2023 Fall

"Phase Transformation *in* Materials"

09.25.2023

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Summary I: 1.5 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 $\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} > 0$

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

3) Ordered Alloys $\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} < 0$

$\Delta H_{mix} < 0$ → 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.

4) a. Simple Eutectic Systems $\Delta H^L_{mix} = 0 \quad \Delta H^S_{mix} >> 0$

→ miscibility gap extends to the melting temperature.

b. Simple Peritectic Systems

→ Considerable difference between the melting points

5) Phase diagrams containing intermediate phases

Stable composition ≠ Minimum G with stoichiometric composition

Summary I: 1.5 Binary phase diagrams

- Equilibrium in Heterogeneous Systems

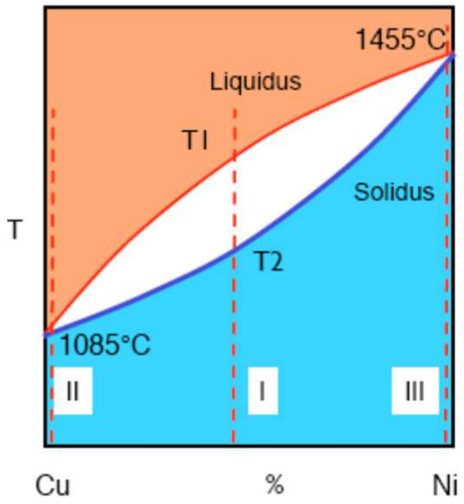
$G_0^\beta > G_0^\alpha > G_0^{\alpha+\beta}$ ➡ α + β separation ➡ unified chemical potential

- Binary phase diagrams

1) Simple Phase Diagrams

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

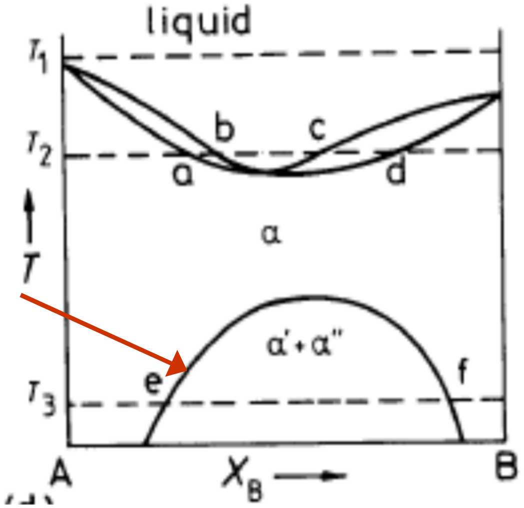
Assume: (1) completely miscible in solid and liquid.
(2) Both are ideal soln.



2) Variant of the simple phase diagram

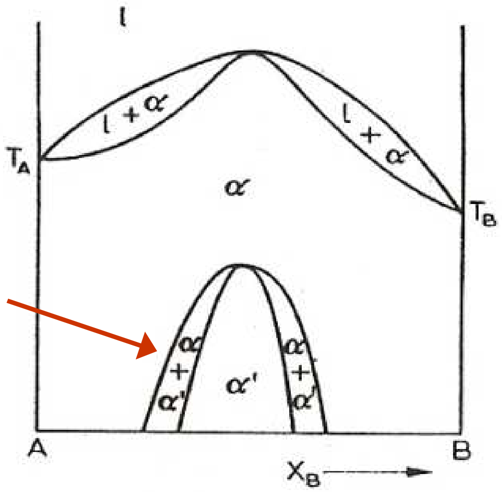
$$\Delta H^\alpha_{mix} > \Delta H^l_{mix} > 0$$

miscibility gab



$$\Delta H^\alpha_{mix} < \Delta H^l_{mix} < 0$$

Ordered phase



Summary II:

1.5.6

• 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.

1.5.7

• 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.

1.5.8

• Equilibrium Vacancy Concentration

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

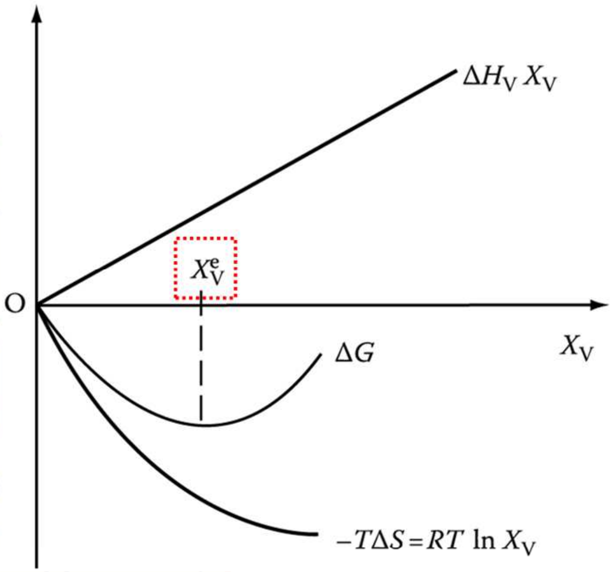


Fig. 1.37 Equilibrium vacancy concentration.

1.7

• Influence of Interfaces on Equilibrium

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

1.8

• Gibbs-Duhem Equation:

$X_A d\mu_A + X_B d\mu_B$

: Be able to calculate the change in chemical potential that result from a

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

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

Q6: “Influence of Interfaces on Equilibrium”?

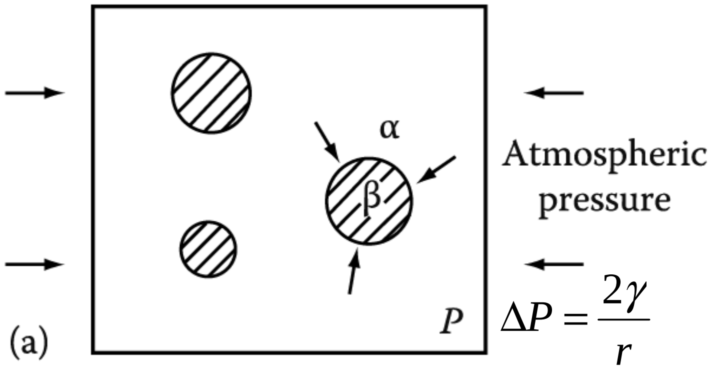
$$\Delta G = \frac{2\gamma V_m}{r}$$ **Gibbs-Thomson effect**

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

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

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



The concept of a pressure difference is very useful for spherical liquid particles, 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 $A = 4\pi r^2$ $\Delta G = \frac{2\gamma V_m}{r}$

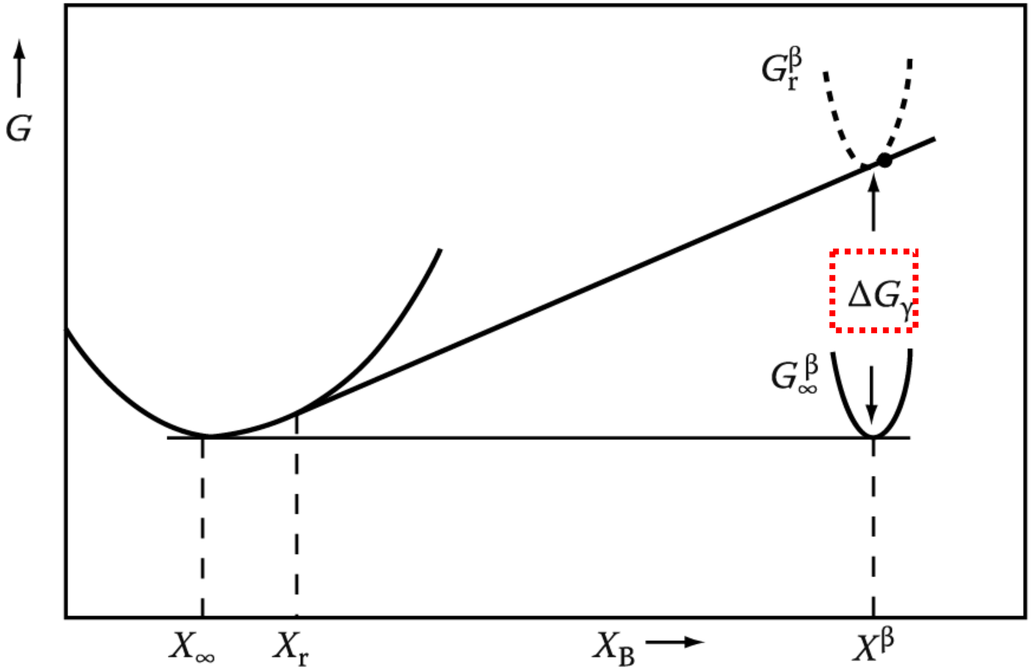


Fig. 1.38 The effect of interfacial E on the solubility of small particle

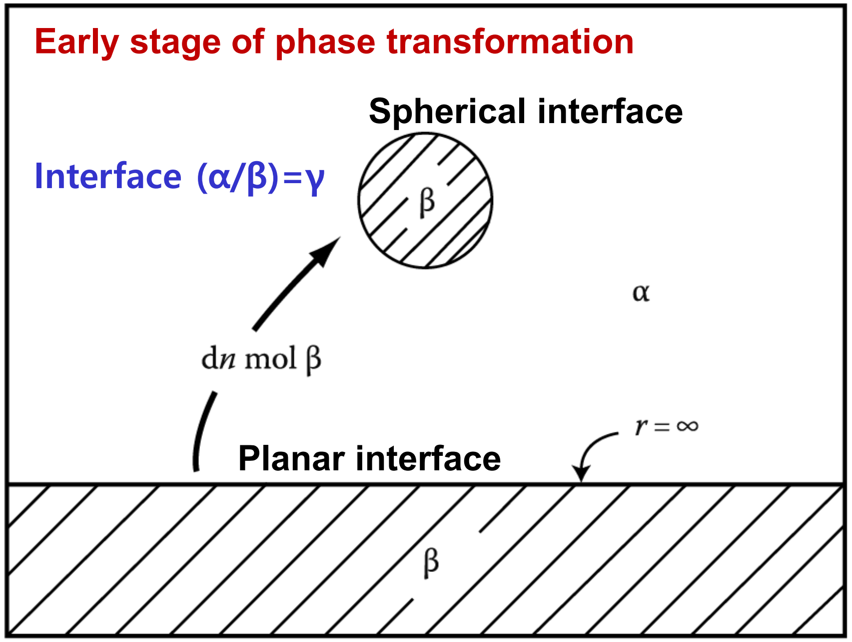


Fig. 1.39 Transfer of dn mol of β from large to a small particle.

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.

