2021 Fall

“Phase Transformation *in* Materials”

09.27.2021

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

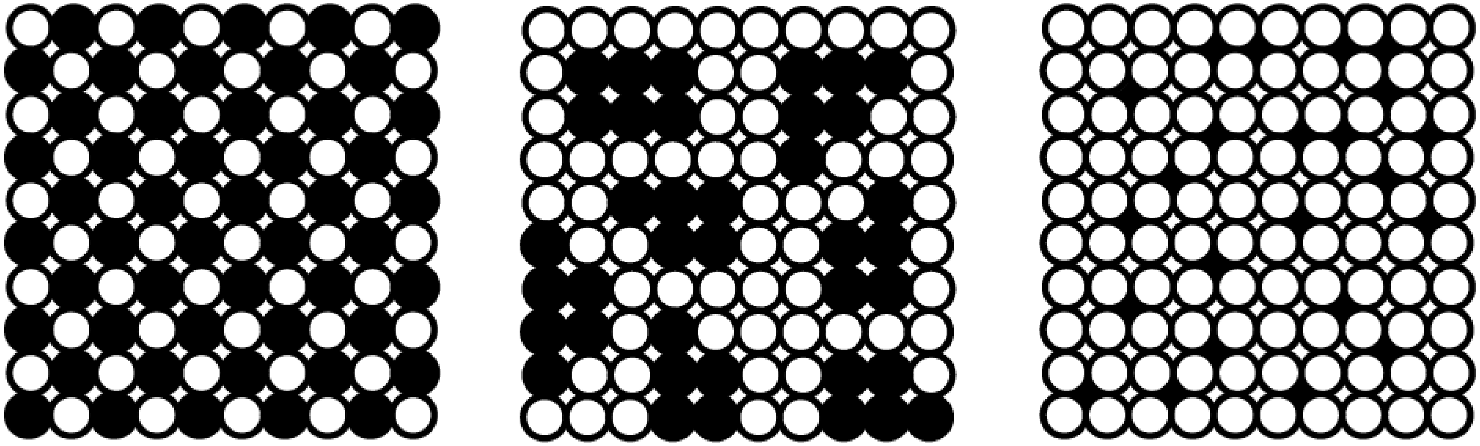
- Binary System mixture/ solution / compound

Ideal solution ($\Delta H_{mix}=0$) **Random distribution**

Regular solution $\boxed{\Delta H_{mix} = P_{AB}\varepsilon}$ where $\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$ $\boxed{\varepsilon \approx 0}$

$\Delta H_{mix} > 0$ or $\Delta H_{mix} < 0$

Real solution **Ordered structure**



(a) $\varepsilon < 0$, $\Delta H_{mix} < 0$

Ordered alloys

P_{AB} ↑ ⟶ Internal E ↓

(b) $\varepsilon > 0$, $\Delta H_{mix} > 0$

Clustering

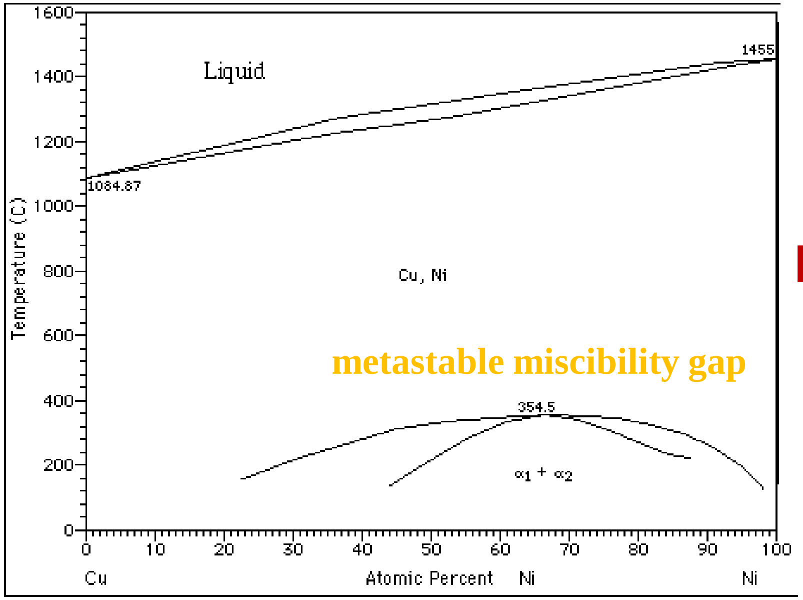
P_{AA}, P_{BB} ↑

(c) when the size difference is large

strain effect

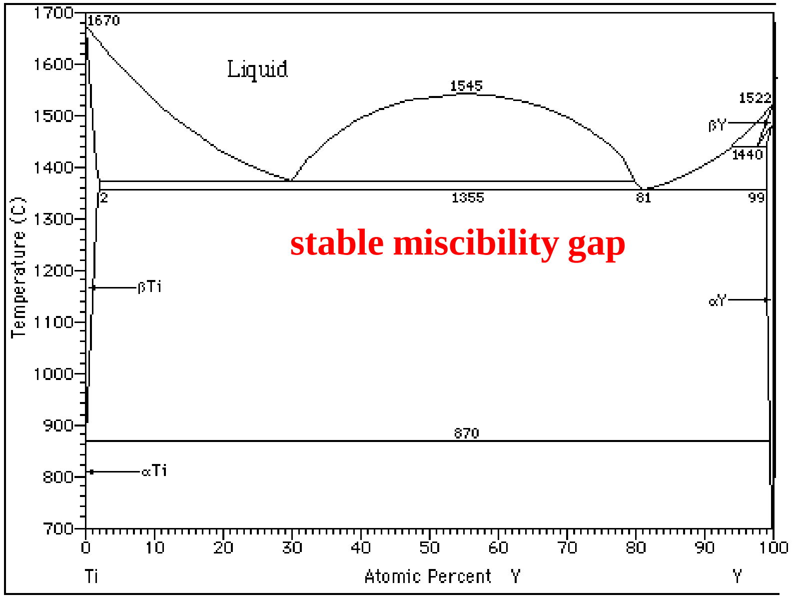
Interstitial solution

$\Delta H_{mix}^{S} > 0$: **Solid solution → solid state phase separation (two solid solutions)**



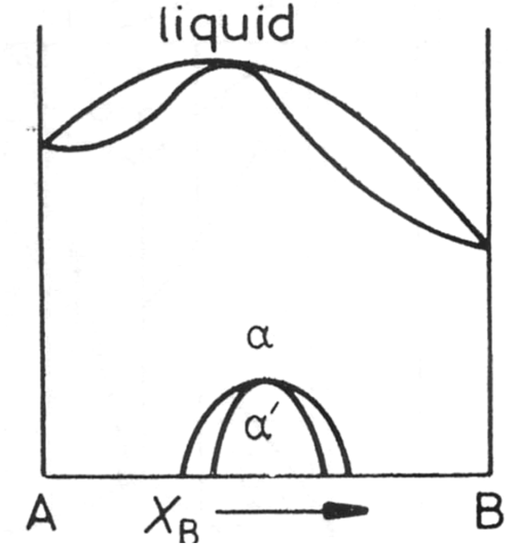
metastable miscibility gap

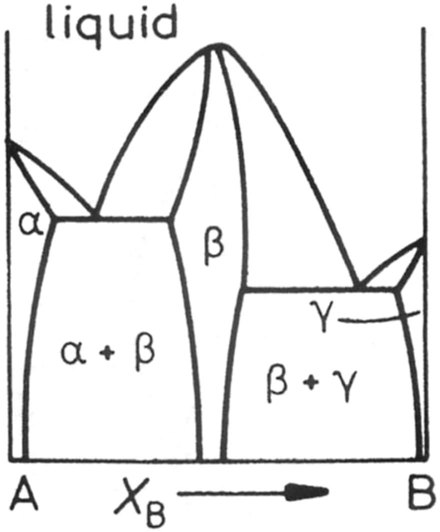
$\Delta H_{mix}^{S} >> 0$: **liquid state phase separation (up to two liquid solutions)**



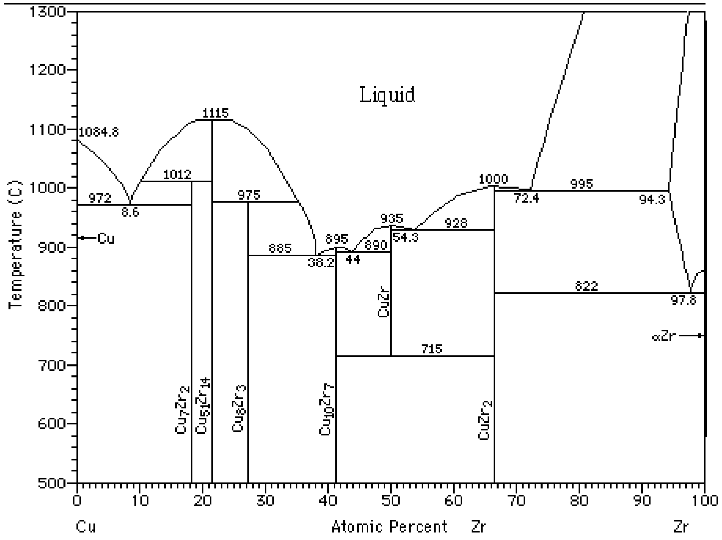
stable miscibility gap

$\Delta H_{mix}^{S} < 0$: **Solid solution → ordered phase**



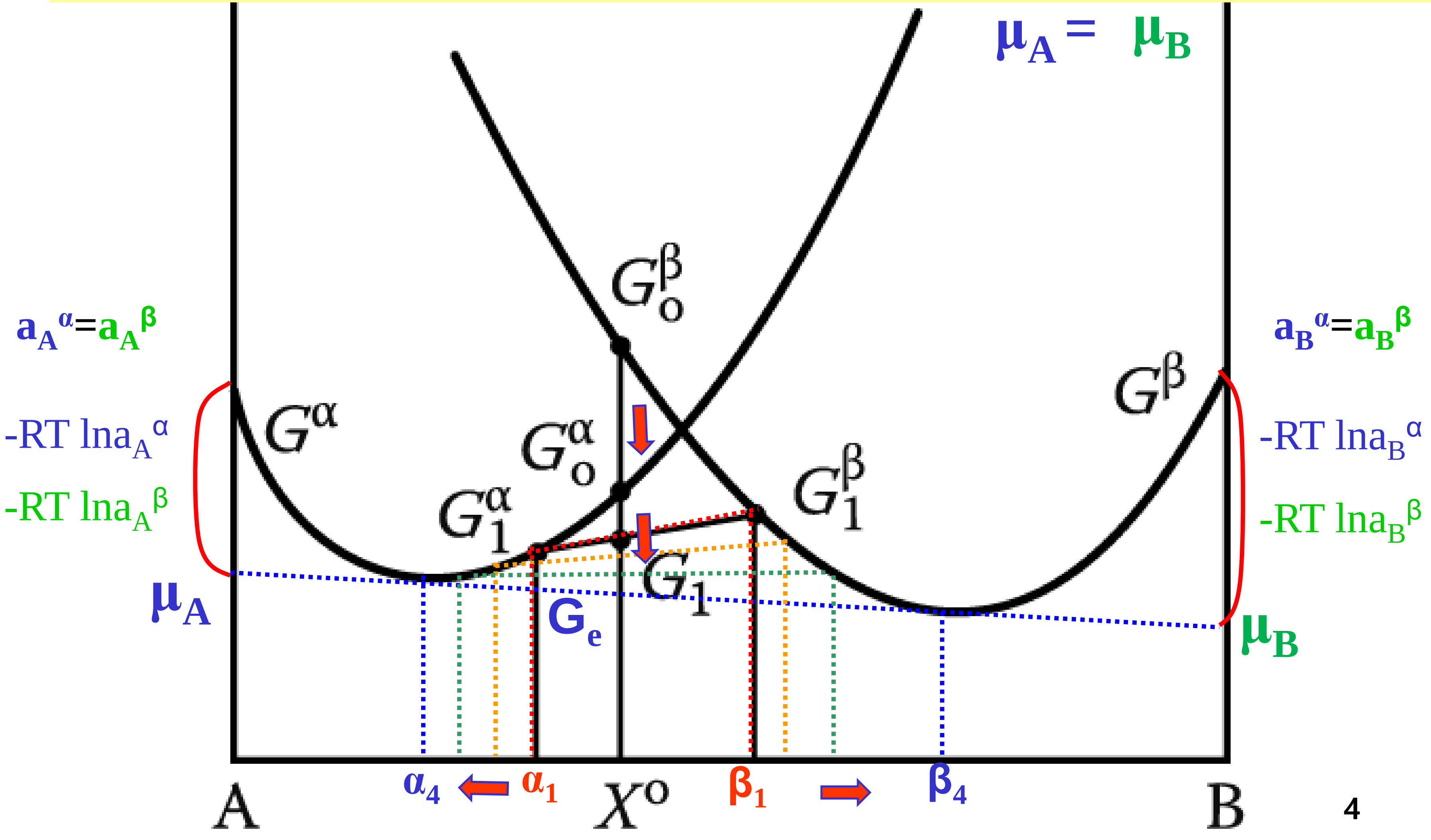


$\Delta H_{mix}^{S} << 0$: **Compound : AB, A_2B…**



Equilibrium in Heterogeneous Systems

In X^0, $G_0^\beta > G_0^\alpha > G_1$ ➡ α + β separation ➡ unified chemical potential



