

# **Chapter -**

# **Gaseous State**

## Unit-2

## Gaseous State

### Kinetic theory of gases (KTG)

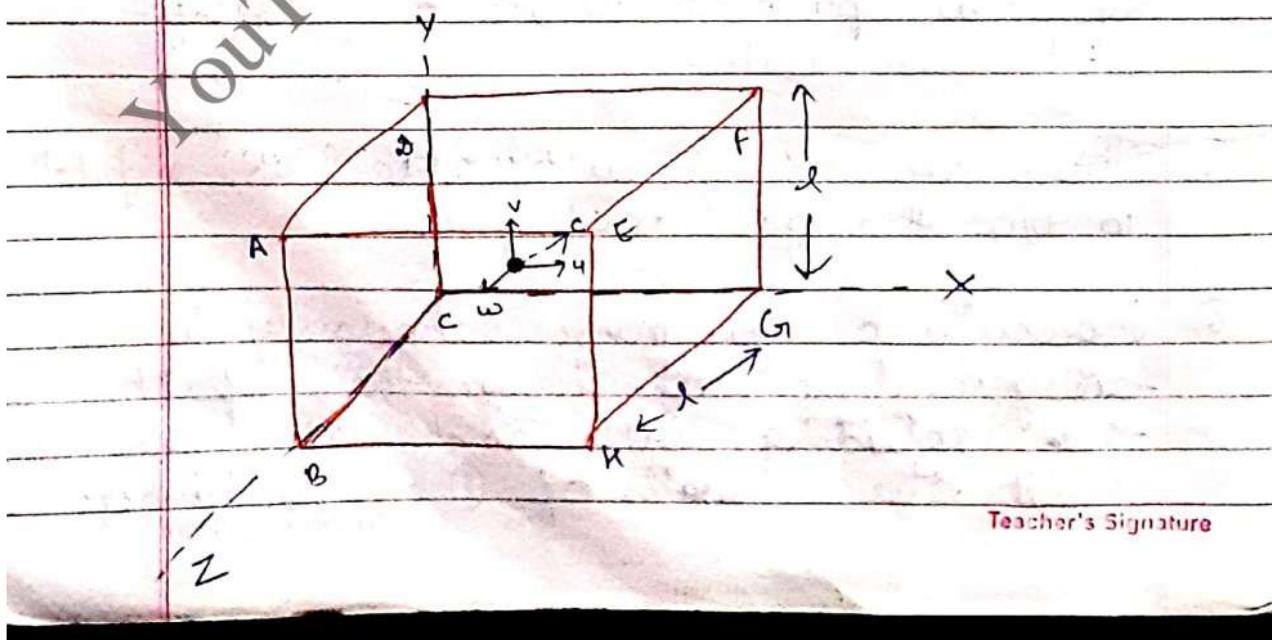
Main postulates →

- ① Each gas is made of minute particles as molecules.
- ② Molecule of 1 gas are similar but diff from the molecule of another gas.
- ③ Volume of gas molecule is negligible in comparison of total volume in which gas occupied by the whole gas (Total volume means the volume in which gas molecule can move freely)
- ④ Gas molecule are considered to be solid spherical particles which are totally elastic in nature.
- ⑤ There are no force of attrac" or repul" in b/w the gas molecules.
- ⑥ Molecules of gas move continuously in straight line at change their path after colliding with each other as with the walls of the container.

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- ⑦ The collision are perfectly elastic i.e there is no loss of energy as a result of collision.
- ⑧ Pressure of gas is in fact the result of the collision of the gas molecule on the inner wall of the container.
- ⑨ Effect of gravity is negligible on the motion of the molecule.
- ⑩ The energy and the velocity of all the molecules are not same that's why avg energy and avg velocity is taken into account.
- ⑪ The avg K.E of the gas molecule is proportional to the absolute temp.

Derivation of kinetic gas eqn



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Let imagine that a certain quantity of gas is enclosed in a cube containing

- (1) Length of cube side = 1 cm
- (2) Total no of molecules =  $n$
- (3) Mass of each molecule =  $m$  gm
- (4) molecules are moving with velocity  $c_1, c_2, c_3, \dots$
- (5) Avg velocity of molecule =  $c$  cm/s

The velocity  $c$  of a particular molecule can be resolved into 3 component  $u, v, w$ .

The component velocity  $u$  has effect on face EFGH and ABCD but has no effect on the other walls.

The momentum before collision on face EFGH =  $mu$

The momentum after collision on face ABCD =  $-mu$

Change in momentum after collision  
 $= mu - (-mu) = 2mu$

Distance b/w wall is less hence time taken in 1 collision is equal to the

$$t = \frac{d}{u}$$

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So collision per sec will be = 4

Hence change in momentum per second  
will be =  $\frac{\Delta p_x}{\Delta t}$

$$= 2m u \times \frac{4}{t} + 2mv^2$$

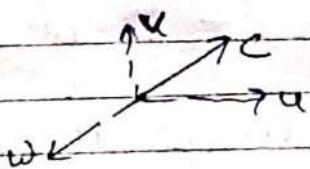
Similarly change in momentum per sec for other two component of velocity will be  $\frac{2m v^2}{t}$  and  $\frac{2m w^2}{t}$

Total change of momentum per sec  
for a molecule

$$= \frac{2m u^2}{t} + \frac{2m v^2}{t} + \frac{2m w^2}{t}$$

$$\equiv \frac{2m}{t} (u^2 + v^2 + w^2) = \frac{2mc^2}{t}$$

{ i.e. From dynamic  $u^2 + v^2 + w^2 = c^2$  }



Since in box total no of molecule is  $n$ .

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Total change of momentum per second  
all molecule =  $\frac{2mnC^2}{l}$

Acc to 2nd law of motion rate of  
change of momentum is equal to F

$$F = \frac{2mnC^2}{l}$$

$$P = \frac{F}{A} = \frac{2mnC^2}{Al} = \frac{2mnC^2}{l \times 6l^2}$$

(Area of cube = Area of 6 cube walls)

$$P = \frac{1}{3} \frac{mnC^2}{l^3} = \frac{1}{3} \frac{mnC^2}{V}$$

$$\left. \begin{array}{l} PV = \frac{1}{3} mnC^2 \\ \end{array} \right\} \text{Kinetic Energy Eqn}$$

Derivation of gas law from kinetic  
Eqn :-

### ① Boyle's law

$$PV = \frac{1}{3} mnC^2 = \frac{2}{3} \left( \frac{1}{2} mnC^2 \right) = \frac{2}{3} k \cdot e$$

Acc to KTG  $\rightarrow k \cdot e \propto T$

$$\frac{2}{3} mnC^2 \propto T$$

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$$\frac{1}{2}mnC^2 = kT$$

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

i.e.  $T$  is constant  $\{ PV = \text{constant} \}$

mathematically  
form of Boyle's law

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

Hence at const. Temp' pressure of definite amount of gas is inversely propotional to its volume.

