Chap. 10. Free E - composition and Phase Diagrams of Binary Sys.

①

10.2. Free E. and activity.

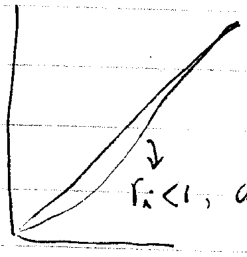
$\Delta G^M = RT(X_A \ln a_A + X_B \ln a_B)$

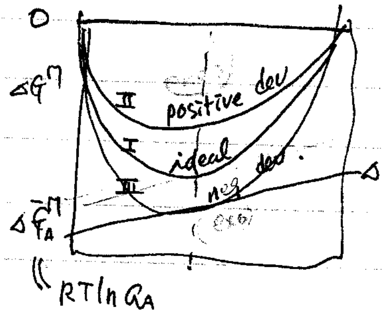
↳ the diff. bet'n the f.E. of a mole of homo. sol'n and the f.E

if it is ideal $\Delta G^{M,id} = RT(X_A \ln X_A + X_B \ln X_B)$.

As $\Delta H^{M,id} = 0$ $\Delta G^{M,id} = -T\Delta S^{M,id}$

∴ the shape of the curve of $\Delta G^{M,id}$ = only $f(T)$.





$\gamma_{II,B} > 1 > \gamma_{III,B}$

∴ ΔG^M- comp ~ activity

5/29/95

10.3. The F.E. of Regular Sol'n.

i) Regular sol'n에서 α가 ΔG^M curve에 미치는 영향.

↙ gen'l term ~~difference bet'n ideal~~ if $G^{xs} = \Delta H^M$ only ≠ f(T).

$$\Delta G^{M} - \Delta G^{M,id} = +G^{xs} = +RT\alpha X_A X_B = +\Delta H^M = \Omega$$

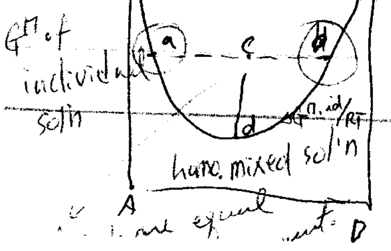
For curve II, $|\Delta G^M| < |\Delta G^{M,id}|$, then $\Delta H^M > 0$ ∴ $\alpha > 0$.

for curve III, $|\Delta G^M| > |\Delta G^{M,id}|$ then $\Delta H^M < 0$ ∴ $\alpha < 0$.

Fig 10.3. Change in $\Delta G^M/RT$ as α ↑.

- As α ↑, the shape of the curve Changes.
- the significance of the shape of ΔG^M !!

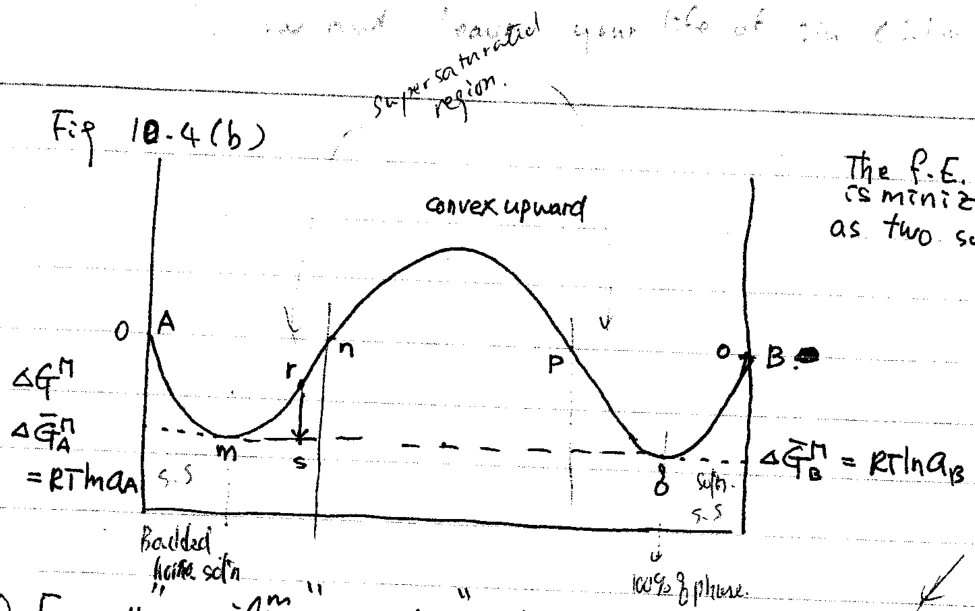
ii) $\Delta G^{M,id}/RT$ Curve는 두 (a.b) sol'n 섞으면 homo. sol'n을 만들고. 더 안정하다 그러나 α=3.0인 경우는 다르다



