

the result of the establishment of a bal.  
between the tendency of the ext. influence (T.P.)

"S-G" Concentrated  
"L-G" not discussed.

①

Date . . .

acting on the sys. to cause a change in the system  
and the tendency of the sys. to resist the change

## 1. Thermo & Phase Diagram.

comp. fixed,  
p.v. work. ~~not simple sys.~~

1. ~~單純~~  
2nd law

### 1.1. Equil<sup>m</sup>.

$$(1.1) \quad G = H - TS \quad A = U - TS$$

$$(1.2) \quad H = U + PV$$

$$(1.3) \quad dG = 0 \text{ at equil}^m \text{ (T,P const)} \quad dA = 0 \text{ at equil}^e \text{ (T,V const)}$$

$$(1.4) \quad \Delta G = G_2 - G_1 < 0 \text{ for any phase transf.}$$

- How fast does a phase transf. occur? not answered by Ther.
- intensive prop. indep. of the size of the sys. T.P.
- extensive  $\Rightarrow \propto$  to the quantity. V.U.H.S.G.

(2)

### 1.2. Single Component Sys.

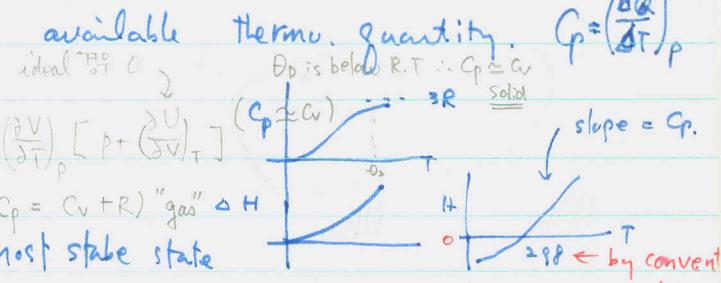
1. Gibbs F.E. as a fn of Temp. at Fixed pressure (1 atm) :  $G(T)$

i)  $C_p$ : easily measured and available thermo. quantity.  $C_p = \left(\frac{\partial G}{\partial T}\right)_P$

$$(1.5) \quad C_p = \left(\frac{\partial H}{\partial T}\right)_P \quad C_p - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

$\downarrow$  cf.  $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_V > (C_p = C_V + R)$  "gas"  $\Delta H$

$H = 0$ . for a pure element in most stable state



$$(1.6) \quad H_T = H_{298} + \int_{298}^T C_p dT \quad (\text{Eq. 1.2b})$$

Fig. 1.2

ii) The variation of entropy.  $dS = \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{C_p dT}{T}$

$$(1.7) \quad \therefore \frac{S_T}{T} = \left(\frac{\partial S}{\partial T}\right)_P$$

$$(1.8) \quad \therefore S_T = S_0 + \int_0^T \frac{C_p}{T} dT \quad (\text{Eq. 1.2c})$$

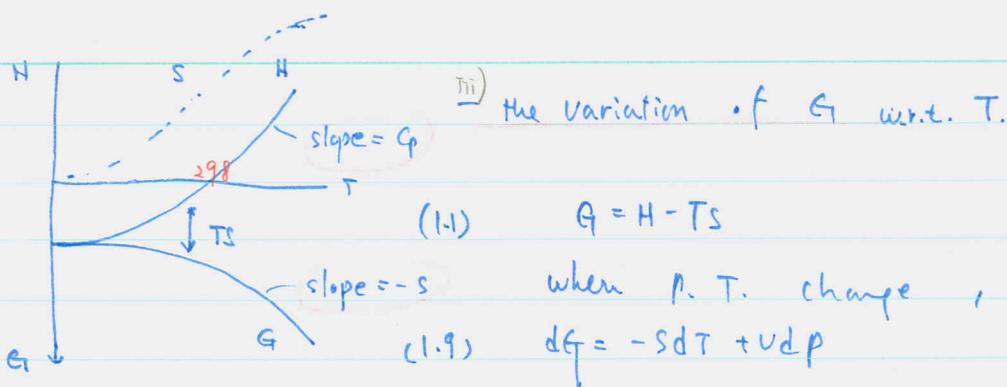
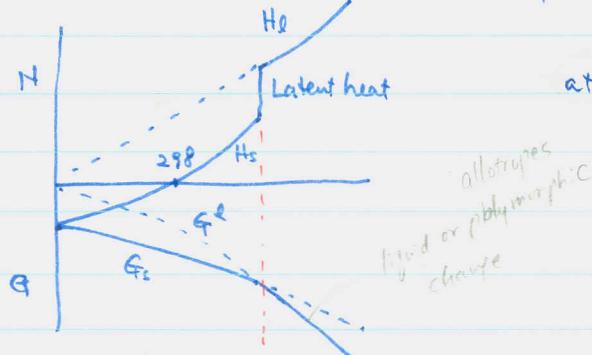


Fig 1.3

At const pressure  $dP = 0$ 

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \left(-\int_0^T \frac{C_p dT}{T}\right)$$

at low temp  $G^e < G^L$ . $G^S$  low slope ( $-S$ ) $G^L$  high slope ( $-C_p$ ).  $\Rightarrow G^L \downarrow$  as  $T \uparrow$ 

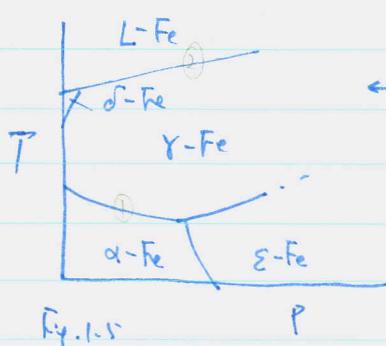
full equilibrium

Fig 1.4. solid stable : liquid stable

## 2. Pressure Effects on Gibbs Free Energy : G(P)

The equil<sup>m</sup> temp in 1.1 section at 1 atm.

→ changes as P varies.

← Effect of P on the equil<sup>m</sup> Temp. of pure Fe  
As P↑, T<sub>0f</sub> & T<sub>f0</sub> depressed.T<sub>0f</sub> of melting raised.At P↑  $\epsilon$ -Fe stable at R.T. (low)

$$\left(\frac{\partial \Delta G_{\text{trans}}}{\partial P}\right)_T = \Delta V_{\text{trans}}$$

$$(1.11) \quad dG = -SdT + VdP \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

- two phases in equil<sup>m</sup> w/ diff. molar Vol. ( $V_m$ )  $\left(\frac{\partial G}{\partial P}\right)_T = V_m V^P$   
will have diff. amount of change in G

∴ equil<sup>m</sup>  $\frac{df}{dp}$  to maintain equil<sup>m</sup> w/ diff. pressure ??

