Unit : Kinetic theory of gases

Topics covered :

- Postulates of Kinetic theory of Gases
- Derivation of the Kinetic gas equation
- Comprenibility factor
- Deviation of real gases from ideal behaviour
- Causes of Deviation
- van der Waals equation of state for real gases

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Unit : Gases

Kinetic theory of gases ⊛ [This theory explains the behaviour of a hypothetical ideal gas]

It is based on the following postulates:

1. A gas consists of some basic units called molecules.
   ↓
   minute particles

   These molecules are so small that their actual volume is a negligible fraction of total volume occupied by gas.

2. The molecules move in a random direction with random speed.

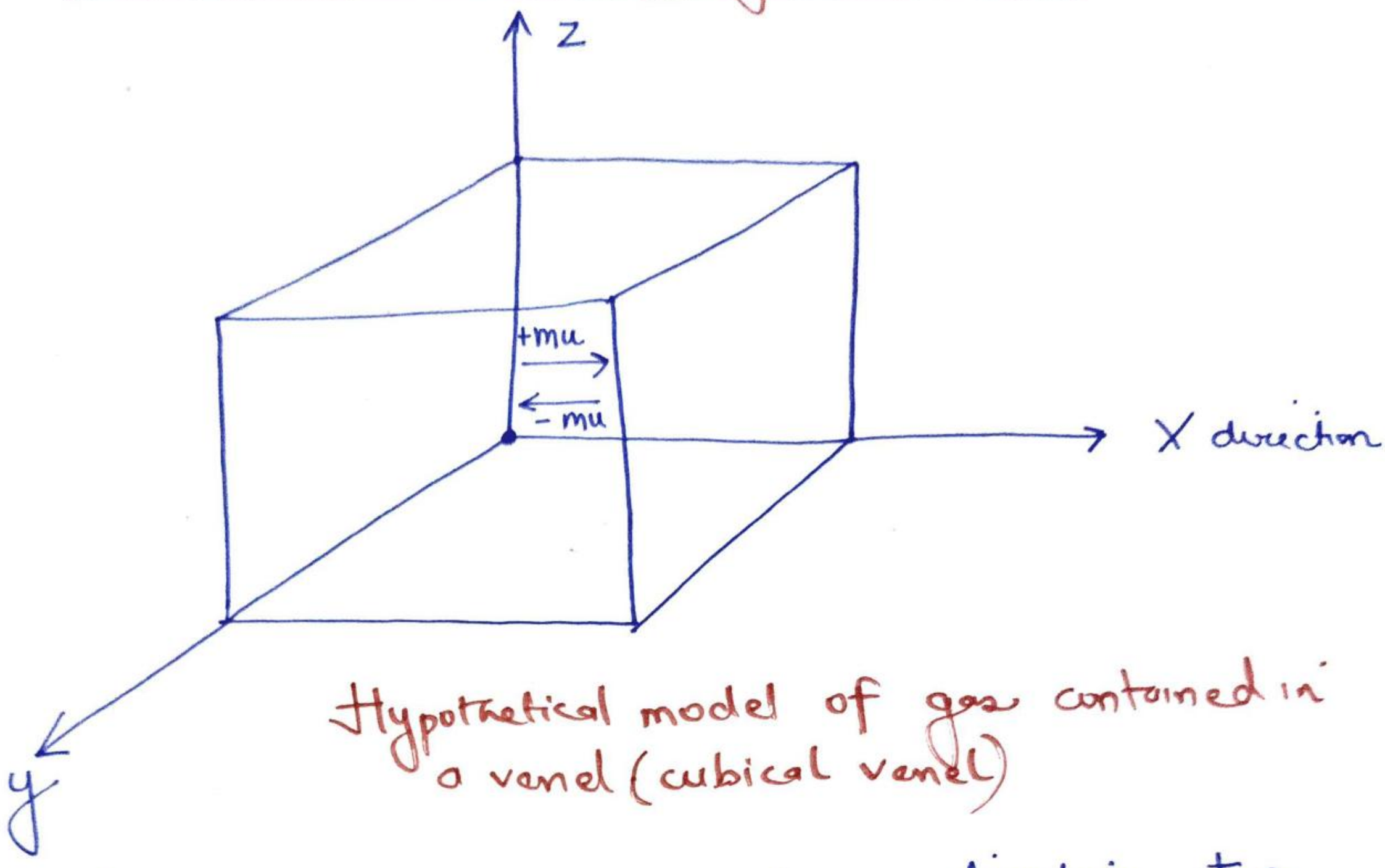
3. The molecules undergo collision among themselves and to the walls of container. Those collision are perfectly elastic.
   ↓ (there is no net loss of energy when gas molecule collide ē one another OR ~~agar~~ against the wall of the vessels.)

4. There are no attractive forces between molecules OR b/w molecules and the walls of the vessel in which gas ~~is~~ is contained. The molecules move completely independent of one another.

5. The pressure of gas is due to the bombardment of molecules on the walls of the containing vessel. (Collision with walls account for the pressure of the gas)

Based on these assumptions, a formula (equation) can be derived that connects the pressure, volume, no. of molecules, individual mass and mean velocity. This equation is known as Kinetic gas equation.

① Derivation of Kinetic gas equation.



