* 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 inter molecular attractions.

$$W = \int_{V_1}^{V_2} P.dV \qquad \because P = \frac{a}{V^2}$$

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

If V_1 and V_2 represents the gram-molecular volumes on the high and the low pressure sides respectively, the external workdone by the gas is $(P_2V_2 - P_1V_1)$

Hence the total work done by the gas is

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

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

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

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

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

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

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

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

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

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

Suppose the fall in tempr. is δT

$W = JH$

$= J[M C_p \delta T]$

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

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

$\delta T = \left[\frac{(P_1 - P_2)}{J M C_p}\right] \times \left[\frac{2a}{RT} - b\right]$ — (ii)

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

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

i.e. $\frac{2a}{RT} > b$ or, $T < \frac{2a}{Rb}$ — (iii)

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

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

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

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

This tempr. is called the tempr. of inversion and is represented by T_i.

$\therefore T_i = \frac{2a}{Rb}$ — (iv)

(iii) δT will be ~~ng~~ negative, if $\left(\frac{2a}{RT} - b\right)$ is -ve.

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

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

$\therefore T > T_i$

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

Results :—

(i) If the gas is at the tempr. of inversion, then no cooling or heating is observed when it is passes through the porous plug.

(ii) If the gas is at a tempr. lower than tempr. of inversion, cooling will take place when it passes through the porous plug. This is called regenerating cooling or Jould-Kelvin cooling. This principle has been used in the liquefaction of the so called paramonent gases like nitrogen, oxygen, hydrogen & helium.

(iii) If the gas is at tempr. higher than the tempr. of inversion, instead of cooling, heating is observed when the gas is passed through the porous plug.