

J.N. College, Marhauai Vander Waals' Eqn of State

An Ideal gas :- An ideal gas is one which strictly obeys the Boyle's law and Charles's law under all conditions of temperature & pressure. Its molecules do not exert force of attraction on one another. The internal energy is, therefore, wholly kinetic depending on the temperature only.

Eqn. of State of an Actual gas :-

The ideal gas eqn.  $PV = RT$  does not correctly represent the behaviour of real gases as revealed by experiments. This eqn., as derived from kinetic theory is based on two assumptions, namely:

- (i) The molecules of a gas are infinitesimally small in size.
  - (ii) They do not exert mutual attraction on one another.
- Actually the molecules of a real gas do possess a finite size and also attract one another. Hence the eqn. of state of an actual gas will be different from that of an ideal gas.

Derivation of Vander Waals' eqn. of state :-

Vander Waals modified the ideal gas eqn. by making allowance for the finite size of the molecules and for their mutual attraction.

The eqn. of state for 1 mole of an ideal gas occupying a volume  $V_i$  at a pressure  $P_i$  is

$$P_i V_i = RT \quad \text{--- (1)}$$

Let us now consider 1 mole of an actual gas occupying an observed volume  $V$  at an observed pressure  $P$ . Let us apply corrections for the finite size of the molecules of the gas and their

mutual attractions.

### Corrections for finite size of molecules -

The molecules of a gas occupy a finite volume in space. Therefore the volume actually available for the molecules to move freely is less than the volume of the gas. Therefore, a real gas occupying a volume  $V$  is equivalent to an ideal gas. Therefore, a real gas occupying a volume  $V$  is equivalent to an ideal gas (whose molecules are of negligible size) of smaller volume  $V_i$  such that

$$V_i = V - b \quad \text{--- (ii)}$$

$b$  is a constant for 1 mole of the gas and is called the 'covolume'. It has been shown that  $b$  is four-times the actual volume of the molecules present in the gas, because each molecule is surrounded by a sphere of space within which no other molecule can enter.

### Correction for Intermolecular Attraction :-

A molecule in the body of the gas is uniformly surrounded by other molecules. Hence it is attracted equally in all directions i.e. it experiences no resultant force. A molecule near the wall of the containing vessel, however, experiences an inward pull due to unbalanced attractions of the molecules behind it as shown in fig. On account of this pull, the molecule collides against the wall with a smaller momentum i.e. the effective pressure of the gas is reduced. Thus the observed

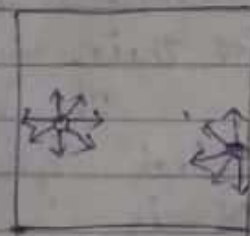


Fig. 1

pressure  $p$  exerted by a real gas is less than the pressure  $P_i$  which would have been exerted by an ideal gas (in which there is no molecular attraction.) Therefore

$$P = P_i - B$$

(iii)

or  $P_i = P + B$

The reduction in pressure,  $B$ , depends upon the inward pull on a molecule near the wall due to the attraction of molecules behind it, as well as on the number of molecules colliding against unit area of the wall per second. Each of these factors is proportional to the density of the gas (number of molecules in unit volume of the gas). Therefore,  $B$  will be directly proportional to the square of the density of the gas or inversely to the volume occupied by a given mass of the gas. Thus

$$B = \frac{a}{V^2}$$

where  $a$  is constant for 1 mole of the gas.  $a/V^2$  is called 'internal pressure'. Substituting this value of  $B$  in equ<sup>n</sup>. (iii), we get

$$P_i = P + \frac{a}{V^2} \quad \text{--- (iv)}$$

Substituting for  $V_i$  and  $P_i$  from equ<sup>n</sup>. (ii) and (iv) in equ<sup>n</sup>. (i), we obtain

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

This is Vander Waals' equation of state for 1 mole of an actual gas.

