

Chapter 10

Liquids and solids

They are similar to each other

- ◆ Different than gases.
- ◆ They are incompressible.
- ◆ Their density doesn't change much with temperature.
- ◆ These similarities are due
 - to the molecules staying close together in solids and liquids
 - and far apart in gases
- ◆ What holds them close together?

Intermolecular forces

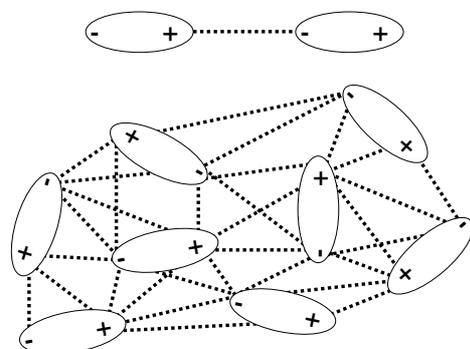
- ◆ Inside molecules (intramolecular) the atoms are bonded to each other.
- ◆ Intermolecular refers to the forces between the molecules.
- ◆ Holds the molecules together in the condensed states.

Intermolecular forces

- ◆ Strong
 - covalent bonding
 - ionic bonding
- ◆ Weak
 - Dipole dipole
 - London dispersion forces
- ◆ During phase changes the molecules stay intact.
- ◆ Energy used to overcome forces.

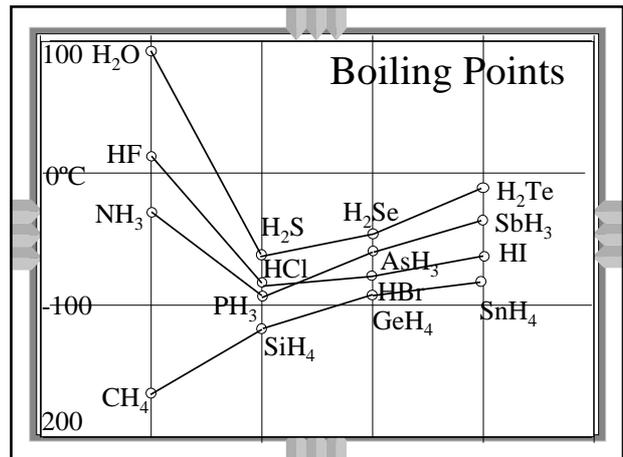
Dipole - Dipole

- ◆ Remember where the polar definition came from?
- ◆ Molecules line up in the presence of an electric field. The opposite ends of the dipole can attract each other so the molecules stay close together.
- ◆ 1% as strong as covalent bonds
- ◆ Weaker with greater distance.
- ◆ Small role in gases.

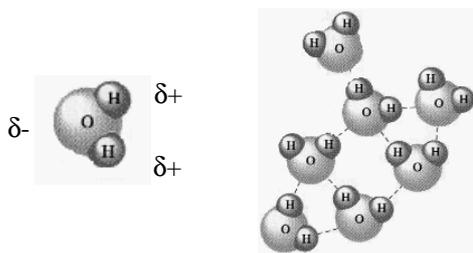


Hydrogen Bonding

- ◆ Especially strong dipole-dipole forces when H is attached to F, O, or N
- ◆ These three because-
 - They have high electronegativity.
 - They are small enough to get close.
- ◆ Effects boiling point.



Water



Each water molecule can make up to four H-bonds

London Dispersion Forces

- ◆ Non - polar molecules also exert forces on each other.
- ◆ Otherwise, no solids or liquids.
- ◆ Electrons are not evenly distributed at every instant in time.
- ◆ Have an instantaneous dipole.
- ◆ Induces a dipole in the atom next to it.
- ◆ Induced dipole- induced dipole interaction.

Example



London Dispersion Forces

- ◆ Weak, short lived.
- ◆ Lasts longer at low temperature.
- ◆ Eventually long enough to make liquids.
- ◆ More electrons, more polarizable.
- ◆ Bigger molecules, higher melting and boiling points.
- ◆ Weaker than other forces.

Van der Waal's forces

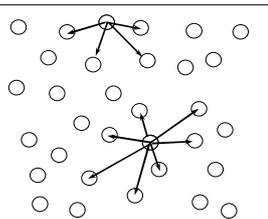
- ◆ London dispersion forces and Dipole interactions
- ◆ Order of increasing strength
 - LDF
 - Dipole
 - H-bond
 - Real bonds

Liquids

- ◆ Many of the properties due to internal attraction of atoms.
 - Beading
 - Surface tension
 - Capillary action
 - Viscosity
- ◆ Stronger intermolecular forces cause each of these to increase.

