2015 Fall

"Phase Transformation *in* Materials"

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Contents for previous class

Chapter 1 Thermondynamics and Phase Diagrams

- **Equilibrium** $\boxed{dG = 0}$

Lowest possible value of G

No desire to change ad infinitum

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

- **Single component system**

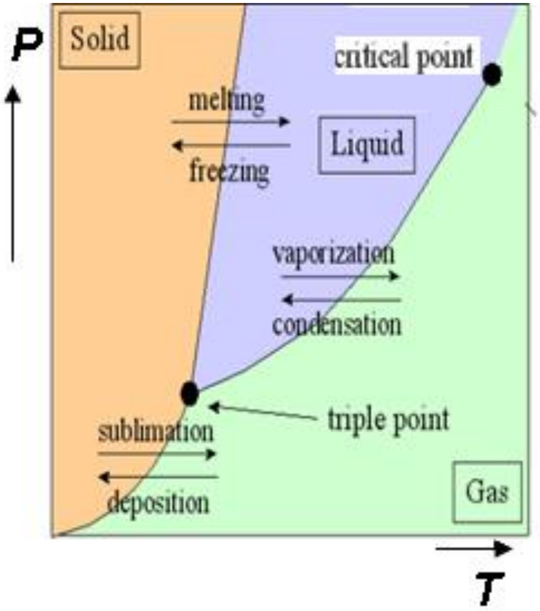
Gibbs Free Energy as a Function of Temp. and Pressure

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S\,, \quad \left(\frac{\partial G}{\partial P}\right)_T = V} \qquad \boxed{\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}}$$

Clausius-Clapeyron Relation

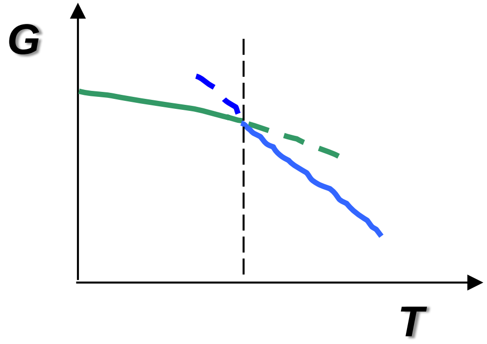
- **Classification of phase transition**

First order transition: CDD/Second order transition: CCD



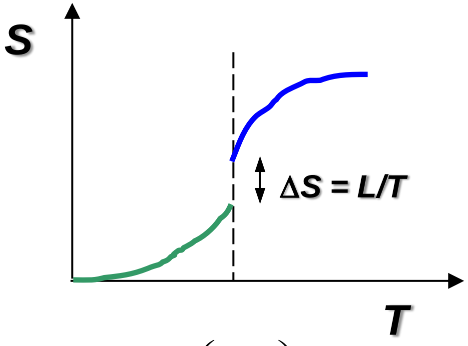
The First-Order Transitions

Latent heat
Energy barrier
Discontinuous entropy, heat capacity



- 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

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

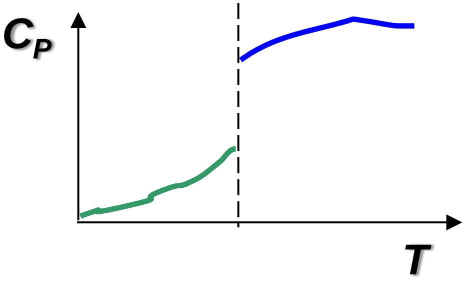


$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

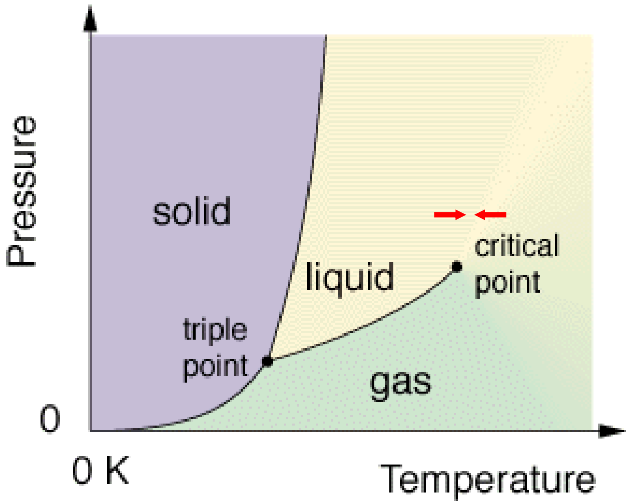
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

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



The Second Order Transition



No Latent heat
Continuous entropy

- 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

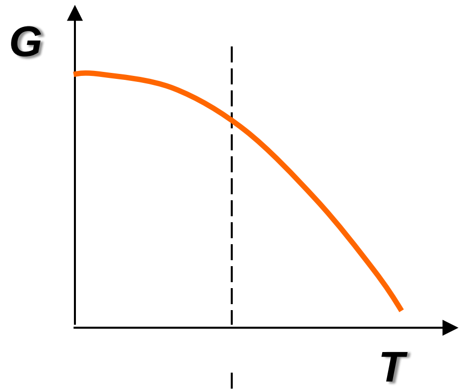
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

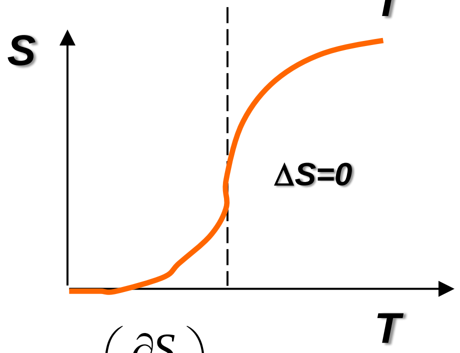
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

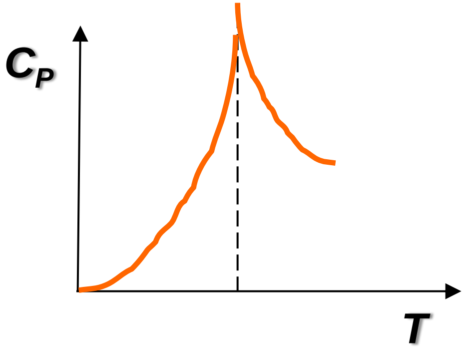
  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Second-order transition



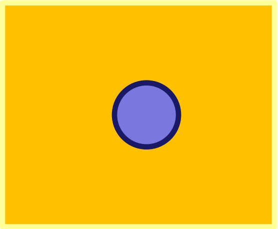


$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \rightarrow \infty$$



Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



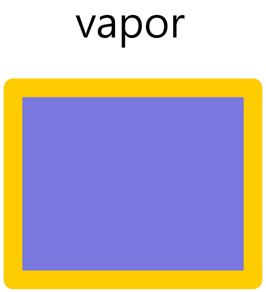
<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

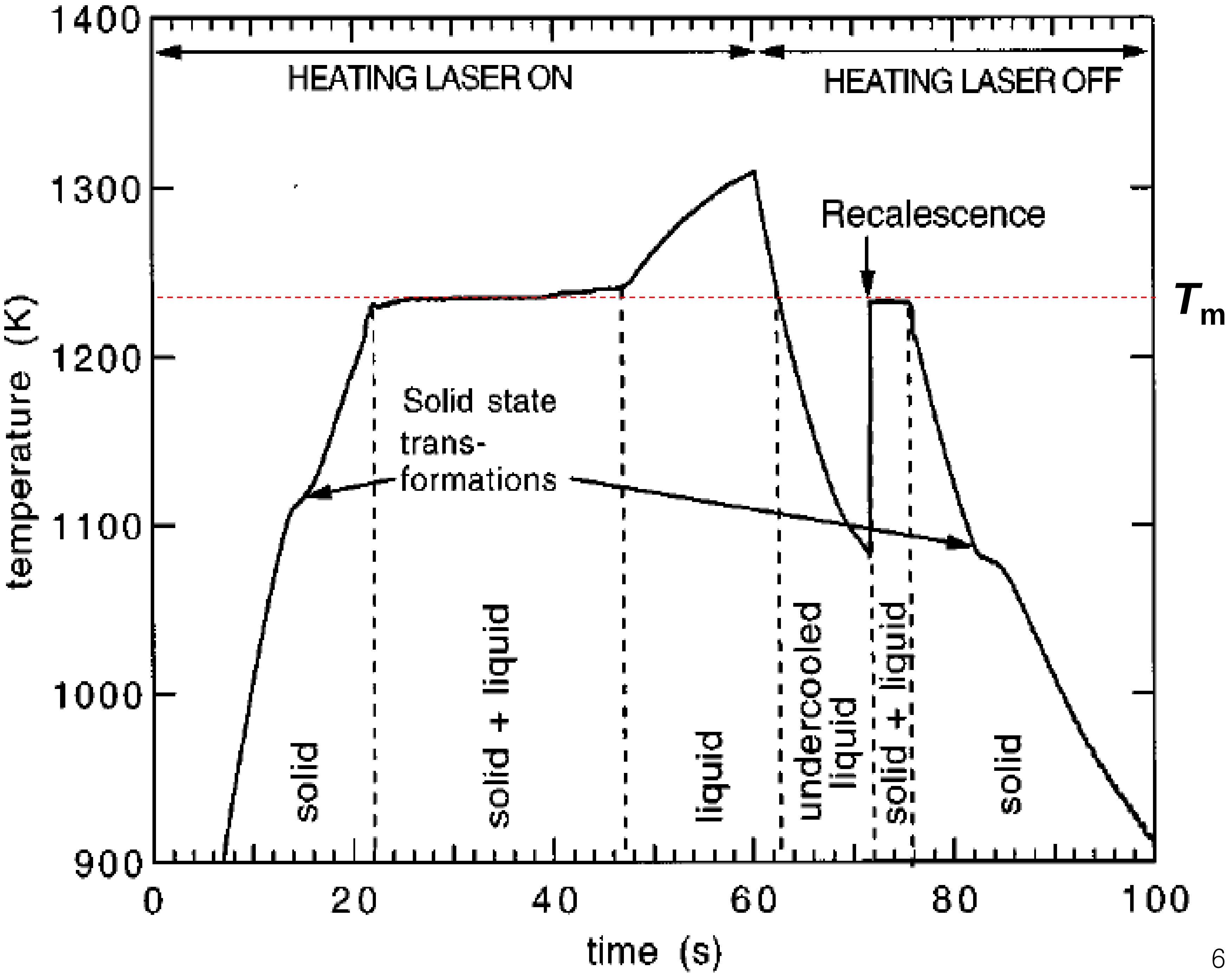
No superheating required!

- Interfacial energy ⇨ No ΔT_N

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



Melting: Liquid ← Solid


HEATING LASER ON
HEATING LASER OFF
Recalescence
T_m
Solid state trans- formations
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid
temperature (K)
1400
1300
1200
1100
1000
900
time (s)
0
20
40
60
80
100

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: Binary system

Q1: “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 $\boxed{\text{composition}}$.