For  $\mu$  moles of the gas the equ<sup>n</sup> would be

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

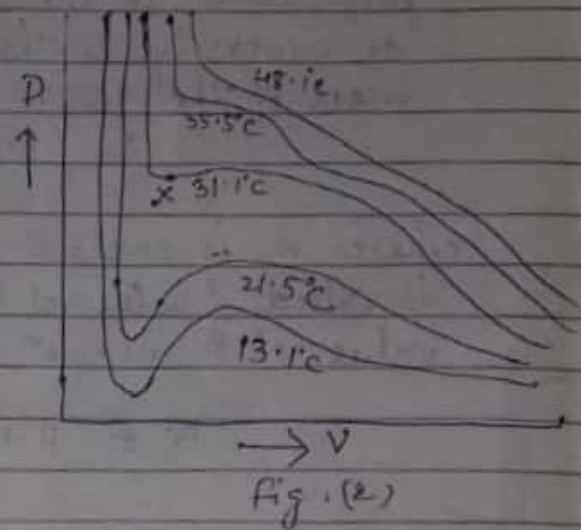
② Critical constants of a gas in terms of the constants 'a' and 'b' of the Van der Waals' eqn.

The three critical constants of a gas are: the critical temperature  $T_c$ , the critical pressure  $P_c$  and the critical volume  $V_c$ . To determine their values, let us write the Van der Waals' eqn. in the following form

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{--- (i)}$$

If  $P$  is plotted against  $V$  at different constant values of  $T$ , a set of isotherms is obtained in fig. (2). The isothermal through the critical point  $x$  is horizontal at  $x$  i.e. the slope of the isothermal at  $x$  is zero. Therefore at  $x$

$$\left(\frac{dP}{dV}\right)_T = 0$$



Also, the curvatures of this isothermal on the two sides of the critical point  $x$  are opposite i.e. the point  $x$  is a point of inflexion. Therefore at  $x$

$$\left(\frac{d^2P}{dV^2}\right)_T = 0$$

Applying these two conditions to the Van der Waals eqn. (i), we get

$$\left(\frac{dP}{dV}\right)_T = \frac{RT}{(V-b)^2} - \frac{2a}{V^3} = 0, \quad \text{--- (ii)}$$

$$\text{and } \left(\frac{d^2P}{dV^2}\right)_T = \frac{-2RT}{(V-b)^3} + \frac{6a}{V^4} = 0 \quad \text{--- (iii)}$$

But at the critical point  $P = P_c$ ,  $V = V_c$  and  $T = T_c$ . Hence from (i)

$$P_c = \frac{RT_c}{(V_c - b)} - \frac{a}{V_c^2} \quad \text{--- (iv)}$$

From (ii)

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \quad \text{--- (v)}$$

and from (iii)

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4} \quad \text{--- (vi)}$$

Dividing eqn. (v) by (vi) we get

$$\frac{1}{2} (V_c - b) = \frac{1}{3} V_c$$

$$\boxed{V_c = 3b} \quad \text{--- (vii)}$$

Substituting  $V_c = 3b$  in eq. (v), we get

$$\frac{RT_c}{4b^2} = \frac{2a}{27b^3}$$

$$\boxed{T_c = \frac{8a}{27bR}} \quad \text{--- (viii)}$$

Substituting  $V_c = 3b$  and  $T_c = \frac{8a}{27bR}$  in eqn. (iv), we get

$$P_c = \frac{R}{2b} \left( \frac{8a}{27bR} \right) - \frac{a}{9b^2}$$

$$P_c = \frac{R}{2b} \left( \frac{8a}{27bR} \right) - \frac{a}{9b^2}$$

or

$$P_c = \boxed{\frac{a}{27b^2}} \quad \text{--- (ix)}$$

$$\therefore \frac{RT_c}{P_c V_c} = \frac{R \cdot \frac{8a}{27bR}}{\frac{a}{27b^2} \cdot 3b} = \frac{8}{3} = 2.67.$$

$\frac{RT_c}{P_c V_c}$  is called the "critical coefficient" and is the

same for all gases.

Determination of 'a' and 'b' :-

From eq<sup>n</sup>. (viii) and (ix), we have

$$\frac{T_c^2}{P_c} = \left( \frac{8a}{27bR} \right)^2 \frac{27b^2}{a}$$

$$a = \frac{27R^2}{64} \left( \frac{T_c^2}{P_c} \right)$$

Again from eq<sup>n</sup>. (viii) and (ix) we have

$$\frac{T_c}{P_c} = \frac{8a}{27bR} \times \frac{27b^2}{a}$$

$$b = \frac{R}{8} \left( \frac{T_c}{P_c} \right)$$

Thus 'a' and 'b' can be determined if  $T_c$  and  $P_c$  are known.  $T_c$  and  $P_c$  can be obtained directly from experiments.