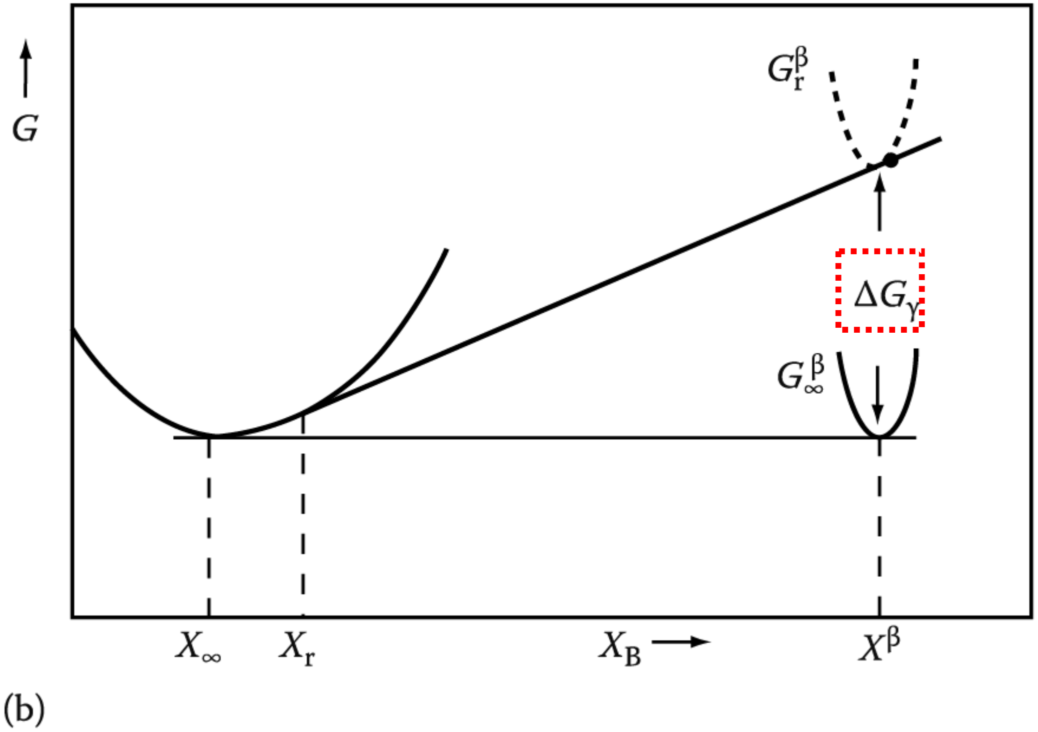


Fig. 1.38 The effect of interfacial energy on the solubility of small particles.

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/m^2, V$_m$=10^{-5} m^3,T=500K**

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

For r=10 nm, solubility~10% increase

Total Free Energy Decrease per Mole of Nuclei $\Delta G_0 = -V\Delta G_V + A\gamma + V\Delta G_s$

Chapter 5.1

: 변태를 위한 전체 구동력, 핵생성을 위한 구동력은 아님

Driving Force for Precipitate Nucleation $\boxed{\alpha \rightarrow \alpha + \beta}$ 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)

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

: driving force for β precipitation

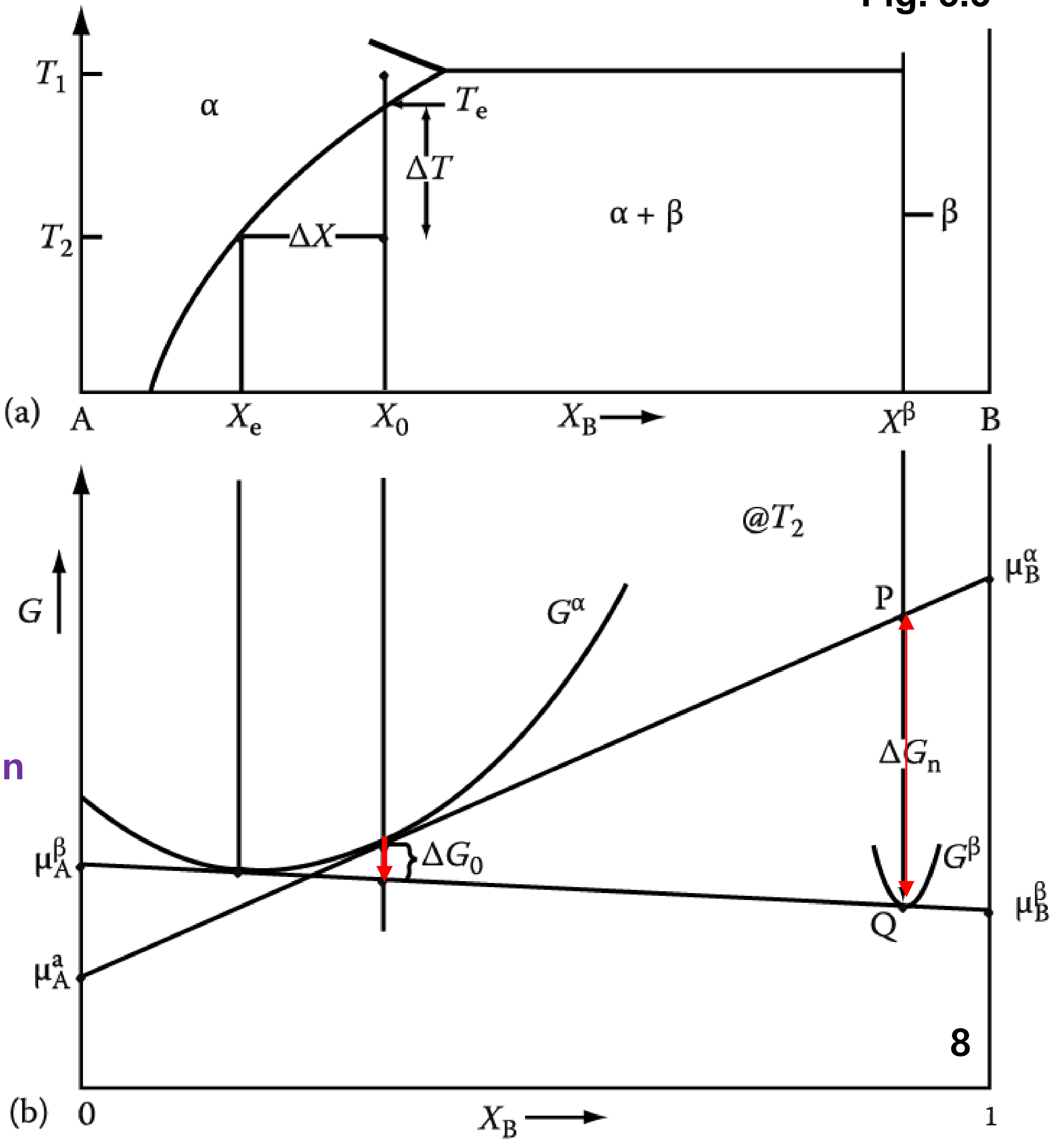
For dilute solutions,

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

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

∝undercooling below T_e

Fig. 5.3



Q7: “Gibbs-Duhem Equation”?

: Be able to calculate the change in chemical potential that result from a change in alloy composition.

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

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

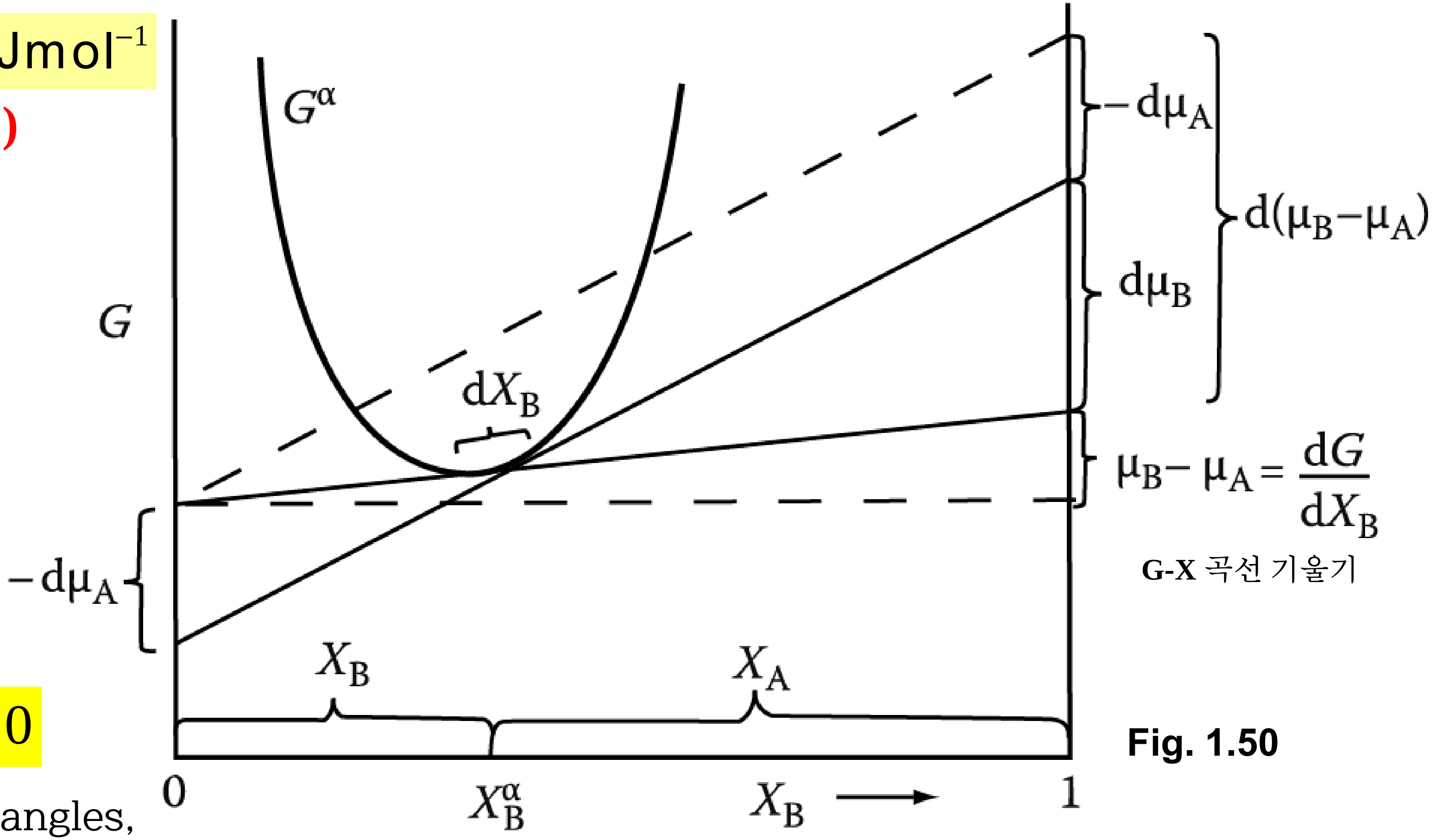
합금조성의 미소변화 (dX)로 인한 화학퍼텐셜의 미소변화**(dμ)** 를 계산

1.8 Additional Thermodynamic Relationships for Binary Solutions

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

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

(T, P: constant)



G-X 곡선 기울기

Fig. 1.50

Gibbs-Duhem Equation

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

Comparing two similar triangles,

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

d^2G/dX^2

($\because d^2G/dX_B^2 = d^2G/dX_A^2$)

Substituting right side Eq.
& Multiply X_AX_B

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

Eq. 1.75

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. 1.75**

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

$$\xrightarrow{\gamma_B = a_B/X_B}$$

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. 1.79

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

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

Eq. 1.80

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

Eq. 1.81

The Gibbs-Duhem Equation

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

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

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

Summary II: Binary phase diagrams

- 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.

