2015 Fall

"Phase Transformation *in* Materials"

09.21.2015

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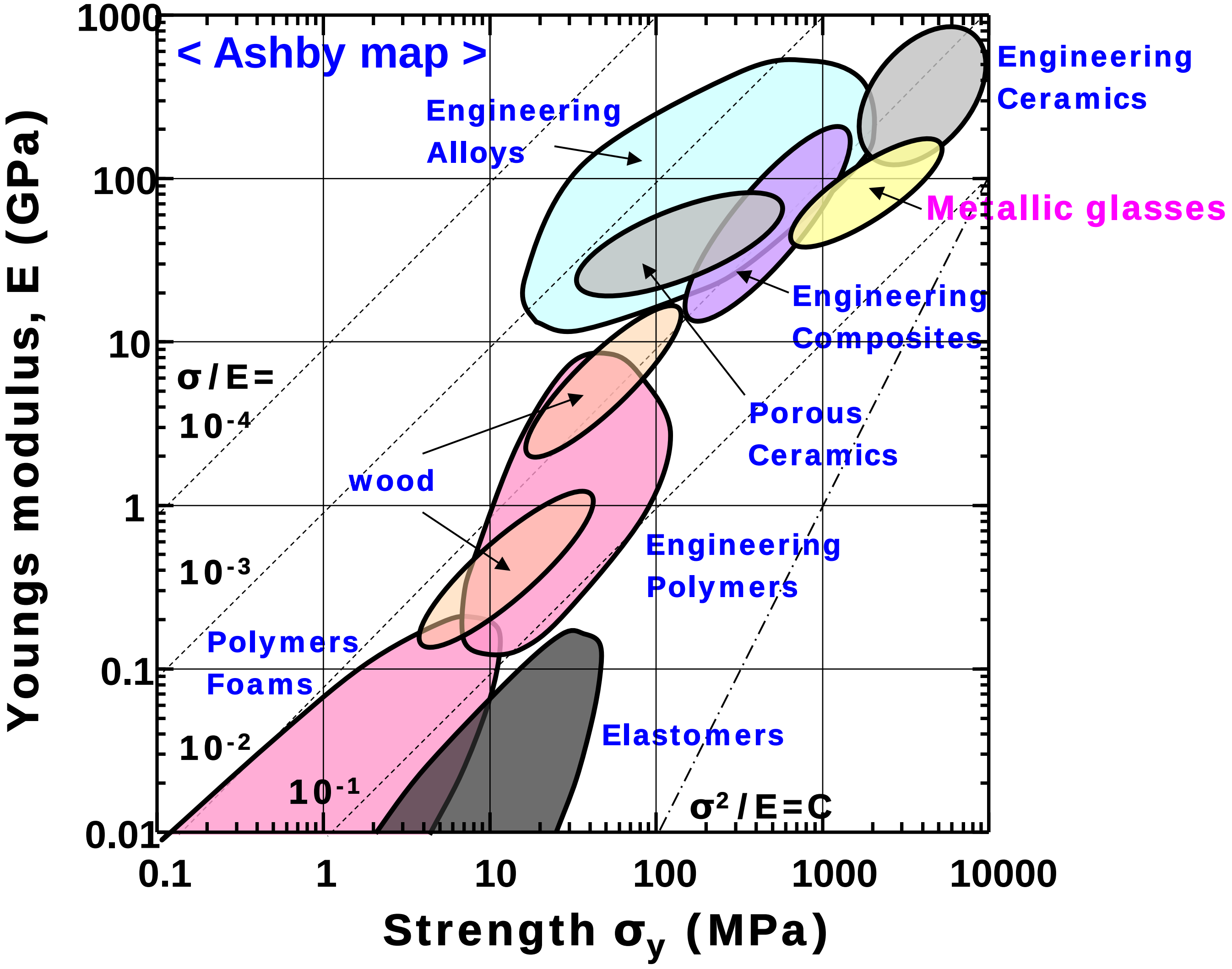
Q: Materials design

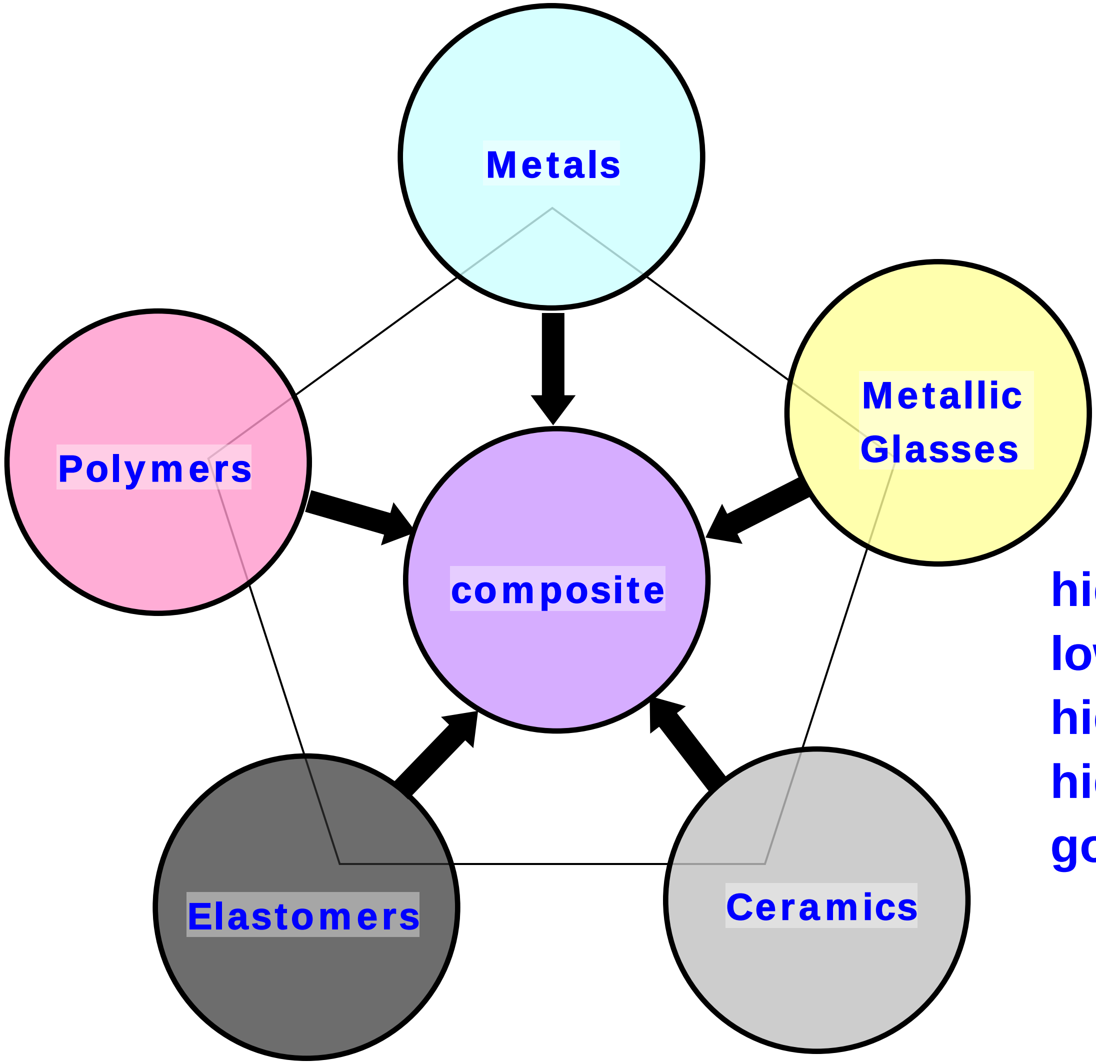
Proposal for final presentation?

Materials Design



Materials Design

Menu of engineering materials



High GFA

High plasticity

higher strength
lower Young's modulus
high hardness
high corrosion resistance
good deformability
⋮

Topic proposal for materials design

Please submit 3 materials that you want to explore for materials design and do final presentations on in this semester. Please make sure to thoroughly discuss why you chose those materials (up to 1 page on each topic). The proposal is due by September 23rd on eTL.

Ex) stainless steel/ graphene/ OLED/
Bio-material/ Shape memory alloy
Bulk metallic glass, etc.

Contents for previous class

- Equilibrium in Heterogeneous Systems

- Binary phase diagrams

How the equilibrium state of an alloy can be obtained from the free energy curves at a given temperature

→ How equilibrium is affected by temperature

a) Variation of temp.: $G^L > G^S$
b) At low temp. (∵ decrease of $-T\Delta S_{mix}$ effect): Decrease of curvature of G curve

1) Simple Phase Diagrams

2) Systems with miscibility gap

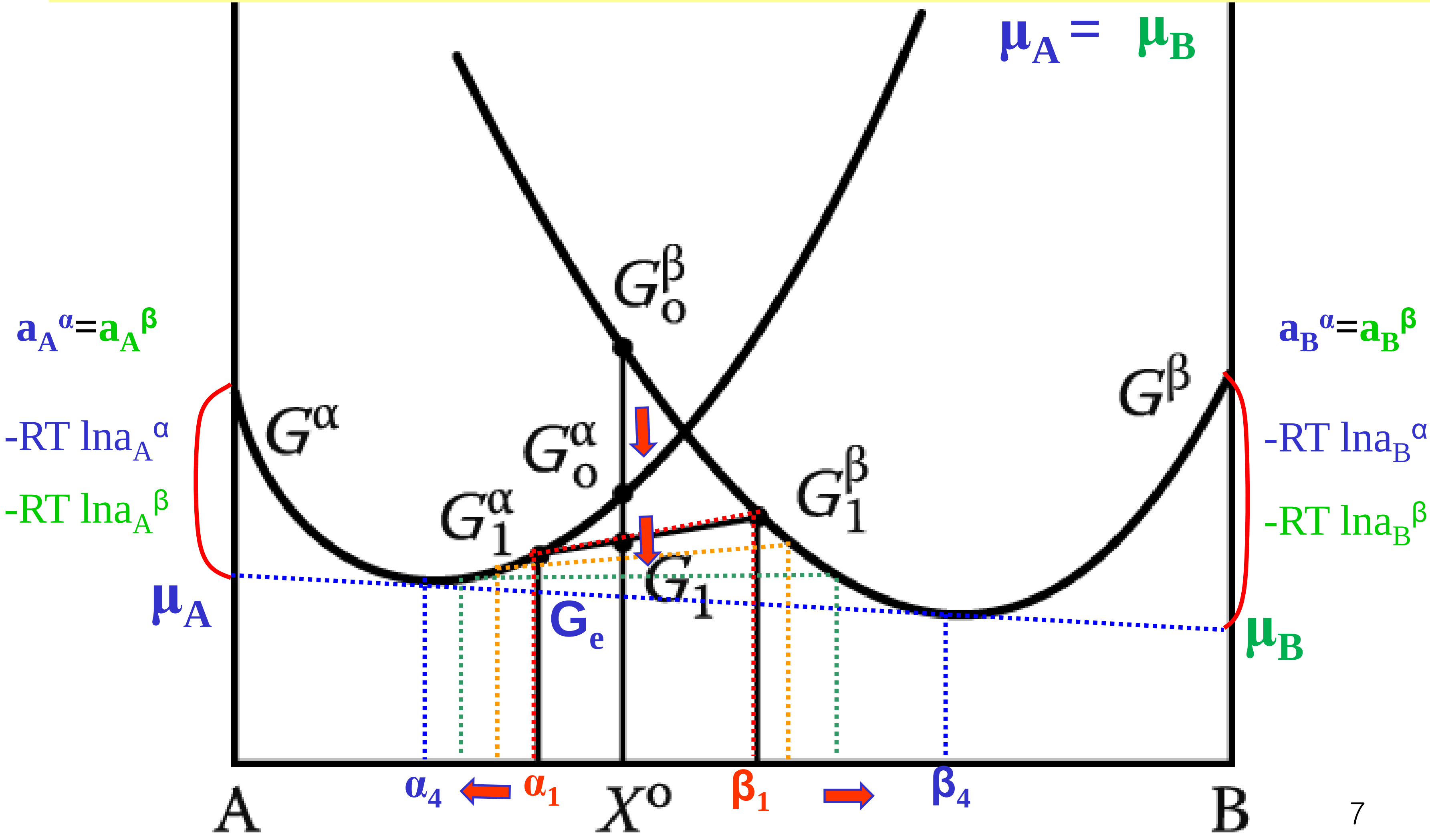
4) Simple Eutectic Systems

3) Ordered Alloys

5) Phase diagrams containing intermediate phases

Equilibrium in Heterogeneous Systems

In X^0, $G_0^\beta > G_0^\alpha > G_1$ → $\alpha + \beta$ separation → unified chemical potential



1.5 Binary phase diagrams

1) Simple Phase Diagrams

1) Variation of temp.: $G^L > G^s$

2) Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

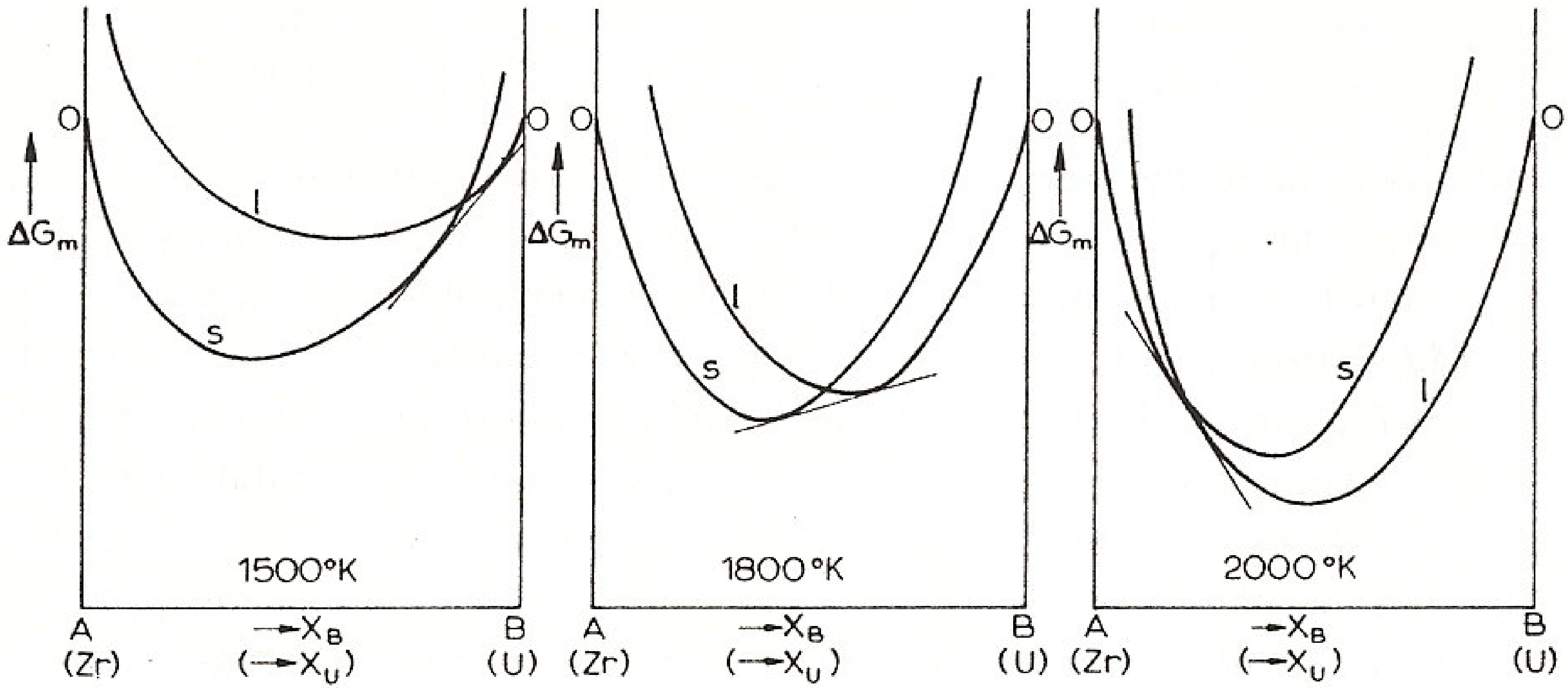


Fig. 26. Free energy curves for liquid and solid phases in the U–Zr system at 1500°, 1800° and 2000 °K.

1.5 Binary phase diagrams

1) Simple Phase Diagrams

1) Variation of temp.: $G^L > G^s$

2) Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

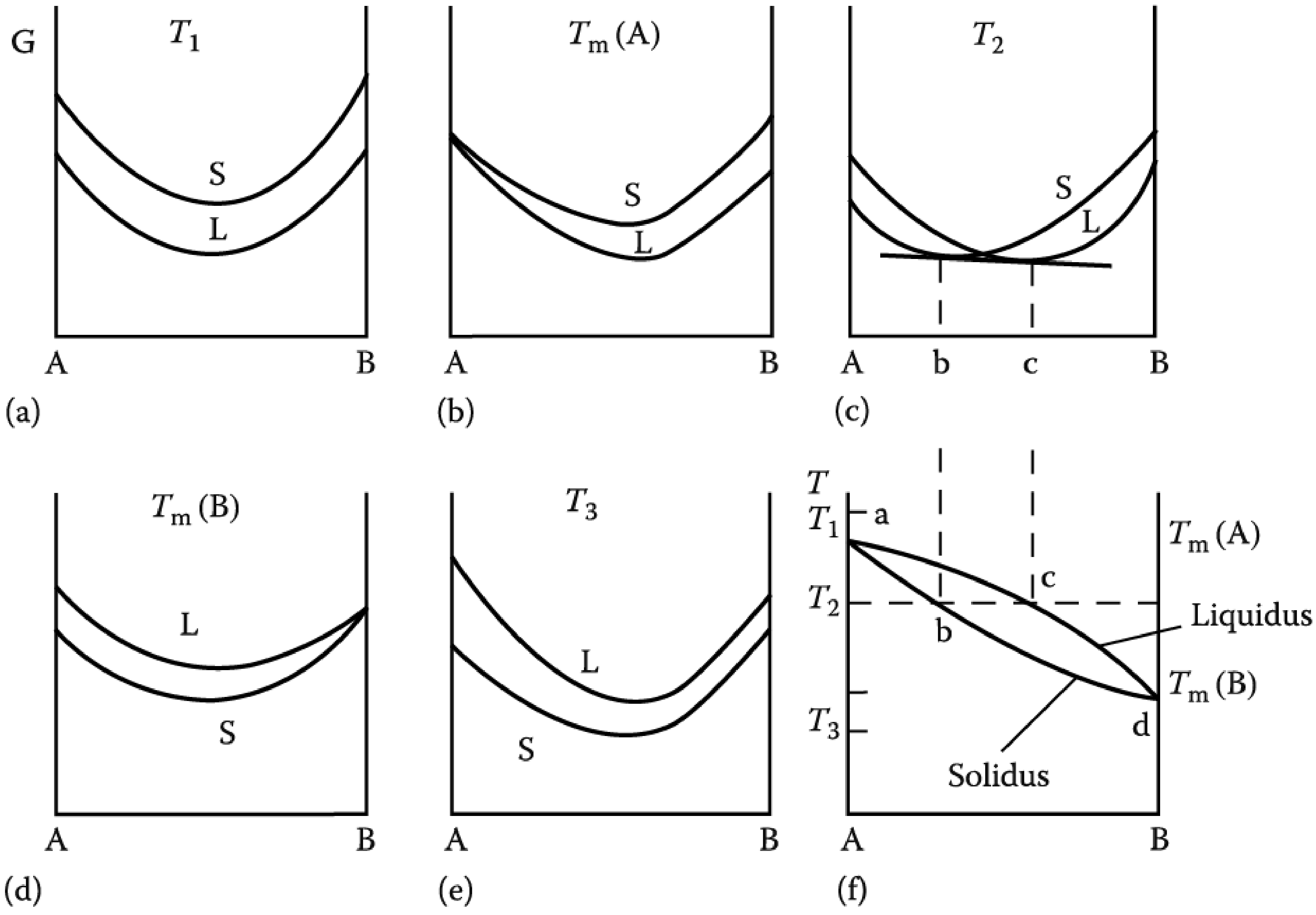
Assumption:

(1) completely miscible in solid and liquid.

