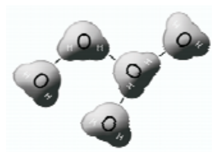
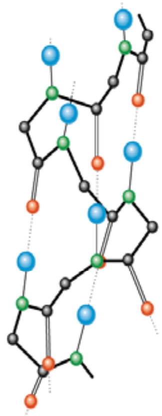
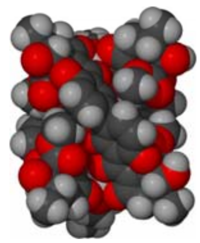


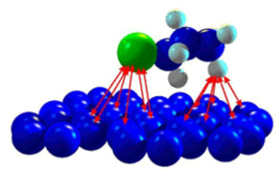


Chapter 12

Intermolecular Forces and Physical Properties of

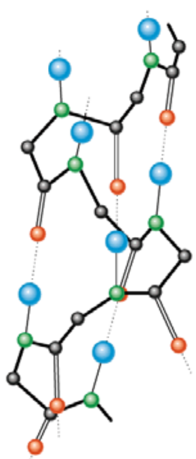
Liquids and Solids





Preview

- Intermolecular forces.
- Properties of liquids.
  - Vapor pressure.
- Properties of solids.
  - Lattice and unit cells.
  - Closest packing.
  - Types of crystalline solids.
- Changes of states.
- Phase diagram.



Chapter 12 Section 1

The Three Phases of Matter

Gas | Liquid | Solid

Gas	Liquid	Solid
Molecules are far apart from each other, having continuous motion, and have little interactions	The motion of the molecules is slower as compared to gas, achieving a slight movement and disorder.	The molecules are locked in place but can vibrate about their positions.

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Chapter 12 Section 1

The Three Phases of Matter

	Gas	Solid
Density	Low	High
Compressibility	High	Low
Internal attraction forces	Low	High

Liquid lies somehow in between, but it is closer in its structural properties to solid (Condensed phases).

$H_2O(s) \rightarrow H_2O(l) \quad \Delta H^o_{fus} = 6.02$ kJ/mol

$H_2O(l) \rightarrow H_2O(g) \quad \Delta H^o_{vap} = 40.7$ kJ/mol

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Chapter 12 Section 1

Intermolecular Forces

- The force holding atoms together to form a molecule is known as ***intramolecular force***. (covalent and ionic bonding)
- The force holding a collection of molecules together in the condensed phases is caled ***intermolecular force***.
  - The magnitude of intermolecular forces is what determines whether the particles that make up a substance are gas, liquid, or solid.

Intramolecular forces >> ***Inter***molecular forces

Intermolecular forces (solid) > Intermolecular forces (liquid) > Intermolecular forces (gas)

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Chapter 12 Section 1

Intermolecular Forces

- The *change in state* is due to the *change in intermolecular interaction.*
- Intermolecular forces decrease as more energy is added.
- What *holds atoms* together is *intramolecular forces*.

$H_2O(s)$	$\rightarrow$ $H_2O(l)$	ΔH^o_{fus}	= 6.02 kJ/mol
$H_2O(l)$	$\rightarrow$ $H_2O(g)$	ΔH^o_{vap}	= 40.7 kJ/mol
$H_2O(g)$	$\rightarrow$ $2H(g) + O(g)$	$\Delta H^o_{diss.}$	= 934 kJ/mol

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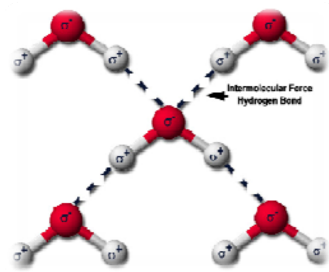
Chapter 12 Section 1

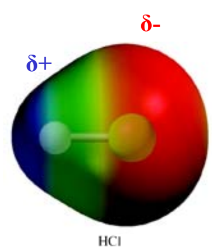
Types of Intermolecular Forces

- Dipole-Dipole Interaction.
- Hydrogen Bonding.
- London Dispersion Forces.
- Ion-Dipole Interaction.



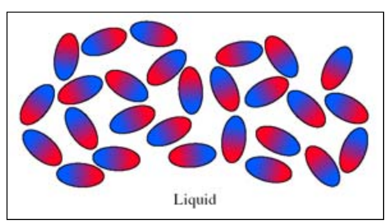
Chapter 12 Section 1

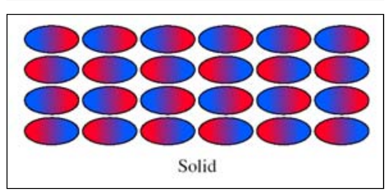
Dipole-Dipole Interaction



- It exists as a weak electrostatic attraction between ***polar molecules***.
- In a condensed state, the molecules orient themselves to maximize electrostatic attractions and minimize the electrostatic repulsions.

  Dipole-dipole force is 1% as strong as covalent and ionic bonds. It becomes weaker as the distance between the molecules gets larger.





Chapter 12 Section 1

Dipole-Dipole Interaction

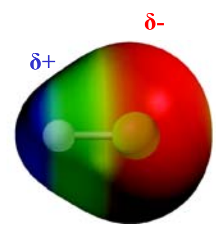
- The attractive forces between polar molecules depend on the ***magnitude of the dipole***.
- Larger intermolecular force between the molecules requires more energy to separate between the particles and, as a result, the substance will boil at higher temperatures.

