

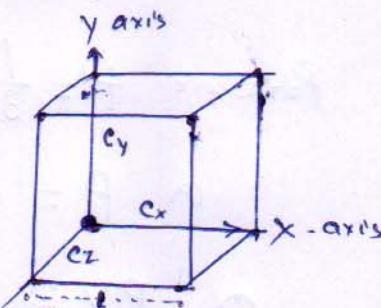
## Kinetic theory of gases: -

### Postulates of Kinetic theory of Gases

- (1) All gases are composed of a large number of very tiny particles called molecules. Molecules of a gas are alike but differ from molecules of other gases.
- (2) The volume of a gas molecule is negligible in comparison to the total volume of the gas.
- (3) Molecules of a gas are in the state of constant ~~random~~ motion in all directions and motion increases with increase of temperature.
- (4) Molecules of a gas have kinetic energy only. They do not have potential energy.
- (5) The gas molecules collide with each other and with the walls of container.
- (6) Gas molecules are small and perfectly elastic spheres and exert no force of attraction or repulsion on one another or walls of the container.  
After collision gas molecules begin to move in the opposite direction with the same velocity.
- (7) The pressure of the gas is due to collision of molecules with the inner walls of the container.
- (8) The average kinetic energy of gas molecules is directly proportional to the absolute Temperature.  
i.e.  $K.E \propto T$ .

### Derivation of Kinetic Gas Equation : -

Let a Cubical Container having length  $l$  contains  $n$  molecules of gas having mass  $m$  each of them are moving with velocity  $c$ . The velocity of the molecule is  $c_x$  along  $x$ -direction,  $c_y$  along  $y$  direction and  $c_z$  along  $z$  direction respectively  
i.e.  $c^2 = c_x^2 + c_y^2 + c_z^2$



Let us consider the gas molecule is moving along  $x$ -axis and collide with the wall and back to opposite direction with same velocity  $c_x$ , because gas molecule is perfectly elastic sphere.

Now, the change in momentum per Collision along  $x$ -axis

$$\begin{aligned}
 &= \text{Momentum before Collision} - \text{Momentum after Collision} \\
 &= mc_x - (-mc_x) \\
 &= 2mc_x
 \end{aligned} \tag{1}$$

Distance travelled by gas molecule between two successive collisions is  $2l$ .

$$\therefore \text{Number of Collision per second} = \frac{C_x}{2l} \quad \text{--- (2)}$$

$$\therefore \text{Change in momentum along } x \text{ direction Hall per second due to } \frac{C_x}{2l}$$

$$\text{Collisions} = 2m C_x \times \frac{C_x}{2l} = \frac{m C_x^2}{l} \quad \text{--- (3)}$$

$$\therefore \text{Change in momentum per second due to the collision of one gas molecule on two opposite faces along X-axis} = \frac{m C_x^2}{l} + \frac{m C_y^2}{l} + \frac{m C_z^2}{l} = \frac{2m C^2}{l}$$

Therefore the rate of change in momentum due to the collision per molecule on six faces of the cube =  $\frac{2m C_x^2}{l} + \frac{2m C_y^2}{l} + \frac{2m C_z^2}{l}$

$$= \frac{2m}{l} (C_x^2 + C_y^2 + C_z^2)$$

$$= \frac{2m C^2}{l} \quad \text{--- (4)}$$

$$\text{Therefore the rate of change in momentum for } n \text{ molecules} = \frac{2m n C^2}{l}$$

According to Newton's 2nd law, the rate of change of momentum is equal to force

And we also know that force per unit area is the Pressure of gas

$$\text{Hence, force} = \frac{2m n C^2}{l}$$

$$\text{and area} = 6l^2$$

$$\therefore \text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{2m n C^2}{6l^2}$$

$$= \frac{2m n C^2}{3 \cdot 6 l^3} \quad [\because l^3 = V]$$

$$\therefore \text{Pressure } P = \frac{1}{3} \frac{m n C^2}{l^3} = \frac{1}{3} \frac{m n C^2}{V} \quad \text{--- (5)}$$

$$\text{or } P = \frac{1}{3} \frac{M C^2}{V} \quad [\because m n = M]$$

$$\text{or } P V = \frac{1}{3} M C^2 \quad \text{--- (6)}$$

The above equation is called  
the Kinetic gas equation.