- **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:** $X_A d\mu_A + X_B d\mu_B = 0$

: 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

Total Free Energy Decrease per Mole of Nuclei $\Delta G_0 = -V\Delta G_V + A\gamma + V\Delta G_s$

⇕ **Chapter 5.1**

: 변태를 위한 전체 구동력, 핵생성을 위한 구동력은 아님

Driving Force for Precipitate Nucleation $\boxed{\alpha \rightarrow \alpha + \beta}$ 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)

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

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

: driving force for β precipitation

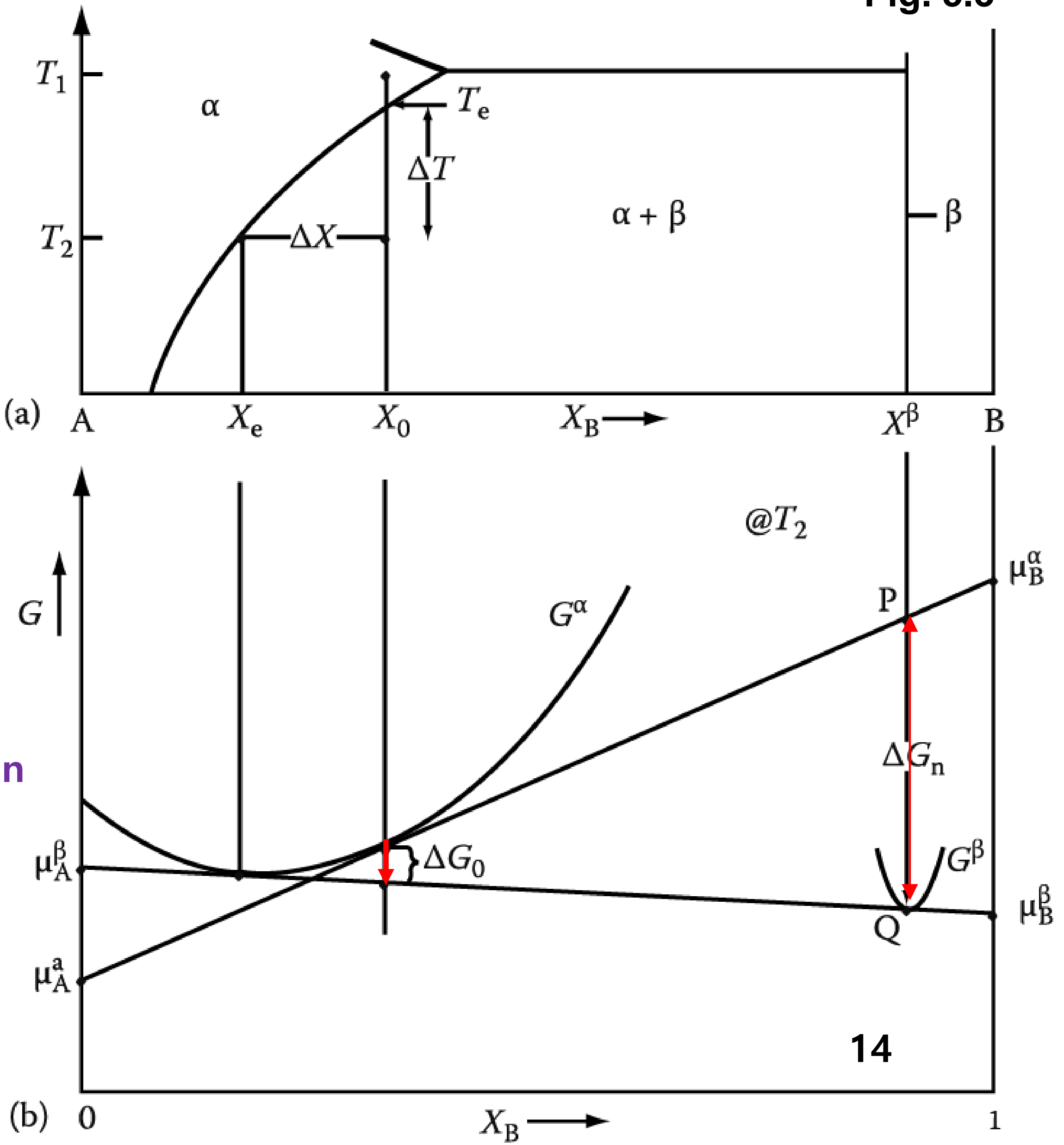
For dilute solutions,

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

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

$\propto$ undercooling below T_e

Fig. 5.3



Contents for today's class

- **Ternary Phase Diagram**

1.7

Q1: “Ternary Phase Diagram”?

What are ternary phase diagram?

Diagrams that represent the equilibrium between the various phases that are formed between three components, as a function of temperature.

Normally, pressure is not a viable variable in ternary phase diagram construction, and is therefore held constant at 1 atm.

www.sjsu.edu/faculty/selvaduray/page/phase/ternary_p_d.pdf

Gibbs Phase Rule for 3-component Systems

$F = C + 2 - P$

For isobaric systems:

$F = C + 1 - P$

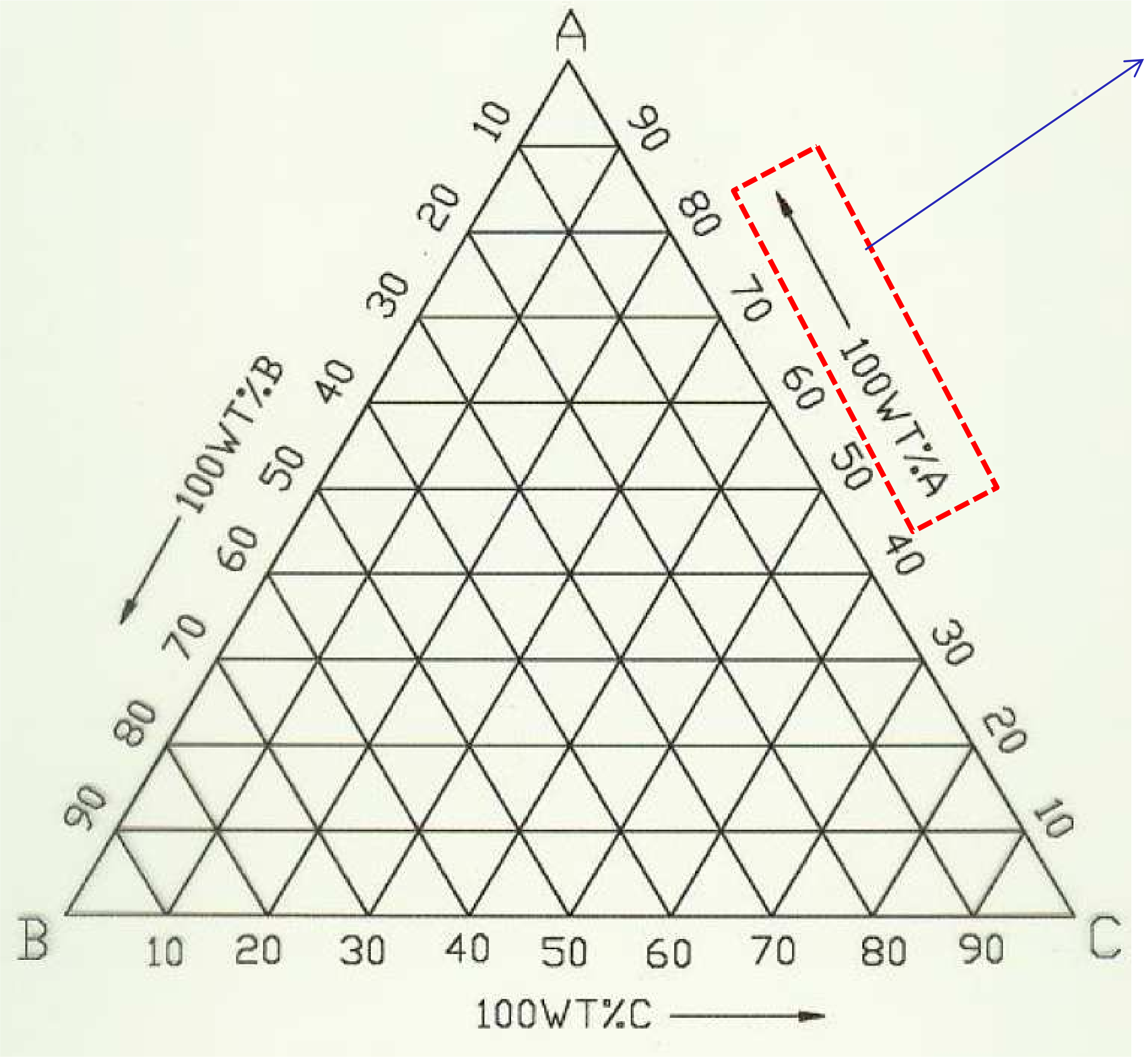
For $C = 3$, the maximum number of phases will co-exist when $F = 0$

$P = 4$ when $C = 3$ and $F = 0$

Components are “independent components”

Gibbs Triangle

An Equilateral triangle on which the pure components are represented by each corner.