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

$$\begin{array}{ccc} A - A, & & B - B \\ | & & | \\ A & & B \end{array}$$

Alluvial mining

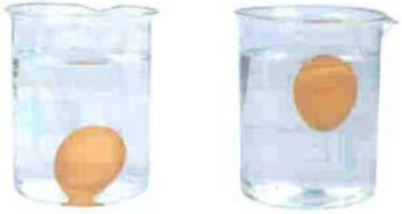
사금 채취

키질

Winnowing

wash rice

쌀 씻기



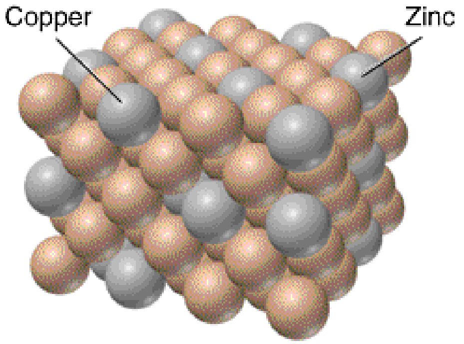
달걀 고르기

Select egg

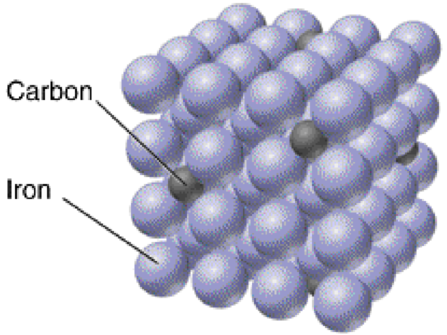
- **Solution** ; A – A – A ; → atomic scale mixture/ **Random distribution**

  | |

  A – B – A   Solid solution : substitutional or interstitial



A Brass, a substitutional alloy



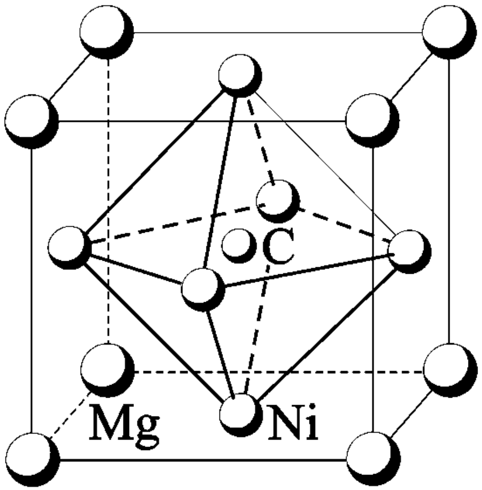
B Carbon steel, an interstitial alloy

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

  | | | |

  B – A – B – A

MgCNi3



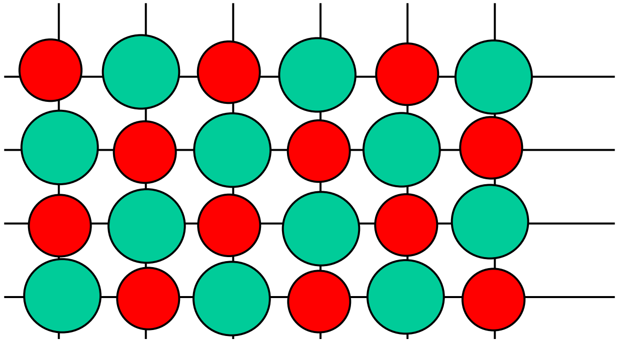
Q2: What is “Alloying”?

Ordered Compounds or Solid Solutions

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

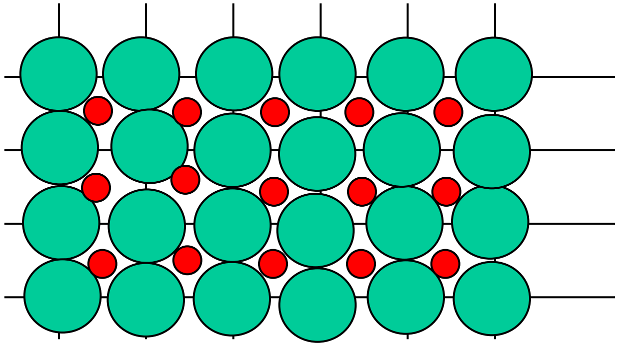
Ordered Substitutional and Interstititials Compounds

Substitutional
element replaces host atoms
in an orderly arrangement



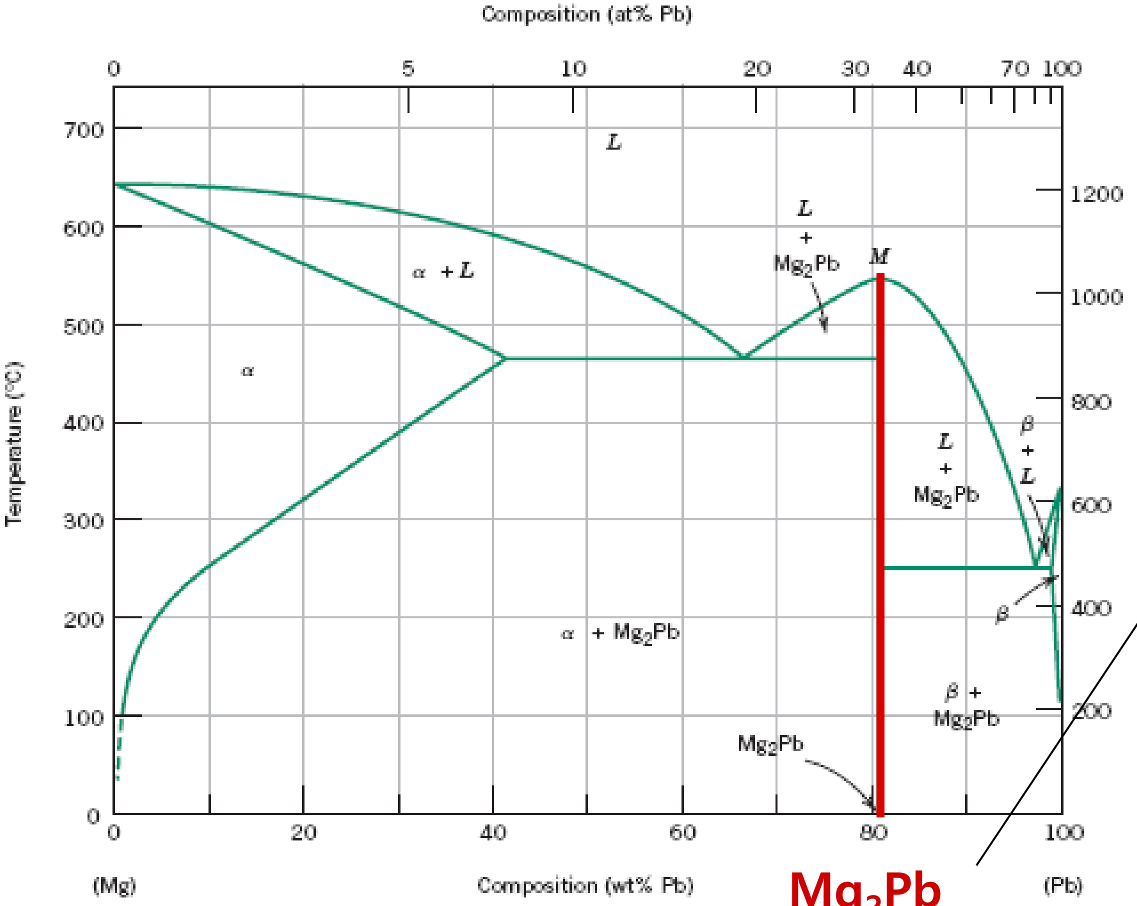
e.g., Ni_3Al (hi-T yield strength),
$Al_3(Li,Zr)$ (strengthening)

Interstitial
element goes into holes
in an orderly arrangement

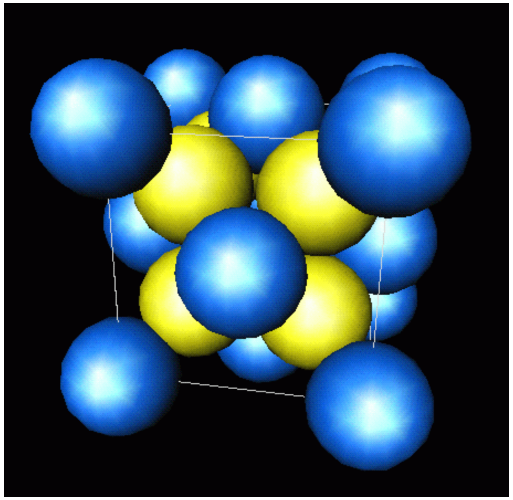


e.g., small impurities, clays
ionic crystals, ceramics.

Intermetallic Compounds



Mg_2Pb



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**

A – B – A

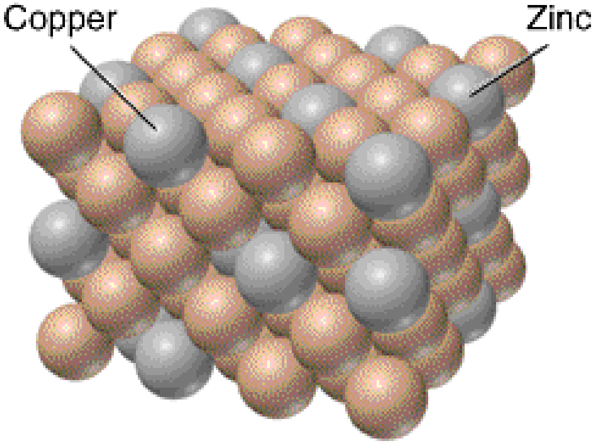
Two Possibilities for Solid Solutions: B atoms in A atoms

Substitutional

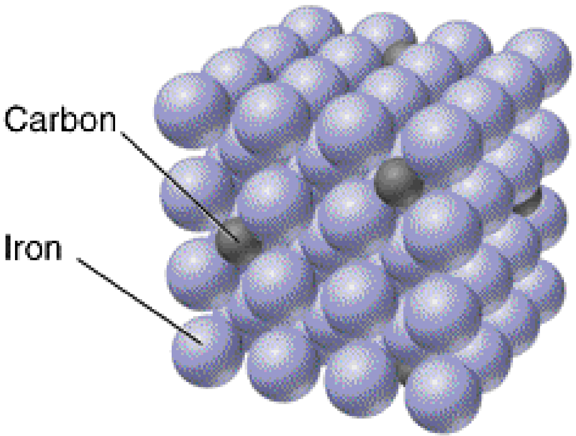
'new element replaces host atoms'

Interstitials

'new element goes in holes'



A Brass, a substitutional alloy



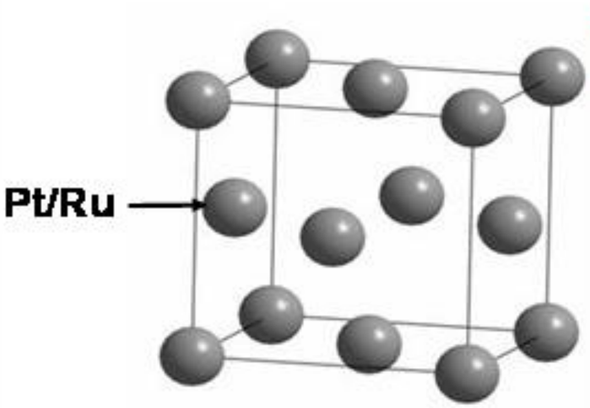
B Carbon steel, an interstitial alloy

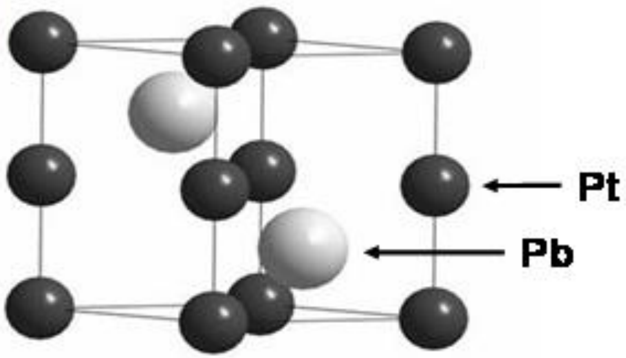
Q3: “Solution vs. Intermetallic compound”?