## Relation between Kinetic Energy and Temperature of a gas.

The relationship between Kinetic Energy and Temperature can be derived from the Kinetic gas equation.

We know from Kinetic gas equation

$$PV = \frac{1}{3} mn c^2 \quad \dots \textcircled{1}$$

$$\text{or } PV = \frac{2}{3} \times \frac{1}{2} mn c^2$$

$$\text{or, } PV = \frac{2}{3} \times \frac{1}{2} Mc^2 \quad \dots \textcircled{2} \quad [ \because mn = M \\ M = \text{mass of the gas} ]$$

$$\therefore PV = RT \quad (\text{For 1 mol of gas}) \quad \textcircled{3}$$

From eqn  $\textcircled{2}$  and  $\textcircled{3}$

$$RT = \frac{2}{3} \times \frac{1}{2} Mc^2$$

$$RT = \frac{2}{3} \times K.E.$$

$$\therefore K.E. = \frac{3}{2} RT$$

$$[\because K.E. = \frac{1}{2} Mc^2]$$

Where  $M$  is mass  
of C is velocity

$$\text{or } K.E. \propto T \quad [\text{Where } \frac{3}{2} R \text{ is constant}]$$

So, It is clear that K.E. of translation of an ideal gas is independent of the nature of the gas and its pressure. It depends only upon the temperature of the gas.

**Derivation of the gas-laws on the basis of Kinetic gas equation.**

(1) Derivation of the Boyle's Law:-

According to Kinetic theory of gases, the average Kinetic energy ( $\frac{1}{2} mn c^2$ ) is directly proportional to absolute Temperature (T)

$$\text{i.e. } \frac{1}{2} mn c^2 = RT$$

$$\frac{3}{2} \times \frac{1}{3} mn c^2 = RT$$

$$\frac{3}{2} PV = RT$$

$$[\because \frac{1}{3} mn c^2 = PV]$$

$$\text{or } PV = \frac{2}{3} RT$$

Therefore, the product of Pressure and Volume is a Constant at a Constant temperature,

i.e

$$PV = \text{constant}$$

or  $P \propto \frac{1}{V}$  at Constant Temperature T

This is Boyle's law

## 2. Derivation of Charles' Law from Kinetic Gas Equation.

We know,

$$PV = \frac{2}{3}RT$$

$$\text{or } V = \frac{2}{3} \cdot \frac{R}{P} \cdot T$$

$$V = \frac{2R}{3P} \cdot T$$

If Pressure P is constant,

then  $V \propto T$

## 3. Avagadro's Law Derivation:-

When two gases have the same pressure and volume,  
then  $P_1 V_1 = P_2 V_2$

We know from Kinetic gas eq<sup>n</sup>  $PV = \frac{1}{3} m n c^2$

Applying Kinetic gas eq<sup>n</sup>

$$\frac{1}{3} m_1 n_1 c_1^2 = \frac{1}{3} m_2 n_2 c_2^2$$

$$\frac{2}{3} \cdot \frac{1}{2} m_1 n_1 c_1^2 = \frac{2}{3} \cdot \frac{1}{2} m_2 n_2 c_2^2$$

$$\text{or } \frac{1}{2} m_1 n_1 c_1^2 = \frac{1}{2} m_2 n_2 c_2^2 \quad \text{--- (1)}$$

When the temperature of these two gases is also the same,  
then their Kinetic energy per mole will also be the same

$$\text{i.e. } \frac{1}{2} m_1 c_1^2 = \frac{1}{2} m_2 c_2^2 \quad \text{--- (2)}$$

Dividing equation (1) by (2)

$$\text{We get, } n_1 = n_2$$

Thus the equal volumes of all gases under the same  
conditions of temperature and pressure have the same number  
of moles. This is Avagadro's Law.

