2019 Spring

“Phase Equilibria *in* Materials”

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Eun Soo Park

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

Contents for previous class

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

- **Gibbs Free Energy in Binary System**

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

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

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

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

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

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

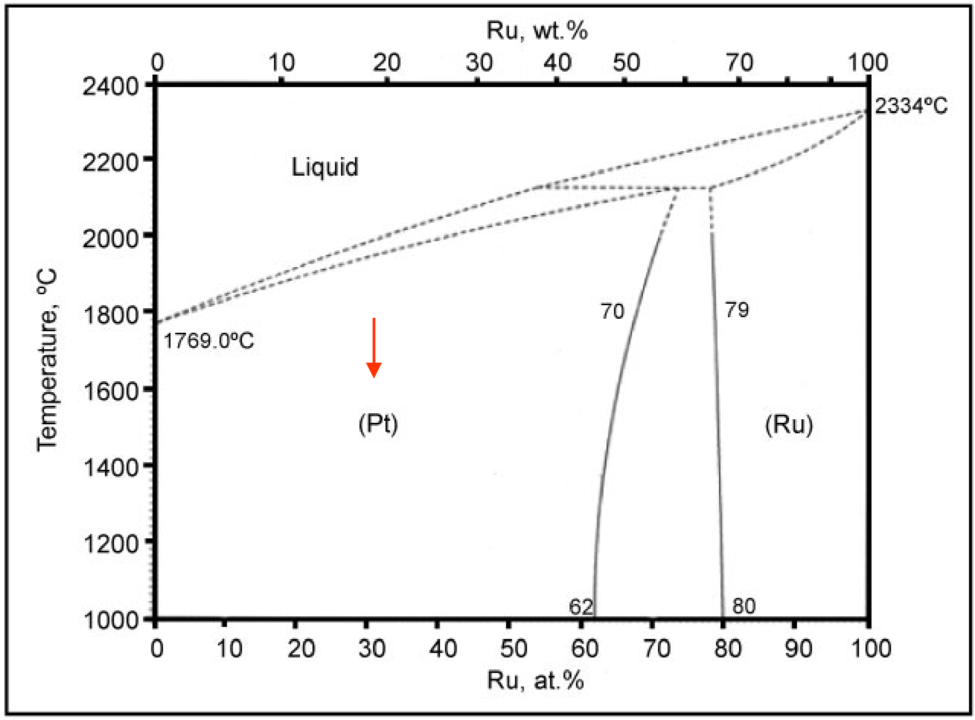
* **Binary System (two components)** → A, B

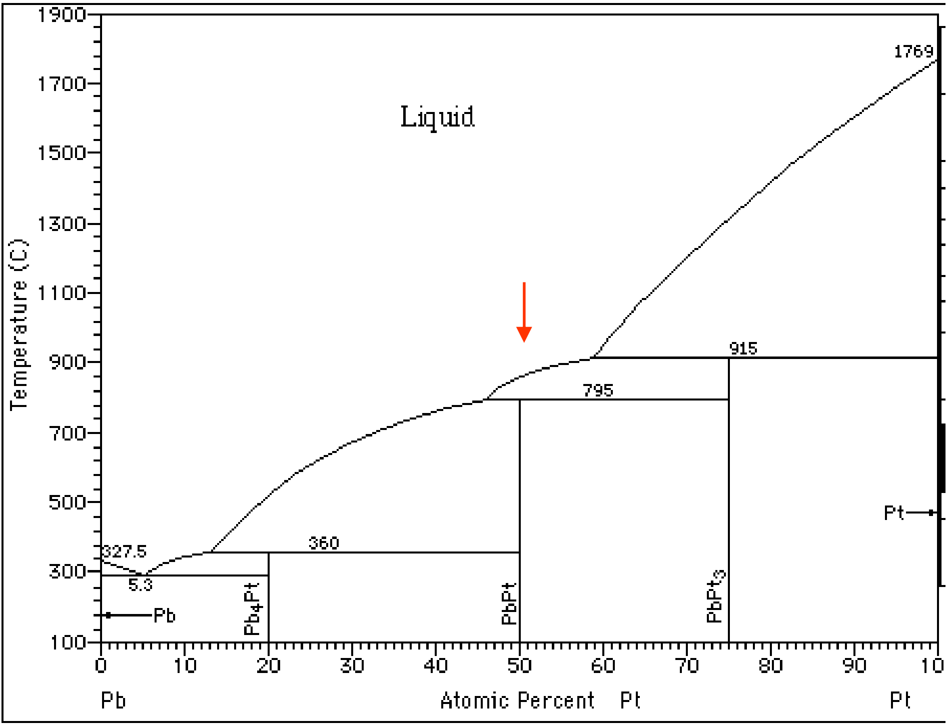
: Equilibrium depends on not only pressure and temperature but also composition.

Solid Solution vs. Intermetallic Compounds

- atomic scale mixture/ Random distribution on lattice

- fixed A, B positions/ Ordered state





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

PbPt – NiAS structure

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.

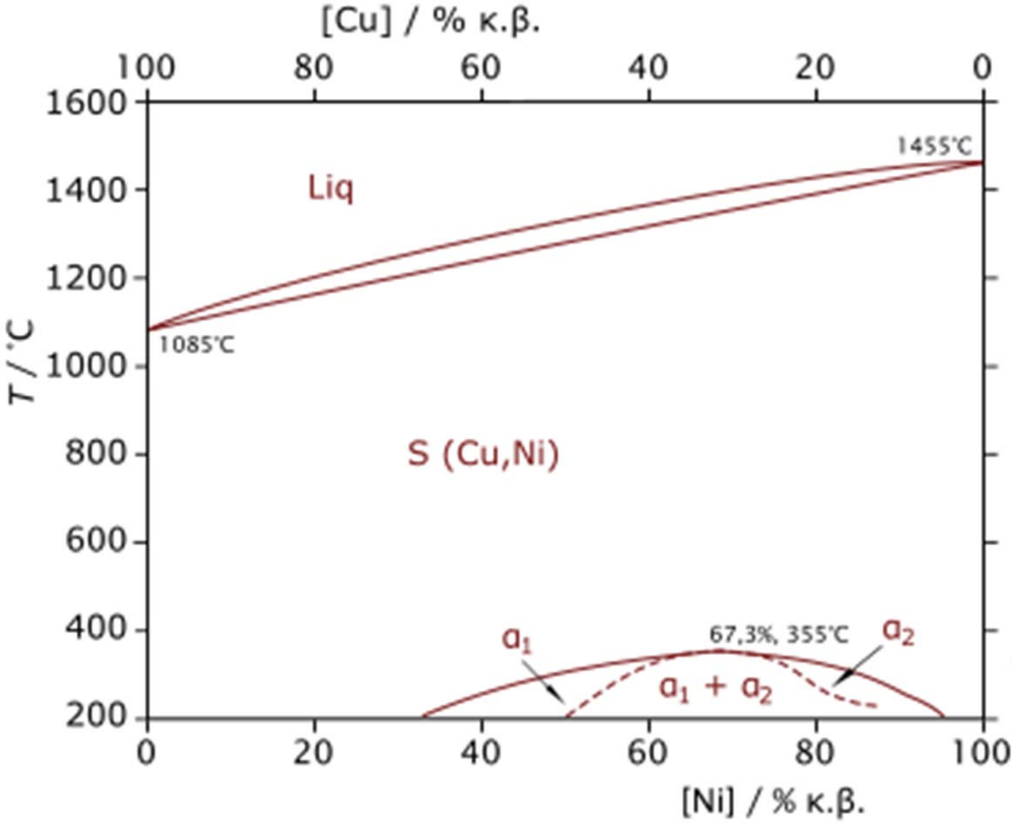
- ***Solid solution:***
  - Crystalline solid
  - Multicomponent yet homogeneous
  - Impurities are randomly distributed throughout the lattice

- **Factors favoring solubility of B in A (Hume-Rothery Rules)**
  - ***Similar atomic size:*** **$\Delta r/r \leq 15\%$**
  - ***Same crystal structure*** **for A and B**
  - ***Similar electronegativities:*** **$|\chi_A - \chi_B| \leq 0.6$ (preferably ≤ 0.4)**
  - ***Similar valence***

- **If all four criteria are met:** ***complete solid solution***

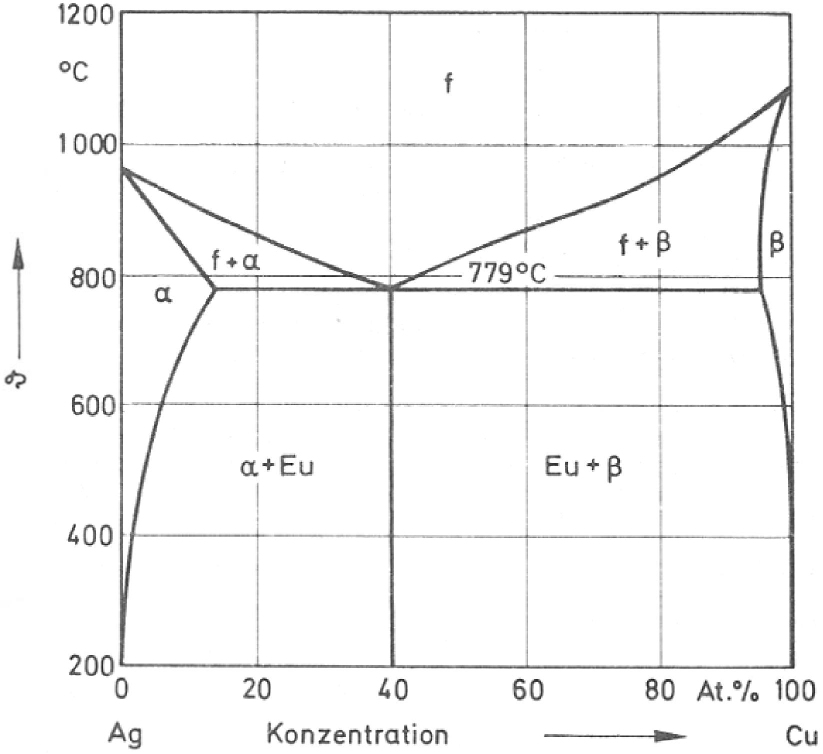
- **If any criterion is not met:** ***limited solid solution***

Cu-Ni Alloys



complete solid solution

Cu-Ag Alloys



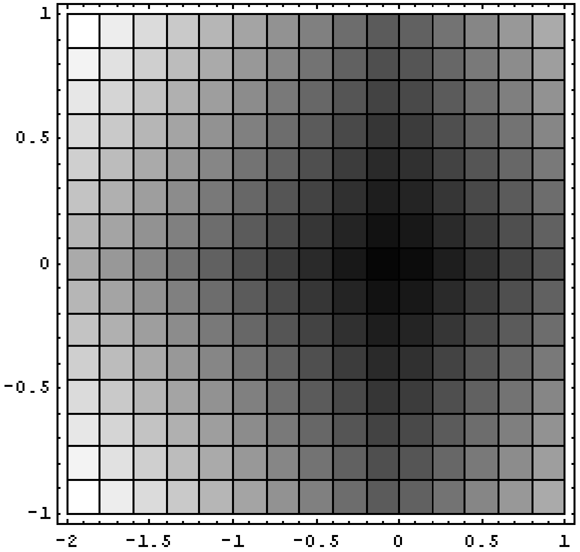
limited solid solution

Assumption: a simple physical model for “binary solid solutions”

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

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~ small enough
(∵ μ_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**