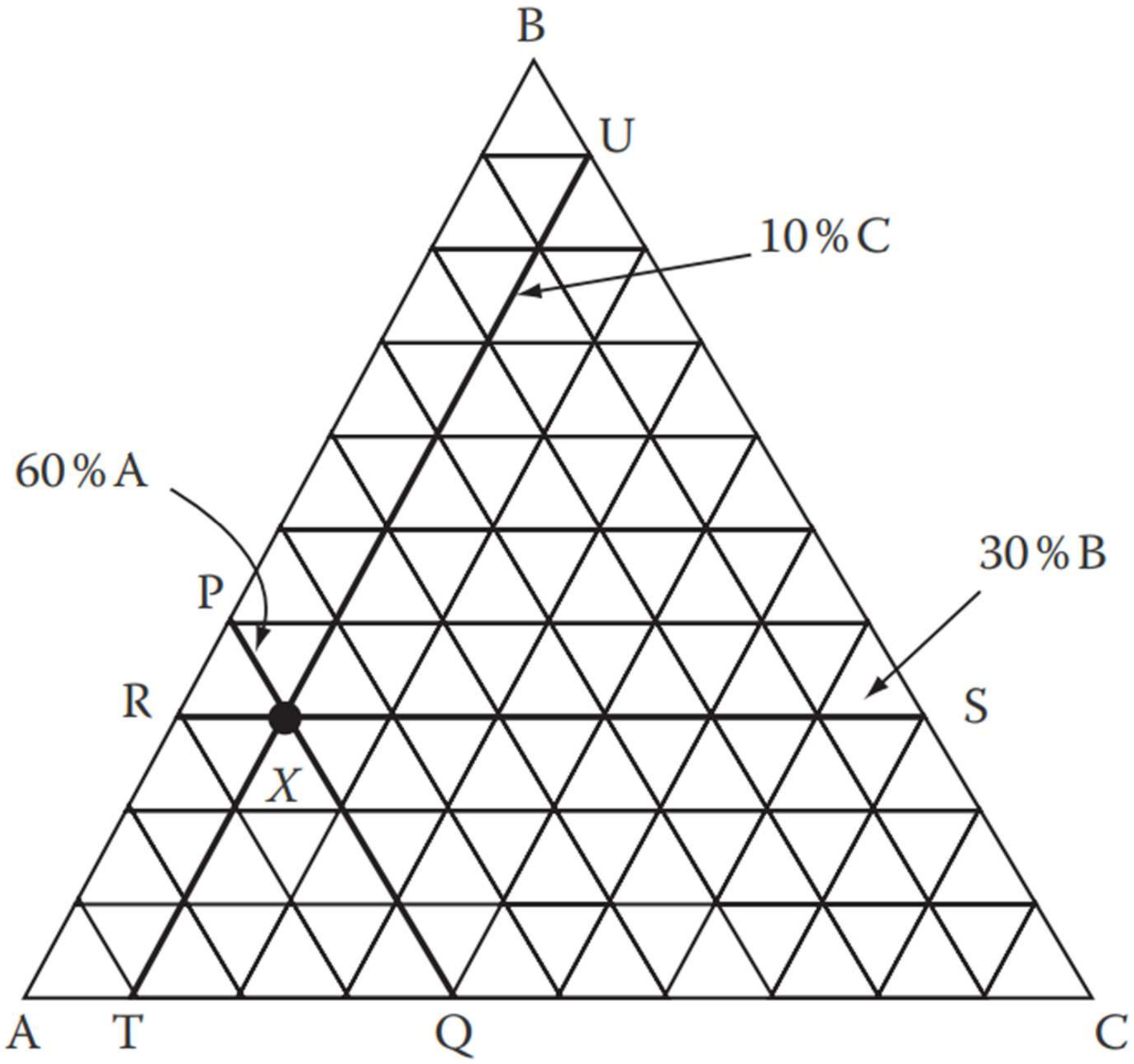
Concentration can be expressed as either “wt. %” or “at.% = molar %”.

$$X_A+X_B+X_C = 1$$

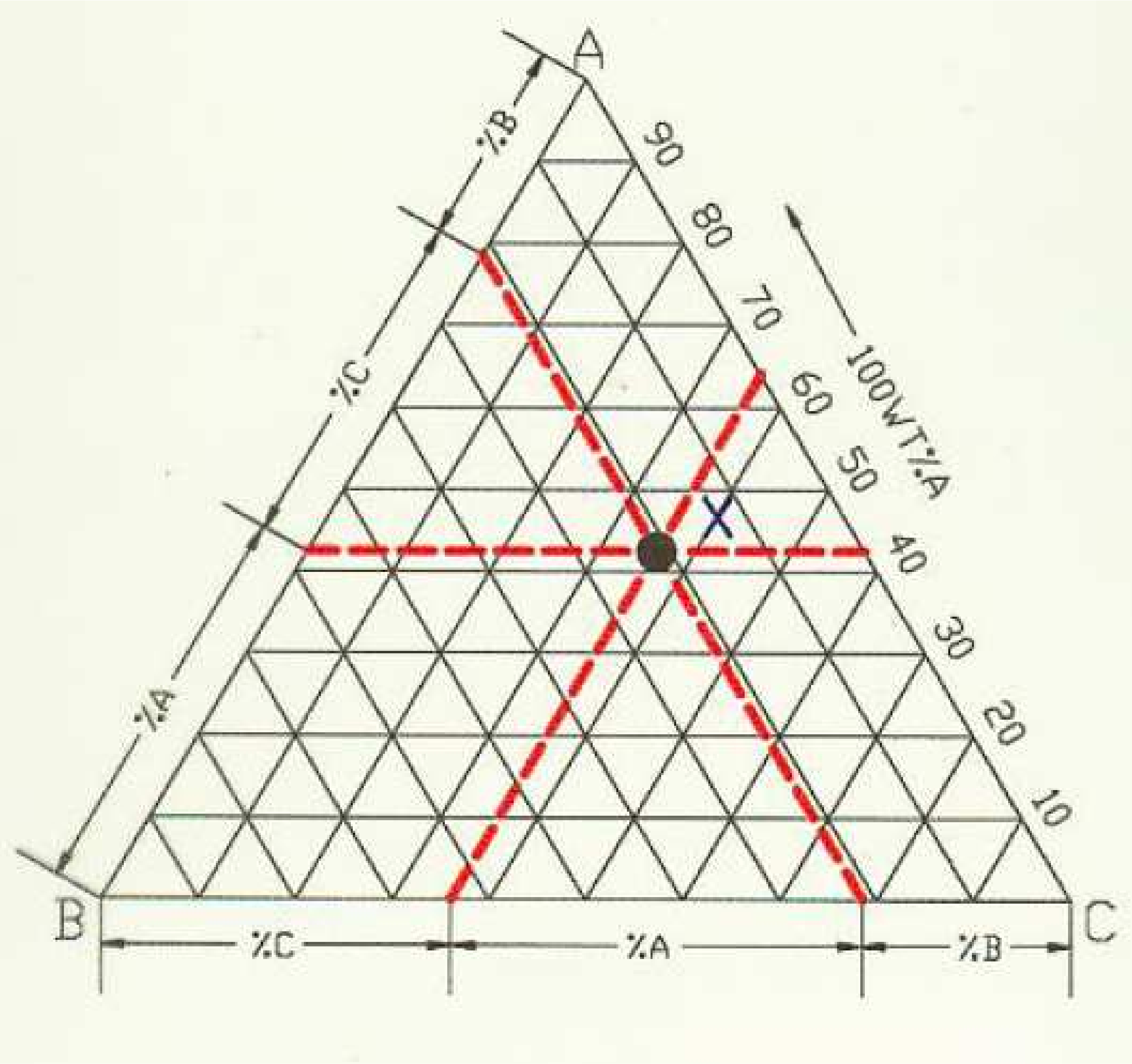
Used to determine the overall composition

Gibbs Triangle

An Equilateral triangle on which the pure components are represented by each corner.



