$$dx = M\,dy + N\,dz$$

exact: $\left(\frac{\partial M}{\partial z}\right)_y = \left(\frac{\partial N}{\partial y}\right)_z$

$$f(P, v, T) = 0$$

$$S = S(T, P)$$

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

$$C_p = \frac{\delta Q_p}{n\,dT}$$

$$\delta Q_p = dU + p\,dV$$

$$C_p = \frac{T\,d(S/n)}{dT}$$

$$T\,dS = dU + p\,dV$$

$$\delta Q_p = T\,dS$$

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

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

$$\delta Q = dU + \delta W$$

$$\boxed{T\,dS = dU + p\,dv}$$

$$du = T\,dS - P\,dv$$

M N

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

$$du = T\,ds - p\,dV$$

$$dx = M\,dy + N\,dz$$

exact $\quad \left(\frac{\partial M}{\partial z}\right)_y = \left(\frac{\partial N}{\partial y}\right)_z$

$$f(p, v, T) = 0$$

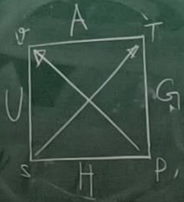
$$h = u + pv$$

$$dh = du + p\,dv + v\,dp$$

$$dh = \delta Q + v\,dp$$

$$\underset{\text{exact diff}}{dh} = \underset{M}{T}\,ds + \underset{N}{v}\,dp$$

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




$$dA = -p\,dV - s\,dT$$

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

$$dH = T\,dS + v\,dp \qquad dG = (-)S\,dT + v\,dp$$

$$\delta Q = dU + \delta W$$

$$\boxed{T\,ds = dU + p\,dv}$$

$$du = \underset{M}{T}\,ds \underset{N}{- P}\,dv$$

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

$dh$
$dy$
$dA$
$dG$

$p, v, T$

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

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

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

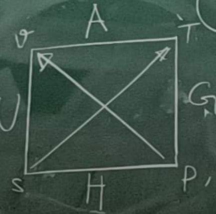
$du = T\,dS - p\,dV$

Maxwell Relations

$dx = M\,dy + N\,dz$

exact $\left(\frac{\partial M}{\partial z}\right)_y = \left(\frac{\partial N}{\partial y}\right)_z$

$f(P, v, T) = 0$




$dA = -p\,dV - s\,dT$

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

$dH = T\,dS + v\,dp$

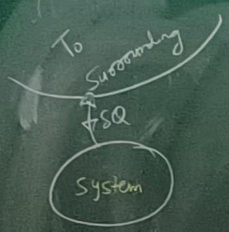
$dG = (-)S\,dT + v\,dP$

$\delta Q = dU + \delta W$

$\boxed{T\,ds = dU + p\,dv}$

$du = \underset{M}{T}\,ds - \underset{N}{P}\,dv$

$\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_v$




$$A = U - TS$$

$$\delta Q = dU + \delta W$$

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

Second law

$$dS_{sys} + dS_{surr} \geq 0$$

$$ds + \frac{(-\delta Q)}{T_0} \geq 0$$

$$\delta Q \leq T_0\, dS$$

$$\delta Q - dU \leq T_0\, dS - dU$$

$$\int \delta W_{1-2} \leq \int T_0\, ds - \int dU$$

$$W_{1-2} \leq T_0 (S_2 - S_1) - (U_2 - U_1)$$

$$W_{1-2} \leq (U_1 - T_0 S_1) - (U_2 - T_0 S_2)$$

If system $\underset{(\text{initial})}{T_1} = \underset{(\text{final})}{T_2} =$ surrounding temp $= T_0$

$$W_{1-2} \leq \underbrace{(U_1 - T_1 S_1)} - \underbrace{(U_2 - T_2 S_2)}$$

$$W_{1-2} \leq A_1 - A_2$$

Departure function

A

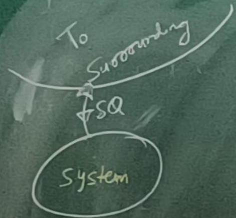
G

$$dh = \left( C_P \quad \beta \quad K \right)$$

$$du =$$

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

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




$$\dot{W}_s \le \dot{G}_i - \dot{G}_e$$

if a material flowing across a CV such that

$$T_i = T_e = T_0$$
(surround)

rate of change of Gibbs free energy = Maximum shaft work

Departure function

A

G

$$dh = \begin{pmatrix} C_P & \beta & K \end{pmatrix}$$

$$du =$$

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

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

Prove that: $ds = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$

$S(T,P)$

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

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

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

$$\boxed{ds = \left(\frac{C_p}{T}\right) dT - \left(\frac{\partial V}{\partial T}\right)_P dP}$$

$$\boxed{T\,ds = C_p\, dT - \beta v\, dP}$$


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

Departure function

~~A~~

~~G~~

$dh = $

$du = $ $\left( C_p \quad \beta \quad K \right)$

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

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

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

$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$

$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P$

<u>P T</u>

$T\,dS = C_V\,dT + \frac{T\beta}{k}\,dV$

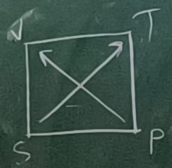
$S(T, v)$

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

$\left(\frac{C_V}{T}\right) dT + \left(\frac{\partial P}{\partial T}\right)_v dv$

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

$$\boxed{\begin{gathered} f(P, v, T) = 0 \\ (P, v, T) \quad \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v = -1 \end{gathered}}$$




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

Departure function

A

G

$dh = \big(C_P \quad \beta \quad K\big)$

$du =$

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

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

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

$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$

$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P$

PT

$T\,ds = C_V\,dT + \frac{T\beta}{k}\,dV$

$S(T, v)$

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

$\left(\frac{C_V}{T}\right) dT + \left(\frac{\partial P}{\partial T}\right)_V dv$ —— (a)

$\frac{\beta}{k} = \frac{(-)\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = (-)\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V$ —— (b)

from cyclic relation

$f(P, v, T) = 0$

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

from (a) & (b)

$ds = \frac{C_V}{T}\,dT + \frac{\beta}{k}\,dV$

$\boxed{T\,ds = C_V\,dT + \frac{\beta}{k}\,dV}$

Departure function

A

G

$dh = (C_P \quad \beta \quad k)$

$du =$

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

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

p.T.

$$dh = C_p\,dT + (v - T\beta v)\,dP$$

$$du = C_v\,dT + \left(\frac{T\beta}{\kappa} - P\right)dv$$

$h(T,P)$

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

$$dh = C_p\,dT + \left(v - T\left(\frac{\partial v}{\partial T}\right)_P\right)dP$$

$$\boxed{dh = C_p\,dT + (v - T\beta v)\,dP}$$

∴ using formula for $\beta$

$$dh = (\delta Q_p)_n$$

$$C_p = \frac{1}{n}\frac{\delta Q_p}{dT}$$

$$C_p = \left(\frac{\partial h}{\partial T}\right)_P$$

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

$$\boxed{\left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P}$$

$$\left(\frac{\partial h}{\partial P}\right)_T = T\left(\frac{-\partial v}{\partial T}\right)_P + v$$

$$dh = T\,ds + v\,dP$$

$$\left(\frac{\partial h}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T + v$$


Departure function

A

G

$$dh = \left(C_p \quad \beta \quad \kappa\right)$$

$$du =$$

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

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