

## Kinetic theory of gases

According to the kinetic theory of gases, gases are made up of various smallest particles called molecules. These molecules are always in motion along a straight line in all directions with the different velocities. They collide among themselves as well as with the wall of the vessel. Due to the collisions, velocities of the molecules and the direction of motion always change. As soon as the molecules collide with the walls, there is change in their momentum. The rate of change of momentum is the force exerted by the gas per unit area of the wall. The force per unit area measures the pressure of the gas.

### Assumptions of Postulates :-

- (i) Gases are made up of smallest particles called molecules. These molecules are perfectly elastic.
- (ii) The dimensions of molecules are negligible.
- (iii) The molecules are always in motion in all directions with different velocities.
- (iv) The molecules always collide among themselves and with the walls of the vessel.
- (v) Among the molecules, there is neither force of attraction nor force of repulsion.
- (vi) Between two collisions, the molecules move with uniform velocity in a straight line. The distance between two collisions is called free path.

The mean of the different consecutive free paths of the different molecules is called mean free path.

(vii) The time taken in collision is neglected in comparison to the time taken in travelling a free path by the molecule.

(viii) The pressure of the gas in all directions is the same.

(ix) At the same temperature and same pressure all the gases contain same no. of molecules in a certain volume.

### Vander Waal's equation of state

While deriving the perfect gas equation  $PV = RT$  on the basis of kinetic theory, it was assumed that

- (i) the size of the molecule of the gas is negligible
- (ii) the forces of inter-molecular attraction are absent. But in actual practice, at a high pressure, the size of the molecules of the gas becomes significant and cannot be neglected in comparison with the volume of the gas. Also, at high pressure, the molecules come closer and the forces of intermolecular attraction are appreciable.

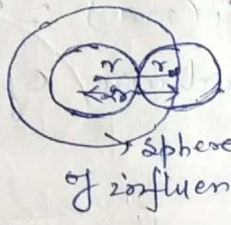
Therefore correction should be applied in the gas equation

i) Correction for Pressure :- A molecule in the interior of a gas experiences of attraction in all directions and the resultant cohesive force is zero. A molecule near the walls of the container experiences a resultant force inwards. Due to this reason, the observed pressure of the gas is less than the actual pressure. The correction for pressure  $p$  depends upon (i) the no. of molecules striking unit area of the walls of the container per second (ii) the no. of molecules present in the given volume. Both these factors depend on the density of gas.

∴ correction for pressure  $p \propto p_2 \propto \frac{1}{V^2}$   
 (ii) Correction for volume ∴  $p = \frac{a}{V^2}$   
 ∴ Correct pressure =  $P + p = \left(P + \frac{a}{V^2}\right)$

The molecules have the finite size and the actual space for the movement of the molecules is less than the volume of the vessel. The molecules have the sphere of influence around them and due to this factor, the correction for volume is  $b$  where  $b$  is approximately four times the actual volume of the molecules. Therefore the corrected volume of the gas =  $(V - b)$ .

Let the radius of one molecule is  $r$   
 The volume of the molecule ( $x$ ) =  $\frac{4}{3} \pi r^3$



Each molecule is surrounded by its sphere of influence and radius of it is equal to two times of the radius of each molecule.

The volume of the sphere of influence of each molecule,  $S = \frac{4}{3} \pi (2r)^3 = 8x$

Consider a container of volume  $V$ . Let  $n$ -molecules are allowed to enter one by one.

~~The~~ volume available for the first molecule =  $V$

~~The~~ volume available for the second molecule =  $V - S$

~~The~~ volume available for the third molecule =  $V - 2S$

volume available for  $n$ th molecule =  $V - (n-1)S$

Average available volume per molecule =

$$= \frac{V + (V - S) + (V - 2S) + \dots + \{V - (n-1)S\}}{n}$$

$$= \frac{1}{n} [nV - \{1 + 2 + 3 + \dots + (n-1)\}S]$$

$$= \frac{1}{n} \left[ nV - \frac{n(n-1)}{2} \cdot s \right] \checkmark$$

$$= V + \frac{s}{2} - \frac{ns}{2}$$

As the no. of molecules is very large,  $\frac{s}{2}$  can be neglected.

$$\therefore \text{Average volume} = V - \frac{ns}{2} \quad [s = 8x]$$

$$= V - \frac{n \cdot 8x}{2}$$

$$= V - 4(nx)$$

$$= V - b$$

where  $b = 4(nx) =$  four times the actual volume of the molecules.

Thus; the Van der Waals equation of state for a gas is

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