(2) Both are ideal soln.

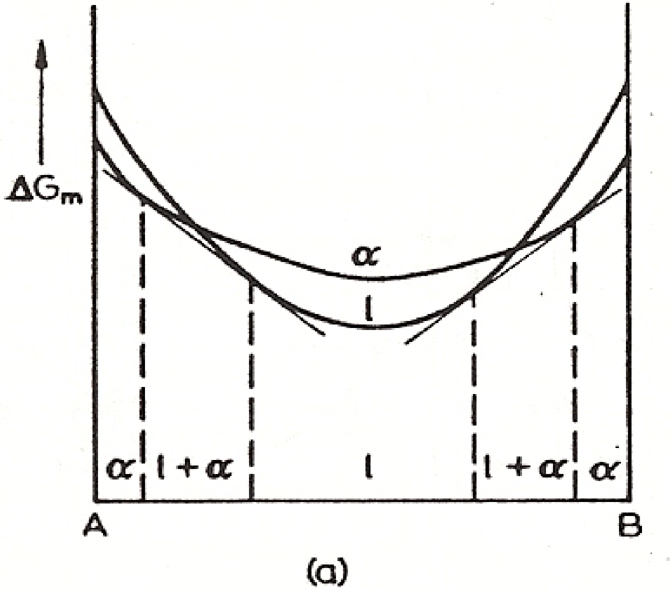
(3) $T_m(A) > T_m(B)$

(4) $T_1 > T_m(A) > T_2 > T_m(B) > T_3$

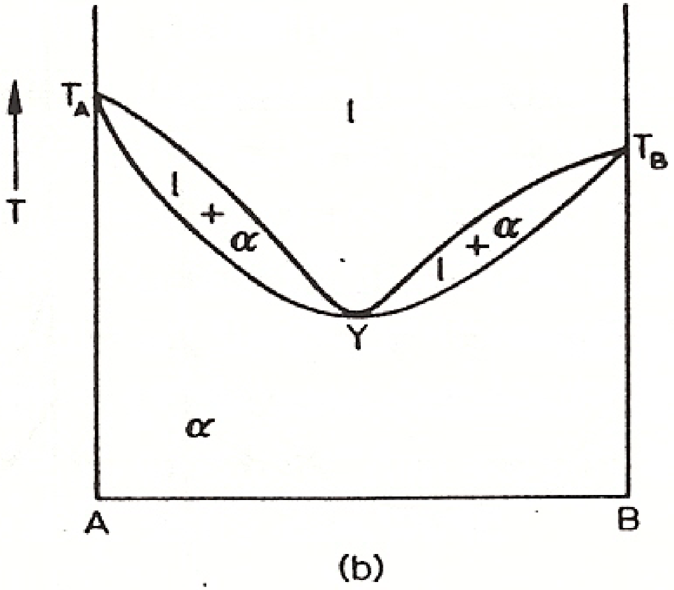


2) Variant of the simple phase diagram

$$\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$$



(a)



(b)

congruent minima

2) Variant of the simple phase diagram

$$\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$$

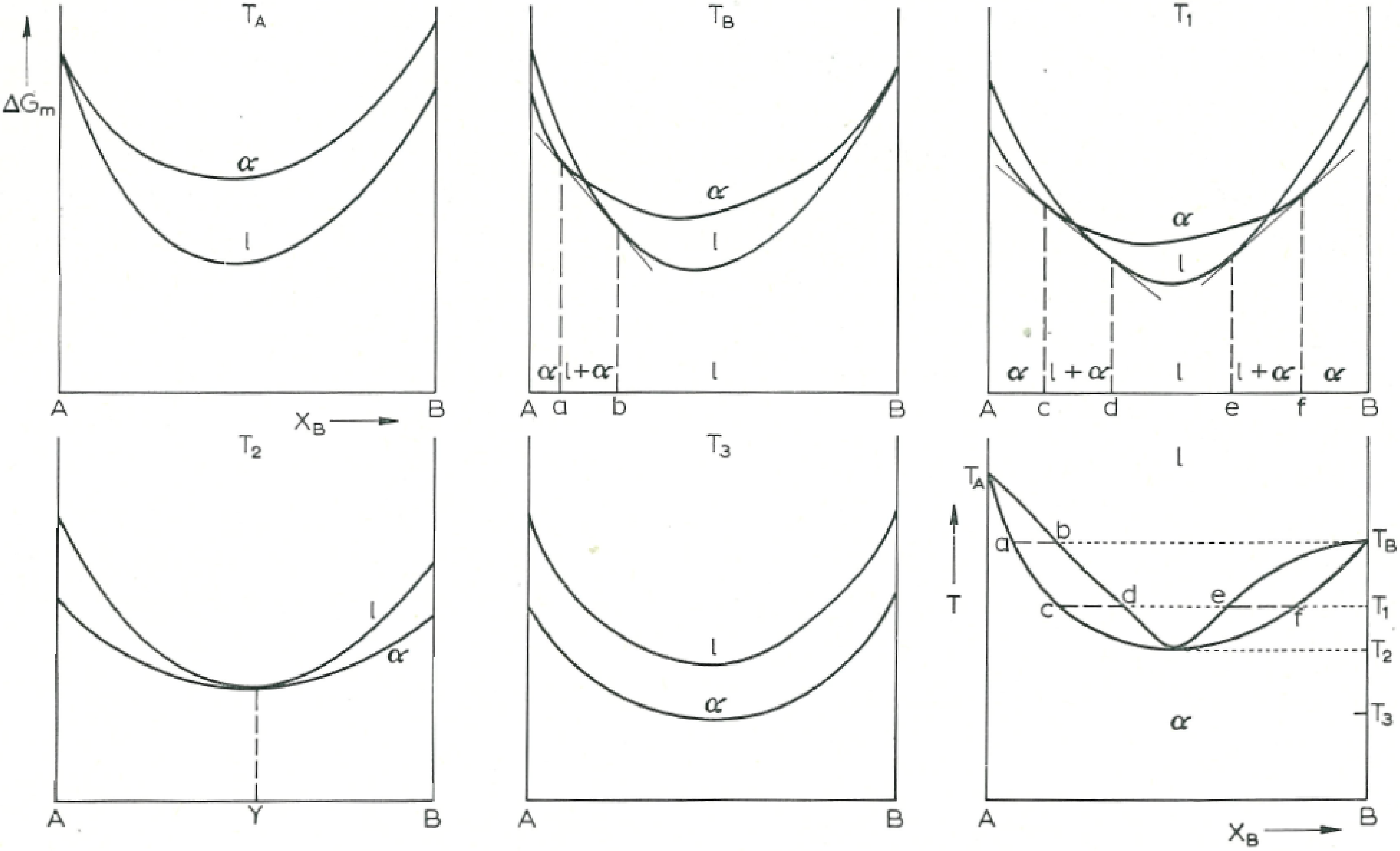
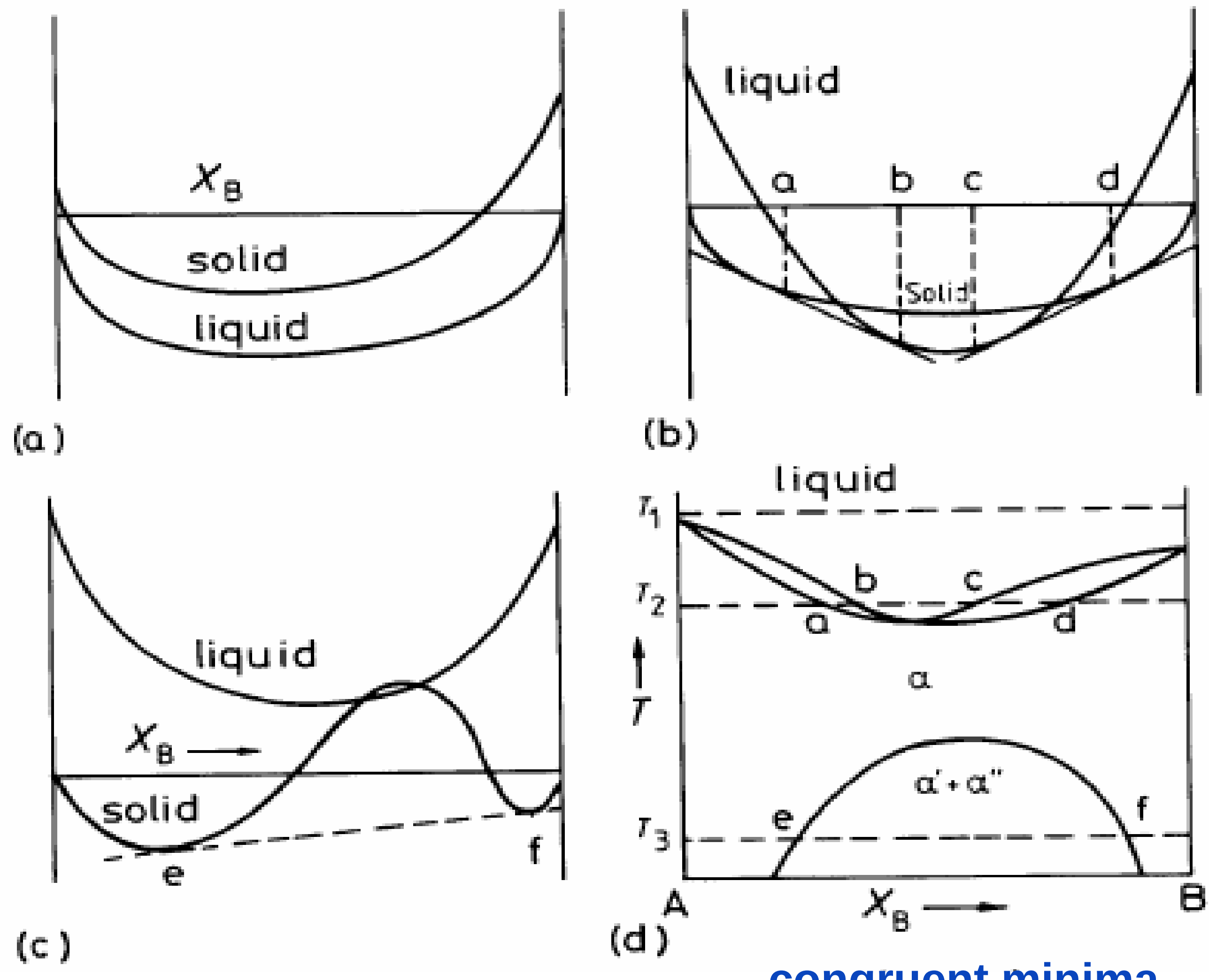


Fig. 30. Derivation of the phase diagram (Fig. 29b) from free energy curves for the liquid and solid phases. $T_A > T_B > T_1 > T_2 > T_3$.

2) Variant of the simple phase diagram

Systems with miscibility gab $\Delta H_{mix} > 0 \quad \Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix}$



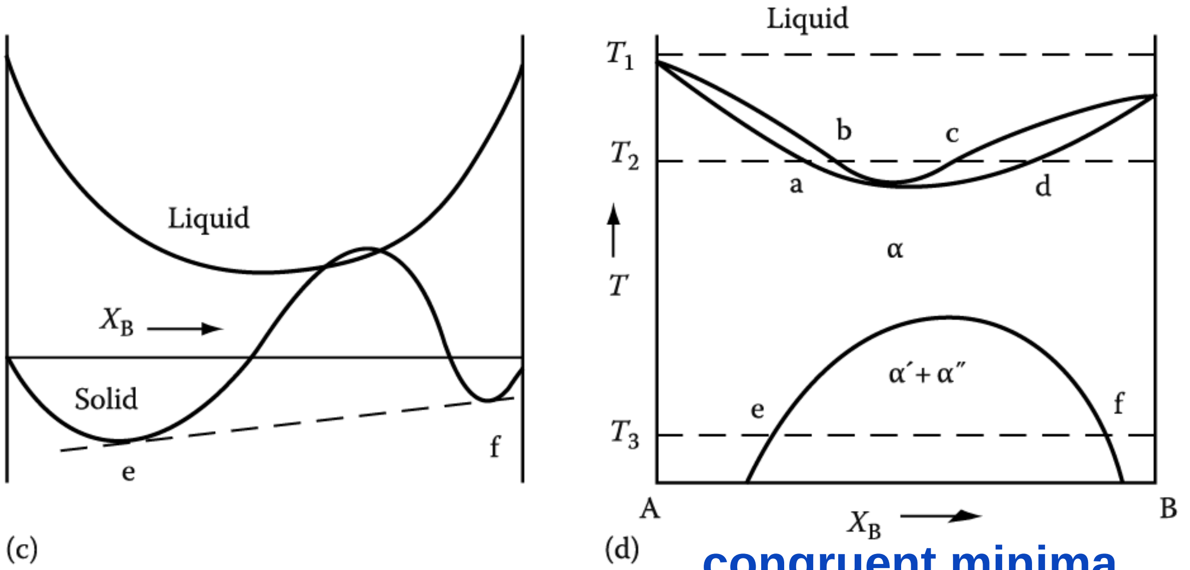
congruent minima

1.5 Binary phase diagrams

2) Systems with miscibility gab

$$\Delta H^{L}_{mix} = 0 \qquad \Delta H^{S}_{mix} > 0$$

- **When A and B atoms dislike each other,** $\Delta H_{mix} > 0$
- **In this case, the free energy curve at low temperature has a region of negative curvature,** $\dfrac{d^2G}{dX_B^2} < 0$
- **This results in a ‘miscibility gap’ of α′ and α″ in the phase diagram**



congruent minima

1.5 Binary phase diagrams

4) Simple Eutectic Systems $\Delta H_{mix}^{L} = 0 \quad \Delta H_{mix}^{S} >> 0$

- **$\Delta H_m >> 0$ and the miscibility gap extends to the melting temperature.** **(when both solids have the same structure.)**

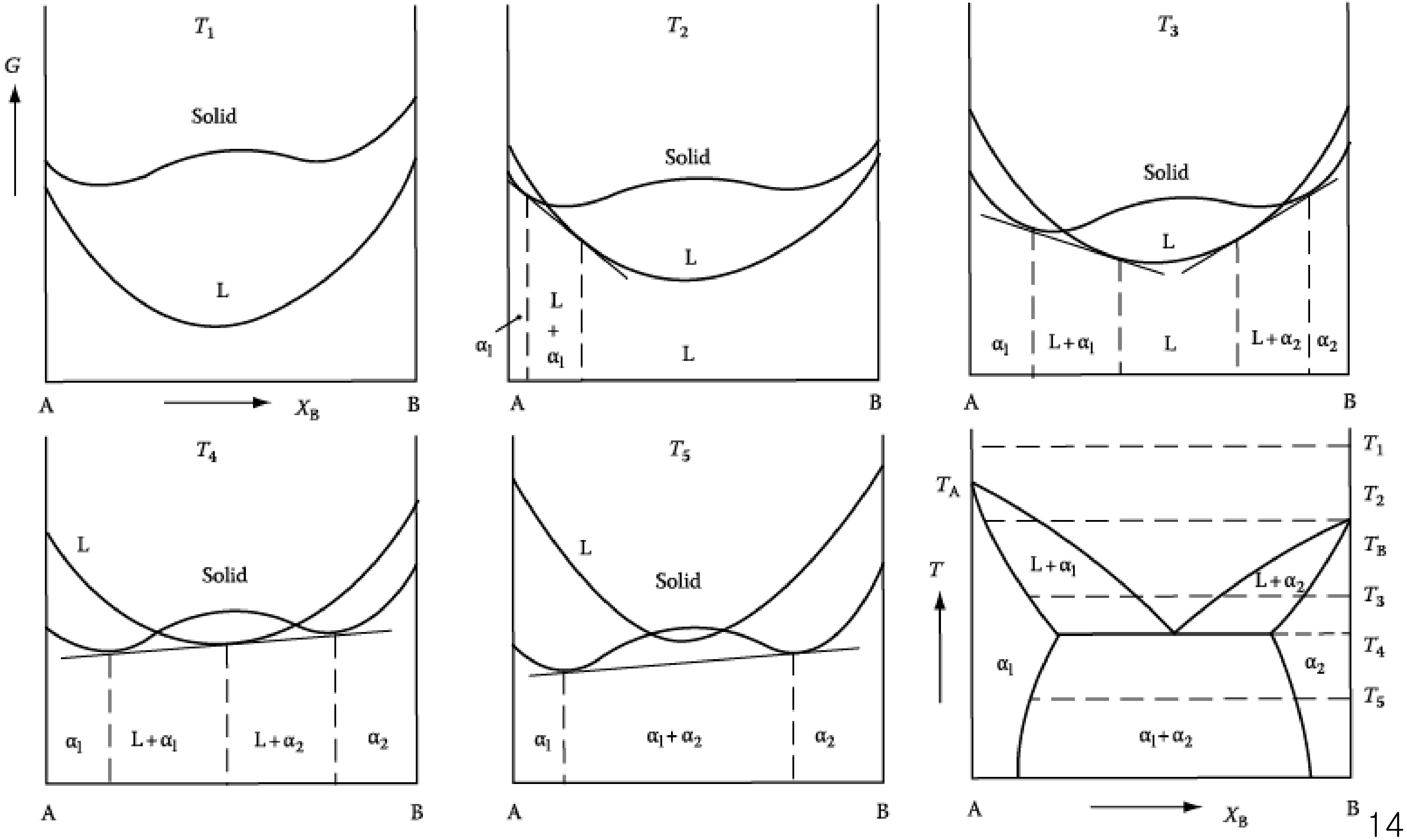


Fig. 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure.

(when each solid has the different crystal structure.)

