

$$H = U + pV$$

$$G = H - TS$$

$$A = U - TS$$

$$dU = \delta Q - \delta W$$

$$(F1) \quad dU = dQ - p dV \quad \text{with} \quad T dS = dQ_{rev}$$

$$\boxed{dU = T dS - p dV}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p; \quad \left(\frac{\partial U}{\partial S}\right)_V = T$$

$$dH = dU + p dV + V dp$$

$$dH = T dS - \cancel{p dV} + \cancel{p dV} + V dp$$

$$(F2) \quad \boxed{dH = T dS + V dp}$$

$$\left(\frac{\partial H}{\partial p}\right)_S = V; \quad \left(\frac{\partial H}{\partial S}\right)_p = T$$

$$dA = dU - T dS - S dT$$

$$dA = \cancel{T dS} - p dV - \cancel{T dS} - S dT$$

$$(F3) \quad \boxed{dA = -p dV - S dT}$$

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

$$dG = dH - S dT - T dS$$

$$dG = \cancel{T dS} + V dp - S dT - \cancel{T dS}$$

$$(F4) \quad \boxed{dG = -S dT + V dp}$$

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

Maxwell Relations

$$\frac{\partial}{\partial z} \left(\frac{\partial y}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{\partial y}{\partial z} \right)$$

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

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

$$(2) \quad \left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S$$

$$(4)^* \quad -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

Definitions

(2)

$$\boxed{\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \beta}$$

Coefficient of Thermal Expansion

$$\boxed{-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \kappa}$$

Isothermal Compression

Cycle Rule

$$\left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial P}{\partial V} \right)_T = -1$$

$$(\beta V) \left(\frac{\partial T}{\partial P} \right)_V \left(-\frac{1}{V\kappa} \right) = -1$$

$$\boxed{\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}}$$

Thus Maxwell Relations

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

$$\textcircled{4} \quad \boxed{-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P = V\beta}$$

For Gas

$$\eta_J = \left(\frac{\partial T}{\partial V} \right)_U$$

Constant U
free expansion

$$\mu_{JT} \left(\frac{\partial T}{\partial P} \right)_H$$

constant H (Isolated $q, w=0$)

Define C_v and C_p

$$\left(\frac{\partial Q}{\partial T} \right)_v \equiv C_v$$

$$du = dq - pdv$$

$$\left(\frac{du}{dT} \right)_v = \left(\frac{\partial Q}{\partial T} \right)_v - p \left(\frac{dv}{dT} \right)_{v, \text{const}} \rightarrow 0$$

$$\left(\frac{du}{dT} \right)_v = C_v$$

$$\left(\frac{\partial Q}{\partial T} \right)_p \equiv C_p$$

$$dH = du + pdv + vdp$$

$$dH = dq + vdp$$

$$\left(\frac{dH}{dT} \right)_p = \left(\frac{dq}{dT} \right)_p + 0$$

$$\left(\frac{\partial H}{\partial T} \right)_p = C_p$$

$$du = dq - pdv$$

divide by dT at constant v

$$\left(\frac{\partial u}{\partial T} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v - 0$$

$$\left(\frac{\partial u}{\partial T} \right)_v = C_v = T \left(\frac{\partial s}{\partial T} \right)_v$$

$$\left(\frac{\partial s}{\partial T} \right)_v = \frac{C_v}{T}$$

$$dH = Tds + vdp$$

Replace dq with Tds divide by dT at const p

$$\left(\frac{dH}{dT} \right)_p = T \left(\frac{\partial s}{\partial T} \right)_p$$

$$C_p = T \left(\frac{\partial s}{\partial T} \right)_p$$

$$\left(\frac{\partial s}{\partial T} \right)_p = \frac{C_p}{T}$$

Entropy as a function of (T, P) or (T, V) (4)