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

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

For variable T and P

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

1.3 Binary Solutions

1) Ideal solution

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

$$= \underbrace{(G_A + RT \ln X_A)}_{\mu_A} X_A + \underbrace{(G_B + RT \ln X_B)}_{\mu_B} X_B$$

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

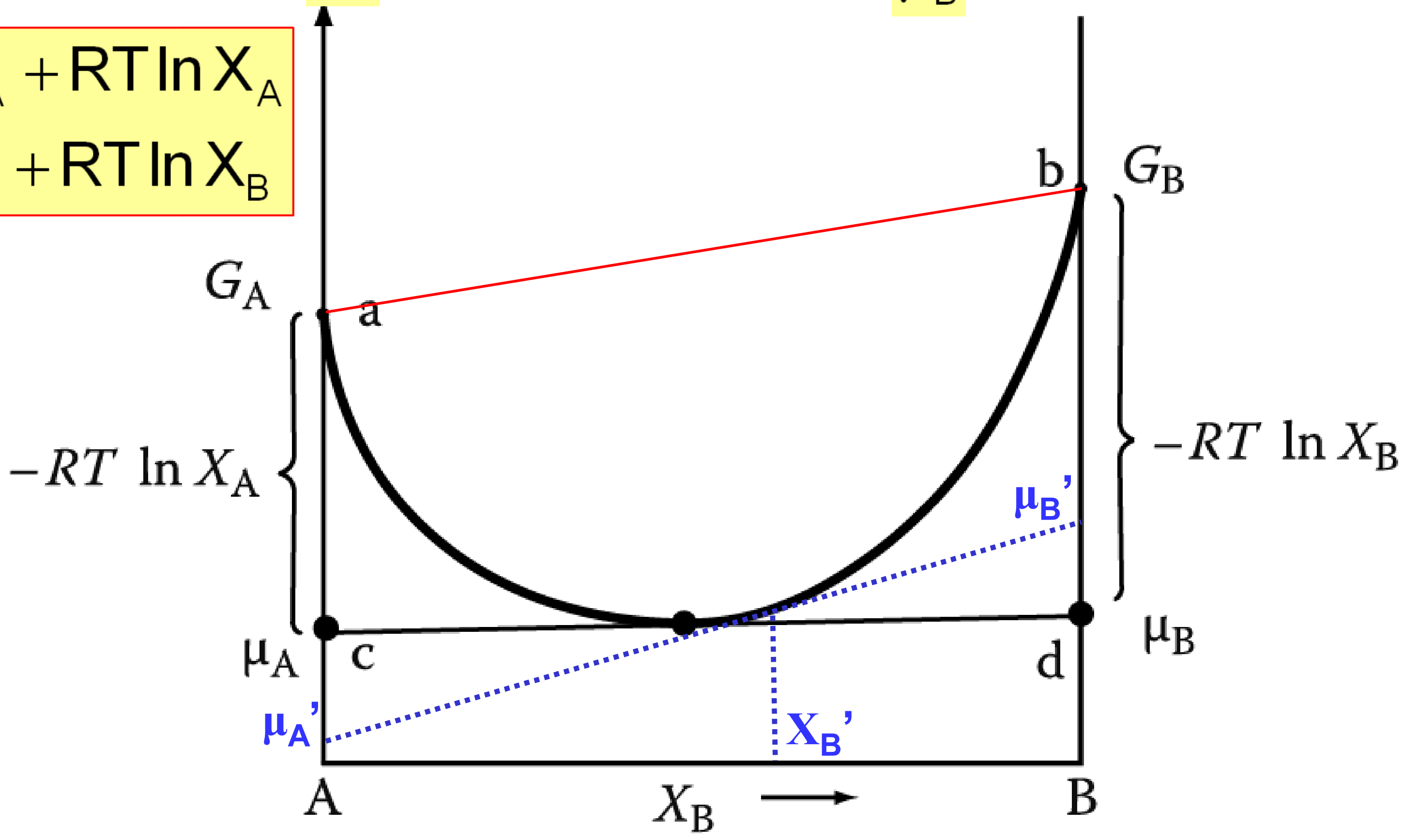


Fig. 1.12 The relationship between the free energy curve and Chemical potentials for an ideal solution.

Contents for today's class

- Binary Solid Solution

  Ideal solution and Regular solution

  : Chemical potential and **Activity**

  Real solution

  - Ordered phases: SRO & LRO, superlattice, Intermediate phase (intermetallic compound)
  - Clustering

- Equilibrium in heterogeneous system

Q1: What is “Regular Solution”?

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

Regular Solutions

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

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

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

Structure model of a binary solution

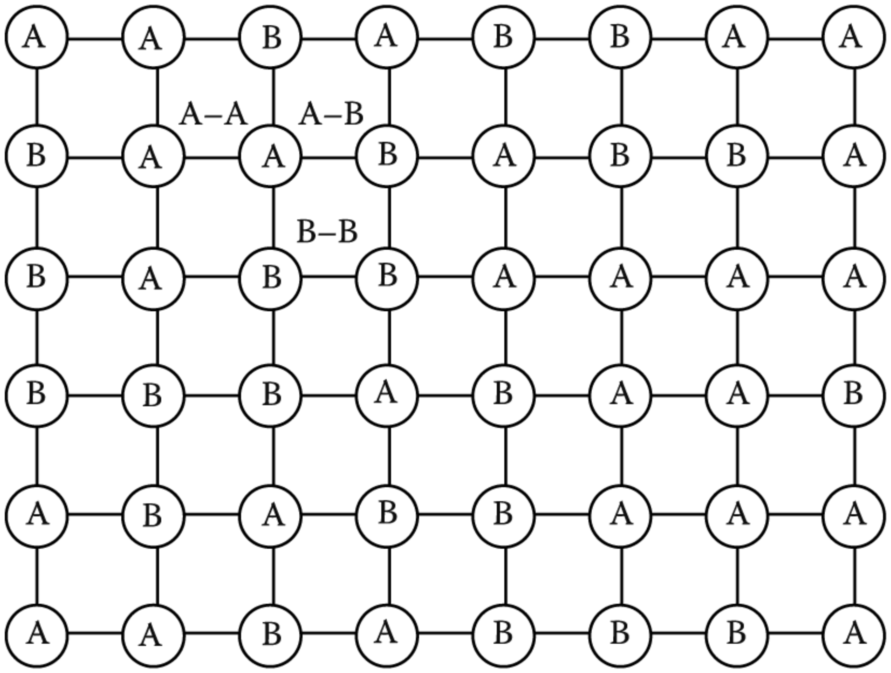


Fig. 1.13 The different types of interatomic bond in a solid solution.

Q2: How can you estimate "ΔH_{mix} of regular solution"?

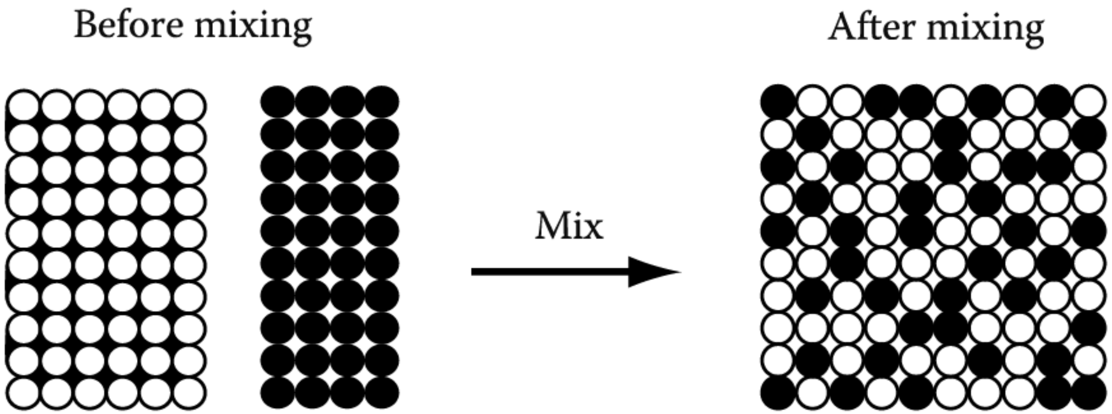
$$\boxed{\Delta H_{mix} = \Omega X_A X_B \text{ where } \Omega = N_a z \varepsilon}$$

Regular Solutions

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

Internal energy of the solution

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



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

Regular Solutions

Completely random arrangement

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

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

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

N_a : Avogadro's number

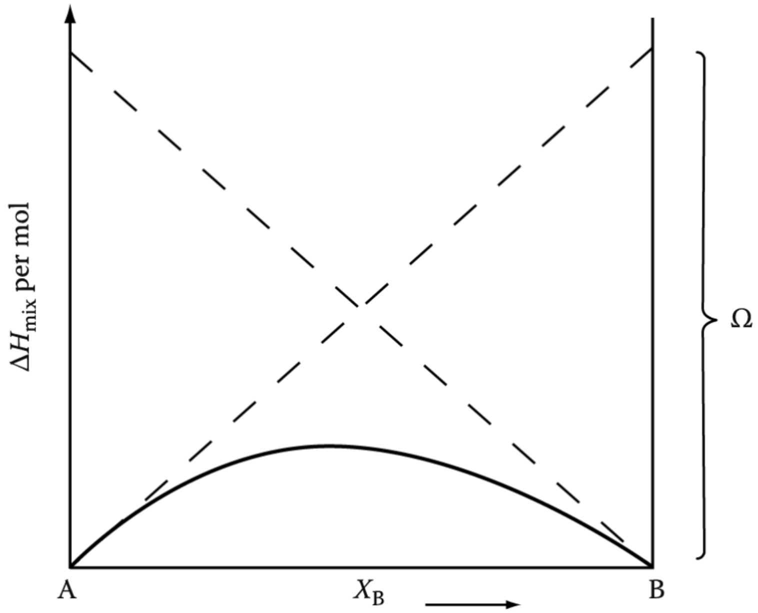
z : number of bonds per atom

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

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

$$\boxed{\Delta \mathbf{H}_{\mathbf{mix}} = \mathbf{\Omega X_A X_B} \ \text{where} \ \mathbf{\Omega = N_a z \varepsilon}}$$

Regular solution



Ω >0

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

Q3: How can you estimate

"Molar Free energy for regular solution"?