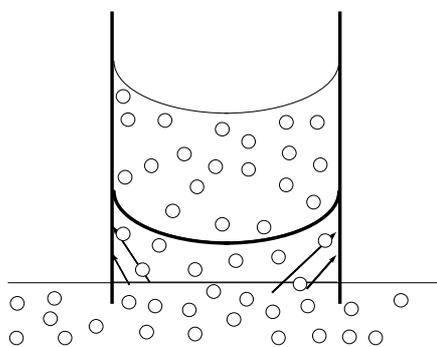
Surface tension

- ◆ Molecules at the the top are only pulled inside.
- ◆ Molecules in the middle are attracted in all directions.
- ◆ Minimizes surface area.



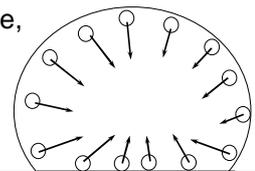
Capillary Action

- ◆ Liquids spontaneously rise in a narrow tube.
- ◆ Intermolecular forces are cohesive, connecting like things.
- ◆ Adhesive forces connect to something else.
- ◆ Glass is polar.
 - It attracts water molecules.



Beading

- ◆ If a polar substance is placed on a non-polar surface.
 - There are cohesive,
 - But no adhesive forces.



Viscosity

- ◆ How much a liquid resists flowing.
- ◆ Large forces, more viscous.
- ◆ Large molecules can get tangled up.
- ◆ Cyclohexane has a lower viscosity than hexane.
- ◆ Because it is a circle- more compact.

How much of these?

- ◆ Stronger forces, bigger effect.
 - Hydrogen bonding • H next to O, N, or F
 - Dipole-dipole • Polar molecules
 - LDF • All molecules
- ◆ In that order

Model of a Liquid

- ◆ Can't see molecules so picture them as-
- ◆ In motion but attracted to each other
- ◆ With regions arranged like solids but
 - with higher disorder.
 - with fewer holes than a gas.
 - Highly dynamic, regions changing between types.

Phases

- ◆ The phase of a substance is determined by three things.
 - The temperature.
 - The pressure.
 - The strength of intermolecular forces.

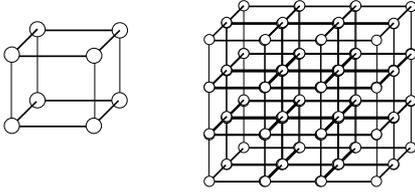
Solids

- ◆ Two major types.
- ◆ Amorphous- those with much disorder in their structure.
- ◆ Crystalline- have a regular arrangement of components in their structure.

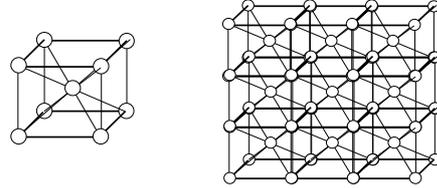
Crystals

- ◆ Lattice- a three dimensional grid that describes the locations of the pieces in a crystalline solid.
- ◆ Unit Cell- The smallest repeating unit in of the lattice.
- ◆ Three common types.

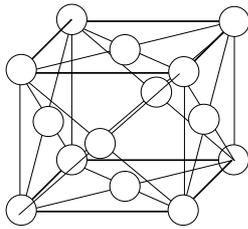
Cubic



Body-Centered Cubic



Face-Centered Cubic



The book drones on about

- ◆ Using diffraction patterns to identify crystal structures.
- ◆ Talks about metals and the closest packing model.
- ◆ It is interesting, but trivial.
- ◆ We need to focus on metallic bonding.
- ◆ Why do metal atoms stay together?
- ◆ How their bonding affects their properties.

Solids

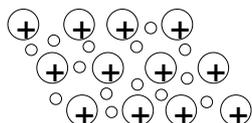
- ◆ There are many amorphous solids.
- ◆ Like glass.
- ◆ We tend to focus on crystalline solids.
- ◆ two types.
 - Ionic solids have ions at the lattice points.
 - Molecular solids have molecules.
- ◆ Sugar vs. Salt.

Metallic Bonds

- ◆ How atoms are held together in the solid.
- ◆ Metals hold onto their valence electrons very weakly.
- ◆ Think of them as positive ions floating in a sea of electrons.

Sea of Electrons

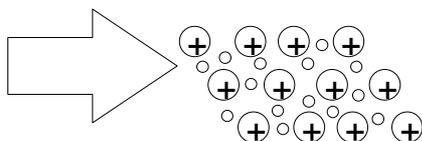
- ◆ Electrons are free to move through the solid.
- ◆ Metals conduct electricity.