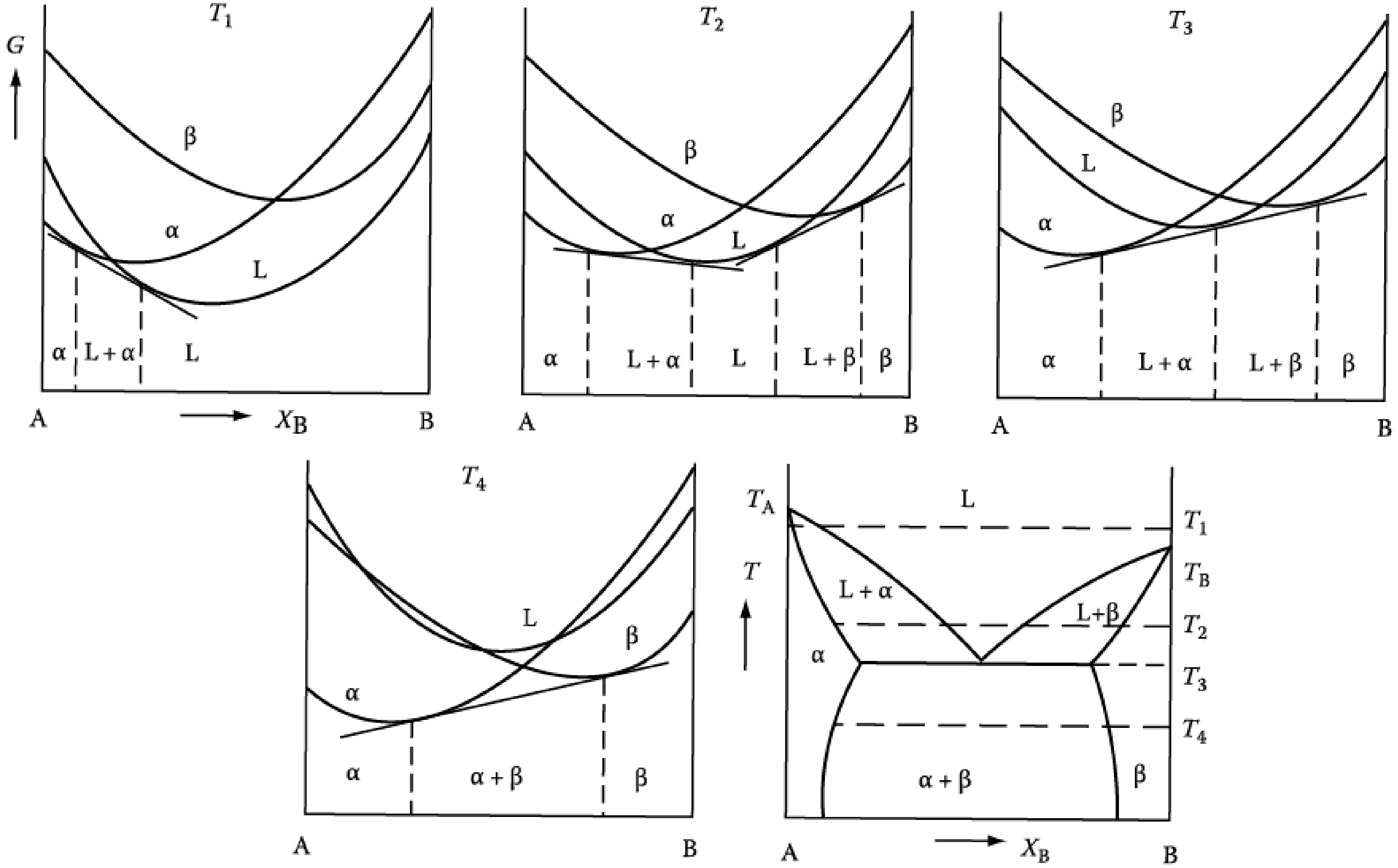


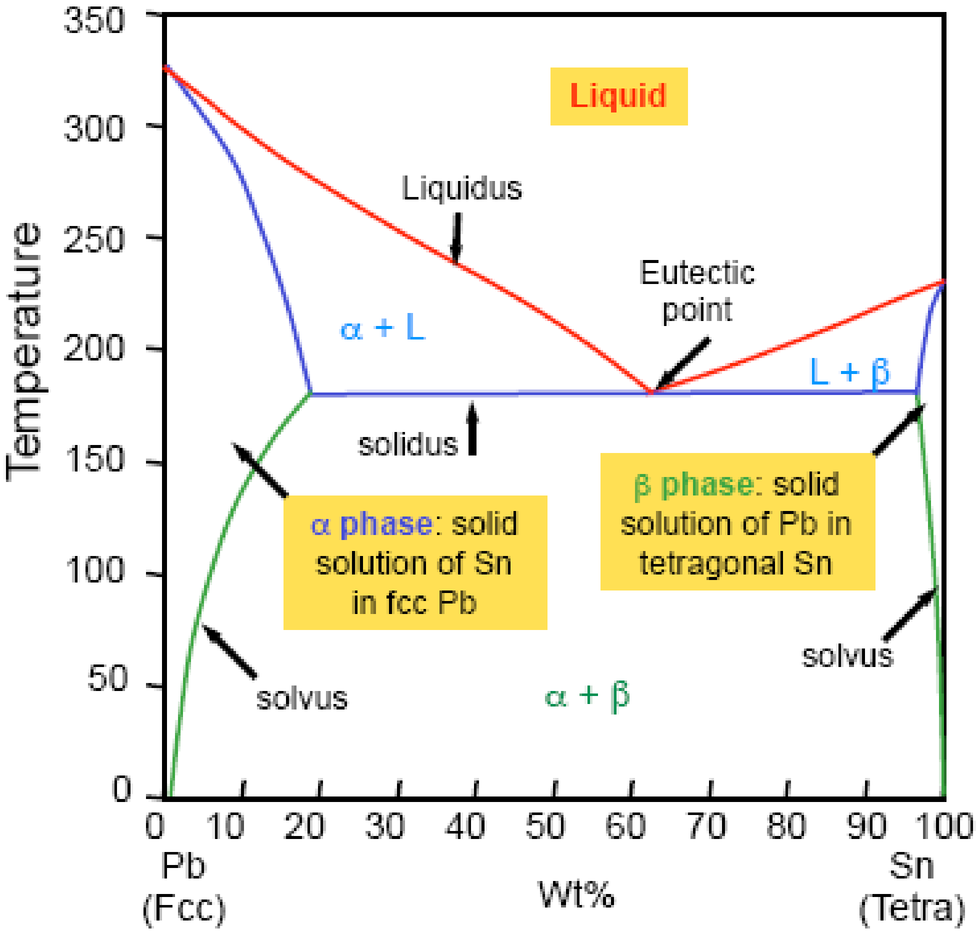
Fig. 1.32 The derivation of a eutectic phase diagram where each solid phases has a different crystal structure.

Eutectic Systems

$$\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} >> 0$$

The Pb-Sn system is characteristic of a valley in the middle. Such system is known as the **Eutectic** system. The central point is the Eutectic point and the transformation though this point is called Eutectic reaction: **L**✦α+β

Pb has a fcc structure and Sn has a tetragonal structure. The system has three phases: L, α and β.


Pb-Sn phase diagram

Solidification of Eutectic Systems

Alloy II

At point 1: Liquid

Solidification starts at eutectic point (where liquidus and solidus join)

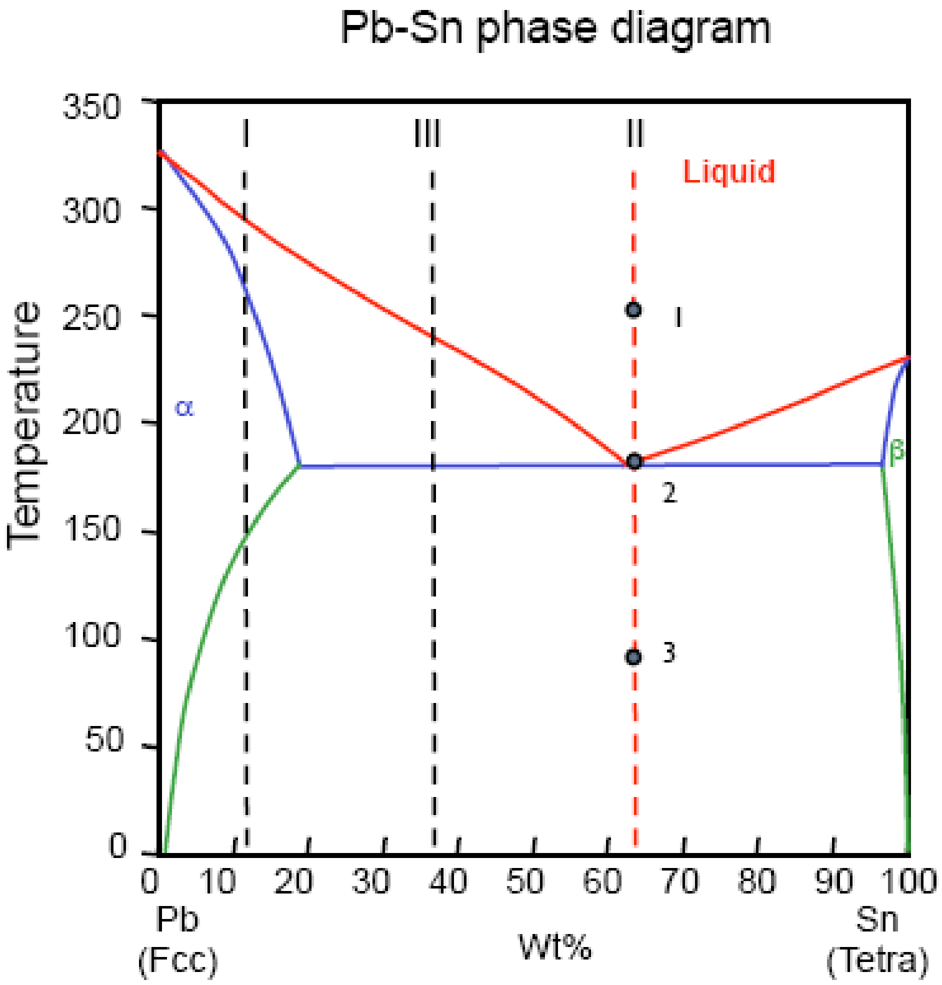
At point 2: L✦(α+β) (eutectic reaction)

The amounts of α and β increase in proportion with time.

Solidification finishes at the same temperature.

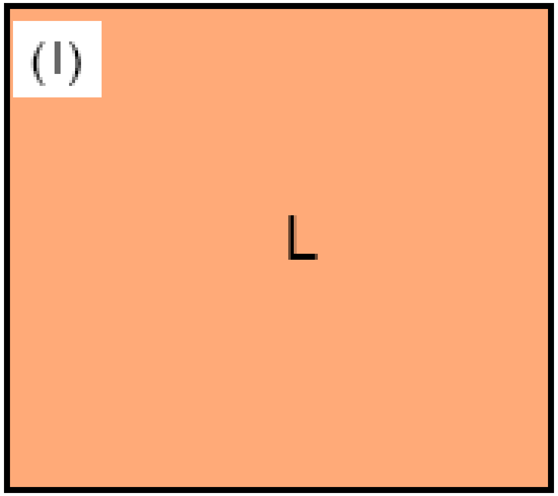
At point 3: α+β

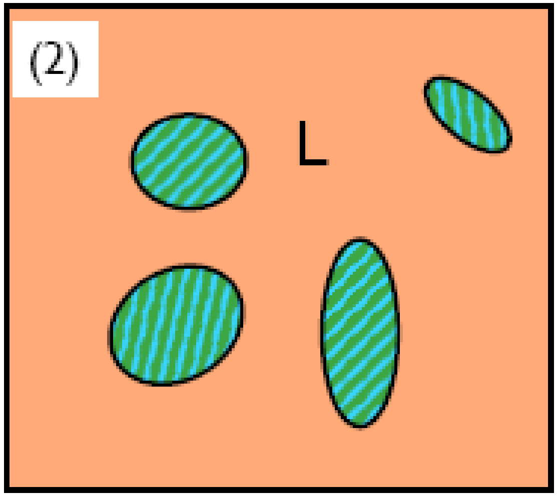
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β.



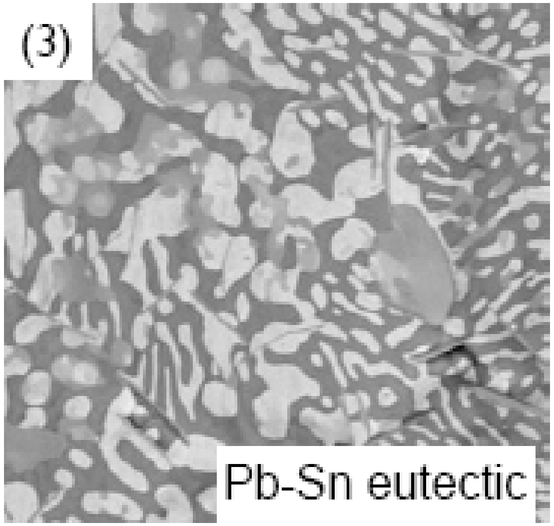
1.5 Binary phase diagrams

Alloy II





Nucleation of colonies of α and β laminates



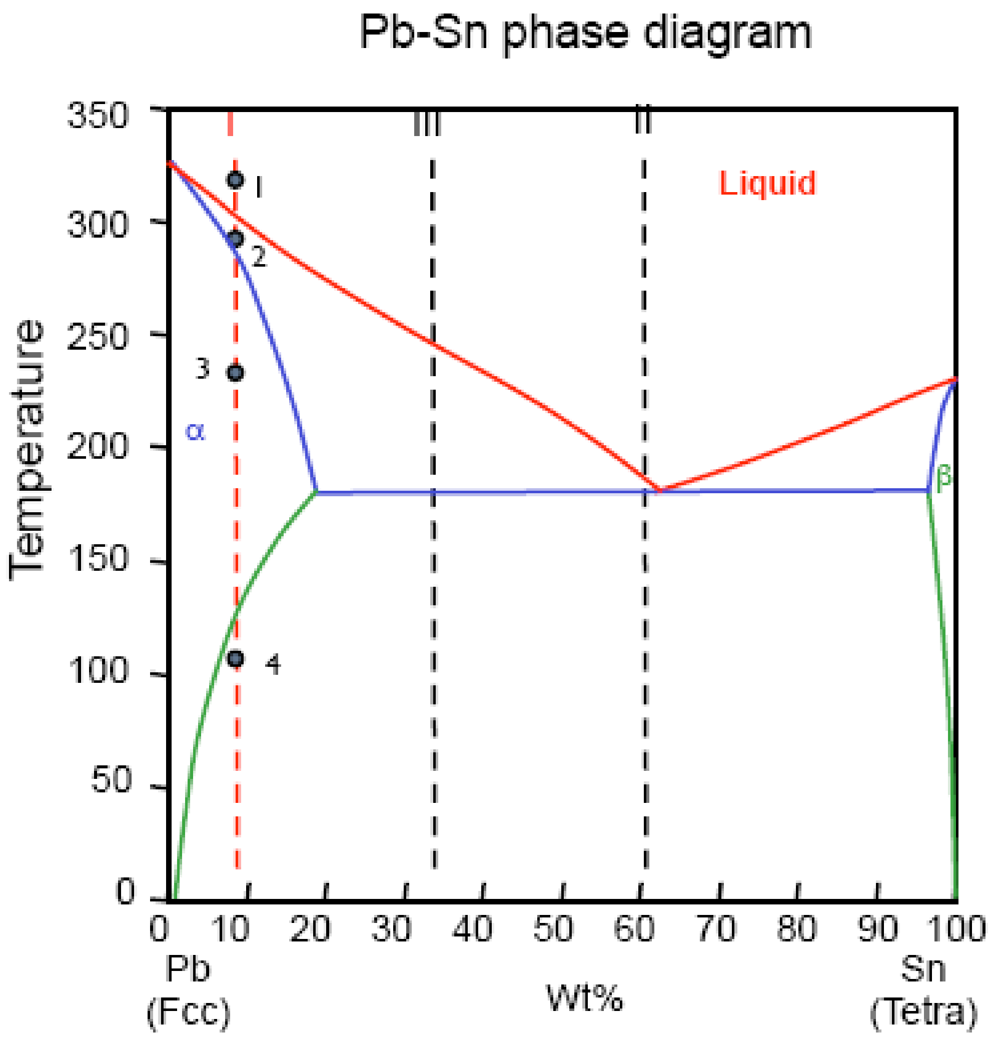
Eutectic structure of intimate mix of α and β to minimise diffusion path

Solidification of Eutectic Systems

Alloy I :

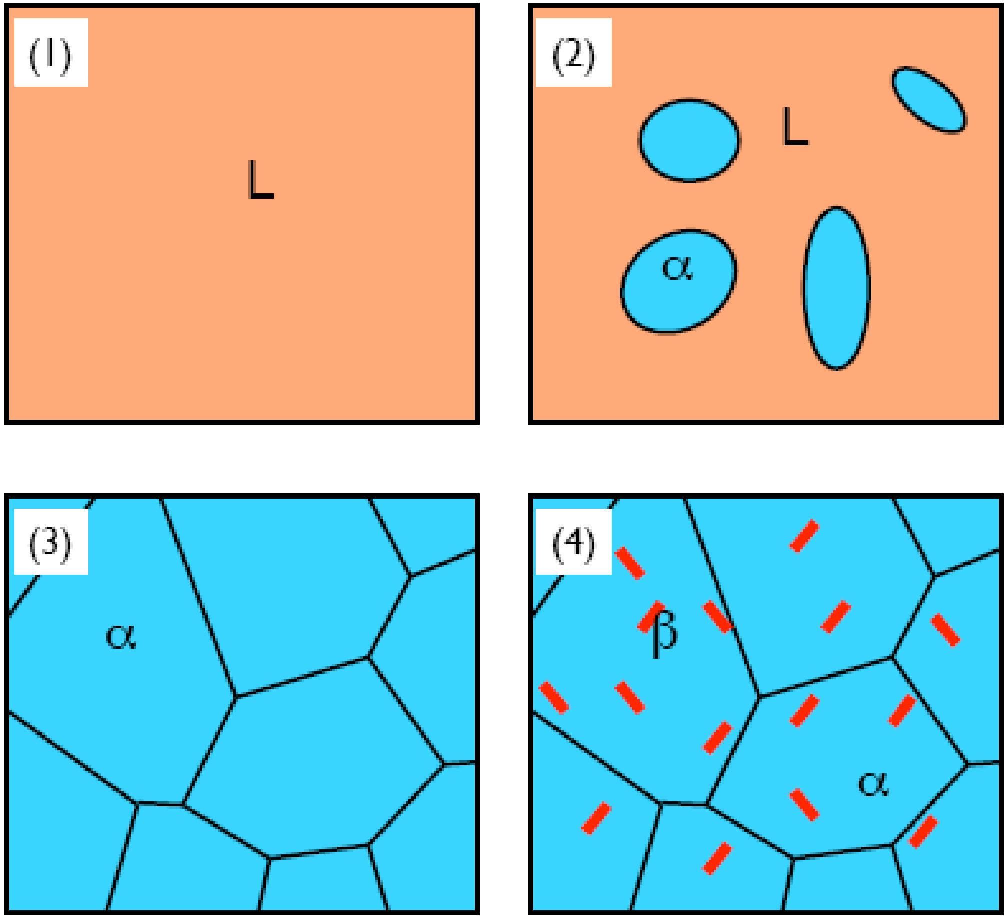
At point 1: Liquid
Solidification starts at liquidus
At point 2: L+α
The amount α ↑ with ↓ T
Solidification finishes at solidus
At point 3: α
Precipitation starts at solvus
At point 4: α+β
Further cooling leads to formation and growth of more β precipitates whereas Sn% in α decreases following the solvus.