Hypothetical model of gas contained in a vessel (cubical vessel)

A gas molecule can move in any direction at a given time: in the x-direction,
in the y- direction
in the z- direction

Let's consider the motion in the x-direction:

Let the velocity be = u_x

length of cube = l

mass of molecule = m

Velocity of molecule = v

Momentum in the x-direction = $+mu_x$ (mass x velocity)

" " " −x direction = $-mu_x$
(negative x direction)

Change in momentum = $mu_x - (-mu_x)$

= $mu_x + mu_x$

= $2mu_x$

(When an individual molecule collides with a wall its momentum

get doubled).

Total time taken from one end to other and vice versa $= t = \frac{\text{distance}}{\text{speed/velocity}}$

$$= \frac{2l}{u_x}$$ (Since length of cube anumed to be l)

Now Rate of change of momentum $= \frac{\text{change in momentum}}{\text{time taken}}$

$$= \frac{2mu_x}{\frac{2l}{u_x}}$$

$$= \frac{mu_x^2}{l}$$

According to Newton second law, rate of change of momentum is the force exerted by the molecules on the wall.

$\therefore$ Force = Rate of change of momentum

$$= \frac{mu_x^2}{l}$$

Since Pressure $= \frac{\text{force}}{\text{Area}}$

Pressure on wall $= \frac{mu_x^2}{l(l^2)}$ — Area

$$P = \frac{mu_x^2}{l^3}$$

$$P = \frac{mu_x^2}{V} \Longrightarrow \text{(volume of container (cube) } = l^3)$$

If there are N molecules in container (so far we have discussed case of a single molecule, now for N particles/molecules), In such situation pressure exerted by N molecules will be

Pressure:

$$P = \frac{m\left[U1_x^2 + U2_x^2 + U3_x^2 + \cdots Un_x^2\right]}{V}$$

Now, If velocities are equal i.e,

$$U_{1x}^2 + U_{2x}^2 + U_{3x}^2 + \cdots = NU_x^2$$

$$P = \frac{m[NU_x^2]}{V}$$

$$P = \frac{NmU_x^2}{V} \quad \text{—} \quad (i)$$

Since velocity in each direction is equal ie,

$$U_x^2 = U_y^2 = U_z^2$$

Total velocity $U^2 = U_x^2 + U_y^2 + U_z^2$

OR $U^2 = 3U_x^2$

$$U_x^2 = \frac{U^2}{3} \rightarrow$$ mean square velocity ∴ it is can be written as c^2

$$\boxed{U_x^2 = c^2/3}$$

On putting this U_x^2 value in (i)

$$\therefore \quad P = \frac{Nmc^2}{3V}$$

$$\boxed{PV = \frac{1}{3}mNc^2}$$ → This is called Kinetic gas equation ↓ (connecting P, V, no. of molecules, mass and mean velocity).

Kinetic energy of a ~~gas~~ gas molecule is directly proportional to absolute temperature of gas ($K.E \propto T$)

Derivation: Consider an ideal gas equation

$$PV = nRT$$ (n → no. of moles)

Put PV value from Kinetic gas equation in ideal gas equation

$$\frac{1}{3}mNc^2 = nRT$$

$$mc^2 = \frac{3nRT}{N}$$

Multiply both sides by $\frac{1}{2}$

$$\frac{1}{2} \cdot mc^2 = \frac{1}{2}\left(\frac{3nRT}{N}\right)$$

$$\text{Kinetic energy } \left(\frac{1}{2}mc^2\right) = \frac{3}{2}\frac{nRT}{N}$$

$$K.E = \left(\frac{3nR}{2N}\right)T$$

(Since $\frac{3}{2}, n, R, N$ all are constants)

$$\boxed{K.E \propto T}$$

All gas laws can be easily derived from K.E gas equation

{ Boyle's law
Charles "
Avogadro's "
Ideal gas equation }

Boyle's law ⟹ According to this law PV is constant at constant Temperature (Pressure x volume)

Start with Kinetic gas equation → $PV = \frac{1}{3} mNc^2$

$PV = \frac{2}{3} \times \frac{1}{2} mNc^2$ [Divide and multiply by 2]

$PV = \frac{2}{3} N \left[\frac{1}{2} mc^2\right]$

K.E.

Thus PV = constant [since K.E is constant at constant temp and $\frac{2}{3}$ and N is also constant]

Charle's law ⟹ According to this law $V \propto T$ at constant pressure

Start Kinetic gas equation ⟹ $PV = \frac{1}{3} mNc^2$

$PV = \frac{2}{3} \left(\frac{1}{2} mNc^2\right)$ [Multiply and divide by 2]

$$PV = \frac{2}{3} \times \underbrace{\frac{1}{2} m c^2}_{K.E.} \times N$$

Since K.E varies ∝ temperature

$\therefore V \propto T$ At constant Pressure [for a definite amount of gas ie: N = constant at constant pressure]

Avogadro's law

According to this law, equal volume of all gases under some conditions of temperature and pressure contains equal number of molecules ie.

$$N_1 = N_2$$

for any two gases, Kinetic gas equation ($PV = \frac{1}{3} m N c^2$) can be written as

$$P_1 V_1 = \frac{1}{3} m_1 N_1 c_1^2$$

OR $P_1 V_1 = \frac{2}{3} \times \frac{1}{2} \times m_1 N_1 c_1^2$ [Multiply & Divide by 2]

