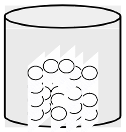
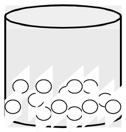
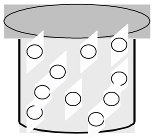
AP Chemistry: *Intermolecular Forces, Liquids, and Solids*

Sec 1. A Molecular Comparison of Liquids and Solids

- Physical properties of liquids and solids are due to **intermolecular forces**.
    - These are forces *between* molecules.
- Physical properties of substances are understood in terms of kinetic-molecular theory.
    - Gases are highly compressible and assume the shape and volume of their container.
        - Gas molecules are far apart and do not interact much with one another.
    - Liquids are almost incompressible and assume the shape but not the volume of the container.
        - Liquid molecules are held together more closely than gas molecules but not so rigidly that the molecules cannot slide past one another.
    - Solids are incompressible and have a definite shape and volume.
        - Solid molecules are packed closely together.
        - The molecules are so rigidly packed that they cannot easily slide past one another.
- Solids and liquids are *condensed phases*.
- Converting a gas into a liquid or solid requires the molecules to get closer to each other.
    - We can accomplish this by cooling or compressing the gas.
- Converting a solid into a liquid or gas requires the molecules to move farther apart.
    - We can accomplish this by heating or reducing the pressure of the gas.
- The forces holding solids and liquids together are called intermolecular forces.

Some Properties of Solids, Liquids, and Gases

Property	Solid	Liquid	Gas
			
Shape	Has definite shape	Takes the shape of the container	Takes the shape of its container
Volume	Has a definite volume	Has a definite volume	Fills the volume of the container
Arrangement of Particles	Fixed, very close	Random, close	Random, far apart
Interactions between articles	Very strong	Strong	Essentially none

B. Intermolecular Forces

- The covalent bond holding a molecule together is an *intra*molecular force.
- The attraction between molecules is an *inter*molecular force.
    - Intermolecular forces are much weaker than intramolecular forces (e.g., 16 kJ/mol versus 431 kJ/mol for HCl).
- When a substance melts or boils, intermolecular forces are broken (not the covalent bonds).
- When a substance condenses, intermolecular forces are formed.
    - Boiling points reflect intermolecular force strength.
    - A high boiling point indicates strong attractive forces.
- Melting points also reflect the strength of attractive forces.
- *van der Waals* forces are the intermolecular forces that exist between neutral molecules.

- An **ion-dipole** force is an interaction between an ion (e.g., Na^+) and the partial charge on a polar molecule/dipole (e.g., water).
- It is the strongest of all intermolecular forces.
  - Especially important for solutions of ionic substances in polar liquids.
  - Example: NaCl(*aq*)

Dipole-Dipole Forces

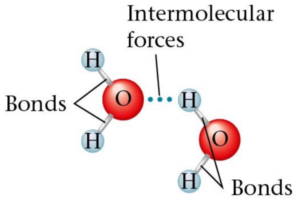
- **Dipole-dipole forces** exist between neutral polar molecules.
- Polar molecules attract one another.
  - The partially positive end of one molecule attracts the partially negative end of another.
- Polar molecules need to be close together to form strong dipole-dipole interactions.
- Dipole-dipole forces are weaker than ion-dipole forces.
- If two molecules have about the same mass and size, then dipole-dipole forces increase with increasing polarity.