Metals are Malleable

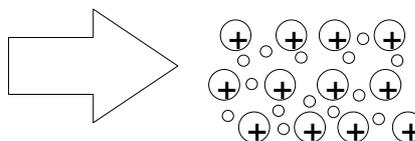
- ◆ Hammered into shape (bend).
- ◆ Ductile - drawn into wires.
- ◆ Because of mobile valence electrons

Malleable

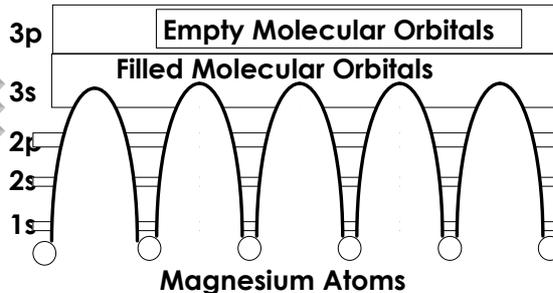


Malleable

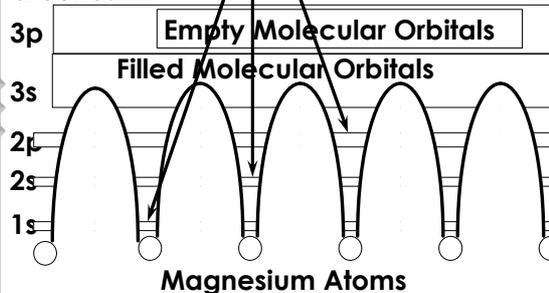
- ◆ Electrons allow atoms to slide by but still be attracted.

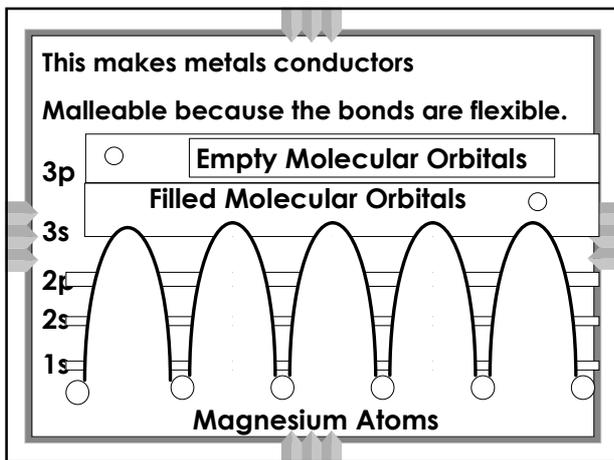
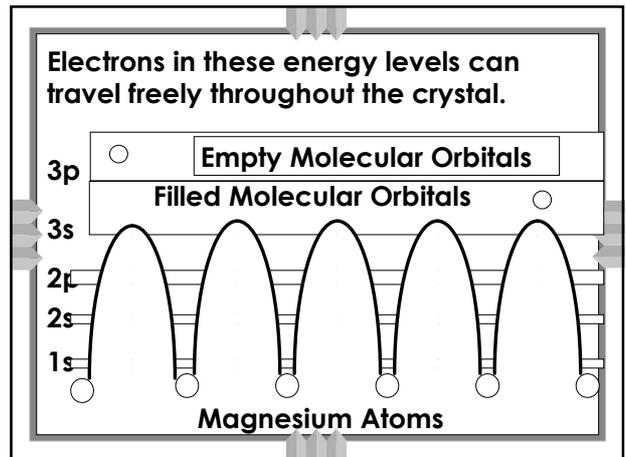
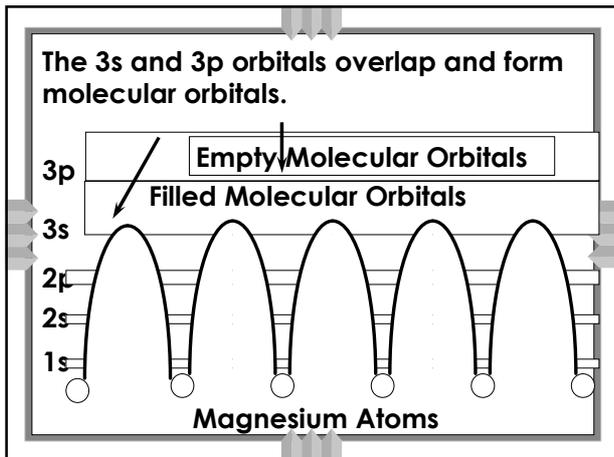


Metallic bonding



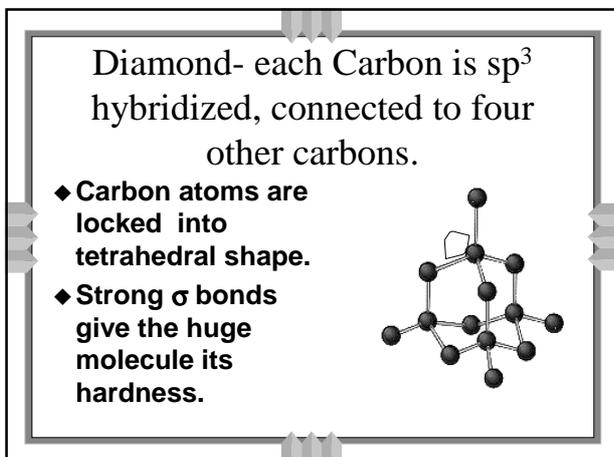
The 1s, 2s, and 2p electrons are close to nucleus, so they are not able to move around.





