

Chap. 8.

1st law  $dU = dq - PdV$   
 2nd law  $dH = Tds - PdV$   
 $dH = d(U+PV) = Tds + vdp$   
 $d(H-Ts) = -sdT + vdv$  c/8

8.6. The Thermo Prop. of ideal gases & mixture of ideal gases

A. (a) Isothermal, free E - P Relationship of an ideal gas.

at const T. fixed comp.

(5.25)  $dG = vdp$

for 1 mole of an ideal gas  $dG = \frac{RT}{P} dp = RT d \ln P$

(8.9)  $G(P_2, T) - G(P_1, T) = RT \ln \frac{P_2}{P_1}$

don't know the absolute G value. → need ref. state → standard state

⇒ Standard State : the state of 1 mole of pure gas at 1 atm.  
 $G(P=1, T) \rightarrow G^\circ(T)$

(8.9)  $G(P_2, T) - G(P=1, T) = RT \ln P_2$   
 $G^\circ(T)$

\* at const. T.

$\therefore G(P, T) = G^\circ(T) + RT \ln P$

or  $G = G^\circ + RT \ln P$   $P = P/P^\circ$  no dimension

B. (a) Mixtures of Perfect Gases.

- mole fraction  $X_A = \frac{n_A}{n_A + n_B + n_C}$   $X_A + X_B + X_C = 1$

Dalton's law  $P = P_A + P_B + P_C$

- of Partial Pressure.

(partial pressure.

$\frac{P_A}{P} = X_A$

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(2)

partial molar Prop.

the value of the ext. prop. for the arbitrary quan.

①

$$\bar{Q}_i = \left( \frac{\partial Q'}{\partial n_i} \right)_{T, P, n_j, n_k, \dots}$$

→ the change in the value of Q' of the mixture for an infinitesimal addition of the comp. i, at const T, P per mole of i added.

proof!

For the addition of i to be infinitesimal

$\bar{Q}_i$  should be dep. on composition, the comp. of the sys → const ⇒ then Q to be sufficiently large that the addition of a mole become affect no change in overall composition.

②

Partial m. Q of Thermo Rule of 300221?

(5.15)

$$\bar{G}_i = \left( \frac{\partial G'}{\partial n_i} \right)_{T, P, n_j, n_k, \dots} = \mu_i$$

chemical pot. of the comp. in the mixture = the partial molar G of a comp. in a n

for one comp.  $\left( \frac{\partial G'}{\partial P} \right)_{T, comp} = V'$  - 열역학 (11.7.1.1)

$\mu_i = G_i$

(2 phase of equil. sys i.e. water & ice)

이런 식으로 take T, P

$$\left[ \frac{\partial}{\partial n_i} \left( \frac{\partial G'}{\partial P} \right)_{T, comp} \right]_{T, P, n_j} = \left( \frac{\partial V'}{\partial n_i} \right)_{T, P, n_j}$$

by definition,  $\left( \frac{\partial V'}{\partial n_i} \right)_{T, P, n_j} = \bar{V}_i$

and as G is a state function. → 열역학 (9.1.1) (2.1.1.1)

$$\frac{\partial}{\partial n_i} \left[ \left( \frac{\partial G'}{\partial P} \right)_{T, comp} \right]_{T, P, n_j} = \left[ \frac{\partial}{\partial P} \left( \frac{\partial G'}{\partial n_i} \right)_{T, P, n_j} \right]_{T, comp}$$

$$\therefore \left( \frac{\partial \bar{G}_i}{\partial P} \right)_{T, comp} = \bar{V}_i \quad \leftarrow (5.25)$$

③ For the perfect gas A in a mixture of perfect gases.

$$d\bar{G}_A = \bar{V}_A dP$$

The partial molar vol.,  $\bar{V}_A$ , in a gas mixture.  
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in a perfect gas mixture  
large D  
ideal gas

$$\bar{V}_A = \frac{V}{\sum n_i} = \frac{x_A RT}{P_A} \quad (1)$$

from  $P_A = x_A P$  Differentiate it at const T. and comp.

$$\therefore d\bar{G}_A = \bar{V}_A dp = \frac{x_A RT}{P_A} \cdot \frac{dP_A}{x_A} = RT \frac{dP_A}{P_A}$$

$$\int_{G^0}^{\bar{G}_A} d\bar{G}_A = \int_{P=1}^{P_i=P_A} RT \ln P_A = RT \ln \frac{P_A}{1} = \bar{G}_A - G_A^0$$

$$\therefore \bar{G}_A = G_A^0 + RT \ln P_A = G_A^0 + RT \ln x_A + RT \ln P$$

(8.15)

④ The Heat of Mixing of Perfect Gases.

the pressure the gas mix at T

for each component gas in the mixture  $\bar{G}_i = G_i^0 + RT \ln x_i + RT \ln P$

$$(8.16) \quad \frac{\partial(\bar{G}_i/T)}{\partial T} = \frac{\partial(G_i^0/T)}{\partial T}$$

$$(8.17) \quad \left[ \frac{\partial(\bar{G}_i/T)}{\partial T} \right]_{p, \text{comp.}} = -\frac{H_i^0}{T^2} \quad \& \quad \left[ \frac{\partial(\bar{G}_i/T)}{\partial T} \right]_{p, \text{comp.}} = -\frac{\bar{H}_i}{T^2}$$

$$(8.18) \quad \therefore \bar{H}_i = H_i^0$$

$\therefore$  the enthalpy of the gas mixture = the enthalpy of the unmixed comp. gas

the change in the enthalpy due to the mixing.

$$\Delta H^{\text{mix}} = \sum n_i \bar{H}_i - \sum n_i H_i^0 = 0$$

assembly of noninteracting particle.

$$\bar{H}_i = f(T) \text{ only} \neq f(P)$$

Free E. of Mixing of Perfect gas mixture.

$$(8.15) \quad \bar{G}_i = G_i^0 + RT \ln P_i \quad \text{each component gas. in mix}$$

$$(8.9) \quad G_i = G_i^0 + RT \ln P_i \quad \text{before}$$

$$P_1 = \frac{1}{3} \text{ atm} \quad P_2 = \frac{2}{3} \text{ atm}$$

④

$$\left[ \begin{array}{c} P_1 = 1 \text{ atm} \\ n = 1 \text{ mol} \end{array} \right] + \left[ \begin{array}{c} P_2 = 1 \text{ atm} \\ n = 2 \text{ mol} \end{array} \right] = \left[ \begin{array}{c} P_m = 1 \text{ atm} \\ n = 3 \text{ mol} \end{array} \right] \quad \text{state}$$

Unmixed  $\rightarrow$  mixed component.

$$\begin{aligned} \Delta G(1 \rightarrow 2) &= G'_{\text{mixture}} - G'_{\text{unmixed comp.}} \\ &= \Delta G'_{\text{mix}} = \sum n_i \bar{G}_{i, \text{mix}} - \sum n_i G_i \\ &= \sum n_i RT \ln \left( \frac{P_i}{P_i^*} \right) \quad \text{if } P_i = P_j = P_k = \dots = 1 \\ &= \sum n_i RT \ln X_i \end{aligned}$$

gases are all the same  
if mixing is carried at const. total vol  
 $\sum n_i$

$\ln X_i < 0 \quad \therefore \Delta G'_{\text{mix}} < 0 \rightarrow \text{sp. pr.}$

### The Entropy of Mixing of Perfect Gases.

$$\Delta H'_{\text{mix}} = 0.$$

$$\Delta G'_{\text{mix}} = \Delta H'_{\text{mix}} - T \Delta S'_{\text{mix}}$$

then

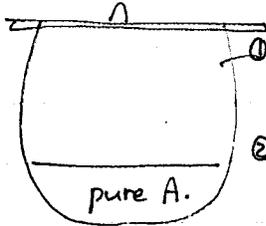
$$\Delta S'_{\text{mix}} = - \sum n_i R \ln \left( \frac{P_i}{P_i^*} \right) = - \sum n_i R \ln X_i$$

if  $P_i = P_k = P_{\text{mix}}$   
 $\text{sp. pr.}$

4/14/06

# 9.2 Raoult's Law and Henry's Law.

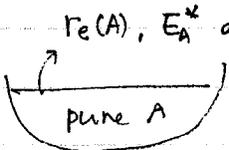
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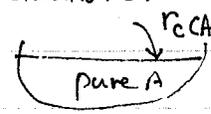
① vac. initially at T.

