2021 Fall

"Phase Transformation *in* Materials"

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Chapter 1

Thermondynamics 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

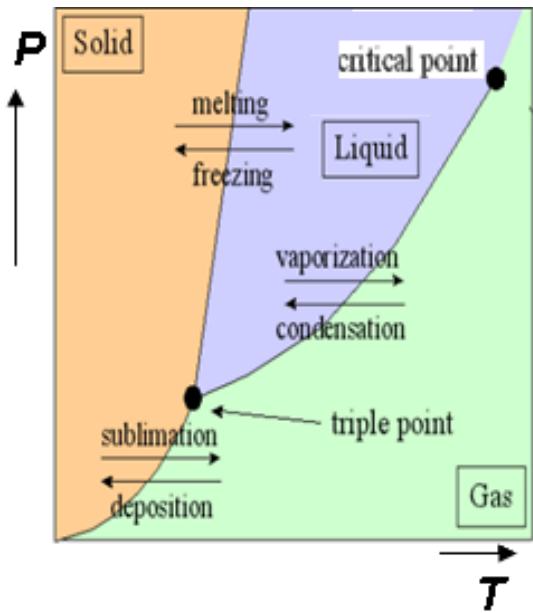**Gibbs Free Energy as a Function of Temp. and Pressure**

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

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

Clausius-Clapeyron Relation

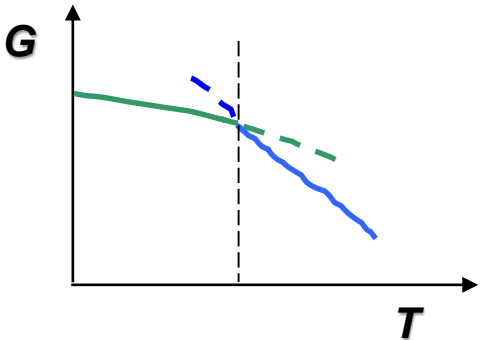**Driving force for solidification** $$\Delta G = \frac{L\Delta T}{T_m}$$

- Classification of phase transition

First order transition: CDD/Second order transition: CCD

The First-Order Transitions

Latent heat
Energy barrier
Discontinuous entropy, heat capacity
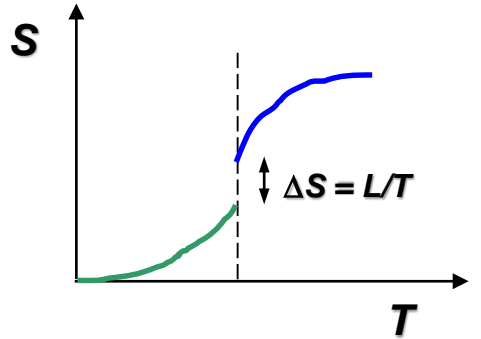

- First Order Phase Transition at T_T:

  – G is <u>continuous</u> at T_T

  – First derivatives of G (V, S, H) are <u>discontinuous</u> at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$
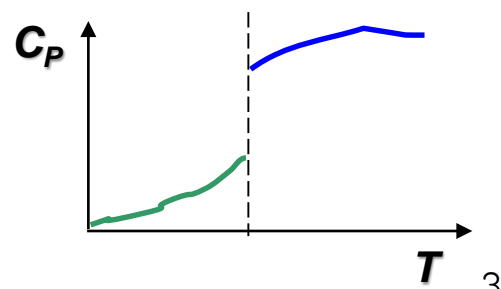
  – Second derivatives of G (α, β, C_p) are <u>discontinuous</u> at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$
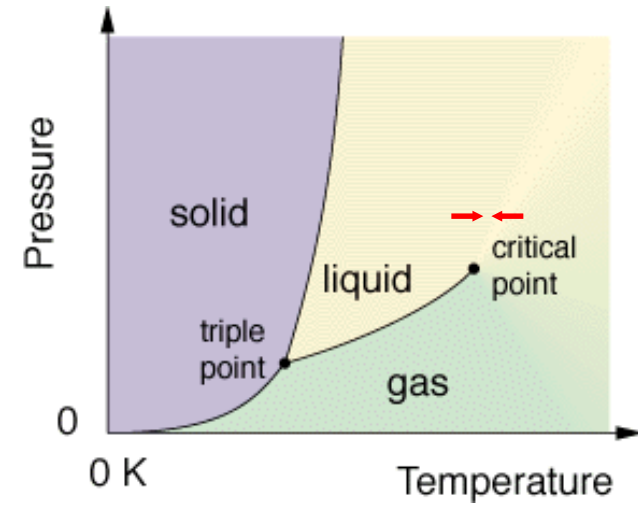
  – Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

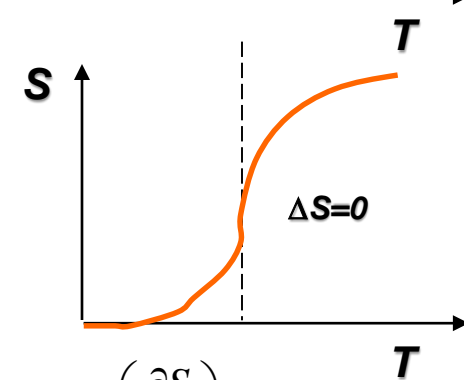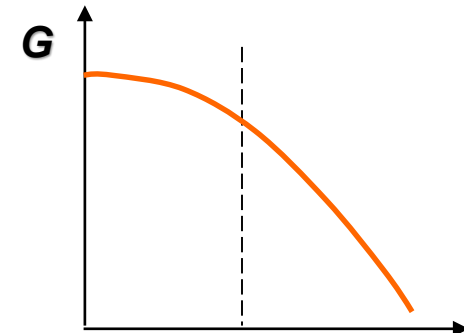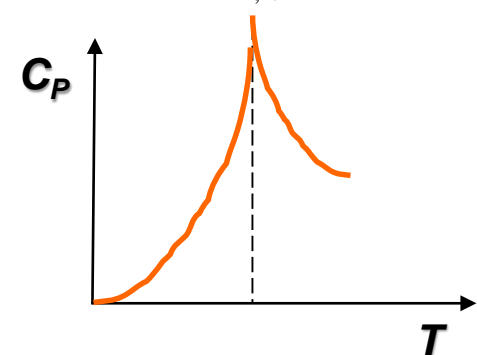$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

$\Delta S = L/T$

The Second Order Transition

No Latent heat
Continuous entropy

Second-order transition

- Second Order Phase Transition at T_T:

  – G is <u>continuous</u> at T_T

  – First derivatives of G (V, S, H) are <u>continuous</u> at T_T

  $$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$
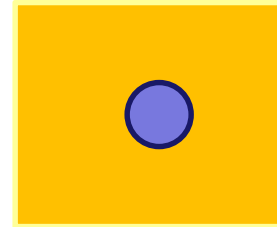
  – Second derivatives of G (α, β, C_p) are <u>discontinuous</u> at T_T

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

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

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

$\Delta S = 0$

Melting and Crystallization are Thermodynamic Transitions

Solidification: **Liquid** $\longrightarrow$ **Solid**

\<Thermodynamic\>

- **Interfacial energy** $\Longrightarrow$ **ΔT_N**

Liquid T_m **Undercooled Liquid**   **Solid**

No superheating required!

- **Interfacial energy** $\Longrightarrow$ **No ΔT_N**

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

vapor

Melting: **Liquid** $\longleftarrow$ **Solid**

HEATING LASER ON — HEATING LASER OFF

Recalescence

T_m

Solid state trans-formations

temperature (K)

solid

solid + liquid

liquid

undercooled liquid

solid + liquid

solid

time (s)

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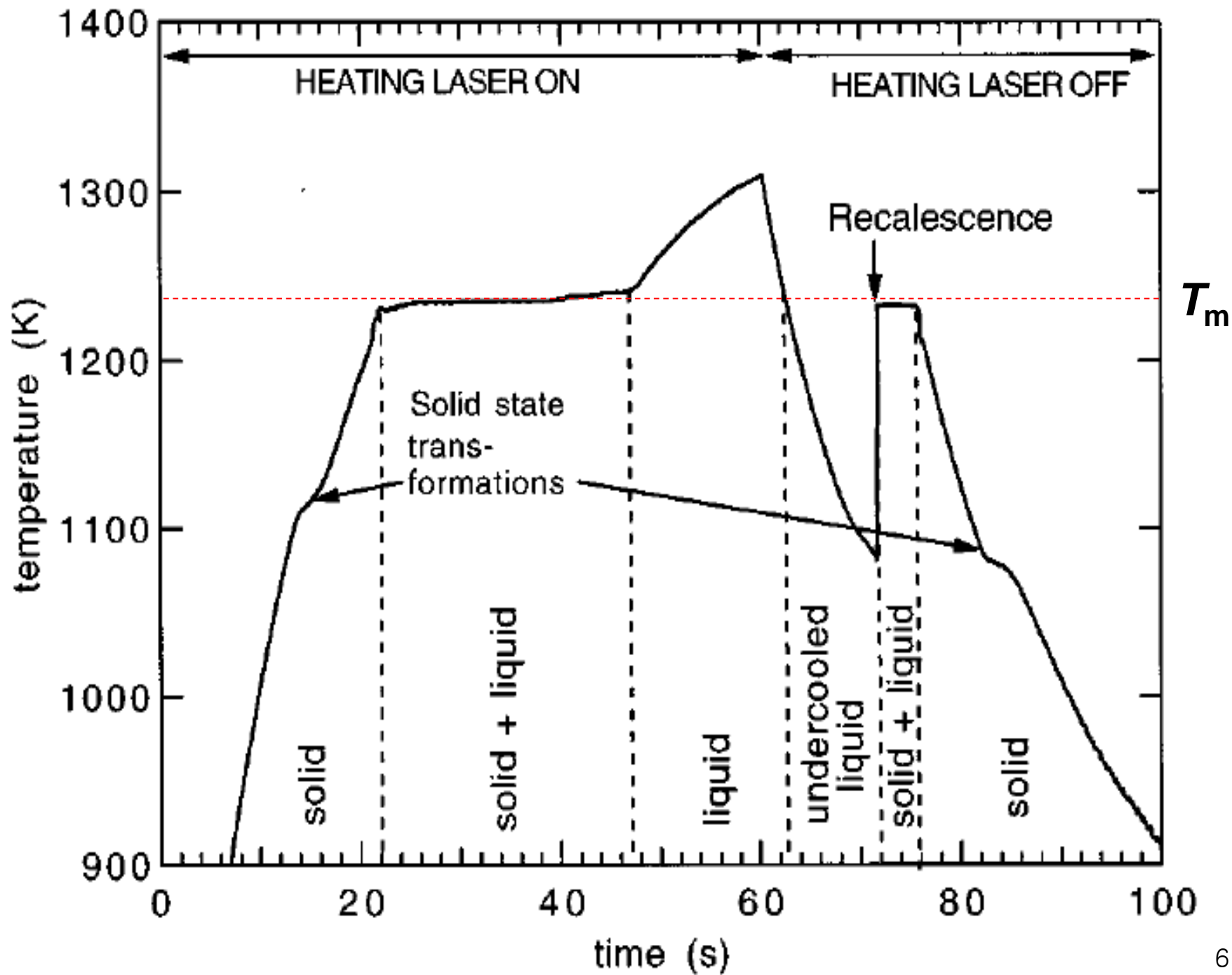
Contents for today's class

- **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 (H_2O)

: **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
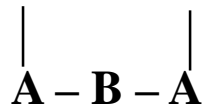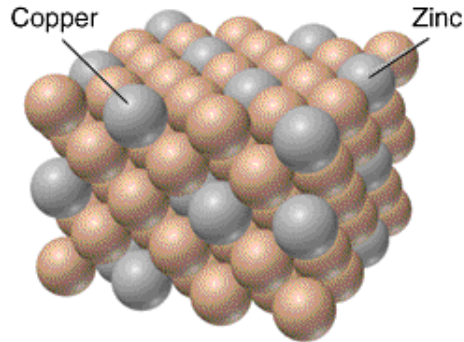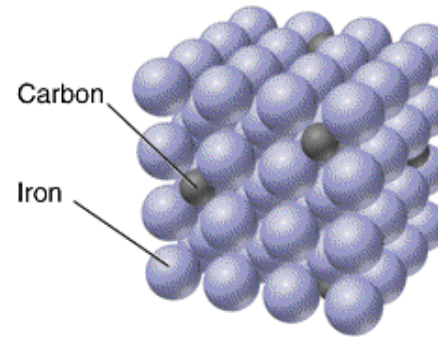
사금 채취

Winnowing

키질

wash rice

쌀 씻기

Select egg

달걀 고르기

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

        | |

    A – B – A   **Solid solution : substitutional or interstitial**
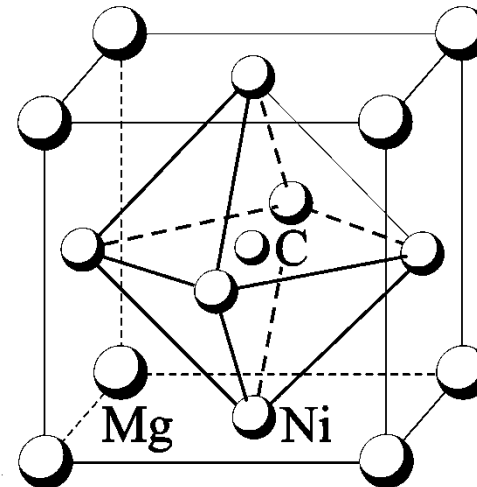

A Brass, a substitutional alloy

B Carbon steel, an interstitial alloy

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

     | | | |

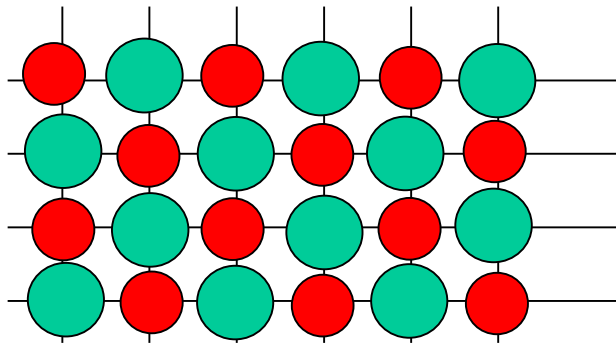   **B – A – B – A**

MgCNi3

Q2: What is "Alloying"?