Carbon- A Special Atomic Solid

- ◆ There are three types of solid carbon.
- ◆ Amorphous- soot - uninteresting.
- ◆ Diamond- hardest natural substance on earth, insulates both heat and electricity.
- ◆ Graphite- slippery, conducts electricity.
- ◆ How the atoms in these network solids are connected explains why.

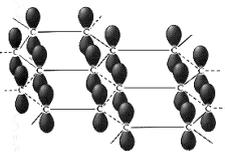


Why is it an insulator?

All the electrons need to be shared in the covalent bonds
Can't move around

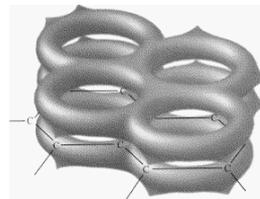
Graphite is different.

- ◆ Each carbon is connected to three other carbons and sp^2 hybridized.
- ◆ The molecule is flat with 120° angles in fused 6 member rings.
- ◆ The π bonds extend above and below the plane.



This π bond overlap forms a huge π bonding network.

- ◆ Electrons are free to move throughout these delocalized orbitals.
- ◆ Conducts electricity
- ◆ The layers slide by each other.
- ◆ Lubricant



Molecular solids.

- ◆ Molecules occupy the corners of the lattices.
- ◆ Different molecules have different forces between them.
- ◆ These forces depend on the size of the molecule.
- ◆ They also depend on the strength and nature of dipole moments.

Those without dipoles.

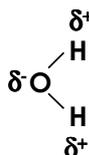
- ◆ Most are gases at 25°C .
- ◆ The only forces are London Dispersion Forces.
- ◆ These depend on number of electrons.
- ◆ Large molecules (such as I_2) can be solids even without dipoles. (LDF)

Those with dipoles.

- ◆ Dipole-dipole forces are generally stronger than L.D.F.
- ◆ Hydrogen bonding is stronger than Dipole-dipole forces.
- ◆ No matter how strong the intermolecular force, it is always much, much weaker than the forces in bonds.
- ◆ Stronger forces lead to higher melting and freezing points.

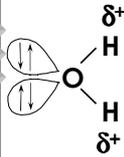
Water is special

- ◆ Each molecule has two polar O-H bonds.



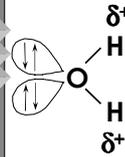
Water is special

- ◆ Each molecule has two polar O-H bonds.
- ◆ Each molecule has two lone pair on its oxygen.



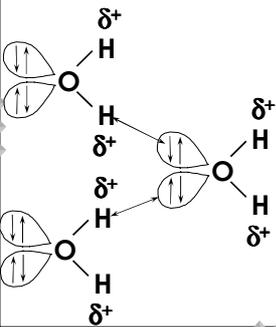
Water is special

- ◆ Each molecule has two polar O-H bonds.
- ◆ Each molecule has two lone pair on its oxygen.
- ◆ Each oxygen can interact with 2 hydrogen atoms.



Water is special

- ◆ This gives water an especially high melting and boiling point.



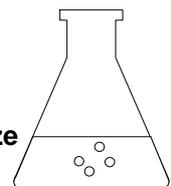
Ionic Solids

- ◆ The extremes in dipole-dipole forces- atoms are actually held together by opposite charges.
- ◆ Huge melting and boiling points.
- ◆ Atoms are locked in lattice so hard and brittle.
- ◆ Every electron is accounted for so they are poor conductors-good insulators.
- ◆ Until melted or dissolved.

Phase Changes

Vapor Pressure

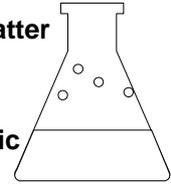
- ◆ Vaporization - change from liquid to gas at boiling point.
- ◆ Evaporation - change from liquid to gas below boiling point
- ◆ Heat (or Enthalpy) of Vaporization (ΔH_{vap}) - the energy required to vaporize 1 mol at 1 atm.



- ◆ Vaporization is an endothermic process - it requires heat.
- ◆ Energy is required to overcome intermolecular forces.
- ◆ Responsible for cool beaches.
- ◆ Why we sweat.