Similarly $P_2 V_2 = \frac{2}{3} \times \frac{1}{2} \times m_2 N_2 c_2^2$

Late when $V_1 = V_2$

$P_1 = P_2$

$$\Rightarrow \frac{2}{3} \times \frac{1}{2} m_1 N_1 c_1^2 = \frac{2}{3} \times \frac{1}{2} m_2 N_2 c_2^2$$

$$\left(\frac{1}{2} m_1 c_1^2\right) N_1 = \left(\frac{1}{2} m_2 c_2^2\right) N_2$$

$$(K.E)_1 N_1 = (K.E)_2 N_2$$

Since $K.E = \frac{1}{2} m c^2$

If two gases are also at the same temperature then K.E is also same $((K.E)_1 = (K.E)_2)$

Thus $\boxed{N_1 = N_2}$

Ideal gas equation

On combining Boyle's law, Charle's law, Avogadro's law, we get

Boyle's law $V \propto \frac{1}{P}$ (at constant T & n)

Charle's law $V \propto T$ (at constant P & n)

Avogadro law $V \propto n$ (at constant T & P)

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

$$\propto T$$

$$\propto n$$

$$\Rightarrow V \propto \frac{Tn}{P}$$

$$PV \propto nT$$

OR $\boxed{PV = nRT}$ Ideal gas equation

Deviations of Real Gases from Ideal behaviour.

* The equation $PV = nRT$ derived from the postulates of Kinetic theory of gases is valid for an ideal gas only.

* Real gases obey this equation only under certain conditions i.e at low pressure and at high temperature.

* Higher the pressure and lower the temperature, the greater are the deviations from ideal behaviour.

Compressibility factor (Z)
OR
Compression factor (Z)

The deviations from ideal behaviour are represented in terms of the compressibility factor Z.

Here $Z = \frac{(PV)_{real}}{(PV)_{ideal}}$ $Z = \frac{P V_{real}}{P V_{ideal}}$

$Z = \frac{PV}{nRT}$ $(PV_{ideal} = nRT)$

$Z = \frac{P}{RT}\left(\frac{V}{n}\right)$

$$\boxed{Z = \frac{PV_m}{RT}}$$

$(\because V_m = \frac{V}{n}$ = molar volume i.e. volume occupied by 1 mol of gas)

For an ideal gas, $Z = 1$ under all conditions of temperature and pressure.

