

# Chap. 5 Auxiliary Functions.

The power of thermo is in its provision of the criteria for equil<sup>m</sup>.

The 1<sup>st</sup> & 2<sup>nd</sup> law.  $dU = Tds - PdV$ .  
for a closed sys.   
external pressure.   
pV work is only work.

- (S, V are inconvenient) choice of indep. variable.
- T, P are the most convenient choice.
- V, T for the partition.  $\rightarrow$  fixed volume fixes  $E_i$  & Partition function.
- $A = U - TS$  the Helmholtz free E.
- $G = (U + PV) - TS = H - TS$  the Gibbs free E.

## 5.2. The Enthalpy, H.

- for a closed sys w/ const P.

$$U_2 - U_1 = \int p \cdot P(V_2 - V_1)$$

(2.5) can be used for  $(U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1 = \Delta H = \int p$   
 $\rightarrow$  applicable for a sys w/ PV work.

## 5.3 The Helmholtz free Energy, A.

$$(A_2 - A_1) = (U_2 - U_1) - (T_2 S_2 - T_1 S_1)$$

for a closed sys.

$$(U_2 - U_1) = \int p - w$$

$$\therefore (A_2 - A_1) = \int p - w - (T_2 S_2 - T_1 S_1)$$

if isothermal  $T_1 = T_2 = T$ .

$$(A_2 - A_1) + T(S_2 - S_1) - \int p = -w \quad \left( \because ds = \frac{d\int_{rev} p}{T} \right)$$

(5.3) ∴ (A<sub>2</sub> - A<sub>1</sub>) + TΔS<sub>irr</sub> = -W

- for a reversible isothermal process ΔU = 0 ∫<sub>rev</sub> = W<sub>max</sub>.  
TΔS<sub>irr</sub> = 0.  
A<sub>2</sub> - A<sub>1</sub> = ΔA = -W<sub>max</sub>.

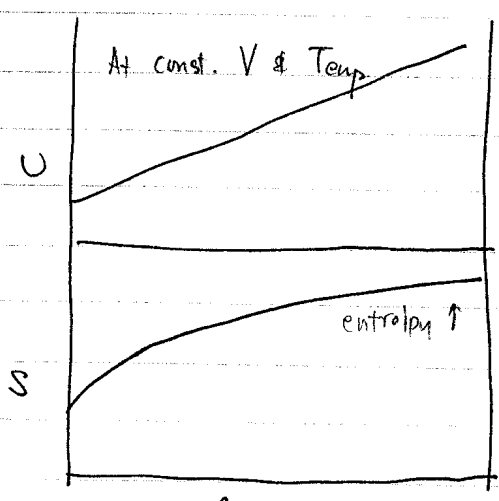
- for an isothermal process at const. V. (= no P-V work).  
(A<sub>2</sub> - A<sub>1</sub>) + TΔS<sub>irr</sub> = 0.  
i.e. for an increment (of a process)  
→ dA + TdS<sub>irr</sub> = 0.

for an irreversible process which is spontaneous.

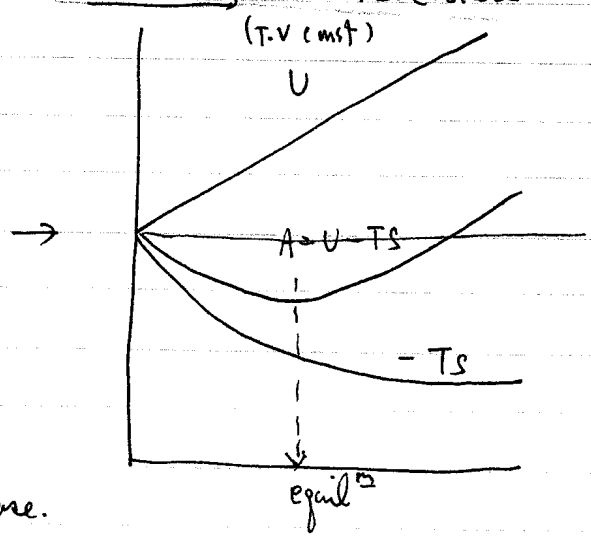
TdS<sub>irr</sub> > 0 ∴ dA < 0 → reaction.

for a reversible process TdS<sub>irr</sub> = 0  
w/ (iso & const. V)

then dA = 0 = -SdT + pdV means reversible → equil



n<sub>v</sub> = # of atoms in vapor phase.