1.5 Binary phase diagrams

1) Simple Phase Diagrams

1) Variation of temp.: $G^L > G^s$

2) Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

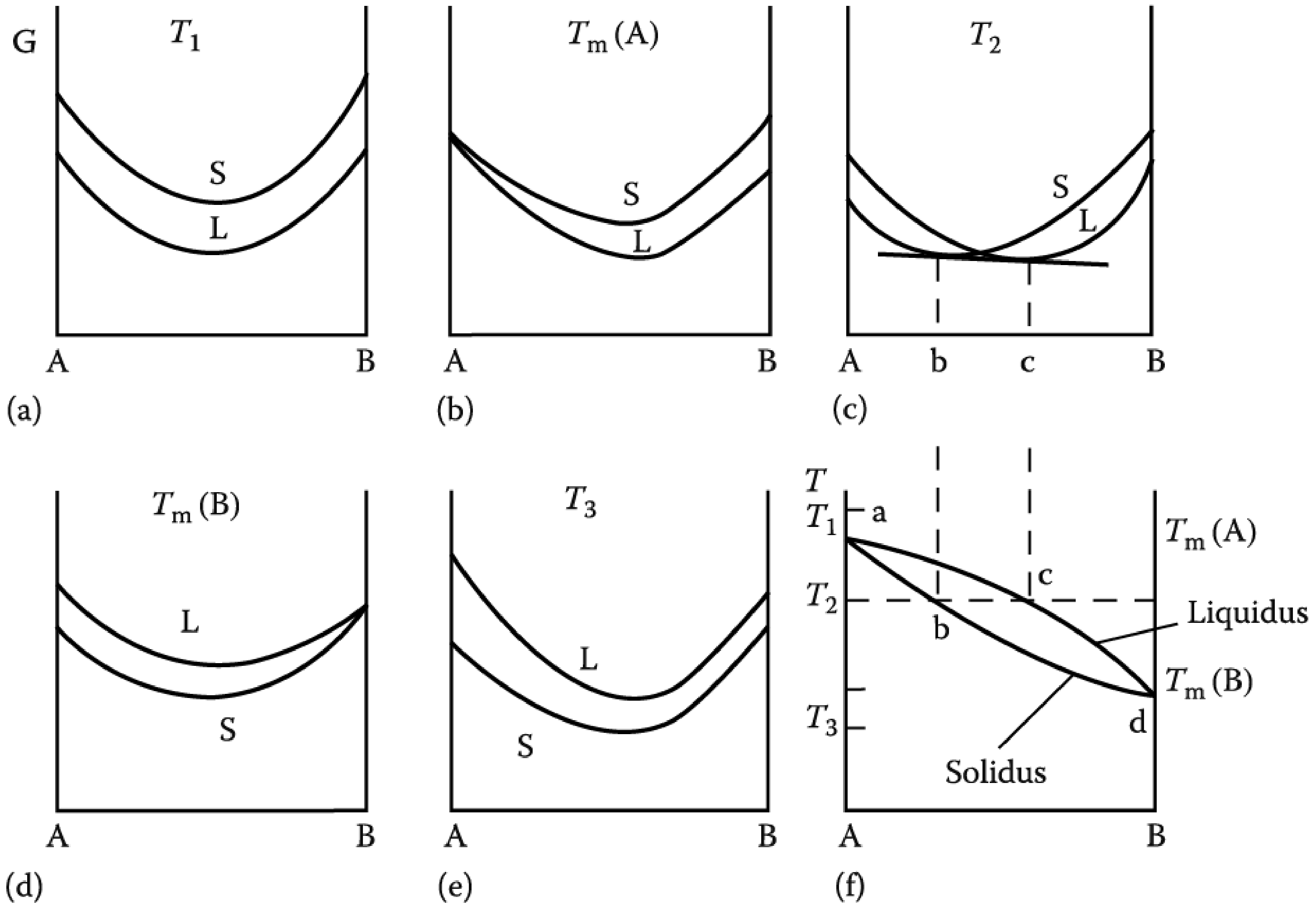
Assumption:

(1) completely miscible in solid and liquid.

(2) Both are ideal soln.

(3) $T_m(A) > T_m(B)$

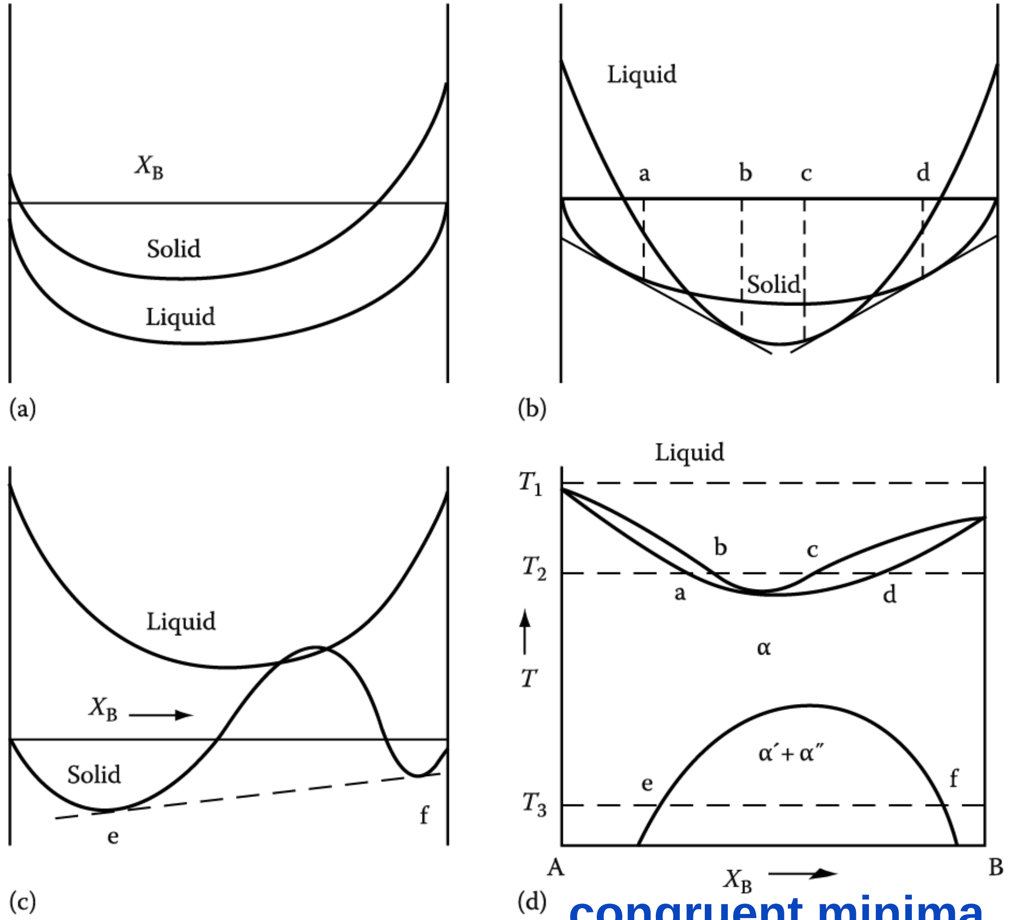
(4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$



1.5 Binary phase diagrams

2) Systems with miscibility gab

$$\Delta H_{mix}^{L} = 0 \qquad \Delta H_{mix}^{S} > 0$$



congruent minima

How to characterize G^s mathematically in the region of miscibility gap between e and f ?

2) Variant of the simple phase diagram

$$\Delta H_{mix} < 0$$

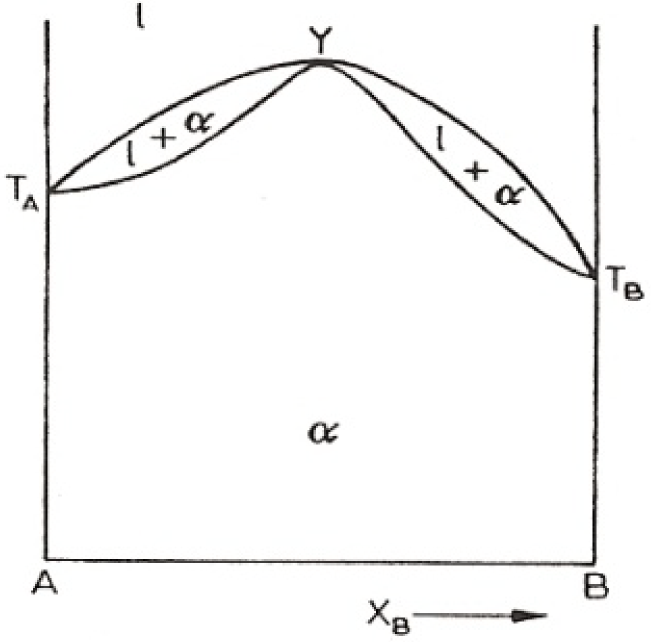


Fig. 32. Phase diagram with a maximum in the liquidus.

congruent maxima

$$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$$

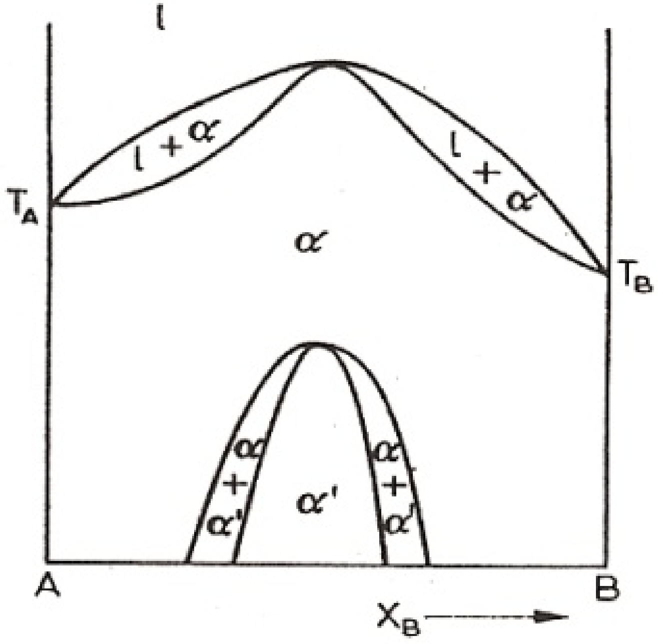


Fig. 33. Appearance of an ordered α′ phase at low temperatures.

1.5 Binary phase diagrams

4) Simple Eutectic Systems $\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} >> 0$

- $\Delta H_m >> 0$ and the miscibility gap extends to the melting temperature. (when both solids have the same structure.)

