2015 Fall

"Phase Equilibria *in* Materials"

09.23.2015

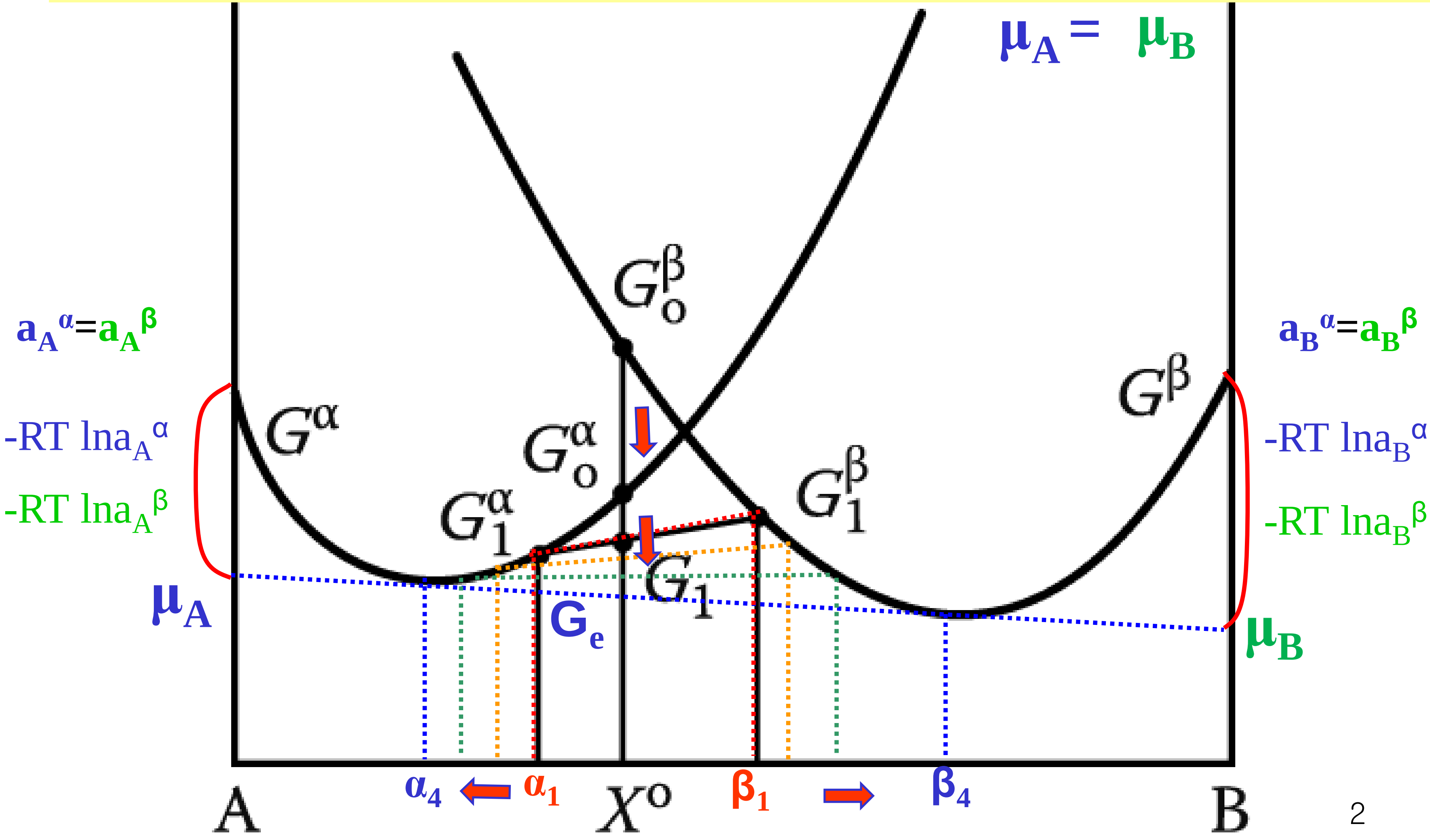
Eun Soo Park

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

Contents for previous class

Equilibrium in Heterogeneous Systems

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



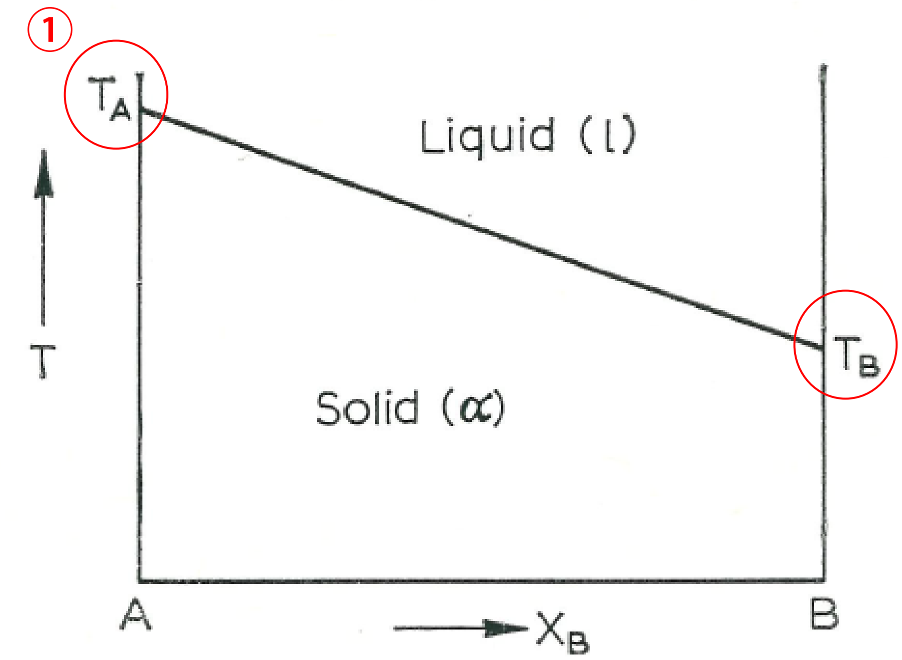
- Two-Phase Equilibrium

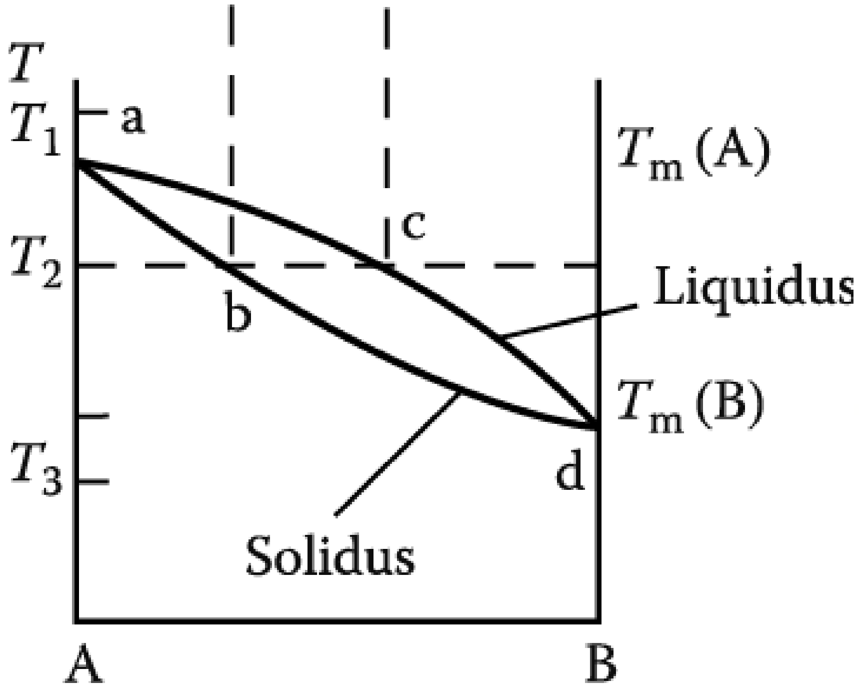
1) Simple Phase Diagrams

Assumption: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.
(3) $T_m(A) > T_m(B)$

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

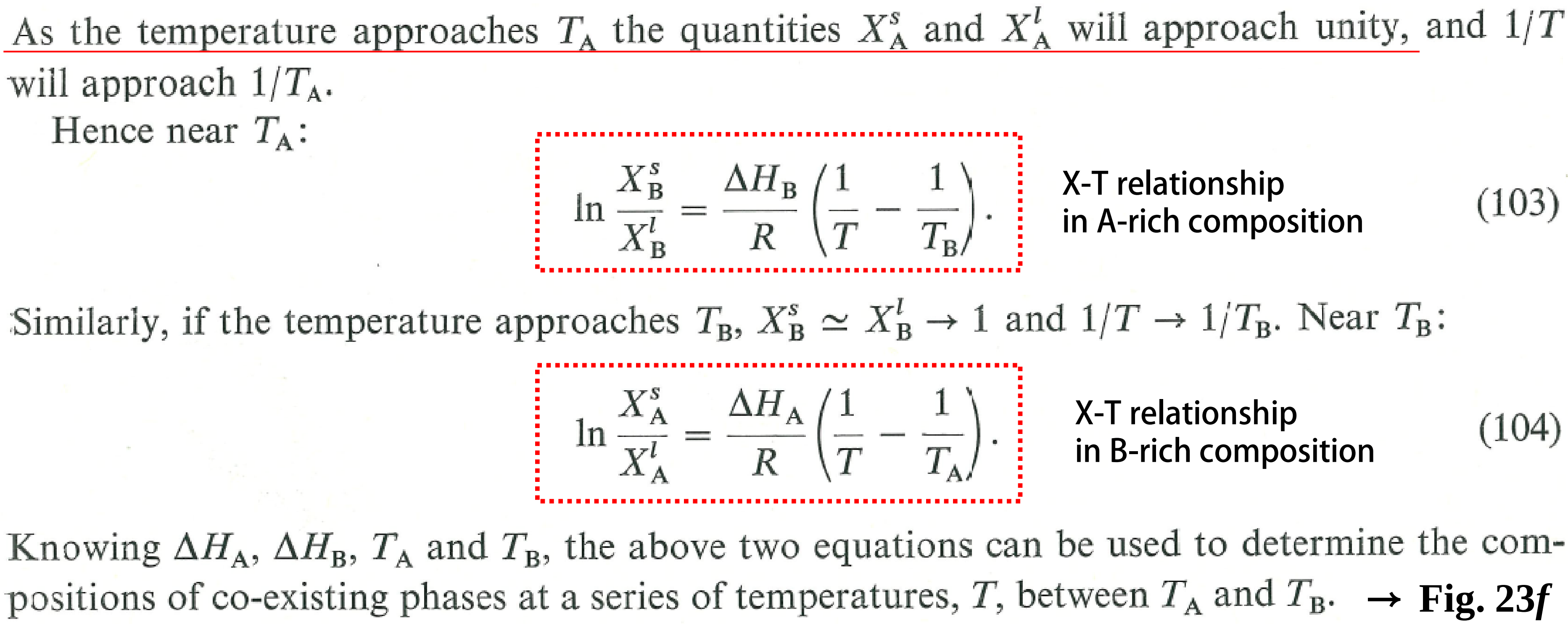
Since $S^s \neq S^l$, then $dT/dX_A = 0$. Thus the condition $X^s_A = X^l_A$ is only associated with $dT/dX_A = 0$, *i.e.* with a minimum or a maximum in the line T_AT_B of Fig. 22. Except for this particular case therefore $X^s_A \neq X^l_A$. There is a difference between the composition of the liquid and solid phase in the general case.





*** Consider the free energy curves for liquid and α phase at a temperature T, where $T_A > T > T_B$. The standard states are pure *solid* A and pure *liquid* B at temperature T. → Derive the free energy curves for the liquid and α phases.**

② X-T relationship in A-rich and B-rich compositions



As the temperature approaches T_A the quantities X_A^s and X_A^l will approach unity, and $1/T$ will approach $1/T_A$.

Hence near T_A:

$$\boxed{\ln \frac{X_B^s}{X_B^l} = \frac{\Delta H_B}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right).} \qquad (103)$$

X-T relationship
in A-rich composition

Similarly, if the temperature approaches T_B, $X_B^s \simeq X_B^l \to 1$ and $1/T \to 1/T_B$. Near T_B:

$$\boxed{\ln \frac{X_A^s}{X_A^l} = \frac{\Delta H_A}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right).} \qquad (104)$$

X-T relationship
in B-rich composition

Knowing ΔH_A, ΔH_B, T_A and T_B, the above two equations can be used to determine the compositions of co-existing phases at a series of temperatures, T, between T_A and T_B. → **Fig. 23*f***

Referring to Fig. 23f, if A is regarded as the solvent, for very dilute solutions of B in A we can write

$$X_A \to 1 \quad \text{and} \quad -\ln X_A \simeq X_B.$$

In terms of eqn. (104):

$$X_A^l - X_A^s = \frac{\Delta H_A}{R}\left(\frac{T_A - T}{T T_A}\right).$$

Since $X_A^l = 1 - X_B^l$ and $X_A^s = 1 - X_B^s$

$$X_B^s - X_B^l = \frac{\Delta H_A}{R}\left(\frac{T_A - T}{T T_A}\right). \tag{105}$$

As T approaches T_A (in dilute solutions of B in solvent A), the denominator on the right-hand side of eqn. (105) can be written RT_A^2. Therefore

$$X_B^s - X_B^l = \frac{\Delta H_A}{RT_A^2}(T_A - T) \tag{106}$$

or,

③ ΔH effect for G curvature
: initial slope of solidus
and liquidus curve

$$\left(\frac{dX_B^s}{dT} - \frac{dX_B^l}{dT}\right)_{T=T_A} = \frac{\Delta H_A}{RT_A^2}. \tag{107}$$

Equations (106) and (107) are referred to as the Van't Hoff relation. They give the depression of the freezing point for a liquid solution in equilibrium with a solid solution. The difference in initial slopes of the solidus and liquidus curves, the slopes at $T = T_A$ and $X_A = 1$, are dependent on the latent heat of fusion of pure A (ΔH_A) but independent of the nature of the solute.

* Consider actual (or so-called regular) solutions

in which $\Delta H_m \neq 0$, but $\Delta S_m = \Delta S_{m,\text{ideal}}$.

$$\Delta G_m^l = \Delta H_m^l + X_A^l \Delta G_A + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).$$

Since

$$\Delta G_A = \Delta H_A - T\Delta S_A$$

then,

$$\Delta G_m^l = \Delta H_m^l + X_A^l \Delta H_A - \boxed{X_A^l T\Delta S_A} + RT(X_A^l \ln X_A^l + X_B^l \ln X_B^l).$$

The free energy curve for the solid phase is:

$$\Delta G_m^s = \Delta H_m^s - X_B^s \Delta G_B + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s)$$

or,

$$\Delta G_m^s = \Delta H_m^s - X_B^s \Delta H_B + \boxed{X_B^s T\Delta S_B} + RT(X_A^s \ln X_A^s + X_B^s \ln X_B^s).$$

④ Temperature effect for G variation
: role of **ΔS**

1) Simple Phase Diagrams

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

b) T ↓ → Decrease of curvature of G curve

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

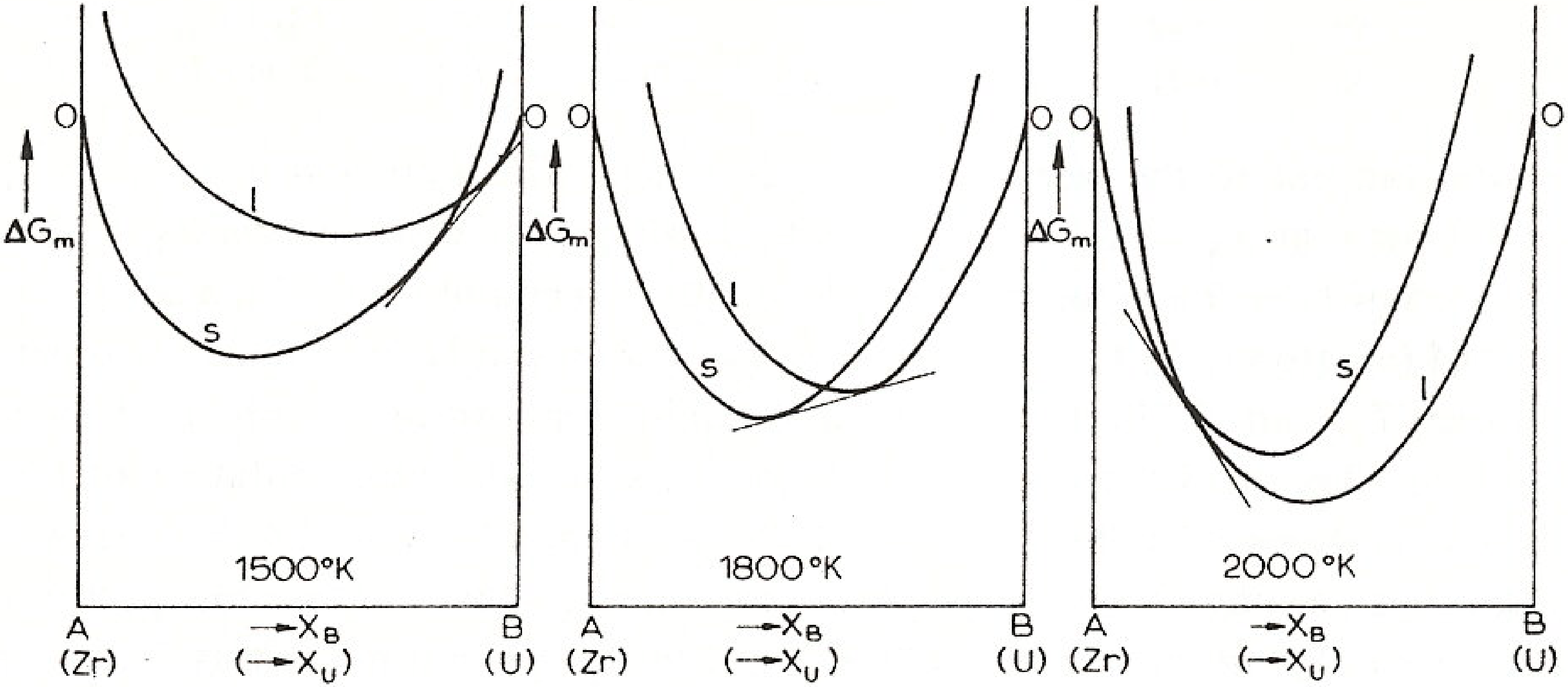


Fig. 26. Free energy curves for liquid and solid phases in the U–Zr system at 1500°, 1800° and 2000 °K.

It was assumed that $\Delta H_m^l = \Delta H_m^s$

1.5 Binary phase diagrams

1) Simple Phase Diagrams

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

b) $T \downarrow \rightarrow$ Decrease of curvature of G curve

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

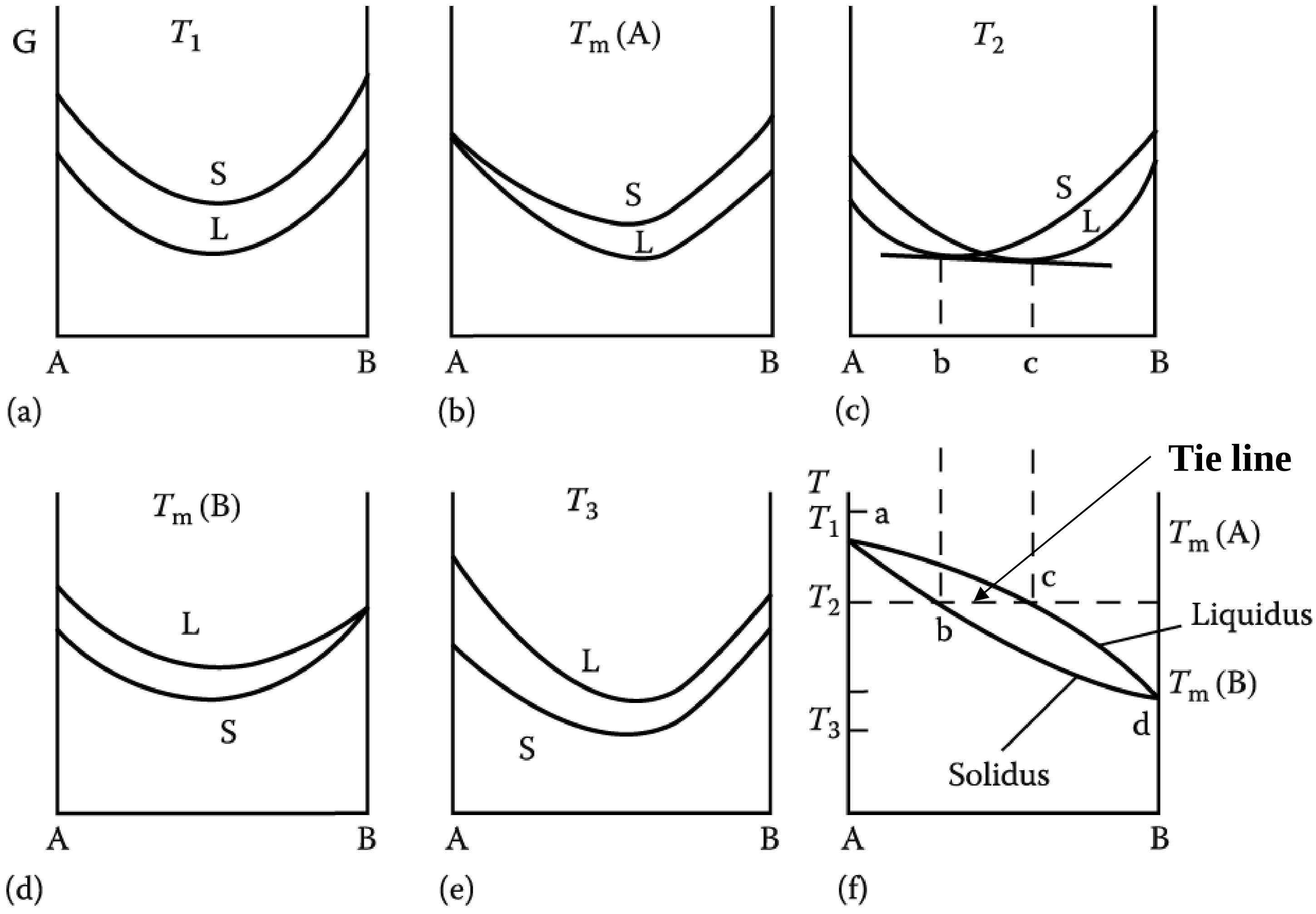
Assumption:

(1) completely miscible in solid and liquid.