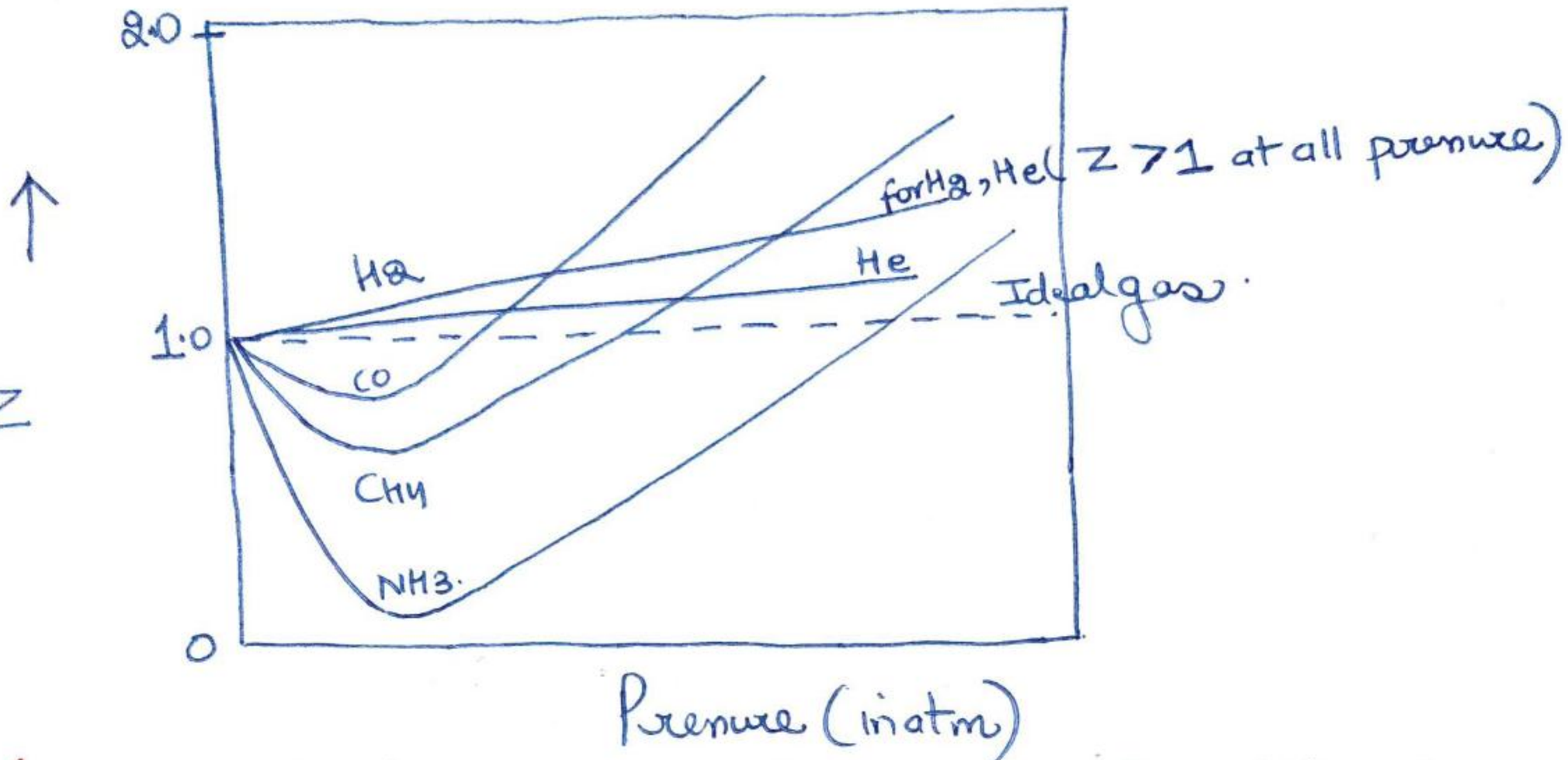


Fig 1: Plot for the compressibility factor for different gases over a range of pressure at a constant temperature

$\Longrightarrow$ At extremely low pressure, Z close to unity which means that the gas behave almost ideally.

$\Longrightarrow$ At moderately low pressure,

PV is less than $(PV)_{ideal}$

i.e $\Longrightarrow Z = \dfrac{PV}{PV_{ideal}}$

Thus $Z < 1$

This is due to the fact at low pressure, long range attractive forces are dominant and favor compression.

eg: CO, CH_4, NH_3 are more compressible than ideal gas ie $(Z<1)$ (fig 1)

⇒ At very high pressure :-

The compressibility factor Z goes on decreasing with increase in pressure, passes through a minimum at a certain stage and then begins to increase ↑se in pressure. The gases now become less compressibile than an ideal gas i.e. PV is more than PV ideal so that $Z > 1$ $\left\{ Z = \frac{PV}{PV_{ideal}} \right\}$

At very high pressure, repulsive forces are dominant.

A gas which obeys the gas laws and the gas equation $PV = nRT$ at all temperature and pressure is said to be an ideal gas.

But no real gas strictly obeys the gas equation at all temperature and pressure.

Deviation from ideal behavior are observed mainly at high P and low T.

In case of ideal gas, $PV = nRT$, $Z = 1$.

In case of Real gas $PV \neq nRT$, $Z \neq 1$

Thus in case of Real gas, Z can be > 1 or < 1

case 1 When $Z < 1$, it is a negative deviation

It shows that gas is more comprenible than expected from ideal behaviour. This is caused by predominance of attractive forces among molecules of this gas (Refer fig 1)

Case II: when $Z > 1$, it is a positive deviation

It shows that gas is len comprenible than expected from ideal behaviour. This is caused by predominance of the strong repulsive forces among molecule. (Refer fig 1)

For some gas, at a particular pressure, the extent of deviation depends upon temperature (fig 2).

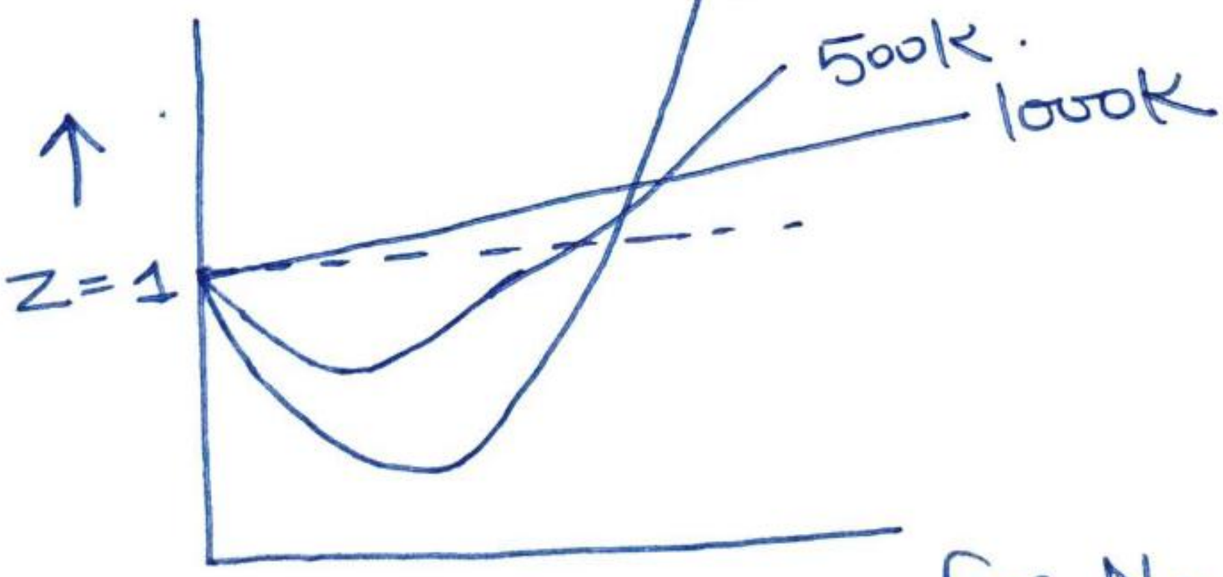


fig 2: for N_2 gas at different temp

As the temperature increases, the minimum in the curve shifts upward. Ultimately, a temperature is reached at which the value of Z remain close to 1. The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature OR Boyle Point

Causes of deviation from Ideal Behaviour:

⇓

⇒ Faulty assumptions in Kinetic theory of gases.