Alloying: atoms mixed on a lattice → partial or complete solid solution

Solid Solution vs. Intermetallic Compounds

Crystal structure

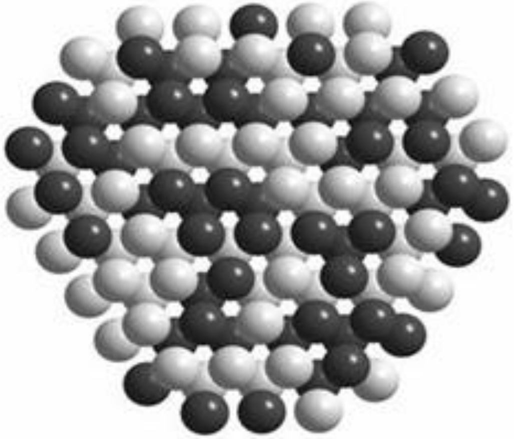


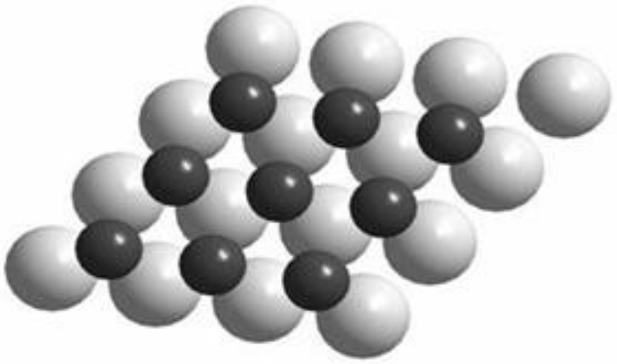


$Pt_{0.5}Ru_{0.5}$ – Pt structure (fcc)

PtPb – NiAS structure

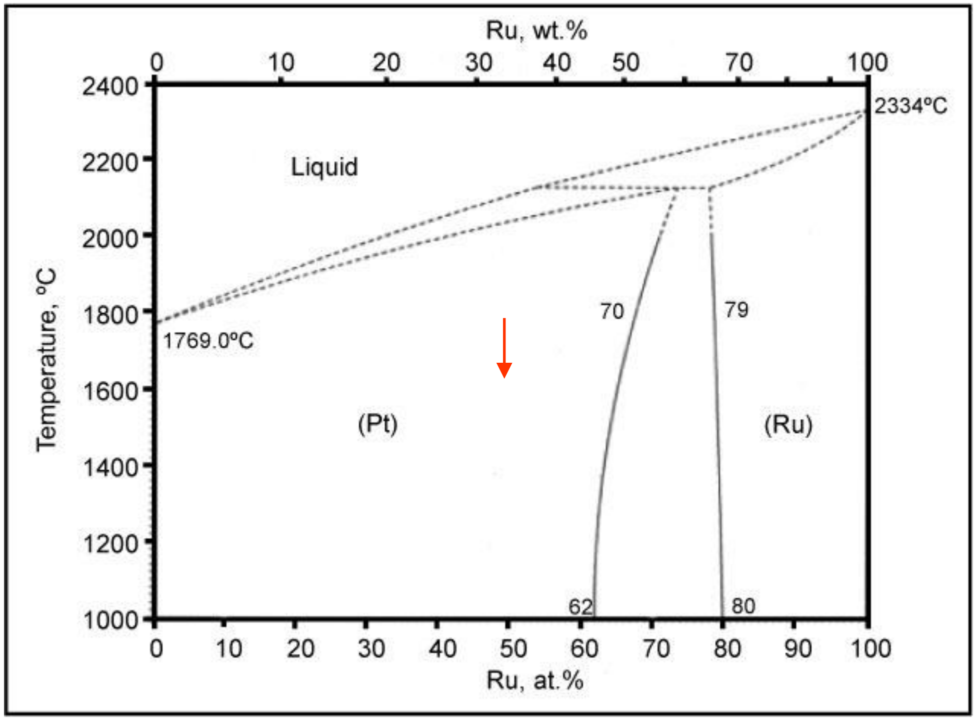
Surface

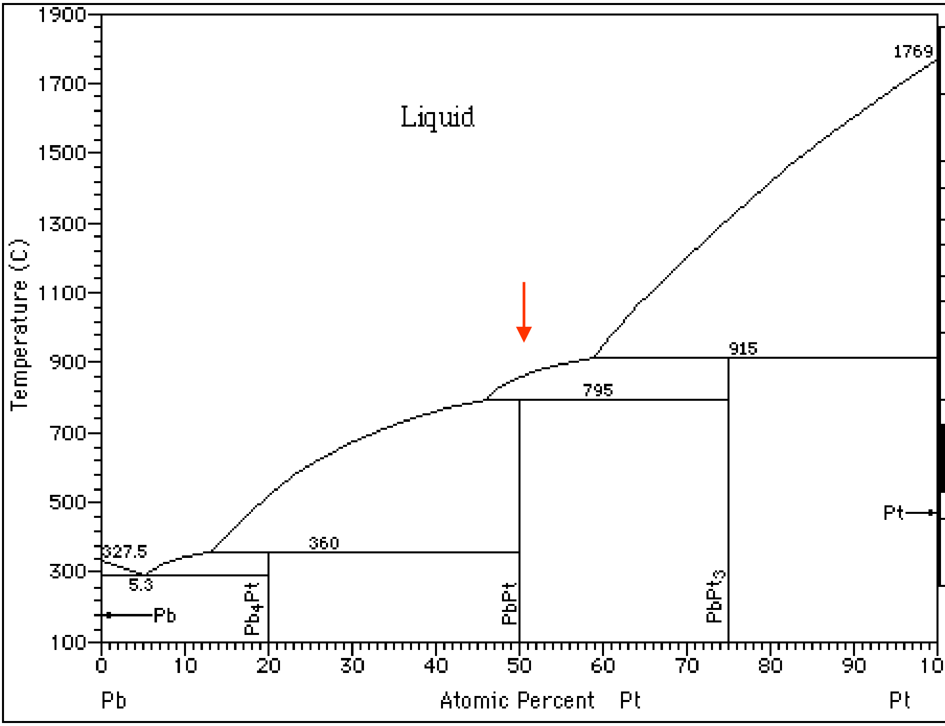




ruthenium 루테늄《백금류의 금속 원소;기호 Ru, 번호 44》

Solid Solution vs. Intermetallic Compounds





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

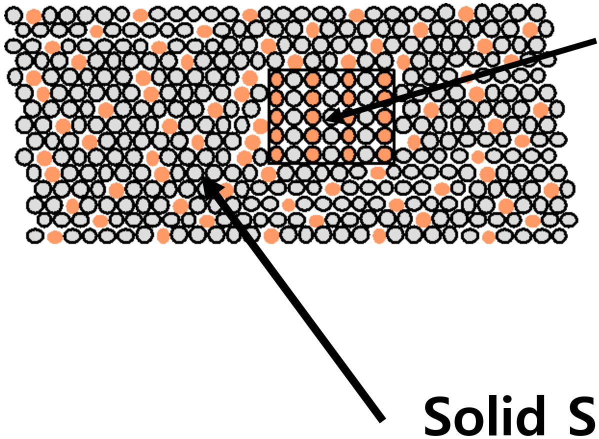
PbPt – NiAS structure

Assumption: a simple physical model for "binary solid solutions"

: in order to introduce some of the basic concepts of the thermodynamics of alloys

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)

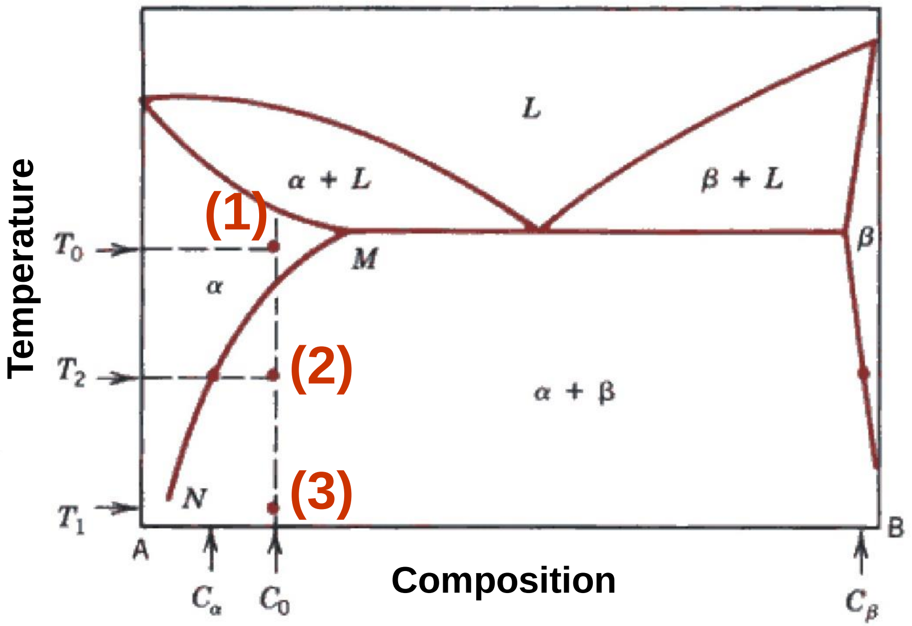


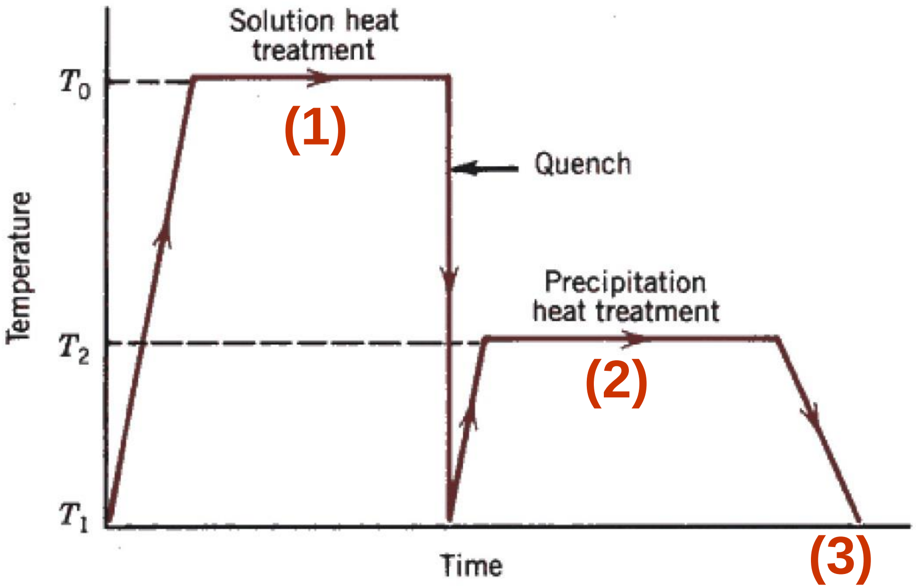
Second phase particle
--different composition
--often different structure.