(P.T.V) only by changin temp!!

$\frac{dG}{dp} = \frac{V_m V^P}{T}$

22일) equilibrium 상태의 T, P의 관계식은?

### - Clausius - Clapeyron

two phases in equilibrium ( $\alpha, \beta$ )

$$(1.12) \quad dG^\alpha = V_m^\alpha dp - S^\alpha dT$$

$$- dG^\beta = V_m^\beta dp - S^\beta dT$$

$$(1.13) \quad \text{at equilibrium} \quad G^\alpha = G^\beta \quad dG^\alpha = dG^\beta$$

$$\therefore \left( \frac{dp}{dT} \right)_{eq} = \frac{S^\beta - S^\alpha}{V_m^\beta - V_m^\alpha} = \frac{\Delta S}{\Delta V_m}$$

Clapeyron Eq.  
(solid - liquid)

in a different form  $\frac{dp}{dT} = \frac{\Delta H}{\Delta V_m}$  ( $= \frac{\Delta S}{\Delta V_m}$ )을 정해진다.

$$\nabla \rightarrow G^\beta = H^\beta - TS^\beta \quad G^\alpha = H^\alpha - TS^\alpha$$

$$- dG^\beta = H^\beta - TS^\beta \quad \Delta G = G^\beta - G^\alpha$$

$$\therefore \Delta G = \Delta H - T\Delta S$$

$$\nabla \rightarrow \text{at equilibrium} \quad \Delta G = G^\beta - G^\alpha = 0. \quad \therefore \Delta H - T\Delta S = \Delta G = 0.$$

$$(1.14) \quad \therefore (1.13) \rightarrow \left( \frac{dp}{dT} \right)_{eq} = \frac{\Delta H}{T \Delta V_m}$$

Clapeyron eq.

ii) when applied to solid-gas phases, assuming ideal gas behavior

$$\Delta V_m = V_{\text{vap}} - V_s \approx V_{\text{vap}} = \frac{RT}{P} \quad \therefore \frac{dp}{P} = \frac{dH}{RT^2} dt$$

$$(\Delta H_p = \Delta H + bT + cT^{-2})$$

$\frac{\partial \ln P}{\partial T}$

Integrate

$$d\ln P = \frac{\Delta H}{RT^2} dt$$

Clausius - Clapeyron eq.

(solid-gas)

$$\ln P = \frac{H}{T} + B \ln T + C \quad (\text{boiling pt } P=1.)$$

example. 1.  $\gamma$ -Fe : smaller molar Vol than  $\alpha$ -Fe.

$$\Delta V_m = V_m^\gamma - V_m^\alpha < 0 \quad \gamma: \text{high temp. phase}$$

in reverse.  $\leftarrow \Delta H = H^\gamma - H^\alpha > 0. \leftarrow \text{liquid has a higher entropy than solid}$

if you know the slope  $\therefore \frac{dp}{dT} < 0.$  in Fy 1.5 !!

you can find.  $\Delta V_m (= V_m^\gamma - V_m^\alpha) < 0 \text{ or } > 0$

$$2. \Delta V_m = V_m^\gamma - V_m^\alpha > 0, \Delta H > 0 \quad \therefore \left( \frac{dp}{dT} \right)_{eq}^{40^\circ} > 0.$$

$$3. \gamma/\epsilon \Delta V_m = V_m^\gamma - V_m^\alpha > 0, \Delta H > 0 \quad \therefore \left( \frac{dp}{dT} \right)_{eq}^{40^\circ} > 0.$$

highest density

$$\left(\frac{\partial \Delta G_{\text{ext}}}{\partial p}\right)_T = \Delta V_{\text{molar}} < 0 \therefore \text{as } p \uparrow \Delta G \downarrow$$

As  $P \uparrow$ , the area of a phase w/ the smallest molar vol. like  $\gamma\text{-Fe} \uparrow$   
i.e., become stabilized.

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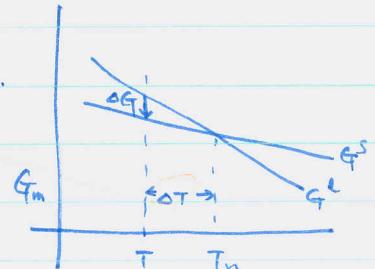
### 3. The Driving Force for the solidification. ( $= \Delta G_{\text{trs}}$ or $\Delta G_{\text{solidifn}}$ ) (= transformation)

- Phase transf. deals w/  $\Delta G$  of two phases of interest at temp. away from  $T_m$ .

By: liquid metal undercooled by  $\Delta T$  below  $T_m$ .  
solidification accompanied by  $\Delta G \downarrow$

$$\text{At } T. \quad G^L = H^L - TS^L$$

$$(1.15) \quad G^S = H^S - TS^S \quad \Delta G = \Delta H - T\Delta S$$



$$\text{At equil } T_m \quad G^L = G^S \quad \therefore \Delta G = 0. \quad \therefore \Delta H = T_m \Delta S$$

$$(1.16) \quad \Delta S = \frac{\Delta H}{T_m} = -\frac{L}{T_m} (\approx R) \quad \boxed{\text{the entropy of fusion.} \approx R}$$

Richard's Rule → experimentally.  
for most metals

∴ metals w/ high bond strength → tend to have  
high  $T_m \& L!!$

(near equil  $\overset{m}{\sim}$  temp or  $T_m$ )

- For small undercooling ( $\Delta T$ )  $\Delta G_p (= G^L - G^S) \xrightarrow{\text{no count}} \therefore \Delta G_p dT = 0$   
 $\therefore \Delta H, \Delta S \not\propto f(T)$

$$(1.15) + (1.16) \quad \Delta G \approx \Delta H - T \frac{\Delta H}{T_m} = L - T \frac{L}{T_m}$$

(1.17)

$$\therefore \Delta G \approx \frac{L \Delta T}{T_m} = R \Delta T \quad \boxed{\text{useful!!}}$$

A, B have the same Xtal Struc.

