Chapter 11 States of Matter; Liquids and Solids

These Notes are to SUPPLIMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

The author is providing these notes as an addition to the students reading the text book and listening to the lecture. Although the author tries to keep errors to a minimum, the student is responsible for correcting any errors in these notes.

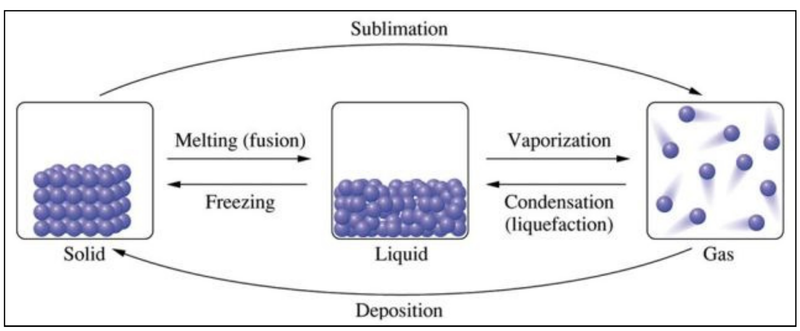
Note: Corrections for Significant Digits were recently made. They are marked SD See also 1025 Ch 2 Notes

Gases are compressible fluids. Gases are composed of molecules in constant random motion in mostly empty space.

Liquids are incompressible fluids. Liquids are molecules in constant random motion, but are more tightly packed so there is much less free space.

Solids are nearly incompressible and are rigid and not fluid. Solids are composed of particles that exist in close contact and do not move about but oscillate or vibrate about fixed sites.

Gases follow the Ideal Gas Law $PV = nRT$



Changes of State or phase transition:

Melting is the change of a solid to a liquid state — ice → water

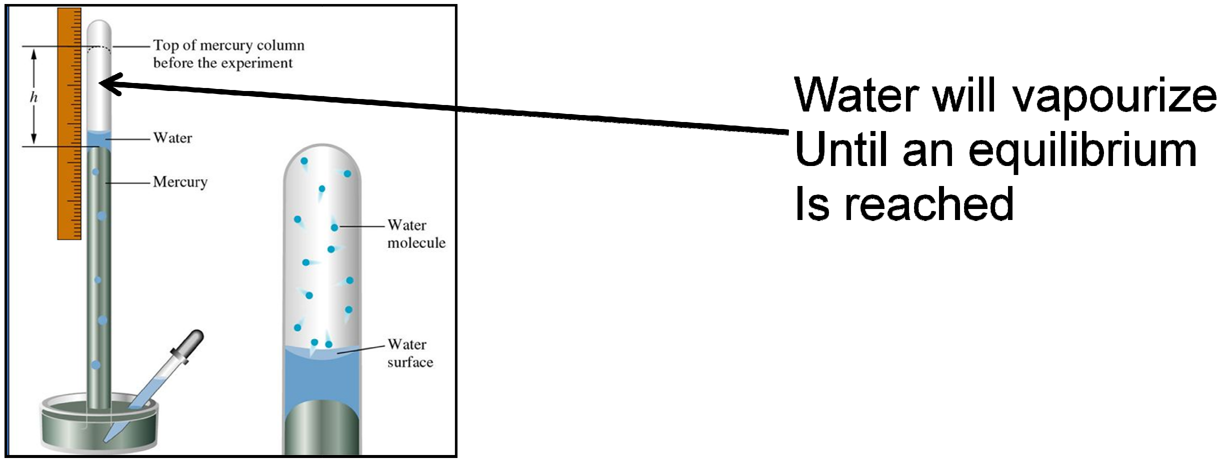
Freezing is the change of a liquid to a solid state — water → ice

Vaporization is the change of a solid or liquid to a vapor. — $H_2O_{Liq} \rightarrow H_2O_{Vap}$

Sublimation is the change of a solid directly to a vapour. — Ice can go to a vapour directly, snow disappears.
Iodine Crystals to a vapor
Freeze drying food

Condensation is the change of a gas to either a liquid or a solid. — Water on a car windshield

Liquefaction is the change of a gas to a liquid. — e.g. Distillation



Per above picture – the water sitting above the mercury will vaporize until equilibrium is reached.

Hard Boiled Egg: If it takes 5 minutes to prepare a hardboiled egg at sea level, how long will it take on top of at 5,000 ft mountain?

Vapor Pressure is the partial pressure of the vapor over the liquid measured at equilibrium at a given temperature. Water vapor and liquid water are in equilibrium.

Vapor Pressure of water [Table 5.6, p 199] Note the higher partial pressure of water for higher temperature.

Temp ^oC	**0**	**10**	**20**	**30**	**40**	**60**	**80**	**100**
Pressure mm Hg	**4.6**	**9.2**	**17.5**	**31.8**	**55.3**	**149.4**	**355.1**	**760.0**

STUDENT/TEST QUESTION:

1. What does it mean when the Pressure of water at 100 ^oC is 760.0 mm Hg?\

2. If it takes 5 minutes to heat an egg to hard boiled at sea level, how long will it take on top of a 10,000 ft mountain and why?

