Thermodynamics and Energy Conversion (EN 203)
Indian Institute of Technology Bombay
Auxiliary Functions and Maxwell's Relationships

1. Auxiliary Functions

$dU = TdS - PdV$ (1)

$dH = TdS + VdP$ (2)

$dA = -PdV - SdT$ (3)

$dG = VdP - SdT$ (4)

$$T = \left.\frac{\partial U}{\partial S}\right|_V = \left.\frac{\partial H}{\partial S}\right|_P \quad (5)$$

$$P = -\left.\frac{\partial U}{\partial V}\right|_S = -\left.\frac{\partial A}{\partial V}\right|_T \quad (6)$$

$$V = \left.\frac{\partial H}{\partial P}\right|_S = \left.\frac{\partial G}{\partial P}\right|_T \quad (7)$$

$$S = -\left.\frac{\partial A}{\partial T}\right|_V = -\left.\frac{\partial G}{\partial T}\right|_P \quad (8)$$

Let $z = z(x, y)$ be a state function and the exact differential dz be $dz = Ldx + Mdy$

Then
$$\left.\frac{\partial L}{\partial y}\right|_x = \left.\frac{\partial M}{\partial x}\right|_y \quad (9)$$

2. Maxwell's relationships

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V \quad (10)$$

$$\left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P \quad (11)$$

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V \quad (12)$$

$$\left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P \quad (13)$$

3. Thermodynamic state functions in terms of *P* and *T*

$$dV = V\alpha dT - V\beta dP \quad (14)$$

$$dS = \frac{C_P}{T}dT - V\alpha dP \quad (15)$$

$$dU = (C_p - PV\alpha)dT + V(P\beta - T\alpha)dP \quad (16)$$

$$dH = C_p dT + V(1 - T\alpha)dP \quad (17)$$

$$dA = -(S + PV\alpha)dT + PV\beta dP \quad (18)$$

$$dG = -SdT + VdP \quad (19)$$

Where $\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P$ and $\beta = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$

4. General Mathematical relations

Chain Rule
$$\left.\frac{\partial x}{\partial y}\right|_z = \left.\frac{\partial x}{\partial a}\right|_z \times \left.\frac{\partial a}{\partial y}\right|_z \quad (20)$$

Reciprocal Relation
$$\left.\frac{\partial x}{\partial y}\right|_z = 1\Big/\left.\frac{\partial y}{\partial x}\right|_z \quad (21)$$

Cyclic Relation
$$\left.\frac{\partial x}{\partial y}\right|_z \times \left.\frac{\partial y}{\partial z}\right|_x \times \left.\frac{\partial z}{\partial x}\right|_y = -1 \quad (22)$$