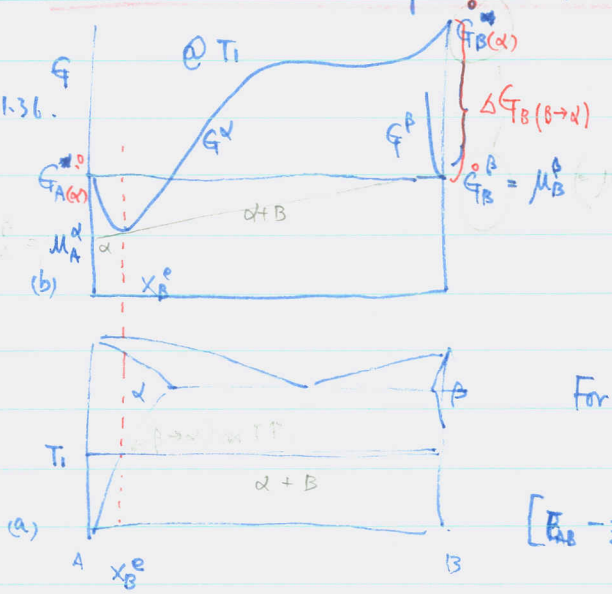
7. The Effect of Temp on Solid Solubility.

Fig 1.36.



Phase diagram B soluble in A
A insoluble in B.

for X^e_B (max. solubility of B in A)

$$\mu^\alpha_B = \mu^\beta_B \simeq G^{\circ}_{B(\beta)}$$

For a regular soln.

$$\mu^\beta_B = G^{\circ\beta}_B + \underbrace{\Omega(1-X_B)^2}_{RT\ln\gamma_B} + RT\ln X_B$$

$$= G^{\circ\beta}_B + RT\ln a_B \quad (a_B \to 1)$$

$$\left[\varepsilon_{AB} - \tfrac{1}{2}(\varepsilon_{AA}+\varepsilon_{BB})\right]$$

$$\mu^\alpha_{B(\alpha)} = G^{\circ\alpha}_B + \Omega(1-X_B)^2 + RT\ln X_B.$$

$$\Omega = N_a z \varepsilon$$

From fig 1.36 b. $\simeq G^{\circ\alpha}_B - \mu^{\alpha(\beta)}_B = \Delta G_{B(\beta\to\alpha)}$ the diff in f.E. bet'n pure B (in the stable β-form) and unstable α-form.

(1.51) $\therefore \Delta G_{B(\beta\to\alpha)} = -RT\ln X^e_B - \Omega(1-X^e_B)^2$

(1.52) If $X^e_B \ll 1$ (1.51) → $\boxed{X^e_B = \exp\left(-\dfrac{\Delta G_B + \Omega}{RT}\right)}$

Since $\Delta G_{B(\beta\to\alpha)} = \Delta H_{B(\beta\to\alpha)} - T\Delta S_{B(\beta\to\alpha)}$

(1.53) $X^e_B = A\exp\left(-\dfrac{Q}{RT}\right)$

(1.54) where $A = \exp\left(\dfrac{\Delta S_B}{R}\right)$, $\boxed{Q = \Delta H_B + \Omega}$

① ② $N_a z \varepsilon$

② the change in E. when 1 mole of B w/ α-struc. dissolves in A to make a dilute soln.

$\therefore$ Q = Heat absorbed when 1 mole of B in β dissolves in A(α) to make a dilute soln.

$(B(\beta) \to B^\alpha \text{ in } A(\alpha))$

$$\Delta S_B = \Delta S_{B(\beta\to\alpha)} \neq f(T)$$

명백히. $X^e_B \uparrow$ as $T \uparrow$, rate determined by Q.

Date

8. Equil^m vac. Conc.

- Always there are vacancies in the lattice. $\Delta S_{thermal} \simeq$ small
  vacancy (removal of atoms) cause U (int. E) and $\Delta S_{conf.}$ to ↑.
  ∴ G of the alloy $\equiv$ f(vac. conc.) and X_v^e will give G_{min}.
  ↳ conc. of vac. variable

- Assume that calculation of X_v^e is identical to that of ΔG^m for A & B when $\Delta H^m > 0$ (endo)

- Since X_v^e normally small, ignore vac-vac interactions
  ∴ $\Delta H \simeq \Delta H_v X_v$
  ↳ ΔH/mole vac. added.