TABLE 12.1 Dipole Moments and Boiling Points of Compounds with Similar Molecular Masses

Compound	Structural Formula	Dipole Moment (D)	Boiling Point (°C)
Propane	$CH_3CH_2CH_3$	0.1	−42
Dimethyl ether	CH_3OCH_3	1.3	−25
Methyl chloride	CH_3Cl	1.9	−24
Acetaldehyde	CH_3CHO	2.7	21
Acetonitrile	CH_3CN	2.9	82

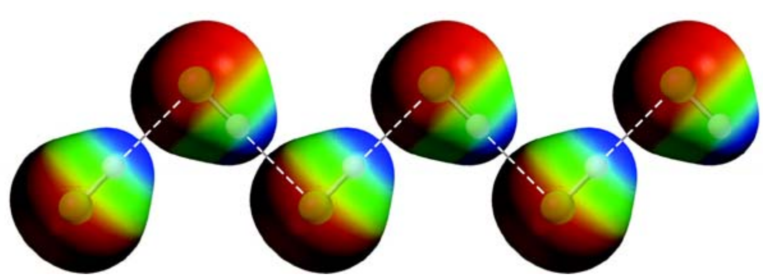
Chapter 12 Section 1

Hydrogen Bonding



HF molecule

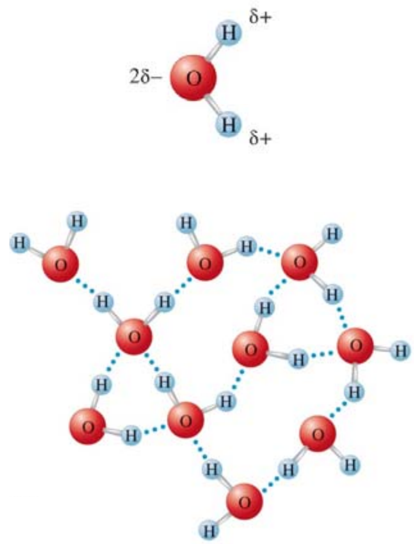
- It is associated only with small, highly electronegative atoms, especially N, O, and F atoms.
- Hydrogen bonds between HF molecules take place between the H atom with a large δ+ charge and a lone pair of the F atom.



Chapter 12 Section 1

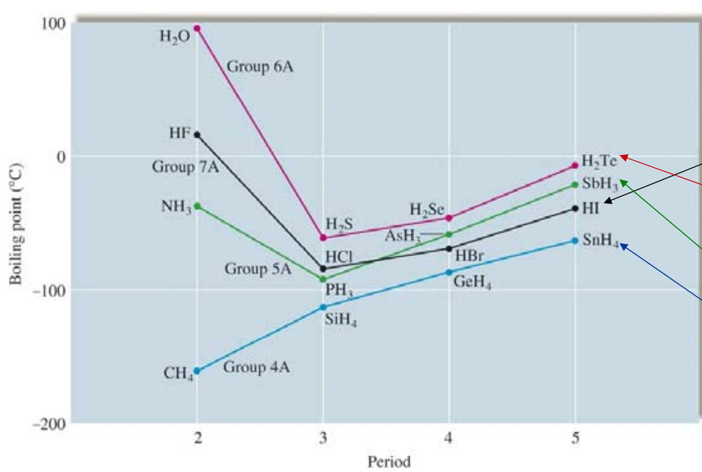
Hydrogen Bonding

- O atoms undergo strong hydrogen bonding with H atoms in H_2O resulting in a high boiling temperature for water.
- ***Two factors*** explain the strengths of hydrogen bonding:
  - The great polarity of the bond.
  - The close approach of the dipoles allowed by the smaller size of the atoms.



Chapter 12 Section 1

Hydrogen Bonding



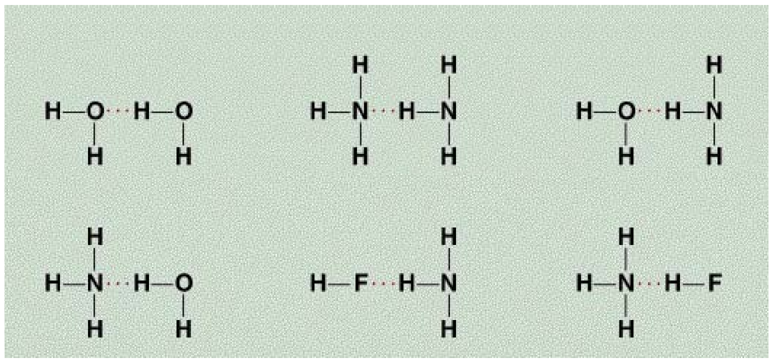
The boiling points of the covalent hydrides of the elements in groups 4A, 5A, 6A, and 7A

As going down a group (increase in MM), the intermolecular force increases. Exceptions are O, F and N atoms

Chapter 12 Section 1

Hydrogen Bonding

- Nitrogen-, oxygen-, and fluorine-containing molecules exhibit hydrogen bonding between themselves or even with other molecules of the same type.

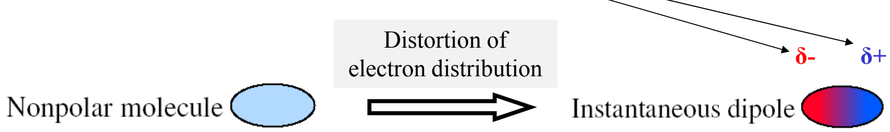


Chapter 12 Section 1

London Dispersion Forces

- It is the only force present in non-polar molecules and noble gases.
- The electron charge is uniformly distributed around the nucleus (electron cloud).

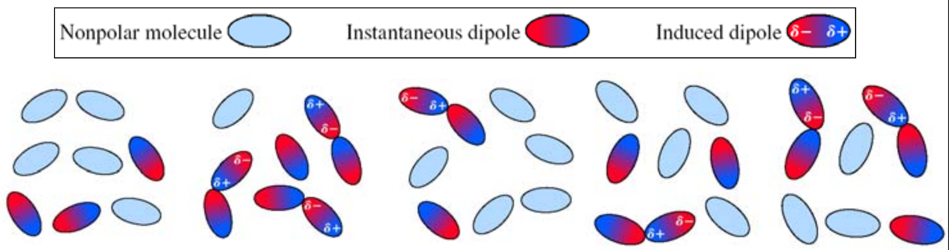
  However, an ***non-uniform*** electron distribution could develop on an atom at some instances. This would lead to ***instantaneous dipole*** within the atom, and a *distorted* electron density would result.



Chapter 12 Section 1

London Dispersion Forces

- The ***instantaneous dipole*** in a molecule or atom can induce (polarize) similar dipole in neighboring atoms, which then can polarize the next molecules, and so on.
- This type of interaction is extremely weak and short-lived, yet it is especially ***significant for large atoms*** because they are more capable to be polarized.