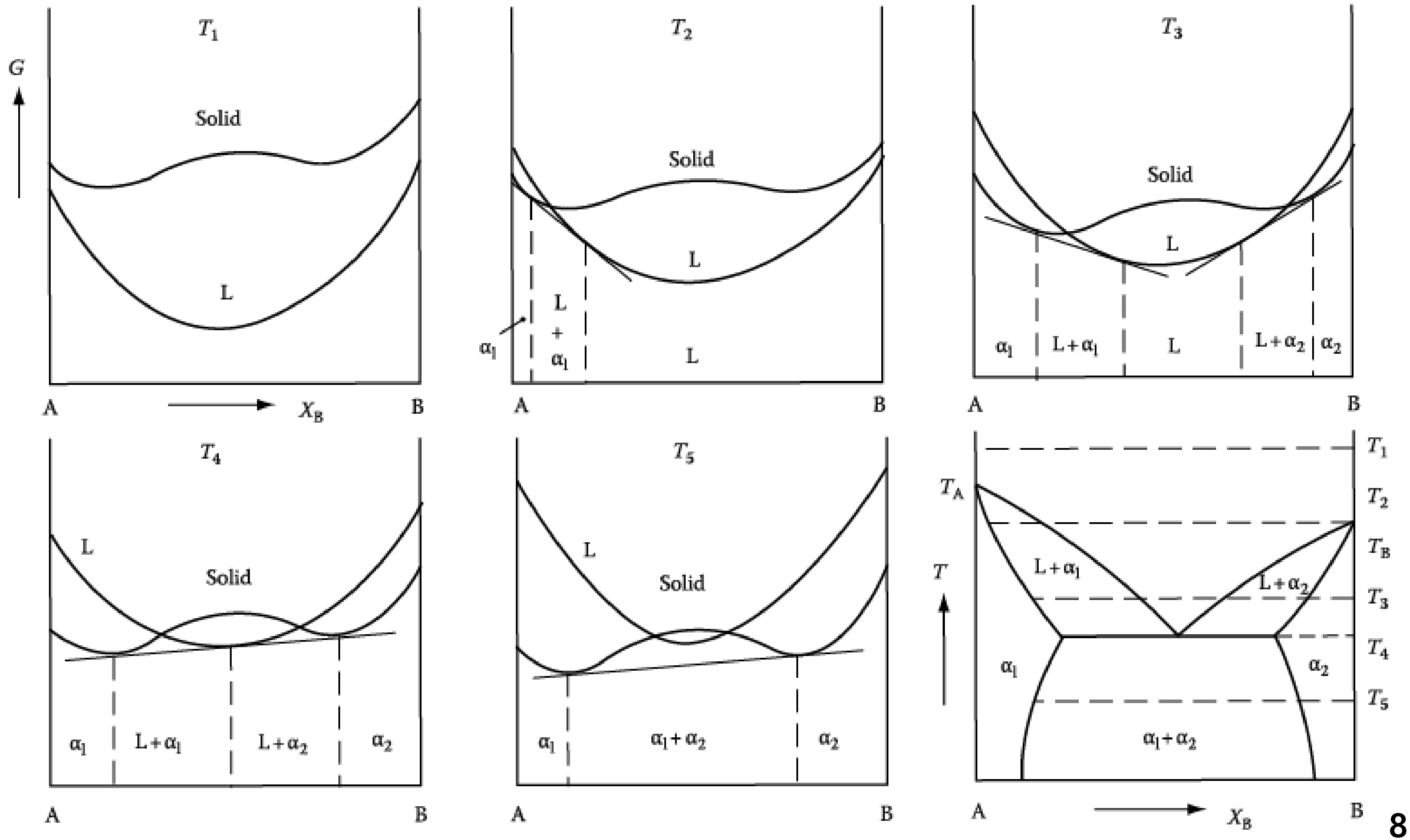


Fig. 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure.

(when each solid has the different crystal structure.)

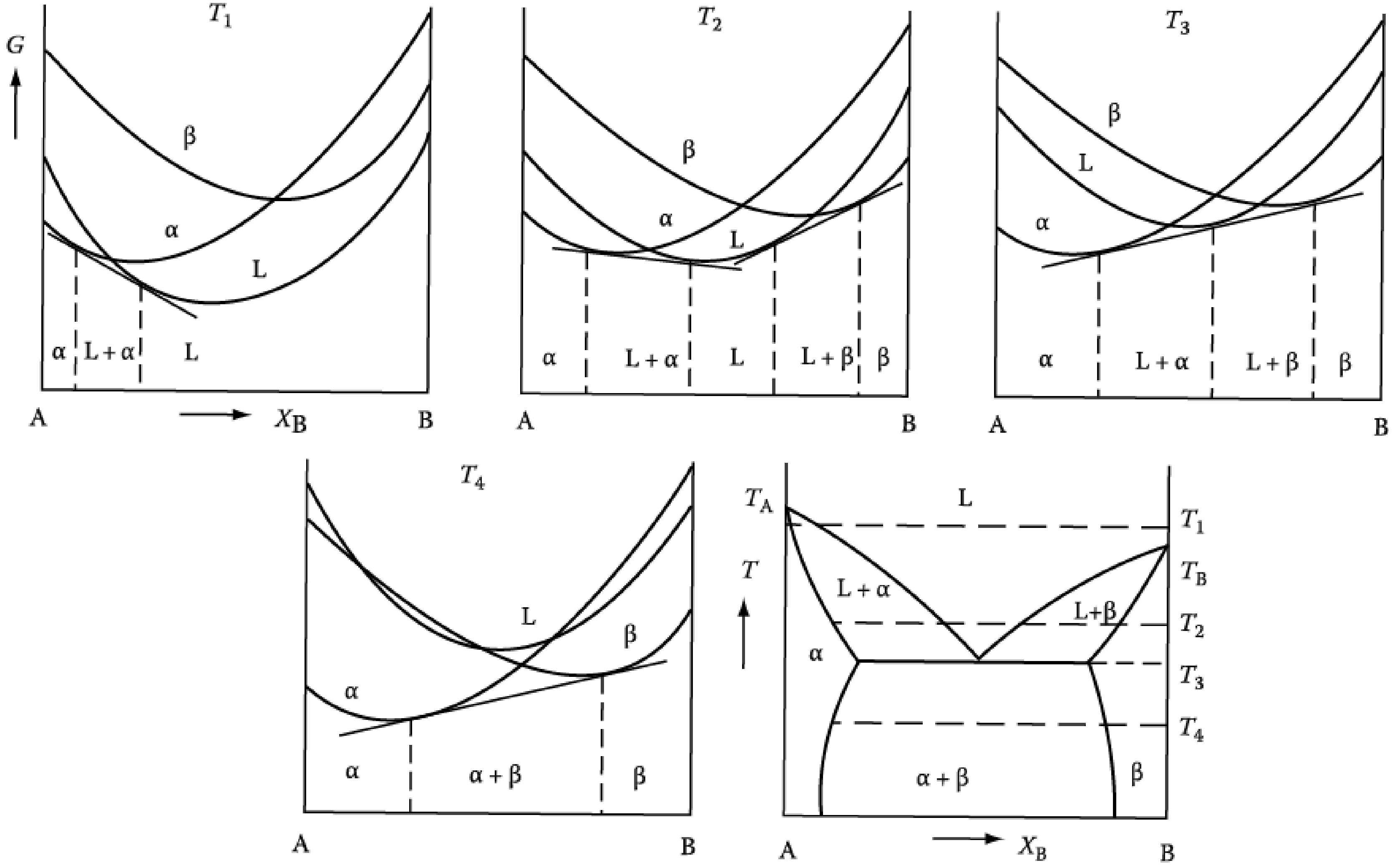
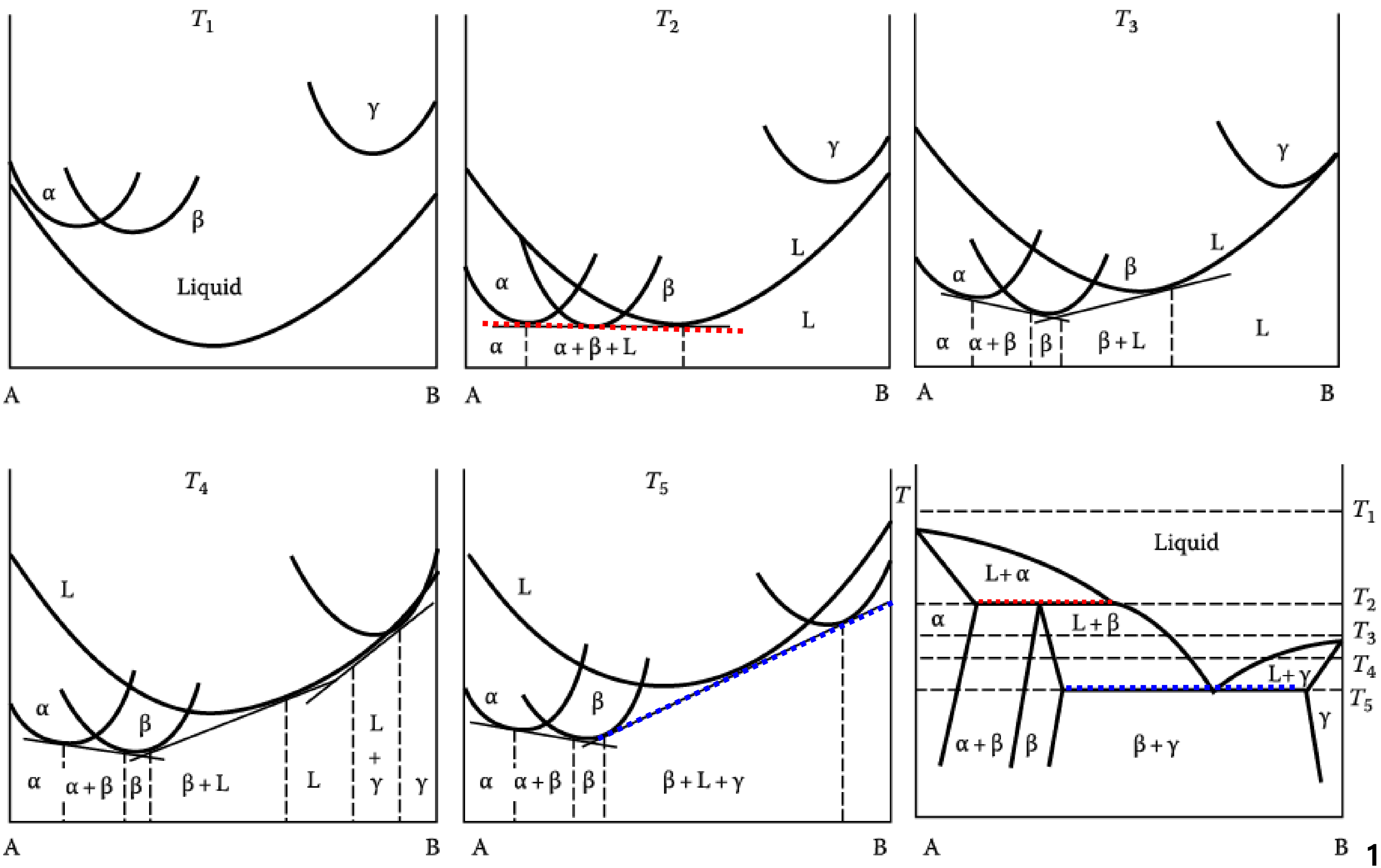


