

2019 Spring

“Phase Equilibria *in* Materials”

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Contents for previous class

Chapter 1 Thermodynamics and Phase Diagrams

- **Equilibrium** - $dG = 0$ **Lowest possible value of G**
No desire to change ad infinitum

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

- **Single component system**

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

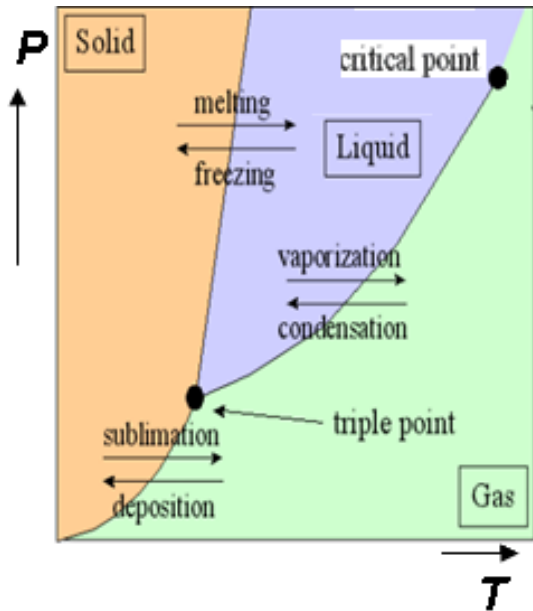
$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

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

Clausius-Clapeyron Relation

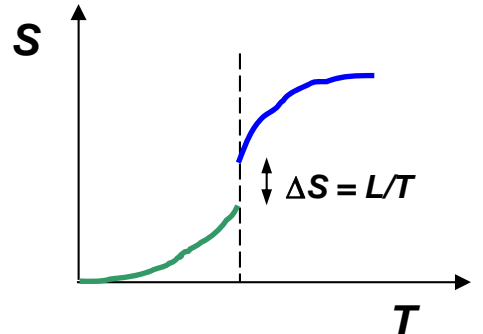
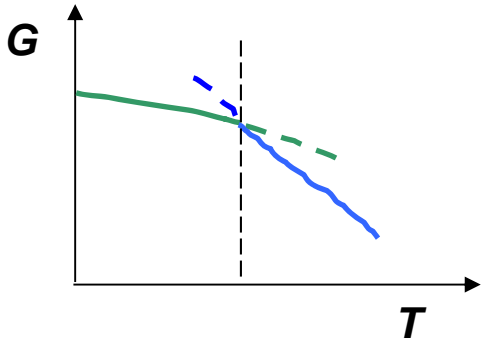
- **Classification of phase transition**

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

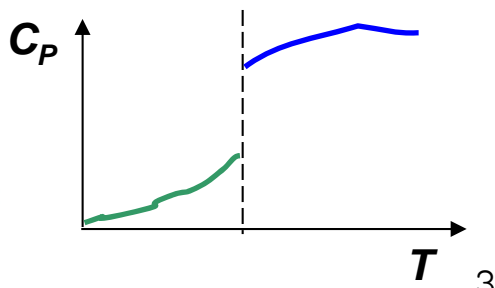


The First-Order Transitions

Latent heat
Energy barrier
 Discontinuous entropy, heat capacity

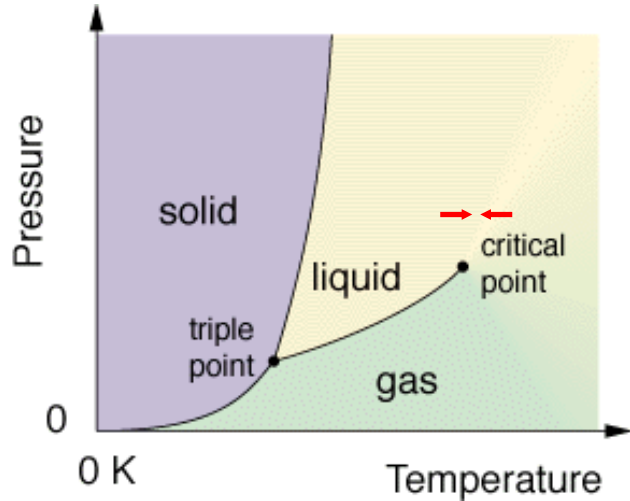


$$C_P = T \left(\frac{\partial S}{\partial T} \right)_{P,N}$$



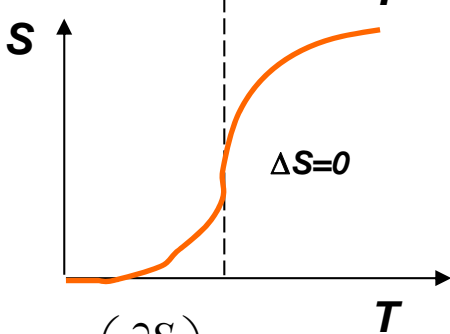
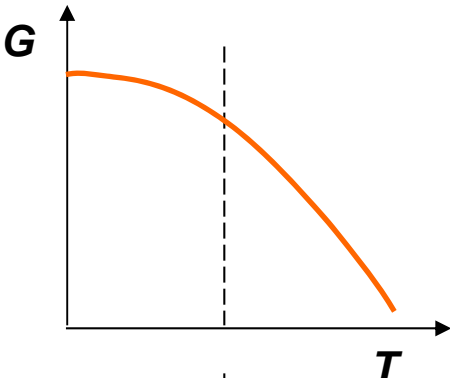
- First Order Phase Transition at T_T :
 - G is **continuous** at T_T
 - First derivatives of G (V, S, H) are **discontinuous** at T_T
- $$V = \left(\frac{\partial G}{\partial P} \right)_T \quad S = - \left(\frac{\partial G}{\partial T} \right)_P \quad H = G - T \left(\frac{\partial G}{\partial T} \right)_P$$
- 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

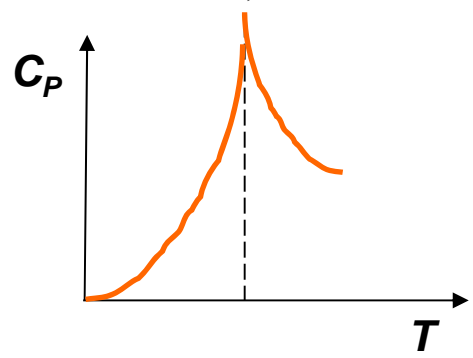


No Latent heat
Continuous entropy

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

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

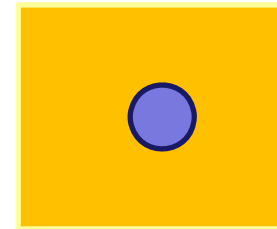
- Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

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

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid \rightarrow Solid



<Thermodynamic>

• Interfacial energy $\Rightarrow \Delta T_N$

Liquid

T_m

Undercooled Liquid

Solid

No superheating required!

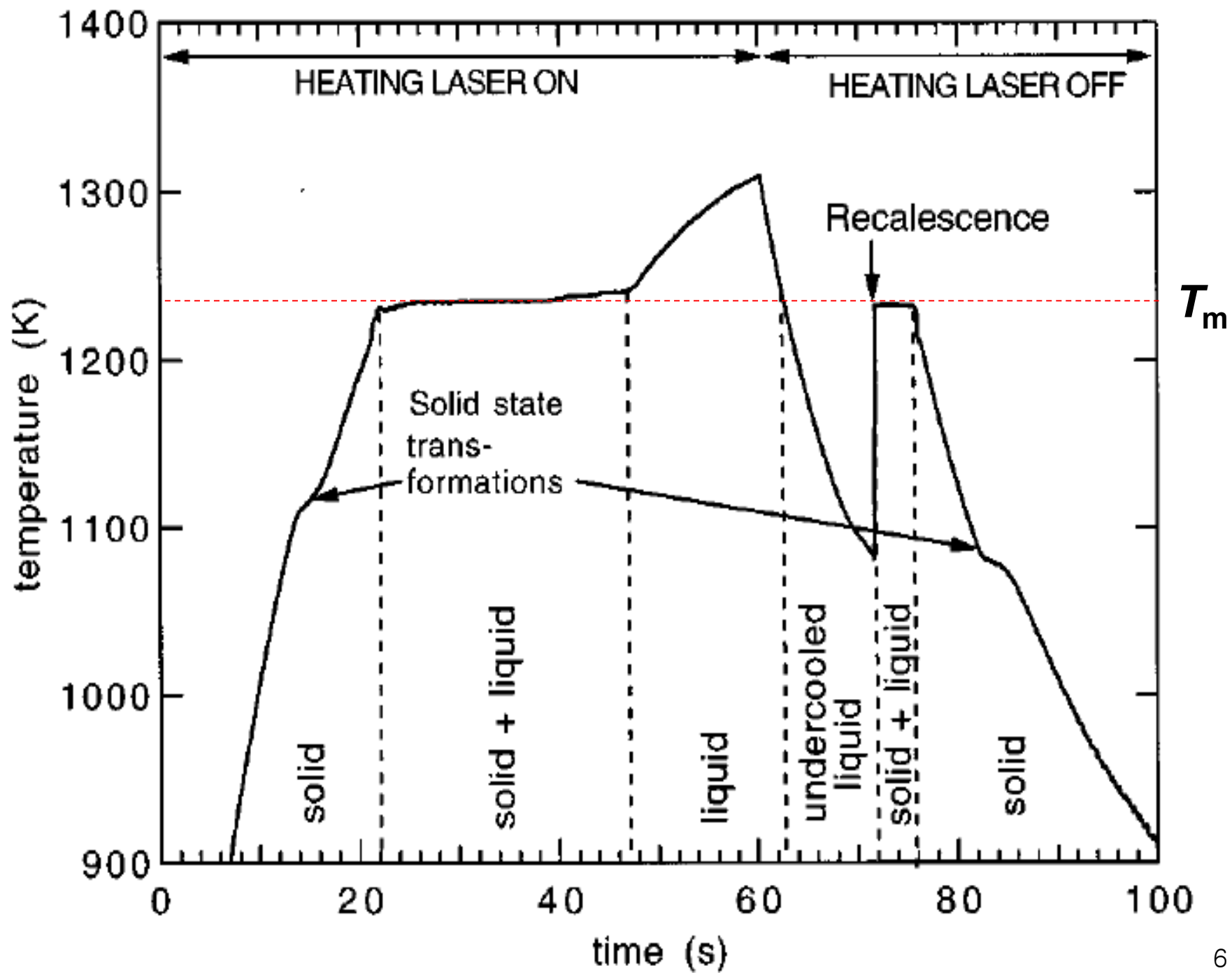
• Interfacial energy \Rightarrow No ΔT_N

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

vapor



Melting: Solid \leftarrow Liquid



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.