3. Why / How is BP effected by a change in pressure?

Dynamic equilibrium is one in which the molecular processes are continuously occurring.

$$\mathbf{H_2O_{\,liq} \quad \longleftrightarrow \quad H_2O_{\,gas}}$$

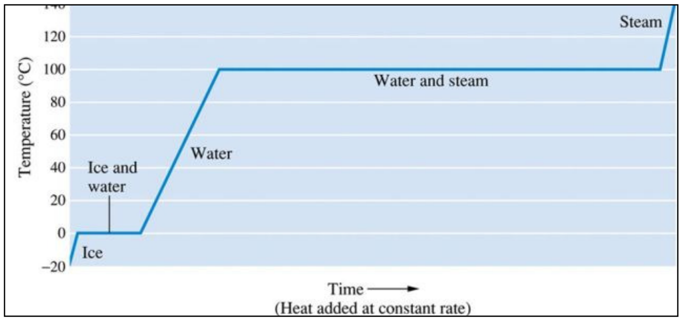
Boiling Point is the temperature at which the vapor pressure of a liquid equals the pressure exerted on the liquid
At temp goes up, vapor pressure goes up [see table above], til vp = atmospheric pressure = bp
BP varies with atmospheric pressure.

Freezing Point is the temperature where a pure liquid changes to a crystalline solid

Melting Point is the temperature at which a crystalline solid changes to a liquid
FP and MP's are not affected by slight change in atmospheric pressure

Heat of Phase Transition

- Add heat to ice at – 20°C. The temperature changes until 0°C.
- Then there is a plateau as the ice melts. This is called the **heat of phase transition.**
- After the ice melts, the temp increases up to 100 °C.
- At 100 °C, the water is turned to steam.



<u>**Heat of fusion**</u> is the heat needed to melt a solid.

For ice [$H_2O_{solid} \rightarrow H_2O_{liq}$] **ΔH_{fus} = 6.01 kJ / mole.**

<u>**Heat of vaporization**</u> is the heat needed to vaporize a liquid.

For water at 100°C **ΔH_{vap} = 40.7 kJ / mole.**

<u>**Example 11.1**</u> **How many kg of CCl_2F_2 must be evaporated to freeze 525 g of water at 0°C to ice at 0°C? Heat of vaporization of CCl_2F_2 is 17.4 kJ/mol. = heat from the vaporization**

Reword as: Water $_{Liquid}$ – ENERGY $\rightarrow$ Water $_{Ice}$

<u>**SIGNIFICANT DIGITS COUNT**</u>			
	2 H	2 * 1.008	2.016
	1 O	1 * 16.00	<u>16.00</u>
			18.016
		Rounds to	18.02 g/mole

$$525 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{-6.01 \text{ kJ}}{1 \text{ mol } H_2O} = \mathbf{-175.\ kJ}$$

Heat removed from the water (3 SD)

The energy removed from the water is used to vaporize the ChloroFluoroMethane:

ENERGY + CCl_2F_2 $_{Liquid}$ -> CCl_2F_2 $_{Vapor}$

<u>**SIGNIFICANT DIGITS COUNT**</u>			
	1 C	1 * 12.01	12.01
	2 Cl	2 * 35.45	70.90
	1 O	2 * 19.00	<u>38.00</u>
			120.91
		Rounds to	120.91 g/mole

$$175.\text{ kJ} \times \frac{1 \text{ mol } CCl_2F_2}{17.4 \text{ kJ}} \times \frac{120.91 \text{ g } CCl_2F_2}{1 \text{ mol } CCl_2F_2} = 1216.\text{ g } CCl_2F_2 = \mathbf{1.22\ kg\ CCl_2F_2}\ \mathbf{(3\ SD)}$$

<u>**STUDENT AT BOARD**</u>

<u>Example 11.1x</u> Ammonia heat of vaporization is 23.4 kJ / mole.

How much heat is required to vaporize 1.00 kg of NH_3?

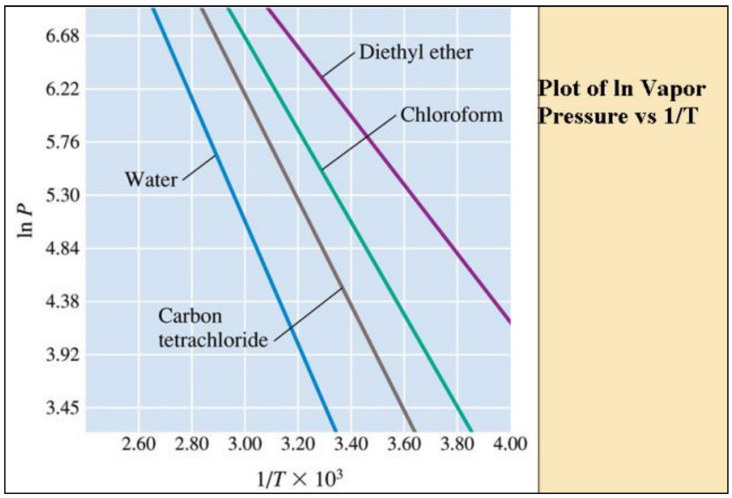
How many grams of water at 0^oC can be converted to ice at 0^oC with this much NH_3?