(4) Graham's Law of Diffusion: —

If  $M$  is the total mass of a gas, then the Kinetic gas equation,

$$PV = \frac{1}{3} m n c^2 \text{ reduces to}$$

$$PV = \frac{1}{3} M c^2$$

$$\text{or } c^2 = \frac{3PV}{M} = \frac{3P}{\frac{M}{V}} = \frac{3P}{D} \quad \left[ \frac{M}{V} = \text{Density} \right]$$

$$\text{or } c^2 = \frac{3P}{D}$$

$$c = \sqrt{\frac{3P}{D}} \quad (1)$$

Where  $D$  is the density of the gas, we know that the rate of diffusion ( $\tau$ ) of a gas varies with the mean velocity ( $c$ ),  $(\because \tau \propto c^2)$

from the above eqn (1)

$$c \propto \sqrt{\frac{1}{D}} \quad \text{where } P \text{ is constant}$$

Thus the rate of diffusion of a gas is inversely proportional to the square root of density of the gas at constant pressure.

This is the Graham's law of diffusion.

(5) Dalton's Law of Partial Pressure: —

Let  $n_1$  molecules each of mass  $m_1$  of a gas A are taken in a container of volume  $V$ . Then the pressure  $P_A$  for the gas is given by Kinetic gas Eqn.

$$P_A = \frac{m_1 n_1 c_1^2}{3V}$$

Similarly for gas B,

$$P_B = \frac{m_2 n_2 c_2^2}{3V}$$

If both the gases are present in  $3V$  the same containers, then total pressure,

$$P = \frac{m_1 n_1 c_1^2}{3V} + \frac{m_2 n_2 c_2^2}{3V} \\ = P_A + P_B$$

Similarly for  $n$  gases, the total pressure,

$$P = P_A + P_B + P_C + \dots + P_n$$

This is Dalton's Law of Partial Pressure.

## Ideal gas and real gas

At very low pressures and very high temperatures, the gases tend to obey the gas laws.

A gas which obeys the gas laws under all circumstances has been named as ideal or perfect gas, while a gas which does not obey the gas laws is known as a real gas.

The gas which obeys the equation of state  $PV = nRT$  strictly is called ideal gas.

Gases which do not obey the equation of state  $PV = nRT$  are called real gases.

All gases are real and no one is ideal in true sense.  
Other differences may be mentioned below

1. Equation of State i.e.  $PV = nRT$

ideal gases strictly obey

Real gases do not obey

2. Compressibility factor  $Z$ . ( $Z = \frac{PV}{nRT}$ )

Compressibility factor  $Z = 1$  for ideal gases  
" " "  $Z \neq 1$  for Real gases

3. Molar Volume -

Molar Volume is 22.4 for ideal gases

Molar volume is not exact 22.4 for real gases

4. Intermolecular attraction :-

Inter molecular attraction do not exist in ideal gases

Inter molecular attraction exist in Real gases

5. PV Vs P Curve :-

In ideal gas PV Vs P Curve is Horizontal st. line.

In Real gas PV Vs P Curve is not so.

6. PV Vs Z Curve :-

In ideal gas PV Vs Z Curve is Horizontal st. line.

But In Real gas PV Vs Z Curve is not so.

## Causes of deviation from ideal behaviour

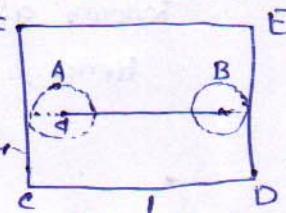
### and Vander Waals' Equation

Vander Waals observed that the failure of ideal behaviour i.e.  $PV = nRT$  relation is due to neglect of the following factors:-

(a) Volume of gas molecules is negligible by comparison with the total volume of the gas.

(b) The gas molecules exert no attraction upon one another.  
So Vander Waals made necessary correction by ideal gas.

