Recall Gases

- At ordinary temperatures and pressures, all gases follow the ideal gas law
- There is no equivalent equation of state that can be written to correlate the properties of liquids and solids

Liquids and Solids Differ from Gases

1. Molecules are much closer together in liquids and solids than in gases
   - In gases, molecules are separated by ten or more molecular diameters
   - In liquids and solids, the molecules are in contact with each other
2. Intermolecular forces play a major role in the behavior of liquids and solids, whereas they are negligible in gases

Behavior of Liquids and Solids

- Phase equilibria
  - Gas-liquid
    - Vapor pressure
    - Boiling point
    - Critical properties
- Relationships
  - Particle structure
  - Interparticle forces
  - Physical properties

Table 9.1: Phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Molecular Spacing</th>
<th>Density</th>
<th>Volume of One Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam (H2O(g))</td>
<td>at 100°C, 1 atm 0.0050 g/mL</td>
<td>at 100°C, 1 atm 31 L</td>
<td></td>
</tr>
<tr>
<td>Water (H2O(l))</td>
<td>at 100°C, 1 atm 0.95 g/mL</td>
<td>19 mL</td>
<td></td>
</tr>
<tr>
<td>Ice (H2O(s))</td>
<td>at 0°C, 1 atm 0.92 g/mL</td>
<td>20 mL</td>
<td></td>
</tr>
</tbody>
</table>
Liquid-Vapor Equilibrium

- Vaporization
  - Liquid is converted into a gas
  - In an open container, evaporation continues until all the liquid is converted into vapor
  - In a closed container, the process of vaporization is countered by the process of condensation:
    - Liquid $\rightleftharpoons$ Vapor
    - The double arrow indicates a *dynamic equilibrium*

Equilibrium

- When the rate at which the liquid vaporizes is equal to the rate at which the vapor condenses, a *dynamic equilibrium is established*
- The *liquid level in the container does not change*
- Molecules are entering the vapor phase from the liquid and condensing from the vapor phase to the liquid at the same rate

Equilibrium in Bromine

Vapor Pressure

- Once equilibrium between a liquid and its vapor is reached, the number of molecules per unit volume does not change with time
  - The pressure exerted by the vapor over the liquid remains constant
  - The vapor pressure is temperature dependent

Pressure and Volume

- As long as both liquid and vapor are present, the vapor pressure is independent of the volume of the container
Example 9.1, (Cont’d)

Vapor Pressure and Temperature

- The vapor pressure of a liquid increases as the temperature rises
  - Increase in $P$ is not linear with temperature
  - Water
    - $VP$ is 24 mmHg at 25 °C
    - $VP$ is 92 mmHg at 50 °C
  - To make a linear plot, the natural logarithm is required
Vapor Pressure Equation

\[ \ln P = -\frac{\Delta H_{vap}}{RT} + b \]

The Clausius-Clapeyron Equation

- For many purposes, a two-point equation is useful
  - Two pressures
  - Two temperatures

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

- Notes:
  - Temperatures must be in Kelvin
    - \( R = 8.31 \text{ J/mol} \cdot \text{K} \)
    - \( \Delta H_{vap} \) must be in J for use with this value for \( R \)

Example 9.2

Boiling Point

- When heat is applied to a liquid in an open container, bubbles eventually form at the bottom
  - At a certain temperature, large bubbles form throughout the liquid; i.e., the liquid boils
  - The temperature at which a liquid boils depends on the pressure above it
    - If the pressure is 1 atm, the temperature at which the liquid boils is called the normal boiling point
    - When the term boiling point is used, the normal boiling point is implied
    - The boiling point is the temperature at which the vapor pressure equals the prevailing pressure

Boiling Point and Prevailing Pressure

- Variation on atmospheric pressure will change the boiling point
  - At high elevation, atmospheric pressure is lower, so the boiling point is lower
  - To elevate the boiling point and allow food to cook more quickly, a pressure cooker can be used
Carbon Dioxide

- Consider carbon dioxide
  - $\text{CO}_2$ as a liquid is sealed into an evacuated glass tube
  - As the tube is heated, some liquid is converted to vapor, and the pressure rises to 44 atm at 10 °C
  - At 31 °C, the pressure is 73 atm
  - Suddenly, the meniscus between liquid and vapor disappears and only vapor is present

