DIFFERENTIAL FORM OF ENERGY PROPERTIES

Energy properties like $(U, H, G,$ and $A)$ are related to the reference properties $(P, T, V,$ and $S)$ as follows:

First law of thermodynamics: $dU = dQ + dW$ here $dW = -PdV$ and $dQ = TdS$. So,

$$dU = TdS - PdV = U(S, V) \tag{1}$$

Enthalpy H is given by $H = U + PV$. Therefore,

$$\begin{aligned} dH &= dU + d(PV) \\ &= dU + PdV + VdP \\ &= (TdS - PdV) + PdV + VdP \quad \text{(Using equation (1))} \\ &= TdS + VdP \\ \Rightarrow dH &= TdS + VdP = H(S, P) \end{aligned} \tag{2}$$

Gibb's free energy G is given by $G = H - TS$. Therefore,

$$\begin{aligned} dG &= dH - d(TS) \\ &= dH - TdS - SdT \\ &= (TdS + VdP) - TdS - SdT \quad \text{(Using equation (2))} \\ &= VdP - SdT \\ \Rightarrow dG &= VdP - SdT = G(P, T) \end{aligned} \tag{3}$$

Helmholtz free energy A is given by $A = U - TS$. Therefore,

$$\begin{aligned} dA &= dU - d(TS) \\ &= dU - TdS - SdT \\ &= (TdS - PdV) - TdS - SdT \quad \text{(Using equation (1))} \\ &= -PdV - SdT \\ \Rightarrow dA &= -PdV - SdT = A(V, T) \end{aligned} \tag{4}$$

Now using the exact differential property of equation (1) to (4), we derive the well known Mazwell's equations as follows,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P, \quad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T, \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{5}$$

MNEMONIC DIAGRAM

$$\begin{tikzcd} V \arrow[r, dash, "A"] \arrow[d, dash, "U"'] & T \arrow[d, dash, "G"] \\ S \arrow[r, dash, "H"'] \arrow[ur] & P \arrow[ul] \end{tikzcd}$$

V, T, P, S - "**V**ijay's **T**uppakki is **P**akka **S**uperhit" and A, G, H, U - Alphabetical order. Using the above diagram, derive the differential form of equation (1) to (4).