STATES OF MATTER

Matter: Anything that occupies space and has a definite mass

- Matter mainly exists in three different states – solid, liquid and gas

Comparison between the three states of matter

PROPERTIES	SOLID	LIQUID	GAS
Shape and volume	Definite	No definite shape but has definite volume	No definite shape and volume
Inter molecular force of attraction	Strong	In between solids and gases	Weak
Arrangement of particles	Closely packed	Loosely packed	Far apart
Kinetic energy	Very Low	In between solids and gases	Very high
Diffusability	Very Low	In between solids and gases	Very high
Compressibility	Very Low	In between solids and gases	Very high

INTERMOLECULAR FORCES

- Various attractive or repulsive forces between particles (Atoms or molecules) of a matter
- Attractive forces are termed as ***van der Waals forces***

Various van der waal forces are given below

1. **Dispersion Forces or London Forces**
   - *Weak attractive force between electrically symmetric molecules having no dipole moment(non polar molecules)*
   - *As they approaches , their charge cloud is distorted , so a temporary dipole is generated and also a weak force is formed*
   - *As the moves away , the dipole is removed , so force is dispersed*
2. **Dipole - Dipole Forces**
   - *Forces act between the molecules possessing permanent dipole(polar molecules)*
   - *This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.*
   - *Decreases with the increase of distance between the dipoles*
3. **Dipole–Induced Dipole Forces**
   - *Forces operates between the polar molecules and the non-polar molecules.*
   - *Polar molecule induces dipole non-polar molecule by deforming its electronic cloud.*
   - *So force of attraction is generated*

4. **Hydrogen bond**

GAS LAWS

1. Boyle’s Law (Pressure – Volume Relationship)

- *At constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.*

  Ie

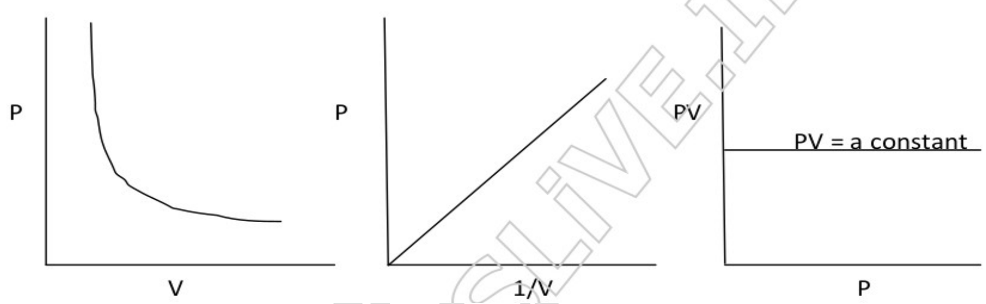
  $P \alpha \frac{1}{V}$

  $P = k \times \frac{1}{V}$ (k is constant)

  pv= constant

  $P_1V_1 = P_2V_2$

- The plot at constant temperature is known as **Isotherm**



We know $d = \frac{m}{V}$ so, $V = \frac{m}{d}$ →(1)

we know PV = k → (2)

(1) in (2) $P \times \frac{m}{d} = k$ re arranging $d = P \times \frac{m}{k}$

that is *At constant temperature, pressure is directly proportional to the density of a fixed mass of the gas*

2. Charles’ Law (Temperature – Volume Relationship)

- *At constant pressure, volume of a fixed mass of gas is directly proportional to its temperature.*