Critical Temperature and Pressure

- For every liquid, there is a temperature above which only vapor can exist
  - This is the critical temperature
  - At this temperature, the pressure is called the critical pressure
  - Together, the critical temperature and pressure are called the critical point

Permanent Gases

- Permanent gases are substances with critical temperatures below 25 °C.
  - Usually stored in cylinders at 150 atm or greater
  - Only vapor is present in the tank
  - Pressure in the tank drops as the gas is released
Condensable Gases

- Condensable gases have critical temperatures above 25 °C.
  - Carbon dioxide
  - Hydrocarbon gases
  - Ammonia
  - Chlorine
  - Sulfur dioxide

- For these substances, the liquid-vapor equilibrium accounts for the pressure in the tank
  - Pressure will not change until all the liquid is gone

Phase Diagrams

- Phase diagrams are graphical representations of the pressure and temperature dependence of a pure substance
  - Pressure on the y-axis
  - Temperature on the x-axis

- Three places to consider
  - In a region, one phase exists
  - On a line, two phases exist in equilibrium
  - At a point, three phases exist in equilibrium

Phase Diagram of Water

- Curve b (green) is the vapor pressure-temperature curve of liquid water
- Curve c (red) is the vapor pressure curve of ice
- Line a (blue) gives the temperature-pressure dependence for ice in equilibrium with water
- Point X is the **triple point**
  - All three phases are in equilibrium
  - There is only one triple point for a pure substance
  - For water, the triple point is at 0.01 °C and 4.56 mmHg

Example 9.3

**Example 9.3 Conceptual**

Consider a sample of H2O at point X in Figure 9.6.

(a) What phase is it in, present?
(b) If the sample were sealed at constant pressure, what would happen?
(c) How would you correct the sample to vapor without changing its temperature?

**Solution**

1. Use the phase diagram from Figure 9.6.
2. Note that P increases moving vertically, T increases moving to the right.

- X is the triple point. For liquid water, and water, vapor are present.
- Moving left to the solid line, this graph moves the solid area, which is implies that the sample is frozen completely.
- Reduce the pressure to below the triple point value perhaps to 4 mm Hg.

Sublimation

- Sublimation is the process by which a solid passes directly into the vapor phase without first being converted to a liquid
- Sublimation can happen only at a temperature below the triple point
- Water can sublime if the pressure is reduced
  - Freeze drying
  - Cold winter days
- Iodine sublimes readily because its triple point pressure is much higher than that of water
**Melting Point**

- For a pure substance, the melting point and freezing point are identical
  - The effect of pressure on the freezing point is very small
  - An increase in pressure favors the more dense phase
    - This is usually the solid phase
    - Water is denser than ice, so water is anomalous
    - The slope of the solid-liquid line depicts the behavior of the freezing point as pressure is increased or decreased
      - Positive slope: solid is denser than liquid
      - Negative slope: liquid is denser than solid

**Molecular Substances: Intermolecular Forces**

- Many gases, most liquids and many solids are molecular
  - Molecules are the structural units of such matter
  - Properties of molecular substances include
    - They are nonconductors of electricity when pure
    - They are insoluble in water but soluble in nonpolar solvents such as CCl₄ or benzene
    - They have low melting points
  - These properties depend on the intermolecular forces between the molecules of the substance

**Dispersion Forces**

- All substances have dispersion forces
  - Also called London or van der Waals forces
  - Stem from induced dipoles in molecules
  - Motion of electrons in the molecule causes transient dipoles to form
  - Increase with the number of electrons in the molecule
  - As molar mass increases, dispersion forces become stronger

**Figure 9.9 and Table 9.3**

<table>
<thead>
<tr>
<th>Substance</th>
<th>MM (g/mol)</th>
<th>b.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4</td>
<td>250</td>
</tr>
<tr>
<td>Ne</td>
<td>20</td>
<td>71</td>
</tr>
<tr>
<td>Ar</td>
<td>40</td>
<td>84</td>
</tr>
<tr>
<td>Ne</td>
<td>40</td>
<td>160</td>
</tr>
<tr>
<td>Ar</td>
<td>84</td>
<td>254</td>
</tr>
<tr>
<td>CH₄</td>
<td>16</td>
<td>86</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>44</td>
<td>130</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>56</td>
<td>76</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>58</td>
<td>0</td>
</tr>
</tbody>
</table>

