

2023 Fall

“Phase Transformation *in* Materials”

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Chapter 1

Thermodynamics and Phase Diagrams

- **Equilibrium** $dG = 0$ Phase Transformation
 $\Delta G = G_2 - G_1 < 0$

Lowest possible value of G

No desire to change ad infinitum

- **Single component system**

Gibbs Free Energy as a Function of **Temp.** and **Pressure**

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$$

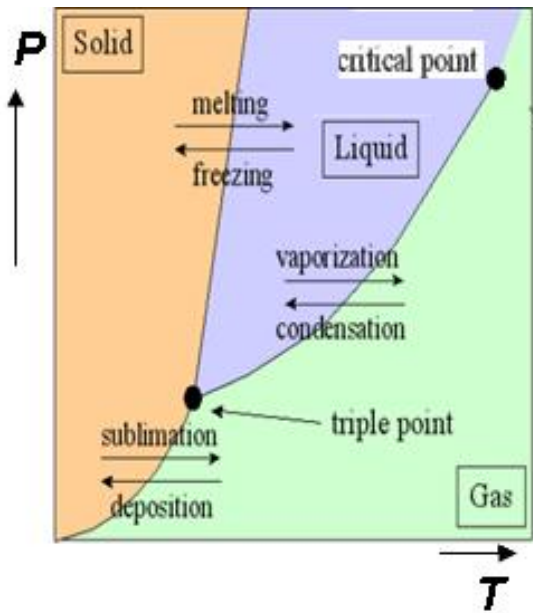
Clausius-Clapeyron Relation

Driving force for solidification

$$\Delta G = \frac{L\Delta T}{T_m}$$

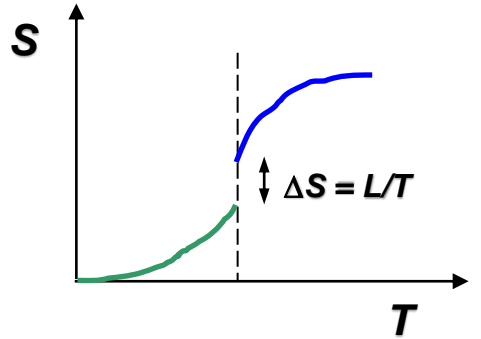
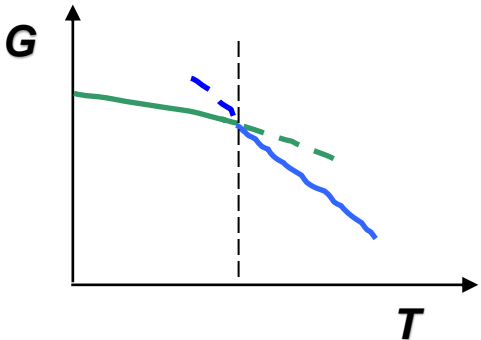
- **Classification of phase transition**

First order transition: **CDD**/Second order transition: **CCD**

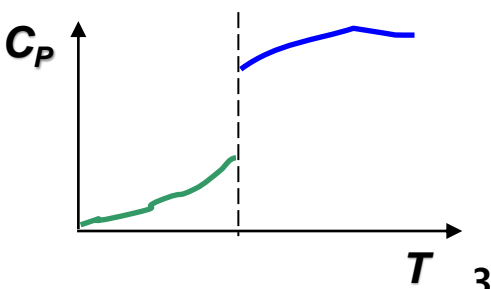


The First-Order Transitions

Latent heat
 Energy barrier
 Discontinuous entropy, heat capacity



$$C_P = T \left(\frac{\partial S}{\partial T} \right)_{P,N}$$



• First Order Phase Transition at T_T :

- G is **continuous** at T_T
- First derivatives of G (V, S, H) are **discontinuous** at T_T

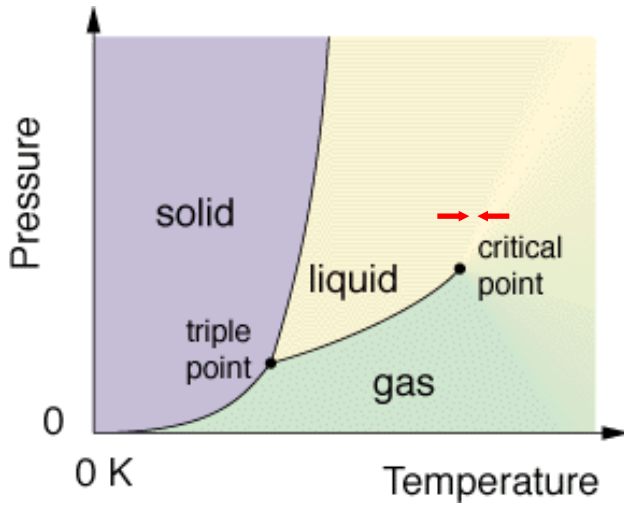
$$V = \left(\frac{\partial G}{\partial P} \right)_T \quad S = - \left(\frac{\partial G}{\partial T} \right)_P \quad H = G - T \left(\frac{\partial G}{\partial T} \right)_P$$

- Second derivatives of G (α , β , C_p) are **discontinuous** at T_T

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \beta = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

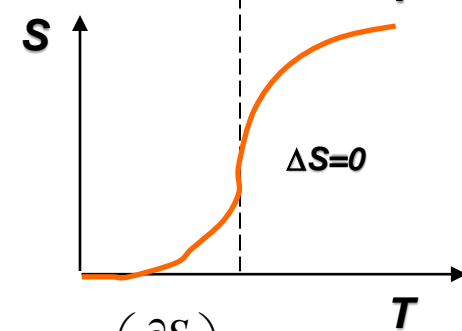
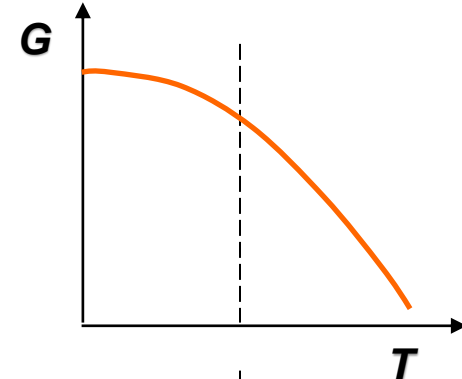
- Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

The Second Order Transition

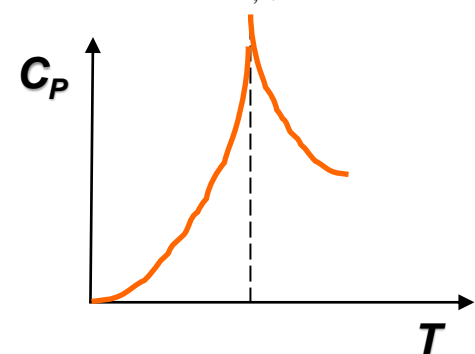


No Latent heat
Continuous entropy

Second-order transition



$$C_P = T \left(\frac{\partial S}{\partial T} \right)_{P,N} \rightarrow \infty$$



• Second Order Phase Transition at T_T :

– G is **continuous** at T_T

– First derivatives of G (V , S , H) are **continuous** at T_T

$$V = \left(\frac{\partial G}{\partial P} \right)_T \quad S = - \left(\frac{\partial G}{\partial T} \right)_P \quad H = G - T \left(\frac{\partial G}{\partial T} \right)_P$$

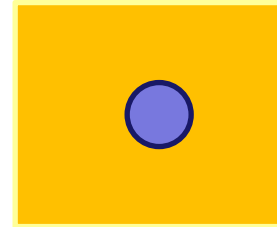
– Second derivatives of G (α , β , C_p) are **discontinuous** at T_T

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \beta = \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

– **Examples:** Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid \longrightarrow Solid



<Thermodynamic>

• Interfacial energy $\Rightarrow \Delta T_N$

Liquid

T_m Undercooled Liquid

Solid

No superheating required!

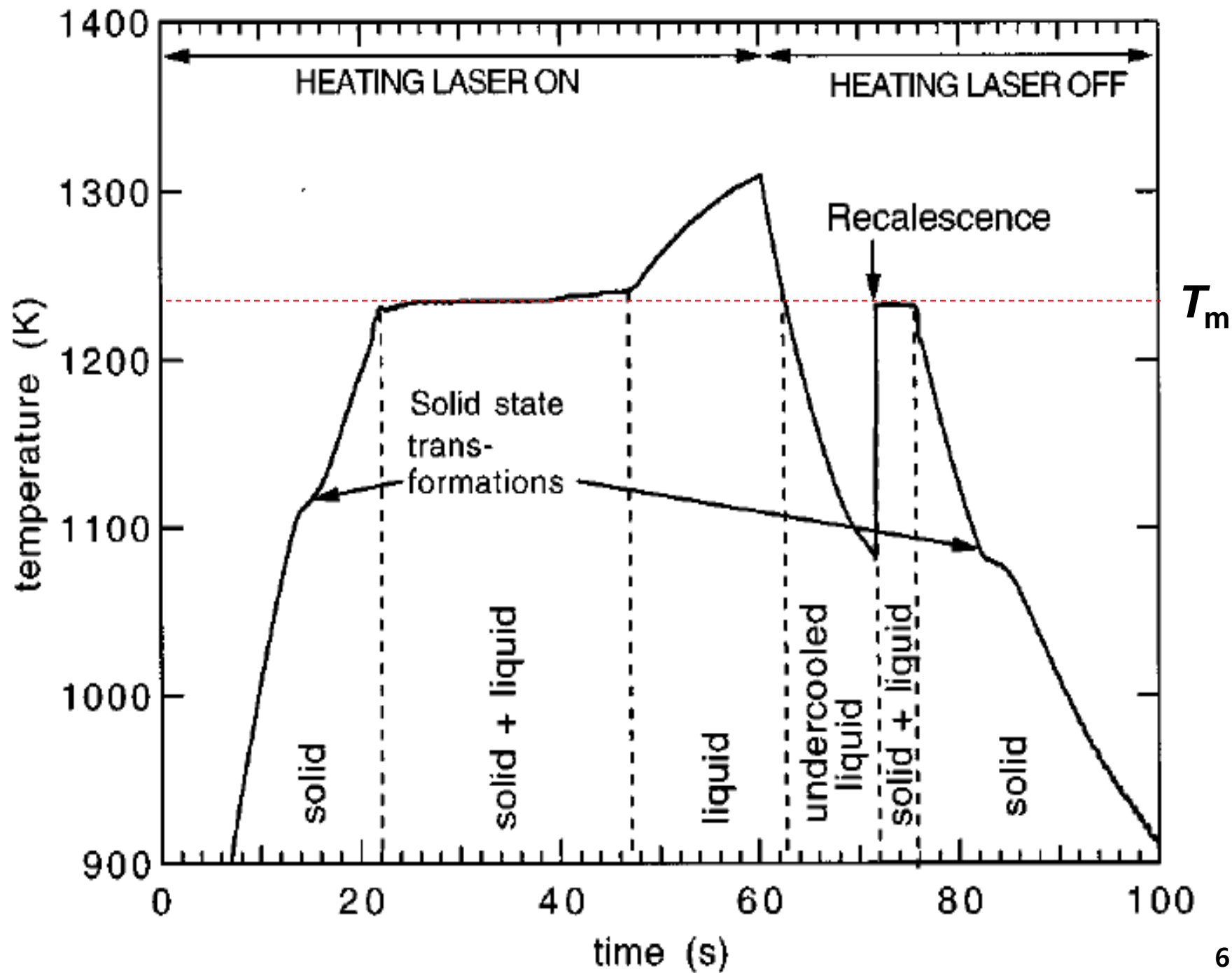
• Interfacial energy \Rightarrow No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

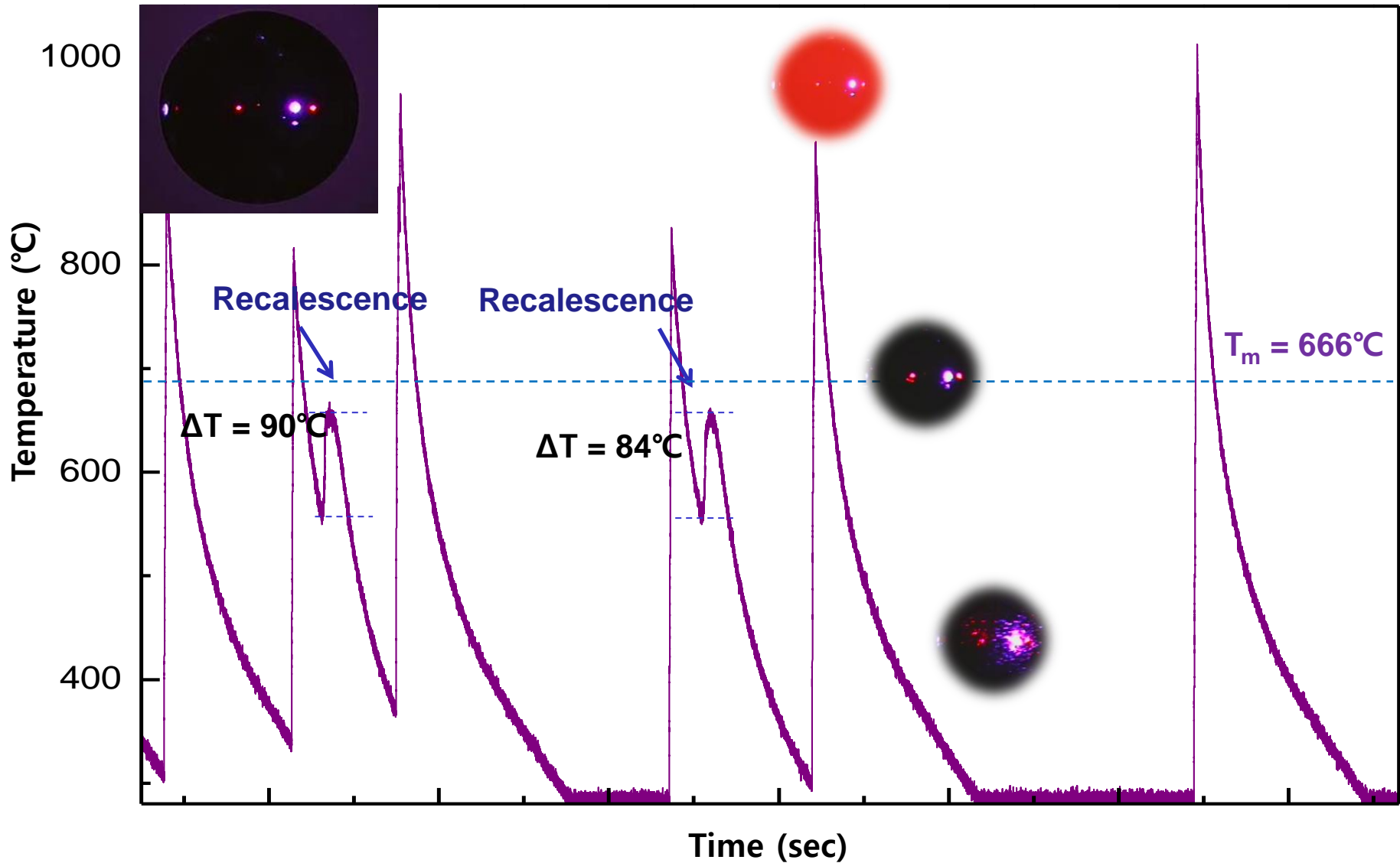
vapor



Melting: Liquid \longleftarrow Solid



Cyclic cooling curves of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$



Contents for today's class

- **Binary System** mixture/ solution / compound
Hume-Rothery Rules for Alloys
- **Gibbs Free Energy in Binary System**
Ideal solution and Regular solution
- **Chemical potential** and Activity

Multi-component system:

Q1: What are binary systems?

“Mixture vs. Solution vs. Compound”

* **Single component system** One element (Al, Fe), One type of molecule (H₂O)

: Equilibrium depends on **pressure** and **temperature**.

* **Binary system (two components)** → A, B

: Equilibrium depends on not only **pressure and temperature** but also **composition**.

- **Mixture** ; A – A, B – B ; → the physical combination of two or more substances on which the identities and boundaries are retained.



Alluvial mining



사금 채취



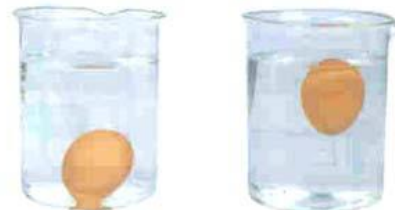
키질

Winnowing

wash rice



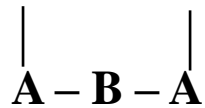
쌀 씻기



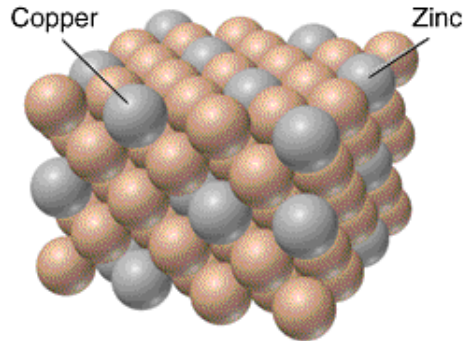
달걀 고르기

Select egg

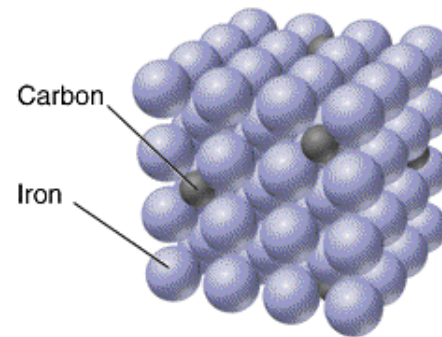
- **Solution** ; A - A - A ; \rightarrow atomic scale mixture/ **Random distribution**



Solid solution : substitutional or interstitial

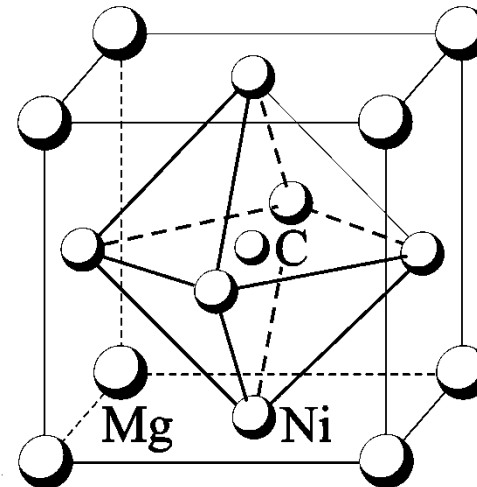


A Brass, a substitutional alloy



B Carbon steel, an interstitial alloy

- **Compound** ; A - B - A - B ; \rightarrow fixed A, B positions/ **Ordered state**



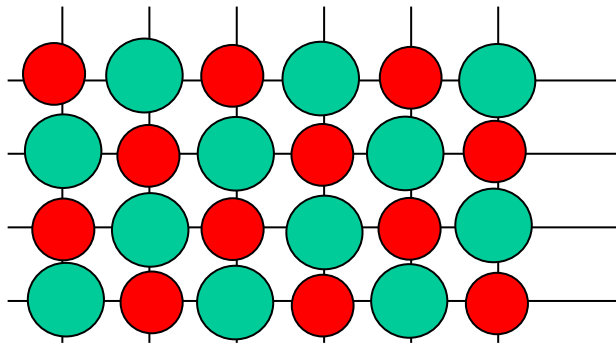
Q2: What is “Alloying”?

Ordered Compounds or Solid Solutions

"Alloying": atoms mixed on a lattice Ordered Compounds and Solid Solutions

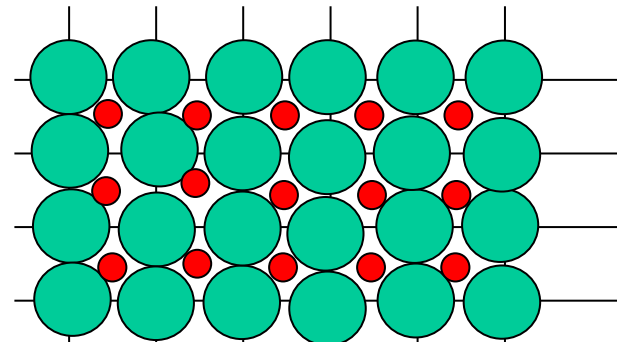
Ordered Substitutional and Interstitials Compounds

Substitutional
element replaces host atoms
in an orderly arrangement



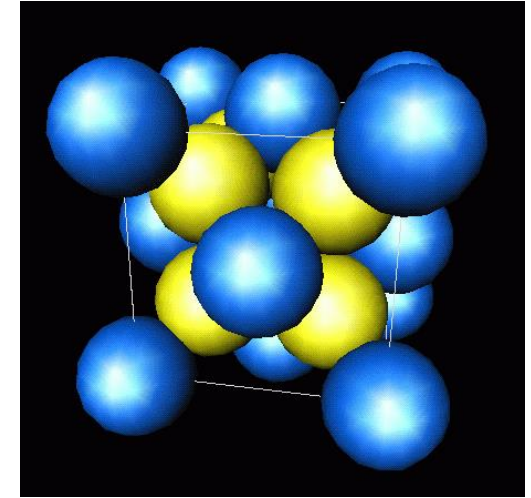
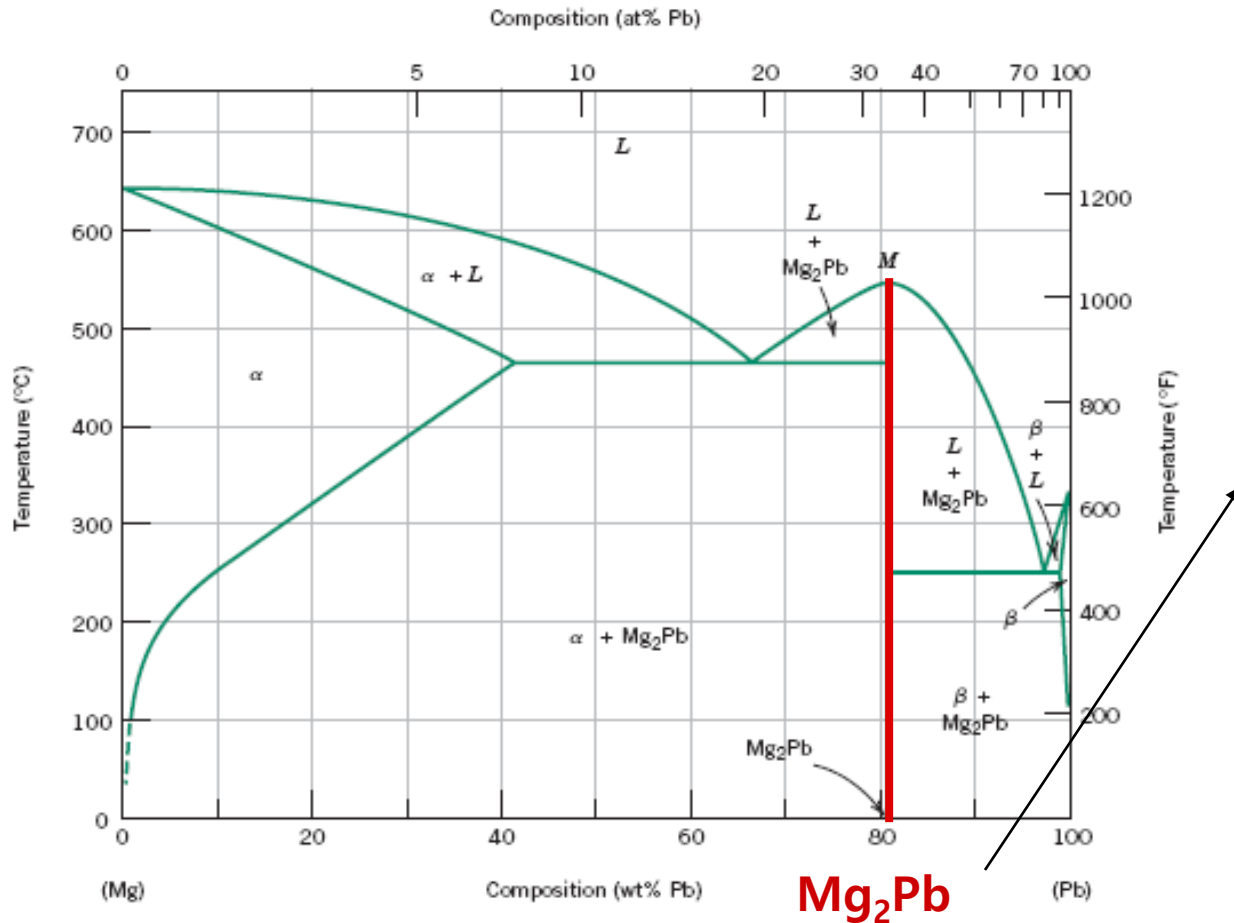
e.g., Ni_3Al (hi-T yield strength),
 $\text{Al}_3(\text{Li},\text{Zr})$ (strengthening)

Interstitial
element goes into holes
in an orderly arrangement



e.g., small impurities, clays
ionic crystals, ceramics.

Intermetallic Compounds

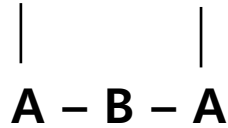


Antifluorite Structure:

- FCC unit cell with anions occupying FCC sites
- Cations occupying 8 octahedral interstitial sites

Intermetallic compounds form lines - not areas - because stoichiometry (i.e. composition) is exact.