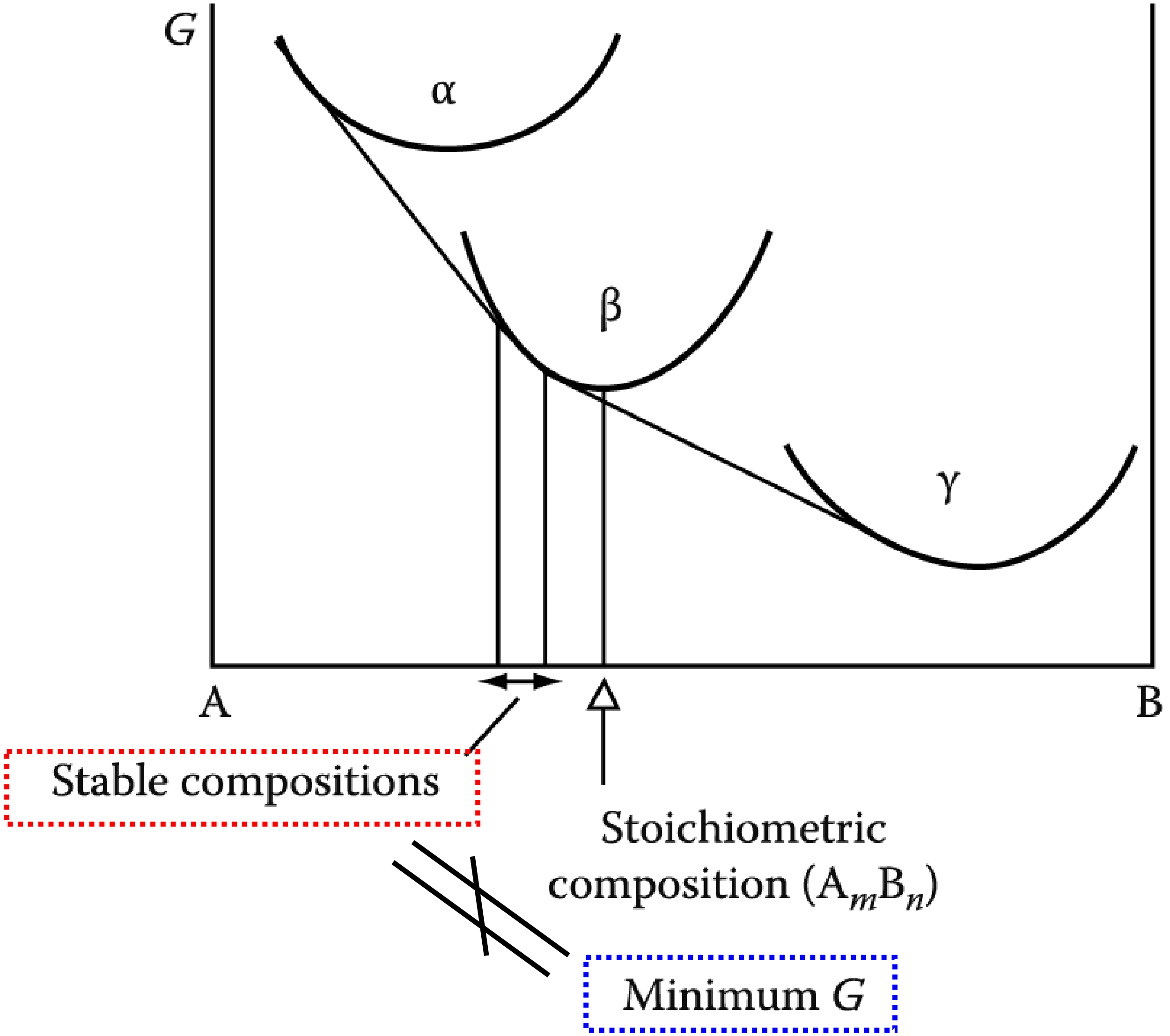
Fig. 1.32 The derivation of a eutectic phase diagram where each solid phases has a different crystal structure.

1.5 Binary phase diagrams

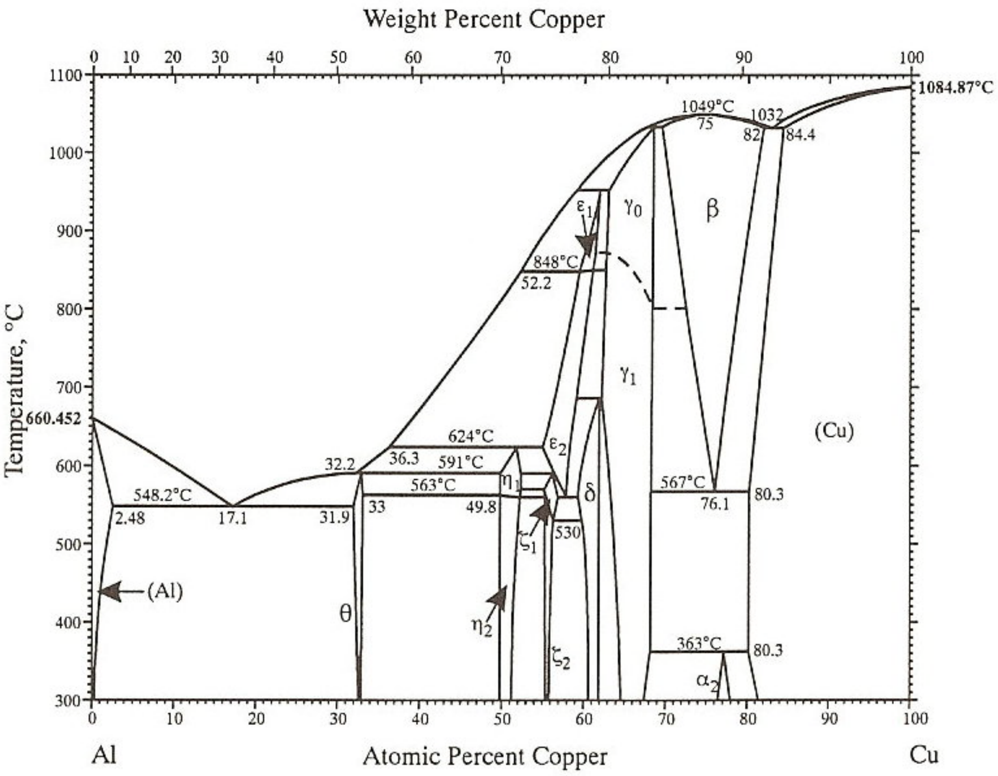
5) Phase diagrams containing intermediate phases

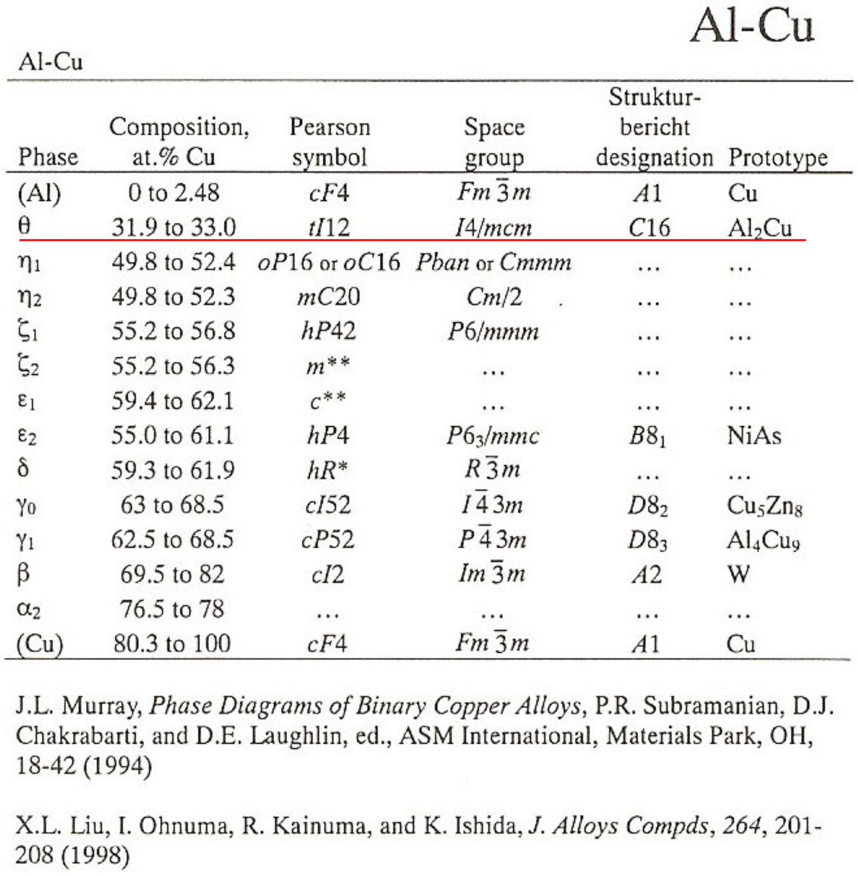


5) Phase diagrams containing intermediate phases



θ phase in the Cu-Al system is usually denoted as $CuAl_2$ although the composition $X_{Cu}=1/3$, $X_{Al}=2/3$ is not covered by the θ field on the phase diagram.





Al-Cu

Al-Cu

Phase	Composition, at.% Cu	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Al)	0 to 2.48	*cF*4	$Fm\bar{3}m$	*A*1	Cu
θ	31.9 to 33.0	*tI*12	*I*4/*mcm*	*C*16	Al_2Cu
η1	49.8 to 52.4	*oP*16 or *oC*16	*Pban* or *Cmmm*	…	…
η2	49.8 to 52.3	*mC*20	*Cm*/2	…	…
ζ1	55.2 to 56.8	*hP*42	*P*6/*mmm*	…	…
ζ2	55.2 to 56.3	*m***	…	…	…
ε1	59.4 to 62.1	*c***	…	…	…
ε2	55.0 to 61.1	*hP*4	$P6_3/mmc$	$B8_1$	NiAs
δ	59.3 to 61.9	*hR**	$R\bar{3}m$	…	…
γ0	63 to 68.5	*cI*52	$I\bar{4}3m$	$D8_2$	Cu_5Zn_8
γ1	62.5 to 68.5	*cP*52	$P\bar{4}3m$	$D8_3$	Al_4Cu_9
β	69.5 to 82	*cI*2	$Im\bar{3}m$	*A*2	W
α2	76.5 to 78	…	…	…	…
(Cu)	80.3 to 100	*cF*4	$Fm\bar{3}m$	*A*1	Cu

J.L. Murray, *Phase Diagrams of Binary Copper Alloys*, P.R. Subramanian, D.J. Chakrabarti, and D.E. Laughlin, ed., ASM International, Materials Park, OH, 18-42 (1994)

X.L. Liu, I. Ohnuma, R. Kainuma, and K. Ishida, *J. Alloys Compds*, *264*, 201-208 (1998)

Summary I : Binary phase diagrams

1) Simple Phase Diagrams

Both are ideal soln. → 1) Variation of temp.: $G^L > G^S$ 2) Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

2) Systems with miscibility gap

$$\Delta H^L_{mix} = 0 \qquad \Delta H^S_{mix} > 0$$

1)Variation of temp.: $G^L > G^S$ 2)Decrease of curvature of G curve + Shape change of G curve by H

4) Simple Eutectic Systems

$$\Delta H^L_{mix} = 0 \qquad \Delta H^S_{mix} >> 0$$

→ miscibility gap extends to the melting temperature.

3) Ordered Alloys

$$\Delta H^L_{mix} = 0 \qquad \Delta H^S_{mix} < 0$$

$\Delta H_{mix} < 0$ → A atoms and B atoms like each other. → Ordered alloy at low T

$\Delta H_{mix} << 0$ → The ordered state can extend to the melting temperature.

5) Phase diagrams containing intermediate phases

Stable composition ≠ Minimum G with stoichiometric composition

Contents for previous class

- Equilibrium in Heterogeneous Systems

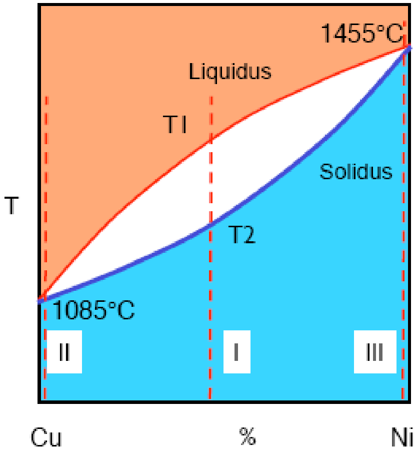
$G_0^{\beta} > G_0^{\alpha} > G_0^{\alpha+\beta}$ → **α + β separation** → **unified chemical potential**

- Binary phase diagrams

1) Simple Phase Diagrams

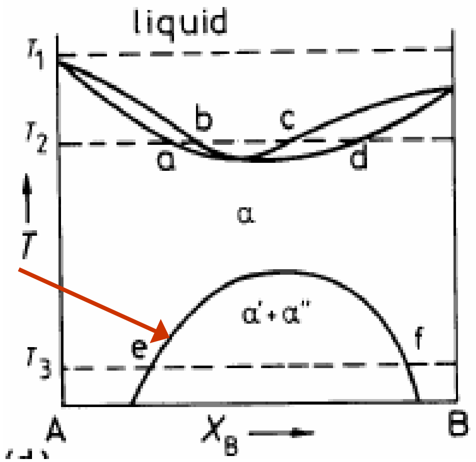
$\Delta H_{mix}^{L} = 0 \ \Delta H_{mix}^{S} = 0$

Assume: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.