Ordered Compounds or Solid Solutions

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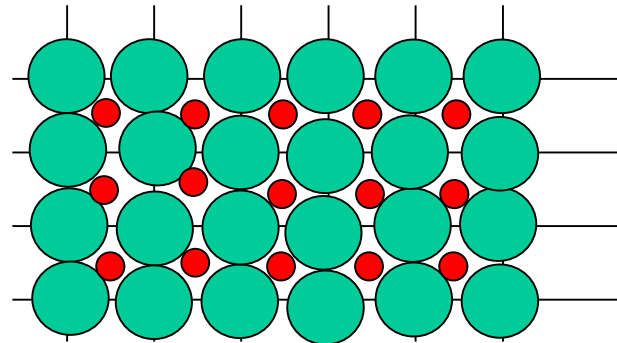## Ordered Compounds and Solid Solutions

Ordered Substitutional and Interstititials Compounds

Substitutional
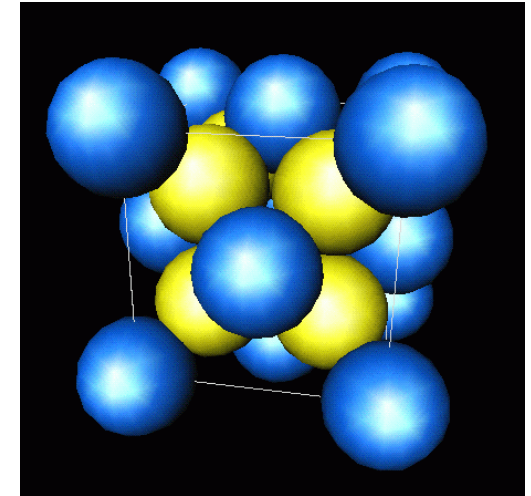**element replaces host atoms**
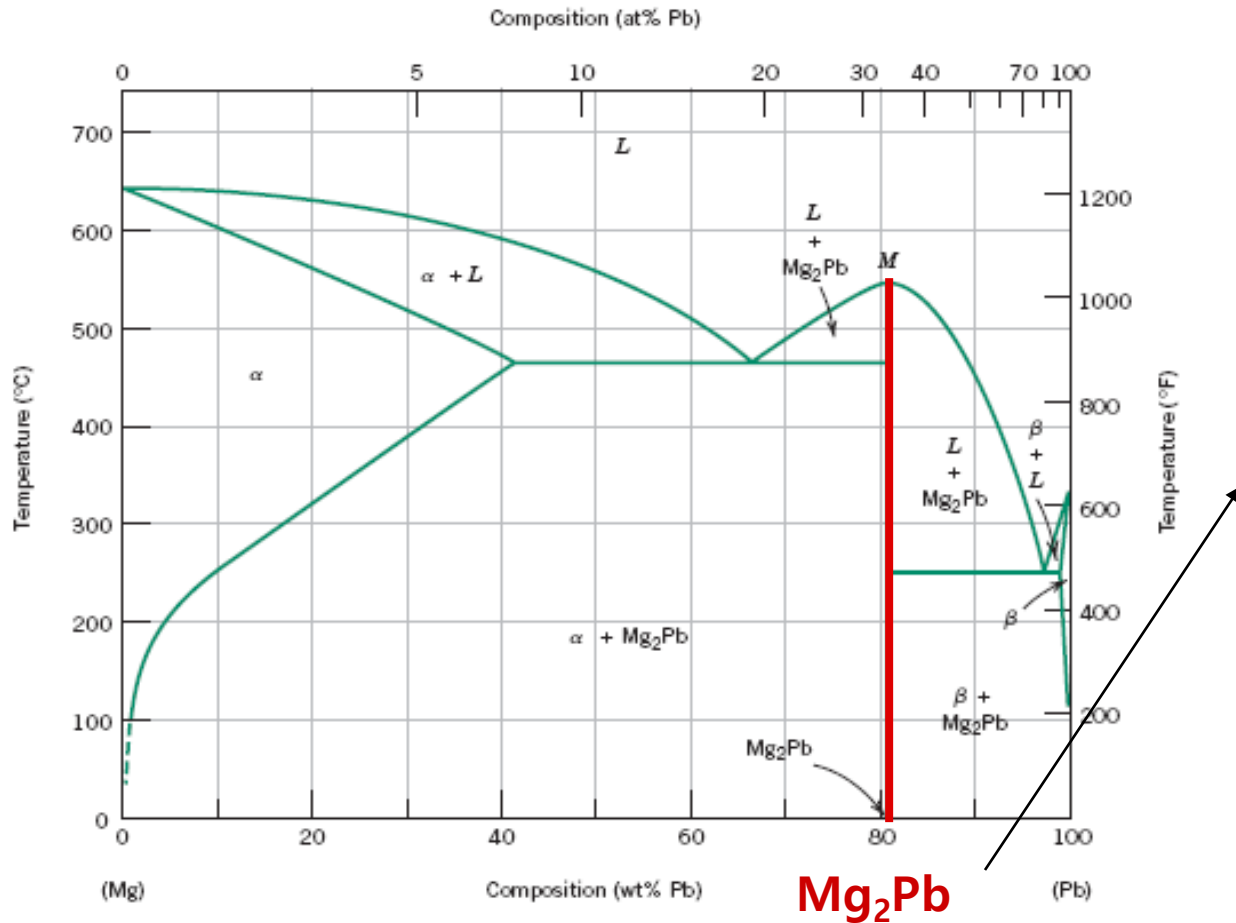**in an orderly arrangement**

Interstitial
element goes into holes
in an orderly arrangement

e.g., Ni_3Al (hi-T yield strength), $Al_3(Li,Zr)$ (strengthening)

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

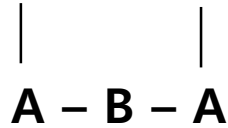# Intermetallic Compounds

Mg$_2$Pb

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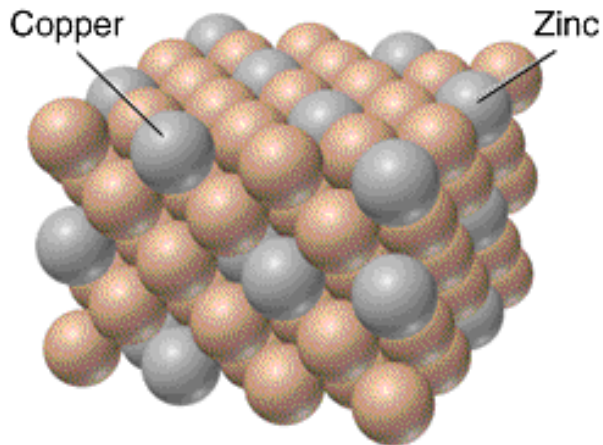
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- **Solution** ; **A – A – A** ; → **atomic scale mixing, Random distribution**

         | |
    A – B – A

Two Possibilities for Solid Solutions: B atoms in A atoms

Substitutional	Interstitials
'new element replaces host atoms'	**'new element goes in holes'**

A Brass, a substitutional alloy
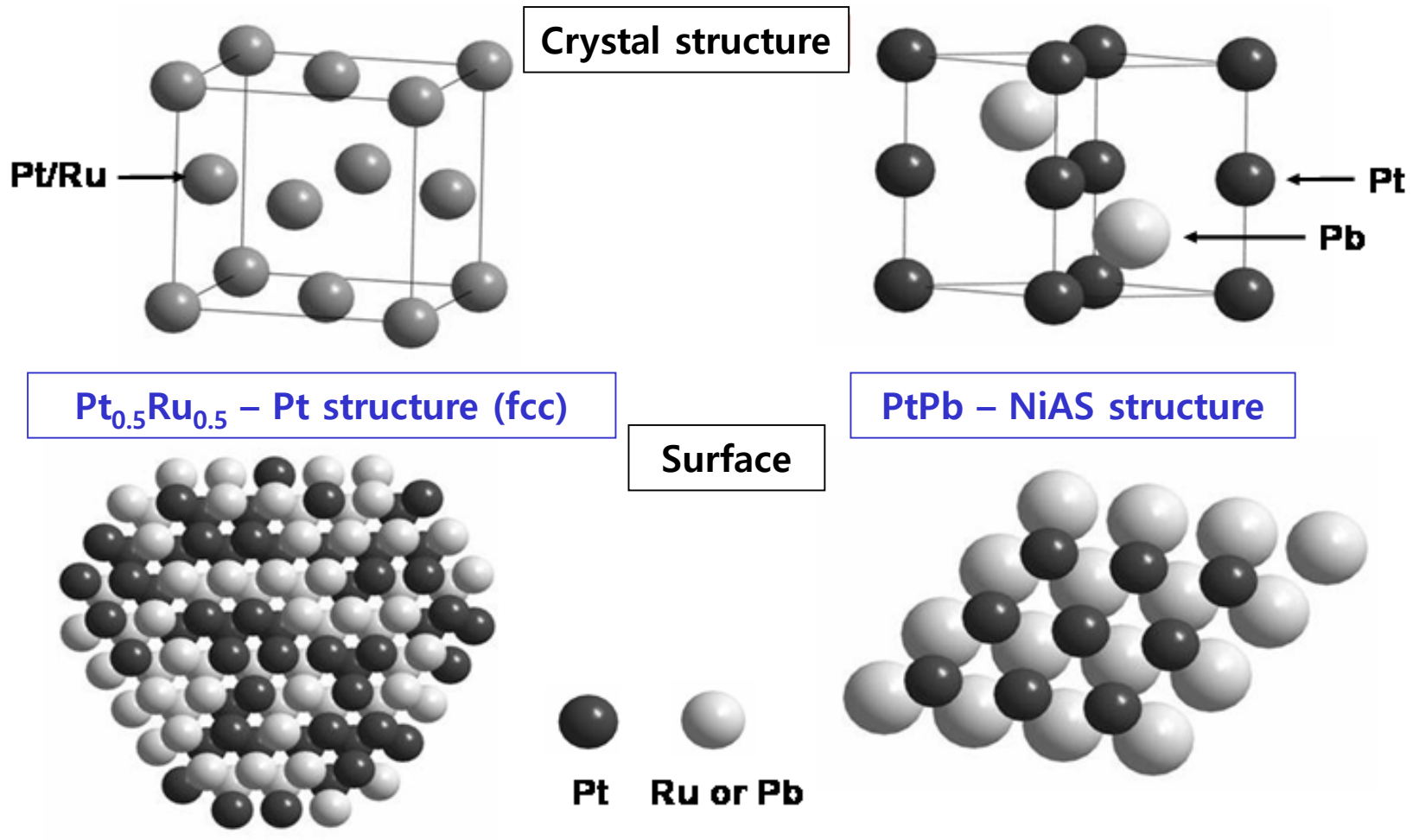
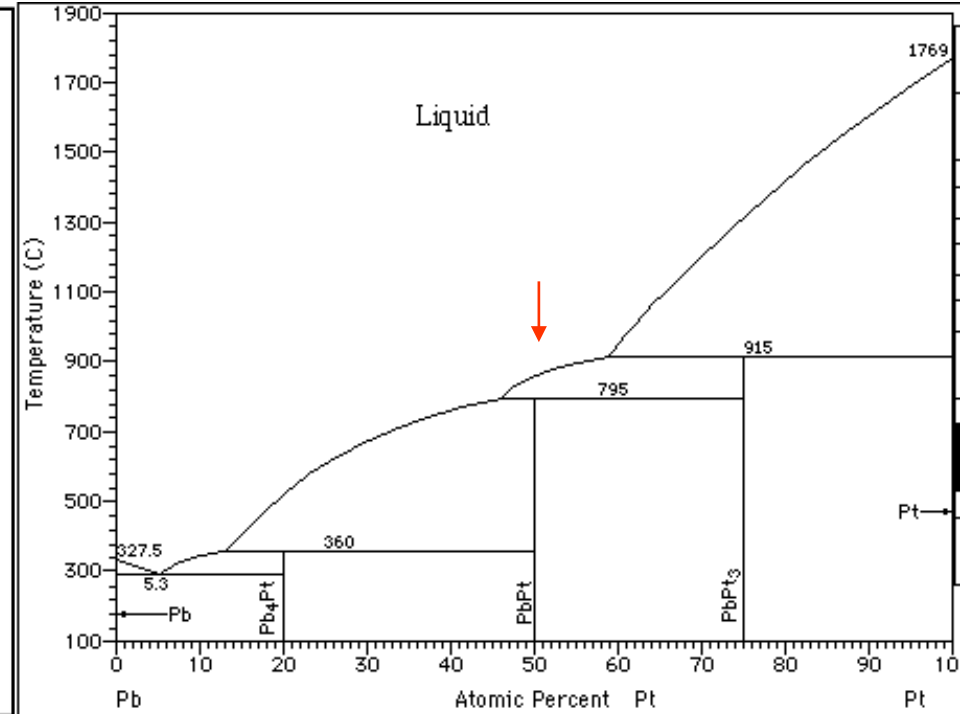**B** Carbon steel, an interstitial alloy