London Dispersion Forces

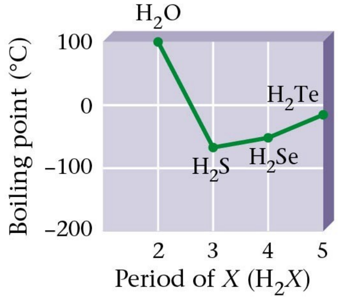
- These are the weakest of all intermolecular forces.
- It is possible for two adjacent nonpolar molecules to affect each other.
  - In helium atoms the average distribution of electrons around the nucleus is spherically symmetrical.
  - At a given instant both electrons might be on the same side of the nucleus.
  - In that instant a dipole is formed (called an instantaneous dipole).
  - One instantaneous dipole can induce another instantaneous dipole in an adjacent molecule (or atom).
  - These two temporary dipoles attract each other.
  - The attraction is called the **London dispersion force** or simply a dispersion force.
    - London dispersion forces exist among all molecules.
- What affects the strength of a dispersion force?
  - Molecules must be very close together for these attractive forces to occur.
  - **Polarizability** is the ease with which an electron cloud can be deformed.
    - The larger the molecule (the greater the number of electrons) the more polarizable it is.
  - Lon`don dispersion forces increase as molecular weight increases.
  - London dispersion forces depend on the shape of the molecule.
    - The greater the surface area available for contact, the greater the dispersion forces.
    - London dispersion forces between spherical molecules are smaller than between more cylindrically shaped molecules.
      - Example: *n*-pentane vs. neopentane.

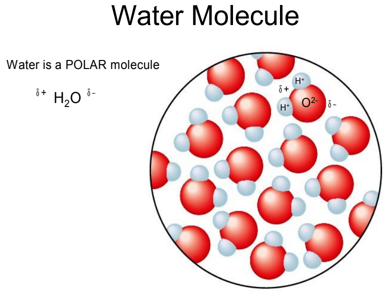
Hydrogen Bonding

- From experiments: boiling points of compounds with H-F, H-O, and H-N bonds are abnormally high.
  - Their intermolecular forces are abnormally strong.
- Hydrogen bonding is a special type of intermolecular attraction.
  - This is a special case of dipole-dipole interactions.
  - H-bonding requires:
    - H bonded to an electronegative element (most important for compounds of F, O, and N).
    - It also requires an unshared electron pair on a nearby electronegative ion or atom (usually F, O, or N on another molecule).
  - Electrons in the H-X bond (X is the electronegative element) lie much closer to X than H.
  - H has only one electron, so in the H-X bond, the $H^{\delta+}$ presents an almost bare proton to the $X^{\delta-}$.
  - Therefore, H-bonds are strong.
- Hydrogen bonds have exceedingly important biological significance.



    - They are important in stabilizing protein structure, in DNA structure and function, etc.
- An interesting consequence of H-bonding: Ice floats.
    - The molecules in solids are usually more closely packed than those in liquids.
        - Therefore, solids are usually more dense than liquids.
    - In liquid water the hydrogen bonding interactions between the water molecules are random.
    - Ice is ordered with an open structure to optimize H-bonding.
        - In water the H-O bond length is 1.0 angstrom.
            - The O···H hydrogen bond length is 1.8 angstrom.
        - Water molecules in ice are arranged in an open, regular hexagon.
            - Each H $^{\delta+}$ points toward a lone pair on O.
            - Therefore, ice is less dense than water.
    - Ice floats, so it forms an insulating layer on top of lakes, rivers, etc. Therefore, aquatic life can survive in winter.
    - Water expands on freezing.
        - Frozen water in pipes may cause them to break in cold weather.





Comparing Intermolecular Forces

- Dispersion forces are found in all substances.
    - Their strength depends on molecular shapes and molecular weights.
- Dipole-dipole forces add to the effect of dispersion forces.
    - They are found only in polar molecules.
- H-bonding is a special case of dipole-dipole interactions.
    - It is the strongest of the intermolecular forces involving neutral species.
    - H-bonding is most important for H compounds of N, O, and F.
- If ions are involved, ion-dipole interactions (if a dipole is present) and ionic bonding are possible.
    - Ion-dipole interactions are stronger than H-bonds.
- Keep in mind that ionic or covalent bonds are much stronger than these interactions!

Sec 2. Some Properties of Liquids

Viscosity

- **Viscosity** is the resistance of a liquid to flow.
- A liquid flows by sliding molecules over one another.
- Viscosity depends on:
    - The attractive forces between molecules:
        - The stronger the intermolecular forces, the higher the viscosity.
    - The tendency of molecules to become entangled.
        - Viscosity increases as molecules become entangled with one another.
    - The temperature:
        - Viscosity usually decreases with an increase in temperature.

