Applications of Maxwell's thermodynamic relations

(1) Clausius - Clapeyron's ~~eqd~~ equation

From Maxwell's 2nd relation

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

Multiplying by 'T' we get

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

$$\rightarrow \left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \quad \text{—(a)} \quad [\because T\partial S = \partial Q]$$

Here $\left(\frac{\partial Q}{\partial V}\right)_T$ represents the quantity of heat absorbed per unit increase in volume at const. 'T'. This quantity of heat absorbed at constant temperature is the latent heat (L)

Thus $\partial Q = L$ and $\partial V = V_2 - V_1$ for unit mass of a substance

Thus equ^n (a) becomes

$$\left(\frac{L}{V_2 - V_1}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\text{or} \quad \frac{L}{V_2 - V_1} = T\frac{dP}{dT}$$

$$\text{or} \quad \boxed{\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}}$$

This is Clausius - Clapeyron's heat equ^n.

(2) The T.dS equation

(a) ~~d~~. The entropy S of a pure substance can be taken as a function of temperature and volume

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

Multiplying both sides by T

$$T\,dS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{—(1)}$$

2. But $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ —(2)

and from Maxwell's relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad -(3)$$

from (1), (2) and (3)

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

↳ 1st T.ds equation

(ii) Entropy 'S' is also a function of temperature and pressure

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad -(4)$$

Multiplying both sides by T

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \quad (4)$$

$$\text{But } C_P = T\left(\frac{\partial S}{\partial T}\right)_P \quad -(5)$$

and from Maxwell's relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad -(6)$$

Substituting in eqn (4)

$$\boxed{TdS = C_P\, dT - T\left(\frac{\partial V}{\partial T}\right)_P dP}$$

↳ 2nd TdS equation.

(1) Thermodynamic Potential $U(S, V)$

According to the 1st and 2nd law of thermodynamics

$$dU = dQ - PdV$$
$$= TdS - PdV \qquad (\because dQ = TdS)$$

Taking partial differentials of U w.r.t S, and V we have

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Since dU is a perfect differential (i.e., U is a single valued), we have

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

↳ This is Maxwell's 1st thermodynamic relation.

(2) Thermodynamic Potential, $F(T, V)$

$$F = U - TS$$

$$\therefore dF = d(U - TS) = dU - TdS - SdT$$

But $dU = TdS - PdV$

$$\therefore dF = -PdV - SdT$$

Taking partial differentials of F w.r.t T and V, we get

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

Since dF is a perfect differential

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V$$

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

↳ This is Maxwell's 2nd thermodynamic relation

(3) Thermodynamic Potential, $H(S,P)$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

But $dU = TdS - PdV$

$$\therefore dH = TdS + VdP$$

Taking partial differential w.r.t 'S' and 'P' we get

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad , \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

Since dH is perfect differential

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right]_P$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

↳ This is Maxwell's 3rd relation.

(4) Thermodynamic Potential $G(P,T)$

$$G = H - TS$$

$$\Rightarrow dG = dH - TdS - SdT$$

But $dH = TdS + VdP$

$$\Rightarrow dG = VdP - SdT$$

Taking partial differential w.r.t 'P' and 'T'

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

As dG is perfect differential

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T$$

$$\Rightarrow \boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}$$

↳ Maxwell's 4th relation