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### 1.3. Binary Solutions. (no hetero sys. - different Xtal Struc)

In single component sys. = the same comp., P & T. as variables  
in alloys (binary, ternary) - comp., P, T. ← all variables.  
phase transf. of interest occurs at a fixed P (= 1 atm).

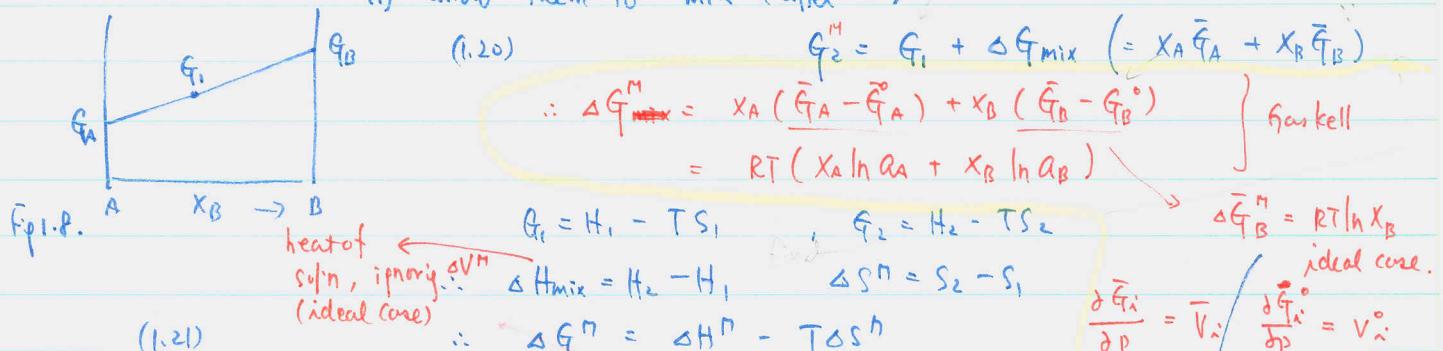
#### 1.3a. The Gibbs F.E. of Binary Solns

- Calculation of G.F.E. of soln when A, B have the same Xtal Struc.  
make a solid soln of the same struc.

$$(1.18) \quad X_A + X_B = 1$$

(1.19) - Steps i) bring together. (before mixing)  $G_1 = X_A G_A + X_B G_B (= X_A G_A^\circ + X_B G_B^\circ)$

ii) allow them to mix (after  $\rightarrow$ )



#### 2. Ideal Solns

-  $\Delta H_{\text{mix}}^M (\Delta H^M) = 0$  ideal (no interaction)

$\therefore$  Gibbs-Helmholtz eq.

$$\left. \frac{\partial (\frac{\bar{G}_i - \bar{G}_i^\circ}{T})}{\partial T} \right|_{p, \text{comp}} = 0$$

$$\Delta \bar{G}_i^M = RT \ln \alpha_A$$

$$\therefore \frac{\partial \bar{G}_i^M}{T} \neq f(T)$$

$$\Delta H^M = X_A \Delta \bar{H}_A^M + X_B \Delta \bar{H}_B^M = 0.$$

$$G = H - TS \quad \left( \frac{\partial G}{\partial T} \right)_P = -S \quad \left( \frac{\partial G}{\partial P} = -S \frac{\partial T}{\partial P} + V \right) \quad G = H + T \left( \frac{\partial G}{\partial T} \right)_P \quad \text{at const } P \rightarrow GdT = HdT - TdS$$

$$\text{If } T \text{ multiply.} \quad - \left( \frac{GdT - TdG}{T^2} \right) = - \frac{HdT}{T^2} \Rightarrow \left( \frac{d(\frac{G}{T})}{dT} \right)_P = - \frac{H}{T^2}$$

$$(1.22) \quad \Delta G^M = -T\Delta S^M$$

$S$  related to randomness. statistical theory

most often observed  
high probability

$$(1.23) \quad \text{Boltzman eq} \quad S = k \ln w \quad (w = \Omega)$$

$$S = S_{\text{th}} + S_{\text{conf.}}$$

If no vol. change or heat change during mixing

then  $\Delta S^M$  is only due to  $\Delta S_{\text{conf.}}$

$$S_1 = k \ln 1 = 0 \quad S_2 = k \ln w_{\text{conf.}}$$

$$(1.24) \quad \frac{\text{the # of distinguishable ways of arranging atoms}}{w_{\text{conf}}} = \frac{(N_A + N_B)!}{N_A! N_B!} \quad \text{Avogadro's #.}$$

$$N_A = X_A N_a, \quad N_B = X_B N_b.$$

Stirling approx.  $\ln N! \approx N \ln N - N \quad \& \quad N_a k = R$ .

$$(1.25) \quad \text{gives} \quad \Delta S^M = -R(X_A \ln X_A + X_B \ln X_B) > 0.$$

$$(1.26) \quad \therefore (1.22) \quad \Delta G^M = RT(X_A \ln X_A + X_B \ln X_B)$$

$$(1.27) \quad \therefore G^M = G_2 \left( \frac{\Delta G^M + G_1}{\Delta G^M + G_1} \right) = X_A G_A^\circ + X_B G_B^\circ + RT(X_A \ln X_A + X_B \ln X_B)$$

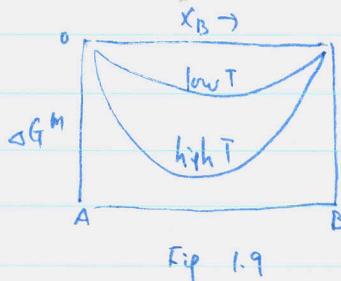


Fig. 1.9

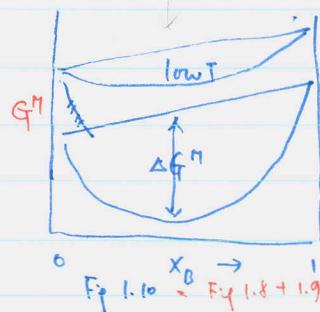


Fig. 1.10

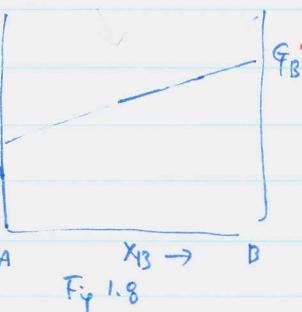


Fig. 1.8

# Q/

### 3. Chemical Potential.

Partial Molal quantity  $\bar{Q}_i = \left( \frac{\partial Q_i'}{\partial n_i} \right)_{T, P, n_j, \dots, n_i}$   $\mu_i$  chemical pot.