(2) Both are ideal soln.

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

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



Contents for today's class

- Equilibrium in Heterogeneous Systems

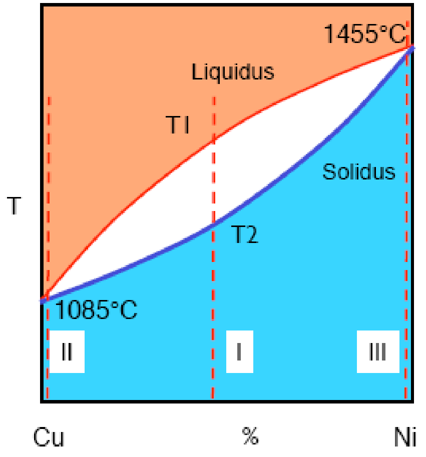
$G_0^{\beta} > G_0^{\alpha} > G_0^{\alpha+\beta}$ ➡ α + β separation ➡ unified chemical potential

- Binary phase diagrams

1) Simple Phase Diagrams

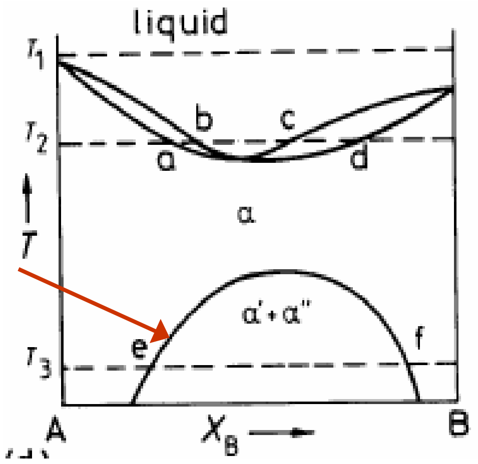
$$\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} = 0$$

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



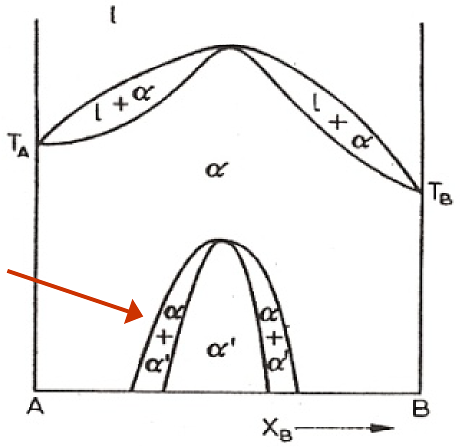
2) Variant of the simple phase diagram

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



miscibility gab

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



Ordered phase

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

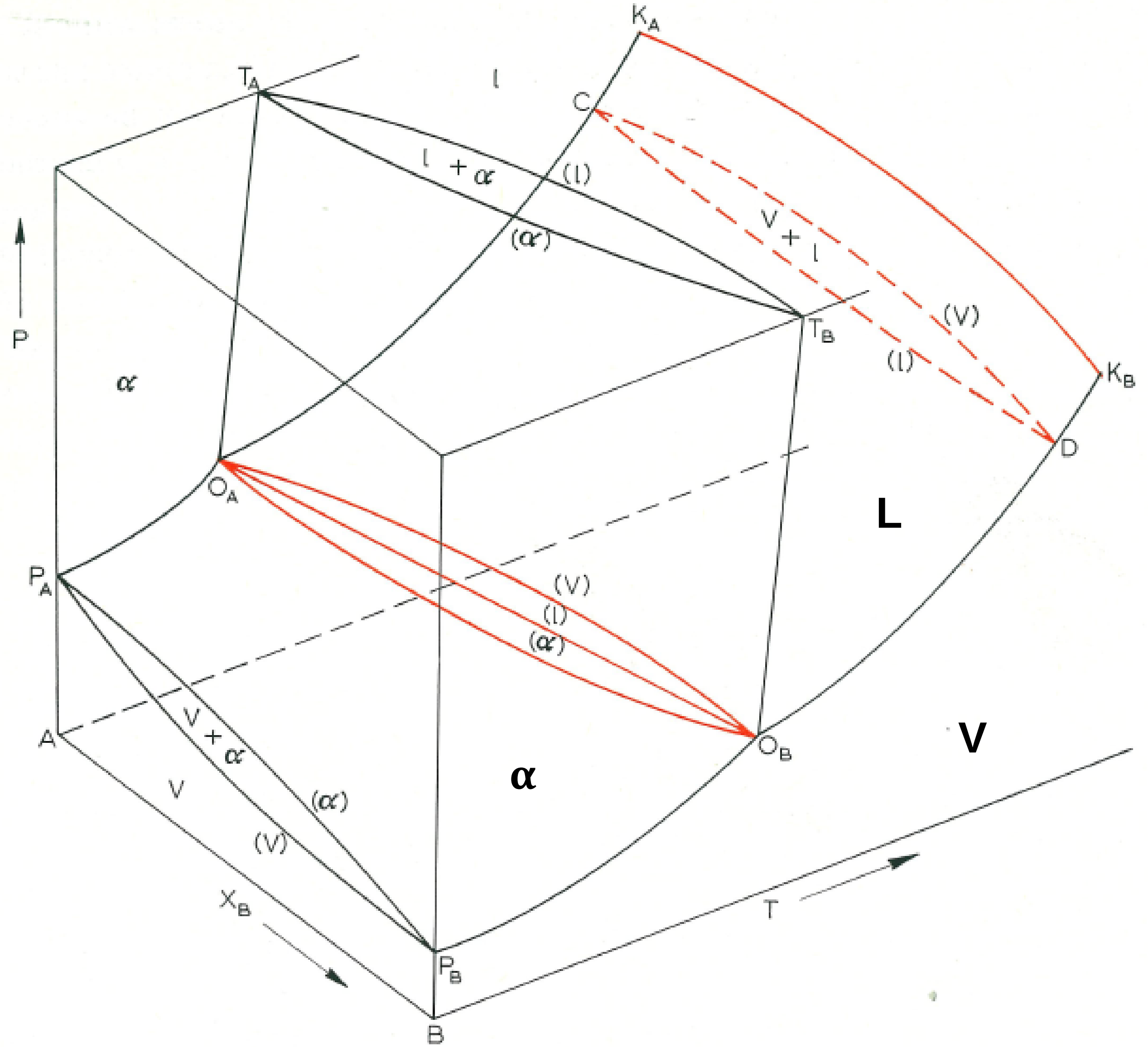


Fig. 35. Pressure–temperature–composition phase diagram for a system with continuous series of solutions

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

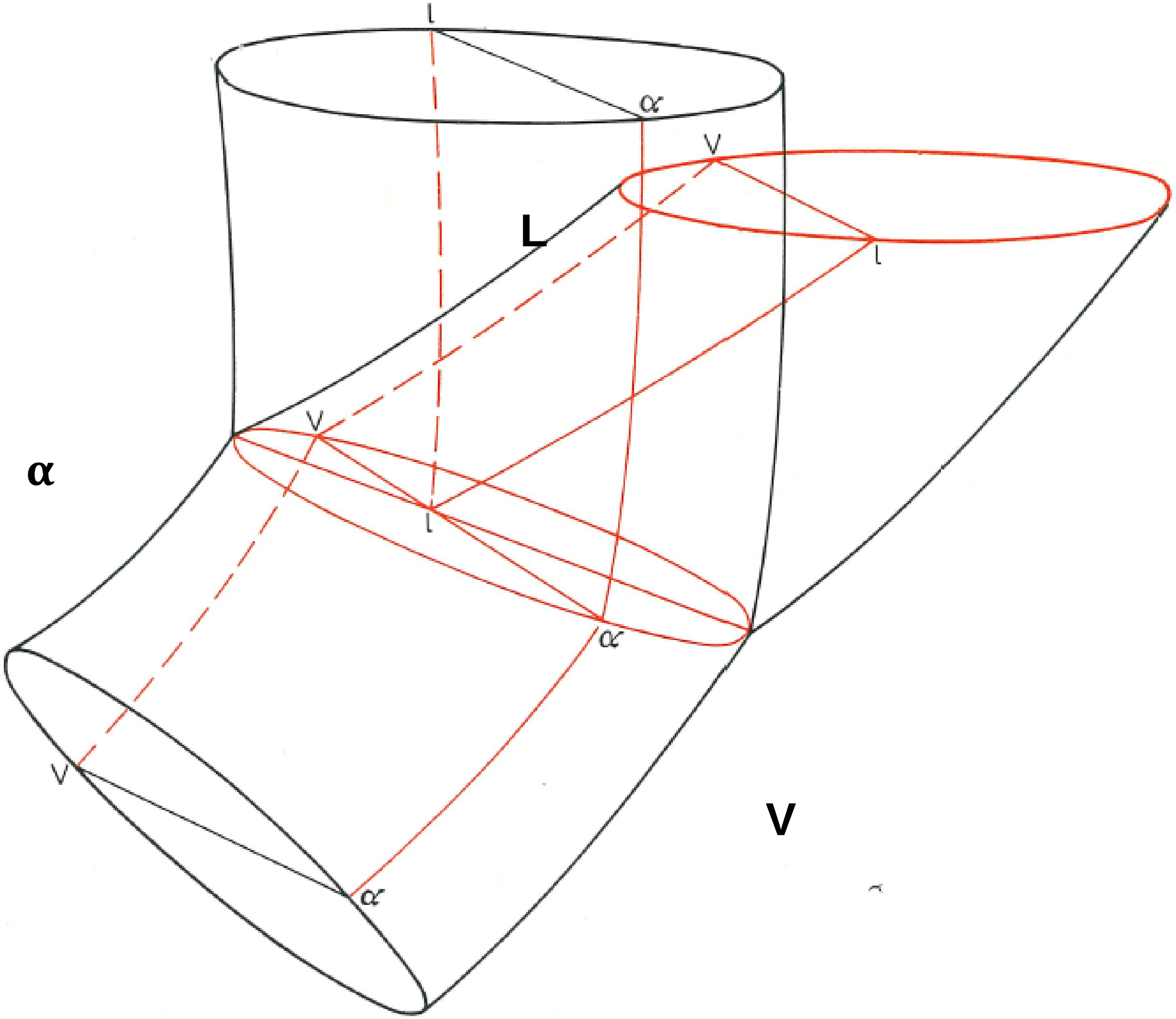


Fig. 36. Formation of a three-phase tie line $Vl\alpha$.

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

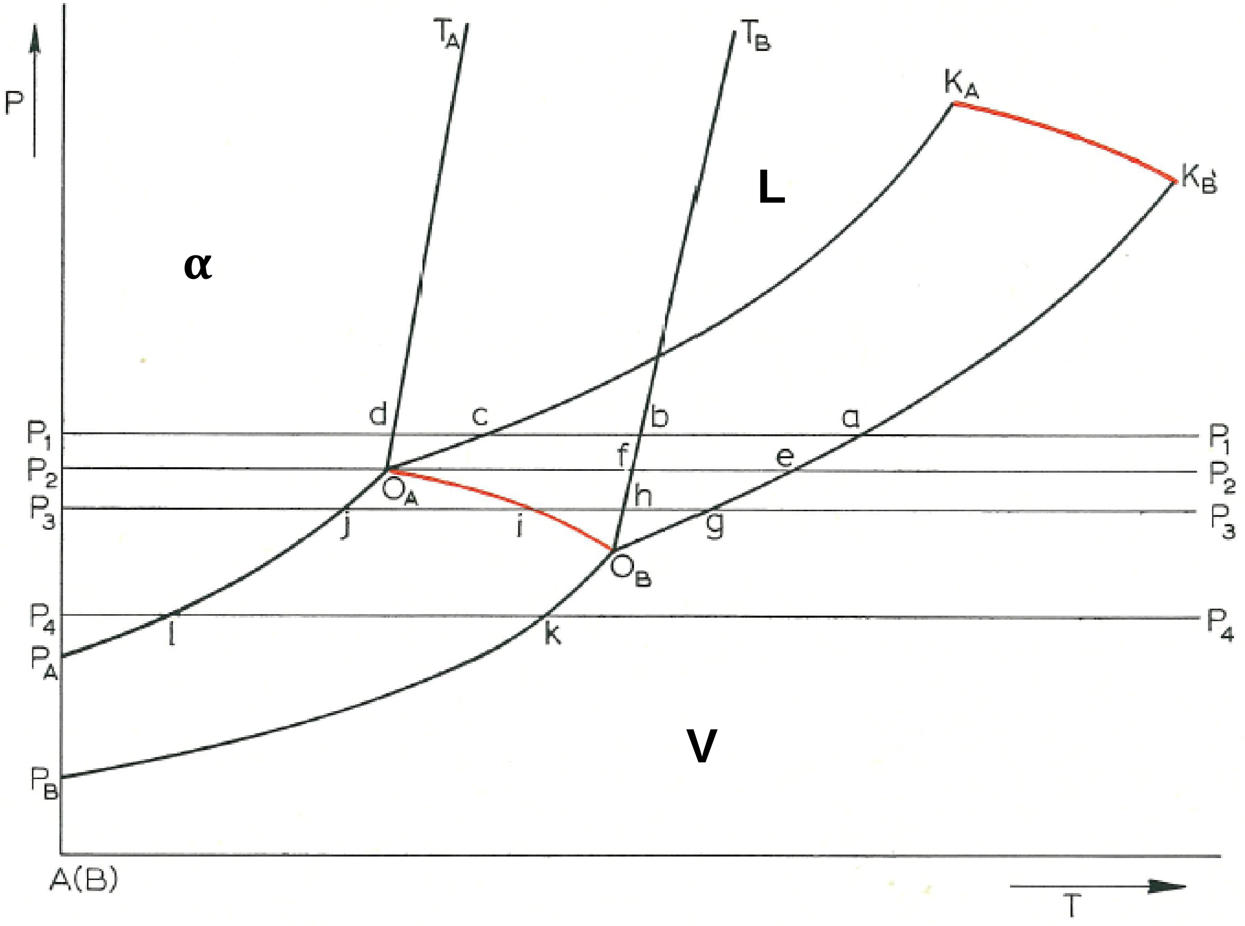


Fig. 37. Two-dimensional projection of Fig. 35 on the P–T plane for component A. P_AO_A — equilibrium between V_A and α_A; P_BO_B — V_B and α_B; O_AT_A — l_A and α_A; O_BT_B — l_B and α_B; O_AK_A — V_A and l_A; O_BK_B — V_B and l_B; O_AO_B — V_{AB}, l_{AB} and α_{AB}; O_A — V_A, l_A and α_A; O_B — V_B, l_B and α_B; K_AK_B — $V_{AB} = l_{AB}$.

3.2.6 Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions

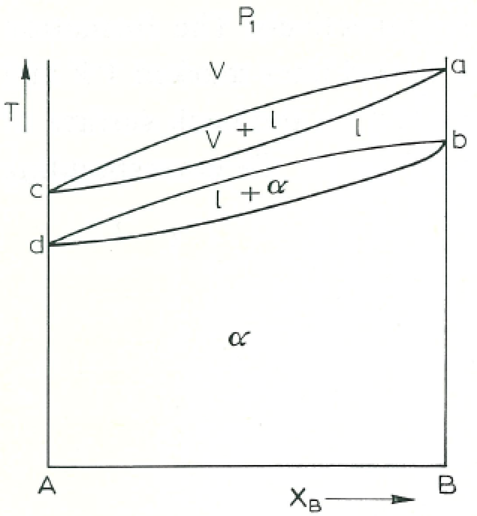


Fig. 38. *T–X* section through Fig. 35 at a pressure P_1 where $K_B > P_1 > O_A$.

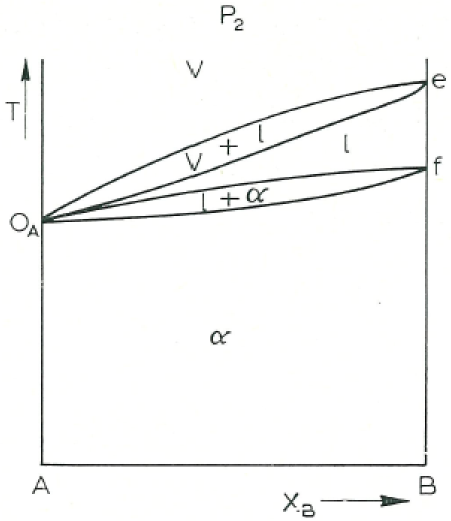


Fig. 39. *T–X* section through Fig. 35 at a pressure P_2 where $P_2 = O_A$

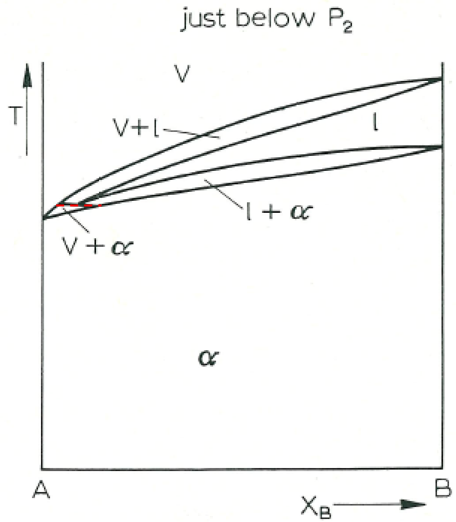


Fig. 40. *T–X* section through Fig. 35 at a pressure just below P_2.

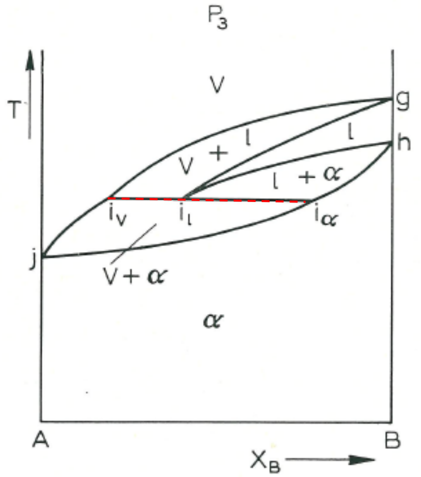


Fig. 41. *T–X* section through Fig. 35 at a pressure P_3 where $O_A > P_3 > O_B$.

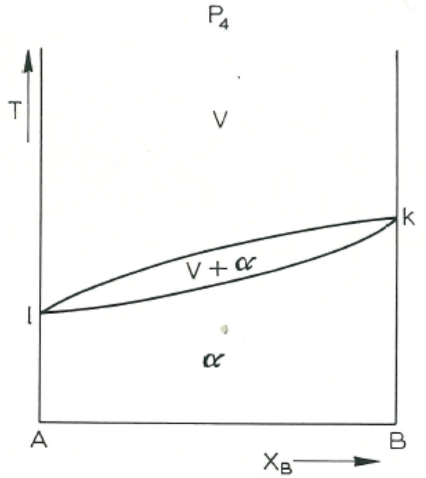


Fig. 42. *T–X* section through Fig. 35 at a pressure P_4 where $O_B > P_4 > P_B$.