$NH_{3\ Liquid}$ **+ ENERGY** → $NH_{3\ Vapour}$ 1.00 kg of NH_3 , $\Delta H_{Vap} = 23.4$ kJ / Mole

$Water_{Liquid}$ **– ENERGY** → $Water_{Ice}$ How much water is converted with ENERGY from above.

<u>CONCEPT CHECK 11.1, page 427</u>   **<u>STUDENT AT BOARD</u>**

<u>Clausius – Clapeyron Equation:</u> The vapor pressure of a substance depends on temperature.



Plot of the Logarithm of vapor pressure vs 1 / T

Determine the vapor pressure at one temperature from the value at another

Two Point Clausius – Clapeyron Equation:

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

Example 11.2 What is the vapor pressure of water at 85 ^oC if water boils at 100 ^oC and $\Delta H_{vap} = 40.7$ kJ/mol.

$P_1 = 760$ mm Hg $T_1 = 100\ ^oC = 373\ ^oK$

P_2 = To Be Found $T_2 = 85$ oC $= 358\ ^oK$ <u>(**SD**)</u>

$$\mathrm{Ln}\ \frac{P_2}{760\text{ mm Hg}} = \frac{40.7 \times 10^3\text{ J/mol}}{R = 8.31\text{ J/K mol}}\left[\frac{1}{373^oK} - \frac{1}{358^oK}\right] = \mathbf{4997.71^oK \quad x \quad 1.123 \times 10^{-4}\ /^oK = -550.}$$

P_2 / 760 mm Hg = antln (-550) = 0.577

P_2 = 760 mm Hg * 0.577 = 439 mm Hg

Example 11.3 Calculate the ΔH_{vap} for ether [$H_3C\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$] from the vapor pressure at 18°C is 400 mm Hg and 35°C is 760 mm Hg.

$$\ln \frac{760 \text{ mm Hg}}{400 \text{ mm Hg}} = \frac{\Delta H_{vap}}{R = 8.31 \text{ J/K mol}} \times \left[\frac{1}{291^\circ K} - \frac{1}{308^\circ K} \right]$$

$$\ln \frac{760 \text{ mm Hg}}{400 \text{ mm Hg}} = \frac{\Delta H_{vap}}{8.31 \text{ J/K mol}} \times 1.896\ 10^{-4}$$

$$0.642 = (2.28 \times 10^{-5} \times \Delta H_{vap} / \text{J/mol})$$

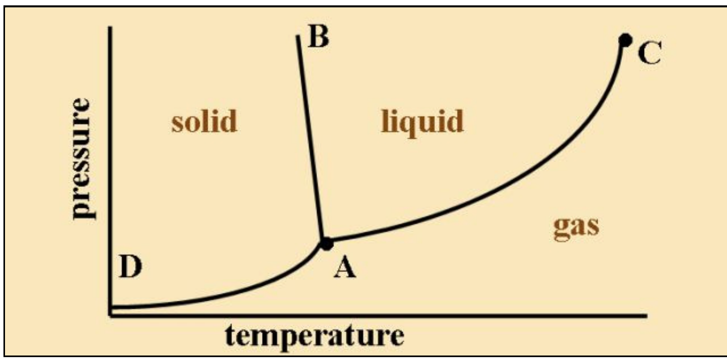
$$\Delta H_{vap} = 2.82 \times 10^{4} \text{ J/mol}$$

CLASS PROJECT

Exercise 11.3 SeF_4 is a clear liquid. It has a vp of 757 mm Hg at 105 °C and 522 mm Hg at 95 °C. What is the heat of vaporization of SeF_4?

Phase Diagram: Melting Point Curve & Vapor Pressure Curves for Liquid and Solids

The Phase Diagram is a graphical way to summarize conditions which different states are stable



Phase Diagram
A-B = Melting Point
A-C = Liquid / Gas, BP at 1 atm
A-D = Solid / Gas = vapor pres
A = Triple Point

DISCUSS ALL LINES AND BORDERS

A = Triple Point represents the temperature and pressure at which all 3 phases of a substance coexists in equilibrium.

TP_{CO2} = -57 °C at 5.1 atm Solid CO_2 goes to Gas directly at Room Temperature **[Class Explain]** **NEW**

TP_{water} = 0.01°C at 0.00603 atm [4.58 mm Hg]

Freeze Dry Food: If you warm a solid at its triple point, it will sublime – pass directly from the solid to gas
Put it in a vacuum at 0.00603 atm

Supercritical fluid: Temperature of a Liquid / Gas is warmed to above the L / G temperature and critical pressure.