② started evaporation & continued until  $P_A$  (saturated vapor pressure)

③ a dynamic equil<sup>m</sup> bet'n the rate of evap. and of



$r_e(A)$ ,  $E_A^*$  activation E.



$r_e(A) \propto$  the # of A atoms in the vapor phase.

$r_e = r_e \cdot 10^{23}$

(11.1) Thus,  $r_e(A) = k P_A^0$  and at equil<sup>m</sup>  $r_e(A) = k' P_A^0$

(11.2)  $r_e(A) \propto \frac{n_i^*}{n} = \frac{1}{kT} \int_{E^*}^{\infty} \exp\left(\frac{-E_i}{kT}\right) dE = \exp\left(\frac{-E^*}{kT}\right)$  ref exponential

$n = \sum_i \exp\left(\frac{-E_i}{kT}\right) = \text{avg. } E/\text{atom}$

(11.2) for liquid B  $r_e(B) = k' P_B^0$  (11.2)  $n_i = \frac{n e^{-\beta E_i}}{P}$

(A) \* Consider the effect of small addition of B to A.

if bulk comp. = surface comp.,  $X_A$ .

at equil<sup>m</sup>

(11.3, 4)

$r_e(A) X_A = k P_A$ ,  $r_e(B) X_B = k' P_B$

from (11.1)  $A \& B$  size comparable  
area reduced by this factor

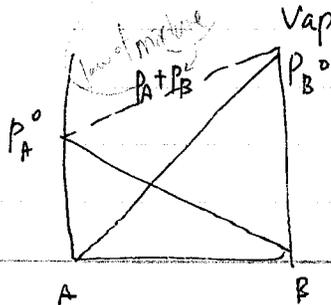
(11.5) (11.1) + (11.3)

(11.6) (11.2) + (11.4)

$P_A = X_A P_A^0$   
 $P_B = X_B P_B^0$

Raoult's Law.

Vapor pressure exerted by i = the mole fraction of i x vap.p. of



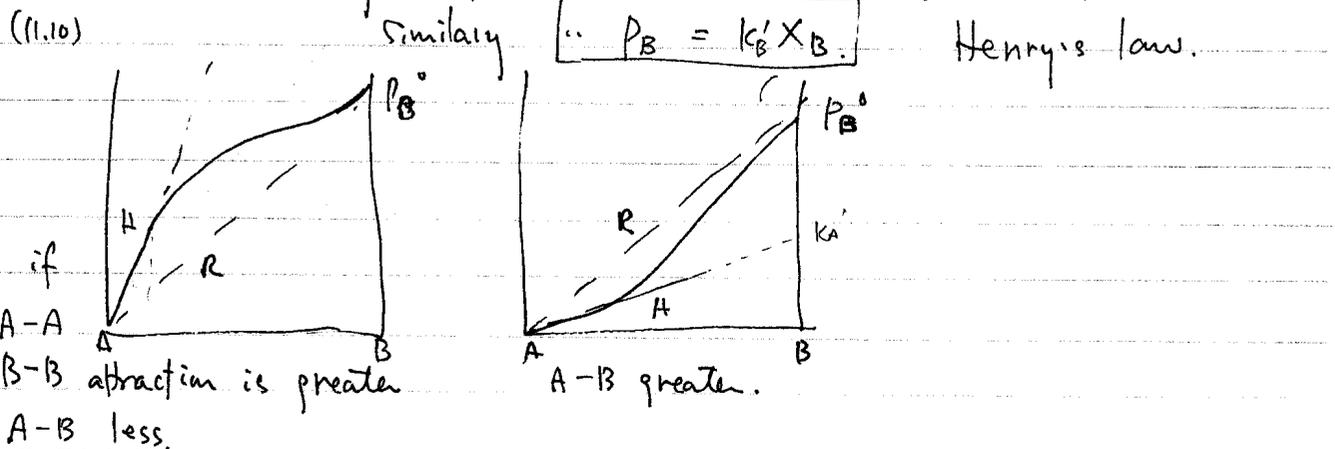
- Requirement:  $r_e(A) \& r_e(B)$  is ind. of comp. of the magnitudes of A-A, B-B, A-B interactions identical

(B) if A-B interaction  $\gg$  A-A or B-B interaction. high E. area  
 a dilute solution of A to B. A atom at the surface surrounded  
 A in a deeper potential E well than are the A atoms at  
 the surface of pure liquid  $\rightarrow$  difficult to be lifted to

(11.7) evaporation rate is decreased from  $r_e(A)$  to  $r'_e(A)$  ( $r'_e(A) < r_e(A)$ )  
 $r'_e(A) X_A = k P_A \rightarrow k = \frac{r'_e(A)}{P_A} X_A = \frac{r_e(A)}{P_A} X_A$   
 from  $r_e(A) = k P_A^\circ \rightarrow r_e(A) = \frac{r'_e(A)}{P_A} X_A P_A^\circ$

(11.8)  $\therefore P_A = \frac{r'_e(A)}{r_e(A)} X_A P_A^\circ$   $r'_e(A) < r_e(A)$   
 $P_A = k'_A X_A$  (11.9)

Beyond a critical value of  $X_A$ ,  $r'_e(A)$  thus becomes comp.-dependent  
 (11.9) obey only over initial conc. range in reality.



q.3. Activity of a comp. in solution.

$a_i = \frac{f_i}{f_i^\circ} = \frac{P_i}{P_i^\circ}$  if the vapor above the sol'n is ideal  
 pure (standard state) at T.

if the component i behaves ideally in solution

### 9.4. The Gibbs - Duhem Eq.

- In many cases, the extensive prop. of a component in a multicomponent sol'n are amenable to exp. measurement !!
- The other comp's prop ← obtained by a pen'l relationship.  
⇒ G-D eq.