Contents for today’s class

CHAPTER 4

Binary Phase Diagrams

Three-Phase Equilibrium Involving Limited Solubility of the Components in the Solid State but Complete Solubility in the Liquid State

*** Three-Phase Equilibrium : Eutectic Reactions**

a) Structural Factor: Hume-Rothery Rules

Empirical rules for substitutional solid-solution

complete solid solution ↔ **limited solid solution**

Similar atomic radii, the same valency and crystal structure

b) The eutectic reaction

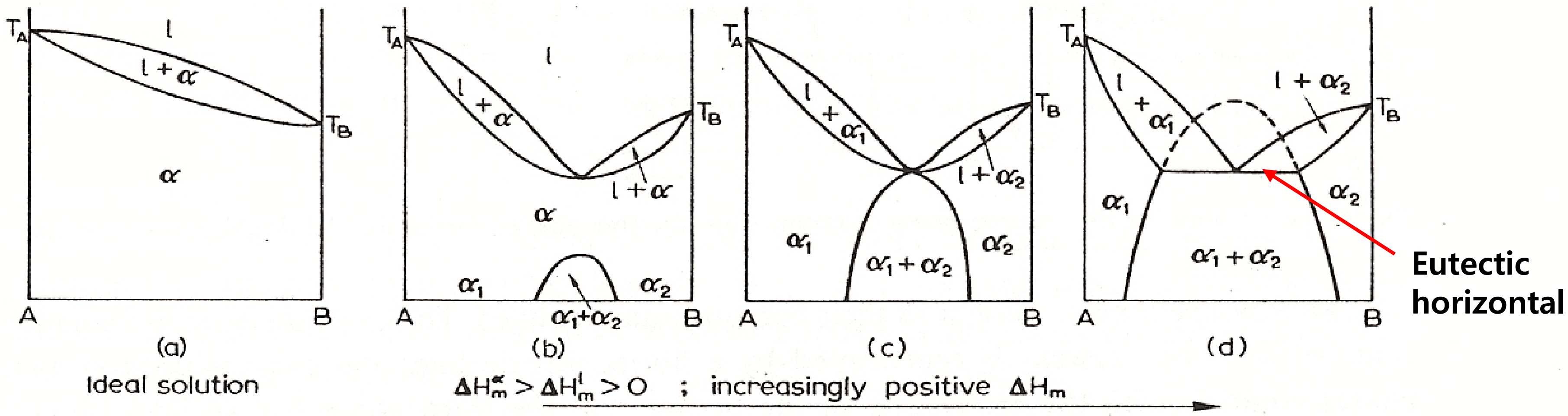
c) Limiting forms of eutectic phase diagrams

d) Retrogade solidus curves

* Simple Eutectic Systems

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

- **Three-Phase Equilibrium Involving Limited Solubility of the Components in the Solid State but Complete Solubility in the Liquid State**



Eutectic horizontal

Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

* Simple Eutectic Systems

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

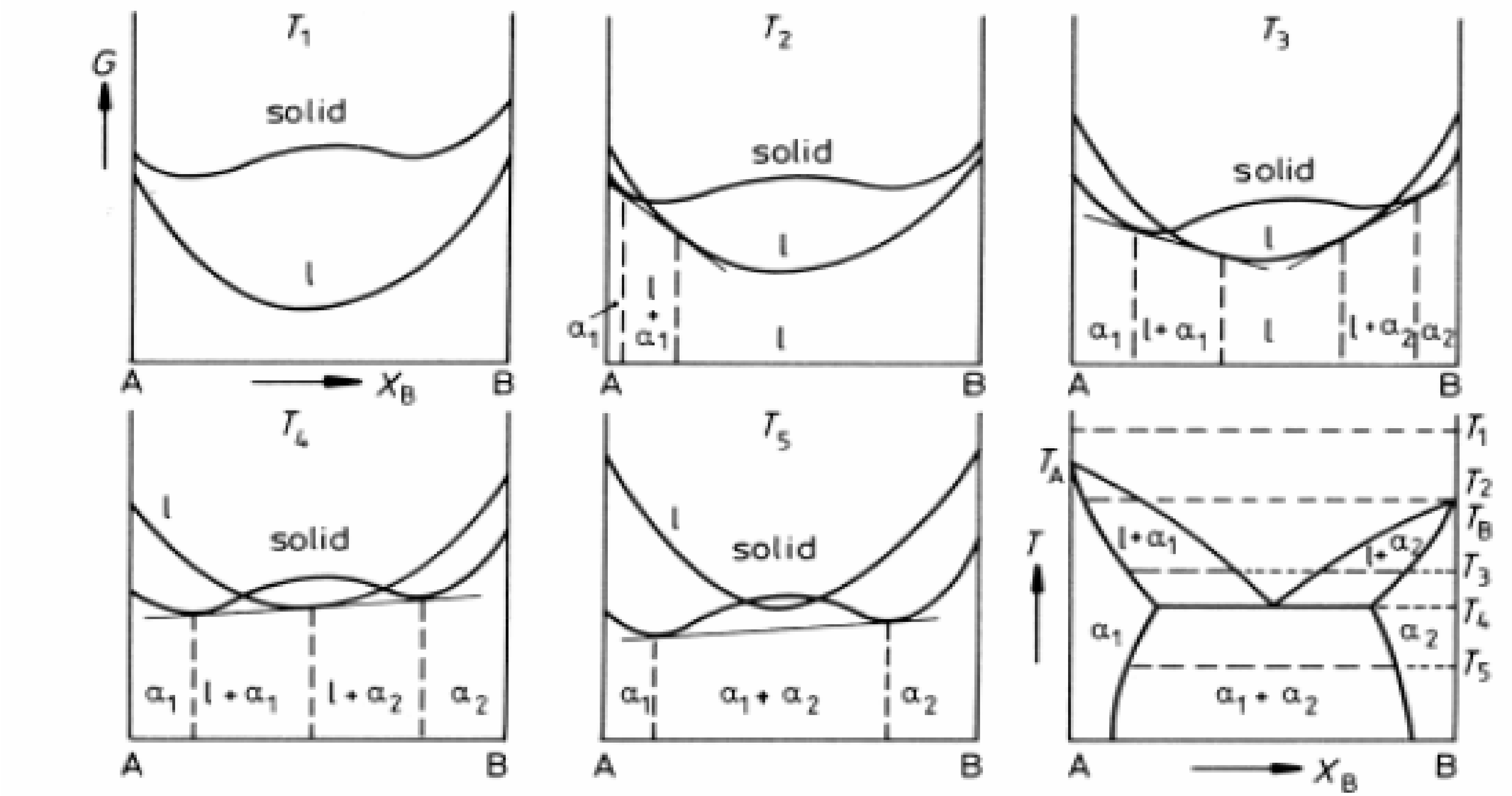


Fig 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure. (After A.H. Cottrell, *Theoretical Structural Metallurgy*, Edward Arnold, London, 1955,©Sir Alan Cottrell.)

(when each solid has the different crystal structure.)

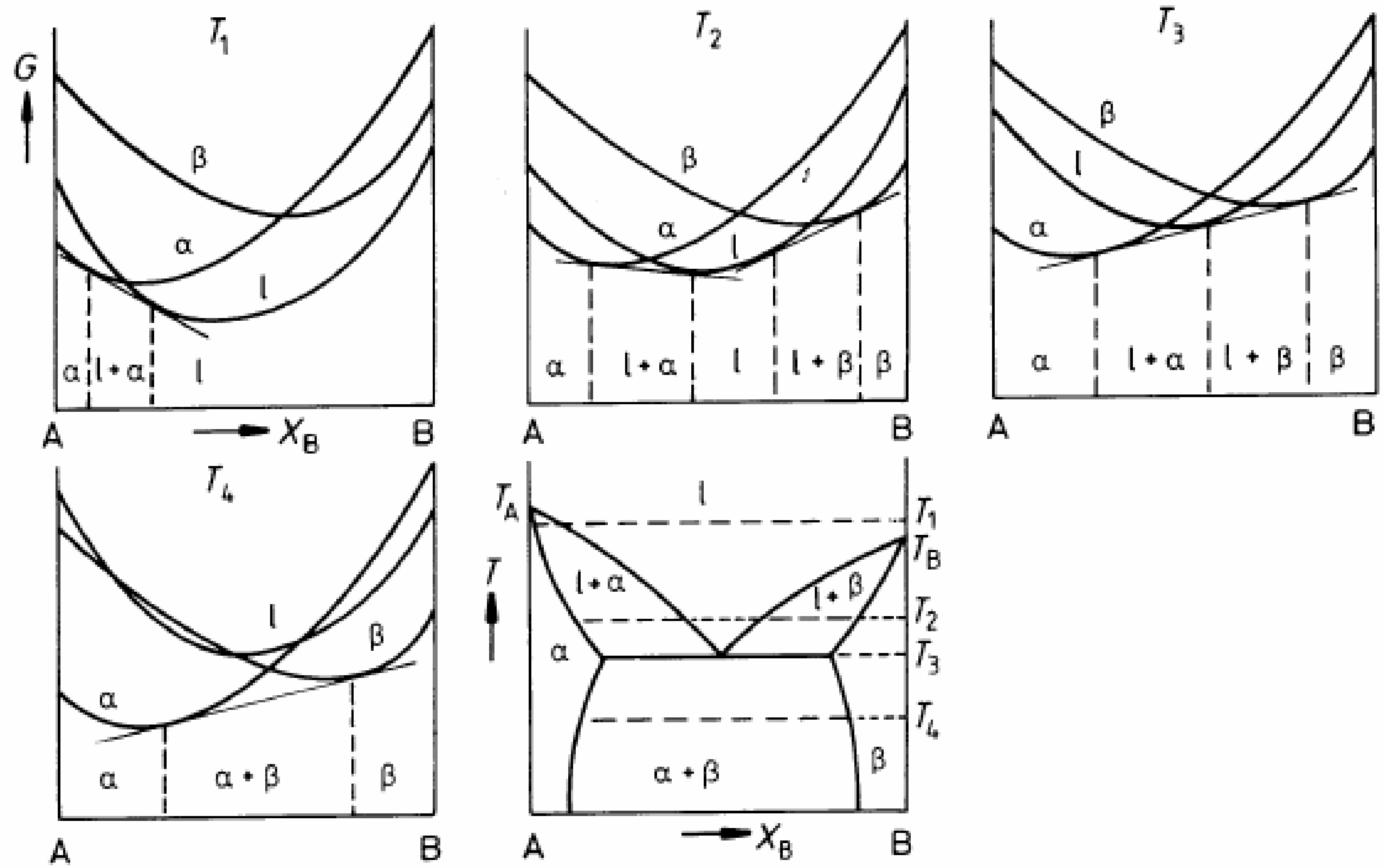
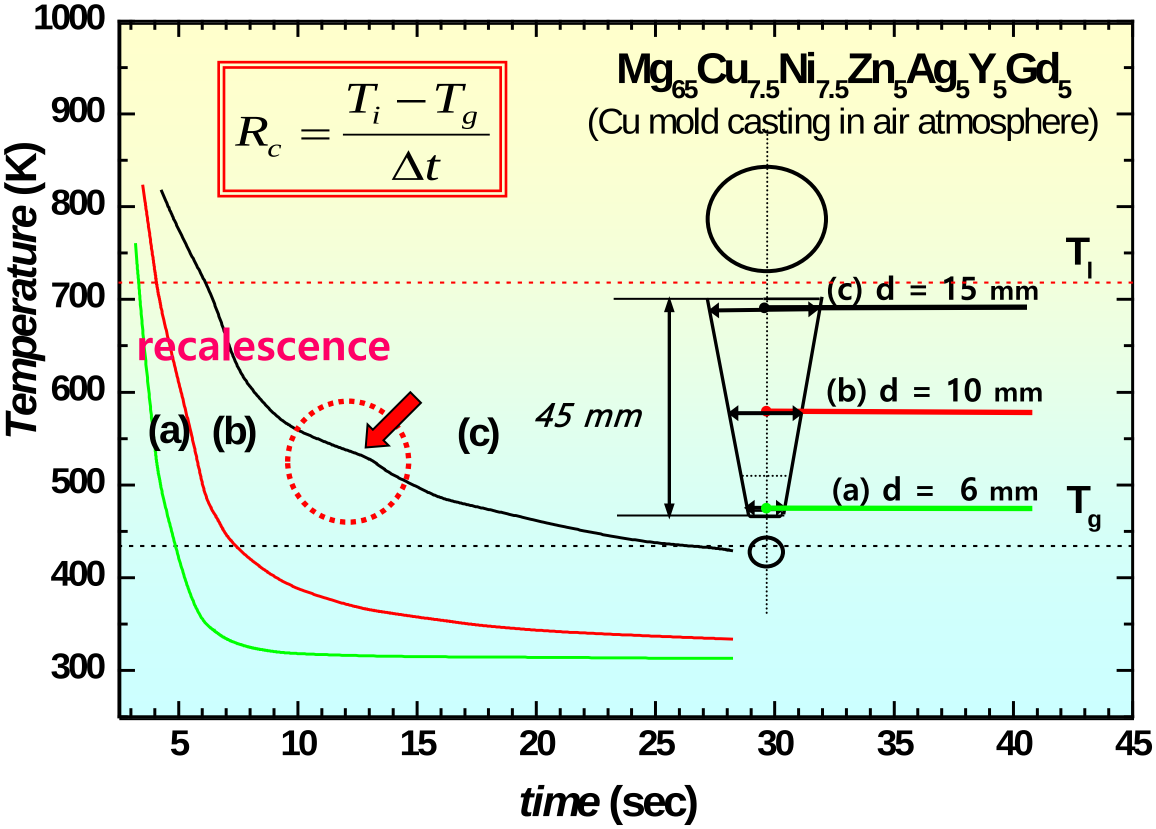


Fig. 1.33 The derivation of a eutectic phase diagram where each solid phase has a different crystal structure. (After A. Prince, *Alloy Phase Equilibria*, Elsevier, Amsterdam, 1966.)

Measurement of R_c in Mg BMG (D_{max}=14 mm)



top position : recalescence

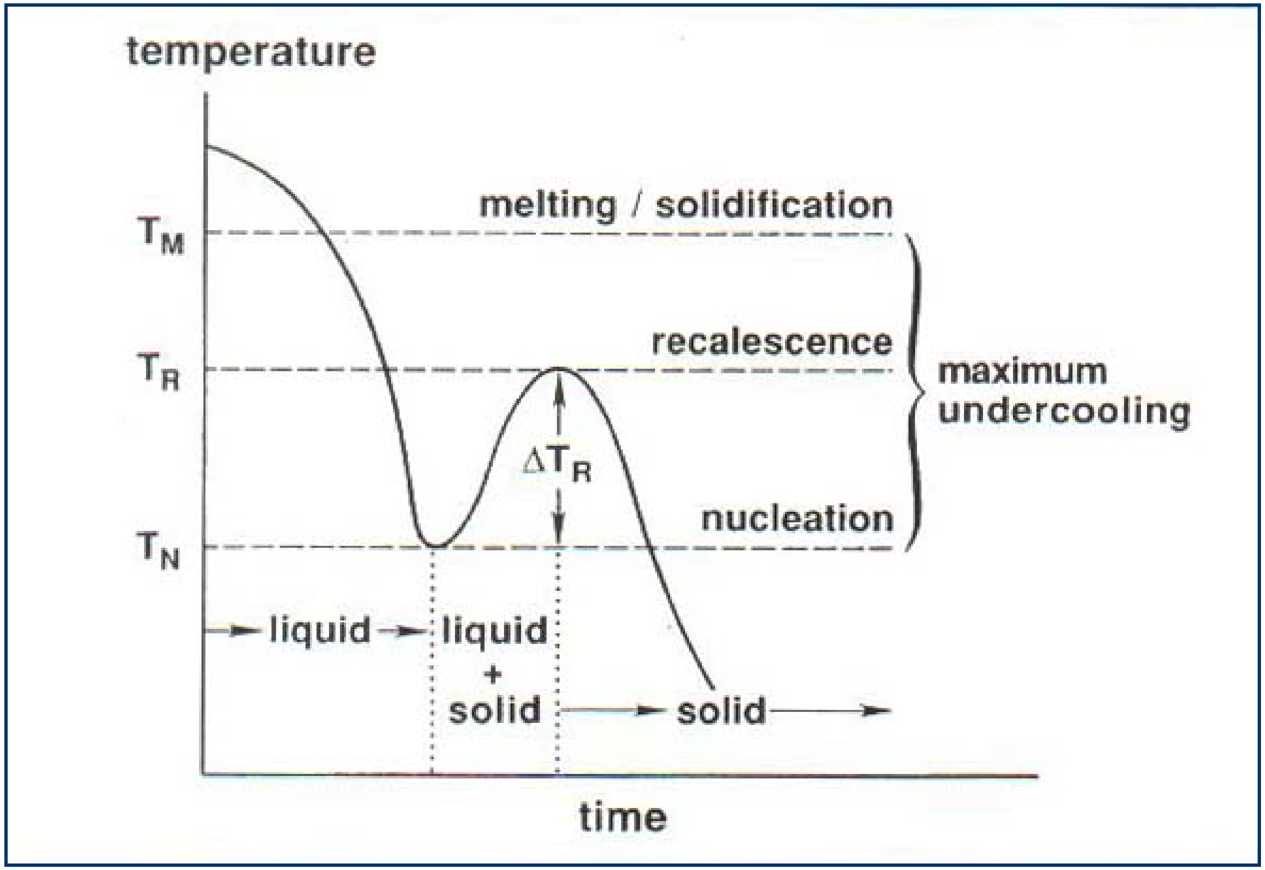
middle position : 64K/s

bottom position : 137 K/s

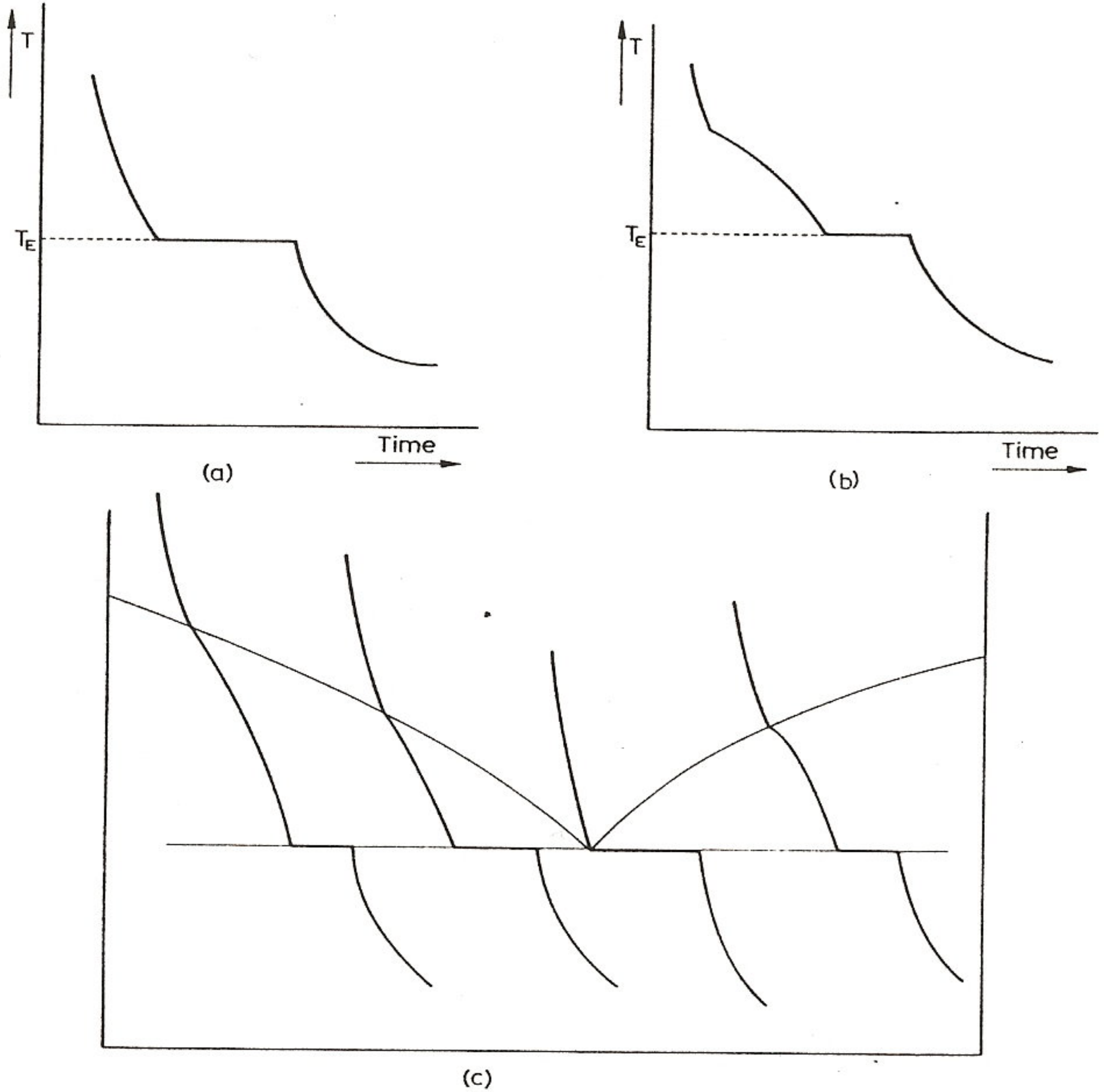
* **Cooling curves** measured at the center of the three transverse cross sections

* JAP 104, 023520 (2008)

Nucleation Theory as Applied to solidification



- **The recalescence process is illustrated by a temperature versus time plot, showing the temperature rise on nucleation due to release of the heat of fusion.**
- **A sudden glowing in a undercooled liquid of metal caused by liberation of the latent heat of transformation**
- **The higher the recalescence temperature, the larger the microstructural scale in the solid.**



(a)

(b)

(c)

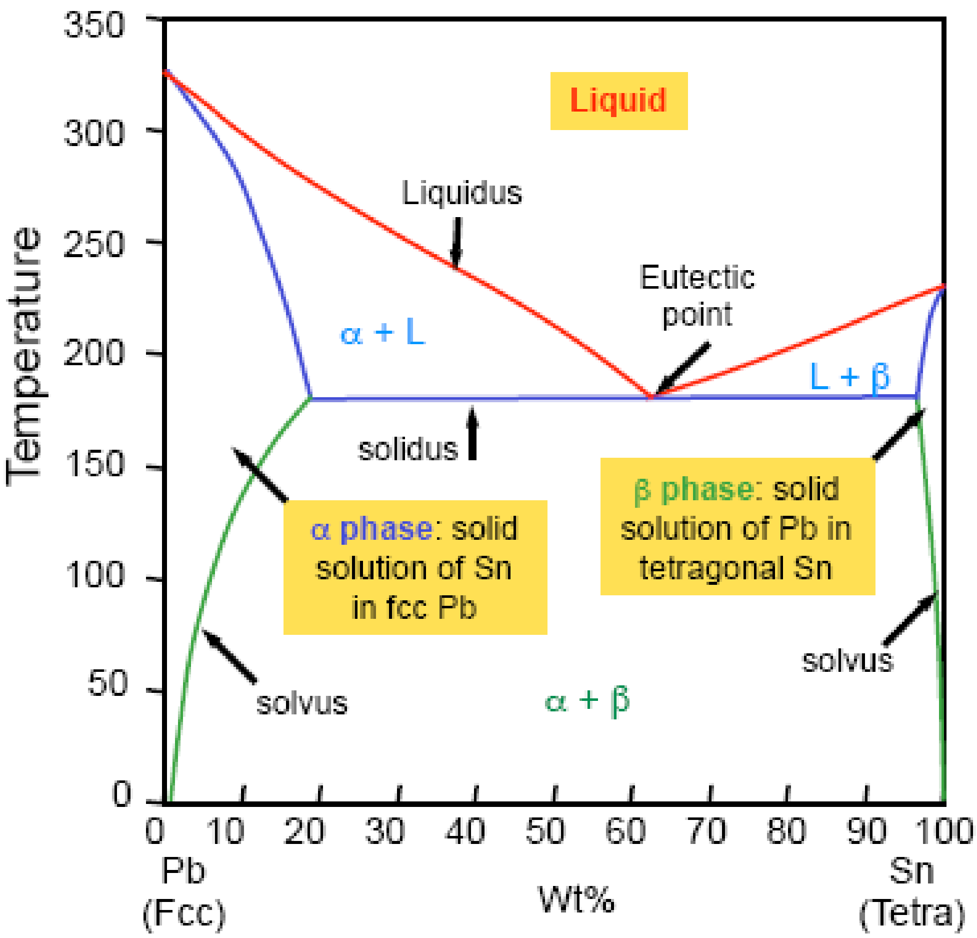
Fig. 48. Cooling curve for (a) the eutectic alloy, (b) hypo-eutectic alloy *N*, and (c) a series of alloys, allowing the determination of the liquidus and eutectic horizontal.