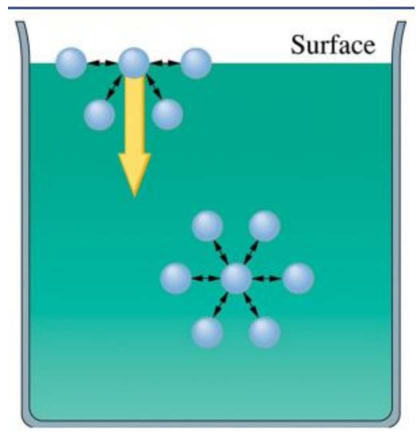
C = Critical Temperature is temp above which the liquid state of a substance no longer exists regardless of the pressure.
Critical Pressure is the vapor pressure at the critical temperature
Critical Point is the point [C] where the temperature and pressure have their critical values

Example 11.4 The critical temperature of ammonia is 132 ^oC and of nitrogen is -147 ^oC. Ammonia can be liquefied at room temperature by compressing the gas, but nitrogen requires a low temperature as well. Why?

CT for N_2 is -147 ^oC. N_2 cannot be a liquid above that temperature! **NEW**

Surface Tension and Viscosity

A molecule in a liquid is attracted in all directions. The same molecule at the surface has no net attraction on the surface. The surface is thus reduced as much as possible. Raindrops fall as a sphere.



Surface Tension is the energy required to increase the surface area of a liquid by a unit amount.
Soaps reduce surface tension, thus help dissolve materials.
A pin will float on the surface of water until you add a drop of a soap.

Capillary rise is the rising column of water in a small diameter tube.
Capillary rise is due to the water molecules being attracted to the glass tube.

Mercury has a downward curving meniscus. Due to the Hg/Hg attraction is greater than Hg/Glass
Viscosity is the resistance to flow that is exhibited by all liquids and gases.

1. Intermolecular Forces – the forces of interaction between molecules, are usually weakly attractive.

Van der Waals forces is the general term for those intermolecular forces that include **Dipole-Dipole** and **London Forces**.

Neon Single atoms that donot bond together

BP -246^oC at 1 atm

ΔH_{vap} [heat of vaporization] = 1.77 kJ / mol

0.23 kJ / mol push back the atmosphere as the vapor forms

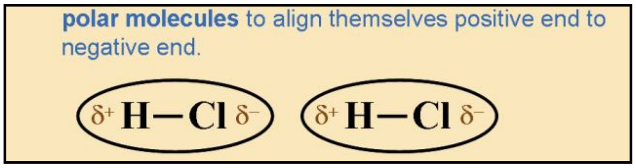
1.54 kJ / mol overcome intermolecular attractions

Divide 1.54 kJ/Mol by 5 to give 0.3 kJ/mol for each single atom-atom attraction

Hydrogen Energy of Attraction of each atom of H_2 = 432 kJ / mol

So the energy of attraction for neon [0.3 kJ/mol] is @ 1000 time weaker than the H-H bond energy!

A Dipole-Dipole force is the attractive intermolecular force resulting from the tendency of polar molecules to align themselves such as the + end of one end of a molecule is near the – end of another

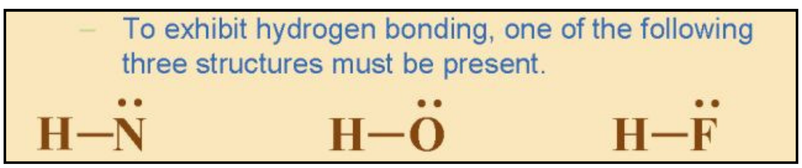


B London Forces or Dispersion Forces are the weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about nuclei. All covalent bonded molecules exhibit LF. E.g. any alkane. Pentane BP 36°C, 2-Methyl butane BP 28°C, 2,2-Dimethyl propane BP 9.5°C. London Forces increase with Molecular Mass.

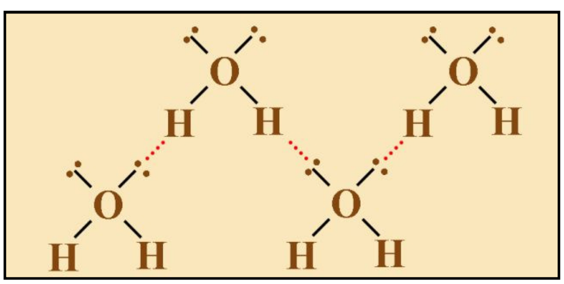
C Hydrogen Bonding H_2O

Hydrogen Bonding is a weak to moderate attractive force that exists between a hydrogen atom covalently bonded to a very electronegative atom X and a lone pair of electrons on another small electronegative atom.

