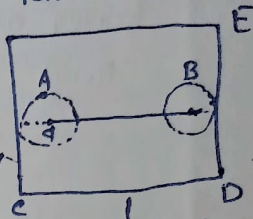


Causes of deviation from ideal behaviour and Vander Waals Equation

Vander Waals observed that the failure of ideal behaviour i.e. $PV = nRT$ relation is due to neglect of the following factors:-

- Volume of gas molecules is negligible in comparison with the total volume of the gas.
 - The gas molecules exert no attraction upon one another.
- So Vander Waals made necessary correction in ideal gas.

(A) **Volume Correction**:- Consider a molecule A of a gas in a closed space having volume V , moving parallel to CD , suppose it strikes the face of the vessel DE at B, F and come back, now $CD = l$, the distance travelled by the molecule is not $2l$, but it is $2(l-d)$. where d is diameter of the molecule.



If we consider the motion of all the molecules in this way, we find that effective volume in which the molecules are free to move is less than the total volume.

When the pressure is increased, there is decrease not in the whole volume but a part of it, (i.e. $V-b$), where b is the volume of the portion which can not be compressed.

This constant b is four times the total volume of the molecules and not equal to the volume occupied by the molecules because.

(i) When all the molecules are moving about, they obstruct each other's motion much more than if some of them were at rest.

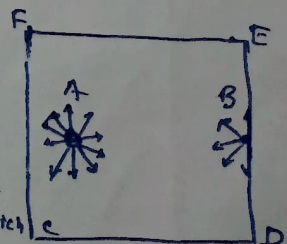
(ii) Each molecule is surrounded by its sphere of influence, radius of which is greater than the radius of the molecule within which no other molecule can penetrate.

The factor ' b ' is known as effective volume, Co-volume, or vibratory volume.

(B) **Pressure Correction**:- If we consider the molecule A inside the vessel, it is attracted by other molecules in all directions with the same force and net force on it is zero.

But when it strikes the wall of the vessel it is pulled back by other molecules.

Its velocity and hence the momentum with which it strikes the wall would be less than the momentum with which it strikes the wall would be less than the momentum with which it will strike in the absence of the force of attraction.



Naturally, when the momentum becomes less the pressure decreases.

It is evident that if we double the number of molecules per cc. of the gas, the decrease in Pressure will be four times. It is due to the fact that the decrease in pressure is proportional to²

- (i) the number of attracting molecules per unit volume.
- (ii) the number of attracted molecules striking a unit area of the walls of containing vessel per unit time.

Both the above factors are proportional to the number of molecules per cc. or density of the gas.

$$\therefore \text{Decrease in Pressure, } P \propto (\text{Density of the gas})^2$$

$$\propto \frac{1}{V^2}$$

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

where a is the proportionality constant. The factor, $\frac{a}{V^2}$ is known as Cohesive Pressure.

$$\text{Hence, Real Pressure} = \text{Observed Pressure} + \text{decrease in Pressure}$$

$$= P + \frac{a}{V^2}$$

This value of real pressure should be substituted in the perfect gas equation, Now substituting $(V-b)$ for V and $(P + \frac{a}{V^2})$ for P , we have,

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

For n moles,

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

The unit of 'a' and 'b' is the factor $\frac{a}{V^2}$ is added to P , hence dimension of $\frac{a}{V^2}$ will be the dimension of P .

$$\therefore P = \frac{n^2 a}{V^2}$$

$$\text{or } a = \frac{PV^2}{n^2} = \frac{\text{atmosphere} \times \text{litre}^2}{\text{mol}^2} = \text{atm} \cdot \text{litre}^2 \text{mol}^{-2}$$

The factor b is subtracted from V , hence the dimension of b will be the dimension of V

$$\therefore V = nb$$

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