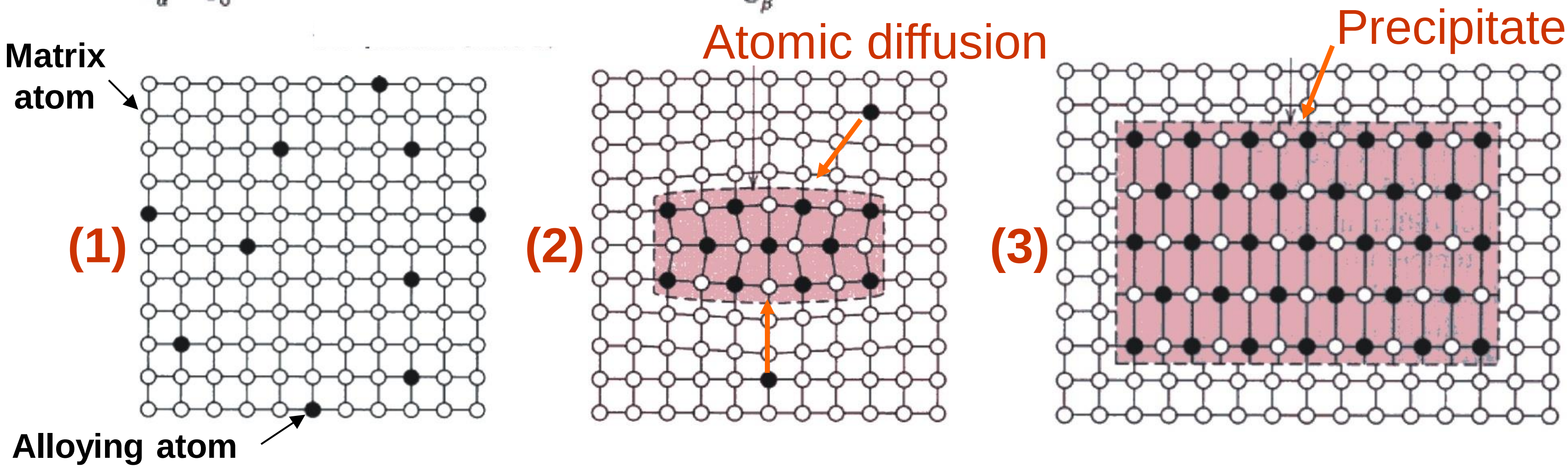
Solid Solution phase: B atoms in A

5) Microstructure control : ② Secondary phase control

c. Mechanism of Precipitation



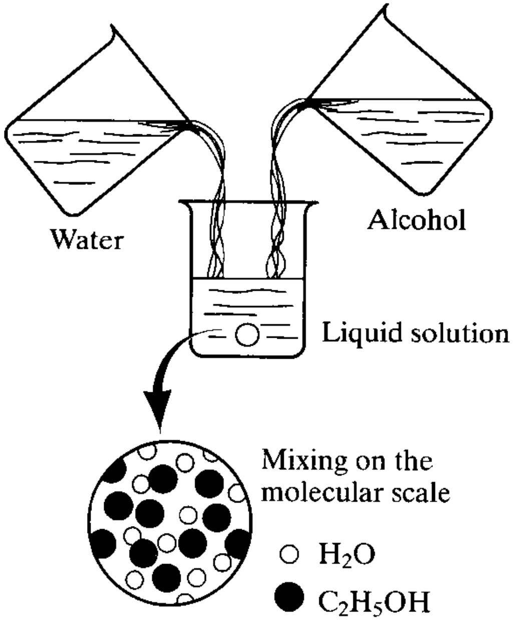


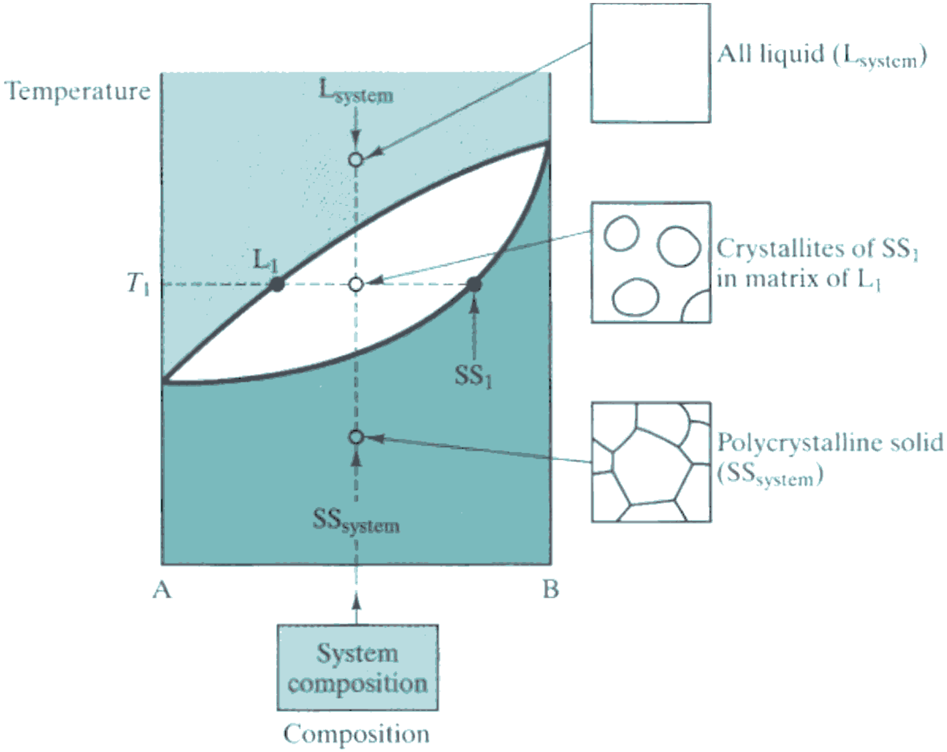


Q4: “Solubility”?

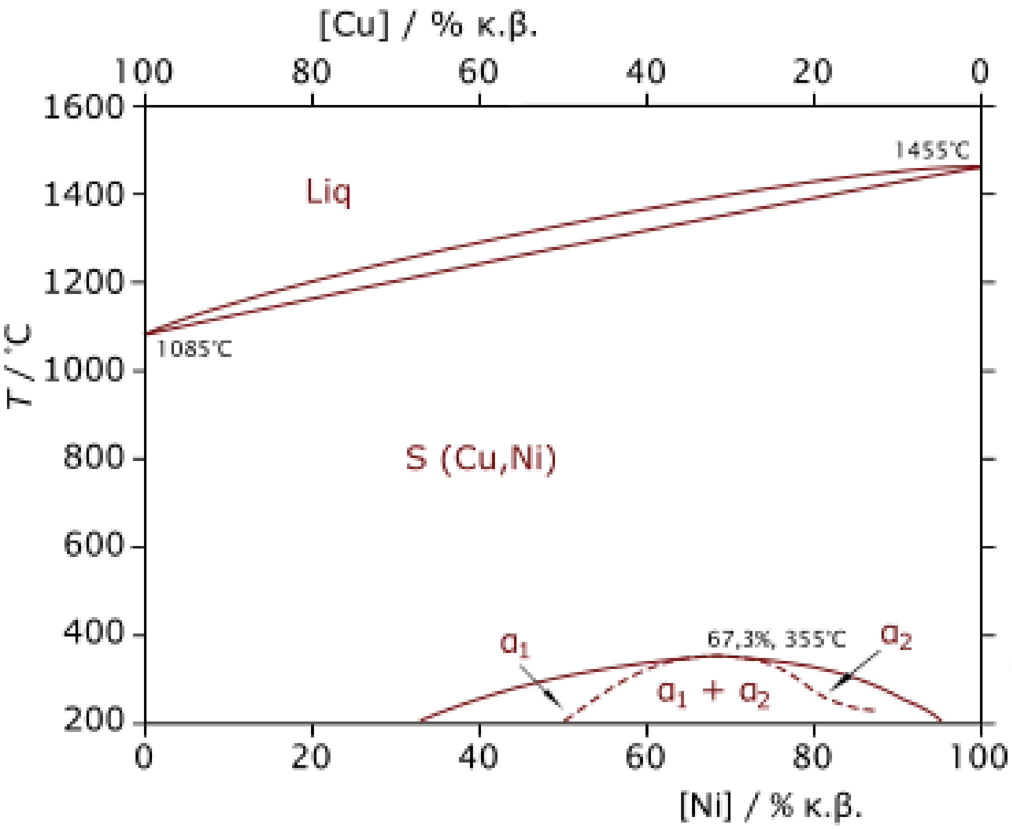
Solubility

- 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



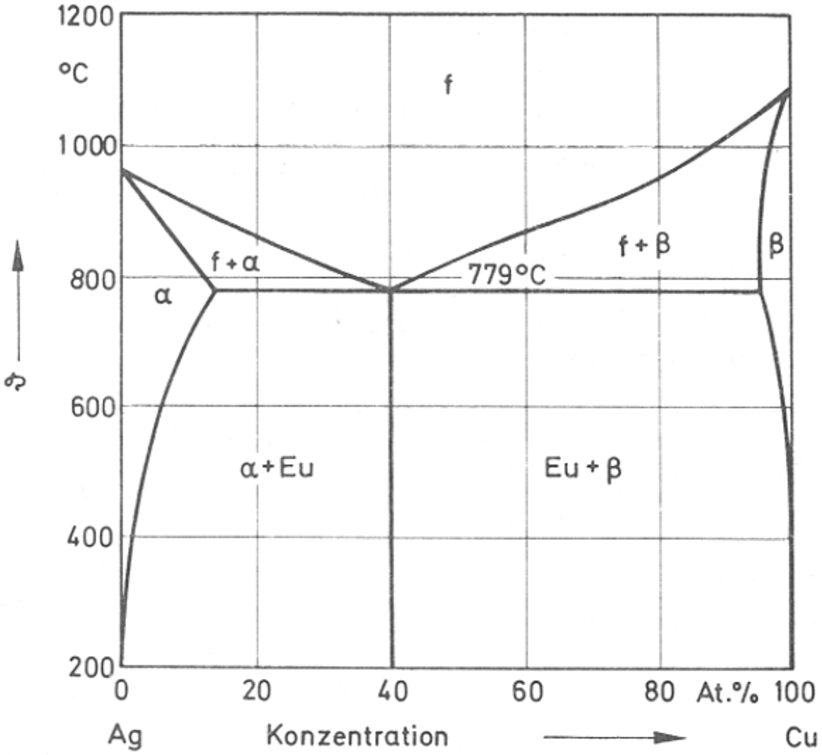


Cu-Ni Alloys



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.

