[illegible]

Give the theory of Joule-Thomson effect. explain the importance of temperature of inversion.

We Know

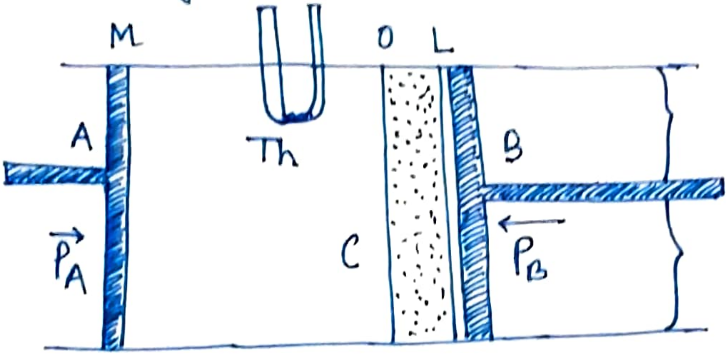
$$\frac{\delta U}{\delta V} = 0$$ is true only for perfect gases.

Actually a small cooling effect was observed by Joules for the real gases. This shows that U depends on the volume occupied by the gas. Where U is internal energy. When a real gas at high pressure is allowed to pass through porous or orifice towards the low pressure, its temperature changes. This change in temperature of the gas due to throttling process is called Joule-thomson effect. This effect occupies very significant place in the evaporation liquification of gases. When the gas is allowed to pass through the porous plug at high pressure arising out of the compressor (P) and the temperatures of the gas after considerable time of passage are recorded at T_1 ad T_2, Joule ad thomson fond the folloing facts :

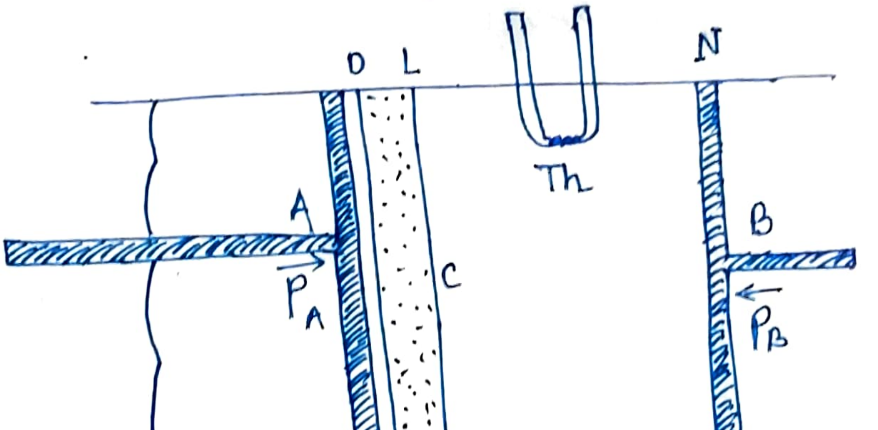
⇒ Except Hydrogen, for almost all ordinary gases cooling effect was observed. For Hydrogen, heating effect was observed.

⇒ The temperature drop of the gas was proportional to the pressure difference across the two sides of the porous plug (i.e. the drop in pressure).

⇒ The temperature droop was dependent on the initial temperature for a given pressure difference. The less the initial temp, the greater is the temp – drop. For every gas there exists an initial temp called Inversion temperature $\left(T_i = \frac{2a}{R b}\right)$ for which Joule-Thomson effect or the cooling effect becomes zero.



(a)



(b)

Let us consider a cylinder thermally insulated and provided with insulating pistons on opposite sides of the porous plug. Let us consider there a mass of the fluid traversing the porous plug from left to right and assume that the steady state on both sides of the plug has been attained. Suppose

P_A, V_A, T_A, U_A and P_B, V_B, T_B, U_B be the pressure, volume, temperature and ~~molecules~~ mol. of the internal energy of one ~~molecules~~ mol. of the fluid before and after traversing the orifice (plug) respectively.

According to first law of thermodynamics,

$$\Delta Q = dU + pdv$$

or, $$0 = dU + pdv.$$

or, $$pdv = -dU$$

or. workdone by the system (gas) = decrease in its internal energy.

or, $$P_B V_B - P_A V_A = U_A - U_B$$

or, $$U_A + P_A V_A = U_B + P_B V_B$$

or, $$U + Pv = \text{constant} \ldots$$

or. the total heat function (Enthalpy) $H = U + PV$ remains constant during adiabatic throttling process. ——①

On differentiation, eqn ① gives.

$$dH = (dU + p\,dV) + V\,dp$$ since $\underline{dQ = Tds = \text{II law}}$ $= dU + pdv = \text{I la}$

or. $$0 = Tds + V\,dp$$ ——②.