*Strictly speaking, the noble gases are not true molecular substances, like molecules, the noble gases are attracted to one another by dispersion forces.*
Dipole Forces

- Molecules with permanent dipoles display dipole forces
- Dispersion forces are also present but are much weaker
- Adjacent molecules line up so that the negative pole of one molecule is as close as possible to the positive pole of another molecule
- Result is an electrostatic attractive force that causes molecules to associate with each other

Table 9.4

<table>
<thead>
<tr>
<th>TABLE 9.4 Boiling Points of Nonpolar Versus Polar Substances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substances</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>N₂</td>
</tr>
<tr>
<td>SiH₄</td>
</tr>
<tr>
<td>GeH₄</td>
</tr>
<tr>
<td>BF₃</td>
</tr>
</tbody>
</table>

Example 9.4

Hydrogen Bonding

- Unusually strong type of dipole force
- H attached to (n) N, O, or F
- The H from one molecule can associate itself with the negative end of the dipole of another
  - Dipole arises from the difference in the electronegativity between H and (N, O, or F)
  - Small size of H allows the unshared pair from the negative end of the dipole to approach the H closely
- HF, H₂O and NH₃: unusually high boiling points as a result of hydrogen bonding

Table 9.5

<table>
<thead>
<tr>
<th>TABLE 9.5 Effect of Hydrogen Bonding on Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>NH₃</td>
</tr>
<tr>
<td>NH₃</td>
</tr>
<tr>
<td>NH₃</td>
</tr>
<tr>
<td>NH₃</td>
</tr>
</tbody>
</table>

Note: Molecules in blue show hydrogen bonding.
### Example 9.5

Would you expect to find hydrogen bonds in:

(a) water and H₂O

(b) ethene or C₂H₄

(c) hydrogen, H₂

**Strategy**

1. Lewis structures for (a) and (b) are given; draw the Lewis structure for hydrogen.
2. Pos of bonding (orions, one of the following) give rise to the presence of hydrogen: H:O, H:O, or H:O

### Example 9.5, (Cont’d)

**Example 9.5**

Water

- Hydrogen bonding in water accounts for
  - High specific heat
  - High boiling point
  - Higher density of the liquid phase relative to the solid

**Figure 9.11**

Covalent Bonds vs. Intermolecular Forces

- Three types of intermolecular forces
  - Dispersion
  - Dipole
  - Hydrogen bond

- All three intermolecular forces are weak relative to the strength of a covalent bond
  - Attractive energy in ice is 50 kJ/mol
  - Covalent bond in water is 928 kJ/mol
Solids: Network Covalent, Ionic and Metallic

- Network covalent solids
  - Continuous network of covalent bonds
  - Crystal is one large molecule
- Ionic solids
  - Oppositely-charged ions held together by strong electrical forces
- Metallic solids
  - Structural unit are +1, +2 and +3 metals with associated electrons

Figure 9.12

Network Covalent Solids

- Characteristics
  - High melting points, often above 1000 °C
  - Covalent bonds must be broken to melt the substance
- Examples
  - Graphite and diamond: allotropes
    - Diamond is three-dimensional and tetrahedral
    - Graphite is two-dimensional and planar

Figure 9.13

Compounds of Silicon

- Quartz
  - SiO$_2$
    - Major component of sand
    - Glass
- Layered structures
  - Talc
- Silicate lattices
  - Chains in 1, 2 and 3 dimensions
  - Zeolites
Ionic Solids

- Characteristics
  - Nonvolatile; high melting points (600-2000 °C)
  - Nonconductors of electricity in the solid state
    - Conduct when melted or dissolved in water
  - Many are soluble in water but not in nonpolar solvents

Strengths of Ionic Bonds

- Coulomb’s Law
  \[ E = \frac{k \cdot Q_1 \cdot Q_2}{d} \]
  \[ d = r_{\text{anion}} + r_{\text{cation}} \]
- Strength of ionic bond depends on
  - Charges of the ions (higher charges produce stronger bonds)
  - Sizes of the ions (smaller internuclear distances result in stronger bonds)

Metals

- Characteristics of metals
  - High electrical conductivity
  - Highly mobile electrons in structure
  - High thermal conductivity
    - Heat is carried through the structure by collision between electrons
  - Ductility and malleability
    - Can be drawn into wire or hammered into sheets
  - Luster
    - Polished metal surfaces reflect light
  - Insolubility in water and other common solvents