A

B

Alluvial mining



사금 채취



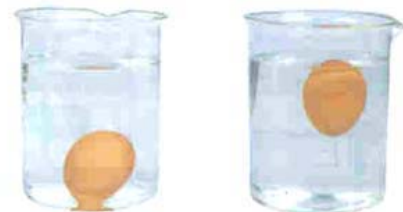
키질

Winnowing

wash rice



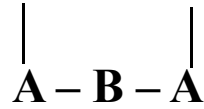
쌀 씻기



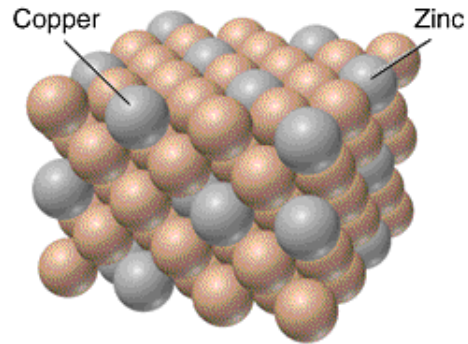
달걀 고르기

Select egg

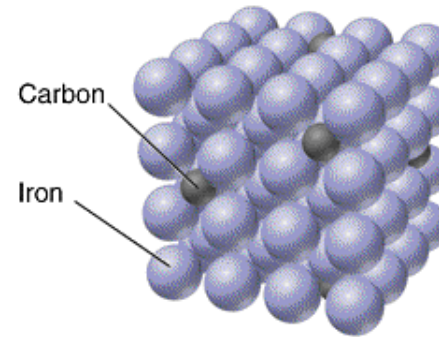
- **Solution** ; A - A - A ; → atomic scale mixture/ **Random distribution**



Solid solution : substitutional or interstitial



A Brass, a substitutional alloy

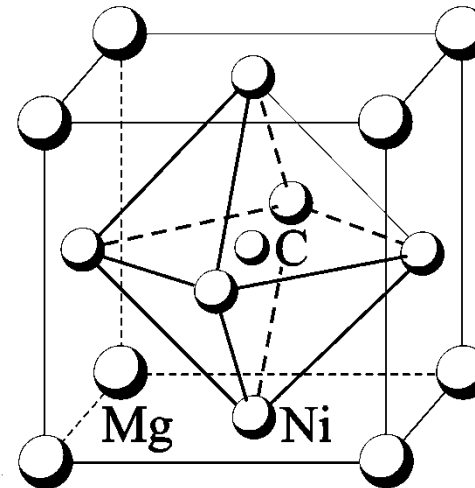


B Carbon steel, an interstitial alloy

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



MgCNi₃



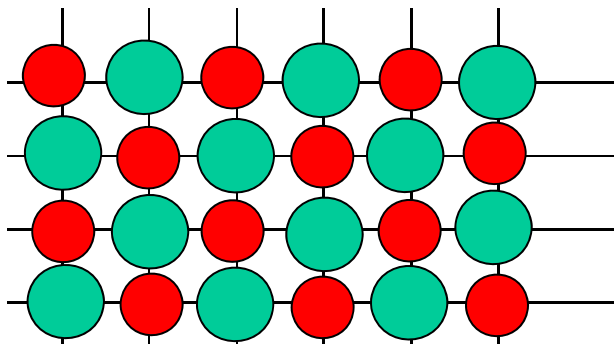
Q2: What is “Alloying”?

Ordered Compounds or Solid Solutions

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

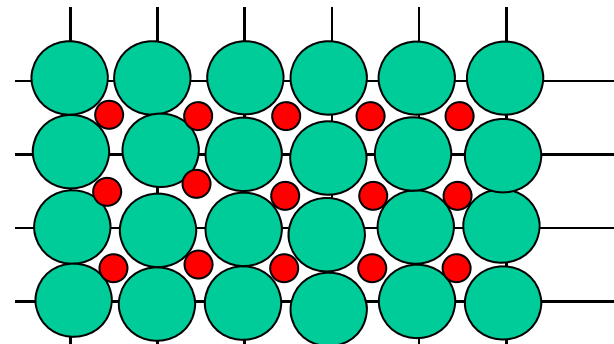
Ordered Substitutional and Interstitials Compounds

Substitutional
element replaces host atoms
in an orderly arrangement



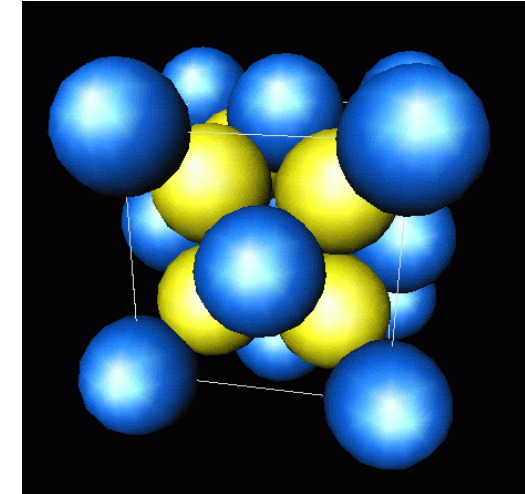
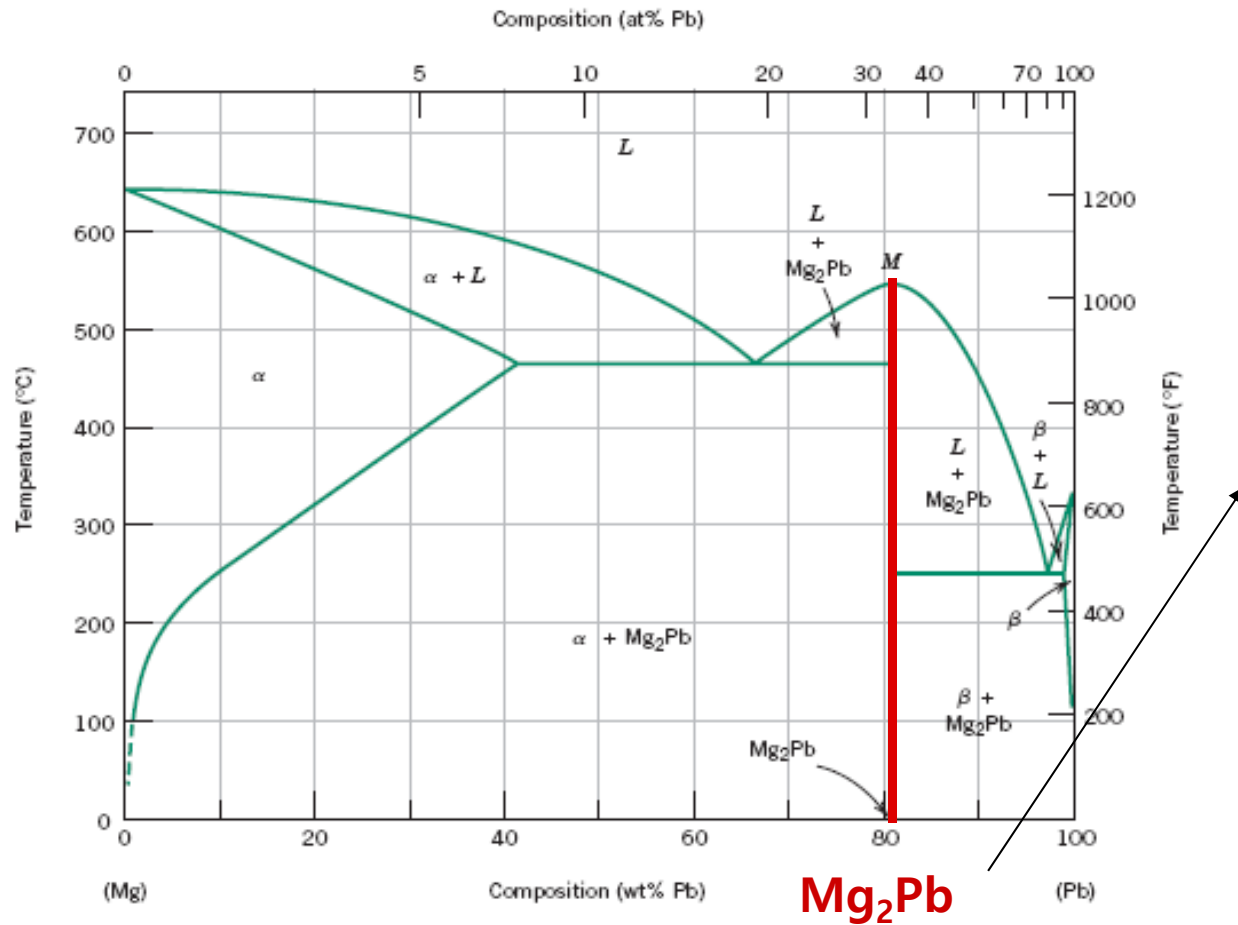
e.g., Ni_3Al (hi-T yield strength),
 $\text{Al}_3(\text{Li},\text{Zr})$ (strengthening)

Interstitial
element goes into holes
in an orderly arrangement



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

Intermetallic Compounds

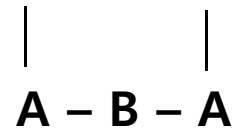


Antifluorite Structure:

- 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.

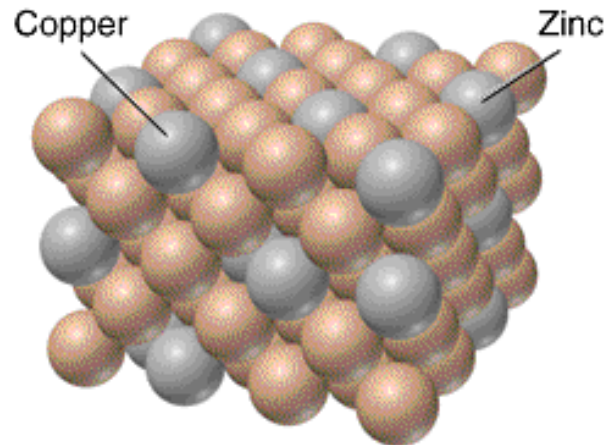
- **Solution** ; A – A – A ; → atomic scale mixing, **Random distribution**



Two Possibilities for Solid Solutions: B atoms in A atoms

Substitutional

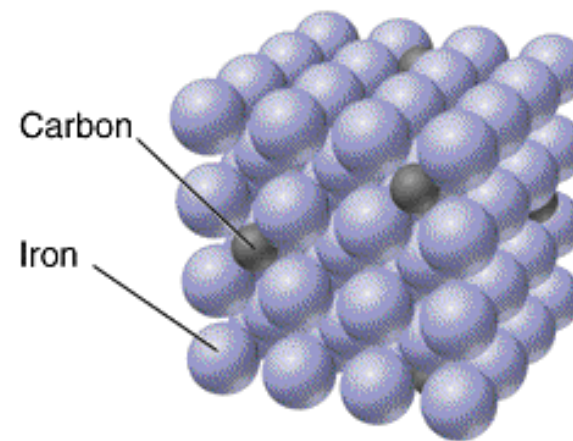
‘new element replaces host atoms’



A Brass, a substitutional alloy

Interstitials

‘new element goes in holes’

