Vander waal's equation of state for real gases:

(b) Pressure Correction:

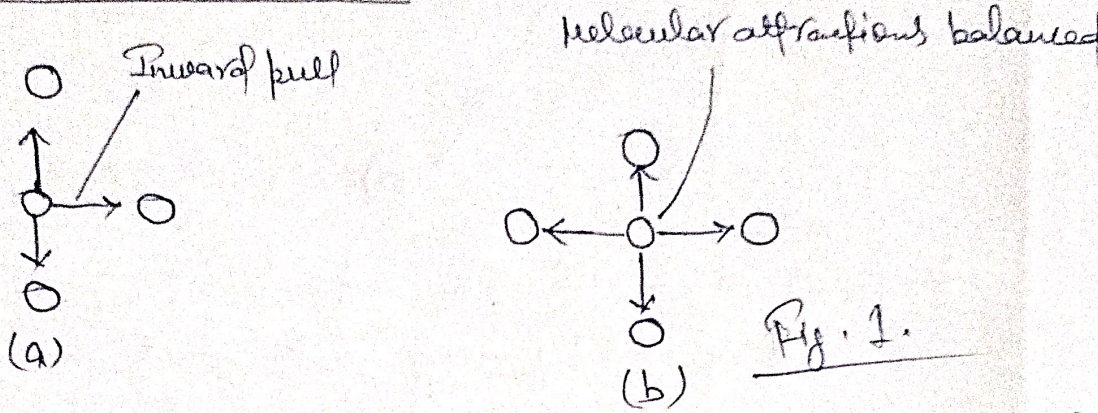


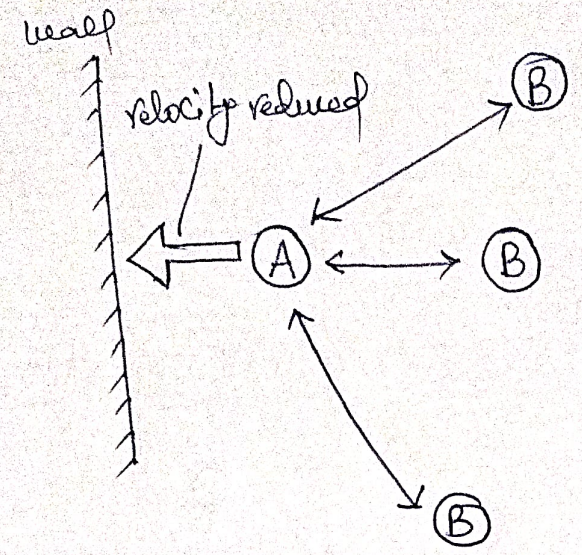
Fig. 1.

A molecule in the interior of gas is attracted by molecule on all sides. The molecules that exert the force on the container will get attracted by molecules of the immediate layer which are assumed not to be exerting pressure. These attracting characteristics cancel each other out. A molecule poised to impact the vessel's wall, on the other hand, is drawn only by molecules on one side. It feels forced to go inside as a result. Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas P, will be less than ideal pressure if the pressure P, is less than P_{ideal} by a quantity P, we have,

$$P = P_{ideal} - P$$

$$\Rightarrow P_{ideal} = P + P \quad -(2)$$

The value of P is determined by the force of attraction between molecules (A) striking the wall of the container and molecules (B) pulling them inward as shown in the fig. 2. The net force of attraction is, therefore, is



proportional to the Concentration of (A) type molecules and also of (B) type of molecules.

Therefore, $P \propto C_A \times C_B$

$\Rightarrow P \propto \frac{n}{V} \times \frac{n}{V}$

$\Rightarrow P \propto \frac{n^2}{V^2}$

$\Rightarrow P = a\frac{n^2}{V^2}$ (where, a is the Constant of proportionality which depends on the nature of gas. A higher value of 'a' reflects the increased attraction between gas molecules, n = Number of moles of real gas, V = Volume of the gas).

Hence, ideal pressure from eq. (2),

$$P_{ideal} = P + \frac{an^2}{V^2} \quad -(3)$$

Substituting the values of ideal volume and ideal pressure in ideal gas equation i.e. $PV = nRT$, the modified equation (Van der waal's equation) is obtained as

$$\boxed{\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad -(4)}$$ → Van der waals equation or Real gas equation.

The units of a = L^2 atm mol^{-1}; b = $L\,mol^{-1}$

The numerical values of a and b are in order of $10^{-1} - 10^{-2}$ & $10^{-2} - 10^{-4}$ respectively.