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

$$G = X_A G_A + X_B G_B + \underbrace{\Omega X_A X_B}_{\Delta H_{mix}} + \underbrace{RT(X_A \ln X_A + X_B \ln X_B)}_{-T\Delta S_{mix}}$$

Regular Solutions

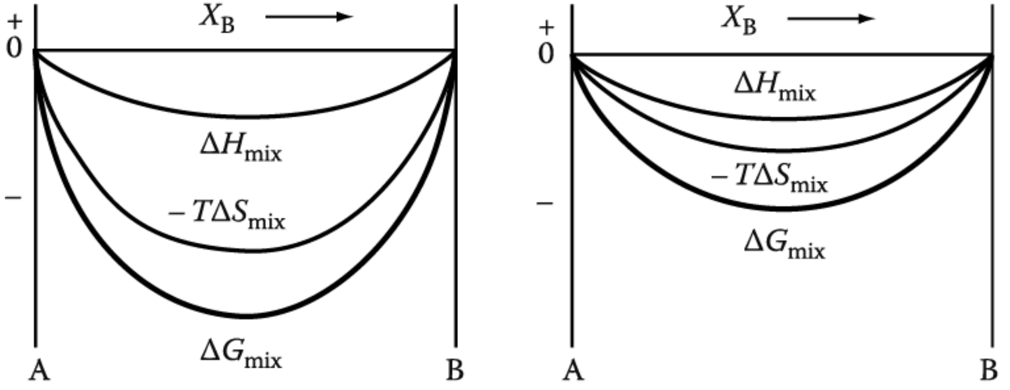
$$G_2 = G_1 + \Delta G_{mix}$$

$$G = X_A G_A + X_B G_B + \overset{\Delta H_{mix}}{\boxed{\Omega X_A X_B}} + \overset{-T\Delta S_{mix}}{\boxed{RT(X_A \ln X_A + X_B \ln X_B)}}$$

Reference state

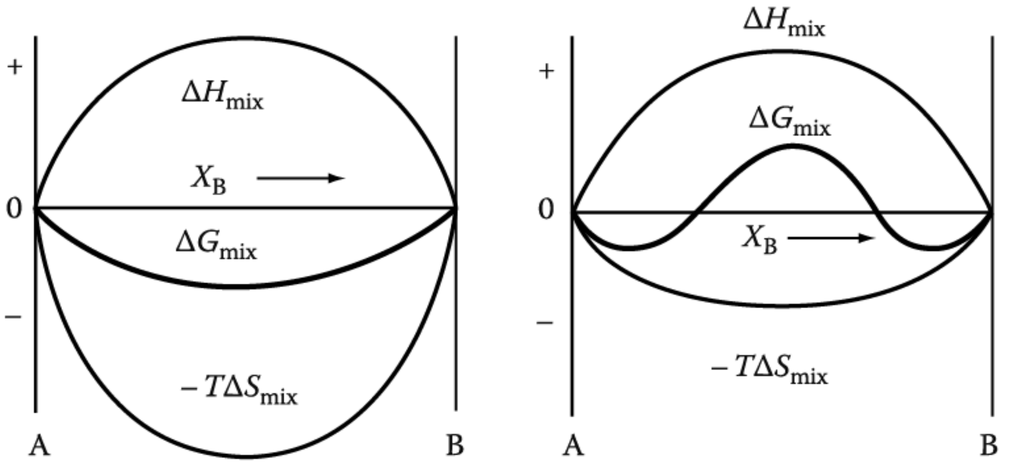
Pure metal $G_A^0 = G_B^0 = 0$

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



(a) Ω < O, high *T*

(b) Ω < O, low *T*

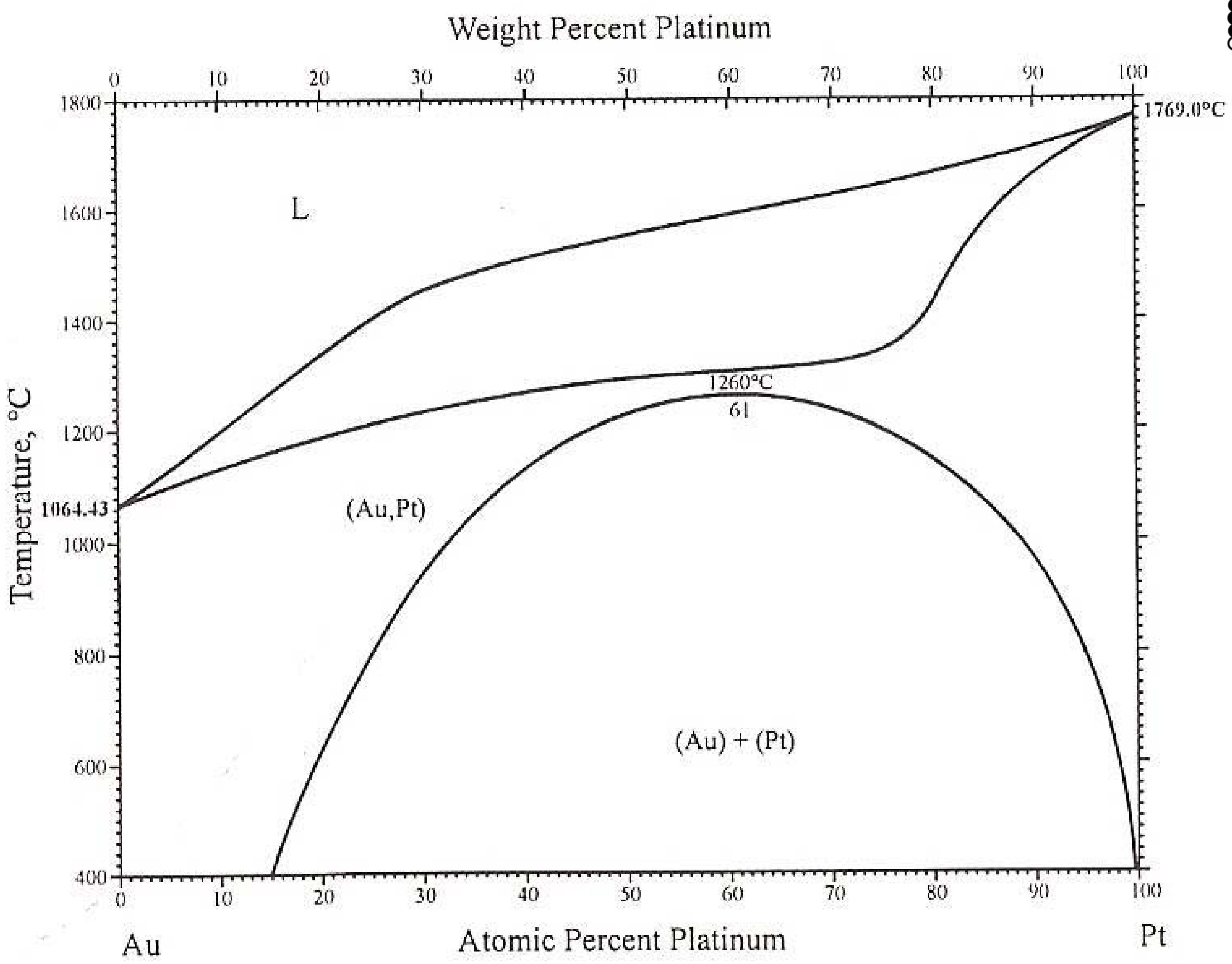


(c) Ω > O, high *T*

(d) Ω > O, low *T*

Q4: How can you calculate “critical temperature, T_c”?

$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim$ **+17** kJ/mol



Regular Solutions

Reference state

Pure metal $G_A^0 = G_B^0 = 0$ $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

$$\Delta G_m = \overset{\Delta H_{mix}}{\boxed{zNX_A(1-X_A)\left[H_{AB} - \frac{H_{AA}+H_{BB}}{2}\right]}} + \overset{-T\Delta S_{mix}}{\boxed{NkT[X_A \ln X_A + (1-X_A)\ln(1-X_A)].}} \quad (97)$$

(a) With $H_{AB} < \frac{1}{2}(H_{AA}+H_{BB})$, H_{AB} will be more negative than the mean of $H_{AA}+H_{BB}$. This implies that dissimilar atoms attract more strongly than similar atoms. There will be a tendency towards the formation of a superlattice or a compound.

(b) With $H_{AB} > \frac{1}{2}(H_{AA}+H_{BB})$, ΔH_m will be positive. With H_{AB} greater than the mean of $H_{AA}+H_{BB}$ similar atoms will attract each other more strongly than dissimilar atoms. There will be a tendency towards the formation of a mechanical mixture of A and B rather than towards the formation of a homogeneous solution. The tendency towards phase separation into phases A and B is dependent on ΔH_m predominating over ΔS_m. With increase in temperature the entropy term becomes more significant and eventually predominates over the enthalpy term. At low temperatures the system will consist of virtually pure A and pure B. As the temperature rises the entropy effect gives rise to increasing association of A and B atoms, *i.e.* to increasing mutual solubility of A and B. Eventually a temperature will be reached, the critical temperature, at which complete solubility of A and B is attained. The entropy effect is exerting such a predominating role that it completely swamps the enthalpy effect and a homogeneous solution results.

$$\boxed{\Delta G_m = NCX_A(1-X_A)+NkT[X_A \ln X_A+(1-X_A)\ln(1-X_A)]}$$

where,
$$C = z\left[H_{AB} - \frac{H_{AA}+H_{BB}}{2}\right]$$
: energy term

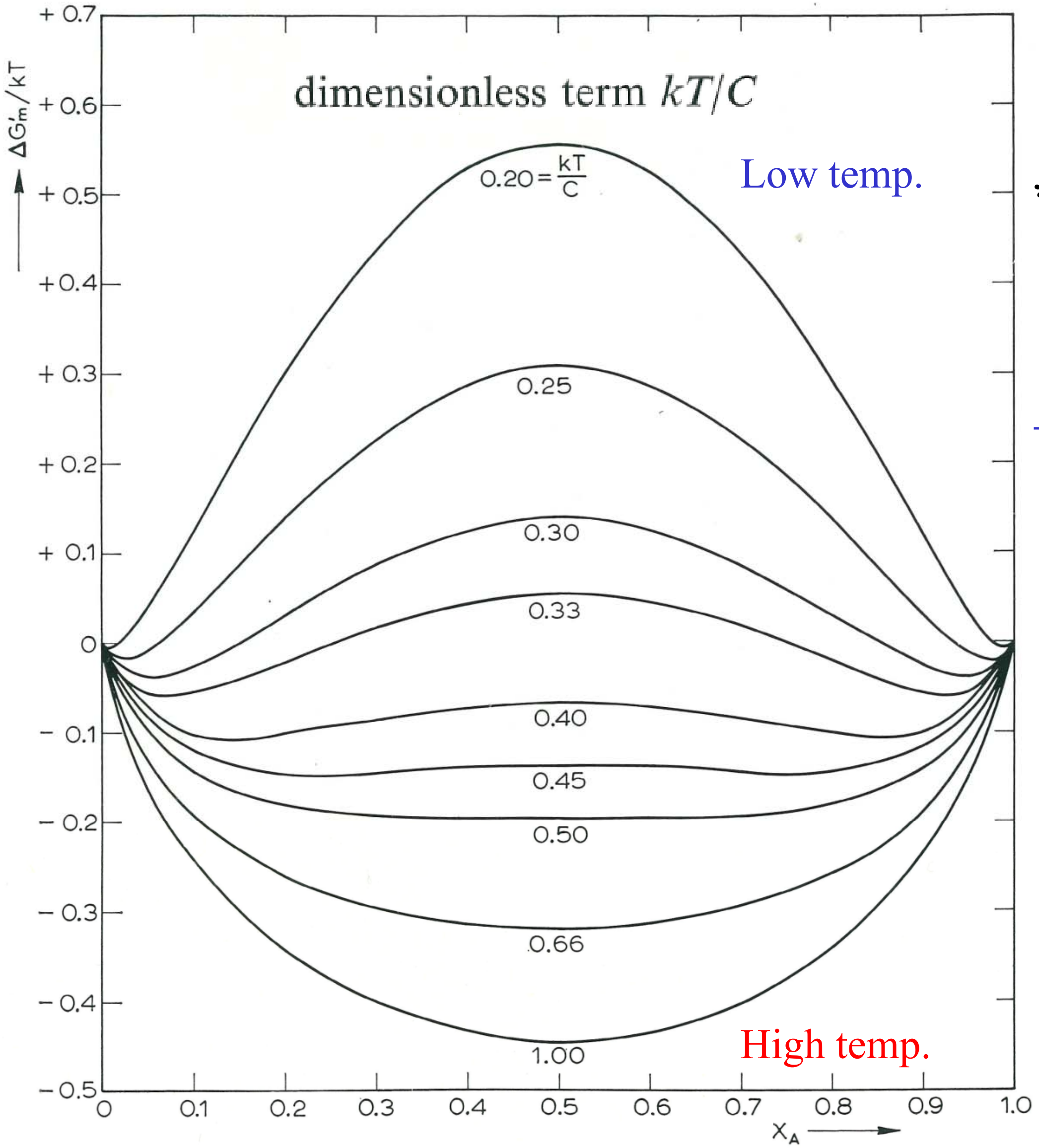


Fig. 14. Variation of free energy with composition for a homogeneous solution with $\Delta H_m > 0$. Free energy–composition curves are given for various values of the parameter kT/C.