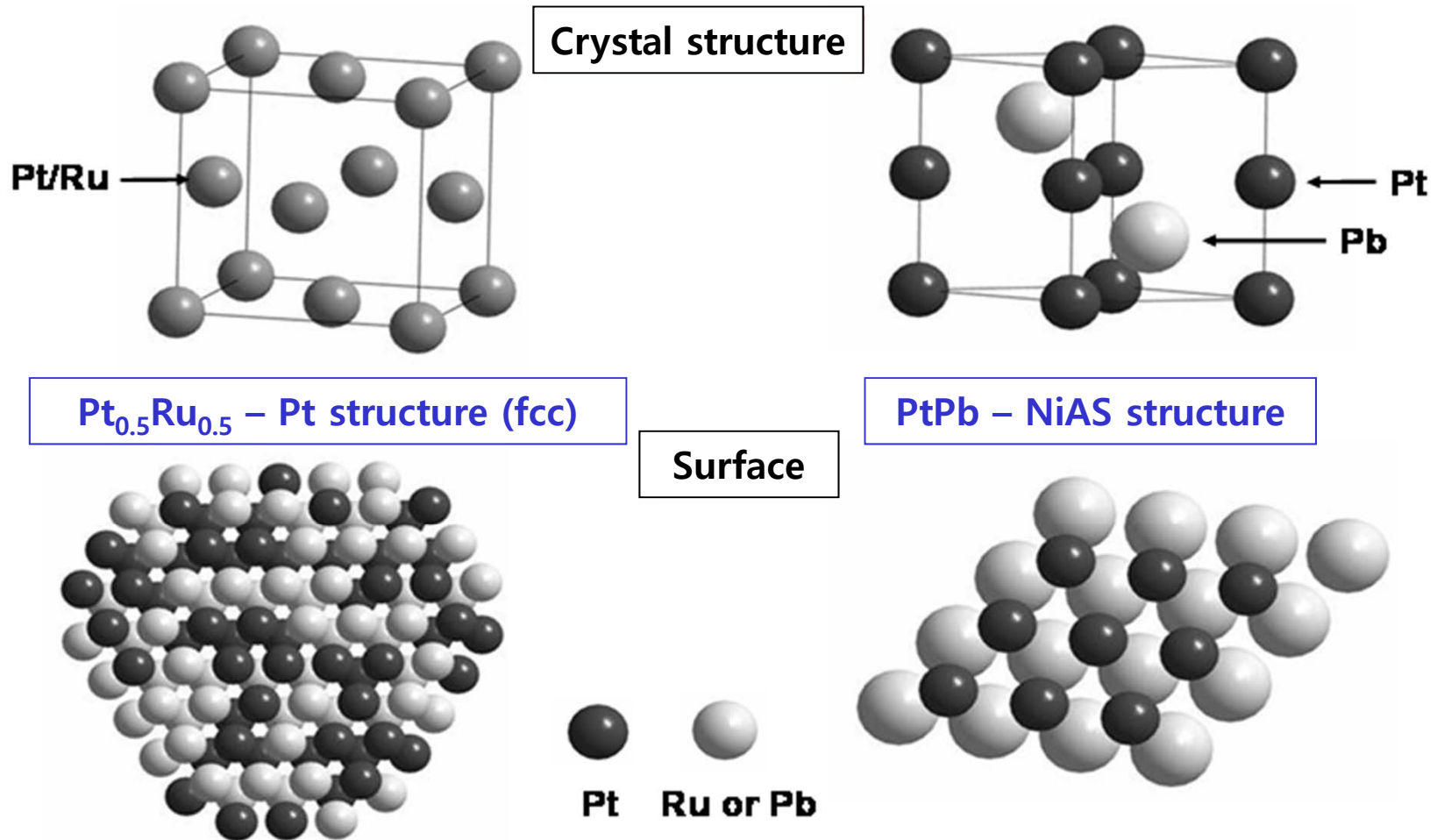


B Carbon steel, an interstitial alloy

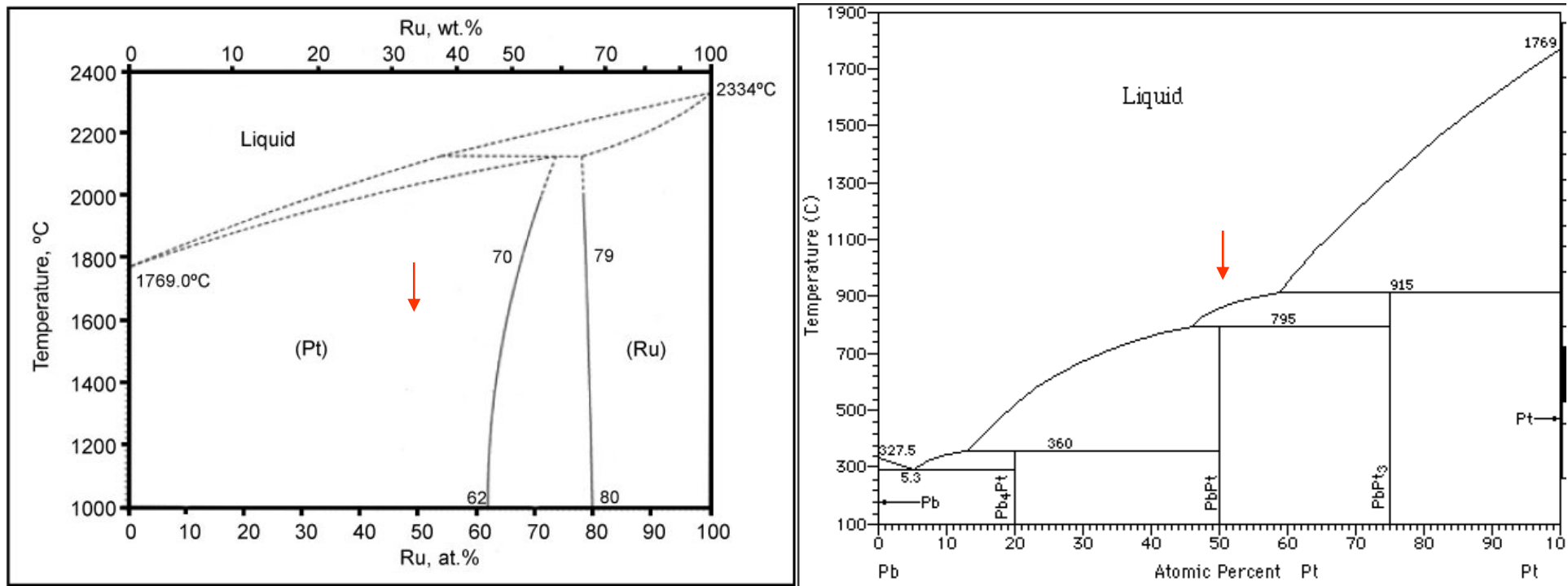
Q3: “Solution vs. Intermetallic compound”?

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

Solid Solution vs. Intermetallic Compound



Solid Solution vs. Intermetallic Compounds



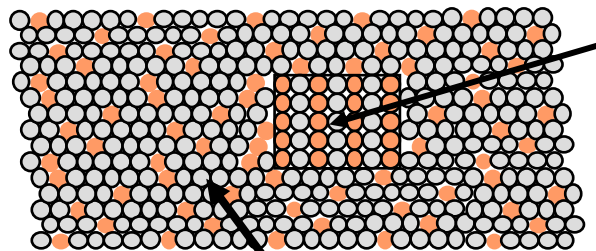
$Pt_{0.5}Ru_{0.5}$ – Pt structure (fcc)

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)

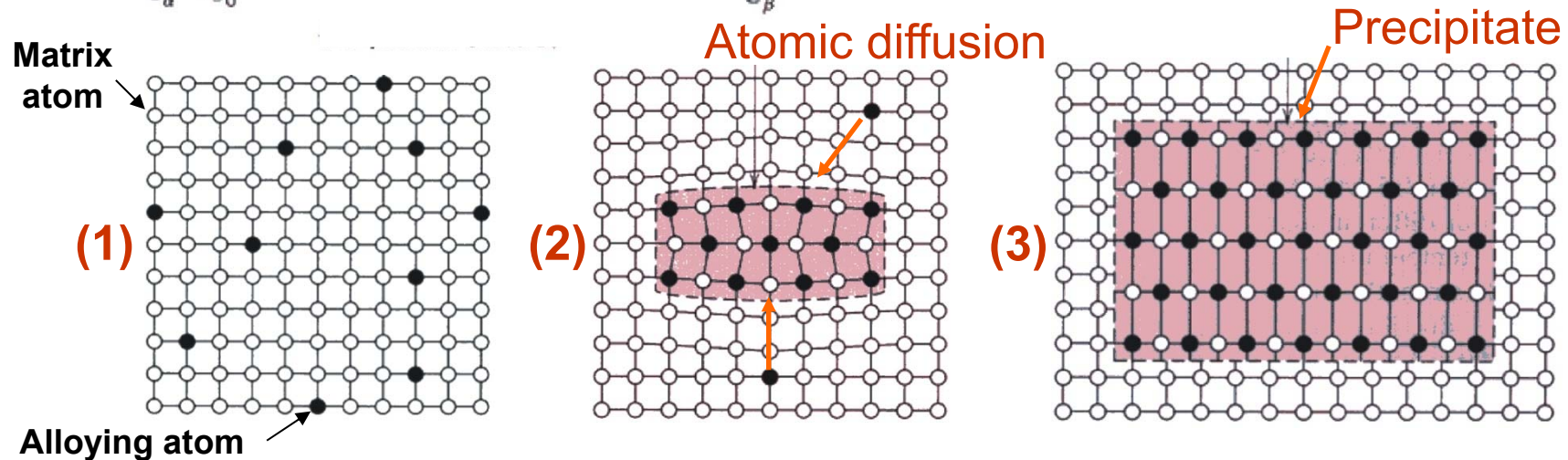
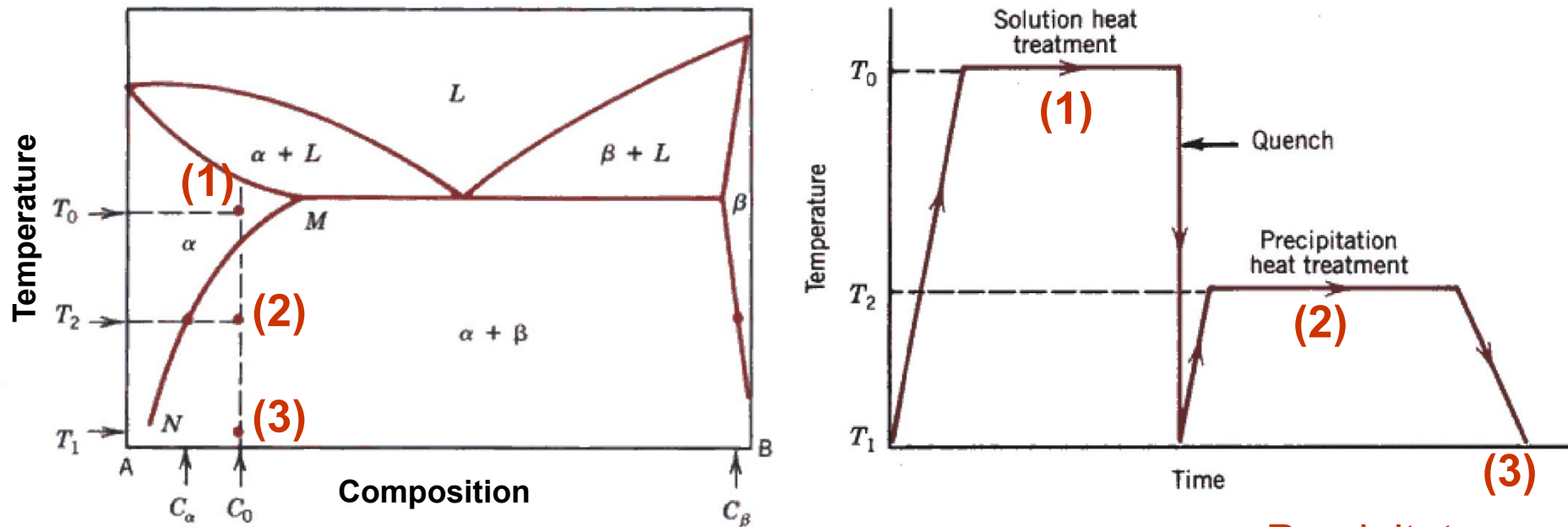


Second phase particle
--different **composition**
--often different **structure**.

Solid Solution phase: B atoms in A

5) Microstructure control : ② Secondary phase control

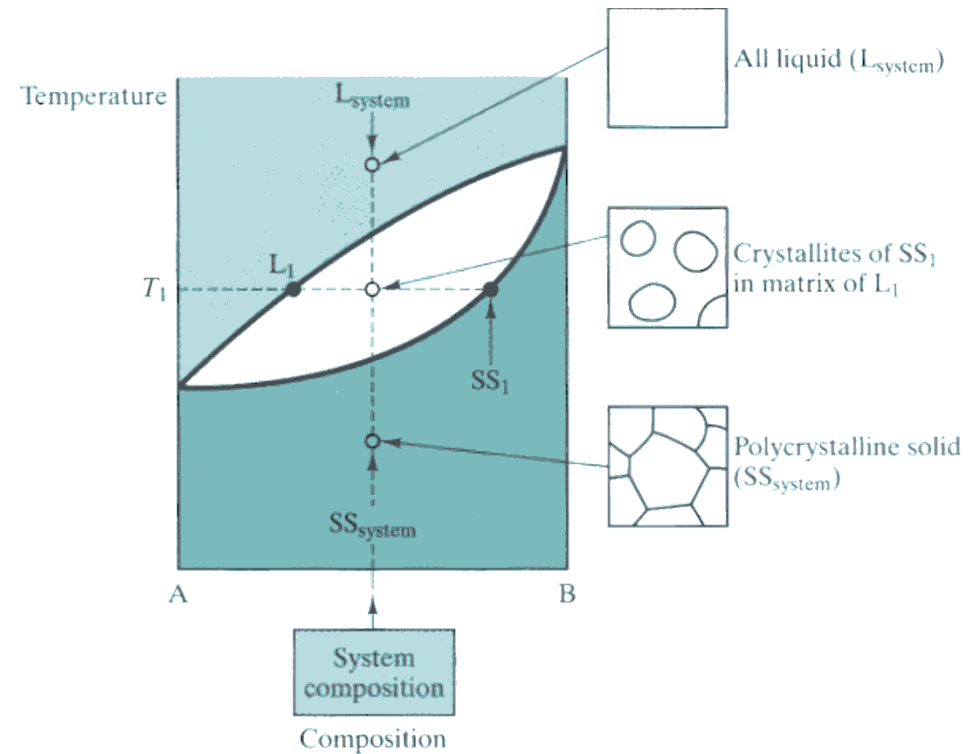
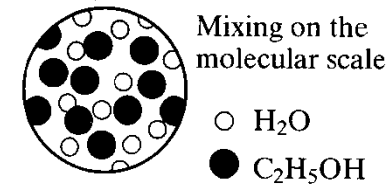
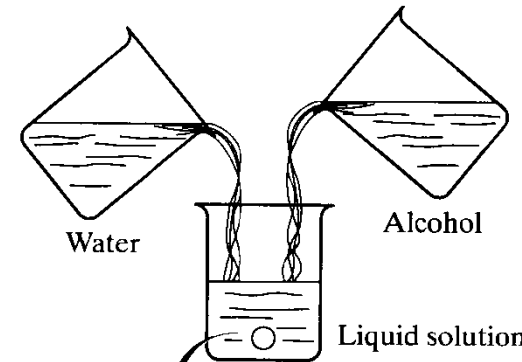
c. Mechanism of Precipitation