## ② Charles law

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

$$V = \frac{2kT}{3P}$$

at const. Pressure  $V = \text{constant} \times T$   
 $\left\{ \frac{V}{T} = \text{constant} \right\}$

mathematical form of Charles law

at const. press' volume of definite amount of gas is directly proportional to its absolute temp'.

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### ③ Avogadro's law

$$PV = \frac{1}{3} m_1 n_1 c_1^2 \quad (\text{for one gas}) \quad \text{--- } ①$$

$$PV = \frac{1}{3} m_2 n_2 c_2^2 \quad (\text{for another gas}) \quad \text{--- } ②$$

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

Their temp<sup>r</sup> is same hence  $c_1^2$  will be equal.

$$\frac{1}{2} m_1 c_1^2 = \frac{1}{2} m_2 c_2^2 \quad \text{--- } ④$$

$$③ \div ④ \quad n_1 = n_2$$

Under the similar cond<sup>n</sup> of press and temp<sup>r</sup> equal volume of gases have same no. of molecules.

### ④ Ideal gas eqn

$$V \propto \frac{1}{P} \quad (\text{at const } T)$$

$$V \propto T \quad (\text{at const } P)$$

$$V \propto n \quad (\text{at const } P, T)$$

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

$$V = \frac{RTn}{P} \Rightarrow \{ PV = nRT \}$$

Ideal gas eqn  
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$$\begin{aligned}
 R &= 0.0831 \text{ Latm mol}^{-1}\text{K}^{-1} \\
 &= 0.0831 \text{ L bar mol}^{-1}\text{K}^{-1} \\
 &= 8.314 \text{ J Mol}^{-1}\text{K}^{-1} \\
 &= 8.314 \times 10^7 \text{ erg mol}^{-1}\text{K}^{-1} \\
 &= 8.314 \times 10^7 \text{ dyne cm mol}^{-1}\text{K}^{-1} \\
 &= 2 \text{ cal mol}^{-1}\text{K}^{-1}
 \end{aligned}$$

(5)

Graham's law of diffusion

$$PV = \frac{mn c^2}{3}$$

$$c^2 = \frac{3PV}{mn} = \frac{3PV}{M} = \frac{3P}{d}$$

$$c = \sqrt{\frac{3P}{d}}$$

at same P, T

$$\begin{aligned}
 M &= \text{Total mass} \\
 d &= \frac{M}{V}
 \end{aligned}$$

for gas 1

$$c_1 = \sqrt{\frac{3P}{d_1}}$$

for gas 2

$$c_2 = \sqrt{\frac{3P}{d_2}}$$

$$\frac{c_1}{c_2} = \sqrt{\frac{d_2}{d_1}}$$

Since  $r_{ms}$  is directly proportional to rate of diffusion.

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fence  $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$

at const temp and press the rate of diffusion of a gas is inversely proportional to the square root of its density.

### ⑥ Dalton's law of partial pressure

$$K \cdot \epsilon = K \cdot \epsilon_1 + K \cdot \epsilon_2 + K \cdot \epsilon_3 + \dots$$

$$\frac{1}{2} m c^2 = \frac{1}{2} m_1 c_1^2 + \frac{1}{2} m_2 c_2^2 + \dots$$

$$PV = \frac{1}{3} m n c^2 \quad \left\{ \because \text{Container is same} \right\}$$

$$PV = \frac{2}{2} \times \frac{1}{2} m n c^2 \quad \left\{ \because V \text{ constant} \right\}$$

$$\frac{3}{2} PV = \frac{1}{2} m n c^2 = K \cdot \epsilon$$

$$\frac{3}{2} PV = \frac{3}{2} P_1 V + \frac{3}{2} P_2 V + \dots$$

$$P = P_1 + P_2 + P_3 - \dots \rightarrow \text{law of partial press}$$

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Kinetic Energy & Temp :-

$$K.E = \frac{1}{2}mc^2$$

from KTG  $PV = \frac{1}{3}mnC^2$

$$PV = \frac{2}{3}n \times \frac{1}{2}mc^2 = \frac{2}{3}nK.E$$

$$K.E = \frac{3PV}{2n}$$

from ideal gas  $\frac{PV}{T} = nR$   $\frac{PV}{T} = \rho RT$

$$K.E = \frac{3}{2}nRT \quad (\text{for } 1 \text{ mole})$$

$$K.E = \frac{3}{2}nRT \quad (for n \text{ mole})$$

$$K.E \propto T$$

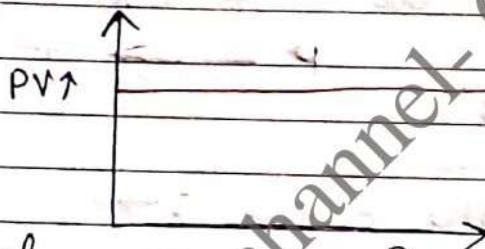
K.E of 1 mole of an ideal gas is directly proportional to its absolute temp does not depend upon nature of gas.

## Real Gas :-

all gases behave as ideal gas at high temp<sup>o</sup> and low press<sup>r</sup> but their ideal behaviour deviated at low temp<sup>o</sup> and high pressure. Such gases are k/a real gases.

### Deviation from ideal behaviour:-

acc to Boyle's law  $PV \propto \text{const.}$  at const temp<sup>r</sup> and if  $PV$  is plotted against  $P$  a straight line parallel to  $x$  axis must be obtain.