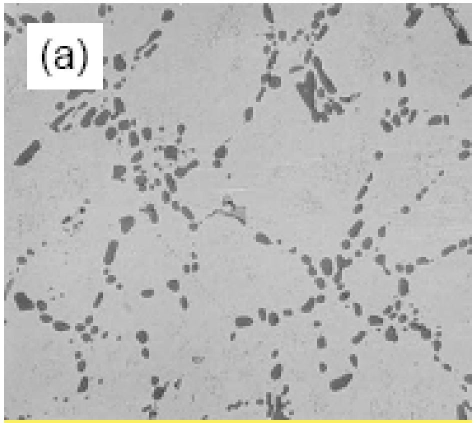
Pb-Sn phase diagram



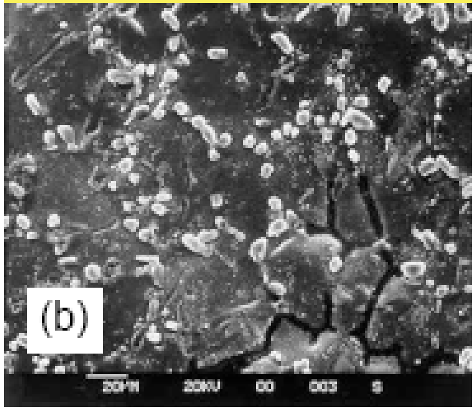
1.5 Binary phase diagrams

Alloy I





Precipitates in a Al-Si alloy;
(a) optical microscopy,
(b) scanning electron
microscopy of fracture surface



1.5 Binary phase diagrams

Solidification of Eutectic Systems

Alloy III

At point 1: Liquid

Solidification starts at liquidus

At point 2: L✦L+α (pre-eutectic α)

The amount α ↑ with ↓T

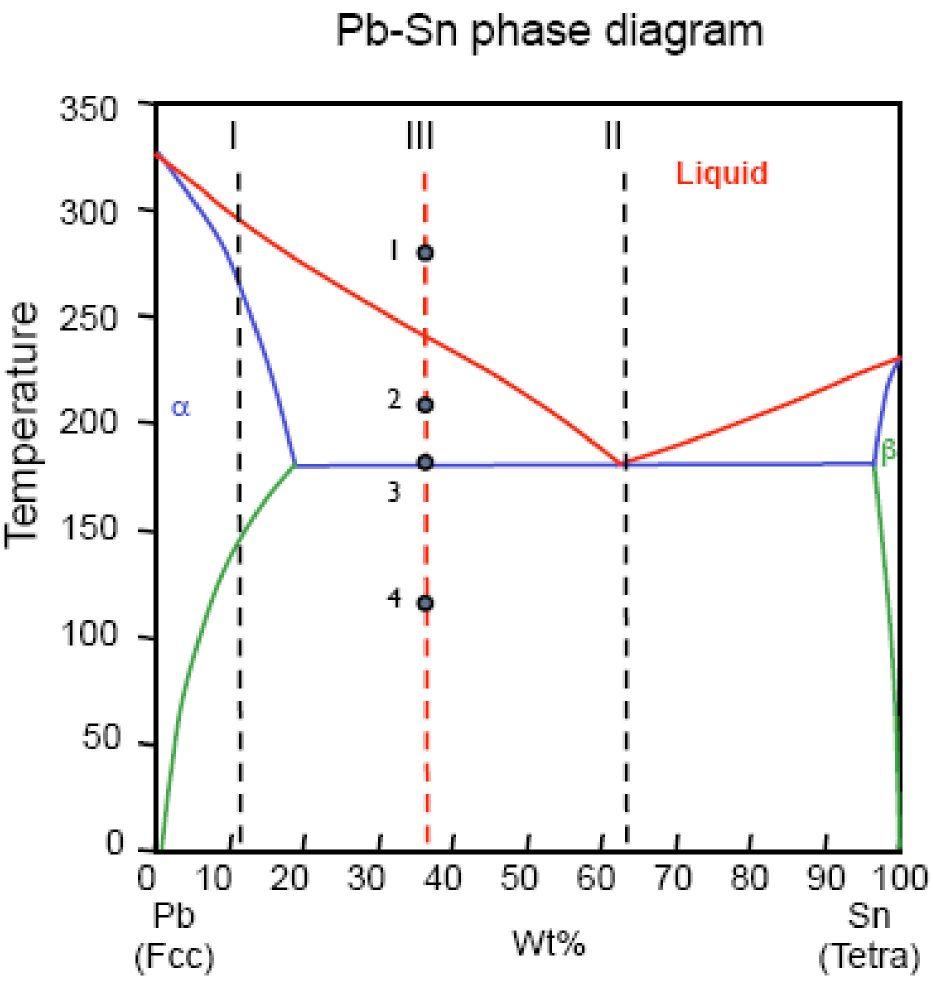
At point 3: L✦ (α+β) (eutectic reaction)

Solidification finishes at the eutectic temperature

At point 4: α+β (pre-eutectic α + (α+β) eutectic mixture)

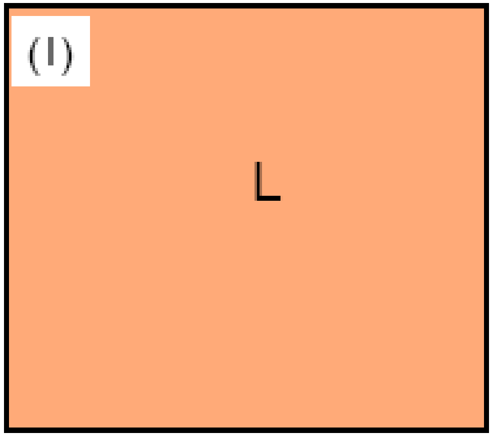
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β.

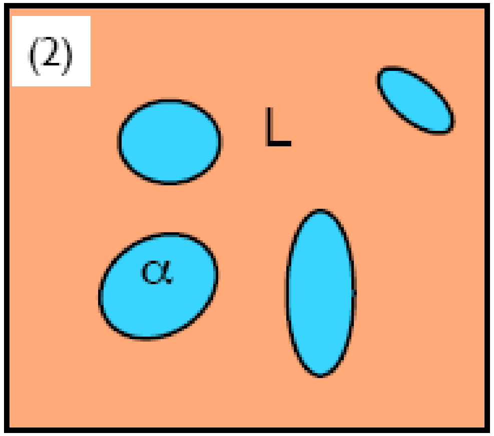
The cooling curve of this alloy is a combination of the two cooling curves shown in slide 9.

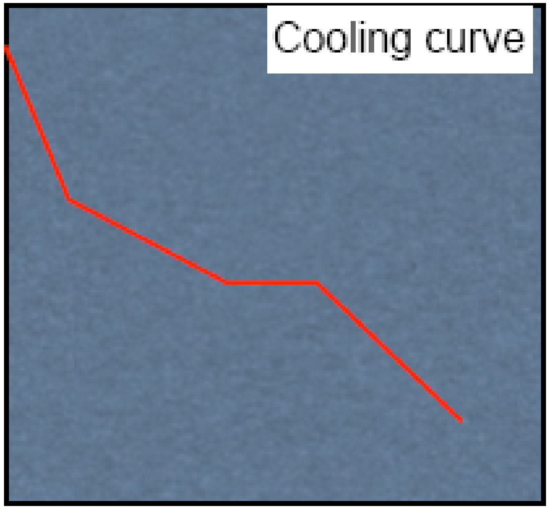


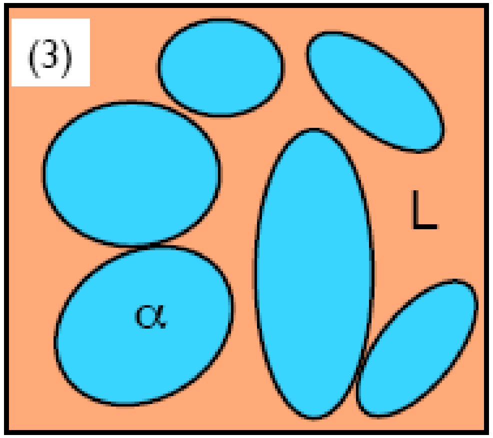
1.5 Binary phase diagrams: Hypoeutectic

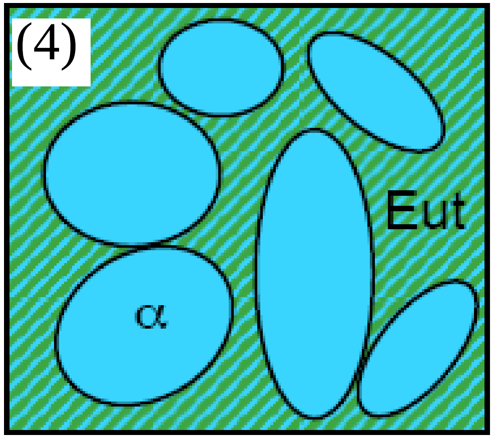
Alloy III

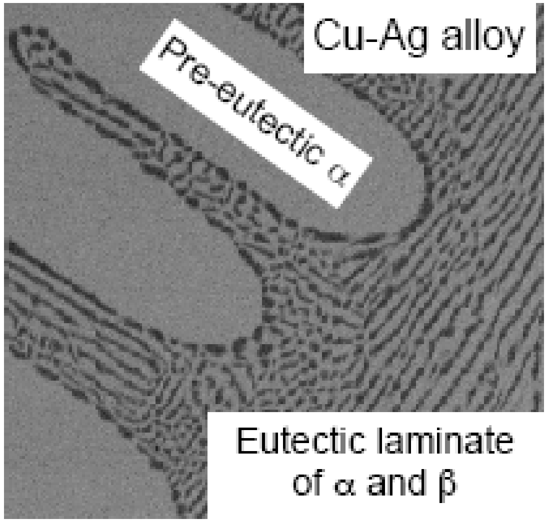





Cooling curve



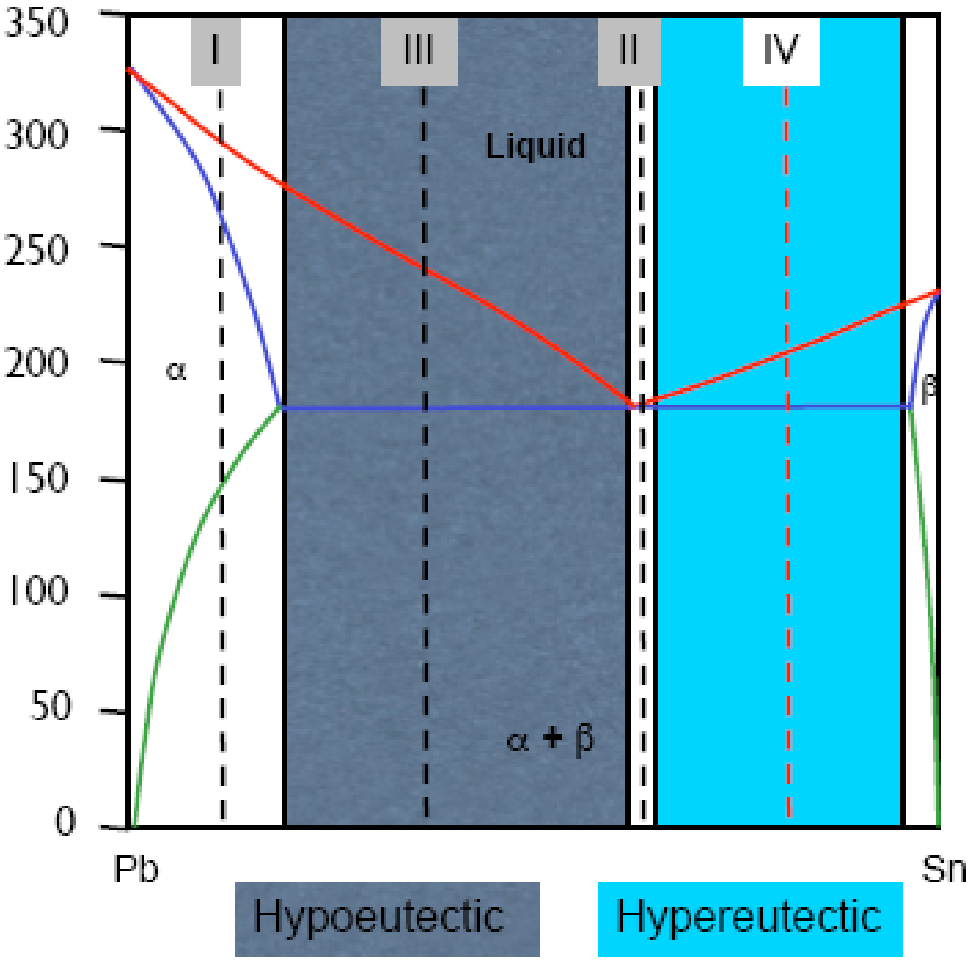



Cu-Ag alloy

Solidification of Eutectic Systems

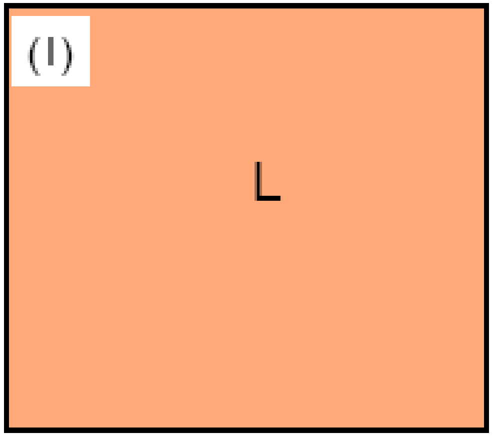
Alloy IV

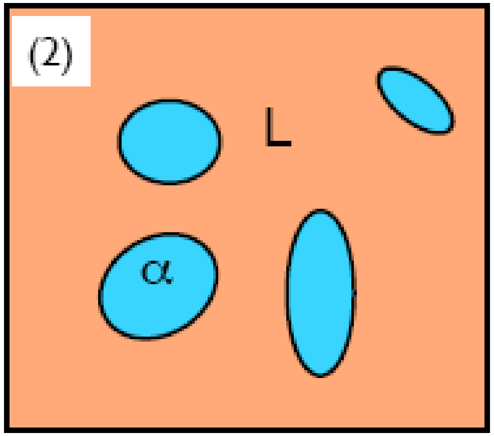
Can you describe the solidification process of alloy IV, including microstructure evolution, morphology of phases and cooling curve?

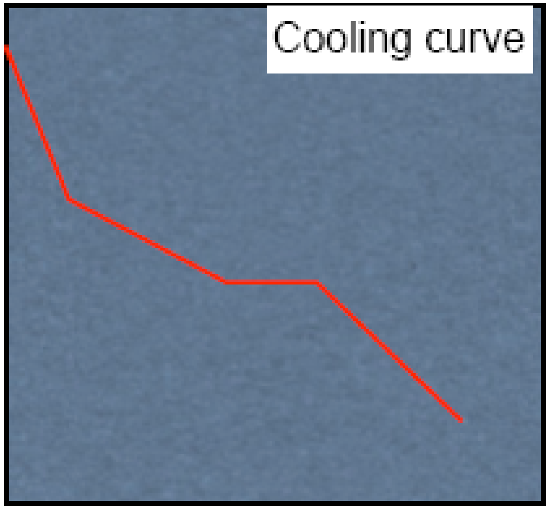


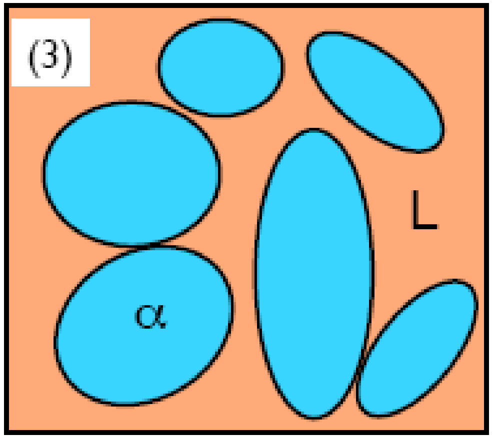
1.5 Binary phase diagrams : Hypereutectic

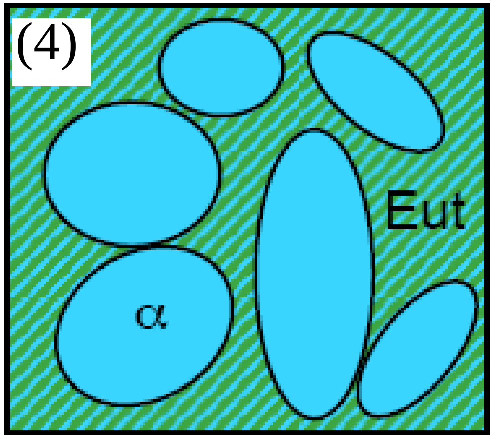
Alloy IV

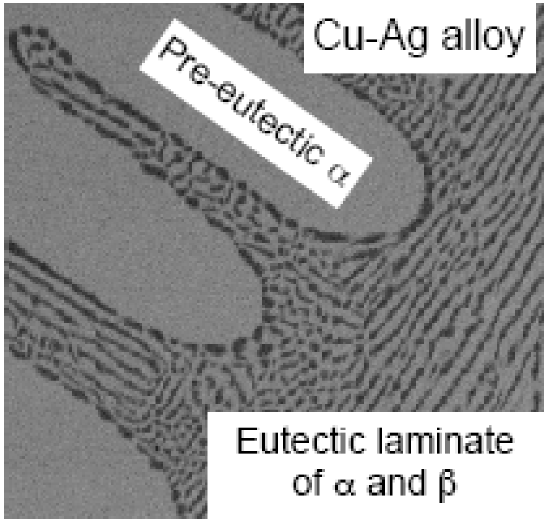





Cooling curve






Cu-Ag alloy

Eutectic laminate of α and β

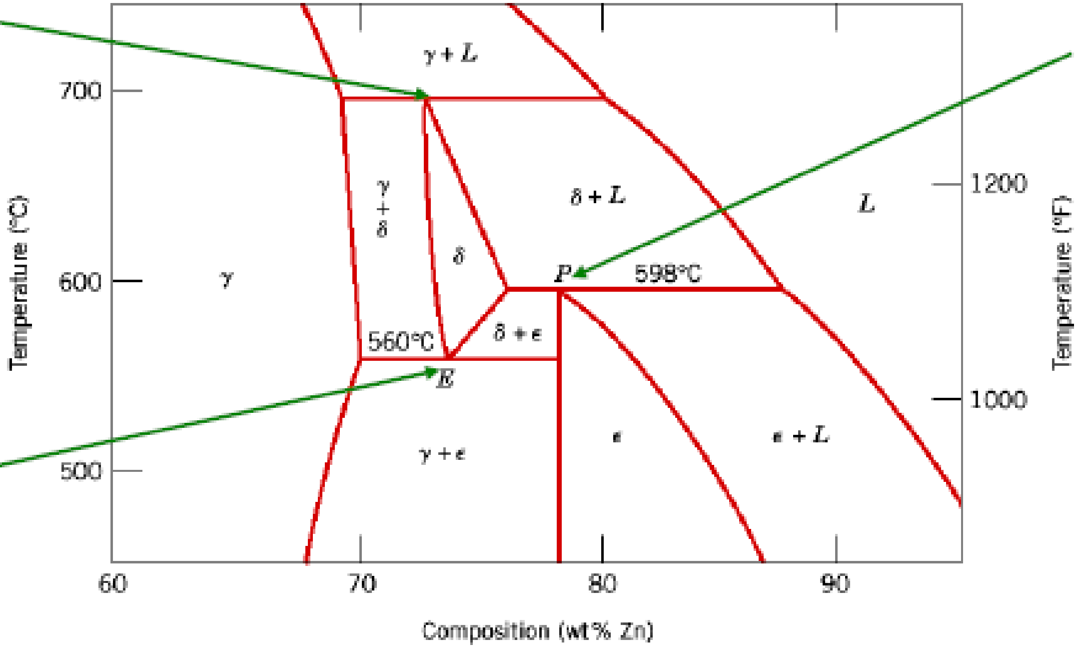
Cu-Zn Phase Diagram

Eutectoid and Peritectic Reactions

peritectic:
$\gamma + L \rightleftharpoons \delta$

peritectic:
$\delta + L \rightleftharpoons \varepsilon$

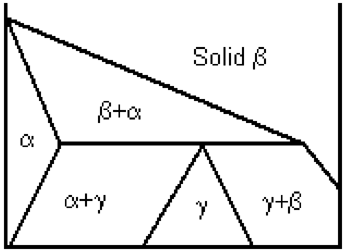
eutectoid:
$\delta \rightleftharpoons \gamma + \varepsilon$