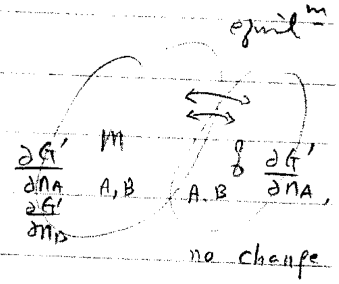
convex downwards.

the most stable configuration of A & B is homo. mixture.

Fig 10.4(b)



The f.E. of a sys. of comp. be
is minized when the sys. occ
as two sol'ns (separat. but prop


equil^m
$\frac{\partial G'}{\partial n_A}$
$\frac{\partial G'}{\partial n_B}$
m
A, B
γ
A. B
$\frac{\partial G'}{\partial n_A}$,
no change

① For. the equil^m "coexistence. of two separate sol'ns ∴ at const - T. P.

Requires that "$\bar{G}_A$ (in sol'n m) = $\bar{G}_A$ (in sol'n γ)." (a)

$\bar{G}_A = G_A^o + RT\ln a_A$

$\bar{G}_B$ (") = $\bar{G}_B$ ("). (b)

Substraction G_A^o from a), ~~(4)~~ (b).

$\Delta \bar{G}^M_{A,m} = RT\ln a_A$ (in sol'n m) = $RT\ln a_A$ (in sol'n γ). = $\Delta \bar{G}^M_{A,\gamma}$

② ∴ a_A (in m) = a_A (in γ) (c), a_B (in m) = a_B (in γ). (d).

eq(c)&(d) These are the Criteria for equil^m coexistence. of two sol'n co at T. P

③ ∴ As $\Delta \bar{G}^M_{A,m} = \Delta \bar{G}^M_{A,\gamma}$ → the tangent to the curve at m and γ. the same.
(activity 같다)

역 ↕ the value of α is sufficiently large → consequent tendency towards clustering of like atoms → phase separation.

!! Graph explanation !!

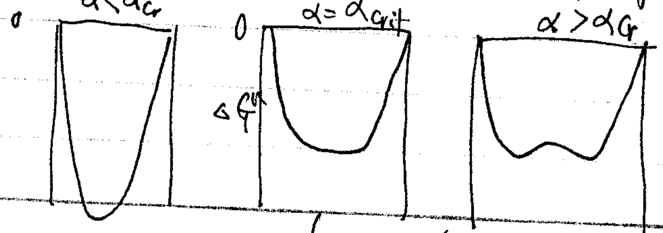
~~12.4.~~ 5/25

10.4. Criterion of phase Stability in Regular Sys.

For a given T !!

i) a critical value α below which. a homo. sol'n.) are stabl
above which ph separated phase)

p 270 ~~305~~ !!
[illegible]



(Fig. 10, 5).

$$\frac{\partial \Delta G^M}{\partial X_B} = \frac{\partial^2 \Delta G^M}{\partial X_B^2} = \frac{\partial^3 \Delta G^M}{\partial X_B^3} = 0$$ at one composi

$$\boxed{\begin{aligned}\Delta H^M &= \Delta G^{xs} = RT\alpha X_A X_B \\ &= \Omega X_A X_B\end{aligned}}$$ ③

$= 0 \rightarrow$ immiscibility becomes imminent.

$$\Delta G^M = RT(X_A \ln X_A + X_B \ln X_B) + RT\alpha X_A X_B .$$

$$\frac{\partial \Delta G^M}{\partial X_B} = RT\left[\ln\frac{X_B}{X_A} + \alpha(X_A - X_B)\right]$$ ~~$\rightarrow X_A = X_B = 0.5$~~

$$\frac{\partial^2 \Delta G^M}{\partial X_B^2} = RT\left[\frac{1}{X_A} + \frac{1}{X_B} - 2\alpha\right]$$ then $\alpha = 2$

$$\frac{\partial^3 \Delta G^M}{\partial X_B^3} = RT\left[\frac{1}{X_A^2} - \frac{1}{X_B^2}\right] = 0 \qquad X_A = X_B = 0.5$$

