Energy Equation → ① st

For a PVT system :- From 1^{st} law of thermodynamics $dQ = dU + pdV$
From 2^{nd} law of thermodynamics $Tds = dQ$

By combining 1^{st} & 2^{nd} law of thermodynamics,

$$dU = Tds - pdV \rightarrow ①$$

(or)

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

1^{st} Maxwell relation $\Big\} \rightarrow \left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(or)

$$\left(\frac{\partial u}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - p \rightarrow 1^{st} \text{ energy equation}$$

Derivation of change in internal energy

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

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

$$\downarrow$$

$$dU = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV$$

$$dU = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

as,

$$C_V = \left(\frac{\partial u}{\partial T}\right)_V$$

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

(2)nd Energy Equation

$\longrightarrow$ $dQ = dU + pdV \rightarrow$ 1st law of thermodynamics

$\longrightarrow$ $TdS = dQ \rightarrow$ 2nd law of thermodynamics.

By Combining (1) & (2).

$$dU = TdS - pdV \longrightarrow (1)$$

(or)

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

2nd maxwell relation $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$

(or)

$$\left(\frac{\partial u}{\partial p}\right)_T = T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T \rightarrow \text{2nd energy equation}$$

Derivation of changes in internal energy

Take U as dependent variables; T & 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: -

$PV = RT$

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

$$\text{as} \left(\frac{\partial P}{\partial T}\right)_V = P/T$$

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

(or)

$$dU = C_v dT + \left\{T \times P/T - P\right\} dV,$$

$$\Delta V = \int_{T_1}^{T_2} C_v\, dT \quad \therefore \Delta V = C_v (T_2 - T_1).$$

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

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

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

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

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

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

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

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

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

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

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

sub (3) in (1)

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

(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

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

$$dh = Tds + vdp$$

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

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

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

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

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

$\mu_j \rightarrow$ ideal gas

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

$$\mu_j = \frac{-1}{C_p}\left\{ v - T\frac{R}{P} \right\} \qquad \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P}$$

$$\mu_j = -1/C_p \underbrace{\left\{ v - \underbrace{T\, R/P}_{v} \right\}}_{0}$$

$$\boxed{\mu_j = 0}$$

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