14
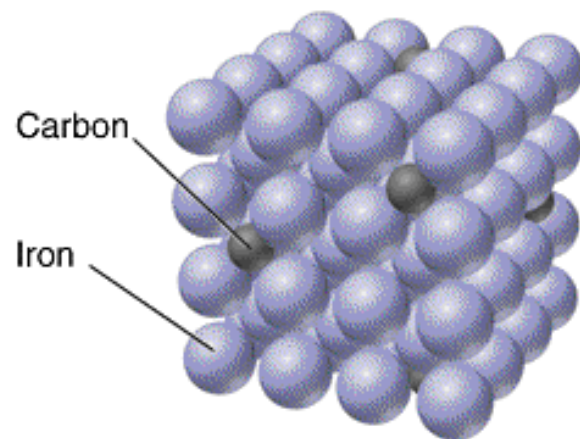
Q3: "Solution vs. Intermetallic compound"?

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

Solid Solution vs. Intermetallic Compound

Crystal structure

Pt/Ru →

← Pt

← Pb

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

PtPb – NiAS structure

Surface

Pt   Ru or Pb

ruthenium 루테늄《백금류의 금속 원소;기호 Ru, 번호 44》

Solid Solution vs. Intermetallic Compounds
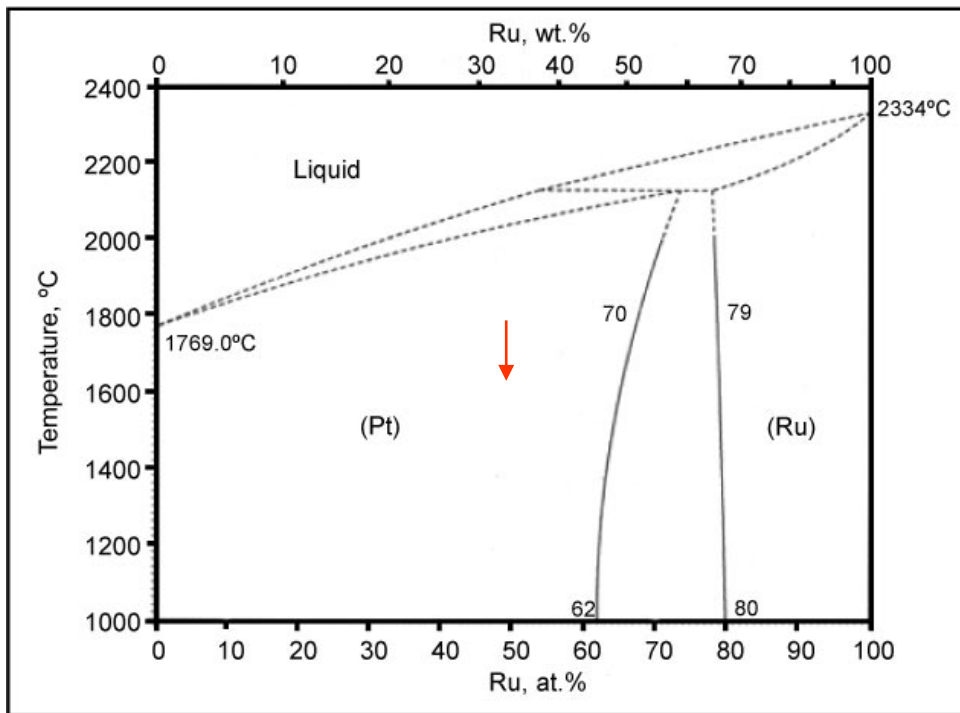
Pt$_{0.5}$Ru$_{0.5}$ – Pt structure (fcc)

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

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- **Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)**
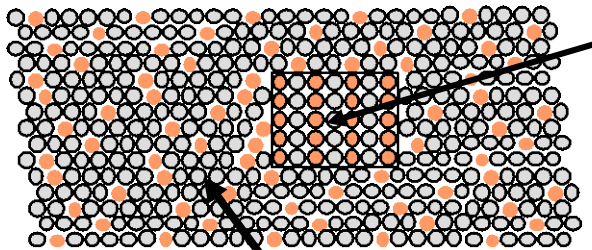
**Second phase particle
--different composition
--often different structure.**

Solid Solution phase: B atoms in A

c. Mechanism of Precipitation

Matrix atom

Alloying atom

Atomic diffusion

Precipitate
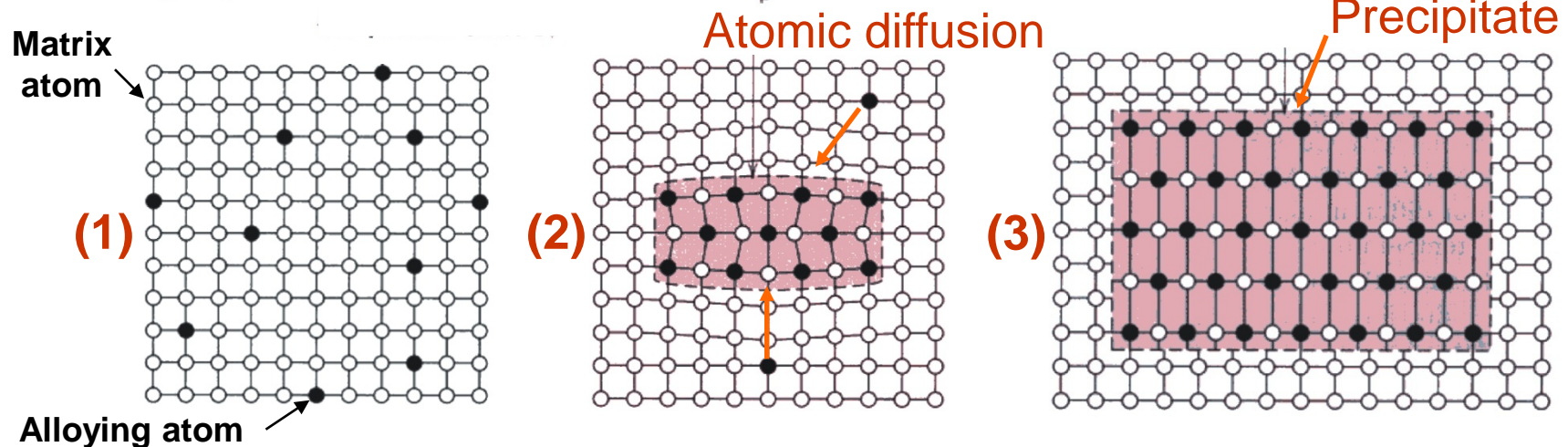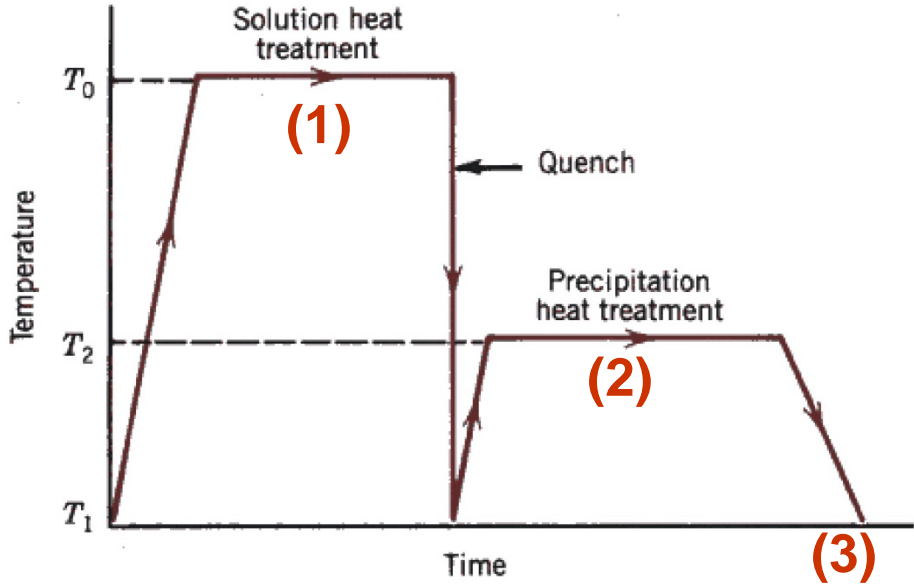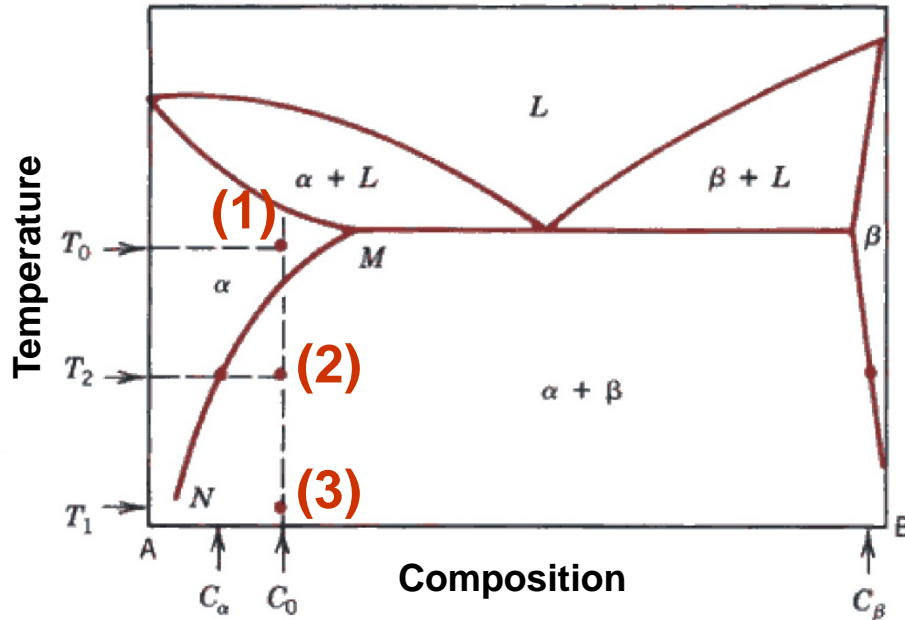
Q4: How can we classify "Solubility"?