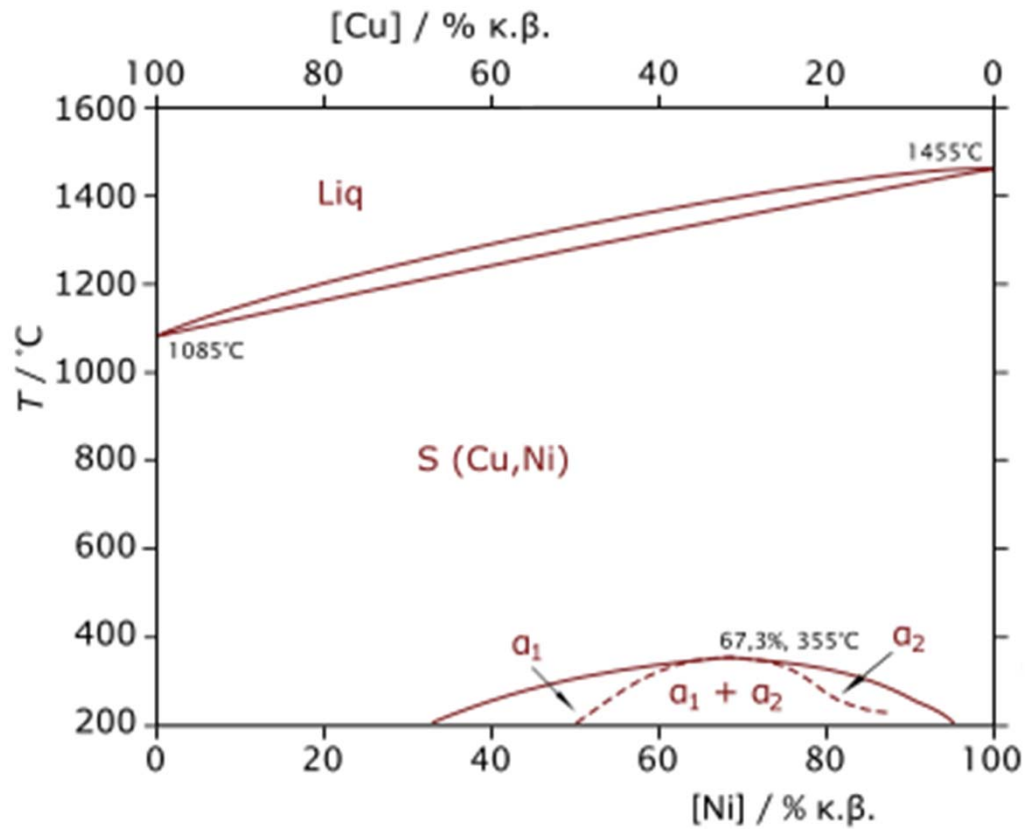
Q4: How can we classify “Solubility”?

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

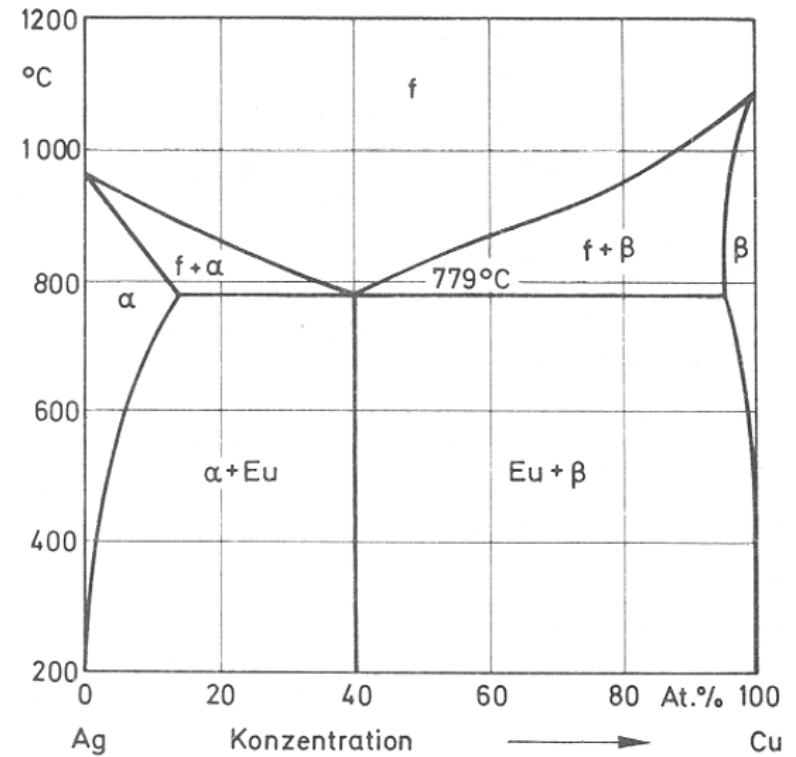


Cu-Ni Alloys



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.

