

**Udai Pratap (Autonomous) College, Varanasi****E-learning Material**

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| <b>Module/ Lecture</b> | <b>03</b>   |
| <b>Topic</b>           | <b>Van der Waals Equation<br/>and<br/>Critical Constants</b>  |
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## Van der Waals Equation and Critical Constants

### Van der Waals Equation

The history of **equations of state** goes back to two laws namely Boyle's Law and Charles' Law.

According to Boyle's law: For a fixed mass of gas at constant temperature, the volume is inversely proportional to the pressure. Mathematically

$$pV = \text{constant} \quad (1)$$

According to Charles' law: For a fixed mass of gas at constant pressure, the volume is directly proportional to the absolute temperature. Mathematically

$$\frac{V}{T} = \text{constant} \quad (2)$$

Combining these two laws, one get the ideal gas equation

$$pV = RT \quad (3)$$

which was arrived by assuming that molecules are point masses having negligible volume and exerts no force of attraction/repulsion on one another. An improvement over the ideal gas equation of state based on elementary molecular arguments was suggested in 1873 by Van Der Waals who noted that gas molecules actually occupy more than the negligibly small volume presumed by the ideal gas model and also exert long-range attractive forces on each other. Thus, not all of the volume of a container would be available to the gas molecules and the force they exert on the container wall would be reduced because of the attractive force that exists between molecules. Van der Waals suggested following two corrections

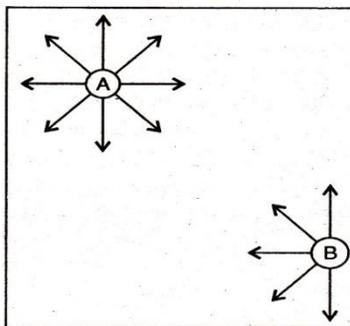
1. **Correction for the finite size of Molecule :** Consider one mole of a gas enclosed in a container of volume  $V$ . If this gas is composed of point masses all this Volume could be available to them for free motion. When molecular size is taken into account, the volume available to single molecule for free movement will somewhat less than  $V$ . Let us denote this reduction by  $b$  (which known as covolume). Therefore the factor  $V$  occurring in the perfect gas Equation should be replaced by  $(V-b)$ .

The magnitude of  $b$  is equal to four times the total molecular volume for one mole of a Van der Waals gas.

2. **Correction for Intermolecular Attraction:** The pressure factor appearing in the perfect gas Equation will also have to be corrected because of the presence of intermolecular attractive force in the real gas.

A molecule interior of the volume, say  $A$ , will have to face attractive force due to its neighboring molecules which are present in all its sides. Since it is equally attracted in all the directions, net force on it will be zero.

On the molecule at the surface or near the surface, say  $B$  will face the attractive force due to its neighboring molecules having which are present on on hemisphere only. Thus there will be resultant inward force perpendicular to the surface.



The force on the single molecule at the surface will obviously be proportional to the number  $n_v$  of the attracting molecules per unit volume.

Also the number of molecules in unit area of the surface multiplied by the above mentioned force on one molecule will give a net inward force per unit area or Net inward pressure called cohesive pressure.

The Number of molecules in unit area is again proportional to number of molecules per unit volume  $n_v$ .

Thus extra cohesive inward pressure  $p'$  due to attraction of neighboring molecules will be proportional to  $n_v^2$ ,

$$\begin{aligned} \text{i.e.} \quad p' &\propto n_v^2 \\ &\propto \frac{1}{V^2} \\ &= \frac{a}{V^2} \end{aligned}$$

where  $a$  is a constant of proportionality.

Now the net pressure (equivalent to perfect gas) on the gas will be the sum of observed external pressure on the gas and the drop caused by the intermolecular attraction.

Thus pressure  $p$  in the perfect gas equation must be replaced by  $(p + \frac{a}{V^2})$ . On introducing the two corrections, the equation of state of the real gas will be

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (4)$$

Equation (4) is known as Van der Waals equation of state, where  $a$  and  $b$  are Van der Waals constants.

For  $n$  moles of the real gas above equation becomes

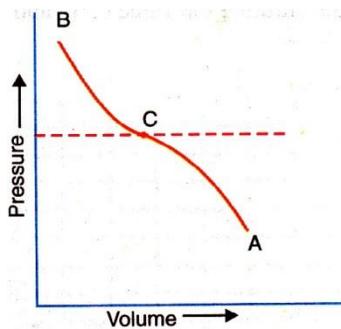
$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (5)$$

## Critical Constants of a real gas

1. **Critical Temperature:** Critical temperature of a gas is the highest temperature at which gas can be liquefied by applying pressure alone. It is denoted by  $T_c$ .
2. **Critical Pressure:** The amount of pressure necessary to liquefy the gas at its critical temperature is known as critical pressure. It is denoted by  $p_c$ .
3. **Critical Volume:** The volume of one mole of the gas at its critical temperature and critical pressure is known as its critical volume. It is denoted by  $V_c$ .

**Derivation of expressions for Critical Constants of a real gas:** The values of critical constants in terms of Van der waals constants can be deduced as follows

If we plot the curve between pressure vs Volume we see that at critical point C  $\frac{\partial p}{\partial V} = 0$ . The point C is also called the **point of inflexion**, and at point of inflexion  $\frac{\partial^2 p}{\partial V^2} = 0$ .



Hence at critical point C, we have  $\frac{\partial p}{\partial V} = 0$  and  $\frac{\partial^2 p}{\partial V^2} = 0$ .

Van der Waals equation for state of real gas is ,

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

or 
$$p = \frac{RT}{(V-b)} - \frac{a}{V^2} \quad (1)$$

Now from Eq. (1)

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \quad (2)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{RT}{(V-b)^3} - \frac{6a}{V^4} \quad (3)$$

But Eqns. (2) and (3) vanish at  $T = T_c$ ,  $p = p_c$ ,  $V = V_c$ . Thus from Eqns. (2) & (3) we have,

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

$$\frac{RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4} \quad (5)$$

Dividing Eq. (4) by Eq. (5), we get

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

i.e. 
$$V_c = 3b \quad (6)$$

Substituting the value of this value of  $V_c$  in Eq. (4), we get

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

$$T_c = \frac{8a}{27Rb} \quad (7)$$

Also at critical point Van der Waals Equation becomes

$$\left(p_c + \frac{a}{V_c^2}\right)(V_c - b) = RT_c \quad (8)$$

Substituting the values of  $T_c$  and  $p_c$  from Eqns. (6 & 7) into Eq. (8) we get

$$\left(p_c + \frac{a}{9b^2}\right)(3b - b) = R \frac{8a}{27Rb}$$

i.e. 
$$p_c = \frac{a}{27b^2} \quad (9)$$

Thus all the critical; constant of Van der Waals gas are obtained in Equations (7-9) in terms of constants a and b. Since critical point for any gas can be obtained experimentally, hence the constant a and b can be determined from these relation.

We should also note that the critical coefficient

$$\frac{RT_c}{p_c V_c} = \frac{8}{3} \quad (10)$$