$$(1.28) \quad \therefore dG' = \mu_A dN_A \quad (\text{T.P. } n_B \text{ const.})$$

$G'$ : whole system.  $G$ : molar F.E.  $\therefore$  indep. of size

$$(1.29) \quad \mu_A = \left( \frac{\partial G'}{\partial n_A} \right)_{T, P, n_B} (= \bar{G}_A)$$

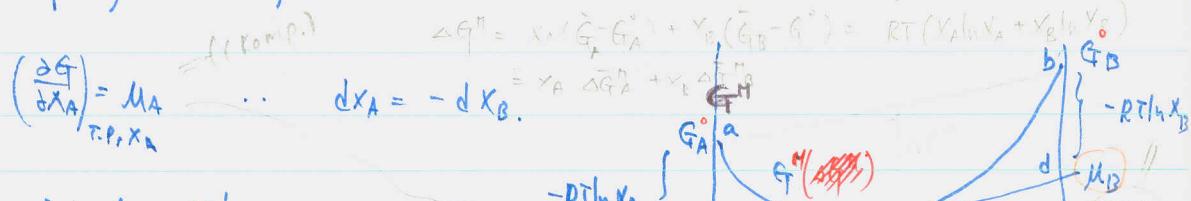
$$(1.30) \quad \text{For a binary sol'n at T.P. const. } dG' = \mu_A dn_A + \mu_B dn_B.$$

$\Leftrightarrow$  If T.P. changing  $dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \dots$   
 & multi-component sys.

For molar quantity, the expression will change

(1.30)  $\rightarrow$

$$(1.31) \quad \overset{\text{H}}{G} = \mu_A X_A + \mu_B X_B \quad (= \bar{G}_A X_A + \bar{G}_B X_B) \quad [J/mol] \quad (1.26)$$



for ideal sol'n.

$$(1.32) \quad \mu_A = G_A^° + RT \ln X_A \quad (\rightarrow \bar{G}_A = G_A^° + RT \ln X_A)$$

$$\mu_B = G_B^° + RT \ln X_B$$

$$\therefore \bar{G}_A - G_A^° = \Delta \bar{G}_A^m \quad \Delta G^m = X_A \Delta \bar{G}_A^m + X_B \Delta \bar{G}_B^m \quad \text{ideal}$$

Fig. 1.12

#### 4. Regular Soln (Quasi-Chemical Model.)

$$= -T \Delta S^m$$

$$= RT (X_A \ln X_A + X_B \ln X_B)$$

$$= X_A \left\{ RT \ln X_A \right\} + X_B \left\{ RT \ln X_B \right\}$$

ideal soln  $\Delta H^m = 0$

real soln  $\Delta H^m > 0$  or  $\Delta H^m < 0$  (endo)  $\Delta \bar{G}_A^m$   $\Delta \bar{G}_B^m$

assumed that

Quasi-chemical approach.  $\Delta H^m$  is only due to the bond  $E$ .

$\rightarrow$  automatically assume  $\Delta H^m \approx 0$  (vol. of A.B equal)

interatomic bond  $E$ , distance maintained the same. (indep. of comp.)

1. A-A  $E_{AA}$ , 2. B-B  $E_{BB}$  3. A-B  $E_{AB}$

↓ # of pair

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

i) when A & B are mixed

the # of A atoms  $\times$  # of bonds / atom

= the # of A-B bond  $\rightarrow$  the # of A-A bonds  $\times 2$ .

$$\therefore n_A Z = \overset{\text{Avg. # of bonds}}{P_{AB}} + 2P_{AA}$$

$$n_B Z = P_{AB} + \overset{\text{mixed}}{2P_{BB}}$$

$$\therefore P_{AA} = \frac{n_A Z}{2} - \frac{P_{AB}}{2}$$

$$P_{BB} = \frac{n_B Z}{2} - \frac{P_{AB}}{2}$$

$$\frac{n_A Z}{2}$$

$$E_{AB}$$

$$\therefore \Delta E = \left( \frac{n_A Z}{2} - \frac{P_{AB}}{2} \right) E_{AA} + \left( \frac{n_B Z}{2} - \frac{P_{AB}}{2} \right) E_{BB} + P_{AB} E_{AB} - (P_{AA} E_{AA} + P_{BB} E_{BB})$$

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

unmixed

$$\text{for mixing } \Delta H^\eta = \Delta E^\eta + P \Delta V^\eta \quad (V^\eta \rightarrow 0)$$

$$\Delta H^\eta = \Delta E^\eta$$

(1.33).

$$\therefore \Delta H^\eta = P_{AB} \Sigma$$

(1.34)

$$\text{where } \Sigma = \Sigma_{AB} - \frac{1}{2} (\Sigma_{AA} + \Sigma_{BB})$$

If  $\Sigma = 0$  ( $\Sigma_{AB} = \frac{1}{2} (\Sigma_{AA} + \Sigma_{BB})$ )  $\Delta H^\eta = 0$ . (Completely randomly arranged)

(1.45) and entropy of mixg  $\Delta S^\eta = -R(X_A \ln X_A + X_B \ln X_B)$

Margules  $\rightarrow \ln X_A = \alpha X_B + \frac{1}{2} \alpha^2 X_B^2 + \dots$  (A term)  $\rightarrow R \ln(X_A) = \alpha X_B^2$  Regular soln 2nd eq.

If Regular soln  $\Delta H^\eta \leq RT$ , the same random distribution of atom = ideal soln.

Then  $P_{AB}$  can be calculated to relate regular and Q-c.

Neighboring sites



$$P: A \text{ atom for site 1} = \frac{n_A}{N_A - \text{avogadro} \#} = X_A$$

$$: B \quad " \quad = X_B$$

$$P: A \text{ for 1, B for 2} = X_A X_B$$

$$B \text{ for 1, A for 2} = X_A X_B$$

$\therefore P \text{ of neighboring w/ A-B pair} = 2X_A X_B$

P: A for 1 site, A for 2 site  $= X_A^2$

B " " B "  $= X_B^2$ .