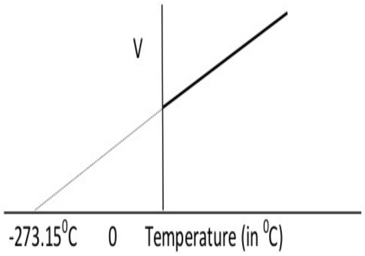
  $V \alpha T$

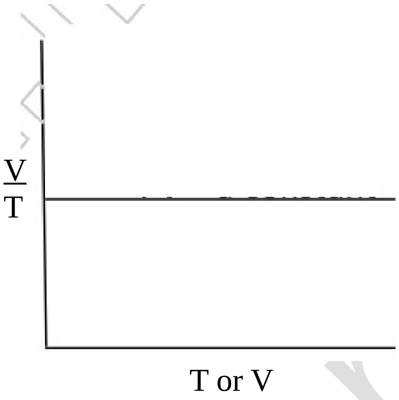
  $V = k \times T$

  $\frac{V}{T} = k$

  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

- Plot at constant pressure is known as **Isobar**

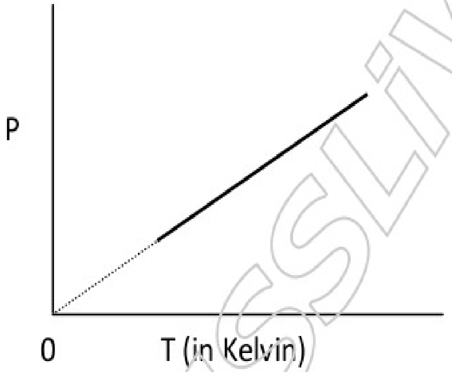




If we extend the graph to temperature axis (X-axis), the graph will meet at -273.15 0 C. At this temperature, the **volume** of the gas becomes **zero**. This lowest hypothetical or **imaginary temperature at which gases are supposed to occupy zero volume is called *Absolute zero*** and the scale of temperature based on absolute zero is called ***Absolute scale***

3) Gay Lussac's Law (Pressure - Temperature Relationship)

- *It states that at constant volume, pressure of a fixed amount of a gas is directly proportional to the temperature.*
  $P \alpha T$
  $P = \text{a constant} \times T$
  $P/T = \text{constant}$
- *The graph obtained at constant volume is termed as an* **Isochore**



4) Avogadro Law (Volume – no. of moles or Amount Relationship)

- *It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles or molecules.*
  (At constant temperature and pressure , volume is directly proportional to number of moles)

  $V \alpha n$,

  $V = k \times n$,

Number of moles = $\frac{\text{Given mass(g)}}{\text{Molecular Mass}}$, $n = \frac{w}{M}$ – (1)

$n = \frac{V}{k}$ – (2)

(2) in (1) – $\frac{V}{k} = \frac{w}{M}$

Re arranging --- $M = k \times \underline{w}$

$M = k\,d$

$M \propto d$

ie, **the density of a gas is directly proportional to its molar mass.**

Standard Temperature and Pressure (STP)

Standard temperature and pressure (also called NTP, the normal temperature and pressure) means 273.15 K (0°C) temperature and 1 bar pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71 L mol^{-1}

IDEAL GAS EQUATION

- **Gas obeys Boyles law, Charls law and avogadro law is known as Ideal gas**

The combination of the three gas laws (Boyle's law, Charles' and Avogadro law) give a single equation which is known as I**deal gas equation.**

According to Boyle's law: $V \propto \frac{1}{P}$ (At constant T and n)

According to Charles' Law: $V \propto T$ (At constant p and n)

According to Avogadro Law: $V \propto n$ (At constant p and T)

Combining these $V \propto \frac{nT}{P}$

$V = \frac{R\,nT}{P}$, $pV = nRT$, R is the universal gas constant

1. L atm/K/mol ---- 0.0821

2. L bar/K/mol ---- 0.08314 (8.314×10^{-2})

3. Pa m /K/mol ---- 8.314

4. J/K/mol ---- 8.314

Combined Gas Law

From ideal gas equation PV = nRT, that is $\frac{PV}{T} = nR$ (n and constant)

so $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

5) Dalton's Law of Partial Pressures

- *This law states that at constant temperature, the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of the component gases.*

The partial pressure of a gas in a mixture of gases is the pressure that the gas would exert, when it alone occupies the whole volume.

Mathematically,

$P_{Total} = P_1 + P_2 + P_3 + \ldots\ldots P_n$ (at constant T, V)

where P_{Total} is the total pressure exerted by the mixture of gases and P_1, P_2, P_3 etc. are partial pressures of gases.

Application of Dalton's law:

Dalton's law can be used to calculate the pressure of a gas collected over water surface. Here the gas is always moist. Therefore, pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas.

Pressure exerted by saturated water vapour is called ***aqueous tension****.*

<u>Partial pressure in terms of mole fraction</u>

Consider three gases at constant temperature T and constant volume V, exert partial pressures P_1, P_2 and P_3.

From ideal gas equation, $P = n\frac{RT}{V}$

So, $P_1 = n_1 \frac{RT}{V}$, $P_2 = n_2 \frac{RT}{V}$ and $P_3 = n_3 \frac{RT}{V}$

So $P_{total} = P_1+P_2+P_3$

$$= n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$= (n_1+n_2+n_3) \frac{RT}{V}$$

Divide P_1 by P_{total} ---- $\frac{P_1}{P_{total}} = \frac{n_1}{n_1+n_2+n_3} = x_1$ x_1 is the molefraction of first gas