Eutectic Systems

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

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)

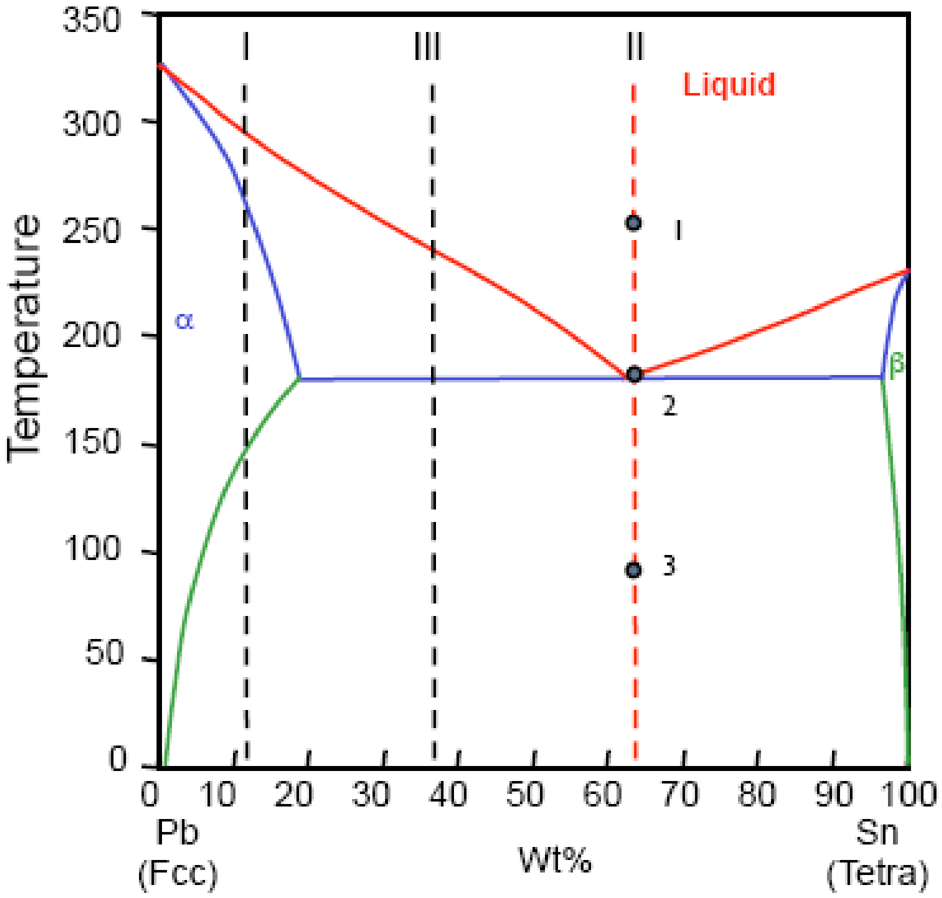
The amounts of α and β increase in proportion with time.

Solidification finishes at the same temperature.

At point 3: α+β

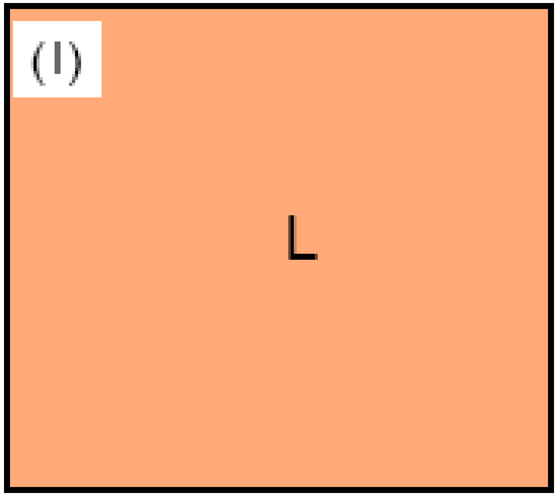
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β.

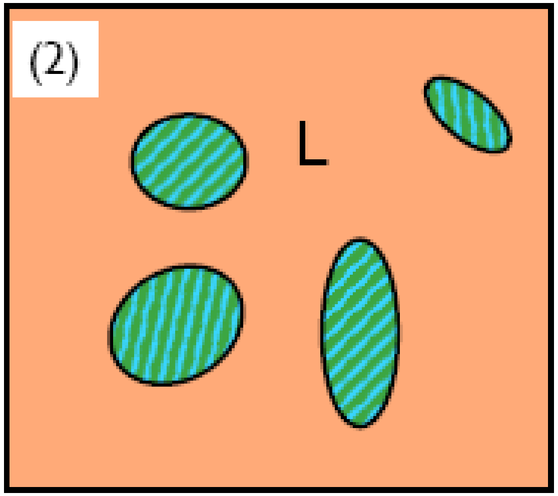
Pb-Sn phase diagram



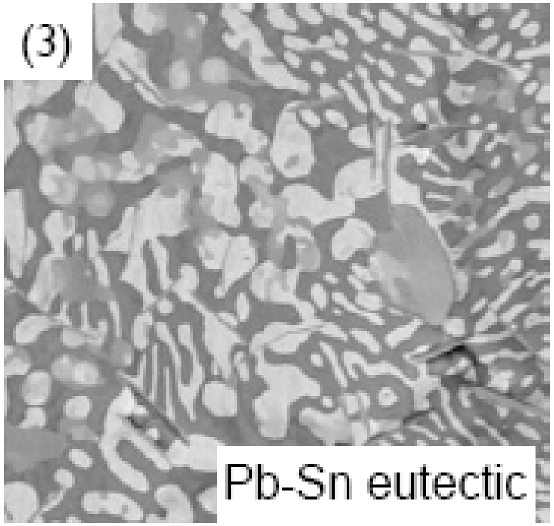
1.5 Binary phase diagrams

Alloy II





Nucleation of colonies of α and β laminates



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

4.3.2 Eutectic Solidification: L→α + β

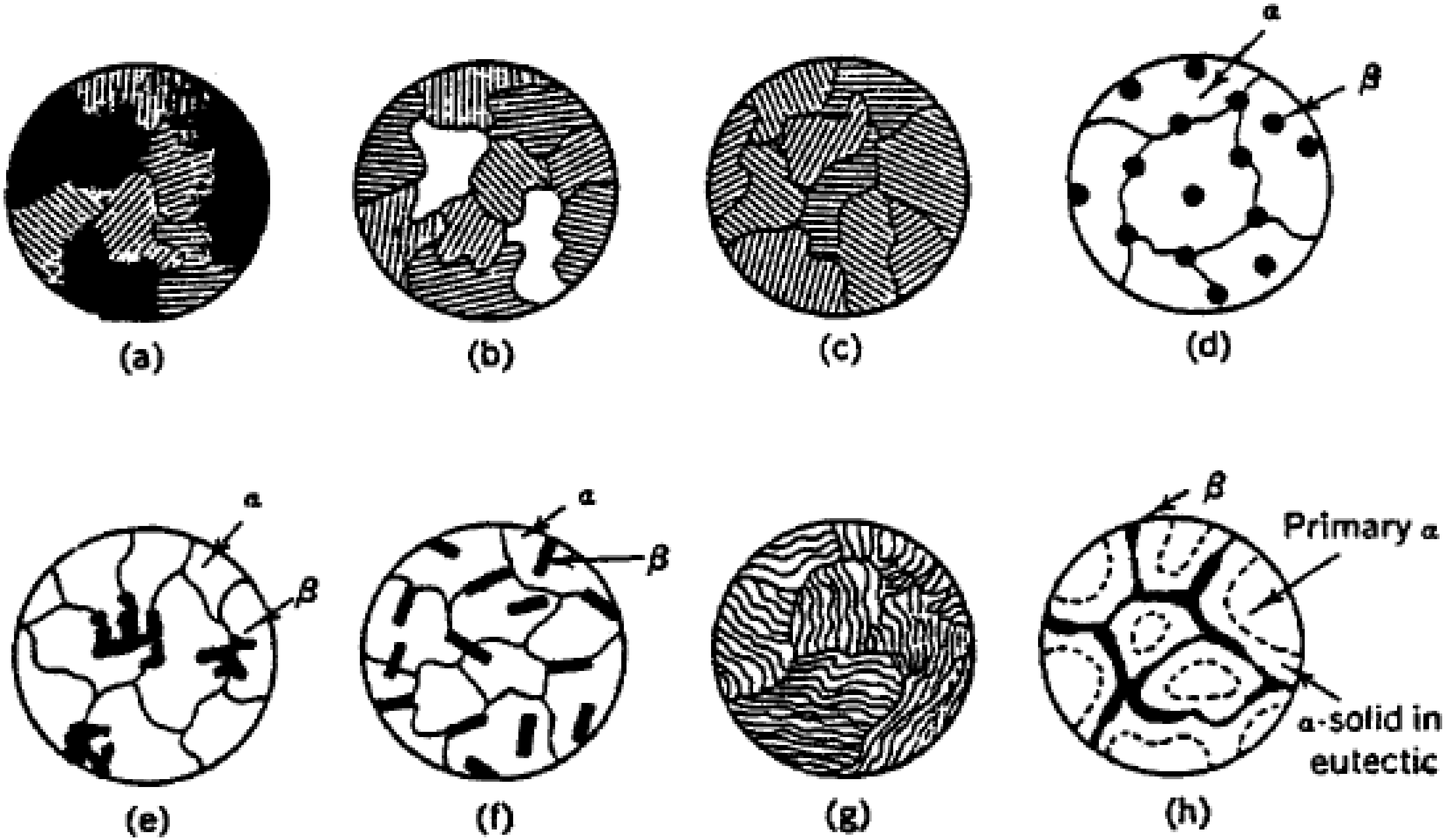


Fig. 14 Schematic representation possible in eutectic structures. (a), (b) and (c) are alloys shown in fig. 13; (d) nodular; (e) Chinese script; (f) acicular; (g) lamellar; and (h) divorced.

4.3.2 Eutectic Solidification

During solidification both phases grow simultaneously behind an essentially planar solid/liquid interface.

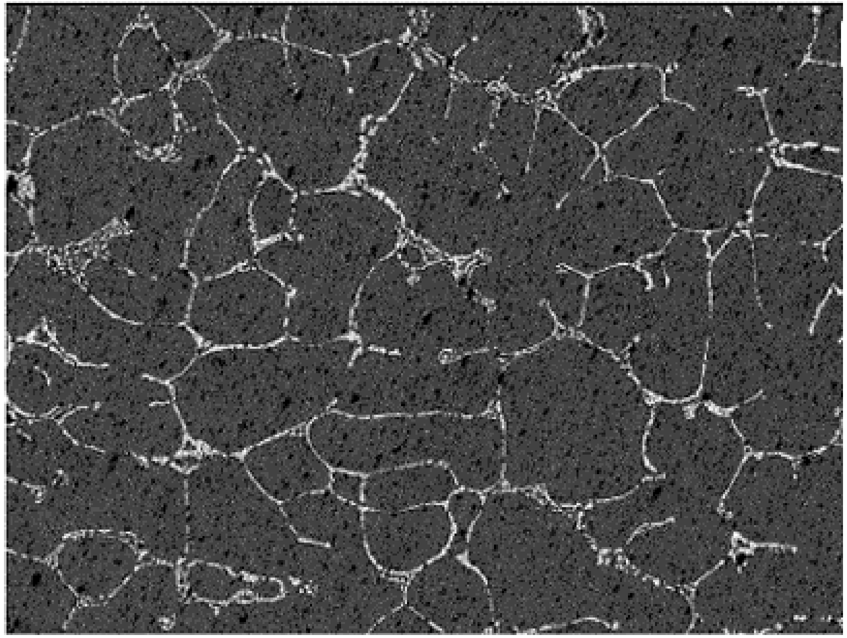
Normal eutectic

both phases have low entropies of fusion.

Anomalous eutectic

One of the solid phases is capable of faceting, i.e., has a high entropy or melting.

Fig. 4.30 Rod-like eutectic. Al_6Fe rods in Al matrix. Transverse section. Transmission electron micrograph (x 70000).

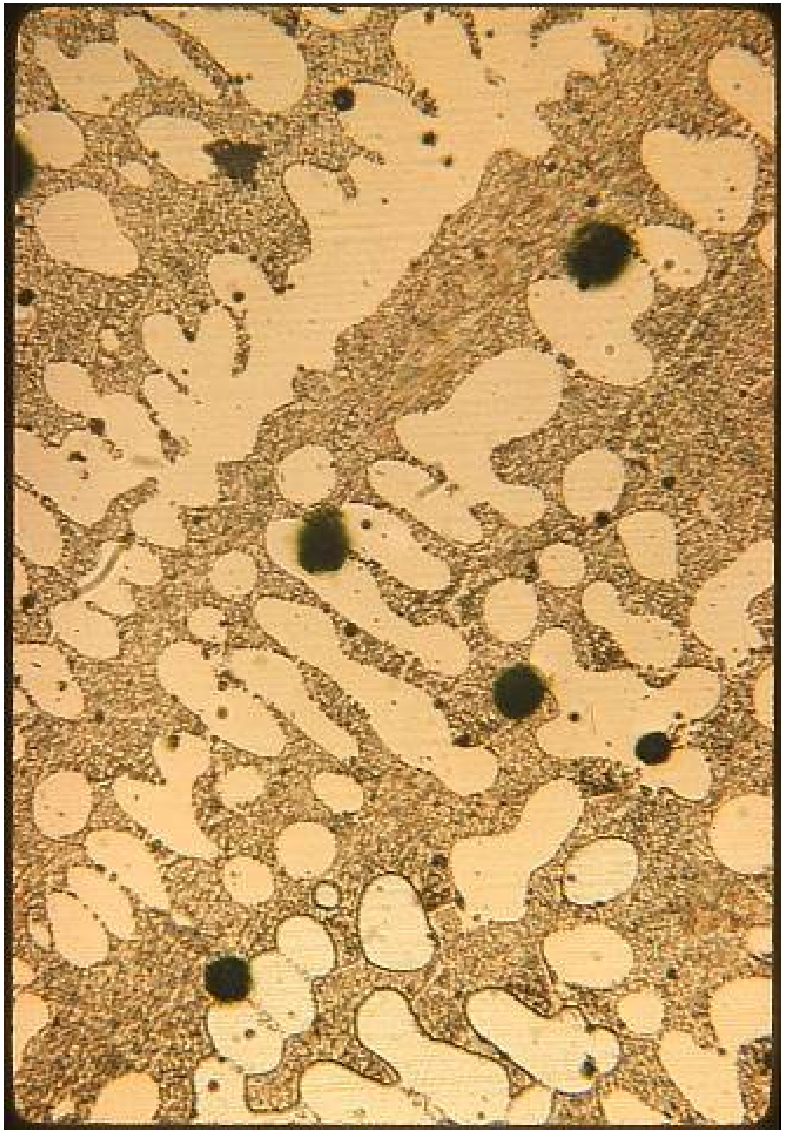


The microstructure of the Pb-61.9%Sn (eutectic) alloy presented a coupled growth of the (Pb)/βSn eutectic. There is a remarkable change in morphology increasing the degree of undercooling with transition from regular lamellar to anomalous eutectic.

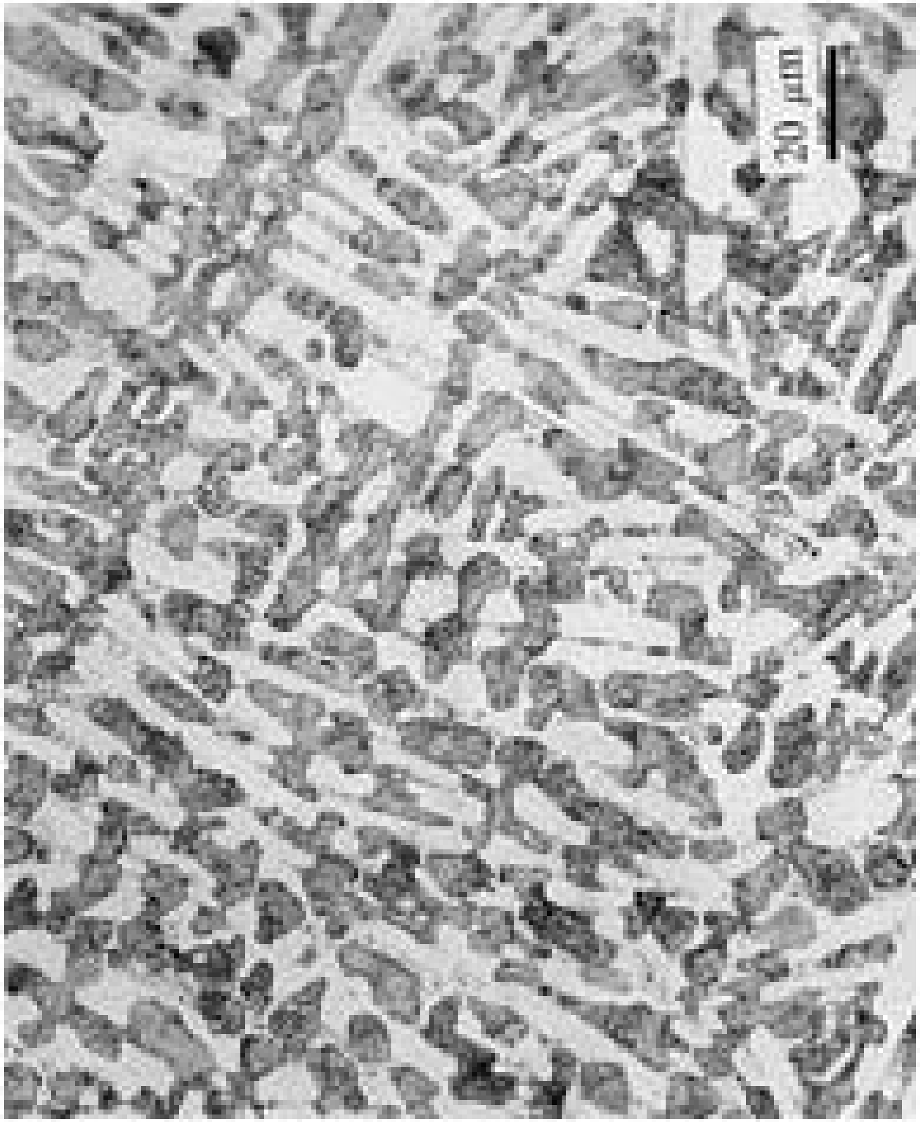
http://www.matter.org.uk/solidification/eutectic/anomalous_eutectics.htm

D.A. Porter and K.E. Eastering, "Phase Transformations in Metals and Alloys"

Eutectic



Divorced Eutectic



Solidification of Eutectic Systems

Alloy I :