Eutectoid: one solid phase transforms into two other solid phases upon cooling

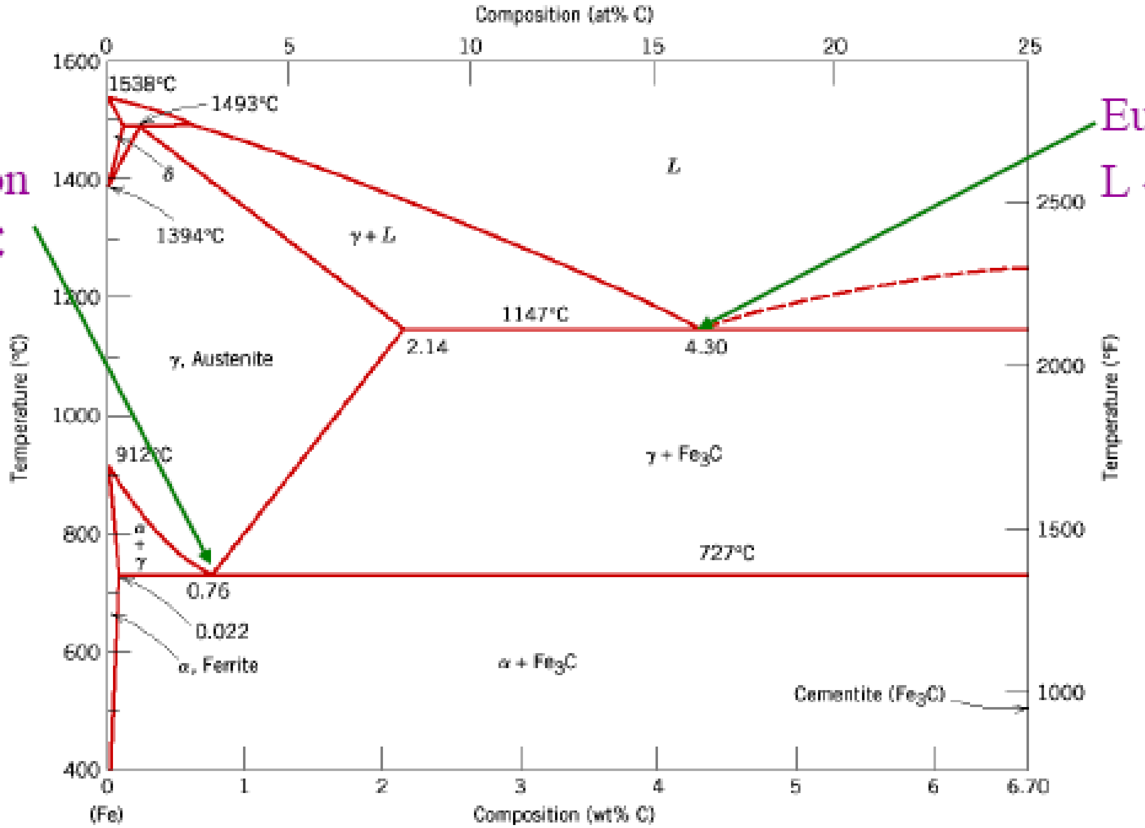
Peritectic: one solid and one liquid phase transform into another solid phase upon cooling

Peritectoid: two other solid phases transform into another solid phase upon cooling



The Iron–Iron Carbide (Fe–Fe_3C) Phase Diagram

*In their simplest form, steels are alloys of Iron (Fe) and Carbon (C). The Fe-C phase diagram is a fairly complex one, but we will only consider the part up to around **7%** carbon of the diagram.*



Eutectoid reaction

$\gamma \leftrightarrow \alpha + Fe_3C$

Eutectic reaction

$L \leftrightarrow \gamma + Fe_3C$

912°C 1394°C 1538°C

α **(BCC)** ↔ γ **(FCC)** ↔ δ **(BCC)** ↔ **liquid** Pure iron

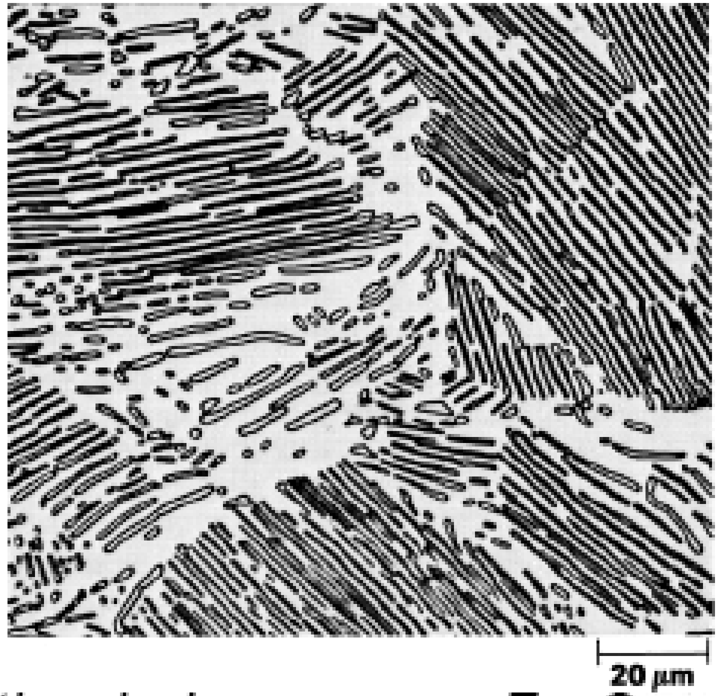
Development of Microstructure in Iron - Carbon alloys

- Microstructure depends on composition (carbon content) and heat treatment.
- In the discussion below we consider slow cooling in which equilibrium is maintained.

Eutectoid steel

When alloy of eutectoid composition (0.76 wt % C) is cooled slowly it forms a lamellar or layered structure of α and cementite (Fe_3C). This structure is called **pearlite.**

Mechanically, pearlite has properties intermediate to soft, ductile ferrite and hard, brittle cementite.



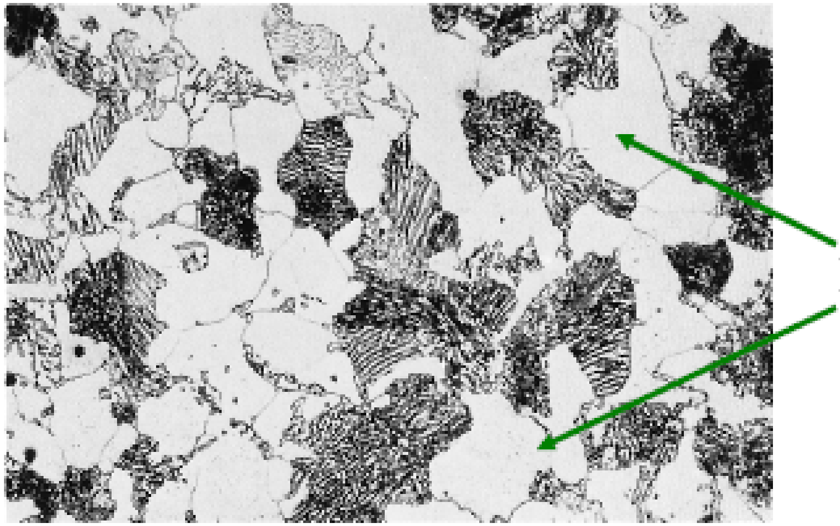
the dark areas are Fe_3C *layers, the light phase is* α *-ferrite*

Microstructure of hypoeutectoid steel

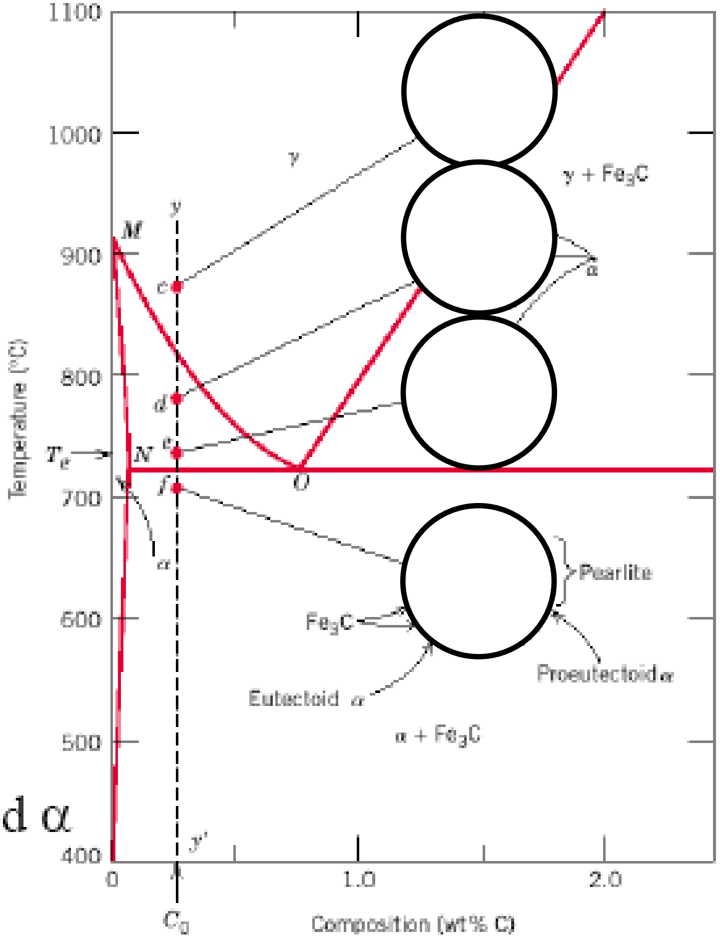
Compositions to the left of eutectoid (0.022-0.76 wt % C) **hypoeutectoid** alloys

- *less than eutectoid* (Greek)

Hypoeutectoid alloys contain proeutectoid ferrite (*formed above the eutectoid temperature*) plus the eutectoid pearlite that contain eutectoid ferrite and cementite.



Preutectoid α

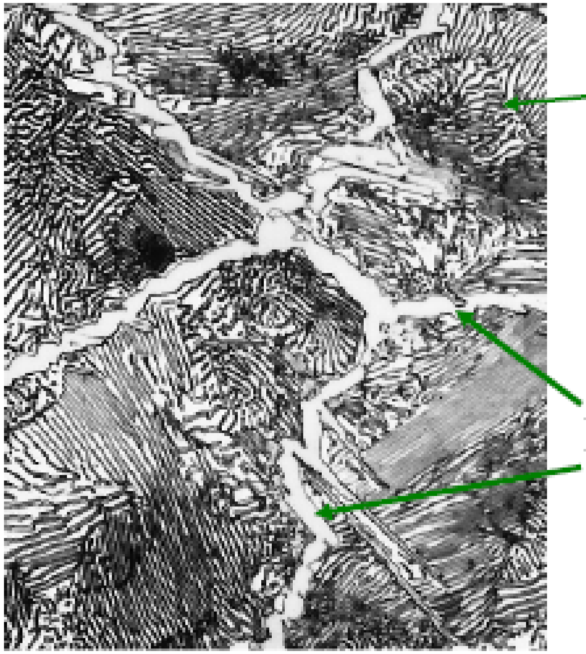


Microstructure of hypereutectoid steel

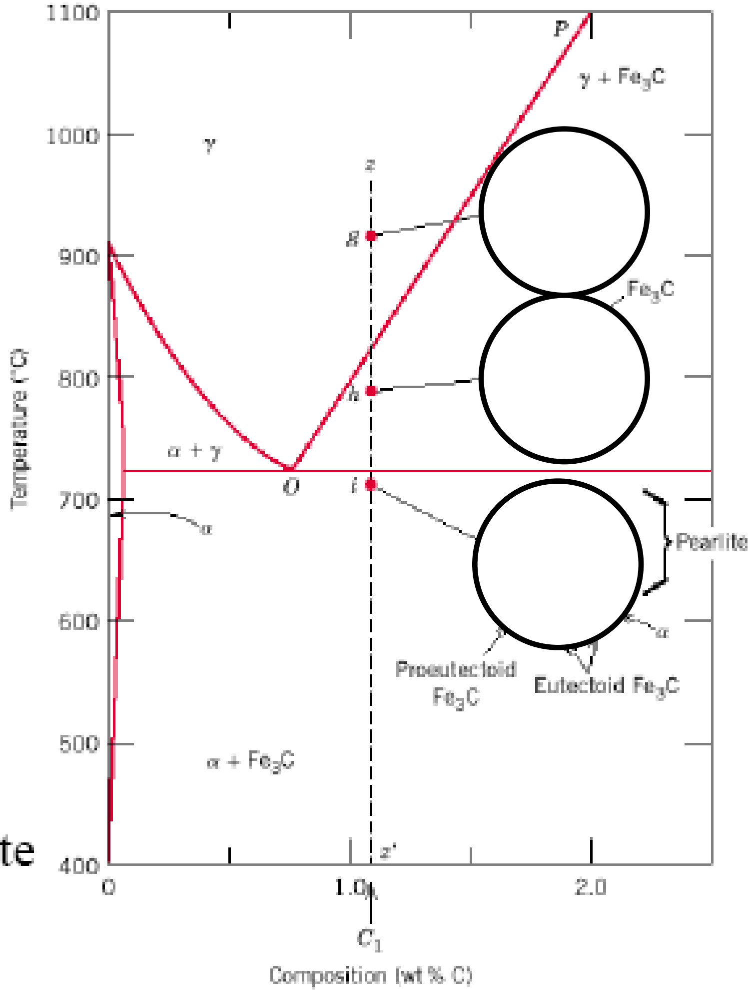
Compositions to the right of eutectoid (0.76 - 2.14 wt % C) **hypereutectoid** alloys.

- *more than eutectoid* (Greek)

$$\gamma \rightarrow \gamma + \mathbf{Fe_3C} \rightarrow \alpha + \mathbf{Fe_3C}$$


pearlite

Preutectoid cementite



2) Variant of the simple phase diagram

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

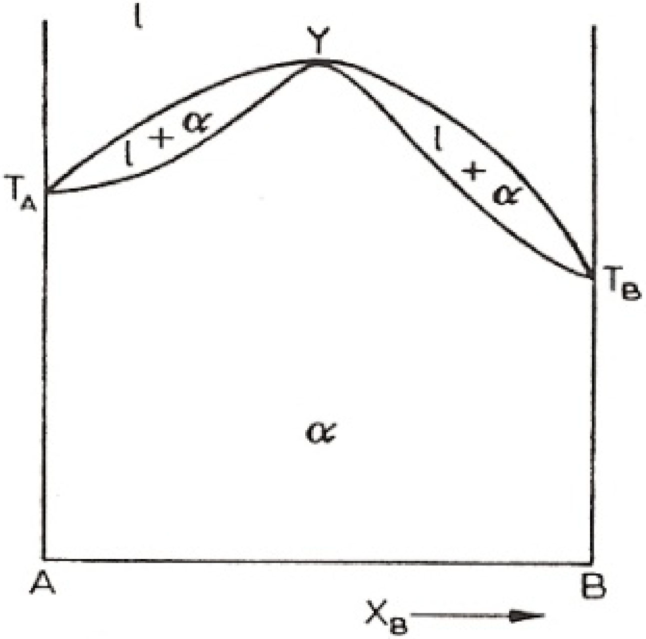


Fig. 32. Phase diagram with a maximum in the liquidus.

congruent maxima

$$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$$

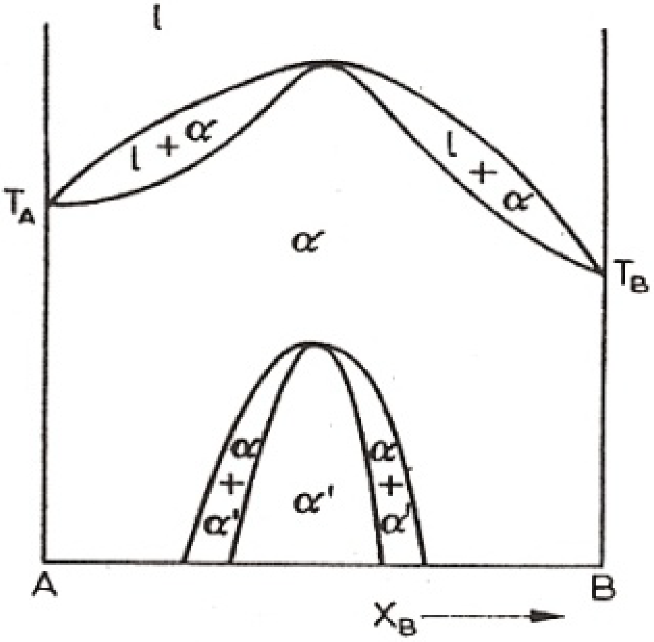
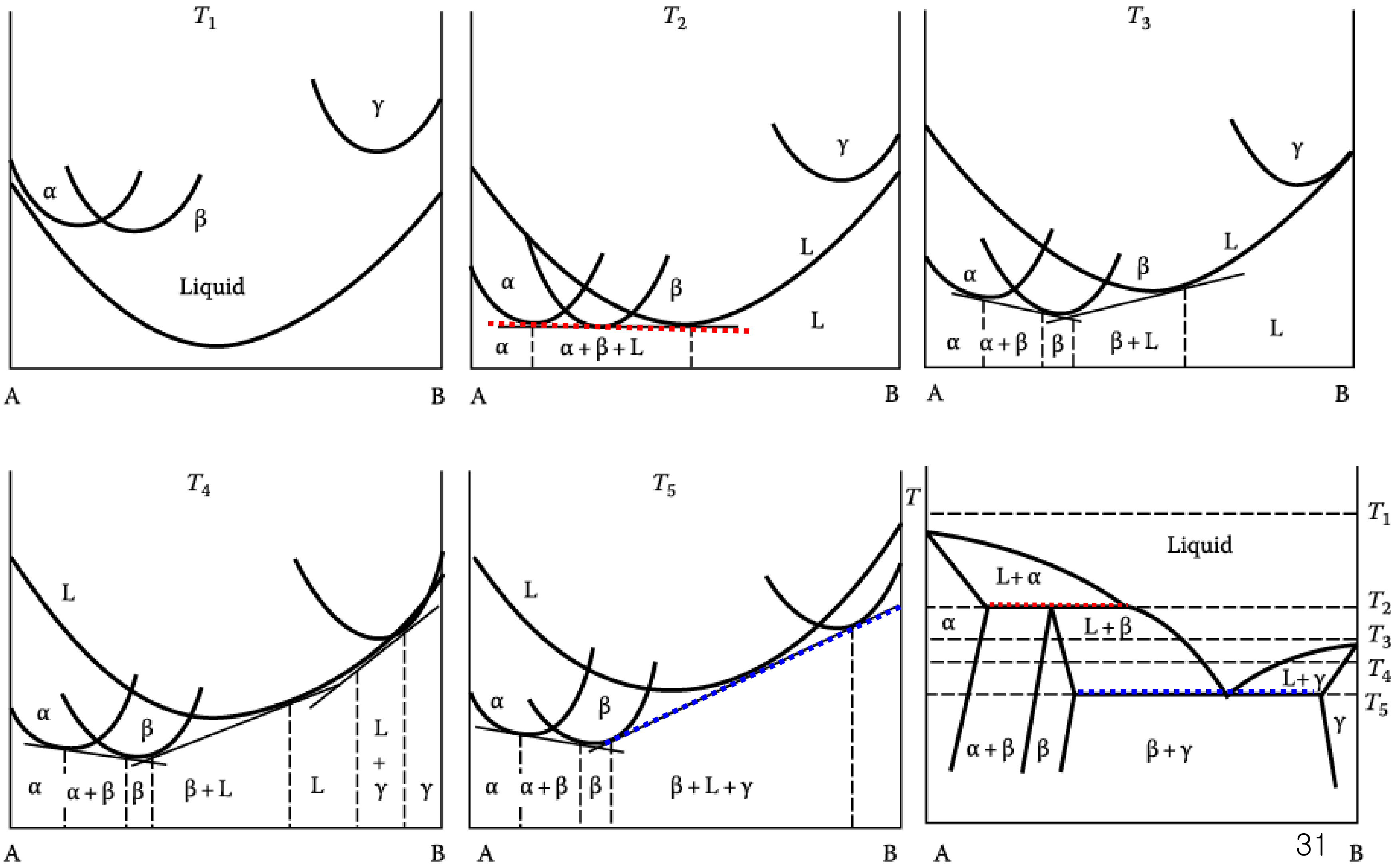


Fig. 33. Appearance of an ordered α′ phase at low temperatures.