Solubility

- **Unlimited Solubility**

  - **Hume Rothery' Conditions**
    - Similar Size
    - Same Crystal Structure
    - Same Valance
    - Similar Electronegativity

  - Implies <u>single phase</u>

- **Limited Solubility**
  - Implies <u>multiple phases</u>

- **No Solubility**
  - oil and water region

Water   Alcohol

Liquid solution

Mixing on the molecular scale

○ H_2O

● C_2H_5OH

Temperature

L_{system}

T_1 L_1

SS_1

SS_{system}

A   B

System composition

Composition

All liquid (L_{system})

Crystallites of SS_1 in matrix of L_1

Polycrystalline solid (SS_{system})
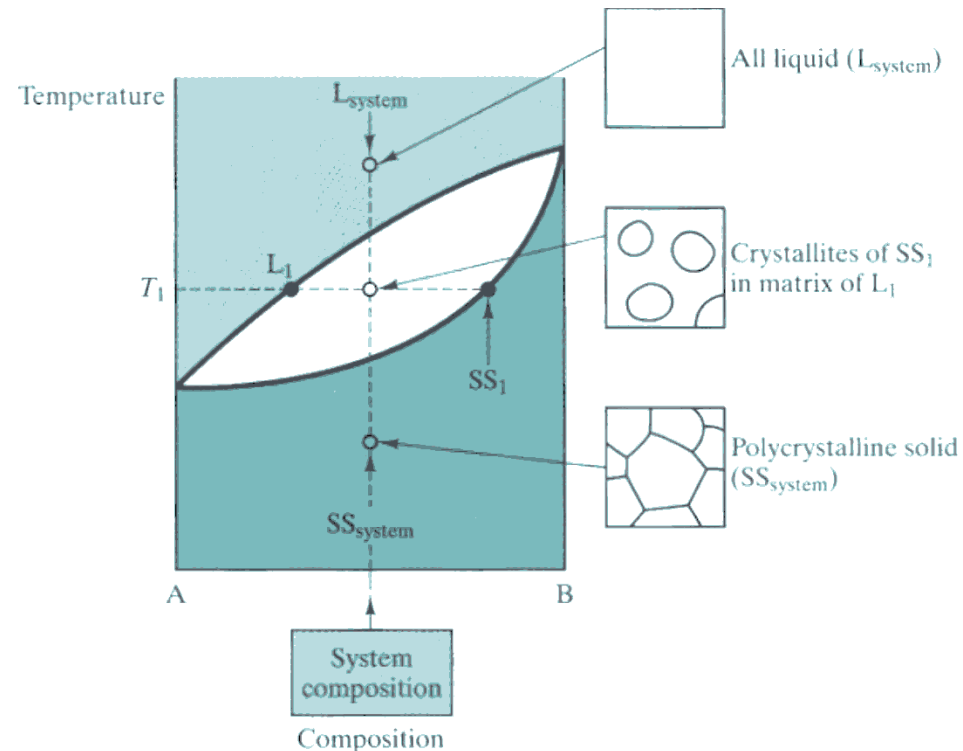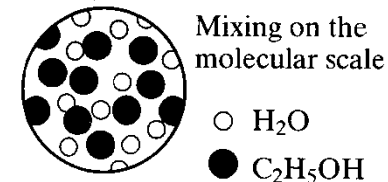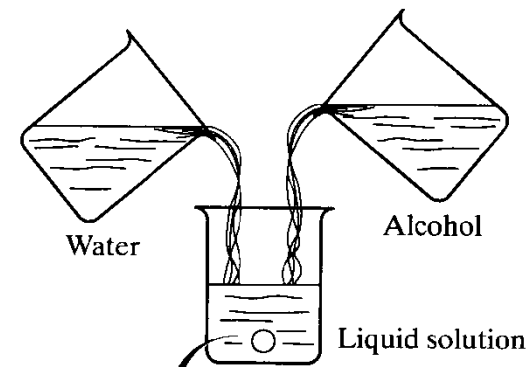
Cu-Ni Alloys
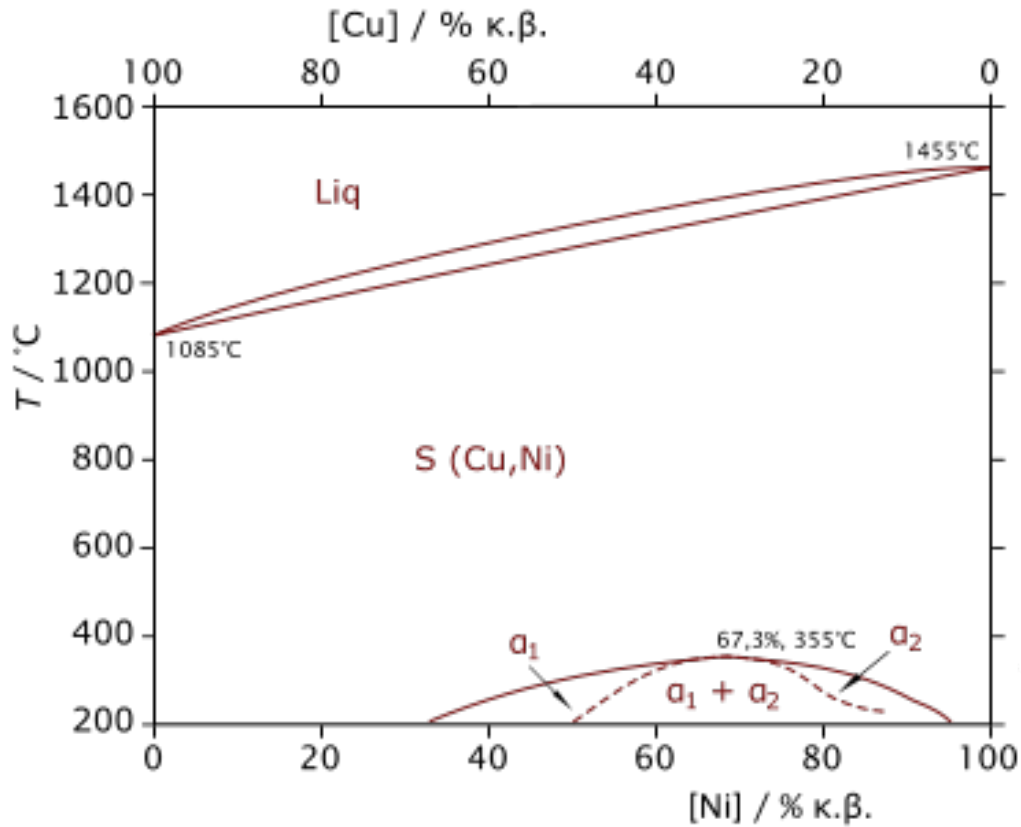
complete solid solution

Cu-Ag Alloys

limited solid solution

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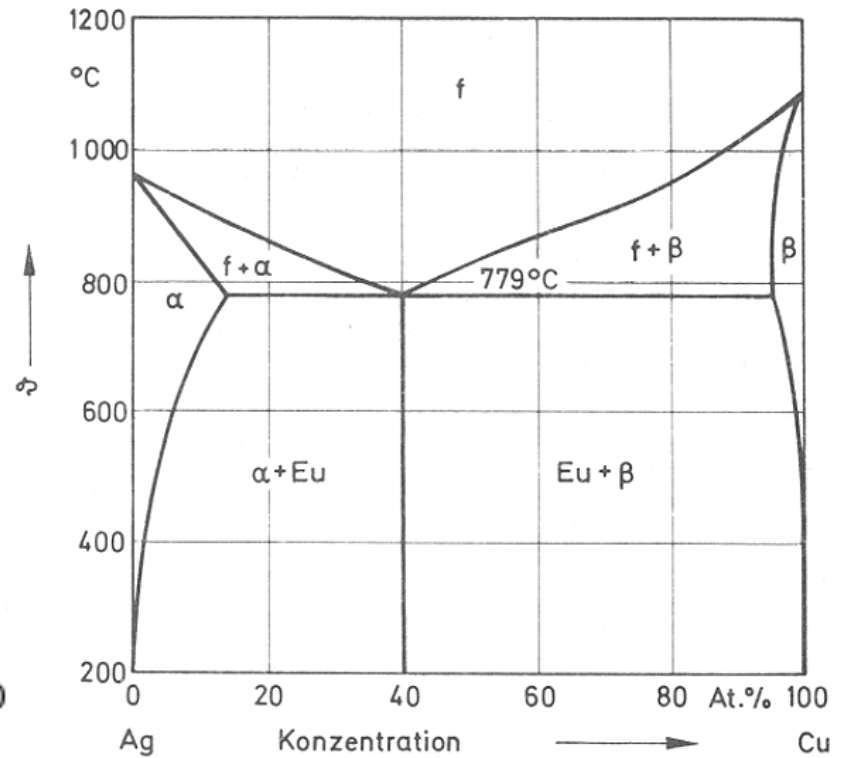
* Complete immiscibility of two metals does not exist.

: 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.
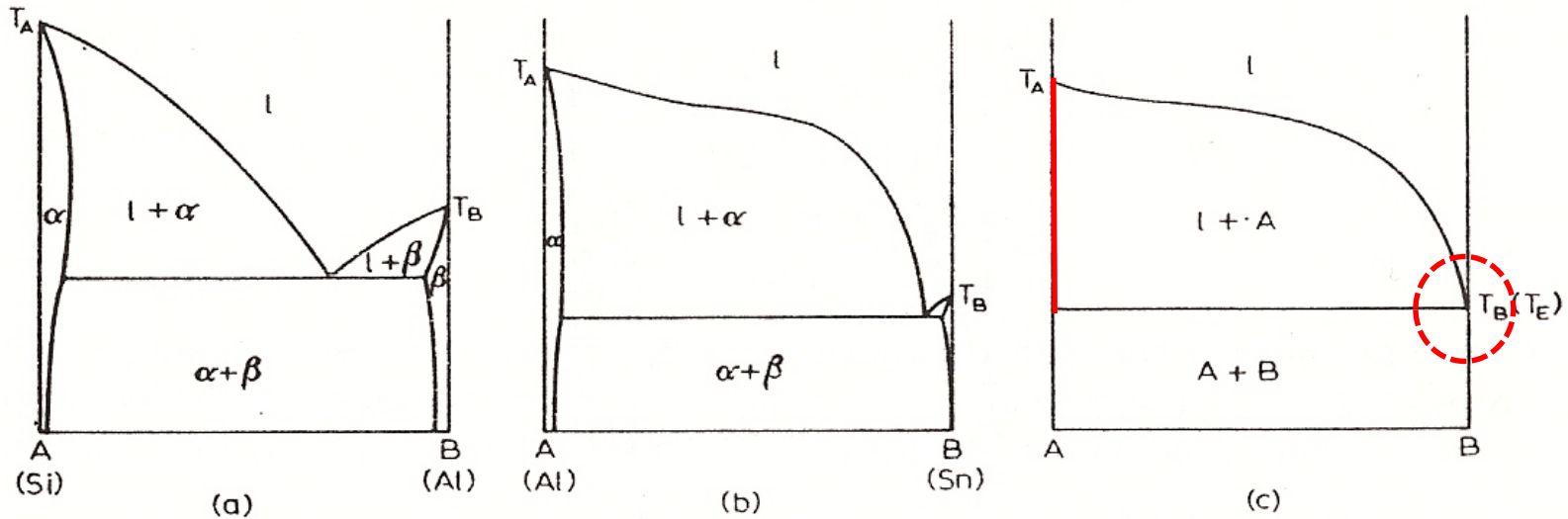
Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.
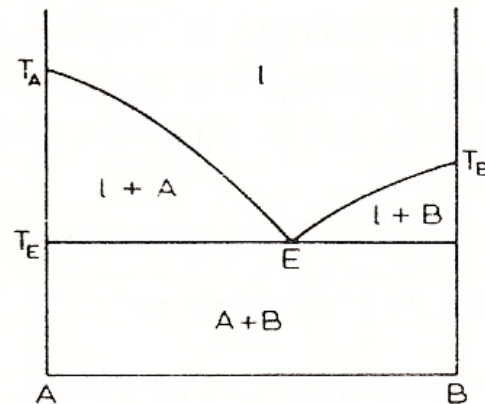
Fig. 54. Impossible form of a binary eutectic phase diagram.