$\therefore$ $\alpha = 2$. critical value., above which phase separat

(11.72) $\alpha = \frac{\alpha'}{RT}$ (const) inverse fn. of T.

positive deviation. separation only possible ... ! $\Delta H^M > 0$, reg

$\therefore$ for any given regular w/ $\Delta H^M > 0$

$\exists$ a critical temp. T_{cr}, above which $\alpha < 2 \rightarrow$ h

const. for one sol'n — below which $\alpha > 2$. $\rightarrow$ se

(12.1) $\Omega = \alpha RT = \alpha_{cr} R T_{cr}$ $\qquad T_{cr} = \frac{\Omega}{2R}$. (T_{cr}은 $\Delta H^M > 0$인 sol'n에서 Separation이 일어나는 온도. $T_{cr} > T$이면 $\alpha > 2$가 되어 분리시작)

p ~~3~~ 271 !! 참조.

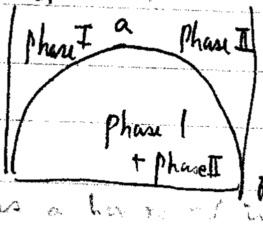


Fig 10.6(b) is the locus of the double tangent. Fig. 10.6(a)

iii) 온도에 따른 activity 변화.

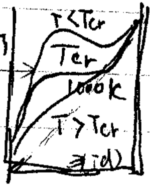
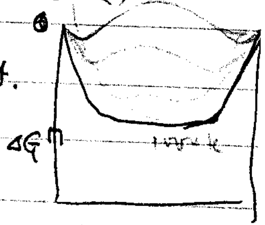


Fig. 10.6(c)



horizontal inflexion

at T_{cr}, p. [illegible] has a horizontal inflexion at $X_B = 0.5$

this shows

$$\because\ \Delta \bar{G}_B^M = \Delta G^M + X_A \frac{\partial \Delta G^M}{\partial X_B} = RT \ln a_B .$$

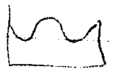
(12.2)
$$\frac{\partial \Delta \bar{G}_B^M}{\partial X_B} = X_A \frac{\partial^2 \Delta G^M}{\partial X_B^2} = \frac{RT}{a_B}\frac{\partial a_B}{\partial X_B}$$

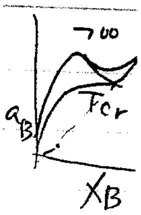
(12.3)
$$\left(\frac{\partial^2 \Delta \bar{G}_B^M}{\partial X_B^2}\right) = X_A\left(\frac{\partial^3 \Delta G^M}{\partial X_B^3}\right) - \left(\frac{\partial^2 \Delta G^M}{\partial X_B^2}\right) = \frac{RT}{a_B}\frac{\partial^2 a_B}{\partial X_B^2} - \frac{RT}{a_B^2}\left(\frac{\partial a_B}{\partial X_B}\right)^2$$

at T_{cr} and $X_B = 0.5$, the 2nd & 3rd der. = 0 $\qquad$ 0 $\qquad$ 0

$\frac{RT}{a_B}\left(\frac{\partial^2 a_B}{\partial X_B^2}\right) - \frac{RT}{a_B^2}\left(\frac{\partial a_B}{\partial X_B}\right)$

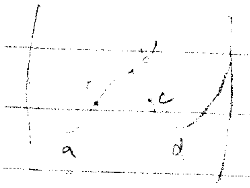
iii-a) As at T_{cr} and $X_B = 0.5$ $\frac{\partial^2 \Delta G^M}{\partial X_B^2} = \frac{\partial^3 \Delta G^M}{\partial X_B^3} = 0$.

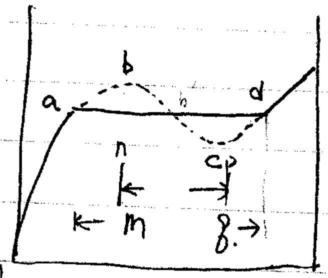
then  이렇게 되니 ← $\Omega = \alpha RT \downarrow$ ∴ $\frac{\partial a_B}{\partial X_B} = \frac{\partial^2 a_B}{\partial X_B^2} = 0$ from (12.3) ∴



iii-b). when $T < T_{cr}$ $= \alpha_{cr} R T_{cr}$, shows a max. and a min.

spinodal compositions.





Curve ab → a_B in phase I, which is super w/ B.