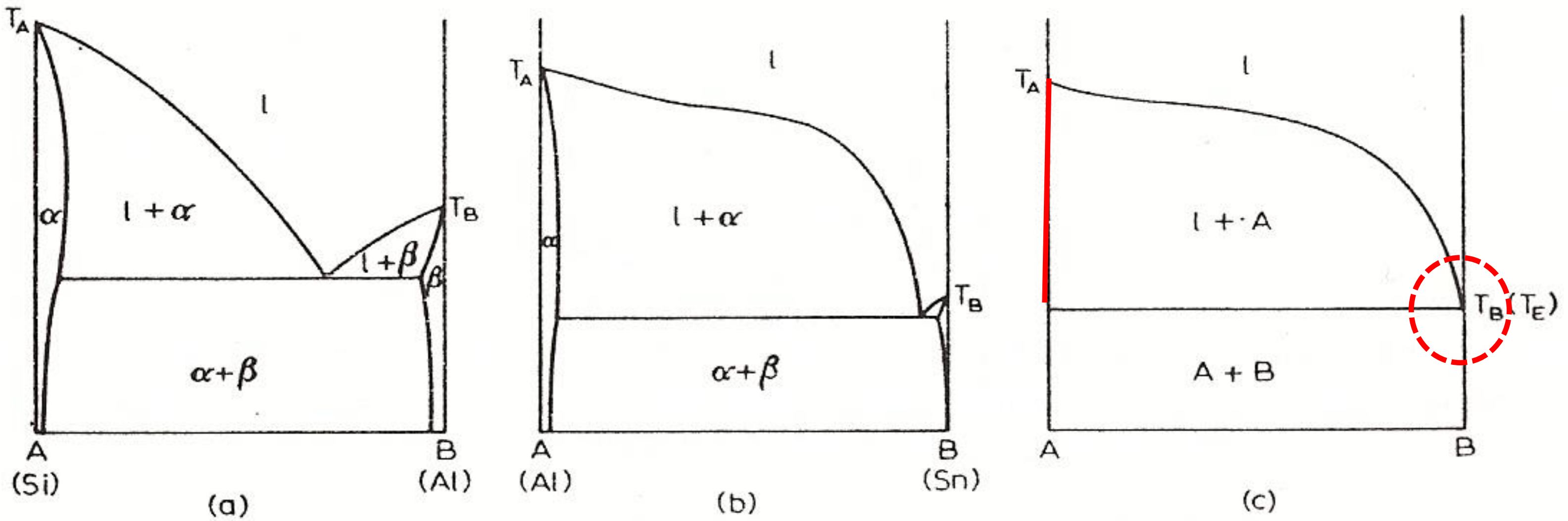


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

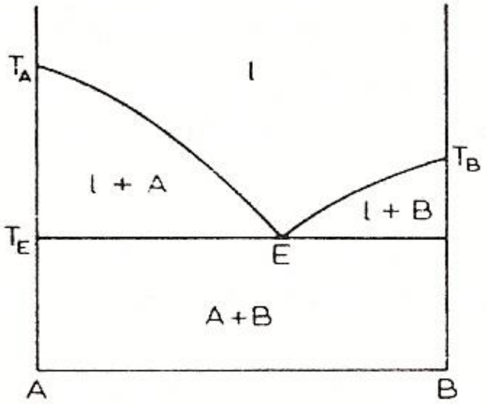
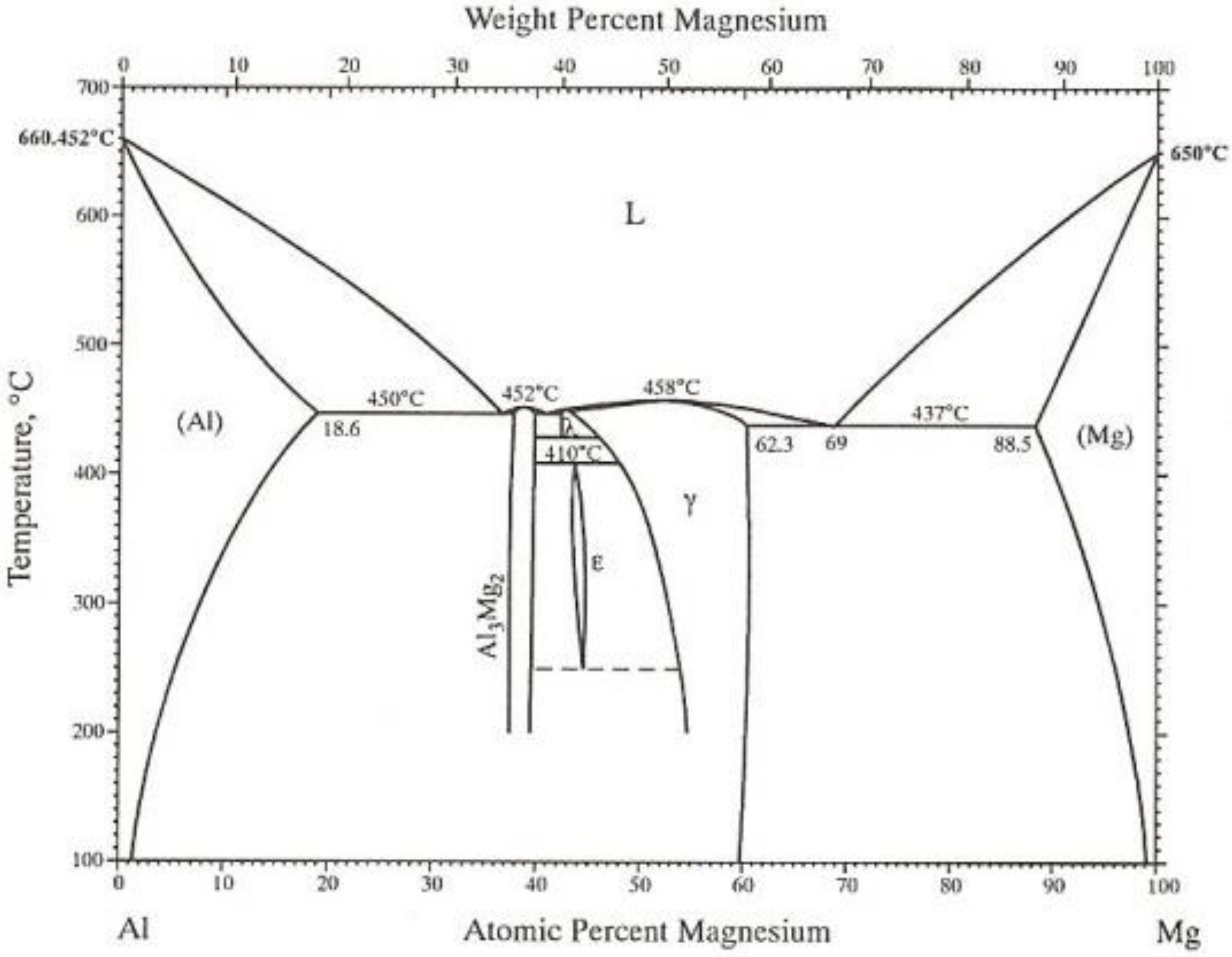
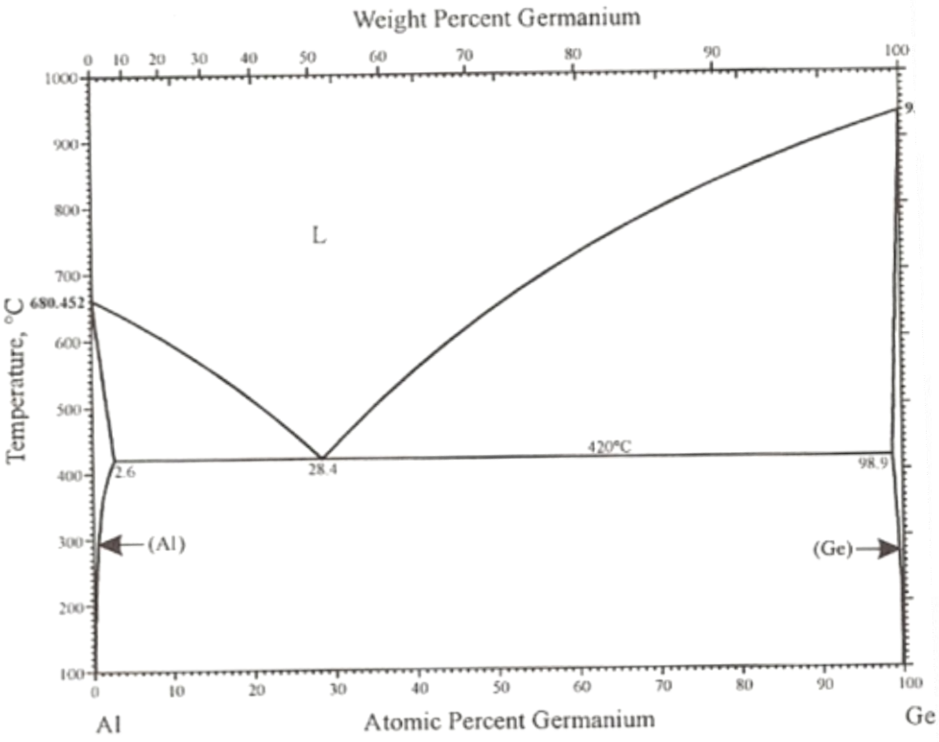
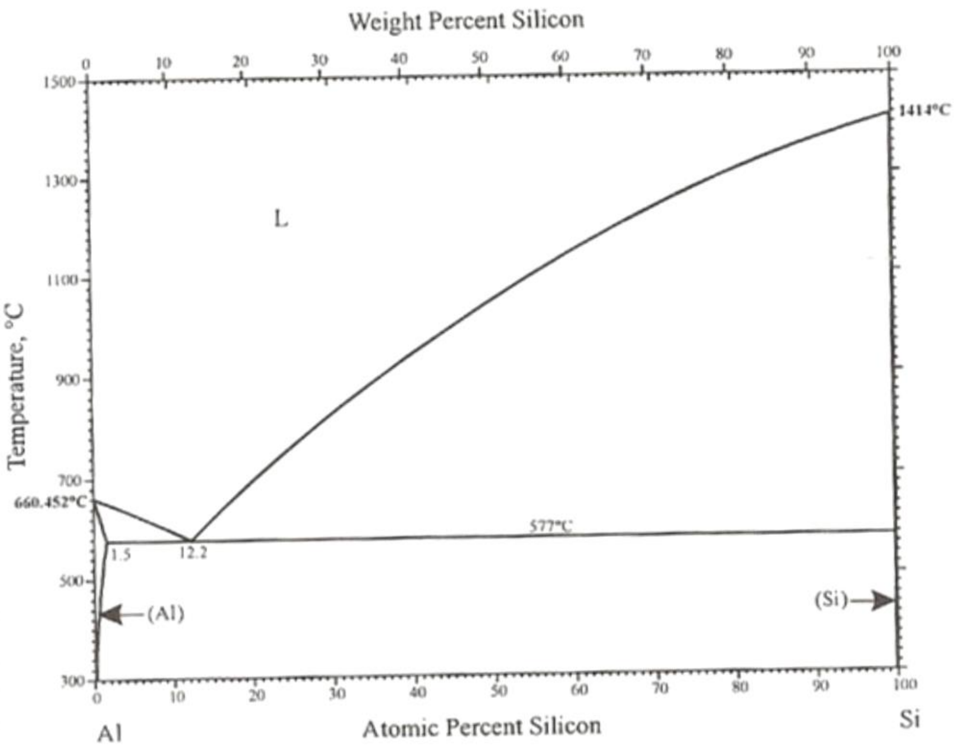
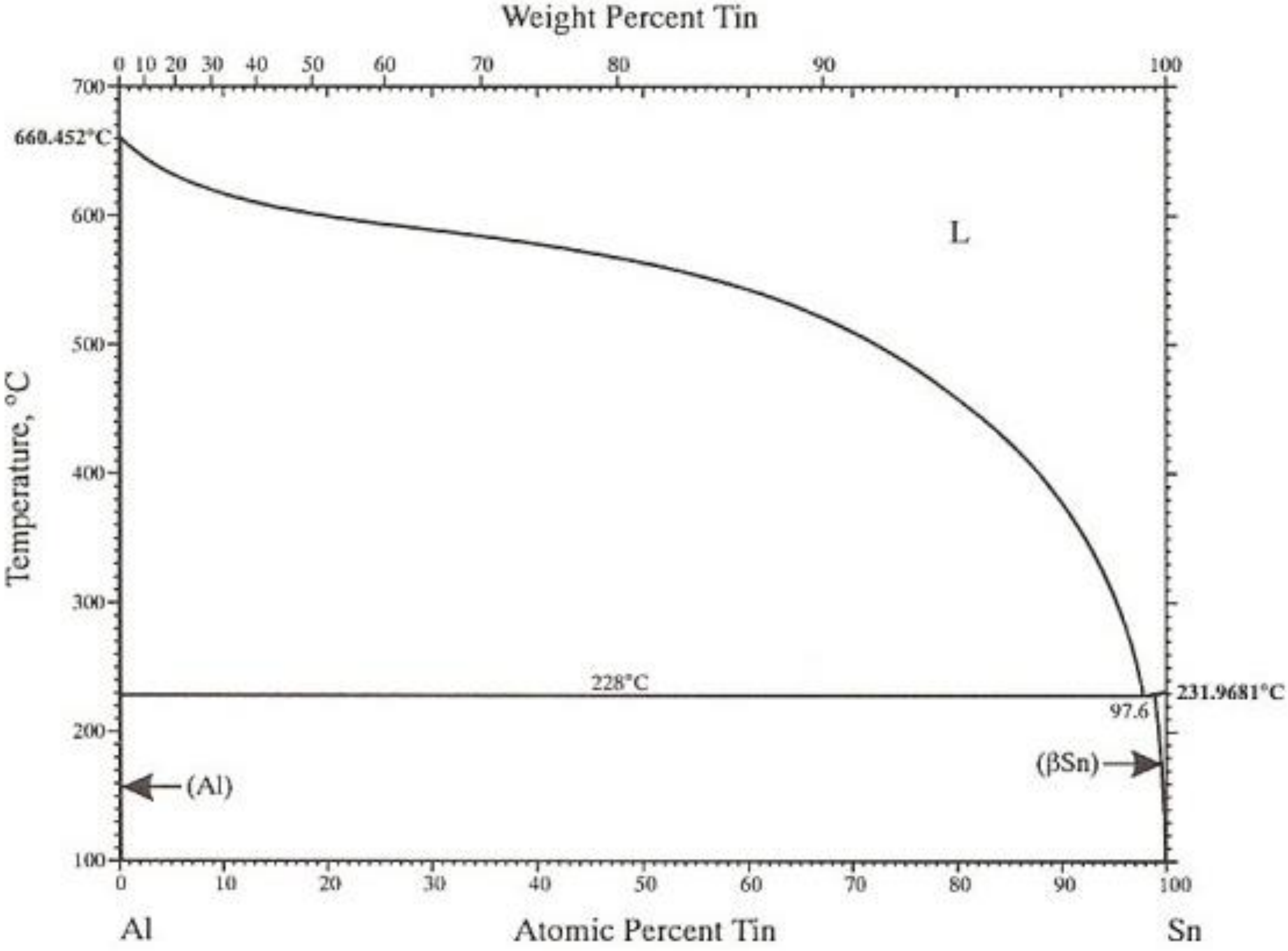


Fig. 54. Impossible form of a binary eutectic phase diagram.