#### Effect of

#### Pressure:-

But Amagat performed experiment on some gases and found that no gas strictly obey Boyle's law. The deviation from ideal behaviour is best represented in terms of compressibility factor  $Z$ .

$$Z = \frac{PV}{PV_{\text{ideal}}}$$

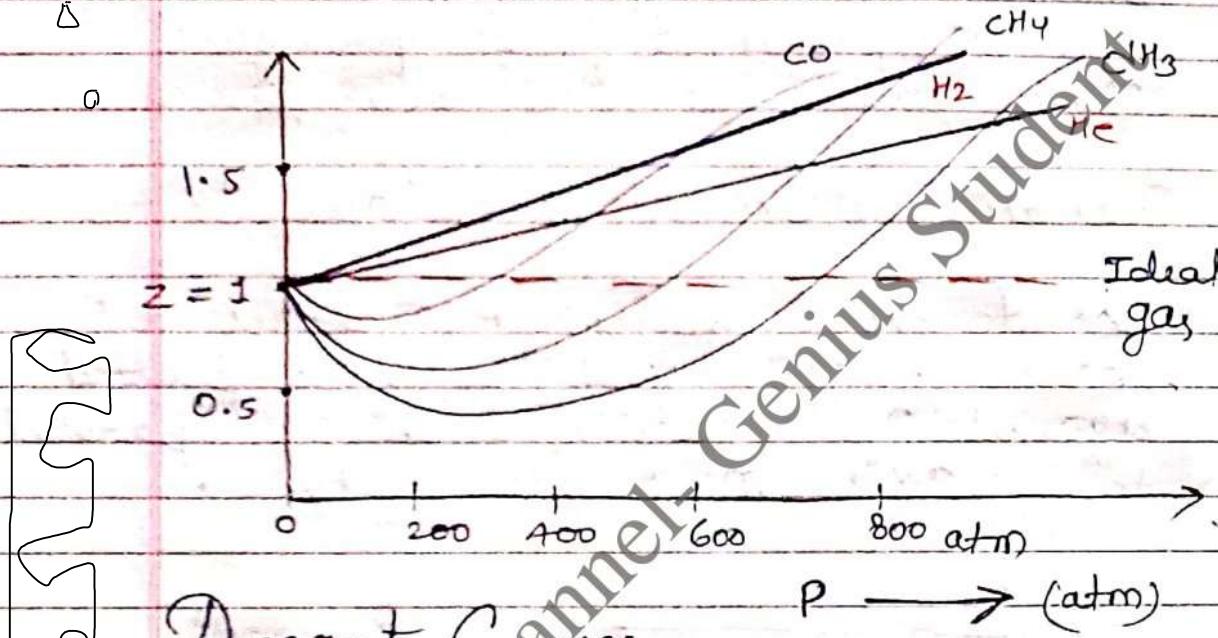
$$PV_{\text{ideal}} = nRT$$

for 1 mole

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 $PV_{\text{ideal}} = RT$

$$\text{So } z = \frac{PV}{RT} \text{ (for 1 mole)}$$

$$z = \frac{PV}{nRT} \text{ (for n mole)}$$



Amagat Curves

Observations of the curve :-

(1) for ideal gas  $z = 1$  at all press

(2) for H and He  $z > 1$  at all press  
i.e. H<sub>2</sub> and He are less compressible than an ideal gas.

(3) At extremely low press the gases have  $z = 1$  showing that they behave almost ideally.

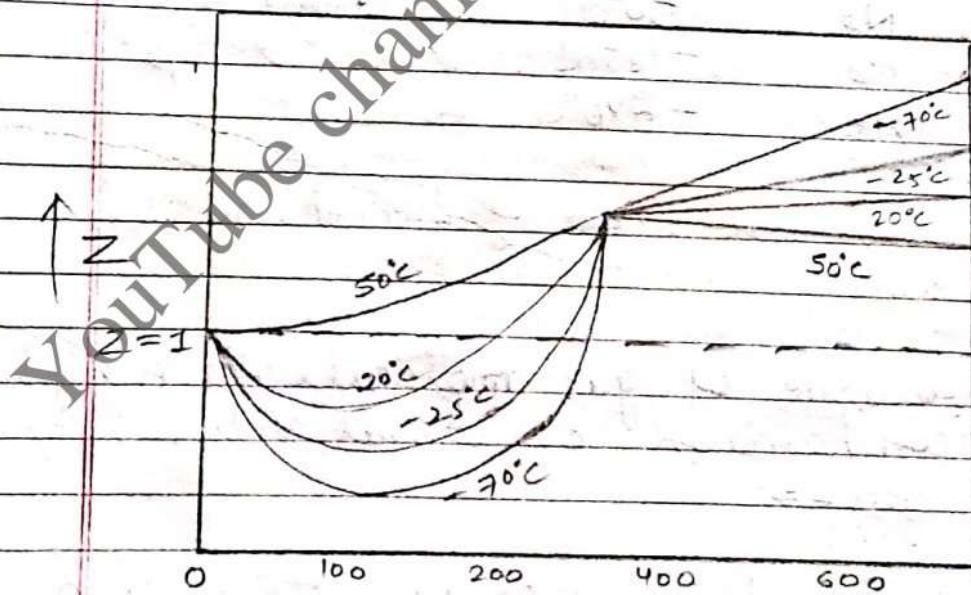
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④ At very high pressure  $Z > 1$  indicating that they are less compressible than an ideal gas. This is due to the fact that repulsive forces b/w the molecules are dominating.

⑤ At moderately range of pressure  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$  are more compressible than ideal gas i.e.  $Z < 1$ .

The obvious reason is that at low pressure attractive forces are more dominating and hence favours compression.

Effect of temperature :-



Amagat curves  
for  $\text{N}_2$  gas at  
different temp<sup>o</sup>.

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As the temp<sup>r</sup> increases the deviation from ideal behaviour decreases and the dip (downwards) slope becomes smaller.

At 50°C the curves becomes almost horizontal b/w 0 to 100 atm. Within this range Boyle's law is obeyed and this temp<sup>r</sup> is called Boyle temp<sup>r</sup>.

Boyle Temp<sup>r</sup> → The temp<sup>r</sup> at which a real gas follows the Boyle's law of an ideal gas, over the moderately wide range of pressure is called Boyle's temp<sup>r</sup>.

for N <sub>2</sub>	50°C	} Boyle's temp <sup>r</sup>
H <sub>2</sub>	165°C	
He	-240°C	

Cause of deviation from the ideal behaviour :-

- ① The volume of gas molecule is negligible in comparison of total volume of the gas →

This postulate is nearly true under normal cond'n of temp<sup>r</sup> and press<sup>r</sup> becoz under these cond'n volume

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of the gas molecule is 0.04% of total volume of the gas which is negligible.

