Liquids & Solids

Chapter 10

"Condensed States" (def: reduced to a more compact or dense form)

- held in these phases because of attractive forces between the particles

1. Ionic Solids
   - held in the solid phase by ionic bonds

2. Molecular Substances
   - held in solid phase (& liquid phase) by molecular attractions between neighboring molecules
   - the type of molecular attraction depends on the type of molecule

A) Dipole-Dipole Forces
   - forces of attraction between neighboring dipoles (polar molecules)
   - positive end of one dipole is attracted to the negative end of the next dipole

Ex. +H-Cl- ←→ +H-Cl-

B) Hydrogen Bonds
   - a particularly strong dipole attraction
   - occurs when H is bonded to an atom of small radius & high electronegativity (Ex. F,O,N)
   - stronger because:
     i. the bonds are more polar (larger electronegative difference)
     ii. the very small size of the hydrogen atoms allows the molecules to get very close to each other
   - accounts for the unusually high MP & BP of HF, H_2O, & NH_3 compared to compounds formed from H & elements from the same group

Compound	HF	HCl	HBr	HI	H_2O	H_2S	H_2Se	H_2Te	NH_3	PH_3	AsH_3	SbH_3
MP	-83.1	-114.8	-88.5	-50.8	0	-85.5		-49	-77.7	-133.5	-113.5	-88.5
BP	19.54	-84.9	-67.0	-35.38	100	-60.7	-42	-2	-33.35	-87.4	-55	-17

(attractive force $\propto$ charge & $\propto \frac{1}{r}$)

C) London Dispersion Forces (Fritz London)
   - "Van der Waals" forces
   - occurs between all molecules but only important for nonpolar substances
   - the only type of attractive force between nonpolar molecules

- asymmetrical electron distribution produces a temporary dipole
- this induces a similar dipole in a neighboring particle

Ex. $^{e}{}_{e}{}^{-}$H-H^{+} ←→ - $^{e}{}_{e}{}^{-}$H-H^{+} +

- the interaction is very weak and very short lived
- the larger the particle the stronger the force because:
  i. at any given temperature, larger particles are moving more slowly ($KE=\frac{1}{2}mv^2$)
  ii. as atomic number increases, the number of electrons present in the particle increases (greater chance of a momentary dipole arrangement)

Ex.

Compound	He	Ne	Ar	Kr	Xe	F_2	Cl_2	Br_2	I_2
MP (°C)	-269.7	-248.6	-189.4	-157.3	-111.9	-219.62	-100.98	-7.2	113.5

Liquid State
- definite volume
- no definite shape
- low compressibility

Surface Tension
- molecular attractions between molecules across a liquid's surface
- directly dependent on the strength of the intermolecular forces
- (in a zero gravity environment, molecular attractions pulling into the body of the liquid would cause the sample to be spherical)

Ex. CCl_4 or $CHCl_3$ → Which has higher surface tension?
- both molecules are tetrahedrons
- CCl_4=nonpolar $CHCl_3$=polar (use models)
  London Dispersion Forces Dipole Attraction (=stronger)

Capillary Action
- the spontaneous rising of a liquid in a narrow tube
- for H_2O → polar H_2O molecules are attracted to polar molecules in the container wall
- these are Adhesive forces
- the H_2O pulls itself up the wall until the weight of the H_2O balances the tendency of the H_2O to pull up the wall
- the meniscus is concave
  - the adhesive forces between the H_2O and the glass are stronger than the cohesive forces between neighboring H_2O molecules
- $Hg_{(l)}$=nonpolar
  - convex meniscus
  - cohesive forces are stronger than adhesive forces

Viscosity
- a measure of a liquid's resistance to flow

- dependent on:
    1. strength of IMF
    2. shape of the molecules

Ex. glycerol $C_3H_5(OH)_3$

H

|

H-C-OH Large capacity to form H bonds

|

H-C-OH Complex structure inhibits flow

|

Vaporization – (evaporation)

- particlaes of a liquid overcome intermolecular forces and escape from the body of the liquid
- is a cooling process
    - losing particles of hightest KE
    - KE of remaining liquid decreases
- is an endothermic process
    - energy is needed to overcome the molecular attractions