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Chapter 12 Section 1

London Dispersion Forces

- Dispersion force is the only type of force that exists in ***nonpolar molecules***.
- Dispersion force becomes more significant when the electrons are more mobile within a molecule. This is found more in large size molecules (greater molar masses)

TABLE 12.2 Molar Masses, Boiling Points, and States of the Halogens at Room Temperature

Molecule	Molar Mass (g/mol)	Boiling Point (°C)	State (Room Temp.)
F_2	38.0	−188	Gas
Cl_2	70.9	−34	Gas
Br_2	159.8	59	Liquid
I_2	253.8	184	Solid

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London Dispersion Forces in Noble Gases

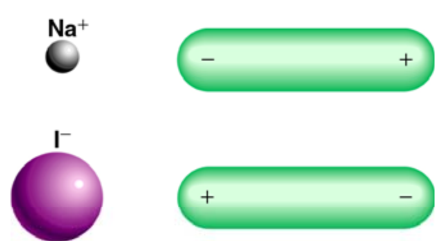
- Dispersion force is the only type of force that exists in ***noble gases***.
- The weaker the dispersion force between the atoms in a noble gas, the lower the freezing point temperature.

TABLE 10.2 The Freezing Points of the Group 8A Elements

Element	Freezing Point (°C)
Helium*	−269.7
Neon	−248.6
Argon	−189.4
Krypton	−157.3
Xenon	−111.9

Ion-Dipole Interactions

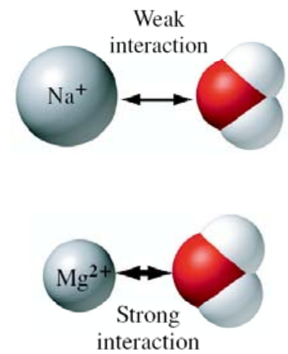
- It is shown by an attraction force between an ion (positive or negative) and a polar molecule.



- Cations generally interact more strongly with dipoles than anions of the same magnitude of charge because cation size is smaller.

Ion-Dipole Interactions

- A higher charge cation interacts more strongly when compared with a lower charge cation from the same period. That is because of the magnitude of the charge and its smaller size.



Intermolecular Forces

- What type(s) of intermolecular forces exist between each of the following molecules, atoms, and ions?

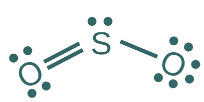
HI

HI is a polar molecule: *dipole-dipole forces*. There are also *London dispersion forces* between HI molecules.

CF_4

CF_4 is nonpolar: ONLY *London dispersion forces*.

SO_2



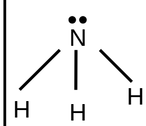
SO_2 is a polar molecule: *dipole-dipole forces*. There are also *dispersion forces* between SO_2 molecules.

Chapter 12 Section 1

Intermolecular Forces

- What type(s) of intermolecular forces exist between each of the following molecules, atoms, and ions?

NH_3



NH_3 is a polar molecule with N and H atoms: *dipole-dipole forces* and *hydrogen bonding*. There are also *London dispersion forces* between HI molecules.

Ar

Ar is a noble gas: ONLY *London dispersion forces*.

K^+ with HCl

An ion with a polar molecule: *ion-dipole interaction.*

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Chapter 12 Section 2

Properties of Liquids

- Why does water bead as droplets when it fall down from a leave of a tree?

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Chapter 12 Section 2

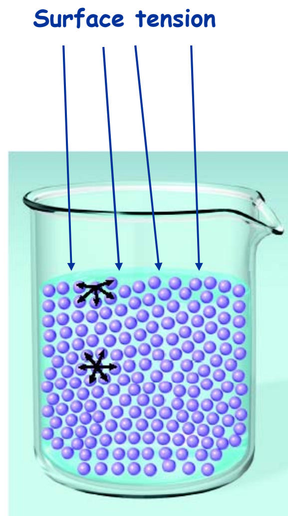
Properties of Liquids

- Why does not the clip sink in water??

Chapter 12 Section 2

Surface Tension

- ***Surface tension*** : Molecules on the surface will be pulled inward. This causes the surface of the liquid to tighten like an elastic film, thus minimizing its surface area “droplets will form”.
- Liquids with larger intermolecular forces (such as those with polar molecules or hydrogen bonding) will have higher surface tensions.

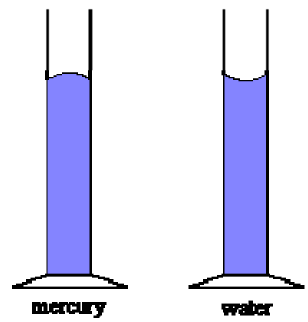


Capillary Action

- It is the rising of liquid in a narrow tube.
  - ***Cohesive*** forces (Intermolecular).
  - ***Adhesive*** forces (between the liquid molecules and the container's inside wall).
- In a glass tube (container made of polar substances):
  - Water forms a concave meniscus.

    cohesion < adhesion
  - Mercury forms a convex meniscus.

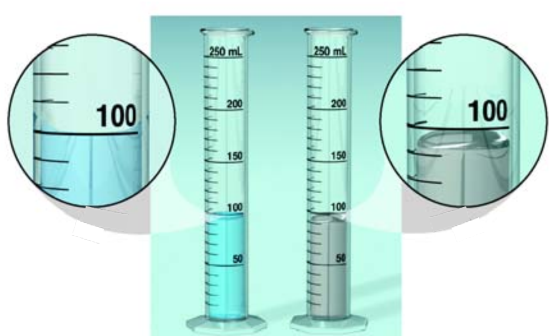
    cohesion > adhesion



Remember that glass is made up from polar substances (mainly SO_2)

Chapter 12 Section 2

Capillary Action



- Water forms a concave meniscus.

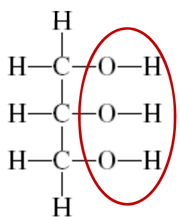
  cohesion < adhesion
- Mercury forms a convex meniscus.

  cohesion > adhesion

Chapter 12 Section 2

Viscosity

- It is the measure of liquid's resistance to flow. The higher the viscosity, the more slowly a liquid flows.
  - Liquids with larger intermolecular interaction tend to be more viscous.



