Study material: For B.Sc. part-I

Subject: Physical Chemistry, paper-I (A)

Topic: Gaseous State

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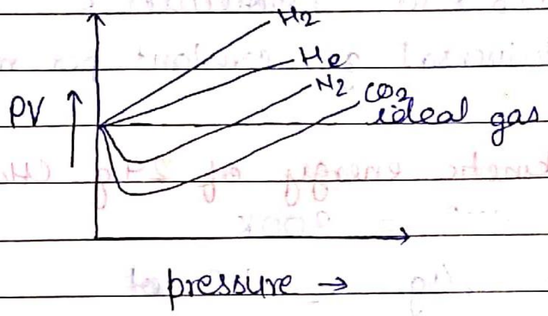
Deviation of real gases from ideal gas behaviour →

The gas which obeys the ideal gas equation [PV = nRT] compeletly at all pressures and temperatures is called an ideal gas, but no gas has been found to obey this equation compeletly as evident from following figure.



[Boyle's law PV = k
Temperature and no of mole constant]

All the existing gases are real gases and they don't obey ideal gas equation compeletly, this is due to two faulty assumption in kinetic theory of gases.

[I] The total volume of gaseous molecule is negligible in comparision to the volume of the vessel.

[II] There acts neighter attractive nor repulsive force among gaseous molecule

The deviation of a real gas from ideal gas behaviour is more pronounced when the density of the gas is high at high pressure and low temperature. $d = PM/RT$

Conversely, a real gas tends to behave as an ideal gas at low pressure and high temperature.

van der Waals equation →

van der Waals modified the ideal gas equation [$PV = nRT$] so that real gases may also obey it, for this purpose he made two corrections in ideal gas equation.

[I] Volume correction →

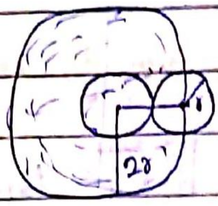
The gaseous molecules occupy some spaces and therefore the space available to a gaseous molecule to move is smaller than the volume of vessel.

Corrected volume = $V - v$

V → volume of vessel.

v → volume excluded by gaseous molecule.

Let two molecules of a gas with radius r are in a position to collide with each other, their centers can't come closer than $2r$.



volume of gaseous molecule $= \frac{4}{3}\pi r^3$.

Volume excluded mutually by two molecules $= \frac{4}{3}\pi (2r)^3$
$= 8 \cdot \frac{4}{3}\pi r^3$.

volume excluded mutually by one molecule $= 4 \cdot \frac{4}{3}\pi r^3$

volume excluded mutually by one mole molecules of gas $= 4 \cdot N_A \cdot \frac{4}{3}\pi r^3$

$= b$

= van der Waals constant.

volume excluded by n molecule of gas, $v = nb$

$\therefore$ Corrected volume $= V - v$
$= (V - nb)$.

van der Waals constant (b):→

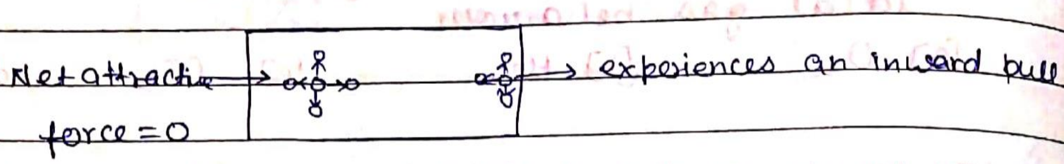
The effective volume [which is 4 times of the actual volume] of 1mol molecules of a gas is called its van der Waals constant b.

Unit of b = $L\,mol^{-1}$

$v = nb$

$\Rightarrow b = \frac{v}{n} = \frac{L}{mol} = L\,mol^{-1}$.

[II] Pressure correction:→



An attractive force acts among the molecules of a gas but when a gaseous molecule is in the bulk, it experiences zero net attractive force on the other hand when a gaseous molecules is in position to collide with the wall of vessel, it experiencs inward pull.

As a result molecule collid with the wall less effectively, therefore, the observed pressure of gas is lower than that expected in absence of intermolecular attraction.

Corrected pressure = $P + p$

P → observed pressure of gas.
p → decrease in pressure due to inter-molecular attraction.

The decrease in pressure due to intermolecular attraction is directly proportional to number of molecules colliding with the wall as well as number of molecules behind the wall.

$p \propto$ number of molecules colliding with the wall
$\propto$ molar concentration of gas $\left(\frac{n}{v}\right)$

$p \propto$ number of molecules behind the wall
$\propto$ molar concentration of gas $\left(\frac{n}{v}\right)$.

$$\therefore \quad p \propto \frac{n}{v} \times \frac{n}{v}$$

$$\boxed{p = \frac{an^2}{v^2}}$$

where, a → proportionality constant
= van der Waals constant.

Greater the value of 'a' greater will be the decrease in pressure (p) and stronger will be the intermolecular attraction.

In other words 'a' is the measure of strength of intermolecular attractive force

He H_2 O_2 N_2 CH_4 CO_2 NH_3 Cl_2 SO_2 H_2O →
value of 'a' increases
strength of intermolecular attractive force increases.

Unit of a = $atm\,L^2\,mol^{-2}$

On putting corrected pressure and corrected volume in the ideal gas equation $PV = nRT$, we have

$$(P+p)\,(V-v) = nRT$$

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

It is van der Waals equation for n moles of real gas.

for 1 mol of a real gas it becomes.

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