- $\Delta S_{conf} \gg \Delta S_{thermal}$ by vibration of atoms due to vac. existence.
  (엔트로피 변화 영향이 ~~before~~ or pin)

$$\Delta S = X_v \Delta S_v - R\underbrace{\left[X_v \ln X_v + (1-X_v)\ln(1-X_v)\right]}_{\text{due to mixing}}$$

(thermal entropy) (VAC 에 의한 ΔG)

(1.55) $$G = G_A^\circ + \Delta G_v = G_A^\circ + X_v(\Delta H_v - T\Delta S_v) + RT\left[X_v \ln X_v + (1-X_v)\ln(1-X_v)\right]$$

$$= G_A^\circ + (\Delta H - T\Delta S)$$

$$= G_A^\circ + \Delta H_v X_v - T\Delta S_v X_v + RT[\ \ ]$$

For X_v^e

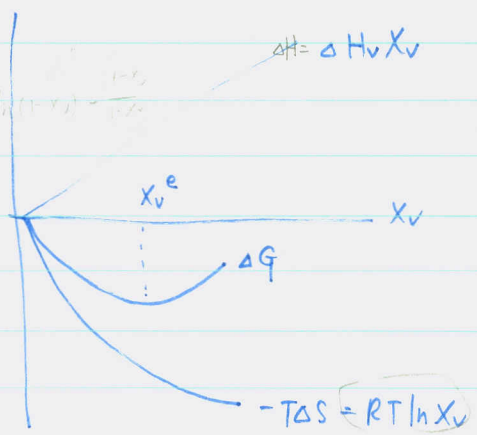
$$\left.\frac{dG}{dX_v}\right|_{X_v = X_v^e} = 0$$

$$\therefore \Delta H_v - T\Delta S_v + RT \ln X_v^e = 0$$

(1.56) $$\therefore X_v^e = \exp\left(\frac{\Delta S_v}{R}\right) \cdot \exp\left(\frac{-\Delta H_v}{RT}\right)$$

$\simeq 3 \neq f(T)$

(1.57) or $$X_v^e = \exp\left(\frac{-\Delta G_v}{RT}\right)$$

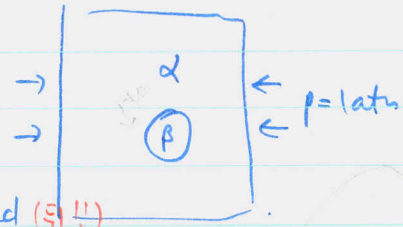


In practice $\Delta H_v \sim 1$ eV/atom
$X_v^e \sim 10^{-4} \sim 10^{-3}$ at T_m of solid.

1.6. The Influence of Interfaces on Equil^{m}

So far assumed a perfect single Xtal.
In reality, various defects exist. (disl. g.b., interphase interface)

1 In the early stages of phase transf.
fine β in α matrix



due to the curvature $\Delta p = \frac{2\gamma}{r}$ exerted (식 1.11) on the β.

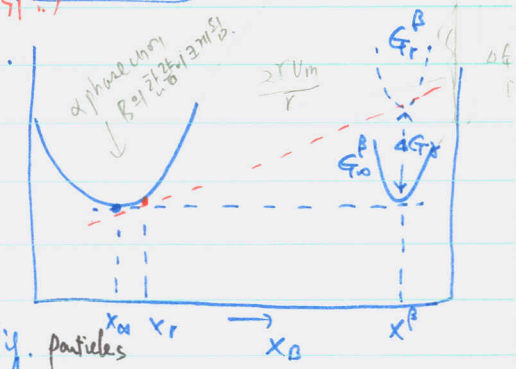
$\rightarrow U + pV$.

$G = H - TS$

$(dG = -SdT + Vdp)$

$\therefore \Delta G = \Delta p \cdot V$ — molar vol. of β.

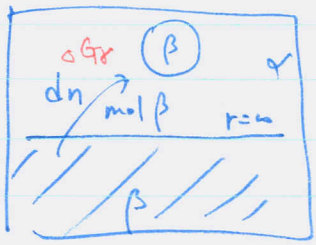
(1.58) $\boxed{\Delta G_\gamma = \frac{2\gamma V_m}{r}}$: Gibbs-Thompson effect or capillary effect.



the concept of a Δp → good for spherical liq. particles
less ~~important~~ convenient in solids. → usually nonspherical

2 two β particles in α matrix : one w/ radius r, one w/ " ∞ (flat). in α.

if the molar f.e. difference bet'n two particles is ΔG_γ



the transfer of dn mole of β from β_∞ to β_r.

$dG = \Delta G_r \, dn$.

If the surface Area of β_∞ unchanged.
then dG is due to the increase in the <u>interfacial area</u> of the β_r (dA).

$dG = \gamma \, dA$.