Heat of Vaporization (ΔH_{vap}) – Enthalpy of Vaporization

- the amount of energy needed to vaporize one mole of a liquid at a pressure of 1 atm
- for H_2O**,** ΔH_{vap}=41.2 kj/mol (also listed as 40.7 kj/mol)
    - must overcome strong hydrogen bonds

Vapor Pressure

- the pressure exerted by the particles escaping from the body of the liquid
- depends on:
    1. Molecular Weight
        - Heavy particles move more slowly & have a smaller tendency to escape
    2. Intermolecular Forces
        - The stronger the force, the less tendency to escape

        Ex. H_2O – light molecule but has a low vapor pressure due to strong hydrogen bonds
    3. Temperature
        - Increasing temperature increases vapor pressure
        - At higher temperature a greater number of molecules have enough KE to escape
- Vapor pressures at 2 different temperatures are related

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

Where P_1=vapor pressure at T_1 (Kelvin)
P_2=vapor pressure at T_2
ΔH_{vap}=heat of vaporization
R=gas constant=8.31j/mol*K (energy term)

10.6 (p479)

- P_1=23.8 torr ΔH_{vap}=43.9 kj/mol T_1=25°C P_2=? if T_2=50°C

S+P (p188)

- for $CCl_{4\,(l)}$ P_1=0.132atm @ 296K P_2=0.526atm @ 331K ΔH_{vap}= ?

- for CCl_4, what is the vapor pressure at 38°C?

S+P (p119)

- $CH_3OH_{(l)}$ P_1=0.0526atm @ 5°C P_2=0.132atm @ 34.9 °C ΔH_{vap}= ?

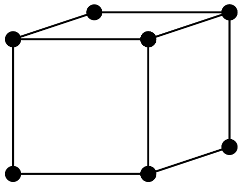
Solid State

- has definite shape
- has definite volume

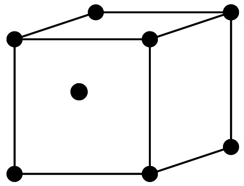
$\}$ strong short range forces between the particles

- has a crystal structure
    - a highly regular arrangement of particles
    - called lattice – the position of the particles in a crystalline solid
        - made up by repetition of a "unit cell" (the unit that, upon repetition, produces the entire lattice

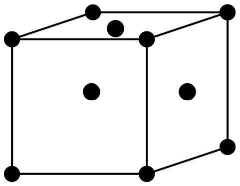
ex:



Simple cube



Bodycentered cubic



Face-centered cubic

- X-ray diffraction is used to determine the lattice structure
- (X-rays directed at the crystal, scattered by particles, resulting patterns analyzed)
- Some solids are amorphous
    - Have no crystal structure

      Ex: glass, plastics

Types of Crystalline Solids

1. Atomic Solids
2. Molecular Solids
3. Ionic Solids

1. Atomic Solids

- the lattice points are occupied by atoms
- metals and network solids

Metals

- have low ionization energy and release their valence electrons
- results in a regular array of kernels at the lattice points in a "sea of mobile electrons"
- the bonds are strong but nondirectional
- it is difficult to separate the atoms but it is easy to move them
- have high thermal and electrical conductivity (mobile electrons)
- are malleable and ductile (nondirectional bonds)

(most are durable and have high melting points)

(exist for a long time without significant deterioration)

Alloys

- a substance that has metallic properties but contains a mixture of elements
- substitutional alloy
    - some of the host atoms are replaced by atoms of similar size
    - ex: Brass 66% Cu, 33% Zn (sterling Silver 93% Ag, 7% Cu)
- interstitial alloy (interstitial – a space left between atoms
- interstials in the metal are occupied by small atoms
- changes the properties of thehost metal
- ex: steel → C atoms in holes between Fe atoms
    - directional bonding of C atoms makes the alloy stronger and harder

Network Solids

- Atoms at the lattice points held in place by strong covalent bonds
- Have high melting points, are brittle, do not conduct electricity or heat.