Overall Composition

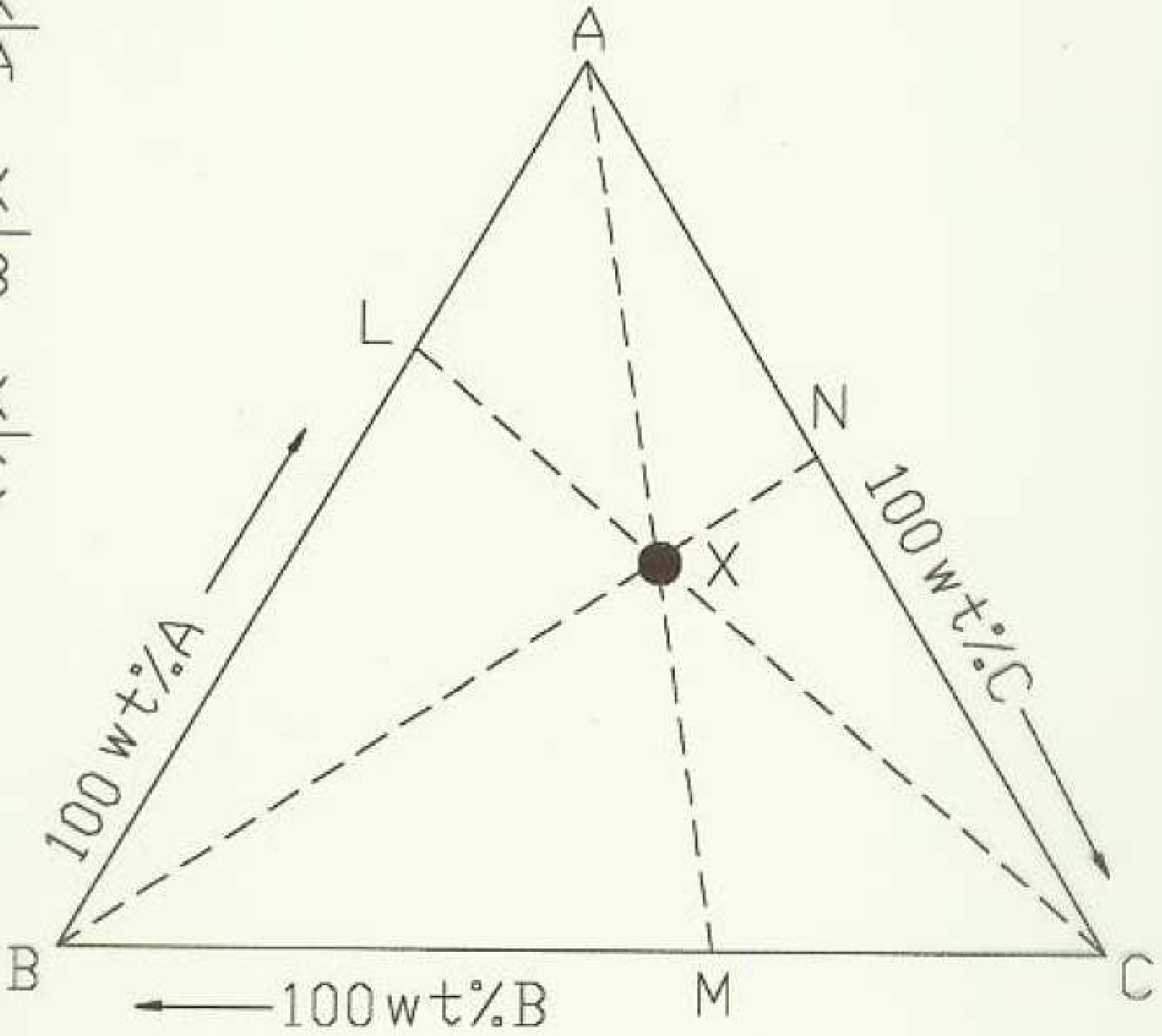


Overall Composition

$$\%A = \frac{MX}{MA}$$

$$\%B = \frac{NX}{NB}$$

$$\%C = \frac{LX}{LC}$$



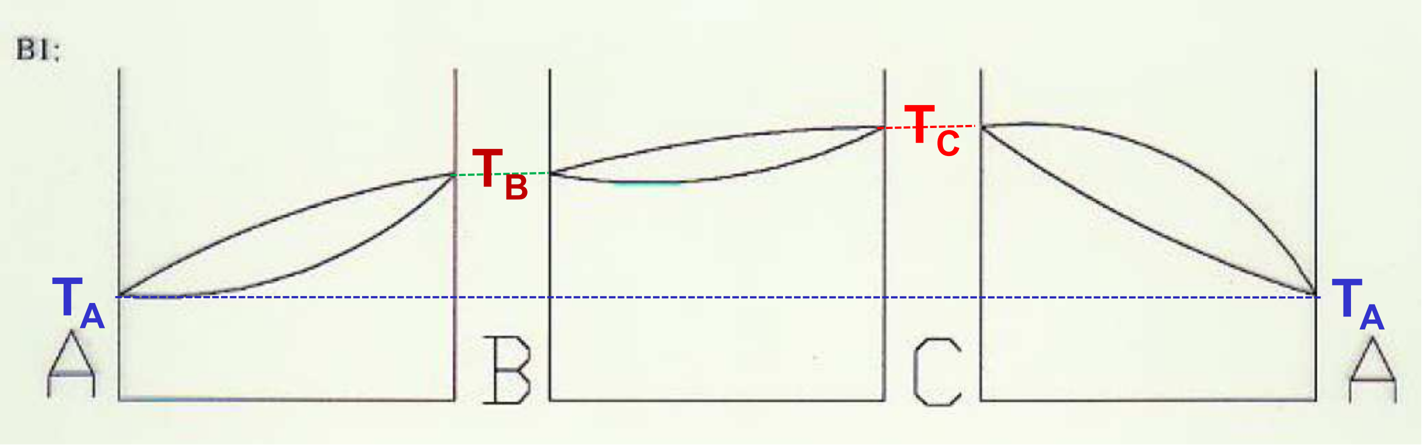
Ternary Isomorphous System

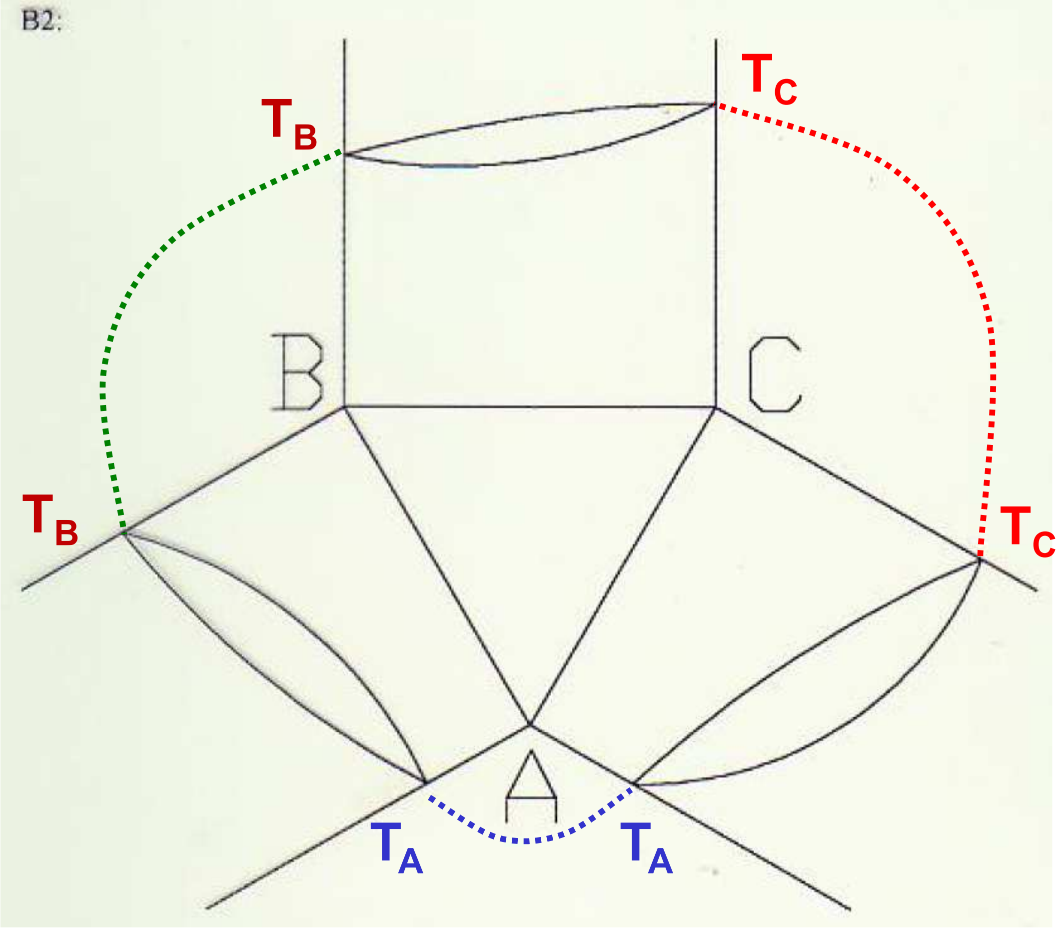
Isomorphous System: A system (ternary in this case) that has only one solid phase. All components are totally soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility.

The Liquidus surface: A plot of the temperatures above which a homogeneous liquid forms for any given overall composition.

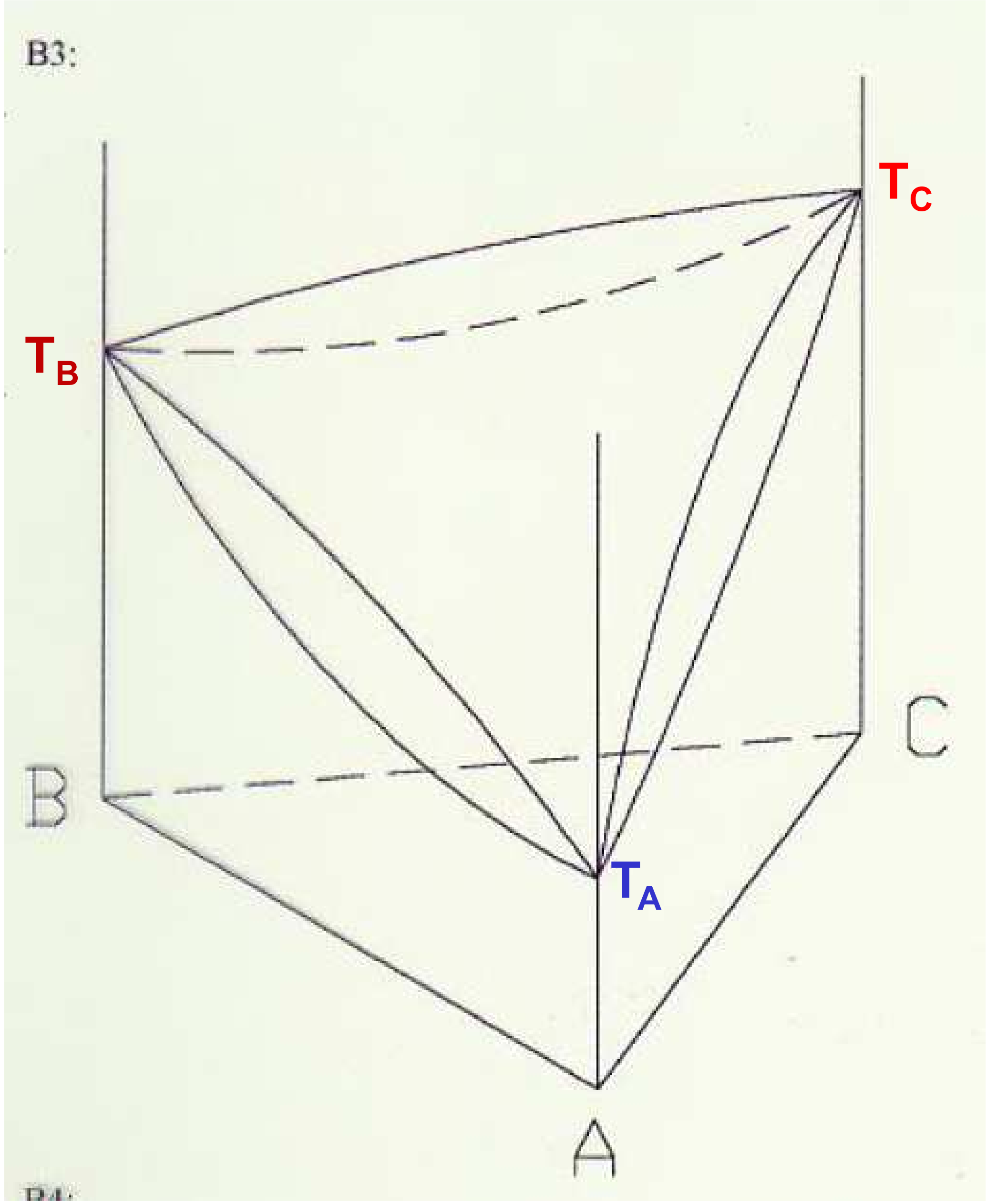
The Solidus Surface: A plot of the temperatures below which a (homogeneous) solid phase forms for any given overall composition.