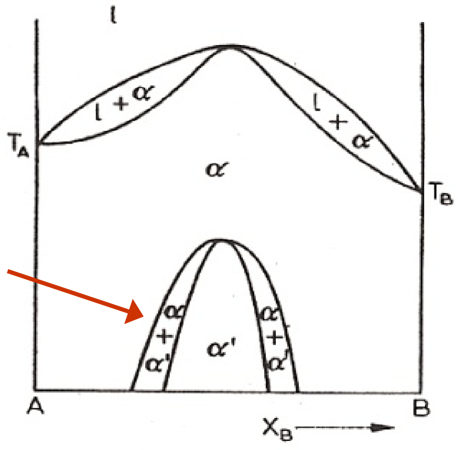
2) Variant of the simple phase diagram

$\Delta H_{mix}^{\alpha} > \Delta H_{mix}^{l} > 0$



miscibility gab

$\Delta H_{mix}^{\alpha} < \Delta H_{mix}^{l} < 0$



Ordered phase

Contents for today's class

- Gibbs Phase Rule $F = C - P + 1$ (constant pressure)
- Effect of Temperature on Solid Solubility
- Equilibrium Vacancy Concentration
- Influence of Interfaces on Equilibrium
- Gibbs-Duhem Equation: Be able to calculate the change in chemical potential that result from a change in alloy composition.

Q1: “Gibbs Phase Rule”?

Gibbs' Phase Rule allows us to construct phase diagram to represent and interpret phase equilibria in heterogeneous geologic systems.

$F = C - P + 1$ **(constant pressure)**

The Gibbs Phase Rule

Degree of freedom **(number of variables that can be varied independently)**

= the number of variables – the number of constraints

- Number of phases : p, number of components : c,
- # of controllable variable : composition (c-1)p, temperature : p, pressure : p
- # of restrictions :

(p-1)c from chemical equilibrium $\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \cdots = \mu_i^{p}$

p-1 from thermal equilibrium $T^{\alpha} = T^{\beta} = T^{\gamma} = \cdots = T^{p}$

p-1 from mechanical equilibrium $P^{\alpha} = P^{\beta} = P^{\gamma} = \cdots = P^{p}$

- Number of variable can be controlled with maintaining equilibrium

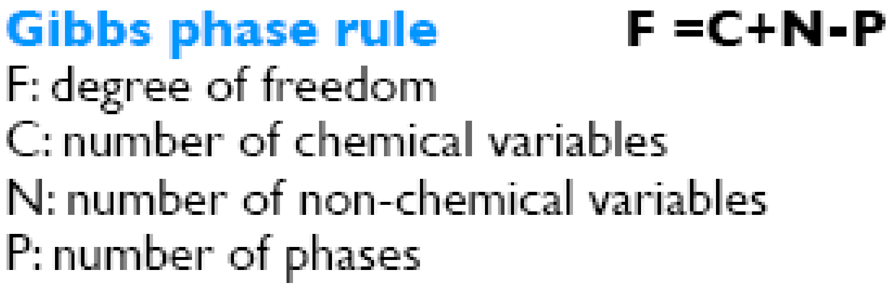
$$f = \boxed{(c-1)p + p + p} \boxed{- (p-1)c - (p-1) - (p-1)} = c - p + 2$$

$$\boxed{f = c - p + 2}$$

- If pressure is constant : $f = (c-1)p + p - (p-1)c - (p-1) = \boxed{c - p + 1}$

The Gibbs Phase Rule

In chemistry, Gibbs' phase rule describes the possible number of degrees of freedom (F) in a closed system at equilibrium, in terms of the number of separate phases (P) and the number of chemical components (C) in the system. It was deduced from thermodynamic principles by Josiah Willard Gibbs in the 1870s.



Gibbs phase rule $F = C + N - P$

F: degree of freedom
C: number of chemical variables
N: number of non-chemical variables
P: number of phases

In general, Gibbs' rule then follows, as:

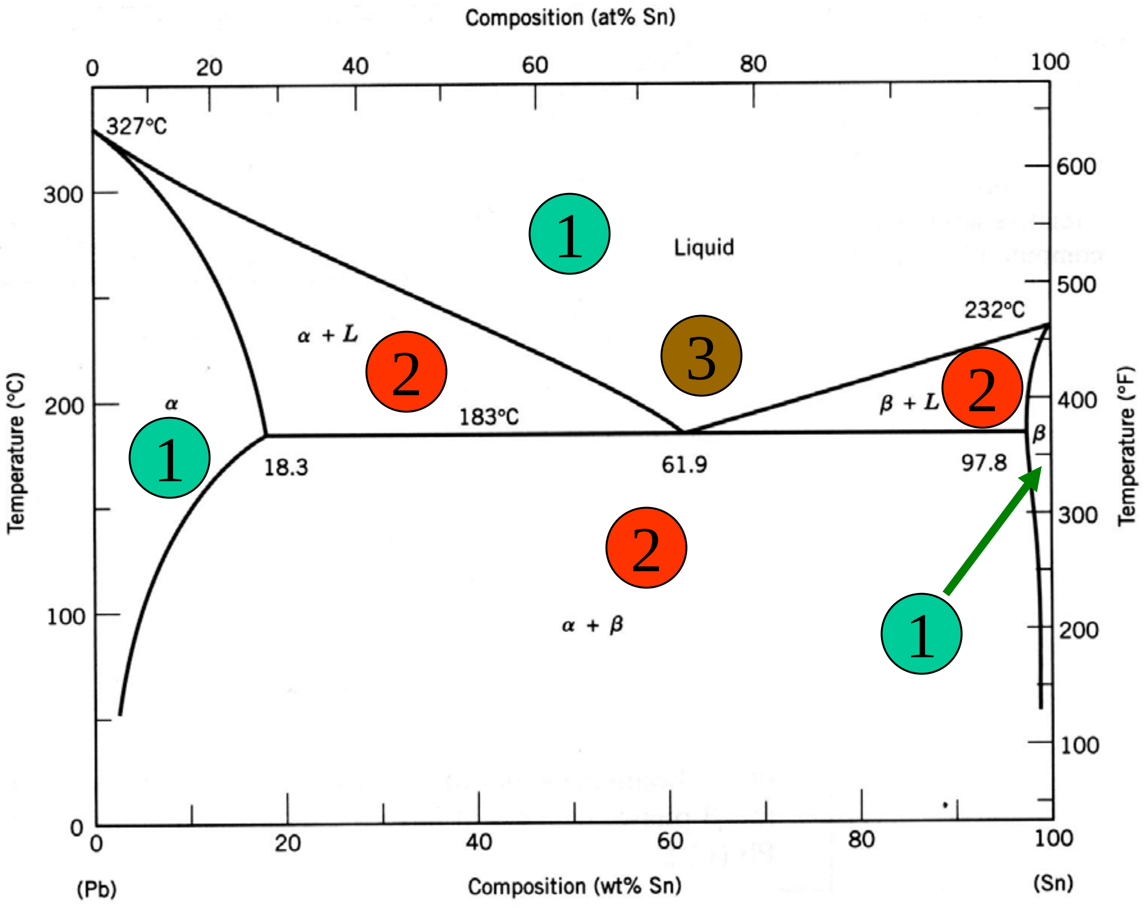
$$F = C - P + 2$$ (from T, P).

From Wikipedia, the free encyclopedia

The Gibbs Phase Rule

For Constant Pressure,

P + F = C + 1



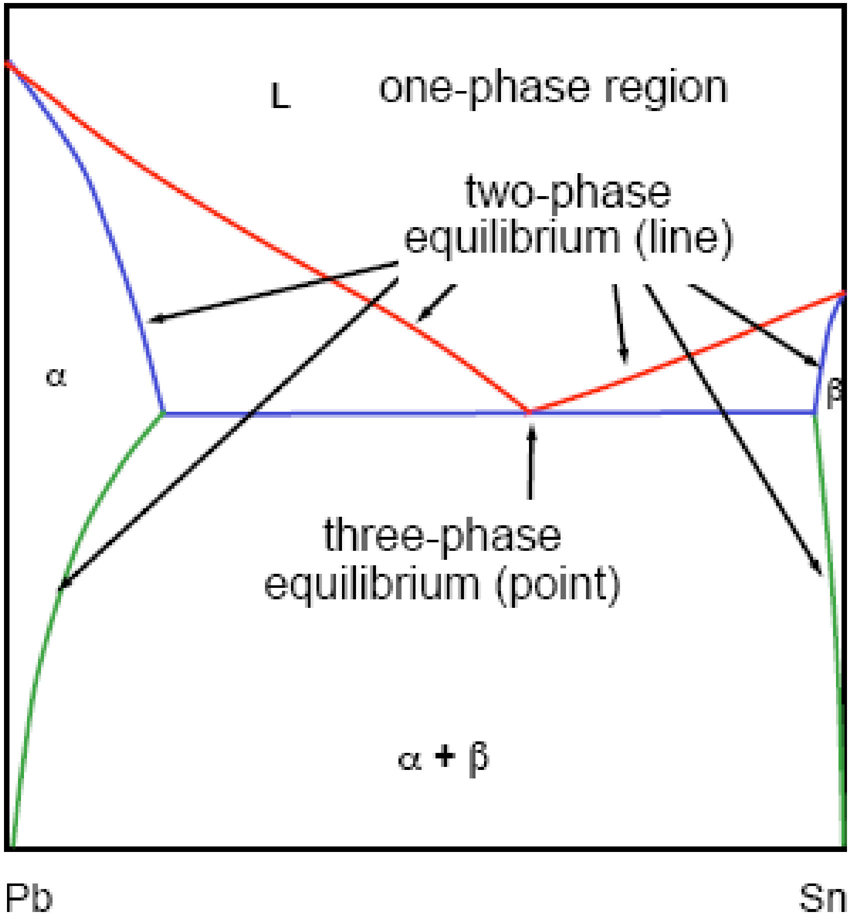
① **single phase**
F = C - P + 1
= 2 - 1 + 1
= 2
can vary T and composition independently

② **two phase**
***F = C - P* + 1**
= 2 - 2 + 1
= 1
can vary T *or* composition

③ **eutectic point**
F = C - P + 1
= 2 - 3 + 1
= 0
can’t vary T or composition

The Gibbs Phase Rule

Application of Gibbs phase rule:
For a binary system at ambient pressure:
C=2 (2 elements)
N=1 (temperature, no pressure)
For single phase: F=2: % and T
(a region)
For a 2-phase equilibrium: F=1:
% or T (a line)
For a 3-phase equilibrium: F=0, (invariant point)



Q2: “Effect of Temperature on Solid Solubility”?

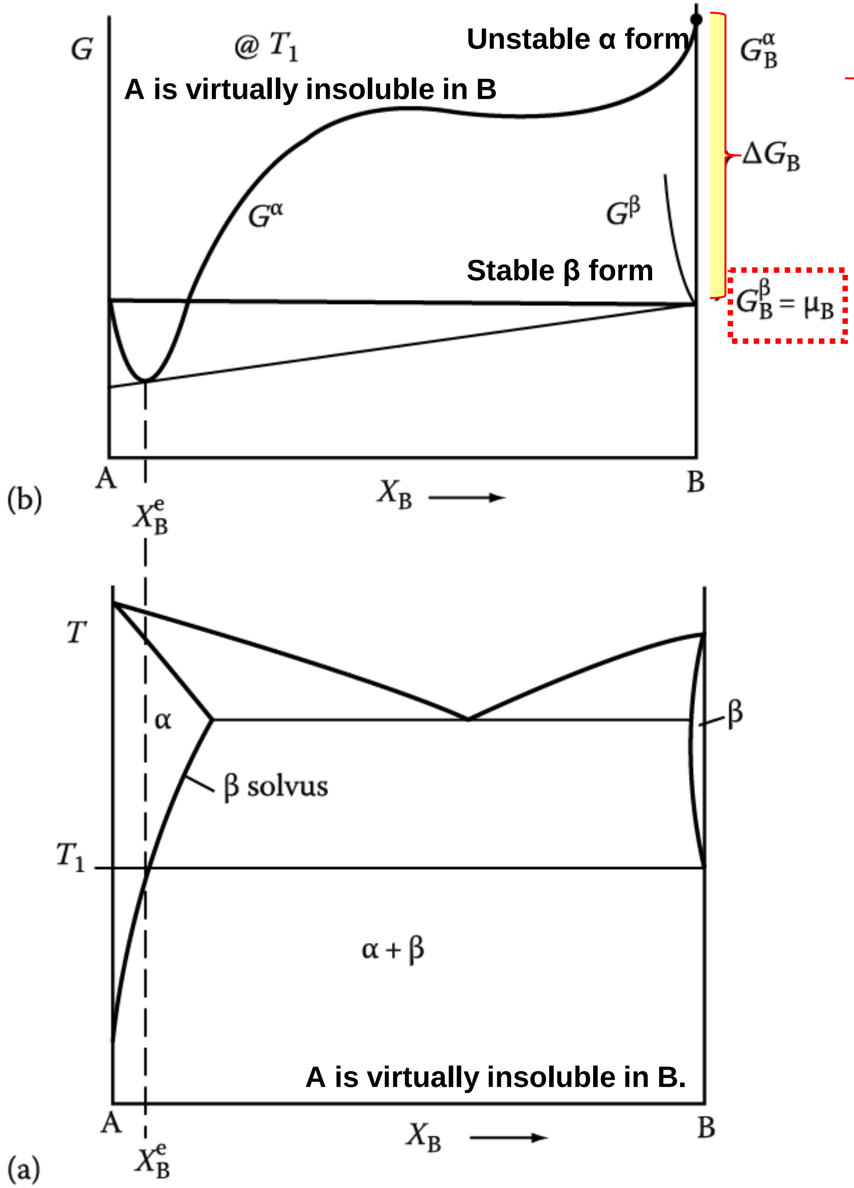
$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$

a) $T\uparrow \Rightarrow X_B^e\uparrow$

b) X_B^e can never be equal to zero.