At point 1: Liquid

Solidification starts at liquidus

At point 2: L+α

The amount α ↑ with ↓ T

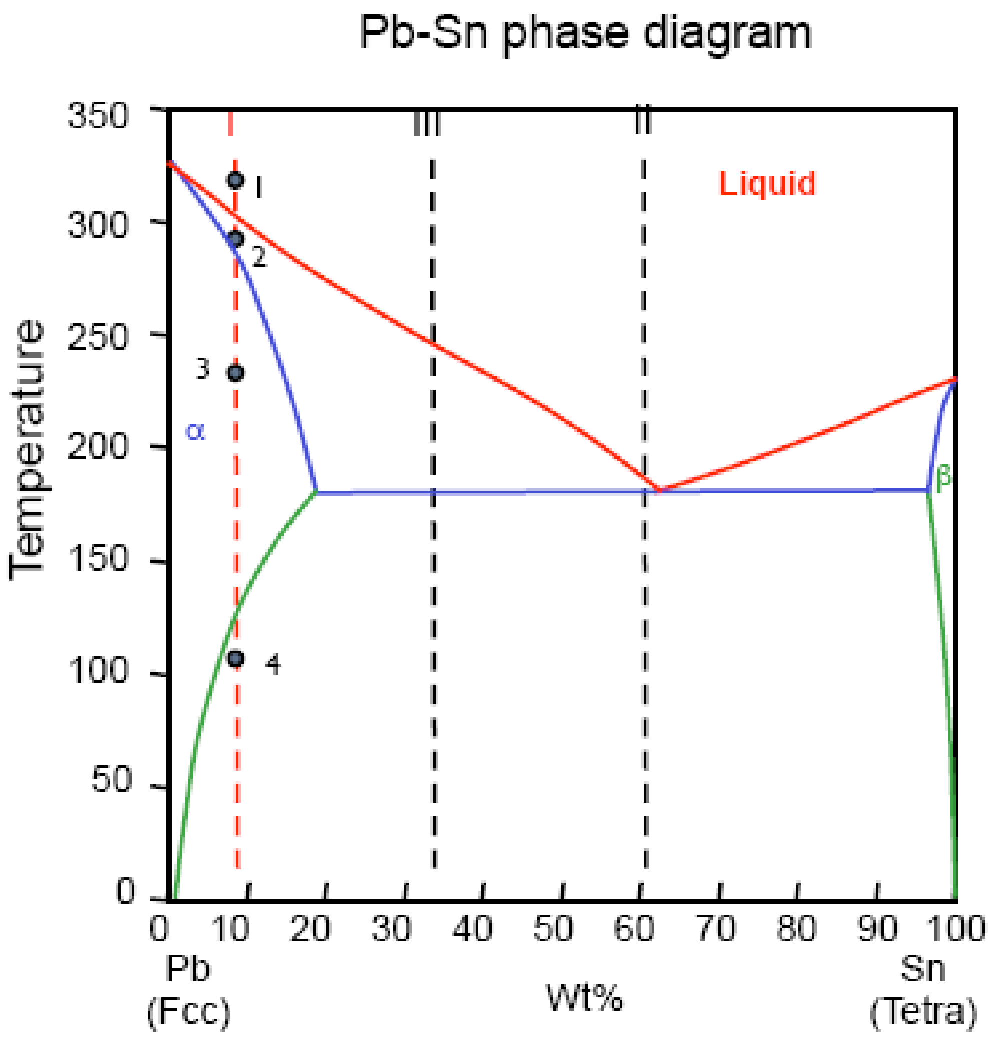
Solidification finishes at solidus

At point 3: α

Precipitation starts at solvus

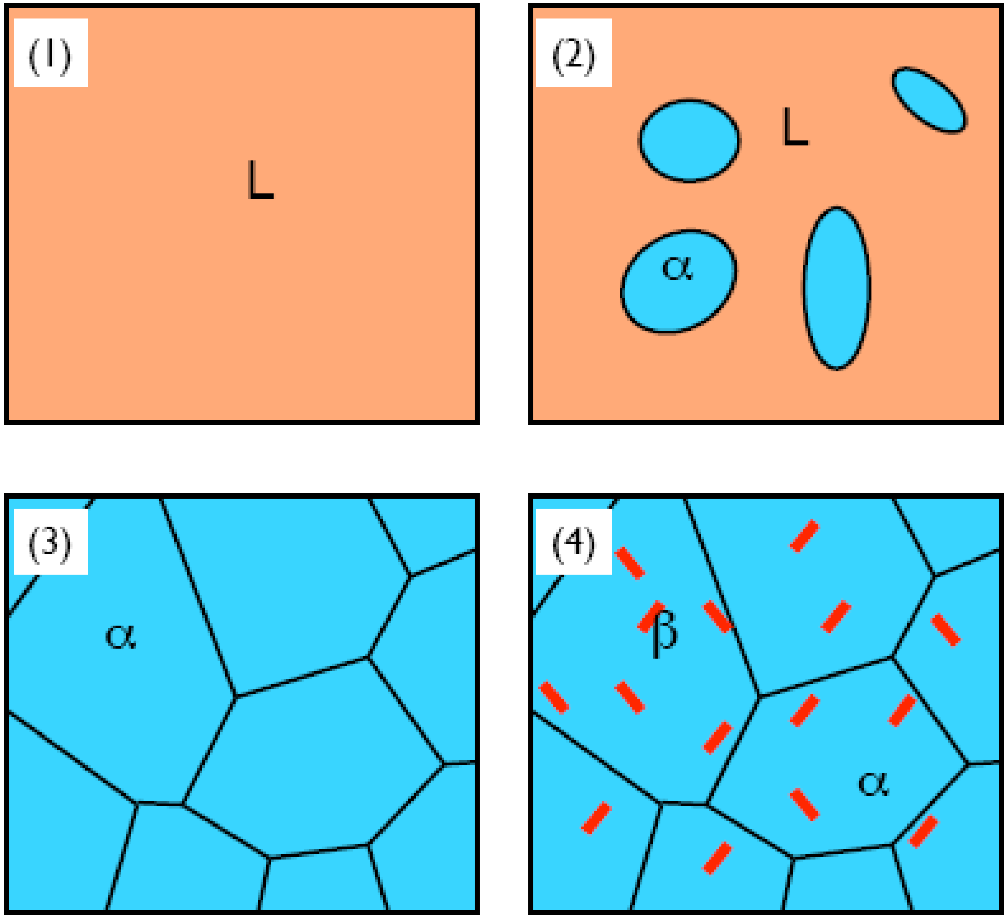
At point 4: α+β

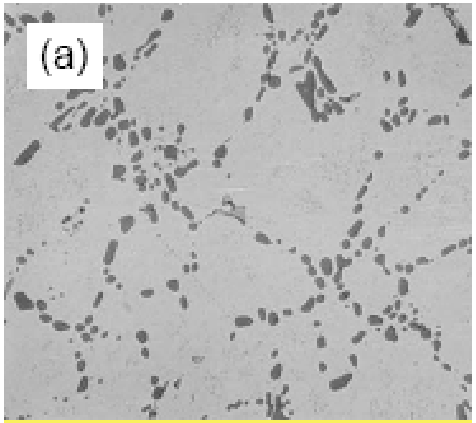
Further cooling leads to formation and growth of more β precipitates whereas Sn% in α decreases following the solvus.



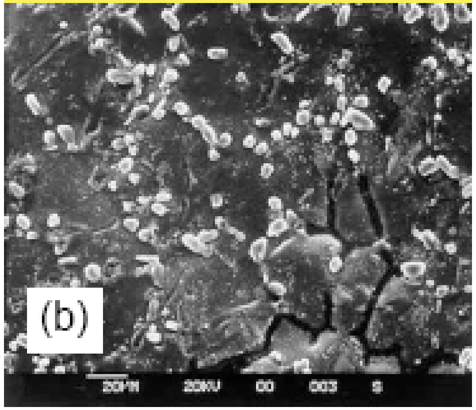
1.5 Binary phase diagrams

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

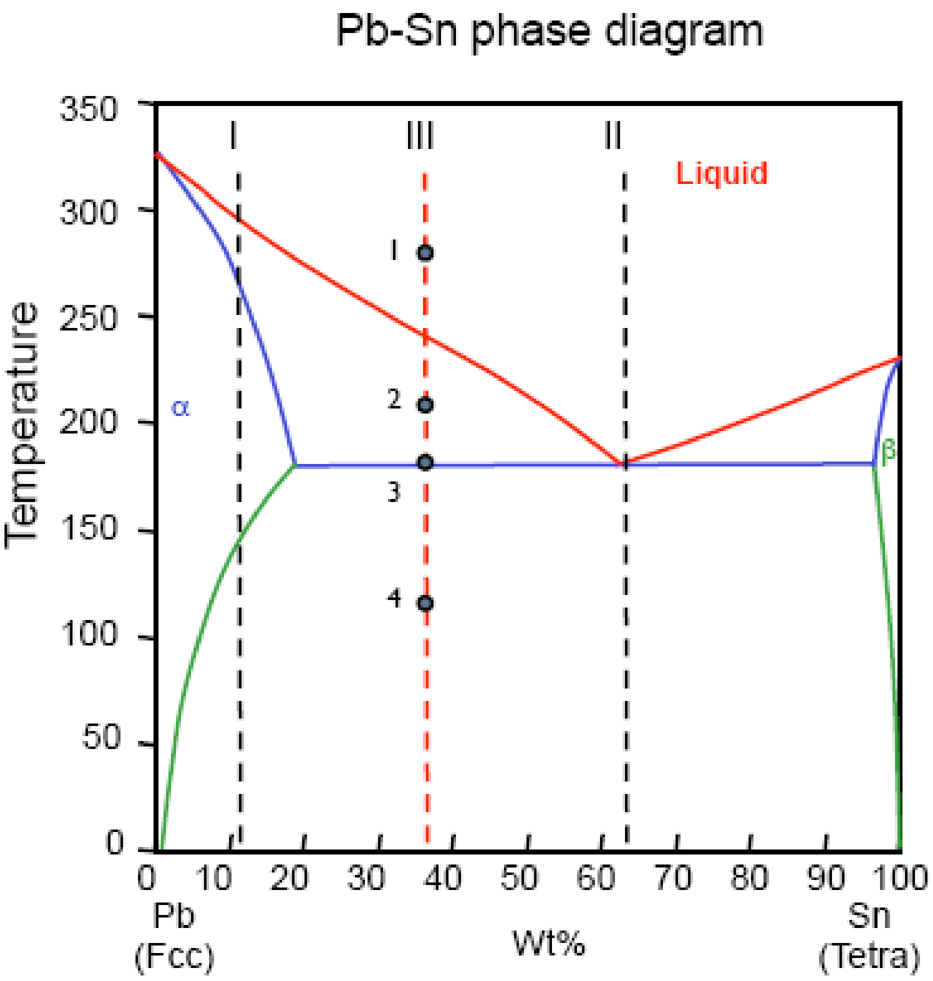
At point 3: L✦ (α+β) (eutectic reaction)

Solidification finishes at the eutectic temperature

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

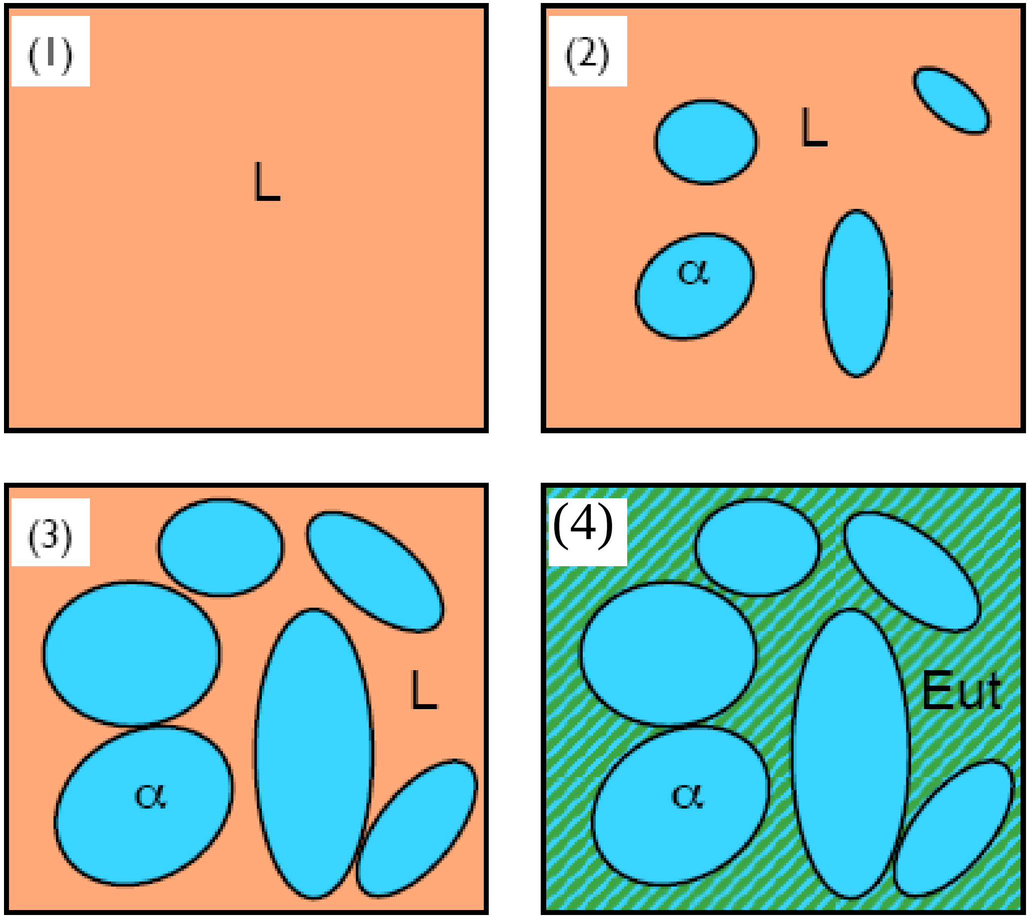
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β.

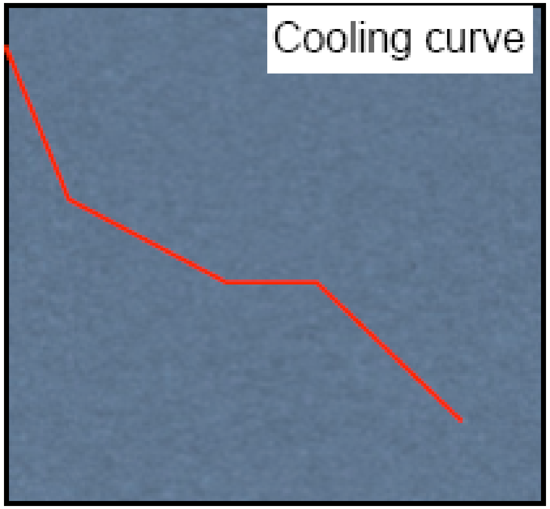
The cooling curve of this alloy is a combination of the two cooling curves shown in slide 9.

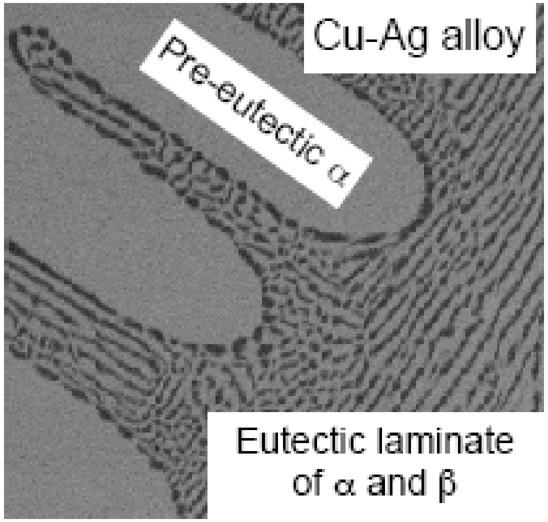


1.5 Binary phase diagrams: Hypoeutectic

Alloy III



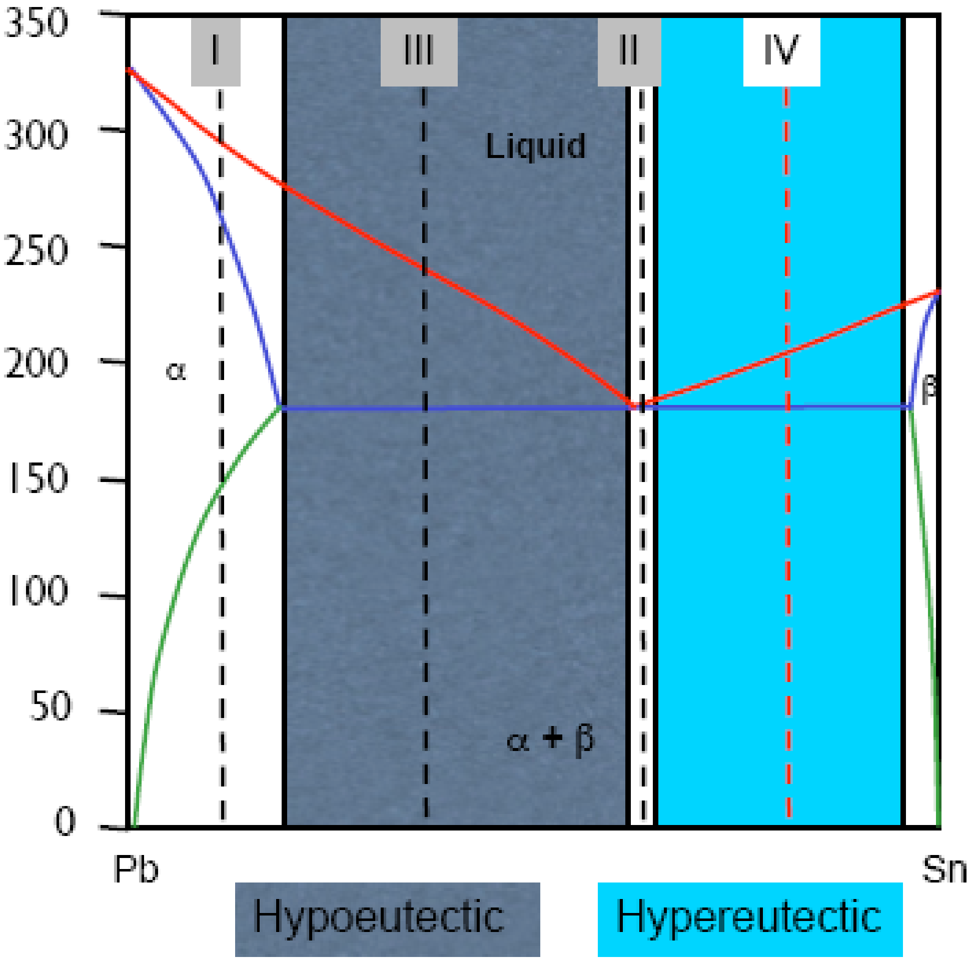

Cooling curve


Cu-Ag alloy

Solidification of Eutectic Systems

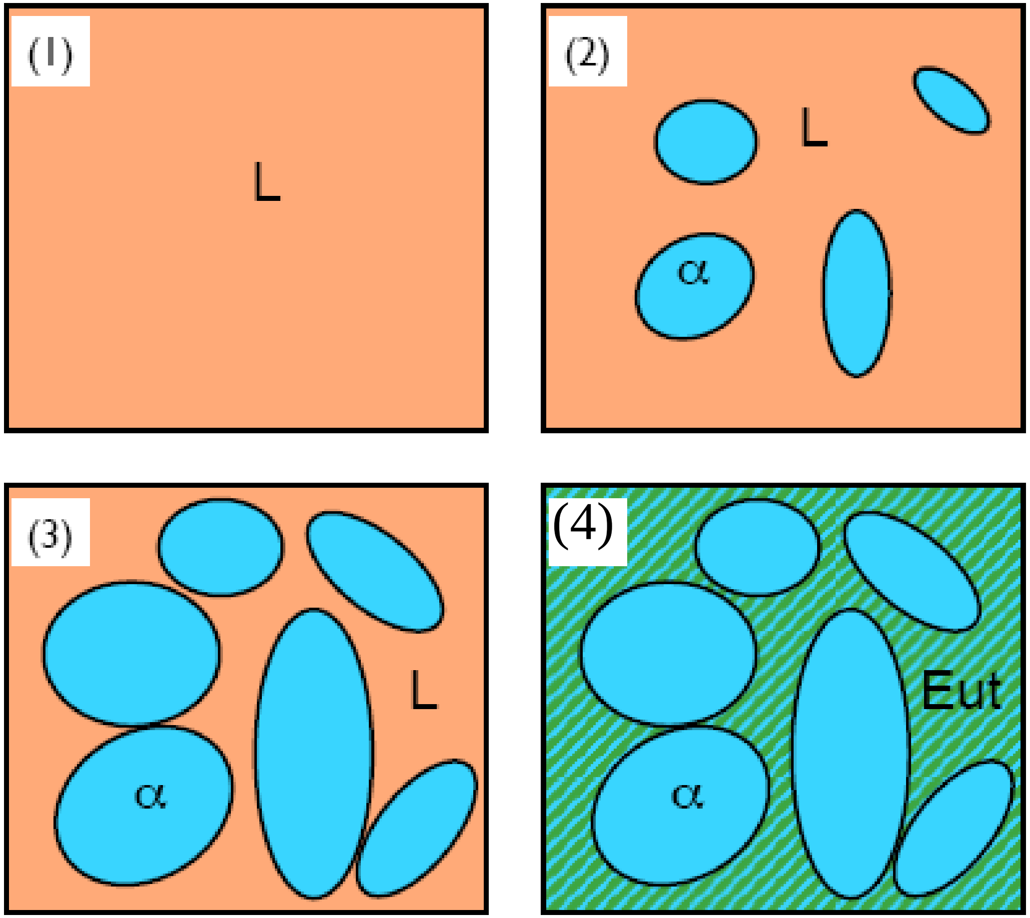
Alloy IV

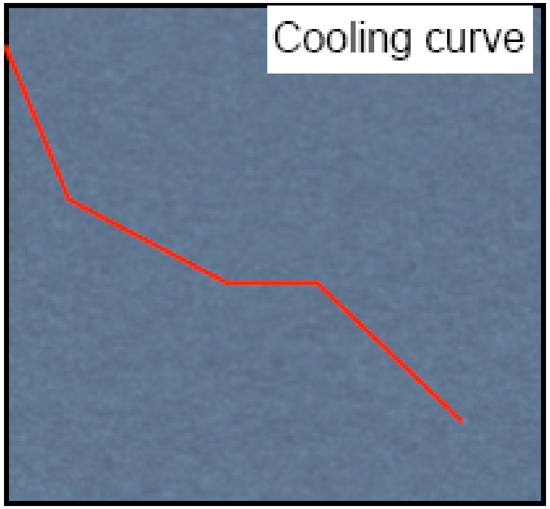
Can you describe the solidification process of alloy IV, including microstructure evolution, morphology of phases and cooling curve?