Ex. Diamonds

graphite SiO_2 (quartez mp=1713°C)

2. Molecular Solids

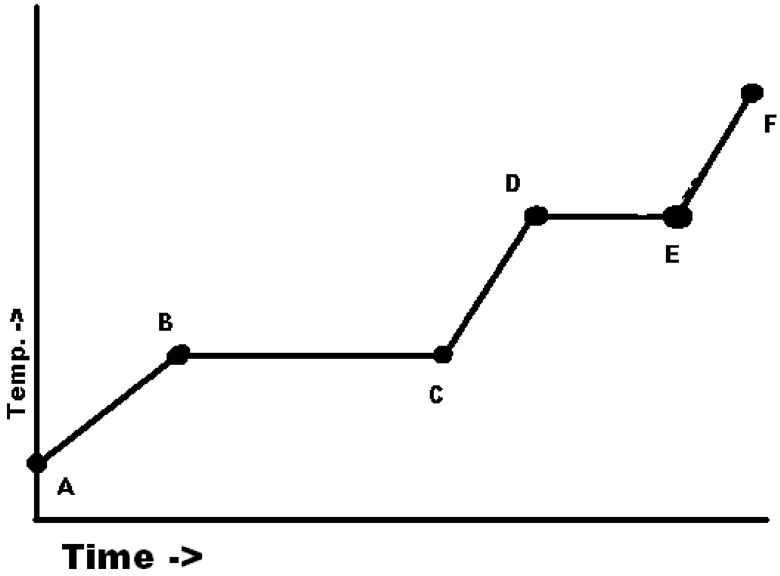
- Have molecules at the lattice points
- Have weak attractive forces between the molecules (D-D, H bonds, LDF)
- Have low melting points, do not conduct electricity, are soft

3. Ionic Solid
   - Cations and anions occupy the lattice points
   - Held together by strong electrostatic attraction between the ions
   - Have high melting points, are hard (brittle)
   - Do not conduct electricity as solids but fused or dissolved in H_2O are good conductors (mobilize the ions)

Changes of State

Heating Curve

- A plot of temperature vs time as energy is added at a constant rate



A-B – solid heating up, KE increases

B-C – solid turns into liquid

Normal Melting Point

- temperature at which the solid and liquid have the same vapor pressure at conditions of 1 atm pressure (total press on the system = 1 atm)
- as solid melts KE remains the same and pot energy increases

Heat of Fusion (H_{fus})

- the amount of energy needed to melt the solid at it's melting point

C-D - liquid heating up, KE increases

D-E – liquid turning into a gas

Normal Boiling Point

- Temperature at which the vapor pressure of a liquid equals 1 atm.

(At any temperature, if vapor pressure = external pressure, the liquid will boil)

- As phase change occurs, KE is constant but PE increases
- Energy needed to vaporize the liquid at its boiling point is the Heat of Vaporization (ΔH_{vap})
  ($\Delta H_{vap} > \Delta H_{fus}$ because ?)

E-F – gas heating up, KE increases

(Other possible changes)

Sublimation

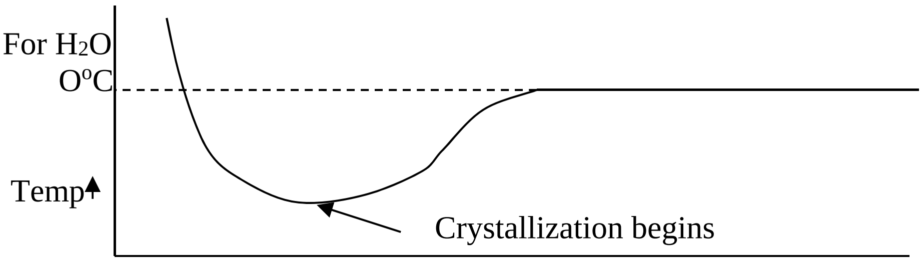
- change from solid to gaseous state without passing through the liquid state

Ex. $CO_2(s) \rightarrow CO_2(g)$

$I_2(s) \rightarrow I_2(g)$

Super Cooling

- cooling a liquid below its normal freezing point without freezing occurring
- as cooling occurs, the particles of the liquid do not achieve the organization (right positions) needed to form the solid
- at some point, the correct positioning finally occurs
- the exothermic process of freezing raises the temperature back up to the melting point



Time →

<u>Fig 10.46</u>
(p 483)