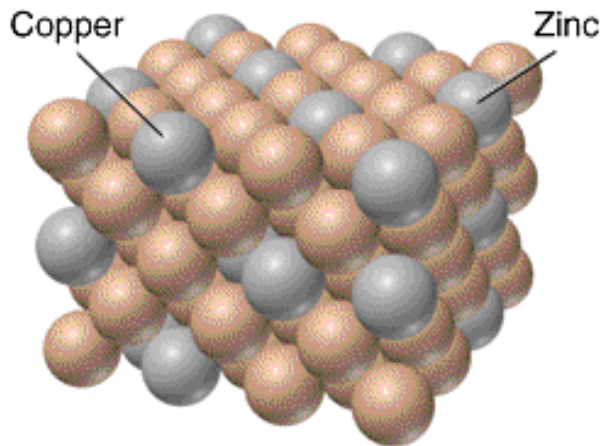
- **Solution** ; A – A – A ; → atomic scale mixing, **Random distribution**



Two Possibilities for **Solid Solutions**: B atoms in A atoms

Substitutional

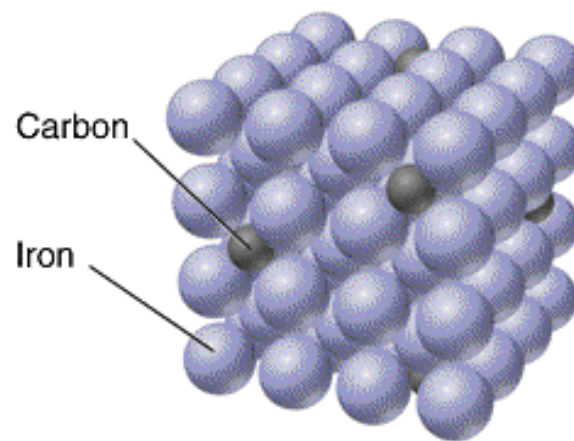
‘new element replaces host atoms’



A Brass, a substitutional alloy

Interstitials

‘new element goes in holes’

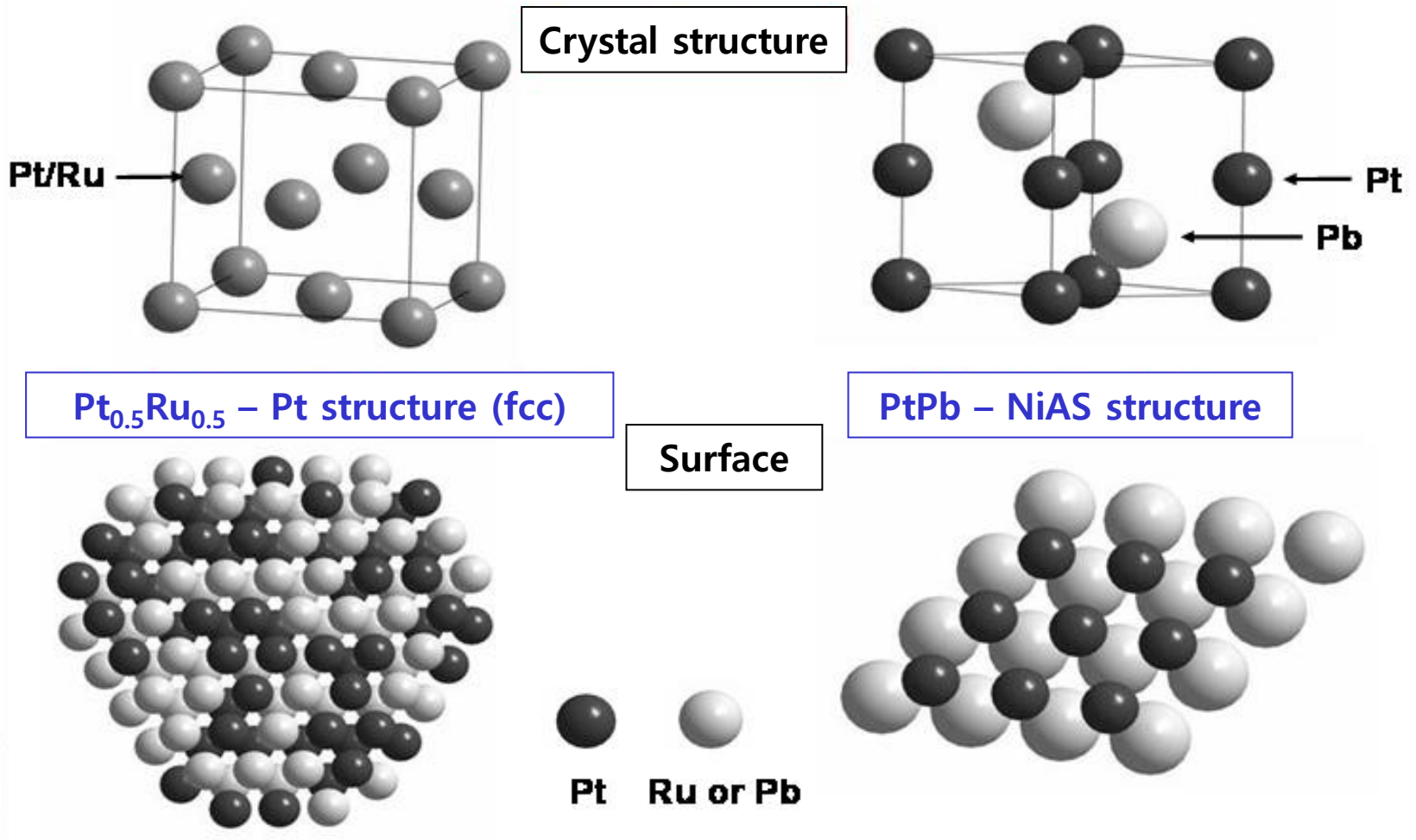


B Carbon steel, an interstitial alloy

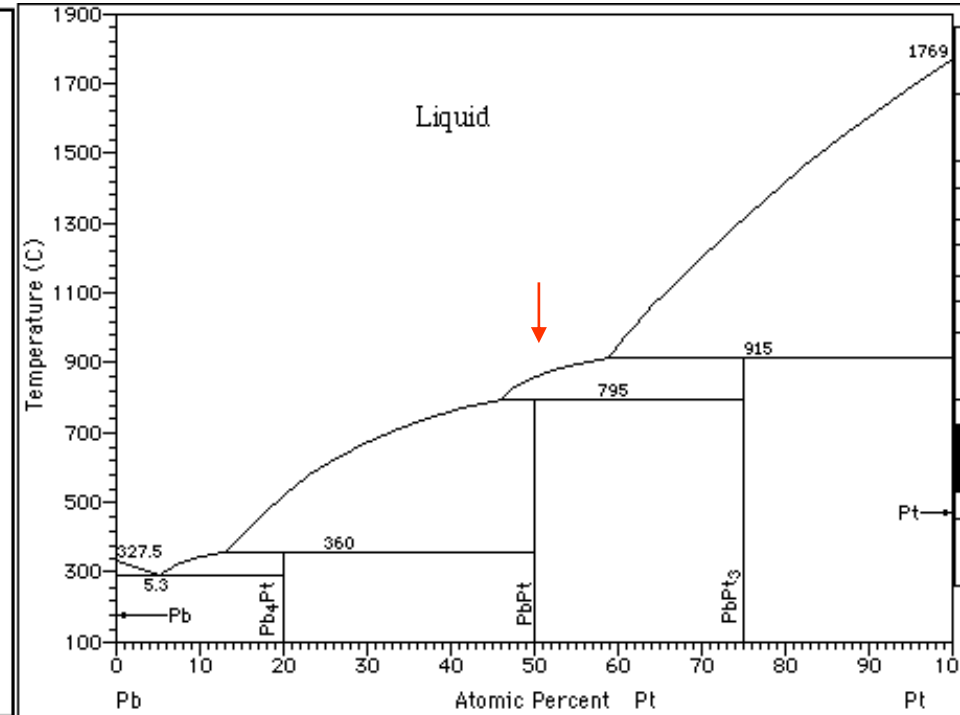
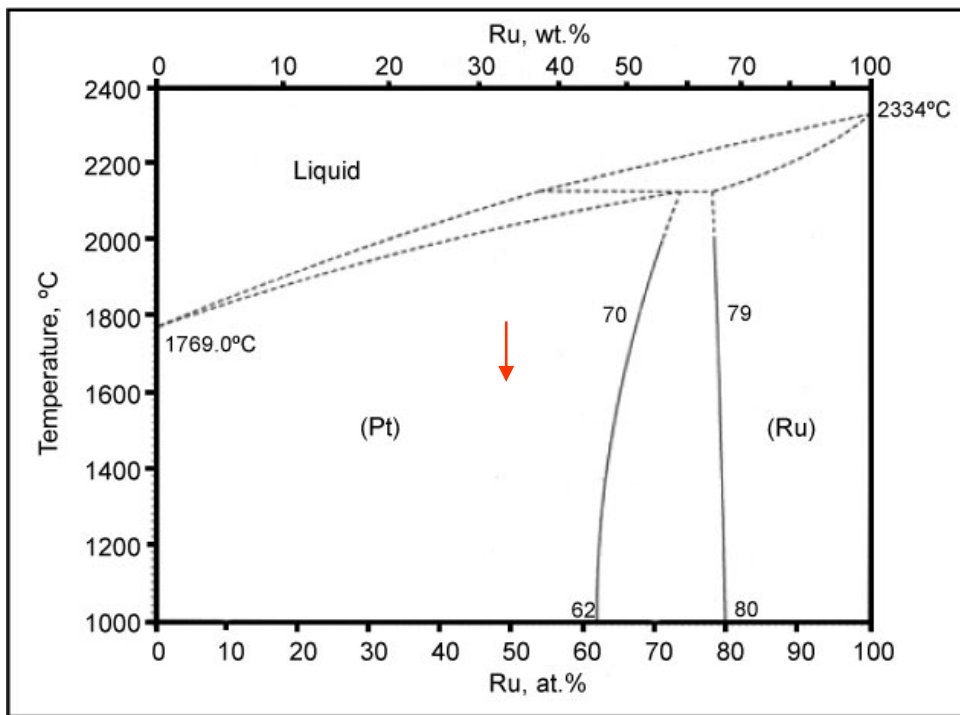
Q3: “Solution vs. Intermetallic compound”?

Alloying: atoms mixed on a lattice → solid solution and ordered compound

Solid Solution vs. Intermetallic Compound



Solid Solution vs. Intermetallic Compounds



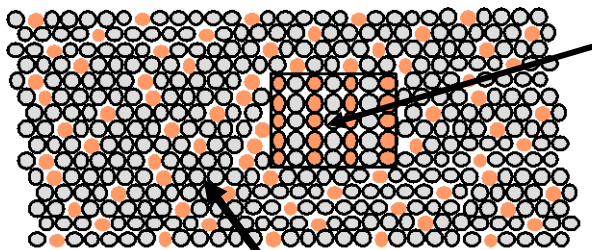
$Pt_{0.5}Ru_{0.5}$ – Pt structure (fcc)

PbPt – NiAS structure

Assumption: a simple physical model for “binary solid solutions”
: in order to introduce some of the basic concepts of the thermodynamics of alloys

Particles of New Phase in Solid-Solution Alloys

- Solid solution of **B** in A plus particles of a new phase (usually for a larger amount of B)

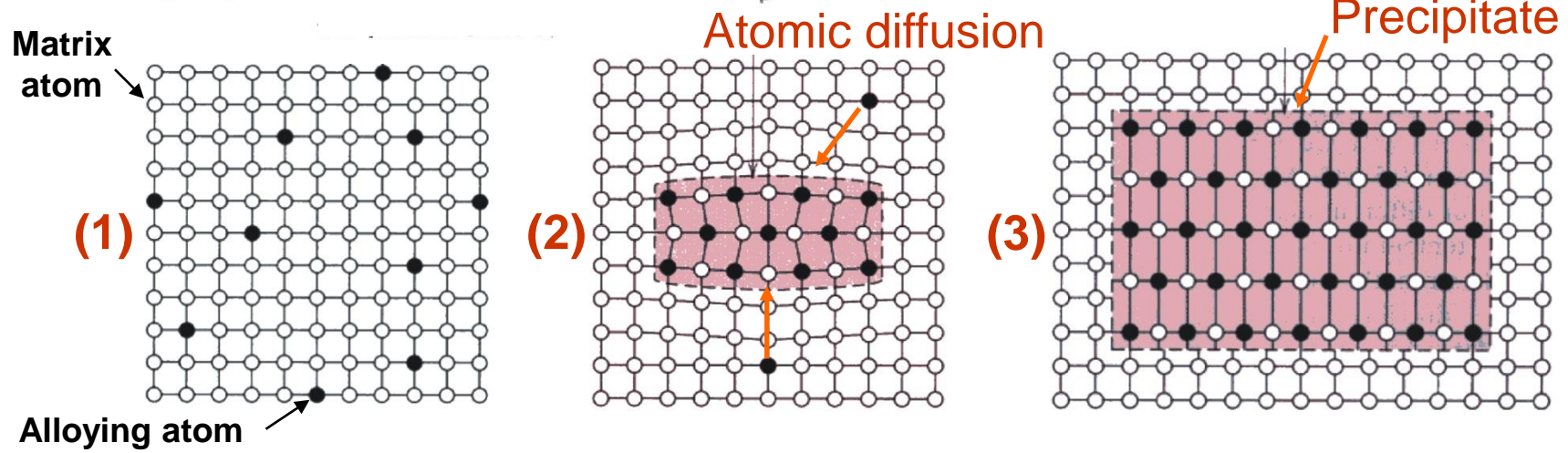
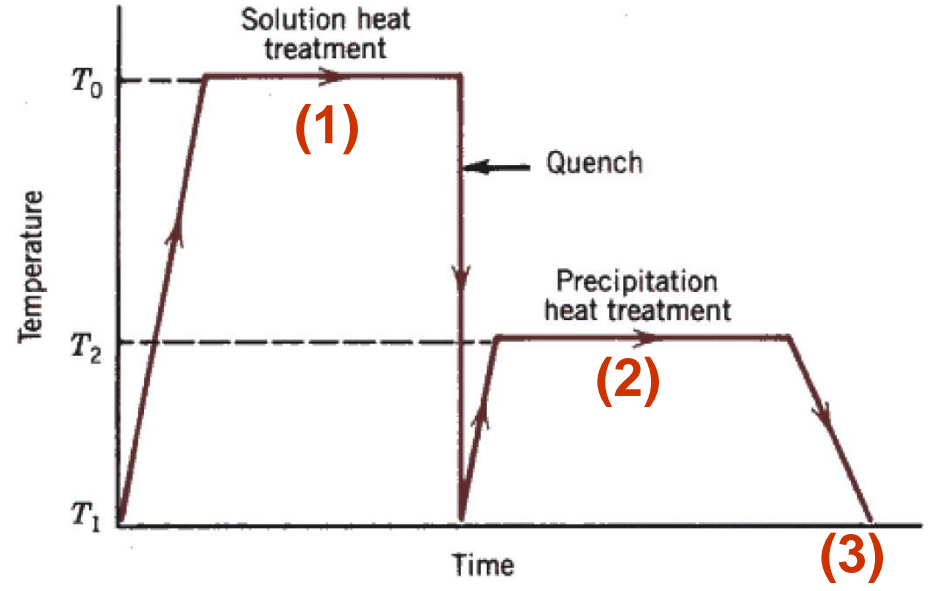
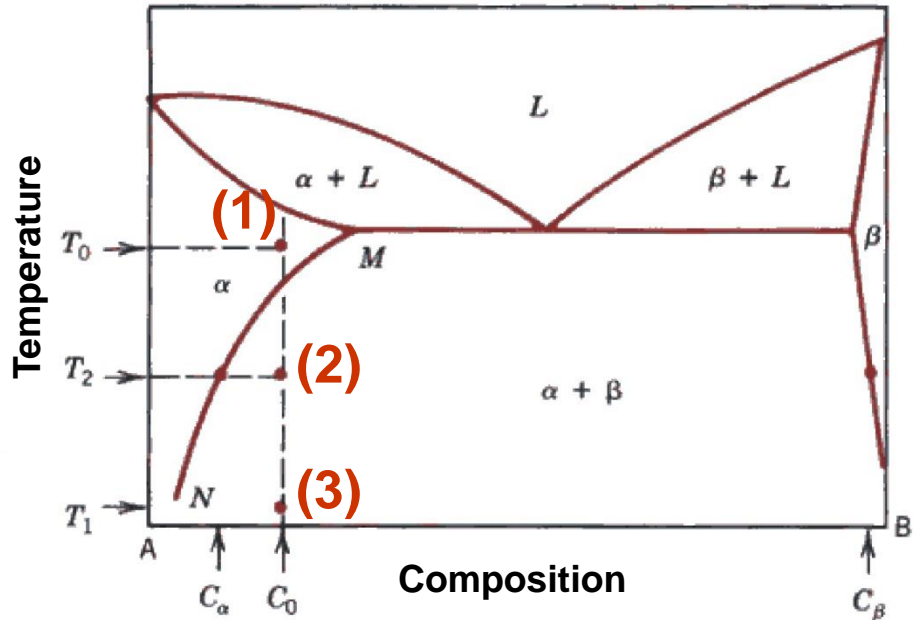


Second phase particle
--different **composition**
--often different **structure**.

Solid Solution phase: B atoms in A

5) Microstructure control : ② Secondary phase control

c. Mechanism of Precipitation



Q4: How can we classify “Solubility”?

Solubility

- Unlimited Solubility

- Hume Rothery' Conditions

- Similar Size
 - Same Crystal Structure
 - Same Valance
 - Similar Electronegativity

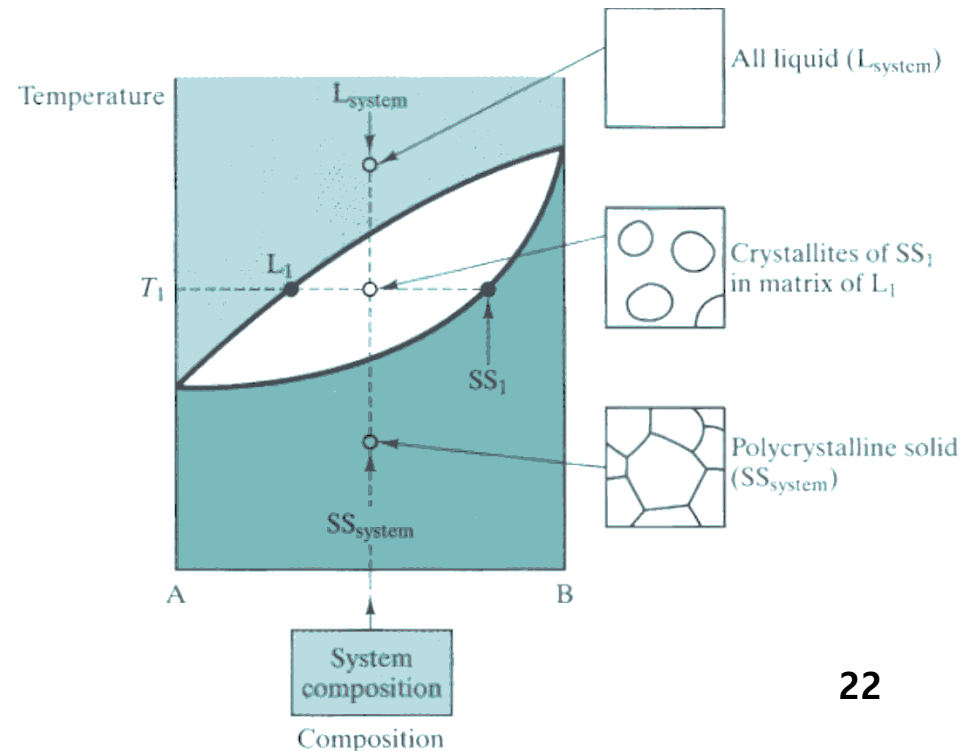
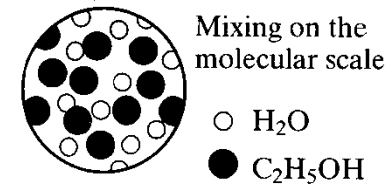
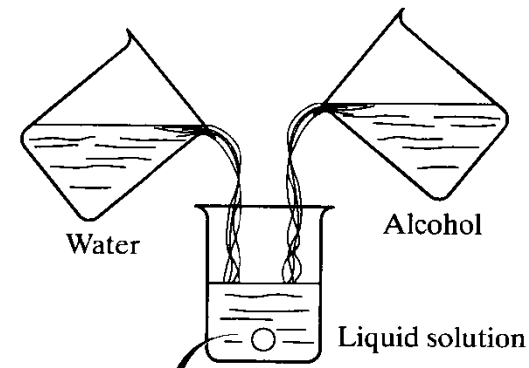
- Implies single phase

- Limited Solubility

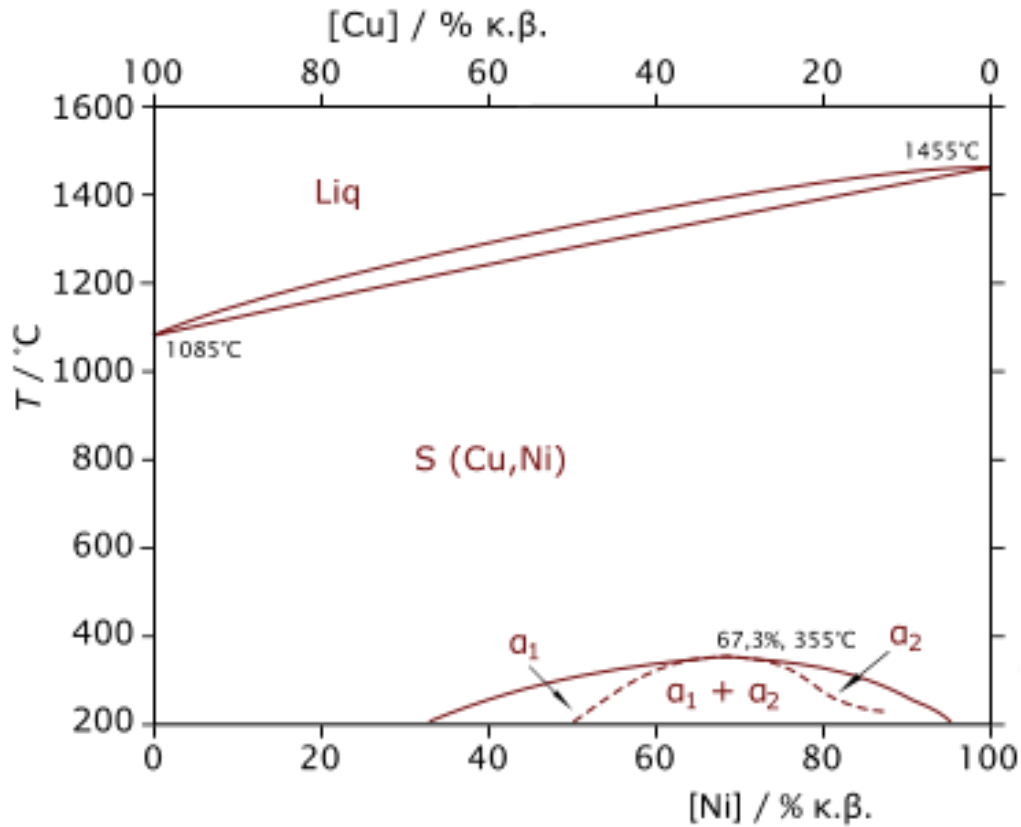
- Implies multiple phases

- No Solubility

- oil and water region

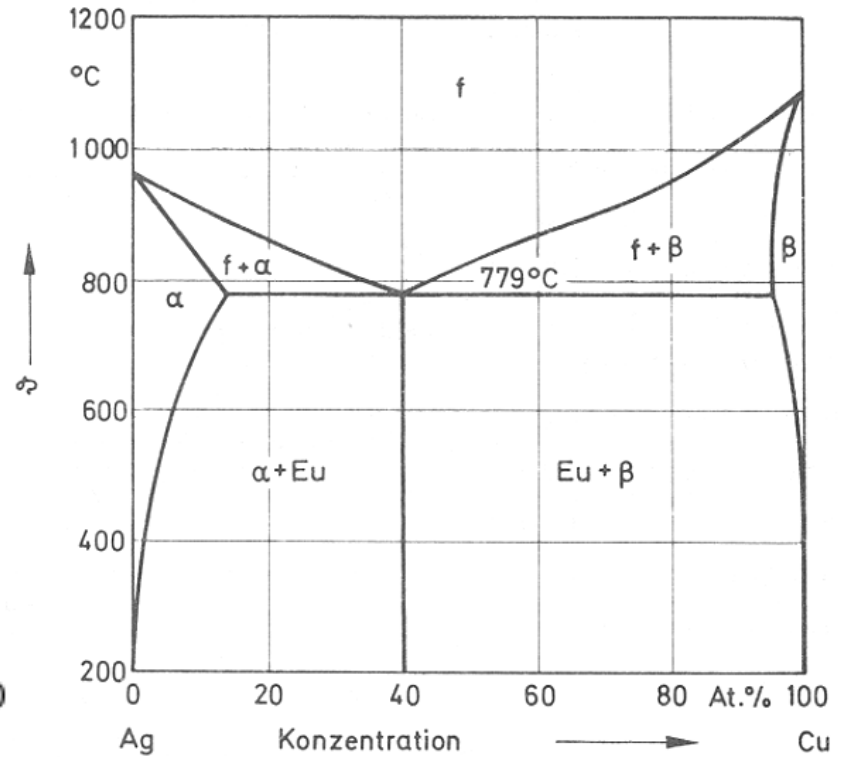


Cu-Ni Alloys



complete solid solution

Cu-Ag Alloys



limited solid solution

* Complete immiscibility of two metals does not exist.

: The solubility of one metal in another may be so low (e.g. Cu in Ge $< 10^{-7}$ at%.) that it is difficult to detect experimentally, but there will always be a measure of solubility.