Compound	Formula	Mw	Dipole	BP
Fluoromethane	CH_3F	34	1.81 D	- 78 °C
Methanol	CH_3OH	32	1.70 D	65 °C



Group 6A: O, S, Se, Te **NEW**



Boiling Points vs Mw: H_2O = 100 °C H_2S = -60 °C H_2Se = -40 °C H_2Te = 0 °C.

Thus Oxygen has a different type of bonding – hydrogen bonding. The Hydrogen of one molecule is attracted to the Oxygen Electron Pair from another molecule. The –OH has a dipole Moment:

Δ- Δ+
-O---H

D. Covalent Bonding H_2 H – H bond ΔH to break the H-H bond is 432 kJ/mol

Boiling Points of liquids depends on intermolecular forces.

Surface Tension also depends on intermolecular forces. **Surface Tension** is the energy needed to increase the surface area of a liquid.

Viscosity of a liquid depends on intermolecular forces.

Example 11.5 Identify the Intermolecular Forces:

Name	Structure	Bond Type	London	Dipole Dipole	Hydrogen Bonding
A. Methane	CH_4	NonPolar Symetrical	Yes	No	No
B. TriChloroMethane	$CHCl_3$	Unsymetrical & Polar	Slight	Yes	No
C. Butanol	$CH_3CH_2CH_2CH_2$-OH	Hydroxyl & Polar	Slight	Yes	Yes

Students Do

A. Propanol $CH_3CH_2CH_2$-OH
B. Carbon Dioxide CO_2
C. Sulfur Dioxide SO_2

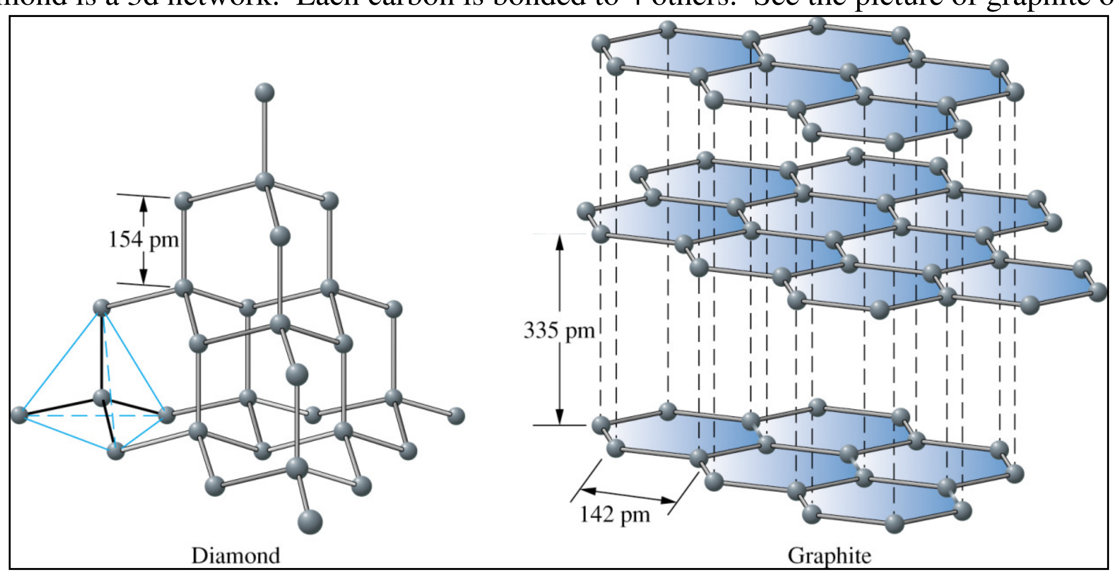
11.6 Classification of Solids

1. Molecular Solid consist of atoms or molecules held together by intermolecular forces. E.g. solid neon, ice, solid CO_2 – dry ice.

2 Metallic Solid consists of positive cores of atoms held together by a surrounding "sea" of electrons – metallic bonding. E.g. iron, copper and silver.

3. Ionic Solid consists of cations and anions held together by the electrical attraction of opposite charges – ionic bonds.

4. Covalent Network Solid consists of atoms held together in large networks or chains by covalent bonds. E.g. diamond is a 3d network. Each carbon is bonded to 4 others. See the picture of graphite on p 445:



Example 11.7 Show the types of solids:

	Solid Ammonia	NH_3	Molecular Structure = molecular solid
	Cesium	Cs	Metallic
	Cesium Iodide	CsI	Ionic
	Silicon	Si	Expected to form covalent bonds as with carbon = covalent network.
Students Do	Zinc	Zn	
	Sodium Iodide	NaI	
	Silicon Carbide	SiC	
	Methane	CH_4	

Physical Properties:

Melting Points.