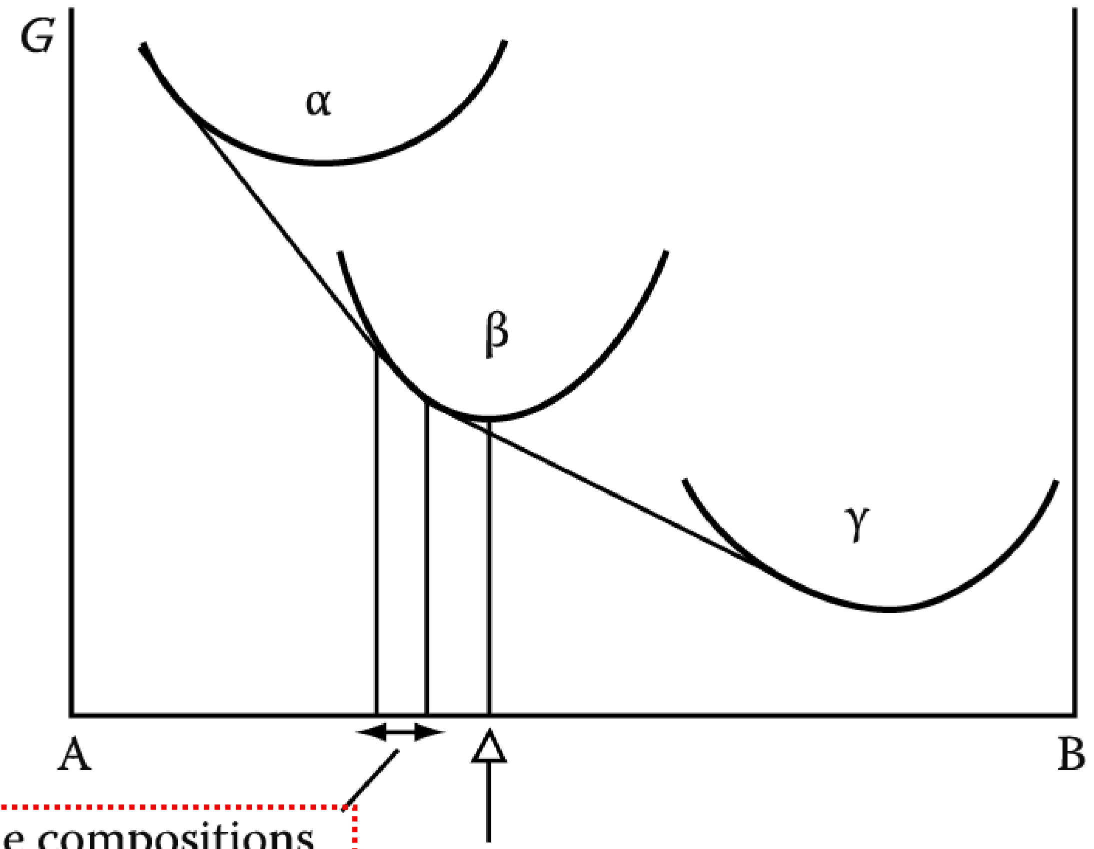
1.5 Binary phase diagrams

5) Phase diagrams containing intermediate phases



1.5 Binary phase diagrams

5) Phase diagrams containing intermediate phases



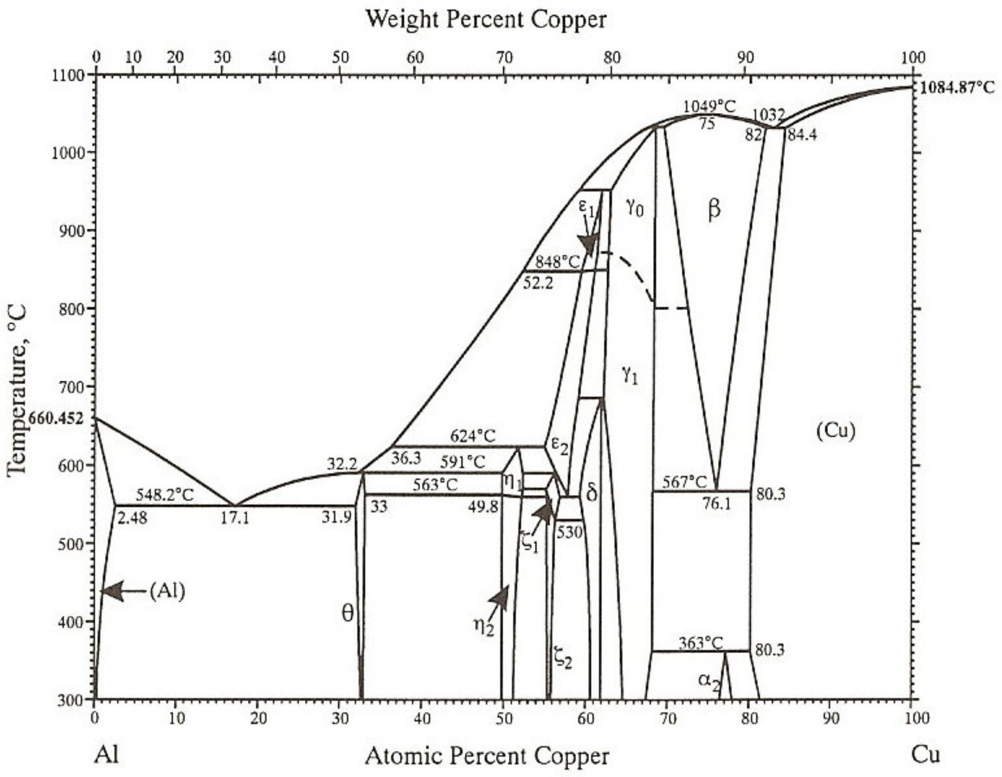
Stable compositions

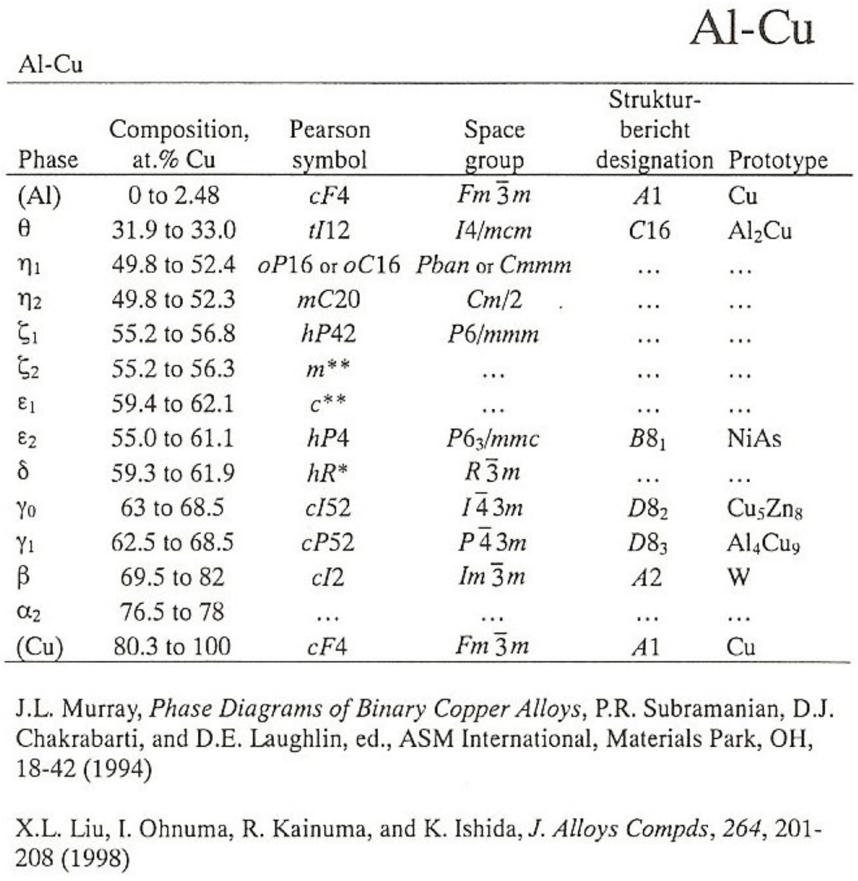
≠

Minimum G

Stoichiometric composition (A_mB_n)

θ phase in the Cu-Al system is usually denoted as $CuAl_2$ although the composition $X_{Cu}=1/3$, $X_{Al}=2/3$ is not covered by the θ field on the phase diagram.





Al-Cu

Al-Cu

Phase	Composition, at.% Cu	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Al)	0 to 2.48	*cF*4	*Fm*$\bar{3}$*m*	*A*1	Cu
θ	31.9 to 33.0	*tI*12	*I*4/*mcm*	*C*16	Al_2Cu
η_1	49.8 to 52.4	*oP*16 or *oC*16	*Pban* or *Cmmm*	…	…
η_2	49.8 to 52.3	*mC*20	*Cm*/2	…	…
ζ_1	55.2 to 56.8	*hP*42	*P*6/*mmm*	…	…
ζ_2	55.2 to 56.3	*m***	…	…	…
ε_1	59.4 to 62.1	*c***	…	…	…
ε_2	55.0 to 61.1	*hP*4	$P6_3/mmc$	$B8_1$	NiAs
δ	59.3 to 61.9	*hR**	*R*$\bar{3}$*m*	…	…
γ_0	63 to 68.5	*cI*52	*I*$\bar{4}$3*m*	$D8_2$	Cu_5Zn_8
γ_1	62.5 to 68.5	*cP*52	*P*$\bar{4}$3*m*	$D8_3$	Al_4Cu_9
β	69.5 to 82	*cI*2	*Im*$\bar{3}$*m*	*A*2	W
α_2	76.5 to 78	…	…	…	…
(Cu)	80.3 to 100	*cF*4	*Fm*$\bar{3}$*m*	*A*1	Cu

J.L. Murray, *Phase Diagrams of Binary Copper Alloys*, P.R. Subramanian, D.J. Chakrabarti, and D.E. Laughlin, ed., ASM International, Materials Park, OH, 18-42 (1994)

X.L. Liu, I. Ohnuma, R. Kainuma, and K. Ishida, *J. Alloys Compds*, *264*, 201-208 (1998)

- Equilibrium in Heterogeneous Systems

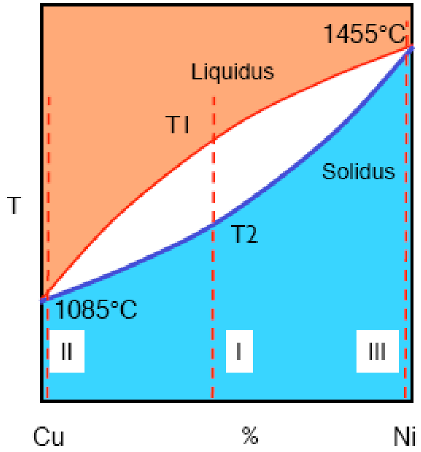
$G_0^{\beta} > G_0^{\alpha} > G_0^{\alpha+\beta}$ → **α + β separation** → **unified chemical potential**

- Binary phase diagrams

1) Simple Phase Diagrams

$\Delta H^{L}_{mix} = 0 \ \Delta H^{S}_{mix} = 0$

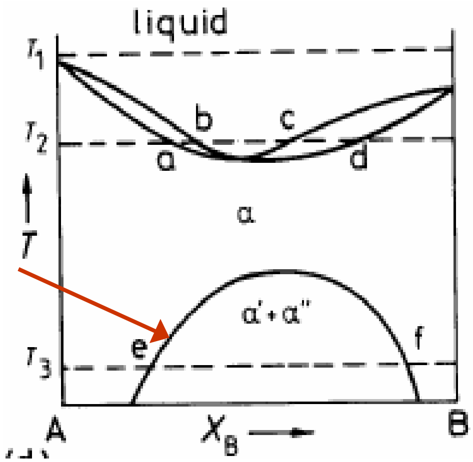
Assume: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.



2) Variant of the simple phase diagram

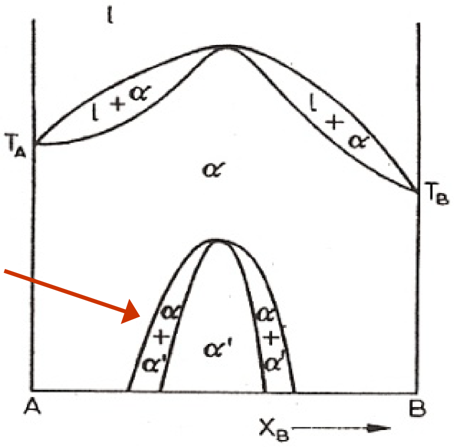
$\Delta H^{\alpha}_{mix} > \Delta H^{l}_{mix} > 0$

miscibility gab



$\Delta H^{\alpha}_{mix} < \Delta H^{l}_{mix} < 0$

Ordered phase



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

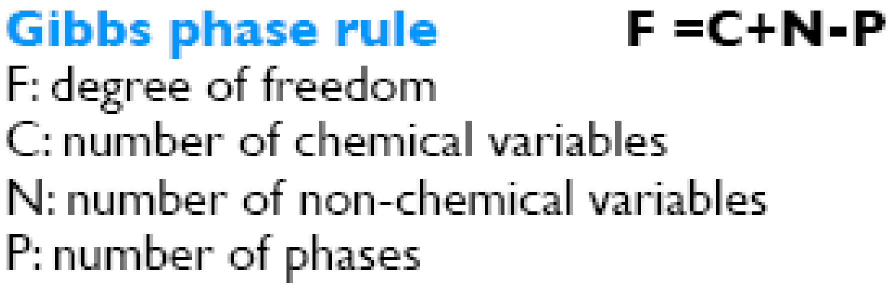
$$f = (c-1)p + p + p - (p-1)c - (p-1) - (p-1) = c - p + 2$$

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

- 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:

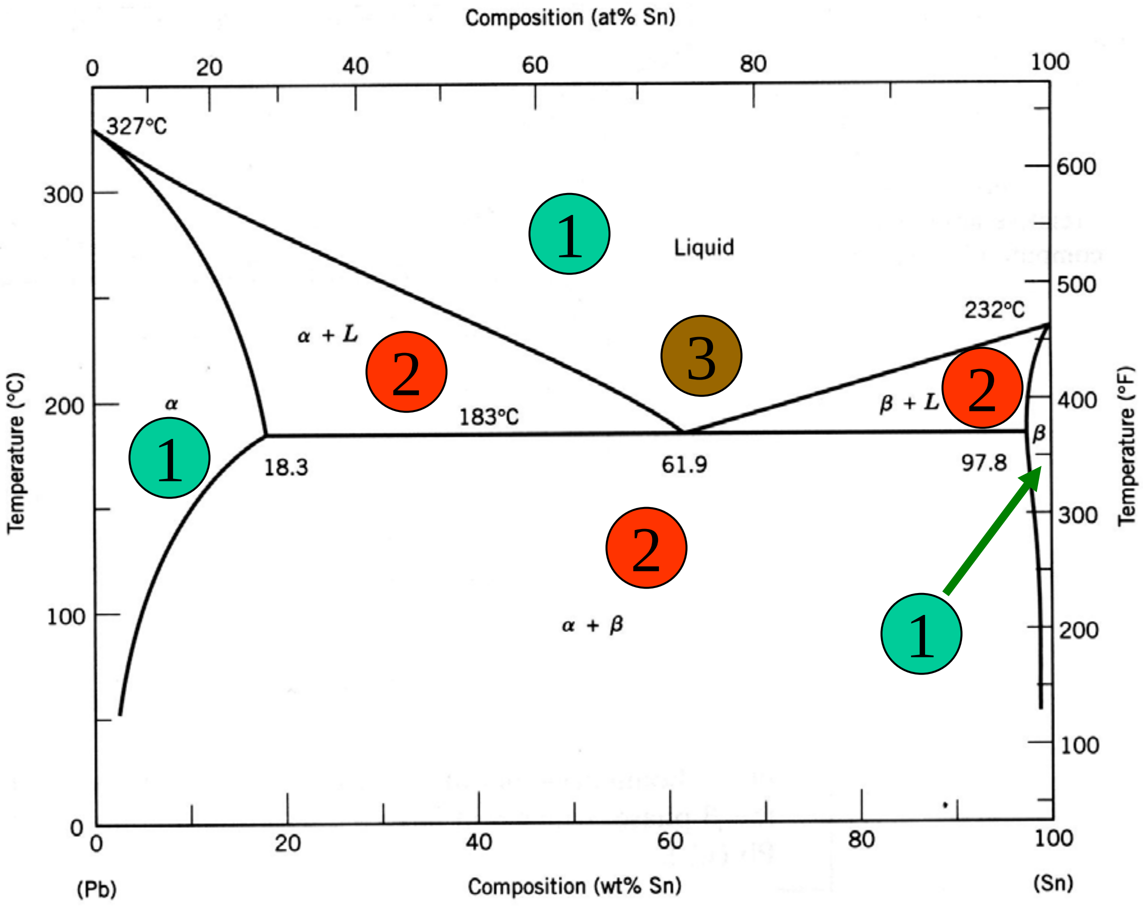
$$F = C - P + 2 \quad \text{(from T, P).}$$