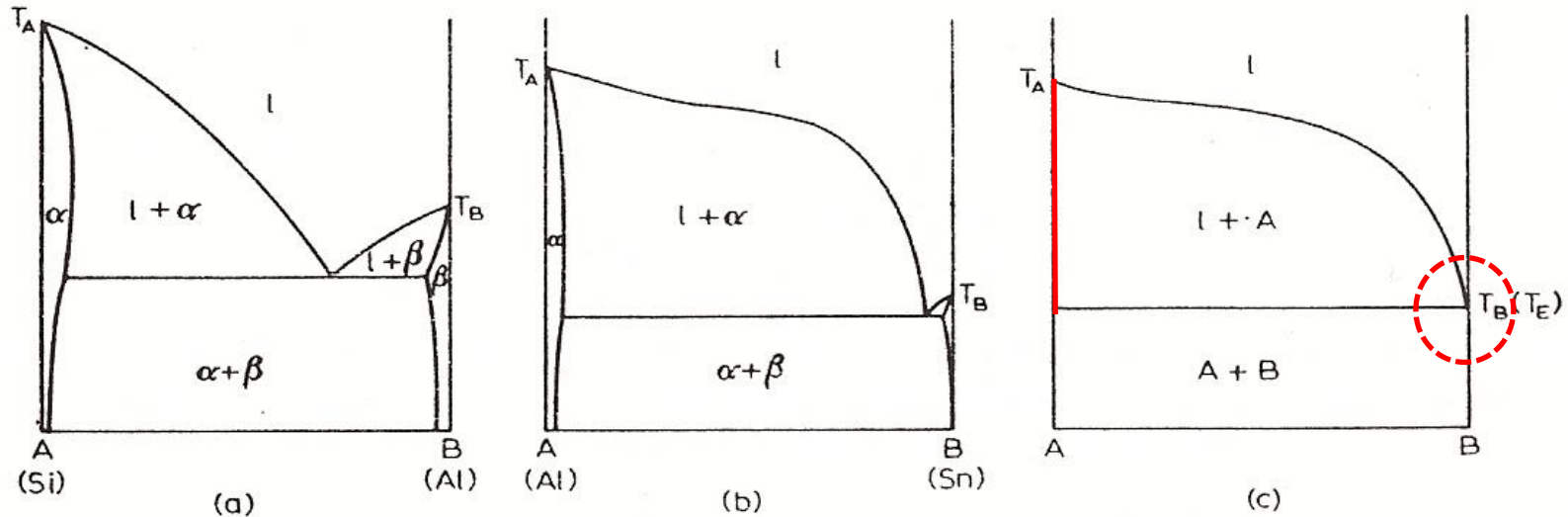


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

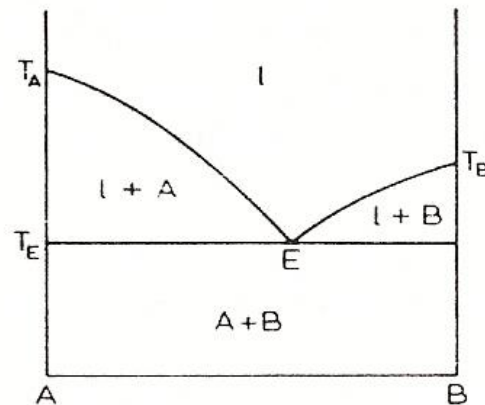
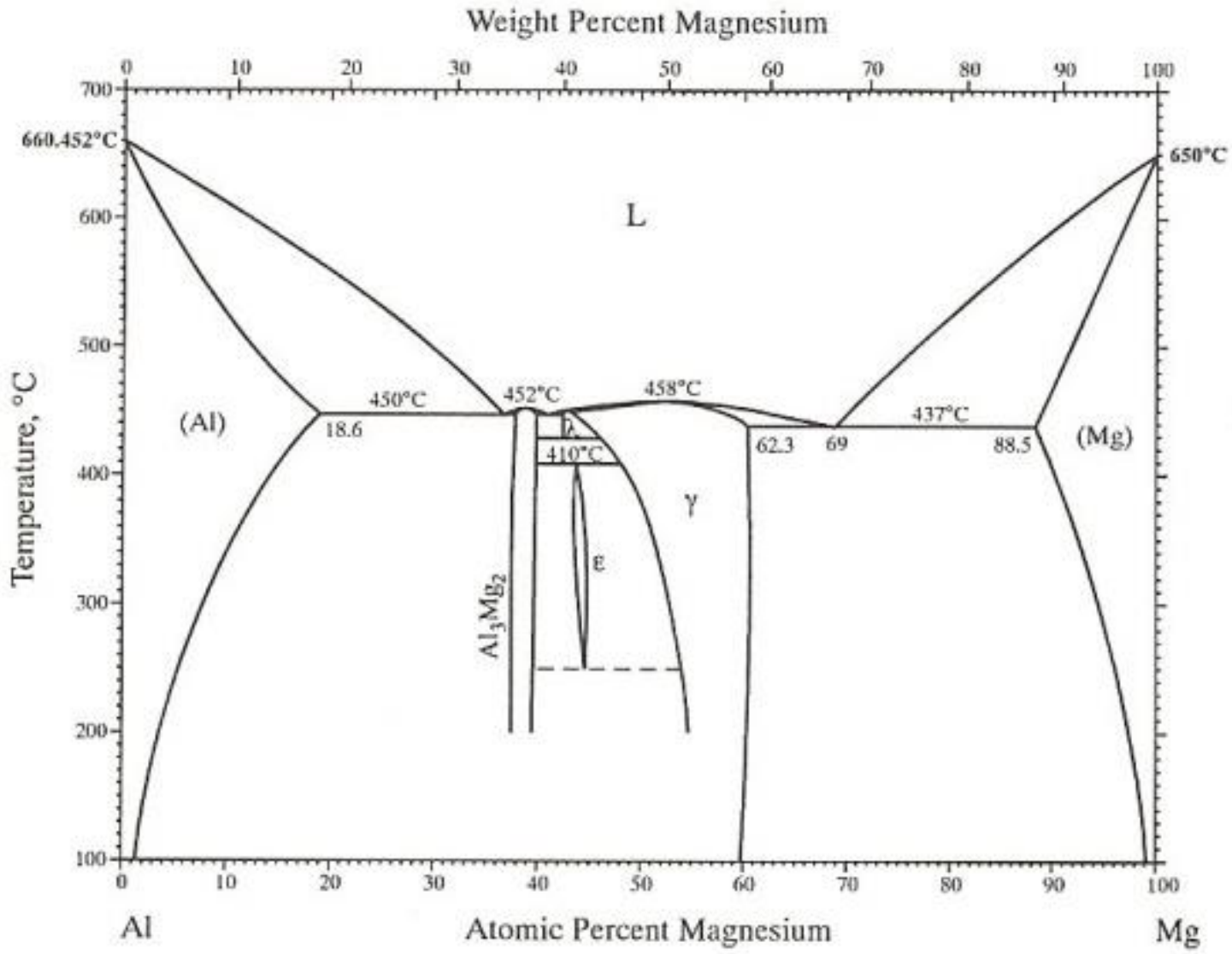
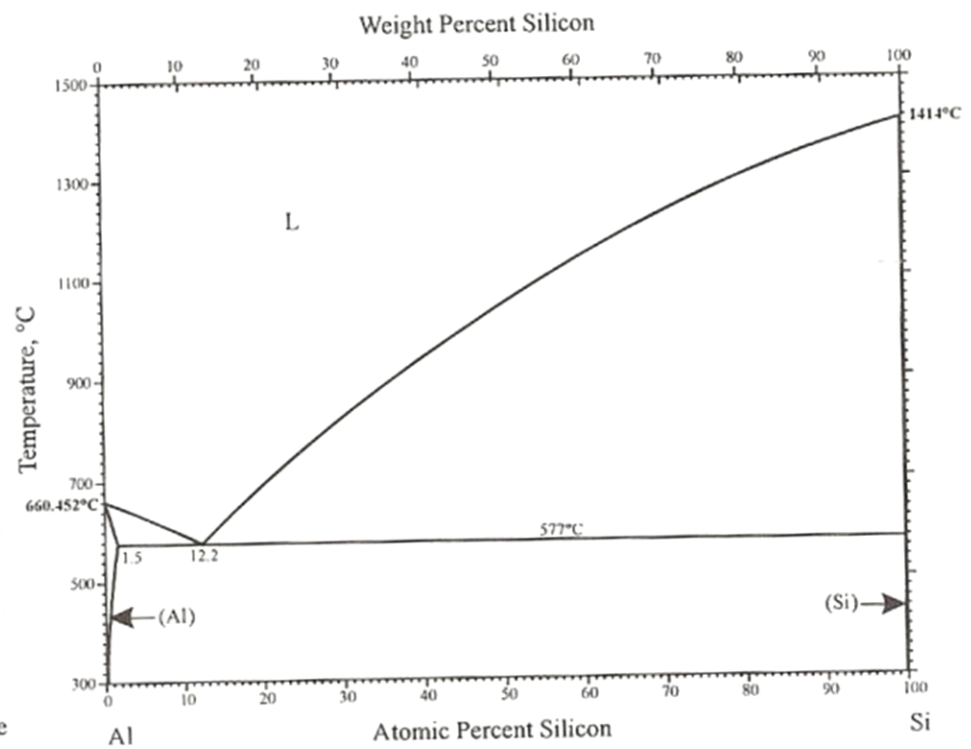
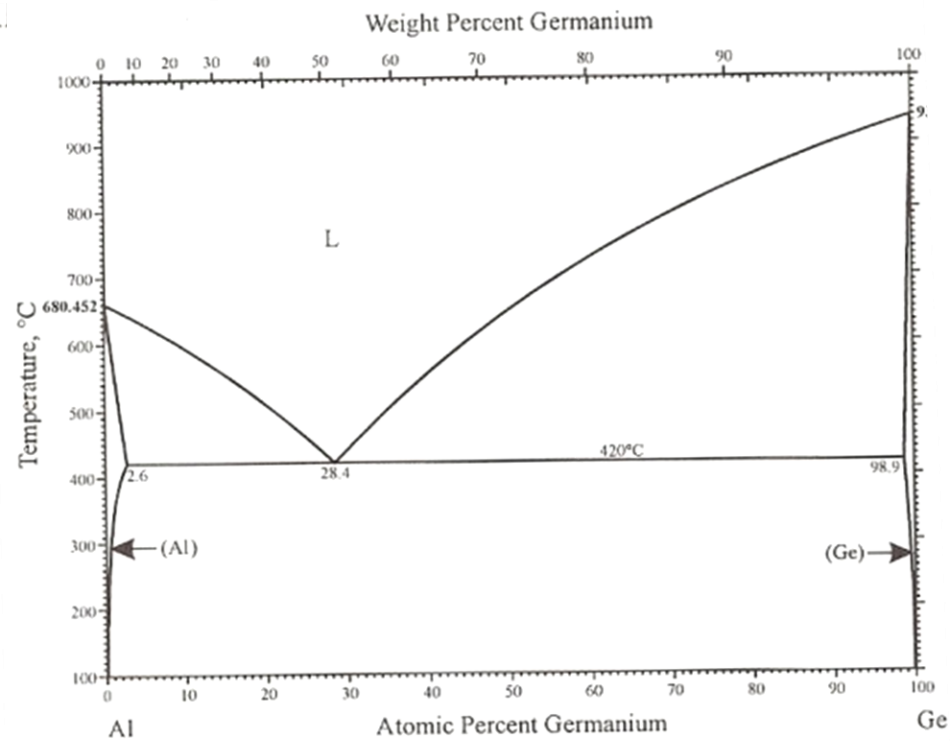
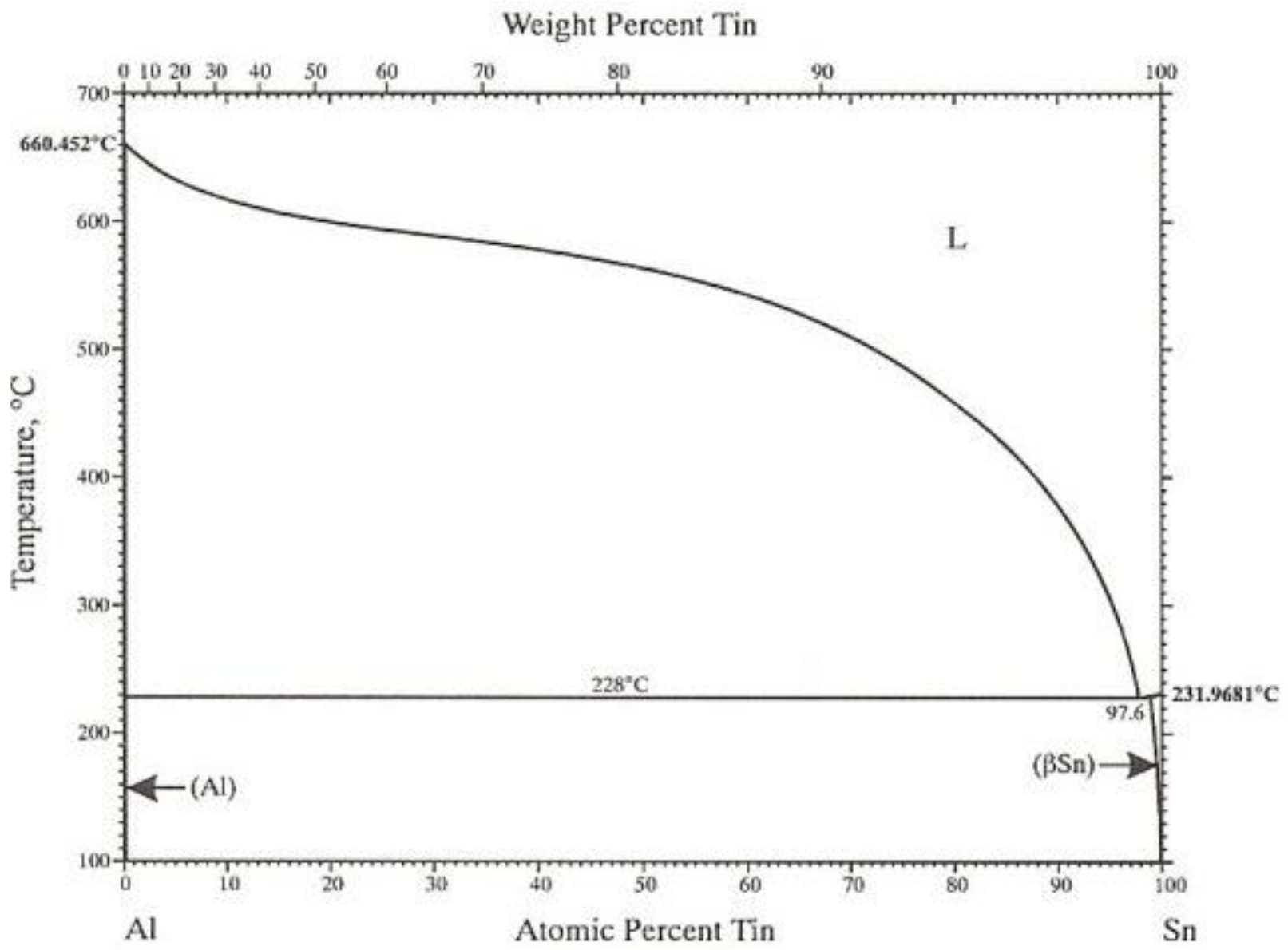


Fig. 54. Impossible form of a binary eutectic phase diagram.





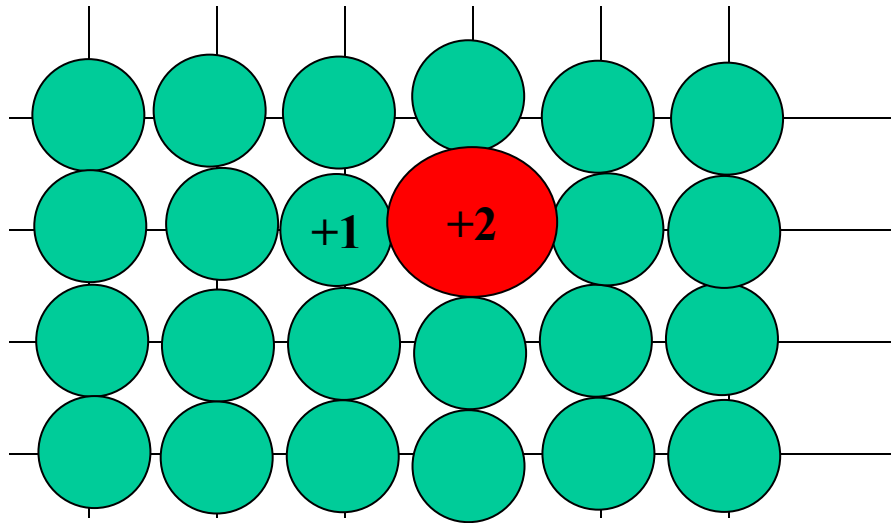


**Q5: Can we roughly estimate
what atoms will form solid solutions?**

“Hume-Rothery Rules”

Hume-Rothery Rules for Alloys (atoms mixing on a lattice)

Will mixing 2 (or more) different types of atoms lead to a solid-solution phase?



Empirical observations have identified 4 major contributors through :

Atomic Size Factor , Crystal Structure, Electronegativity, Valences

Hume-Rothery Rules for Mixing

Empirical rules for substitutional solid-solution formation were identified from experiment that are not exact, but give an expectation of formation.

Briefly,

1) Atomic Size Factor **The 15% Rule**

If "size difference" of elements are greater than $\pm 15\%$, the lattice distortions (i.e. local lattice strain) are too big and solid-solution will not be favored.

$$\text{DR}\% = \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \times 100\% < \pm 15\% \text{ will } \underline{\text{not disallow}} \text{ formation.}$$

2) Crystal Structure **Like elemental crystal structures are better**

For appreciable solubility, the crystal structure for metals must be the same.

3) Electronegativity **DE ~ 0 favors solid-solution.**

The more electropositive one element and the more electronegative the other, then "intermetallic compounds" (order alloys) are more likely.

4) Valences **Higher in lower alright. Lower in higher, it's a fight.**

A metal will dissolve another metal of higher valency more than one of lower valency.

Hume-Rothery Empirical Rules in Action

Is solid-solution favorable, or not?

- Cu-Ni Alloys

Rule 1: $r_{\text{Cu}} = 0.128 \text{ nm}$ and $r_{\text{Ni}} = 0.125 \text{ nm}$.

$$\text{DR}\% = \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \times 100\% = 2.3\% \quad \text{favorable } \checkmark$$

Rule 2: Ni and Cu have the FCC crystal structure. favorable \checkmark

Rule 3: $E_{\text{Cu}} = 1.90$ and $E_{\text{Ni}} = 1.80$. Thus, $\text{DE}\% = -5.2\%$ favorable \checkmark

Rule 4: Valency of Ni and Cu are both +2. favorable \checkmark

Expect Ni and Cu forms S.S. over wide composition range.

At high T, it does (helpful processing info), but actually phase separates at low T due to energetics (quantum mechanics).

Hume-Rothery Empirical Rules in Action

Is solid-solution favorable, or not?

- Cu-Ag Alloys

Rule 1: $r_{\text{Cu}} = 0.128$ nm and $r_{\text{Ag}} = 0.144$ nm.

$$\text{DR}\% = \frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \times 100\% = 9.4\% \quad \text{favorable } \checkmark$$

Rule 2: Ag and Cu have the FCC crystal structure. favorable \checkmark

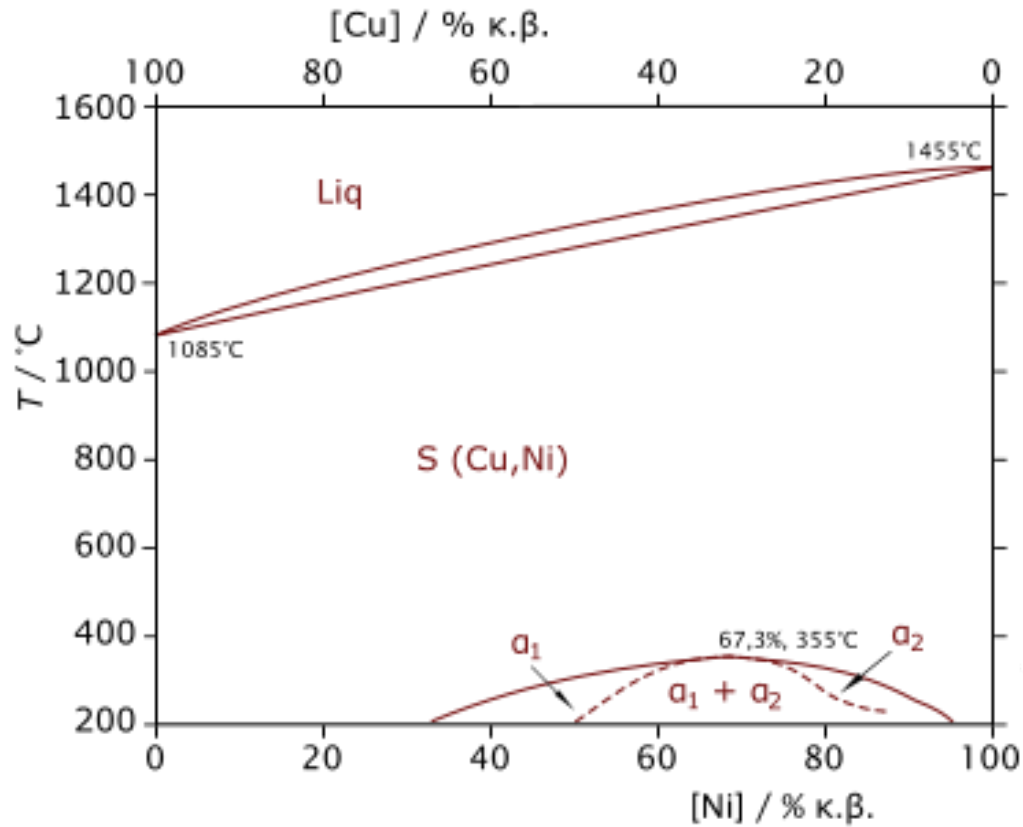
Rule 3: $E_{\text{Cu}} = 1.90$ and $E_{\text{Ni}} = 1.80$. Thus, $\text{DE}\% = -5.2\%$ favorable \checkmark

Rule 4: Valency of Cu is +2 and Ag is +1. **NOT favorable**

Expect Ag and Cu have limited solubility.

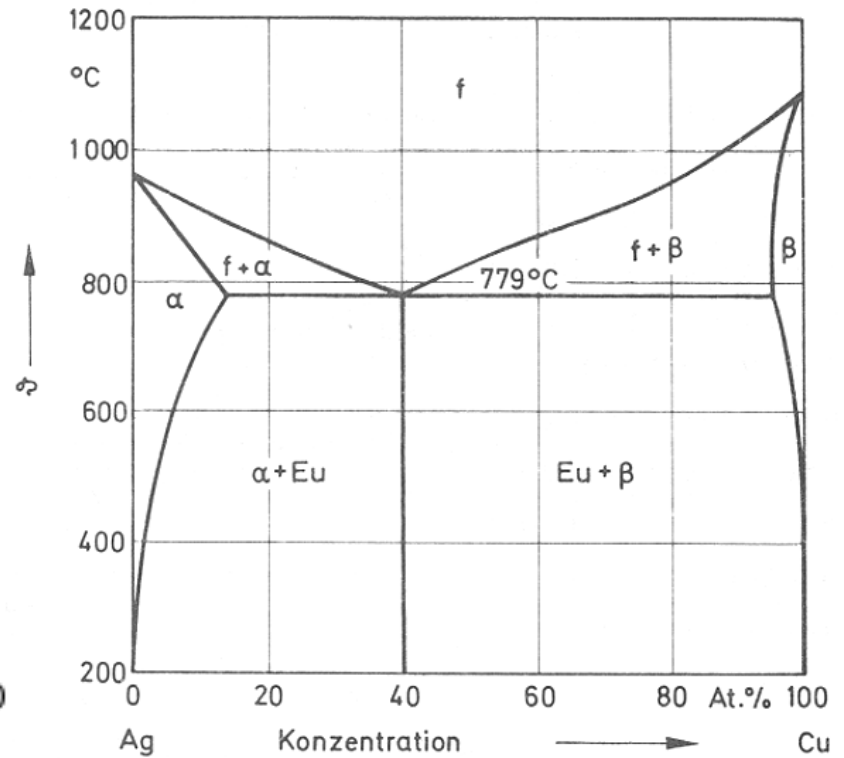
In fact, the Cu-Ag phase diagram (T vs. c) shows that a solubility of only 18% Ag can be achieved at high T in the Cu-rich alloys.

Cu-Ni Alloys



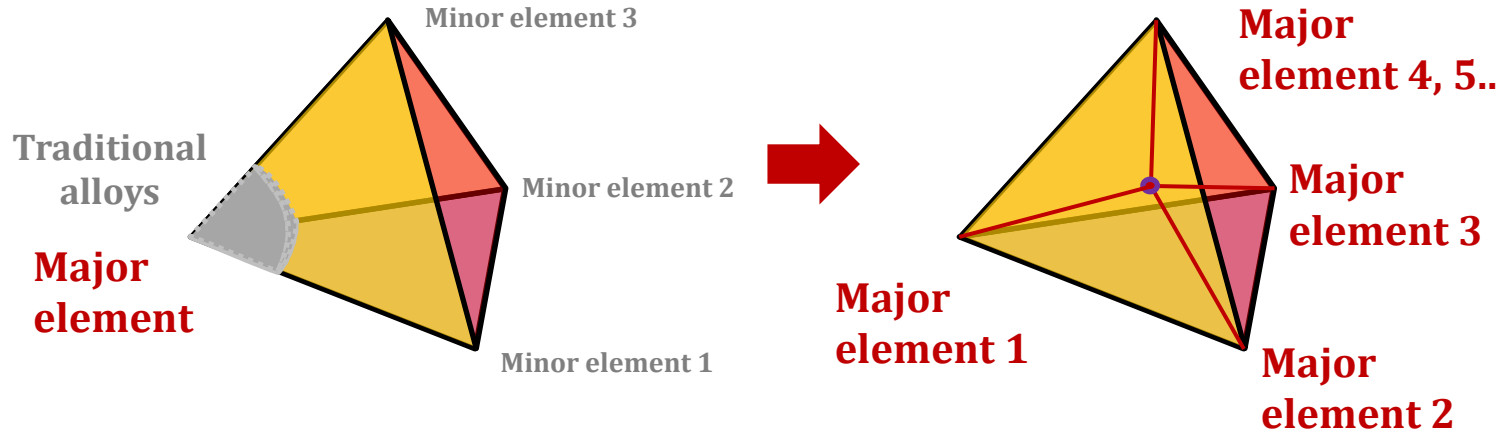
complete solid solution

Cu-Ag Alloys



limited solid solution

High entropy alloy (HEA)



Conventional alloy system

Ex) 304 steel - Fe₇₄Cr₁₈Ni₈

High entropy alloy system

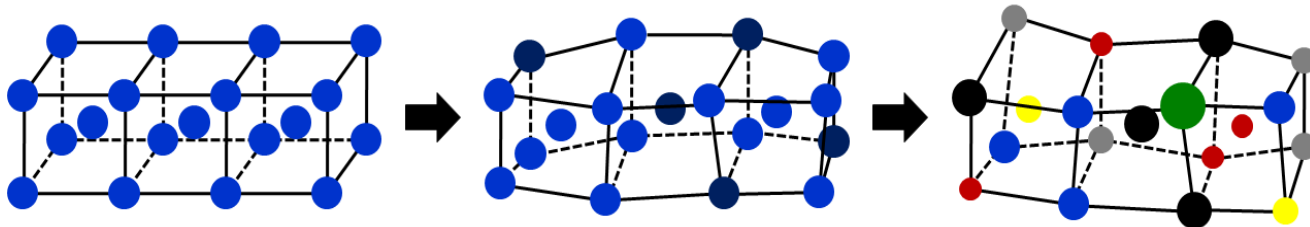
Ex) Al₂₀Co₂₀Cr₂₀Fe₂₀Ni₂₀

(1) Thermodynamic : high entropy effect

(2) Kinetics : sluggish diffusion effect

(3) Structure : severe lattice distortion effect

(4) Property : cocktail effect



Yong Zhang et al., Adv. Eng. Mat. P534-538, 2008

Severe lattice distortion → Sluggish diffusion & Thermal stability

**Q6: How to calculate
“Gibbs Free Energy of Binary Solutions”?**

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

Binary Solutions: binary solid solution/ a fixed pressure of 1 atm

2) Gibbs Free Energy of Binary Solutions

* Composition in mole fraction X_A, X_B $X_A + X_B = 1$

Step 1. bring together X_A mole of pure A and X_B mole of pure B

Step 2. allow the A and B atoms to mix together to make a homogeneous solid solution.