1. **Molecular Solids:** low melting points due to weak intermolecular attractions.
   MP also is reflected in types of intermolecular attraction. Usually below 300 ^oC

2. **Metallic:** Low MP's for Group 1 & II A, increase moving right to transitions metals. Transition have high MP's. Continue moving right MP's go down. Hg MP -39 ^oC, Tungsten MP 3410 ^oC

3. **Ionic Solid:** Chemical Bonds must be broken – high MP's. NaCl 801 ^oC MgO 2800 ^oC

4. **Covalent Network Soli**d: Chemical Bonds must be broken, high MP's. Quartz 1610 ^oC, Diamond 3550 ^oC

Name	Type of Solid	MP ^oC	BP ^oC
Neon, Ne	Molecular	-249	-246
Hydrogen Sulfide, H_2S	Molecular	-86	-61
Chloroform, $CHCl_3$	Molecular	-64	62
Water, H_2O	Molecular	0	100
Acetic Acid, CH_3COOH	Molecular	17	118
Mercury, Hg	Metallic	-39	357
Sodium, Na	Metallic	98	883
Tungsten, W	Metallic	3410	5660
Cesium Chloride, CsCl	Ionic	645	1290
Sodium Chloride, NaCl	Ionic	801	1413
Magnesium Oxide, MgO	Ionic	2800	3600
Quartz, SiO_2	Covalent Network	1610	2230
Diamond, C	Covalent Network	3550	4827

Hardness

1. **Molecular Solids:** Weak intermolecular forces = soft
2. **Metallic:** Mallable
3. **Ionic Solid:** Strong attractive forces = hard
4. **Covalent Network Soli**d: Rigid structure = very hard [Diamond is very hard]

Electrical Conductivity

1. **Molecular Solids:** Non-conductor
2. **Metallic:** Good Conductors
3. **Ionic Solid:** Conductor in liquid state only.

4. Covalent Network Solid: Non-conductor

Type of solid	MP	Forces	Hardness & Brittleness	Electrical Conductivity
Molecular	Low	Van der Waals	Soft & Brittle	Nonconductive
Metallic	Variable	Metallic Bond	Variable Mallable	Conductor
Ionic	High->VH	Ionic Bond	Hard & Brittle	Nonconductive Solid Conductive Liquid
Covalent Network	Very High	Covalent Bond	Very Hard	Non conductive

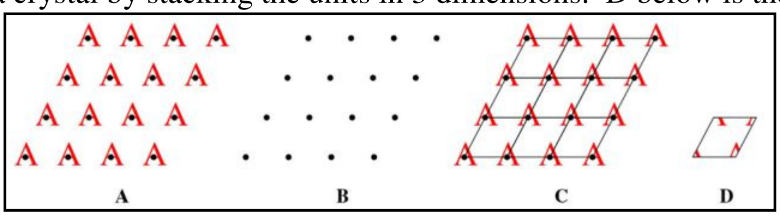
Crystalline Solids

Crystalline Solids is composed of one or more crystals; each crystal has a well defined ordered structure in 3D
Amorphous Solid has a disordered structure; it lacks the well defined arrangement of basic units found in a crystal.

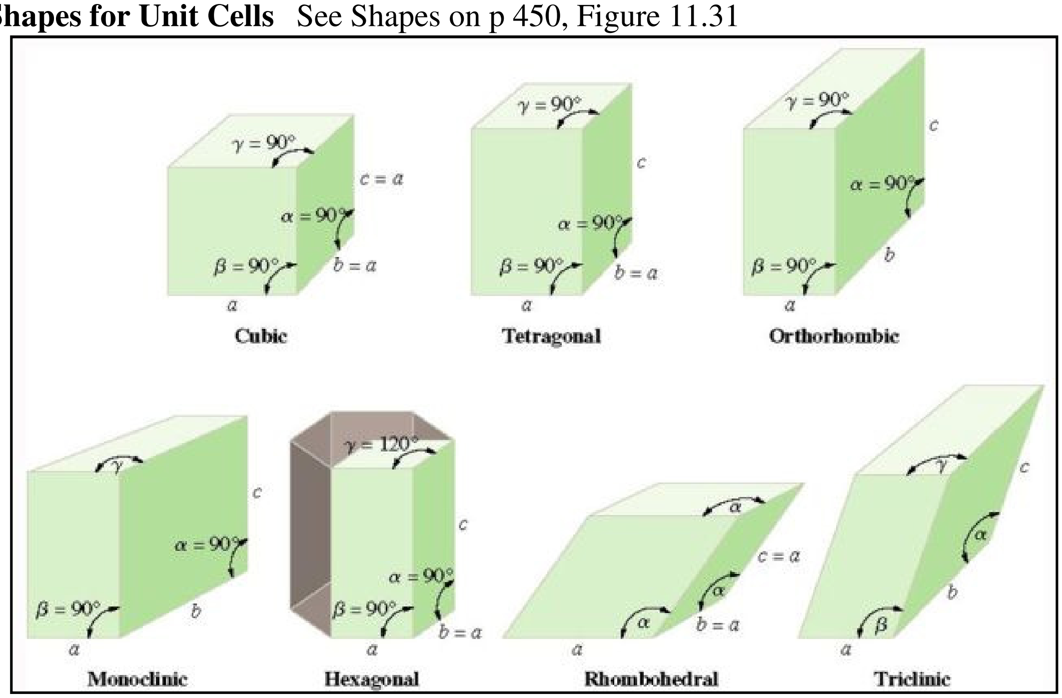
A Crystal is a 3D ordered arrangement of basic units