Q is an extensive prop.  $Q' = Q'(T, P, n_i, n_j, n_k \dots)$   
at const T, P.

$$(11.15) \quad dQ' = \left( \frac{\partial Q'}{\partial n_i} \right)_{T, P, n_j, n_k} dn_i + \left( \frac{\partial Q'}{\partial n_j} \right) dn_j + \dots$$

partial molar value.  $\bar{Q}_i = \left( \frac{\partial Q'}{\partial n_i} \right)_{T, P, n_j, n_k \dots}$

(11.16)  $\therefore dQ' \stackrel{\text{by definition}}{=} \bar{Q}_i dn_i + \bar{Q}_j dn_j + \bar{Q}_k dn_k + \dots$   
if  $\bar{Q}_i$  is the value of Q/mole of  $n_i$ .  
 ↳ the increase in the value of  $Q'$  for the mixture sol'n when 1 mole of  $n_i$  added to a large ju ← don't cause mean change by adding 1 mo.

$$(11.17) \quad Q' = n_i \bar{Q}_i + n_j \bar{Q}_j + n_k \bar{Q}_k + \dots$$

$$(11.18) \quad \therefore dQ' = n_i d\bar{Q}_i + n_j d\bar{Q}_j + n_k d\bar{Q}_k + \dots + \bar{Q}_i dn_i + \bar{Q}_j dn_j + \bar{Q}_k dn_k + \dots$$

from (11.16) & (11.18).

$$n_i d\bar{Q}_i + n_j d\bar{Q}_j + n_k d\bar{Q}_k + \dots = 0$$

$$(11.19) \quad \text{Generally} \quad \sum n_i d\bar{Q}_i = 0$$

(11.19) ÷ n (total # of moles)

$$(11.20) \quad \boxed{\sum X_i d\bar{Q}_i = 0} \quad \text{G-D Eq.}$$

5/7/95  
 9.5 The free E. of solution

$dG = TdS - PdV + \sum \mu_i dn_i$   
 $dG = TdS - PdV + \sum \mu_i dn_i$   
 $dG = TdS - PdV + \sum \mu_i dn_i$

(9)

\* Molar free E. of a sol'n & partial molar f. E. of Sol'n of comp'ts.

- w/ free E. as an ext. prop.

(11.21) (11.17)  $\rightarrow$  ext  $\rightarrow G' = n_A \bar{G}_A + n_B \bar{G}_B$

(11.22) For 1 mole of sol'n.  $\rightarrow G'' = x_A \bar{G}_A + x_B \bar{G}_B$

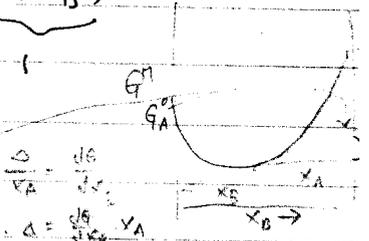
(11.23)  $dG = x_A d\bar{G}_A + x_B d\bar{G}_B + \bar{G}_A dx_A + \bar{G}_B dx_B$   
 0 by G-D.

(11.24)  $\therefore dG = \bar{G}_A dx_A + \bar{G}_B dx_B \rightarrow \frac{dG}{dx_A} = \bar{G}_A - \bar{G}_B$

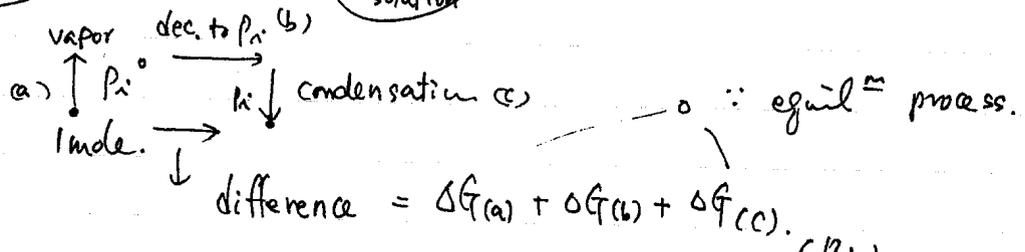
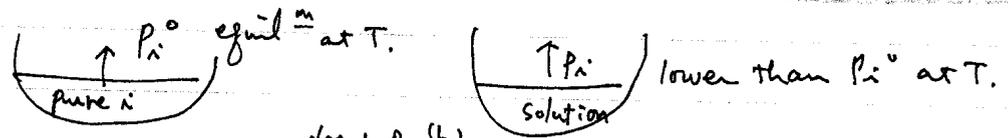
(11.26)  $x_B \times (11.24) \Rightarrow x_B \frac{dG}{dx_A} = x_B \bar{G}_A - x_B \bar{G}_B$

(11.26) + (11.22)  $G'' + x_B \frac{dG}{dx_A} = \bar{G}_A (x_A + x_B)$

(11.27)  $\therefore \bar{G}_A = G'' + x_B \frac{dG}{dx_A}$   
 $\therefore \bar{G}_B = G'' + x_A \frac{dG}{dx_A}$



\* The free E. change due to the formation of a sol'n.



difference =  $\Delta G(a) + \Delta G(b) + \Delta G(c)$   
 $= \Delta G(b) = RT \ln \left( \frac{P_i}{P_i^0} \right)$

⑥

$= \bar{G}_i$  (partial molar F.E. of  $i$ )

$\Delta \bar{G}_i^M = \bar{G}_i - G_i^0$        $G_i^0 = \text{molar F.E.}$

Since  $a_i = \frac{P_i}{P_i^0}$  (11.12),

$\Delta G_{(b)} = G_i(\text{in solution}) - G_i(\text{pure}) = R$   
 $\Delta \bar{G}_i^M = \bar{G}_i - G_i^0 = RT \ln a_i$

This process is a part of mixing a soln (in this case,  $i$  component)  
 ∴ Call it " $\Delta \bar{G}_i^M$ ", the partial m.f.E. of the soln of  $i$ .

- If at  $T, P = \text{const.}$  w/  $n_A$  of  $A$ ,  $n_B$  moles of  $B$  to form bin

the free E. of before mixing =  $n_A G_A^0 + n_B G_B^0$  (1)

after =  $n_A \bar{G}_A + n_B \bar{G}_B$  (2)

prime on ( $G'$ )

for any quantity  $\Rightarrow$  free E. change due to mixing (2)-(1)

not molar.

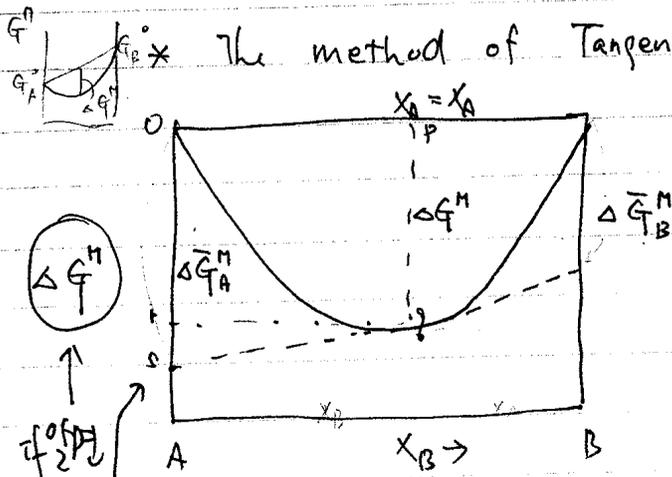
$\Delta G'^M = n_A (\bar{G}_A - G_A^0) + n_B (\bar{G}_B - G_B^0)$

integral F.E. of mixing

from (11.28)  $\Delta G'^M = n_A \Delta \bar{G}_A^M + n_B \Delta \bar{G}_B^M = RT (n_A \ln a_A + n_B \ln a_B)$

1 mole  $\Rightarrow \Delta G^M = X_A \Delta \bar{G}_A^M + X_B \Delta \bar{G}_B^M = RT (X_A \ln a_A + X_B \ln a_B)$

The method of Tangent Intercepts.



from (11.27, a, b): page ⑤ or ⑥

$\Delta \bar{G}_A^M = \Delta G^M + X_B \frac{d\Delta G^M}{dX_A}$   
 $\Delta \bar{G}_B^M = \Delta G^M + X_A \frac{d\Delta G^M}{dX_B}$

At  $X_A = X_B$

$\Delta G^M = p\delta$   
 $\frac{d\Delta G^M}{dX_A} = \frac{r\delta}{r\gamma}$

$\therefore \Delta \bar{G}_A^M = p\delta + \frac{r\delta}{r\gamma} = p\delta + \frac{r\delta}{r\gamma}$

5/12/15 3:30 (10:45)

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Q.6. The prop. of Raoultian ideal sol'n.

