

**Ideal Gas Law** :- The ideal gas law is the equation of state of a hypothetical ideal gas. It is a good approximation of the behaviour of many gases under many conditions, although it has several limitations.

**Boyle's Law** :- states that for a given mass of gas held at a constant temperature the gas pressure is inversely proportional to the gas volume.

**Charles Law** :- states that for a given fixed mass of gas held at a constant pressure the gas volume is directly proportional to the gas temperature.

**Ideal Gas Law** :- The ideal gas law states that the product of the pressure and the volume of one gram molecule of an ideal gas is equal to the product of the absolute temperature of the gas and the universal gas constant.  $PV=nRT$  where,

P is the pressure.

V is the volume.

n is the amount of substance.

R is the ideal gas constant.

#### **Derivation of the Ideal Gas Law :-**

The ideal gas law is derived from the observational work of Robert Boyle, Gay-Lussac and Amedeo Avogadro. Combining their observations into a single expression, we arrive at the Ideal gas equation, which describes all the relationships simultaneously.

The three individual expressions are as follows:

#### **Boyle's Law**

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

#### **Charles's Law**

$$V \propto T$$

#### **Avagadro's Law**

$$V \propto n$$

Combining these three expressions, we get

$$V = \frac{RnT}{P} = \frac{nRT}{P}$$

The above equation shows that volume is proportional to the number of moles and the temperature while inversely proportional to the pressure.

This expression can be rewritten as follows:

Multiplying both sides of the equation by P to clear off the fraction, we get

$$PV = nRT$$

The above equation is known as the ideal gas equation.

#### **Properties of ideal gases :-**

- An ideal gas can not be liquefied because the gaseous molecule has no intermolecular attraction.
- The coefficient of thermal expansion( $\alpha$ ) depends on the temperature of the gases and does not depend on nature.
- The coefficient of compressibility( $\beta$ ) similarly depends on the pressure and will be the same for all gases.

- When pressure is plotted against volume at a constant temperature a rectangular hyperbola curve is obtained according to Boyle's law.
- When PV is plotted against pressure at a constant temperature a straight line parallel plot is obtained.
- If the ideal gas passes through a porous plug from higher pressure to lower pressure within the insulated enclosure, there will be no change in the specific heat or temperature. This confirms that the ideal gases have no intermolecular attraction.

#### **Properties of real gases :-**

- Real gas could be liquefied because the gaseous molecule has the property of intermolecular attraction which helps to coalesce the molecule .
- The coefficient of thermal expansion ( $\alpha$ ) depends on the nature of the gaseous molecule .
- The coefficient of compressibility (P) was also found to depend on the nature of the gases .
- When pressure is plotted against volume a rectangular hyperbola curve is obtained only at a high temperature above the critical temperature.
- But a temperature below the critical temperature ( $T_c$ ), the molecule can be liquefied after certain pressure depends on temperature. Liquid and gas can be indistinguishable properties in the critical point of the gases. When PV is plotted against pressure for real or Van der Waals gases, the Amagat curve is obtained.
- Real gases pass through porous plugs from higher pressure to lower pressure within the insulated enclosure, there occurs a change of temperature.
- Real gases have intermolecular attraction and when expanded, the molecules have to spend more kinetic energy to overcome intermolecular attraction. Therefore, the temperature drops down.

#### **What is Critical Pressure ?**

The critical pressure of a substance is the pressure that must be applied in order to liquefy that substance at its critical temperature. For example, 217.7 atmospheres of pressure must be applied to water in order to liquefy it at its critical temperature (which is 647.09 Kelvin).

#### **Define Critical Temperature ?**

Critical temperature ( of a substance) can be defined as the highest possible temperature value at which the substance can exist as a liquid. At temperatures

above the critical temperature of a given gaseous substance, it can no longer be liquified, regardless of the amount pressure applied to it.

### Consequences of the Absorption of Light :-

- Light is a form of energy. According to the principle of photochemical activation, only that part of the light which is absorbed by any system can cause photochemical change or reaction. However, it is not essential that every time, the energy which is absorbed by any system can bring about a photochemical reaction. Absorption of light means absorption of radiation energy. Absorption of radiation energy by a substance may lead to the following changes:
- **Thermal Change :-** The kinetic energy of the molecules may be increased giving rise to an increase in temperature. i.e., heat will be generated.
- **Excitation :** The internal energy of the molecules or atoms may be raised. This will result in elevating the electrons to higher energy levels. In spectroscopic terminology, it is assumed that the atoms or molecules are raised from the ground state energy levels to the excited state energy levels.
- **Dissociation :** The molecule breaks down to form smaller molecules, atoms or free radicals. Excitation and dissociation may occur simultaneously.
- **Emission :** Part of the absorbed radiation may be re-emitted giving rise to fluorescence or phosphorescence.
- The first of the four processes are not important when visible and ultraviolet light are considered. When the light of shorter wavelengths is used, in addition to the above processes ionisation and physical interaction of the photons and matter become also prominent.