Crystal Lattice is the geometric arrangement of lattice points of a crystal in which we choose one lattice point at the same location within each of the basic units of the crystal. Crystal Lattice shows only the arrangements of the basic units of the crystal. *Look at a repeating pattern on wall paper.*

Unit Cell is the smallest boxlike unit [each box having faces that are parallelograms] form which you can imagine constructing a crystal by stacking the units in 3 dimensions. D below is the smallest Unit Cell.



Seven Basic Shapes for Unit Cells See Shapes on p 450, Figure 11.31



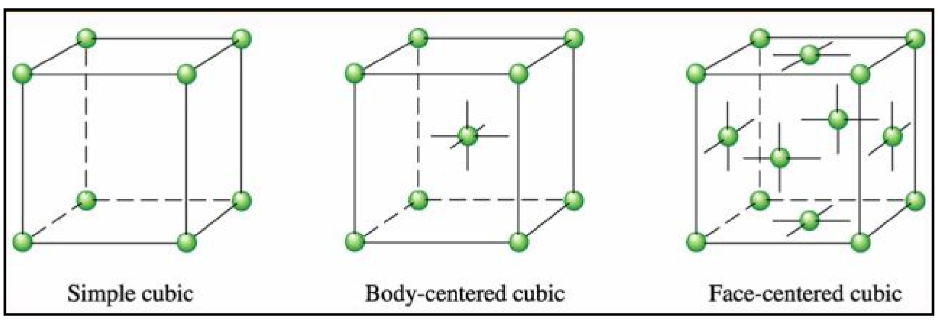
Crystal System	Edge Length	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Cu
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	TiO_2 (rutile), Sn (white tin)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$CaCO_3$ (aragonite), $BaSO_4$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90°, \gamma \neq 90°$	$PbCrO_4$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	C (graphite), ZnO
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaCO_3$ (calcite), HgS (cinnabar)
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$

Cubic Unit Cell – 3 types

1. **Simple cubic unit cell** is a cubic unit cell in which lattice points are situated only at the corners

2. **Body-centered cubic unit cell** is a in which there is a lattice point at the center of the cubic cell in addition to those at the corners

3. **Face-centered cubic unit cell** is a cubic unit cell in which there are lattice points at the centers of each face of the unit cell in addition to those at the corners.



Crystals Defects – crystals can have chemical impurities and defects in the formation of the lattice.

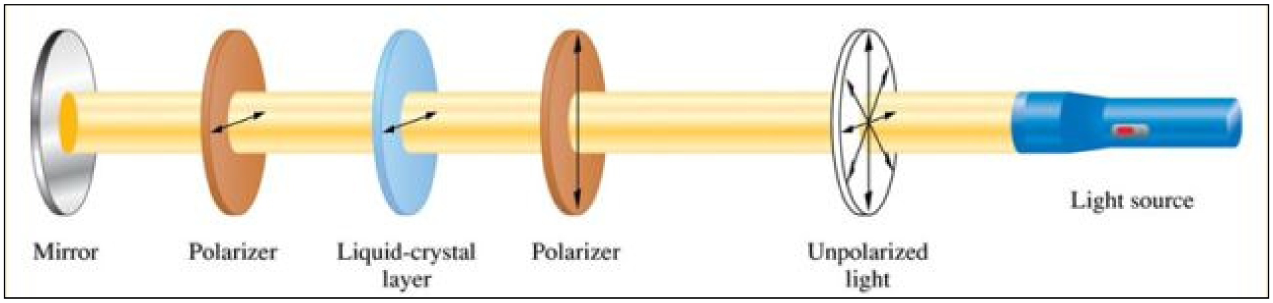
Chemical Impurities: Ruby is Aluminum Oxide Al_2O_3 with some Al^{+3} replace with Cr^{+3}

Lattice Defects:
A. Crystal Planes misaligned
B. Missing ioins – NaCl can have equal number of missing Na and Cl
C. Unequal number of missing cations or anions.

