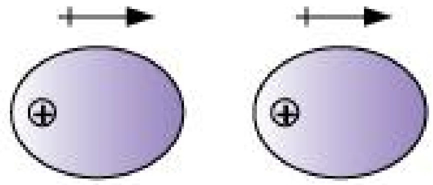
States of Matter

Intermolecular forces:

(Also known as **van der Waals forces**)

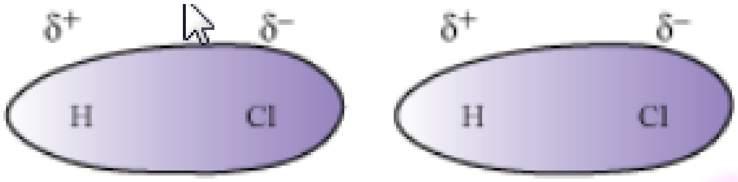
- Dispersion forces or London forces (Forces between atoms or non-polar molecules)



Atom with instantaneous dipole, more electron density on the right hand side

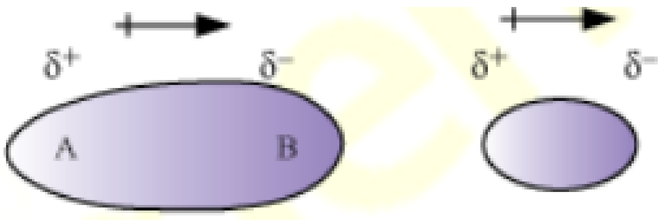
Atom with induced dipole

- Dipole-dipole forces (Forces between molecules possessing permanent dipole)



Dipole-dipole interaction between two HCl molecules

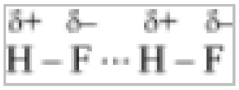
- Dipole-induced forces (Forces between a molecule having permanent dipole and a molecule lacking permanent dipole)



Permanent dipole (a polar molecule)

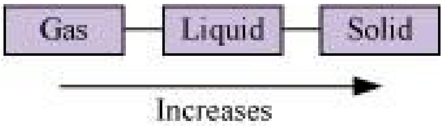
Induced dipole in a non-polar molecule

- Ion-dipole interaction (Interaction of an ion with the oppositely charged site of a polar moleule)
- Hydrogen bond (Force between hydrogen attached to an electronegative atom of one molecule and an electronegative atom of different molecule)



$\overset{\delta+}{H}-\overset{\delta-}{F}\cdots\overset{\delta+}{H}-\overset{\delta-}{F}$

Intermolecular interactions:



Thermal energy: Energy of a body due to motion of its atoms or molecules

Boyle's Law

- Relation between pressure (*p*) and volume (*V*)
- Statement − At constant temperature, the pressure of a fixed amount (number of moles, *n*) of a gas is inversely proportional to its volume.

Charles' Law

- Relation between temperature (*T*) and volume (*V*)
- Statement − At constant pressure, the volume of a fixed amount of a gas is directly proportional to its absolute temperature.

Standard Temperature and Pressure(STP)

The standard values are 0^0C or 273K for temperature and 1 atm or 760 mm of Hg for pressure and are commonly known as **S.T.P.**

Gay-Lussac's Law

- Relation between pressure and temperature

- Statement − At constant volume, the pressure of a fixed amount of a gas is directly proportional to the temperature.

Avogadro Law

- Relation between volume (V) and amount of substance (number of moles n)
- Statement − Under the same conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules.

Ideal Gas

- The gas which strictly follows Boyle's law, Charles' law and Avogadro law

Ideal Gas Equation

- Equation obtained by the combination of Boyle's law, Charles' law and Avogadro law

$\Rightarrow pV = n\mathrm{R}T$ …….(i)

R = Proportionality constant, known as Universal Gas Constant

Equation (i) is called ideal gas equation.

Kinetic molecular theory of gases:

- Gases are made of large number of identical particles called molecules, which are very small. The actual volume of the molecules is negligible in comparison to the total volume of the molecules. They are considered as the point masses.
- The forces of attraction and repulsion between the particles are supposed to be negligible at ordinary temperature and pressure.
- Particles of a gas are always in constant and random motion.
- Molecules are supposed to be perfectly hard spheres and the collisions between them are perfectly elastic.
- The pressure exerted on the walls of the containing vessel is due to the collision of the molecules on the walls of the container.

- The average kinetic energy of the particles of a gas is directly proportional to the absolute temperature of the gas.

Deviation from ideal gas behaviour (real gas):

van der Waals equation

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

$$\text{Compressibility factor (Z)} = \frac{pV}{nRT}$$

Z=1 (for ideal gas, at all temperatures and pressures)

At very low pressures, $Z \approx 1$

At high pressures, $Z > 1$

At intermediate pressures, $Z < 1$

The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called **Boyle temperature** or **Boyle point.**

Liquefaction of gases:

A gas can be liquefied by cooling or applying pressure or by the combined effect of both.

Critical temperature (T_c), critical volume (V_c), and critical pressure (p_c):

The temperature at which a gas liquefies is called its critical temperature.

The volume of one mole of a gas at critical temperature is called its critical volume.