When pressure is decreased total volume of the gas will increase while the volume of the gas molecules remains same. Hence the volume of the gas molecule cannot be taken as negligible.

Eg → if pressure of the gas is decreased to thousand atm the volume of the gas molecule will be 14% of the total volume which is not negligible.

② There is no force of attrac<sup>n</sup> b/w the gas molecules →

This postulate was also found in correct at low temp<sup>r</sup> and high pressure. Because in both cond<sup>n</sup> volume decreases gas molecules comes close to each other. And molecule certainly have attrac<sup>n</sup> for each other.

Evidence →

① Liquific<sup>n</sup> of gas

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gases can be liquified at low temp<sup>r</sup> and high press<sup>r</sup>. This is possible only due to attrac<sup>n</sup> force b/w gas molecules.

## ② Joule Thomson effect

When a gas at high press<sup>r</sup> is allowed to expand in vaccum, temp<sup>r</sup> of the gas reduces i.e. cooling effect is observed. This is known as Joule Thomson effect.

This effect can be explained on the basis of force of attrac<sup>n</sup> b/w the molecules.

When the gas expands, gas molecules go apart from each other, and for this work is done against the force of attrac<sup>n</sup>. The energy for this work is taken from K.E. due to which K.E. increases and so temp<sup>r</sup> increases ( $K.E. \propto Temp^r$ )

## Vanderwaal interaction

### (i) Volume correction $\rightarrow$

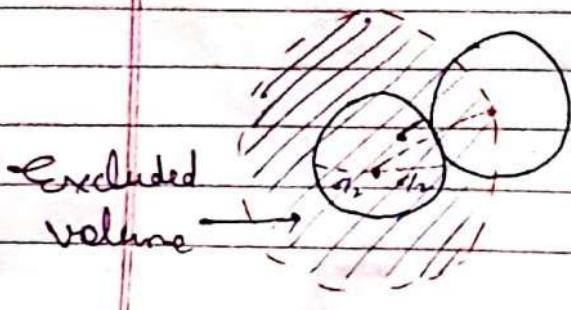
If molecules occupied some volume then the space available for their movement must be reduced.

If  $b$  is effective volume of molecule in 1 mole of gas and  $V$  is the total volume of  $n$  mole of the gas then the total volume occupied by the molecules =  $nb$

Volume available for compression :  $V_i = V - nb$

This is also free space available for the movement of molecule and  $b$  is also called as excluded volume per mole.

Calculation of excluded volume



Excluded volume for a pair of molecule shown by the enclosed by dashed line.

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The volume of one molecule =  $\frac{4}{3}\pi(\frac{r}{2})^3$

$$= \frac{1}{8} \left( \frac{4}{3}\pi r^3 \right)$$

Excluded volume of shaded sphere

$$= \frac{4}{3}\pi r^3$$

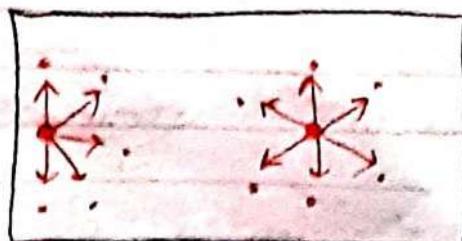
Excluded volume for 1 molecule =  $\frac{\left( \frac{4}{3}\pi r^3 \right)}{2}$

Excluded volume per molecule =  $\frac{4}{3}\pi r^3$   
Actual volume of molecule

Excluded volume per mole =  $4N \times \frac{1}{8} \left( \frac{4}{3}\pi r^3 \right)$

## (ii) Pressure Correction $\rightarrow$

In real gas, molecule is attracted by each other and pressure of real gas is less than pressure of ideal gas.



$\rightarrow$  It's very write yourself.

$$\text{pressure of real gas } P = P_i - P'$$

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$P' = \text{constant}$  in press<sup>r</sup>

$$P' \propto \frac{n^2 M}{V^2}$$

$M = M \cdot M$  of gas  
= constant

$$P' = \frac{an^2}{V^2}$$

$$P_i' = P + P' = P + \frac{an^2}{V^2}$$

$$\rightarrow P_i \cdot V_i = nRT$$

ideal gas eq<sup>n</sup>

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

vanderwaal  
gas eq<sup>n</sup>

$$\text{if } n=1 \quad \left( P + \frac{a}{V^2} \right) (V - b) = RT$$

- ~~unit~~ unit of  $a, b$

$a, b$  are vanderwaal constant

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

$$a = \frac{PV^2}{n^2} = \frac{\text{atm} (\text{litr})^2}{(\text{mol})^2} = \text{atm litr}^2 \text{mol}^{-2}$$

$$V = nb$$

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

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- Dimension of  $a, b$  in SI unit system

~~$a = \text{atm} \cdot a = \frac{\text{pressure} \times \text{Volume}^2}{(\text{mole})^2}$~~ 
$$= \frac{\text{Nm}^{-2} (\text{m}^3)^2}{(\text{mole})^2}$$

$$a = \text{Nm}^4 \text{ mole}^{-2}$$

$$b = \frac{\text{Volume}}{\text{mole}} = \frac{V}{n} = \text{m}^3 \text{ mole}^{-1}$$

Maxwell Boltzmann Distribution law  
of molecules velocities :-

All the molecules of a gas do not move with the same speed. This is becaz they are havin continuously collision as a result of which there is interechange of momentum b/w them.

Hence some molecule move with very high velocity some other move with low velocity and some molecules become totally sluggish. They is the sample of a gas. Velocity of a molecule differs from 0 to  $\infty$ .

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In 1860 JC Maxwell give a law "Acc to this law velocities of molecule distributed from 0 to great range".

