CLAPEYRON EQUATION :-

Clapeyron Equation which involves the relationship between the saturation pressure, Saturation temperature, the enthalpy of evaporation and the specific volume of the two phases involved. This equation provides a basis for calculation of properties in a two phase region. It gives the slope of a curve separating the two phases in the PT diagram.

Let, Entropy (s) is a function of temperature (T) and volume (V).

$$s = f(T, V)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_V \cdot dT + \left(\frac{\partial s}{\partial V}\right)_T \cdot dV \quad\text{---}\quad ①$$

When the phase is changing from Saturated liquid to saturated vapour, temperature remains constant. so ds equation reduces to

$$ds = \left(\frac{\partial s}{\partial V}\right)_T \cdot dV \quad\text{---}\quad ②$$

∴ Temperature remains constant ⇒ $dT = 0$.

From Maxwell Equations, we know that.

$$\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Substituting in equation ②

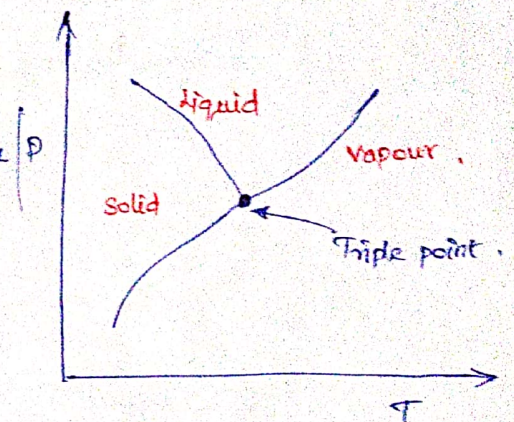$$ds = \left(\frac{\partial P}{\partial T}\right)_V \cdot dV \quad\text{---}\quad ③$$

The term $\left(\frac{\partial P}{\partial T}\right)$ is the slope of the Saturation curve.

Integrating the above equation between Saturated liquid (f) and Saturated vapour (g)

$$\int_{S_f}^{S_g} ds = \frac{dP}{dT} \int_{V_f}^{V_g} dV.$$

$$[s]_{S_f}^{S_g} = \frac{dP}{dT} [V]_{V_f}^{V_g}.$$

$$S_g - S_f = \frac{dP}{dT} [V_g - V_f]$$

$$\frac{dp}{dT} = \frac{S_g - S_f}{V_g - V_f}.$$

$$\boxed{\frac{dp}{dT} = \frac{S_{fg}}{V_{fg}}.} \quad\text{——} \quad ④$$

$$\therefore S_{fg} = S_g - S_f.$$
$$V_{fg} = V_g - V_g.$$

From second law of thermodynamics,

$$ds = \frac{dQ}{dT}.$$

for constant pressure process,

$$dQ = dh.$$

$$ds = \frac{dh}{T}.$$

$$S_{fg} = \frac{h_{fg}}{T}..$$

Substituting in equation ④.

$$\frac{dp}{dT} = \frac{S_g - S_f}{V_g - V_f} = \frac{S_g}{V_{fg}}$$

$$\boxed{\frac{dp}{dT} = \frac{h_{fg}}{TV_{fg}}.} \quad\text{——} \quad ⑤$$

This equation is known as clapeyron Equation.

JOULE - THOMSON CO-EFFICIENT

Joule Thomson coefficient is defined as the change in temperature, with change in pressure keeping the enthalpy remains constant. It is denoted by (μ).

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \quad \quad ——① $$

Throttling Process :-

Throttling process is defined as the fluid expansion through a minute orifice or slightly opened valve. During the throttling process, pressure and velocity are reduced. But there is no heat transfer and no work done by the system. In this process, enthalpy remains constant.