(A) Volume Correction:- Consider a molecule A of a gas in a closed space having volume V, moving parallel to CD, suppose it strikes the face of the vessel DE at B, F and come back. Now  $CD = l$ , the distance travelled by the molecule is not  $2l$ , but it is  $2(l-d)$ . Where d is diameter of the molecule.



If we consider the motion of all the molecules in this way, we find that effective volume in which the molecules are free to move is less than the total volume.

When the pressure is increased, there is decrease but in the whole volume but a part of it, (i.e.  $V-b$ ), where  $b$  is the volume of the portion which cannot be compressed.

This constant  $b$  is four times the total volume of the molecules and not equal to the volume occupied by the molecules because,

(i) When all the molecules are moving about, they obstruct each other's motion much more than if some of them were at rest.

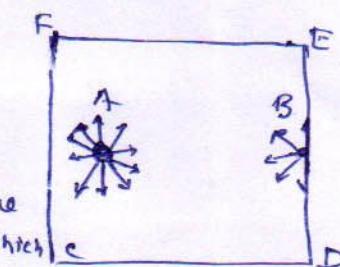
(ii) Each molecule is surrounded by its sphere of influence, radius of which is greater than the radius of the molecule within which no other molecule can penetrate.

The factor ' $b$ ' is known as effective volume, co-volume, or vibratory volume.

(B) Pressure Correction:- If we consider the molecule A inside the vessel, it is attracted by other molecules in all directions with the same force and net force on it is zero.

But when it strikes the wall of the vessel it is pulled back by other molecules.

Its velocity and hence the momentum with which it strikes the wall would be less than the momentum with which it strikes the wall in the absence of the force of attraction. Naturally, when the momentum becomes less the pressure decreases.



It is evident that if we double the number of molecules per cc. of the gas, the decrease in pressure will be four times. It is due to the fact that the decrease in pressure is proportional to-

(i) The number of attracting molecules per unit volume.

(ii) The number of attracted molecules striking a unit area of the walls of containing vessel per unit time.

Both the above factors are proportional to the number of molecules per cc. or density of the gas.

$\therefore$  Decrease in Pressure,  $P \propto (\text{Density of the gas})^2$

$$\propto \frac{1}{V^2}$$

$$P = \frac{a}{V^2}$$

where 'a' is the proportionality constant. The factor,  $\frac{a}{V^2}$  is known as cohesive pressure.

Hence, Real Pressure = Observed Pressure + decrease in Pressure

$$= P + \frac{a}{V^2}$$

This value of real pressure should be substituted in the perfect gas equation. Now substituting  $(V-b)$  for V and  $(P + \frac{a}{V^2})$  for P, we have,

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

For n moles,

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

The unit of 'a' and 'b' is the factor  $\frac{a}{V^2}$  is added to P, hence dimension of  $\frac{a}{V^2}$  will be the dimension of P -

$$\therefore P = \frac{n^2 a}{V^2}$$

$$\text{or } a = \frac{PV^2}{n^2} = \frac{\text{Atmosphere} \times \text{litre}^2}{\text{mol}^2} = \text{atm} \cdot \text{litre}^2 \text{mol}^{-2}$$

The factor b is subtracted from V, hence the dimension of b will be the dimension of V

$$\therefore V = nb$$

$$b = \frac{V}{n} = \frac{\text{litre}}{\text{mol}} = \text{litre mol}^{-1}$$

## Limitations of Vander Waal's equation,

and equations of state regarding behaviour of real gases.

The Vander Waal's equation is successful to explain the P-V-T behaviour of real gases at high temperature and low pressure. However, when the values of  $a$  and  $b$  are substituted in Vander Waal's equation the P-V-T relationship shows a deviation when pressure is too high or the temperature is too low.

This is so, because the value of  $a$  and  $b$  vary with temperature. Several other equations of state have been proposed to express the P-V-T behaviour of real gases.

Some important equations of state are given below.