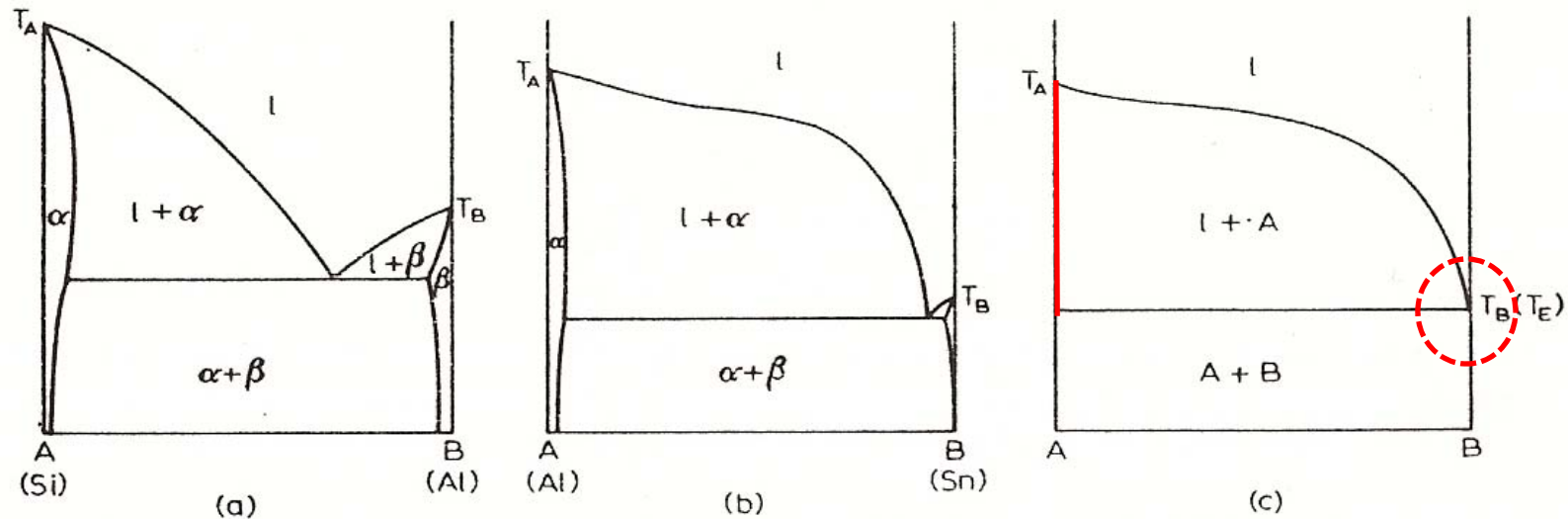


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

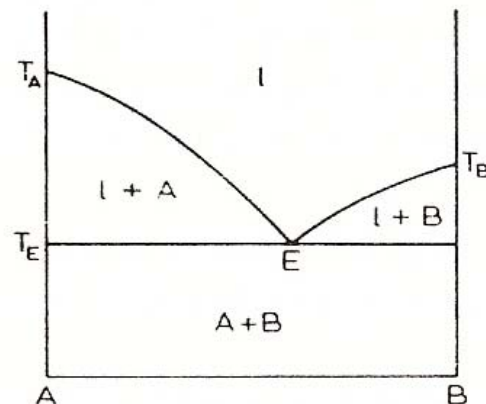
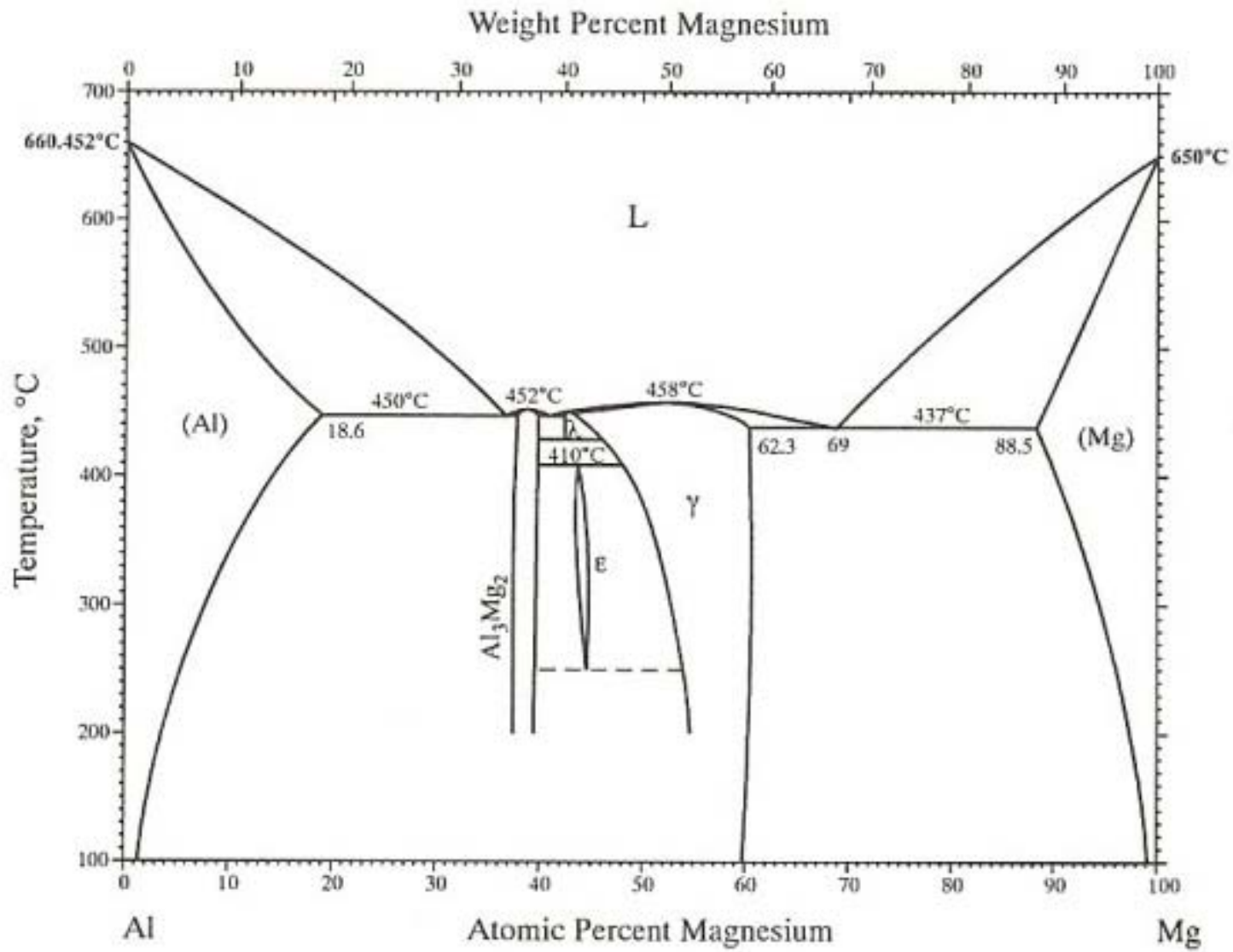
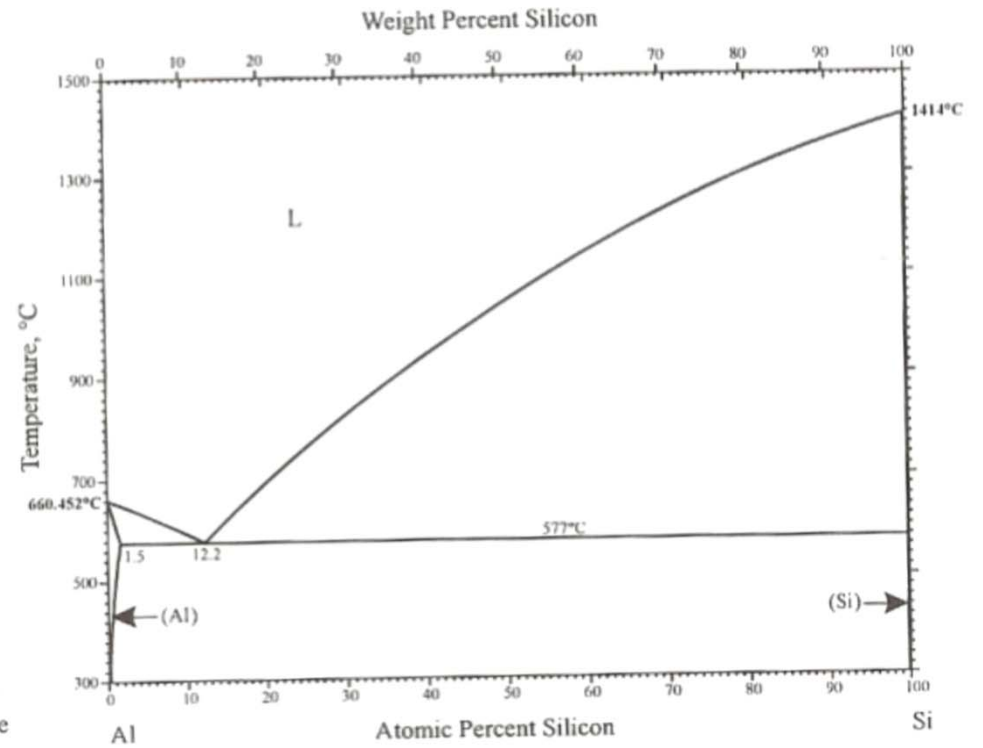
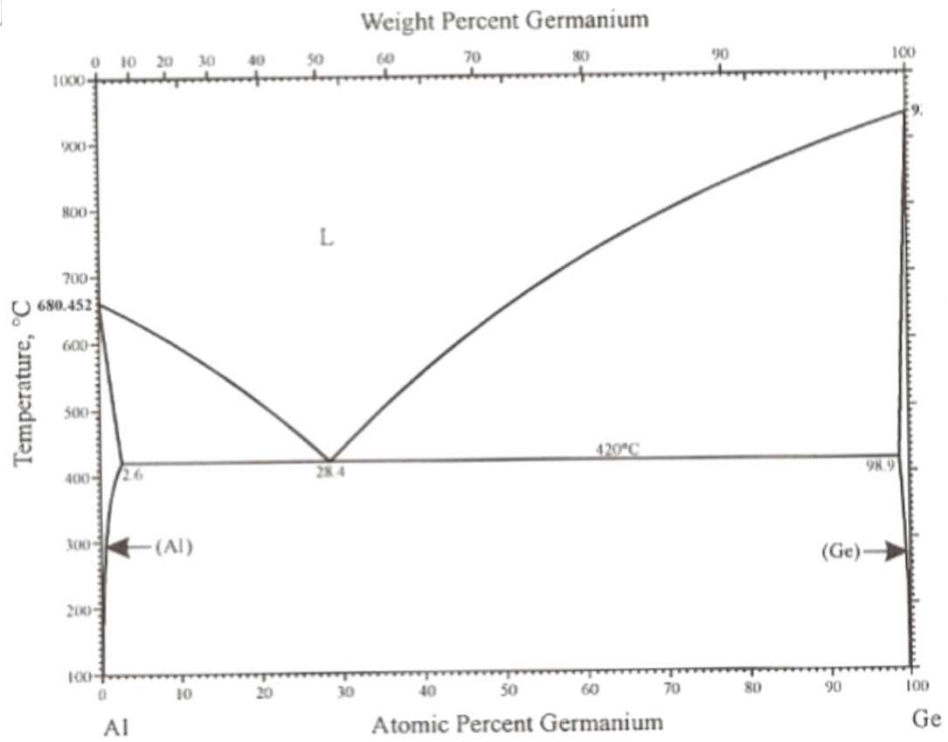
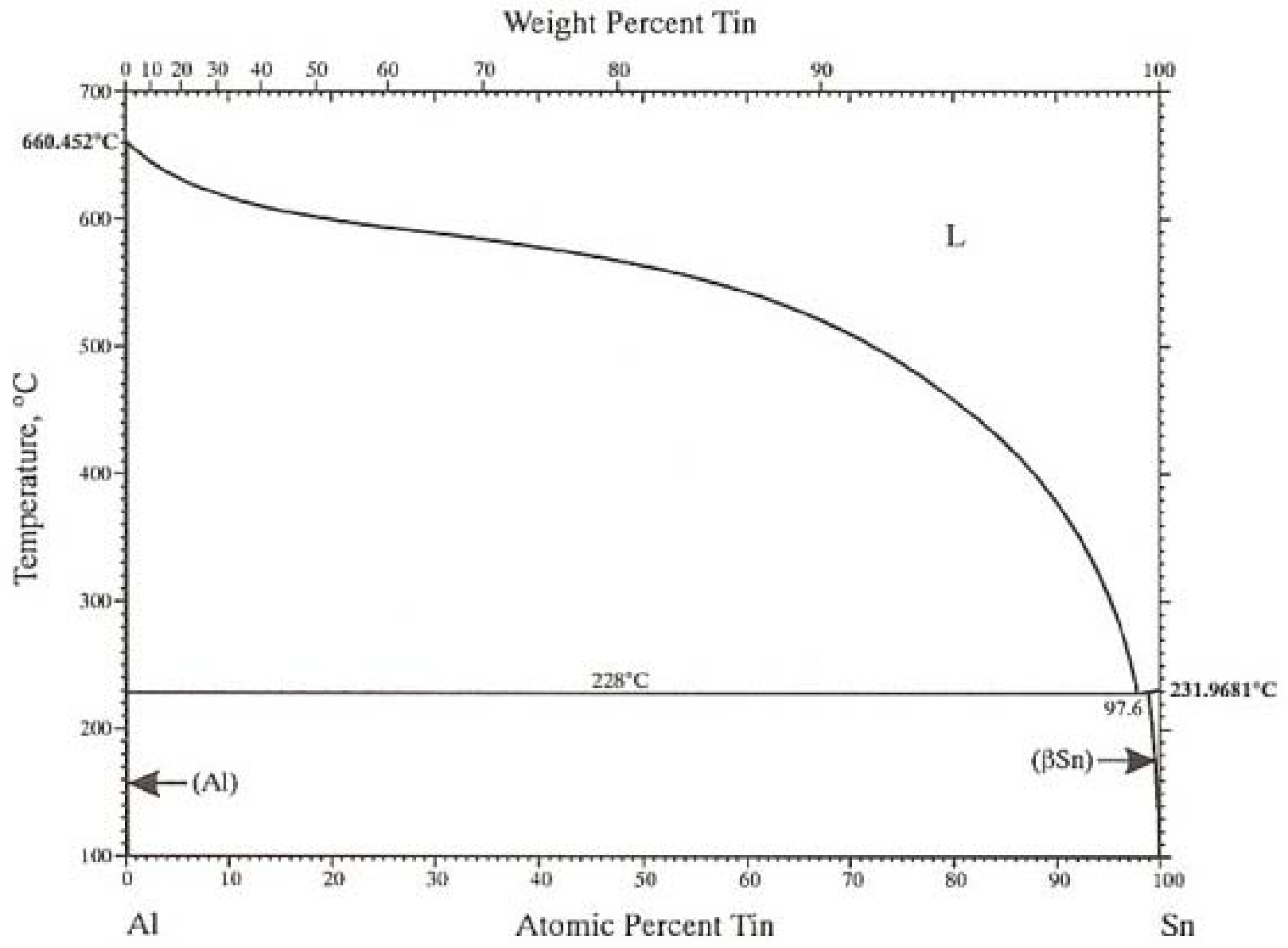


Fig. 54. Impossible form of a binary eutectic phase diagram.





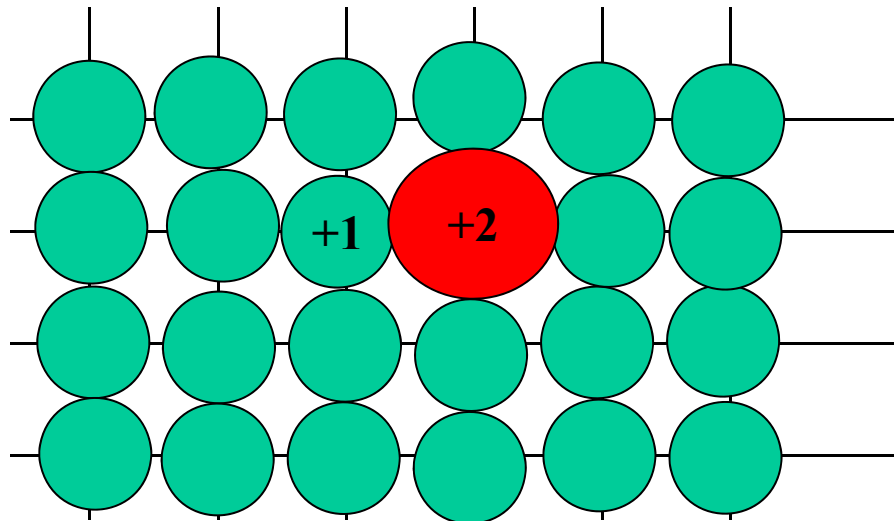


**Q5: Can we roughly estimate
what atoms will form solid solutions?**

“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: $r_{\text{Cu}} = 0.128$ nm and $r_{\text{Ni}} = 0.125$ 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: $r_{\text{Cu}} = 0.128 \text{ nm}$ and $r_{\text{Ag}} = 0.144 \text{ nm}$.