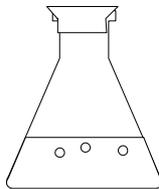
Condensation

- ◆ Change from gas to liquid.
- ◆ Achieves a dynamic equilibrium with vaporization in a closed system.
- ◆ What is a closed system?
- ◆ A closed system means matter can't go in or out.
- ◆ Put a cork in it.
- ◆ What the heck is a "dynamic equilibrium?"



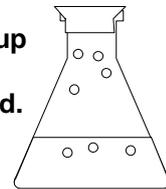
Dynamic equilibrium

- ☞ When first sealed the molecules gradually escape the surface of the liquid



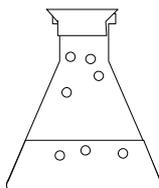
Dynamic equilibrium

- ☞ When first sealed the molecules gradually escape the surface of the liquid
- ☞ As the molecules build up above the liquid some condense back to a liquid.



Dynamic equilibrium

- ☞ As time goes by the rate of vaporization remains constant
- ☞ but the rate of condensation increases because there are more molecules to condense.
- ☞ Equilibrium is reached when



Dynamic equilibrium

**Rate of Vaporization =
Rate of Condensation**

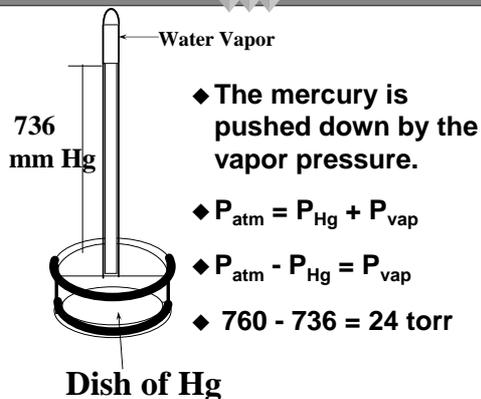
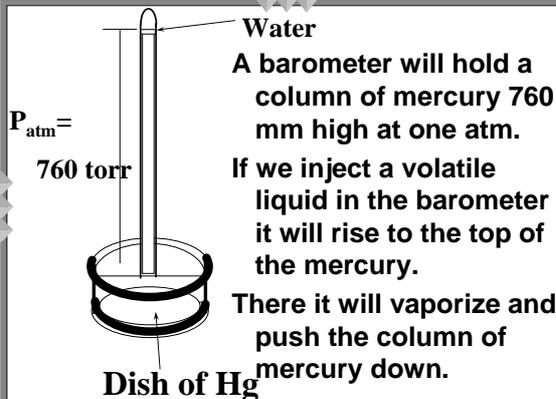
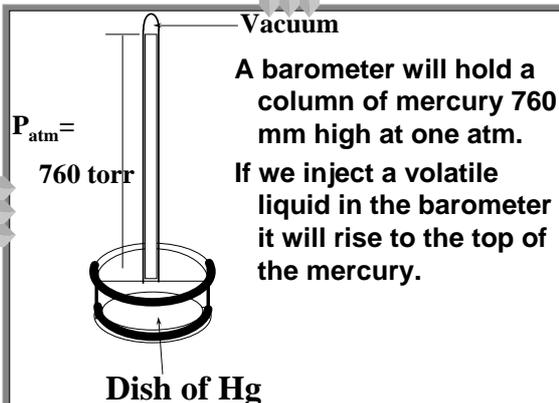
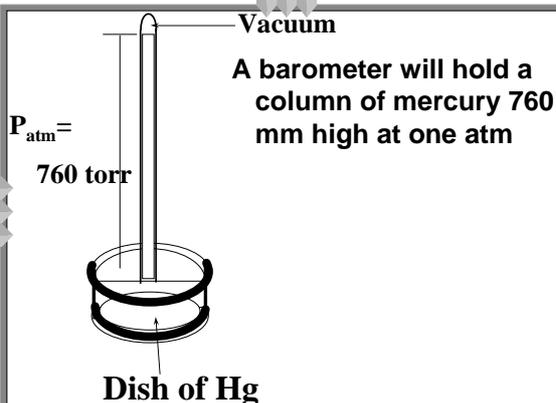
- ◆ Molecules are constantly changing phase "Dynamic"
- ◆ The total amount of liquid and vapor remains constant "Equilibrium"

Vapor pressure

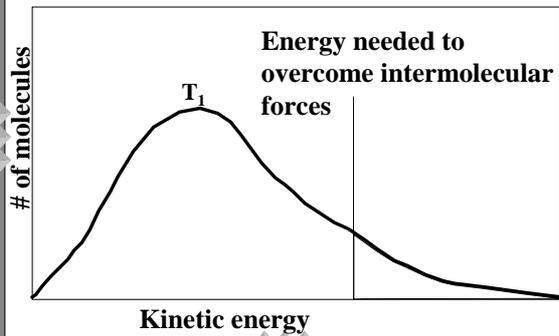
- ◆ The pressure above the liquid at equilibrium.
- ◆ Liquids with high vapor pressures evaporate easily.
- ◆ They are called volatile.
- ◆ Decreases with increasing intermolecular forces.
 - Bigger molecules (bigger LDF)
 - More polar molecules (dipole-dipole)

