Subject ⇒ Chemistry
Chapter ⇒ Gaseous State (Group-A)
Topic ⇒ Van der Waals equation.

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Vander Waals Equation

Van der Waal obtained the equation for real gases by applying the corrections for volume and pressure as follows

(i) Volume Correction

The volume of gas is the free space in the container in which molecules move about.

Volume V of an ideal gas is the same as the volume of the container.

The volume of a real gas is, therefore, ideal volume minus the volume occupied by gas molecules.

If b is the effective volume of molecules per mole of the gas.

The volume in the ideal gas equation is corrected as $(V-b)$

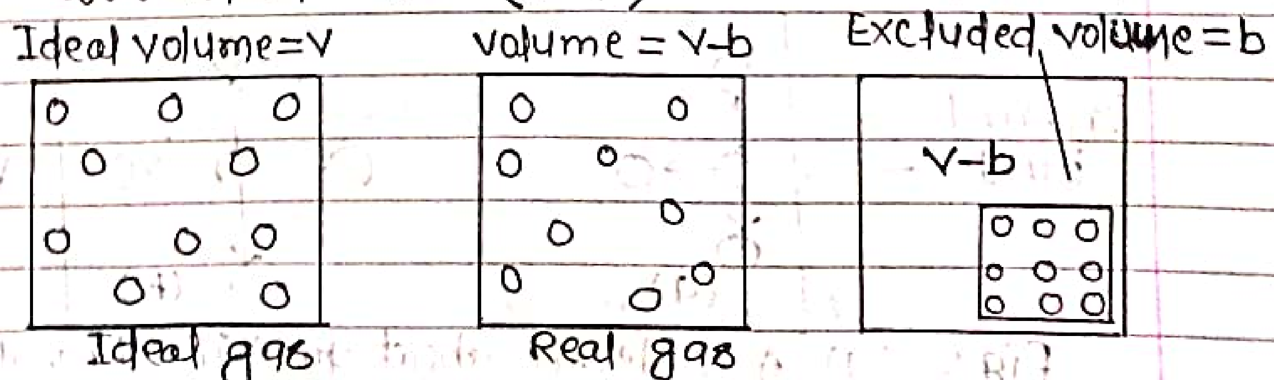

Fig:- Volume of Real gas

for n moles of the gas,

The corrected volume = $(V - nb)$

Where b = Excluded volume which is constant and characteristic for each gas.

The excluded volume is not equal to the actual volume of the gas molecules.

The excluded volume is four times the actual volume of gas molecules is calculated as-

Excluded volume for two molecules $= \frac{4}{3}\pi(2r)^3$

$= 8(4/3\pi r^3)$

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

$= 4V_m$

Where V_m = Actual volume of a single molecule

Thus, excluded volume of the gas molecules is four times the actual volume of molecules.

(ii) Pressure correction

A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull.

Fig:- (a) A molecule about to strike the wall has a net inward pull
(b) A molecule in the interior of gas has balanced attraction

Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas P will be less than the ideal pressure.

If the actual pressure P is less than P_{ideal} by a quantity p, we have

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

or $$P_{ideal} = P + p$$

p is determined by the force of attraction between molecules (A) striking the wall of container and the molecules (B) pulling them inward. The net force of attraction, therefore, proportional to the concentration of (A) type molecules and also of concentration of (B) type molecules.

i.e.

$$p \propto C_A \times C_B$$

or, $$p \propto \frac{n}{V} \times \frac{n}{V}$$

or, $$p = \frac{an^2}{V^2}$$

Where n = Total no. of gas molecules in volume V.

a = Proportionality constant characteristic of the gas.

Thus, the pressure P in the ideal gas equation is corrected as.

$$\left(P + \frac{an^2}{V^2}\right)$$ for n mole of gas.

Putting the values of corrected pressure and volume in the ideal gas equation $PV = nRT$ we get

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

This is known as van der waals equation for n moles of a gas.

For 1 mole of gas (n = 1) van der waals equation becomes

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

This eqn is known as van der waals equation. Where a and b are van der waals constants.

Significance of van der waals constants a and b

Constant a is a measure of the intermolecular forces of attraction in a gas.

The values of constant a for the easily liquefiable gases are greater than those for permanent gases like H_2 and He.

The value of a increases with the ease of liquefaction of the gas.

Constant b is the effective volume of the gas molecules.

The constancy in the value of b for any gas over a wide range of temperature and pressure confirms that the gas molecules are incompressible.

S.I. unit of constant a and b

If pressure and volume are taken in S.I. units,

$$a = \frac{(\text{Pressure})(\text{Volume})^2}{(\text{mol})^2} = \frac{(Nm^{-2})(m^3)^2}{(\text{mol})^2}$$

$\therefore$ $a = N m^4 mol^{-2}$

And b = volume mol^{-1}

$\therefore$ $b = m^3 mol^{-1}$ (S.I.)