The pressure of a gas at its critical temperature is called its critical pressure.

Methods of Liquefaction of Air
(1) Lind process
(2) Linde-Claude process

Liquid State

Vapour Pressure: Vapour pressure in the state of equilibrium between liquid phase and vapour phase.

Boiling point: The temperature at which the vapour pressure of a liquid is equal to the external pressure.

Surface tension (γ):

- Force acting per unit length perpendicular to the line drawn on the surface of liquid
- Its SI unit is Nm^{-1}.

Viscosity:

It is the measure of the resistance to flow, which arises due to the internal friction between the layers of fluid as they slip past one another while the liquid flows.

$$\boxed{F = \eta A \frac{du}{dz}}$$

Where, F = Force

A = Area of contact

$\frac{du}{dz} = \text{Velocity gradient}$

= Proportionality constant known as coefficient of viscosity

Coefficient of viscosity (η) is the measure of viscosity. Its SI unit is $N\ s\ m^{-2}$.

Greater the viscosity, more slowly does the liquid flow.

General characteristics of solid state:

- Definite mass, volume and shape
- Short intermolecular distances
- Strong intermolecular forces
- Fixed lattice positions of the constituent particles
- Incompressibility and rigidity

Classification of the solid state:

- Crystalline
- Amorphous (sometimes called pseudo solids or super-cooled liquids)

Differences between the crystalline and amorphous solids

Crystalline	Amorphous
Have definite characteristic geometrical shape	Have irregular shape
Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
When cut with a sharp edged tool, the newly generated pieces are plain and smooth	When cut with a sharp edged tool, the newly generated pieces are with irregular surfaces
Have definite and characteristic heat of fusion	Do not have definite heat of fusion
Are true solids	Are pseudo solids
Anisotropic in nature	Isotropic in nature
Have long-range order	Have only short-range order

Classification of crystalline solids (On the basis of the nature of intermolecular forces)

Molecular solids

- Non-polar molecular solids →These consist either atoms or the molecules formed by non-polar covalent bonds. Example: H_2, Cl_2, I_2
- Polar molecular solids → The molecules ion these types of solids are held together by strong dipole-dipole interactions. Example: Solid SO_2, solid NH_3
- Hydrogen-bonded molecular solids → The molecules of such solids contain polar covalent bonds between H and f, O or N atoms. Example: Ice (H_2O)

Ionic solids

Ions are the constituent particles; e.g., NaCl, KNO_3

Metallic solids

Each metal atom is surrounded by electrons; e.g., Fe, Cu

Covalent or network solids

Formed by covalent bonds; e.g., diamond, silicon carbide

Crystal lattice: A regular three-dimensional arrangement of points in space.

- There are 14 Bravais lattices

Unit cells: There are two categories of unit cells –

- **Primitive unit cells:** There are seven types of primitive unit cells –
- Cubic ($a = b = c$, $\alpha = \beta = \gamma = 90°$); e.g., NaCl
- Tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$); e.g., $CaSO_4$
- Orthorhombic ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$); e.g., KNO_3

- Hexagonal ($a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$); e.g., ZnO
- Rhombohedral or Trigonal ($a = b = c$, $\alpha = \beta = \gamma \neq 90°$); e.g., $CaCO_3$
- Monoclinic ($a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 120°$)
- Triclinic ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$); e.g., $Na_2SO_4.10H_2O$
- **Centred unit cells:** There are three types of centred unit cells –
- Body-centred unit cells: Contain one constituent particle at its body centre along with the ones present at corners
- Face-centred unit cells: Contain one constituent particle at the centre of each face along with the ones present at corners
- End-centred unit cells: Contain one constituent particle at the centre of any two faces along with the ones present at corners

Number of atoms in a unit cell:

- Total number of atoms in one primitive cubic unit cell = 1
- Total number of atoms in one body-centred cubic unit cell = 2
- Total number of atoms in one face-centred cubic unit cell = 4

Close-packed structures:

- **Coordination number:** The number of the nearest neighbours of a particle
- **Packing efficiency:** The percentage of total space filled by the particles

Close-Packing in One dimension

Only one way of arrangement, i.e., the particles are arranged in a row, touching each other

Close-Packing in Two Dimensions

Square close-packing in two dimensions

Close-Packing in Three Dimensions

Three-dimensional close-packing is obtained by stacking two-dimensional layers (square close-packed or hexagonal close-packed) one above the other.

- There are two highly efficient lattices of close-packing –
- Hexagonal close-packed (*hcp*)
- Cubic close-packed (*ccp*) [also called face-centred cubic (*fcc)* lattice]
- In *hcp* and *ccp,* 74% space is filled, i.e., packing efficiency = 74%.

The remaining space is present in the form of voids.

There are two types of voids –

- Octahedral voids
- Tetrahedral voids

The packings other than *hcp* and *ccp* are not close packings as they have less packing efficiency.

- Packing efficiency in bcc = 68%
- Packing efficiency in simple cubic lattice = 52.4%

Number of octahedral voids = Number of close-packed particles

Number of tetrahedral voids = 2 × Number of close-packed particles

In ionic solids, the bigger ions (usually anions) form the close-packed structure and the smaller ions (usually cations) occupy the voids.