Surface Tension

- Bulk molecules (those in the liquid) are equally attracted to their neighbors.
- Surface molecules are attracted only inward toward the bulk molecules.
    - Therefore, surface molecules are packed more closely than bulk molecules.

    - This causes the liquid to behave as if it has a “skin.”
- **Surface tension** is the amount of energy required to increase the surface area of a liquid by a unit amount.
- Stronger intermolecular forces cause higher surface tension.
    - Water has a high surface tension (H-bonding).
    - Hg(*l*) has an even higher surface tension (there are very strong metallic bonds between Hg atoms).
- *Cohesive forces* are intermolecular forces that bind molecules to one another.
- *Adhesive forces* bind molecules to a surface.
    - Illustrate this by looking at the meniscus in a tube filled with liquid.
        - The *meniscus* is the shape of the liquid surface.
        - If adhesive forces are greater than cohesive forces, the liquid surface is attracted to its container more than to the bulk molecules. Therefore, the meniscus is U-shaped (e.g., water in a glass).
        - If cohesive forces are greater than adhesive forces, the meniscus is curved downward (e.g., Hg(*l*) in glass)
- **Capillary action** is the rise of liquids up very narrow tubes.
    - Liquid climbs until adhesive and cohesive forces are balanced by gravity.

Sec 3. Structures of Solids

- **Crystalline solid**: well-ordered, definite arrangement of molecules, atoms or ions.
    - Example: quartz, salt, sugar
    - The intermolecular forces are similar in strength.
        - Thus they tend to melt at specific temperatures.
- **Amorphous solid**: molecules, atoms, or ions do not have an orderly arrangement.
    - Example: rubber, glass.
    - Amorphous solids have intermolecular forces that vary in strength.
        - Thus they tend to melt over a range of temperatures

Unit Cells

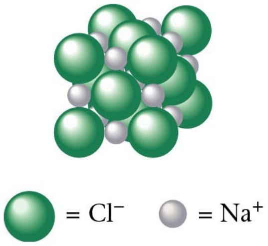
- Crystalline solids have an ordered, repeating structure.
- The smallest repeating unit in a crystal is a **unit cell**.
    - The unit cell is the smallest unit with all the symmetry of the entire crystal.
    - The three-dimensional stacking of unit cells is the **crystal lattice**.
- There are three types of cubic unit cell.
    - **Primitive cubic.**
        - Atoms are at the corners of a simple cube with each atom shared by eight unit cells.

    - **Body-centered cubic.**
        - There are atoms at the corners of a cube plus one in the center of the body of the cube.
          The corner atoms are shared by eight unit cells, and the center atom is completely enclosed in one unit cell.

    - **Face-centered cubic.**
        - There are atoms at the corners of a cube plus one atom in the center of each face of the cube. Eight unit cells share the corner atoms and two unit cells share the face atoms.

The Crystal Structure of Sodium Chloride

- Face-centered cubic lattice.
- There are two equivalent ways of defining this unit cell:
  - Cl^- (larger) ions at the corners of the cell, or
  - Na^+ (smaller) ions at the corners of the cell.



- The cation to anion ratio in a unit cell is the same for the crystal.
  - In NaCl each unit cell contains the same number of Na^+ and Cl^- ions.
- Note that the unit cell for $CaCl_2$ needs twice as many Cl^- ions as Ca^{2+} ions.

Close Packing Spheres

- Crystalline solids have structures that maximize the attractive forces between particles.
- Their particles can be modeled by spheres.
  - Each atom or ion is represented by a sphere.
- Molecular crystals are formed by close packing of the molecules.
- Maximum intermolecular forces in a crystal are achieved by the close packing of spheres.
  - When spheres are packed as closely as possible there are small spaces between adjacent spheres.
  - The spaces are called *interstitial holes*.
  - A crystal is built up by placing close packed layers of spheres on top of one another.
  - There is only one place for the second layer of spheres.
  - There are two choices for the third layer of spheres:
    - The third layer eclipses the first (ABAB arrangement).
      - This is called **hexagonal close packing** (hcp);
    - The third layer is in a different position relative to the first (ABCABC arrangement).
      - This is called **cubic close packing** (ccp).
      - Note: The unit cell of a ccp crystal is face-centered cubic.
  - In both close-packed structures, each sphere is surrounded by 12 other spheres (6 in one plane, 3 above, and 3 below).
- **Coordination number:** the number of spheres directly surrounding a central sphere.
- If unequally sized spheres are used, the smaller spheres are placed in the interstitial holes.
  - Example: Li_2O
    - The larger O^{2-} ions assume the cubic close-packed structure with the smaller Li^+ ions in the holes.