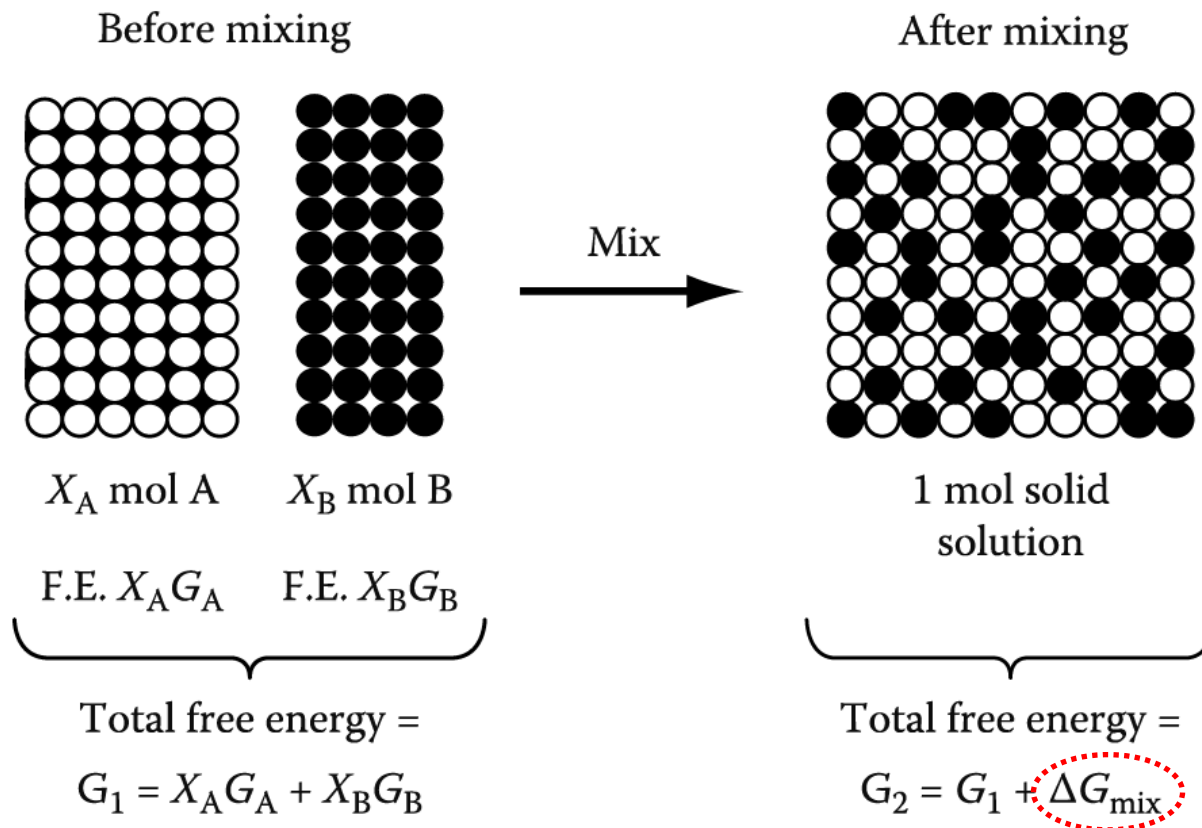


Fig. 1.7

1.3 Binary Solutions

Gibbs Free Energy of The System

In Step 1

- The molar free energies of pure A and pure B

pure A; $G_A(T, P)$

pure B; $G_B(T, P)$

X_A, X_B (mole fraction)

$$G_I = X_A G_A + X_B G_B \quad J/mol$$

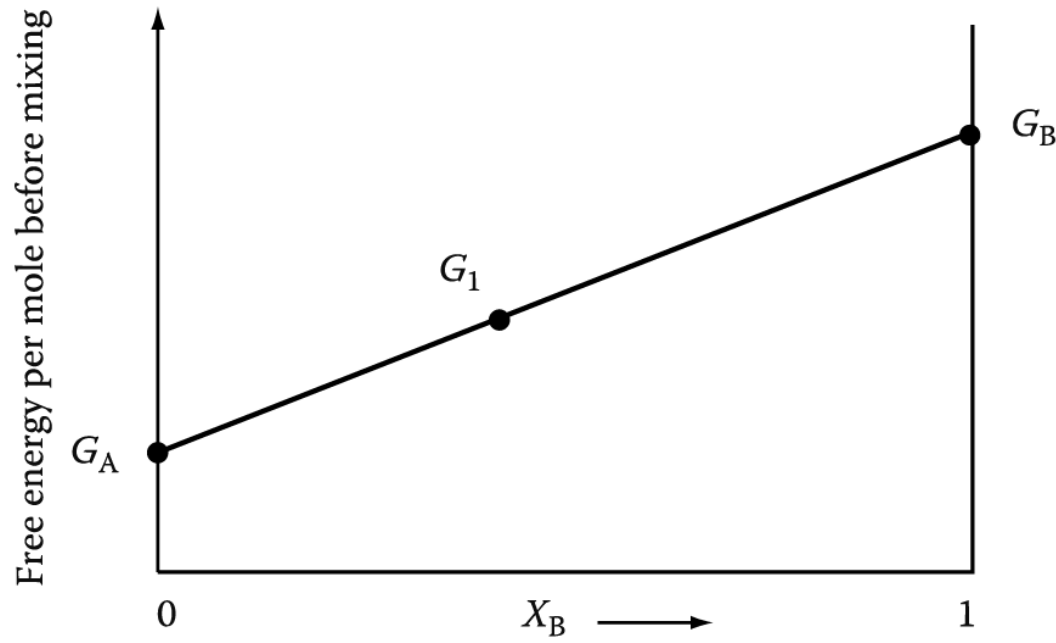


Fig. 1.8 A

 Free energy of mixture

1.3 Binary Solutions

Gibbs Free Energy of The System

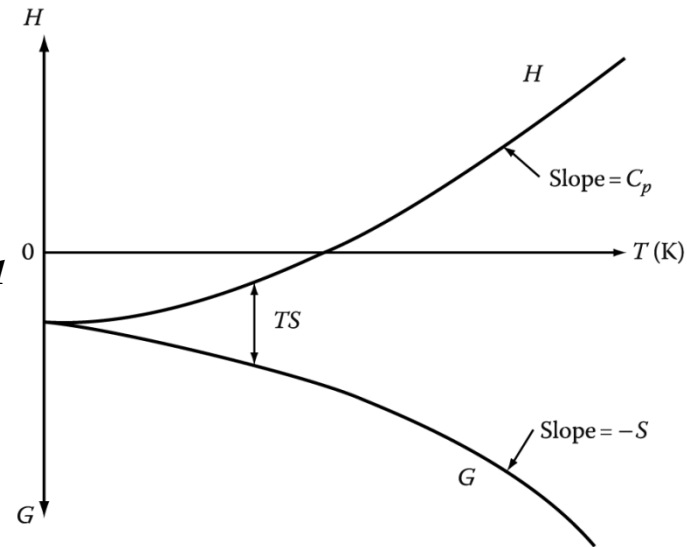
In Step 2

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

Since $G_1 = H_1 - TS_1$ and $G_2 = H_2 - TS_2$

And putting $\Delta H_{mix} = H_2 - H_1$ $\Delta S_{mix} = S_2 - S_1$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



ΔH_{mix} : *Heat of Solution* i.e. **heat absorbed or evolved** during step 2

ΔS_{mix} : *difference in entropy* between the mixed and unmixed state.

Fig. 1.3

➡ How can you estimate ΔH_{mix} and ΔS_{mix} ?

**Q7: How can you estimate
“ ΔG_{mix} of ideal solid solution”?**

$$\Delta G_{mix} = -T\Delta S_{mix}$$



$$\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

1.3 Binary Solutions

Mixing free energy, ΔG_{mix}

- Ideal solution

Assumption 1; $\Delta H_{mix} = 0$:

; A & B = complete solid solution

(A,B ; same crystal structure)

; no volume change

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$


$$\Delta G_{mix} = -T\Delta S_{mix} \text{ J/mol}$$

Entropy can be computed from randomness

by Boltzmann equation, i.e.,

$$S = k \ln w$$

w : degree of randomness, k : Boltzman constant

→ **thermal**; vibration (no volume change)

→ **Configuration**; number of distinguishable ways of arranging the atoms

$$S = S_{th} + S_{config}$$

Excess mixing Entropy

If there is no volume change or heat change,

$$w_{config} = 1 \rightarrow \text{before_solution_}(pureA_pureB)$$

$$w_{config} = \frac{(N_A + N_B)!}{N_A! N_B!} \rightarrow \text{after_solution_}(N_A, N_B) \leftarrow \text{Number of distinguishable way of atomic arrangement}$$

$$\Delta S^{mix} = S^{after} - S^{before} = k \ln \frac{(N_A + N_B)!}{N_A! N_B!} - k \ln 1$$

Since we are dealing with 1 mol of solution,

$$\rightarrow N_A = X_A N_0, N_B = X_B N_0, N_A + N_B = N_0$$

using Stirling's approximation $\ln N! \approx N \ln N - N$

and $R = kN_0$ (the universal gas constant)

$$= k[(N_0 \ln N_0 - N_0) - (X_A N_0 \ln X_A N_0 - X_A N_0) - (X_B N_0 \ln X_B N_0 - X_B N_0)]$$

$$= -R(X_A \ln X_A + X_B \ln X_B)$$

Excess mixing Entropy

$$\Delta S^{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta G_{mix} = -T\Delta S_{mix}$$



$$\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

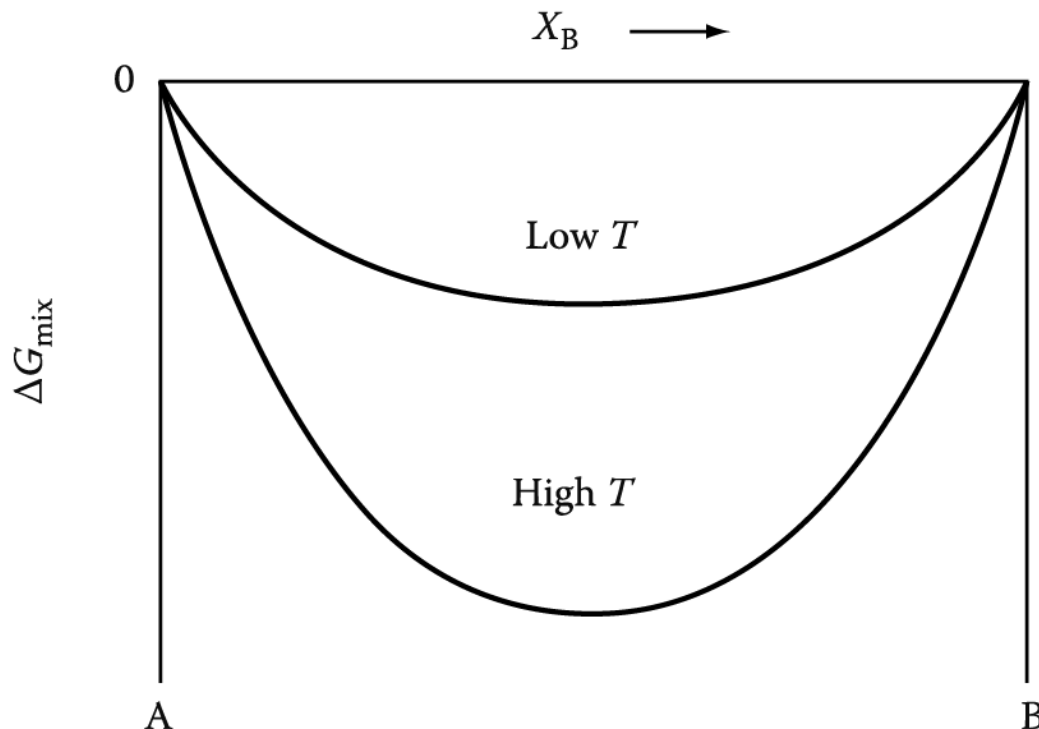


Fig. 1.9 Free energy of mixing for an ideal solution

Q8: How can you estimate

“Molar Free energy for ideal solid solution”?

$$G_2 = G_1 + \Delta G_{mix}$$



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

1.3 Binary Solutions

1) Ideal solution

Since $\Delta H_{mix} = 0$ for ideal solution,

$$G_2 = G_1 + \Delta G_{mix}$$



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

Compare $G_{solution}$ between high and low Temp.

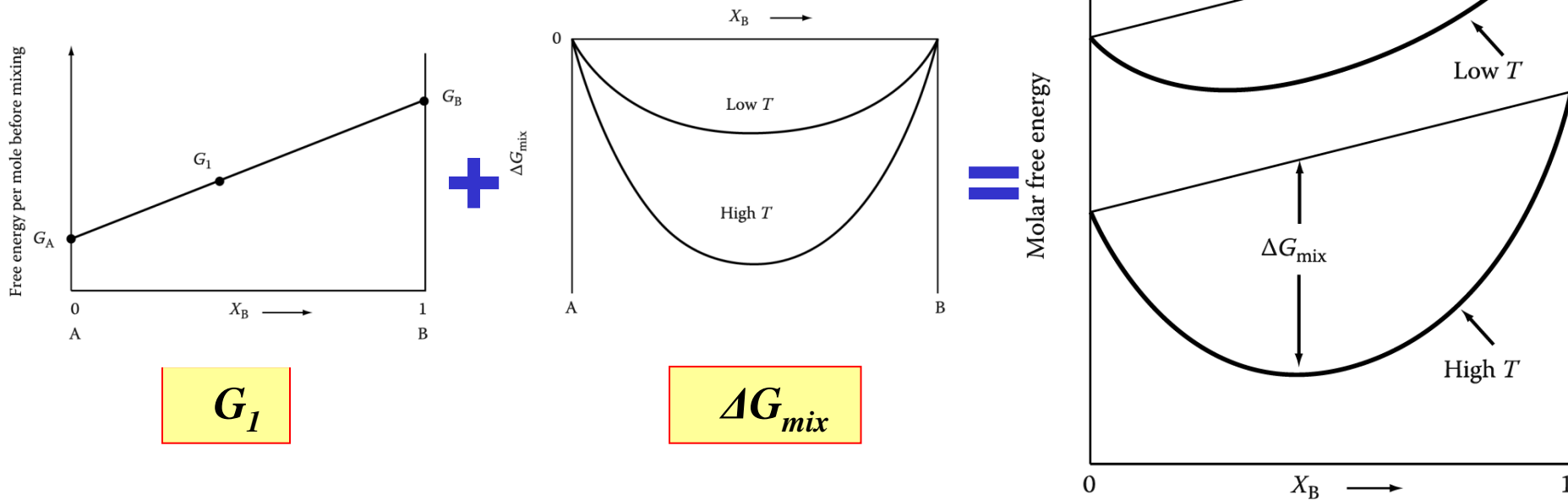


Fig. 1.10 The molar free energy (free energy per mole of solution) for an ideal solid solution. A combination of Figs. 1.8 and 1.9.

Q9: How the free energy of a given phase will change when atoms are added or removed?

“Chemical potential”

1.3 Binary Solutions

1) Ideal solution

$$G = H - TS = E + PV - TS$$

Chemical potential

The increase of the total free energy of the system by the increase of very small quantity of A, dn_A , will be proportional to μ_A .

→ $dn_A \sim$ small enough
($\because \mu_A$ depends on the composition of phase)

$$dG' = \mu_A dn_A \quad (T, P, n_B: \text{constant})$$

μ_A : partial molar free energy of A
or chemical potential of A

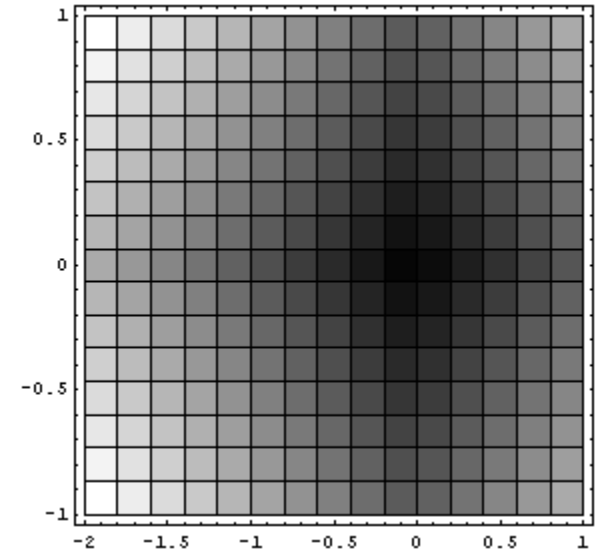
$$\mu_A = \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B}$$

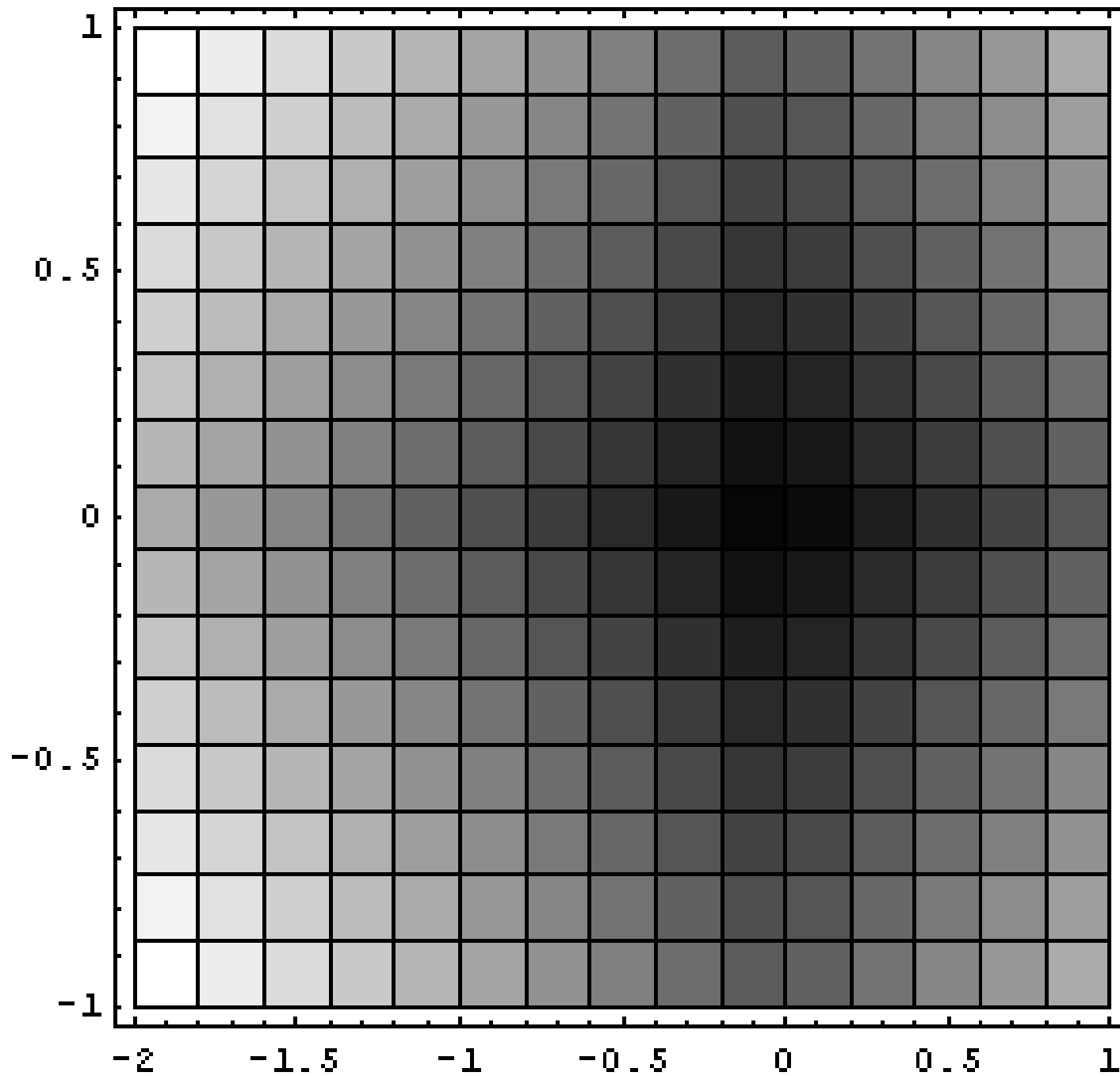
$$\mu_B = \left(\frac{\partial G'}{\partial n_B} \right)_{T, P, n_A}$$

For A-B binary solution, $dG' = \mu_A dn_A + \mu_B dn_B$

For variable T and P

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$





1.3 Binary Solutions

1) Ideal solution

$$G = H - TS = E + PV - TS$$

Chemical potential

The increase of the total free energy of the system by the increase of very small quantity of A, dn_A , will be proportional to μ_A .

→ $dn_A \sim$ small enough
($\because \mu_A$ depends on the composition of phase)

$$dG' = \mu_A dn_A \quad (T, P, n_B: \text{constant})$$

μ_A : partial molar free energy of A
or chemical potential of A

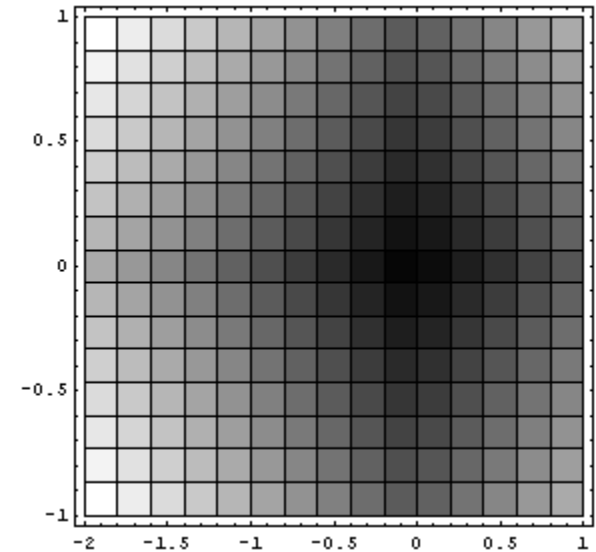
$$\mu_A = \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B}$$

$$\mu_B = \left(\frac{\partial G'}{\partial n_B} \right)_{T, P, n_A}$$

For A-B binary solution, $dG' = \mu_A dn_A + \mu_B dn_B$

For variable T and P

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$



Q10: “Correlation between chemical potential and free energy”?

Correlation between chemical potential and free energy

For 1 mole of the solution **(T, P: constant)**

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

$$dG = \mu_A dX_A + \mu_B dX_B$$

$$\frac{dG}{dX_B} = \mu_B - \mu_A$$

$$\mu_A = \mu_B - \frac{dG}{dX_B}$$

$$G = \left(\mu_B - \frac{dG}{dX_B} \right) X_A + \mu_B X_B$$

$$= \mu_B X_A - \frac{dG}{dX_B} X_A + \mu_B X_B$$

$$= \mu_B - \frac{dG}{dX_B} X_A$$

$$= \mu_B - \frac{dG}{dX_B} (1 - X_B)$$

$$\mu_B = G + \frac{dG}{dX_B} X_A$$

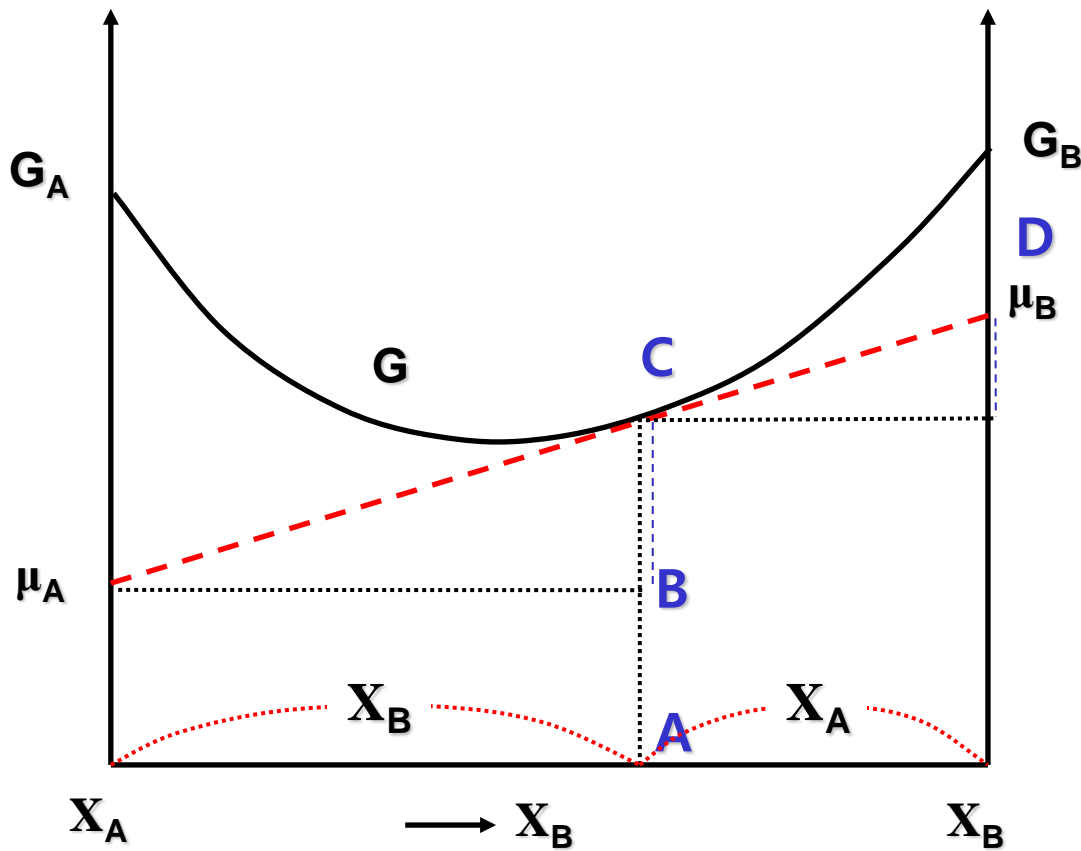
Correlation between chemical potential and free energy

For 1 mole of the solution

(T, P: constant)

1) Ideal solution

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



$$\mu_B = G + \frac{dG}{dX_B} (1 - X_B)$$

$$\mu_B = G + \frac{dG}{dX_B} X_A$$

$$= \overline{CA} + \overline{DC}$$

$$\mu_A = \mu_B - \frac{dG}{dX_B}$$

$$= \mu_B - (X_A + X_B) \frac{dG}{dX_B}$$

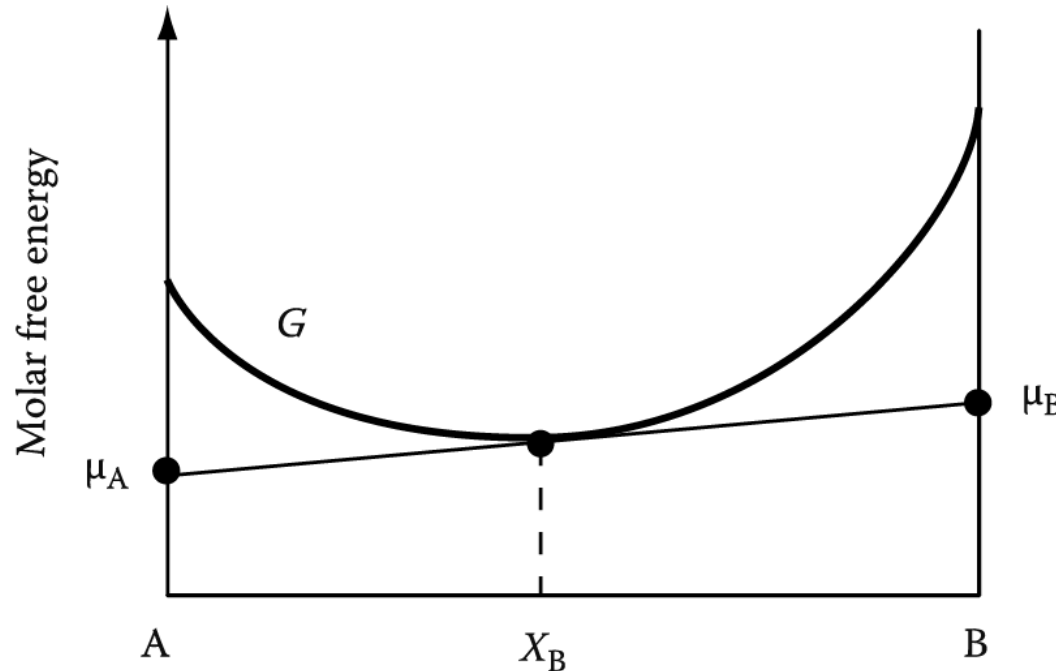
$$= \overline{DA} - \overline{DC} - \overline{CB} \quad 51$$

Correlation between chemical potential and free energy

For 1 mole of the solution (T, P: constant)

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

$$\mu_A = \mu_B - \frac{dG}{dX_B}$$



$$\mu_B = G + \frac{dG}{dX_B} X_A$$

Fig. 1.11 The relationship between the free energy curve for a solution and the chemical potentials of the components.