*** Variation of free energy with composition for a homogeneous solution with $\Delta H_{mix} > 0$**

→The curves with *kT/C* < 0.5 show two minima, which approach each other as the temperature rise.

$$\boxed{\Delta G_m = NCX_A(1-X_A)+NkT[X_A \ln X_A+(1-X_A)\ln(1-X_A)]}$$

where,

$$C = z\left[H_{AB} - \frac{H_{AA}+H_{BB}}{2}\right]$$

Taking the curve *kT/C* = 0.25 as an example, we can substitute *C*=4*kT* in upper eq. to obtain

$$\frac{\Delta G_m}{N} = \Delta G'_m = kT[\overbrace{4X_A(1-X_A)}^{\Delta H_{mix}}+\overbrace{X_A \ln X_A+(1-X_A)\ln(1-X_A)}^{\Delta S_{mix}}].$$

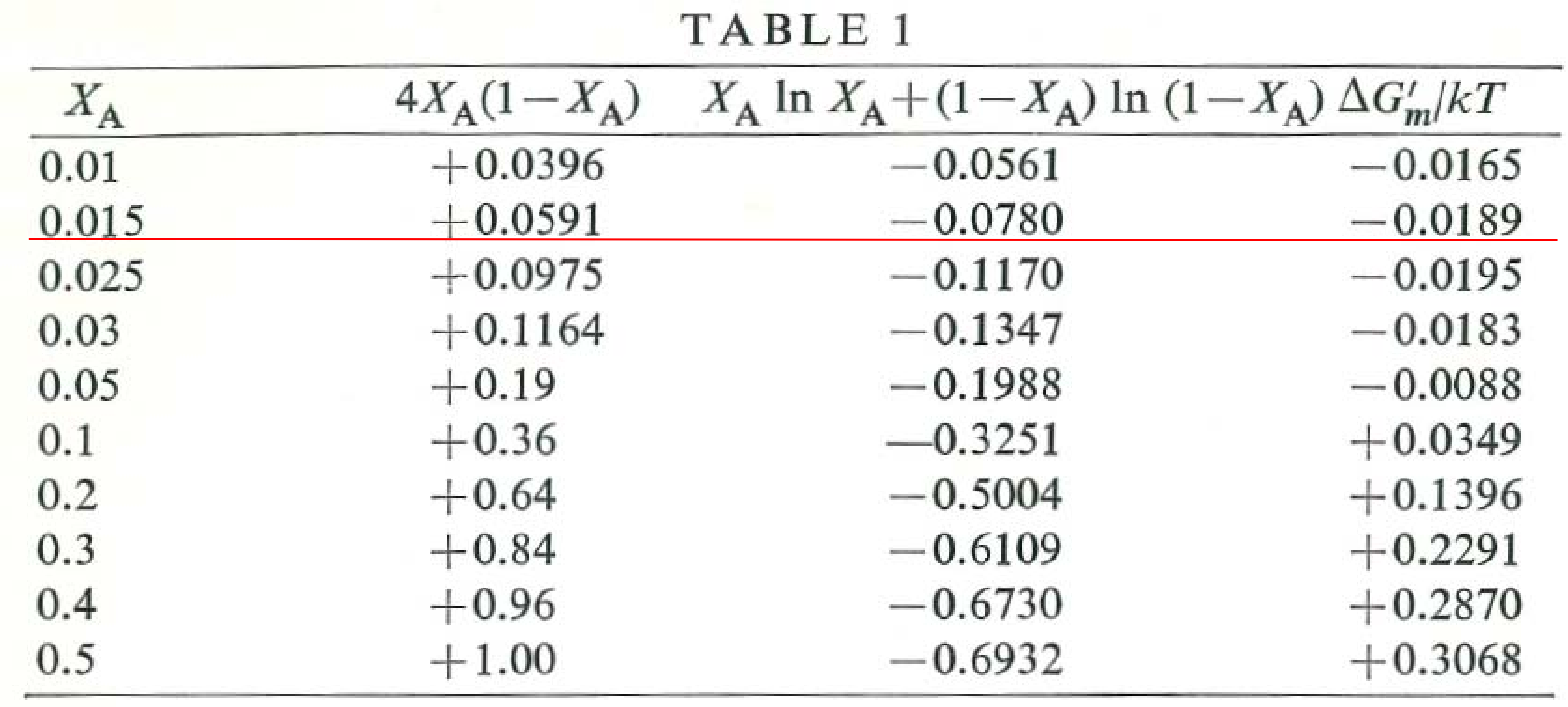


TABLE 1

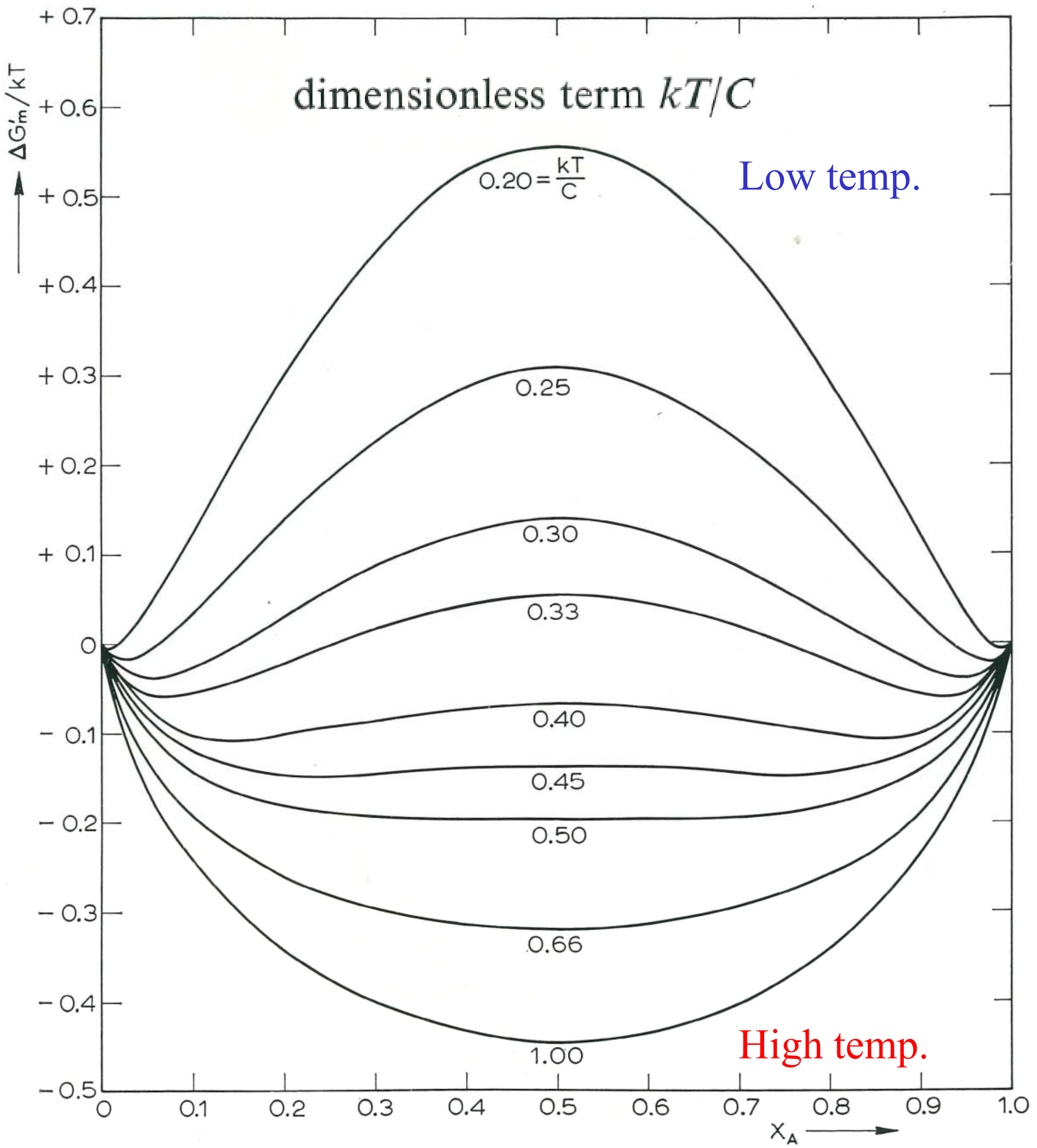
X_A	$4X_A(1-X_A)$	$X_A \ln X_A+(1-X_A)\ln(1-X_A)$	$\Delta G'_m/kT$
0.01	+0.0396	−0.0561	−0.0165
0.015	+0.0591	−0.0780	−0.0189
0.025	+0.0975	−0.1170	−0.0195
0.03	+0.1164	−0.1347	−0.0183
0.05	+0.19	−0.1988	−0.0088
0.1	+0.36	−0.3251	+0.0349
0.2	+0.64	−0.5004	+0.1396
0.3	+0.84	−0.6109	+0.2291
0.4	+0.96	−0.6730	+0.2870
0.5	+1.00	−0.6932	+0.3068

*** Free energy curve exhibit two minima at $X_A = 0.02$ and $X_A = 0.98$.**

$$\boxed{\Delta G_m = NCX_A(1-X_A)+NkT[X_A \ln X_A+(1-X_A)\ln(1-X_A)]}$$

where,

$$C = z\left[H_{AB} - \frac{H_{AA}+H_{BB}}{2}\right]$$

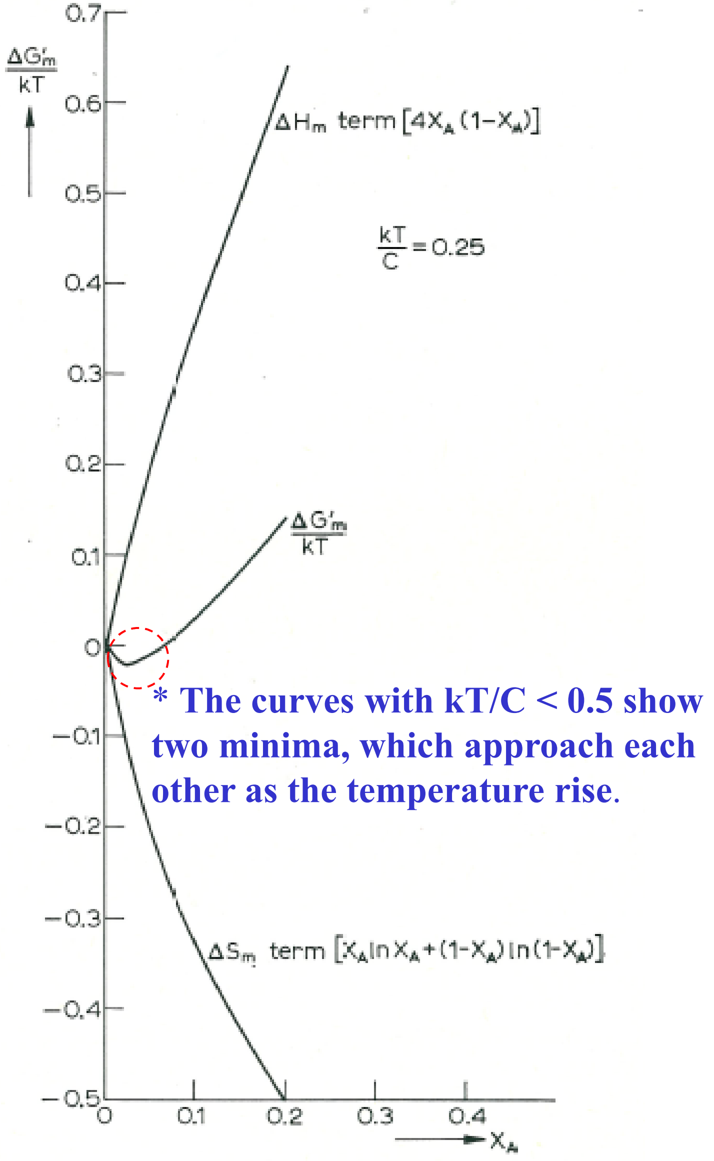


dimensionless term kT/C

Low temp.