Joule - Thomson Experiment :-

The arrangement of porous plug experiment. In this experiment, a stream of gas at a pressure P_1 and temperature T_1 is allowed to flow continuously through a porous plug. The gas comes out from the other side of the porous plug at a pressure P_2 and temperature T_2.
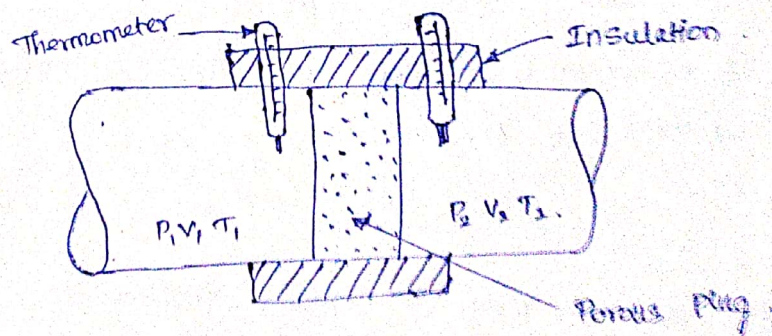
The whole apparatus is completely insulated. Therefore, no heat transfer take place.

$$Q = 0 $$

The system does not exchange work with the surrounding.

$$W = 0 $$

From steady flow energy equation, we know that.

$$gz_1 + \frac{V_1^2}{2} + h_1 + q = gz_2 + \frac{V_2^2}{2} + h_2 + W \quad ——② $$

Since there is no considerable change velocity $V_1 = V_2$ and $Z_1 = Z_2$.
$Q = 0$, $W = 0$, $V_1 = V_2$ and $Z_1 = Z_2$ are applied in steady flow energy equation. So the equation ① becomes.

$$h_1 = h_2.$$

Enthalpy at inlet h_1 = Enthalpy at outlet h_2.

It indicates that the enthalpy is constant for throttling process.

It is assumed that a series of experiments performed on a real gas keeping the initial pressure P_1 and temperature T_1, constant with various reduced down steam pressures $(P_2, P_3, P_4 \ldots)$. It is found that the down steam temperature also changes. The results from these experiments can be plotted as a constant enthalpy curve on T-p (Temperature - Pressure) plane.
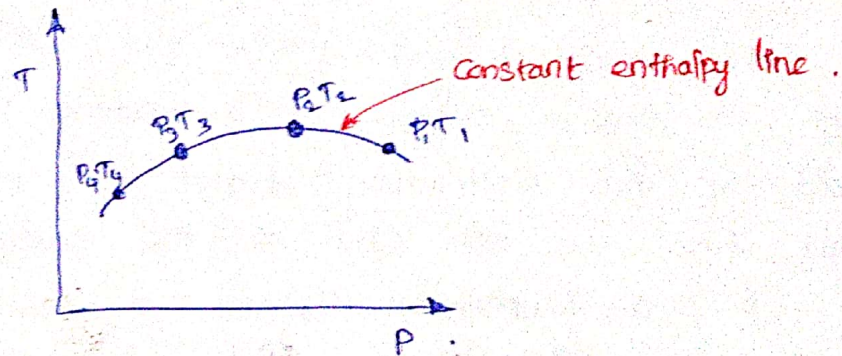
The slope of a constant enthalpy is known as Joule-Thomson coefficient, it is denoted by μ.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h.$$

For real gas, μ may be either positive or negative depending upon the thermodynamic state of the gas.

Case (1) :-

There is always pressure drop in throttling process. So ΔP and temperature change are negative. Therefore μ is positive.

$$\mu = \left(\frac{\partial T}{\partial P}\right)$$

This throttling process produces cooling effect.

Case (ii) :-

There is always pressure drop in throttling process. So ΔP is negative.

When the temperature change is positive, μ is negative.

$$\mu = \left(\frac{\partial T}{\partial P}\right)$$

This throttling process produces heating effect.

Case (iii) :-

When μ is zero, the temperature of the gas remains constant with throttling. The temperature at which $\mu=0$ is called inversion temperature for a given pressure.

Inversion curve :-

The maximum point on each curve is called inversion point and the locus of the inversion point is called inversion curve.