All together  $\frac{1}{2} Z N_A$  pairs of bonds

$$(1.35) \quad \therefore P_{AB} = 2 X_A X_B \cdot \frac{1}{2} Z N_A = N_A Z X_A X_B. \quad P_{AA} = \frac{1}{2} Z N_A X_A^2 \\ P_{BB} = \frac{1}{2} Z N_B X_B^2$$

$$(1.35) \quad P_{AB} = N_A Z X_A X_B.$$

If  $\varepsilon < 0$ , A-B preferred. and  $P_{AB} \uparrow$

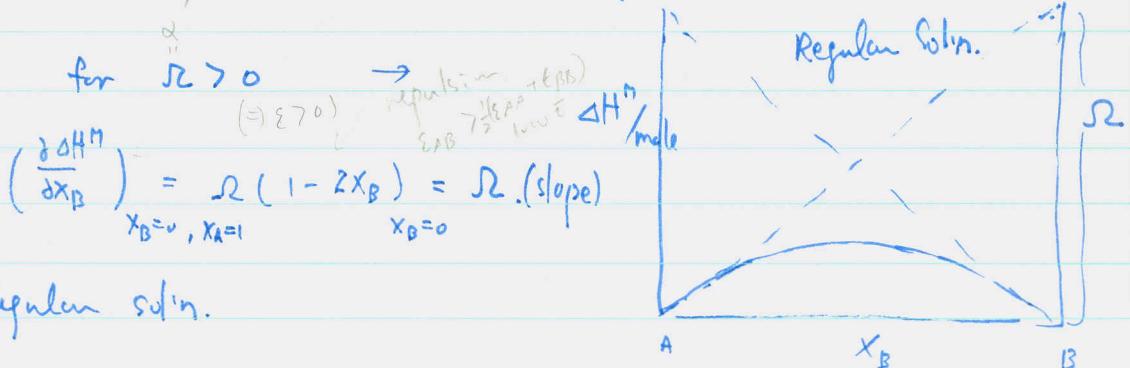
$\varepsilon > 0$  AA, BB preferred  $P_{AB}$  less than in a random soln.

If  $\varepsilon$  is close to zero. (1.35) holds !!.

(1.36)

$$(1.36) \quad \text{Then } \Delta H^\infty = N_A Z \sum X_A X_B = \Sigma X_A X_B \quad (\Sigma = N_A Z \Sigma) \\ \neq f(T) \quad \Sigma = \Sigma (X_B - X_B^2)$$

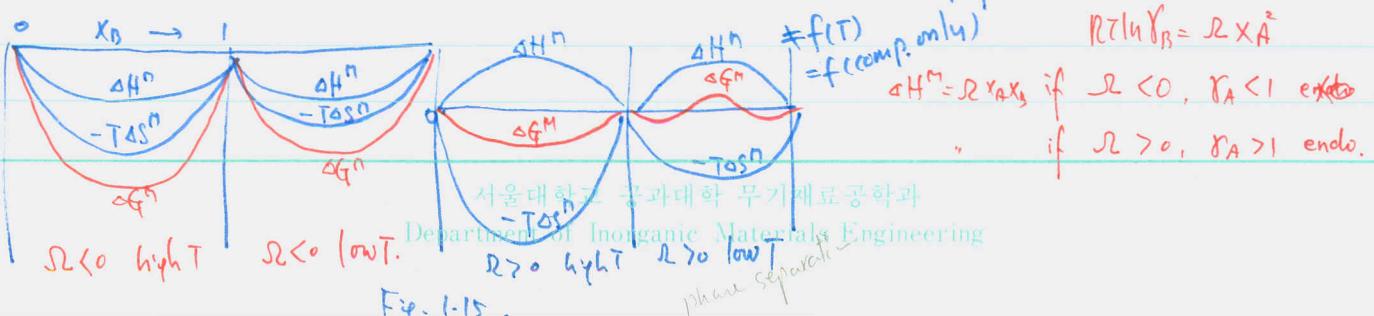
If real solns follow (1.36), they are called as "Regular soln"



For a Regular soln.

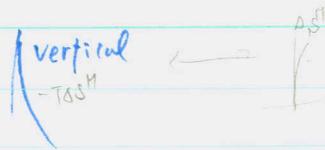
Fig 1.14.

$$(1.38) \quad \Delta G_m^{\infty} = \Delta H_m^{\infty} - T \Delta S_m^{\infty} = \Sigma X_A X_B + RT (X_A \ln X_A + X_B \ln X_B) \quad \text{regular.} \quad RT \ln Y_A = \Sigma X_B^2$$



- Slope in the  $\Delta G^\circ$  vs. comp. diagram.

$$\Delta S^\circ = -R(X_A \ln X_A + X_B \ln X_B)$$



$$\left(\frac{\partial \Delta S^\circ}{\partial X_A}\right)_{X_B=0} = -R(\ln X_A + 1 - \ln(1-X_A) - \frac{(1-X_A)}{1-X_A}) = -R \ln \frac{X_A}{1-X_A} \Big|_{X_A=0} = \Delta$$

$\therefore -T\Delta S^\circ = -\infty$  slope.  $\Rightarrow$  this implies  $\Delta G^\circ \downarrow$  w/ a small solute addition.

- total free E. of an alloy. (Regular soln.)

$$(1.39) \quad G^\circ = G_A^\circ + G_B^\circ + RT(X_A \ln X_A + X_B \ln X_B) \quad \text{for Regular soln.}$$

$G_A^\circ + G_B^\circ$  ← original.       $\Delta G^\circ$

$$= X_A [G_A^\circ + RT(1-X_A)^2 + RT \ln X_A] + X_B [G_B^\circ + RT(1-X_B)^2 + RT \ln X_B]$$

$$(\because X_A X_B = X_A X_B (X_A + X_B) = X_A^2 X_B + X_A X_B^2)$$

$$(1.31) \quad G^\circ = \mu_A X_A + \mu_B X_B$$

$$(1.40) \quad \therefore \mu_A = G_A^\circ + RT(1-X_A)^2 + RT \ln X_A$$

$(\approx \bar{G}_A^\circ)$

$$\therefore \Delta \bar{G}_A^\circ = \mu_A - G_A^\circ = RT(1-X_A)^2 + RT \ln X_A$$