### S.4. The Gibbs Free Energy, G.

from (S.2) 
$$\begin{aligned}
 (G_2 - G_1) &= (H_2 - H_1) - (T_2 S_2 - T_1 S_1) \\
 &= (U_2 - U_1) + (P_2 V_2 - P_1 V_1) - (T_2 S_2 - T_1 S_1)
 \end{aligned}$$

for a closed sys., the 1<sup>st</sup> law.

$$(U_2 - U_1) = q - w.$$

and if  $T_1 = T_2 = T$ .  
 when  $T$  is the temp. of  $1$   
 and if  $P_1 = P_2 = P$ .

then 
$$(G_2 - G_1) = q - w + P(V_2 - V_1) - T(S_2 - S_1)$$

total work done during the process

$$\therefore w = w' + P(V_2 - V_1)$$

chemical, electrical etc..

$$\therefore (G_2 - G_1) = q - w' - T(S_2 - S_1).$$

$$(G_2 - G_1) + T(S_2 - S_1) - q =$$

again

$$q \leq T(S_2 - S_1)$$

reversible case

$$\Delta TS$$

$$T \Delta S_{irr} > 0$$

$$\therefore w' \leq - (G_2 - G_1)$$

Again the equality can be written.

$$\boxed{-w' = (G_2 - G_1) + T \Delta S_{irr}}$$

always true! when T, P const

- In the case of an isothermal, isobaric process, no work other than P-V. then  $w' = 0$ .

$$\boxed{\therefore (G_2 - G_1) + T \Delta S_{irr} = 0}$$

always true!

a process can only occur <sup>always</sup> spontaneously ( $w/ \Delta S > 0$ ) if  $(G_2 - G_1) < 0$

$\therefore$  As the condition for thermo. equil<sup>m</sup>,  $dS_{irr} = 0$  (no more spontaneous mov)  
 then equil<sup>m</sup> is defined by  $\underline{dG = 0}$  ( $= -s dT + v dP$ )  
 for const. T, P

- For a sys. undergoing a process at const. T, P.  
 the Gibbs free Energy, G, can only decrease (i.e.  $G_2 - G_1 < 0$ ) or remain const.

3/29/95 (12)

S.S. For a enclosed sys.

- S.(10)  $H = U + PV$
- S.(11)  $A = U - TS$
- S.(12)  $G = H - TS$

$$\begin{aligned} dU &= Tds - PdV \\ dH &= Tds + vdp \\ dA &= -s dT - PdV \\ dG &= -s dT + v dP \end{aligned}$$

(1st + 2nd law) in a closed sys.  
 $dU = Tds - PdV + \sum \mu_i dn_i$   
 $dH = dU + Tds + v dP + \sum \mu_i dn_i$   
 $dA = dU - Tds - PdV + \sum \mu_i dn_i$   
 $dG = dH - Tds - s dT + \sum \mu_i dn_i$

## 5.6 Variation of the composition and size of the sys.

if the composition and size of a sys vary.