1.5.7 Effect of T on solid solubility

$$\boxed{T\uparrow \;\Rightarrow\; X_B^e\uparrow}$$



$$\mu_B^\alpha = {}^oG_B^\alpha + \Omega(1-X_B)^2 + RT\ln X_B = \mu_B^\beta \simeq {}^oG_B^\beta$$

$$\Delta G_B^{\beta\to\alpha} = {}^0G_B^\alpha - {}^oG_B^\beta = {}^oG_B^\alpha - \mu_B^\beta = {}^oG_B^\alpha - \mu_B^\alpha$$

$${}^oG_B^\alpha - \mu_B^\alpha = -\Omega(1-X_B)^2 - RT\ln X_B$$

$$\Delta G_B^{\beta\to\alpha} = -\Omega(1-X_B)^2 - RT\ln X_B$$

$$RT\ln X_B = -\Delta G_B^{\beta\to\alpha} - \Omega(1-X_B)^2$$

$$(here,\ X_B^e << 1)$$

$$RT\ln X_B^e = -\Delta G_B^{\beta\to\alpha} - \Omega$$

$$>> \qquad X_B^e = \exp\left(-\frac{\Delta G_B^{\beta\to\alpha} + \Omega}{RT}\right)$$

$$\Delta G_B^{\beta\to\alpha} = \Delta H_B^{\beta\to\alpha} - T\Delta S_B^{\beta\to\alpha}$$ 이므로

$$X_B^e = \boxed{\exp\left(\frac{\Delta S_B^{\beta\to\alpha}}{R}\right)} \exp\left(-\frac{\boxed{\Delta H_B^{\beta\to\alpha} + \Omega}}{RT}\right)$$

$$\boxed{X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}} \qquad \boxed{T\uparrow \;\Rightarrow\; X_B^e\uparrow}$$

Q : heat absorbed (enthalpy) when 1 mole of β dissolves in A rich α as a dilute solution.

* Limiting forms of eutectic phase diagram

The solubility of one metal in another may be so low.

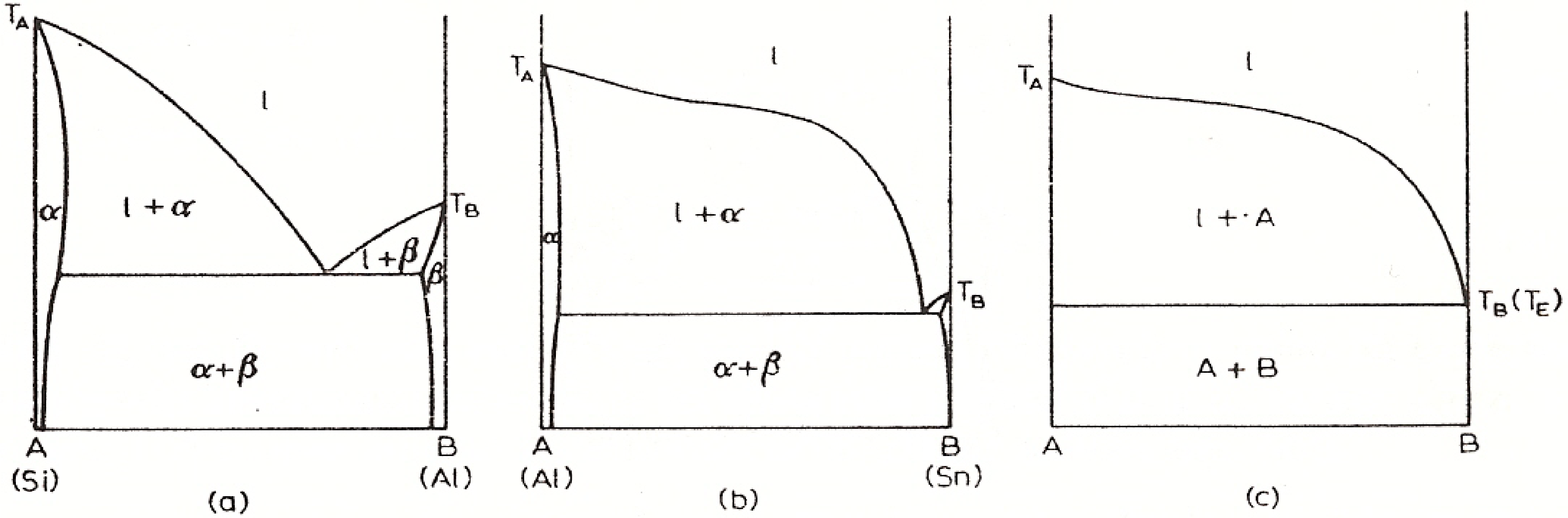


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$

a) $T\uparrow \Rightarrow X_B^e\uparrow$

b) It is interesting to note that, except at absolute zero, X_B^e can never be equal to zero, that is, no two compo-nents are ever completely insoluble in each other.

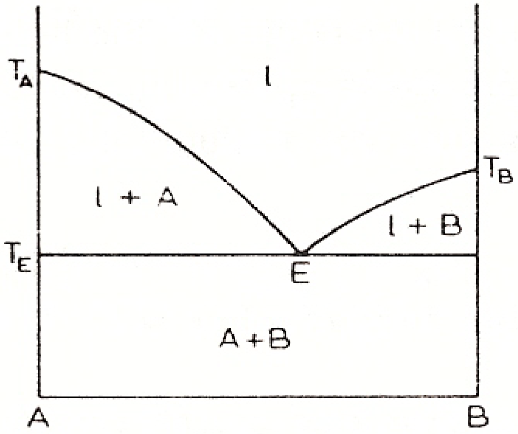
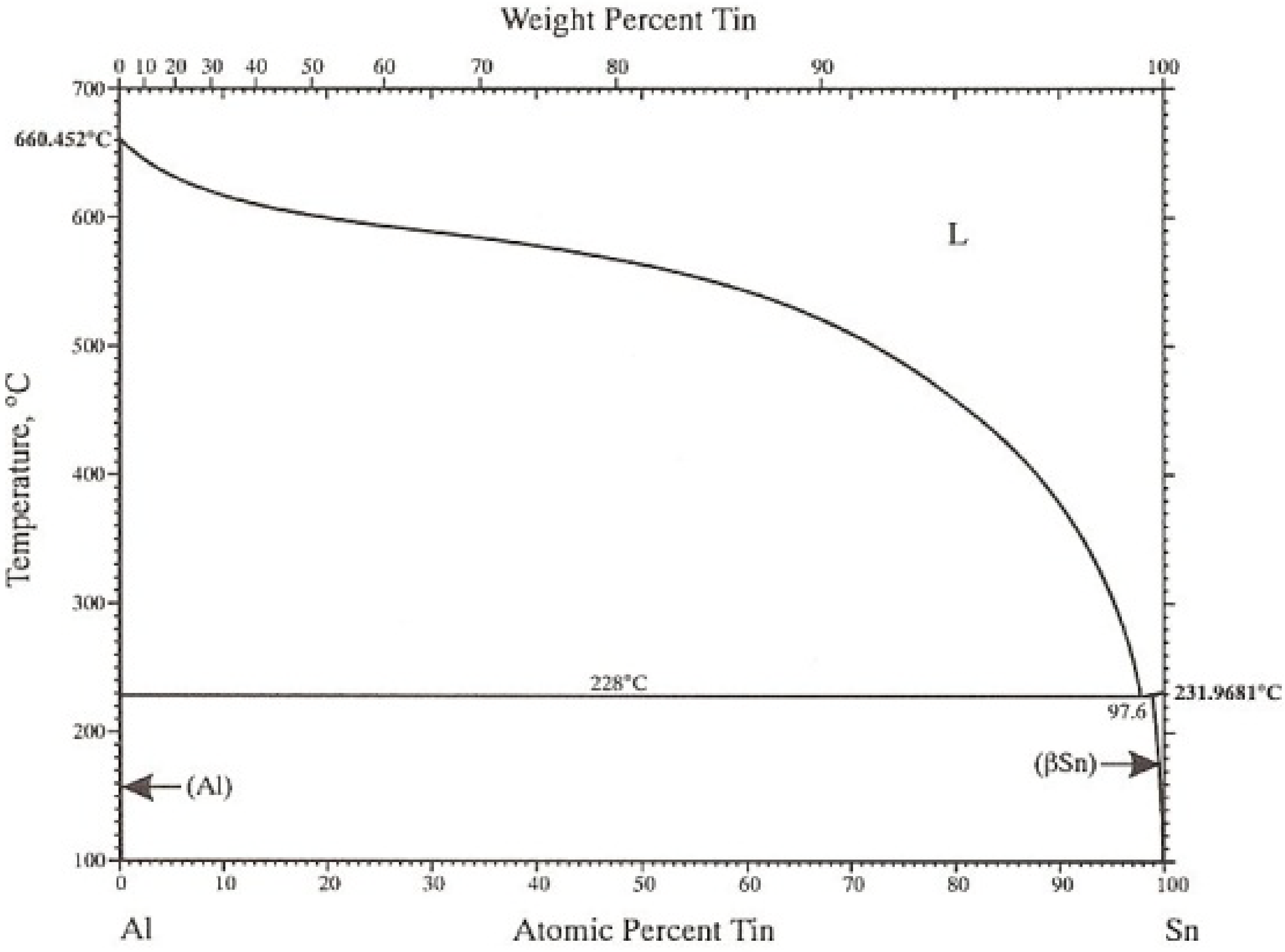


Fig. 54. Impossible form of a binary eutectic phase diagram.


Weight Percent Tin
0
10
20
30
40
50
60
70
80
90
100
700
660.452°C
600
500
400
300
200
100
Temperature, °C
L
228°C
231.9681°C
97.6
(βSn)
(Al)
0
10
20
30
40
50
60
70
80
90
100
Al
Atomic Percent Tin
Sn

Q3: “Equilibrium Vacancy Concentration”?

$$X_V^e = \exp\frac{-\Delta G_V}{RT}$$

1.5.8. Equilibrium Vacancy Concentration

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

G of the alloy will depend on the concentration of vacancies and X_V^e will be that which gives the minimum free energy.

1) Vacancies increase the internal energy of crystalline metal due to broken bonds formation. **(Here, vacancy-vacancy interactions are ignored.)**

$$\Delta H \cong \Delta H_V X_V$$

2) Vacancies increase entropy because they change the **thermal vibration frequency** and also the **configurational entropy**.