High temp.

Fig. 14. Variation of free energy with composition for a homogeneous solution with $\Delta H_m > 0$. Free energy–composition curves are given for various values of the parameter kT/C.



*** The curves with kT/C < 0.5 show two minima, which approach each other as the temperature rise.**

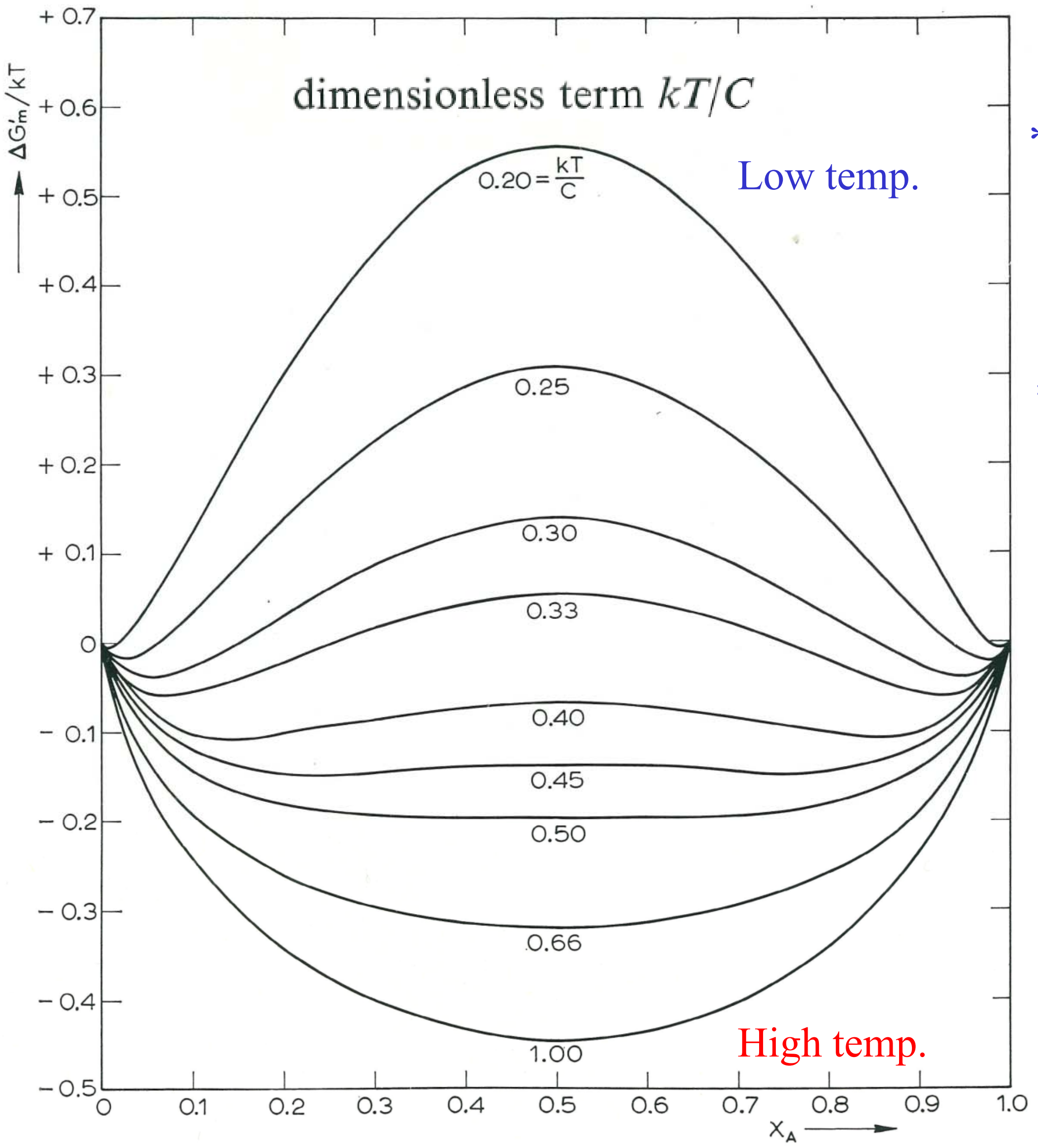
$\Delta H_m > 0$ and $kT/C = 0.25$

$$\boxed{\Delta G_m = NCX_A(1-X_A)+NkT[X_A \ln X_A+(1-X_A)\ln(1-X_A)]}$$

where,

$$C = z\left[H_{AB} - \frac{H_{AA}+H_{BB}}{2}\right]$$

: energy term



Low temp.

High temp.

Fig. 14. Variation of free energy with composition for a homogeneous solution with $\Delta H_m > 0$. Free energy–composition curves are given for various values of the parameter kT/C.

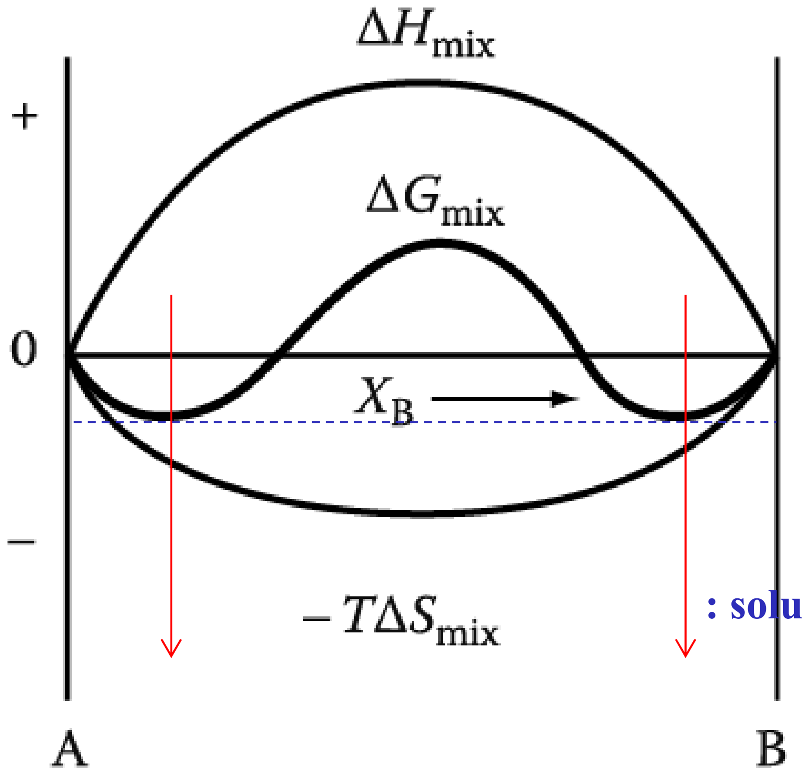
*** The curves with $kT/C < 0.5$ show two minima, which approach each other as the temperature rise.**

*** With $kT/C \geq 0.5$ there is a continuous fall in free energy from $X_A=0$ to $X_A=0.5$ and $X_A=1.0$ to $X_A=0.5$. The free energy curve thus assumes the characteristic from one associates with the formation of homogeneous solutions.**

$$\boxed{\Delta G_m = NCX_A(1-X_A)+NkT[X_A \ln X_A+(1-X_A)\ln(1-X_A)]}$$

where,

$$C = z\left[H_{AB} - \frac{H_{AA}+H_{BB}}{2}\right]$$



: **solubility limit**

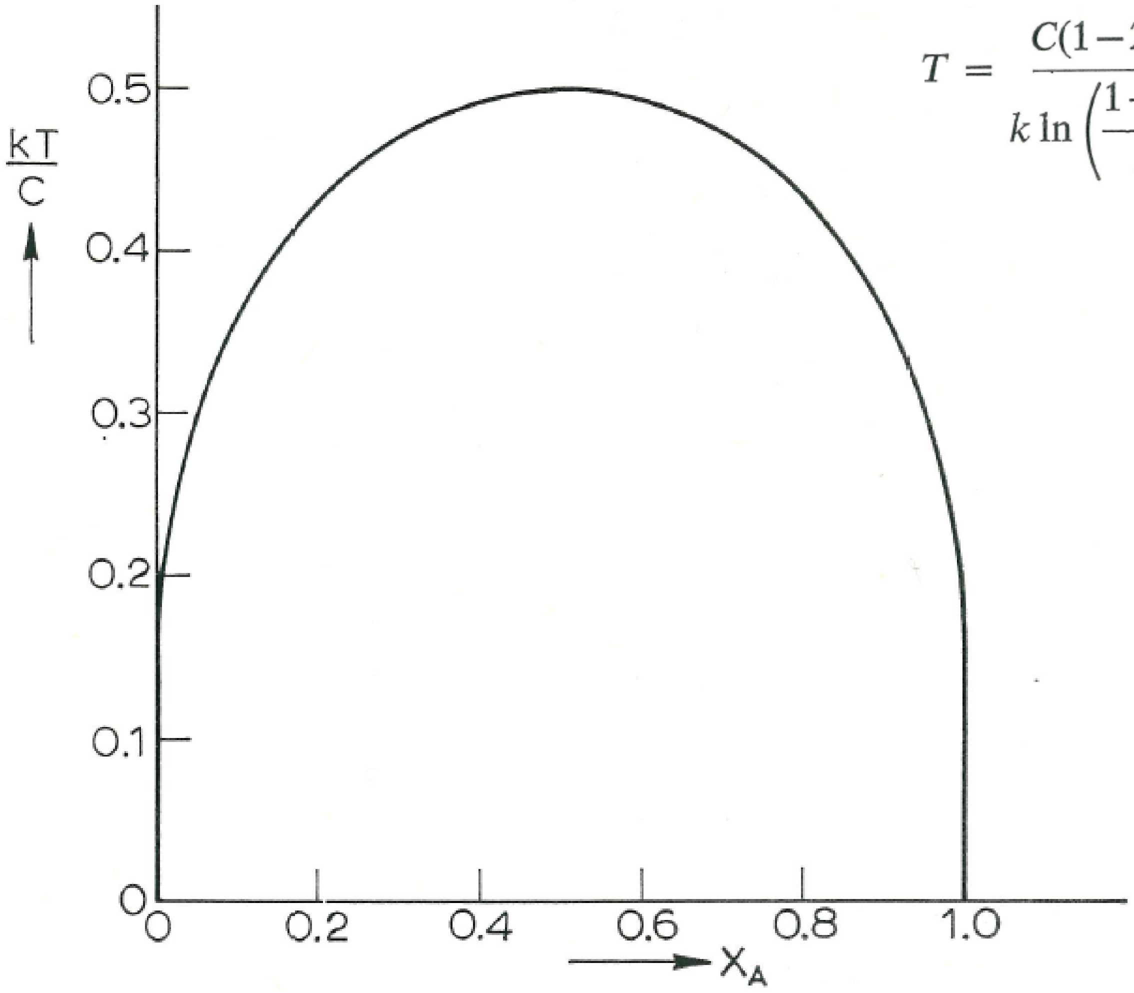
(d) Ω > O, low *T*

$$\frac{d(\Delta G_m)}{dX_A} = NC(1-2X_A)+NkT[\ln X_A-\ln(1-X_A)] = 0$$

$$\ln\left(\frac{X_A}{1-X_A}\right) = -\frac{C(1-2X_A)}{kT}$$

$$\boxed{T = \frac{C(1-2X_A)}{k\ln\left(\frac{1-X_A}{X_A}\right)}.}$$

Fig. 14. Variation of free energy with composition for a homogeneous solution with $\Delta H_m > 0$. Free energy–composition curves are given for various values of the parameter kT/C.



$$T = \frac{C(1-2X_A)}{k\ln\left(\frac{1-X_A}{X_A}\right)} \quad \text{eqn. (100)}$$

Figure. 21. Solubility curve obtained from eqn. (100)
by plotting the concentration A in two-existing phases as a function of kT/C.

