

# Kinetic Theory of Gases

## 6. Correction in Ideal Gas equation to achieve van der Waals gas equation of state

**Correction for finite size:** if  $V$  is volume available for one mole of gas (volume of container). If size of molecule take into account then  $(V - b)$  is volume available for real gas which is less than  $V$ .  $b$  is popularly known as co volume which is dependent on the nature of gas.

**Example:** If  $V_m$  is molecular volume of real gas then prove that  $b = 4NV_m$  if  $N$  is total number of molecule in container.

**Solution:** The volume available to first molecule =  $V$

The volume available to second molecule =  $V - V_s$

Where  $V_s$  volume of exclusion i.e. around any molecule,

a spherical volume is  $V_s = \left(\frac{4\pi d^3}{3}\right)$  will be denied to

every other molecule.

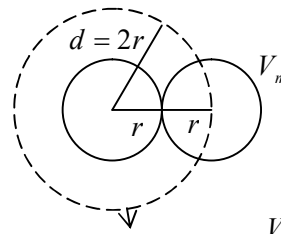
$$\text{Volume of exclusion } V_s = \frac{4\pi(2r)^3}{3}$$

Similarly volume available to  $N^{\text{th}}$  molecule =  $V - (N - 1)V_s$

Average volume available for each molecule

$$\langle V \rangle = \frac{1}{N} \sum_{i=1}^N V - (i-1)V_s = V - \frac{N(N-1)V_s}{2N} = V - \frac{N}{2}V_s = V - \frac{N}{2}8V_m = V - 4NV_m$$

$$(V - b) = V - 4NV_m \quad \text{so } b = 4NV_m$$



Volume of exclusion

$$V_s = 4\pi \frac{(2r)^3}{3}$$

$$V_s = 8V_m$$

**Correction for intermolecular attraction:** A molecule in the equally in all direction so that there is no resultant force on it.

But for outermost layer close to surface there will be net inward force. So whenever a molecule strikes the walls of container, the momentum exchange will be less than for Ideal gas.

These forces are cohesive in nature and proportional to number of molecule.

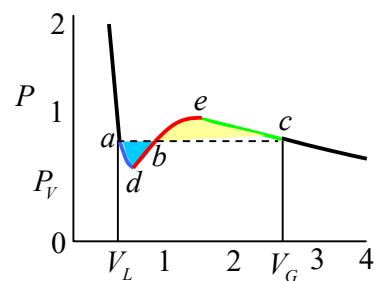
So for real gas change in pressure is  $\frac{a}{V^2}$ . So for real gas pressure will be  $\left(P + \frac{a}{V^2}\right)$

So gas equation reduce to  $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

$$\text{Then } P = \frac{RT}{V - b} - \frac{a}{V^2}$$

### Maxwell Equal Area

James Clerk Maxwell replaced the isotherm between  $a$  and  $c$  with a horizontal line positioned so that the areas of the two hatched regions are equal (means area of  $adb$  and  $bec$  are equal). The flat line portion of the isotherm



now corresponds to liquid-vapor equilibrium. As shown in figure.

The portions  $a-d$  and  $c-e$  are interpreted as metastable states of **super-heated liquid** and **super-cooled vapor** respectively. The equal area rule can be expressed as:

$$P_v (V_G - V_L) = \int_{V_L}^{V_G} P dV$$

where  $P_v$  is the vapor pressure (flat portion of the curve),  $V_L$  is the volume of the pure liquid phase at point  $a$  on the diagram, and  $V_G$  is the volume of the pure gas phase at point  $c$  on the diagram. The sum of these two volumes will equal the total volume  $V$ .

**Example:** One mole of a certain gas is contained in a vessel of volume  $V$ . At a temperature  $T_1$  the gas pressure is  $p_1$  atm and at a temperature  $T_2$  the pressure is  $p_2$  atm. Find the Van der Waals parameters for this gas.

**Solution:** it is given no of mole  $n = 1$

$$\left( P_1 + \frac{a}{V^2} \right) (V - b) = RT_1 \quad (i)$$

$$\left( P_2 + \frac{a}{V^2} \right) (V - b) = RT_2 \quad (ii)$$

from (i) and (ii)

$$a = \frac{V^2(T_1 P_2 - T_2 P_1)}{(T_2 - T_1)}$$

$$b = V - \frac{R(T_2 - T_1)}{(P_2 - P_1)}$$