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

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

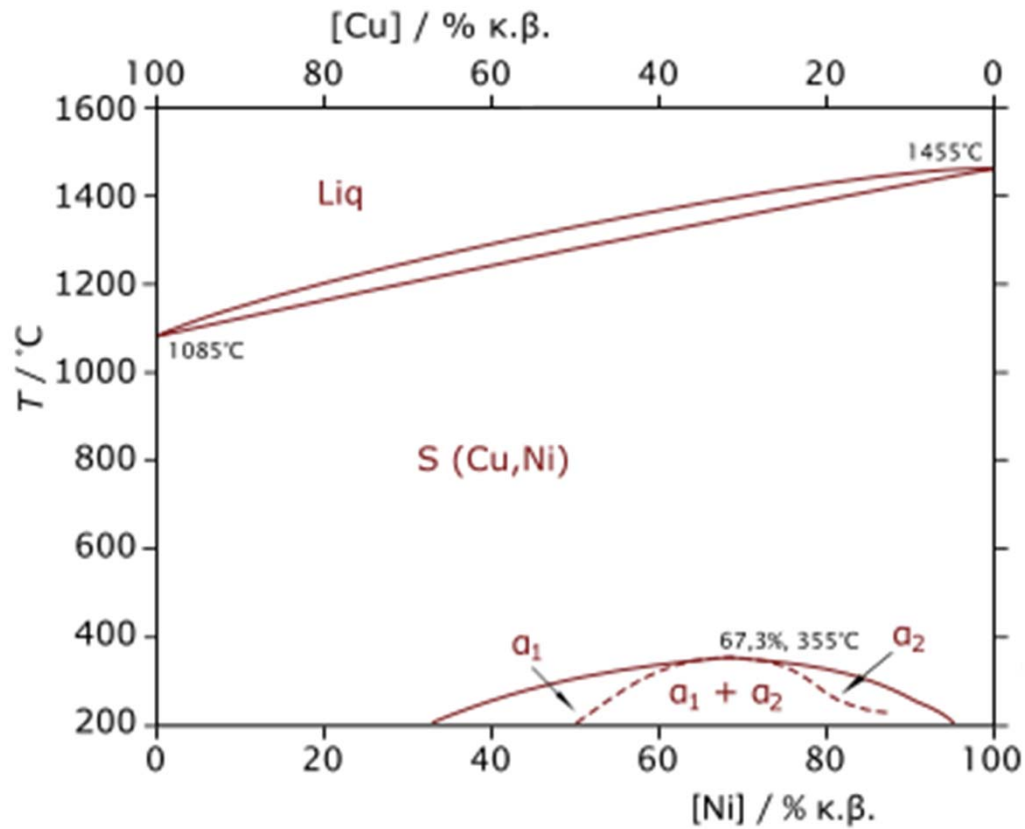
Rule 3: $E_{\text{Cu}} = 1.90$ and $E_{\text{Ni}} = 1.80$. Thus, $\text{DE}\% = -5.2\%$ favorable \checkmark

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

Expect Ag and Cu have limited solubility.

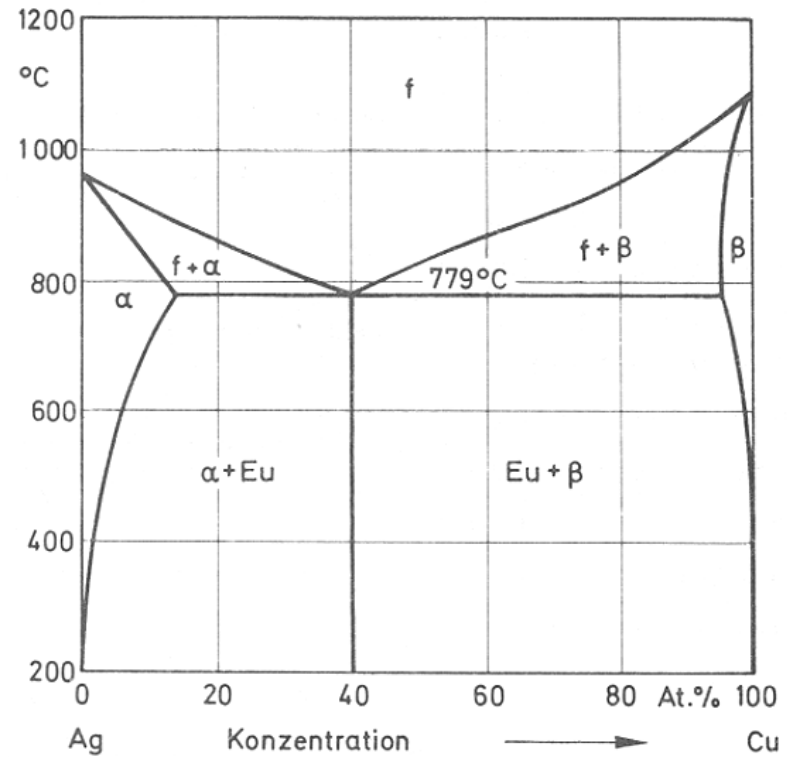
In fact, the Cu-Ag phase diagram (T vs. c) shows that a solubility of only 18% Ag can be achieved at high T in the Cu-rich alloys.

Cu-Ni Alloys



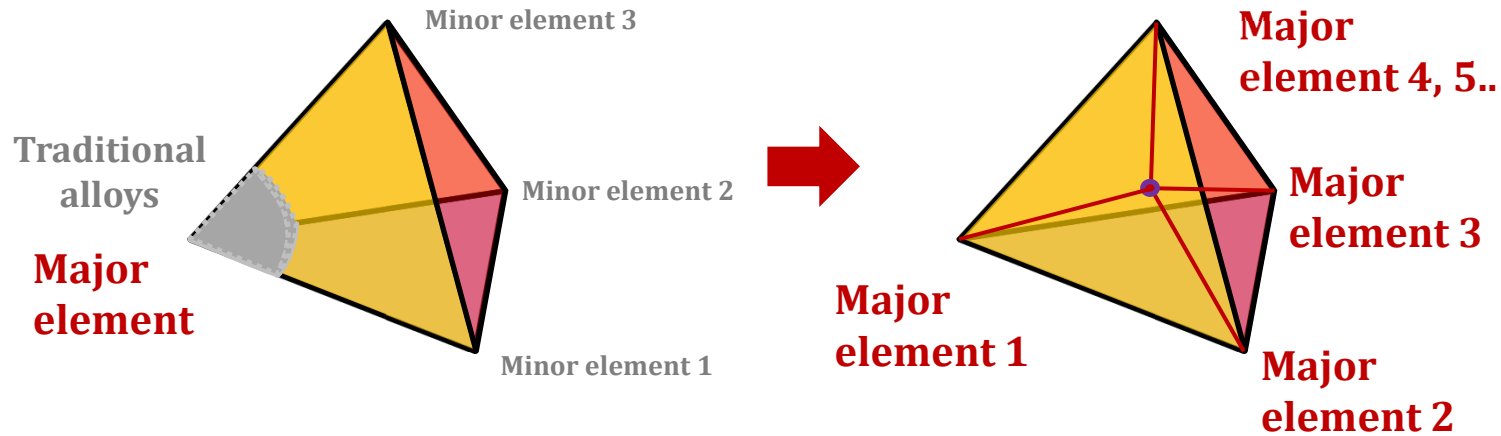
complete solid solution

Cu-Ag Alloys



limited solid solution

High entropy alloy (HEA)



Conventional alloy system

Ex) 304 steel - Fe₇₄Cr₁₈Ni₈

High entropy alloy system

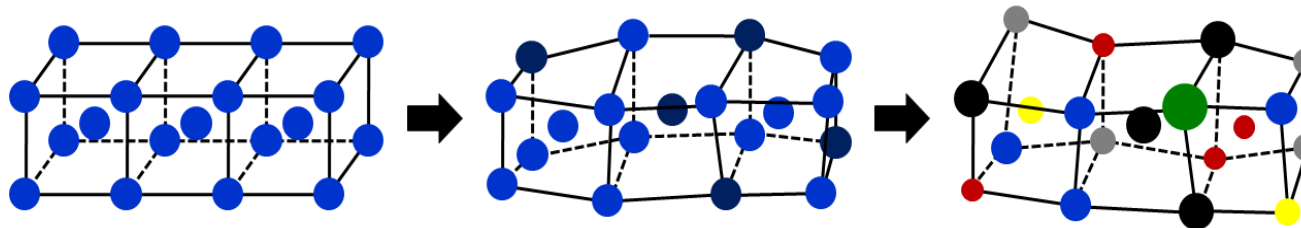
Ex) Al₂₀Co₂₀Cr₂₀Fe₂₀Ni₂₀

(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”?**

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

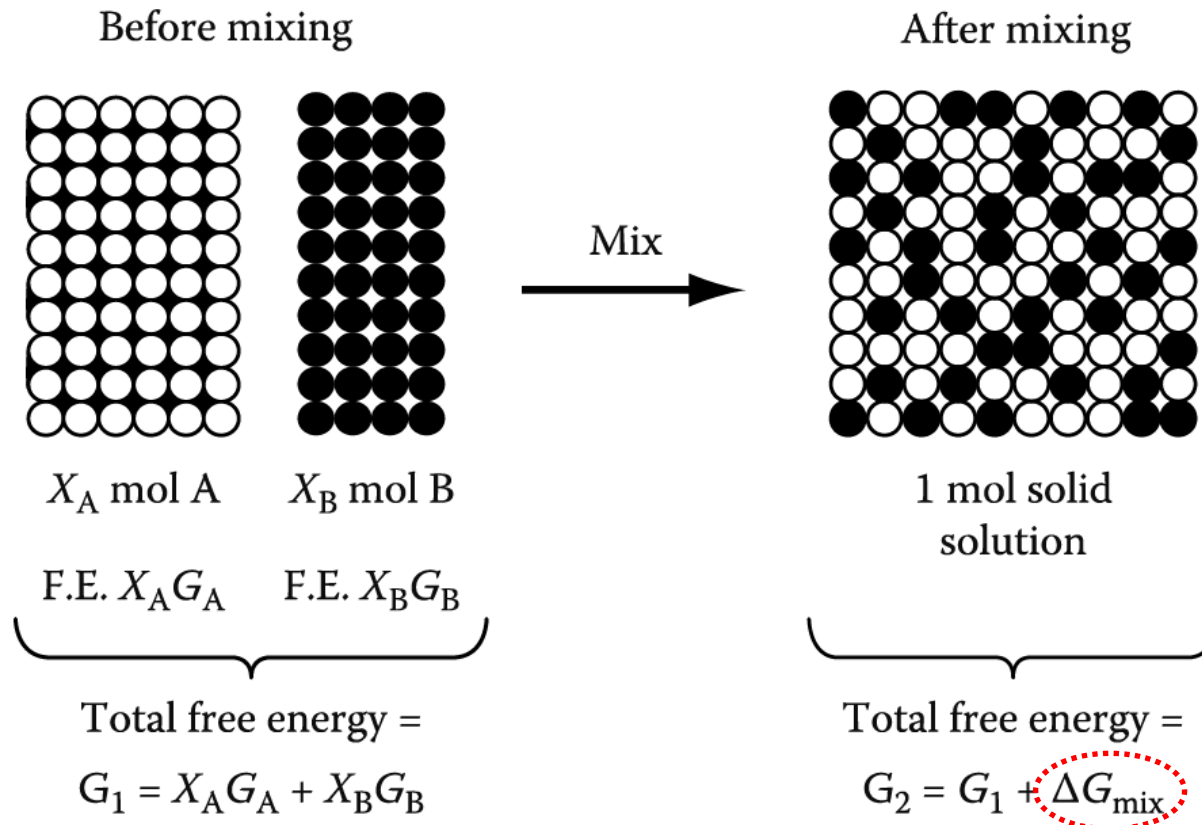
Binary Solutions: binary solid solution/ a fixed pressure of 1 atm

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.