### (a) Berthelot Equation:-

The Berthelot Equation may be represented as

$$P = \frac{RT}{V-b} - \frac{a}{TV^2}$$

Here  $b$  has the same significance as in the Vander Waal's equation, but  $a$  has the dimension of Temperature.

This is particularly more accurate than Vanderwaal's equation when used to calculate molecular masses of gases.

### (b) Dieterici equation:-

$$P(V-b) = RT e^{-\frac{a}{RTV}}$$

The above Dieterici equation gives more satisfactory results at high pressure than the Vander Waal's equation.

Dieterici made allowance in his equation for the effect of intermolecular attraction on the pressure by incorporating the term  $e^{-\frac{a}{RTV}}$ .

### (c) Clausius Equation:-

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

where  $c$  is the new constant. This equation is fairly satisfactory but does not hold for all the gases.

### (d) Virial Equation:-

Virial equation may be represented as

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

This equation was developed by Karmes, Lighth and Onnes.

The Virial (meaning force) equation is in terms of volume for one mole of a gas.

In terms of Pressure, the equation is

$$PV = RT + BP + CP^2 + DP^3 + \dots$$

It expresses PV as a power series of the Pressure.

At any given temp. B, C, D etc are called 2nd, 3rd, 4th Virial Co-efficient and they are function of Temperature. Virial Constant have different values for different gases.

The 1st term RT (Also taken as A) is always Positive and Increases with rise in temperature.

The 2nd Co-efficient B is a negative at low temp. but increases (becomes more Positive) as the temp. is raised Continuously.

The temp. at which  $B = 0$  i.e  $PV = RT$  is called Boyle's Temperature. Since at this temp. Boyle's law is Valid over a wide temp-pressure. It is possible to calculate Virial Co-efficient from Inter-molecular Potential energy.

But this energy is not accurately known and the Calculation of higher Virial Coefficients is a formidable problem.

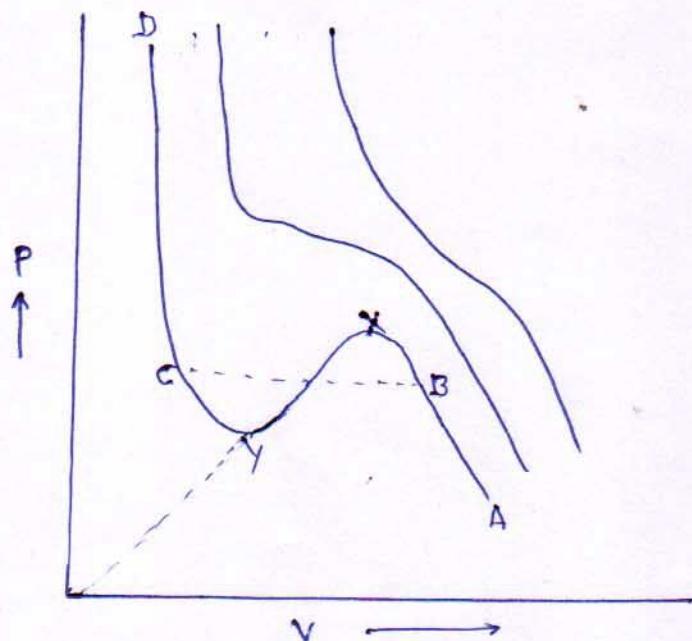
A common feature to all equations of state is that they must reduce to the ideal gas equation at low pressure:

$$P \xrightarrow{\text{Low}} 0 \quad \frac{PV}{RT} = 1$$

## Critical Constants and its relation with Vander Waal's Constant

**Critical Constants:** - A gaseous state is defined by  $P$ ,  $V$  and  $T$ . Generally one of them, particularly the temperature  $T$  is maintained constant. The curve showing the variation of Volume ( $V$ ) at constant temperature ( $T$ ) with pressure  $P$  are called Isotherms.

