van der waal's Equation and critical constants:

Thomson studied the isotherms of CO_2 drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical tempratures. These isotherms shoul really exhibit a complete continuity of state from gas to liquid.

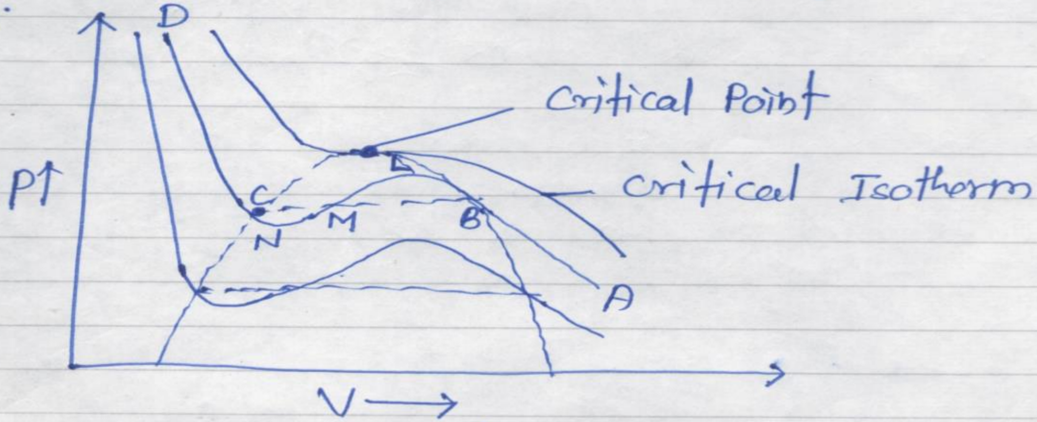


Fig: Curve MLB represents a gas compressed in a way that it would remain stable.

The curve MNC represents the superheated liquid.

This type of continuity of state is predicted by van der Waals cubic equation.

According to it, for any given values of P and T there should be three values of V. These values are indicated by points B, M and C of the wavy curve. The three values of V become closer as the horizontal part of the isotherm rises. At the critical point, these valu become identical. This enables the calculation of T_c, P_c & V_c in terms of van der Waals constants.

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

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT = 0$$

Multiplying the whole equation by V^2

$$PV^3 + aV - \underline{Pb}V^2 - ab - RTV^2 = 0$$

or $PV^3 - (RT + Pb)V^2 + aV - ab = 0$ —— ①

At the critical point

$$V^3 = V_c^3$$

$$(V - V_c)^3 = 0$$

$$V^3 - V_c^3 + 3VV_c^2 - 3V_cV^2 = 0$$ —— ②

Thus at the critical point P becomes Pc, replace P in ① by ~~b~~ Pc and divide whole equ by P

$$V^3 - \left(\frac{RT_c}{P_c} + b\right)V^2 + \left(\frac{a}{P_c}\right)V - \left(\frac{ab}{P_c}\right) = 0$$ —— ③

Equating coefficient of ② and ③.

$$3V_c = \left(\frac{RT_c}{P_c} + b\right)$$ —— ④

$$3V_c^2 = \frac{a}{P_c}$$ —— ⑤

$$V_c^3 = \left(\frac{ab}{P_c}\right)$$ —— ⑥

from ⑤ and ⑥

$$\frac{3\cancel{V_c^2}}{\cancel{V_c^3}} = \frac{\cancel{a}}{\cancel{P_c}} \times \frac{\cancel{P_c}}{\cancel{a}b}$$

$$\boxed{V_c = 3b}$$ —— ⑦

Put the value of V_c in ⑤.

$$3(3b)^2 = \frac{a}{P_c}$$

$$27b^2 = \frac{a}{P_c} \quad \text{or} \quad \boxed{P_c = \frac{a}{27b^2}} \text{ —— } ⑧$$

