UG SEM II (MJC-2T) Physical chemistry

1. Gaseous state

Vander waal's equation of state for real gases:

Van der waal, in 1873 studied the postulates of kinetic theory in detail and found that there are two faulty postulates.

(i) The molecules in a gas are point masses and possess no volume.

(ii) There are no intermolecular attraction in a gas.

Van der waal's was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation, $PV = nRT$.

His corrections are given below;

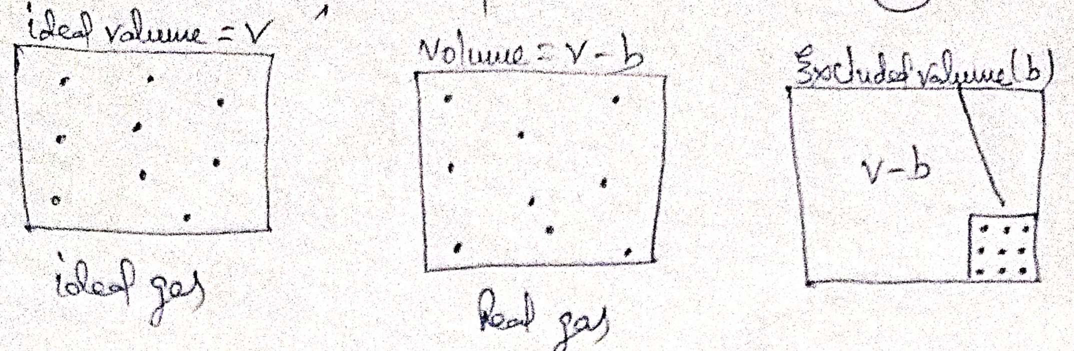
(a) Volume correction: Volume of the gas in the available space for the movement of gas molecules must be considered. Volume V of an ideal gas is the same as the volume of the container. The dot molecule of ideal gas has zero-volume and the entire space in the container is available for their movement. But Van der waals assume that molecules of real gas are rigid spherical particles which possess a definite volume.

Therefore, Volume of real gas = ideal volume − effective volume of gas molecules

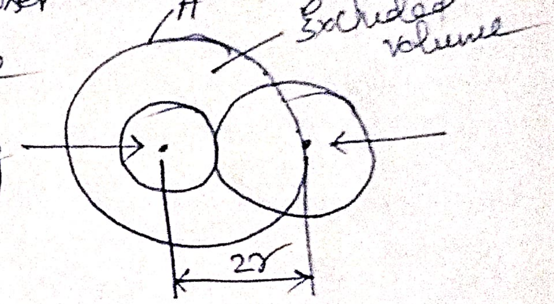
If 'b' is the effective volume (or excluded volume) of molecules per mole of the gas then,

Corrected volume should be, $V - b = V_{ideal}$

For 'n' moles, $V_{ideal} = V - nb$ — (1)



Now let us consider two molecules of radius 'r' colliding with each other (fig. below). Obviously, they can't approach each other closer than 'r'. Therefore, the space indicated by the sphere A having radius 2r will not be available to all other molecules of the gas.



In other words, the dotted space is excluded volume per pair of molecules.

Thus, excluded volume for two molecules =

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

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

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

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

For n moles $= n \times 4 \times \frac{4}{3}\pi r^3 = nb$