The mathematically expressn for the maxwell distributn law is following:-

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

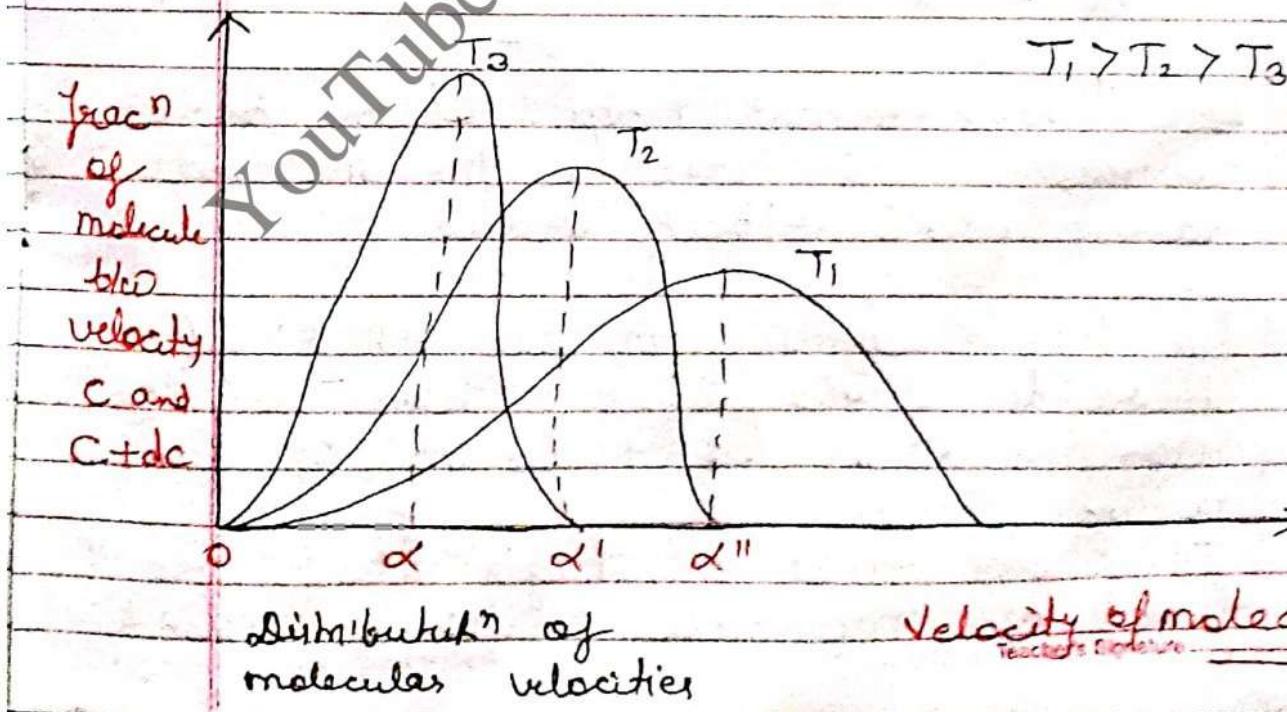
$P$  = probability of the molecule having velocity b/w  $c$  and  $c+dc$

$\frac{dn}{n}$  = frac<sup>n</sup> of the molecule having velocity b/w  $c$  and  $c+dc$

$M$  = molecular mass of gas

$T$  = absolute Temp

$c$  = velocity



## Observation of distrib<sup>n</sup> curve :-

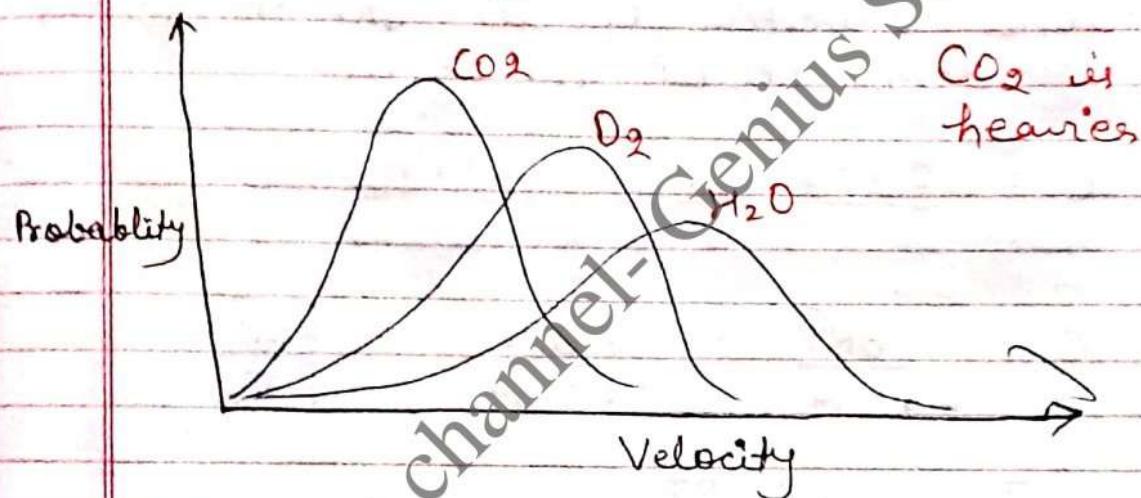
- ① The no of molecules having very low and very high velocity is very low.
- ② for every curve frac<sup>n</sup> of those molecule whose velocity is more than zero has with big velocity, reaches a maxima and then radially decreases as velocity increases.
- ③ The velocity corresponding to the maxima of the curve is known as most probable velocity and denoted by  $\alpha$ .
- ④ The most probable velocity increases with temp in temp  $\alpha < \alpha' < \alpha''$
- ⑤ On increasing temp height of the curve decreases. i.e. frac<sup>n</sup> of the molecule having MPS velocity decreases.
- ⑥ On increasing temp the curves shift towards right side, height of the maxima decreases and width of the curve increases.

It shows that at high temp no of frac<sup>n</sup> of molecule having velocity

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then avg velocity increases. But  
frac<sup>n</sup> of molecule having most probable  
velocity decreases.

- ⑦ Distribut<sup>n</sup> of velocity also depends on  
molecular weight at const. temp.  
distribut<sup>n</sup> of molecular velocities is  
higher in lighter gases than in  
a heavier gas.