Weight Percent Magnesium
0
10
20
30
40
50
60
70
80
90
100
700
660.452°C
650°C
600
L
500
Temperature, °C
(Al)
450°C
18.6
452°C
458°C
λ
410°C
62.3
69
437°C
88.5
(Mg)
400
γ
ε
300
Al_3Mg_2
200
100
0
10
20
30
40
50
60
70
80
90
100
Al
Atomic Percent Magnesium
Mg


Weight Percent Germanium
0
10
20
30
40
50
60
70
80
90
100
1000
900
800
700
660.452
600
500
400
300
200
100
Temperature, °C
L
9
420°C
2.6
28.4
98.9
(Al)
(Ge)
0
10
20
30
40
50
60
70
80
90
100
Al
Atomic Percent Germanium
Ge


Weight Percent Silicon
0
10
20
30
40
50
60
70
80
90
100
1500
1300
1100
900
700
500
300
1414°C
Temperature, °C
L
660.452°C
577°C
1.5
12.2
(Al)
(Si)
0
10
20
30
40
50
60
70
80
90
100
Al
Atomic Percent Silicon
Si

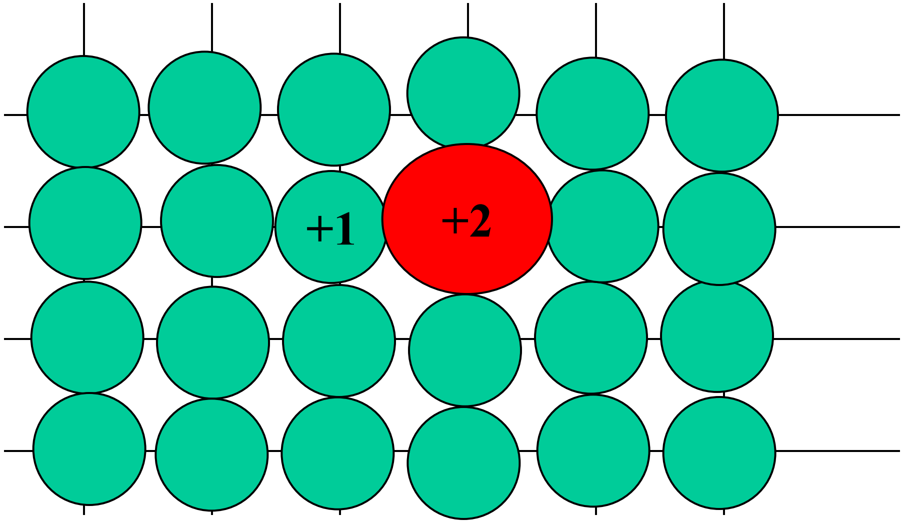

Weight Percent Tin
0
10
20
30
40
50
60
70
80
90
100
700
660.452°C
600
L
500
400
300
228°C
231.9681°C
97.6
200
(βSn)
(Al)
100
Temperature, °C
0
10
20
30
40
50
60
70
80
90
100
Al
Atomic Percent Tin
Sn

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 ±15%, the lattice distortions (i.e. local lattice strain) are too big and solid-solution will not be favored.

$$\mathrm{DR\%} = \frac{r_{\mathrm{solute}} - r_{\mathrm{solvent}}}{r_{\mathrm{solvent}}} \times 100\% < \pm 15\%$$ **will not disallow 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%= $$\frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$$ **= 2.3%** **favorable √**

Rule 2: Ni 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 Ni and Cu are both +2. **favorable √**

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_{Cu} = 0.128 nm and r_{Ag}= 0.144 nm.

DR%= $$\frac{r_{solute} - r_{solvent}}{r_{solvent}} x100\%$$ **= 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 √

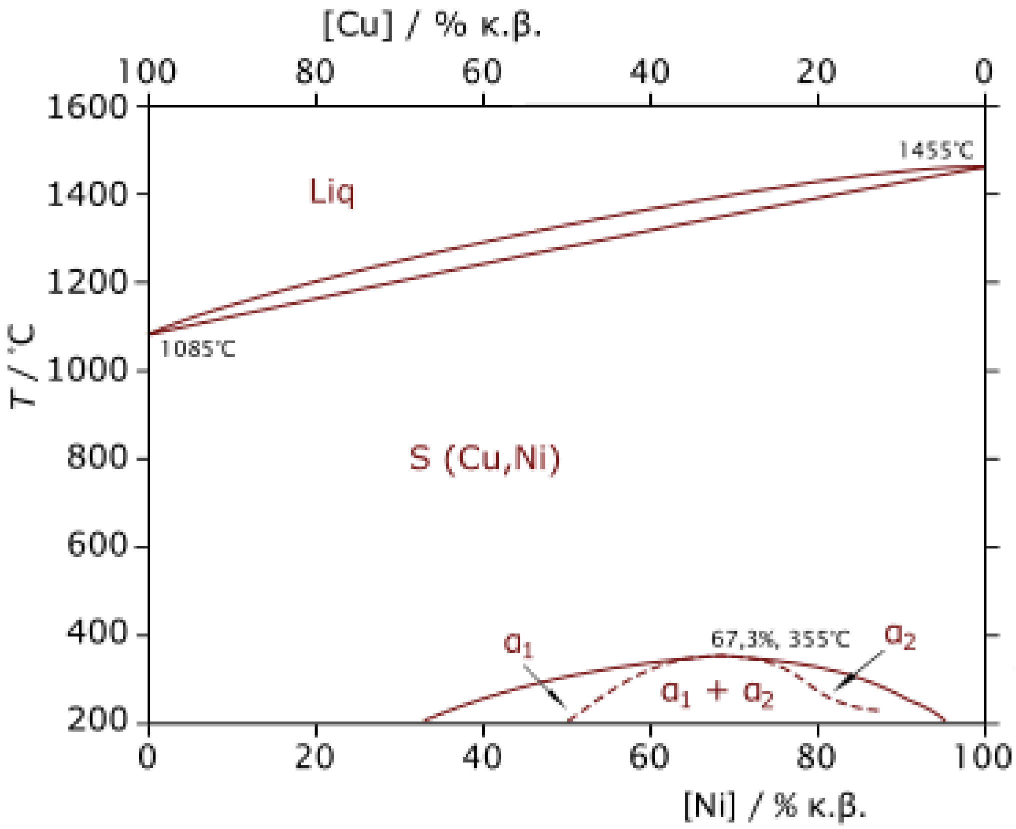
Rule 4: Valency of Cu is +2 and Ag is +1. **NOT favorable**

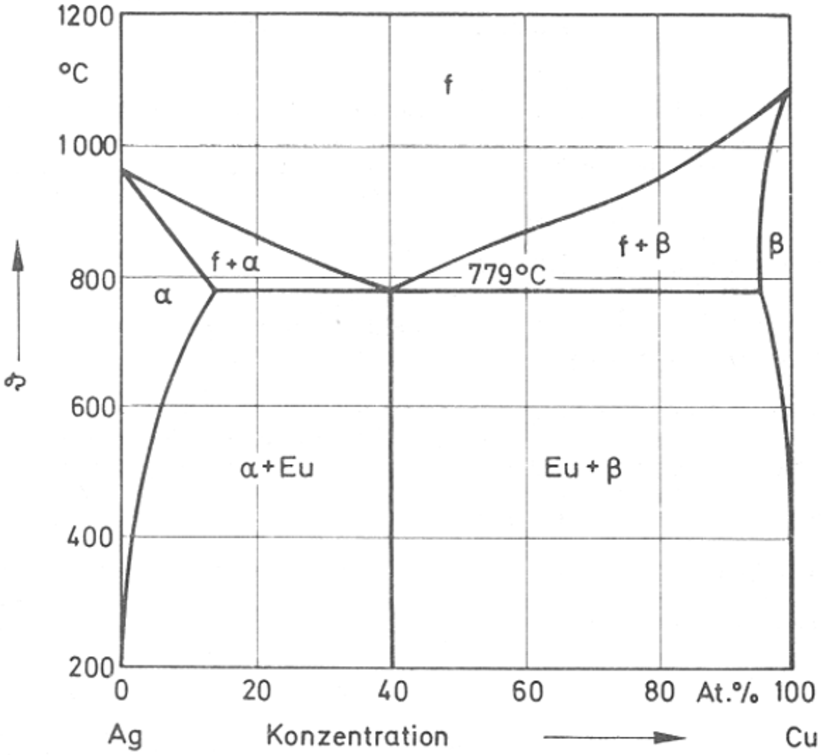
Expect Ag and Cu have <u>limited solubility</u>.

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

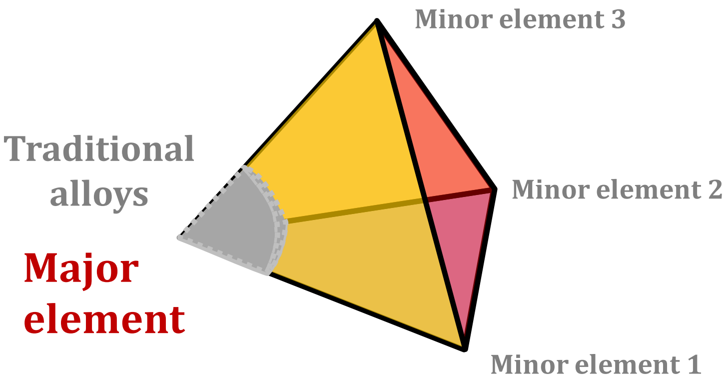




complete solid solution

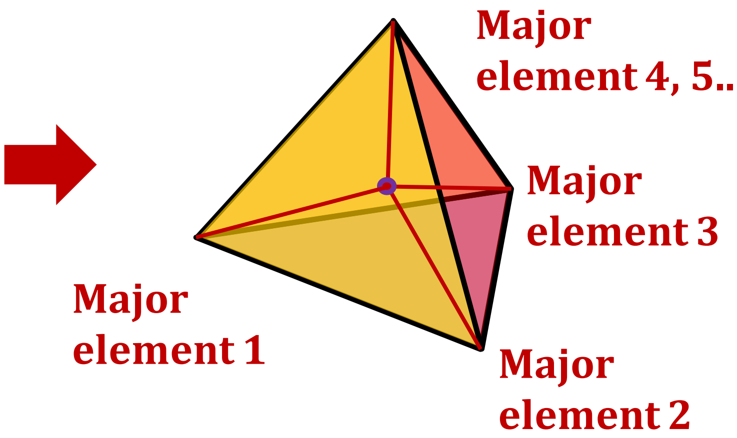
limited solid solution

High entropy alloy (HEA)



Conventional alloy system

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



High entropy alloy system

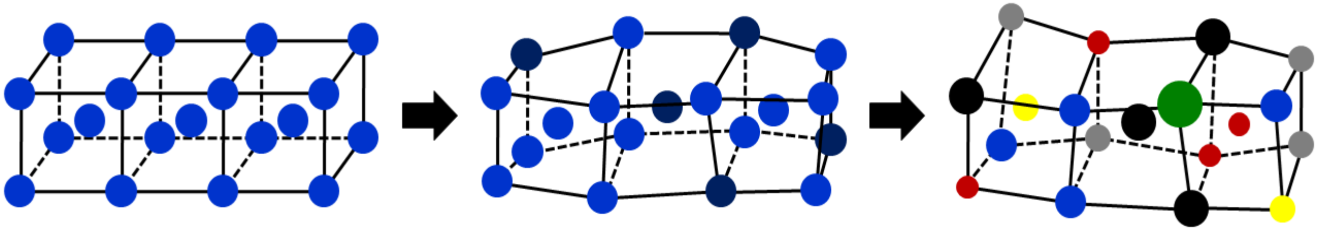
Ex) $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$

(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

Q6: “Gibbs Free Energy of Binary Solutions”?