G is a func. of T, P, & # of moles. of all the species  
 (5.13)  $G = G(T, P, n_1, n_2, n_3, \dots)$

differentiate.  $dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_i, n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_i, n_j} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_T dn_i$

if  $n_i$  remains const.  $dG = -SdT + VdP$

$$\therefore \left(\frac{\partial G}{\partial T}\right)_{P, n_i} = -S, \quad \left(\frac{\partial G}{\partial P}\right)_{T, n_i} = V$$

5.7 The chemical potential.  $\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq n_i} = \mu_i$

$\mu_i$  is the amount by which the capacity of the system for doing work, other than the work of expansion, is increased, per mol of  $i$  added at const T, P.  $i \neq j$  when system is large enough to notice the change.

$$(5.17) \quad dG = -SdT + VdP + \sum \mu_i dn_i$$

applicable to open system which exchange matter as well as to closed sys. which undergo composition change

to open sys. (5.18)  $dU = Tds - PdV + \sum_{s.v. j \neq i} \left(\frac{\partial U}{\partial n_j}\right) dn_j$

$$(5.19) \quad dH = Tds + VdP + \sum_{s.p. j \neq i} \left(\frac{\partial H}{\partial n_j}\right) dn_j$$

$$(5.20) \quad dA = -SdT - PdV + \sum_{T, V, j \neq i} \left(\frac{\partial A}{\partial n_j}\right) dn_j$$

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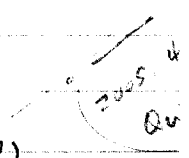
$$\therefore \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_j} = \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_j} = \left( \frac{\partial H}{\partial n_i} \right)_{S, p, n_j} = \left( \frac{\partial A}{\partial n_i} \right)_{T, V, i}$$

( $\frac{\partial}{\partial n_i}$  은  $\frac{\partial}{\partial n_i}$  on !!)

- (S.22)  $\therefore dU = Tds - PdV + \sum \mu_i dn_i$
- (S.23)  $dH = Tds + Vdp + \sum \mu_i dn_i$  particularly one
- (S.24)  $dA = -SdT - PdV + \sum \mu_i dn_i$  called
- (S.25)  $dG = -SdT + Vdp + \sum \mu_i dn_i$  → fundamental.

from the 1<sup>st</sup> law.  $dU = dq - dw$

the comparison give  $dq = Tds$   
 $dw = PdV + \sum \mu_i dn_i$



S.8. Thermodynamic Relations

- (S.26)  $T = \left( \frac{\partial U}{\partial S} \right)_{V, \text{Comp}} = \left( \frac{\partial H}{\partial S} \right)_{P, \text{Comp}}$  Chemical work  
 $= \int H dm$   
 (magnetization)  
 mag. field strength
- (S.27)  $P = - \left( \frac{\partial U}{\partial V} \right)_{S, \text{Comp}} = - \left( \frac{\partial A}{\partial V} \right)_{T, \text{Comp}}$   $= \int \sigma dA$   
 (surface)
- (S.28)  $V = \left( \frac{\partial H}{\partial P} \right)_{S, \text{Comp}} = \left( \frac{\partial G}{\partial P} \right)_{T, \text{Comp}}$   $+ \int \rho dE$   
 (electrostatic)
- (S.29)  $S = - \left( \frac{\partial A}{\partial T} \right)_{V, \text{Comp}} = - \left( \frac{\partial G}{\partial T} \right)_{P, \text{Comp}}$

S.9 Maxwell's Relations.

$Z = Z(x, y)$   $dZ = \left( \frac{\partial Z}{\partial x} \right) dx + \left( \frac{\partial Z}{\partial y} \right) dy = \frac{(x, y)}{x} dx + \dots$

if state func. Department of Inorganic Materials Engineering  
 x, y = indep. variable

$$\left[ \frac{\partial}{\partial y} \left( \frac{\partial Z}{\partial x} \right)_y \right]_x = \left( \frac{\partial L}{\partial y} \right)_x$$

$$\left[ \frac{\partial}{\partial x} \left( \frac{\partial Z}{\partial y} \right)_x \right]_y = \left( \frac{\partial M}{\partial x} \right)_y$$

Since  $Z$  is a state func., the change in  $Z$  is indep. of the order of differentiation, i.e.,

$$\left[ \frac{\partial}{\partial y} \left( \frac{\partial Z}{\partial x} \right)_y \right]_x = \left[ \frac{\partial}{\partial x} \left( \frac{\partial Z}{\partial y} \right)_x \right]_y = \frac{\partial^2 Z}{\partial x \partial y}$$

$$(5.30) \quad \therefore \left( \frac{\partial L}{\partial y} \right)_x = \left( \frac{\partial M}{\partial x} \right)_y$$