Substitutethe value of P_c and V_c in ④

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

$$9\cancel{b} = \left(\frac{27RT_cb}{a} + 1\right)\cancel{b}$$

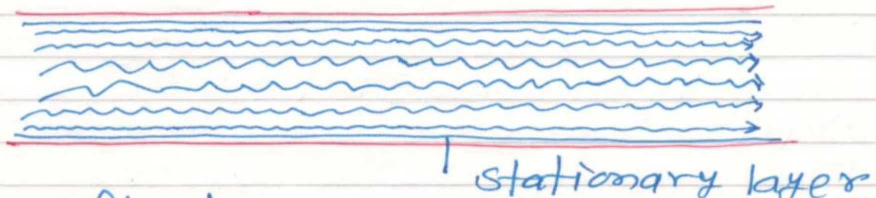
$$9a = 27RT_cb + 1a$$

$$\boxed{T_c = \frac{8a}{27Rb}}$$

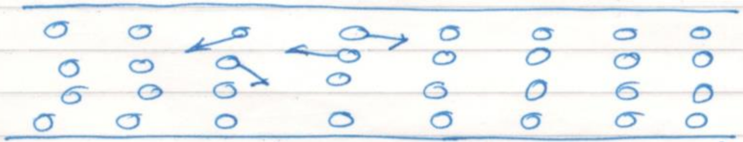
$$\boxed{a = 3V_c^2P_c \qquad b = \frac{V_c}{3}}$$

Viscosity of Gases :

The internal friction which opposes the relative motion of adjacent layers of a fluid is known as viscosity.



When a fluid is flowing through a cylindrical tube, layers just touching the sides of the tube are stationary and velocities of the adjacent layers increases towards the centre of the tube, the layer in the centre of the tube having the maximum velocity. There thus exists a velocity gradient.



But in case of gases because of their continuous movement, there will be an interchange of molecules between two layers with the result that a fraction of momentum of one layer will pass over to the other layer. The net effect will be decreace in the relative rate of movement of one layer with respect to the other. In order to maintain a uniform velocity gradient, one will have to apply a force acting along the direction of movement of the layers. This applied force is a measure of internal friction or viscosity of the fluid.

Coefficient of viscosity :-

$F \propto A$ (area of contact between two layers

$F \propto \frac{du}{dz}$

$$\text{or } F = \eta A \frac{du}{dz}$$

$$\boxed{\eta = \frac{1}{2} m N \langle C \rangle \lambda} \quad \text{———} \; ①$$

where N = no. of molecules per unit volume.

$\langle C \rangle$ = average velocity

λ = Mean free path

$$\boxed{\eta = \frac{1}{2} \rho \langle C \rangle \lambda}$$

where ρ = density of the medium.

Effect of Pressure and Temprature on Viscosity of Gases

$$\langle C \rangle = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \quad \text{———} \; ②$$

$$\lambda = \frac{1}{\sqrt{2}\,\pi \sigma^2 N} \quad \text{———} \; ③$$

substitute the value of $\langle C \rangle$ and λ in ①.

$$\eta = \frac{1}{2} m \cancel{N} \sqrt{\frac{8kT}{\pi m}} \times \frac{1}{\sqrt{2}\,\pi \sigma^2 \cancel{N}}$$

$$= \frac{1}{\cancel{2}} \times \frac{\cancel{2\sqrt{2}}}{\cancel{\sqrt{2}}} \times m \sqrt{\frac{kT}{\pi m}} \quad \frac{1}{\pi \sigma^2}$$

$$\eta = m \sqrt{\frac{kT}{\pi m}} \times \frac{1}{\pi \sigma^2}$$

$$= m \sqrt{\frac{mkT}{\pi m^2}} \times \frac{1}{\pi \sigma^2}$$

$$= \sqrt{\frac{mkT}{\pi}} \quad \frac{1}{\pi \sigma^2}$$

$$\text{or } \boxed{\eta = \frac{\sqrt{mkT}}{\pi^{3/2} \sigma^2}}$$ where σ = Collision Cross section

According to this equation η is independent of pressure.

η is also independent of density.

$$\eta = \frac{\sqrt{mkT}}{\pi^{3/2}\sigma^2}$$

m = costant

k = constand

σ^2 = constant.

$$\therefore \boxed{\eta \propto T^{1/2}}$$

η is increases with increase of temprature.