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

\downarrow page 3 \downarrow Maxwell 4

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

$$dS(T, P) = \frac{C_P}{T} dT - V\beta dP$$

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

\downarrow page 3 \downarrow Maxwell 3

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

$$dS(T, V) = \frac{C_V}{T} dT + \beta K dV$$

What about?

$$dS(P, V) = ?$$

Let's look again at $S(V, T)$ but via (F1)

(5)

$$TdS = du + PdV$$

Expand du

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

$$dS = \frac{1}{T} \left[\left(\frac{\partial u}{\partial T}\right)_V dT + \left[\left(\frac{\partial u}{\partial V}\right)_T + P \right] dV \right]$$

$$dS = \frac{1}{T} [C_V] dT + \left[\left(\frac{\partial u}{\partial V}\right)_T + P \right] dV$$

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

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} C_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[\left(\frac{\partial u}{\partial V}\right)_T + P \right]$$

$$\left(\frac{\partial S}{\partial V}\right)_T \overset{\textcircled{3}}{=} - \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\beta}{\kappa} = \frac{1}{T} \left[\left(\frac{\partial u}{\partial V}\right)_T + P \right] \quad \checkmark$$

$$dS = \frac{C_V}{T} dT - \left(\frac{\partial P}{\partial T}\right)_V dV$$

OR ?

let's Try it for $S(p, T)$ using $F2$

(6)

$$dH = TdS + Vdp$$

$$dS = \frac{dH}{T} - \frac{V}{T} dp \quad \text{now Expand } dH(T, p)$$

$$dS = \frac{1}{T} \left[\left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp - V dp \right]$$

Regroup C_p

$$dS(T, p) = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_p dT + \frac{1}{T} \left(\left(\frac{\partial H}{\partial p} \right)_T - V \right) dp$$

$$dS(T, p) = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp$$

Thus

$$\left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T}$$

$$\left(\frac{\partial S}{\partial p} \right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial p} \right)_T - V \right]$$

$$\left(\frac{\partial S}{\partial p} \right)_T \stackrel{④}{=} - \left(\frac{\partial V}{\partial T} \right)_p = -V\beta = \frac{1}{T} \left[\left(\frac{\partial H}{\partial p} \right)_T - V \right]$$

$$dS(T, p) = \frac{C_p}{T} dT + \left(\frac{\partial V}{\partial T} \right)_p dp$$

↑
or?

Enthalpy as function of $H(T, p)$

⑦

Just use last Equations

$$\frac{1}{T} \left[\left(\frac{\partial H}{\partial p} \right)_T - V \right] = - \left(\frac{\partial V}{\partial T} \right)_p = -V\beta$$

$$\left(\frac{\partial H}{\partial p} \right)_T - V = -T \left(\frac{\partial V}{\partial T} \right)_p = -TV\beta$$

$$\boxed{\left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p = V - TV\beta = V(1 - T\beta)}$$

In general

$$dH(T, p) = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$

$$\boxed{dH = \overset{H}{C_p} dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_p \right] dp}$$

or

$$\boxed{dH(T, p) = C_p dT + V(1 - T\beta) dp}$$

Derive $C_p - C_v$

⑧

Use 1st Law

$$dQ = du + pdV$$

$$dQ = \left(\frac{\partial u}{\partial T} \right)_V dT + \left(\frac{\partial u}{\partial V} \right)_T dV + pdV$$

Regroup

$$dQ = C_v dT + \left[\left(\frac{\partial u}{\partial V} \right)_T + p \right] dV$$

Divide by dT at constant p

$$\left(\frac{dQ}{dT} \right)_p = C_v \left(\frac{\partial T}{\partial T} \right)_p + \left[\left(\frac{\partial u}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p$$

page 5 $S(V, T)$

$$C_p = C_v + T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p$$

$$C_p = C_v + T \left(\frac{\beta}{\kappa} \right) (V\beta)$$

$$C_p = C_v + \frac{TV\beta^2}{\kappa}$$