

(b) Van der Waals Equation of State

The van der Waals equation for real gases are given by,

$$\text{For one mole of gas, } \left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$\text{And for } n \text{ mole of gas, } \left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT .$$

Assumptions for real gas:

1. Gas molecules have finite size
2. There are weak interaction force, which depends only upon distance between them.
3. The molecular density is small and the number of collisions with the walls of the container is exactly same for point and finite size molecules.

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 taken 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 = $V - V_s$

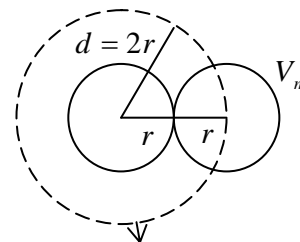
where, V_s is volume of exclusion i.e. around any molecule, a

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

molecule.

$$\text{Volume of exclusion, } V_s = \frac{4\pi(2r)^3}{3} = 8V_m$$

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



Volume of exclusion

Hence, the average volume available to each molecule is,

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

[As for large N , 1 can be neglected]

$$\text{So, } (V - b) = V - 4NV_m \Rightarrow b = 4NV_m$$

Correction for intermolecular attraction

A molecule in the interior of the gas is on average attracted equally in all direction, so that there is no resultant force on it. But for outermost layer closes to the surface of container, there will be net inward force. So whenever a molecule strikes the walls of container, the momentum exchange will be less than that for an Ideal gas.

These forces are cohesive in nature and proportional to number of molecules. So, for real gas change in pressure is $\frac{a}{V^2}$. So for real gas pressure will be $\left(P + \frac{a}{V^2}\right)$

$$\text{So, the gas equation reduces to } \left(P + \frac{a}{V^2}\right)(V - b) = RT. \text{ Then, } P = \frac{RT}{V - b} - \frac{a}{V^2}$$

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 vapour pressure (flat portion of the curve), V_L is the volume of the pure liquid phase at point a as shown in the diagram and V_G is the volume of the pure gas

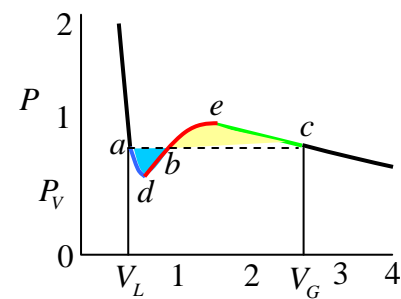


Figure 1

phase at point c as shown in the diagram. The sum of these two volumes will be equal to 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 that the number of mole $n = 1$

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

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

from (i) and (ii)

$$a = \frac{V^2(T_1P_2 - T_2P_1)}{(T_2 - T_1)}$$

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

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