Vapor pressure

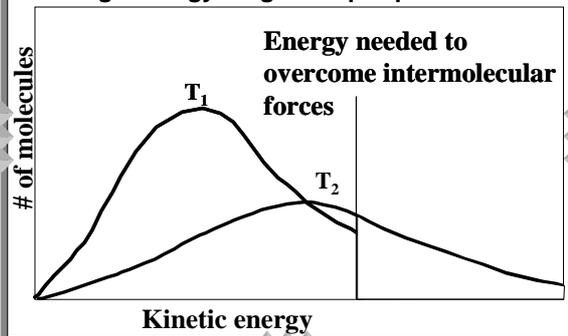
- ◆ Increases with increasing temperature.
- ◆ Easily measured in a barometer.



Temperature Effect



◆ At higher temperature more molecules have enough energy - higher vapor pressure.



Mathematical relationship

- ◆ **ln is the natural logarithm**
 - ln = Log base e
 - e = Euler's number an irrational number like π
- ◆ **ΔH_{vap} is the heat of vaporization in J/mol**

Mathematical relationship

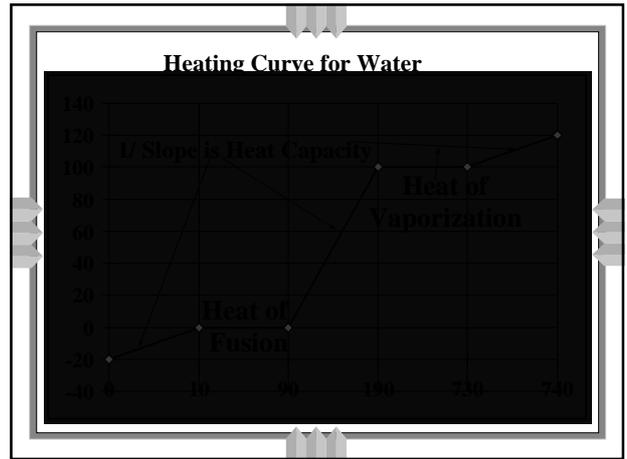
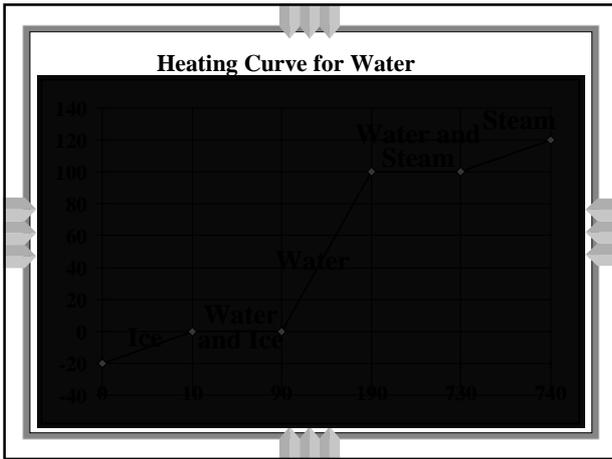
- ◆ **$R = 8.3145 \text{ J/K mol}$.**
- ◆ **Surprisingly this is the graph of a straight line.**
- ◆ **If you graph $\ln P$ vs $1/T$**

Mathematical relationship

- ◆ **The vapor pressure of water is 23.8 torr at 25°C. The heat of vaporization of water is 43.9 kJ/mol. Calculate the vapor pressure at 50°C**
- ◆ **At what temperature would it have a vapor pressure of 760 torr?**

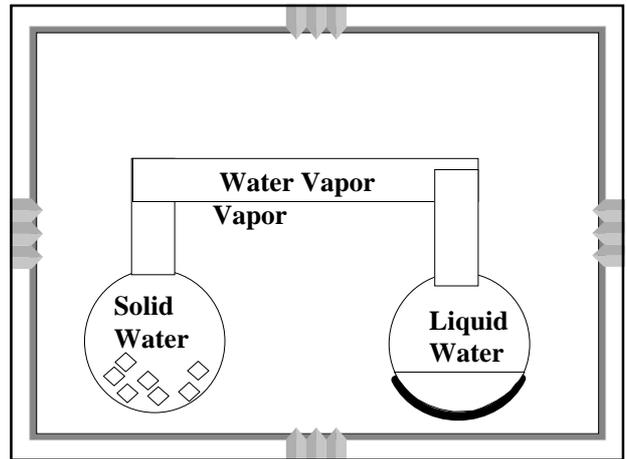
Changes of state

- ◆ **The graph of temperature versus heat applied is called a heating curve.**
- ◆ **The temperature a solid turns to a liquid is the melting point.**
- ◆ **The energy required to accomplish this change is called the Heat (or Enthalpy) of Fusion ΔH_{fus}**