**Debye law of the strong electrolyte :-** Debye-Hückel limiting law that depicts the behaviour of strong electrolytes. The non-ideal behaviour of strong electrolytes, his mathematical treatment considers that each ion is encompassed by an ionic cloud of oppositely charged ions, which retards the motion of ions in the medium. The theory provides a method for calculation of activity coefficients, understanding of diffusion in ionic media, change in the rate of ionic reactions upon addition of salts, and biochemical reactions.

**Debye Huckel Law :-** In the year 1926, Debye and Huckel modified the theory and Onsager modified it further but all the postulates and original theory were retained. It was assumed that the electric field causes the distortion of the charge cloud from the spherical symmetry. After taking this into account, together with some specific requirements of moving ions like viscosity and electrophoretic effects. Onsager helped to derive a theoretical expression to give an empirical relation that is called Kohlrausch's law for the molar conductivity  $\lambda_m$ .

$$\lambda_m = \lambda^\circ_m - Kc\sqrt{c}$$

$\lambda^\circ_m$  is the limiting molar conductivity, K is an empirical constant and c is the electrolyte concentration. The limit of the infinite dilution means limiting. Onsager expressed it through-

$$\lambda_m = \lambda^\circ_m - (A + B\lambda^\circ_m)c\sqrt{c}$$

Here, A and B are constants that are dependent only on known quantities like temperature, charges on the ions, and the dielectric constant and viscosity of the solvent. This is known as the Debye-Huckel-Onsager equation.

### Kinetic Theory of Gases Postulates :-

The kinetic theory of gas postulates is useful in the understanding of the macroscopic properties from the microscopic properties.

- Gases consist of a large number of tiny particles (atoms and molecules). These particles are extremely small compared to the distance between the particles. The size of the individual particle is considered negligible and most of the volume occupied by the gas is empty space.
- These molecules are in constant random motion which results in colliding with each other and with the walls of the container. As the gas molecules collide with the walls of a container, the molecules impart some momentum to the walls. Basically, this results in the production of a force that can be measured. So, if we divide this force by the area it is defined to be the pressure.
- The collisions between the molecules and the walls are perfectly elastic. That means when the molecules collide they do not lose kinetic energy. Molecules never slow down and will stay at the same speed.
- The average kinetic energy of the gas particles changes with temperature i.e. the higher the temperature, the higher the average kinetic energy of the gas.
- The molecules do not exert any force of attraction or repulsion on one another except during collisions.

### Deviation of real gases from ideal behaviour :-

All the gas molecules obey the ideal gas laws only under special conditions of low pressures and high temperatures. The deviations of the real gases, from the ideal gas behaviour, is traced mainly to wrong or incorrect assumptions in the postulates.

They are,

- The particles are point charges and have no volume: Then, it should be possible to compress the gases to zero volume. But, gases cannot be compressed to zero volume indicates that particles do have volume though small and cannot be neglected.
- Particles are independent and do not interact: Particles do interact depending upon their nature. The interactions affect the pressure of the gas. Volume and the interactions differ from gas to gas. Many gas laws have been developed for the real gases incorporating correction factors in the pressure and volume of the gases.

### What is Van der Waals equation ?

Van der Waals equation is given by modifying ideal gas law in 1873. He put the reasons for the deviations of the real gases from ideal behaviour. Van der Waals proposed that the two postulates used in the kinetic theory of gas molecules are not applicable to real gases. These two assumptions are

- The gas molecules are point masses or practically they have no volumes.
- There is no intermolecular attraction in the gas molecules.
- Van der Waals introduced the size effect and the intermolecular attraction effect of the real gases. These two effects or factors in the Van der Waals equation are arising because he considered the size and intermolecular attraction among the gas molecules.

### Equation :-

Van der Waals equation is an equation relating the relationship between the pressure, volume, temperature, and amount of real gases. For a real gas containing 'n' moles, the equation is written as;

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

Where, P, V, T, n are the pressure, volume, temperature and moles of the gas. 'a' and 'b' constants specific to each gas. The equation can further be written as;

1. Cube power of volume:

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

2. Reduced equation (Law of corresponding states) in terms of critical constants:

$$\left(\pi + \frac{3}{\varphi^3}\right)(3\varphi - 1) = 8\tau : \text{ where } \pi = \frac{P}{P_c}, \varphi = \frac{V}{V_c} \text{ and } \tau = \frac{T}{T_c}$$