Weight Percent Tin

L

660.452°C

228°C

231.9681°C

97.6

(Al)

(βSn)

Temperature, °C

Al   Atomic Percent Tin   Sn

26
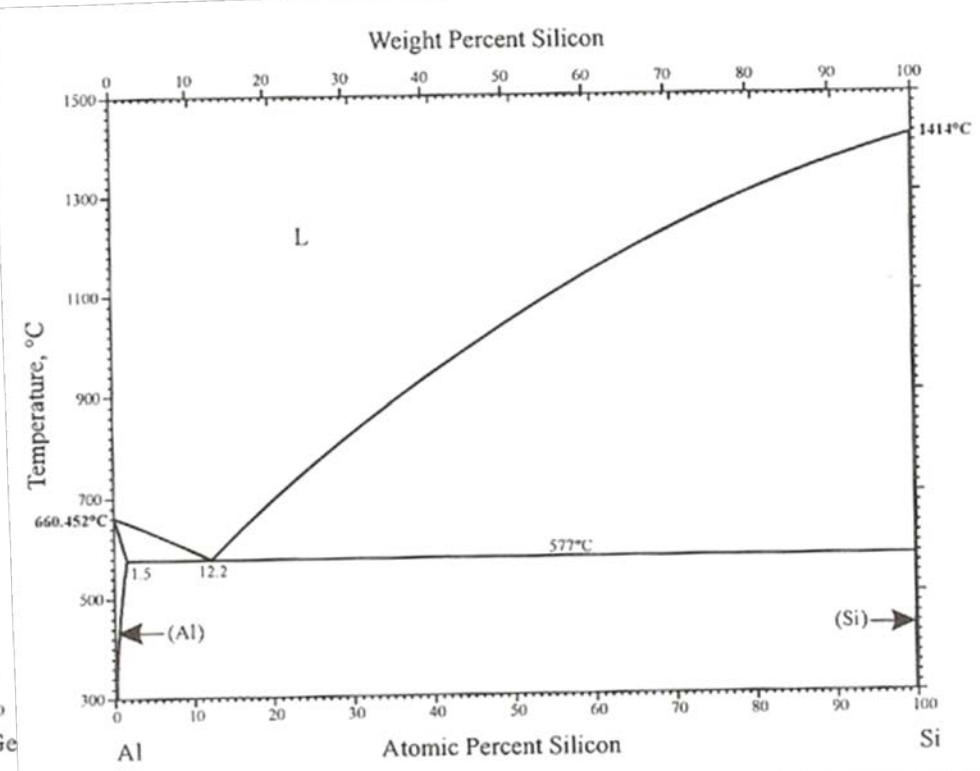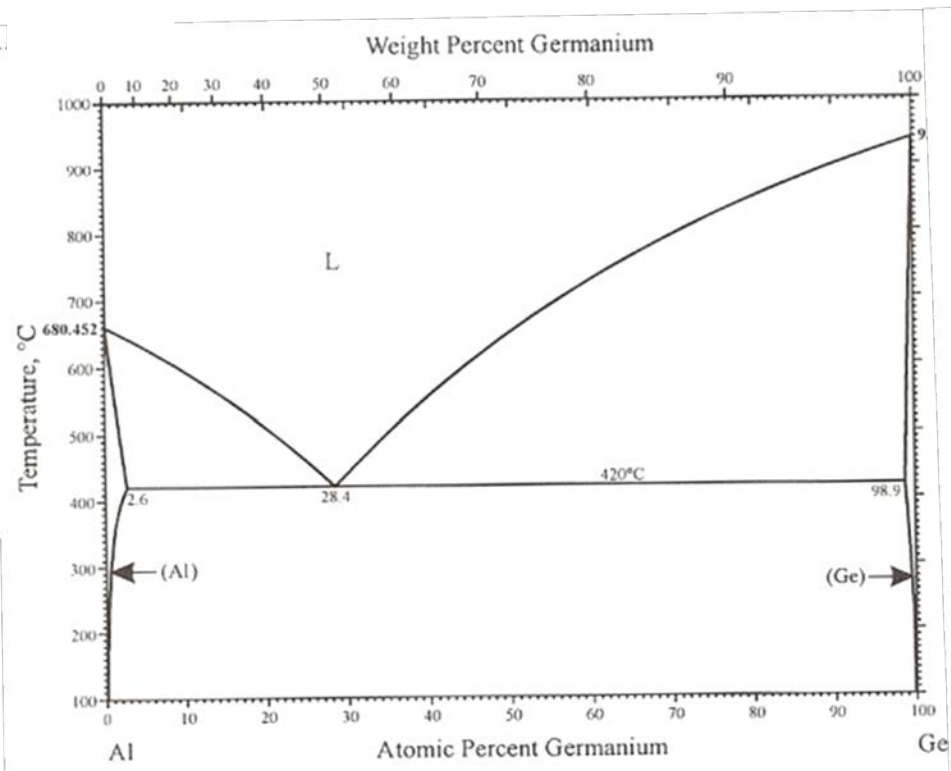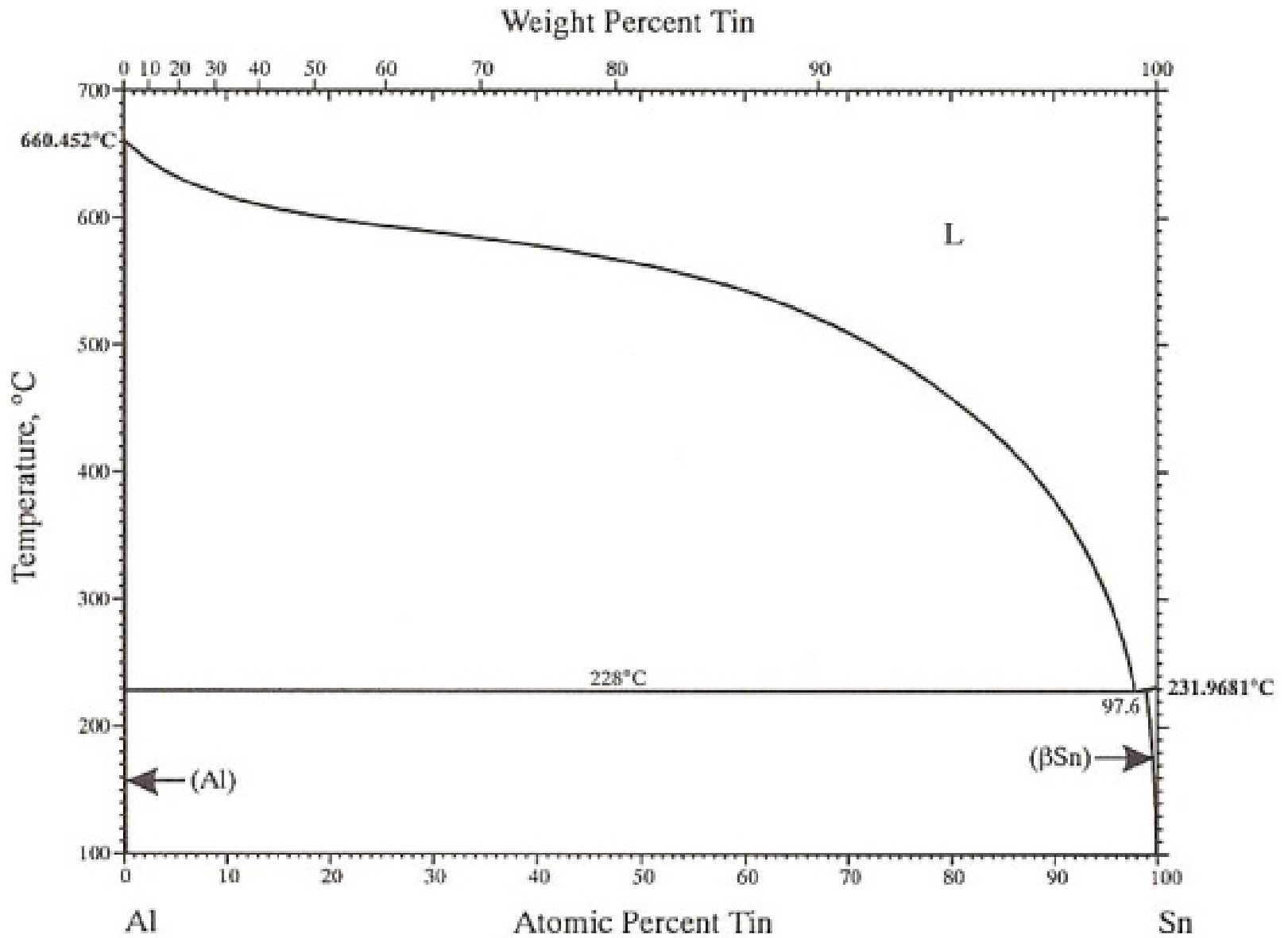
Q5: Can we roughly estimate what atoms will form solid solutions?

"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?
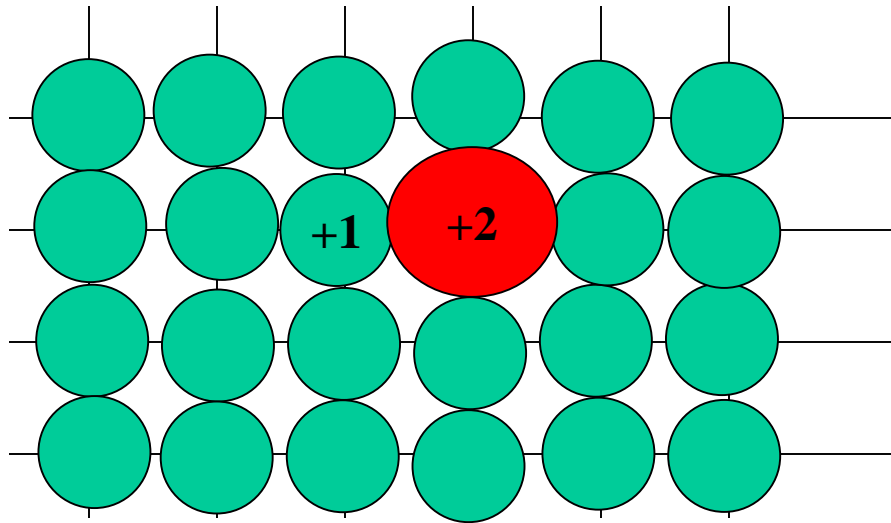
Empirical observations have identified 4 major contributors through :

Atomic Size Factor , Crystal Structure, Electronegativity, Valences

Hume-Rothery Rules for Mixing

Empirical rules for <u>substitutional solid-solution formation </u>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 $\pm15\%$, the lattice distortions (i.e. local lattice strain) are too big and solid-solution will not be favored.

$$DR\% = \frac{r_{solute} - r_{solvent}}{r_{solvent}} \times 100\% \quad < \; \pm15\% \text{ will } \underline{\text{not disallow}} \text{ formation.}$$

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_{Cu} = 0.128 nm and r_{Ni}= 0.125 nm.

DR%= $\dfrac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ **= 2.3%** **favorable** $\surd$

Rule 2: Ni and Cu have the FCC crystal structure. **favorable** $\surd$

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

Rule 4: Valency of Ni and Cu are both +2. **favorable** $\surd$

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).

Is solid-solution favorable, or not?

- **Cu-Ag Alloys**

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

  DR%= $\dfrac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$ **= 9.4%** **favorable √**

  Rule 2: Ag and Cu have the FCC crystal structure. **favorable √**

  Rule 3: E_{Cu} = 1.90 and E_{Ni}= 1.80. Thus, DE%= -5.2% **favorable √**

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

  Expect Ag and Cu have <u>limited solubility</u>.