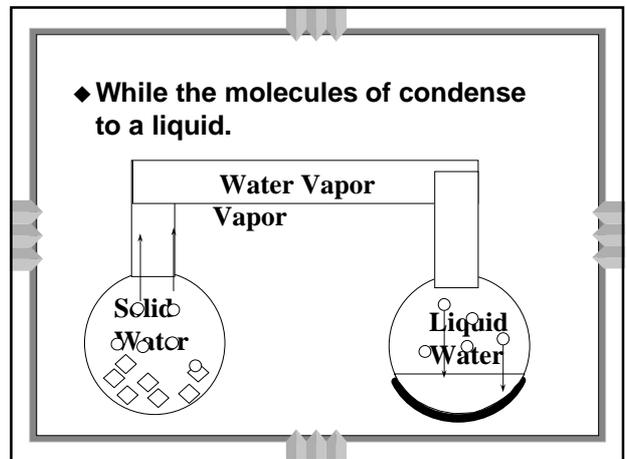
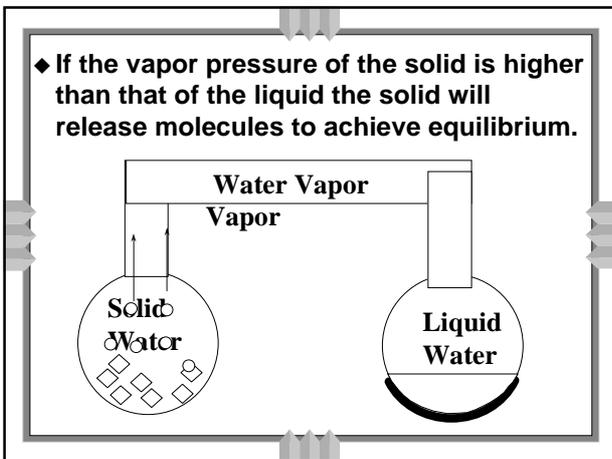
Melting Point

- ◆ Melting point is determined by the vapor pressure of the solid and the liquid.
- ◆ At the melting point the vapor pressure of the solid = vapor pressure of the liquid

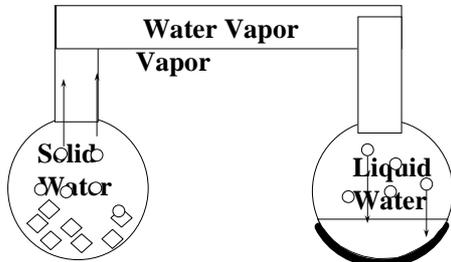


- ◆ If the vapor pressure of the solid is higher than that of the liquid the solid will release molecules to achieve equilibrium.

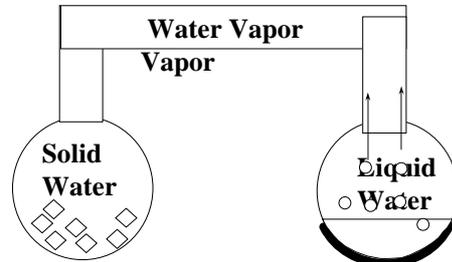
- ◆ While the molecules of condense to a liquid.



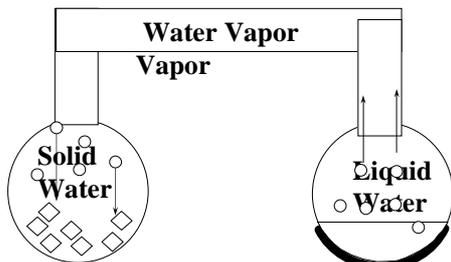
- ◆ This can only happen if the temperature is above the freezing point since solid is turning to liquid.



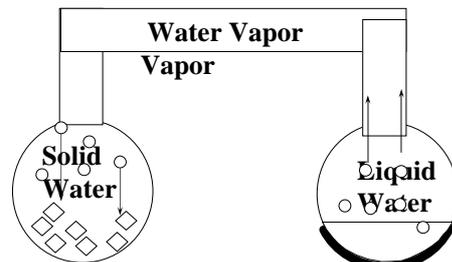
- ◆ If the vapor pressure of the liquid is higher than that of the solid, the liquid will release molecules to achieve equilibrium.