Ternary Isomorphous System

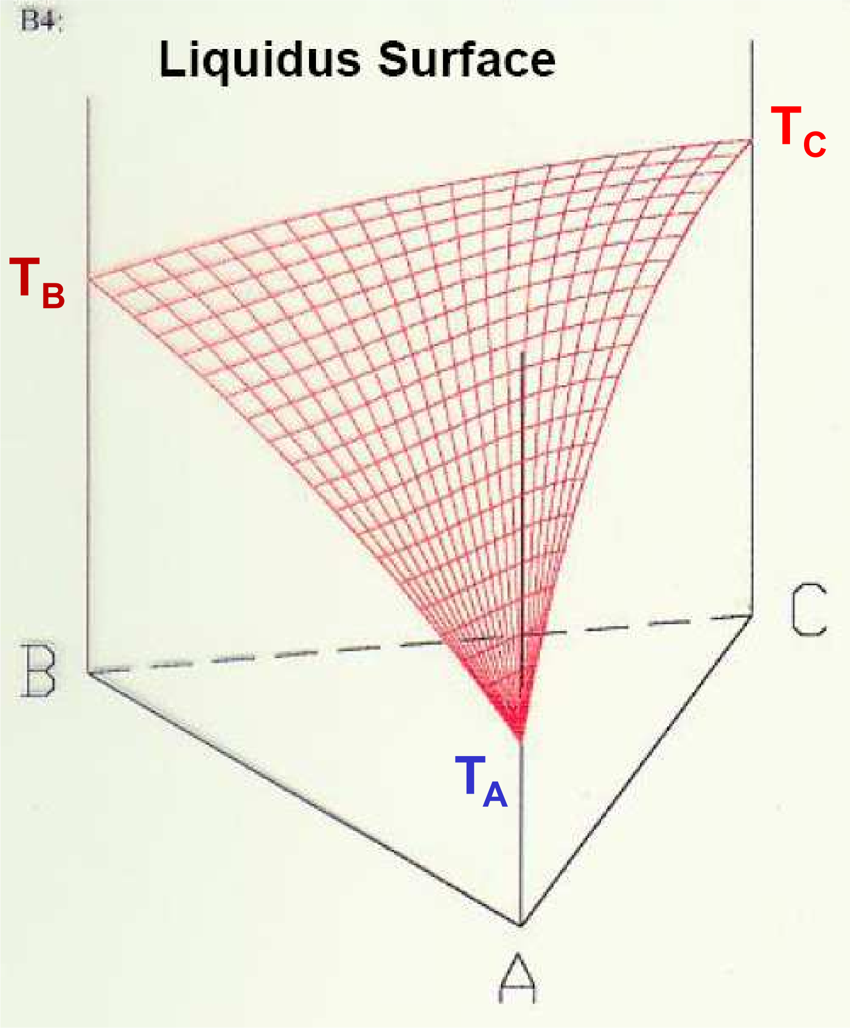


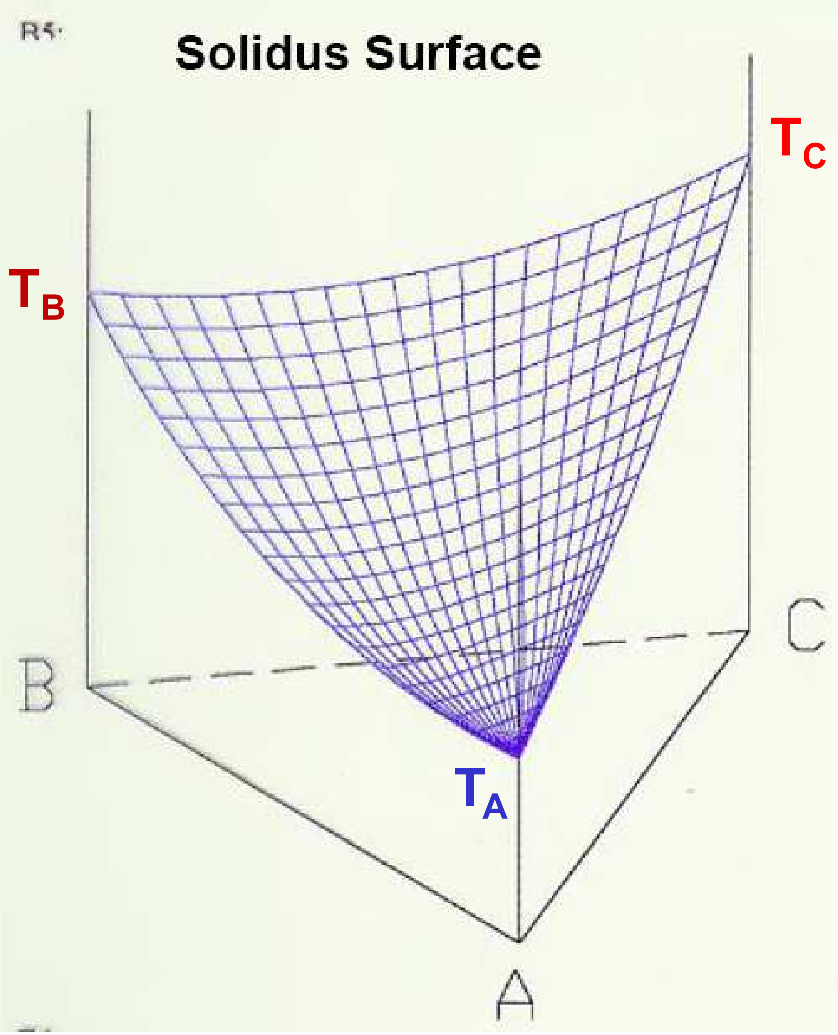


Ternary Isomorphous System

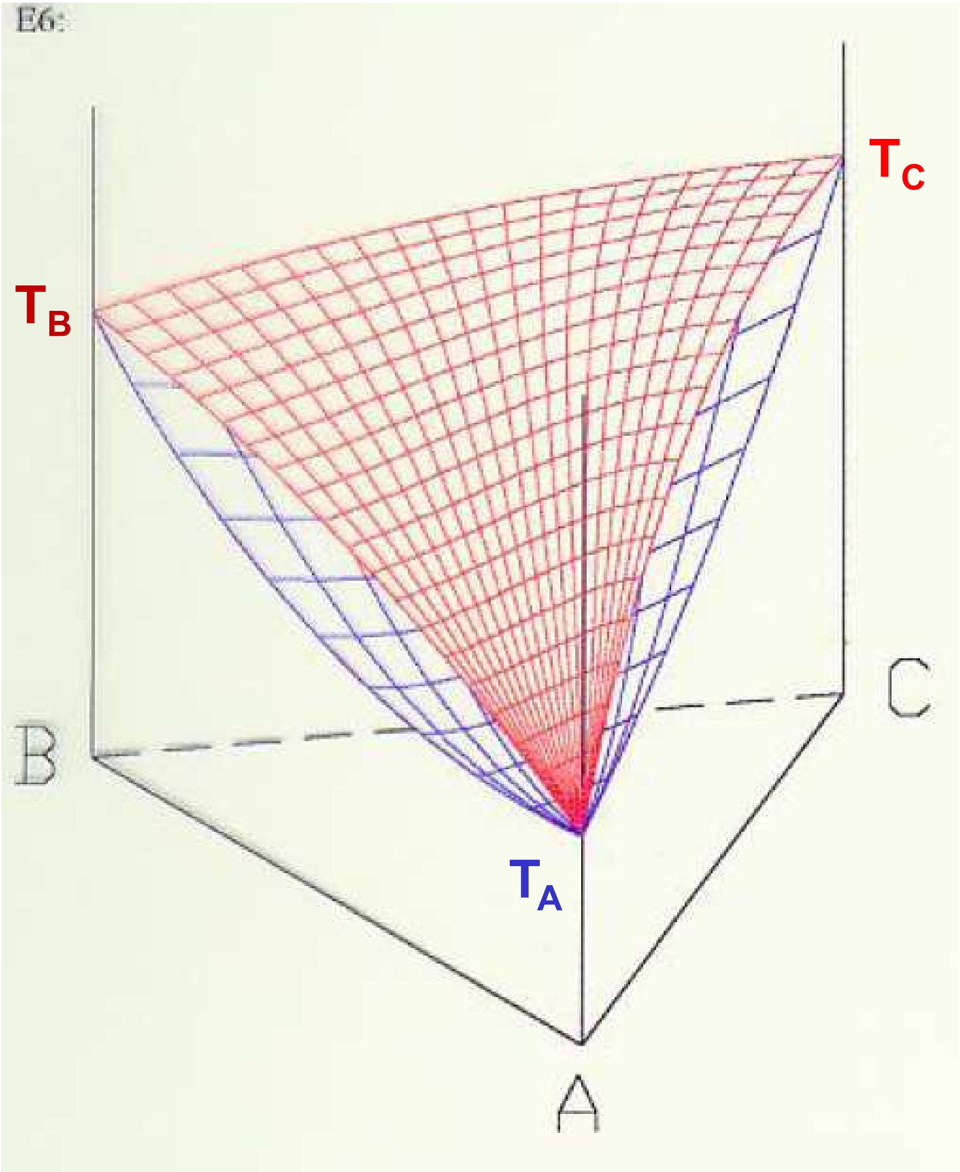


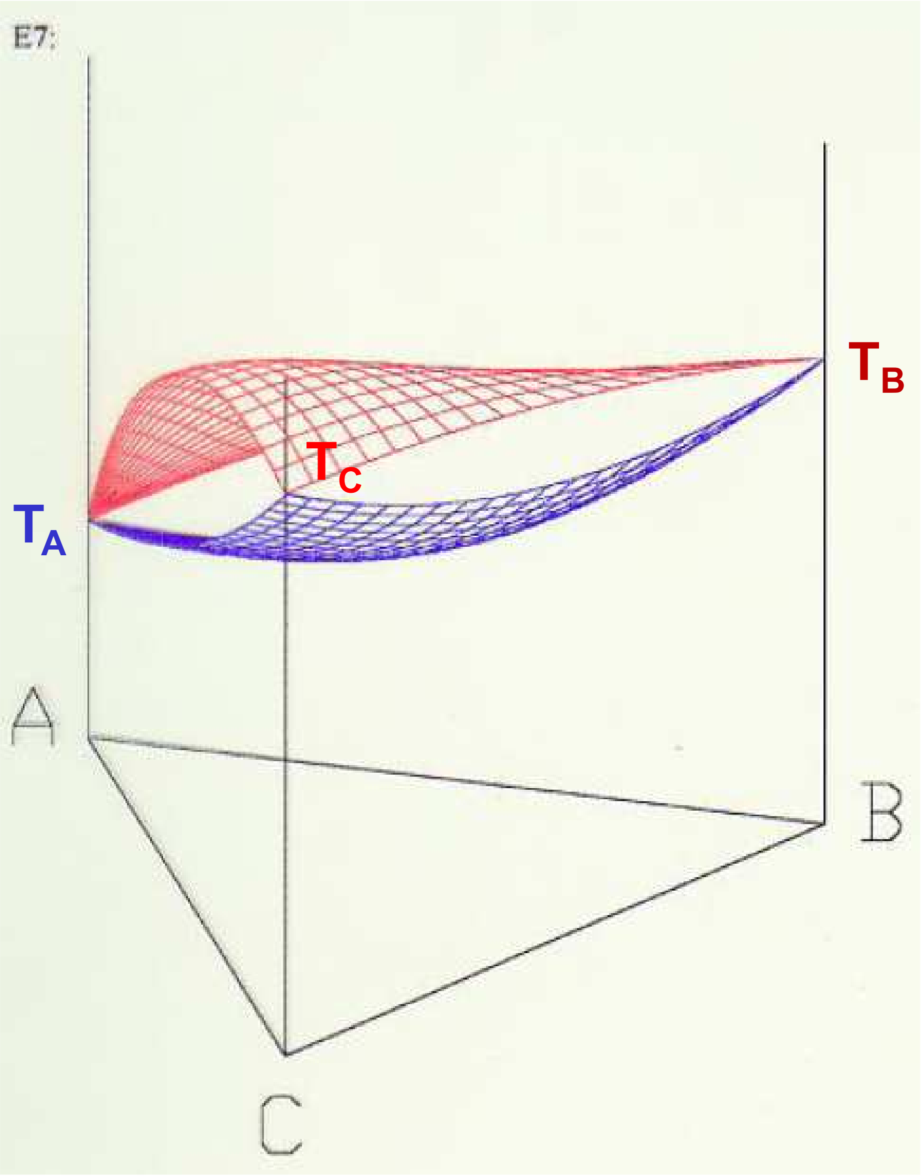
Ternary Isomorphous System





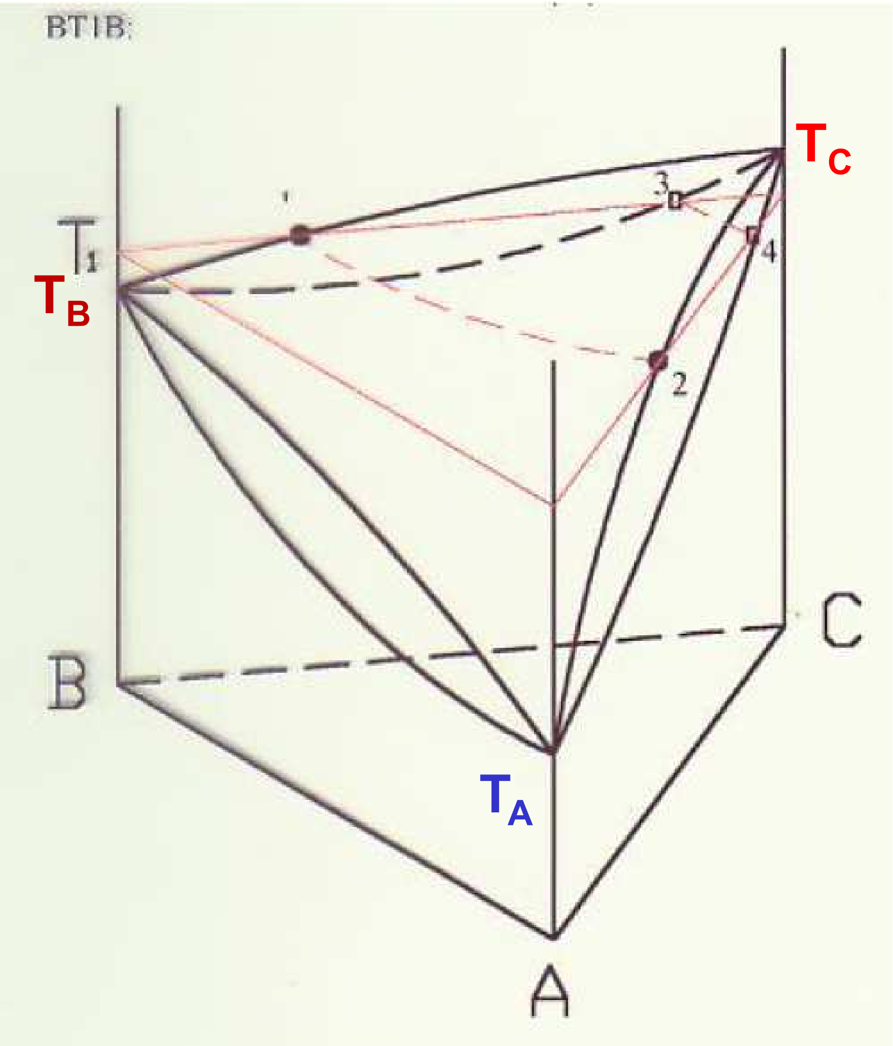
Ternary Isomorphous System

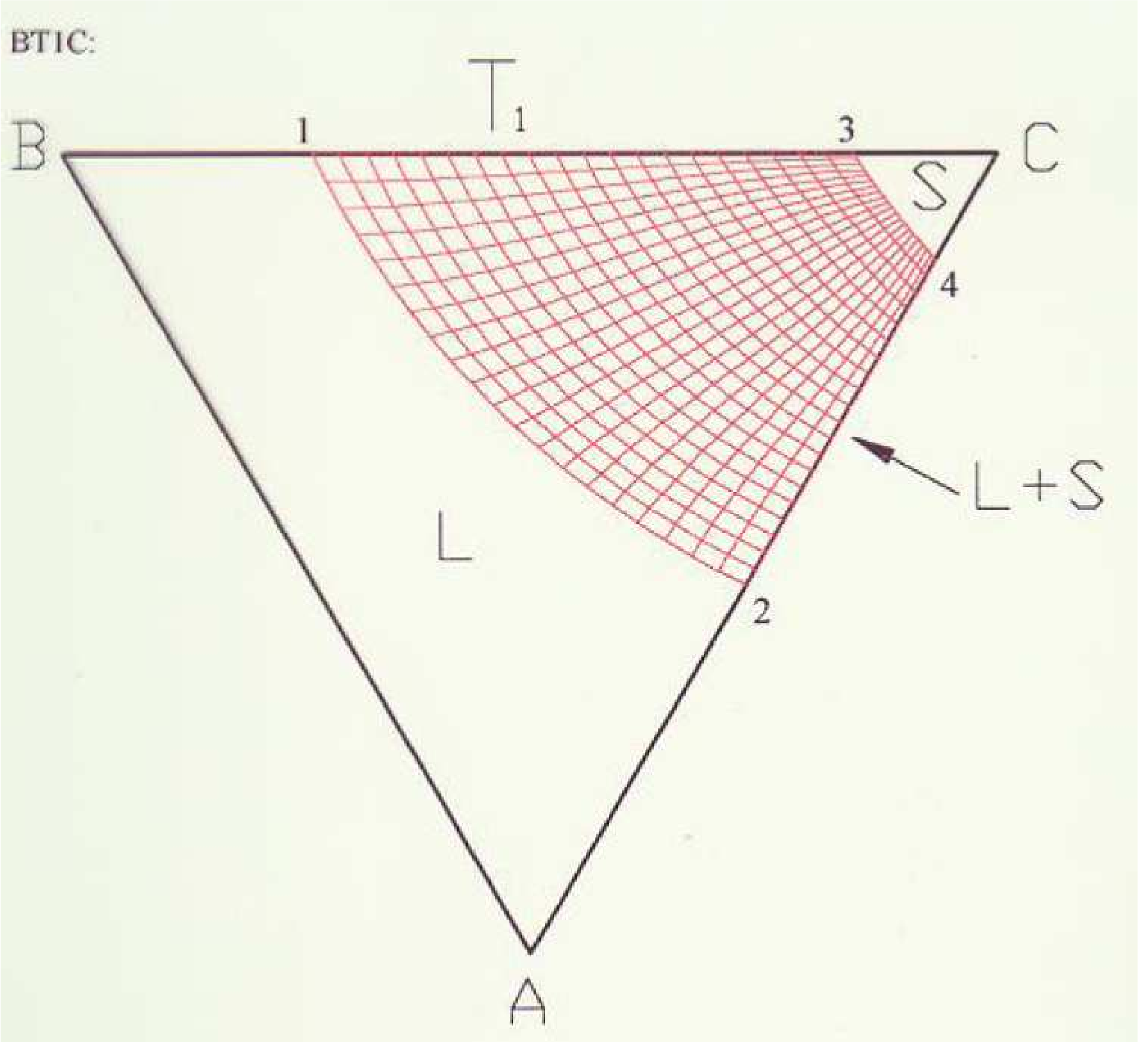




Ternary Isomorphous System

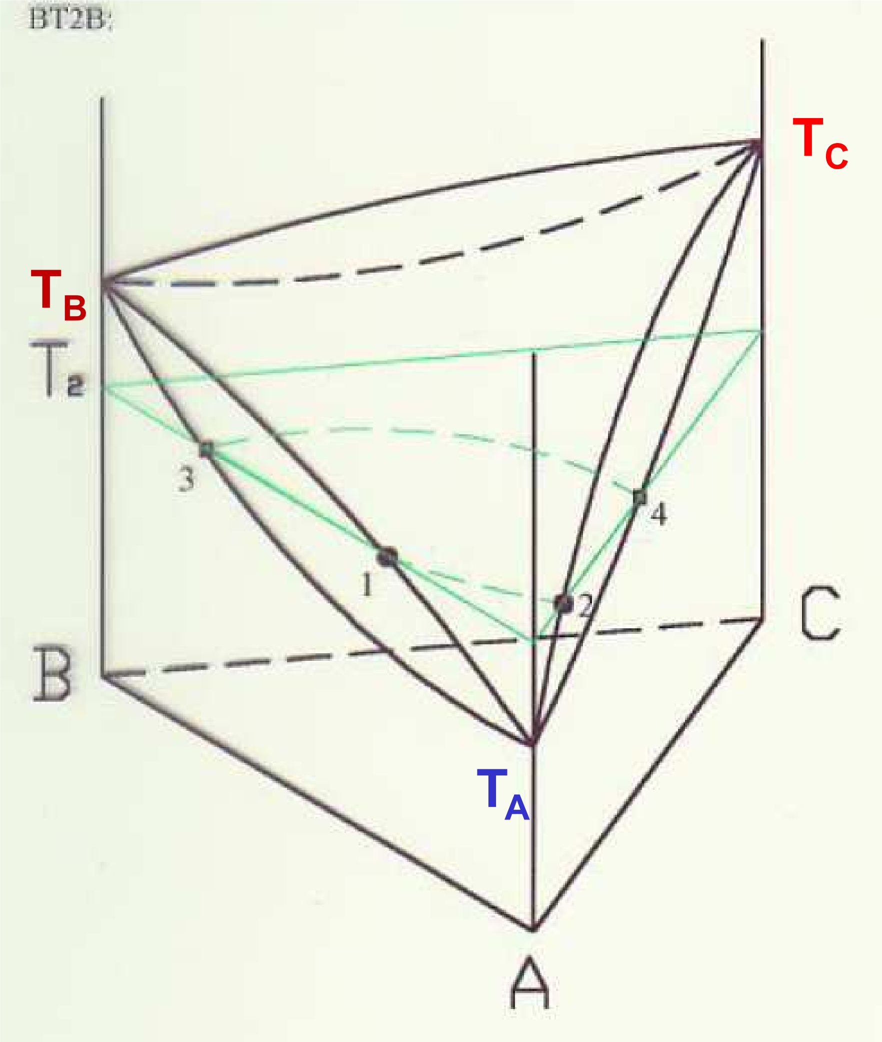