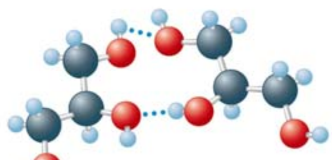


TABLE 12.3 Viscosities of Some Familiar Liquids at 20°C

Liquid	Viscosity ($N \cdot s/m^2$)
Acetone (C_3H_6O)	3.16×10^{-4}
Water (H_2O)	1.01×10^{-3}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Mercury (Hg)	1.55×10^{-3}
Blood	4×10^{-3}
Glycerol ($C_3H_8O_3$)	1.49

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Chapter 12 Section 2

Viscosity

- It is the measure of liquid's resistance to flow. The higher the viscosity, the more slowly a liquid flows.
  - Liquids with larger intermolecular interaction tend to be more viscous.
  - Liquids with more molecular complexity are highly viscous.

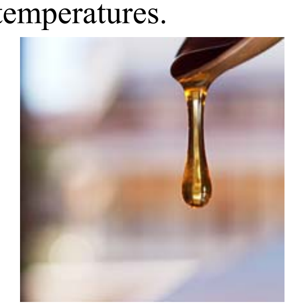
Gasoline ($CH_3 - (CH_2)_8 - CH_3$)

vs.

Grease ($CH_3 - (CH_2)_{25} - CH_3$)

- Viscosity of a liquid typically decreases with the increase in temperature.

For example, honey flows faster at higher temperatures.



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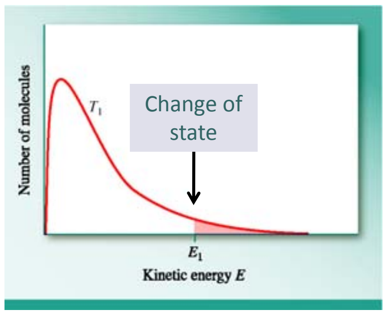
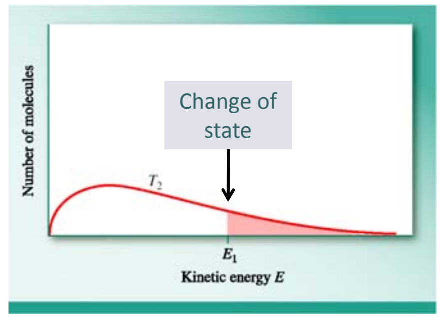
Chapter 12 Section 2

Vapor Pressure

- Molecules in the liquid state are in a continuous motion and have a distribution of kinetic energy.





- $T_1 < T_2$

  A specific amount of KE (E_1) is needed to overcome the intermolecular forces in the liquid phase.

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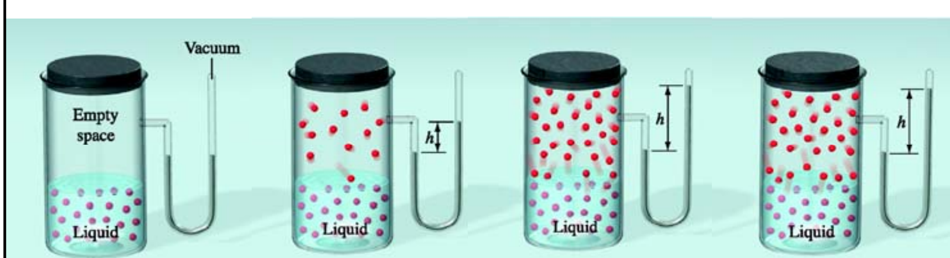
Chapter 12 Section 2

Vaporization Process

- Change of state from liquid to gas.
- Molecules escape the liquid and become gas when they have enough kinetic energy to do so.
- Vapor pressure is developed just above the liquid.



Molecule in the liquid and vapor phases are in ***dynamic equilibrium***

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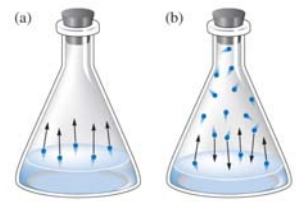
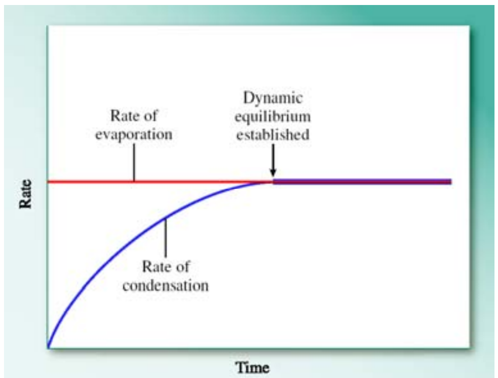
Chapter 12 Section 2

Vapor Pressure

- As more amount of the liquid evaporates, The ***condensation*** rate (returning to the liquid state) of the molecules begins to increase.





- Dynamic equilibrium is established when the rates of evaporations and condensation are equal. (***Equilibrium vapor pressure***)

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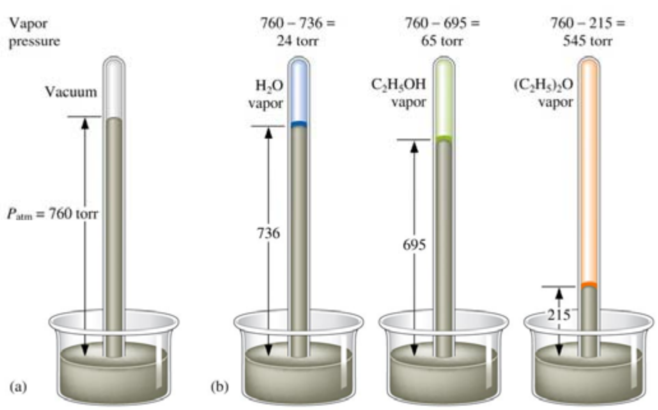
Vapor Pressures of Some Liquids