Curve cd → a_B in phase II "

$\Delta \bar{G}_B^M = \Delta G^M + X_A\left(\frac{\partial \Delta G^M}{\partial X_B}\right)$ |← double →| tangent pt.
$= RT\ln a_B$

max 가 됨 at n
min at p

curve bc, $\frac{\partial a_B}{\partial X_B} < 0$ This violates $\frac{\partial a_i}{\partial X_i}$:

$\Delta \bar{G}_i^M = RT\ln a_i > 0$ ∴ no physical significance. rule

Curve ad : actual const. activity of B in the two-

6/12/95 5/31-6/7 Chap. 13

10.5. Liquid and Solid Standard State

- 이전까지 → the standard state of a component of a condensed sys. : the pure comp. in its stable state at a T & P of interest. 1 atm,

→ As the s. state of a comp. — a ref. state against which the com in any other state can be compared, any state can be chosen as the standard state

① 직선의 식을 구하나
② entropy of mixing 을 얻는다.

Start with
Fig 10.8 look at p ~~389~~ 274 (example with an ideal solutions) Raoultion

Fig. 12.8 (10.8 b)

$G^\circ_{A(s)} - G^\circ_{A(l)} = -\overset{\ominus}{\Delta G^\circ_{m(A)}} = -(\Delta H_{m(A)} - T\Delta S_{m(A)}) \geq 0$

if $C_{p,A(s)} = C_{p,A(l)}$

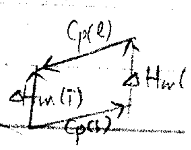
(12.4)
$\Delta G_m^\circ = \Delta H_m^\circ - T_m \Delta S_m^\circ = 0$ $\Delta S_m^\circ = \frac{\Delta H_m^\circ}{T_m}$ → $\Delta G_{m(A)} = \Delta H_m^\circ \left(\frac{T_{m(A)} - T}{T_m}\right)$ < 0

endo

⊖

(b) $\Delta G = -X_A \Delta G^\circ_{m(A)}$

∴ $\Delta G^\circ_{m(B)} > 0$



$\Delta G^\circ_{B(l)} - \Delta G^\circ_{B(s)}$ $\Delta H_m(T) = \Delta H_m$

A(l) B(s) ΔG_m

i) ΔG^M curves 구하는 방법.

~~If they are ideal solutions,~~

At any composition, the formation of a homo. liquid sol'n from pure 의 B(s) = two-step processing.

① the melting of X_B mole of B $\Delta G = X_B \Delta G^\circ_{m(B)}$

② the mixing X_A mole, X_B mole liquid (assume ideal

formation of liquid

(10.5) $\therefore \Delta G^M_{(l)} = X_B \Delta G^\circ_{m(B)} + RT(X_A \ln X_A + X_B \ln X_B)$ → Curve I in F. 12

$(X_A G_A^\circ + X_B G_B^\circ)$

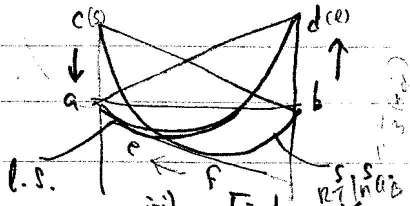
of s.s

(10.6) $\therefore \Delta G^M_{(s)} = RT(X_A \ln X_A + X_B \ln X_B) - X_A \Delta G^\circ_{m(A)}$ → Curve II

ii) Effect of Temp. on the curves $(X_A G_A^\circ + X_B G_B^\circ)$

at ⓔ the tangent to the liquid sol'n is also the tangent to the sol'n at ⓕ liquidus at ⓔ comp equil^m solidus ⓕ

As T ↓ the magnitude of ca ↓, db ↑. then e f position the left.



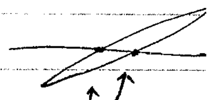
* The loci of e and f with change in T trace o the liquidus & solidus lines, respectively.

iii) Find X_s & X_l on the double tangent line.