Taking $s = s(T, P)$ we have

$$ds = \left(\frac{\delta s}{\delta T}\right) dT + \left(\frac{\delta s}{\delta p}\right) dp$$

or, $$Tds = T\left(\frac{\delta s}{\delta T}\right) dT + T\left(\frac{\delta s}{\delta p}\right)_T dp$$

$$= C_p dT + T\left(\frac{\delta s}{\delta p}\right)_T dp$$

By Maxwell's fourth thermodynamics relation (V- s relation),

$$\left(\frac{\delta s}{\delta p}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_p$$

using this the last expression becomes;

$$Tds = C_p dT + T\left\{-\left(\frac{\delta v}{\delta T}\right)dp\right\}$$

or, $$Tds = C_p dT - T\left(\frac{\delta v}{\delta T}\right)dp \quad \text{③}$$

Making substitution from ③ in ②, we get

$$0 = C_p dT - T\left(\frac{\delta v}{\delta T}\right)dp \; Vdp$$

or, $$dT = \frac{1}{C_p}\left[T\left(\frac{\delta v}{\delta T}\right) - V\right]dp$$

or, $$\left(\frac{\delta T}{\delta p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\delta v}{\delta T}\right) - V\right] = \mu \quad \text{④}$$

Eqn. ④ gives us the differential Joule Coefficient (i.e. μ). If however, the pressure difference be large, we have

$$\Delta T = \int_{P_2}^{P_1} \frac{1}{C_p}\left[T\left(\frac{\delta v}{\delta T}\right)_p - V\right]dp \quad \text{⑤}$$

ΔT gives us the integral Joule-Thomson Coeffecient.

Case I: For a perfect gas,

$$pV = RT$$ for n = number of gm mol

$$\therefore \quad V = \frac{RT}{p}.$$

$$\left(\frac{\delta V}{\delta T}\right)_p = \frac{R}{p}$$

$$\text{or,} \quad T\left(\frac{\delta V}{\delta T}\right) = \frac{R}{p}\cdot T = \frac{pV}{p} = V.$$

$$\text{or,} \quad T\left(\frac{\delta V}{\delta T}\right) - V = 0 \quad \text{———} \quad (6)$$

from eqn. (4) $\left(\frac{\delta T}{\delta p}\right)_H = 0$ Hence, for a perfect gas, the Joule thomson effect vanishes.

Case II: For real gas,

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

Differentiating w.r.t. T at constant pressure, and making desirable calculation, we may find

$$T\left(\frac{\delta V}{\delta T}\right)_p = V - b + \frac{2a}{RT} \quad \text{approx.}$$

From eqn. (4), we get,

$$\left(\frac{\delta T}{\delta p}\right)_H = \frac{1}{C_p}\left[V - b + \frac{2a}{RT} - V\right]$$

$$\therefore \quad \left(\frac{\delta T}{\delta p}\right)_H = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right] \quad \text{approx.} \quad \text{———} \quad (7)$$

(a) When $\frac{2a}{RT} > b$; $\left(\frac{\delta T}{\delta p}\right)_H = \mu$ = positive

(b) When $\frac{2a}{RT} < b$; $\left(\frac{\delta T}{\delta p}\right)_H = \mu$ = negative

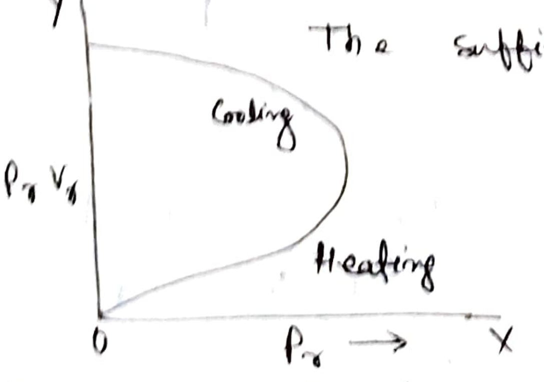
(c) When $\frac{2a}{RT} = b$; $\mu = 0$ i.e., Joule-Thomson effect vanishes.

$\therefore$ $T = \frac{2a}{Rb}$. This temperature is called temperatures of Inversion. That is;

$$\boxed{T_i = \frac{2a}{bR}} \quad \text{———} \quad (8)$$

For ordinary gases, $T_i > T$ at which the J-T expansion was carried out, hence a cooling effect was obtained.

Inversion Temp., since on passing the fluid at this temp the J-T effect changes its sign. Obviously, the temp of Inversion depends upon the initial pressure. A curve giving the inversion temp. at different initial pressures is called the Inversion curve.



The suffix 'r' denote the reduced scale.

Fig. Theoretical Inversion curve