1.3 Binary Solutions

1) Ideal solution

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

$$\mu_A = G_A + RT \ln X_A$$
$$\mu_B = G_B + RT \ln X_B$$

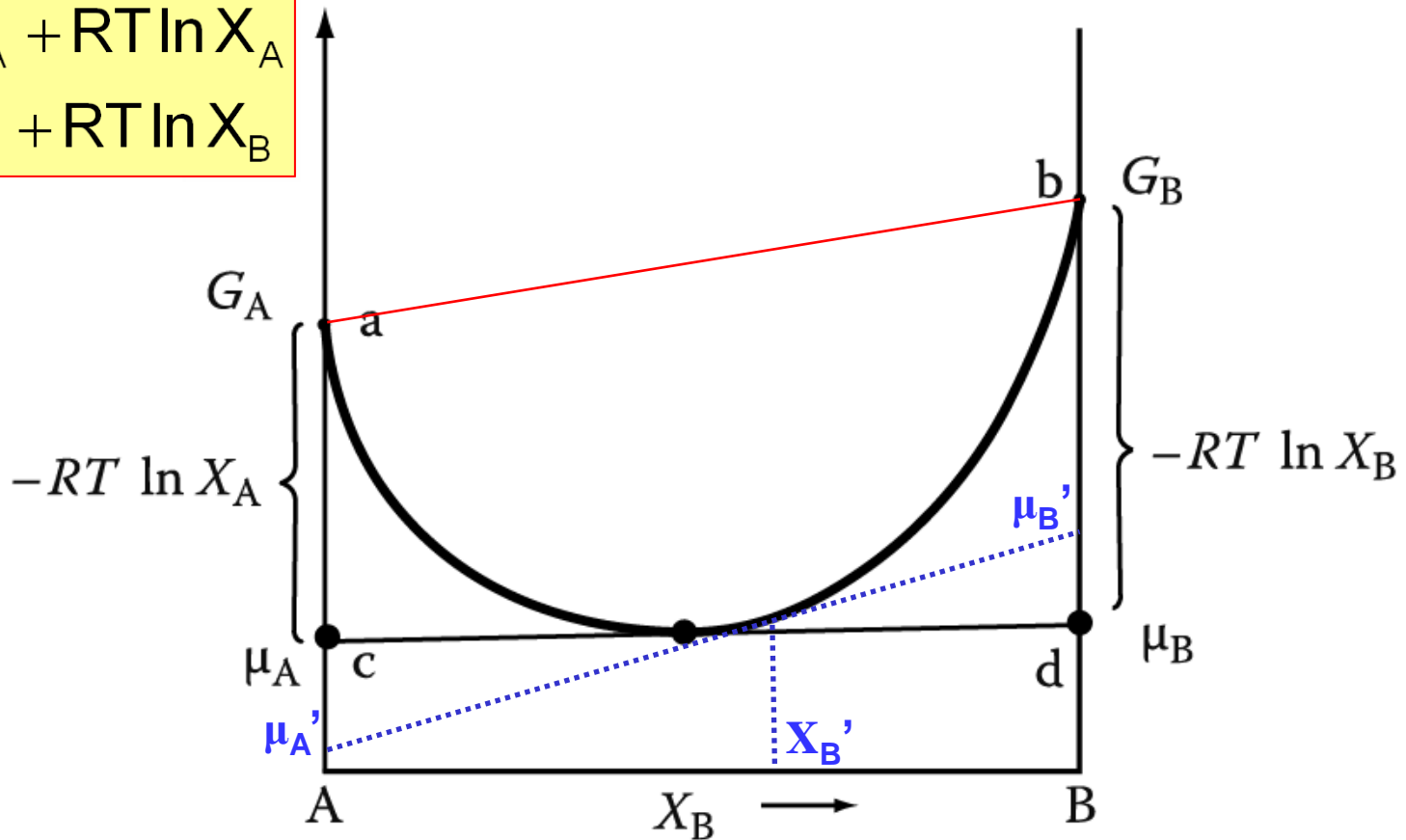


Fig. 1.12 The relationship between the free energy curve and Chemical potentials for an ideal solution.

Contents for today's class

- **Binary System** mixture/ solution / compound
- **Gibbs Free Energy in Binary System**

$$G_1 = X_A G_A + X_B G_B \quad J/mol$$

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

Ideal solution ($\Delta H_{mix} = 0$) $\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$

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

Regular solution

$$\Delta H_{mix} = P_{AB} \varepsilon \quad \text{where } \varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

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

- **Chemical potential and Activity**

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

$$\mu_A = G_A + RT \ln a_A \quad \ln \left(\frac{a_A}{X_A} \right) = \frac{\Omega}{RT} (1 - X_A)^2$$

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient}$$

$dn_A \sim$ small enough ($\because \mu_A$ depends on the composition of phase)

2023 Fall

“Phase Transformation *in* Materials”

09.13.2023

Eun Soo Park

Office: 33-313

Telephone: 880-7221

Email: espark@snu.ac.kr

Office hours: by an appointment

Contents for previous class

- **Binary System** mixture/ solution / compound
- **Gibbs Free Energy in Binary System**

$$G_1 = X_A G_A + X_B G_B \quad J/mol$$

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

Ideal solution ($\Delta H_{mix}=0$) $\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$

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

Regular solution

$$\Delta H_{mix} = P_{AB} \varepsilon \quad \text{where } \varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

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

- **Chemical potential and Activity**

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

$$\mu_A = G_A + RT \ln a_A \quad \ln \left(\frac{a_A}{X_A} \right) = \frac{\Omega}{RT} (1 - X_A)^2$$

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient}$$

$dn_A \sim$ small enough ($\because \mu_A$ depends on the composition of phase)

1.3 Binary Solutions

1) Ideal solution

$$G = H - TS = E + PV - TS$$

Chemical potential

The increase of the total free energy of the system by the increase of very small quantity of A, dn_A , will be proportional to μ_A .

→ $dn_A \sim$ small enough
($\because \mu_A$ depends on the composition of phase)

$$dG' = \mu_A dn_A \quad (T, P, n_B: \text{constant})$$

μ_A : partial molar free energy of A
or chemical potential of A

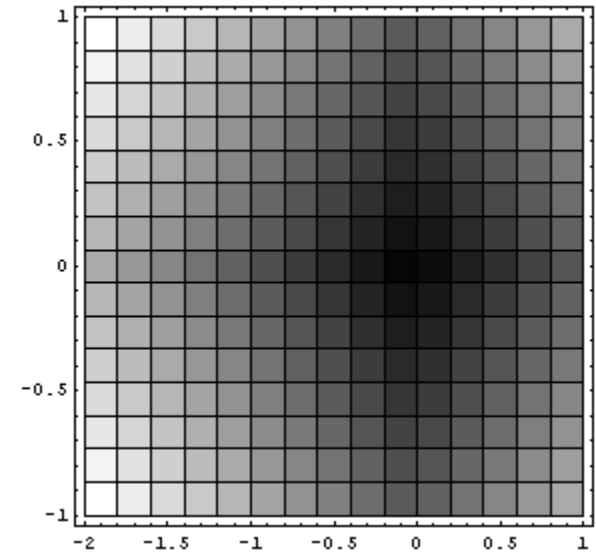
$$\mu_A = \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B}$$

$$\mu_B = \left(\frac{\partial G'}{\partial n_B} \right)_{T, P, n_A}$$

For A-B binary solution, $dG' = \mu_A dn_A + \mu_B dn_B$

For variable T and P

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$



1.3 Binary Solutions

1) Ideal solution

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

$$\mu_A = G_A + RT \ln X_A$$
$$\mu_B = G_B + RT \ln X_B$$

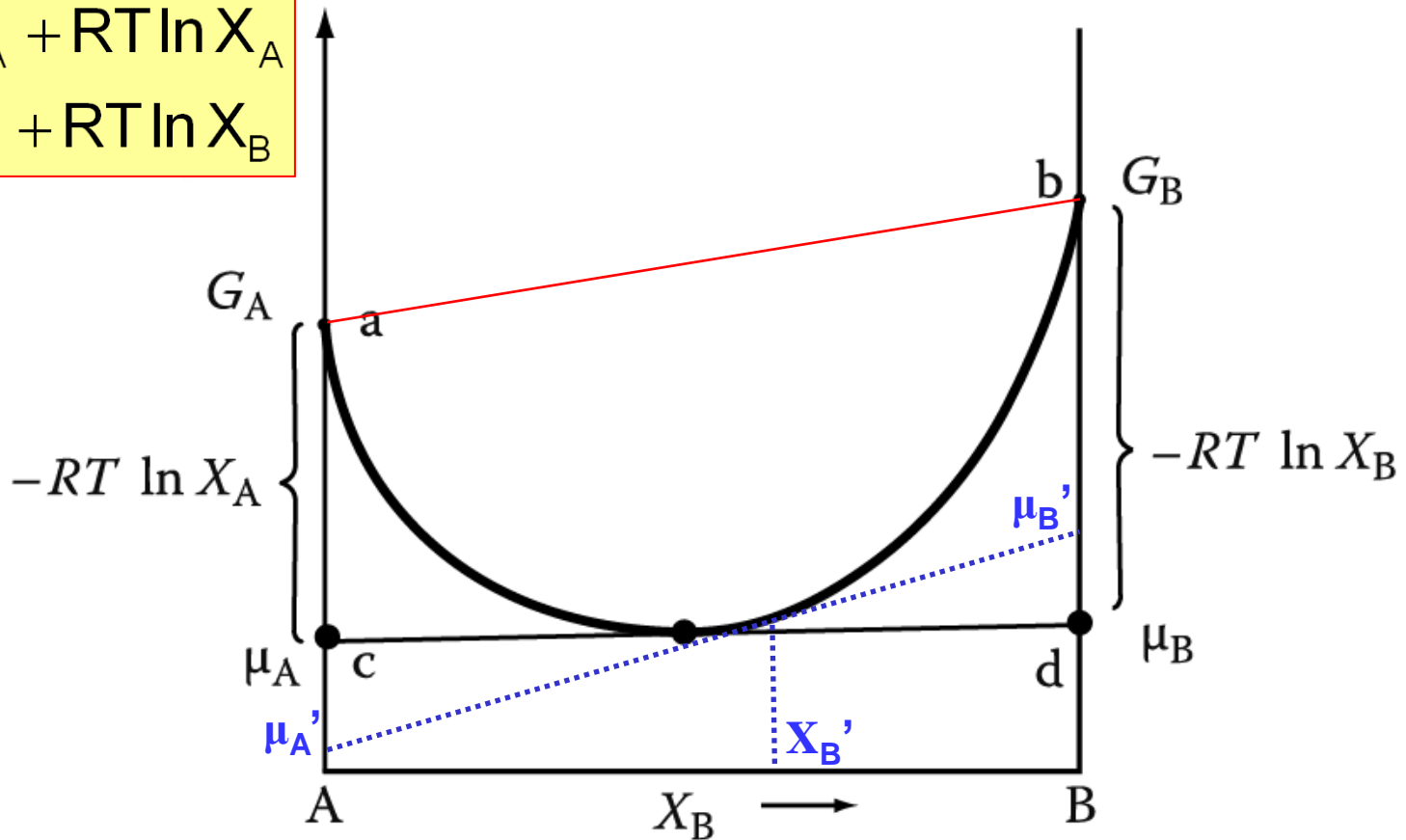


Fig. 1.12 The relationship between the free energy curve and Chemical potentials for an ideal solution.

Contents for today's class II

- Ideal Solution/ **Regular Solution**/ Real solution

1.3 Binary Solutions

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Q1: What is “Regular Solution”?

Regular Solutions

Ideal solution : $\Delta H_{mix} = 0$ \Rightarrow This type of behavior is exceptional in practice and usually mixing is endothermic or exothermic.

Quasi-chemical model assumes that **heat of mixing, ΔH_{mix}** , is only due to **the bond energies between adjacent atoms**.

Assumption: the volumes of pure A and B are equal and do not change during mixing so that the interatomic distance and bond energies are independent of composition.

Structure model of a binary solution

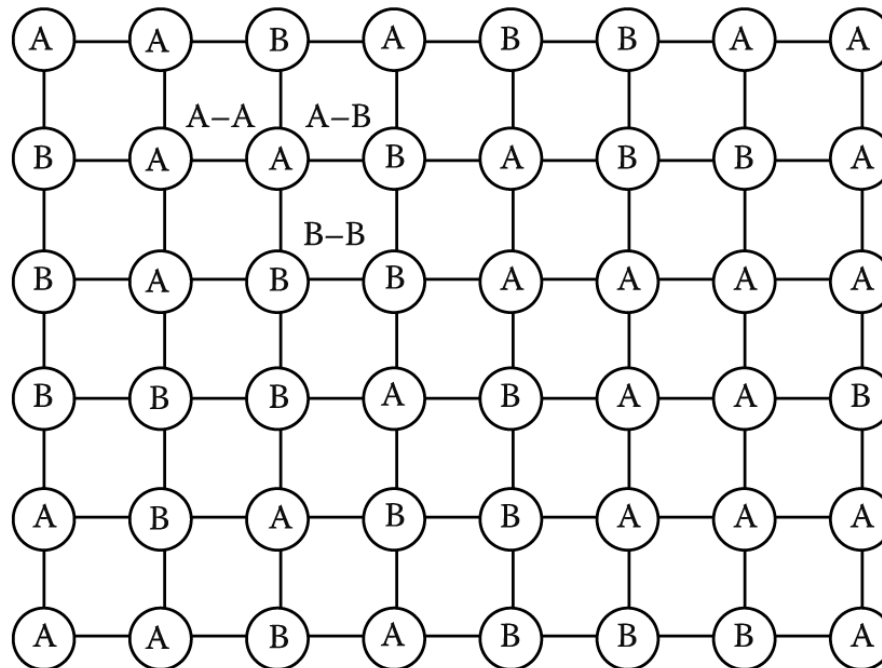


Fig. 1.13 The different types of interatomic bond in a solid solution.

**Q2: How can you estimate
“ ΔH_{mix} of regular solution”?**

$$\Delta H_{\text{mix}} = \Omega X_A X_B \text{ where } \Omega = N_a z \epsilon$$

1.3 Binary Solutions

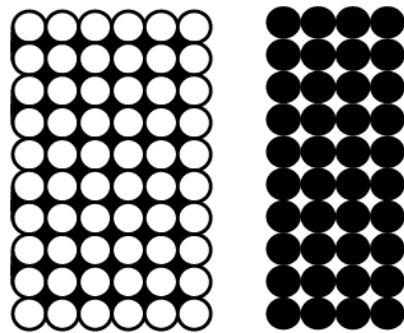
Regular Solutions

	Bond energy	Number of bond
A-A	ϵ_{AA}	P_{AA}
B-B	ϵ_{BB}	P_{BB}
A-B	ϵ_{AB}	P_{AB}

Internal energy of the solution

$$E = P_{AA} \epsilon_{AA} + P_{BB} \epsilon_{BB} + P_{AB} \epsilon_{AB}$$

Before mixing



After mixing

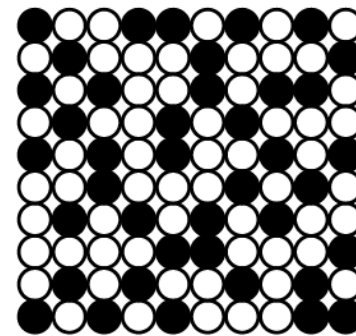


Fig. 1.7

$$\Delta H_{\text{mix}} = P_{AB} \epsilon$$

where $\epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$ 9

1.3 Binary Solutions

Regular Solutions

Completely random arrangement

$$\varepsilon = 0 \quad \rightarrow \quad \varepsilon_{AB} = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

$$\Delta H_{\text{mix}} = 0 \quad \text{ideal solution}$$

$$\Delta S^{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B)$$

$$P_{AB} = N_a z X_A X_B \quad \text{bonds per mole}$$

N_a : Avogadro's number

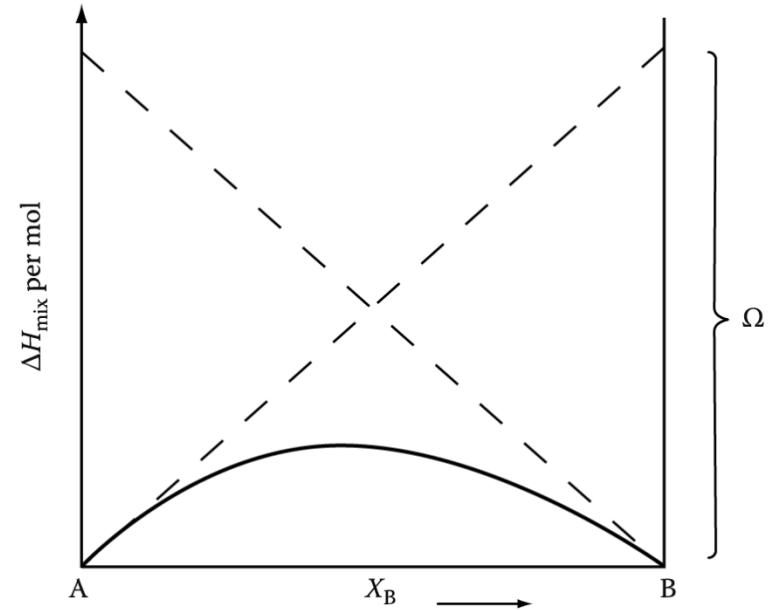
z : number of bonds per atom

$$(1) \quad \varepsilon < 0 \rightarrow P_{AB} \uparrow \quad (2) \quad \varepsilon > 0 \rightarrow P_{AB} \downarrow$$

$$(3) \quad \boxed{\varepsilon \approx 0} \quad \rightarrow \quad \Delta H_{\text{mix}} = P_{AB} \varepsilon$$

$$\Delta H_{\text{mix}} = \Omega X_A X_B \quad \text{where} \quad \Omega = N_a z \varepsilon$$

Regular solution



If $\Omega > 0$,

Fig. 1.14 The variation of ΔH_{mix} with composition for a regular solution.

Q3: How can you estimate

“Molar Free energy for regular solution”?

$$G_2 = G_1 + \Delta G_{mix}$$

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

Regular Solutions

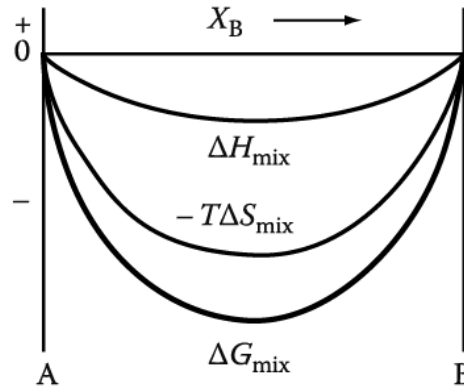
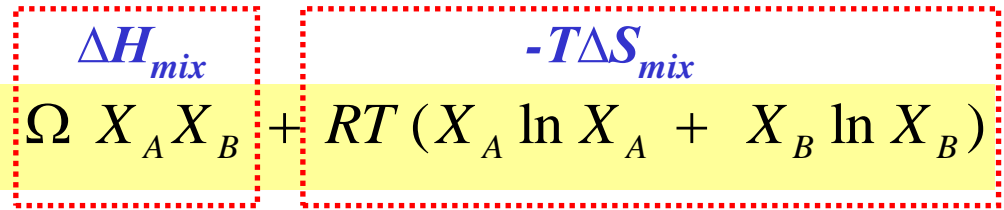
$$G_2 = G_1 + \Delta G_{mix}$$

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

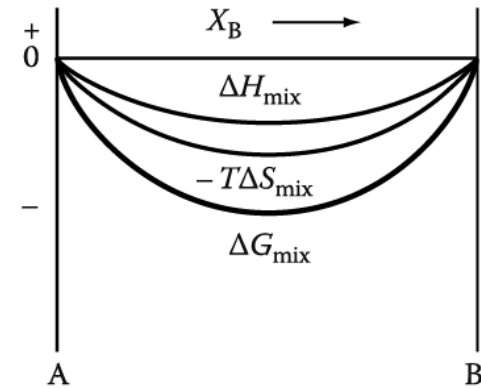
Reference state

Pure metal $G_A^0 = G_B^0 = 0$

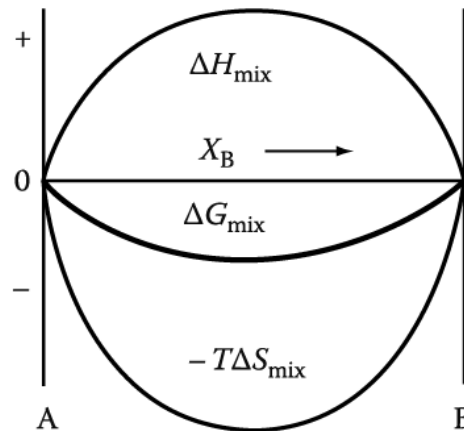
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



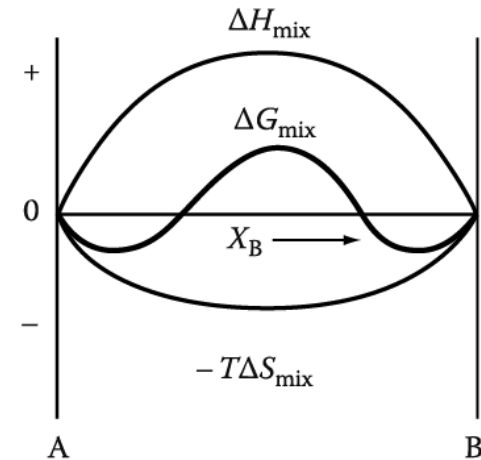
(a) $\Omega < 0$, high T



(b) $\Omega < 0$, low T



(c) $\Omega > 0$, high T



(d) $\Omega > 0$, low T

Fig. 1.5

Q4: “Correlation between chemical potential and free energy”?

Correlation between chemical potential and free energy

For 1 mole of the solution (T, P: constant)

$$G = E + PV - TS \quad G = \mu_A X_A + \mu_B X_B \quad \text{Jmol}^{-1}$$

$$G = H - TS \quad G = X_A G_A + X_B G_B + \Omega X_A X_B + RT (X_A \ln X_A + X_B \ln X_B)$$

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

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

Regular solution

$$\mu_A = G_A + \Omega (1 - X_A)^2 + RT \ln X_A$$

$$\mu_B = G_B + \Omega (1 - X_B)^2 + RT \ln X_B$$

$$\mu_A = G_A + RT \ln X_A$$

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

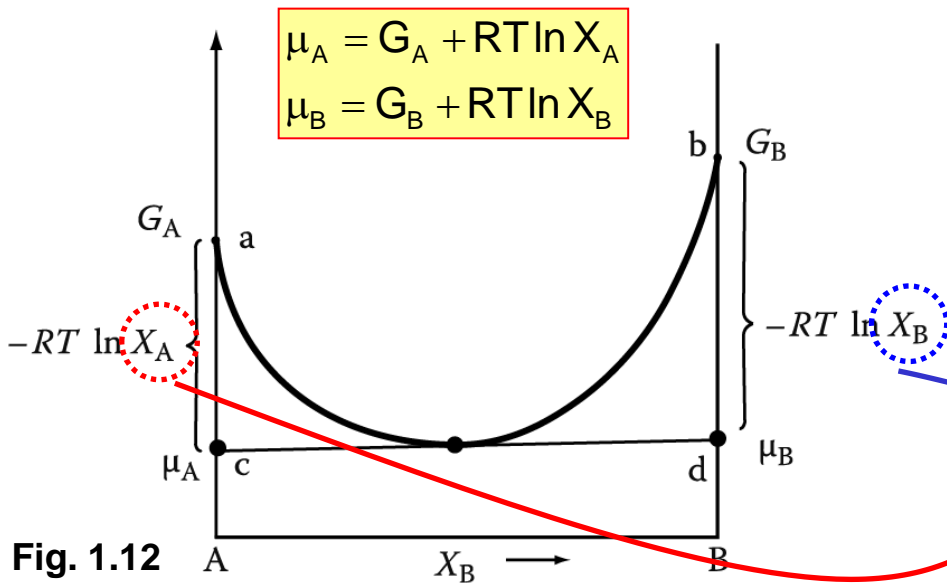
Ideal solution



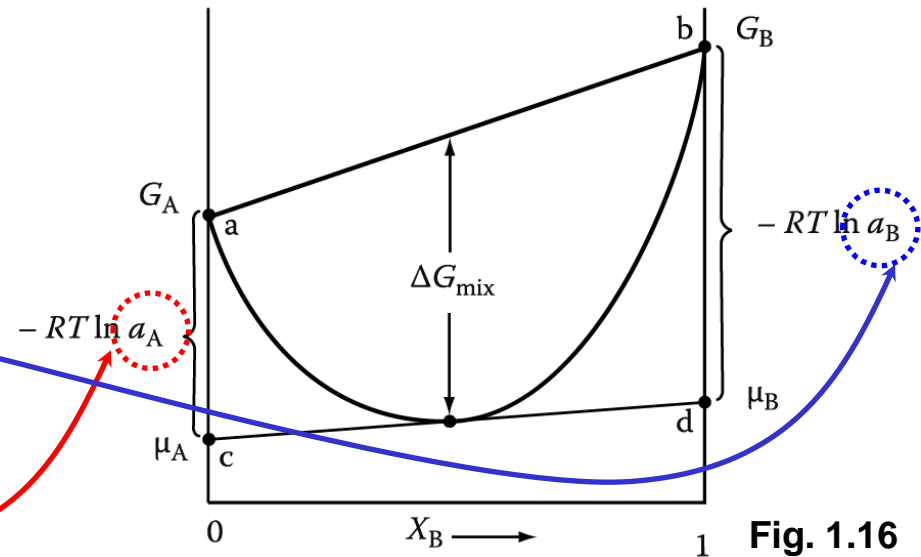
Q5: What is “activity”?