  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
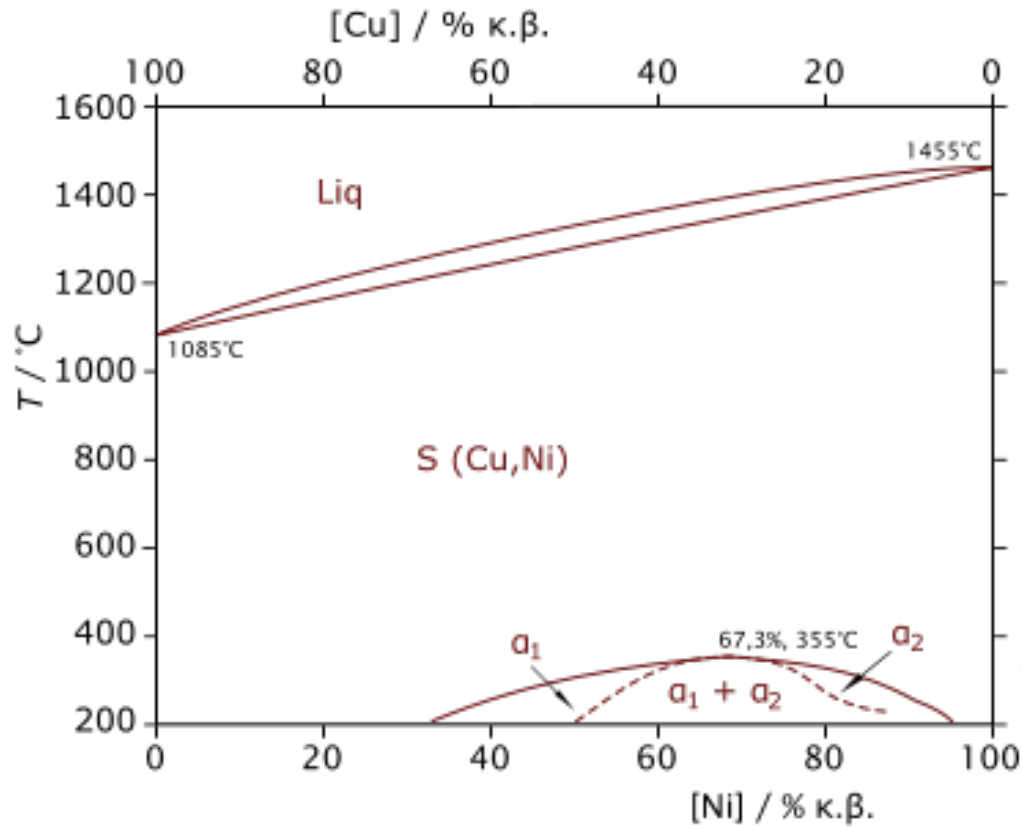
Cu-Ag Alloys

complete solid solution

limited solid solution

Minor element 3

Traditional alloys

Major element

Minor element 2

Minor element 1

Major element 4, 5..

Major element 3

Major element 1

Major element 2
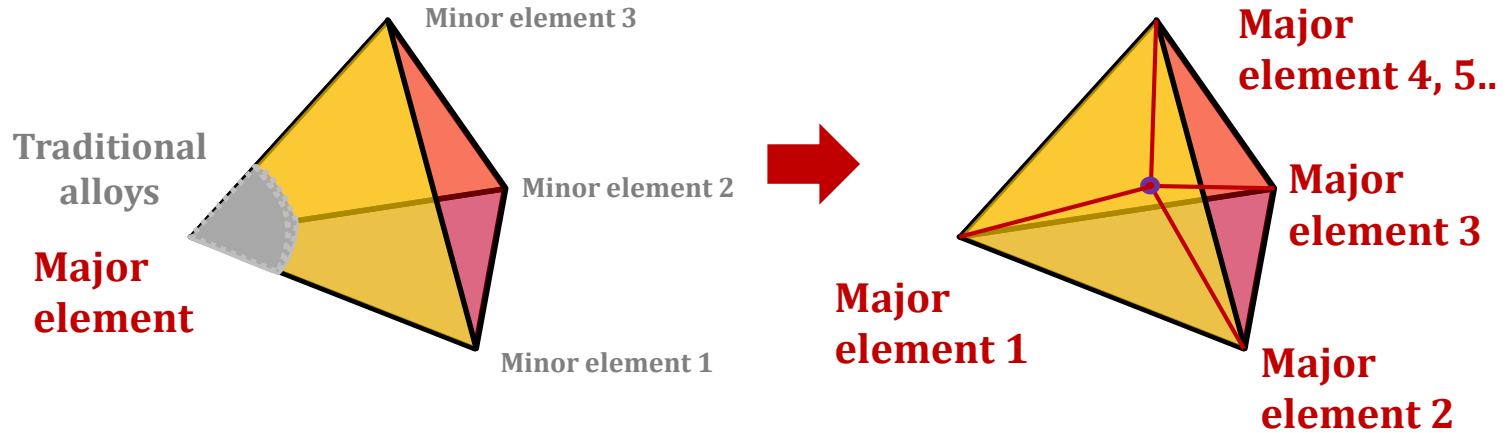
Conventional alloy system

Ex) 304 steel - $Fe_{74}Cr_{18}Ni_8$

High entropy alloy system

Ex) $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$
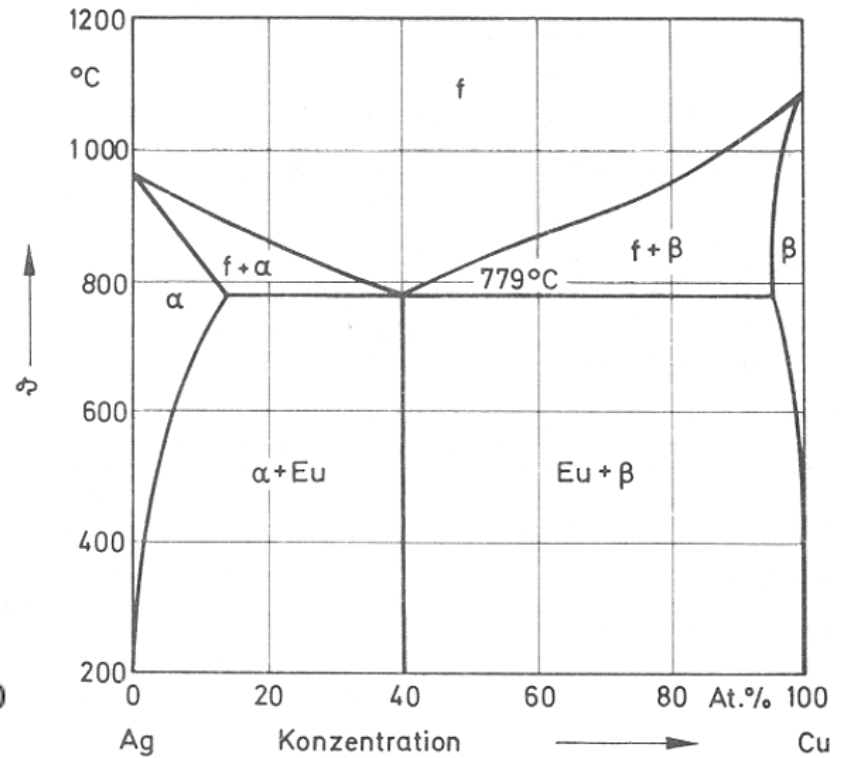
(1) Thermodynamic : high entropy effect

(2) Kinetics : sluggish diffusion effect

(3) Structure : severe lattice distortion effect

(4) Property : cocktail effect
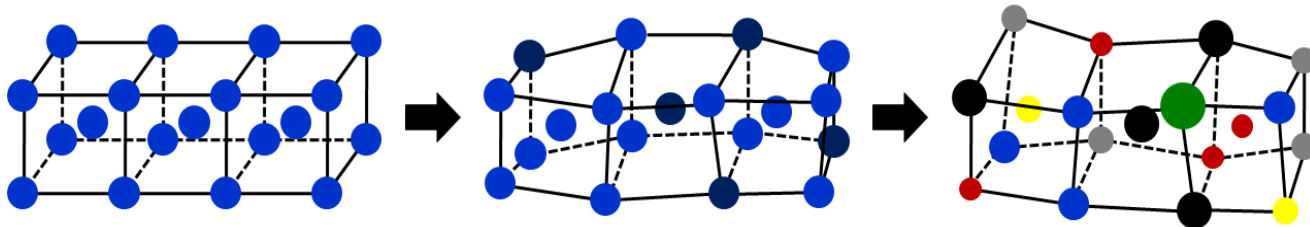
Yong Zhang et al., Adv. Eng. Mat. P534-538, 2008

Severe lattice distortion → Sluggish diffusion & Thermal stability

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Q6: How to calculate

"Gibbs Free Energy of Binary Solutions"?

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

2) Gibbs Free Energy of Binary Solutions

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

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 <u>make a homogeneous solid solution.</u>