(1.59) $\therefore \Delta G_\gamma = \gamma \cdot \frac{dA}{dn}$

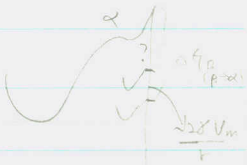
$n = \frac{4}{3}\pi r^3 / V_m$, $A = 4\pi r^2$ $\therefore \frac{dA}{dn} = \frac{8\pi r V_m}{4\pi r^2} = \frac{2V_m}{r}$

(1.58) $\therefore \Delta G_\gamma = \frac{2\gamma V_m}{r}$ Gibbs-Thompson Effect.

- G-T Effect → ~~so~~ ~~N~~ solubility of β in α → sensitive to the size of β
  $x_\infty \to x_r$. Assuming that ① α is a regular sol'n
  in ~~the~~ Figure ② β is almost pure B, $x_B^\beta \sim 1$.

$$(1.52) \to \quad x_B^e = \exp\left[-\frac{\Delta G_B + \Omega}{RT}\right] = x_\infty$$

Similarly $x_r = \exp\left[-\frac{\left(\Delta G_B - \frac{2\gamma V_m}{r}\right) + \Omega}{RT}\right]$



if this is small.

(1.60) $\therefore x_r = x_\infty \exp\left(\frac{2\gamma V_m}{RTr}\right)$

~~(1.60)~~

(1.61) $x_r \cong x_\infty \left(1 + \frac{2\gamma V_m}{RTr}\right)$

- ex. $\gamma = 200\,mJ/m^2$, $V_m = 10^{-5}\,m^3$ $R = 8.3$ J/mol°K $T = 500K$.

$$\frac{x_r}{x_\infty} \simeq 1 + \frac{1}{r(nm)}$$ ← good effective for $r = 1 - 100\,nm$.

for $r = 10$ nm $\frac{x_r}{x_\infty} = 1.1$.

7. Ternary Equil^m.

intercept on A.B.C axes by tangential plane to the f.E. surface as in Fig 1.41.
→ gives the chem pot. of A.B.C

Fig 1.41 → Simple Eutectic.

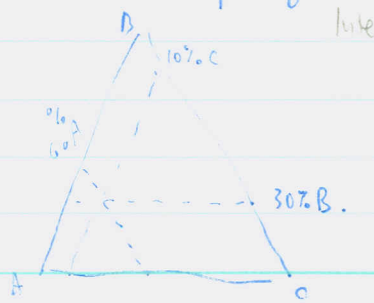


Fig. 1.40 The Gibbs Triangle.

Date . .

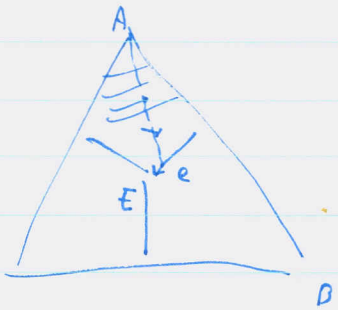
- Construction of phase diagram at T from G-comp curve.

1. Points connected by common tangential plane (∵ equal chem. pot.)
2. Mark these points on an isothermal section of the diagram.
3. get the series of tie line by rolling the tangential plane.

- Relative amount (solid & liquid) determined by a lever rule.

- At lower temp.
  - tie line bundles.
  - tie-triangles
  - ternary eutectic : $L + \alpha + \beta + \gamma$

- The course of solidification. assuming equil^{m} maintained.



$\overline{Ae}$ $\quad$ eE $\quad$ E

$\alpha + L \rightarrow \alpha + \beta + L \rightarrow \alpha + \beta + \gamma$

$L \rightarrow$ Leutetic.

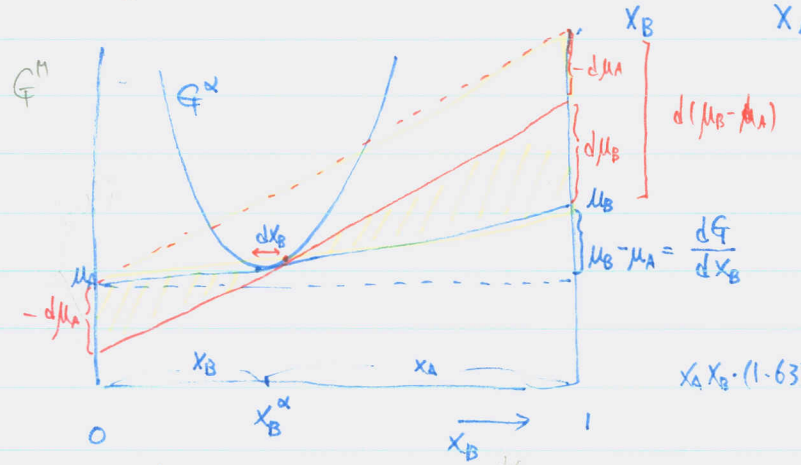
1.8. Add'l Thermo Relationships for Binary Sol'n.