The solubility of the components in each other increases with temperature until a temperature is reached where the components are completely miscible (soluble) in each other.

The temperature at which complete miscibility occurs is called the critical temperature, T_c.

At T_c the term $d^2(\Delta G_m)/d(X_A)^2$ will be zero.

$$C = z\left[H_{AB} - \frac{H_{AA}+H_{BB}}{2}\right]$$

Since

$$\frac{d^2(\Delta G_m)}{d(X_A)^2} = -2NC + NkT_c\left(\frac{1}{X_A} + \frac{1}{1-X_A}\right) = 0$$

then

$$2C = \frac{kT_c}{X_A(1-X_A)} \quad \text{or} \quad \boxed{T_c = \frac{2CX_A(1-X_A)}{k}}$$

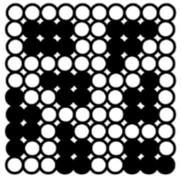
The term T_c will be a maximum when $X_A = (1-X_A) = 0.5$. It follows that

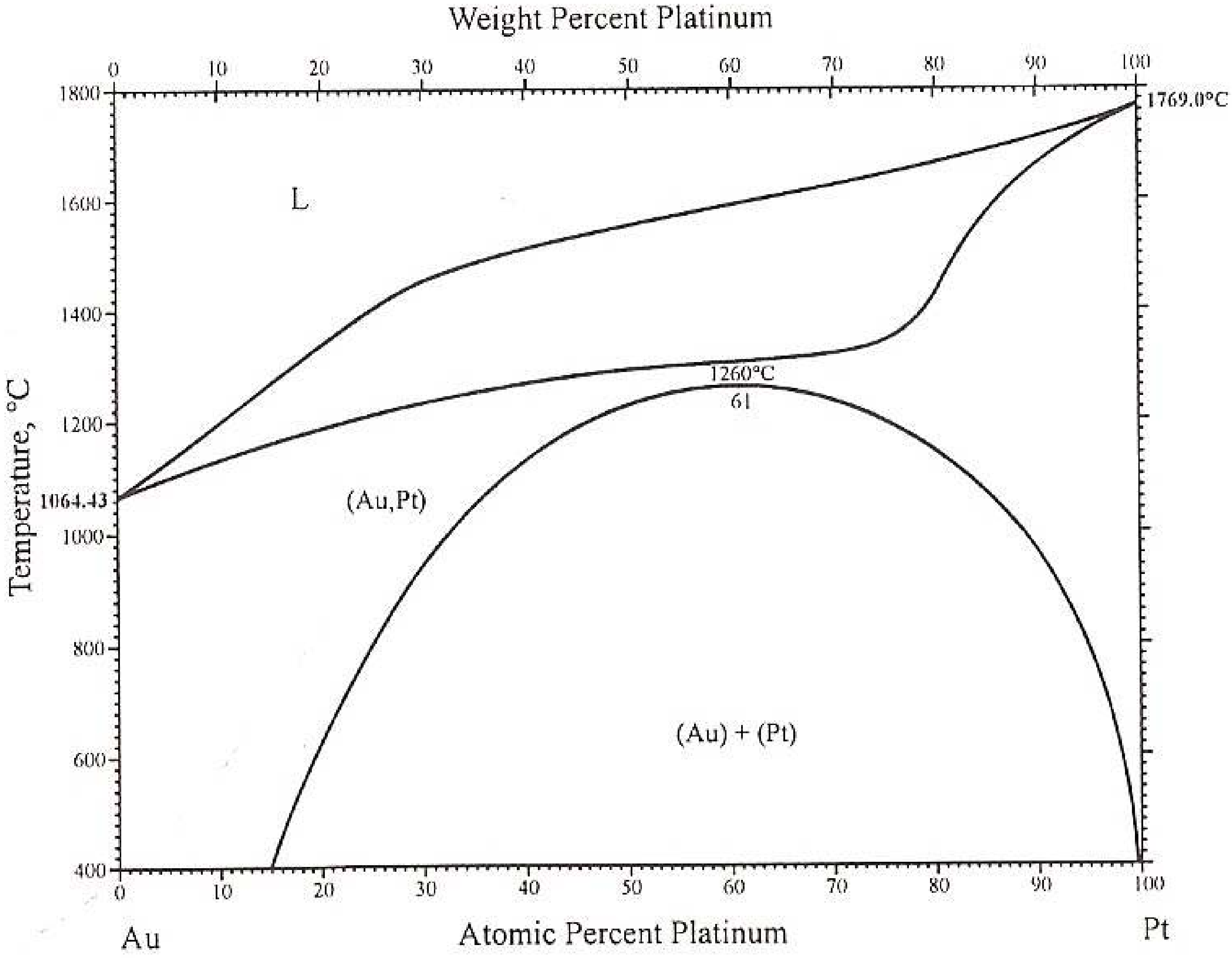
$$T_c = \frac{C}{2k}. \tag{101}$$

A high value of the critical temperature is associated with a high positive value for C $(= z[H_{AB} - \frac{1}{2}(H_{AA}+H_{BB})])$.

The stronger the attraction between similar atoms, the higher T_c. In those binary phase diagrams with a miscibility gap in the solid state the gap has not the symmetrical form shown in Fig. 21. This is primarily because the initial simplifying assumption that the energy is the sum of interaction between pairs of atoms is never absolutely valid. The systems Pd–Ir*, Pt–Ir** and Pt–Au*** all have miscibility gaps in the solid state with varying degrees of asymmetry. Most binary phase diagrams with a positive value of ΔH_m do not show a miscibility gap with a closure at temperature T_c since melting occurs before T_c is reached (for example the Ag–Cu system).

$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +17$ kJ/mol



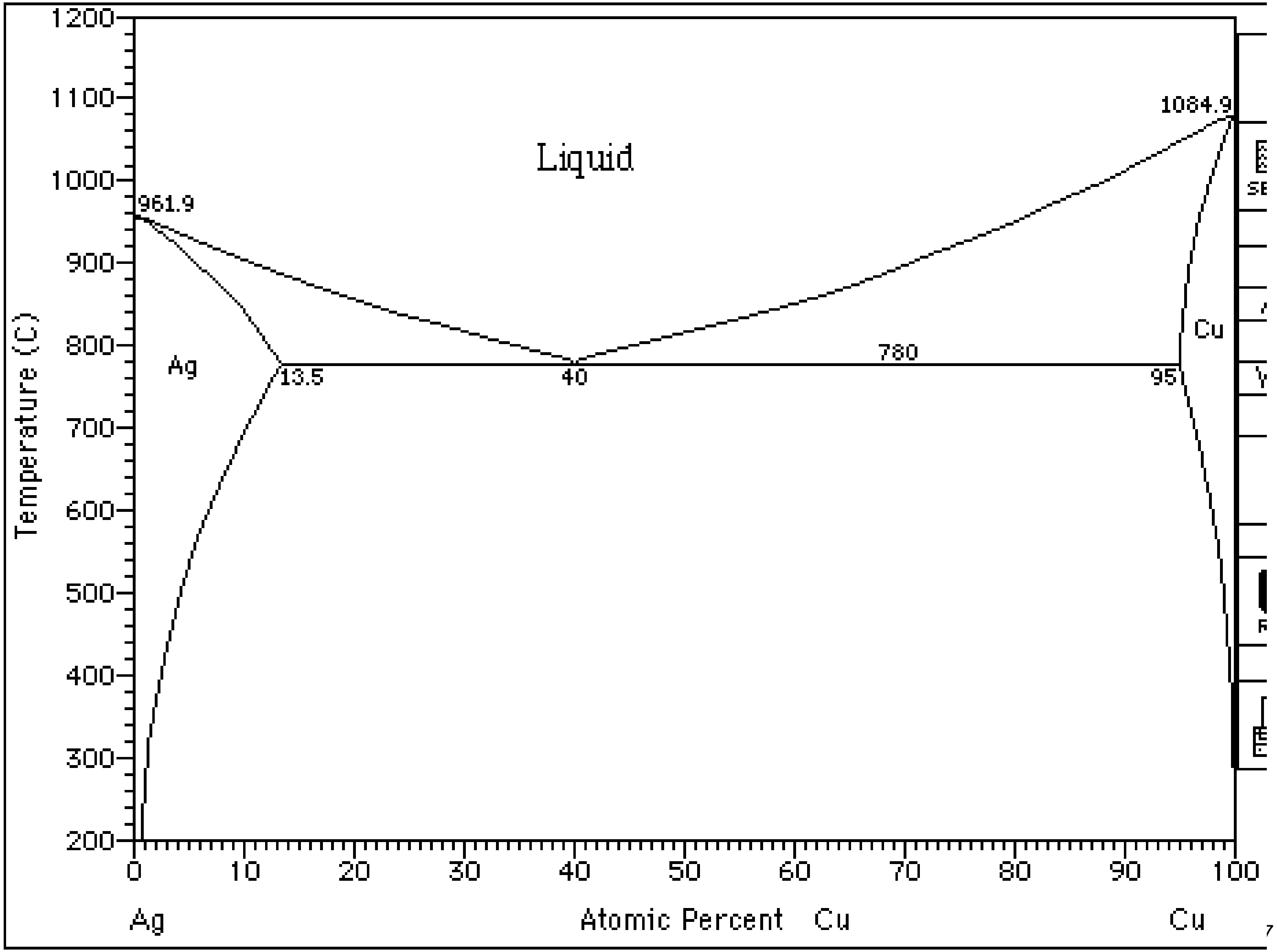


Incentive Homework1:

please find and summary models for asymmetric miscibility gaps as a ppt file.

Ref. Acta Meter. 1 (1953) 202/ Acta Meter. 8 (1960) 711/ etc.

$\varepsilon > 0$, $\Delta H_{mix} > 0$ / $\Delta H_{mix} \sim +5$ kJ/mol



Q5: “Correlation between chemical potential and free energy”?

