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

(i) the number of attracting molecules per unit volume.

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

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

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

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

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

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

Hence, real Pressure = observed Pressure + 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' : The factor $\frac{a}{V^2}$ is added to P, hence dimension of $\frac{a}{V^2}$ will be the dimension of P.

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

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

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

$$\therefore V = nb$$

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