1.3 Binary Solutions

Gibbs Free Energy of The System

In Step 1

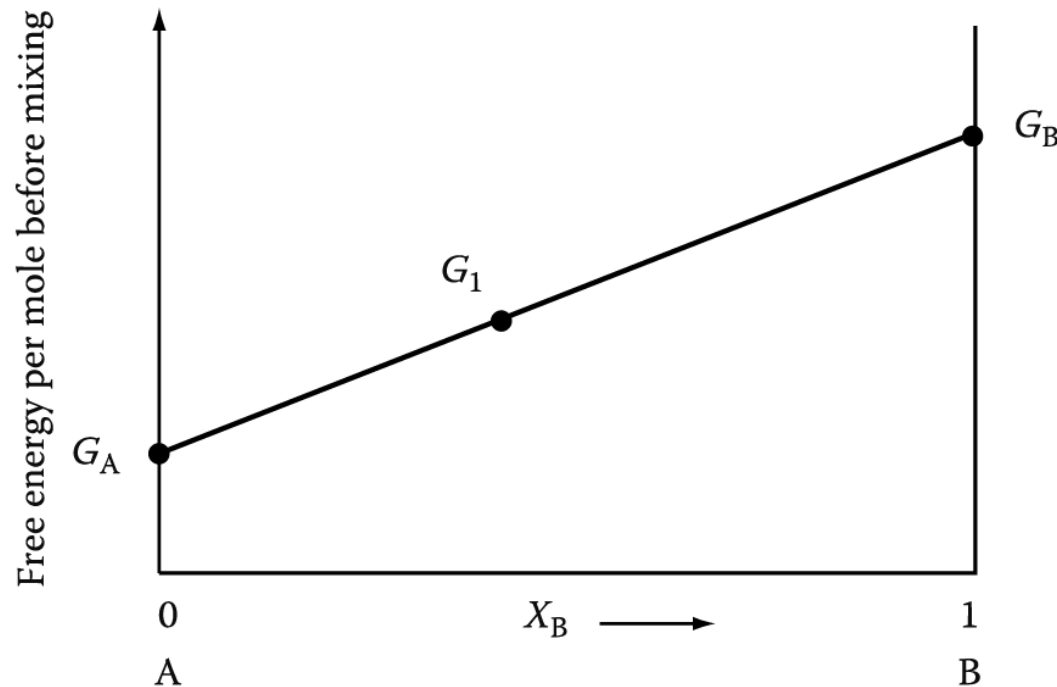
- The molar free energies of pure A and pure B

pure A; $G_A(T,P)$

pure B; $G_B(T,P)$

; X_A, X_B (mole fraction)

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



 Free energy of mixture

1.3 Binary Solutions

Gibbs Free Energy of The System

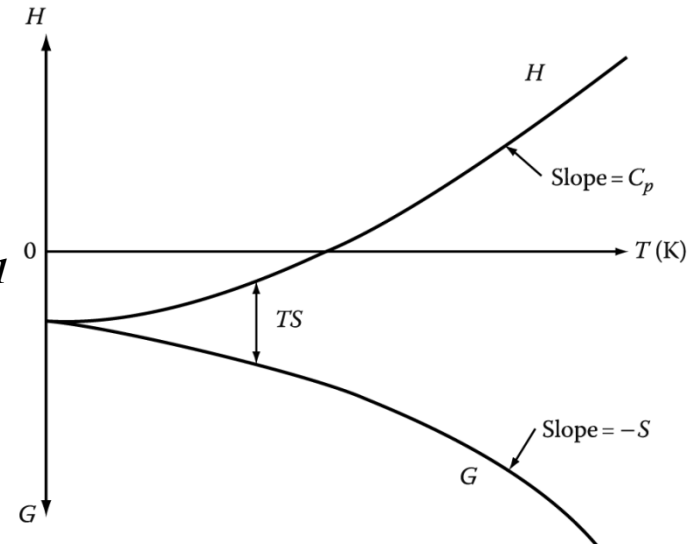
In Step 2

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

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.

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

Gibbs Free Energy of Binary Solutions

**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 : Boltzmann constant

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

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

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

1.3 Binary Solutions

Ideal solution

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)

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

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

1.3 Binary Solutions

Ideal solution

Excess mixing Entropy

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

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



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

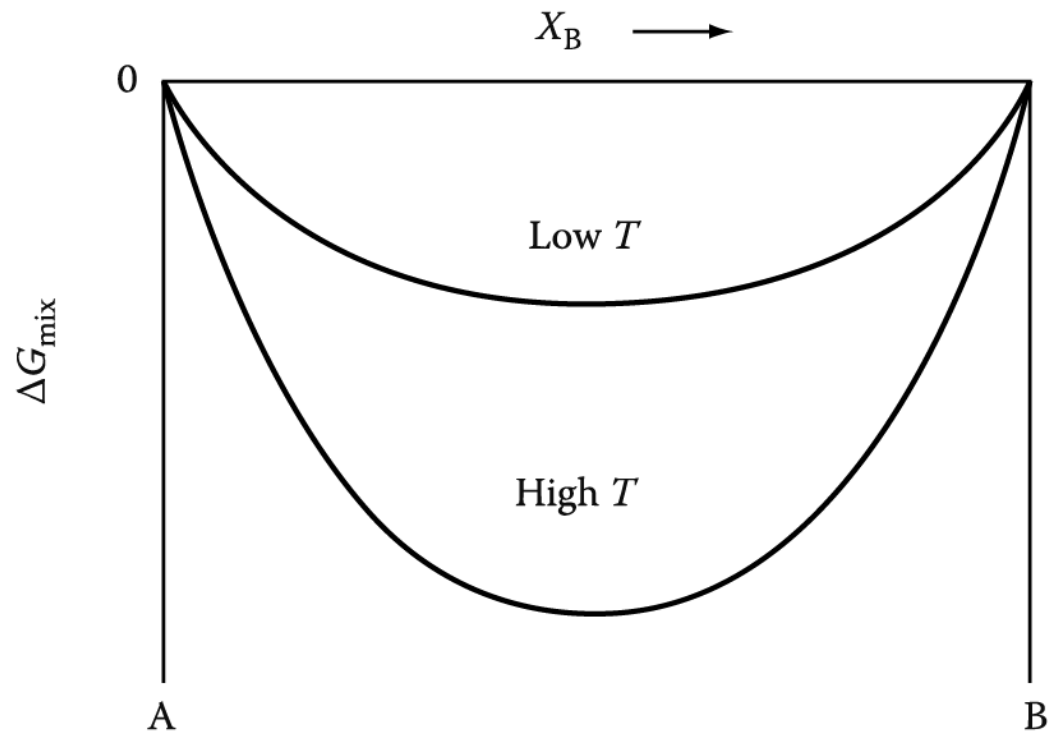


Fig. 1.9 Free energy of mixing for an ideal solution

Gibbs Free Energy of Binary Solutions

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.

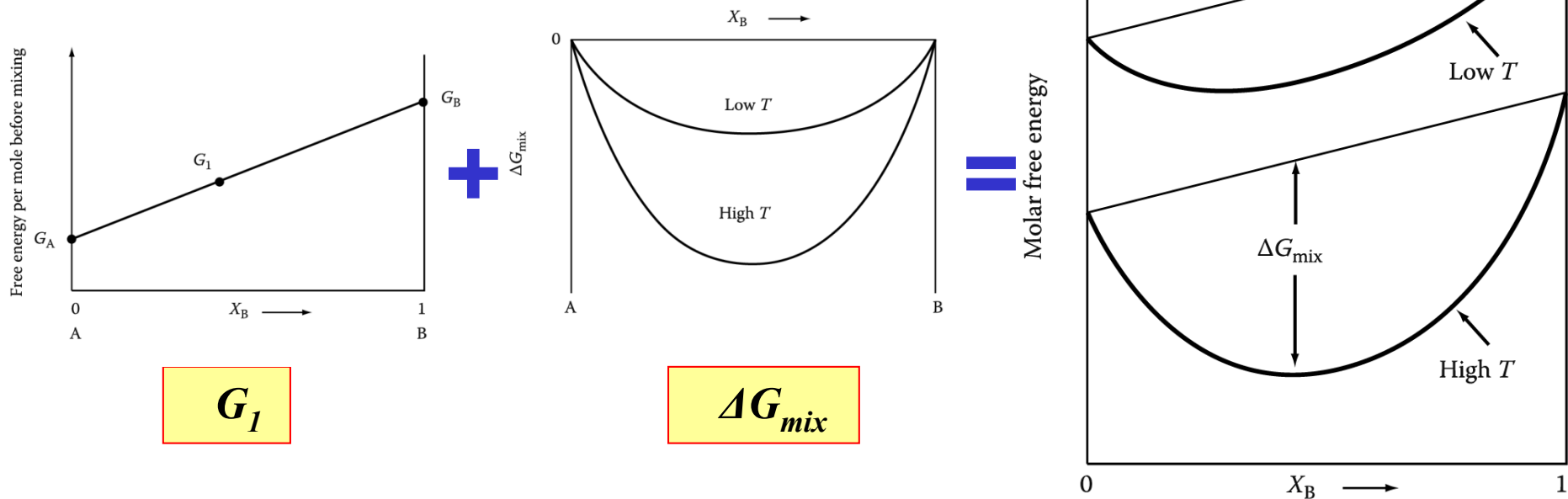


Fig. 1.10 The molar free energy (free energy per mole of solution) for an ideal solid solution. A combination of Figs. 1.8 and 1.9.

Gibbs Free Energy of Binary Solutions

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

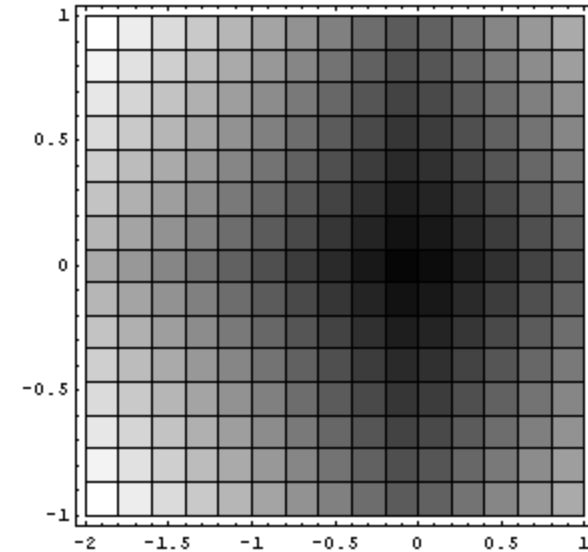
$$\mu_A = \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B}$$

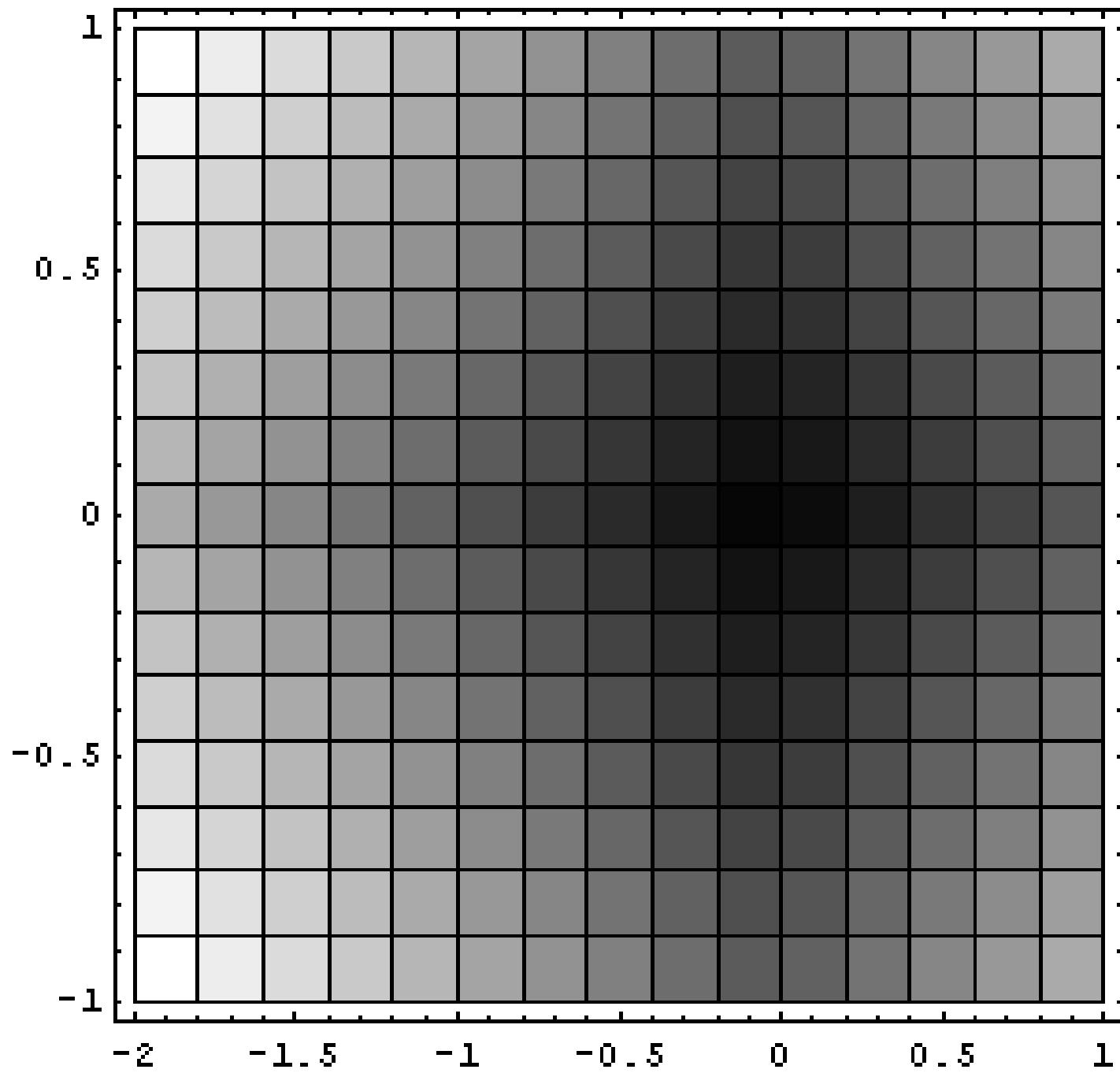
$$\mu_B = \left(\frac{\partial G'}{\partial n_B} \right)_{T, P, n_A}$$