Activity, a : effective concentration for mass action

ideal solution



regular solution



$$\mu_A = G_A + RT \ln a_A$$

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

$$\mu_A = G_A + \Omega (1 - X_A)^2 + RT \ln X_A$$

$$\mu_B = G_B + \Omega (1 - X_B)^2 + RT \ln X_B$$

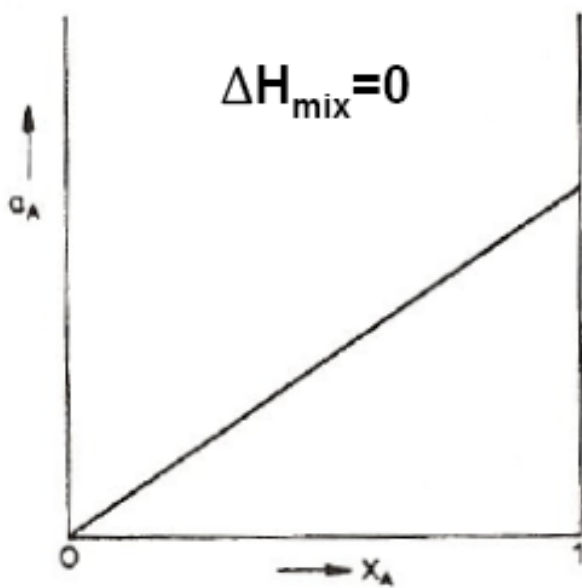
$$\ln \left(\frac{a_A}{X_A} \right) = \frac{\Omega}{RT} (1 - X_A)^2$$

$$\ln \left(\frac{a_B}{X_B} \right) = \frac{\Omega}{RT} (1 - X_B)^2$$

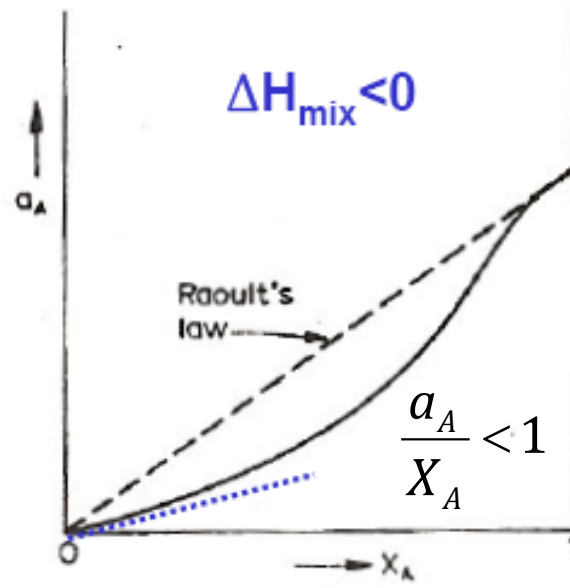
$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient}$$

$$\gamma_B = \frac{a_B}{X_B}$$

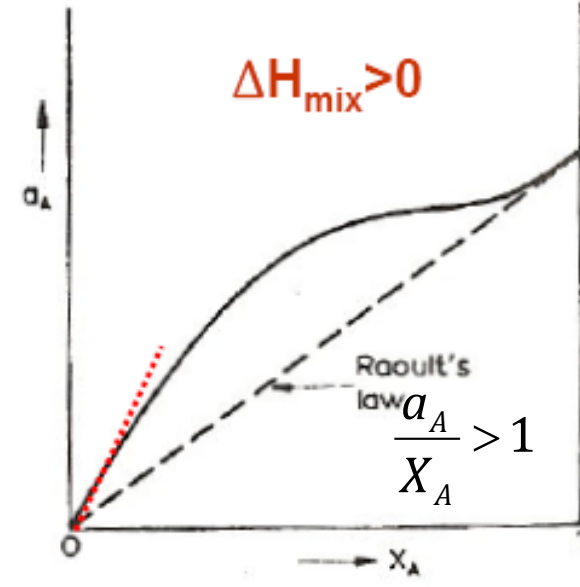
Activity-composition curves for solutions



(a)
Ideal solution
 $A \leftrightarrow B = \frac{1}{2}(A \leftrightarrow A + B \leftrightarrow B)$
e.g. Bi-Sn at 335°C
 $a_A = a_{\text{Sn}}$



(b)
Actual solution
 $A \leftrightarrow B > \frac{1}{2}(A \leftrightarrow A + B \leftrightarrow B)$
e.g. Au-Sn at 600°C
 $a_A = a_{\text{Sn}}$



(c)
Actual solution
 $A \leftrightarrow B < \frac{1}{2}(A \leftrightarrow A + B \leftrightarrow B)$
e.g. Cd-Pb at 500°C
 $a_A = a_{\text{Cd}}$

Degree of non-ideality

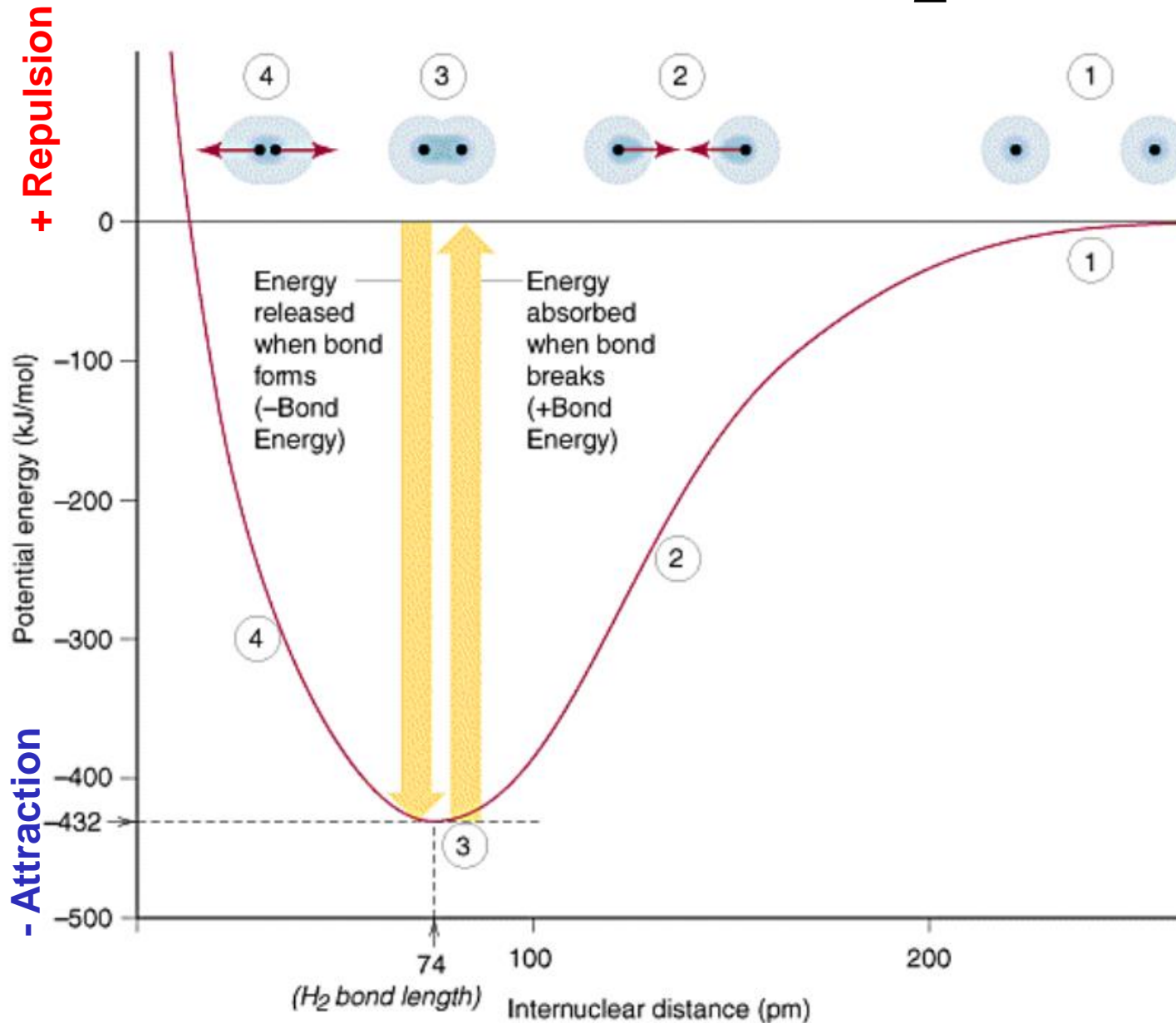
$$\gamma_B = \frac{a_B}{X_B} \cong \text{constant} \quad (\text{Henry's Law})$$

$$\gamma_A = \frac{a_A}{X_A} \cong 1 \quad (\text{Raoult's Law})$$

- For a dilute solution of B in A ($X_B \rightarrow 0$)

$$\Delta H_{\text{mix}} = P_{AB} \varepsilon$$

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



Variation of activity with composition (a) a_B , (b) a_A

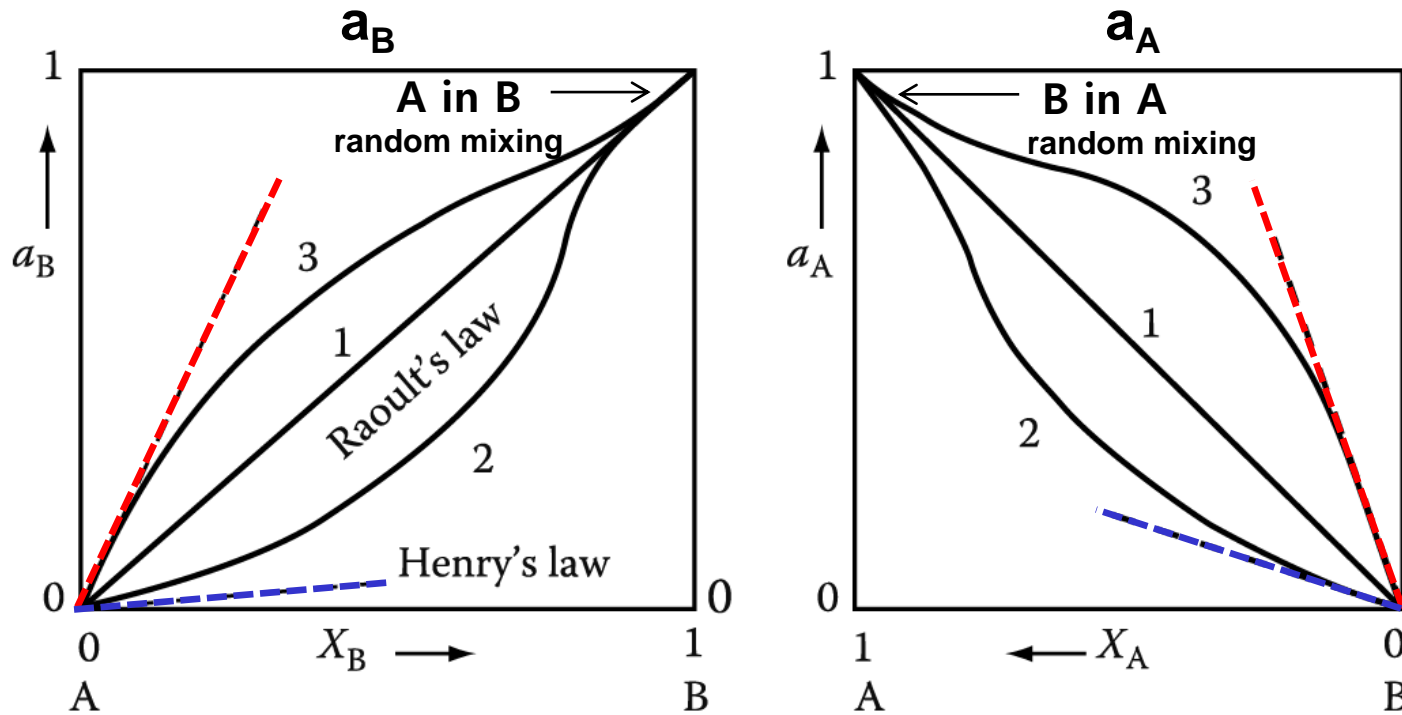


Fig. 1.7

Line 1 : (a) $a_B = X_B$, (b) $a_A = X_A$

Line 2 : (a) $a_B < X_B$, (b) $a_A < X_A$

Line 3 : (a) $a_B > X_B$, (b) $a_A > X_A$

ideal solution...Rault's law

$\Delta H_{\text{mix}} < 0$ ← $\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1-X_A)^2$

$\Delta H_{\text{mix}} > 0$

Q6: “Chemical equilibrium of multi-phases”?

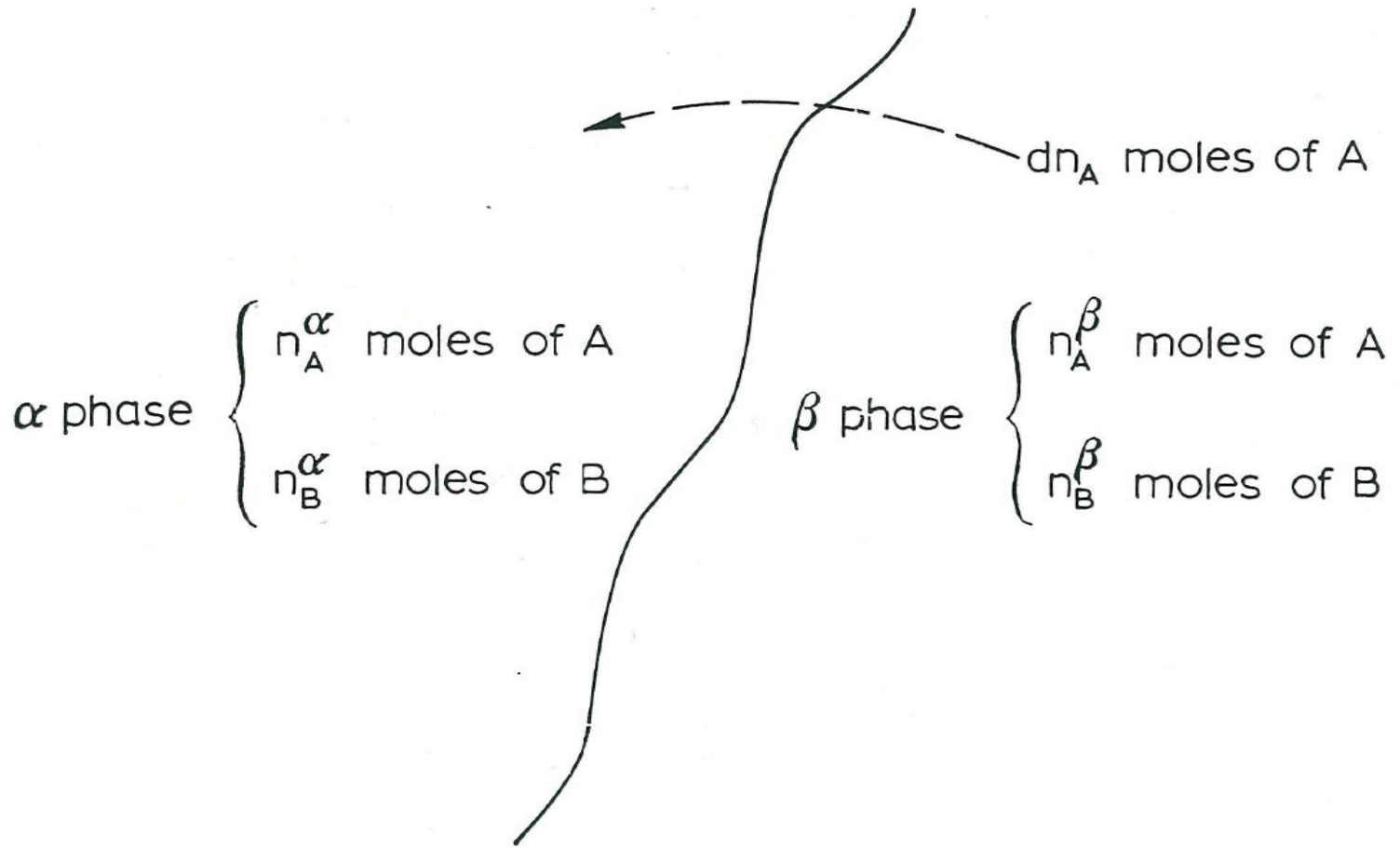


Fig. 10. Transfer of dn_A moles of component A from the β to the α phase.

Activity of a component is just another means of describing the state of the component in a solution.

degree of non-ideality ? $\rightarrow \frac{a_A}{X_A}$

$$\frac{a_A}{X_A} = \gamma_A, \quad a_A = \gamma_A X_A$$

γ_A : activity coefficient

$$\ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT} (1 - X_B)^2$$

$$\mu_A = G_A + RT \ln a_A$$

Activity or chemical potential of a component is important when several condensed phases are in equilibrium.

Chemical Equilibrium (μ , a) \rightarrow multiphase and multicomponent
 $(\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots), (a_i^\alpha = a_i^\beta = a_i^\gamma = \dots)$

$$(\mu_A^\alpha = \mu_A^\beta = \mu_A^\gamma = \dots), (a_A^\alpha = a_A^\beta = a_A^\gamma = \dots)$$

$$(\mu_B^\alpha = \mu_B^\beta = \mu_B^\gamma = \dots), (a_B^\alpha = a_B^\beta = a_B^\gamma = \dots)$$

\vdots

- **Binary System** mixture/ solution / compound

- **Gibbs Free Energy in Binary System**

$$G_1 = X_A G_A + X_B G_B \quad J/mol$$

$$G_2 = G_1 + \Delta G_{mix} \quad J/mol$$

Ideal solution ($\Delta H_{mix}=0$) $\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$

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

Regular solution $\Delta H_{mix} = P_{AB}\epsilon$ where $\epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})$

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

- **Chemical potential and Activity**

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

$$\mu_A = G_A + RT \ln a_A \quad \ln \left(\frac{a_A}{X_A} \right) = \frac{\Omega}{RT} (1 - X_A)^2$$

$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient}$$

μ 는 조성에 의해 결정되기 때문에 dn_A 가 매우 작아서 조성변화 없어야

Contents for today's class II

- Ideal Solution/ Regular Solution/ **Real solution**

Q7: What is “Real Solution”?

sufficient disorder + lowest internal E

1.3 Binary Solutions

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Real solution: sufficient disorder + lowest internal E

Ideal or Regular solution: over simplification of reality

Config. Entropy $S = k \ln w$

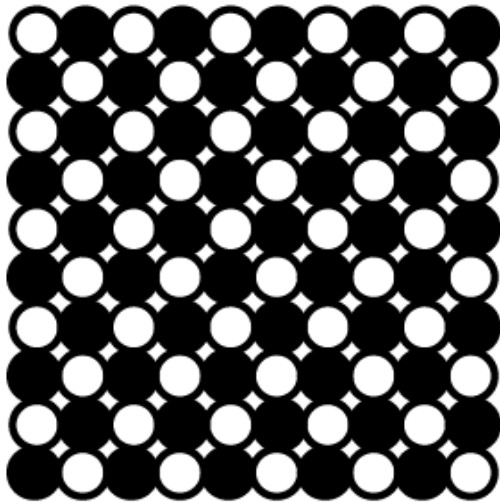
+ mixing enthalpy

$$\Delta H_{mix} = \Omega X_A X_B \text{ where } \Omega = N_a z \epsilon$$

$$S_{thermal} = 0$$

$$\epsilon \approx 0$$

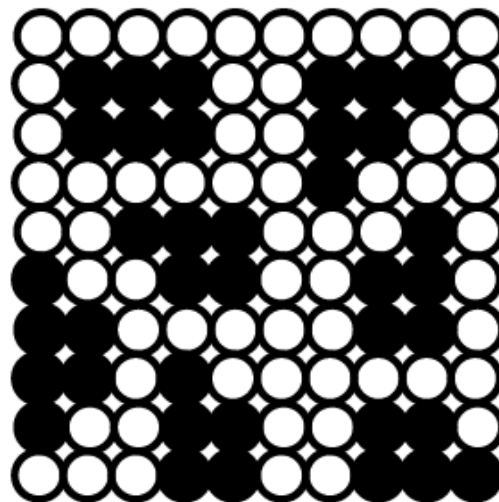
Fig. 1.18



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

Ordered alloys

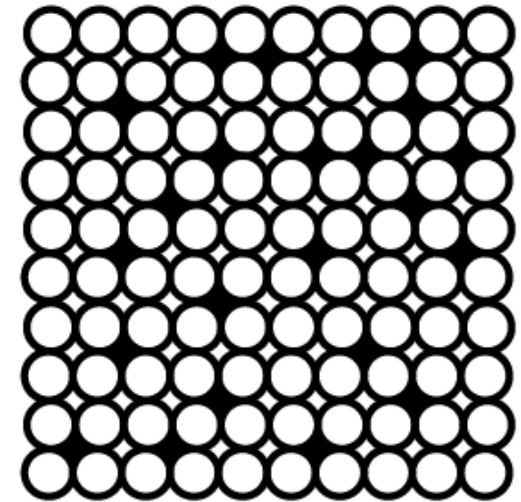
$P_{AB} \uparrow \longrightarrow$ Internal E \downarrow



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

Clustering

$P_{AA}, P_{BB} \uparrow$



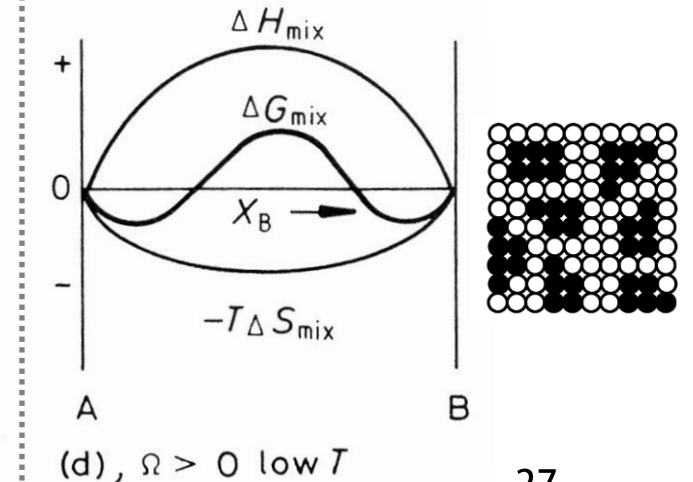
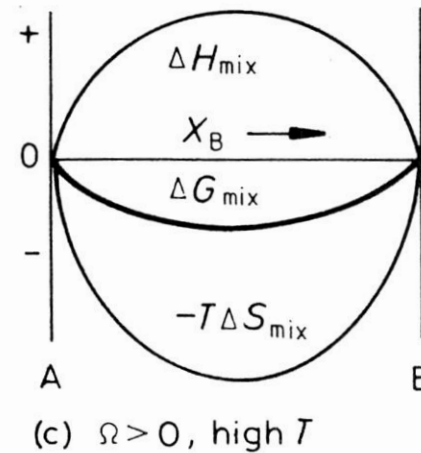
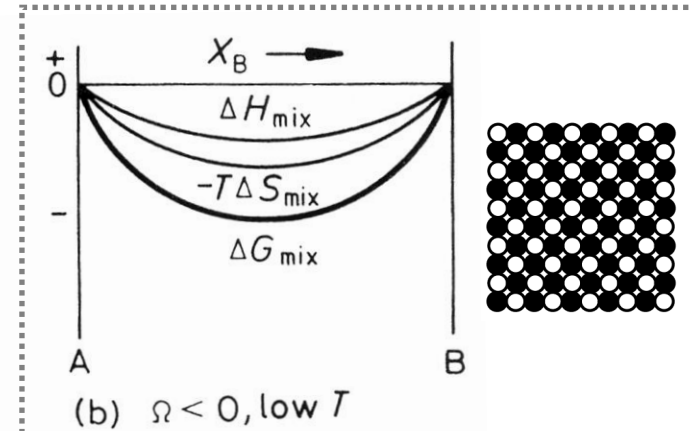
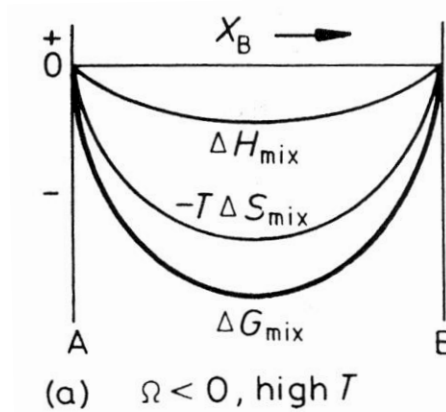
(c) when the size difference is large
strain effect

Interstitial solution

* The degree of **ordering or clustering** will decrease as temp. **increases** due to the increasing importance of **entropy**.

High temp. \longrightarrow Entropy effect \uparrow \longrightarrow Solution stability \uparrow

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



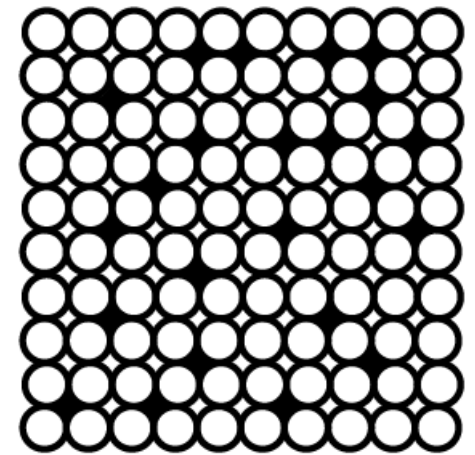
1.3 Binary Solutions

Real solution: sufficient disorder + lowest internal E

2) In systems where there is a size difference between the atom
e.g. interstitial solid solutions,

→ $\Delta E = \Delta H_{\text{mix}} + \text{elastic strain}$

→ quasi-chemical model ~ underestimate ΔE
due to no consideration of elastic strain field



→ **New mathematical models are needed to describe these solutions.**

**Q8: Ordered phase I:
“Short range order (SRO)” in solution**

1.3 Binary Solutions

Ordered phase $\varepsilon < 0, \Delta H_{\text{mix}} < 0$ $P_{AB} \uparrow$

SRO (Short Range Ordering) or **LRO** (Long Range Ordering)

- $\Omega < 0 \Rightarrow$ contain short-range order (SRO)

