

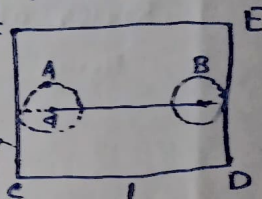
Causes of deviation from ideal behaviour

and Van der Waals Equation

Van der 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 Van der 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.

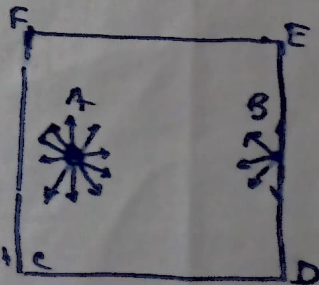
When the pressure is increased, there is decrease not only the whole volume but a part of it, (i.e. $V-b$), where b is the volume of the portion which cannot be compressed.

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

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