① The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.

② The forces of attraction between gas molecules are negligible.

These two assumptions are valid only at low P and high Temperature, when the volume occupied by the gas molecule is negligible as compared to the total volume of gas.

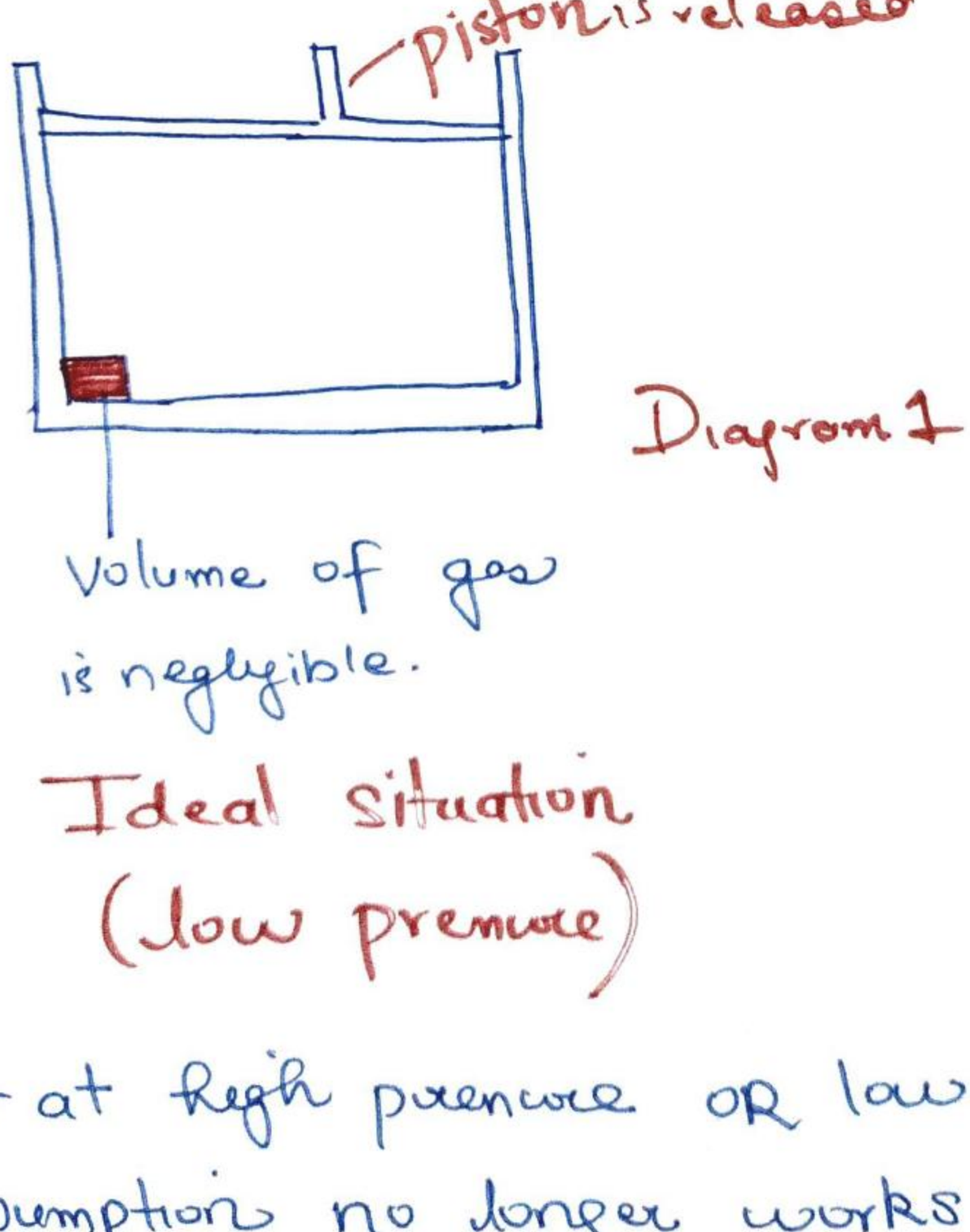


Diagram 1

But at high pressure OR low temp, that assumption no longer works.

The real gas volume becomes larger than the predicted by ideal gas equation at High Prenure (Refer Diagram 1) and also at high prenure, there are more frequent interactions b/w molecules due to ~~strong~~ being in strong proximity ~~c~~ each other. The forces of attraction become appreciable and cannot be ignored.

Equation of state for the Real Gases (vander Waals equation)

Scientist vander Waal modified the ideal gas law ($PV = nRT$) to describle the behaviour of real gases by including the effects of

(1) volume of gas molecules.