$\Delta\Omega = N_a z \varepsilon$ **SRO parameter = s** _ degree of ordering

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

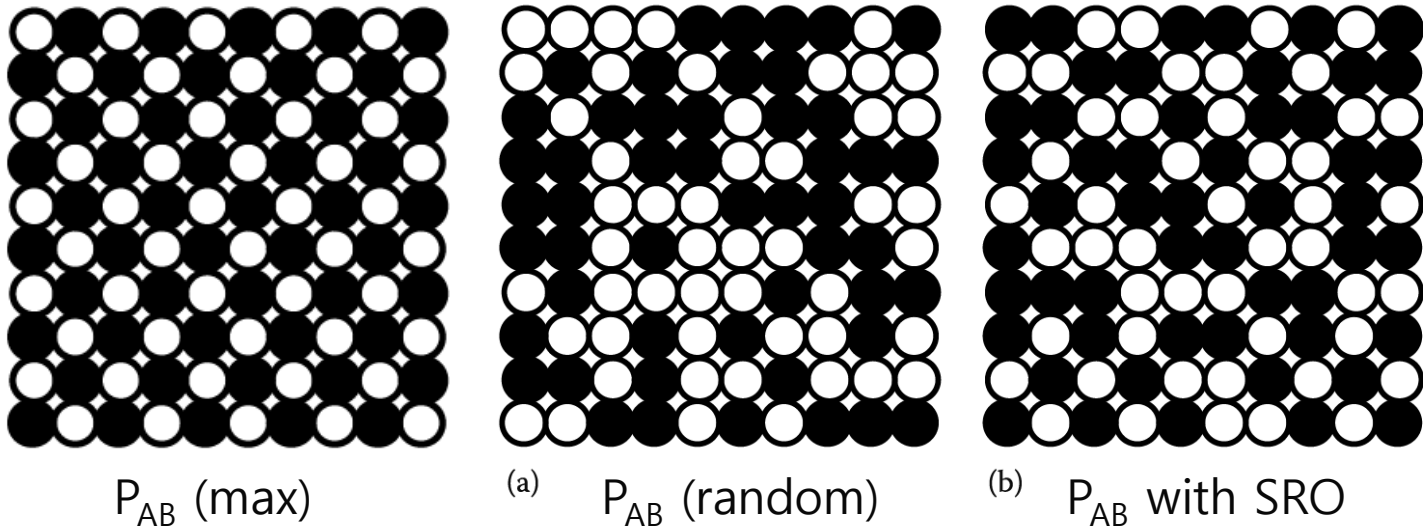
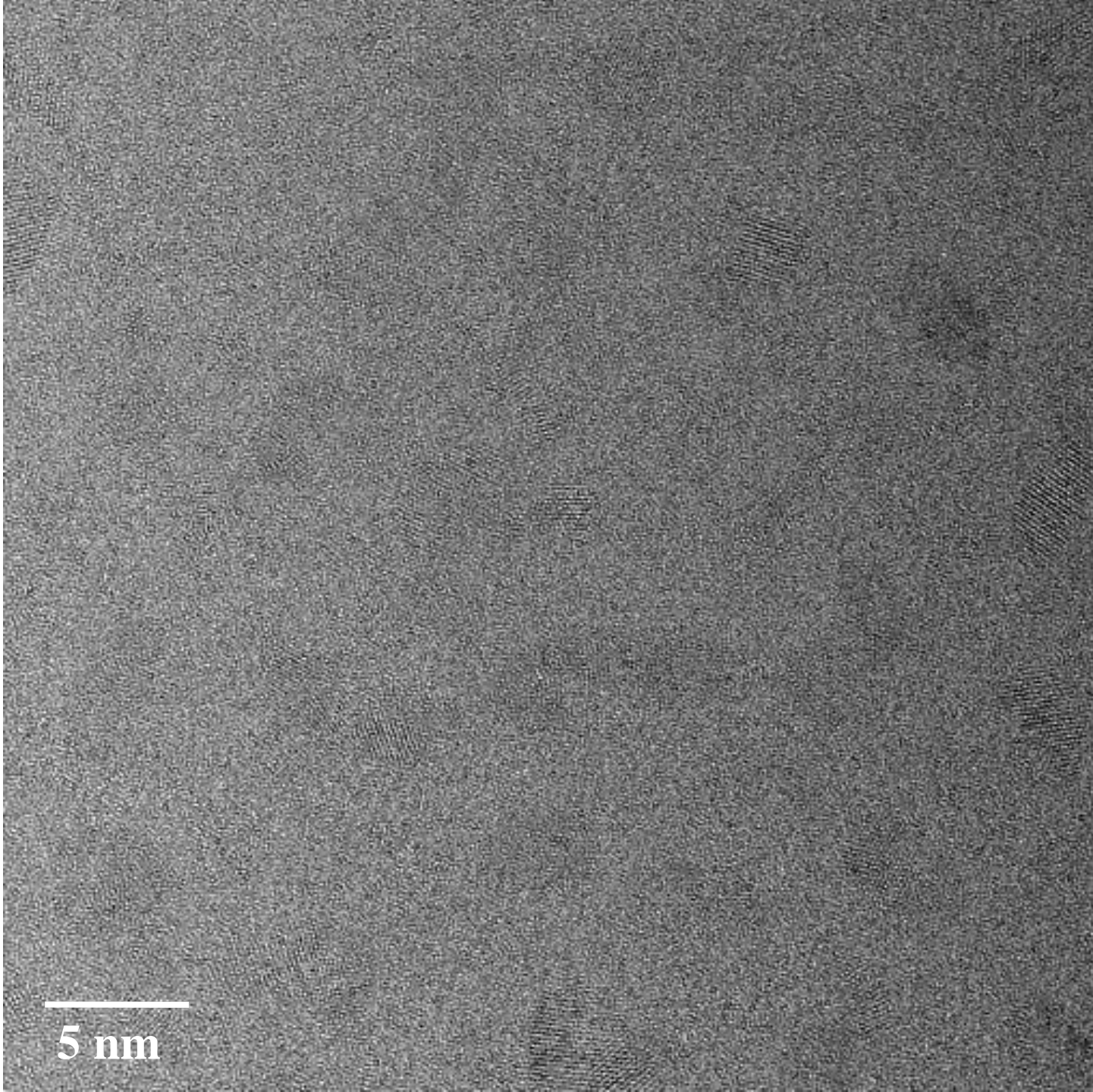
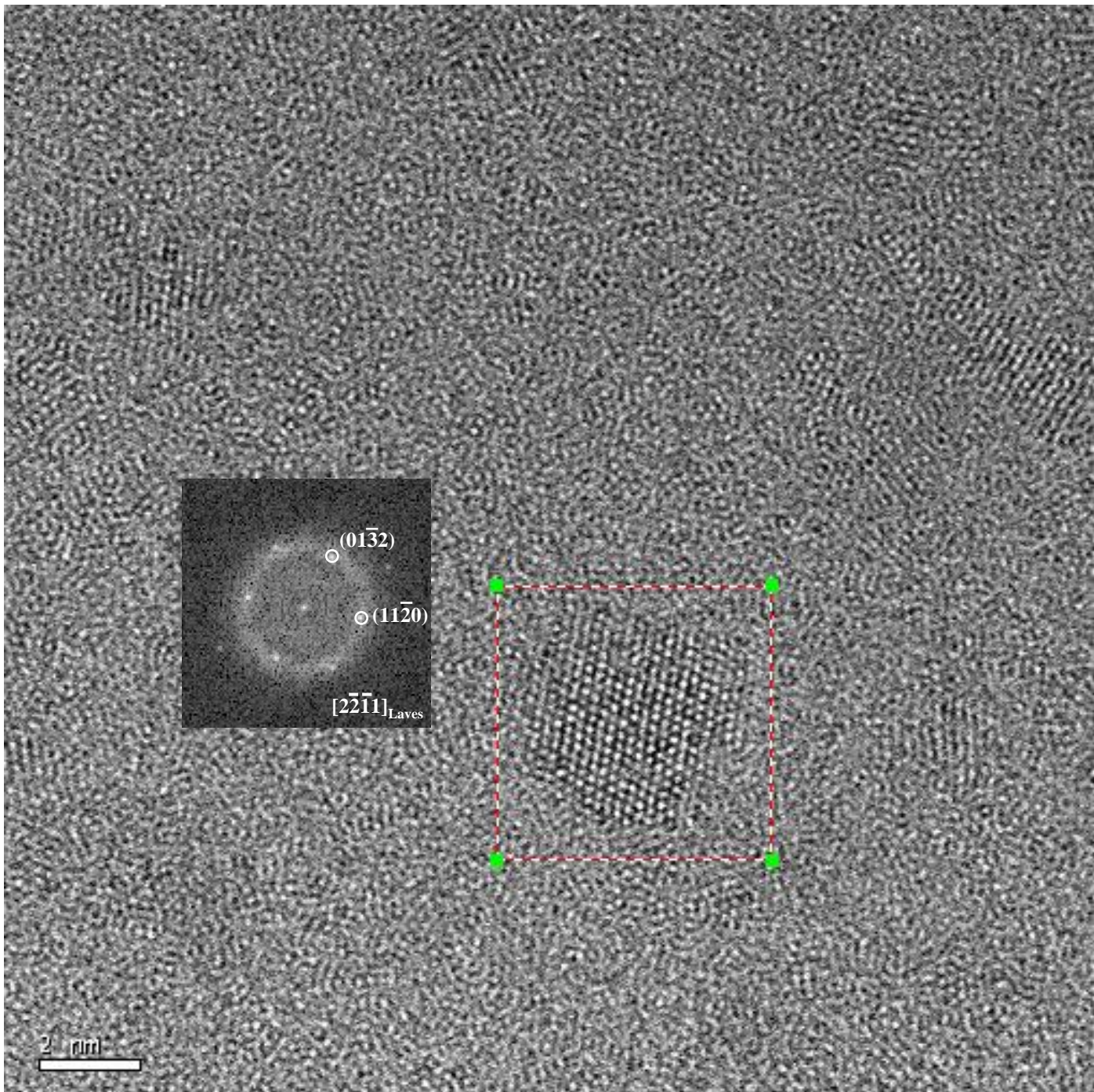


Fig. 1.19 (a) Random A-B solution with a total of 100 atoms and $X_A=X_B=0.5$, $P_{AB} \sim 100$, $S=0$.
(b) Same alloy with short-range order $P_{AB}=132$, $P_{AB}(\text{max}) \sim 200$, $S=(132-100)/(200-100)=0.32$. 30



5 nm



**Q9: Ordered phase II:
“Long range order (LRO)”**

(①superlattice, ②intermediate phase, ③intermetallic compound)

* **Solid solution → ordered phase**

→ random mixing

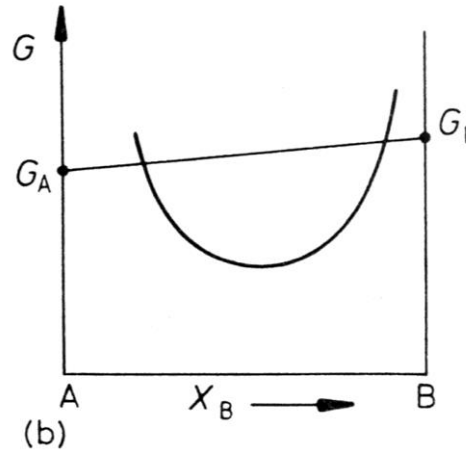
→ entropy ↑

negative enthalpy ↓

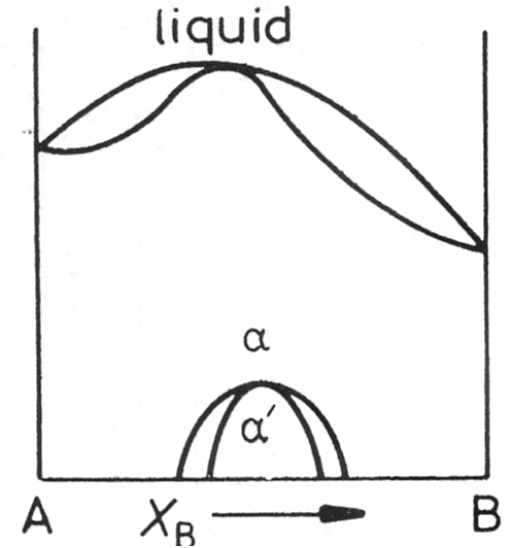
$$\Delta H_{mix}^S < 0$$

Large composition range

→ $G \downarrow$



intermediate phases: (a) for an intermetallic compound with a very narrow stability range, (b) for an intermediate phase with a wide stability range.



* **Compound : AB, A₂B...**

→ entropy ↓

→ covalent, ionic contribution.

→ enthalpy more negative ↓

$$\Delta H_{mix}^S \ll 0$$

Small composition range

→ $G \downarrow$

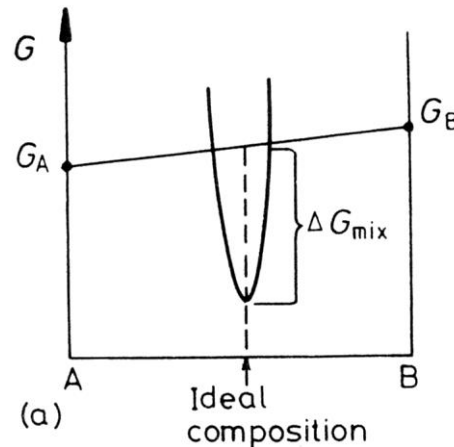
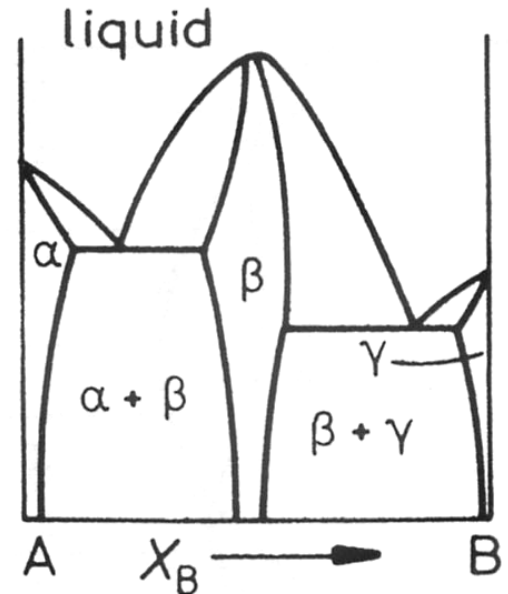


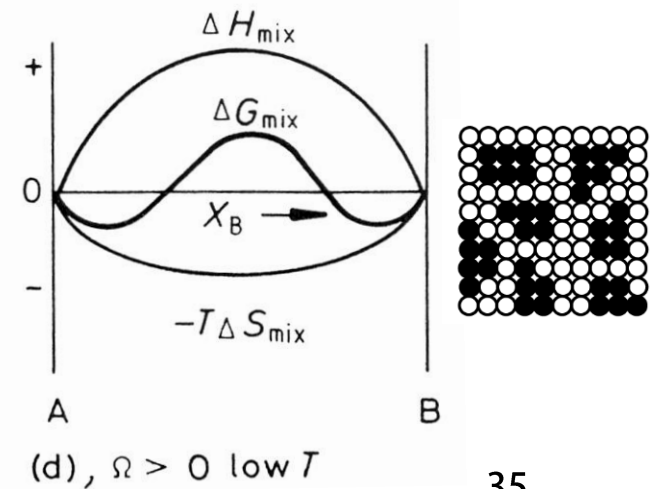
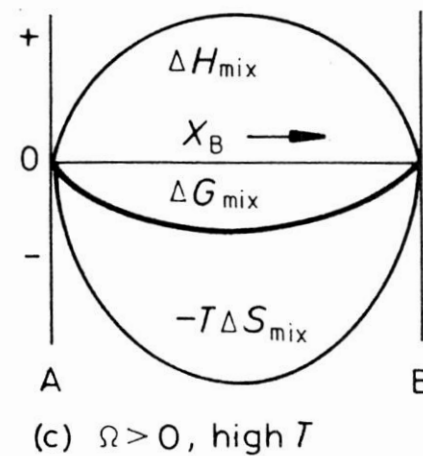
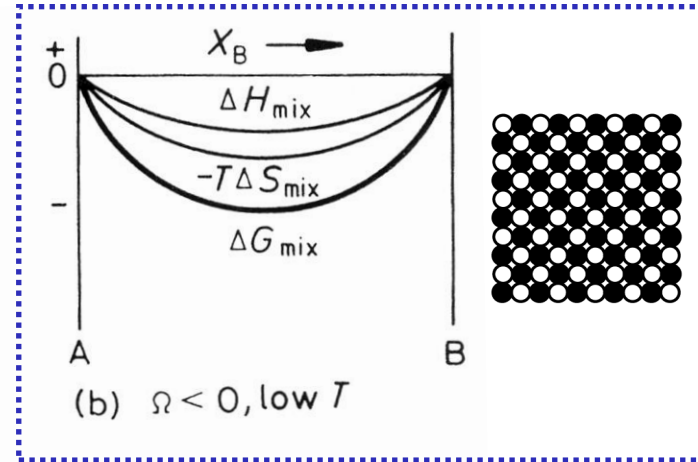
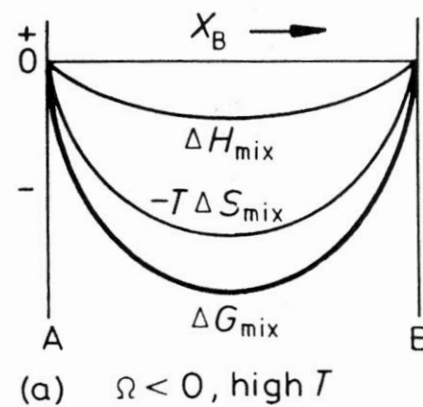
Fig. 1.23 Free energy curves for intermetallic compound with a very narrow stability range, (a) for an intermetallic compound with a very narrow stability range, (b) for an intermediate phase with a wide stability range.



* The degree of **ordering or clustering** will decrease as temp. **increases** due to the increasing importance of **entropy**.

High temp. \longrightarrow Entropy effect \uparrow \longrightarrow Solution stability \uparrow

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



Q9-a: Superlattice

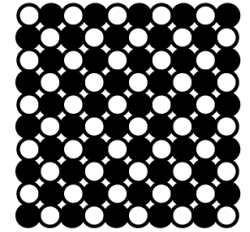
1.3 Binary Solutions

Ordered phase

$$\epsilon < 0, \Delta H_{\text{mix}} < 0$$

* In solutions with compositions that are close to a simple ratio of A:B atoms another type of order can be found.

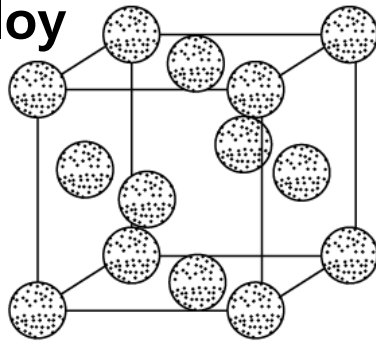
* This is known as long-range order (LRO) CuAu, Cu₃Au and many other intermetallics show LRO.



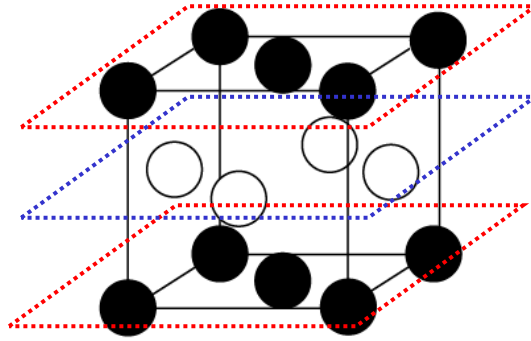
(The atom sites are no longer equivalent but can be labelled as A-sites and B-sites.)

* A superlattice forms in materials with LRO

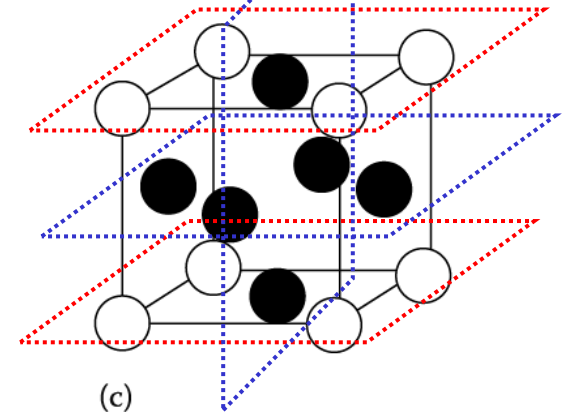
Cu-Au alloy



(a)



(b)



(c)

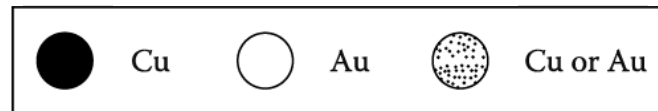


Fig. 1.20

High temp.

Disordered Structure

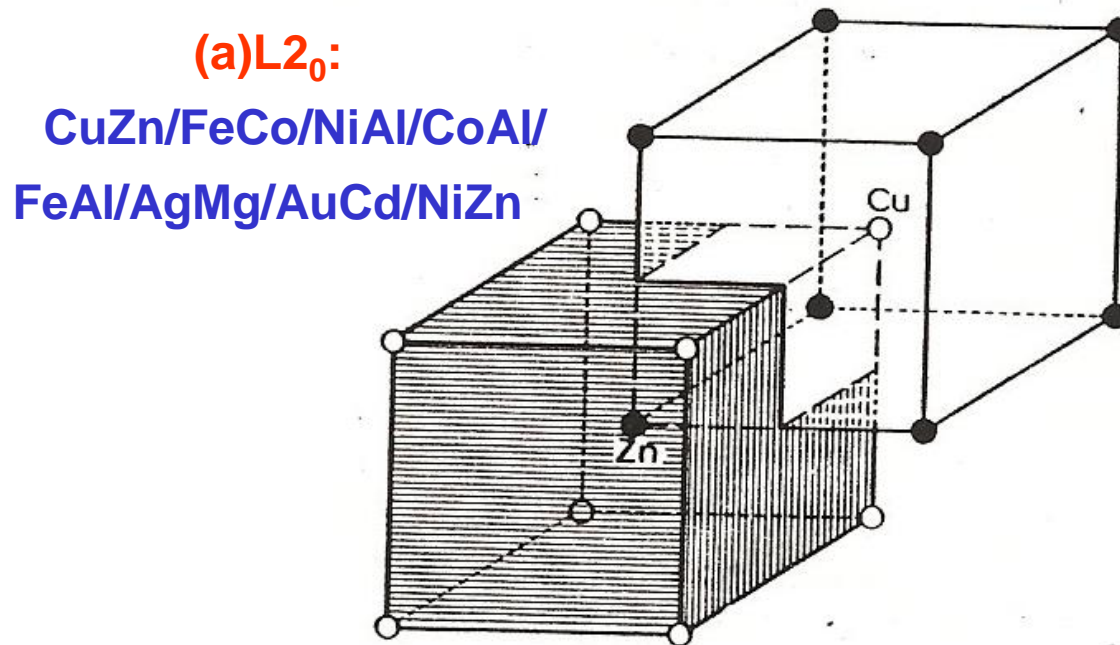
Low temp.

CuAu superlattice

Cu₃Au superlattice

Superlattice formation: order-disorder transformation

- $\epsilon < 0$, $\Delta H_{\text{mix}} < 0$
- **between dissimilar atoms** than between similar atoms
- **Large electrochemical factor**: tendency for the solute atoms to avoid each other and to associate with the solvent atoms
- **Size factor just within the favorable limit**: lead to atomic rearrangement so as to relieve the lattice distortion imposed by the solute atoms



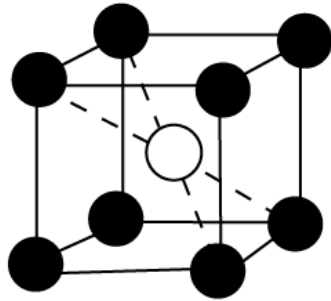
β brass superlattice viewed as two inter-penetrating cubic lattices

1.3 Binary Solutions

Five common ordered lattices

(a) $L2_0$:

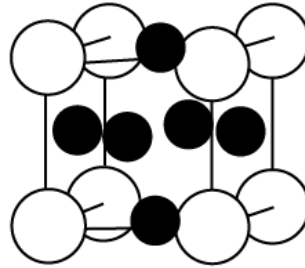
CuZn/FeCo/NiAl/CoAl/
FeAl/AgMg/AuCd/NiZn



(a) ● Cu ○ Zn

(b) $L1_2$:

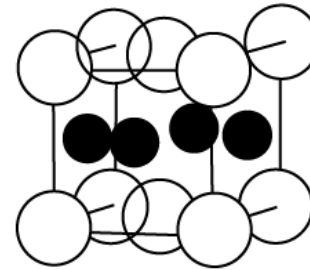
Cu₃Au/Ni₃Mn/Ni₃Fe/Ni₃Al/
Pt₃Fe/Au₃Cd/Co₃V/TiZn₃



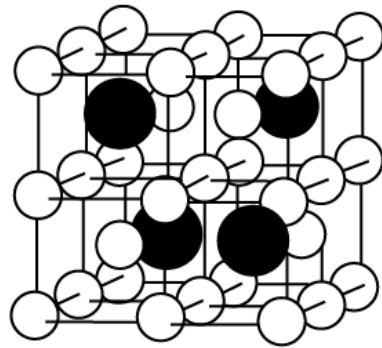
(b) ● Cu ○ Au

(c) $L1_0$:

CuAu/CoPt/FePt



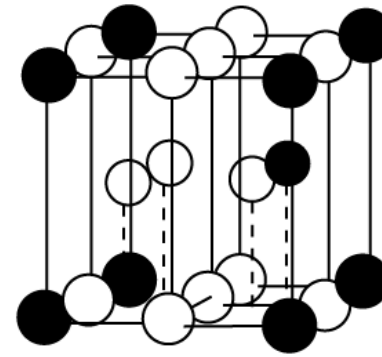
(c) ● Cu ○ Au



(d) ● Al ○ Fe

(d) $D0_3$:

Fe₃Al/Cu₃Sb/Mg₃Li/Fe₃Al/
Fe₃Si/Fe₃Be/Cu₃Al



(e) ● Cd ○ Mg

(e) $D0_{19}$:

Mg₃Cd/Cd₃Mg/Ti₃Al/Ni₃Sn/Ag₃In/
Co₃Mo/Co₃W/Fe₃Sn/Ni₃In/Ti₃Sn

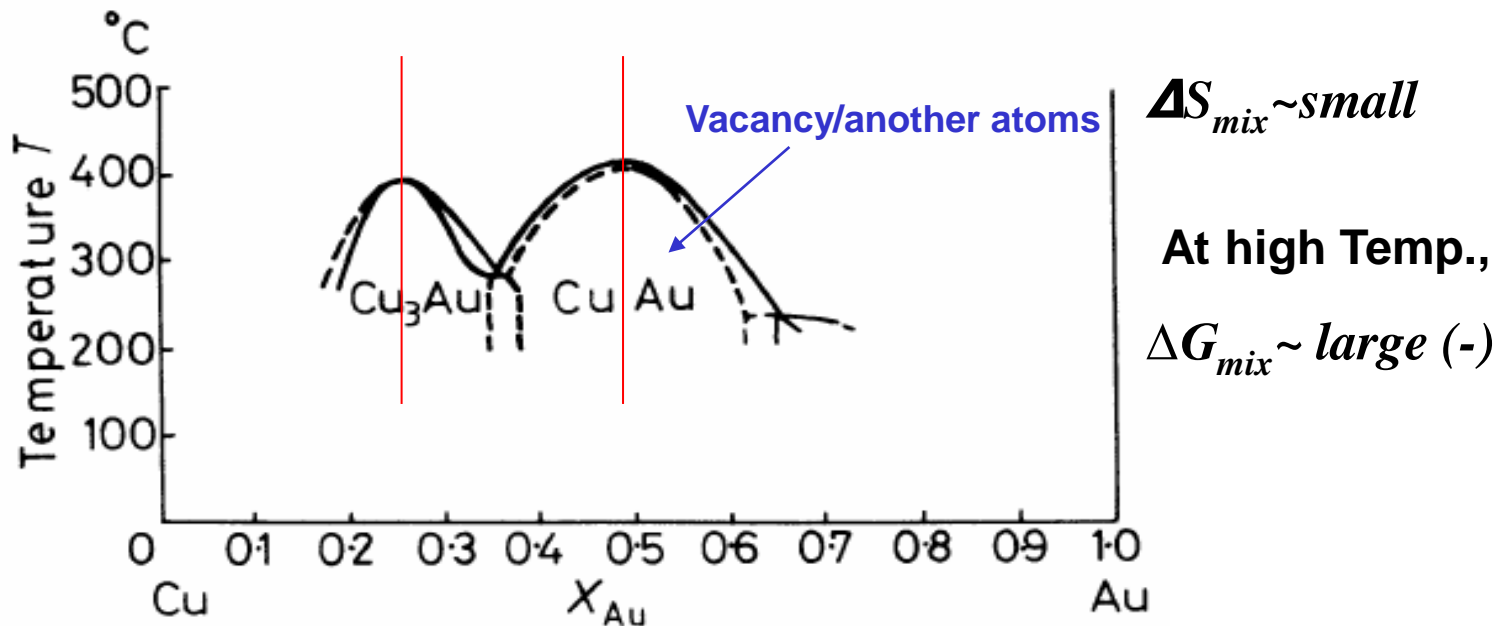
Fig. 1.22

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Ordered phase

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

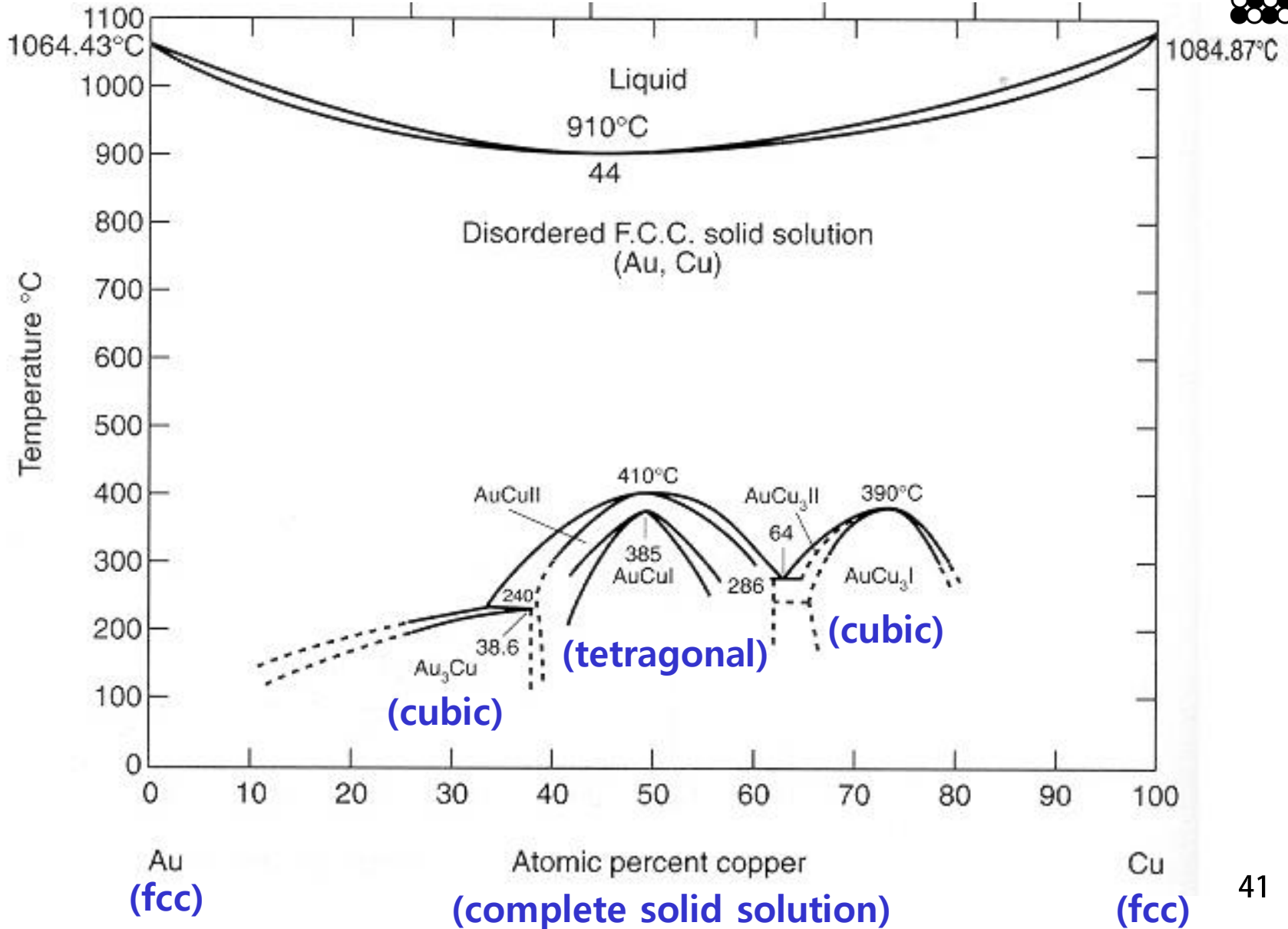
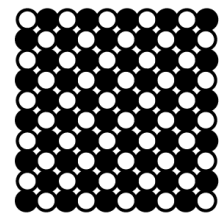
Fig. 1.21. Part of the Cu-Au phase diagram showing the regions where the Cu_3Au and CuAu superlattices are stable.