$\hookrightarrow a_i = X_i$

∴ ideal binary  $\Delta G^{M, id} = RT(X_A \ln X_A + X_B \ln X_B)$

from (11.32)  $\Delta G^M = RT(X_A \ln a_A + X_B \ln a_B)$

→ the General thermo. relationships. let'n state prop. → applicable to the partial molar properties.

(11.35)  $\frac{\partial \bar{G}_i}{\partial P} = \bar{V}_i$  for pure i  $\left(\frac{\partial G_i^0}{\partial P}\right) = V_i^0$

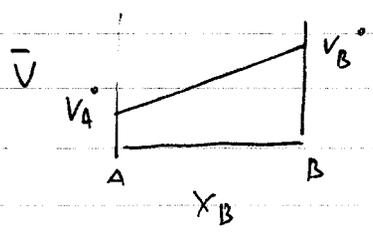
from  $\left[\frac{\partial(\bar{G}_i - G_i^0)}{\partial P}\right]_{T, comp} = (\bar{V}_i - V_i^0)$

→ For an ideal sol'n.  $\Delta \bar{G}_i^M = RT \ln X_i$ ,  $X_i \neq f(P)$

∴  $\frac{\partial \Delta \bar{G}_i^M}{\partial P} = \Delta \bar{V}_i^M = 0$

②  $\Delta V^M = (n_A \bar{V}_A + n_B \bar{V}_B) - (n_A V_A^0 + n_B V_B^0) = n_A \Delta \bar{V}_A^M + n_B \Delta \bar{V}_B^M$

since ideal sol'n  $\Delta \bar{V}_i^M = 0$ , →  $\Delta V^{M, id} = 0$



①  $\bar{V}_A = V_A^0$ ;  $\bar{V}_B = V_B^0$

→ The heat of formation of an ideal sol'n.

(11.39) Gibbs-Helmholtz  $\left[\frac{\partial(\bar{G}_i/T)}{\partial T}\right] = -\frac{\bar{H}_i}{T^2}$ ,  $\left[\frac{\partial(G_i^0/T)}{\partial T}\right]_{p, comp} = -\frac{\bar{H}_i^0}{T^2}$

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$$\left[ \frac{\partial \left( \frac{\bar{G}_i - G_i^\circ}{T} \right)}{\partial T} \right]_{p, \text{comp}} = 0 = - \frac{(\bar{H}_i - H_i^\circ)}{T^2} \quad (= 0)$$

$$\therefore \bar{G}_i - G_i^\circ = \Delta \bar{G}_i^\circ = RT \ln X_i \neq f(T)$$

$$\therefore \Delta \bar{H}_i^\circ = \bar{H}_i - H_i^\circ = 0$$

$$\therefore \Delta H^{M, \text{id}} = n_A \Delta \bar{H}_A^\circ + n_B \Delta \bar{H}_B^\circ \rightarrow \Delta H^{M, \text{id}} = 0$$

→ The Entropy of formation of an ideal sol'n

$$(5.25) \quad \left( \frac{\partial G}{\partial T} \right)_{p, \text{comp}} = -S \quad \therefore \left( \frac{\partial \Delta G^\circ}{\partial T} \right)_{p, \text{comp}} = -\Delta S^\circ$$

from  $\Delta G^{M, \text{id}} = RT (X_A \ln X_A + X_B \ln X_B)$

$$\therefore \Delta S^{M, \text{id}} = -R (X_A \ln X_A + X_B \ln X_B)$$

→ means the entropy of formation of an ideal sol'n  $\neq f(T)$

no size limit →  $\Delta S_{\text{conf}} = k \ln \frac{(N_A + N_B)!}{N_A! N_B!} \rightarrow \Delta S_{\text{conf}} = -R (X_A \ln X_A + X_B \ln X_B)$

for any sol'n  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$   
 ideal sol'n  $\Delta G^{M, \text{id}} = -T \Delta S^{M, \text{id}}$   $\Delta S^\circ = X_A \Delta \bar{S}_A^\circ + X_B \Delta \bar{S}_B^\circ$   
 $\downarrow$   
 $-R \ln X_A$

### 9.7. Nonideal Sol'n

activity coeff  $\gamma_i = \frac{a_i}{X_i}$

$\gamma_i = f(T, \text{comp}) \leftarrow$  determined by experiment

for a sol'n  $\gamma_i$  needed to determine  $a_i$  and  $\Delta \bar{G}_i^\circ (= RT \ln a_i)$

and  $\Delta \bar{G}^\circ = \sum n_i \Delta \bar{G}_i^\circ$

$\gamma_i > 1$  positive dev. from Raoult's law

$\gamma_i < 1$  neg. 서울대학교 공과대학 무기재료공학과  
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II) The tail to minus infinite as  $X_B \rightarrow 0$  can be avoided using  
(In binary A-B sol'n.)

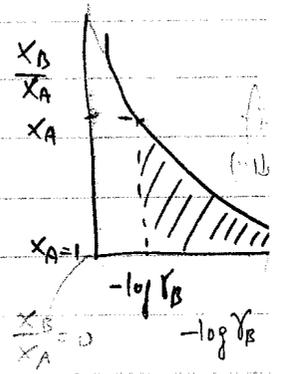
(11.52)  $X_B + X_A = 1$       $dX_A + dX_B = 0 \rightarrow \frac{X_A dX_A}{X_A} + \frac{X_B dX_B}{X_B} = 0$

(11.53)  $\therefore X_A d \log X_A + X_B d \log X_B = 0$

(11.49)  $X_A d \ln a_A + X_B d \ln a_B = 0$

(11.54)  $\therefore d \log \gamma_A = - \frac{X_B}{X_A} d \log \gamma_B$

$\log \gamma_A \Big|_{X_A=X_A} = - \int_{\log \gamma_B \text{ at } X_A=1}^{\log \gamma_B \text{ at } X_A=X_A} (X_B/X_A) d \log \gamma_B$



III) The  $\alpha$ -function as an aid to G-D integration

(11.56)  $\alpha_i = \frac{\ln \gamma_i}{(1-X_i)^2}$       $\alpha_A = \frac{\ln \gamma_A}{X_B^2}$       $\alpha_B = \frac{\ln \gamma_B}{X_A^2}$

from p344 (11.61)  $\ln \gamma_A = -X_B X_A \alpha_B \Big|_{X_A=1}^{X_A=X_A} - \int_{X_A=1}^{X_A=X_A} \alpha_B dX_A$

(11.57)  $\alpha_A = \frac{\ln \gamma_A}{X_B^2}$

$\therefore \ln \gamma_A = \alpha_A X_B^2$

The Relationship bet'n Henry's & Raoult's Laws

Henry's law  $a_B = K_B X_B \rightarrow \log a_B = \log K_B + \log X_B$

$\rightarrow d \log a_B = d \log X_B$      G-D  $\rightarrow X_A d \ln a_A + X_B d \ln a_B = 0$

in Herian Region

$\frac{d \ln a_A}{X_A} = - \frac{X_B}{X_A} d \ln a_B = - \frac{X_B}{X_A} d \ln X_B = - \frac{dX_B}{X_A}$

$= \frac{dX_A}{X_A} = \frac{d \ln X_A}{X_A}$       $\therefore \ln a_A = \ln X_A + \text{const.}$

$a_A = \text{const.} \cdot X_A$

by definition  $a_i = 1$  when  $X_i = 1$       $\therefore \text{const.} \rightarrow 1$

Department of Chemical Engineering  
M... in which the solute B obeys Henry's

IV) The Belton-Fuehan Treatment of the G-D eq.

