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Deg-I (H) - Gaseous State
Topics — Vanderwaal Equation Of State.

Vanderwaal Equation Of State :-

In order to explain the deviation from ideality, Vanderwaal Pointed out that the two assumption in Kinetic theory of gases are faulty.

Faulty Assumption in Kinetic-Theory of gases.

(i) The molecules were Considered as Point-mass i.e. negligiable in Comparision to the total volume of the gases.
(ii) It was assumed that there are no inter-molecular attraction b/w the gaseous molecules & it move independently.

The above two assumptions are true only if the pressr is low or the tempr is high so that the distance b/w the molecules is large. However, if the pressr is high & the tempr is ~~high~~ ~~low~~ low, the gaseous molecules comes closer to each other.

Derivation of vander waal's equation for real-gases.

Vander waals applied the

following Correction to the ideal gas equation.

There are two Correction factors introduced.

(a) Volume Correction factor (b):-

The volume occupied by the molecules Cannot be neglected in comparision to the total volume.

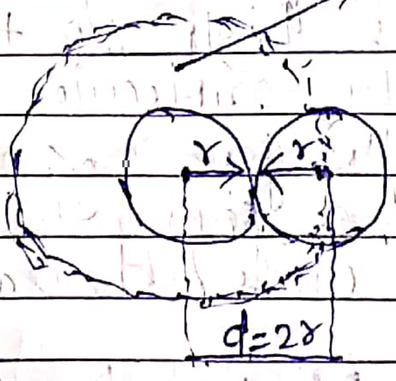
It means that the gaseous molecules are not free to move in volume of the cylinder (whole volume V) but the free volume is less than Observed volume.

Thus free volume for the gases
$= (V - b)$ $\quad b =$ Constant

$b =$ excluded volume
for one mole of gas. $=$ co-volume

for n-moles of gas, the available volume for movement
$= (V - nb)$

Excluded volume



Volume of molecules (assume to be spherical)
$= \frac{4}{3} \pi r^3$

$r =$ Radius of sphere

Excluded volume for pair of Molecules

$= \frac{4}{3}\pi(2r)^3$

$= \frac{4}{3}\pi \cdot 8r^3$

Excluded volume per molecule $= \frac{1}{2} \times 8\left[\frac{4}{3}\pi r^3\right]$

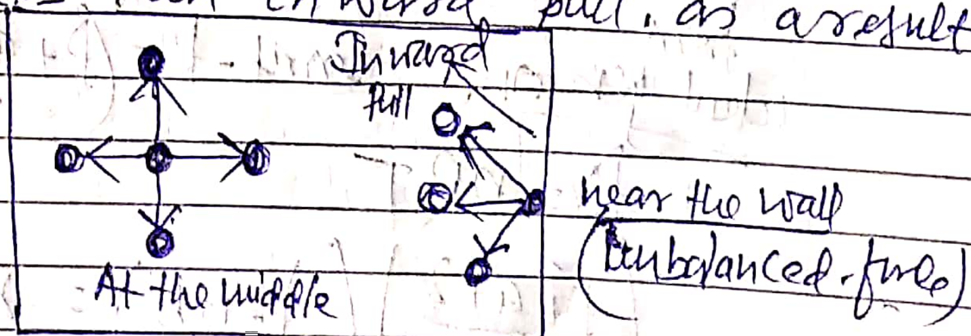
$= 4 \times \frac{4}{3}\pi r^3$

$= 4 \times$ Volume occupied by one molecule.

(b) **Pressure Correction factor (p):—**

Correction due to inter molecular Force.

There are some attractive force exist b/w the molecules of the real gas if molecules at the middle of of the Container. Such molecules is uniformly attracted by neighbouring molecules. there is no resultant pull on the molecule. But when the molecules approach the wall of the Container, it experiences an inward pull, as a result



of attractive force exerted by the neighbouring molecule inside the vessel.

Thus molecules strike the wall with a lesser force than it would have done if there were no attractive force.

Thus there is some decrease in pressure ($p = F/A$). Observed pressure is less than the ideal pressure.

$$\text{Correct pressure} = (P + p)$$

P = observed pressure

p = correction factor.

Vander waal suggested that term p.

$p \propto$ number of molecules drawing a molecule (Inward pull)

$\propto d$

d = density of gases.

$p \propto$ total number of molecules

$\propto d$

Thus $p \propto d^2$

$\left(d = \frac{m}{V}\right)$

$p \propto \frac{1}{V^2}$ a = constant (depends upon nature of gas)

or $p = a/V^2$

for n moles of gases

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

From ideal gas eqn. Correct P = $\left(P + \frac{an^2}{V^2}\right)$

$PV = nRT$

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

For one mole $\left(P + a/V^2\right)(V - b) = RT$

the above equation is Called Vander wall equation Of State.

Significance of Vanderwaal Constant a & b.

Vander waal Constant 'a'

The Constant a measure the force of attraction b/w the molecules of a gas. higher the value of a greater is the strength of force.

For Easily liquifiable gas the value of a is greater than permanent gas like H_2 & He (lower molar mass).

example — NH_3, CH_4, CO_2 etc are more easily liquifiable gas.

unit of a =

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

$$a = \frac{p \times V^2}{n^2} = \frac{atm \times lit^2}{mol^2}$$

Therefore units of a are atm lit^2 mol^{-2}.

Vanderwaal Constant (b) —

It is the effective volume of the gas molecule. The Constancy in the ~~molecule~~ value of b for any gas over a wide range of Temp & Press Conforms that the gas molecule are incompressible. Actually 'b' is not equal to actual volume of the molecules but it is four times the actual volume of molecules.