Before mixing

After mixing

Mix

X_A mol A $\qquad$ X_B mol B

1 mol solid solution

F.E. $X_A G_A$ $\qquad$ F.E. $X_B G_B$

Total free energy =

$G_1 = X_A G_A + X_B G_B$

Total free energy =

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

35
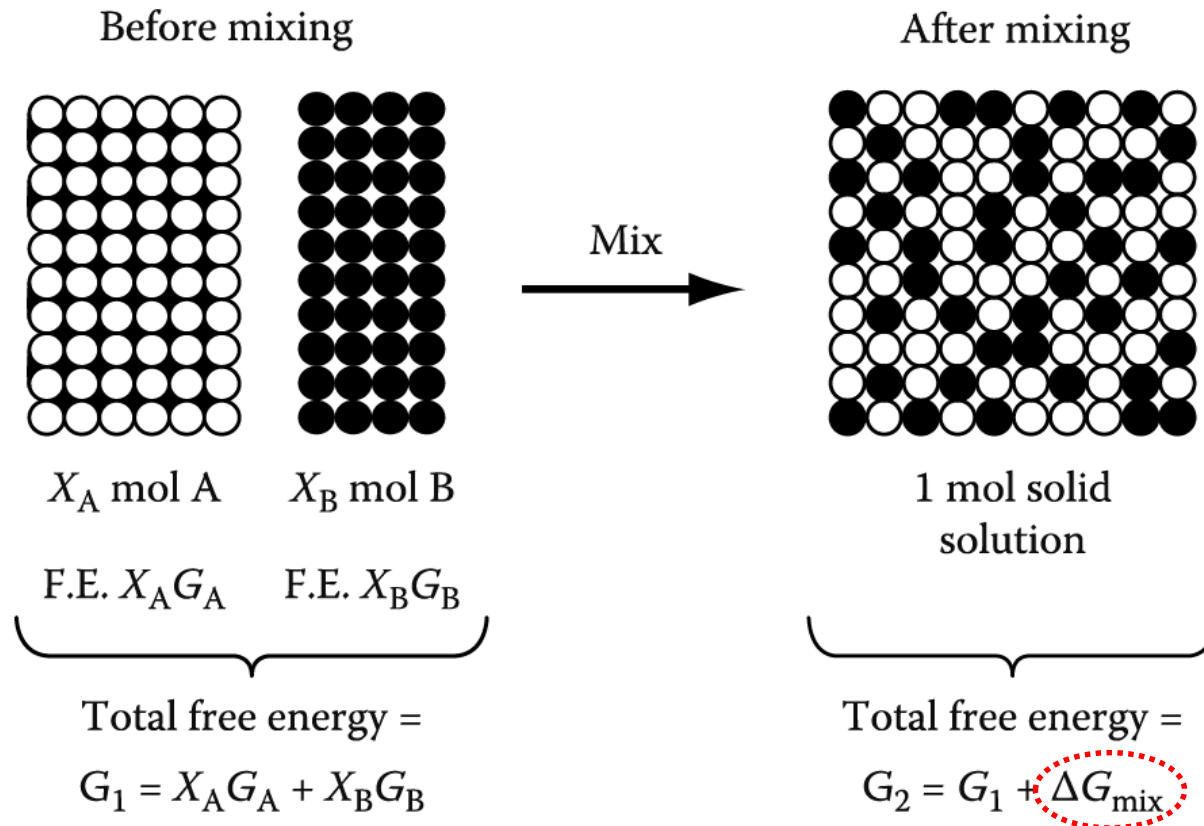
Gibbs Free Energy of The System

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

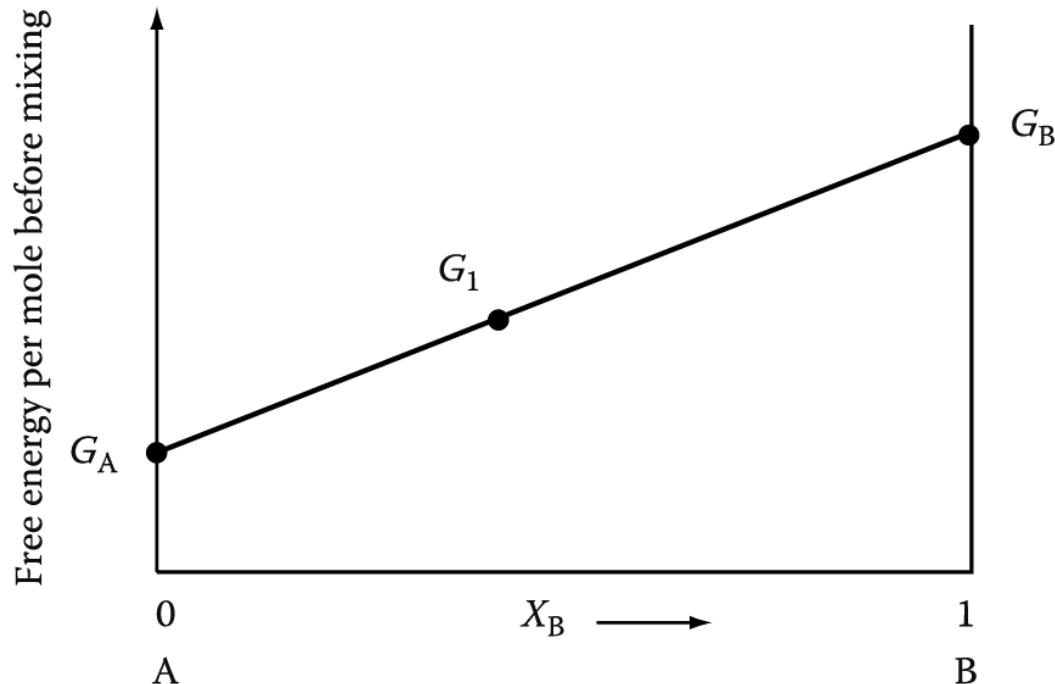# Gibbs Free Energy of The System

In Step 2 $\boxed{G_2 = G_1 + \Delta G_{mix} \quad J/mol}$

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

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

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$
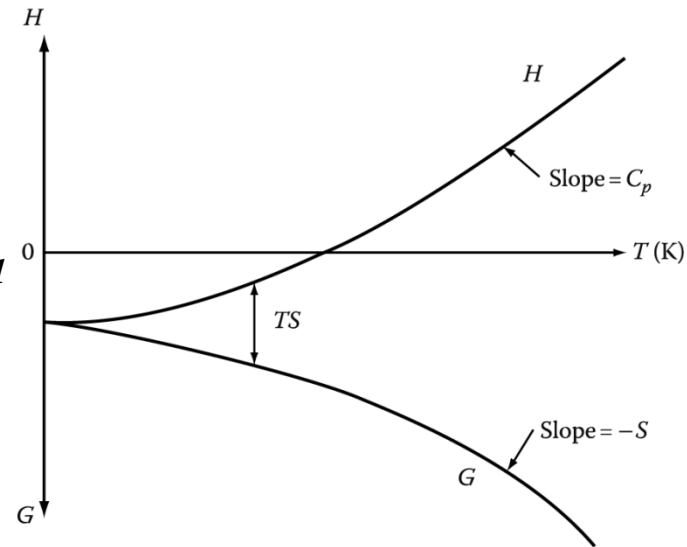
ΔH_{mix} : *Heat of Solution* **i.e. heat absorbed or evolved during step 2**

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

➡ **How can you estimate ΔH$_{mix}$ and ΔS$_{mix}$?**

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Q7: How can you estimate

"ΔG$_{mix}$ of ideal solid solution"?

$$\Delta G_{mix} = -T\Delta S_{mix}$$ ➡ $$\Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

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**

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

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

Entropy can be computed from randomness

by <u>Boltzmann equation</u>, i.e.,

$$\boxed{S = k \ln w}$$

w : degree of randomness, k: Boltzman constant

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

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

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

Excess mixing Entropy

If there is no volume change or heat change,

$$w_{config} = 1 \quad \rightarrow before\_solution\_(pureA\_pureB)$$

$$w_{config} = \frac{(N_A + N_B)!}{N_A! N_B!} \rightarrow after\_solution\_(N_A, N_B) \quad \Longleftarrow$$

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 $\quad \ln N! \approx N \ln N - N$

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

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

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

Excess mixing Entropy

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

$$\Delta G_{mix} = -T\Delta S_{mix} \quad \Longrightarrow \quad \Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$
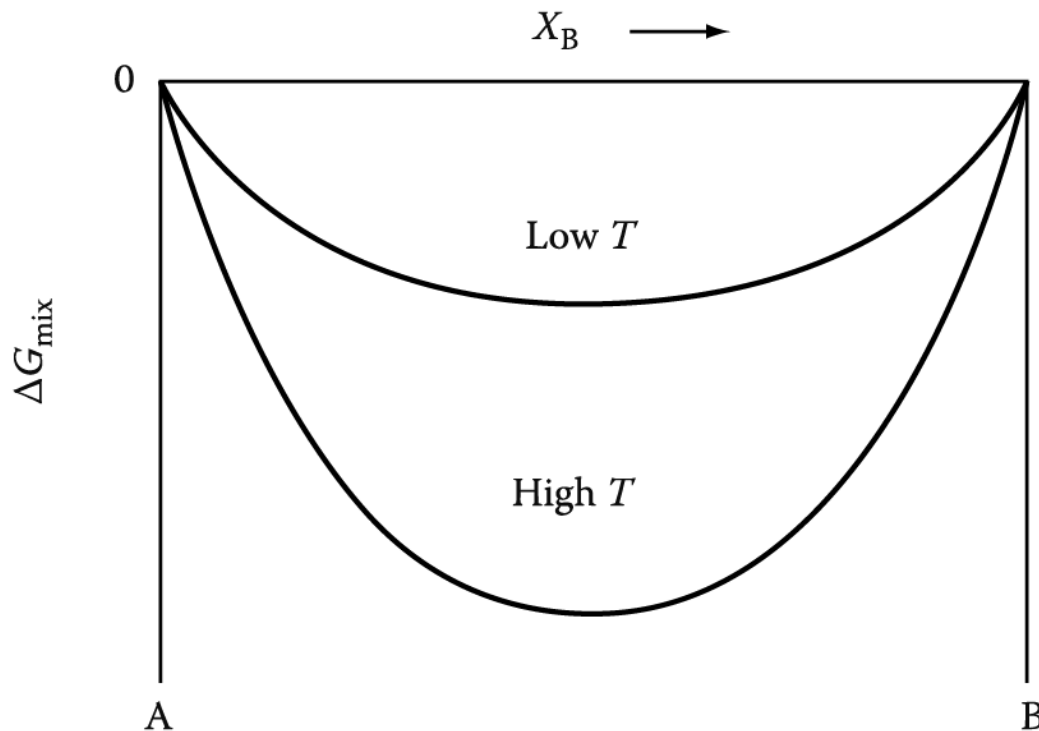

Fig. 1.9 Free energy of mixing for an ideal solution

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Q8: How can you estimate

"Molar Free energy for ideal solid solution"?

$$G_2 = G_1 + \Delta G_{mix}$$ ➡ $$G = X_A G_A + X_B G_B + RT(X_A lnX_A + X_B lnX_B)$$

1.3 Binary Solutions

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.

$$G_1$$

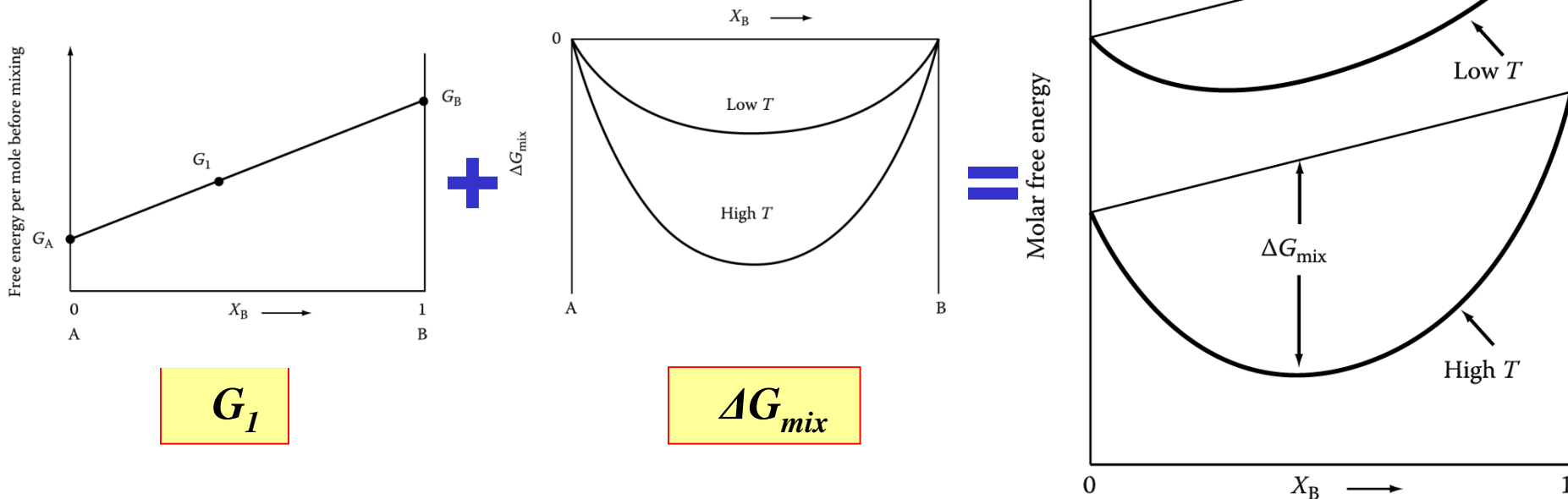$+$

$$\Delta G_{mix}$$

$=$

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"

$G = H\text{-}TS = E+PV\text{-}TS$

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~ small enough
(∵ μ_A depends on the composition of phase)

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

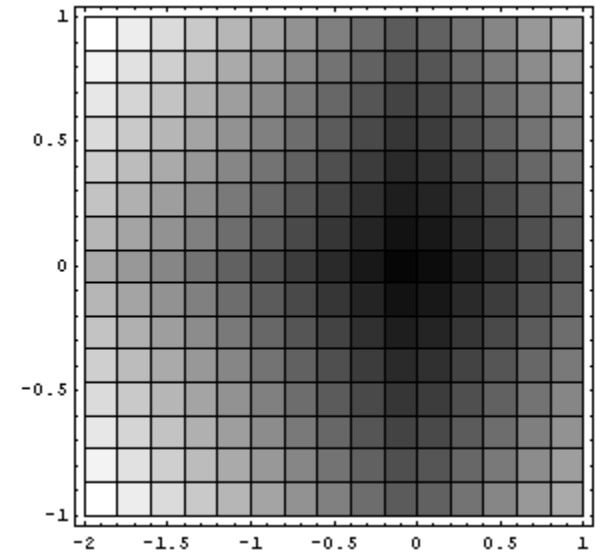μ_A : partial molar free energy of A or chemical potential of A

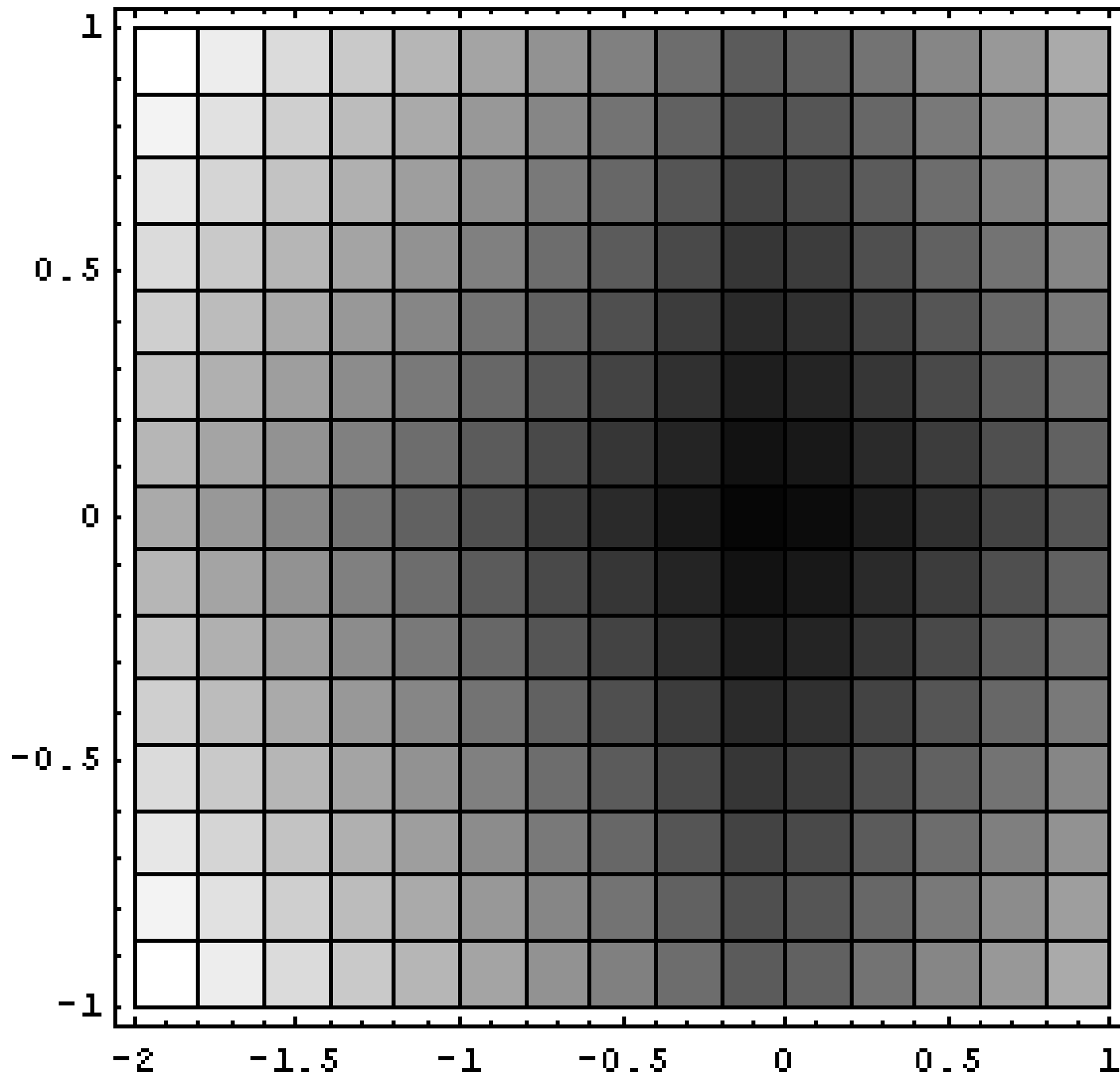$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T, P, n_B} \qquad \mu_B = \left(\frac{\partial G'}{\partial n_B}\right)_{T, P, n_A}$$