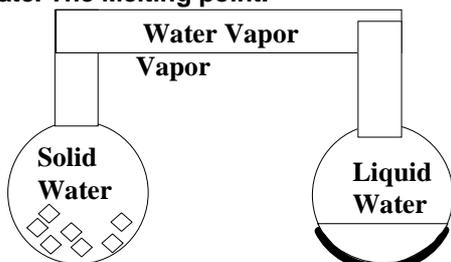
- ◆ While the molecules condense to a solid.



- ◆ The temperature must be below the freezing point since the liquid is turning to a solid.



- ◆ If the vapor pressure of the solid and liquid are equal, the solid and liquid are vaporizing and condensing at the same rate. The Melting point.

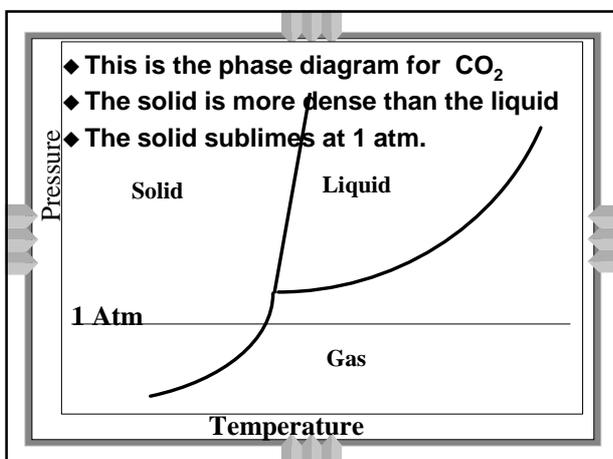
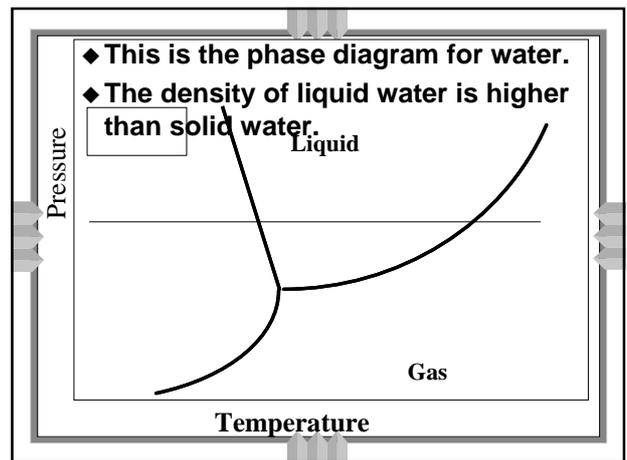
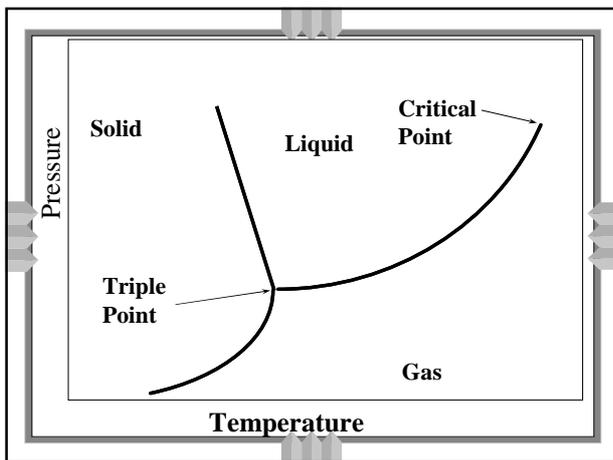
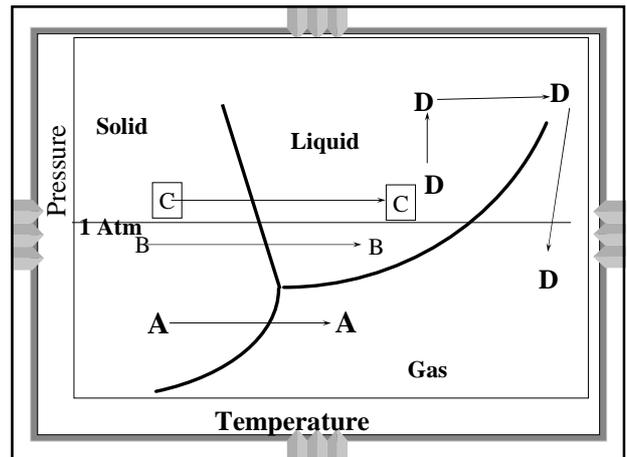


Boiling Point

- ◆ Reached when the vapor pressure equals the external pressure.
- ◆ Normal boiling point is the boiling point at 1 atm pressure.
- ◆ Superheating - Heating above the boiling point.
- ◆ Supercooling - Cooling below the freezing point.

Phase Diagrams.

- ◆ A plot of temperature versus pressure for a closed system, with lines to indicate where there is a phase change.



The End