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

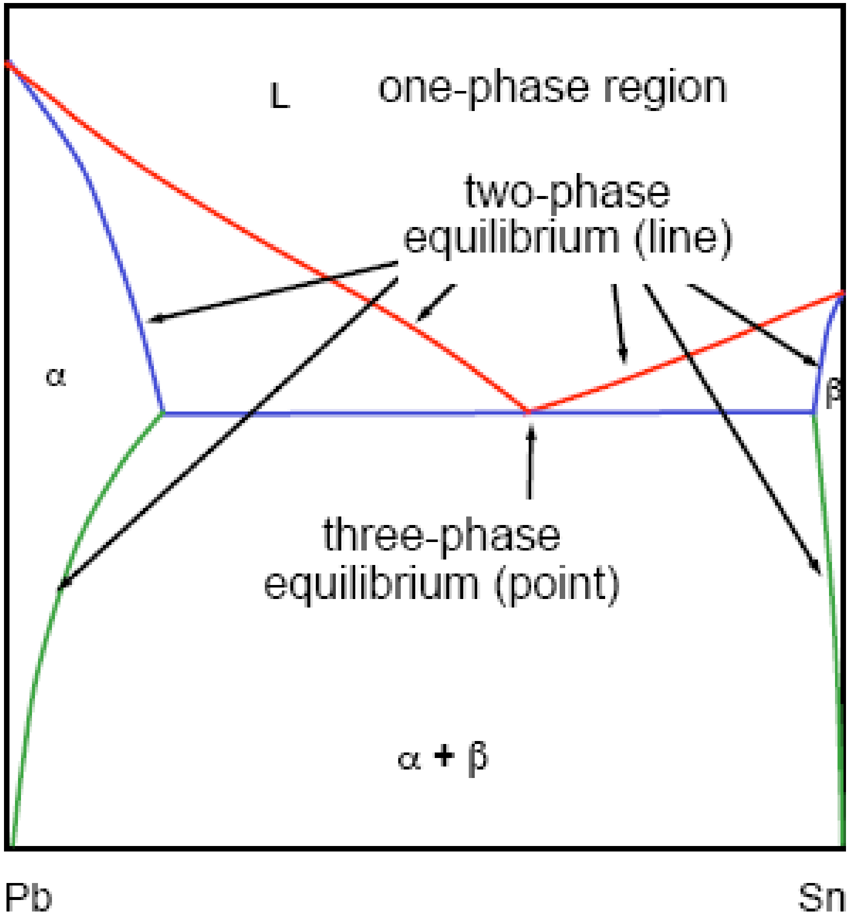
= 2 - 3 + 1

= 0

can't vary T or composition

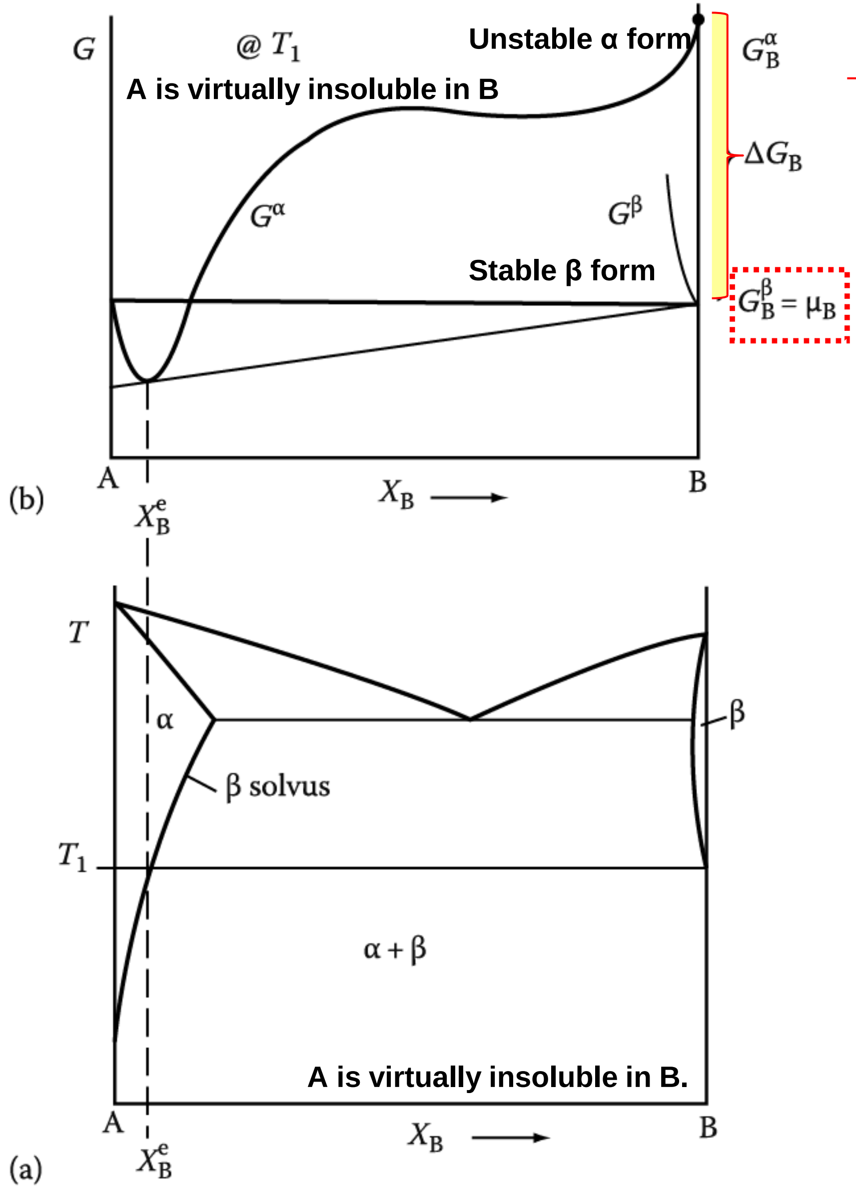
The Gibbs Phase Rule

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)



1.5.7 Effect of T on solid solubility

$$\boxed{T\uparrow \;\Rightarrow\; X_B^e\uparrow}$$



$$\mu_B^\alpha = {}^oG_B^\alpha + \Omega(1-X_B)^2 + RT\ln X_B = \mu_B^\beta \simeq {}^oG_B^\beta$$

$$\Delta G_B^{\beta\to\alpha} = {}^0G_B^\alpha - {}^oG_B^\beta = {}^oG_B^\alpha - \mu_B^\beta = {}^oG_B^\alpha - \mu_B^\alpha$$

$${}^oG_B^\alpha - \mu_B^\alpha = -\Omega(1-X_B)^2 - RT\ln X_B$$

$$\Delta G_B^{\beta\to\alpha} = -\Omega(1-X_B)^2 - RT\ln X_B$$

$$RT\ln X_B = -\Delta G_B^{\beta\to\alpha} - \Omega(1-X_B)^2$$

$$(here,\, X_B^e << 1)$$

$$RT\ln X_B^e = -\Delta G_B^{\beta\to\alpha} - \Omega$$

$$>> \qquad X_B^e = \exp\left(-\frac{\Delta G_B^{\beta\to\alpha} + \Omega}{RT}\right)$$

$$\Delta G_B^{\beta\to\alpha} = \Delta H_B^{\beta\to\alpha} - T\Delta S_B^{\beta\to\alpha}$$ 이므로

$$X_B^e = \boxed{\exp\left(\frac{\Delta S_B^{\beta\to\alpha}}{R}\right)}\exp\left(-\frac{\boxed{\Delta H_B^{\beta\to\alpha} + \Omega}}{RT}\right)$$

$$\boxed{X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}} \qquad \boxed{T\uparrow \;\Rightarrow\; X_B^e\uparrow}$$

Q : heat absorbed (enthalpy) when 1 mole of β dissolves in A rich α as a dilute solution.

* Limiting forms of eutectic phase diagram

The solubility of one metal in another may be so low.

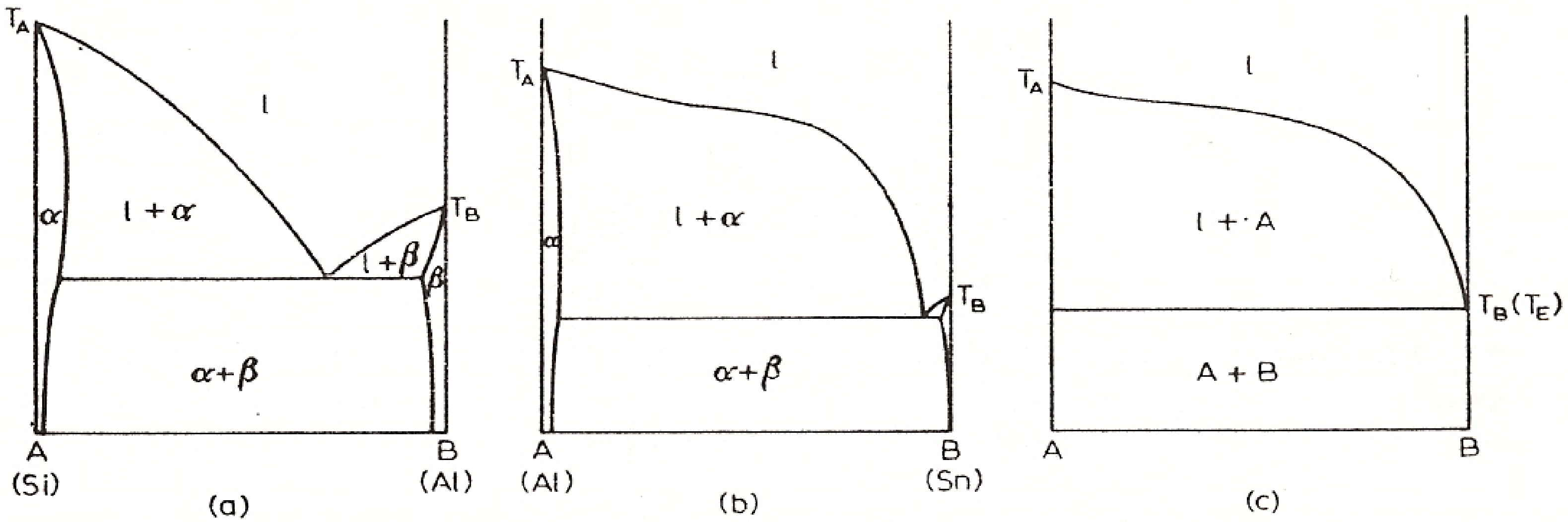


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$

a) $T \uparrow \Rightarrow X_B^e \uparrow$

b) **It is interesting to note that, except at absolute zero, X_B^e can never be equal to zero, that is, no two components are ever completely insoluble in each other.**

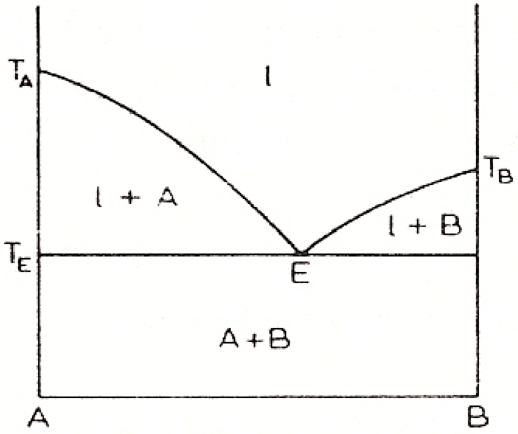
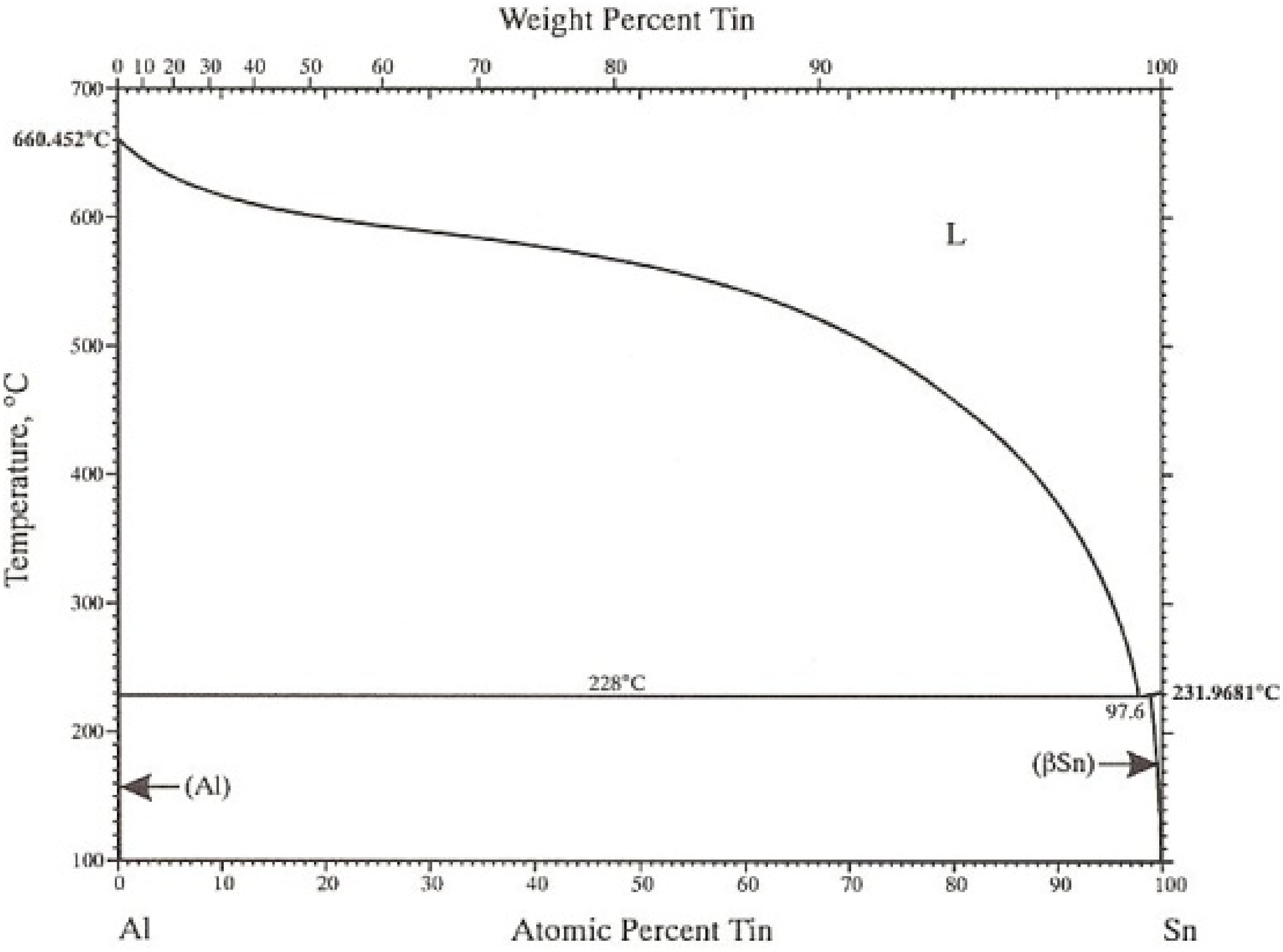


Fig. 54. Impossible form of a binary eutectic phase diagram.


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

a) 평형에 미치는 공공의 영향

1.5.8. Equilibrium Vacancy Concentration

$$\Delta G = \Delta H - T\Delta S$$

G of the alloy will depend on the concentration of vacancies and X_V^e will be that which gives the minimum free energy.

1) Vacancies increase the internal energy of crystalline metal due to broken bonds formation. **(Here, vacancy-vacancy interactions are ignored.)**

$$\Delta H \cong \Delta H_V X_V$$

2) Vacancies increase entropy because they change the **thermal vibration frequency** and also the **configurational entropy.**

Small change due to changes in the vibrational frequencies

"Largest contribution"

- Total entropy change is thus

$$\Delta S = \Delta S_V X_V - \boxed{R\{X_V \ln X_V + (1 - X_V)\ln(1 - X_V)\}}$$

The molar free energy of the crystal containing X_V mol of vacancies

$$\boxed{G = G_A + \Delta G = G_A + \Delta H_V X_V - T\Delta S_V X_V + RT\{X_V \ln X_V + (1 - X_V)\ln(1 - X_V)\}}$$

➡ **With this information, estimate the equilibrium vacancy concentration.**

Equilibrium concentration X_V^e will be that which gives the minimum free energy.

at equilibrium $$\left(\frac{dG}{dX_V}\right)_{X_V = X_V^e} = 0$$

$$\Delta H_V - T\Delta S_V + RT \ln X_V^e = 0$$

A constant ~3, independent of T

Rapidly increases with increasing T

$$X_V^e = \boxed{\exp\frac{\Delta S_V}{R}} \cdot \exp\frac{-\Delta H_V}{RT}$$

putting $\Delta G_V = \Delta H_V - T\Delta S_V$

$$\boxed{X_V^e = \exp\frac{-\Delta G_V}{RT}}$$

- **In practice, ΔH_V is of the order of 1 eV per atom and X_V^e reaches a value of about 10^{-4}~10^{-3} at the melting point of the solid**

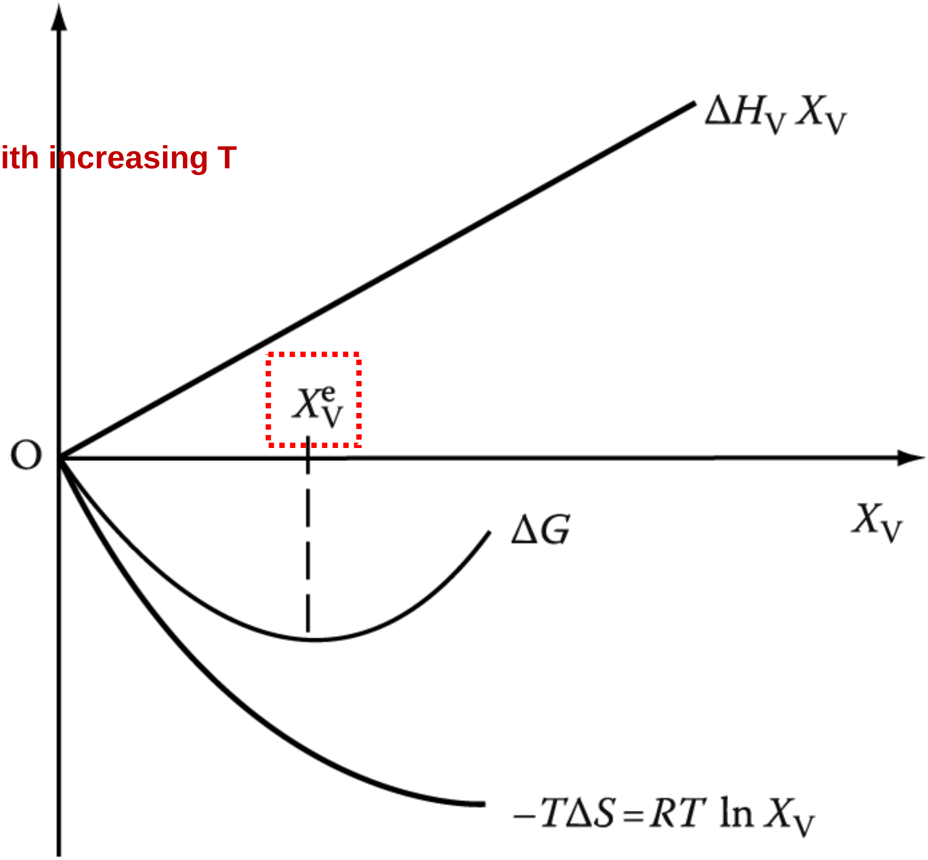


Fig. 1.37 Equilibrium vacancy concentration.

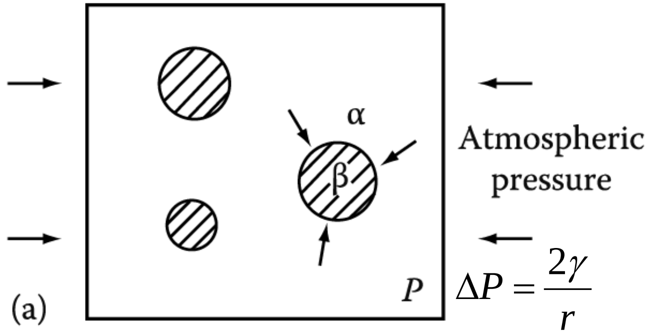
: adjust so as to reduce G to a minimum

The G curves so far have been based on the molar Gs of infinitely large amounts of material of a perfect single crystal. Surfaces, GBs and interphase interfaces have been ignored.

