B. Phase diagram – graphical method of illustrating pressure and temperature dependencies of a pure substance in a closed system
1. Boundary line – points on this line represent pressure/temperature combinations at which two phases are in equilibrium
2. Triple point – a unique combination of pressure and temperature at which all three phases coexist in equilibrium

3. Critical temperature – temperature beyond which a gas cannot be liquefied
4. Critical pressure – pressure required to liquefy a gas at the critical point
5. Critical point – point defined by critical temperature and critical pressure
6. Supercritical fluid – substance that is neither liquid nor gas
    a. Pressure of a gas at the critical point is so high and the molecules are so close together that it is difficult to distinguish between gas and liquid.
    b. Temperature of a liquid at the critical point is so high that it is hard to distinguish between liquid and gas.
7. Effect of pressure on the slope of solid/liquid boundary line depends on the relative densities of the solid and liquid phases.