

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,

$$dU = TdS - PdV = U(S, V) \quad (1)$$

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

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

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

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

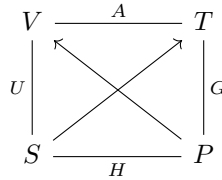
Helmholtz free energy A is given by $A = U - TS$. Therefore,

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

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

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

MNEMONIC DIAGRAM



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).