Interested in the calculation of $d\mu$ (Δ in chem. pot.) due to dx.

G-D $x_A d\mu_A + x_B d\mu_B = 0$ 에서, 좌변 그림에서

Fig. 1.46.

$$(1.63) \qquad -\frac{d\mu_A}{x_B} = \frac{d\mu_B}{x_A} = \frac{d(\mu_B-\mu_A)}{1}$$



the slope of G-comp. curve

$$\frac{dG}{dx_B} = \frac{\mu_B-\mu_A}{1} \qquad (1.64)$$

$x_A x_B \cdot (1.63) \leftarrow (1.64)$

$$-x_A d\mu_A = x_B d\mu_B = x_A x_B \frac{d^2G}{dx_B^2}\cdot dx_B$$

G-D eq.

$$= x_A x_B \frac{d^2G}{dx^2}\cdot dx_B \checkmark$$

$$\left(\because \frac{d^2G}{dx_B^2} = \frac{d^2G}{dx_A^2}\right) \rightarrow (1.68)$$

For a regular sol'n.

$$(1.39) \qquad G = x_A G_A^\circ + x_B G_B^\circ + \Omega x_A x_B + RT(x_A \ln x_A + x_B \ln x_B)$$

$$(1.66) \qquad \frac{d^2G}{dx^2} = \frac{RT}{x_A x_B} - 2\Omega.$$

$$\therefore x_A x_B \frac{d^2G}{dx^2} = RT\left[1 - \frac{2\Omega x_A x_B}{RT}\right] = RT\left[1 - \frac{2\Delta H^M}{RT}\right] = (1.71)$$

for ideal sol'n $\Omega = 0$.

$$(1.67) \qquad \frac{d^2G}{dx^2} = \frac{RT}{x_A x_B}$$

$$(1.68) \qquad (1.44) + (1.43) \rightarrow \mu_B = G_B^\circ + RT \ln \gamma_B x_B$$

①

Differentiate

(1.67) $d\mu_B = RT\left[\ln \gamma_B X_B\right]' = RT\left[\ln \gamma_B + \ln X_B\right]'$

(2) $= RT\left[\frac{d\gamma_B}{\gamma_B} + \frac{dX_B}{X_B}\right]$

$\therefore \frac{d\mu_B}{dX_B} = \frac{RT}{X_B}\left[\frac{X_B}{\gamma_B}\frac{d\gamma_B}{dX_B} + 1\right]$

(1.65) → $X_B\, d\mu_B = X_A X_B \frac{d^2G}{dX^2}\, dX_B = -X_A\, d\mu_A$

+ (1.68) → $\frac{d\mu_B}{dX_B} = \frac{RT}{X_B}\left\{1 + \frac{X_B}{\gamma_B}\frac{d\gamma_B}{dX_B}\right\} = \frac{RT}{X_B}\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$

(1.70) (1.65) $-X_A\, d\mu_A = X_B\, d\mu_B = RT\left[1 + \frac{d\ln\gamma_B}{d\ln X_B}\right] dX_B$

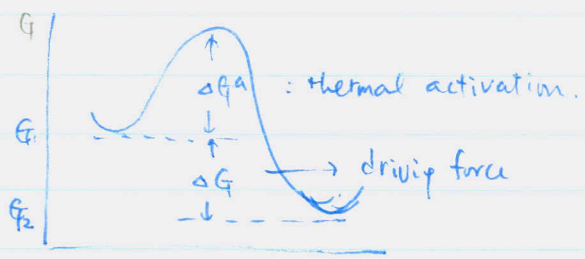
(1.71) $\therefore X_A X_B \frac{d^2G}{dX^2} = RT\left[1 + \frac{d\ln\gamma_A}{d\ln X_A}\right] = RT\left[1 + \frac{d\ln\gamma_B}{d\ln X_B}\right]$

For a regular sol. $= RT\left[1 - \frac{2\Delta H^n}{RT}\right]$

for an ideal sol.

9. The Kinetic of Phase Transf.

- the Thermo fnc. : be used to calculate the driving force for a transf.
  how fast the transf will occur → kinetics.



the probability of an atom reaching the activated state

$= \exp(-\Delta G^a/kT)$

the rate ∝ # of atoms which reached the activate state.

$\therefore$ the rate $\propto \exp\left(-\frac{\Delta G^a}{kT}\right)$ $\qquad \Delta G^a = \Delta H^a - T\Delta S^a$.

$= \underbrace{\exp\left(\frac{\Delta S^a}{k}\right)}_{\text{const}} \exp\left(-\frac{\Delta H^a}{kT}\right)$ $\qquad$ Arrhenius rate eq.