↳ this allows the variation of the individual activities (w/ comp.) to be calculated based on the ratio of the activities (w/ comp.)

→ For an A-B sol'n with known  $a_A/a_B$  as a fn. of comp.

G-D ( $\sum X_i d\bar{Q}_i = 0 = X_A d\bar{Q}_A + X_B d\bar{Q}_B$ )

$X_A d \ln a_A + X_B d \ln a_B = 0$

subtract  $d \ln a_B$  from both <sup>sides</sup> terms. and  $X_B = (1 - X_A)$

$X_A d \ln a_A + (1 - X_A) d \ln a_B - d \ln a_B = - d \ln a_B$

(11.62)  $\rightarrow -X_A d \ln \left( \frac{a_A}{a_B} \right) = + d \ln a_B$

$X_A + X_B = 1$

$dX_A + dX_B = 0$

$X_A \frac{dX_A}{X_A} + X_B \frac{dX_B}{X_B} = 0$

And  $X_A d \ln X_A + X_B d \ln X_B = 0$

Similarly subtract  $d \ln X_B$  from both sides

(11.63)  $\rightarrow d \ln X_B = -X_A d \ln \left( \frac{X_A}{X_B} \right)$

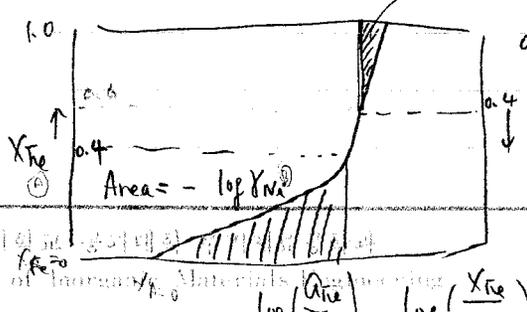
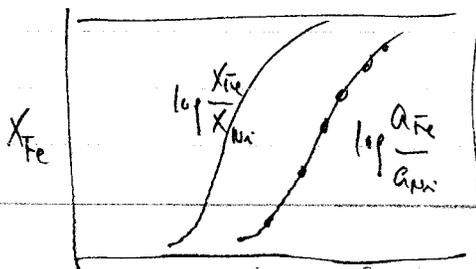
(11.62) - (11.63) =

$d \ln a_B - d \ln X_B = -X_A \left[ d \ln \left( \frac{a_A}{a_B} \right) - d \ln \left( \frac{X_A}{X_B} \right) \right] \rightarrow d \ln \left( \frac{X_A}{X_B} \right)$

$\therefore d \ln X_B = -X_A d \left[ \ln \left( \frac{a_A}{a_B} \right) - \ln \left( \frac{X_A}{X_B} \right) \right]$

$\therefore \log X_B \Big|_{X_B} - \log X_B \Big|_{X_B=1} = - \int_{X_B=1}^{X_B=X_B} X_A d \left[ \log \left( \frac{a_A}{a_B} \right) - \log \left( \frac{X_A}{X_B} \right) \right]$

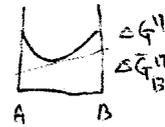
Area =  $-\log X_{Fe}$  at  $X_{Fe} = 0$ .



$\Delta G^M$

\* Direct Calculation of the Integral f. E. of the sol'n. ← (from activity me)

(11.33b)  $\Delta \bar{G}_A^M = \Delta G^M + X_B \frac{d\Delta G^M}{dX_A}$



Rearranging & dividing by  $X_B^2$  results in.

$\frac{\Delta \bar{G}_A^M dX_A}{X_B^2} = \frac{\Delta G^M dX_A + X_B d\Delta G^M}{X_B^2} = \frac{X_B d\Delta G^M - \Delta G^M dX_B}{X_B^2} = d\left(\frac{\Delta G^M}{X_B}\right)$

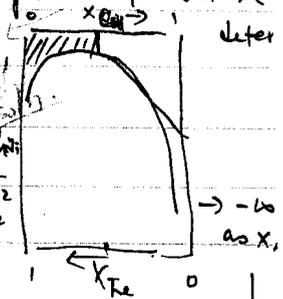
ie  $d\left(\frac{\Delta G^M}{X_B}\right) = \frac{\Delta \bar{G}_A^M dX_A}{X_B^2}$

Integrate bet'n  $X_A = X_A$   $X_A = 0$ .

(11.66)  $\int_{X_A=0}^{X_A} d\left(\frac{\Delta G^M}{X_B}\right) = \frac{\Delta G^M}{X_B} = \int_0^{X_A} \frac{\Delta \bar{G}_A^M}{X_B^2} dX_A \rightarrow \Delta G^M = X_B \int_0^{X_A} \frac{RT \ln a_A}{X_B} dX_A$

∴ if we have inf. about the variation of  $a_A$  w.r.t. Comp.  $\Delta G^M$  will be deter

$\Delta G^M$  (in Ni-Fe) =  $RT X_{Fe} \int_0^{X_{Ni}} \frac{\ln a_{Ni}}{X_{Fe}^2} dX_{Ni}$   
 $\Delta G^M$  (in Cu-Fe) =  $RT X_{Fe} \int_0^{X_{Cu}} \frac{\ln a_{Cu}}{X_{Fe}^2} dX_{Cu}$



w/ Raoultian sol'n :  $a_i = X_i$ .

$\Delta G^M = RT (1-X_i) \int_0^{X_i} \frac{\ln X_i}{(1-X_i)^2} dX_i$

=  $RT (1-X_i) \left[ \frac{X_i \ln X_i}{1-X_i} + \ln(1-X_i) \right]_{X_i}$

=  $RT [X_i \ln X_i + (1-X_i) \ln(1-X_i)]$

Similarity  $\Delta H^M = X_B \int_0^{X_A} \frac{\Delta \bar{H}_A^M}{X_B^2} dX_A$

$\Delta S^M = X_B \int_0^{X_A} \frac{\Delta \bar{S}_A^M}{X_B^2} dX_A$

### 9.9. Regular Sol'n.

1. ideal or Raoultian sol'n  $\rightarrow a_i = X_i, \Delta \bar{H}_i^M = 0, \Delta \bar{V}_i^M = 0.$   
 $\Delta \bar{S}_i^M = -R \ln X_i.$

2. Nonideal  $a_i \neq X_i, \Delta \bar{H}_i^M \neq 0.$

hypothetical nonideal sol'n.  $\rightarrow$  Regular sol'n Behavior.