$$P_{\text{atmosphere}} = P_{\text{vapor}} + P_{\text{Hg Column}}$$

$$P_{\text{vapor}} = P_{\text{atmosphere}} - P_{\text{Hg Column}}$$



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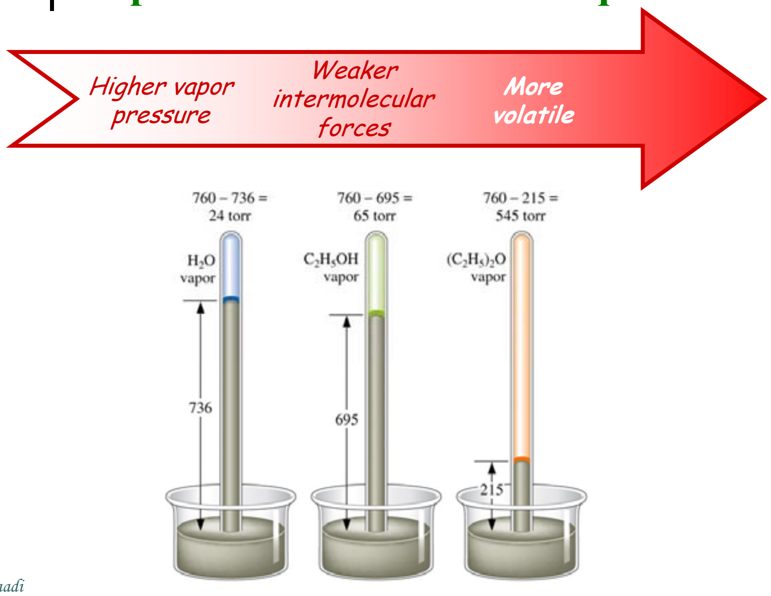
Vapor Pressures of Some Liquids



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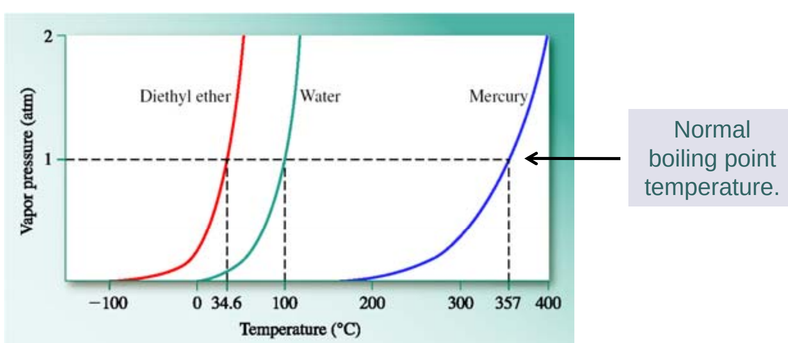
Chapter 12 Section 2

Effect of Temperature on Vapor Pressures

- The vapor pressure increases with the increase in *T*.
- The plot of vapor pressure vs. temperature is not linear.



- However, plotting the natural log of vapor pressures vs. the reciprocal of temperature gives a straight line.

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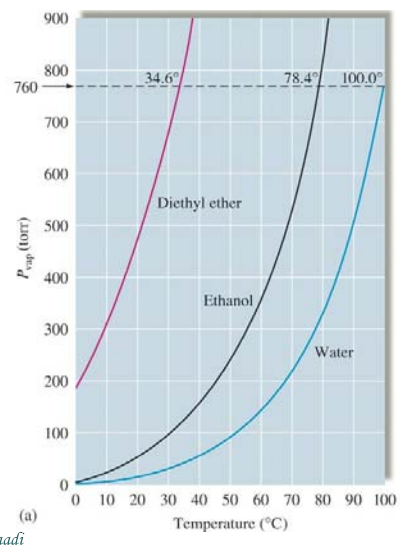
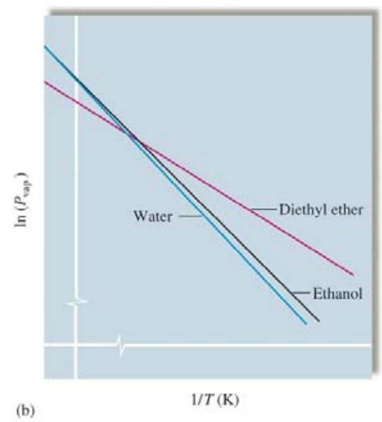
Chapter 12 Section 2

Clausius-Clapeyron Equation



$$\ln P = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$$



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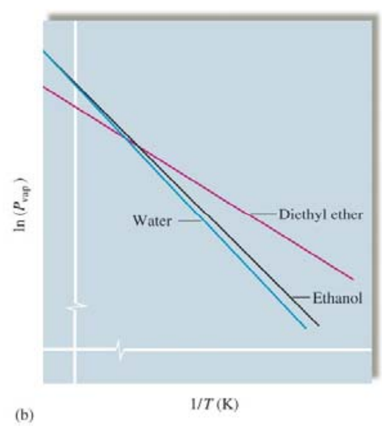
Chapter 12 Section 2

Clausius-Clapeyron Equation

$y = mx + b$

$$\underbrace{\ln P}_{y} = \underbrace{-\frac{\Delta H_{vap}}{R}}_{m}\underbrace{\left(\frac{1}{T}\right)}_{x} + \underbrace{C}_{b}$$

- R = 8.314 J / K · mol
- ΔH_{vap} is the molar heat of vaporization (J/mol)



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Clausius-Clapeyron Equation

- ***Clausius-Clapeyron equation*** can be used to compare between two states of a gas.

State 1

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

State 2

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

Subtracting the 2nd equation from the 1st equation gives:

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

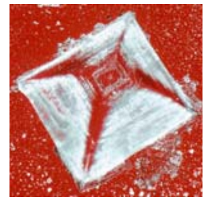
Clausius-Clapeyron Equation

The vapor pressure and heat of vaporization of water at 25°C is 23.8 torr and 43.9 kJ/mol, respectively. Calculate the vapor pressure of water at 50°C.

