Chemistry Study Materials for Class 11 (NCERT Based Notes of Chapter- 05) Ganesh Kumar Date: -22/11/2020

States of Matter

Maxwell-Boltzmann Distribution of molecular speeds

According to Kinetic molecular theory of gases, the molecules of a gas are in continuous random motion and they collide with each other. So the speed and the kinetic energy of the molecules are different at any particular time. Thus we can obtain only an average value of speed of molecules.

The distribution of molecular speeds was first studied by Maxwell and Boltzmann by applying the theory of probability. This is known as *Maxwell-Boltzmann Distribution of molecular speeds*. They plotted a graph between numbers of molecules having different speeds against molecular speeds as follows:



The following conclusions are obtained from the graph:

- 1. The number of molecules having very low and very high speed is very small.
- 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. Average speed (u_{av}): It is the arithmetic mean of the different speeds of molecules in a given sample of gas. If there are 'n' molecules in a sample and u₁, u₂, u₃ u_n are their individual speeds, then average speed is given by,

$$u_{av} = \sqrt{\frac{u_1 + u_2 + u_3 + \dots + u_n}{n}}$$

2. Root mean square (rms) speed: It is the square root of the mean of the squares of the different speeds of the gas molecules. It is given by:

$$u_{rms} = u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2$$

 Most probable speed (u_{mp}): It is the speed possessed by maximum number of gas molecules.

The three types of molecular speeds are related as: $u_{rms} > u_{av} > u_{mp}$. The ratio between the three speeds is:

 u_{mp} : u_{av} : $u_{rms} = 1$: 1.128: 1.224

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.

The deviation from ideal behaviour can be measured in terms of compressibility factor Z, which is the ratio of product PV and nRT.

Mathematically,
$$Z = \frac{PV}{nRT}$$

For ideal gas Z = 1 at all temperature and pressures.

So the graph of Z vs P will be a straight line parallel to pressure axis.

For real gases value of Z deviates from unity.





Z vs P graph for real & ideal gases

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.
- 2. There is no force of attraction between the gas particles.

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, Vander Waal proposed an equation, which is applicable to real gases.

The equation is known as Vander Waal's equation and is given as:

$(P + n^2 a/V^2) (V - nb) = nRT$

Where P is the pressure of the gas, V is the volume, R is the universal gas constant, T is the absolute temperature, n is the no. of moles, 'a' and 'b' are called Vander Wall's constants, 'a' is a measure of magnitude of inter molecular attractive forces within the gas and 'b' is related to the volume of the particles. The unit of 'a' is L^2 atm mol⁻² and that of 'b' is L mol⁻¹. The term n^2a/V^2 is related to pressure correction and term 'nb' is related to volume correction.

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.