- Margules suggested that  $\gamma$  (act. coeff.), at a temp, be represented by a power series of the form.

$$(9.66) \quad \ln \gamma_A = \alpha_1 X_B + \frac{1}{2} \alpha_2 X_B^2 + \frac{1}{3} \alpha_3 X_B^3 + \dots$$
$$\ln \gamma_B = \beta_1 X_A + \frac{1}{2} \beta_2 X_A^2 + \dots$$

by G-D.  $X_A d \ln \gamma_A = -X_B d \ln \gamma_B$  (binary sys) (11.52)

$$X_A (-\alpha_1 + \alpha_2 X_B + \alpha_3 X_B^2 + \dots) = -X_B (-\beta_1 + \beta_2 X_B + \beta_3 X_B^2 + \dots)$$

if these eq are to hold over the entire comp. range.  
then  $\alpha_1 = \beta_1 = 0.$  (Margules showed).

if the  $\gamma$  can be represented by the quadratic terms only.  
then  $\alpha_2 = \beta_2.$

- Hildebrand. in binary A-B

Quadratic form of Margules  $\gamma$

called it  $\left\{ \begin{array}{l} RT \ln \gamma_B = \alpha' X_A^2 \\ RT \ln \gamma_A = \alpha' X_B^2 \end{array} \right.$  (9.68)

Regular sol'n to obey these eq

$\sum_{i=1}^n x_i = 1$   
 $x_A, x_B \neq 0$   
 $\alpha = f(x_A, x_B)$   
 $\alpha = \text{function}$

Gas cell \* R.S. et  $\alpha$  fn of  $x_A$ .  
 p. 344 (6.1)  $\ln \gamma_A = -x_B x_A \alpha_B - \int_{x_A=1}^{x_A} \alpha_B dx_A$

$\alpha_A = \frac{\ln \gamma_A}{(1-x_A)^2}$   
 (주어진 조건에)

if the value of  $\alpha$  for "one" component ( $\alpha_B$ ) is indep. of  $x$   
 then  $\alpha_A = \alpha_B = \alpha$

then  $\ln \gamma_A = -x_A x_B \alpha_B - \alpha_B (x_A - 1)$   
 $= -x_A x_B \alpha_B + \alpha_B x_B = \alpha_B x_B (1 - x_A) = \alpha_B x_B^2$

Eg 11.57  $\ln \gamma_A = \alpha_A x_B^2$

$\therefore \alpha_A = \alpha_B = \alpha = \frac{\alpha'}{RT}$

$\alpha$  for regular sol'n. is an inverse fn of  $T$ .  
 (11.72)  $\therefore$  from Eg 11.71  $\alpha = \frac{\alpha'}{RT}$

Hildebrand defined a regular sol'n.  
 $\Delta \bar{H}^n \neq 0$  and  $\Delta \bar{S}_i^n = \Delta \bar{S}_i^{n, id} = -R \ln x_i$

The Prop. of a Regular Sol'n.: can be examined by excess functi:  
 Excess function Eq 11.72

1. the excess value of an extensive thermo. prop. ( $G^{xs}$ ) =  $\Delta \bar{H}^n$  etc.  
 Always true!  $G = G^{id} + G^{xs}$  (1)  
 the molar free E of the sol'n

(9.74)  $\Delta G^n = \Delta G^{n, id} + G^{xs}$   
 As for any sol'n  $\Delta H^{n, id} = 0$   
 $\Delta G^n = \Delta H^n - T \Delta S^n$  &  $\Delta G^{n, id} = -T \Delta S^{n, id}$

(9.74)  $G^{xs} = \Delta G^n - \Delta G^{n, id} = \Delta H^n - T(\Delta S^n - \Delta S^{n, id})$   
 for a regular sol'n.  $\rightarrow \Delta S^n = \Delta S^{n, id}$   
 (11.76)  $G^{xs} = \Delta H^n$  // regular sol'n

(2)  $RT \ln \gamma_B = \alpha' x_A^2$   $\Delta \bar{H}_i^n = f(x_A)$  effect of mixing process does not  
 effect a noticeable effect

$$\alpha' = \Omega$$

Regular sol'n

(13)

2.  $G^{XS} \neq f(T) \therefore \Delta H^M \neq f(T)$

(11.77)  $\Delta G^M = RT (X_A \ln a_A + X_B \ln a_B)$   
 $= \underbrace{RT (X_A \ln X_A + X_B \ln X_B)}_{\Delta G^{M, id}} + \underbrace{RT (X_A \ln \gamma_A + X_B \ln \gamma_B)}_{G^{XS}}$

For a regular sol'n.

$$\ln \gamma_A = \alpha X_B^2, \quad \ln \gamma_B = \alpha X_A^2$$

from a function  
 $\alpha_i = \frac{\ln \gamma_i}{(1-x_i)^2}$

regular sol'n = sol'n of 5<sup>th</sup> & 12<sup>th</sup> B.S.

$$G^{XS} = RT (X_A \ln \gamma_A + X_B \ln \gamma_B) = RT (X_A \cdot \alpha X_B^2 + X_B \cdot \alpha X_A^2)$$

$$= RT \alpha X_A X_B (X_A + X_B) = 1$$

(11.78)  $G^{XS} = RT \alpha X_A X_B = \alpha' X_A X_B$

(11.79)  $G^{XS} = \alpha' X_A X_B \neq f(T)$  indep. of temp.  
 $\therefore \alpha' = \frac{\alpha'}{RT} \neq f(\text{temp})$  for a regular sol'n.

(11.80)  $\left(\frac{\partial G^{XS}}{\partial T}\right)_{p, \text{com}} = -S^{XS} = -(\Delta S^M - \Delta S^{M, id}) = 0$

### 3. Applicability.

(1) T/X relationship.

$$G^{XS} = X_A \bar{G}_A^{XS} + X_B \bar{G}_B^{XS} = RT \alpha X_A X_B (X_A + X_B)$$

$$= RT \alpha X_B^2 \cdot X_A + RT \alpha X_A^2 \cdot X_B$$

$$\therefore \bar{G}_A^{XS} = \alpha' X_B^2 = RT_1 \ln \gamma_A(T_1) = RT_2 \ln \gamma_A(T_2)$$

(11.80)  $\therefore$  for a regular sol'n.  $\frac{\ln \gamma_A(T_2)}{\ln \gamma_A(T_1)} = \frac{T_1}{T_2}$  Practical Importance

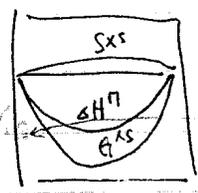
in converting activity at  $T_1$  to activity at  $T_2$ .

Ex 11.27-11.29 Eqs 11-5a the slope of  $\log \gamma_{Ti}$  vs.  $X_{i,sn}^2 = -\alpha$

Pr. ...

When  $\Delta H^M = b X_A X_B$ . if  $b \neq b'$ .  $\rightarrow \Delta S^M \neq \Delta S^M, id$   
 $\rightarrow S^{XS} \neq 0$ .

$\Delta G^{XS} = b' X_A X_B$   
 $\Delta G^M = \Delta G^{ideal} + G^{XS}$   
 $= RT X_A \int_0^{X_B} \frac{\ln \gamma_A}{X_A^2} dX_A$



true for any soln.

from (i.66)  $G^{XS} = RT X_B \int_0^{X_A} \frac{\ln \gamma_A}{X_B^2} dX_A$

started w/  $\Delta G_A^M = \Delta G_A^{id} + X_B$

$\therefore$  for a Raoultian ideal soln, as  $\gamma_A = 1$ ,  $G^{XS} = 0$ .  
 for a Regular soln  $\ln \gamma_A = \alpha X_B^2$ ,  $G^{XS} = RT \alpha X_A X_B$ .  
 Benbich p.32

Statistical model

a liquid solution approximated by quasi-crystalline lattice cause no change lattice vibration

Q.10. The Quasi-Chemical Model of solns.

applied to solns of components which have <sup>1</sup> equal molar vol in pure state and  $\Delta V^M = 0$  <sup>2</sup> interatomic forces are <sup>3</sup> significant over short distance. Random mixing.