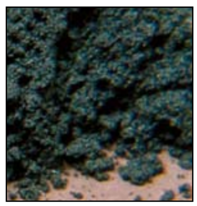
$$\ln\frac{P_1}{P_2} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Crystal Structure

- ***Crystalline Solid***: its components are highly ordered.

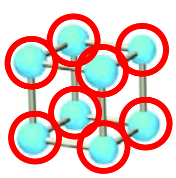


- ***Amorphous Solid***: its components have considerable disorder.

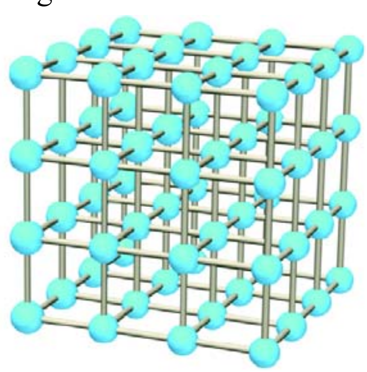


Crystal Structure

- ***Lattice structure*** is a 3-D system of points (at defined positions) that make up a crystalline solid.
- ***Unit cell*** is the basic repeating structural unit in a lattice of a crystalline solid.



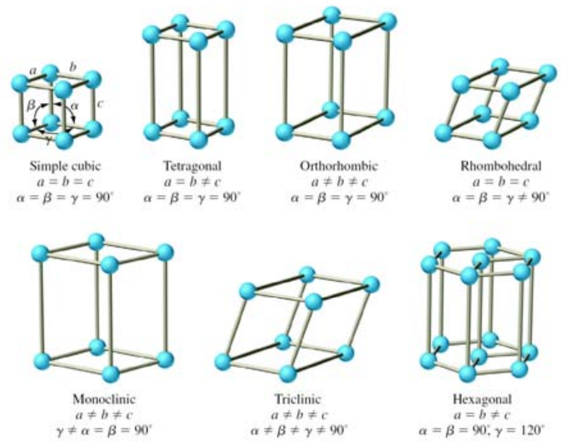
Each ***lattice point*** is occupied by an atom



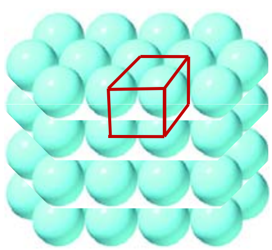
3-D array of unit cells

Unit Cells

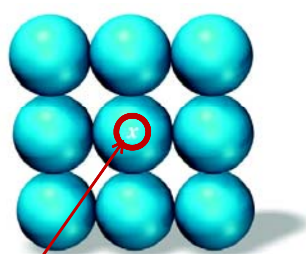
- There are seven types of unit cells, of which the simple cubic cell is the one of the simplest shape.
- Each unit cell generates a characteristic lattice structure.



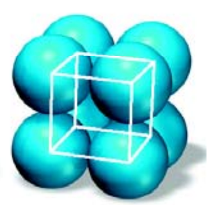
Coordination Number in Crystalline Solids



Packing spheres



Coordination number is 6



Simple cubic cell (scc)

- ***Coordination number*** – number of atoms (particles) surrounding a given atom in a crystal lattice.
  - Indicates how tightly atoms pack.
  - Larger coordination numbers indicate tighter packing.

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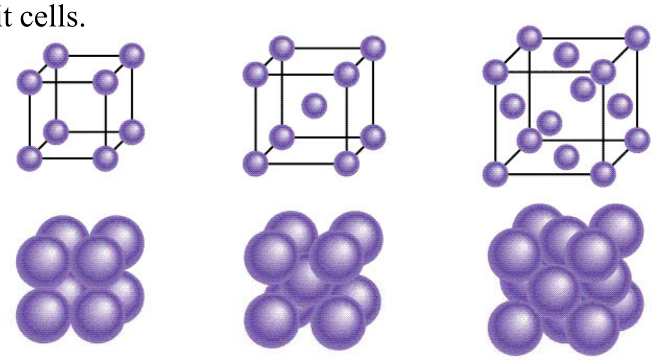
Other Types of Unit Cells

- Different ways of packing result in other types of cubic unit cells.



Simple cubic cell (*scc*)	Body-centered cubic cell (*bcc*)	Face-centered cubic cell (*fcc*)
Coordination number is 6	Coordination number is 8	Coordination number is 12

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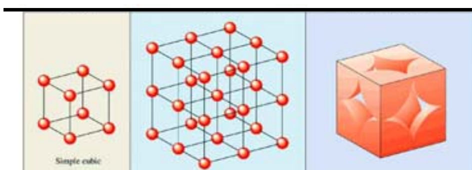
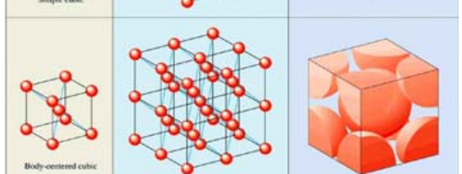
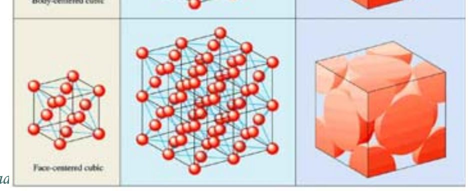
Other Types of Unit Cells

	Unit cell / Lattice / Space-filling unit cell	Net no. of atoms per unit cell
scc		(8 × 1/8 = 1) 1 atom / unit cell
bcc		(8 × 1/8 + 1 = 2) 2 atoms / unit cell
fcc		(8 × 1/8 + 6 × 1/2 = 4) 4 atoms / unit cell

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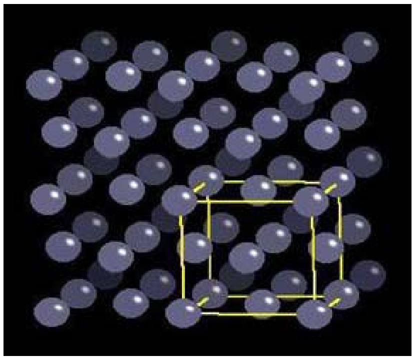
Example of a Unit Cell

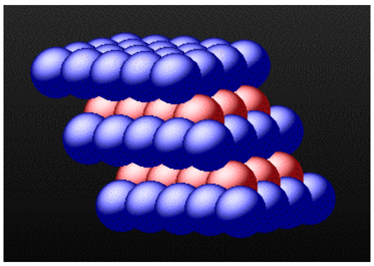


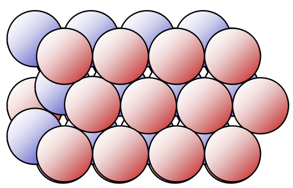
An example of a Faced-Centered Lattice (*fcc*) with its unit cell being shown.