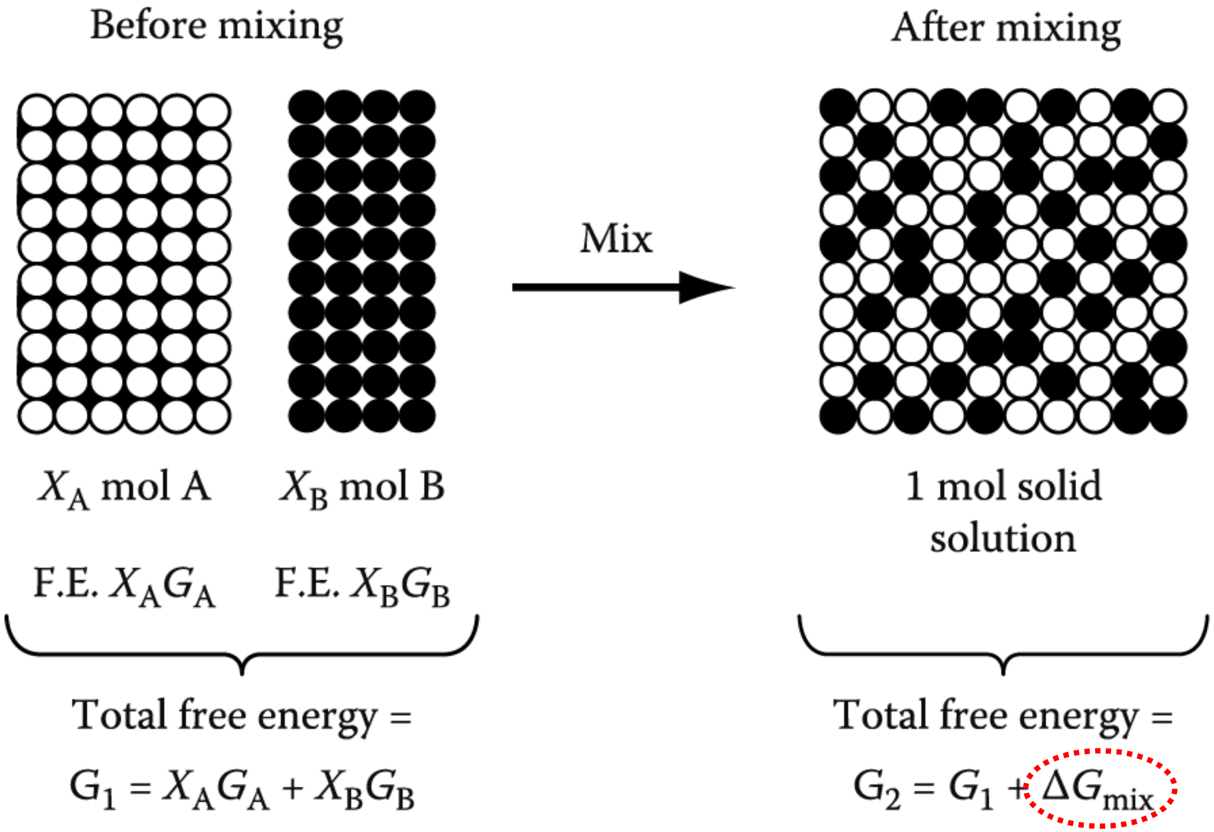
$$\boxed{G_2 = G_1 + \Delta G_{mix} \quad J/mol}$$

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.



Gibbs Free Energy of The System

In Step 1

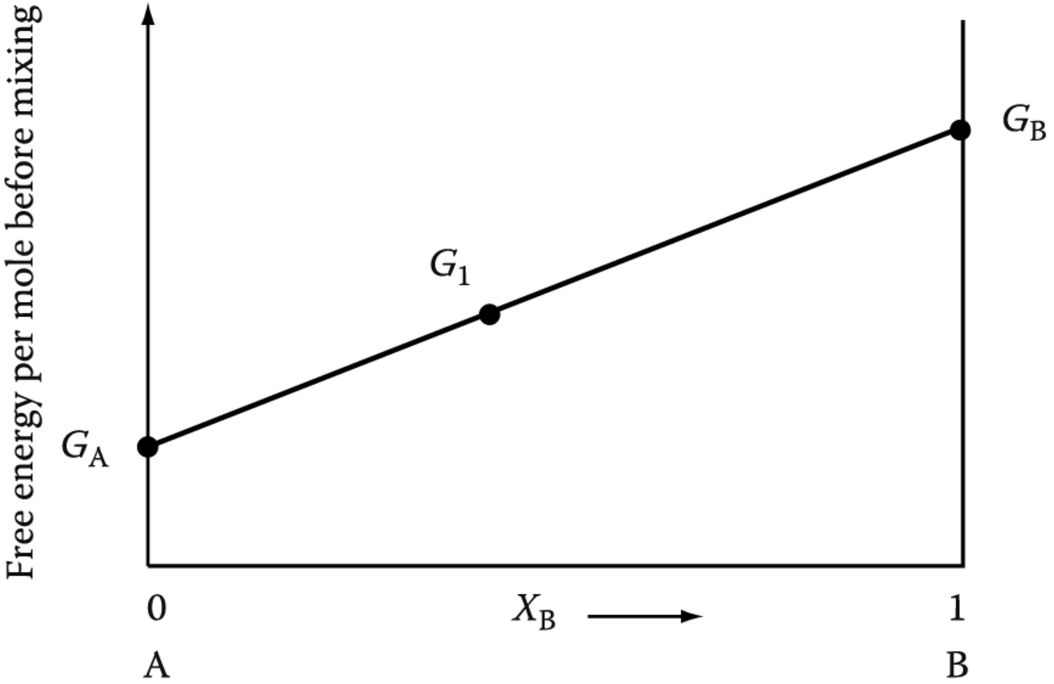
- The molar free energies of pure A and pure B

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**

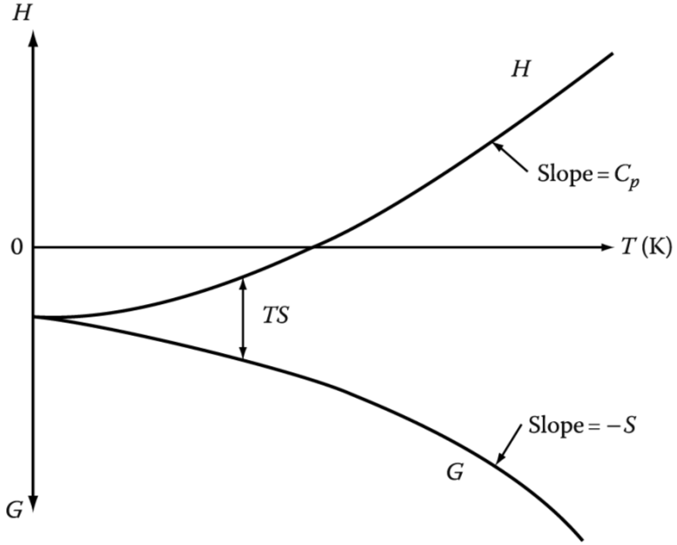
Gibbs Free Energy of The System

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

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



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} ?**

Q7: “ΔG_{mix} of ideal solid solution”?

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

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

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

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

Entropy can be computed from randomness

by Boltzmann equation, 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,

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

$$w_{config} = \frac{(N_A + N_B)!}{N_A!N_B!} \rightarrow after\_solution\_(N_A, N_B)$$ ⬅ **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 $R = kN_0$

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

Excess mixing Entropy

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

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

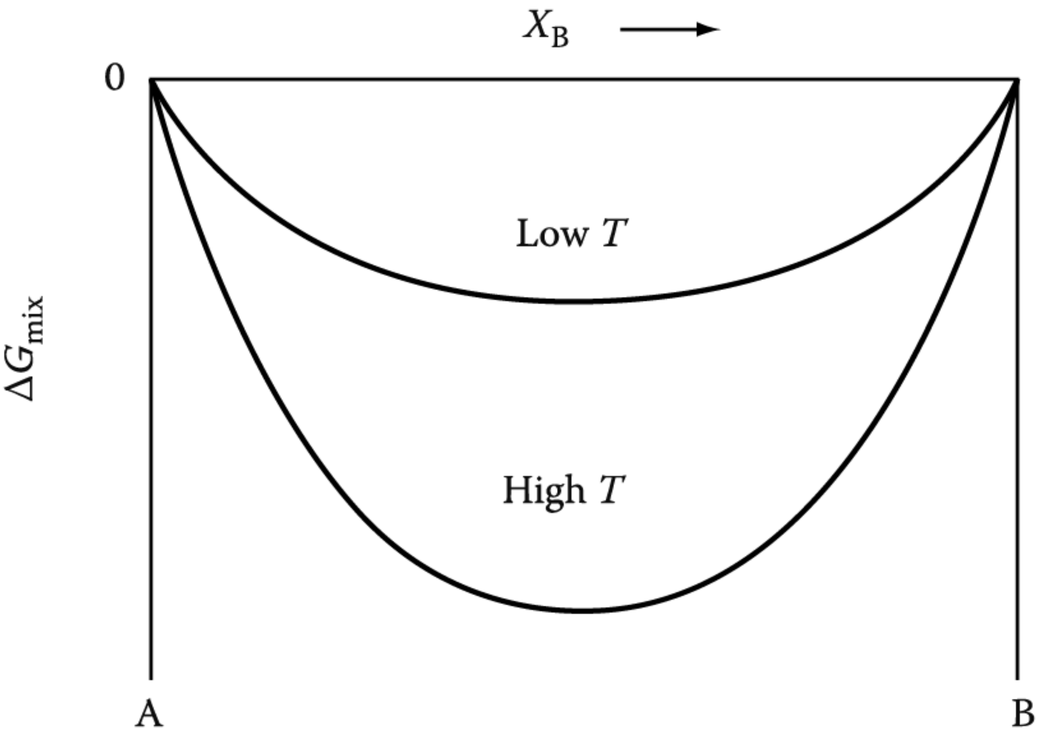


Fig. 1.9 Free energy of mixing for an ideal solution

Q8: “Molar Free energy for ideal solid solution”?

$$\boxed{G_2 = G_1 + \Delta G_{mix}} \Rightarrow \boxed{G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)}$$

1.3 Binary Solutions

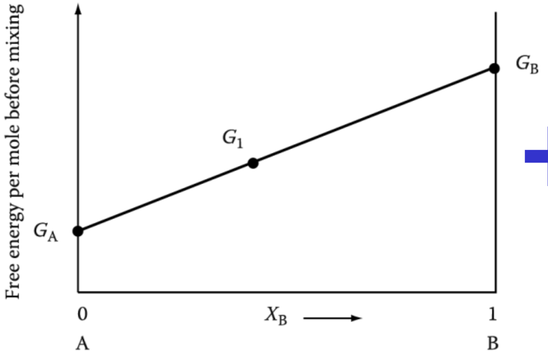
1) Ideal solution

Since ΔH_{mix} = 0 for ideal solution,

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

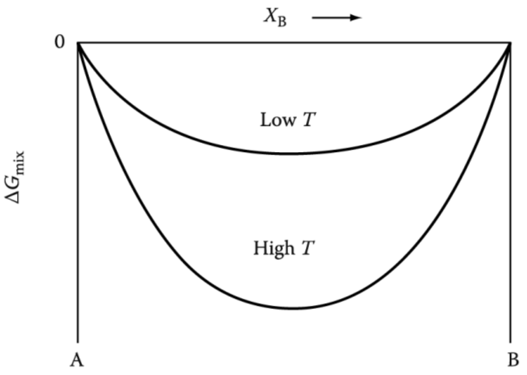
➡ $$\boxed{G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)}$$

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



$$\boxed{G_1}$$

+



$$\boxed{\Delta G_{mix}}$$

=

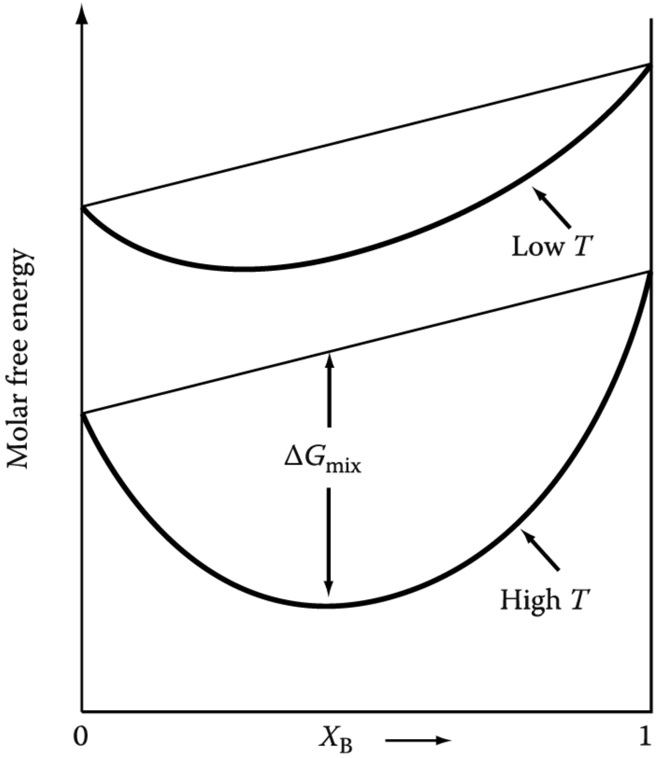


Fig. 1.10 The molar free energy (free energy per mole of solution) for an ideal solid solution. A combination of Figs. 1.8 and 1.9.

