

$$A = U - TS$$

Helmholtz

At const T

$$dA = dU - Tds$$

$$dA_{T,v} \leq 0$$

$$dU = Tds - pdV = dq_{rev} + dw_{rev} = dq_{irr} + dw_{irr}$$

$$dU \leq Tds$$

$$G = H - TS$$

Gibb's

$$dG = dH - Tds$$

$$dG_{T,p} \leq 0$$

$$Tds \geq dq \quad dU = dq + dw$$

$$dU \leq Tds + dw$$

$$dw \geq dU - Tds$$

$$dw \geq dA \equiv dw_{\max}$$

$A \equiv$ work function

$$dG = dH - TdS - SdT = dq + dw + pdV + Vdp - TdS - SdT$$

$$dH = d(U + pV) = dU + pdV + Vdp = dq + dw + pdV + Vdp$$

$$dq_{rev} = TdS \quad dw_{rev} = -pdV + w_{add}$$

$$dG = \cancel{TdS} - \cancel{pdV} + w_{add} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

At const P & T

$$dG = w_{add, max}$$

$$dS_{U,V} / dS_{H,P} \geq 0$$

$$dU_{S,V} \leq 0$$

$$dH_{S,P} \leq 0$$

$$dA_{T,V} \leq 0$$

$$dG_{T,P} \leq 0$$

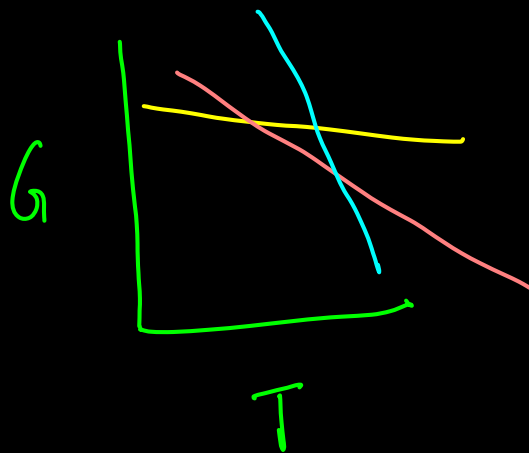
$$dU = TdS - PdV$$

$$dH = TdS + Vdp$$

$$dA = -SdT - PdV$$

$$dG = -SdT + Vdp$$

Fundamental Equations



$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$= TdS - pdV - SdT - TdS$$

$$= -SdT - pdV$$

$$dG = dH - TdS - SdT$$

$$\cancel{TdS} + vdp - \cancel{TdS} - SdT = -SdT + vdp$$

$$dU = Tds - pdv$$

$$dH = Tds + vdp$$

$$dA = -SdT - pdv$$

$$dh = -SdT + vdp$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

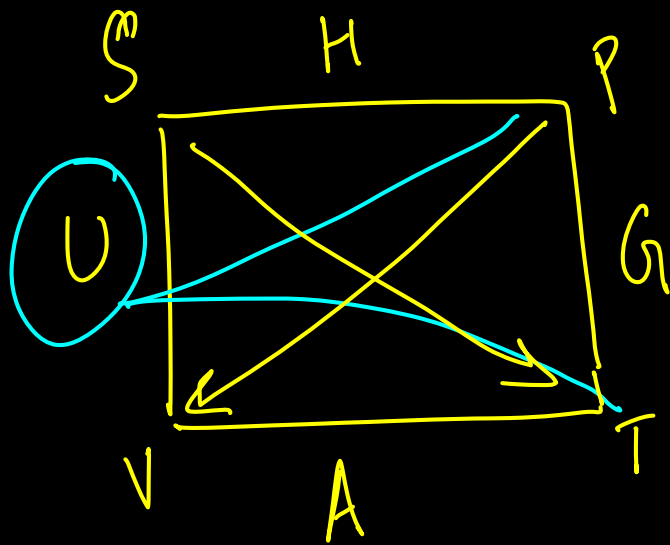
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

Maxwell Relations

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

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



$$dU = TdS - PdV$$

$$dG = -SdT + Vdp$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \quad V = \left(\frac{\partial G}{\partial p}\right)_T$$

$$H = G + TS = G - T \left(\frac{\partial G}{\partial T}\right)_p$$

$$U = H - pV = G - T \left(\frac{\partial G}{\partial T}\right)_p - p \left(\frac{\partial G}{\partial p}\right)_T$$

$$A = U - TS = G - p \left(\frac{\partial G}{\partial p}\right)_T$$

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_p = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

$\approx G(T)$ for small pr. changes for l/s

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$G(p_2, T) = G(p_1, T) + \int_{p_1}^{p_2} V dp$$

$$G(p_2, T) = G(p_1, T) + RT \ln \frac{p_2}{p_1}$$

$$p_1 = \bar{p} = 1 \text{ bar}$$

— always in bar

$$G_m(P, T) = G_m^\ominus(T) + RT \ln P$$

$$-S_m(P, T) = -S_m^\ominus(T) + R \ln P$$

Chemical potential
 $G_m \equiv \mu$

• • • •

$k \ln W$

• 0 • •

$k \ln 4$

0 • • •