Correlation between chemical potential and free energy

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

$G = E + PV - TS$

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

$G = H - TS$

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

$$\longrightarrow \quad \boxed{X_A X_B = X_A X_B (X_A + X_B) = X_A^2 X_B + X_B^2 X_A}$$

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

Regular solution

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

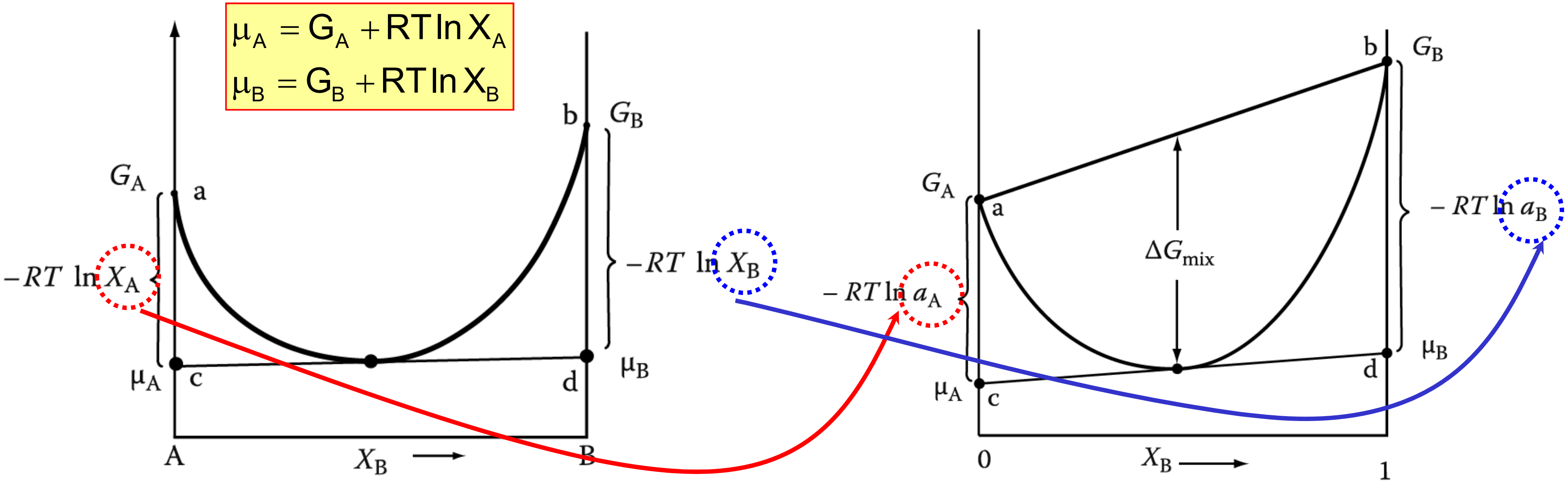
$$\mu_A = G_A + RT \ln X_A$$
$$\mu_B = G_B + RT \ln X_B$$

Ideal solution

Q6: What is “activity”?

Activity, a : effective concentration for mass action

ideal solution **regular solution**



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

$$\mu_A = G_A + \boxed{RT\ln a_A} \qquad \mu_B = G_B + \boxed{RT\ln a_B}$$

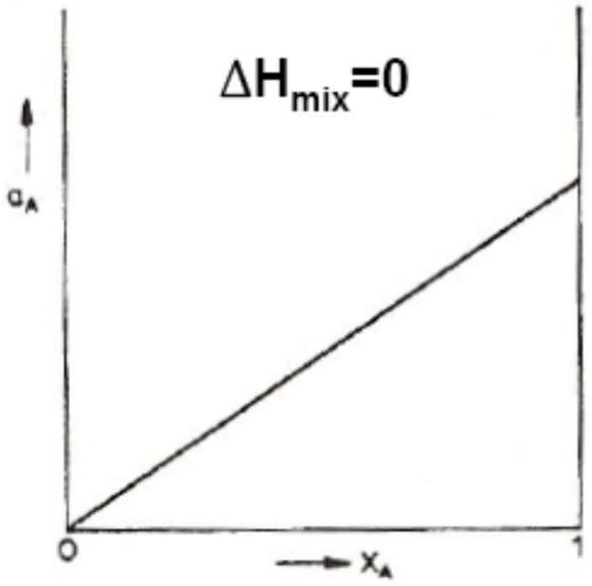
$$\mu_A = G_A + \boxed{\Omega\,(1-X_A)^2 + RT\ \ln\ X_A} \qquad \mu_B = G_B + \boxed{\Omega\,(1-X_B)^2 + RT\ \ln\ X_B}$$

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

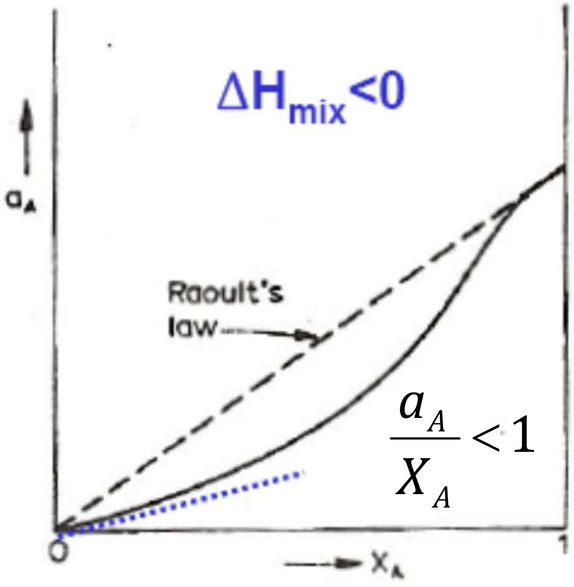
$$\frac{a_A}{X_A} = \gamma_A = \text{activity coefficient} \qquad \gamma_B = \frac{a_B}{X_B}$$

Degree of non-ideality

Activity-composition curves for solutions

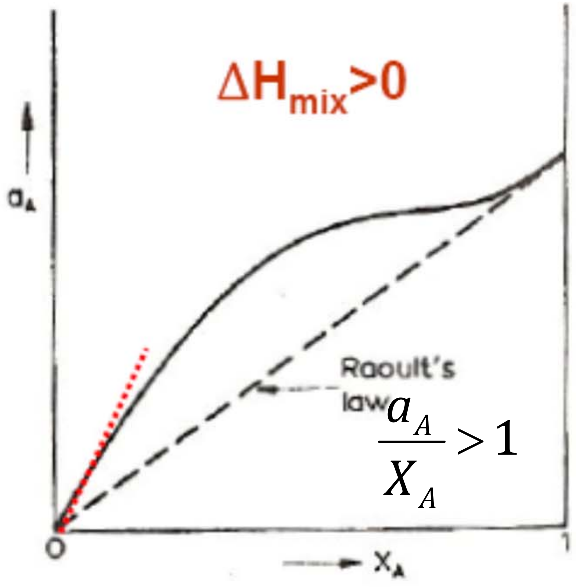


(a)
Ideal solution
$A \leftrightarrow B = \frac{1}{2}(A \leftrightarrow A + B \leftrightarrow B)$
e.g. Bi-Sn at 335°C
$a_A = a_{Sn}$



$$\frac{a_A}{X_A} < 1$$

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



$$\frac{a_A}{X_A} > 1$$

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

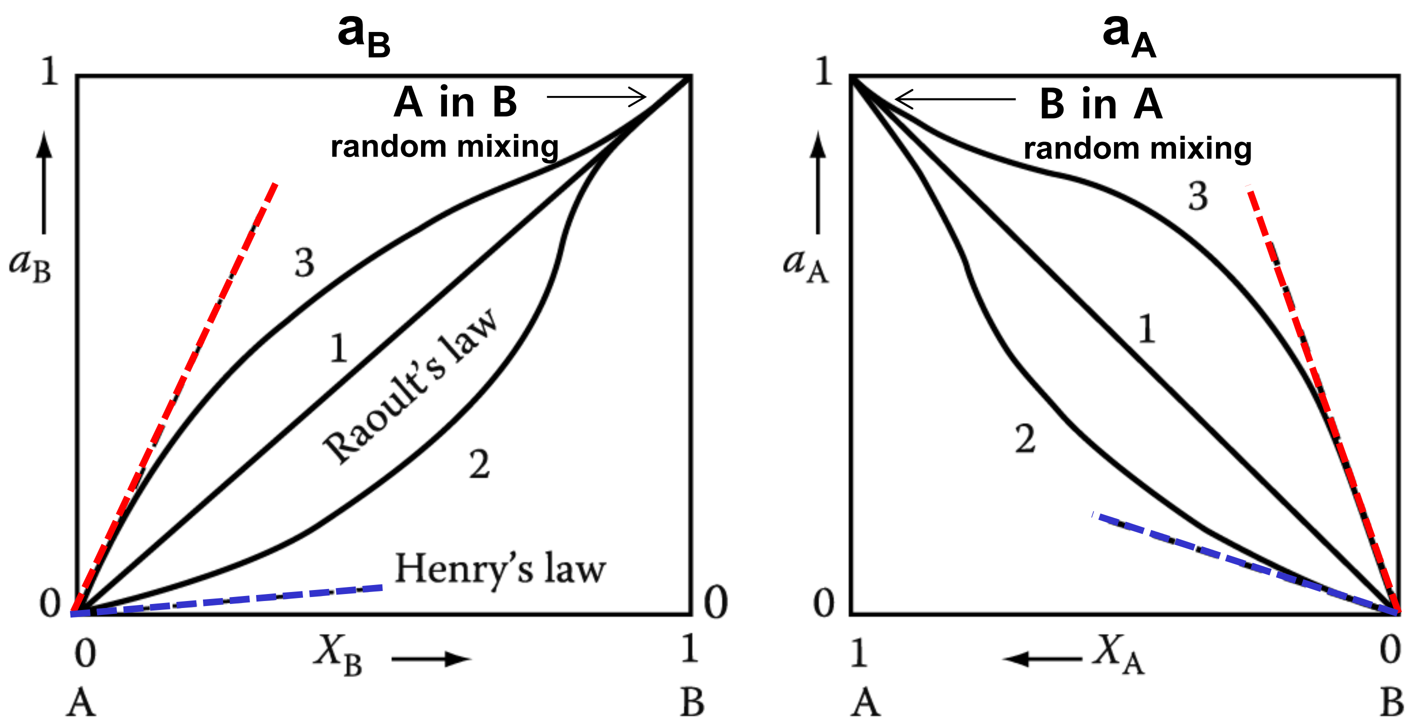
Degree of non-ideality

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

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

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

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



(a)

(b)

Line 1 : (a) $a_B=X_B$, (b) $a_A=X_A$ ideal solution…Rault's law

Line 2 : (a) $a_B<X_B$, (b) $a_A<X_A$ $\Delta H_{mix}<0$

Line 3 : (a) $a_B>X_B$, (b) $a_A>X_A$ $\Delta H_{mix}>0$

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

Q7: “Chemical equilibrium of multi-phases”?