X-ray Diffraction

- When waves are passed through a narrow slit they are diffracted.
- When waves are passed through a diffraction grating (many narrow slits in parallel) they interact to form a diffraction pattern (areas of light and dark bands).
- Efficient diffraction occurs when the wavelength of light is close to the size of the slits.
- The spacing between layers in a crystal is 2–20 angstrom, which is the wavelength range for X-rays.
- X-ray diffraction (X-ray crystallography):
  - X-rays are passed through the crystal and are detected on a photographic plate.
  - The photographic plate has one bright spot at the center (incident beam) as well as a diffraction pattern.
  - Each close-packing arrangement produces a different diffraction pattern.

    - Knowing the diffraction pattern, we can calculate the positions of the atoms required to produce that pattern.
    - We calculate the crystal structure based on a knowledge of the diffraction pattern.

Bonding in Solids

- There are four types of solids.
    - Molecular
    - Covalent network
    - Ionic
    - Metallic

Molecular Solids

- Molecular solids consist of atoms or molecules held together by intermolecular forces.
- Weak intermolecular forces give rise to low melting points.
    - Intermolecular forces: dipole-dipole, London dispersion, and H-bonds.
- Molecular solids are usually soft.
- Efficient packing of molecules is important (since they are not regular spheres).
- Molecular solids exhibit poor thermal and electrical conductivity.
- Examples: Ar, CH_4, CO_2, sucrose.

Covalent-Network Solids

- **Covalent-network solids** consist of atoms held together, in large networks or chains, with covalent bonds.
- They have much higher melting points and are much harder than molecular solids.
    - This is a consequence of the strong covalent bonds that connect the atoms.
- Examples: diamond, graphite, quartz (SiO_2), silicon carbide (SiC), and boron nitride (BN).
- In diamond:
    - Each C atom has a coordination number of 4.
    - Each C atom is tetrahedral.
    - There is a three-dimensional array of atoms.
    - Diamond is hard and has a high melting point (3550°C)
- In graphite:
    - Each C atom is arranged in a planar hexagonal ring.
    - Layers of interconnected rings are placed on top of one another.
    - The distance between adjacent C atoms in the same layer is close to that seen in benzene (1.42 angstrom vs. 1.395 angstrom in benzene).
    - Electrons move in delocalized orbitals (good conductor).
    - The distance between layers is large (3.41 angstrom).
    - The layers are held together by weak dispersion forces.
        - They slide easily past one another.
        - Graphite is a good lubricant.

Ionic Solids

- **Ionic solids** consist of ions held together by ionic bonds.
- Ions (spherical) held together by electrostatic forces of attraction:

$$F = k\frac{Q_1Q_2}{d}$$

- The higher the charges (Q_1, Q_2) and smaller the distance (d) between the ions, the stronger the ionic bond.

- The structure of the ionic solid depends on the charges on the ions and on the relative sizes of the atoms.

- Examples of some ionic lattice types.
    - NaCl structure
        - Each ion has a coordination number of 6.
        - Face-centered cubic lattice.
        - Cation to anion ratio is 1:1.
        - Other similar examples: LiF, KCl, AgCl, and CaO.
    - CsCl structure
        - Cs^+ has a coordination number of 8.
        - Different from the NaCl structure (Cs^+ is larger than Na^+).
        - Cation to anion ratio is 1:1.
    - Zinc blende structure
        - S^{2-} ions adopt a face-centered cubic arrangement.
        - Zn^{2+} ions have a coordination number of 4.
        - The S2- ions are placed in a tetrahedron around the Zn^{2+} ions.
        - Other example: CuCl
    - Fluorite structure (CaF_2)
        - Ca^{2+} ions are in a face-centered cubic arrangement.
        - There are twice as many F^- ions as Ca^{2+} ion in each unit cell.
        - Other examples: $BaCl_2$, PbF_2.