- The **entropy** of mixing of structure with LRO is **extremely small** and **the degree of order decrease** with **increasing temperature** until above some **critical temperature** there is no LRO at all.
- This temperature is a maximum when the composition is the ideal required for the superlattice.
- The critical temperature for loss of LRO increases with increasing Ω or ΔH_{mix} and in many systems the ordered phase is stable up to the melting point.

Ordered Phase

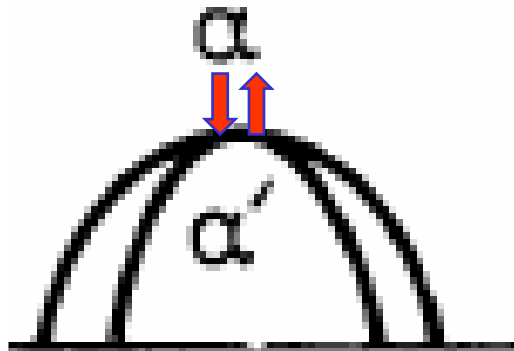
$$\epsilon < 0, \Delta H_{\text{mix}} < 0 / \Delta H_{\text{mix}} \sim -20 \text{ kJ/mol}$$



Q9-b: Order-disorder transition

Order-disorder phase transformation

- Not classical phase change = ~not depend on diffusion process
- **change of temperature allowed a continuous re-arrangement of atoms without changing the phase = "2nd order transition"**
- **boundary: ordered lattice & disordered lattice/phase rule could not applied**
there are cases in which an ordered phase of one composition exists in equilibrium with a disordered phase of a different composition.
- Simple composition of the type AB or AB₃ can the transformation (i.e. at the temperature maximum) be considered diffusionless.

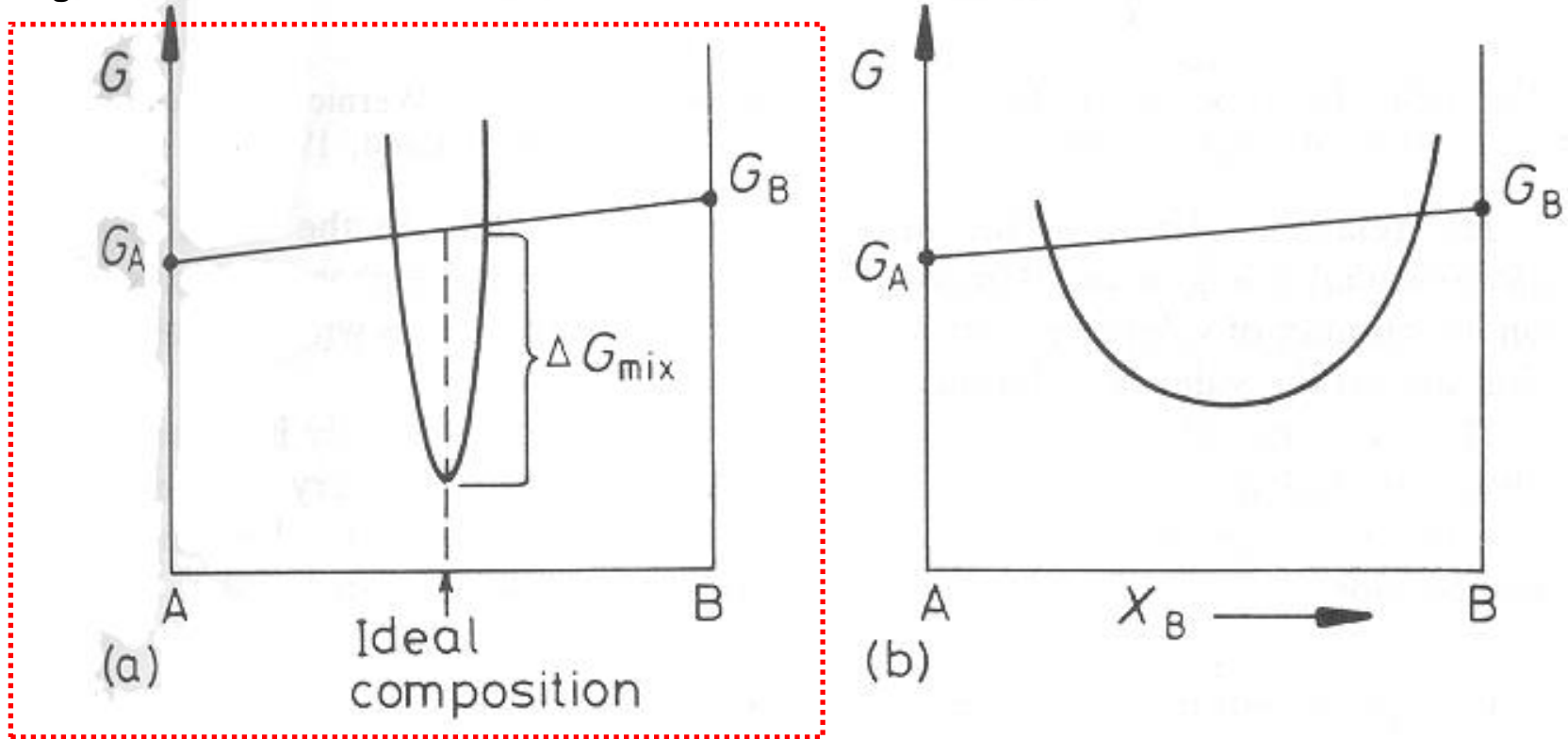


Q9-c:

Intermediate phase vs Intermetallic compound

Intermediate Phase

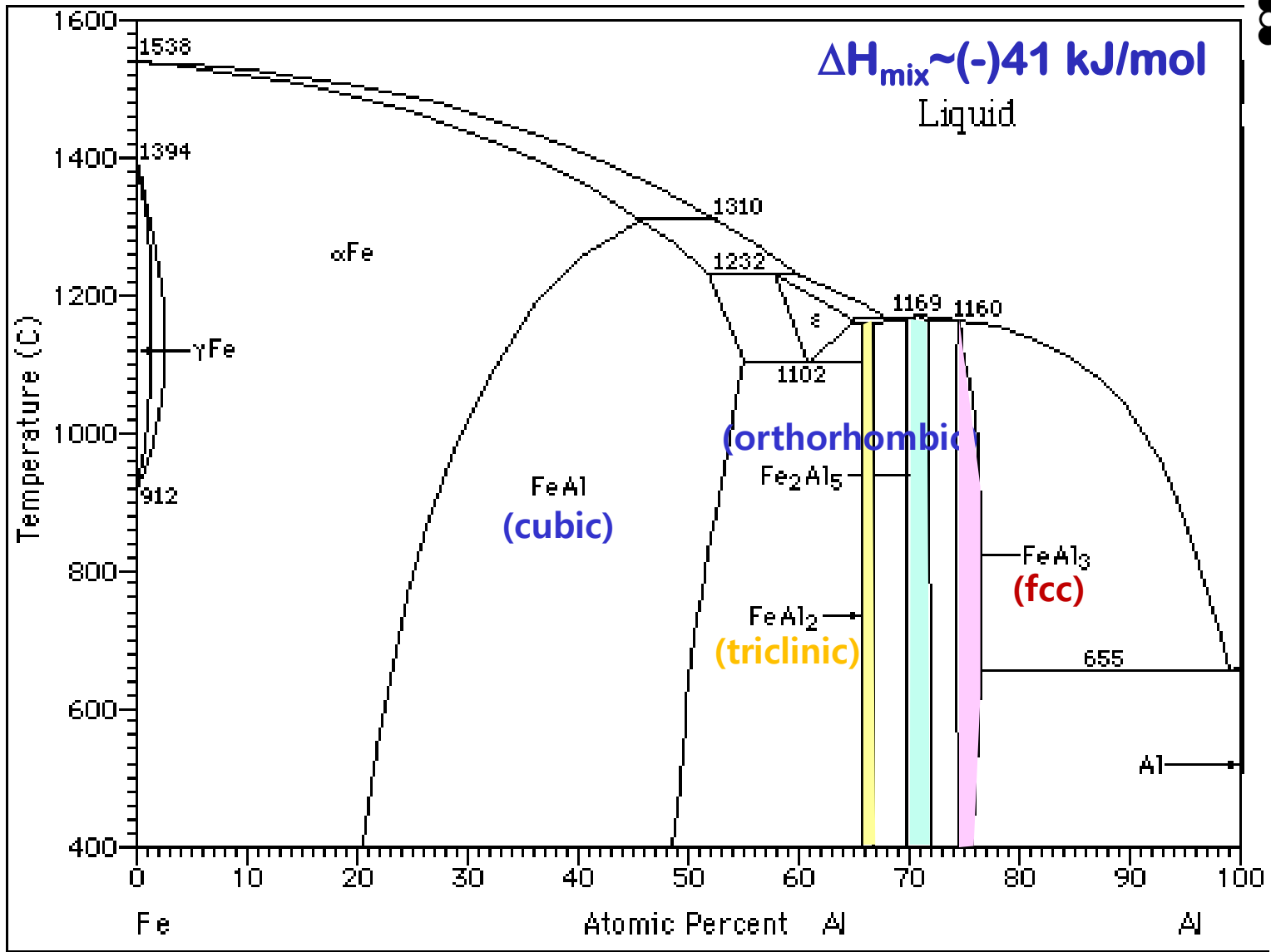
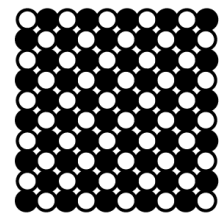
Fig. 1.23



- * **Many intermetallic compounds** have **stoichiometric composition** A_mB_n and a characteristic free energy curve as shown in Fig (a).
- * In other structure, fluctuations in composition can be tolerated by **some atoms occupying 'wrong' position** or by **atom sites being left vacant**, and in these cases the **curvature** of the G curve is much less, Fig (b).

Intermediate Phase

$$\epsilon < 0, \Delta H_{\text{mix}} < 0$$

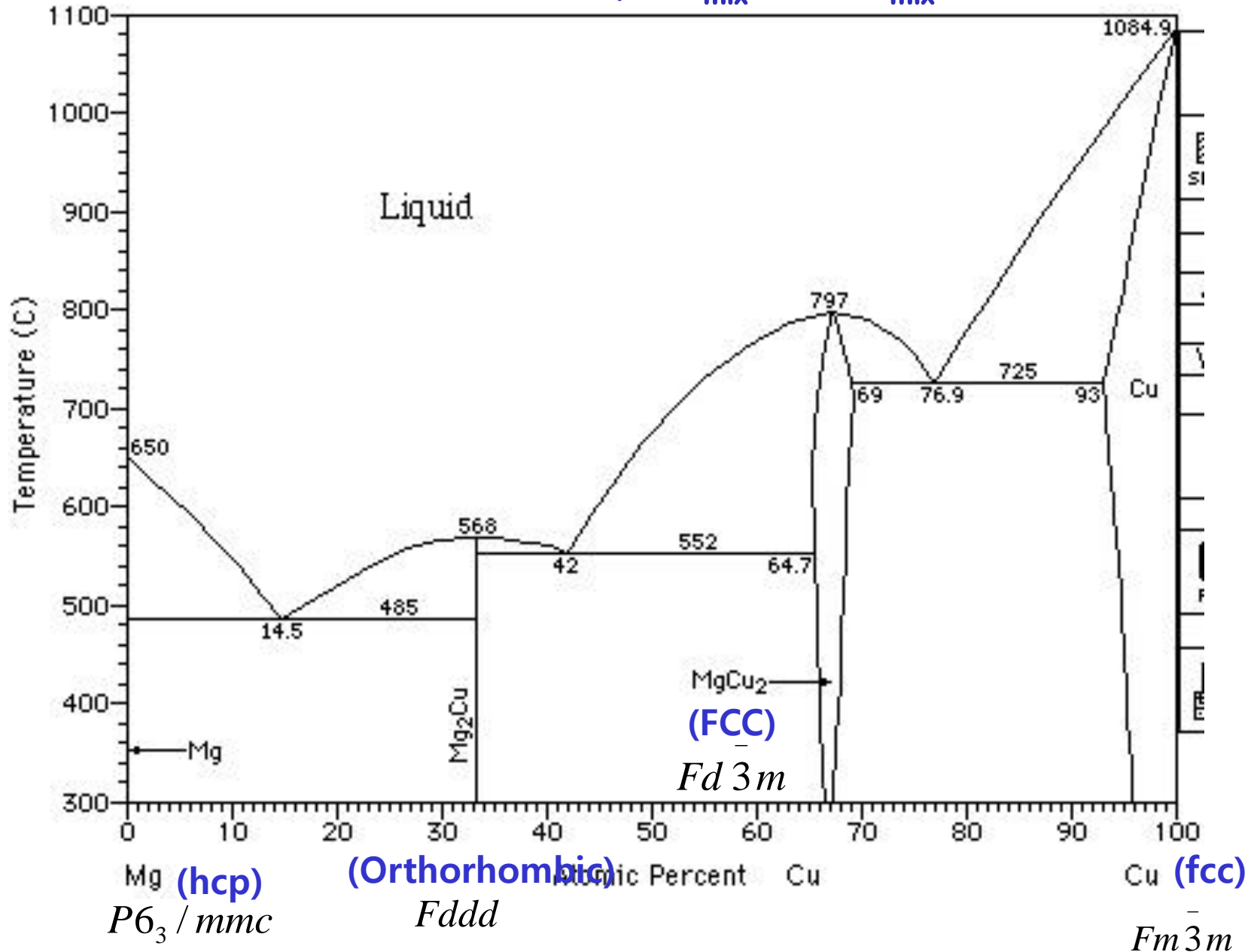


(bcc)

(fcc)

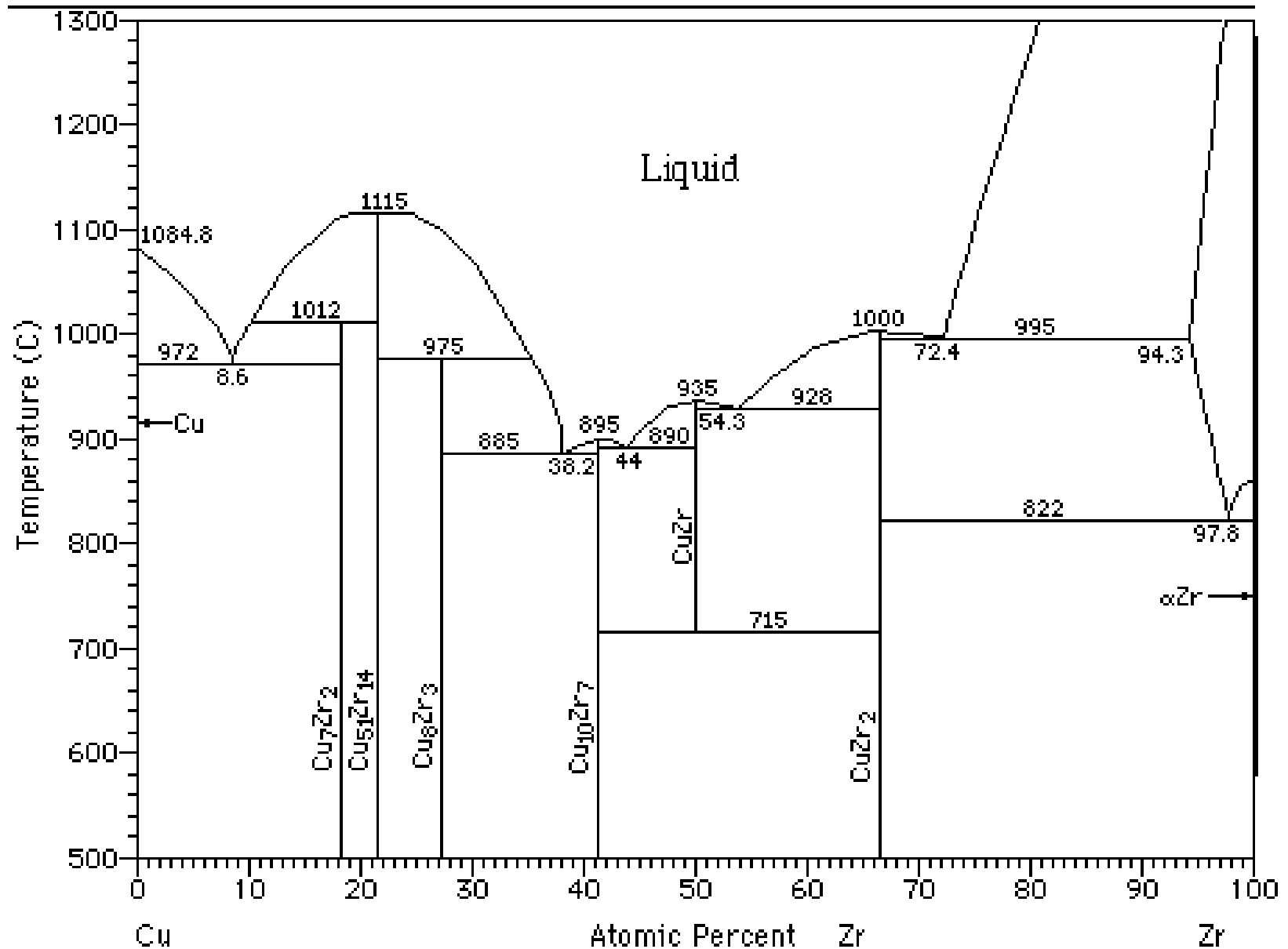
Intermediate Phase

$$\epsilon < 0, \Delta H_{\text{mix}} < 0 / \Delta H_{\text{mix}} \sim -38 \text{ kJ/mol}$$



Intermediate Phase

$$\varepsilon \ll 0, \Delta H_{\text{mix}} \ll 0 / \Delta H_{\text{mix}} \sim -142 \text{ kJ/mol}$$



1.3 Binary Solutions

Intermediate Phase

_"different crystal structure as either of the pure component"

3 main factors

determining the structure of Intermediate phase ?

1) Relative atomic size

- **Laves phase** (size difference: 1.1~1.6 ex: MgCu_2)
fill space most efficiently ~ stable
- **Interstitial compound**: MX , M_2X , MX_2 , M_6X
M= Cubic or HCP ex: Zr, Ti, V, Cr, etc, X= H, B, C, and N

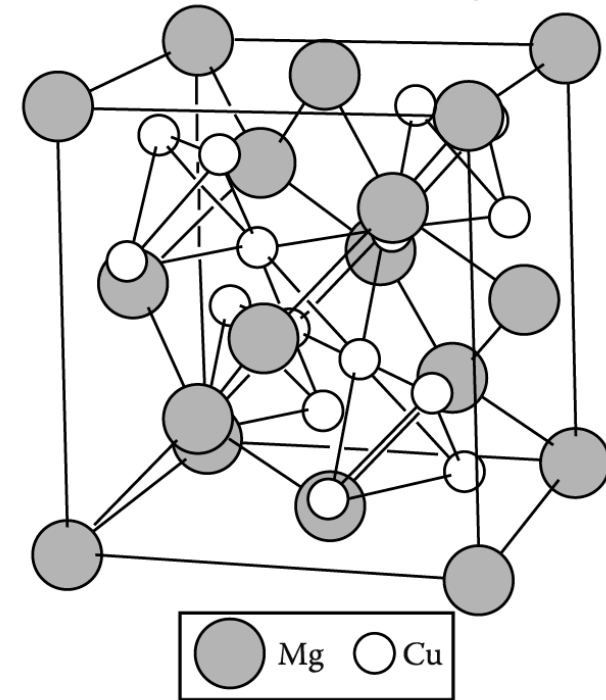
2) Relative valency electron

- **electron phases** ex α & β brass
of valency electrons per unit cell
→ depending on compositional change

3) Electronegativity

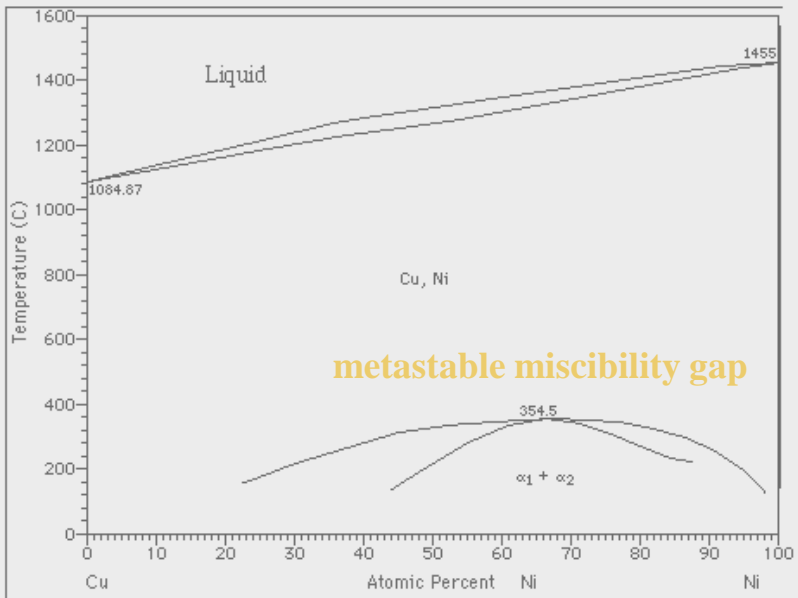
- very different electronegativities → **ionic bond_normal valency compounds**
ex Mg_2Sn

Fig. 1.24

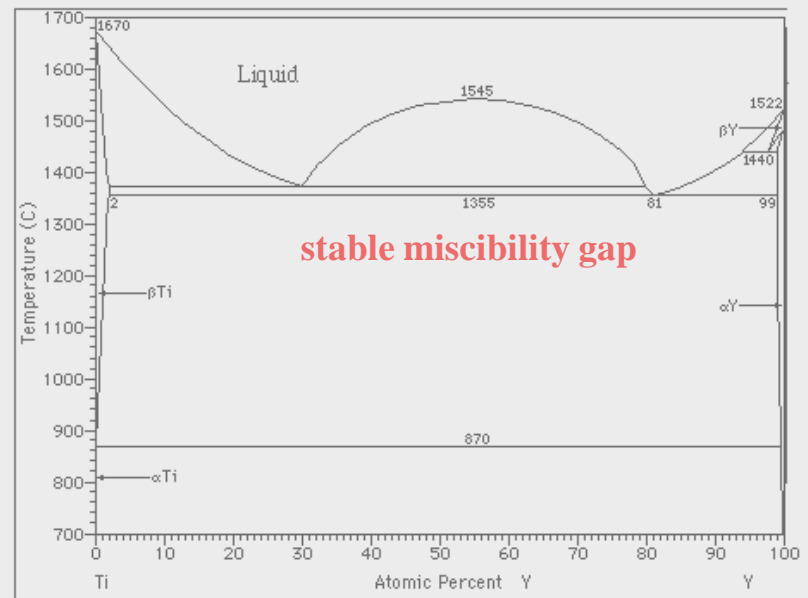


MgCu_2 (A Laves phase)

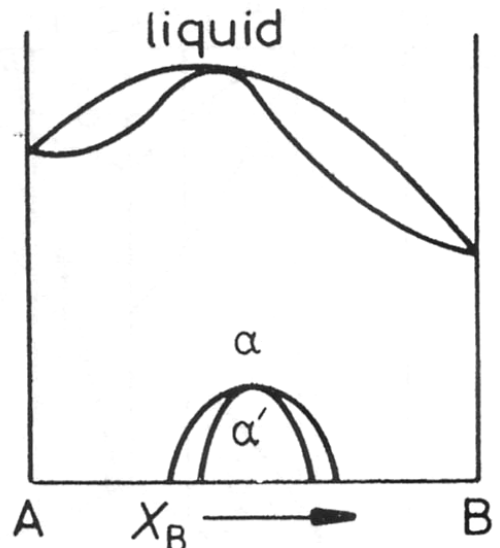
$\Delta H_{mix}^S > 0$: Solid solution \rightarrow solid state phase separation (two solid solutions)



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



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



$\Delta H_{mix}^S \ll 0$: Compound : AB, A₂B...