### Types of Molecular Velocities

- ① Root mean square velocity

Square root of the avg of the square  
of the velocity of molecule is  
known as RMS.

$$C_{rms} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}}$$

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

$$\begin{aligned} PV &= nRT \\ PV &= RT \quad n = 1 \end{aligned}$$

$$c = \sqrt{\frac{3PV}{mn}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}} = 1.7 \sqrt{\frac{P}{d}}$$

## ② Avg velocity

It can be calculated by dividing the total velocities of all the molecules by total no of molecules.

$$\bar{c} = \frac{c_1 + c_2 + c_3 + \dots + c_n}{n}$$

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8P}{\pi d}}$$

$$\bar{c} = 1.6 \sqrt{\frac{RT}{M}}$$

## ③ Most probable speed

The velocity which is possessed by most of the molecule of the gases is Kms MPS.

$$\alpha = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2P}{d}}$$

$$\alpha = 1.4 \sqrt{\frac{RT}{M}}$$

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Relation b/w Rms, MPS, Avg velocity :-

$$C : \bar{C} : \alpha$$

$$1.7 \sqrt{\frac{RT}{M}} : 1.6 \sqrt{\frac{RT}{M}} : 1.4 \sqrt{\frac{RT}{M}}$$

$$1.7 : 1.6 : 1.4 \\ 1 : 0.921 : 0.816$$

$$V \propto \sqrt{\frac{RT}{M}}$$

$$\alpha \sqrt{\frac{\text{erg K}^{-1} \text{mol}^{-1} \times K}{\text{gm mol}^{-1}}} = \sqrt{\frac{\text{erg}}{\text{gm}}}$$

$$\text{erg} = \text{dyne} \times \text{cm}$$

$$\text{dyne} = \frac{\text{gm} \times \text{cm}}{\text{sec}^2}$$

$$\sqrt{\frac{\text{gm} \times \text{cm}^2}{\text{sec}^2 \times \text{gm}}}$$

$$\sqrt{\alpha} \text{ cm/sec}$$

In finding speed we use  $R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$

**Collision No/ frequency**  $\rightarrow$  The no. of collision b/w gas molecules per unit time in per  $\text{cm}^3$  cubic volume.

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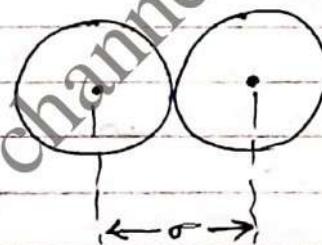
For Homonuclear Diatomic molecule

$$Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 (N')^2 \bar{C}$$

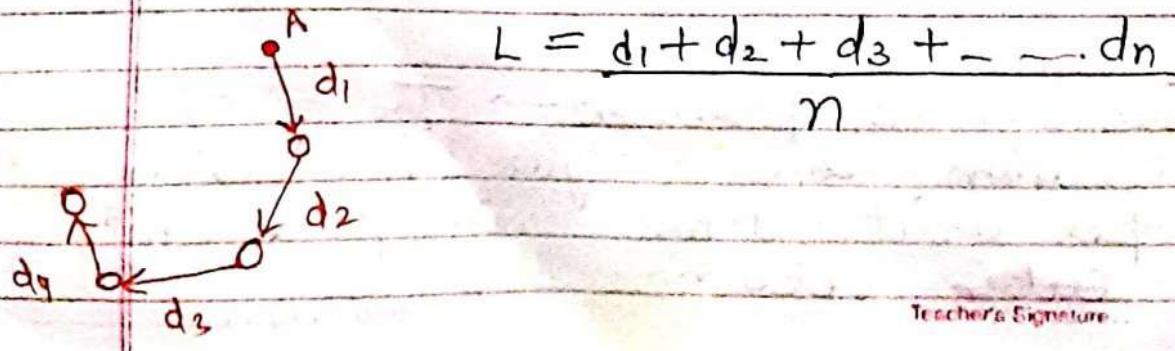
$\sigma$  = Diameter of molecule

$\frac{N'}{C}$  = No of molecule per cubic cm  
 $=$  Avg velocity  
 $= \sqrt{\frac{8RT}{\pi M}}$

Collision diameter  $\rightarrow$  The distance b/w the centres of the molecule when they are closest is called collision diameter



Mean free path  $\rightarrow$  The avg distance travelled by the gas molecule b/w 2 consecutive collision is known as mean free path.



$$L = \frac{d_1 + d_2 + d_3 + \dots + d_n}{n}$$

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$$L = \frac{3n}{d \cdot c} \quad n = \text{boise (unit)}$$

$c = \text{viscosity coefficient}$

$c = \frac{\sigma mg}{\rho}$

$d = \text{density of gas}$

$$c = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

$$L = \frac{3n \sqrt{d}}{d \sqrt{3P}} = n \sqrt{\frac{3}{Pd}}$$

### Liquification of gases

Every gas can be liquify at or below its critical temp by increasing press.

The methods are mainly based on 2 principals :-

- ① Expansion of gases against the intermolecular forces present in them.
- ② By allowing the gases to do some external work.

## Cooling based on Joule Thomson effect :-

Acc to Joule Thomson when a gas is compressed at high presr and allowed to diffuse or expand in low presr area through a fine nozzle, there is fall in temp<sup>r</sup>, i.e cooling effect is observed. This is K/s Joule Thomson effect.

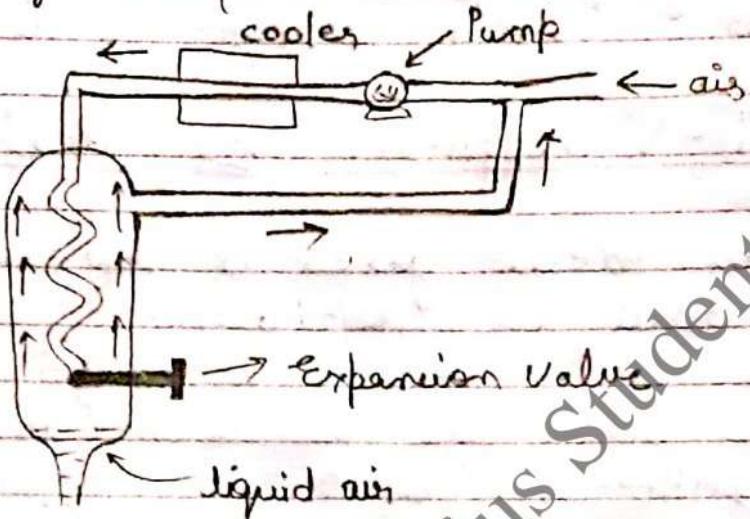
when the gas expand gas molecules go far apart from each other for this expansion work is done against the force of attrac<sup>n</sup> b/w the molecules. for this work energy is taken from the K.E of the molecule and hence temp<sup>r</sup> is lowered. But cooling of gases can be observed below a definite temp<sup>r</sup> which is K/s inversion temp<sup>r</sup>.