The fraction of the octahedral or tetrahedral voids that are occupied depends on the chemical formula of the compound.

Packing Efficiency

Percentage of total space filled by particles

$$\text{packing efficiency} = \frac{\text{Volume of one particle}}{\text{Volume of cubic unit cell}} \times 100\%$$

Calculations involving dimensions of unit cells:

$$\text{Density of a unit cell} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$$

$$\Rightarrow d = \frac{zM}{a^3 N_A}$$

Where,

d → Density

z → Number of atoms present in one unit cell

M → Molar mass

a → Edge length

N_A → Avogadro's number

Imperfections in solids:

- **Line defects**

  -These arise due to irregularities in the arrangement of constituent particles in entire rows of a lattice point

- **Point defects**

  -These arise due to irregularities in the arrangement of constituent particles around a point or an atom

  -There are three types of point defects: Stoichiometric, Impurity and Non-stoichiometric

Stoichiometric defects (intrinsic or thermodynamic defects)

- Vacancy defect

  -Developed when a substance is heated

  -Decreases the density of the substance

- Interstitial defect

  -Increases the density of the substance

- In ionic solids, the vacancy and interstitial defects exist as Frenkel and Schottky defects.

  -Frenkel defect (also called dislocation defect): It occurs when there is a large difference in the size of ions.

  -Schottky defect: It is a vacancy defect and it decreases the density of the substance.

Impurity defects:

These defects arise when foreign atoms are present at the lattice site (in place of the host atoms).

Non-stoichiometric defects:

- Metal excess defect

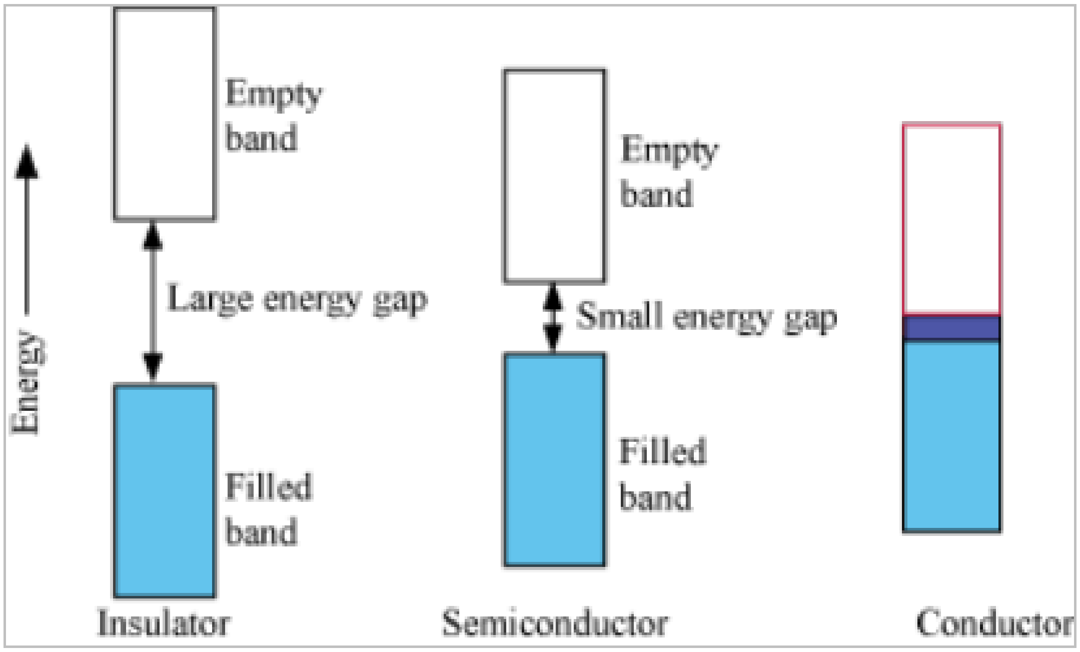
  -Metal excess defect due to anionic vacancies

  -Metal excess defect due to the presence of extra cations

- Metal deficiency defect: Occurs when the metals show variable valency, i.e., the transition metals

Classification of solids on the bases of conductivities:

- Conductors
- Insulators
- Semiconductors



Doping: Adding an appropriate amount of suitable impurity to increase conductivity

- ***n*-type semiconductor**

  -Doped with electron-rich impurities

- ***p*-type semiconductor**

  -Doped with electron-deficient impurities

- Semiconductors are widely used in electronic industries.

Magnetic properties:

Magnetic properties of substances originate because each electron in an atom behaves like a tiny magnet.

-Classification of substances on the basis of magnetic properties:

- Paramagnetic: e.g., O_2

- Diamagnetic: e.g., H_2O
- Ferromagnetic: e.g., CrO_2
- Anti-ferromagnetic: e.g., MnO
- Ferrimagnetic: e.g., Fe_3O_4

Ferromagnetic substances can be made permanent magnets.

These magnetic properties are used in audio, video and other recording devices.