Solids with Different Structures

- Diamond, a network covalent solid
- Potassium dichromate, K_2Cr_2O_7, an ionic solid
- Manganese, a metallic solid

Figure 9.15

Figure 9.16
Crystal Structures

- Solids crystallize into definite geometric forms
- Many times, the naked eye can see the crystal structure
- NaCl forms cubic crystals

Crystal Building Blocks

- Crystals have definite geometric forms because the atoms or ions are arranged in definite, three-dimensional patterns
- Metals crystallize into one of three unit cells
  1. Simple cubic (SC): eight atoms at the corners
  2. Face centered cubic (FCC): simple cubic plus one atom in the center of each face
  3. Body-centered cubic (BCC): simple cubic plus one atom in the center of the cube

Table 9.6

<table>
<thead>
<tr>
<th>Type</th>
<th>NaCl</th>
<th>AlCl3</th>
<th>SC</th>
<th>FCC</th>
<th>BCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>NaCl</td>
<td>AlCl3</td>
<td>SC</td>
<td>FCC</td>
<td>BCC</td>
</tr>
<tr>
<td>Covalent</td>
<td>Covalent</td>
<td>Ionic</td>
<td>Ionic</td>
<td>Ionic</td>
<td>Ionic</td>
</tr>
<tr>
<td>Forces Between</td>
<td></td>
<td>Ion-ion</td>
<td>Ion-ion</td>
<td>Ion-ion</td>
<td>Ion-ion</td>
</tr>
</tbody>
</table>

Example 9.7

- Three other ways to look at the crystalline unit cells:
  1. Number of atoms per unit cell
     - SC: 1  FCC: 4  BCC: 2
  2. Relation between side of cell (s) and radius of atom or ion (r)
     - SC: $2r = s$  FCC: $4r = s\sqrt{2}$  BCC: $4r = s\sqrt{3}$
  3. Percentage of empty space
     - SC: 47.5%  FCC: 32.0%  BCC: 26.0%
Ionic Crystals

- Geometry of ionic crystals is more difficult to describe than that of metals
  - LiCl
    - Larger Cl⁻ ions form a face-centered cube with Li⁺ ions in the “holes” between the anions
  - NaCl
    - Larger Na⁺ ions are slightly too large to fit into the holes between the anions, so the Cl⁻ ions are pushed apart slightly
Example 9.9

Figure 9.9 A. The length of an edge of a cubic cell, $a$, is the distance between the centers of two atoms in the “top” of the cell and the center of the atom in the “bottom.” Taking the ionic radii of $Li^+$, $Na^+$, and $Cl^-$ to be 0.092 nm, 1.88 nm, and 1.81 nm, respectively, determine $a$ for
(a) $NaCl$ (b) $LiCl$

**Stratgy**

Use Figure 9.9 to determine along which lines the ions touch.

**Solution**

(a) $NaCl$

The ions touch along a side.

\[
v = \frac{1}{2}a_0^2 \times \frac{3}{4} + \frac{1}{2} \times \frac{1}{4} = \frac{3a_0^2}{4}
\]

The distance between the ions along a face diagonal.

\[
v = \frac{1}{2}a_0^2 \times \frac{1}{2} + \frac{1}{2} \times \frac{1}{4} = \frac{a_0^2}{4}
\]

(b) $LiCl$

The distance between the ions along a face diagonal.

\[
v = \frac{1}{2}a_0^2 \times \frac{3}{4} + \frac{1}{2} \times \frac{1}{4} = \frac{3a_0^2}{4}
\]

The distance between the ions along a face diagonal.

\[
v = \frac{1}{2}a_0^2 \times \frac{1}{2} + \frac{1}{2} \times \frac{1}{4} = \frac{a_0^2}{4}
\]

**Key Concepts**

1. Use the ideal gas law to determine whether a liquid will completely vaporize in a sealed container
2. Use the Clausius-Clapeyron equation to relate vapor pressure to temperature
3. Use a phase diagram to determine the phases present given the pressure and temperature
4. Identify the type of intermolecular forces in different substances
5. Classify substances as ionic, molecular, network covalent, or metallic
6. Relate unit cell dimensions to atomic or ionic radii