Small change due to changes in the vibrational frequencies

“Largest contribution”

- Total entropy change is thus

$$\Delta S = \Delta S_V X_V - \boxed{R\{X_V \ln X_V + (1 - X_V)\ln(1 - X_V)\}}$$

The molar free energy of the crystal containing X_V mol of vacancies

$$\boxed{G = G_A + \Delta G = G_A + \Delta H_V X_V - T\Delta S_V X_V + RT\{X_V \ln X_V + (1 - X_V)\ln(1 - X_V)\}}$$

➡ **With this information, estimate the equilibrium vacancy concentration.**

Equilibrium concentration X_V^e will be that which gives the minimum free energy.

at equilibrium $$\left(\frac{dG}{dX_V}\right)_{X_V = X_V^e} = 0$$

$$\Delta H_V - T\Delta S_V + RT\ln X_V^e = 0$$

A constant ~3, independent of T

Rapidly increases with increasing T

$$X_V^e = \boxed{\exp\frac{\Delta S_V}{R}} \cdot \exp\frac{-\Delta H_V}{RT}$$

putting $\Delta G_V = \Delta H_V - T\Delta S_V$

$$\boxed{X_V^e = \exp\frac{-\Delta G_V}{RT}}$$

- **In practice, ΔH_V is of the order of 1 eV per atom and X_V^e reaches a value of about 10^{-4}~10^{-3} at the melting point of the solid**

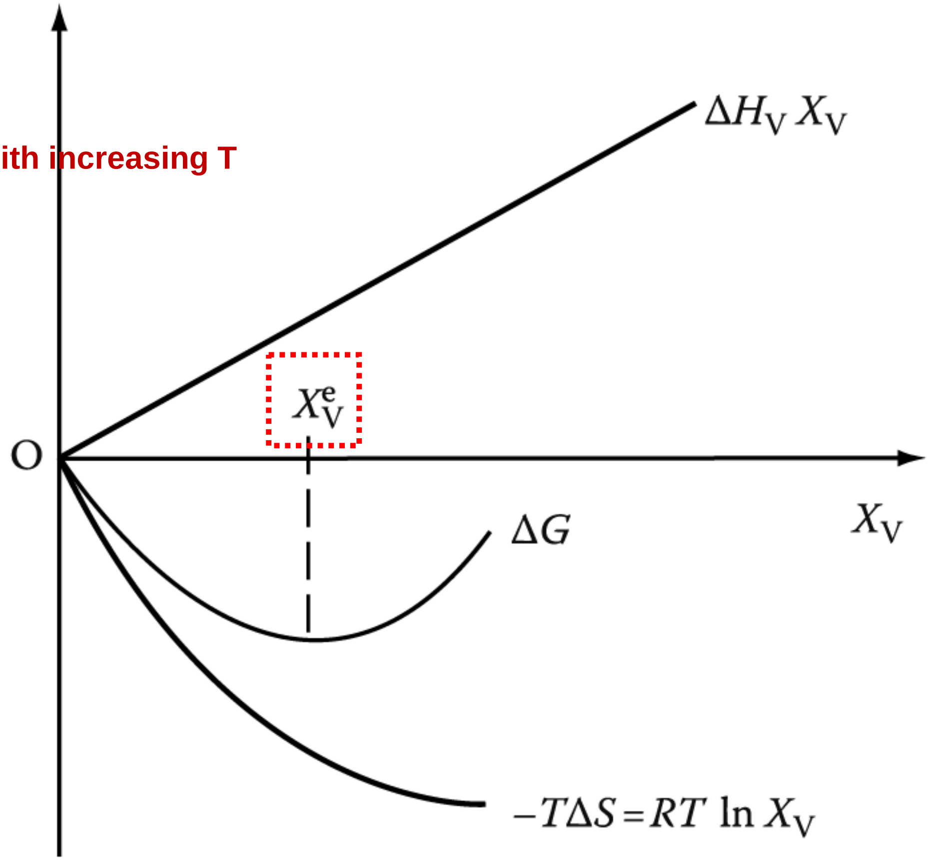


Fig. 1.37 Equilibrium vacancy concentration.

: adjust so as to reduce G to a minimum

Q4: “Influence of Interfaces on Equilibrium”?

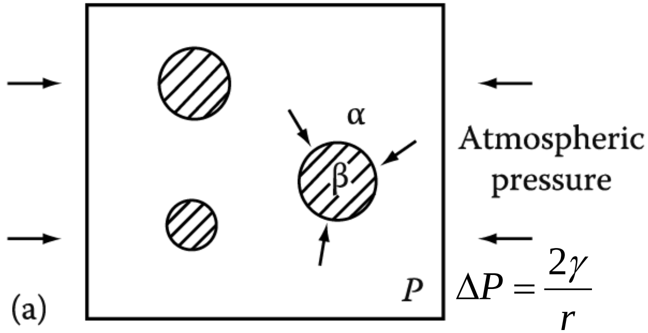
$$\Delta G = \frac{2\gamma V_m}{r}$$ **Gibbs-Thomson effect**

The G curves so far have been based on the molar Gs of infinitely large amounts of material of a perfect single crystal. Surfaces, GBs and interphase interfaces have been ignored.

1.6 Influence of Interfaces on Equilibrium – b) 평형에 미치는 계면의 영향

$$\Delta G = \Delta P \cdot V \Rightarrow \Delta G = \frac{2\gamma V_m}{r}$$

Extra pressure ΔP due to curvature of the α/β



$$\Delta P = \frac{2\gamma}{r}$$

The concept of a pressure difference is very useful <u>for spherical liquid particles</u>, but it is less convenient in solids (often nonspherical shape).

$$dG = \Delta G_\gamma dn = \gamma dA \qquad \Delta G_\gamma = \gamma dA/dn$$

Since $n=4\pi r^3/3V_m$ and $A = 4\pi r^2$ $\Delta G = \frac{2\gamma V_m}{r}$

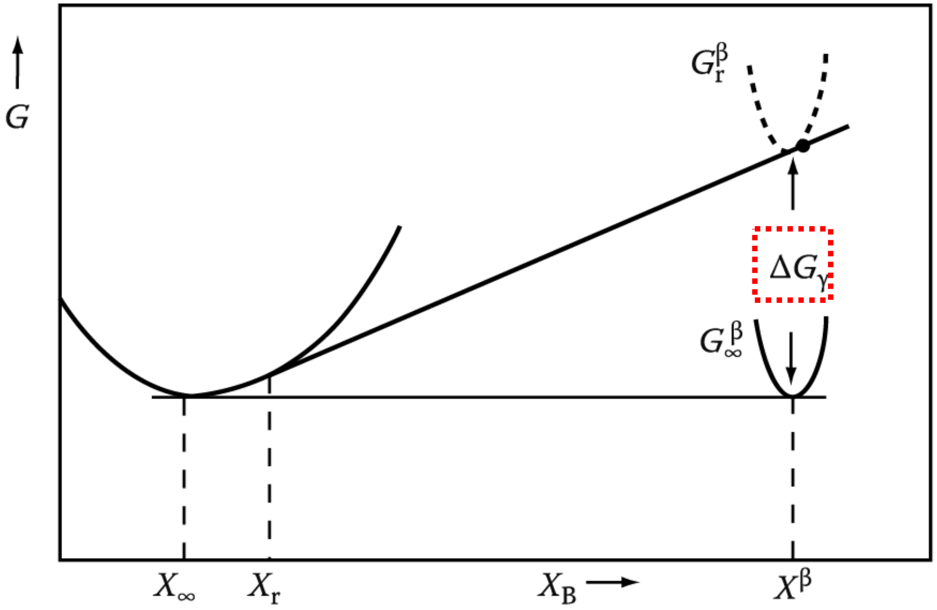


Fig. 1.38 The effect of interfacial E on the solubility of small particle

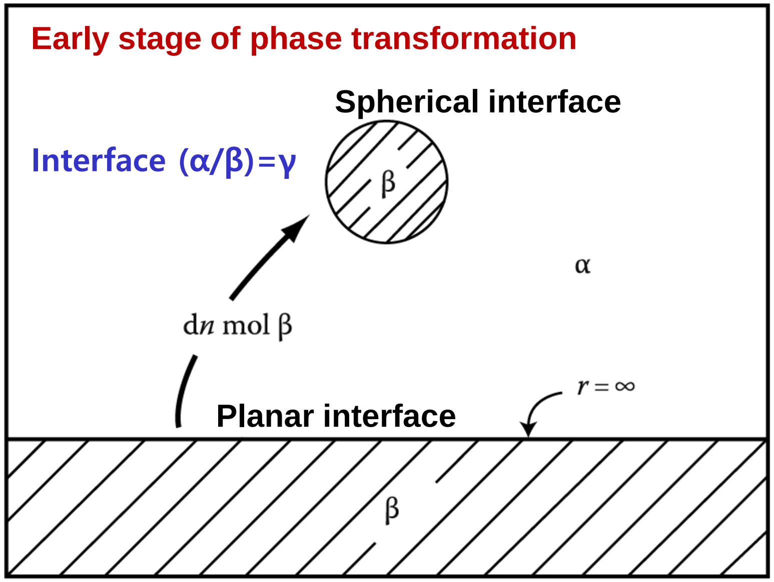


Fig. 1.39 Transfer of dn mol of β from large to a small particle.

Gibbs-Thomson effect (capillarity effect):

Free energy increase due to interfacial energy

$$\boxed{X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}}$$

$$X_B^e = \exp(-\frac{\Delta G_B + \Omega}{RT})$$

$$X_B^{r=\infty} = \exp(-\frac{\Delta G_B + \Omega}{RT})$$

$$X_B^{r=r} = \exp(-\frac{\Delta G_B + \Omega \boxed{- 2\gamma V_m / r}}{RT})$$

$$= X_B^{r=\infty}\exp(\frac{2\gamma V_m}{RTr})$$

Quite large solubility differences can arise for particles in the range r=1-100 nm. However, for particles visible in the light microscope (r>1um) capillarity effects are very small.

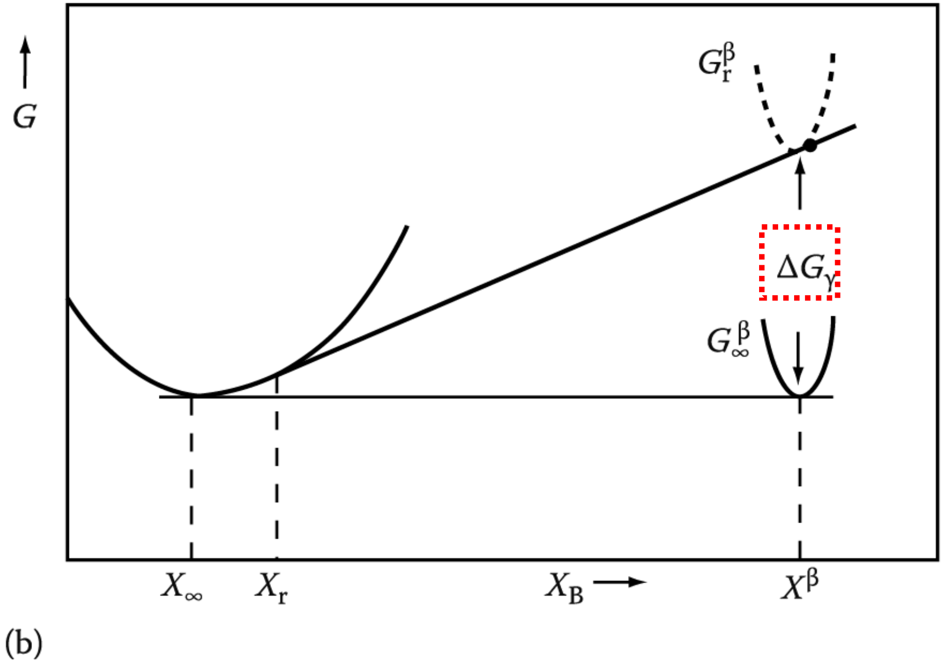


Fig. 1.38 The effect of interfacial energy on the solubility of small particles.