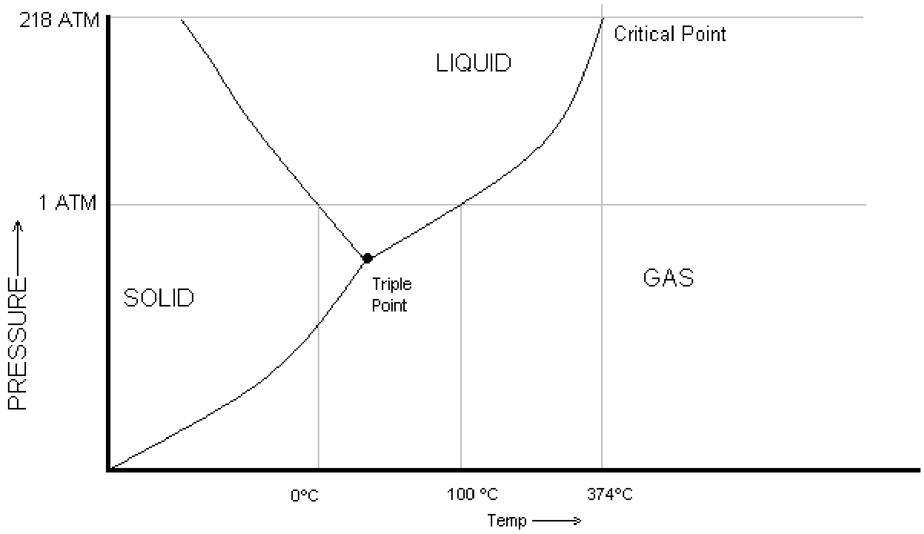
Superheating

- raising the liquid's temperature to a temperature <u>above its boiling point</u>
- heat must be added RAPIDLY
- particles then have a lot of energy but are not near enough to each other to form a bubble
- when particles finally form a bubble its pressure is greater than 1 atm
- causes "bumping" (boiling chips provide air or starter bubbles)

Phase Diagrams

- axes are pressure and temperature
- represents the phase of a substance as a function of P+T

For H_2O



A point on any line represents a point of equilibrium between the two phases.

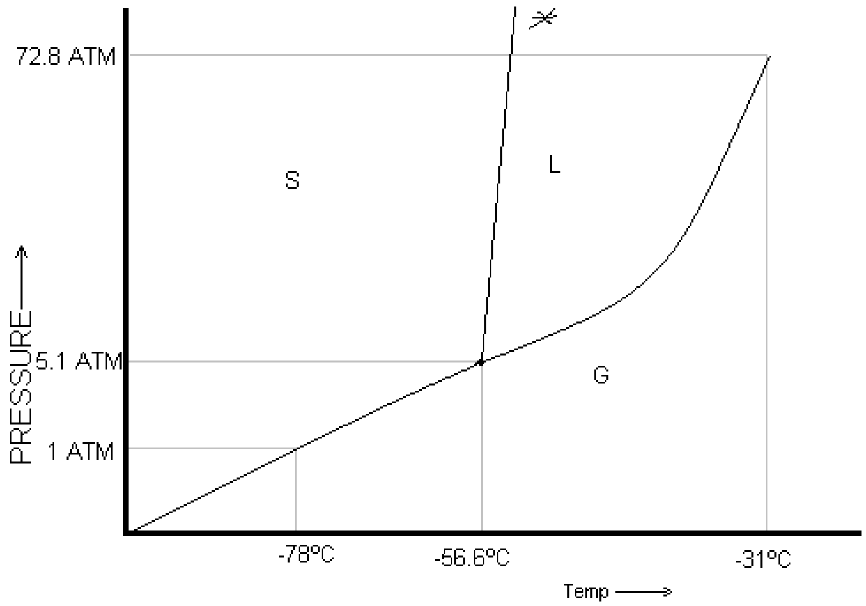
Triple point
- Temperature and pressure
- For H_2O → 4.588 torr, 0.0098 ºC

Critical point
- point of critical temperature and critical pressure

Critical temperature
- the temperature above which the vapor cannot be liquefied

Critical Pressure
- the pressure required to liquefy a gas at the critical temperature

for CO_2



- Critical temperature is a measure of the strength of the attractive forces
- Triple Point = 5.1 atm at -56.6°C
- At 1 atm, CO_2 cannot exist as a liquid, regardless of pressure.