ⓘ for. equil^m bet'n l & s. phase

(10.7) $\Delta \bar{G}^M_A \text{ (in s.s)} = \Delta \bar{G}^M_A \text{ (in l.s.)}$ $\Delta \bar{G}^M_A = \Delta G^M + X_B \frac{\partial}{\partial}$

(10.8) $\Delta \bar{G}^M_B \text{ (in s.s)} = \Delta \bar{G}^M_B \text{ (in l.s)}$



→ At any T. ↳ these fix the solidus, liquidus compositions.

from (10.5) $\frac{\partial \Delta G^M_{(l)}}{\partial X_{A(l)}} = RT[\ln X_{A(l)} - \ln X_{B(l)}] - \Delta G^\circ_{m(B)}$

(10.9) → $X_{B(l)} \times$ $X_{B(l)} \times$ $X_{B(l)} \times$

(11.33a) $\Delta \bar{G}^M_A \text{ (in l.s)} = \Delta G^M_{(l)} + X_{B(l)} \frac{\partial \Delta G^M_{(l)}}{\partial X_{A(l)}}$

$\Delta \bar{G}^M_A \text{ (in s.s)} = RT \ln X_{A(s)} - \Delta G_m^\circ$ (10.12)

from (10.5)+(10.8) $\boxed{\Delta \bar{G}^M_A \text{ (in l.s)} = RT \ln X_{A(l)}}$!! (10.10)

(10.6)+(10.11) Similarly $\Delta \bar{G}^M_B \text{ (in s.s)} = RT \ln X_{B(s)}$ (10.15)

⑤ B

and iii) Find X_S & X_L $\Delta\bar{G}^m_A$ (in l.s) = $\Delta\bar{G}^m_A$ (in s.s) (10.7)

$$\Delta\overline{G}^M_B \text{ (in the liquid solution)} = \Delta\overline{G}^M_B \text{ (in the solid solution)} \qquad (10.8)$$

At " any " temperature T, these two conditions fix the solidus and liquidus compositions, i.e., the position of the points of double tangency. From Eq. (10.5)

i) $\Delta\bar{G}^m_B$(l.s) 에 대한

$$\frac{\partial \Delta G^M_{(l)}}{\partial X_{A(l)}} = RT\,(\ln X_{A(l)} - \ln X_{B(l)}) - \Delta G^\circ_{m(B)}$$

Thus ($\times X_B$)

$$X_{B(l)}\frac{\partial \Delta G^M_{(l)}}{\partial X_{A(l)}} = RT(X_{B(l)}\ln X_{A(l)} - X_{B(l)}\ln X_{B(l)}) - X_{B(l)}\Delta G^\circ_{m(B)} \qquad (10.9)$$

From Eq. (9.33a) $\Delta G^m_l = RT(X_{A_l}\ln X_{A_l} + X_{B_l}\ln X_{B_l}) + X_B\,\Delta G^\circ_{m(B)}$

$$\boxed{\Delta\overline{G}^M_A \text{ (in liquid solutions)} = \Delta G^M_{(l)} + X_{B(l)}\frac{\partial \Delta G^M_{(l)}}{\partial X_{A(l)}}}$$

and thus, adding Eq. (10.5) and (10.9) gives

$$\Delta\overline{G}^M_A \text{ (in liquid solutions)} = RT\ln X_{A(l)} \qquad (10.10)$$

From Eq. (10.6)

ii) ΔG^m_B(s.s) 에 처리

$$\frac{\partial \Delta G^M_{(s)}}{\partial X_{A(s)}} = RT\,(\ln X_{A(s)} - \ln X_{B(s)}) - \Delta G^\circ_{m(A)}$$

and thus

$$X_{B(s)}\frac{\partial \Delta G^M_{(s)}}{\partial X_{A(s)}} = RT(X_{B(s)}\ln X_{A(s)} - X_{B(s)}\ln X_{B(s)}) - X_{B(s)}\Delta G^\circ_{m(A)} \qquad (10.11)$$

$\Delta G^m_{(s)} = RT(X_A\ln X_A + X_B\ln X_B) - X_A\,\Delta G^\circ_{m(A)}$

Adding Eqs. (10.6) and (10.11) gives

$$\Delta\overline{G}^M_A \text{ (in solid solutions)} = \Delta G^M_{(s)} + X_{B(s)}\frac{\partial \Delta G^M_{(s)}}{\partial X_{A(s)}} = RT\ln X_{A(s)} - \Delta G^\circ_{m(A)} \qquad (10.12)$$

Thus, from Eqs. (10.7), (10.10), and (10.12)

$$\boxed{RT\ln X_{A(l)} = RT\ln X_{A(s)} - \Delta G^\circ_{m(A)}} \qquad (10.13)$$