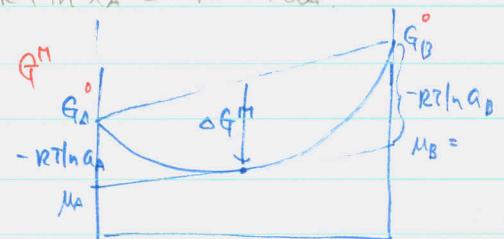
$$RT \ln X_A = RT X_A^2$$

$$= RT \ln \gamma_A + RT \ln X_A = 12T \ln \alpha_A$$

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## 5. Activity

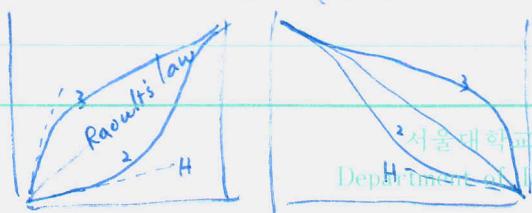
$$(1.41) \quad \begin{aligned} \text{ideal soln} \quad \mu_A &= G_A^\circ + RT \ln X_A \\ \text{real soln} \quad \mu_A &= G_A^\circ + RT \ln \alpha_A \end{aligned}$$



- Difference bet'n  $\alpha_A$  and  $X_A$ . (Real and ideal soln.)

$$(1.40) + (1.41) \quad RT \ln \gamma_A = R(1-X_A)^2 \quad RT \ln \gamma_B = R(1-X_B)^2$$

$$(1.42) \quad RT \ln \left( \frac{\alpha_A}{X_A} \right) = R(1-X_A)^2, \quad RT \ln \left( \frac{\alpha_B}{X_B} \right) = R(1-X_B)^2$$



line 2  $\Delta H^\circ < 0$  exo.  $E_{AB}$  preferre

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endo  $\Delta H^\circ > 0$   $E_{AB}$  avoid. segregat.

$$(1.43) \quad \gamma_A = \frac{\alpha_A}{x_A} \quad \text{the activity coeff. of A.}$$

$$(1.44) \quad \text{For a dilute solution.} \quad \gamma_B = \frac{\alpha_B}{x_B} \approx \text{const. Henry's law.}$$

$$(1.45) \quad x_B \rightarrow 0 \quad \gamma_A = \frac{\alpha_A}{x_A} \approx 1 \quad \text{Raoult's law.}$$

Activity & chem. pot. = a measure of tendency of an atom to leave a solution

if " low, reluctant to leave the sol'n E<sub>A,B</sub> preferred.

G - D equation ①  $dG = \mu_A d\gamma_A + \mu_B d\gamma_B$ . T.P.C. low vap. pressure

### C. Real Solutions.

$$G = \ln \gamma_A + M_B x_B \rightarrow \text{D.G. } x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0$$

$$\text{Assumed that } \frac{x_A d \ln \gamma_A + x_B d \ln \gamma_B}{x_A + x_B} = \frac{x_A d \ln \gamma_A}{x_A + x_B} + \frac{x_B d \ln \gamma_B}{x_A + x_B} = 0.$$

- Regular sol'n  $\Delta H^\ddagger = 0$  ( $|\Delta H^\ddagger| \leq kT$ ), a random arrangement

real sol'n in alloys  $\Delta H^\ddagger \neq 0$ .

??

3つの活性

- Actual arrangement in a real sol'n.

cumromise betw  $\Delta E$  and  $\Delta S$  for min.  $\Delta G^\ddagger$ .

ordering

$$G = H - TS$$

$\underbrace{\text{min}}$        $\underbrace{\text{max}}$

$\epsilon < 0$   $\Delta E \downarrow$  by increasing the # of A-B bonds.

$$\epsilon > 0$$

$\Delta E \uparrow$  " "

of A-A, B-B bonds.

$$\epsilon = [\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})] < 0$$

(Clustering)

- But ordering, clustering tendency ↓ as T ↑ due to high contribution of  $\Delta S$  ( $= -R(x_A \ln x_A + x_B \ln x_B)$ )

→ 높은온도에서는 세련된 첨성과 함께 관찰 된다(강밀화되는 현상)

- If  $\Delta V^\ddagger \neq 0$  (size difference betw atoms) as in Q-C model, the elastic strain  $\epsilon$  fields has to be considered (strain  $\epsilon$  term into  $\Delta H^\ddagger$ )

if  $\Delta V^\ddagger \gg 0$ , (size diff. too large) → tend to form interstitial sol'n.

if " " + strong chemical bonding force  
 $\rightarrow$  tendency for intermetallic

$$\text{for } \Delta H^{\circ} = \Delta E^{\circ} - P\Delta V^{\circ}$$

$$\Delta H^{\circ} = \frac{P}{2} [E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})] \quad \text{for } \Delta S^{\circ} = P_A S_A + P_B S_B$$

I. if  $|E_{AB}| > |\frac{1}{2}(E_{AA} + E_{BB})|$ , then min. of  $H$  corresponds to max. of  $P_{AB}$  (w/ increasingly neg. values of  $\beta$ ) # of A-B pairs (complete ordering of soln)  $\rightarrow$  max. of  $S$   $\rightarrow$  complete random mixing  $\Delta S^{\circ} = S_A - \frac{1}{2}(S_{AA} + S_{BB})$

$\rightarrow$  Minin' of  $G$  occurs as a compromise bet'n maximization of  $P_{AB}$  (w/ increasingly neg. values of  $\beta$ ) and random mixing (w/  $T \uparrow$ )

$\therefore$  The critical parameter are thus  $\beta$  &  $T$  (if  $\beta$  is appreciably negative and  $T$  is not too high)

then  $P_{AB}(\text{actual}) > P_{AB}(\text{random}) \rightarrow$  the assumption of random mixing invalid.