(2) The forces of attraction between gas molecule

$$PV = nRT$$

$V_{corrected} = V - nb$ → excluded volume

$$P_{corrected} = P + \frac{an^2}{V^2}$$

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

a and b are constent different for each gas

(i) Volume Correction

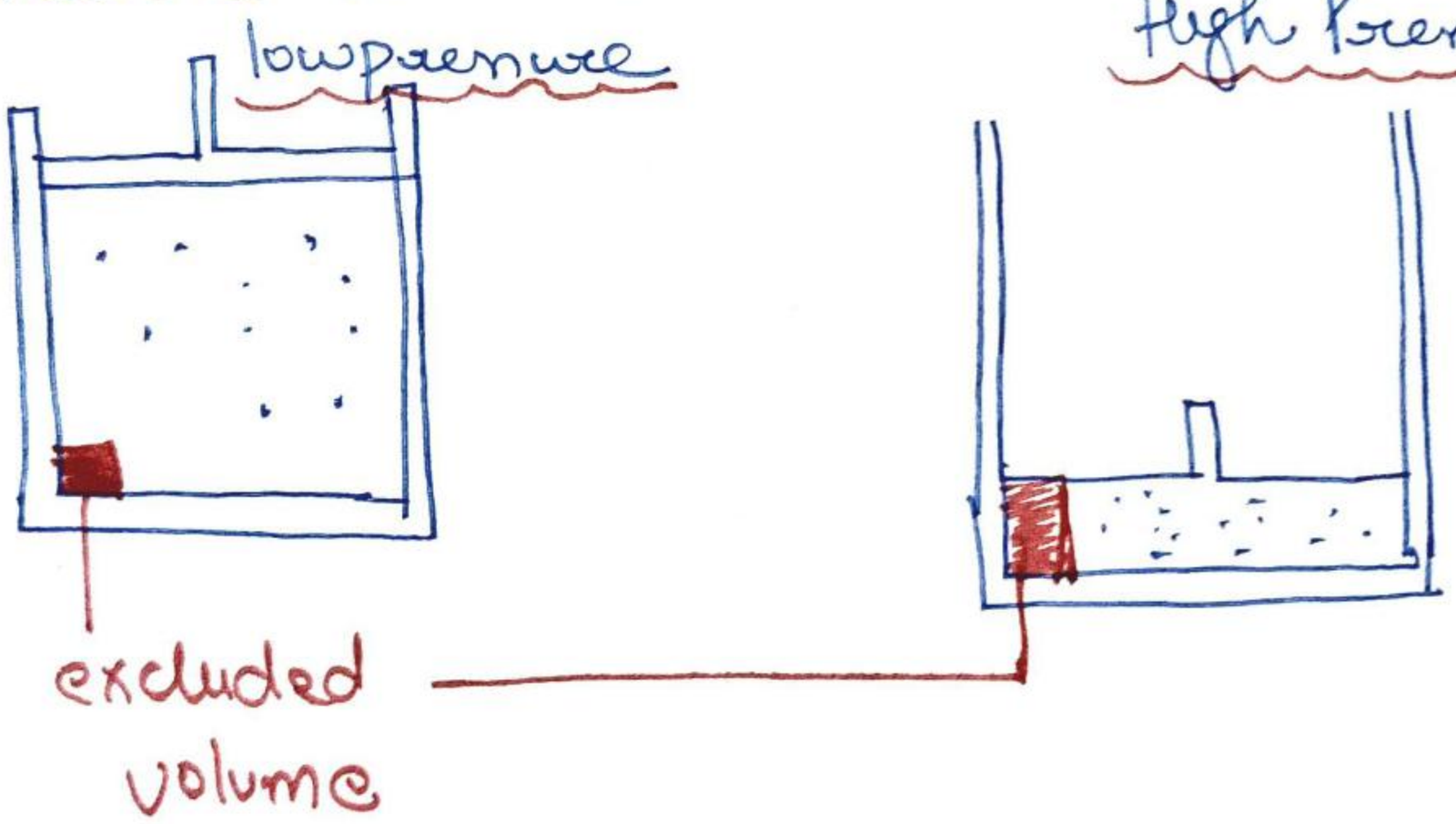
for on ideal gas $PV = nRT$.

Now in real gas, the molecular volume cannot be ignored

∴ Let us assume that 'b' is the volume excluded (out of volume of container) for the moving gas molecules per mole of a gas.

b = actual volume occupied by a mole of gas particles.

Due to n moles of a gas, the volume excluded would be nb



A real gas in container of volume V has only available volume of (V-nb) and this volume can be thought of as an udeal gas in container of volume (V-nb).

Volume term = $V - nb$

corrects for the volume occupied by gaseous molecules

$V_i = V - nb$

no. of moles of real gas

V = volume of gas

b = constant whose value depends on the nature of gas.

(ii) Pressure correction

⇒ The pressure exerted by a real gas would be less than the pressure an ideal gas would have exerted.

⇒ The real gas experiences attraction by its molecule.

∴ If real gas exerts a pressure P, then an ideal gas would exert a pressure equal to

$P + p$ → pressure lost by gas molecules due to attraction.

⇒ Intermolecular attractive forces tends to reduce the pressure from that predicted by Ideal gas law.

p is directly propotional to the extent of attraction between molecules which are hitting the container wall and the molecules which are attracting these.