$\frac{P_1}{P_{total}} = x_1$ $P_1 = x_1.P_{total}$

similarly $P_2 = x_2.P_{total}$

$P_3 = x_3.P_{total}$

Generally $P_n = x_n.P_{total}$

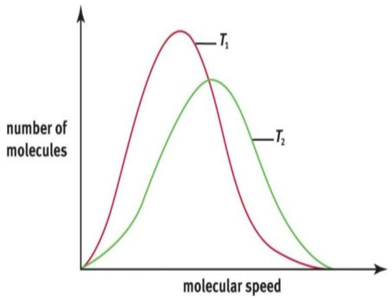
That is *Partial pressure of a gas is proportional to molefraction (Henrys law)*

KINETIC MOLECULAR THEORY OF GASES

In order to explain the gas laws theoretically Maxwell, Boltzmann, Claussius etc. put forward a theory called kinetic molecular theory of gases or microscopic model of gases. The important postulates of this theory are:

1. *Every gas contains a large number of minute and elastic particles (atoms or molecules). The actual volume of the molecules is negligible compared to the volume of the gas.*
2. *There is no force of attraction between the gas particles.*
3. *The particles of a gas are in constant and random motion in straight line. During this motion they collide with each other and also with the walls of the container.*
4. *The pressure of a gas is due to the wall collisions of the particles.*
5. *All collisions are perfectly elastic. i.e. the total energy of particles before and after collisions remains the same.*
6. *At any particular time, different particles of a gas have different speed and hence different kinetic energy.*
7. *The average kinetic energy of gas molecules is directly proportional to absolute temperature.*

Maxwell-Boltzmann Distribution of molecular speeds

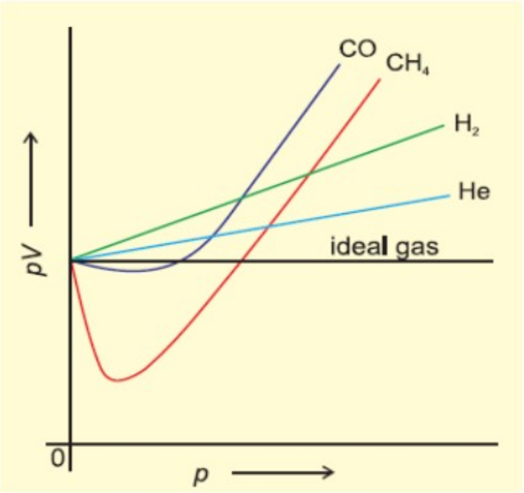


The following conclusions are obtained from the graph:

1. The number of molecules having very low and very high speed is very small.
2. Most of the molecules have a particular speed called most probable speed (u mp) which denotes the maximum in the curve.
3. On increasing the temperature, the curve broadens and the u mp increases.
   The speed distribution also depends on mass of molecules. At a constant temperature, heavier gas molecules have slower speed than lighter gas molecules.

Behavior of real gases – Deviation of real gases from ideal behavior

Real gases do not obey ideal gas equation at all conditions of temperature and pressure.
This can be understood from the PV against P graphs for different gases.
For ideal gases, PV is constant for any pressure. So the graph obtained is a straight line parallel to the pressure axis (X – axis). For H_2 and He, PV increases with increase of pressure. But for CO and CH_4 , the value of PV first decreases, reaches a minimum value and then increases.



PV vs P graph

From the graph it is clear that all gases behave ideally at low pressure. As the pressure increases the deviation from ideal behaviour also increases.

The deviation from real gases from ideal behaviour is due to two wrong assumptions of kinetic theory of gases. They are:

1. **The actual volume of the molecules is negligible compared to the volume of the gas.**
   If this assumption is true , then the Ideal gas and real gas curve will coincide
2. **There is no force of attraction between the gas Particles.**
   If this assumption is true , then A gas will never liquefy

These two assumptions become wrong at high pressure and low temperature. When the pressure increases, the volume of the gas decreases. Then the volume of the gas molecule is also considered. At this condition, there arises inter molecular forces of attraction.

Thus real gases obey ideal gas equation at low pressure and high temperature. Or, real gases deviate from ideal behaviour at high pressure and low temperature.

By considering the above two assumptions, van der Waal proposed an equation, which is applicable to real gases. The equation is known as **van der Waal's equation** and is given as:

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

(a, b are van der waals constants)
a – measure of inter molecular force

The deviation from Idea behavior can be measured in terms of compressibility Factor

$$Z = \frac{pV}{nRT}$$

At very low pressure $z = 1$ – Shows Ideal behavior
At high pressure $z > 1$ – Difficult to compress

Boyle Temperature or Boyle Point

The temperature at which real gases obey ideal gas equation over an appreciable range of pressure is called Boyle temperature or Boyle point. It depends on the nature of the gas.

Liquifaction of gases

Gases can be liquefied by applying pressure at low temperature.