Similarly, from Eqs. (10.5) and (9.33b)

$$\Delta\overline{G}^M_B \text{ (in liquid solutions)} = \Delta G^M_{(l)} + X_{A(l)}\frac{\partial \Delta G^M_{(l)}}{\partial X_{B(l)}} = RT\ln X_{B(l)} + \Delta G^\circ_{m(B)} \qquad (10.14)$$

and from Eqs. (10.6) and (9.33b)

$$\Delta\overline{G}^M_B \text{ (in solid solutions)} = \Delta G^M_{(s)} + X_{A(s)}\frac{\partial \Delta G_{(s)}}{\partial X_{B(s)}} = RT\ln X_{B(s)} \qquad (10.15)$$

⑤C

Thus, from Eqs. (10.8), (10.14), and (10.15),

$$\leftarrow \text{답} \qquad \boxed{RT \ln X_{B(l)} + \Delta G^\circ_{m(B)} = RT \ln X_{B(s)}} \tag{10.16}$$

The solidus and liquidus compositions are thus determined by Eqs. (10.13) and (10.16) as follows. Eq. (10.13) can be written as

$$\text{Finally } ① \quad X_{A(l)} = X_{A(s)} \exp\left(\frac{-\Delta G^\circ_{m(A)}}{RT}\right) \tag{10.17}$$

and, noting that $X_B = 1 - X_A$, Eq. (10.16) can be written as

$$② \quad (1 - X_{A(l)}) = (1 - X_{A(s)}) \exp\left(\frac{-\Delta G^\circ_{m(B)}}{RT}\right) \tag{10.18}$$

Combination of Eqs (10.17) and (10.18) gives

$$①' \quad X_{A(s)} = \frac{1 - \exp(-\Delta G^\circ_{m(B)}/RT)}{\exp(-\Delta G^\circ_{m(A)}/RT) - \exp(-\Delta G^\circ_{m(B)}/RT)} \tag{10.19}$$

and

$$②' \quad X_{A(l)} = \frac{[1 - \exp(-\Delta G^\circ_{m(B)}/RT)]\exp(-\Delta G^\circ_{m(A)}/RT)}{\exp(-\Delta G^\circ_{m(A)}/RT) - \exp(-\Delta G^\circ_{m(B)}/RT)} \tag{10.20}$$

$$= \frac{1 - \exp(-\Delta G^\circ_{m(B)}/RT)}{1 - \exp\left(\frac{\Delta G^\circ_{m,A} - \Delta G^B_m}{RT}\right)}$$

Thus, if $c_{p,i(s)} = c_{p,i(l)}$, in which case

$$\Delta G^\circ_{m(i)} = \Delta H^\circ_{m(i)} \times \left[\frac{T_{m(i)} - T}{T_{m(i)}}\right] \tag{10.4}$$

it is seen that the phase diagram for a system which forms ideal solid and liquid solutions is determined only by the melting temperatures and the molar heats of melting of the components.

Example

The system Ge–Si exhibits complete ranges of liquid and solid solutions. (1) Calculate the phase diagram for the system assuming that the solid and liquid solutions are Raoultian in their behavior and (2) calculate the temperature at which the liquidus (and hence solidus) composition exerts its maximum vapor pressure.

Silicon melts at 1685 K, and its standard Gibbs free energy change on melting is

$$\Delta G^\circ_{m,\mathrm{Si}} = 50{,}200 - 29.8\,T \text{ J}$$

The saturated vapor pressure of solid Si is

$$\log p^\circ_{\mathrm{Si}(s)}\ (\text{atm}) = -\frac{23{,}550}{T} - 0.565 \log T + 9.47$$

Germanium melts at 1213 K and its standard Gibbs free energy change on melting is

$$\Delta G^\circ_{m,\mathrm{Ge}} = 36{,}800 - 30.3\,T \text{ J}$$

ΔG^M [illegible] $= RT \ln X_{(l)}$

from (12.7)(12 [illegible])(12.12)

(10.13) $RT \ln X_{A(l)} = RT \ln X_{A(s)} - \Delta G^\circ_{m(A)}$

(10.16) Similarly $RT \ln X_{B(l)} + \Delta G^\circ_{m(B)} = RT \ln X_{B(s)}$

} w/ T_m, ΔG°_m → phase diagram (c dra

p. 394 - 396 (10) The Choice of the S. states.