Use (5.30) for (5.10) - (5.12) & (3.12).

$$dU = Tds - PdV \quad \left( \frac{\partial T}{\partial V} \right)_s = - \left( \frac{\partial P}{\partial S} \right)_v \quad (5.31)$$

$$dH = Tds + vdp \quad \left( \frac{\partial T}{\partial p} \right)_s = \left( \frac{\partial v}{\partial S} \right)_p \quad (5.32)$$

$$dA = -sdt - PdV \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_v \quad (5.33)$$

$$dG = -sdt + vdp \quad \left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_p \quad (5.34)$$

Power of  
Maxwell's eq  
entropy +  
into P.T.

For a closed sys. of fixed composition.

$$dU = Tds - PdV \rightarrow \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P$$

(5.34b)

$$\text{difficult to measure} \quad = \quad \text{easy to measure} \quad = T \left( \frac{\partial P}{\partial T} \right)_v - P$$

if the sys. is an ideal gas,  $PV = RT$ .  $P = \frac{RT}{V} \therefore \left( \frac{\partial P}{\partial T} \right)_v = \frac{P}{V}$

$$\left( \frac{\partial U}{\partial V} \right)_T = T \cdot \frac{R}{V} - P \left( \frac{RT}{V} \right) = 0.$$

$\therefore$  concludes that the internal E of an ideal gas is indep. of the vol. of the gas !!

Similarly for a closed sys. of fixed composition.

$$(5.10) \quad dH = Tds + vdp \quad \rightarrow \quad \left(\frac{\partial H}{\partial p}\right)_T = T \left(\frac{\partial s}{\partial p}\right)_T + v$$

$$(5.34) \quad \left(\frac{\partial s}{\partial p}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_p \quad \therefore \quad \left(\frac{\partial H}{\partial p}\right)_T = -T \left(\frac{\partial v}{\partial T}\right)_p + v$$

↑ measurable known variable

if a fixed quantity of ideal gas

$$pv = RT \quad v = \frac{RT}{p} \quad p = \text{const} \quad \therefore \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = 0 \quad H \text{ is indep of } p$$

### 5.10 The Transformation formulas.

for a closed sys of fixed comp. w/ 3 state prop. x, y, z.

$$x = x(y, z) \quad dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

for an incremental change of state at const x.

$$\text{then } \left(\frac{\partial x}{\partial y}\right)_z dy = - \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = - \left(\frac{\partial x}{\partial z}\right)_y \rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

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### 5.11 Example of the Use of the thermo. relations.

이것이 이항식  
상대변수 식!

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

isobaric thermal exp.  $\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p$

isothermal compressibility  $\beta = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T$

$$C_p - C_v = \frac{VT\alpha^2}{\beta}$$



5.12 The Gibbs - Helmholtz Eq.

(5.2) G = H - TS

(5.12) dG = -SdT + Vdp → (dG/dT)<sub>p</sub> = -S. Thermodynamic

at const pressure.

∴ G = H + T(dG/dT) → GdT = HdT + TdG.

→ (TdG - GdT) / T<sup>2</sup> = -d(G/T)

(5.37) ∴ d(G/T) / dT = -H / T<sup>2</sup>

Gibbs - Helmholtz Eq. applicable to a closed sys.

d(G<sub>2</sub>/T) - d(G<sub>1</sub>/T) = -(H<sub>2</sub> - H<sub>1</sub>) / T<sup>2</sup>

of fixed comp., p = c

For an isobaric change of state of

d(ΔG/T) / dT = -ΔH / T<sup>2</sup>

a closed sys. (fix comp.)

ΔG can be determined from an exp. ly measured ΔH.

Similar (5.38a)

d(ΔA/T) / dT = -ΔU / T<sup>2</sup>