

* Joule-Kelvin Effect: Temperature of inversion :-

Suppose that Van der Waals equation is obeyed, the attractive forces between the molecules are equivalent to an internal pressure a/v^2 .

When the gas expands from V_1 to V_2 , the work done in overcoming intermolecular attractions.

$$W = \int_{V_1}^{V_2} P_{int} \cdot dV \quad \because P = \frac{a}{V^2}$$

$$\therefore W = \int_{V_1}^{V_2} \frac{a}{V^2} \cdot dV = -\frac{a}{V_2} + \frac{a}{V_1}$$

If V_1 and V_2 represents the gram-molecular volumes on the high and the low pressure sides respectively, the external work done by the gas is $(P_2 V_2 - P_1 V_1)$

Hence the total work done by the gas is

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

$$\text{or, } PV + \frac{a}{V} - bP - \frac{ab}{V^2} = RT$$

$$\text{or, } PV = RT + bP - \frac{a}{V}$$

$\because \frac{ab}{V^2}$ is negligible

$$W = \left[RT + bP_2 - \frac{a}{V_2} \right] - \left[RT + bP_1 - \frac{a}{V_1} \right] = \frac{a}{V_2} + \frac{a}{V_1}$$

$$W = b [P_1 - P_2] + 2a \left[\frac{1}{V_1} - \frac{1}{V_2} \right]$$

But, $V_1 = \frac{RT}{P_1}$ and $V_2 = \frac{RT}{P_2}$

$$\therefore W = b [P_2 - P_1] + 2a \left[\frac{P_1}{RT} - \frac{P_2}{RT} \right]$$

$$\Rightarrow W = -b [P_1 - P_2] + \frac{2a}{RT} [P_1 - P_2]$$

$$\therefore W = (P_1 - P_2) \left(\frac{2a}{RT} - b \right) \quad \text{--- (2)}$$

Suppose the fall in temp^r is δT

$$W = JH$$

$$= JM C_p \delta T$$

Where M is the gram-molecular wt. of the gas.

$$\therefore JM C_p \delta T = (P_1 - P_2) \left(\frac{2a}{RT} - b \right)$$

$$\delta T = \left[\frac{(P_1 - P_2)}{JM C_p} \right] \times \left[\frac{2a}{RT} - b \right] \quad \text{--- (2i)}$$

(i) Since $P_1 - P_2$ is +ve

δT will be positive if $\left(\frac{2a}{RT} - b \right)$ is +ve.

$$\text{i.e. } \frac{2a}{RT} > b \quad \text{or, } T < \frac{2a}{Rb} \quad \text{--- (2ii)}$$

Therefore, cooling will take place if the temp^r of the gas is less than $\frac{2a}{Rb}$.

(ii) For δT to be zero, from eqn (2i), we get,

$$\frac{2a}{RT} - b = 0$$

$$\therefore T = \frac{2a}{Rb}$$

This temp^r is called the temp^r of inversion and is

represented by T_i .

$$\therefore T_i = \frac{2a}{Rb} \quad \text{--- (24)}$$

(iii) δT will be ~~neg~~ negative, if

$$\left(\frac{2a}{RT} - b \right) < -v.$$

$$\text{i.e. } b > \frac{2a}{RT}$$

$$\text{or, } T > \frac{2a}{Rb}$$

$$\therefore T > T_i$$

Therefore, heating will take place if the temp. of the gas is more than the temp. of inversion.

Results: —

- (i) If the gas is at the temp. of inversion, then no cooling or heating is observed when it is passed through the porous plug.
- (ii) If the gas is at a temp. lower than temp. of inversion, cooling will take place when it passes through the porous plug. This is called regenerative cooling or Joule-Kelvin cooling. This principle has been used in the liquefaction of the so called permanent gases like nitrogen, oxygen, hydrogen & helium.
- (iii) If the gas is at temp. higher than the temp. of inversion, instead of cooling, heating is observed when the gas is passed through the porous plug.