Andrews plotted the isotherms for  $\text{CO}_2$  at various temperatures are shown in fig. given below -



A certain Temperature Called Critical Temp  $T_c$  above which it cannot be liquefied no matter how great the pressure may be. The  $T_c$  Value for  $\text{CO}_2$  is  $30^\circ\text{C}$  and therefore above  $30^\circ\text{C}$  liquid  $\text{CO}_2$  does not at all exist. The pressure and volume at this temp. is called Critical Pressure  $P_c$  and Critical Volume  $V_c$ .

The Vander Waal's equation for real gas is given as

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

$$\text{or, } PV - bP + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Multiplying throughout by  $\frac{V^2}{P}$  we get

$$V^3 - V^2 b + \frac{aV}{P} - \frac{ab}{P} - \frac{RTV^2}{P} = 0$$

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

When  $T = T_c$  and  $P = P_c$ , then

$$V^3 - \left( \frac{b + RT_c}{P_c} \right) V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \quad \text{--- (1)}$$

At Critical Points,  $V = V_c$  or,  $V - V_c = 0$

$$(V - V_c)^3 = 0$$

$$\text{or, } V^3 - 3V^2 V_c + 3V_c^2 V - V_c^3 = 0 \quad \text{--- (2)}$$

On equating the powers of  $V$  in eq<sup>n</sup> (1) and (2) we get

$$3V_c = \frac{RT_c}{P_c} + b \quad \text{--- (3)}$$

$$3V_c^2 = \frac{a}{P_c} \quad \text{--- (4)}$$

$$\text{or, } a = 3P_c V_c^2 \quad \text{--- (5)}$$

$$V_c^3 = \frac{ab}{P_c} \quad \text{--- (6)}$$

Dividing eq<sup>n</sup> (6) by eq<sup>n</sup> (4)

$$\frac{V_c^3}{3} = b \quad \text{--- (7)}$$

$$\text{or } V_c = 3b$$

Putting this value in eq<sup>n</sup> (4), we have.

$$3 \times (3b)^2 = \frac{a}{P_c} \quad \text{--- (8)}$$

$$P_c = \frac{a}{27b^2} \quad \text{--- (9)}$$

$$\text{or } a = 27b^2 P_c$$

Putting the value of  $V_c$  and  $P_c$  in equation (3) we get

$$\begin{aligned} 3 \times 3b &= \frac{RT_c}{a/27b^2} + b \\ &= \frac{R \times 27b^2 T_c}{a} + b \end{aligned}$$

$$\text{or } 9 = \frac{R \times 27b \cdot T_c}{a} + 1$$

$$8 = \frac{27RbT_c}{a} \quad \text{or } T_c = \frac{8a}{27RbT_c} \quad \text{--- (10)}$$

$$\therefore b = \frac{8a}{27RT_c}$$

$$b' = \frac{8 \times 27 b^2 P_c}{27 R \cdot T_c}$$

$$l = \frac{8b P_c}{R T_c}$$

$$\text{or } b = \frac{RT_c}{8P_c} \quad \text{--- (11)}$$

Hence we can calculate the values of Vanderwaal's Constant 'a' and 'b' if Critical Pressure, Critical Volume and Critical Temperature i.e.,  $P_c$ ,  $V_c$  and  $T_c$  are known.

Similarly  $P_c$ ,  $V_c$  and  $T_c$  can be calculated if Vanderwaal's constant 'a' and 'b' are known.

## Law of Corresponding States

If the Values of  $P$ ,  $V$  and  $T$  be expressed as fraction of Corresponding Critical values, we get.

$$\frac{P}{P_c} = P_r, \quad \frac{V}{V_c} = V_r \quad \text{and} \quad \frac{T}{T_c} = T_r$$

Where  $P_r$ ,  $V_r$ , and  $T_r$  are called reduced Pressure, Volume, and Temperature respectively,

$$\text{therefore, } P = P_r \cdot P_c, \quad V = V_r \cdot V_c \quad \text{and} \quad T = T_r \cdot T_c$$

Replacing  $P$ ,  $V$  and  $T$  by Van der Waal's equation for real gases

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

$$\left\{ P_r \cdot P_c + \frac{a}{V_r^2 \cdot V_c^2} \right\} (V_r \cdot V_c - b) = R T_r \cdot T_c$$