Chapter 12 Section 3

Closest Packing

- The ***closest packing model*** describes the most efficient way to pack atoms in layers to be close to each other as much as possible.
- Atoms are represented as uniform, hard spheres. Each sphere occupies a *depression* in the upper and lower layers. These layers don't lie directly on top of each other.





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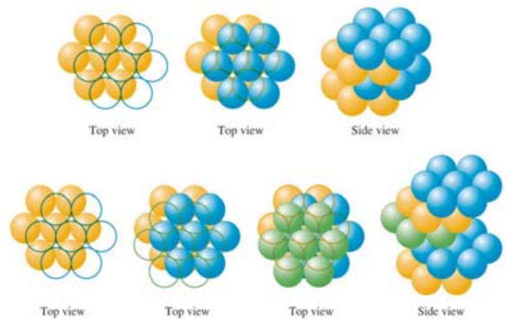
Closest Packing

- The 3rd layer can result in two main types of packing:
  - **ABA** packing: the spheres in *every other layer* occupy the same vertical positions.
  - **ABC** packing: the spheres in *every fourth layer* occupy the same vertical positions.
- These arrangements have the most efficient use of the available space.



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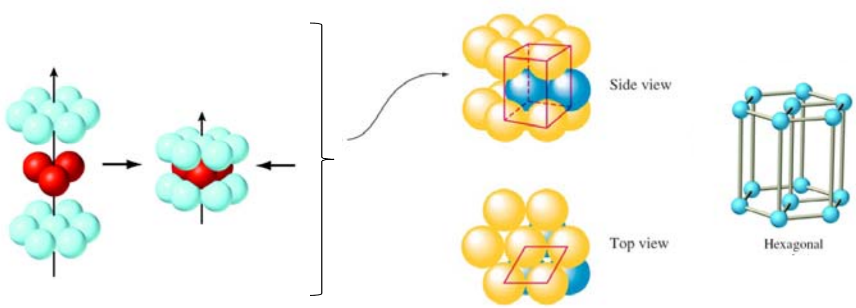
The ABA Closest Packing

- The resulting structure from the ABA packing is the hexagonal close-packed (***hcp***) structure (Mg, Zn, Ti)

  The resulting unit cell is a *hexagonal* unit cell.



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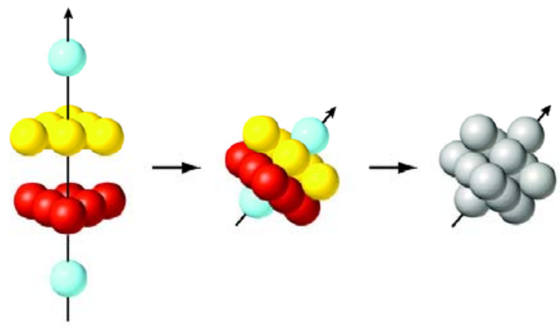
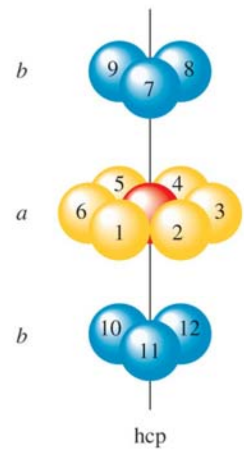
The ABC Closest Packing

- The resulting structure from the ABC packing is the cubic close-packed (***ccp***) structure (Al, Ag, Ni).
  The resulting unit cell is a *faced-centered cubic* (*fcc*) cell.



Coordination Number

- In both types of packing (*hcp* and *ccp*), each sphere has 12 equivalent neighboring spheres:
  - 6 in the same layers,
  - 3 in the layer above, and
  - 3 in the layer below.
- Coordination number = 12



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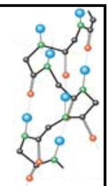
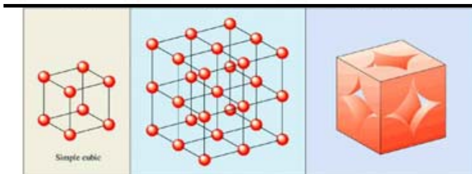
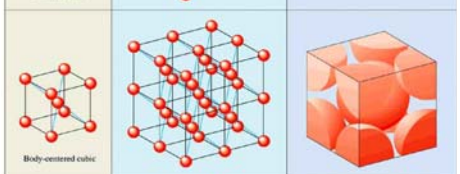
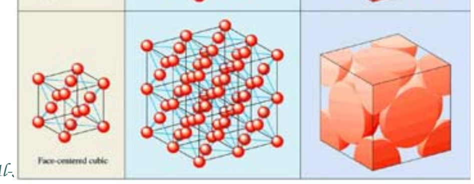
Volume of Unit Cells



Unit cell / Lattice / Space-filling unit cell	No. of atoms per unit cell
	(8 × 1/8 = 1) 1 atom / unit cell
	(8 × 1/8 + 1 = 2) 2 atoms / unit cell
	(8 × 1/8 + 6 × 1/2 = 4) 4 atoms / unit cell

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Chapter 12 Section 3

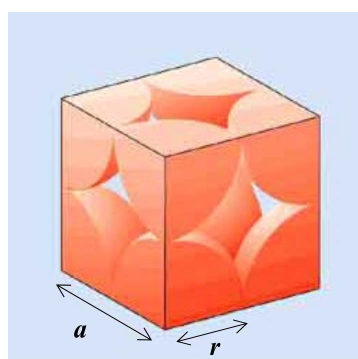
Volume of Unit Cells

- The relationship between the edge length (a) and radius (r) of atoms in a unit cell can be expressed.