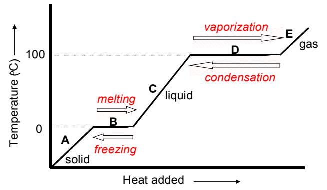
Metallic Solids

- **Metallic solids** consist entirely of metal atoms.
    - Metallic solids can be soft or hard.
    - They have high melting points.
    - They show good electrical and thermal conductivity.
    - They are ductile and malleable.
        - Examples: all metallic elements (i.e., Al, Cu, Fe, Au)
- Metallic solids have metal atoms in hexagonal close-packed, face-centered cubic, or body-centered cubic arrangements.
    - Thus the coordination number of each atom is either 8 or 12.
- Problem that needs to be explained:
    - The bonding is too strong to be explained by London dispersion forces and there are not enough electrons for covalent bonds.
- Resolution:
    - The metal nuclei float in a sea of delocalized valence electrons.
    - **Metals conduct because the valence electrons are delocalized and are mobile.**

11.3 Sec 8 Phase Changes

- **Phase changes** are changes of state.
    - Matter in one state is converted into another state.
        - *Sublimation:* solid --> gas
        - *Melting or fusion:* solid --> liquid
        - *Vaporization:* liquid --> gas
        - *Deposition:* gas --> solid
        - *Condensation:* gas --> liquid
        - *Freezing:* liquid --> solid

Heating Curve for Water

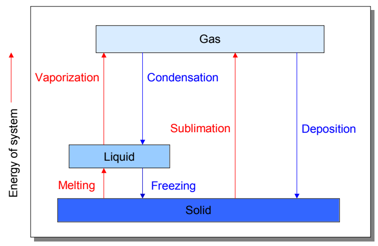


LeMay Jr, Beall, Robblee, Brower, Chemistry Connections to Our Changing World, 1996, page 487

Energy Changes Accompanying Phase Changes

- Energy changes of the system for the changes of state.
    - *Sublimation* is an endothermic process.
    - *Melting* or *fusion*: $\Delta H_{fus} > 0$ (endothermic).
        - **Heat of fusion.**
    - *Vaporization*: $\Delta H_{vap} > 0$ (endothermic).
        - **Heat of vaporization.**
    - *Depostion* is an exothermic process.
    - *Condensation* is an exothermic process.
    - *Freezing* is an exothermic process.
- Generally, the heat of fusion (enthalpy of fusion) is less than the heat of vaporization.

Energy Changes Accompanying Phase Changes



Brown, LeMay, Bursten, Chemistry 2000, page 405

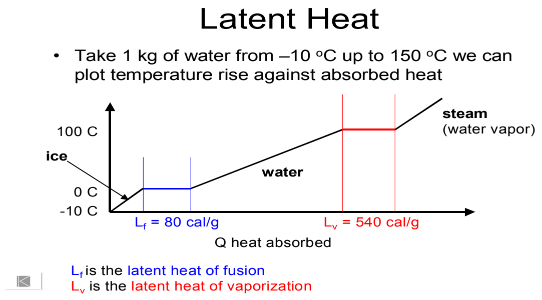
- All phase changes are possible under the right conditions (e.g., water sublimes when snow disappears without forming puddles).

The sequence ---heat solid --> heat liquid --> boil --> heat gas ...is endothermic

- The sequence
  cool gas --> condense --> cool liquid --> freeze --> cool solid ...is exothermic

Heating Curves

- A plot of temperature changes versus heat added s a heating curve.
- During a phase change the temperature remains constant.
    - The added energy is used to disrupt intermolecular interactions rather than to cause a temperature change.
    - These points are used to calculate ΔH_{fus} and ΔH_{vap}.
- *Supercooling*: A liquid is cooled below its freezing point and still remains a liquid.