the ratio. mn/gn in Fig 12.8

For B in any state along aef

$\bar{G}_B = G^\circ_{B(l)} + RT \ln a_B$ w.r.t. B(l

and

$\bar{G}_B = G^\circ_{B(s)} + RT \ln a_B$ w.r.t. B(s

$\therefore G^\circ_{B(l)} - G^\circ_{B(s)} = \Delta G^\circ_{m(B)}$

(10.21) $= RT \ln \dfrac{a_B \text{ wrt. } B(s)}{a_B \text{ wrt. } B(l)}$ $\left(\dfrac{1}{a_{B(l)}}\right.$ m

← [illegible]

Since $\Delta G^\circ_{m(B)} > 0$ $T < T_{m(B)}$

$\therefore a_B$ wrt. B(s) > a_B wrt B(l

if gn = 1, $mn = \exp(-\Delta G^\circ_{m(B)}$

from Eq (10.21)

(xb) + (bd) = (xd)

i.e. $\therefore RT \ln a_B$ w.r.t. B(s) + $(G^\circ_{B(s)} -$

$= RT \ln a_B$ wrt. B(l).

or $\Delta G^\circ_{m(B)} = RT \ln \dfrac{a_B \text{ wrt } B(s)}{a_B \text{ wrt } B(l)}$

if. pure B(l) is chosen as the S.S. (

JKlm unit activity → (mn)

$g n / mn = \exp(\Delta G^\circ_{m(B)}/RT)$
(=1)

ratio bet'n two lines.

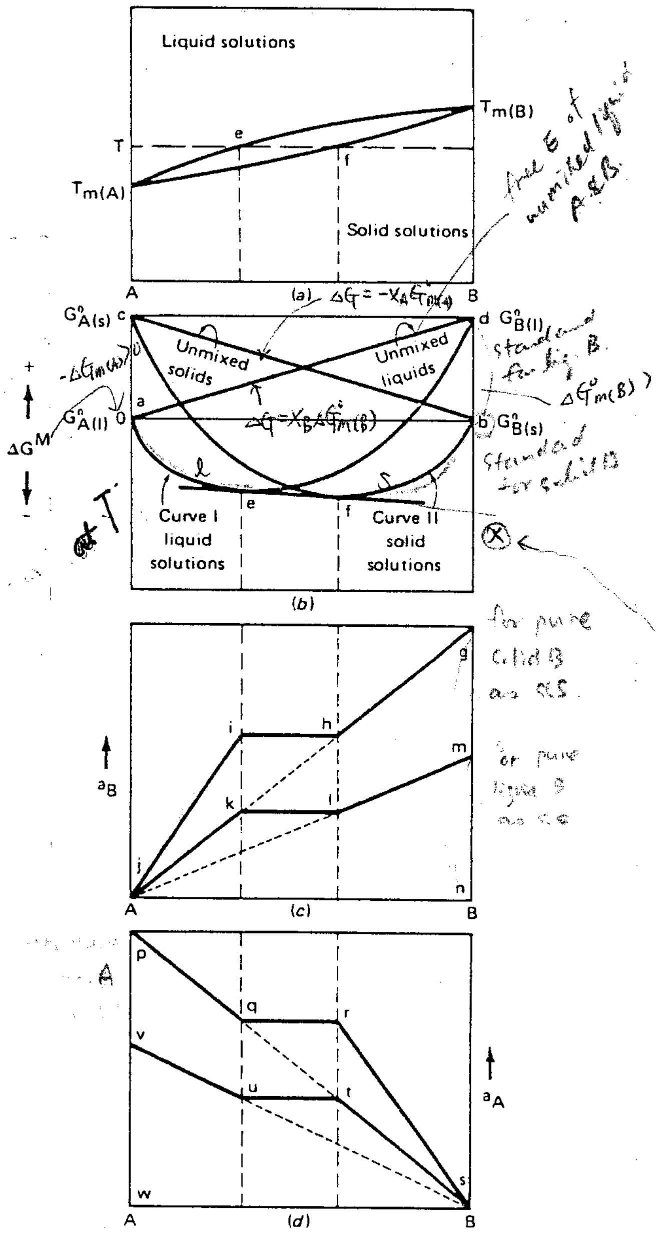

Liquid solutions
$T_{m(B)}$
T
e
f
$T_{m(A)}$
Solid solutions
A
(a)
B
$\Delta G = -X_A \Delta G^\circ_{m(A)}$
free E of unmixed liquid A & B.
$G^\circ_{A(s)}$ c
d $G^\circ_{B(l)}$
standard for liq. B.
Unmixed solids
Unmixed liquids
$-\Delta G_{m(A)} < 0$
+
a
$\Delta G^\circ_{m(B)} > 0$
$G^\circ_{A(l)}$ 0
$\Delta G = X_B \Delta G^\circ_{m(B)}$
b $G^\circ_{B(s)}$
standard for solid B
ΔG^M
l
s
−
at T
Curve I liquid solutions
e
f
Curve II solid solutions
⊗
(b)
for pure solid B as S.S.
g
i
h
m
or pure liquid B as S.S
a_B
k
l
j
n
A
(c)
B
A
p
q
r
v
u
t
a_A
w
s
A
(d)
B