"An inversion temp<sup>r</sup> is that temp<sup>r</sup> below which the applic<sup>n</sup> of Joule Thomson effect leaves to the liquifiction of gases."

$$T_i = \frac{a}{R_b}$$

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In 1895 LINDE used this method for the liquific<sup>n</sup> of air: compression



Linde's apparatus

Purified air (without  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapour) is compressed in a compressor upto 200 atm pres<sup>r</sup>. This compressed air is then passed through a cooling device so that the loss in temp<sup>r</sup> of the gas, during compression, can be nullified. This cooled and compressed air is then allow to enter a fine expansion valve, through a thin tube. By this valve gas is allow to expand at 1 atm pres<sup>r</sup>. Due to J.T effect the gas is cooled. By repeating this process again and again very low temp<sup>r</sup> is obtained and at  $85\text{K}$  air can be liquified.

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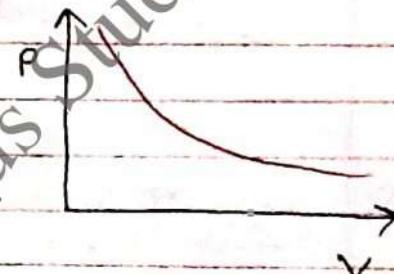
Isotherm :-

A graph plotted b/w pres<sup>r</sup> and volume at const temp<sup>r</sup> is K/Las...isotherm

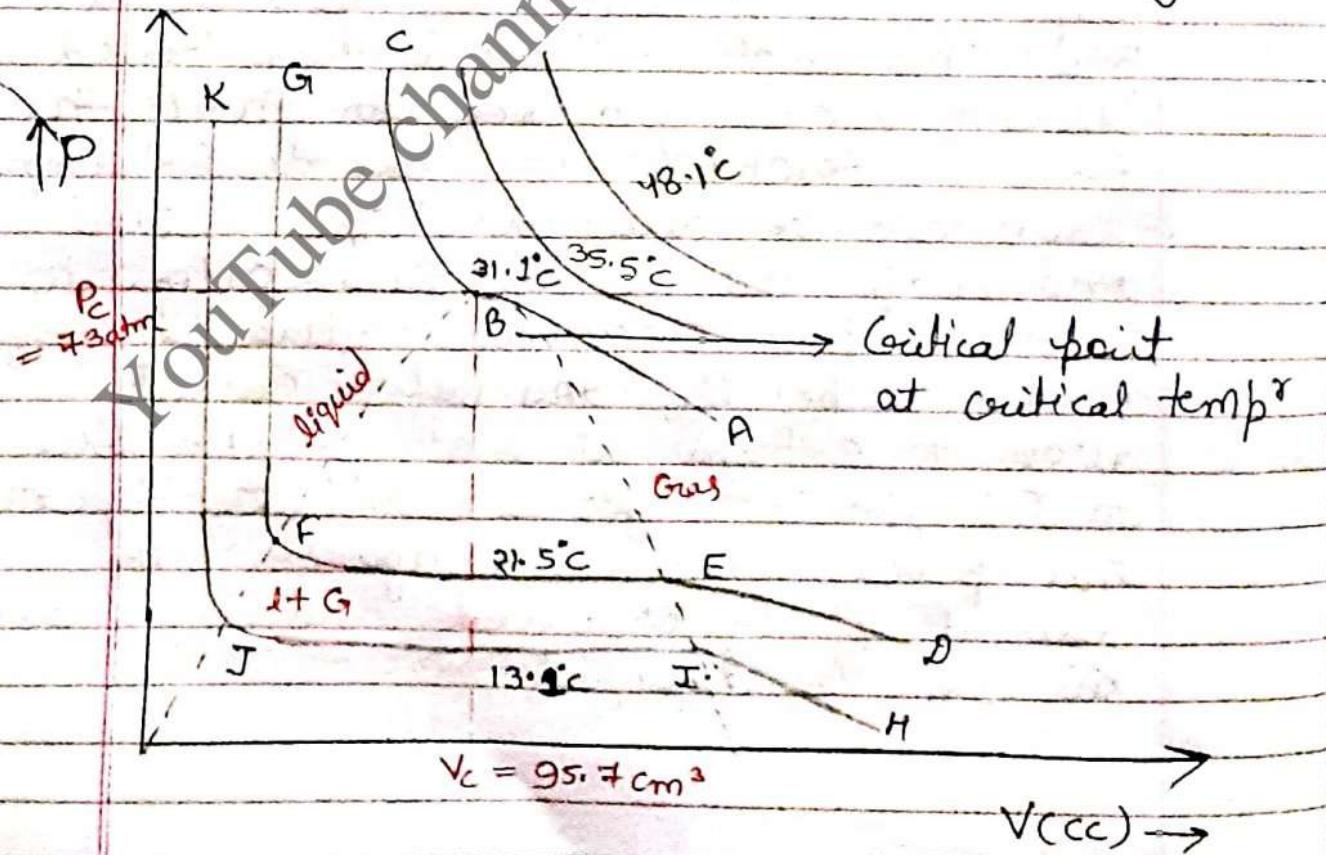
P-V isotherm of Real gases :-

For ideal gases a rectangular hyperboloid is obtain.

Isotherm of an ideal gas —



But curves of  $\text{CO}_2$  gas are not like that of an ideal gas



isotherm of CO<sub>2</sub> gas

This graph gives the observation made by \*Andrews for  $\text{CO}_2$  gas. Consider the isotherm H IJK at the fixed temp $^{\circ}$   $13.1^{\circ}\text{C}$ . At point H,  $\text{CO}_2$  is in gaseous state. By increasing the press. volume increases and reaches to point I. During curve H-I gas nearly follow the Boyle's law. At point I; condensation of the gas starts (due to high P and low temp $^{\circ}$ ) and 2 phases (gas and liquid) are present together during the hz curve I-J. Press remains constant until whole of the gas is condensed at point J. After point J if the press is increases almost vertical curve JK is obtain which shows that at point J there is only liquid phase and there is very little effect of increasing press on volume of liquid, because liquid are almost incompressible. By decreasing the temp $^{\circ}$  hz part of the curve Ires and reduced to a point B. This point is situated on the isotherm at  $31.0^{\circ}\text{C}$ . Above this temp $^{\circ}$  volume increases by increasing press but liquific or condense $^n$  of the gas does not take place.