On Putting the Value of Critical Constants, we have

$$\left\{ P_r \cdot \frac{a}{27b^2} + \frac{a}{V_r^2 9b^2} \right\} (V_r \cdot 3b - b) = R T_r \cdot \frac{8a}{27Rb}$$

$$\left\{ P_r \cdot \frac{a}{27b^2} + \frac{a}{9b^2 V_r^2} \right\} b (3V_r - 1) = T_r \cdot \frac{8a}{27b}$$

$$\text{so, } \left\{ \frac{P_r \cdot a}{27b} + \frac{a}{9b V_r^2} \right\} \{3V_r - 1\} = T_r \cdot \frac{8a}{27b}$$

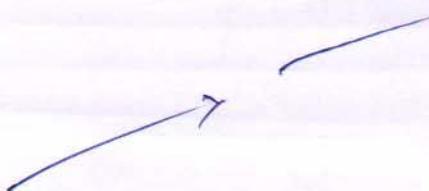
Multiplying throughout by  $27b/8a$  we have

$$(P_r + \frac{3}{V_r^2}) (3V_r - 1) = 8T_r \quad \text{--- (1)}$$

The above eqn (1) is completely free from Constants such as  $R$ ,  $a$  and  $b$ , hence this is applicable to all substances in fluid state.

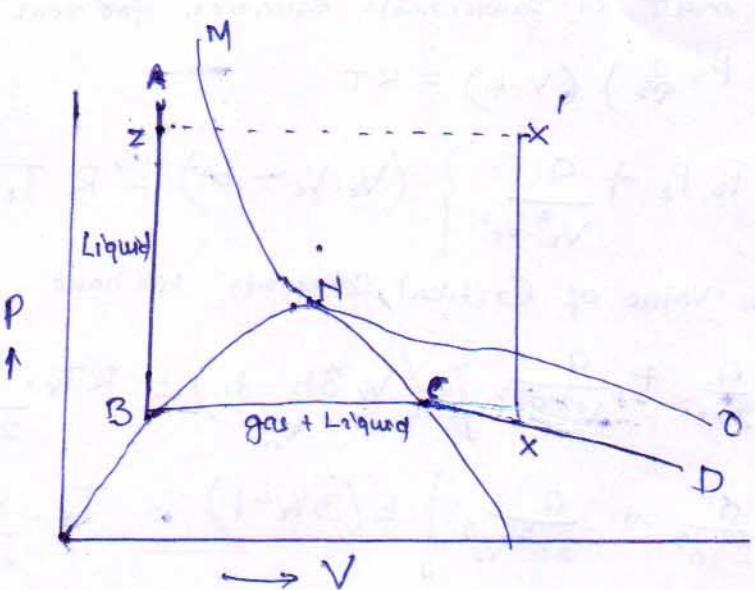
Two or more substances having identical  $P_r$ ,  $V_r$  and  $T_r$  are said to be Corresponding State. This is also called Law of Corresponding States

As b.Ps of liquids are approximately  $\frac{2}{3}$  rd of their Tc's. It means that liquids at their b.Ps are approximately in their Corresponding States.



## Continuity of States

Continuity of States: - When a gas is compressed below Critical Temperature  $T_c$ , the volume of the gas changes along DCBA. The path passes through the region where gas and liquid coexist. However, one can change a gas into liquid and vice-versa without any visible separation of one phase from the another. This is known as continuous transition of state.



If one wants to convert a certain quantity of gas at the point X, the gas at X on ABCD isotherm is heated till it goes above  $T_c$ , at a constant volume and the pressure is allowed to increase up to X, and then pressure is maintained constant while the temperature and volume are allowed to fall to Z.

The system at Z is now totally in liquid state.

This change indicates that a continuous transition takes place in the conversion. Hence the process of change from gas to liquid or from liquid to gas is continuous.