1.6 Influence of Interfaces on Equilibrium – b) 평형에 미치는 계면의 영향

$$\boxed{\Delta G = \Delta P \cdot V \Rightarrow \Delta G = \frac{2\gamma V_m}{r}}$$

Extra pressure ΔP due to curvature of the **α/β**



The concept of a pressure difference is very useful <u>for spherical liquid particles</u>, but it is less convenient in solids (often nonspherical shape).

$$dG = \Delta G_\gamma dn = \gamma dA \qquad \Delta G_\gamma = \gamma dA/dn$$

Since $n = 4\pi r^3/3V_m$ and $A = 4\pi r^2$ $\Delta G = \frac{2\gamma V_m}{r}$

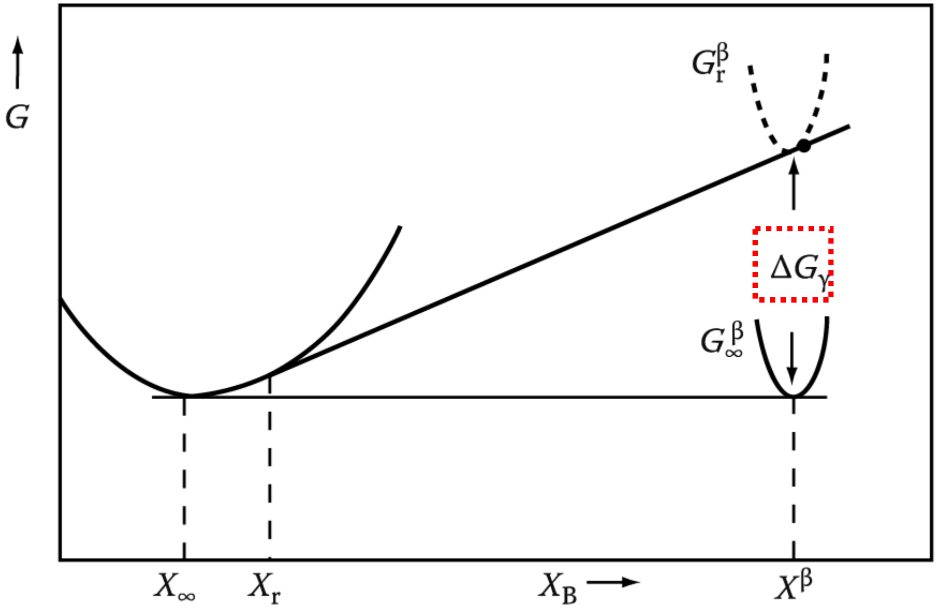


Fig. 1.38 The effect of interfacial E on the solubility of small particle

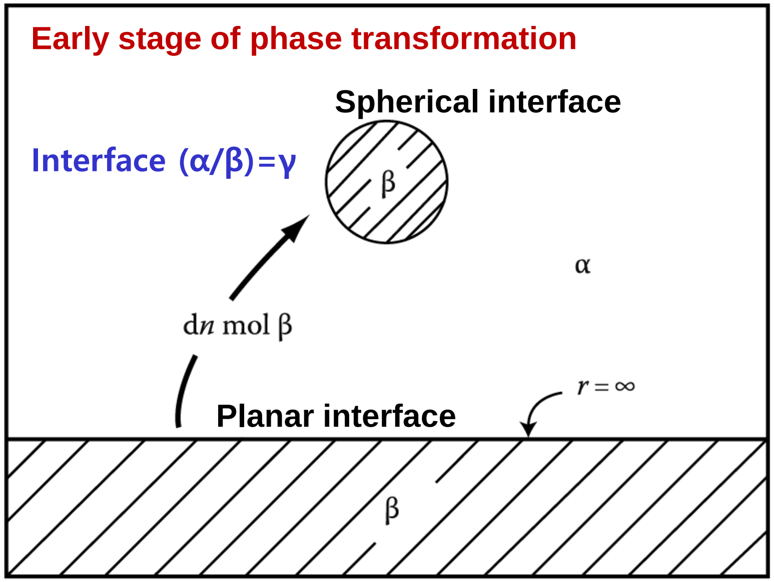


Fig. 1.39 Transfer of dn mol of β from large to a small particle.

Gibbs-Thomson effect (capillarity effect):

Free energy increase due to interfacial energy

$$\boxed{X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}}$$

$$X_B^e = \exp\left(-\frac{\Delta G_B + \Omega}{RT}\right)$$

$$X_B^{r=\infty} = \exp\left(-\frac{\Delta G_B + \Omega}{RT}\right)$$

$$X_B^{r=r} = \exp\left(-\frac{\Delta G_B + \Omega \boxed{- 2\gamma V_m / r}}{RT}\right)$$

$$= X_B^{r=\infty}\exp\left(\frac{2\gamma V_m}{RTr}\right)$$

Quite large solubility differences can arise for particles in the range r=1-100 nm. However, for particles visible in the light microscope (r>1um) capillarity effects are very small.

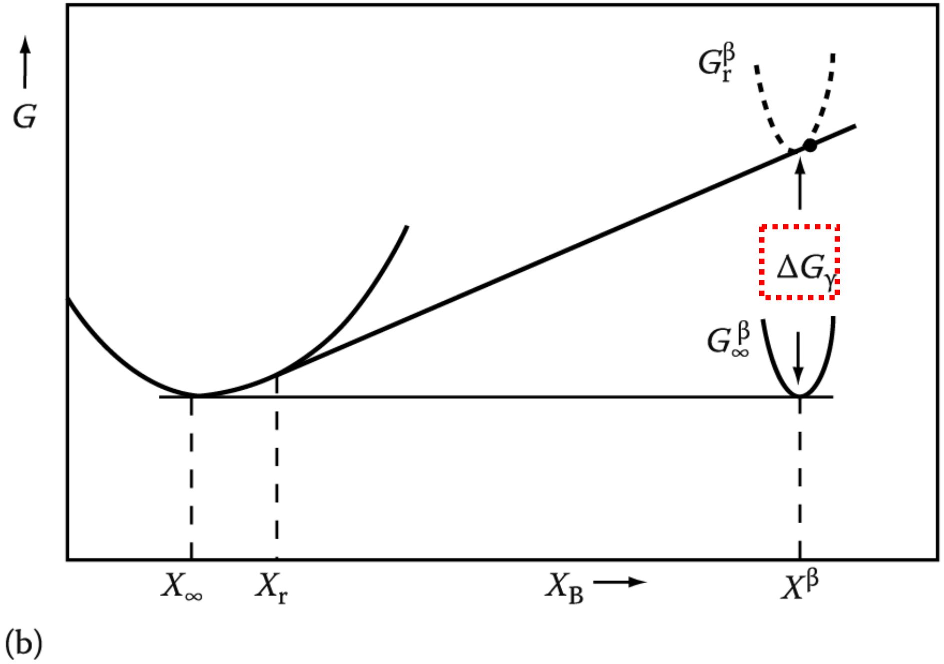


Fig. 1.38 The effect of interfacial energy on the solubility of small particles.

For small values of the exponent,

$$\frac{X_B^{r=r}}{X_B^{r=\infty}} = \exp\left(\frac{2\gamma V_m}{RTr}\right) \approx 1 + \frac{2\gamma V_m}{RTr}$$

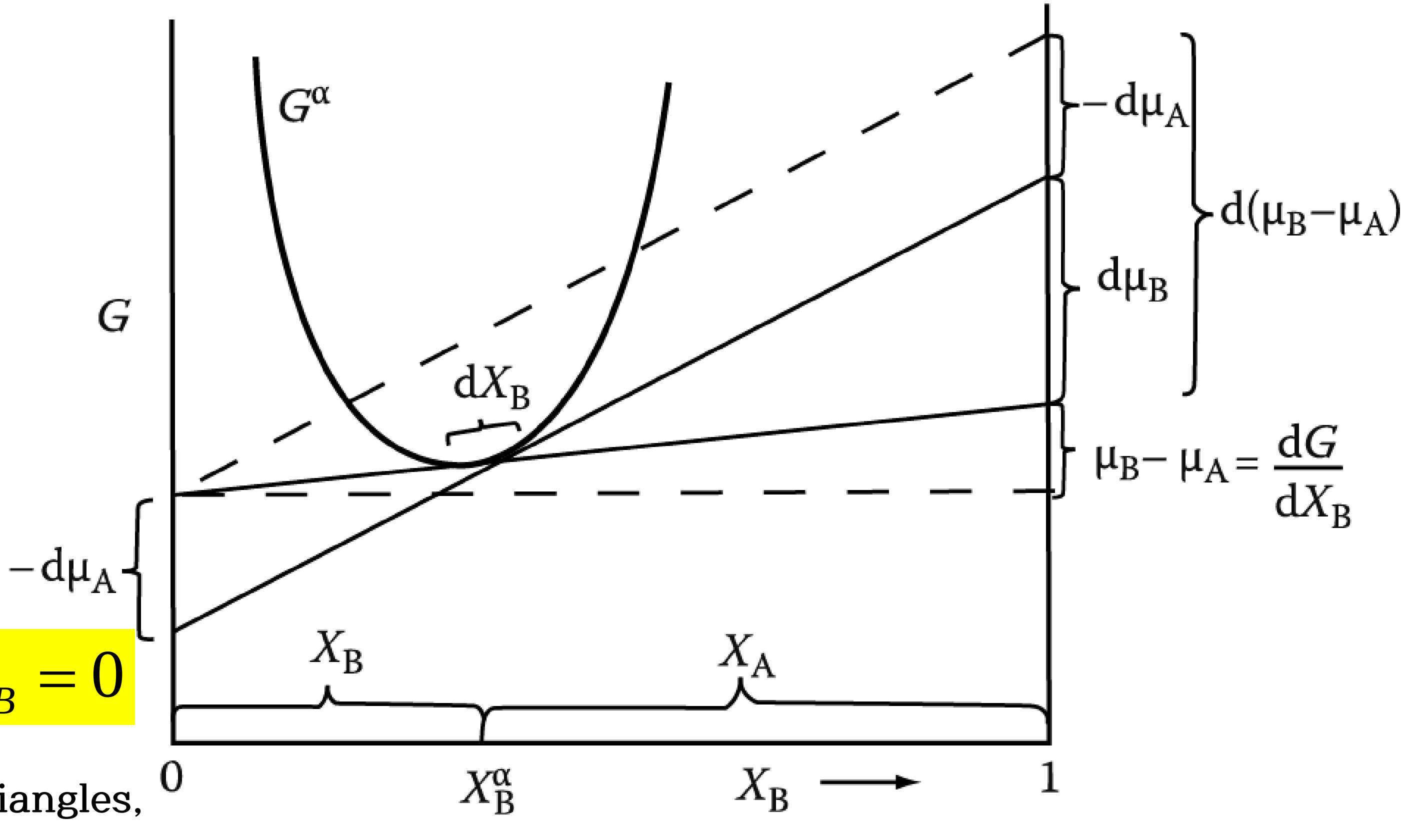
Ex) γ=200mJ/m², V_m=10^{-5} m³,T=500K

$$\boxed{\frac{X_r}{X_\infty} = 1 + \frac{1}{r(nm)}}$$

For r=10 nm, solubility~10% increase

1.8 Additional Thermodynamic Relationships for Binary Solutions

➡ **Gibbs-Duhem equation:** Calculate the change in (dμ) that results from a change in (dX)



$$X_A d\mu_A + X_B d\mu_B = 0$$

Comparing two similar triangles,

$$-\frac{d\mu_A}{X_B} = \frac{d\mu_B}{X_A} = \frac{d(\mu_B - \mu_A)}{1} \Leftarrow \frac{dG}{dX_B} = \frac{\mu_B - \mu_A}{1},$$

$\underline{d^2G/dX^2}$

$d^2G/dX_B^2 = d^2G/dX_A^2$

Substituting right side Eq.
& Multiply X_AX_B

$$\boxed{-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2} dX_B}$$

Eq. 1.65

Additional Thermodynamic Relationships for Binary Solutions

The Gibbs-Duhem Equation 합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(**dμ**) 를 계산

be able to calculate the change in chemical potential (dμ) that result from a change in alloy composition (dX).

① **For a regular solution,**

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

$$\frac{d^2G}{dX^2} = \frac{RT}{X_A X_B} - 2\Omega$$

For a ideal solution, $\Omega = 0$,

$$\frac{d^2G}{dX^2} = \frac{RT}{X_A X_B}$$

② **Different form Eq. 1.65**

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

$\gamma_B = a_B/X_B$ →

Differentiating With respect to X_B,

$$\boxed{\frac{d\mu_B}{dX_B}} = \frac{RT}{X_B}\left\{1 + \frac{X_B}{\gamma_B}\frac{d\gamma_B}{dX_B}\right\} = \frac{RT}{X_B}\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

$$\boxed{\frac{d\mu_B}{dX_B}} = \frac{RT}{X_B}\left\{1 + \frac{X_B}{\gamma_B}\frac{d\gamma_B}{dX_B}\right\} = \frac{RT}{X_B}\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

Eq. 1.69

a similar relationship can be derived for $d\mu_A/dX_B$

$$-X_A d\mu_A = X_B d\mu_B = RT\left\{1 + \frac{d\ln\gamma_A}{d\ln X_A}\right\}dX_B = RT\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}dX_B$$

Eq. 1.70

$$-X_A d\mu_A = X_B d\mu_B = X_A X_B \frac{d^2G}{dX^2}dX_B$$

Eq. 1.65

The Gibbs-Duhem Equation

$$X_A X_B \frac{d^2G}{dX^2} = RT\left\{1 + \frac{d\ln\gamma_A}{d\ln X_A}\right\} = RT\left\{1 + \frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

be able to calculate the change in chemical potential (dμ) that result from a change in alloy composition (dX).

Total Free Energy Decrease per Mole of Nuclei ΔG_0

: 변태를 위한 전체 구동력/핵생성을 위한 구동력은 아님

Driving Force for Precipitate Nucleation $\boxed{\alpha \to \alpha + \beta}$ ΔG_V

$$\Delta G_1 = \mu_A^\alpha X_A^\beta + \mu_B^\alpha X_B^\beta$$

: **Decrease of total free E of system**
by removing a small amount of material
with the nucleus composition (X_B^β) (P point)

$$\Delta G_2 = \mu_A^\beta X_A^\beta + \mu_B^\beta X_B^\beta$$

: **Increase of total free E of system**
by forming β phase with composition X_B^β
(Q point)

$$\boxed{\Delta G_n = \Delta G_2 - \Delta G_1}$$ (length PQ)

$$\boxed{\Delta G_V} = \frac{\Delta G_n}{V_m} \quad \textit{per unit volume of } \beta$$

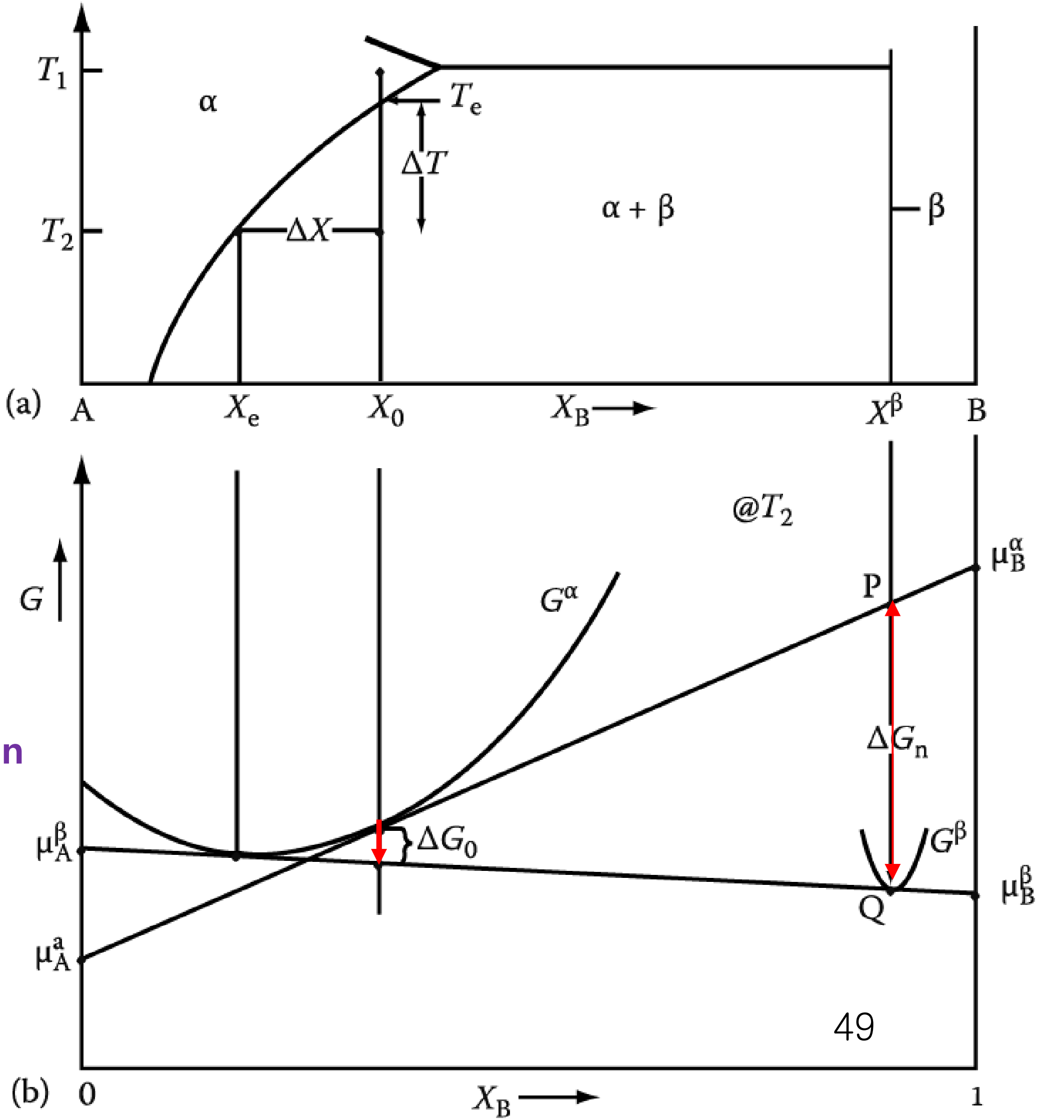
: driving force for β precipitation

For dilute solutions,

$$\Delta G_V \propto \Delta X \quad \textit{where } \Delta X = X_0 - X_e$$

$$\boxed{\Delta G_V \propto \Delta X \propto \Delta T}$$

∝ undercooling below T_e



Contents for previous class : Binary phase diagrams

1) Simple Phase Diagrams

Both are ideal soln. → 1) Variation of temp.: $G^L > G^S$ 2) Decrease of curvature of G curve

(∵ decrease of $-T\Delta S_{mix}$ effect)

2) Systems with miscibility gap

$$\Delta H^L_{mix} = 0 \qquad \Delta H^S_{mix} > 0$$

1)Variation of temp.: $G^L > G^S$ 2)Decrease of curvature of G curve + Shape change of G curve by H

4) Simple Eutectic Systems

$$\Delta H^L_{mix} = 0 \qquad \Delta H^S_{mix} >> 0$$

→ miscibility gap extends to the melting temperature.

3) Ordered Alloys

$$\Delta H^L_{mix} = 0 \qquad \Delta H^S_{mix} < 0$$

$\Delta H_{mix} < 0$ → A atoms and B atoms like each other. → Ordered alloy at low T

$\Delta H_{mix} << 0$ → The ordered state can extend to the melting temperature.

5) Phase diagrams containing intermediate phases

Stable composition $\neq$ Minimum G with stoichiometric composition

- Gibbs Phase Rule

F = C – P + 1 (constant pressure)

Gibbs' Phase Rule allows us to construct phase diagram to represent and interpret phase equilibria in heterogeneous geologic systems.

- Effect of Temperature on Solid Solubility

$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$

a) $T\uparrow \Rightarrow X_B^e\uparrow$

b) X_B^e can never be equal to zero.

- **Effect of Temperature on Solid Solubility**

$$X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$$ **a)** $$T\uparrow \Rightarrow X_B^e\uparrow$$ **b)** X_B^e can never be equal to zero.

- **Equilibrium Vacancy Concentration**

$$X_V^e = \exp\frac{-\Delta G_V}{RT}$$

- **Influence of Interfaces on Equilibrium**

$$\Delta G = \frac{2\gamma V_m}{r}$$ **Gibbs-Thomson effect**

- **Gibbs-Duhem Equation:** **Be able to calculate the change in chemical potential that result from a change in alloy composition.**

$$X_A X_B \frac{d^2G}{dX^2} = RT\left\{1+\frac{d\ln\gamma_A}{d\ln X_A}\right\} = RT\left\{1+\frac{d\ln\gamma_B}{d\ln X_B}\right\}$$

합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화(**dμ**) 를 계산