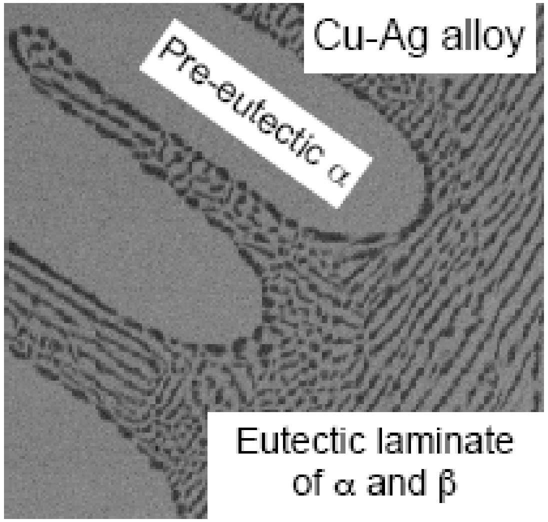


1.5 Binary phase diagrams : Hypereutectic

Alloy IV







4.2.3. Limiting forms of eutectic phase diagram

1) 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.

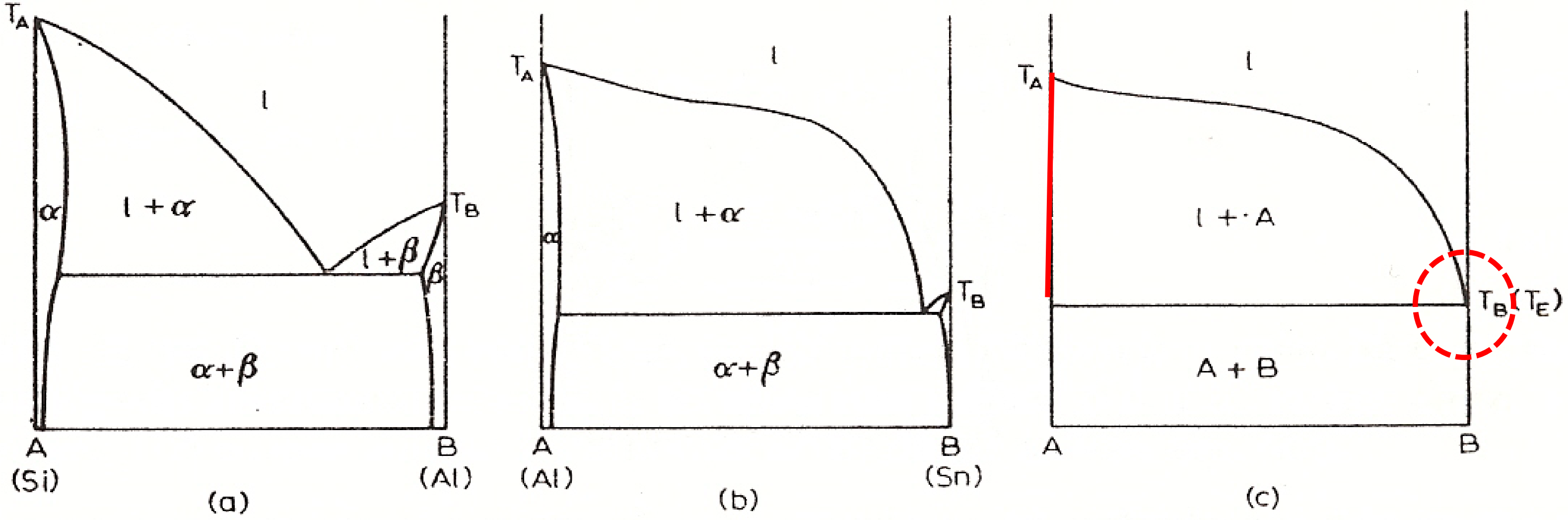


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

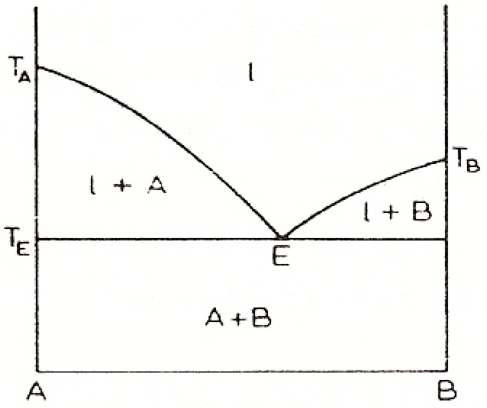
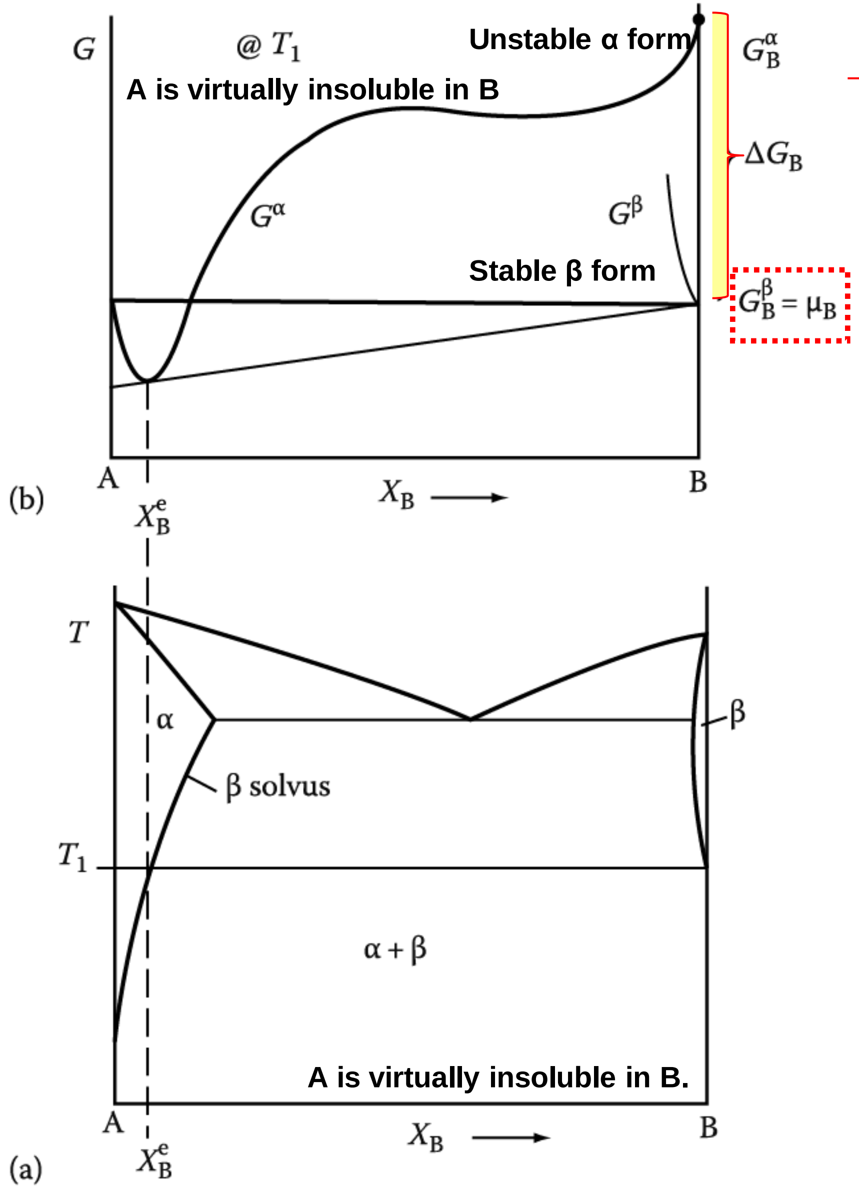


Fig. 54. Impossible form of a binary eutectic phase diagram.

* 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.

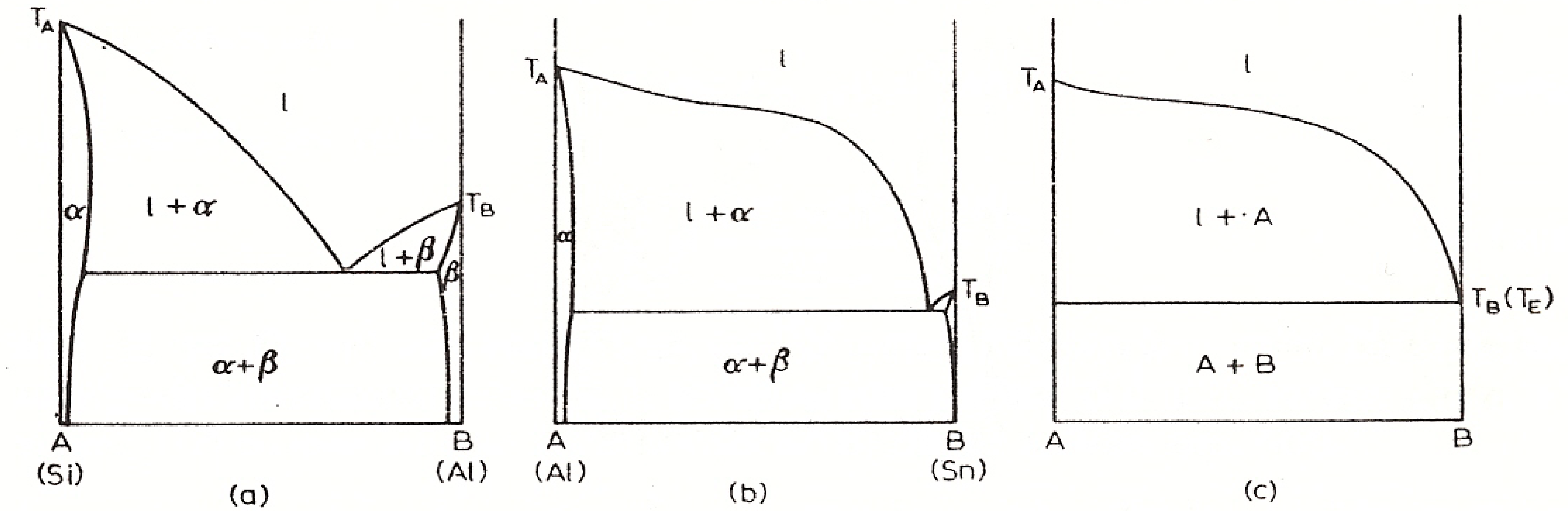


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

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

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.

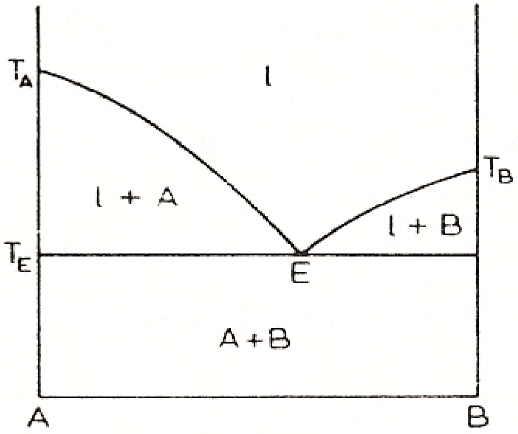
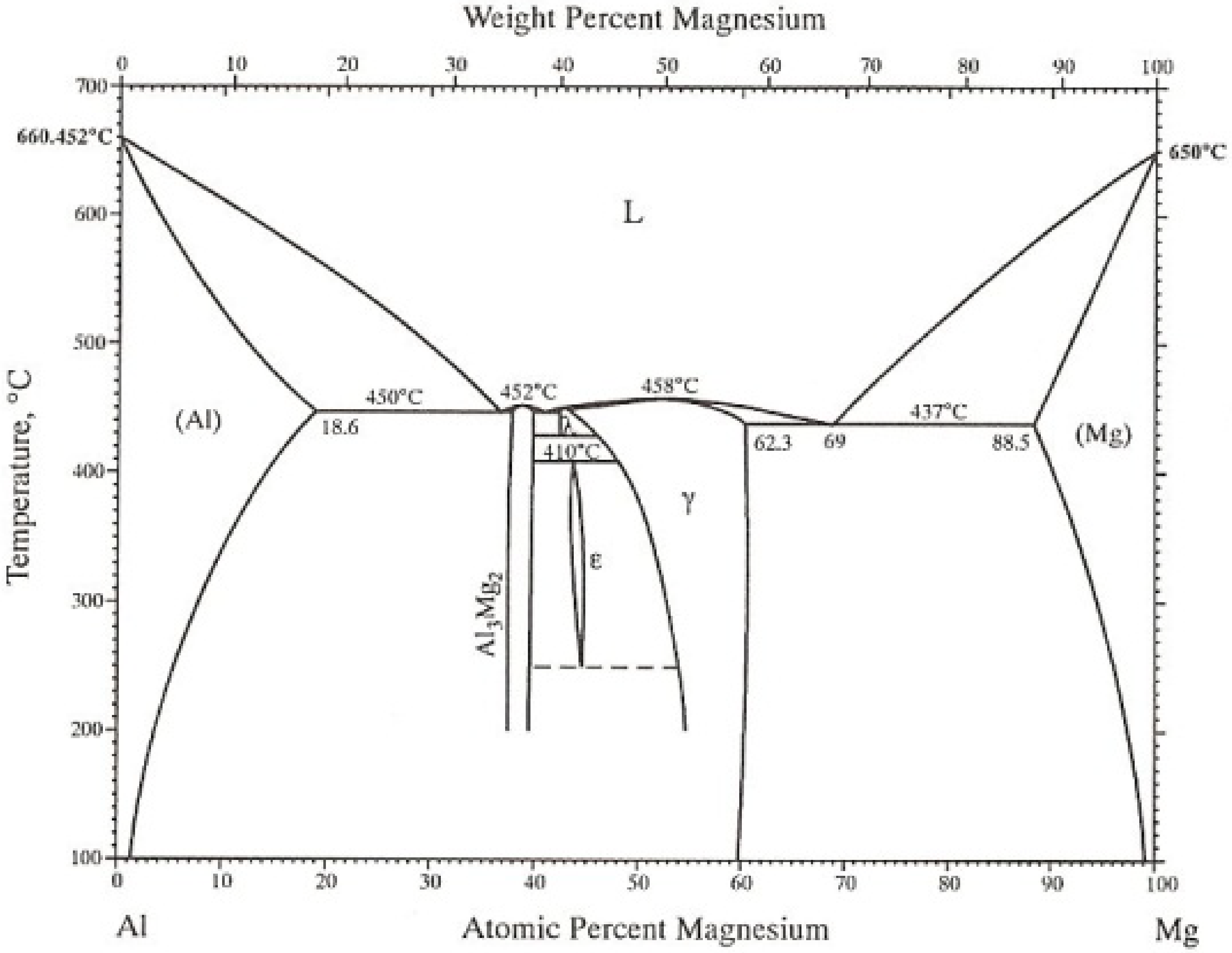
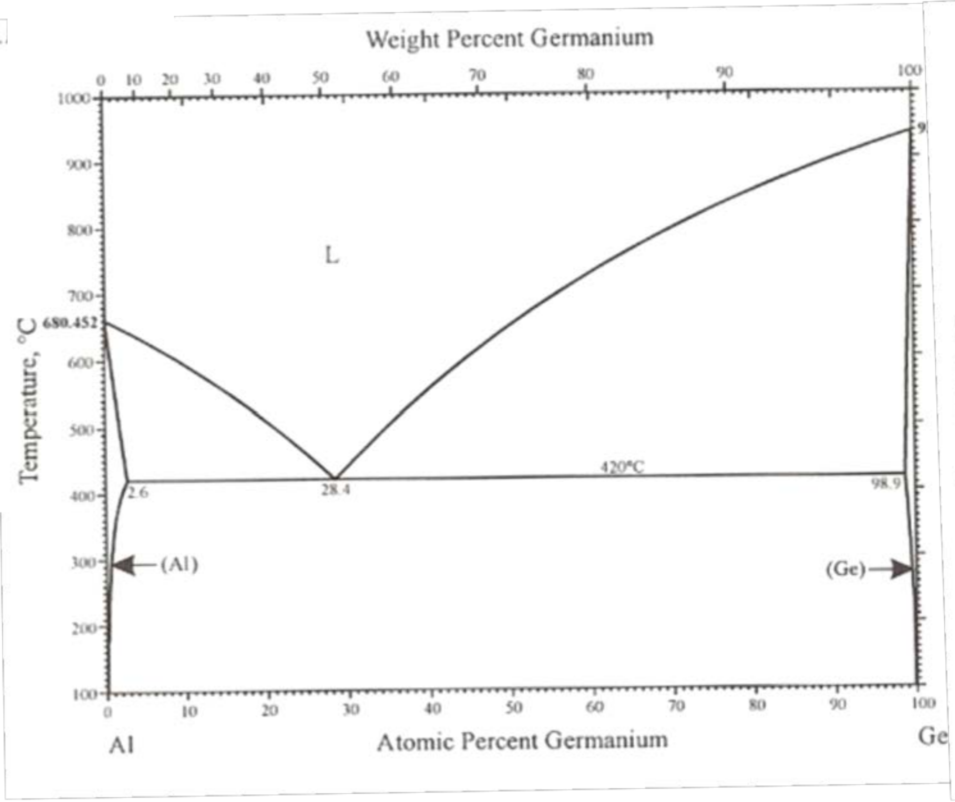
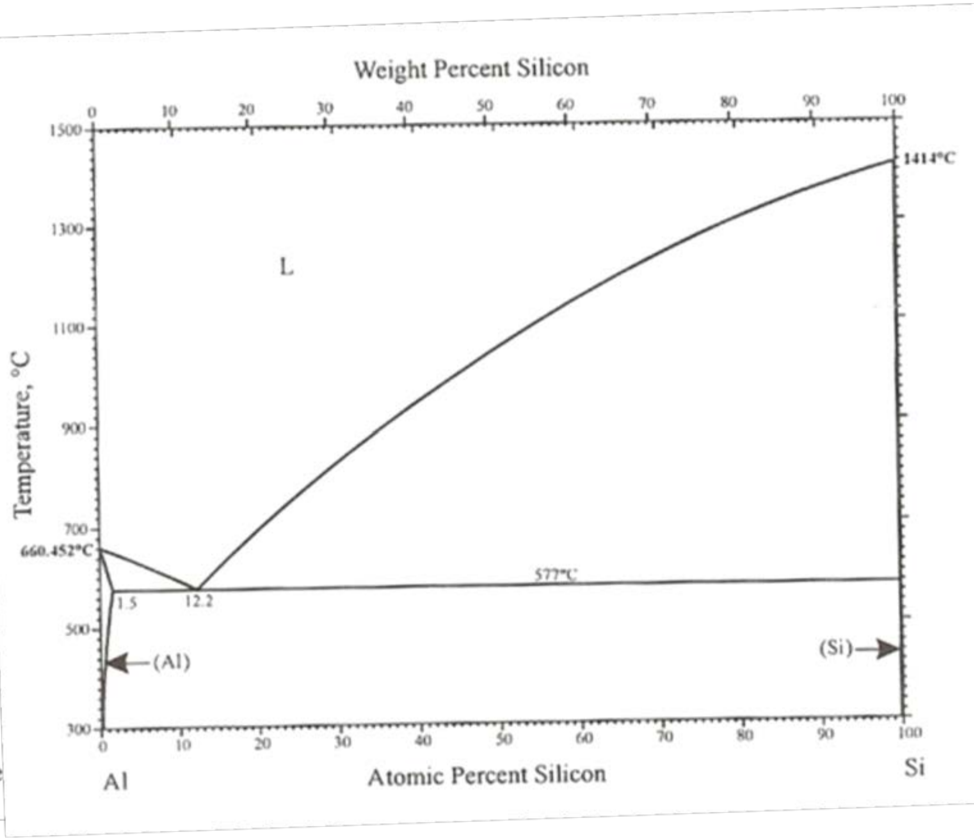
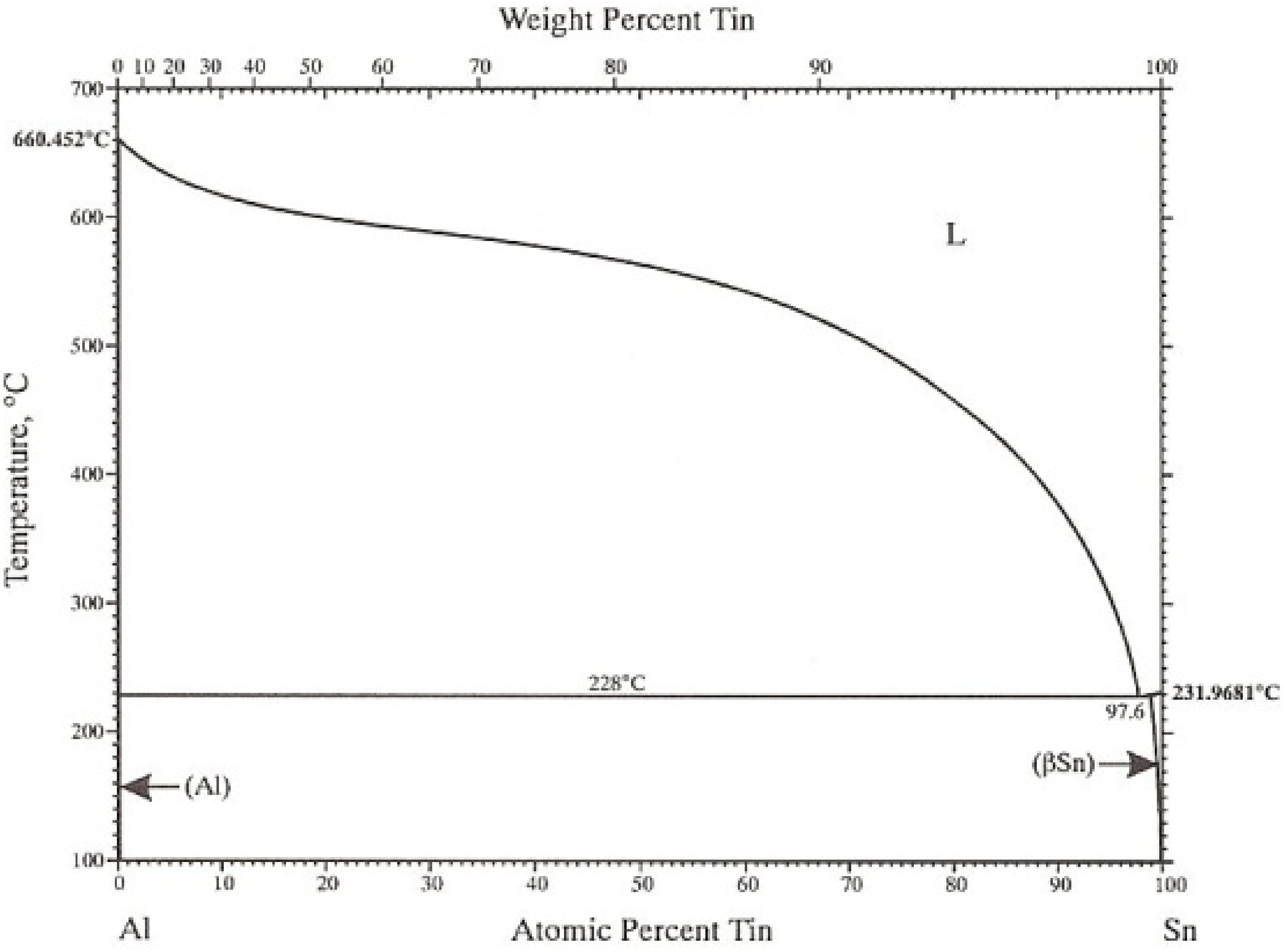


Fig. 54. Impossible form of a binary eutectic phase diagram.