Latent Heat

- Take 1 kg of water from –10 ºC up to 150 ºC we can plot temperature rise against absorbed heat

L_f is the latent heat of fusion
L_v is the latent heat of vaporization

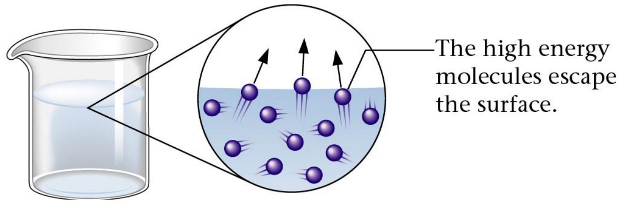
Critical Temperature and Pressure

- Gases can be liquefied by increasing the pressure at a suitable temperature.
- **Critical temperature**: the highest temperature at which a substance can exist as a liquid.
- *Critical pressure*: pressure required for liquefaction at this critical temperature.
    - The greater the intermolecular forces, the easier it is to liquefy a substance.
    - Thus the higher the critical temperature.

Vapor Pressure

Explaining Vapor Pressure on the Molecular Level

- Some of the molecules on the surface of a liquid have enough energy to escape the attraction of the bulk liquid.



- These molecules move into the gas phase.
- As the number of molecules in the gas phase increases, some of the gas phase molecules strike the surface and return to the liquid.
- After some time the pressure of the gas will be constant.
  - The pressure of the vapor at this point is called the equilibrium vapor pressure.
- **Dynamic equilibrium**:
  - A condition in which two opposing processes occur simultaneously at equal rates.
  - In this case, it is the point at which as many molecules escape the surface as strike the surface.
  - **Vapor pressure** is the pressure exerted when the liquid and vapor are in dynamic equilibrium.

Volatility, Vapor Pressure, and Temperature

- If equilibrium is never established, the vapor continues to form.
  - Eventually, the liquid evaporates to dryness.
- Liquids that evaporate easily are said to be **volatile**.
  - The higher the temperature, the higher the average kinetic energy, the faster the liquid evaporates.

Vapor Pressure and Boiling Point

- Liquids boil when the external pressure at the surface of the liquid equals the vapor pressure.
- The **normal boiling point** is the boiling point at 760 mm Hg (1 atm).
- The boiling point temperature increases as the external pressure increases.
- Two ways to get a liquid to boil:
  - Increase temperature or decrease pressure.
    - The boiling point of water is higher at high pressure than at 1 atm.
    - Therefore, the food is cooked at a higher temperature.

Phase Diagrams

- **Phase diagram**: plot of pressure vs. temperature summarizing all equilibria between phases.
- Phase diagrams tell us which phase will exist at a given temperature and pressure.
- Features of a phase diagram:
  - **Vapor-pressure curve**: Generally, as temperature increases, vapor pressure increases.
  - **Critical point**: critical temperature and pressure for the gas.
  - **Normal melting point**: melting point at 1 atm.
  - **Triple point**: temperature and pressure at which all three phases are in equilibrium.
  - Any temperature and pressure combination not on a curve represents a single phase.

Phase Diagrams of H_2O and CO_2

Water:

In general, an increase in pressure favors the more compact phase of the material. (S)
Water is one of the few substances whose solid form is less dense than the liquid form.
The melting point curve for water slopes to the left.
Triple point occurs at 0.0098°C and 4.58 mm Hg.
Normal melting (freezing) point is 0°C.
Normal boiling point is 100°C.
Critical point is 374°C and 218 atm.
Freeze-drying: frozen food is placed in a low-pressure (< 4.58 torr) chamber. The ice sublimes.

Carbon Dioxide:

(1) Triple point occurs at –56.4°C and 5.11 atm (2) Normal sublimation point is –78.5°C. (At 1 atm CO_2 sublimes, it does not melt.), (3) Critical point occurs at 31.1°C and 73 atm.