⇨ **Gibbs Phase Rule**

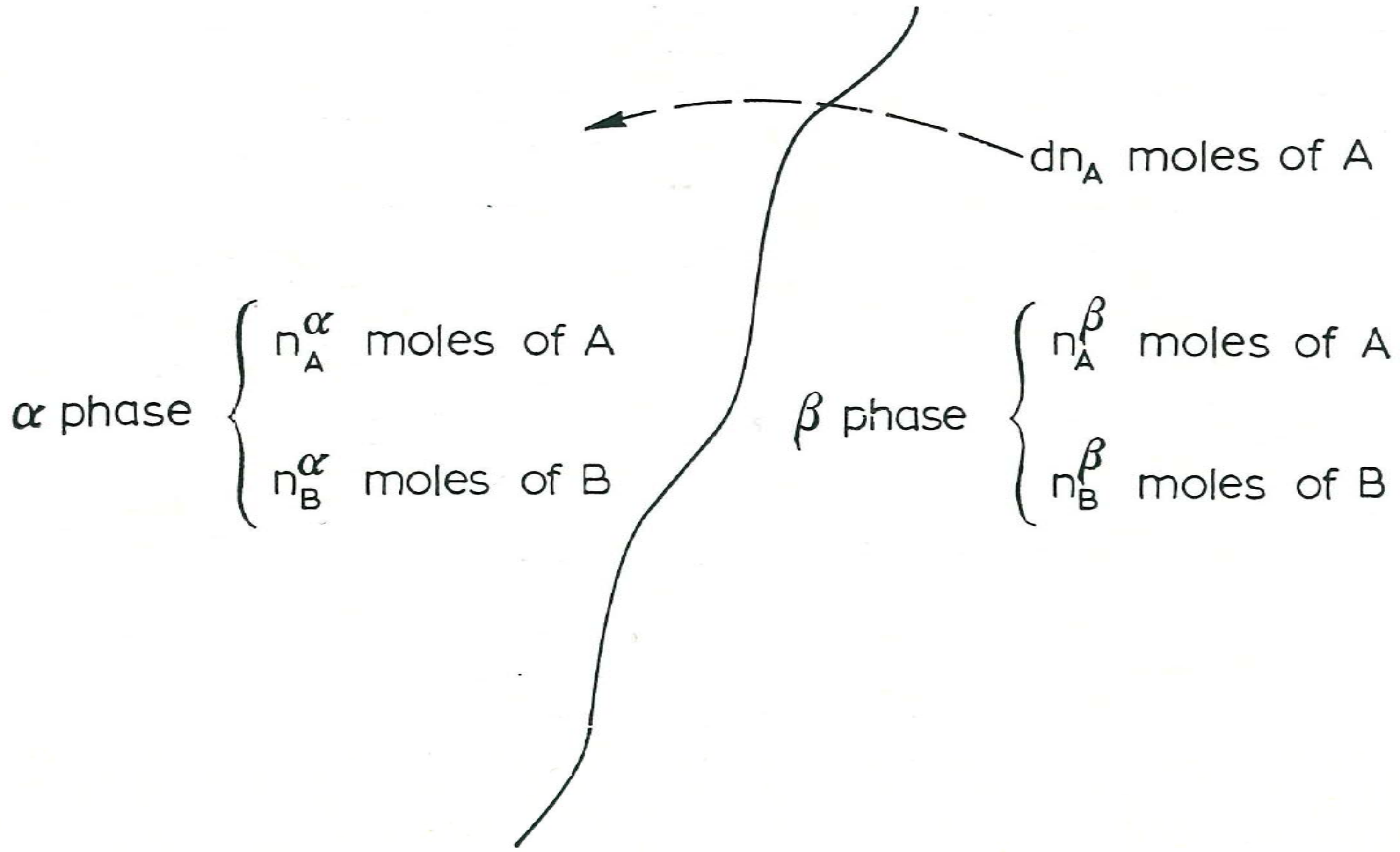


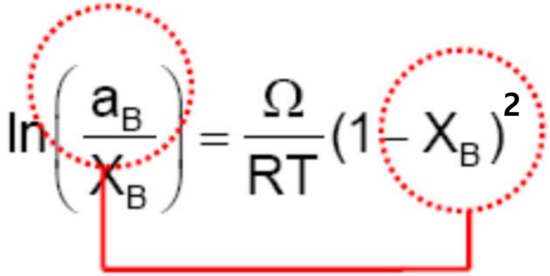
Fig. 10. Transfer of dn_A moles of component A from the β to the α phase.

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

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

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

γ_A : activity coefficient



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

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

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

Chemical Equilibrium (μ, a) → multiphase and multicomponent

$$(\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \ldots), (a_i^\alpha = a_i^\beta = a_i^\gamma = \ldots)$$

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

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

⋮

The Gibbs Phase Rule

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

= the number of variables – the number of constraints

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

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

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

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

- Number of variable can be controlled with maintaining equilibrium

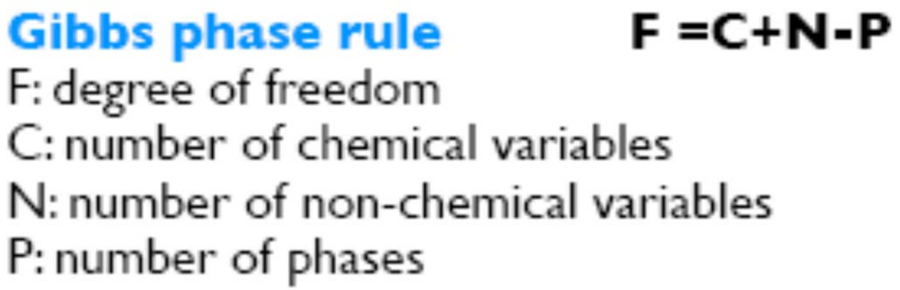
$$f = (c-1)p + p + p - (p-1)c - (p-1) - (p-1) = c - p + 2$$

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

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

The Gibbs Phase Rule

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



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

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

In general, Gibbs' rule then follows, as:

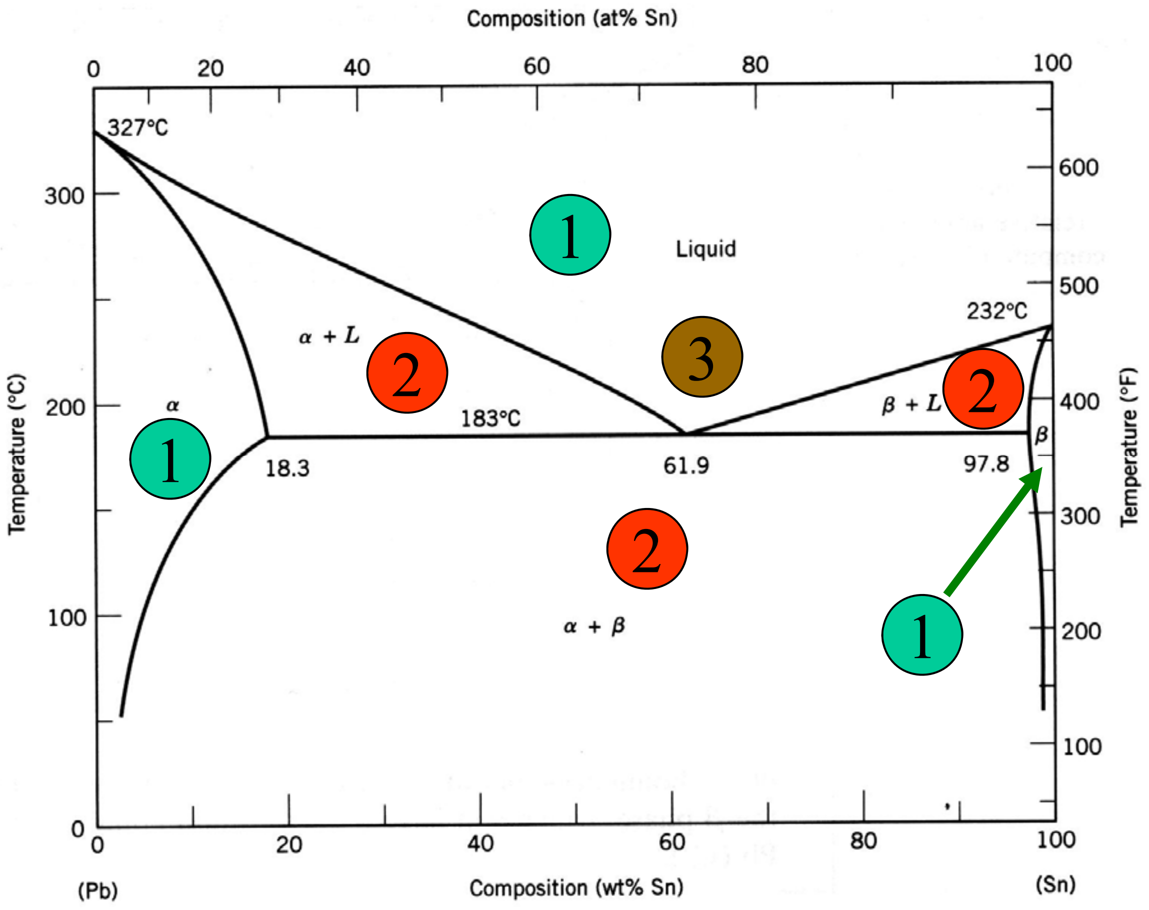
$$F = C - P + 2 \quad \text{(from T, P).}$$

From Wikipedia, the free encyclopedia

The Gibbs Phase Rule

For Constant Pressure,

$P + F = C + 1$



① **single phase**

$F = C - P + 1$

$= 2 - 1 + 1$

$= 2$

can vary T and composition independently

② **two phase**

$F = C - P + 1$

$= 2 - 2 + 1$

$= 1$

can vary T *or* composition

③ **eutectic point**

$F = C - P + 1$

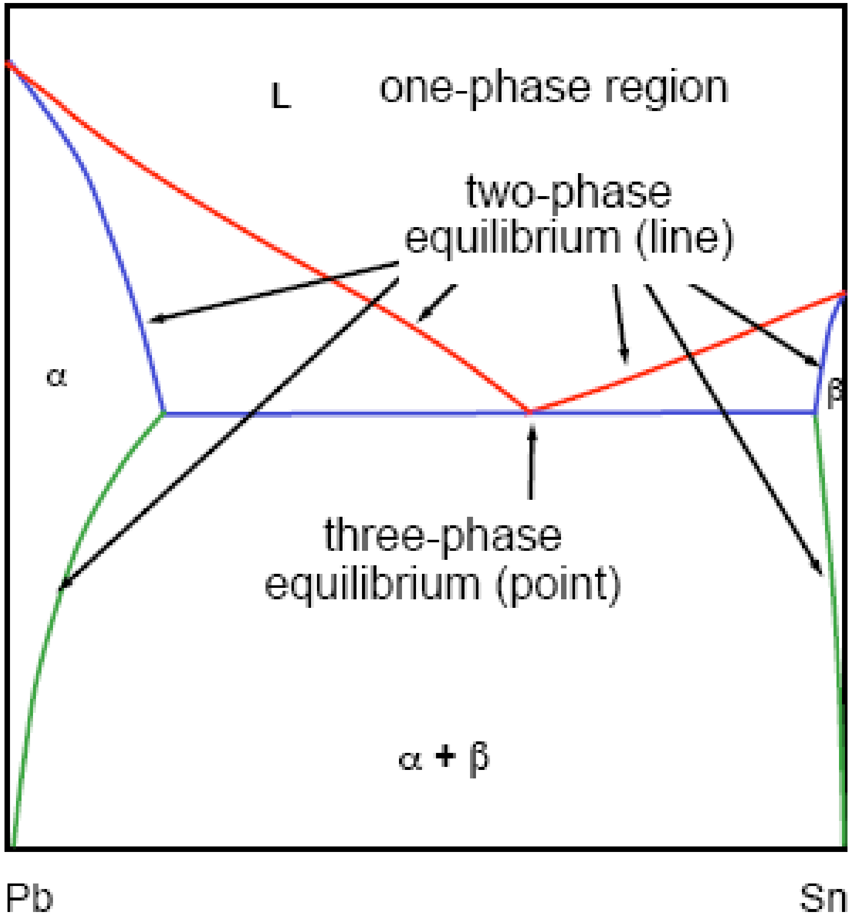
$= 2 - 3 + 1$

$= 0$

can't vary T or composition

The Gibbs Phase Rule

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



- 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

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

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

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

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

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

- Chemical equilibrium → Gibbs phase rule