Weight Percent Magnesium
0
10
20
30
40
50
60
70
80
90
100
700
600
500
400
300
200
100
660.452°C
650°C
L
(Al)
450°C
18.6
452°C
458°C
R
410°C
γ
ε
Al_3Mg_2
62.3
69
437°C
88.5
(Mg)
Temperature, °C
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
680.452
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

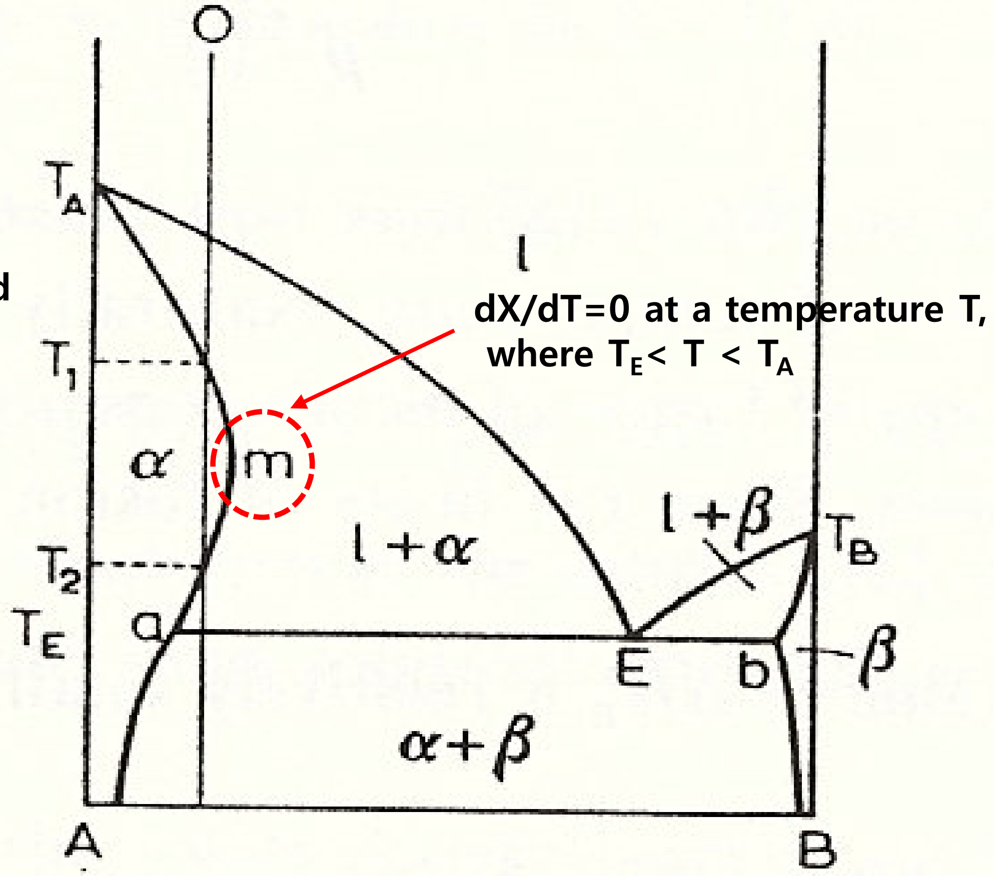

Weight Percent Tin
0 10 20 30 40 50 60 70 80 90 100
700
660.452°C
600
500
400
300
200
100
Temperature, °C
L
228°C
231.9681°C
97.6
(βSn)
(Al)
0 10 20 30 40 50 60 70 80 90 100
Al
Atomic Percent Tin
Sn

4.2.5. 2) Retrograde solidus curves

: A maximum solubility of the solute at a temperature between the melting point of the solvent and an invariant reaction isothermal

Solidus curve in the systems with low solubility
Ex) semiconductor research using Ge and Si as solvent metals

A high value of ΔH_B^S (or a large difference in the melting points of the components) is associate with a significant difference in atomic radii for A and B, which can lead to a large strain energy contribution to the heat of solutions.



dX/dT=0 at a temperature T, where $T_E < T < T_A$

Fig. 57. Partial re-melting associated with retrograde solubility.

Intensive Homework 3: Understanding of retrograde solidus curves from a thermodynamic standpoint

4.2.5. Disposition of phase boundaries at the eutectic horizontal

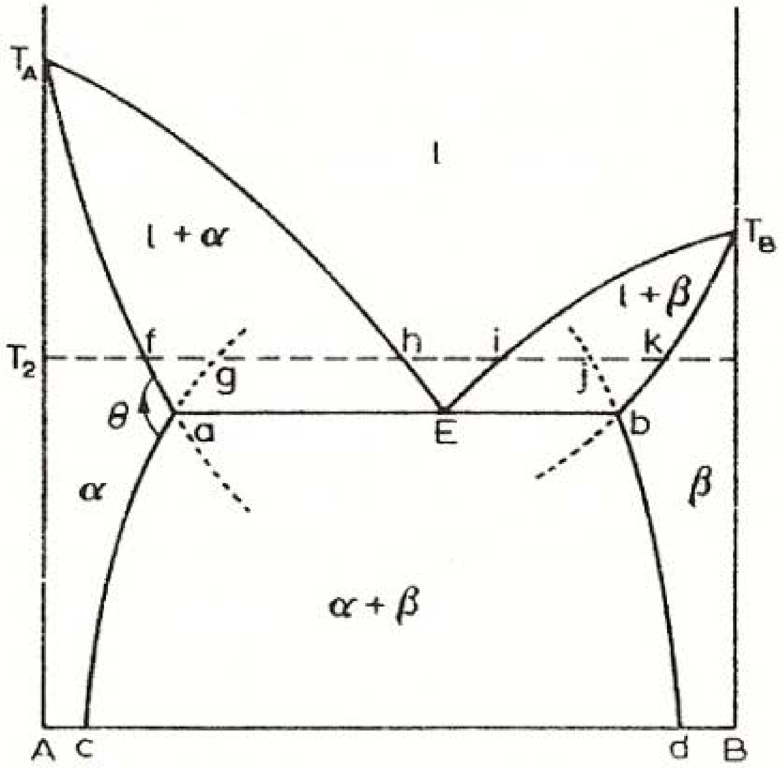


Fig. 58. Disposition of phase boundaries at the eutectic horizontal *aEb*.

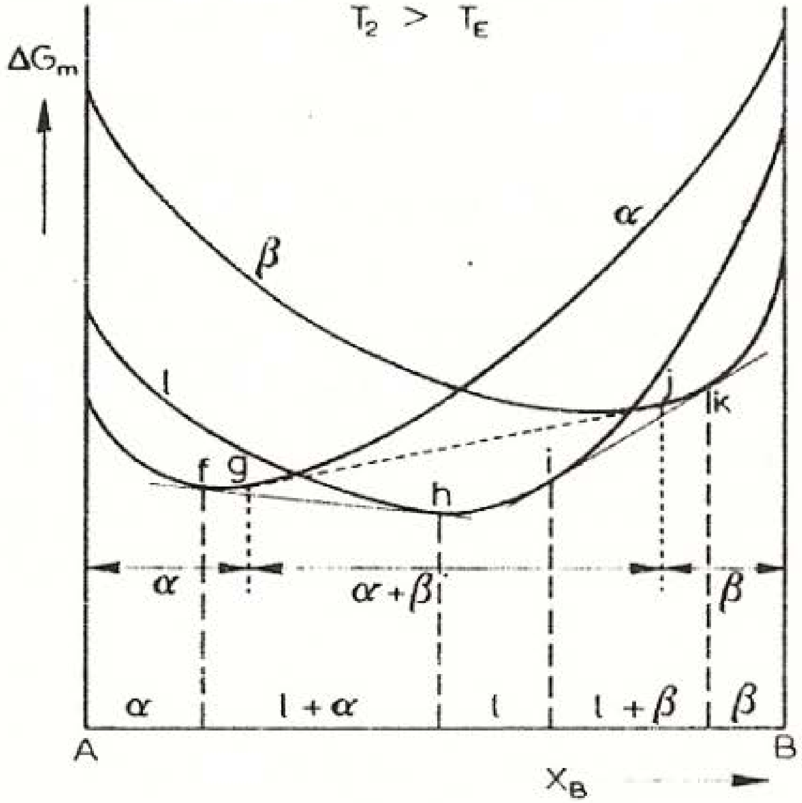


Fig. 59. Free energy curves for the liquid, α and β phases at a temperature T_2 where $T_2 > T_E$.

➡ 3) Θ between solidus and solubility curves must be less than 180°.

4.2.5. Disposition of phase boundaries at the eutectic horizontal

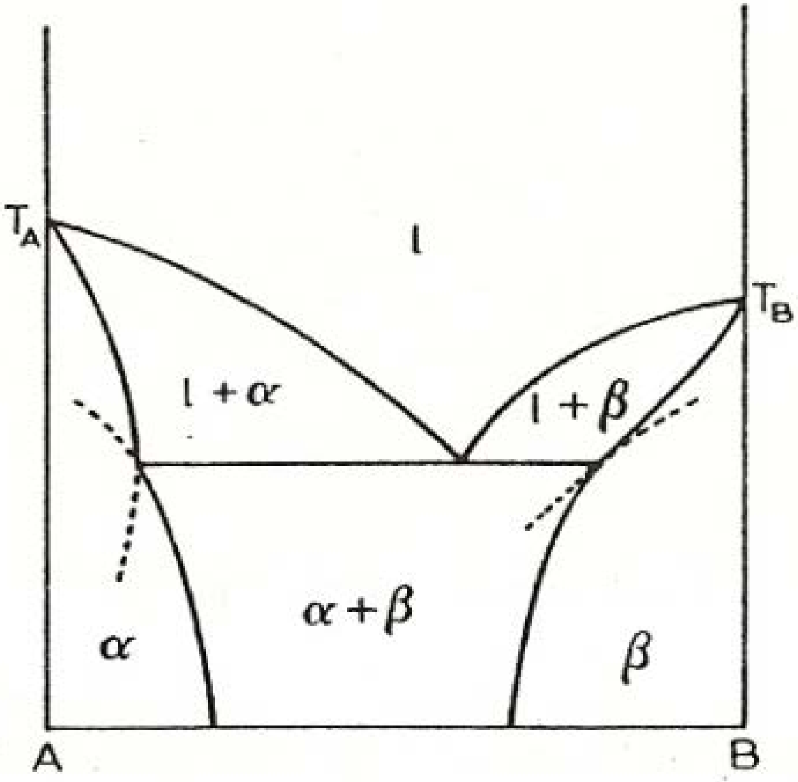


Fig. 60. Impossible dispositions of phase boundaries at a eutectic horizontal.

ϴ between solidus and solubility curves must be less than 180°.

This is a general rule applicable to all curves which meet at an invariant reaction horizontal in a binary diagram, whether they be eutectic, peritectics, eutectoid, etc., horizontals.

Contents for previous class

CHAPTER 4

Binary Phase Diagrams

Three-Phase Equilibrium Involving Limited Solubility of the Components in the Solid State but Complete Solubility in the Liquid State

*** Three-Phase Equilibrium : Eutectic Reactions**

a) Structural Factor: Hume-Rothery Rules

Empirical rules for substitutional solid-solution

complete solid solution ⟷ **limited solid solution**

Similar atomic radii, the same valency and crystal structure

b) The eutectic reaction

c) Limiting forms of eutectic phase diagrams

d) Retrogade solidus curves

Contents for today's class

- Binary phase diagrams

1) Simple Phase Diagrams

*** Pressure-Temperature-Composition phase diagram for a system with continuous series of solutions**

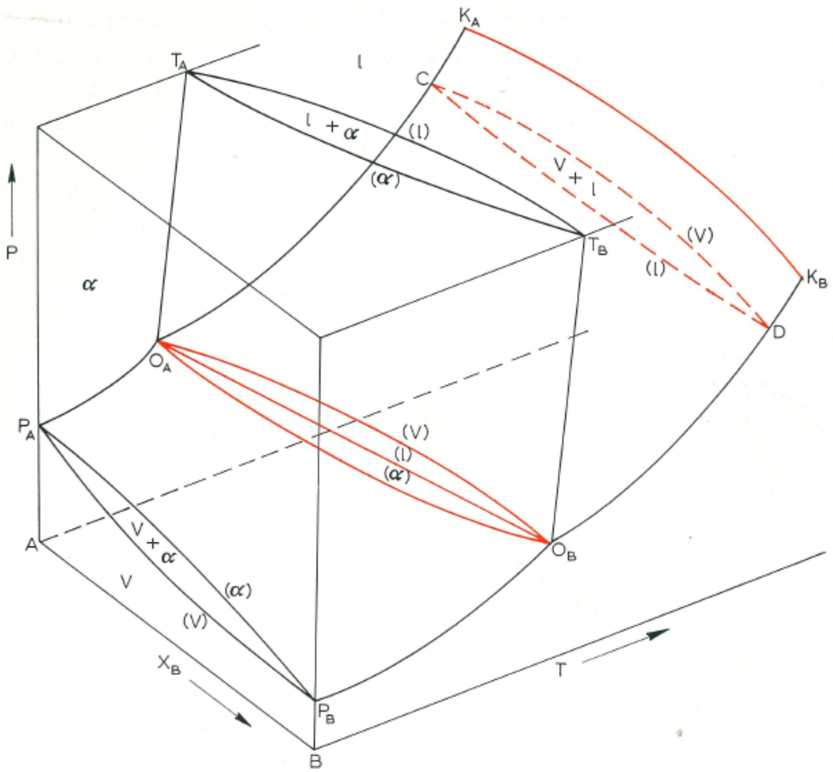
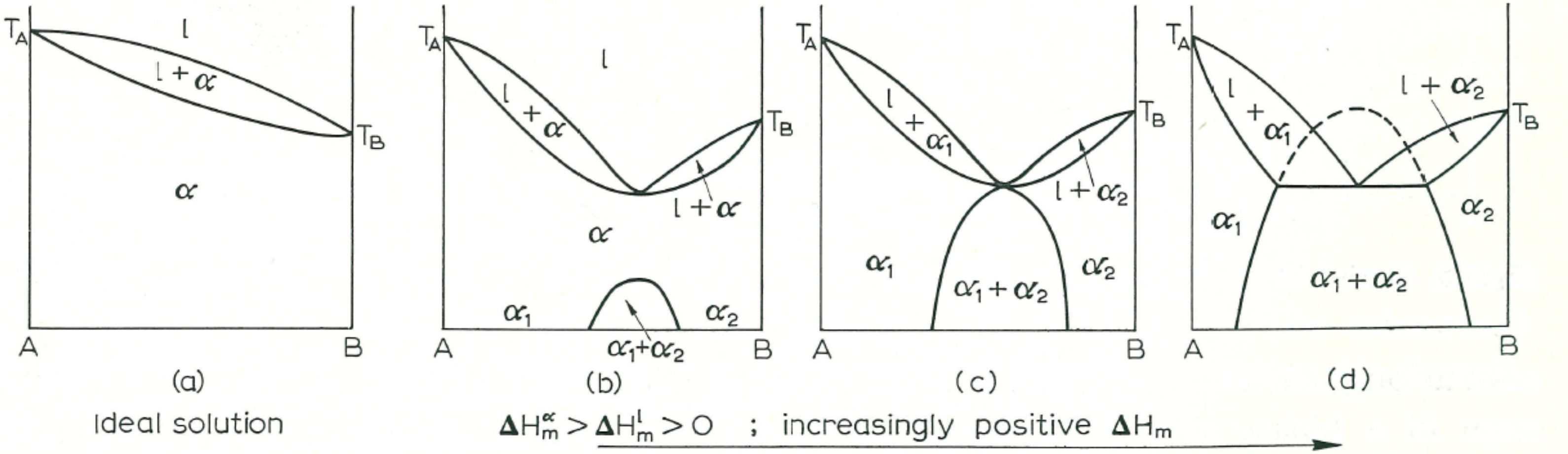


Fig. 35. Pressure–temperature–composition phase diagram for a system with continuous series of solutions

3) Simple Eutectic Systems



(a) Ideal solution

(b)

(c)

(d)

$\Delta H^{\alpha}_{m} > \Delta H^{l}_{m} > 0$; increasingly positive ΔH_m

Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

By plotting a series of the free energy-composition curves at different temperatures we established the manner in which the phase compositions changes with temperature. In other words, we determined the phase limits or phase boundaries as a function of temperature. A phase diagram is nothing more than a presentation of data on the position of phase boundaries as a function of temperature.