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

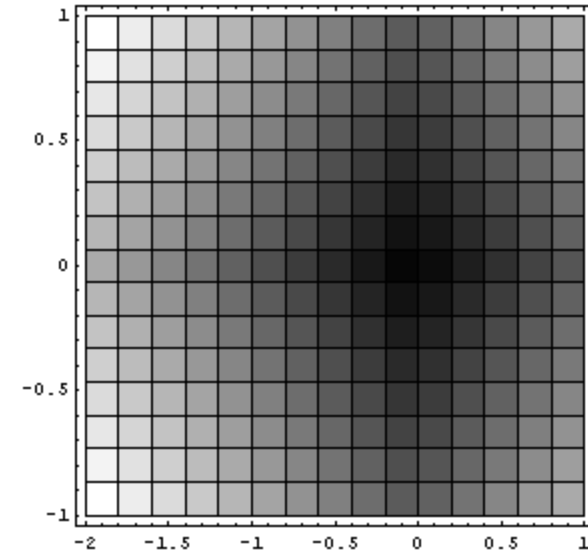
$$\mu_A = \left(\frac{\partial G'}{\partial n_A} \right)_{T, P, n_B}$$

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

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

For variable T and P

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



Gibbs Free Energy of Binary Solutions

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

Correlation between chemical potential and free energy

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

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

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

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

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

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

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

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

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

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

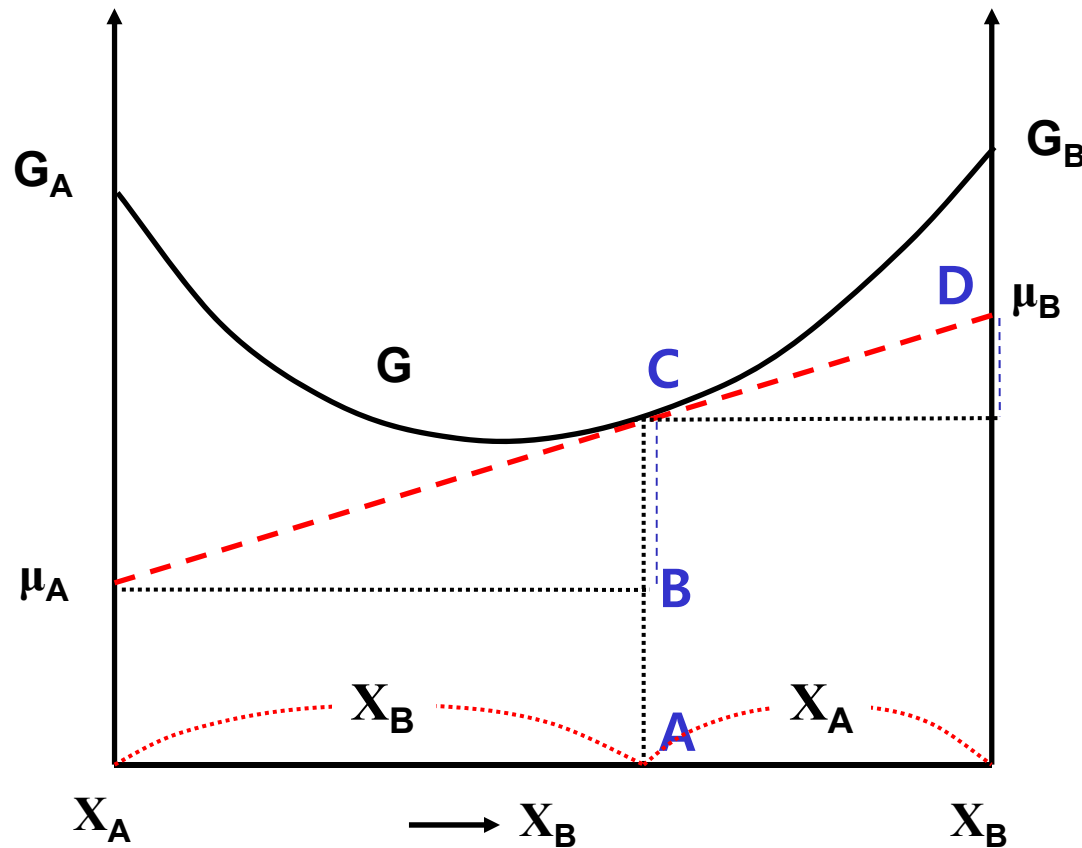
Correlation between chemical potential and free energy

For 1 mole of the solution

(T, P: constant)

1) Ideal solution

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



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

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

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

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

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

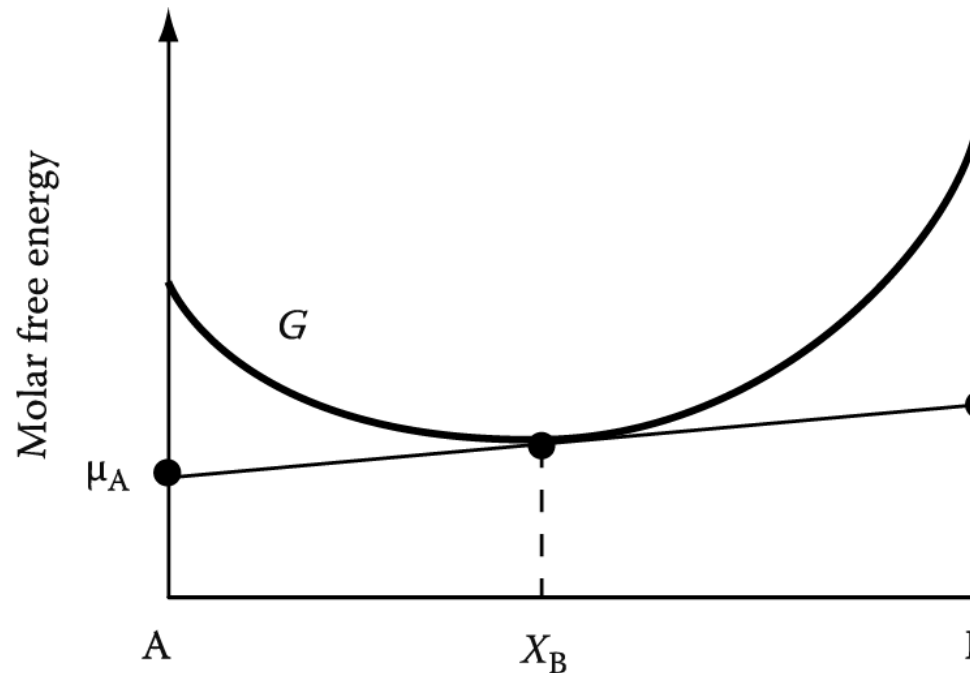
$$= \overline{DA} - \overline{DC} - \overline{CB}$$

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

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

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

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

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

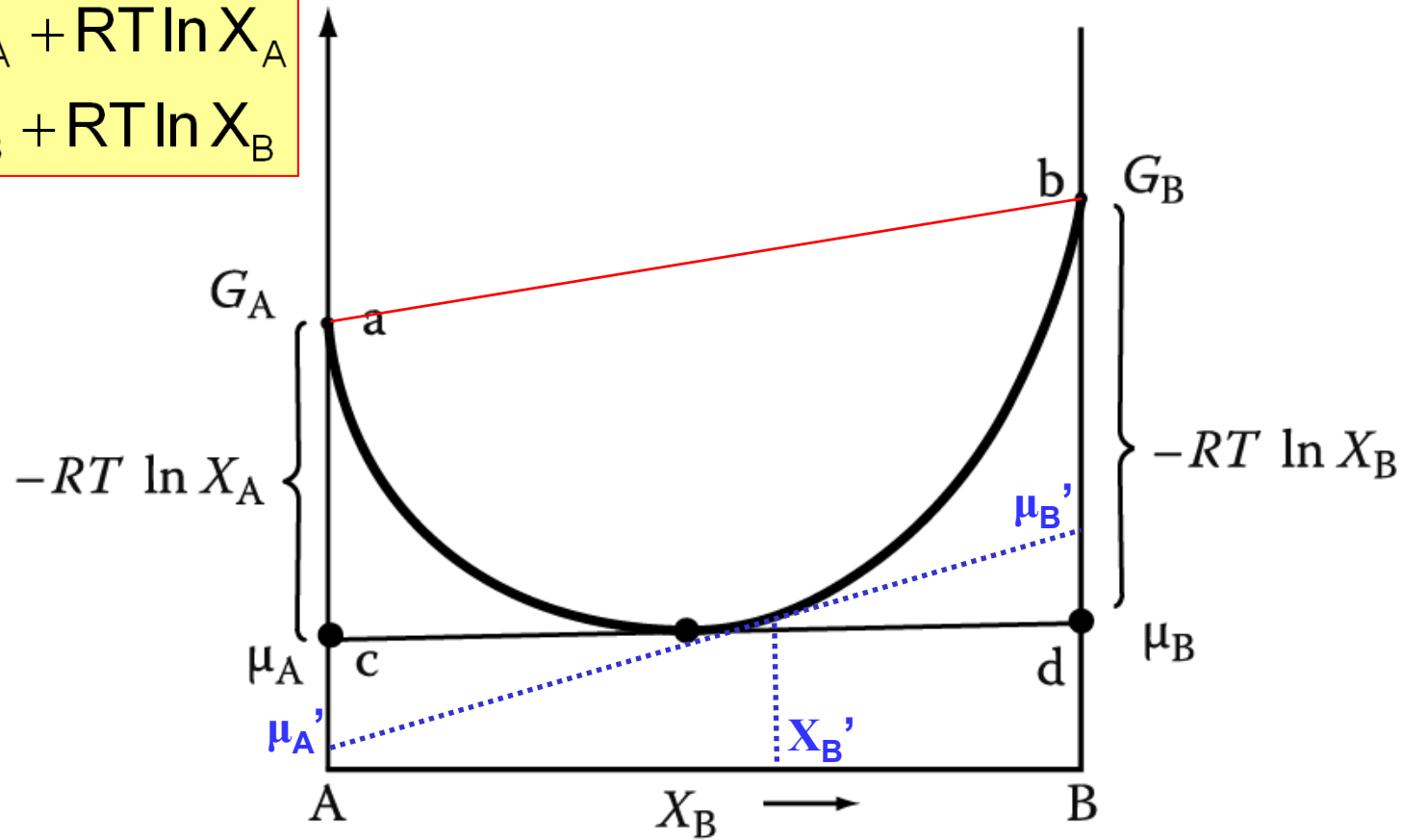


Fig. 1.12 The relationship between the free energy curve and Chemical potentials for an ideal solution.

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

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

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

- **Chemical potential and Activity**

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

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

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

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