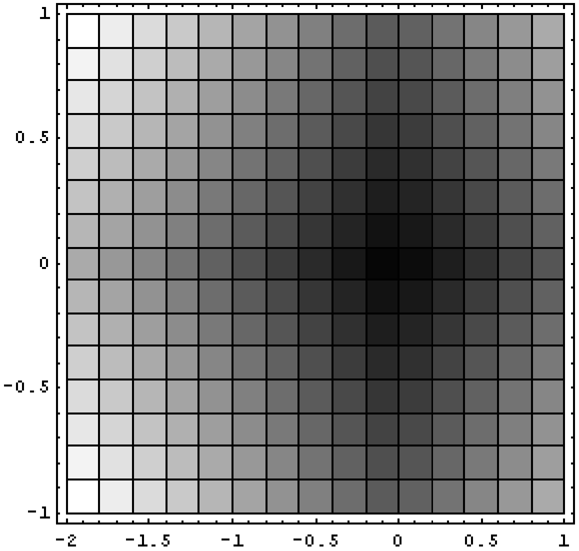
Gibbs Free Energy of Binary Solutions

Q9: “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.

➡ **소량 첨가에 의한 내부 에너지 변화 계산**

$$\boxed{dG' = \mu_A dn_A}$$

(T, P, n_B: constant)

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

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

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

For variable T and P

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

- Consider the chemical potential function over a hypothetical 2D region shown in the figure.
- Particles will tend to move from regions of high chemical potential (shown as lighter shades in plot) to regions of low chemical potential (shown as darker shades in plot). [particles: W → B]
- Various themodynamic properties determine what the chemical potential is. For example, consider charged particles in a fluid.

- A concentration gradient in a fluid may promote movement of particles in one direction, and
- the electric potential gradient may promote movement of the particles in another.
- The chemical potential would account for both concentration and electric components and describe a potential distribution that determines net particle movement.

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

1) Ideal solution

Correlation between chemical potential and free energy

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

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

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

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

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

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

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

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

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

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

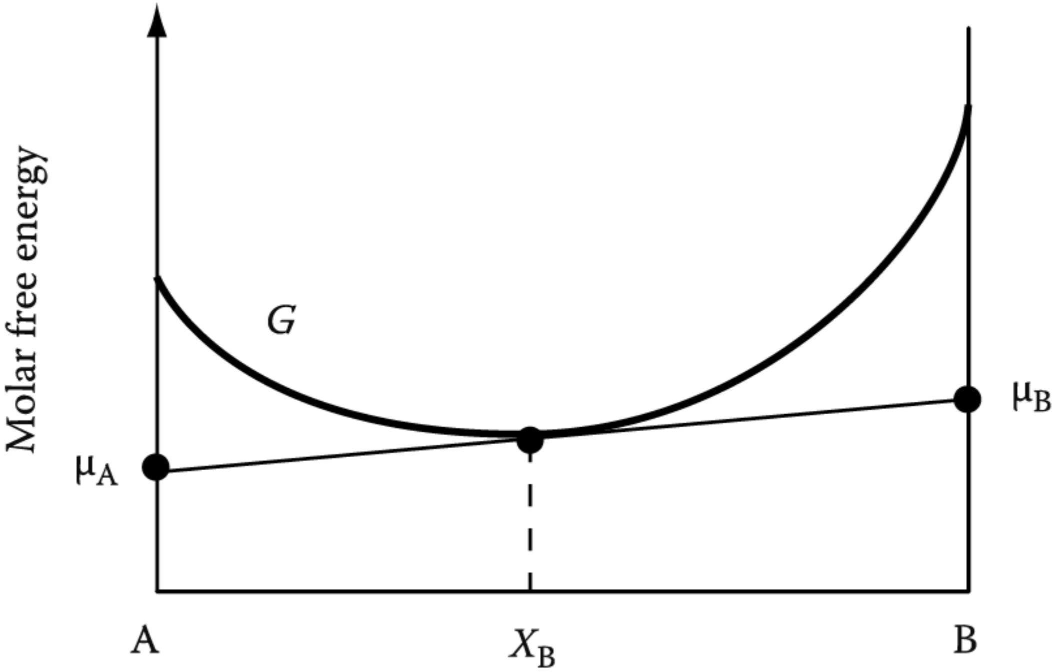
1) Ideal solution

Correlation between chemical potential and free energy

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

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

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



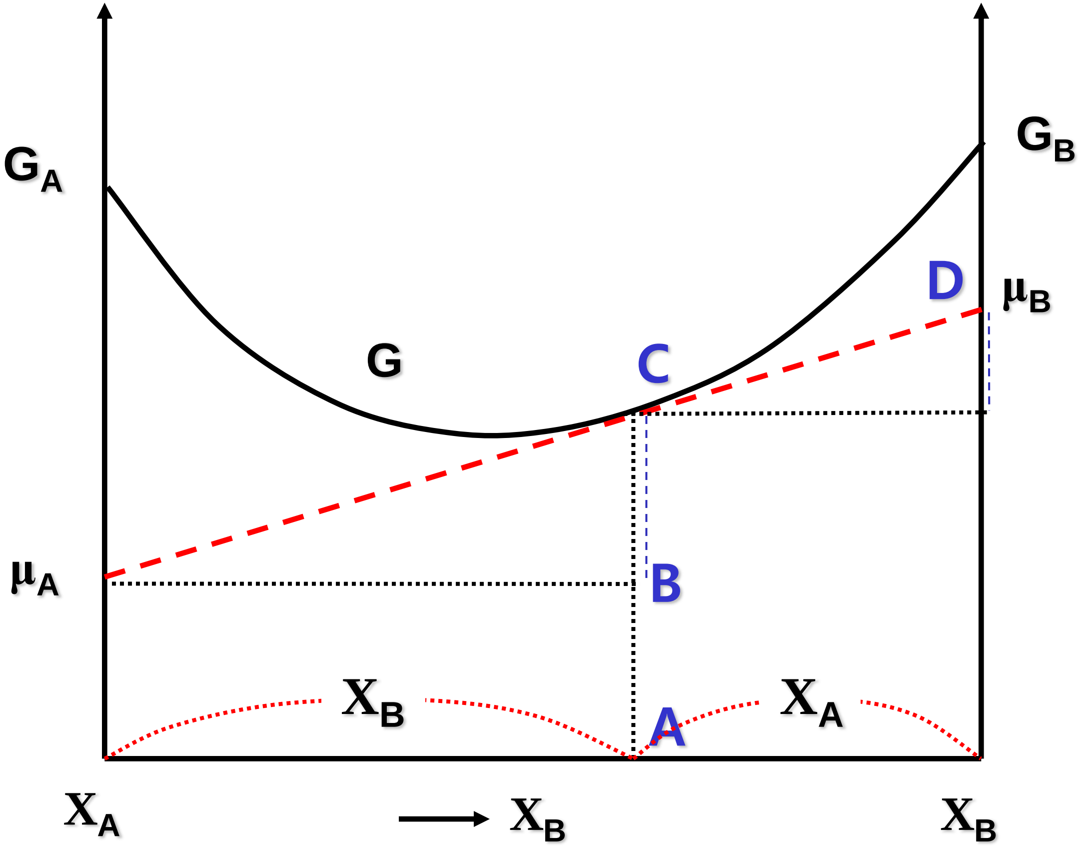
$$\mu_B = G + \frac{dG}{dX_B} X_A$$

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

Correlation between chemical potential and free energy

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

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



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

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

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

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

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

1.3 Binary Solutions

1) Ideal solution

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

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

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

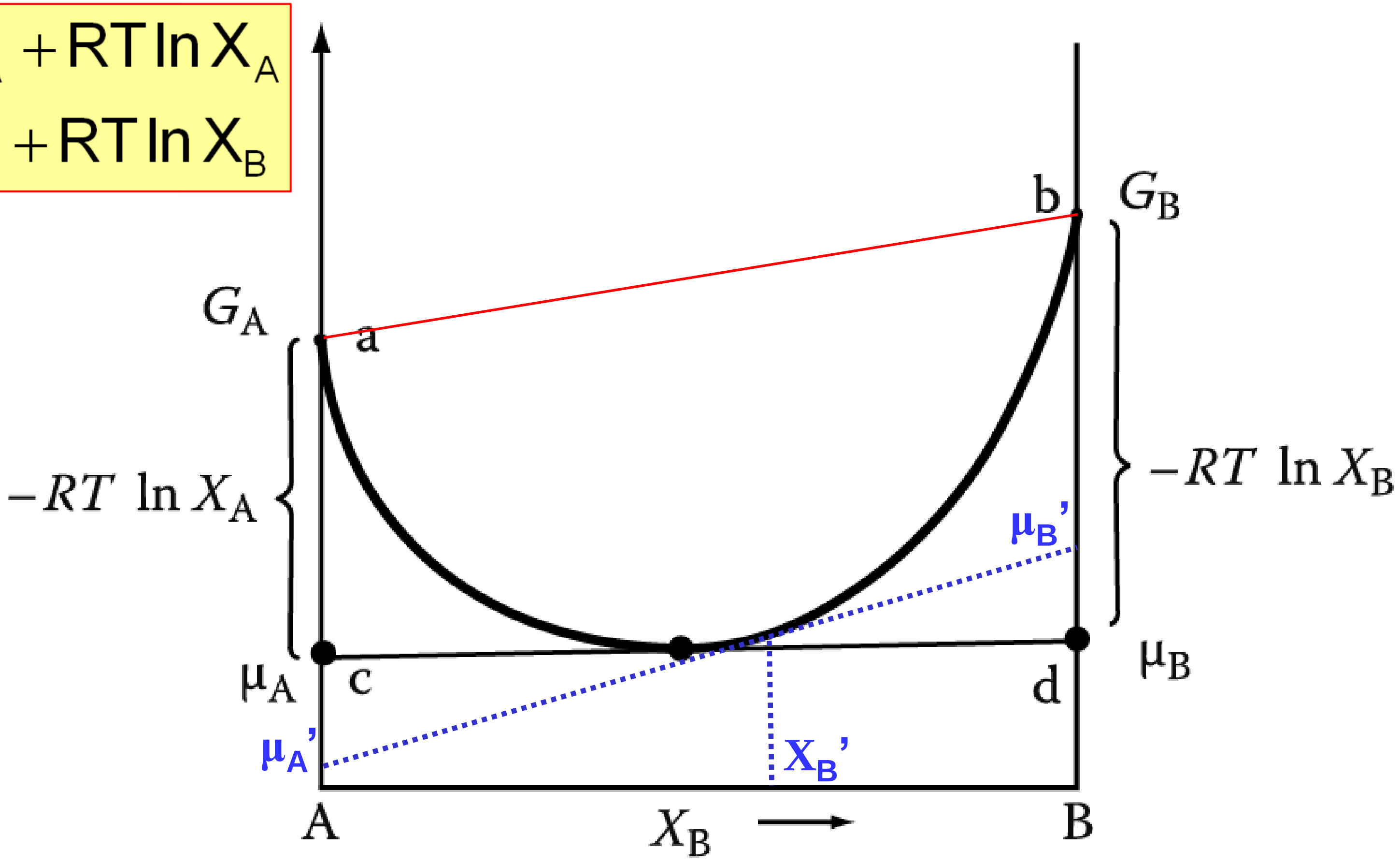


Fig. 1.12 The relationship between the free energy curve and Chemical potentials for an ideal solution.

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

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

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

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

μ는 조성에 의해 결정되기 때문에 dn_A가 매우 작아서 조성변화 없어야