Dr. L. K. Mishra
Deptt of Chemistry

Page No.
Date

Deg I Chem. Hons, Paper – I

Topic :- Gaseous state

The Vanderwaal's equation :-

Vanderwaal applied suitable correction due to molecular volume as well as due to molecular attraction

Correction due to molecular volume

Ideal gas equation for n moles

$$PV = nRT$$

V is the total volume occupied by n moles of the gas. This includes the volume of the molecules as well. But the molecules are incompressible Hence a certain volume, called the excluded volume is not available for the movement of molecules.

If the excluded volume occupied by one mole of a gas is represented by b then for one mole gas the equation should be as follows:-

$$P(V-b) = RT$$

The excluded volume for n moles will be represented by nb

$$P(V-nb) = nRT$$

[b is a Constant known as Vanderwaal's Const

Correction due to molecular attraction

A molecule lying somewhere in the middle of a vessel as shown by Point A in the figure is being attracted uniformely on all sides by the neighbouring molecules. These forces cancel one another and there is no resultant attractive forces on the molecules. However, as the molecule approaches the wall of the vessel as shown by Point B in the figure it experiences attractive forces from the bulk of the molecule behind it.

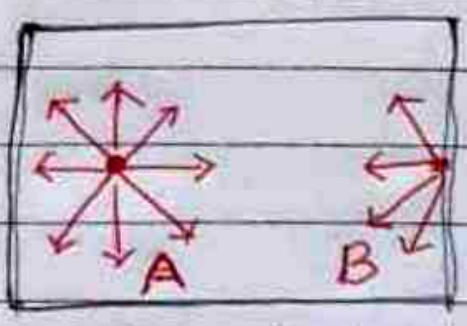

Figure.

Hence it will strike the wall with a lower velocity and would exert a lower Pressure than it would have been done if there were no forces of attraction. It is, therefore, necessary to add a certain quantity to the Pressure P in order to get the corrected Pressure = P + p

Correction factor p is proportional to the square of the density of the gas.

$$p \propto d^2$$

Suppose there are n moles of gas occupying volume V then

$$d \propto \frac{n}{V}$$

$$\text{or } d^2 \propto \frac{n^2}{V^2}$$

$$\therefore p \propto \frac{n^2}{V^2}$$

$$\therefore p = \frac{an^2}{V^2}$$ where a is known as Vanderwaal's Constant and depends on the nature of gas

∴ The corrected gas equation for n moles of a gas may be written as

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

This equation is known as Vanderwaal's equation which is applicable to all real gases.