Energy Equation → 1st

For a PVT system:- From 1st law of thermodynamics $dQ = dU + pdv$

From 2nd law of thermodynamics . $Tds = dQ$

By combining 1st and 2nd law of thermodynamics

$$dU = Tds - pdv \rightarrow (1)$$

(or)

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p$$

1st Maxwell relation equation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

(or)

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \rightarrow \text{1st energy equation}$$

Derivation of change in internal energy

Take U as independent variables; T and V as independent variables

$$\therefore U = u(T,V)$$

$$\downarrow$$

$$\rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dv$$

$$\rightarrow dU = C_v\, dT + \left(\frac{\partial U}{\partial V}\right)_T dv \quad \text{as, } C_v = \left(\frac{\partial u}{\partial T}\right)_V$$

$$\therefore dU = C_v\, dT + \left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\} dv$$

Prepared by: M. Sriram, AP/FT

② nd Energy Equation :-

$\rightarrow dQ = du + pdv \rightarrow$ ① st law of thermodynamics

$\rightarrow Tds = dQ \rightarrow$ 2nd law of thermodynamics.

By Combining ① & ②.

$$dU = Tds - pdV \longrightarrow ①$$

(or)

$$\left(\frac{\partial U}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T$$

(or)

$$\left(\frac{\partial u}{\partial p}\right)_T = T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T$$

2nd Maxwell's relation $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$

↳ ② nd energy equation

Derivation of change in internal energy :-

Take U as dependent variables; T and p as independent variables

$$\therefore U = U(T, p)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_p dT - \left\{T\left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_T\right\} dp$$

Application of Energy Equation

$$PV = RT$$

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

$$dU = C_V dT + \left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\} dV$$

(or)

$$dU = C_V dT + \left\{T \times P/T - P\right\} dV, \text{ as } \left(\frac{\partial P}{\partial T}\right)_V =$$

$$\therefore \Delta U = \int_{T_1}^{T_2} C_V dT$$

$$\Delta U = C_V (T_2 - T_1).$$

Equation of a state for an Van der Waal's gas :-

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

$$\therefore \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}$$

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

$$dU = C_v\, dT + \left\{T\left(\frac{\partial p}{\partial T}\right)_V - p\right\} dV$$

$$\rightarrow dU = C_v\, dT + \frac{a}{V^2} dV$$

$$\Delta U = \int_{T_1}^{T_2} C_v\, dT + \int_{V_1}^{V_2} \frac{a}{V^2} dV$$

$$\Delta U = C_v(T_2 - T_1) - a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$dU = T\,dS - p\,dV \ldots (1) \longrightarrow (\text{or}) \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Take U as dependent variable; T and V as independent variable

$$U = U(T, V) \longrightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \ldots (2)$$

Now,

S as dependent variable; T and V as independent variable

$$S = S(T, V) \longrightarrow \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right) dV \ldots (3)$$

Sub (3) in (1)

$$dU = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV - p\,dV \ldots (4)$$

(or)

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

By comparing ② and ③.

Derivation of Joule - Thomson Co-efficient

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

$$dh = \underset{\downarrow}{Tds} + VdP$$

$$\cancel{dh}^{0} = \left\{C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp\right\} + V dp$$

$$0 = C_p dT + dp\left\{V - T\left(\frac{\partial V}{\partial T}\right)_p\right\}$$

$$C_p dT = -dp\left\{V - T\left(\frac{\partial V}{\partial T}\right)_p\right\}$$

$$\frac{dT}{dp} = \frac{-1}{C_p}\left\{V - T\left(\frac{\partial V}{\partial T}\right)_p\right\}$$

$$\mu_j = \left(\frac{\partial T}{\partial p}\right)_h = \frac{-1}{C_p}\left\{V - T\left(\frac{\partial V}{\partial T}\right)_p\right\} \rightarrow \text{Real gases.}$$

μ_j ideal gas =>

$$PV = RT, \quad V = \frac{RT}{P}, \quad \partial V = \frac{R}{P}\partial T$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{P}$$

$$\mu_j = \frac{-1}{C_p}\underbrace{\left\{V - \underbrace{T\frac{R}{P}}_{V}\right\}}_{0}$$

$$\mu_j = 0$$