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

For variable T and P

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

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$G = H\text{-}TS = E\text{+}PV\text{-}TS$

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

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

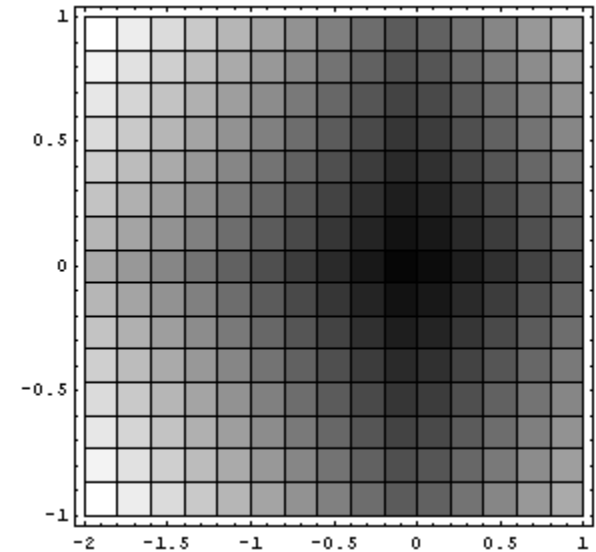μ_A : **partial molar free energy of A or chemical potential of A**

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

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

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

For variable T and P

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

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Q10: "Correlation between chemical potential and free energy"?

Correlation between chemical potential and free energy

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

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

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

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

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

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

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

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

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

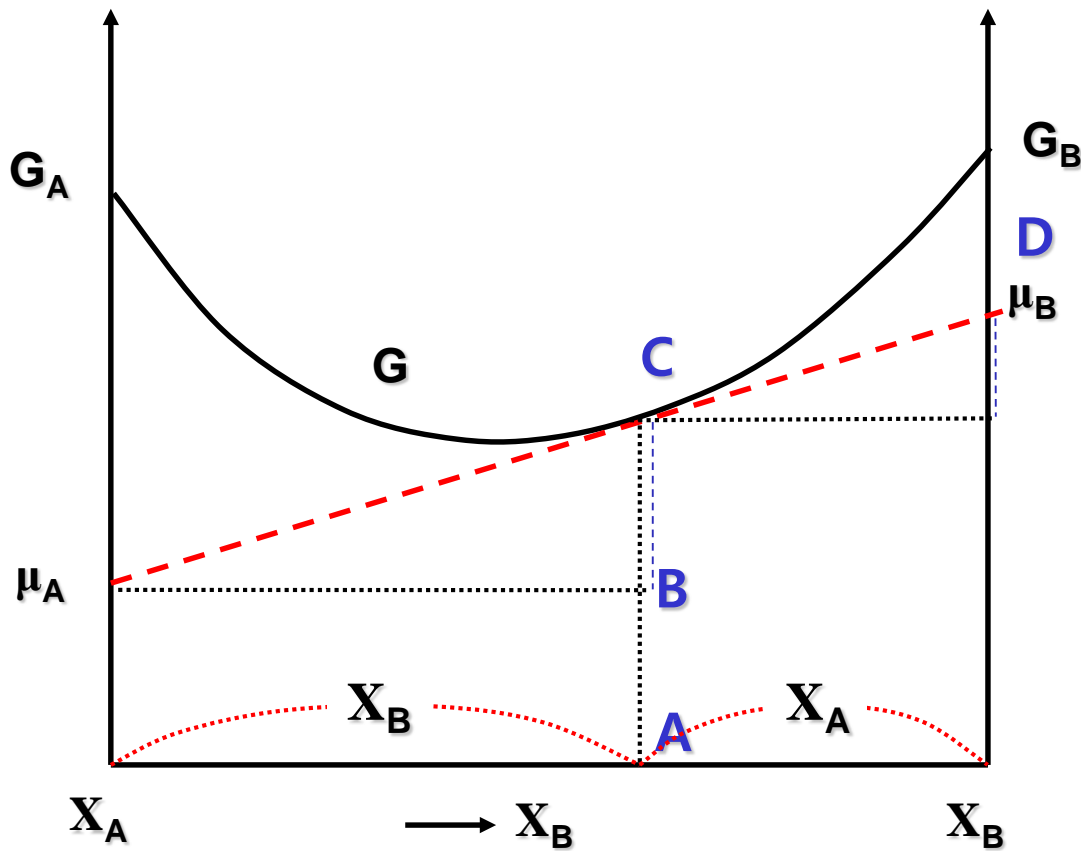$$\mu_B = G + \frac{dG}{dX_B} X_A$$

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Correlation between chemical potential and free energy

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

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

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

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

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

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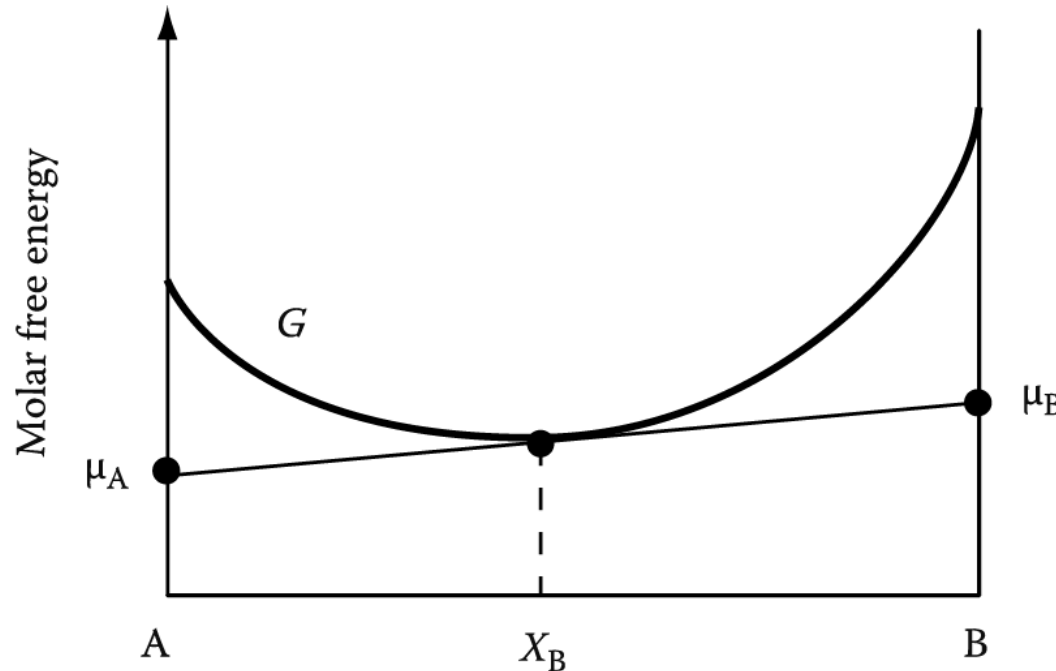
$$= \mu_B - (X_A + X_B)\frac{dG}{dX_B}$$

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

Correlation between chemical potential and free energy

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

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

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

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

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

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

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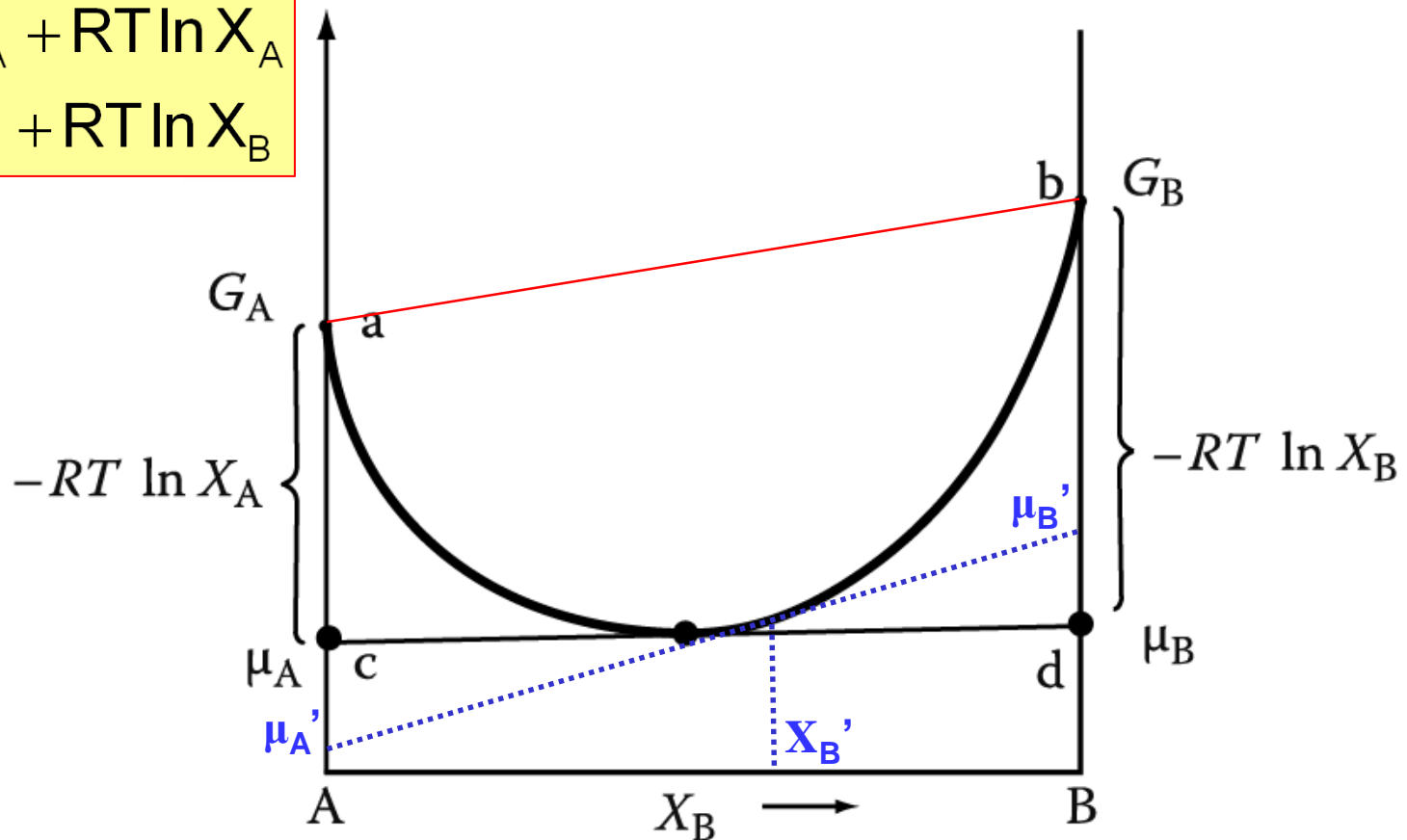
$$\mu_A = G_A + RT \ln X_A$$
$$\mu_B = G_B + RT \ln X_B$$

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

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

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

- **Chemical potential** and **Activity**

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

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

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

dn_A~ small enough ($\because$ μ_A depends on the composition of phase)