Thus  $\text{CO}_2$  gas cannot be liquified above  $31^{\circ}\text{C}$  no matter how much high press $^{\circ}$  is applied. This temp $^{\circ}$  is the critical temp $^{\circ}$  of  $\text{CO}_2$ .

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Ques. What are critical phenomenon and calculate critical constant from van der waal eq<sup>n</sup>.

The phenomena of smooth merging of a gas into its liquid state is called critical phenomena.

The temp<sup>r</sup> above which a gas cannot be liquified even if high press<sup>r</sup> is applied. This is called critical temp  $T_c$ .

At critical temp<sup>r</sup> the lowest press<sup>r</sup> of any gas at which it liquify is K/a, critical press<sup>r</sup> ( $P_c$ ).

At  $T_c$  and  $P_c$  volume of 1 mole of a gas is K/a, critical volume  $V_c$ .

$T_c$ ,  $V_c$ ,  $P_c$  are K/a, critical constant.

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

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$\bullet PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$$

Multiplying by  $\frac{V^2}{P}$  and Rearrange

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

~~$$PV^3 - PV^2 b + av - ab - RTV^2 = 0$$~~

$$PV^3 - (Pb + RT) V^2 + av - ab = 0$$

$$V^3 - V^2 \left( b + \frac{RT}{P} \right) + \frac{av}{P} - \frac{ab}{P} = 0 \quad \text{--- (1)}$$

at critical point

$$V = V_c$$

$$V - V_c = 0$$

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

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

at critical state  $P = P_c, T = T_c$

from eq (1)

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

Eq (2) and (3) are eqn of similar curve. Hence their eqn are equivalent.

By comparing Eq (2) and (3)

$$3V_c = b + RT_c \quad \text{--- (4)}$$

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

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

from Eqn (5) and (6)

$$\frac{3V_c^2}{V_c^3} = \frac{a}{P_c ab} = \frac{1}{b}$$

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

by putting value of  $V_c$  in (5)

$$3 \times 9b^2 = \frac{a}{P_c} \quad P_c = \frac{a}{27b^2} \quad \text{--- (8)}$$

by put value of  $V_c$  and  $P_c$  in (4)

$$3 \times 3b = b + \frac{RT_c}{a} \times 27b^2$$

$$9b - b = \frac{27b^2 R}{a} T_c$$

$$\frac{8a}{27bR} = T_c \quad \text{--- (9)}$$

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## Calculations of Vanderwaal constant

On putting value of  $V_c$  from eqn ⑦  
in eq ④

$$3 \times 3b = b + \frac{RT_c}{P_c}$$

$$b = \frac{RT_c}{8P_c} \quad \text{--- } \textcircled{10}$$

put value of  $b$  in  $P_c$  (eqn 8)

$$P_c = \frac{a 64 P_c^2}{27 R^2 T_c^2}$$

- ⑧

$$\frac{27 R^2 T_c^2}{P_c 64} = a \quad \text{--- } \textcircled{11}$$

From ⑨ put value of  $R$  in ⑪

$$\frac{27 \left( \frac{8a}{T_c 27 + b} \right)^2 T_c^2}{P_c 64} = a$$

$$\frac{64 a^2 T_c^2 \times 27}{T_c^2 \times 27 \times 27 \times b^2 \times P_c \times 64}$$

put value of  $b$  from ⑩ in ⑪

$$\frac{V_c}{3} = \frac{RT_c}{8P_c}$$

$$\frac{RT_c}{P_c V_c} = \frac{8}{3}$$

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Relation b/w critical temp<sup>r</sup> and Boyle's temp<sup>r</sup> :-

$$T_c = \frac{8a}{27Rb} \quad \text{--- (1)}$$

$$T_B = \frac{a}{Rb} \quad \text{--- (2)}$$

$$(1) \div (2)$$

$$\frac{T_c}{T_B} = \frac{8a}{27Rb} \times \frac{Rb}{a}$$

$$\frac{T_c}{T_B} = \frac{8}{27}$$

*w/* The law of corresponding state and reduced eq<sup>n</sup> of state

In Vanderwaal eq<sup>n</sup> constant  $a, b$  depend upon nature of gas. Hence vanderwaal eq<sup>n</sup> cannot be applied equally on all gases. Hence if vanderwaal eq<sup>n</sup> is expressed in terms of reduced pres<sup>r</sup>, temp<sup>r</sup>, and volume then a general eq<sup>n</sup> will be form which can be applied equally on all gases.

$$(i) \quad T_x = \frac{T}{T_c} \quad (ii) \quad P_x = \frac{P}{P_c} \quad (iii) \quad V_x = \frac{V}{V_c}$$

$$T = T_c \phi \quad P = P_c \pi \quad V = V_c \phi$$

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

$$\left( P_c \pi + \frac{a}{(V_c \phi)^2} \right) (V_c \phi - b) = R T_c \circ$$

put value of  $V_c$ ,  $P_c$ ,  $T_c$

$$\left( \frac{a \pi}{27b^2} + \frac{a}{9b^2 \phi^2} \right) (3b\phi - b) = \frac{8a}{27bR} \circ$$

$$\frac{a}{27b^2} \left( \pi + \frac{3}{\phi^2} \right) b(3\phi - 1) = \frac{8a \circ}{27b}$$

$$\left[ \left( \pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 80 \right]$$

Reduced eqn of State

This eqn is applied on any gas.

If all gases have same value of reduced press<sup>r</sup> and reduced temp<sup>r</sup> then their devia<sup>n</sup> from ideal behaviour will be same. This is known as law of corresponding state.

If 2 gases have same value of reduce temp and press<sup>r</sup> then their reduced volume will also be same.

## Continuity of states

If the conversion of liquid phase to vapour phase and vapour phase to liquid phase is done at temp below the critical temp, the conversion is not continuous, in the process both the phases exist together.

This type of change of phases of the substance where two phases can not be distinguish is known as continuity of states.