Fig. 12.8. (*a*) The phase diagram of the system A–B. (*b*) The integral free energies of mixing in the system A–B at the temperature *T*. (*c*) The activities of B at the temperature *T*, and comparison between the solid and liquid standard states of B. (*d*) The activities of A at the temperature *T*, and comparison between the solid and liquid standard states of A.

Temperature effect

$$\frac{a_i \text{ wrt solid } i}{a_i \text{ wrt liq. } i} = \exp\left(\frac{\Delta G^\circ_{m(i)}}{RT}\right) = \exp\left[\Delta H^\circ_{m(i)}\left(\frac{T_{m(i)} - T}{RT\,T_m}\right.\right.$$

WRT $\underline{\underline{B}}$. if $T_{m(B)} > T$ $\left(a_{B(solid)} / a_{B(liq)}\right)(>1)$ increases as T ↓

wrt. A. if $T > T_{m(A)}$ $a_{A(solid)} / a_{A(liq)}$ (<1) increases. as T ↓

p 280. Changing s.s.!!

10-6 Phase Diagram, free E. and Activity

설명됨. Fig. 10.10 - 10.13. and va

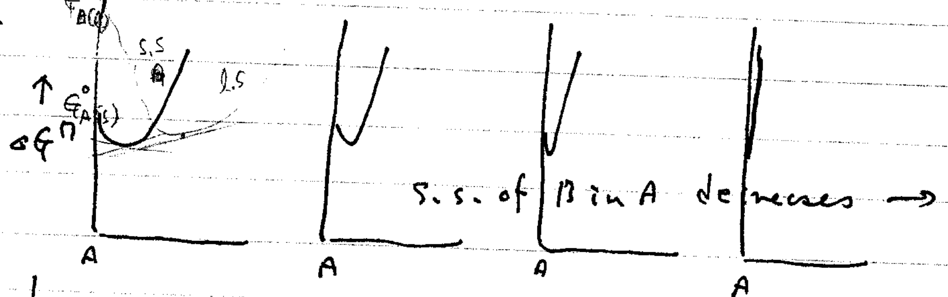
Complete solid solubility of A, B. $\xrightarrow{\text{require}}$ the same Xtal Struc. ~ atomic size, electron

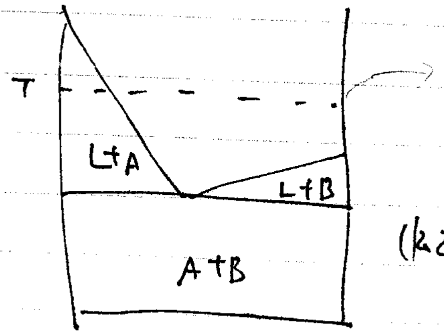
Otherwise, miscibility gap occurs.

p 284 Fig. 10.10 - 13.

p329. if the range of solid solubility in α, β → very small → called insolu

Fig. 12.15





이경우

pure A(s) is in equil^n w/ liquid soln.

$$\bar{G}_{A(s)} = G^\circ_{A(s)} = \bar{G}_{A(l)} = G^\circ_{A(l)} + RT\ln a_{A(l)}$$

w.r.t. A as s. state

(12.22) $\therefore G^\circ_{A(l)} - G^\circ_{A(s)} = \Delta G^\circ_{m(A)} = -RT\ln a_{A(l)}$

if the liquid soln are Raoultian.

(12.23) $\Delta G^\circ_{m(A)} = -RT\ln X_{A(l)}$

Fig 12.16 Bi-Cd Phase Diagram

$$\Delta G^0_{m(Bi)} = \Delta H^\circ_{m(Bi),544} + \int_{544}^{T} \Delta C_{p,Bi}\,dT - T\left[\Delta S^\circ_{m(Bi),544} + \int\right.$$

$$= -RT \ln X_{Bi} \text{ (liquidus)}$$