- *The temperature below which a gas can be liquefied by the application of pressure is called* ***Critical Temperature (T_c).***
- *The pressure that must be applied at the critical temperature to liquefy a gas is called* ***Critical Pressure (P_c).***
- *The volume of 1 mole of a gas at its critical temperature and critical pressure is called* ***Critical Volume (V_c).***
- ***T_c, P_c and V_c are called Critical constants.***
- A gas below its critical temperature can be liquefied by applying pressure and is called the **vapour of the gas.**

THE LIQUID STATE

1. Vapour pressure

- In a liquid, all the molecules do not have the same energy. The molecules having higher energy are escaped to vapour phase. This process is called **evaporation**.
- As the density of the vapour increases the molecules collide with each other and so their energy decreases and returns to the liquid state. This process is called **condensation**.
- After some time, the rate of evaporation becomes equal to rate of condensation and the two processes attain equilibrium. At this condition, the pressure exerted by the vapour is called **vapour pressure**.
  It is defined as the pressure exerted by the vapour in equilibrium with its own liquid.
- It depends on the **nature of the liquid and the temperature**.
  As the temperature increases, the vapour pressure also increases.

2. Boiling Point

The vapour pressure of a liquid increases with temperature. At a particular temperature, the **vapour pressure becomes equal to atmospheric pressure**. At this temperature, the liquid boils. This temperature is called **boiling point.**

“ The temperature at which vapour pressure become equal to atmospheric press”

- *At 1 atm pressure the boiling point is called* ***normal boiling point.***
- *If pressure is 1 bar then the boiling point is called* ***standard boiling point of the liquid.***

The normal boiling point of water is 100 °C (373K), its standard boiling point is 99.6 °C (372.6 K).

At high altitudes (heights) atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures than at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food.

As depth increases, the atmospheric pressure also increases. So water boils at a higher temperature in a mine than at sea level.

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first there is a clear boundary between liquid and vapour phase because liquid is denser than vapour. As the temperature increases more and more molecules go to vapour phase and density of vapours rises. At the same time liquid becomes less dense. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called critical temperature. At critical temperature boiling does not occur.

3. Surface Tension

It is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid.

- It is denoted by Greek letter γ (Gamma). Its SI unit is $N\,m^{-1}$.

The energy required to expand the surface of a liquid by unit area is called surface energy.

- Its SI unit is Jm^{-2} .

Every liquid tries to reduce their energy by decreasing the surface area. So liquid drops assume spherical shape.

Sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid become rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass.

- The magnitude of surface tension of a liquid depends on the **attractive forces between the moleculesand the temperature.**
- When the attractive forces are large, the surface tension is large.
- As temperature increases, surface tension decreases.
- The phenomenon like rise (or fall) of a liquid in a capillary tube (Capillary rise/depression) is due to surface tension.

4. Viscosity

When a liquid flows over a fixed surface, we can assume that there are a large number of layers.

- The layer of molecules which is in contact with the surface is **stationary**.
- The velocity of upper layers increases as the distance of layers from the fixed layer increases.
- *This type of flow in which there is a regular change of velocity in passing from one layer to the next is called* ***laminar flow.***

Viscosity is a measure of internal resistance offered by the different layers of a liquid. (Resistance to flow)

If the velocity of the layer at a distance dz is changed by a value du, then velocity gradient is given by the amount **$\frac{du}{dz}$.**

A force is required to maintain the flow of layers. This force is proportional to the **area of contact of layers** and **velocity gradient**

i.e.

$f \alpha A$ (Where A is the area of contact).

$f \alpha \frac{du}{dz}$ (Where $\frac{du}{dz}$ is the velocity gradient. i.e. the change in velocity with distance)

or,

$$f \alpha A.\frac{du}{dz}$$

or,

$$f = \eta.A.\frac{du}{dz}$$

The proportionality constant ‘ η ’ is called **coefficient of viscosity**.

It is defined as the force when velocity gradient and the area of contact are unity.

Thus ‘ η ’ is measure of viscosity.

- SI unit of viscosity coefficient is **N s m $^{-2}$** or **pascal second (Pa sec)**.
- In cgs system the unit of coefficient of viscosity is **poise.**

1 poise = 1 g cm $^{-1}$ s $^{-1}$ = 10 $^{-1}$ kg m $^{-1}$ s $^{-1}$.

- Greater the viscosity, the more slowly the liquid flows. i.e. viscosity is inversely proportional to fluidity.

The presence of Hydrogen bonding and van der Waals forces, increases viscosity.

- Glass is a very viscous liquid. So it has a tendency to flow though very slightly. Hence the windowpanes of old buildings are thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature, molecules have high kinetic energy and can overcome the intermolecular forces.