Maxwell’s Thermodynamic Relations

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$$dQ = dU + PdV \qquad dQ = TdS$$

$$\Rightarrow dU = dQ - PdV$$

$$dU = TdS - PdV \quad - (1)$$

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy \quad - (2)$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \quad - (3)$$

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \quad - (4)$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right] - P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

$$\left(\frac{\partial u}{\partial x}\right)_y = T\left(\frac{\partial s}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \quad - (5)$$

$$\left(\frac{\partial u}{\partial y}\right)_x = T\left(\frac{\partial s}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \quad - (6)$$

$$\frac{\partial^2 u}{\partial y \partial x} = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial s}{\partial x}\right)_y + T\cancel{\frac{\partial^2 s}{\partial y \partial x}} - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\cancel{\frac{\partial^2 V}{\partial y \partial x}} \quad - (7)$$

$$\frac{\partial^2 u}{\partial x \partial y} = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial s}{\partial y}\right)_x + T\left(\cancel{\frac{\partial^2 s}{\partial x \partial y}}\right) - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\left(\cancel{\frac{\partial^2 V}{\partial x \partial y}}\right) \quad - (8)$$

$$\left\{\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x}\right\}, \quad \frac{\partial^2 s}{\partial y \partial x} = \frac{\partial^2 s}{\partial x \partial y}$$

$$\frac{\partial^2 V}{\partial y \partial x} = \frac{\partial^2 V}{\partial x \partial y}$$

$$\boxed{\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y-\left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y=\left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x-\left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x} \quad -(9)$$

(1) Take $x=S$ & $y=V$

$$\frac{\partial S}{\partial x}=1,\quad \frac{\partial V}{\partial y}=1,\quad \frac{\partial S}{\partial y}=0,\quad \frac{\partial V}{\partial x}=0$$

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

(2) $x=T$ $\quad y=V$

$$\frac{\partial T}{\partial x}=1,\quad \frac{\partial V}{\partial y}=1,\quad \frac{\partial T}{\partial y}=0,\quad \frac{\partial V}{\partial x}=0$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \quad \text{— (11)}$$

(3) $x = S \;,\; y = P$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad \text{— (12)}$$

(4) $x = T \;,\; y = P$

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

(5) $x = P, \quad y = V$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1} \quad \text{—(14)}$$

(6) $x = T, \quad y = S$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1} \quad \text{—(13)}$$

Thermodynamic Potentials or Functions

i) Internal Energy U

ii) Helmholtz free energy $F = U - TS$

iii) Enthalpy $H = U + PV$

iv) Gibbs function $G = U + PV - TS$

1. Internal Energy

U

$dQ = dU + PdV$

$\Rightarrow dU = dQ - PdV$ $\{dQ = TdS\}$

$dU = TdS - PdV$ — (1)

a) For an adiabatic process

$dQ = 0$

$\Rightarrow \boxed{dU = -PdV}$

b) For isochoric adiabatic process

$dV = 0$ $dQ = 0$

$\Rightarrow dU = 0$ $\Rightarrow U = $ a const

2. Helmholtz Free Energy F

$$F = U - TS$$

$$dU = TdS - dW \checkmark$$

const. temp

$$TdS = d(TS)$$

$$dU = d(TS) - dW$$

$$d(U - TS) = -dW$$

$$\Rightarrow \boxed{dF = -dW}$$

where $F = U - TdS$

Helmholtz work f^n

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

$$dF = T\cancel{dS} - PdV - T\cancel{dS} - SdT = -PdV - SdT$$

$$\boxed{dF = -PdV - SdT} \quad \text{--- } (2)$$

a) Isothermal

$dT = 0$

$dF = -PdV$

or $\boxed{PdV = -dF}$

b) Isothermal isochoric process

$dV = 0$

$dT = 0$

$dF = 0$

$F = \text{Const}$

3. Enthalpy H

$H = U + PV$

$dH = dU + PdV + VdP$

$= TdS - \cancel{PdV} + \cancel{PdV} + VdP$

$dH = TdS + VdP$ — (3)

a) For reversible isobaric process

$dP = 0$

$\Rightarrow dH = TdS = dQ$

(b) For an isobaric Adiabatic process

$dP = 0 \quad dQ = 0$

$dH = 0$

$H = \underline{a} \text{ const}$

4. Gibbs Function G

$$G = U - TS + PV$$

$$\boxed{G = F + PV}$$

or $\boxed{G = H - TS}$

Enthalpy = Gibbs free energy + Latent heat

(a) Isothermal process

$$TdS = d(TS)$$

(b) Isothermal Isobaric

$$dH = d(TS)$$

$$\Rightarrow d(H - TS) = 0$$

$$dG = 0$$

$$\Rightarrow \underline{G = \text{Const}}$$

Relation of F and G with Parameters of System

$$F = U - TS$$

$$\Rightarrow dF = -PdV - SdT \quad \text{—} \; (1)$$

$$G = H - TS$$

$$= U + PV - TS$$

$$dG = \underbrace{dU + PdV}_{} + VdP - TdS - SdT$$

$$= T\cancel{dS} + VdP - T\cancel{dS} - SdT$$

$$dG = VdP - SdT \quad \text{—} \; (2)$$

$dP = 0 \qquad dV = 0$

(1) $\rightarrow dF = -SdT$

(2) $\rightarrow dG = -SdT$

$\therefore \boxed{dF = dG}$ — (3)

cases

(a) For isothermal process

$dT = 0$

$dF_T = -PdV$

or $\left(\frac{\partial F}{\partial V}\right)_T = -P$ — (4)

$dG_T = VdP$

$\Rightarrow \left(\frac{\partial G}{\partial P}\right)_T = V$ — (5)

(b) Isobaric process

$dP = 0$

$dG_P = -SdT$

$\Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S$ — (6)

$$\boxed{G = H + T\left(\frac{\partial G}{\partial T}\right)_P} \quad -(7)$$

(c) For isochoric process

$dV = 0$

$dF_V = -S\,dT$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad -(8)$$

$$\boxed{F = U + T\left(\frac{\partial F}{\partial T}\right)_V} \quad -(9)$$

Gibbs-Helmholtz relations

Maxwell’s Thermodynamic Relation from Thermodynamic Potentials or Functions

Internal Energy

$$dU = TdS - PdV$$

Taking partial derivatives

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad - (1)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad - (2)$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S \Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} - (3)$$

Helmholtz Function

$$dF = -P\,dV - S\,dT$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \quad \text{— (4)}$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{— (5)}$$

dF is perfect differential

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

$$\Rightarrow \boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T} \quad \text{— (6)}$$

Enthalpy

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad — 7$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad — 8$$

dH is a perfect differential

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

$$\Rightarrow \boxed{\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S} \quad — 9$$

Gibbs Potential

$$dG = V\,dP - S\,dT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad — (10)$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad — (11)$$

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

$$\Rightarrow \boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \quad — (12)$$

TV SP

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

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

Thankyou