- Simple Cubic Cell

$$a = 2r$$

Volume $= a^3 = 8r^3$



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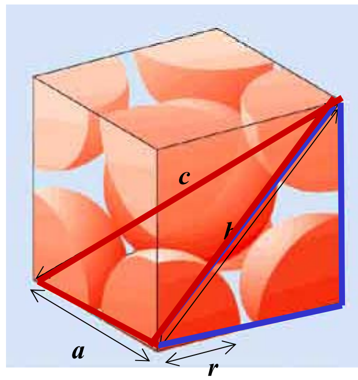
Volume of Unit Cells

- Body-Centered Cubic Cell

$$c = 4r$$
$$b^2 = a^2 + a^2$$
$$c^2 = a^2 + b^2$$
$$c^2 = a^2 + 2a^2 = 3a^2$$
$$3a^2 = 16r^2$$
$$a = 4r/\sqrt{3}$$
$$\text{Volume} = 64r^3/(3)^{3/2}$$



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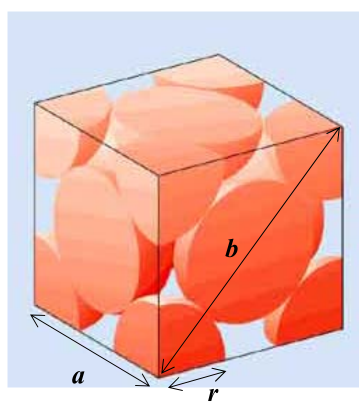
Volume of Unit Cells

- Face-Centered Cubic Cell

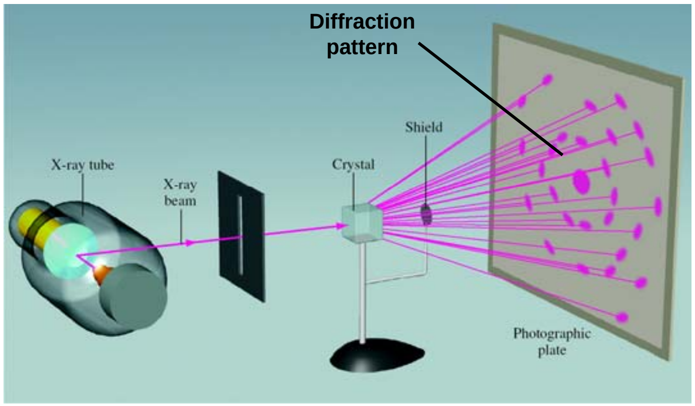
$$a^2 + a^2 = b^2$$
$$b = 4r$$
$$b^2 = 16r^2$$
$$2a^2 = 16r^2$$
$$a^2 = 8r^2$$
$$a = r\sqrt{8}$$
$$\text{Volume} = a^3 = 8^{3/2}r^3$$



Chapter 12 Section 3

How Do We Know the Structures of Crystals

- X-ray diffraction instrument can be used to analyze the structure of various chemical solid materials.



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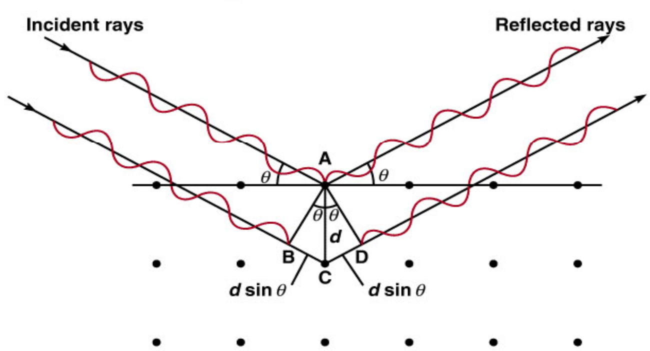
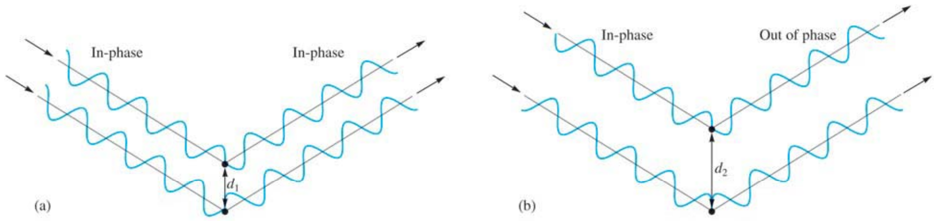
X-Ray Diffraction

- ***Diffraction*** is the scattering of light beams from a regular array of points in which the spacings (d) between the components are comparable with the wavelength of the light (λ). The angle of incident / reflection is given by (θ).



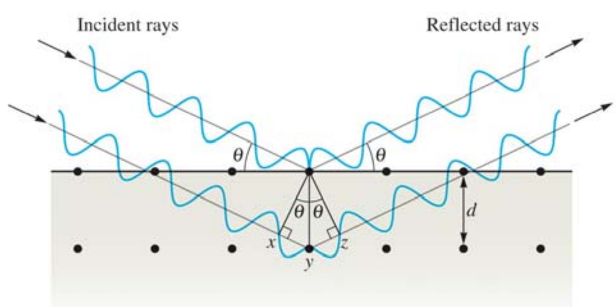
X-Ray Diffraction

- X-rays scattered from two different atoms may: (a) reinforce (constructive interference), or (b) cancel (destructive interference) one another.



- The difference in distances traveled is an integral number (*n*) of wavelength (*λ*).
- The diffraction pattern can be used to determine the interatomic distances.

X-Ray Diffraction



$xy + yz = n\lambda$	(In-phase light)
$xy + yz = 2d \sin\theta$	(From trigonometry)
$\mathbf{2d \sin\theta = n\lambda}$	(Bragg Equation)

X-Ray Diffraction

A topaz crystal has an interplanar spacing of 1.36 Å. Calculate the wavelength of the X ray that should be used if the θ is 15.0°. Assume n = 1.

$$2d \sin\theta = n\lambda$$