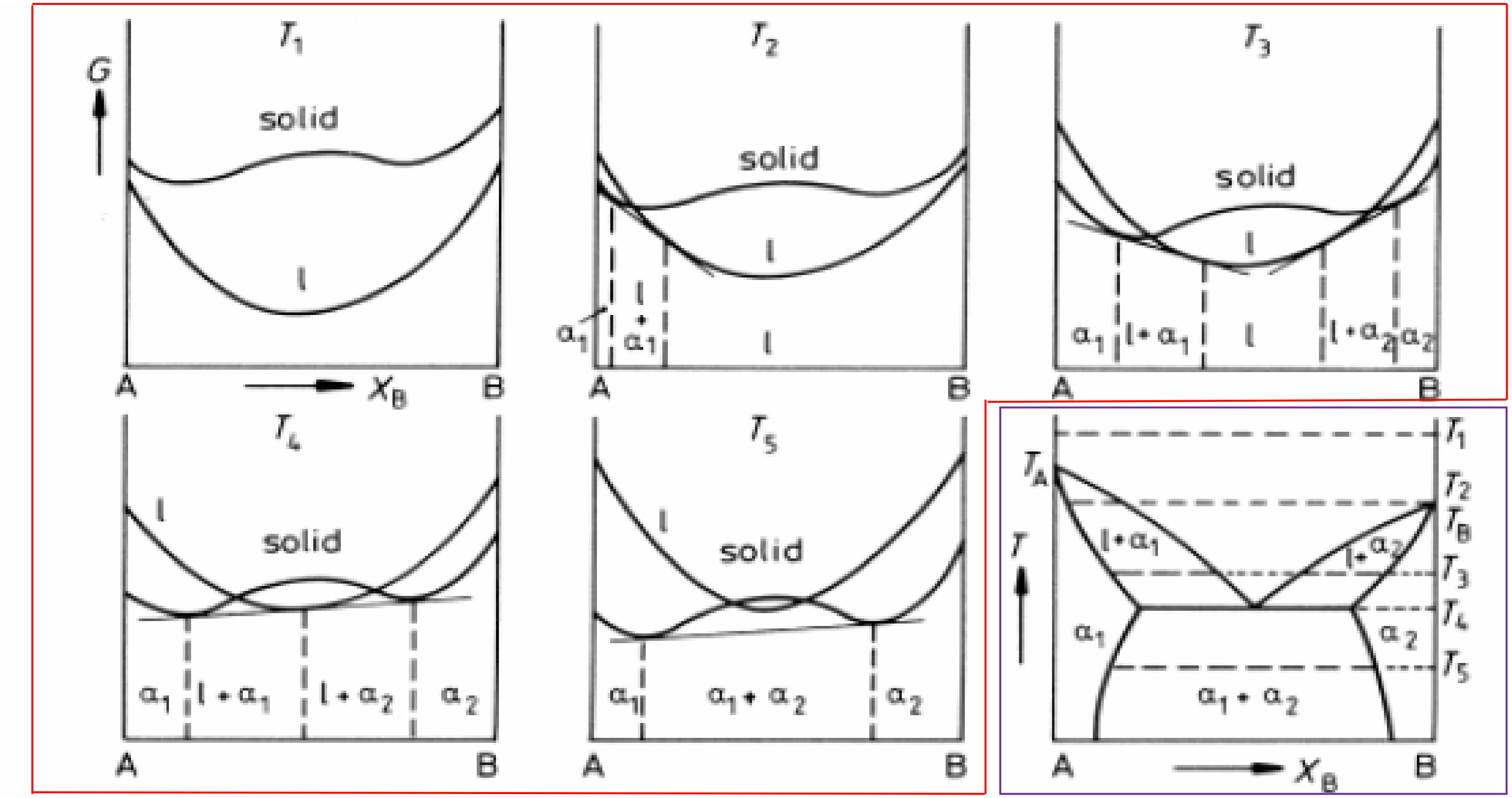
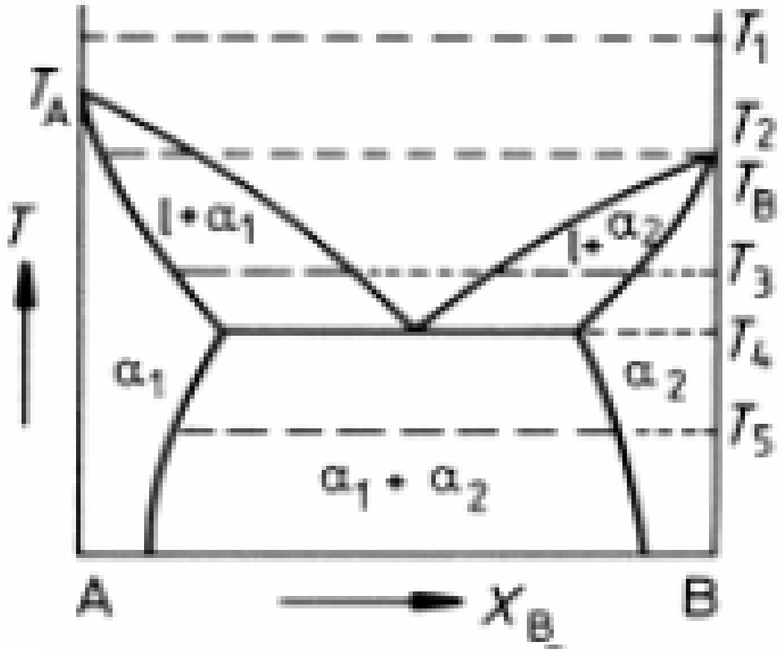
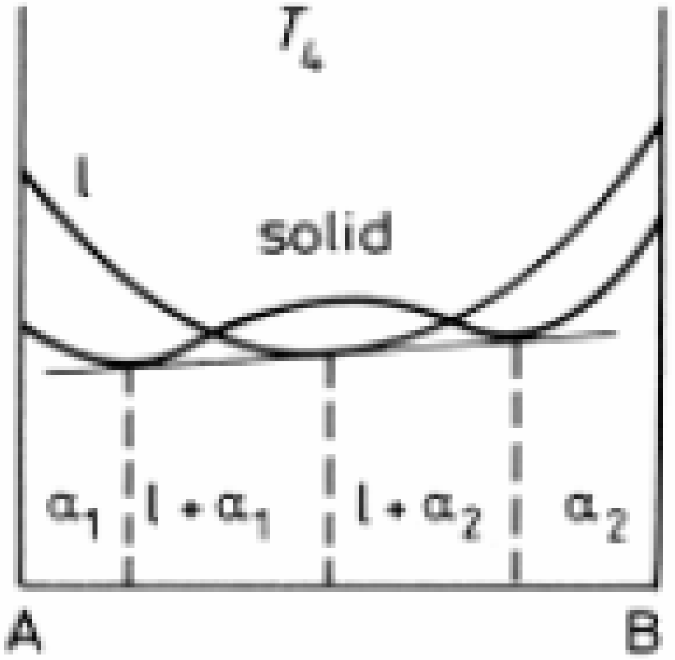


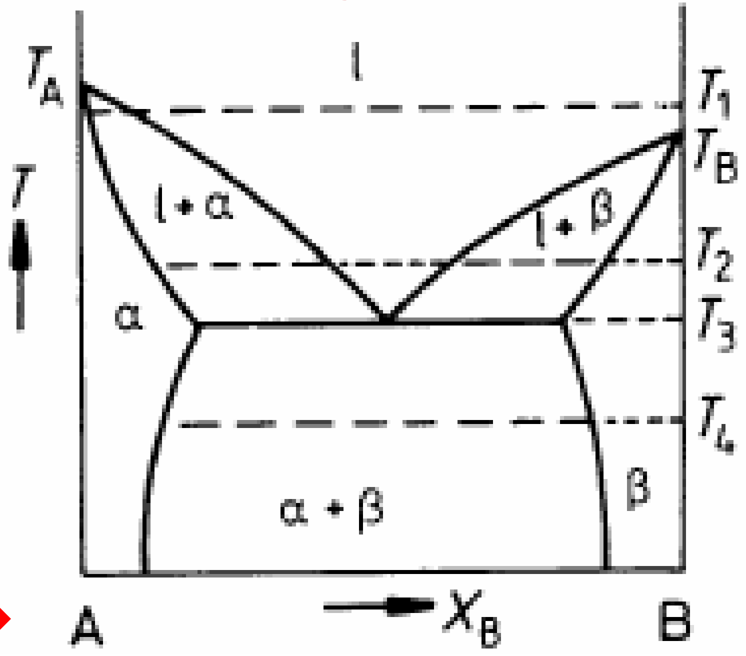
Fig 1.32 The derivation of a eutectic phase diagram where both solid phases have the same crystal structure. (After A.H. Cottrell, *Theoretical Structural Metallurgy*, Edward Arnold, London, 1955,©Sir Alan Cottrell.)

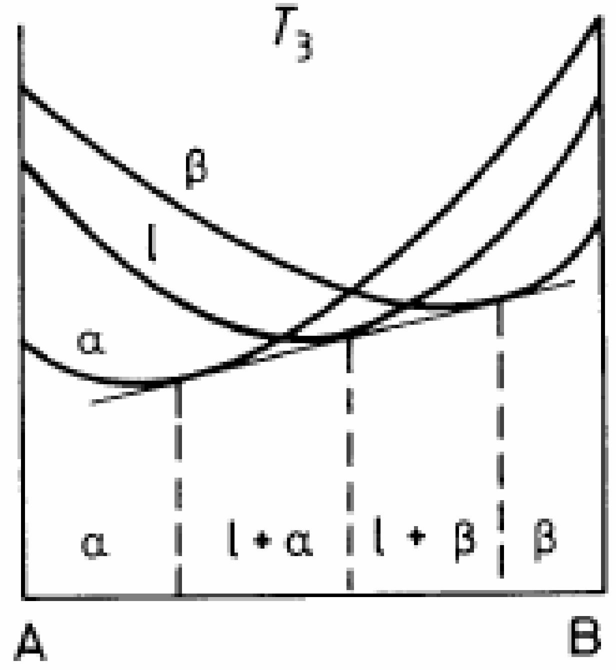
same crystal structure





different crystal structure





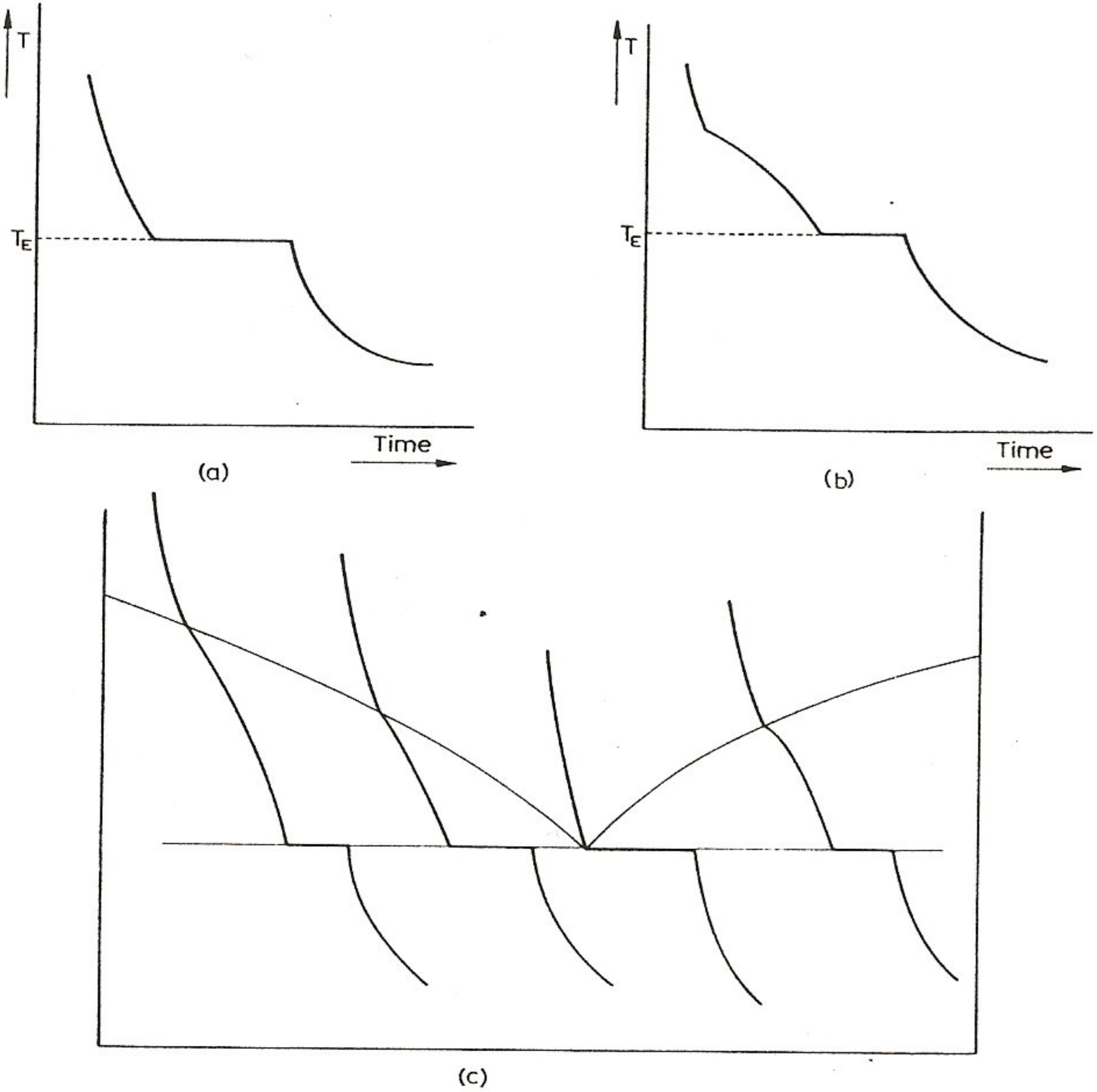


Fig. 48. Cooling curve for (a) the eutectic alloy, (b) hypo-eutectic alloy *N*, and (c) a series of alloys, allowing the determination of the liquidus and eutectic horizontal.

4.2.3. Limiting forms of eutectic phase diagram

1) 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.

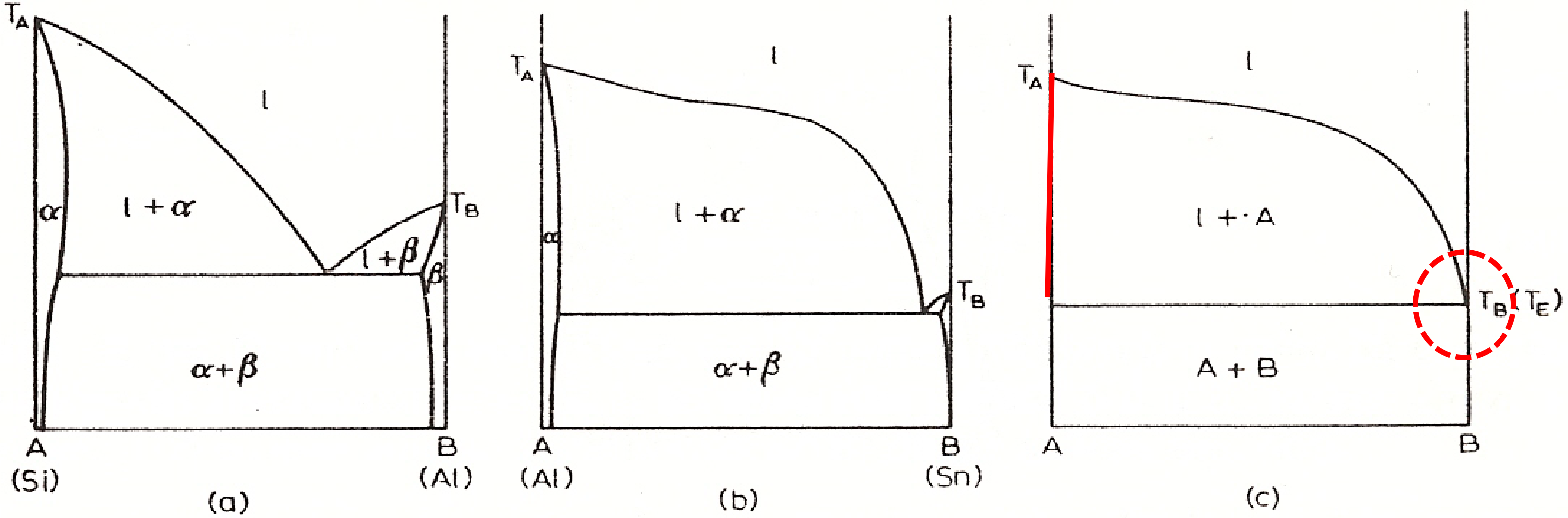


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

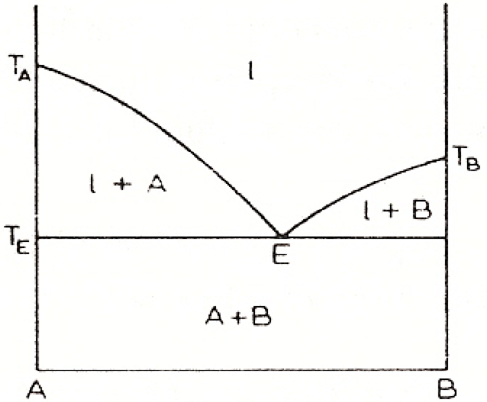


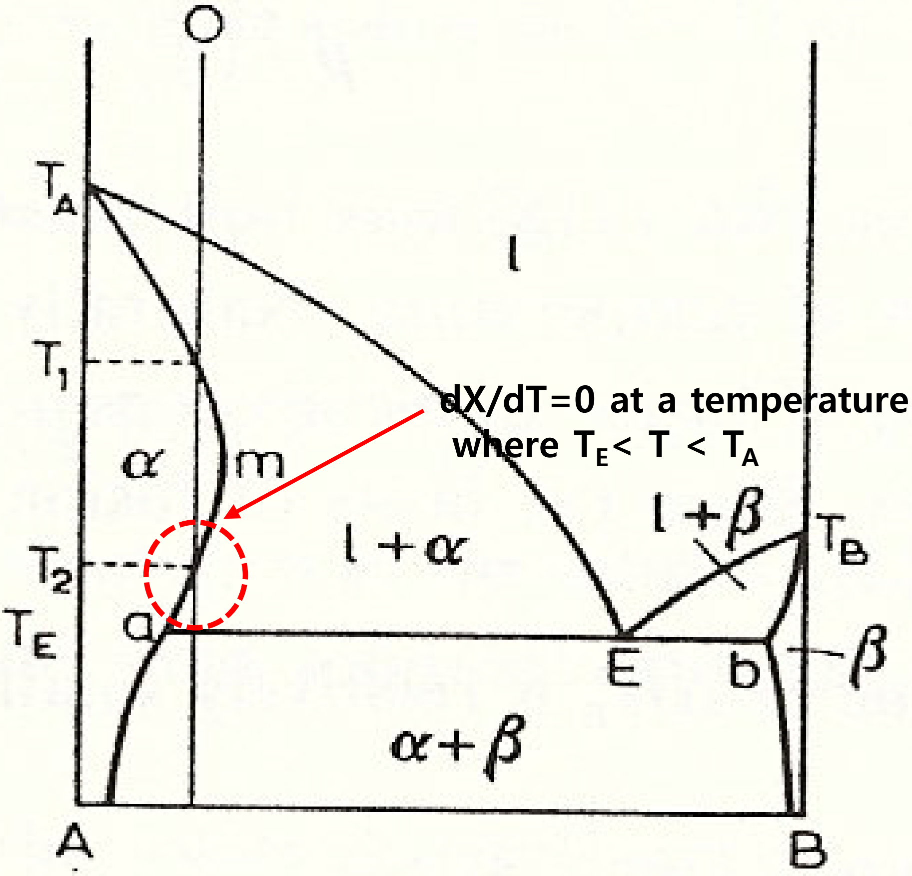
Fig. 54. Impossible form of a binary eutectic phase diagram.

4.2.5. 2) Retrograde solidus curves

: A maximum solubility of the solute at a temperature between the melting point of the solvent and an invariant reaction isothermal

Solidus curve in the systems with low solubility
Ex) semiconductor research using Ge and Si as solvent metals

A high value of ΔH_B^S (or a large difference in the melting points of the components) is associate with a significant difference in atomic radii for A and B, which can lead to a large strain energy contribution to the heat of solutions.



dX/dT=0 at a temperature T, where $T_E < T < T_A$

Fig. 57. Partial re-melting associated with retrograde solubility.

Intensive Homework 2: Understanding of retrograde solidus curves from a thermodynamic standpoint

4.2.5. Disposition of phase boundaries at the eutectic horizontal

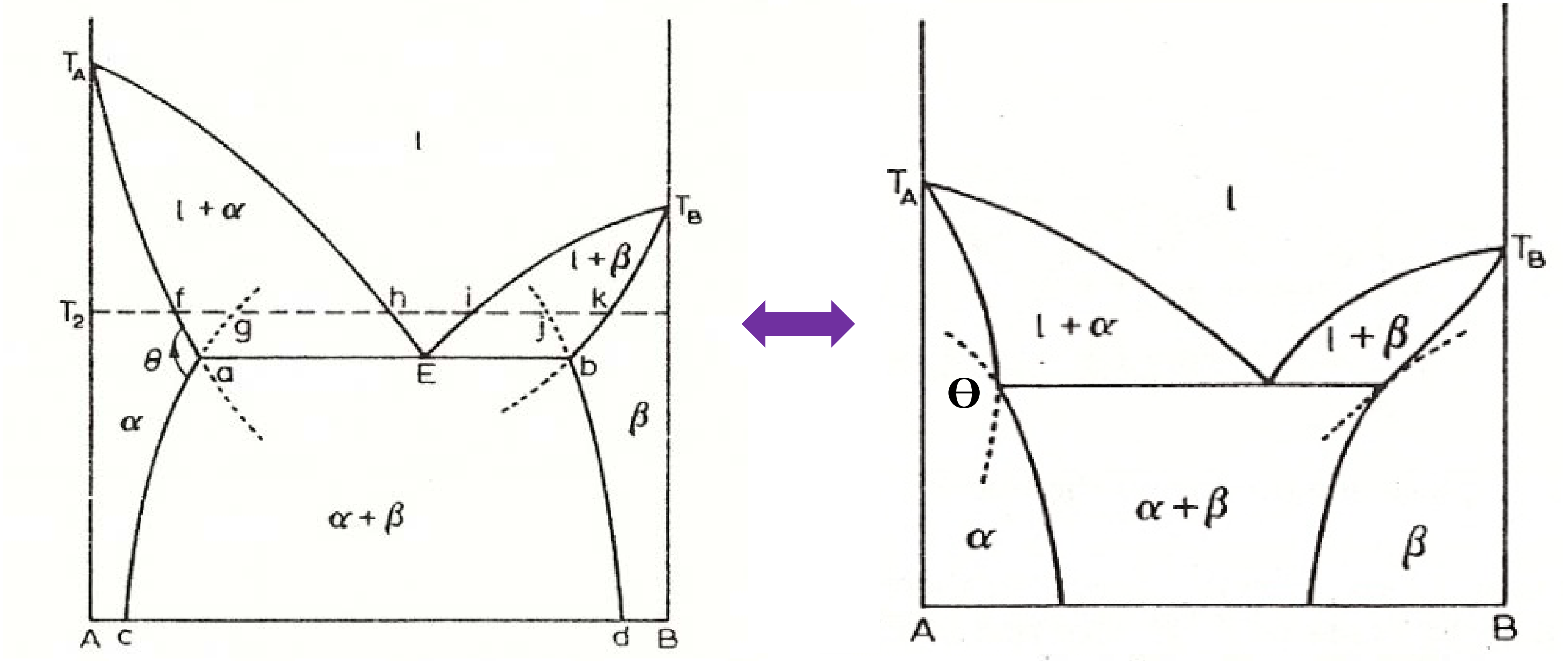


Fig. 60. Impossible dispositions of phase boundaries at a eutectic horizontal.

3) Θ between solidus and solubility curves must be less than 180°.

This is a general rule applicable to all curves which meet at an invariant reaction horizontal in a binary diagram, whether they be eutectic, peritectics, eutectoid, etc., horizontals.