Marwari college Darbhanga

Subject---physics (Sub)

Class--- B.Sc. part 1

group----C

Topic--- Vander waal's equation of state (Thermal physics)

Lacture series –02

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Van der waal's Equation

Van der waal's equation is basically a modified version of the ideal Gas law which state that gases consist of point masses that undergo perfectly elastic collision. However, this law fails to explain the behaviour of real gases.

Van der waal's equation is an equation relating the relationship between the pressure, volume, temperature and amount of real gases. for a real gas containing 'n' moles, the equation is

$$\left(P + \frac{an^2}{V^2}\right)\left(V - nb\right) = nRT \quad \text{—— (1)}$$

where,

P = Pressure
V = Volume
T = Temperature
n = moles of the gas.
'a' and 'b' are constant specific to each other.

The equation can further be written as,

(1) Cube power of volume:-

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

(2) Reduced equation (Law of corresponding State) in terms of critical Const.

$$\left(\pi + \frac{3}{\varphi}\right)\left(3\varphi - 1\right) = 8\tau \quad \text{—— (3)}$$

where $\pi = \frac{P}{P_c}$, $\varphi = \frac{V}{V_c}$, $\tau = \frac{T}{T_c}$

Van der Waal's Equation Derivation

(1) Correction for pressure

Consider a molecule 'A' of the gas, well inside the vessel. It is attracted by other molecules in all direction with the same force and the net force acting on it is zero. But when it strikes the wall of the vessel, (Position A') it is pulled back by other molecules. It's velocity and hence momentum with which it will strike the wall would be less than the momentum with which it will strike in the absence of the force of attraction. This reduction in momentum results in decrease of pressure.
i.e, the observed pressure of the gas is less than the actual pressure.

It is evident that if we double the number of molecules per unit volume of the gas the decrease in pressure will be four times as great. It is due to this simple reson that the decrease in pressure is proportional to:-

(i) The no. of molecules striking a unit area of the walls of the container per unit time and

(ii) The no. of attracting molecules per unit volume.
Each of these factors is proportional to the density of the gas.

∴ Correction for pressure $p \propto \rho^2 \propto \frac{1}{v^2}$

$$p = \frac{a}{v^2}$$

Therefore, the Corrected or real pressure

$$= P + p = \left(P + \frac{a}{V^2}\right) \quad \text{—— (4)}$$

where P = Observed pressure.

(2) Correction for volume

Due to the finite size of a gas molecules, the actual space available for the movement of the molecules is less than the volume of the vessel. The molecules have the sphere of influence around them of radius $(2r)$, within which no other molecule can penetrate.

Here r = Radius of each gas molecules.

Volume of the molecule $= x = \frac{4}{3}\pi r^3$

The Centre of any two molecules can approach each other only by a minimum distance of $2r$. The volume of sphere of influence of each molecule

$$S = \frac{4}{3}\pi(2r)^3 = 8 \times \frac{4}{3}\pi r^3 = 8x$$

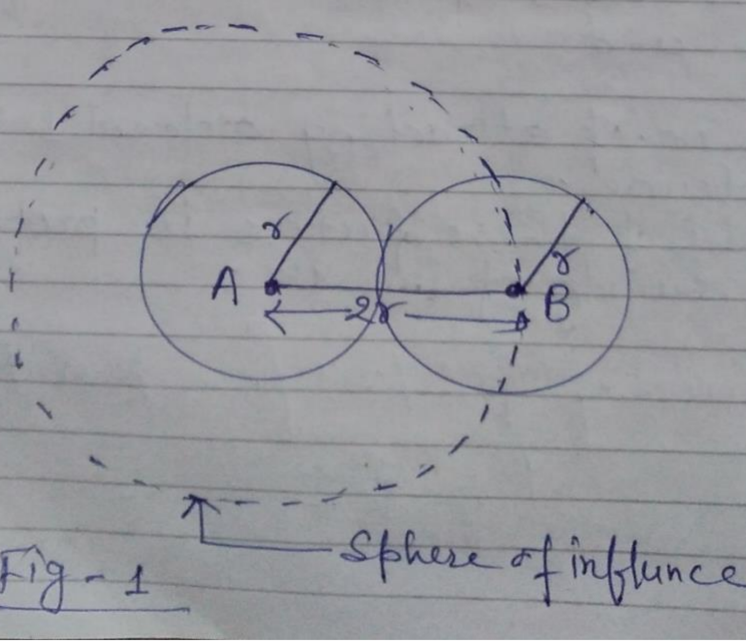

Fig - 1

Let us fill the whole space of the volume V with 'n' molecules one by one.

The volume available for the first molecule $= V$

The volume available for the Second molecule $= V - 8x$
$= V - s$

The volume available for nth molecule
$= [V - (n-1)s]$.

$\therefore$ Average space available for each molecule

$$= \frac{V + (V-s) + (V-2s) + \cdots + [V-(n-1)s]}{n}$$

$$= \frac{nV}{n} - \frac{s}{n}\{1+2+3+\cdots+(n-1)\}$$

$$= V - \frac{s}{n}\cdot\frac{(n-1)n}{2}$$

$$= V - \frac{ns}{2} + \frac{s}{2} \quad \text{—— (5)}$$

As the no. of molecules is very large $s/2$ can be neglected.

$\therefore$ Average space available of each molecule

$$= V - \frac{ns}{2} = V - \frac{n(8x)}{2} \qquad (\because s = 8x)$$

$$= V - 4(nx) = V - b \quad \text{—— (6)}$$

where $b = 4(n-x)$ = four times of actual vol. of the molecules

Thus, the Van der waal's equation of State for a gas is

$$\boxed{\left(P + \frac{a}{V^2}\right)(V-b) = RT} \quad \text{—— (7)}$$