$\therefore p \propto \frac{n}{V}$ (concentration of molecules which are hitting the container wall)

$p \propto \frac{n}{V}$ (concentration of molecules which are attracting these molecules)

● { concentration $= \frac{\text{no. of moles}}{\text{volume}} = \frac{n}{V}$ }

It takes two particle to engage in the pairwise intermolecular interaction. (ie Squared $\frac{n^2}{V^2}$)

$\Rightarrow p \propto \left(\frac{n}{V}\right)\left(\frac{n}{V}\right)$

$\Rightarrow p \propto \frac{n^2}{V^2}$

$\Rightarrow p = \frac{an^2}{V^2}$

constant of proportionality depends upon the nature of gas.

Higher value of a reflects the increased attraction b/w gas molecules.

Hence ideal pressure would be

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

Put these value of ideal volume Vi and ideal pressure P_i in ideal gas equation

$$P_i V_i = nRT$$

(*) correction of volume = +ve

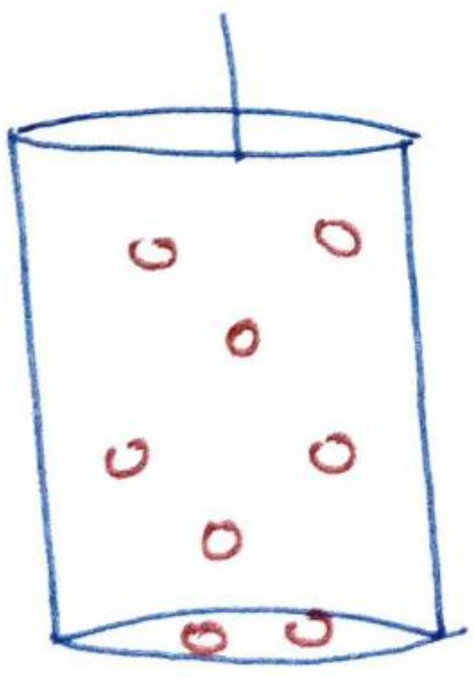
correction of pressure = +ve ($P \propto 1/V$)

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

This is called equation of state for Real gases OR vander Waal equation

Points to remember :-

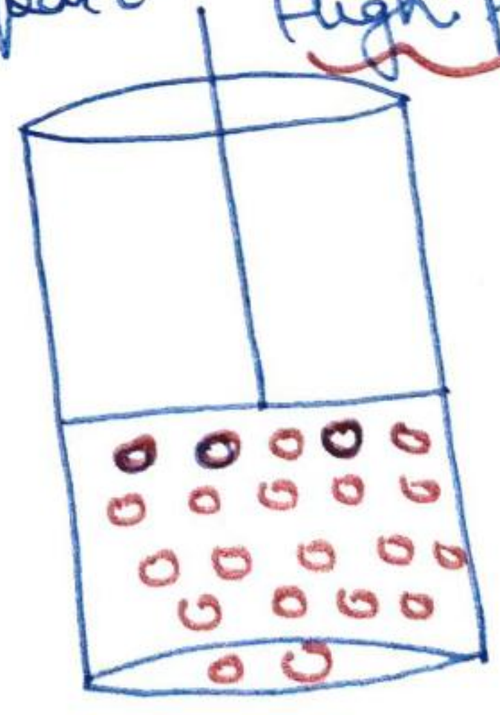
- Molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is same as the volume of container. In contrast the molecules of a real gas have small but measurable volumes. At low pressure, the gaseous molecules are relatively far apart.



Low pressure

(molecules are far apart)

High pressure



(molecules are close to one another)

- As the pressure of gas increases, the intermolecular distance (molecules one close to one another) becomes smaller and smaller. As a result, the volume occupied by the molecules becomes significant compared with the volume of container. Thus total volume occupied by the gas is greater than the volume predicted by ideal gas.

- Moreover, all molecules are attracted to one another by various forces. These forces become important for gases at low temp & high pressure, where intermolecular distances are shorter. Attraction b/w these molecules reduces the number of collision with the container wall. This effect becomes more pronounced as the number of attractive interaction increases. Because the average distance b/w molecules decreases, the pressure exerted by gas on the container wall decreases, and the observed pressure is less than expected.

- The correction for volume is -ve, but the correction for pressure is +ve, to reflect the effect of each factor on V and P respectively (*) Because non-zero molecular volume (as by ideal gas) produce a measured volume that is larger than that predicted by ideal gas law, ∴ we must subtract the molecular volumes to obtain actual volume available. (V - nb)

- Conversely, the attractive intermolecular forces produce a pressure that is less than that expected based on ideal gas law, so $\frac{an^2}{V^2}$ must be added to measured pressure to correct for these effects.

- At high temperature, the molecules have sufficient K.E. to overcome intermolecular attraction forces and effect of non-zero volume predominates

- Conversely, as temperature is lowered, K.E of gas molecule loses. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to liquid)

Significance of a & b

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

a ⇒. Its value is a measure of magnitude of attractive forces among the molecules of gas. If a is large then intermolecular forces of attraction would be large.

b ⇒ Its value is a measure of the effective size of gas molecules. Its value is equal to 4 times the actual volume of gas molecules. It is called as excluded volume OR co-volume.