Based on this, the E of soln is calculated by summing the atom-atom bond E.

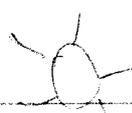
$\Rightarrow$  Consider 1 mole of a crystal  $N_A$  atoms,  $N_B$  atoms.

$X_A = \frac{N_A}{N_A + N_B} = \frac{N_A}{z}$ ,  $X_B = \frac{N_B}{z}$   
 z = coordination #.

- 1. A-A bond  $E_{AA}$   $P_{AA}$
  - 2. B-B bond  $E_{BB}$   $P_{BB}$  if  $E = 0$  when the atoms are infinitely
  - 3. A-B bond  $E_{AB}$   $P_{AB}$   $E_{AA}, E_{BB} \dots < 0$ . Negative quantities
- $z = \text{coordination \#}$ .

$\therefore E = P_{AA} E_{AA} + P_{BB} E_{BB} + P_{AB} E_{AB}$

1) When A & B are mixed



\* The # of A atoms x the # of bonds / atom.  
= the # of A-B bonds + the # of A-A bonds x 2.

(11.82)  $\therefore N_A z = P_{AB} + 2P_{AA} \quad \therefore P_{AA} = \frac{N_A z}{2} - \frac{P_{AB}}{2}$

(11.83) for B.  $N_B z = P_{AB} + 2P_{BB} \quad \therefore P_{BB} = \frac{N_B z}{2} - \frac{P_{AB}}{2}$

(11.84)  $\therefore E = \left(\frac{N_A z}{2} - \frac{P_{AB}}{2}\right) E_{AA} + \left(\frac{N_B z}{2} - \frac{P_{AB}}{2}\right) E_{BB} + P_{AB} E_{AB}$   
 $= \frac{1}{2} N_A z E_{AA} + \frac{1}{2} N_B z E_{BB} + P_{AB} \left[ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right]$

⇒ 2) the E of the unmixed components,  
for  $N_A$  atoms in pure A. (the # of A-A bonds x 2  
= the # of atoms x # of bonds)

$P_{AA} = \frac{1}{2} N_A z$

Similarly  $P_{BB} = \frac{1}{2} N_B z$

3)  $\therefore \Delta E^H = (\text{the energy of sol'n}) - (\text{the E of unmixed components})$   
 $= P_{AB} \left[ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right]$   
 (=  $\Delta U^H$ )

for mixing  $\Delta H^H = \Delta E^H - P \Delta V^H$  (Quasi  $\rightarrow \Delta V^H = 0$ )

(11.85)  $\therefore \Delta H^H = \Delta E^H = P_{AB} \left( E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right)$  # of bonds

for given values of  $E_{AA}$ ,  $E_{BB}$ ,  $E_{AB}$   $\Delta H^H$  depends on  $P_{AB}$   
 (11.86) for ideal sol'n.  $\Delta H^H = 0$ .  $E_{AB} = \frac{E_{AA} + E_{BB}}{2}$

if  $|E_{AB}| > \left| \frac{E_{AA} + E_{BB}}{2} \right|$  then  $\Delta H^H < 0$ . → negative departure from Raoultian ideal

if  $|E_{AB}| < \left| \frac{E_{AA} + E_{BB}}{2} \right|$  then  $\Delta H^H > 0$ . → positive "

$\Delta H^M = \Delta G^M = 0$

$\Delta H^M = \Delta G^M = 0$

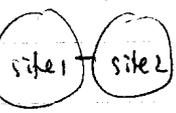
$\Delta H^M = 0 \rightarrow$  no interactions

(1)

if  $\Delta H^M = 0$ , then random mixing  $\Delta S^M = \Delta S^M_{id}$

\* if  $|\Delta H^M| \ll RT$ , the same random of atom  $\approx$  ideal sol'n. \* As

5/24/95



A atom for site 1.  $= \frac{n_A}{a} = x_A$

B " "  $= \frac{n_B}{a} = x_B$

$\sum_{\text{sites}} \left\{ \begin{array}{l} \text{A for site 1} \\ \text{B for site 2} \end{array} \right. = x_A x_B$

$\therefore$  Prob<sup>of</sup> neighbors w/ A-B pair

$\sum_{\text{sites}} \left\{ \begin{array}{l} \text{B for site 1} \\ \text{A for site 2} \end{array} \right. = x_A x_B$

$\Rightarrow 2x_A x_B$

Similarly A-A pairs  $x_A^2 \leftarrow \sum_{\text{sites}}$   
 B-B "  $x_B^2 \leftarrow \text{"}$

$\Delta H^M = \frac{1}{2} z a x_A x_B + \frac{1}{2} z a x_A^2 + \frac{1}{2} z a x_B^2 - \frac{1}{2} z a$

Regular sol'n

$\therefore x_A x_B$  the # of A-B pairs = the # of pairs of sites  $\times$  Probability of  
 (11.87)  $\hookrightarrow P_{AB} = \frac{1}{2} z a \times 2 x_A x_B = z a x_A x_B$

Similarly  $P_{AA} = \frac{1}{2} z a \times x_A^2 = \frac{1}{2} z a x_A^2$   
 $P_{BB} = \frac{1}{2} z a \times x_B^2 = \frac{1}{2} z a x_B^2$

$\alpha' = \alpha RT$

(11.87)  $\Delta H^M = z a x_A x_B [E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})] = \Omega x_A x_B$

(11.85)  
(11.88)

$\Delta H^M$  is "a parabolic" fn of composition.  
 As random mixing is assumed Q-C model  $\Rightarrow$  Regular sol'n.

(11.89)

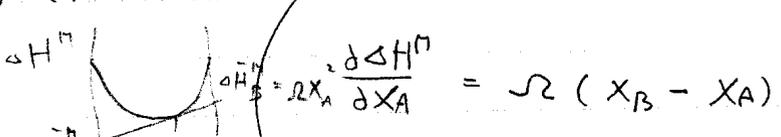
(11.90)

$\Delta H^M = Q x_A x_B = \Omega x_A x_B = RT \alpha x_A x_B \quad \& \quad \frac{\Omega}{RT} \rightarrow \alpha$

(or regular soln)

\*  $\Omega$ 의 값을 찾기

i) (11.33a) i)  $\Delta \bar{H}_A^M = \Delta H^M + X_B \frac{d\Delta H^M}{dX_A}$ ,  $\Delta H^M = \Omega X_A X_B$ .



(11.91a)  $\Delta \bar{H}_A^M = \Omega X_A X_B + X_B \Omega (X_B - X_A) = \Omega X_B^2$  from the intercept.

(11.91b) Similarly  $\Delta \bar{H}_B^M = \Omega X_A^2$

As the mixing is random.  $\Delta \bar{S}_A^M = -R \ln X_A$ ,  $\Delta \bar{S}_B^M = -R \ln X_B$

(11.92)  $\Delta \bar{G}_A^M = \Delta \bar{H}_A^M - T \Delta \bar{S}_A^M = \Omega X_B^2 + RT \ln X_A$

(11.93)  $= RT \ln a_A = RT \ln \gamma_A + RT \ln X_A$

(11.94)  $\therefore RT \ln \gamma_A = \Omega X_B^2$   $\ln \gamma_A = \frac{\Omega}{RT} X_B^2 = \alpha X_B^2$

$\therefore \gamma = f(\Omega) = f(\epsilon_{AA}, \epsilon_{BB}, \epsilon_{AB})$

if  $\Omega < 0$ ,  $\gamma_A < 1$  ex:  $\epsilon_{AB} > \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$

if  $\Omega > 0$ ,  $\gamma_A > 1$  endo

ii) Henry's law.  $\gamma_A \rightarrow k$  as  $X_B \rightarrow 1$ .  $\therefore \ln \gamma_A \rightarrow \ln \gamma_A^0 = \frac{\Omega}{RT} (= \frac{\alpha}{RT})$

$\therefore$  via the relations bet'n Henry's & Raoult's law, Raoult's law is approx by the component  $i$  as  $X_i \rightarrow 1$ .