A generalized equation of the Joule - Thomson coefficient can be derived by using change of enthalpy equation.

change in Enthalpy, $dh = \left[c_p \, dT - T\left(\frac{\partial v}{\partial T}\right)_p dp\right] + v \cdot dp$

Inversion point
Inversion curve
Cooling zone ($\mu=+ve$)
Heating zone ($\mu=-ve$)
constant enthalpy line

$$dh - v \cdot dp = c_p \cdot dT - T\left(\frac{\partial v}{\partial T}\right)_p \cdot dp$$

$$dh - v \cdot dp + T\cdot\left(\frac{\partial v}{\partial T}\right)_p = c_p \cdot dT$$

Dividing by c_p on both sides;

$$\frac{dh}{c_p} - \frac{v \cdot dp}{c_p} + \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p \cdot dp = \frac{c_p \cdot dT}{c_p}$$
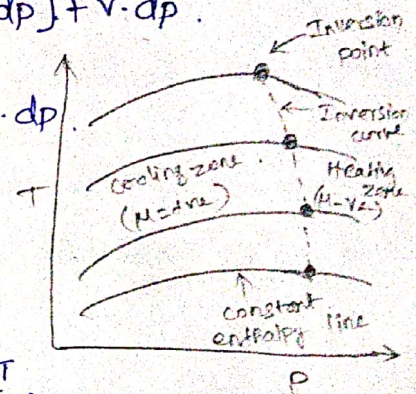
$$dT = \frac{dh}{c_p} + \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]\cdot dp \quad \text{----③}$$

Differentiating this equation with respect to pressure at constant enthalpy.

$$\left(\frac{\partial T}{\partial P}\right)_h = 0 + \left[\frac{1}{c_p} T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] \quad \text{----④}$$

We can determine the Joule Thomson coefficient (μ) in terms of measurable properties such as pressure (P), temperature (T), specific volume (v) and c_p.

Joule – Thomson Coefficient for ideal gas :-

It is defined as the change in temperature with change in pressure, keeping the enthalpy remains constant. It is denoted by (μ).

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right].$$

We know that the equation of state as.

$$Pv = RT$$

Differentiating the above equation of state with respect to T by keeping pressure, p constant.

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} = \frac{v}{T}.$$

$$\mu = \frac{1}{C_P}\left[T \cdot \frac{v}{T} - v\right].$$

∴ $\mu = 0$ It implies that the Joule - Thomson coefficient is zero for ideal gas.

Constant temperature Coefficient :-

let, Enthalpy is a function of pressure and temperature.

$$h = f(P, T)$$

$$dh = \left(\frac{\partial h}{\partial P}\right)_T dp + \left(\frac{\partial h}{\partial T}\right)_P dT \quad \text{——} \quad ⑤$$

For throttling process, enthalpy remains constant.

$$h = c.$$
$$dh = 0.$$

Substitute in equation ⑤.

$$0 = \left(\frac{\partial h}{\partial P}\right)_T dp + \left(\frac{\partial h}{\partial T}\right)_P dT$$

$$\left(\frac{\partial h}{\partial P}\right)_T \cdot dp + \left(\frac{\partial h}{\partial T}\right)_P \cdot dT = 0 \quad \text{——} \quad ⑥$$

Dividing by dT,

$$\left(\frac{\partial h}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_h + \left(\frac{\partial h}{\partial T}\right)_P = 0.$$

$$\left(\frac{\partial h}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_h = -\left(\frac{\partial h}{\partial T}\right)_P.$$

$$\left(\frac{\partial h}{\partial P}\right)_T \left(\frac{1}{\mu}\right) = -\left(\frac{\partial h}{\partial T}\right)_P \qquad \because \mu = \left(\frac{\partial T}{\partial P}\right)_h$$

$$\left(\frac{\partial h}{\partial T}\right)_P = -\frac{1}{\mu}\left(\frac{\partial h}{\partial P}\right)_T$$

$$\boxed{C_P = \left(\frac{\partial h}{\partial T}\right)_P = -\frac{1}{\mu}\left(\frac{\partial h}{\partial P}\right)_T} \qquad \text{———} (7)$$

$$\because C_P = \left(\frac{\partial h}{\partial T}\right)_P$$

The property $C_P = \left(\frac{\partial h}{\partial P}\right)_T$ is known as constant temperature coefficient.