Units of a & b

The units of a and b depend upon the units in which P & V are expressed.

$$\text{Unit of } a = \frac{PV^2}{n^2} = \frac{(\text{Pressure})(\text{Volume})^2}{\text{mol}^2}$$

If P is atm, V = dm^3

$$a = dm^6 \text{ atm mol}^{-2}$$

Unit of b = Same as unit of volume per mole

$$= dm^3 \text{ mol}^{-1}$$

Explaination of behaviour of real gas by vander Waal eq / Different forms of vander Waal equation:

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

At moderate pressure:

V is large and b is negligible in comparison with V

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

for n = 1

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

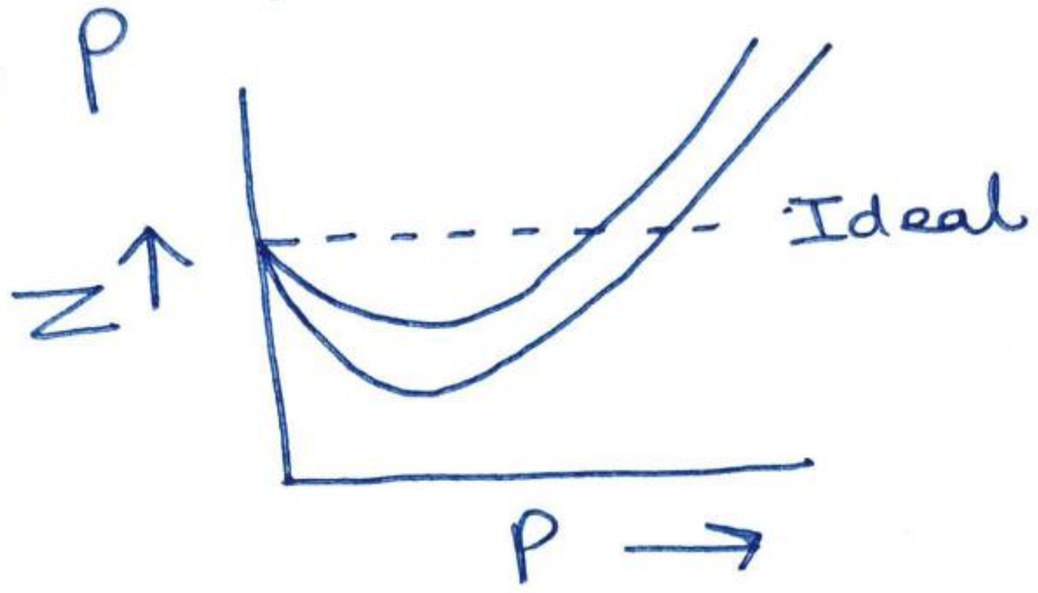
$$PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V} \quad \text{OR} \quad \frac{PV}{RT} = 1 - \frac{a}{RTV}$$

so at constant, P ↑ses (V ↓ses) OR so that $\frac{a}{RTV}$ ↑ses

$$\boxed{Z = 1 - \frac{a}{RT}} \Rightarrow Z < 1$$

This accounts for the initial dip in Z vs P plot at low P



At very low Pressure:

V is large, $\frac{a}{V^2}$ is so small that it can be neglected

Similarly, the correction term b can also be neglected in comparison to V.

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

$$(P)(V) = RT$$

$\boxed{PV = RT}$ Ideal gas equation (for n=1)

This explains why at very low pressure, the real gas behaves like an ideal gas

At high pressure :

V is so small that b cannot be ignored. The factor $\frac{a}{V^2}$ is no doubt large but as P is very high, $\frac{a}{V^2}$ can be neglected in comparison to P.

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

$$P \cdot (V - b) = RT$$

$$PV - Pb = RT$$

$$PV = RT + Pb$$

$$\frac{PV}{RT} = \frac{RT}{RT} + \frac{Pb}{RT}$$

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

OR $$Z = 1 + \frac{Pb}{RT}$$

$$\Rightarrow \boxed{Z > 1}$$

As P is ↑sing, factor $\frac{Pb}{RT}$ ↑ses. This explain why after minima in the curves, the compressibility factor increases continuously with pressure.

At high temperature :

V is very large (at a given P) so that both correction factor ($\frac{a}{V^2}$ and b) becomes negligible. Hence behaves like ideal gas.

Explaination of the exceptional behaviour of hydrogen and helium :

for H_2 and He (small mass, lightest gases known), Z is always greater than 1 , $Z > 1$ (see plot of Z vs P). This is because H_2 and He are very small molecules. The intermolecular forces of attraction in them are negligible, that is 'a' is very small so that $\frac{a}{V^2}$ can be ignored / negligible.

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

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

$$P(V - b) = RT$$

$$PV = RT + Pb$$

$$\frac{PV}{RT} = \frac{RT}{RT} + \frac{Pb}{RT}$$

$$Z = 1 + \frac{Pb}{RT}$$

$Z > 1$ and ↑ses with ↑sein the value of P at const T

measured volume

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

P: measured pressure

$\left(\frac{n}{V}\right)^2$: Ideal Pressure

(Correction factor to account for intermolecular attractions)

$(V - nb)$: Ideal volume

(Correction factor to account for the size of molecule)