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

- The minin' of  $G$  occurs as a compromise bet'n minin' of  $P_{AB}$  (w/ increasingly pos. values of  $\beta$ ) and random mixing (w/  $T \uparrow$ )

(.. if  $\beta$  is appreciably pos. and the  $T$  is not too high)

$P_{AB}(\text{actual}) < P_{AB}(\text{random}) \rightarrow$  assumption of random mixing invalid

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  $\beta$ , nearly random mixing occurs as  $T \uparrow$ . (2) for any  $T$ , nearly random mixing occurs w/ smaller value of  $\beta$ .  $|E_{AB}| \rightarrow |E_{AA} + E_{BB}| = 0$

## 7. Ordered Phases

(1.35)

$$P_{AB} = N_a z X_A X_B$$

(1.33)

$$\delta H^M = P_{AB} \varepsilon$$

(1.37)

$$\Omega = N_a z \varepsilon$$

(1.34)

$$\varepsilon = \varepsilon_{AB} - \frac{1}{2} (\varepsilon_{AA} + \varepsilon_{BB})$$

- If  $\Omega < 0$ , tend to have more A-B pairs parameter  
it's said to have a short-range order (SRO), s,

$$S = \frac{P_{AB} - P_{AB}(\text{random})}{P_{AB}(\text{max}) - P_{AB}(\text{random})}$$

Fig 1.19 !!

# of bonds for a random soln.

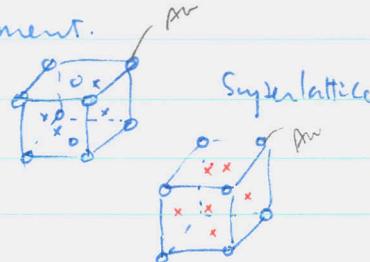
↳ max. # of bonds possible

$$\cancel{(1.35)} \quad P_{ABC(\text{max})} = N_a z \times \cancel{\frac{1}{2}} = 100 \times 4 \times 0.5 \cancel{\times} = 200.$$

# of atoms considered.  
units 3D.

- Cu-Au alloy of fcc.

At high temp. random arrangement.

at low temp.  $X_{Cu} = X_{Au} = 0.5$ . $X_{Cu} : X_{Au} = 3:1$  $\Delta S^M$  for long-range order very smallas  $T \uparrow$ , destroyed.

still LRO since some of the atom sites are vacant or some atoms sit on wrong sites.

ideal ideal comp.

∴ low max. temp. ∵ easy to disrupt LRO (crit?) as  $T \uparrow$ .

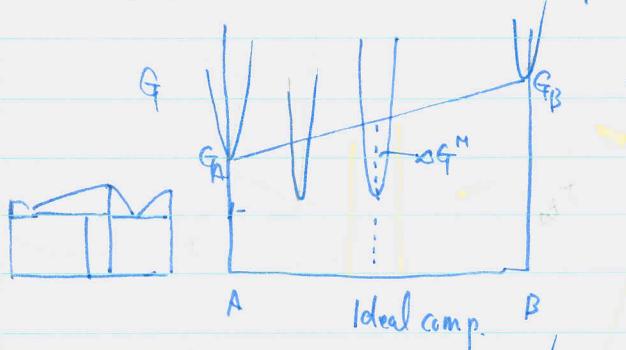
$$(T_{cr} = \frac{\sqrt{R}}{2R})$$

- Ferit.  $\uparrow$  with  $|\Omega|$  or  $|\delta H^M| \uparrow$ . the ordering stable to  $T_m$ .

1.3.8. → Intermediate Phases. - XRD struct diff. from initial atoms.

$\delta H^M > 0$ , but still have strong attraction  $\varepsilon < 0 \rightarrow$  I.P. forms to have  $\Omega_{\text{min}}$ .

- Intermediate phase. normally based on an ideal atom ratio.  $\rightarrow G_{\min}$   
 composition deviation are often giving U shape.

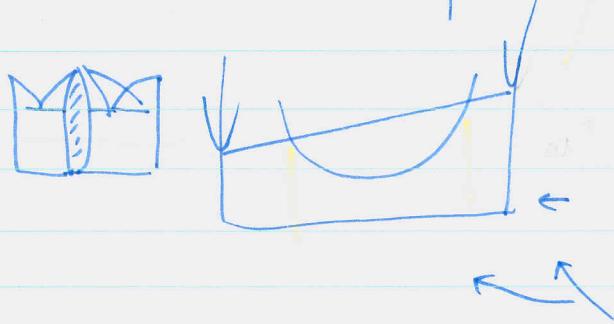


it causes

- the range of compositions relies on the ↓

phase struc. & bond type (metallic, covalent, ionic).

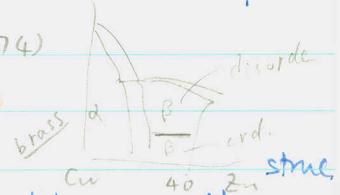
① When small comp. change cause a rapid rise in G, it is called intermetallic compound.  
 is usually stoichiometric:  $A_mB_n$



② If the fluctuation in comp can be tolerated by some atoms occupying 'wrong' position or by atom sites being left vacant, G curve will be less steep.

③ Intermediate phases also can have an order-disorder transf.

- random arrangement : at h. temp. (Fig 5.74)  
 ordered " " : at l. temp.



\* Intermediate phase:

\* Relative atom size, valency & electronegativity → determine a phase

! size diff. by a factor of 1.1-1.6 : Laves phase  $M_2Cu_3$ ,  $M_2Zn_3$ ,  $M_2Ni_3$ .  
 large size diff. → interstitial compound  $MX$ ,  $M_2X$ ,  $M_3X_2$ ,  $M_6X$ .

↓ bond force  
 ↓ ionic force  
 ↓ shared bond H  
 (M: Zr, Ti, V, Cr X: H, B, C, N)

2 relative valency : important for electron phases ( $\alpha$ ,  $\beta$ , brasses)  
 $H-TS = G \propto f(c)$  # of valency elec. / unit cell)

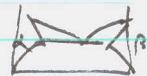
3 electronegativity : degree of attraction of electron.  
 very diff. two atoms → valency compound. ionically bonded

③ / 27

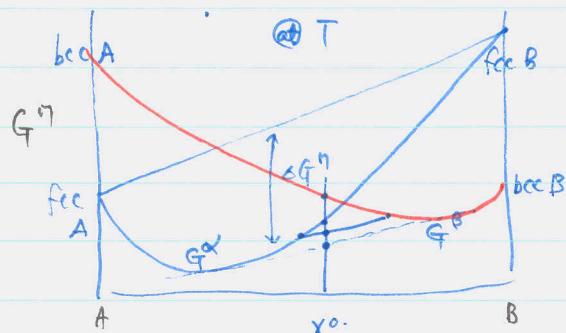
(14)

Date . . .