## Maxwell Boltzmann law of distribution of Molecular Velocities.

Maxwell and Boltzmann using probability consideration. They have shown that the distribution of molecular velocities depends on the temperature and molecular weight of a gas and is given by the expression,

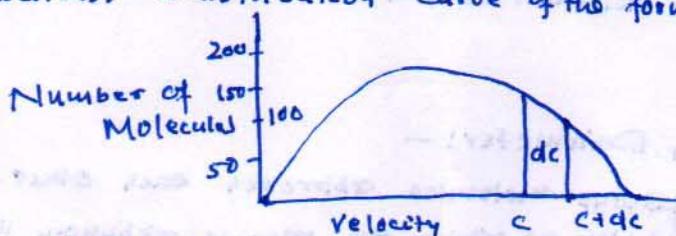
$$\frac{dn_c}{n} = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \frac{Mc^2}{2} e^{-\frac{Mc^2}{2RT}} dc$$

Where  $dn_c$  is the number of molecules out of the total number of  $n$  molecules which have velocities between  $c$  and  $c+dc$ ,  $T$  is Temperature and  $M$  is the molecular wt of the gas. The ratio  $\frac{dn_c}{n}$  gives therefore the fraction of the total number of molecules having velocities between  $c$  and  $c+dc$ .

Dividing both side the above eqn by  $dc$ , we get,

$$\frac{1}{n} \cdot \frac{dn_c}{dc} = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \frac{Mc^2}{2} e^{-\frac{Mc^2}{2RT}} c^2$$

The L.H.S. expression gives the probability of finding the molecules with the velocity  $c$ . It shows the fraction of the total number of molecules for any gas of known molecular wt. at any particular temperature is plotted against the velocities. A distribution curve of the form shown in figure is obtained



The curve shows that the fraction of molecules having velocities between  $c$  to  $c+dc$  is given by the area under the strip of the curve within the velocity range. The area between two coordinates separated by  $dc$  is clearly equal to  $\frac{dn_c}{n} dc$ , hence the area under the whole curve is equal to the total number of molecules and the height of ordinate corresponds to any velocity is virtually a measure of the fraction of the molecules which have the velocity.

The shape of the curve says that the fraction of molecules having too low or too high velocities is very small and the majority of the gas molecules have some intermediate velocity within small range of variation more or less around the peak, known as the most probable velocity.

### (A) Mean Free Path: -

Gas molecules are always in state of rapid motion. Colliding with each other. The distance travelled by a gas molecule before colliding with another molecule is called Free Path, and the average length of a large number of such paths is called Mean free path and it is denoted by symbol 'l'.

The expression of Mean free Path is given as follows

$$l = \frac{1}{\sqrt{2\pi\sigma^2 N}}$$

where  $N$  = Number of Molecules per Cubic Metre of the gas

$\sigma$  = Molecular Diameter in Metres

### (B) Collision Diameter: -

When two gaseous molecules approach each other by continue moving till a point at which the mutual repulsion is so great that they have to retrace their paths.

The distance between centres of two such molecules at the point of the closest approach is called Collision diameter. The collision diameter is denoted by Sigma ' $\sigma$ '.

(C) Collision frequency: - It is denoted by  $N_c$ . The number of collisions suffered by gas molecules per sec. per cubic metre of a gas is called Collision frequency of the gas. It is given by following expression:-

$$N_c = \frac{1}{V} \pi v \sigma^2 N^2 = 2 \sigma^2 N^2 \sqrt{\frac{\pi RT}{M}}$$

Where  $v$  is the average molecular velocity in  $\text{metre sec}^{-1}$ .  $N$  is the number of molecules per cubic metre of the gas.

$\sigma$  is the molecular diameter in Metres.

At a particular temperature, distance travelled by a molecule between two successive collisions depends upon the pressure of the gas.

When the temperature is very high, the molecules are comparatively near to each other and mutual collisions are larger as compared to those at low pressure, then the mean free path ( $l$ ) is expressed as

$$l = \frac{c}{N_c} \quad \text{where } c = \text{Velocity of molecule.}$$