조건: \* Applicability of the Q-C model as  $\Omega \ll 1$ . (i.e.  $|\epsilon_{AB}| \gg \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$ )  
 $\alpha = \Omega = 2R[\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})]$  the magnitude of  $\alpha$   
assumption (random mixing) is true

$$T = 0 - T_0$$

$$\Delta H^M = \Delta E^M - P \Delta V^M \approx 0 \text{ for } \alpha \rightarrow 0$$

$$\rightarrow P_{AB} [E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})]$$

(18)

I. if  $|E_{AB}| > \frac{1}{2}(E_{AA} + E_{BB})$ , then min. of  $H$  corresponds to max.  $\#$  of A-B pairs (complete ordering of  $s$ )  
 $\rightarrow$  max. of  $s \rightarrow$  complete random mix  
 $P_{AB} [E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})]$   
 $\Omega \geq a [E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})]$

\* Minimization of  $G$  occurs as a compromise bet'n maximization of  $P_{AB}$  (w/ increasingly neg. values of  $\Omega$ ) and random mixing (w/  $T$ )  
 $\therefore$  The critical parameter is thus  $\Omega$  &  $T$  for non-ideal  $\rightarrow$  RT (value)  
 (if  $\Omega$  is appreciably negative and  $T$  is not too high  
 then  $P_{AB}(\text{actual}) > P_{AB}(\text{random}) \rightarrow$  the assumption of random invalid.  
 (# of bond A-B)

II. if  $|E_{AB}| < \frac{1}{2}(E_{AA} + E_{BB})$ , then min of  $H$  corresponds to min.  $\#$  of A-B pairs. (clustering)  
 $\rightarrow$  max. of  $s \rightarrow$  complete random mixing

\* The min. of  $G$  occurs as a compromise bet'n min. of  $P_{AB}$ . (w/ increasingly pos. values of  $\Omega$ ) and random mixing (w/  $T \uparrow$ )  
 $\therefore$  if  $\Omega$  is appreciably pos. and  $T$  is not too high,  
 $P_{AB}(\text{actual}) < P_{AB}(\text{random}) \rightarrow$  assumption of random mixing invalid  
 (# of A-B bond)

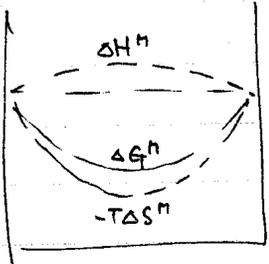
III. In order for Q-C model to be applicable, the compromise should not be far from "random mixing"

- As the  $S$  is a fn of temp., (1) for any value of  $\Omega$ , nearly random mixing occurs as  $T \uparrow$ . (2) for any  $T$ , nearly random mixing occurs w/ smaller value of  $\Omega$ .  $|E_{AB}| \rightarrow \frac{1}{2}(E_{AA} + E_{BB}) = 0$

Date

9. Subregular Soln

In the regular soln model  $\alpha = \frac{\alpha'}{RT}$  (inverse fun of T.  $\neq$  (comp).  
 $\Delta H^m = \alpha X_A X_B$  (parabolic variation).  
 $\alpha = \text{const.} + f(T)$



↳ const.  
 i) to accommodate  $\alpha' = f(\text{comp.})$   
 Subregular solution model.

$$\Omega = a + b X_B + c X_B^2 + d X_B^3 + \dots$$

no physical meaning  
 from curve fitting

$$(\Delta H^m =) \therefore G^{XS} = (a + b X_B) X_A X_B$$

11.27a  $\bar{G}_A = G + X_B \frac{dG}{dX_A}$

Similarly  $\bar{G}_A^{XS} = G^{XS} + X_B \frac{dG^{XS}}{dX_A}$

$$\begin{aligned} \Delta \bar{H}_A^m = \bar{G}_A^{XS} &= (a + b X_B) X_A X_B + X_B \left[ (a + b X_B) X_B + (-a - 2b X_B) \right] \\ &= a X_B^2 + b X_B^2 (X_B - X_A) \end{aligned}$$

$$\bar{G}_B^{XS} = a X_A^2 + 2b X_A^2 X_B$$

Fig 9.26. (New Edition) : the variation of  $G^{XS}$  w/  $X_B$ .

max. min. of the curves can be found at  $\frac{dG^{XS}}{dX_B} = 0$ .

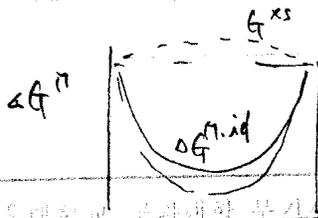
$$G^{XS} = (a + b X_B) X_A X_B = a X_B + (b-a) X_B^2 - b X_B^3$$

$$\therefore \frac{dG^{XS}}{dX_B} = a + 2(b-a) X_B - 3b X_B^2 = 0$$

$$X_B = \frac{2(b-a) \pm \sqrt{(b-a)^2 - 3b^2}}{6b}$$

例:  $A_p - A_n$

at 1350



$$AX^2 + 2Bx + C = 0$$

$$x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

ii) To accommodate the influence of temp.

previously  $Q^{xs} = (a + b x_B) X_A X_B \neq f(T)$  ↗ as T ↑, solution be-  
ide

$$Q^{xs} = (a_0 + b_0 x_B) X_A X_B \left(1 - \frac{T}{T_c}\right) \quad \text{if } \frac{T_c}{T} \gg 1$$

then  $S^{xs} = - \left( \frac{\partial Q^{xs}}{\partial T} \right) = \frac{(a_0 + b_0 x_B) X_A X_B}{T}$

the molar heat of mixing

$$\begin{aligned} H^{xs} = \Delta H^M &= Q^{xs} + TS^{xs} = (a_0 + b_0 x_B) X_A X_B \left(1 - \frac{T}{T_c}\right) + (a_0 + b_0 x_B) X_A X_B \frac{T}{T_c} \\ &= (a_0 + b_0 x_B) X_A X_B \left(1 - \frac{T}{T_c}\right) + (a_0 + b_0 x_B) X_A X_B \frac{T}{T_c} \\ &= [(a_0 + b_0 x_B) X_A X_B] \left[1 - \frac{T}{T_c} + \frac{T}{T_c}\right] \\ &= [(a_0 + b_0 x_B) X_A X_B] \end{aligned}$$

other thought

$$\begin{aligned} Q^{xs} &= a \exp\left(-\frac{b}{RT}\right) \\ &= a \left(1 - \frac{b'}{T}\right) \end{aligned}$$

$$Q^{xs} = a \exp\left(-\frac{T}{T_c}\right) \Rightarrow a \left(1 - \frac{T}{T_c}\right) \quad \text{if } \exp\left(-\frac{T}{T_c}\right) \ll 1$$

$$S^{xs} = + \frac{1}{T} a \exp\left(-\frac{T}{T_c}\right)$$

$$\Delta H^M = a \exp\left(-\frac{T}{T_c}\right) \left[1 - \frac{T}{T_c}\right]$$