## 1.4. Equil<sup>m</sup> in Hetero Sys.



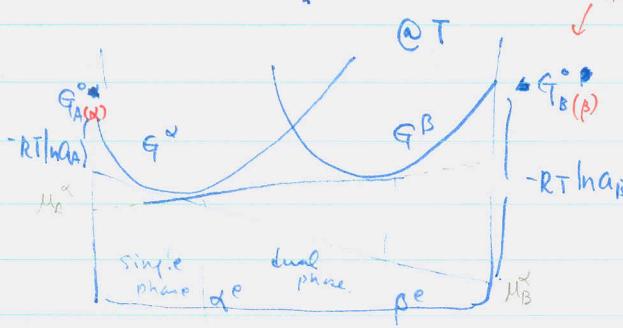
when A, B have two diff. struc. in pure states.  $\rightarrow$  two f.e. curve.



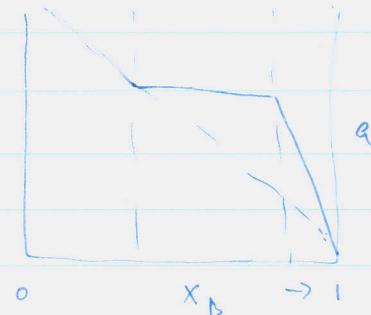
if let say  $\alpha$  fcc.,  $\beta$  bcc

total E. minimized if  $\alpha, \beta$  separate.  
for hetero equil<sup>m</sup>.  
 $\mu_A^\alpha = \mu_A^\beta$      $\mu_B^\alpha = \mu_B^\beta$

(1.46)



✓ Standard free E  
of B in  $\beta$

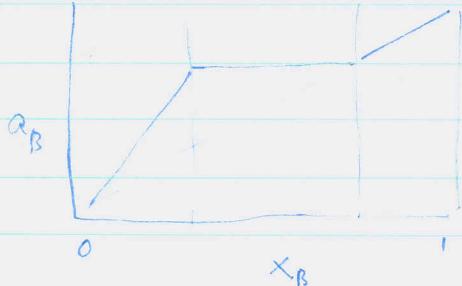


Hetero sys.

nonmixing.

$\rightarrow$  separation.  
 $r > 1$ .

$$a_A^\alpha = \alpha_A^\beta \quad a_B^\alpha = \alpha_B^\beta \quad (1.47)$$



$\Rightarrow \text{diff.} = 2 \text{ comp.}$   
 $\text{e.g. } V_1, V_2, S_1, S_2$

## 1.5 Binary Phase Diagram.

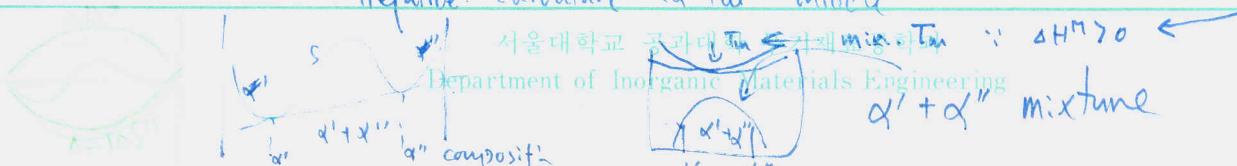
S. J. Kim

1. A Simple Phase Diagram.      Fig 1.29. Text. APB Fig 2. Diagram.

2. Systems w/ a Miscibility Gap.

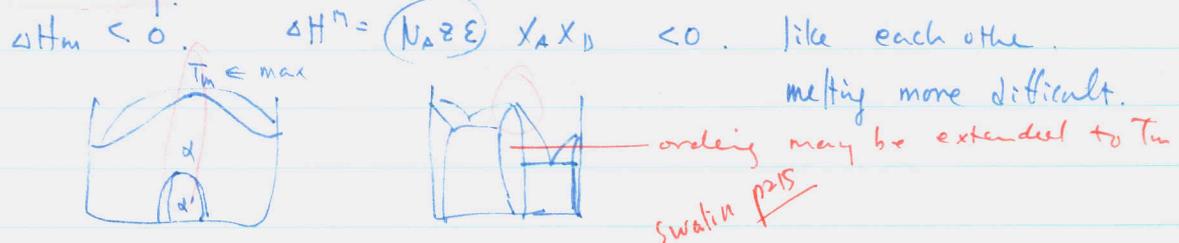
Fig 1.30 liquid  $\approx$  ideal soln, but solid  $\Delta H^\gamma > 0$ . positive dev.  $\Leftrightarrow$   
negative curvature in the middle

dislike.



### 3. Ordered Alloy.

$$\Delta H_m < 0$$



### 4. Simp's Eutectic Systems.

If  $\Delta H^m \gg 0$  separation repellency



Fig. 1.32.

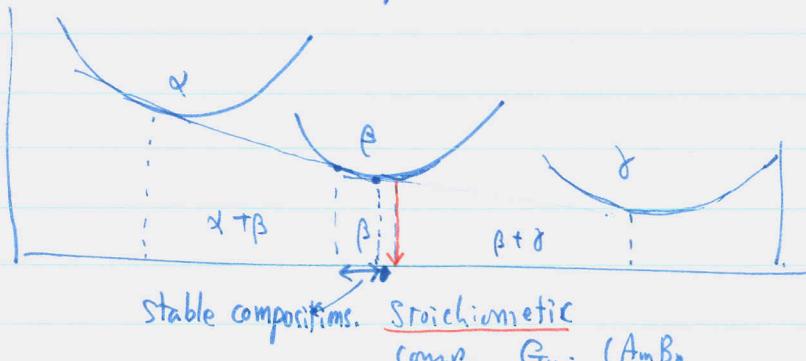
extend to liquid, form eutectic

If A & B have diff. xtal struc. → Fig. 1.33.



### 5. P.D. w/ Intermediate Phases.

- w/ the formation of stable intermediate phases, extra free E. curves appear → Fig 1.34.
- the stable composition range of the phase in the diagram need not include the comp. w/ the min. free. Energy.  
but determined by the relative free energies of adjacent phm.



- ex. the comp. of the equil<sup>n</sup> phase appears to deviate from that predicted by the xtal struc.

$\theta$  in Al-Cu, CuAl<sub>2</sub>

although  $X_{Cu} = \frac{1}{3}$ ,  $X_{Al} = \frac{2}{3}$