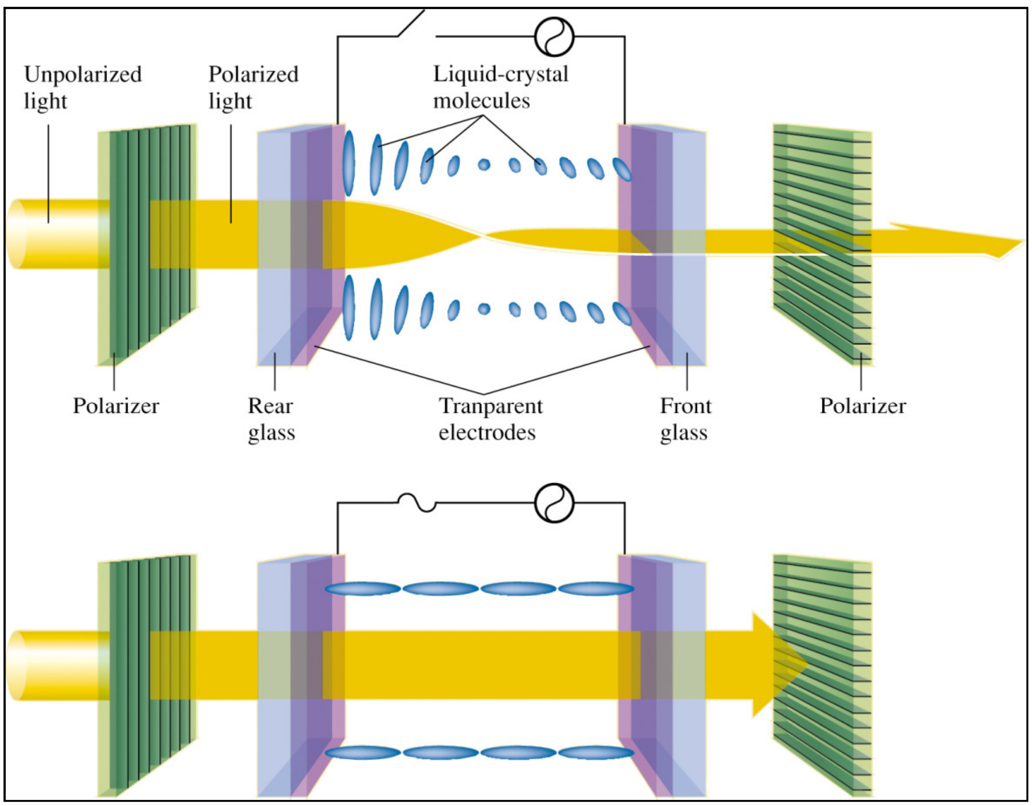
Discuss how Liquid Crystal Displays Work:

Light Source → Up/Down Polarizer → LC Layer → Side/Side Polarizer → Mirror/Detector

Rotates light 90°



| → The Liquid Crystal Layer rotates the light See fig 11.37 p 453



Molecular Solids

Hexagonal close-packed structure is a crystal structure composed of close packed atoms with a stacking of ABABAB

Stack one plane of balls. Put another on top, the 3rd will be equal to the 1st.
See Fig 11.38 on p 454

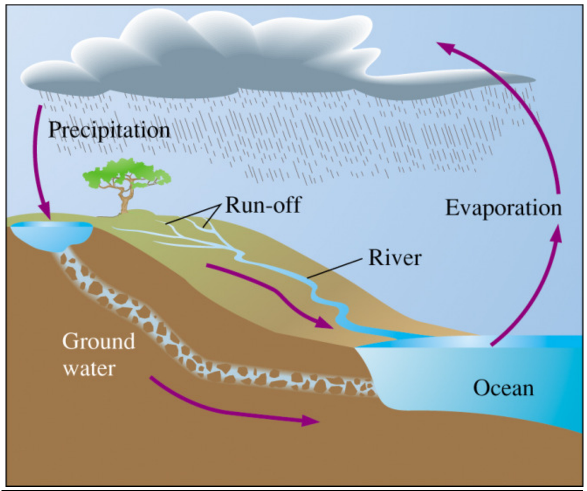
Cubic close-packed structure is a crystal structure composed of close-packed atoms with a stacking of ABCABC.

See book Fig 11.39, p 456

Coordination Number is the number of nearest neighbor atoms. **Max is 12** and atoms will occupy 74% avail space

X-Ray Diffraction is used to determine Crystal Structures

WATER



Water is the only liquid substance found on earth in Significant Amounts
It exists as a Solid – ice, liquid, and gas / vapour

Water forms strong hydrogen bonds.

As a solid, ice is less dense than water and floats on water. Liquid water is at its max density at 4 ^{o}C. As such, ice floats on water and prevents the liquid below from freezing so fish can survive.

Water has a large heat capacity and large heat of vaporization. 30% of the solar energy is absorbed by water as it evaporates. It goes back to the liquid state during condensation – thunderstorms or hurricanes. This is a natural cycle that moves water. Detroit has a more moderate winter due to the thermal capacity of the great lakes.

Water is an excellent solvent. It is Polar and Hydrogen Bonds so it dissolves ionic and polar compounds. It dissolves Mg2+ and Ca2+ which react with soap to give soap scum. A water softener will ion exchange the Mg and Ca for Na to give soft water – no soap scum.

Practice Questions

Review Questions: 11.1, 11.2, 11.4, 11.6, 11.9, 11.13
Concept Questions: 11.23
Practice Problems: 11.31, 11.47, 11.51, 11.57, 11.89