For small values of the exponent,

$$\frac{X_B^{r=r}}{X_B^{r=\infty}} = \exp(\frac{2\gamma V_m}{RTr}) \approx 1 + \frac{2\gamma V_m}{RTr}$$

Ex) **γ=200mJ/m^2, V$_m$=10^{-5} m^3,T=500K**

$$\boxed{\frac{X_r}{X_\infty} = 1 + \frac{1}{r(nm)}}$$

For r=10 nm, solubility~10% increase

Total Free Energy Decrease per Mole of Nuclei $\Delta G_0 = -V\Delta G_V + A\gamma + V\Delta G_s$

: 변태를 위한 전체 구동력, 핵생성을 위한 구동력은 아님

Chapter 5.1

Driving Force for Precipitate Nucleation $\boxed{\alpha \to \alpha + \beta}$ ΔG_V

$$\Delta G_1 = \mu_A^{\alpha} X_A^{\beta} + \mu_B^{\alpha} X_B^{\beta}$$

: Decrease of total free E of system
by removing a small amount of material
with the nucleus composition (X_B^{β}) (P point)

$$\Delta G_2 = \mu_A^{\beta} X_A^{\beta} + \mu_B^{\beta} X_B^{\beta}$$

: Increase of total free E of system
by forming β phase with composition X_B^{β}
(Q point)

$$\boxed{\Delta G_n = \Delta G_2 - \Delta G_1}$$ (length PQ)

$$\boxed{\Delta G_V} = \frac{\Delta G_n}{V_m} \quad \textit{per unit volume of } \beta$$

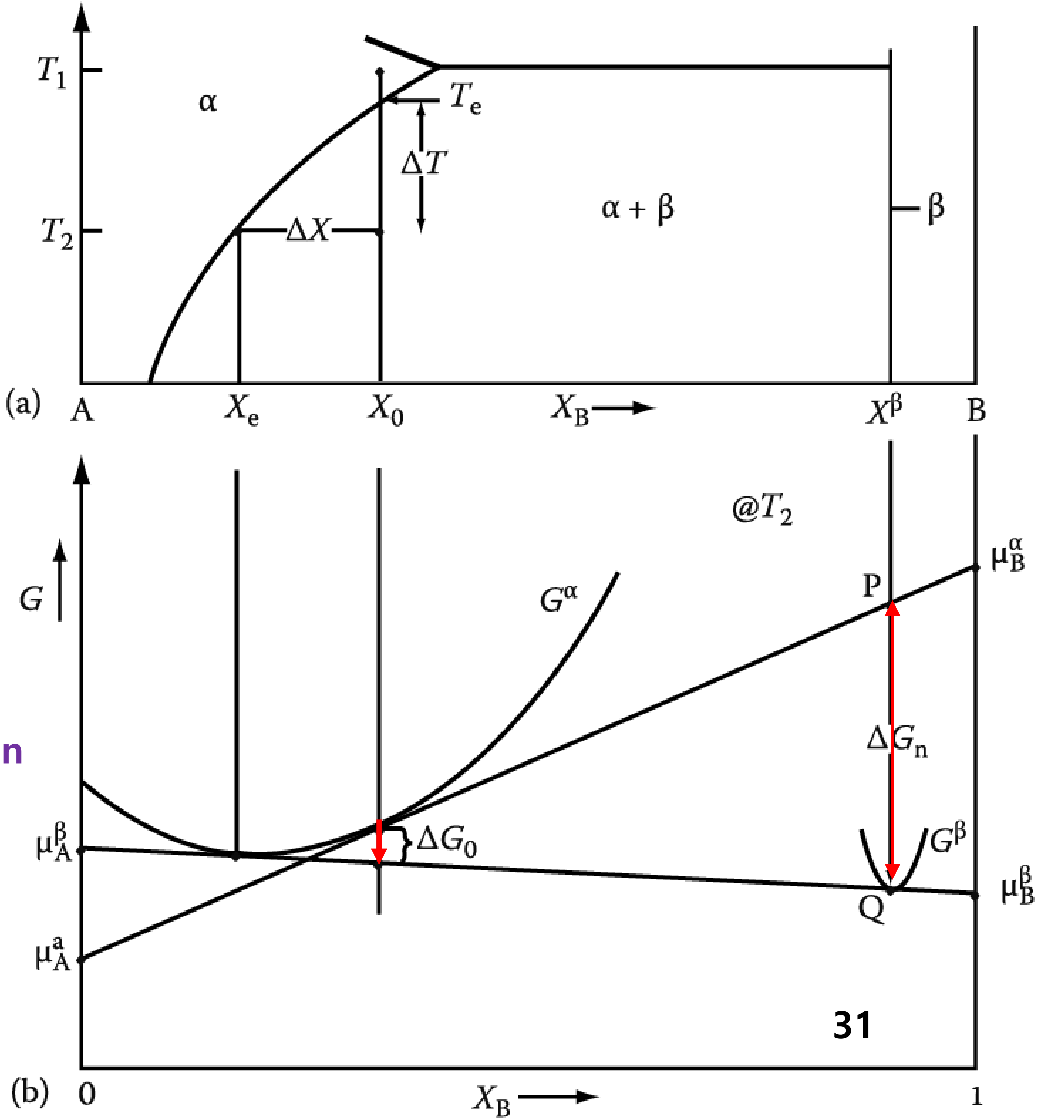
: driving force for β precipitation

For dilute solutions,

$$\Delta G_V \propto \Delta X \quad \text{where } \Delta X = X_0 - X_e$$

$$\boxed{\Delta G_V \propto \Delta X \propto \Delta T}$$

∝undercooling below T_e



Q5: “Gibbs-Duhem Equation”?

: Be able to calculate the change in chemical potential that result from a change in alloy composition.

$$X_A d\mu_A + X_B d\mu_B = 0$$

$$\boxed{X_A X_B \frac{d^2G}{dX^2} = RT\left\{1 + \frac{d\ln\gamma_A}{d\ln X_A}\right\} = RT\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}}$$

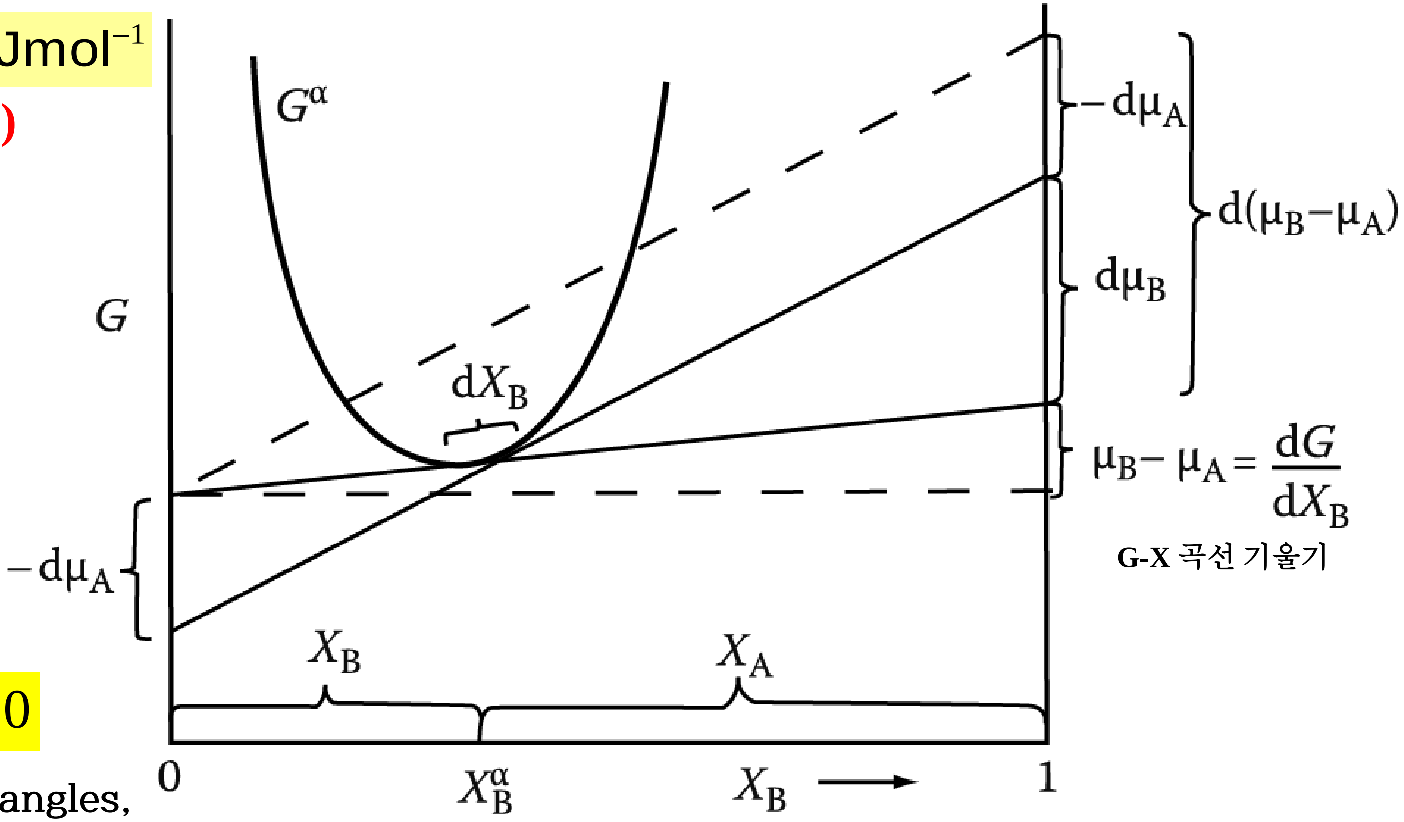
합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화**(dμ)** 를 계산

1.8 Additional Thermodynamic Relationships for Binary Solutions

Gibbs-Duhem equation: Calculate the change in (dμ) that results from a change in (dX)

$$G = \mu_A X_A + \mu_B X_B \quad \mathrm{Jmol^{-1}}$$

(T, P: constant)



G-X 곡선 기울기

Gibbs-Duhem Equation

$$X_A d\mu_A + X_B d\mu_B = 0$$

Comparing two similar triangles,

$$-\frac{d\mu_A}{X_B} = \frac{d\mu_B}{X_A} = \frac{d(\mu_B-\mu_A)}{1} \Leftarrow \frac{dG}{dX_B} = \frac{\mu_B-\mu_A}{1},$$

d^2G/dX^2

($\because d^2G/dX_B^2 = d^2G/dX_A^2$)

Substituting right side Eq.
& Multiply X_AX_B

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2} dX_B$$

Eq. 1.65

Additional Thermodynamic Relationships for Binary Solutions

The Gibbs-Duhem Equation

합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(**dμ**) 를 계산

be able to calculate the change in chemical potential (dμ) that result from a change in alloy composition (dX).

① For a regular solution,

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$$\frac{d^2G}{dX^2} = \frac{RT}{X_A X_B} - 2\Omega$$

For a ideal solution, $\Omega = 0$,

$$\frac{d^2G}{dX^2} = \frac{RT}{X_A X_B}$$

② **Different form**
Eq. 1.65

$$\mu_B = G_B + RT \ln a_B = G_B + RT \ln \gamma_B X_B$$

$$\xrightarrow{\gamma_B = a_B/X_B}$$

Differentiating
With respect to X_B,

$$\boxed{\frac{d\mu_B}{dX_B}} = \frac{RT}{X_B}\left\{1 + \frac{X_B}{\gamma_B}\frac{d\gamma_B}{dX_B}\right\} = \frac{RT}{X_B}\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

$$\boxed{\frac{d\mu_B}{dX_B}} = \frac{RT}{X_B}\left\{1+\frac{X_B}{\gamma_B}\frac{d\gamma_B}{dX_B}\right\} = \frac{RT}{X_B}\left\{1+\frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

Eq. 1.69

a similar relationship can be derived for $d\mu_A/dX_A$

$$-X_A d\mu_A = X_B d\mu_B = RT\left\{1+\frac{d\ln\gamma_A}{d\ln X_A}\right\}dX_B = RT\left\{1+\frac{d\ln\gamma_B}{d\ln X_B}\right\}dX_B$$

Eq. 1.70

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2}dX_B$$

Eq. 1.65

The Gibbs-Duhem Equation

$$X_A d\mu_A + X_B d\mu_B = 0$$

$$X_A X_B \frac{d^2G}{dX^2} = RT\left\{1+\frac{d\ln\gamma_A}{d\ln X_A}\right\} = RT\left\{1+\frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

be able to calculate the change in chemical potential (dμ) that result from a change in alloy composition (dX).

Summary II: Binary phase diagrams

- **Gibbs Phase Rule** F = C − P + 1 (constant pressure)

  Gibbs' Phase Rule allows us to construct phase diagram to represent and interpret phase equilibria in heterogeneous geologic systems.

- **Effect of Temperature on Solid Solubility**

$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$

a) $T\uparrow \Rightarrow X_B^e\uparrow$

b) X_B^e can never be equal to zero.

- **Equilibrium Vacancy Concentration**

$$X_V^e = \exp\frac{-\Delta G_V}{RT}$$

- **Influence of Interfaces on Equilibrium**

$$\Delta G = \frac{2\gamma V_m}{r}$$

Gibbs-Thomson effect

- **Gibbs-Duhem Equation:** $X_A d\mu_A + X_B d\mu_B = 0$

: Be able to calculate the change in chemical potential that result from a change in alloy composition.

$$X_A X_B \frac{d^2G}{dX^2} = RT\left\{1+\frac{d\ln\gamma_A}{d\ln X_A}\right\} = RT\left\{1+\frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(**dμ**) 를 계산