Isothermal section → F = C - P

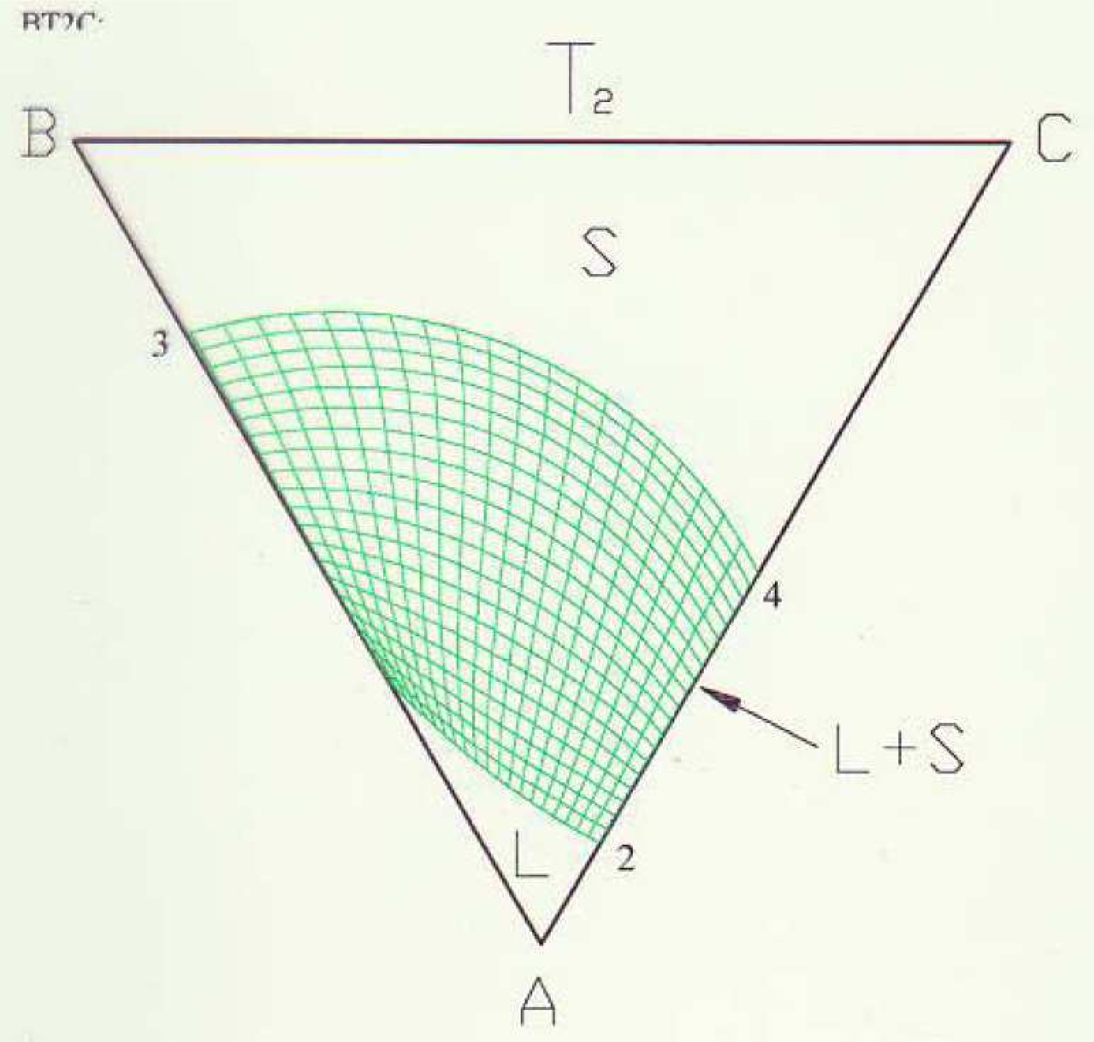




Ternary Isomorphous System

Isothermal section





Ternary Isomorphous System

Isothermal section → $F = C - P$

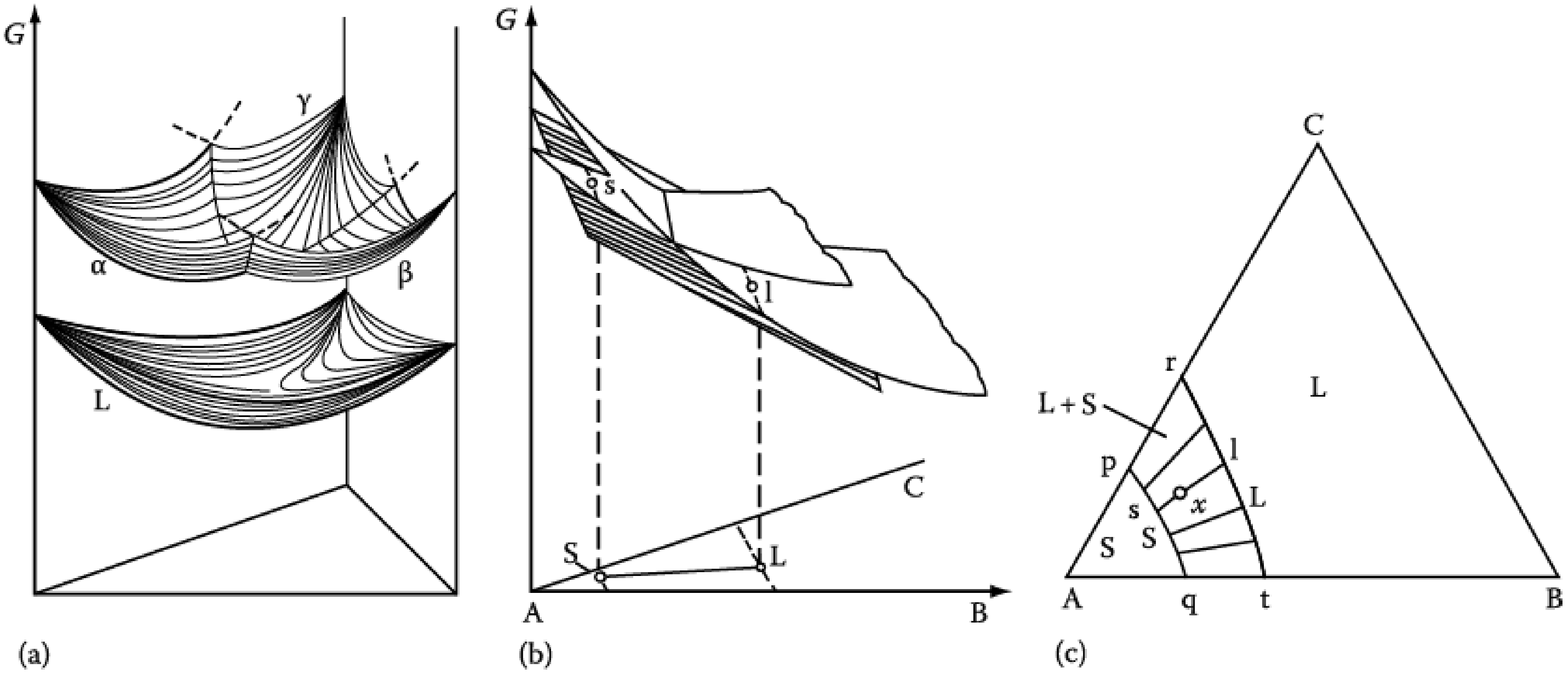
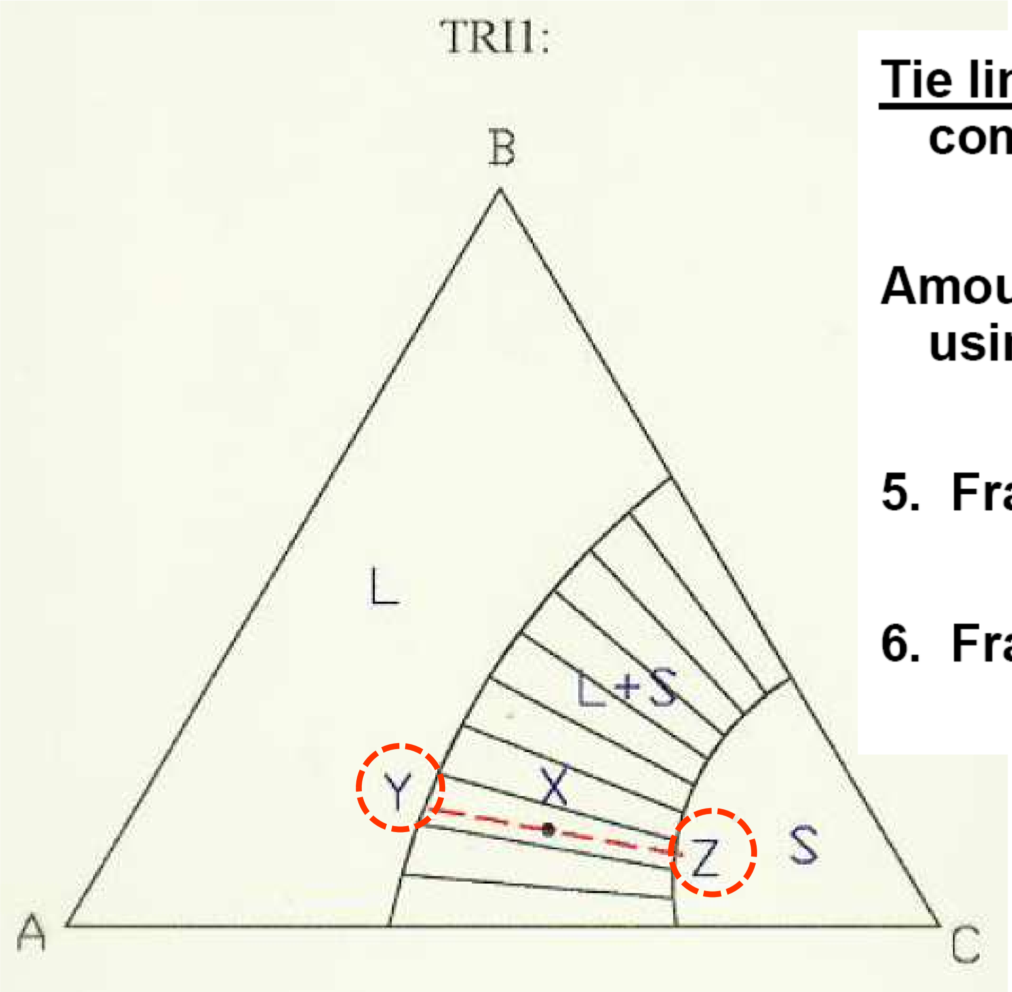


Fig. 1.41 (a) Free energy surface of a liquid and three solid phases of a ternary system. (b) A tangential plane construction to the free energy surfaces defined equilibrium between s and l in the ternary system (c) Isothermal section through a ternary phase diagram

Ternary Isomorphous System

Locate overall composition using Gibbs triangle



Tie line: A straight line joining any two ternary compositions

Amount of each phase present is determined by using the Inverse Lever Rule

5. Fraction of solid = YX/YZ

6. Fraction of liquid = ZX/YZ

Ternary Eutectic System
(No Solid Solubility)

The Ternary Eutectic Reaction:

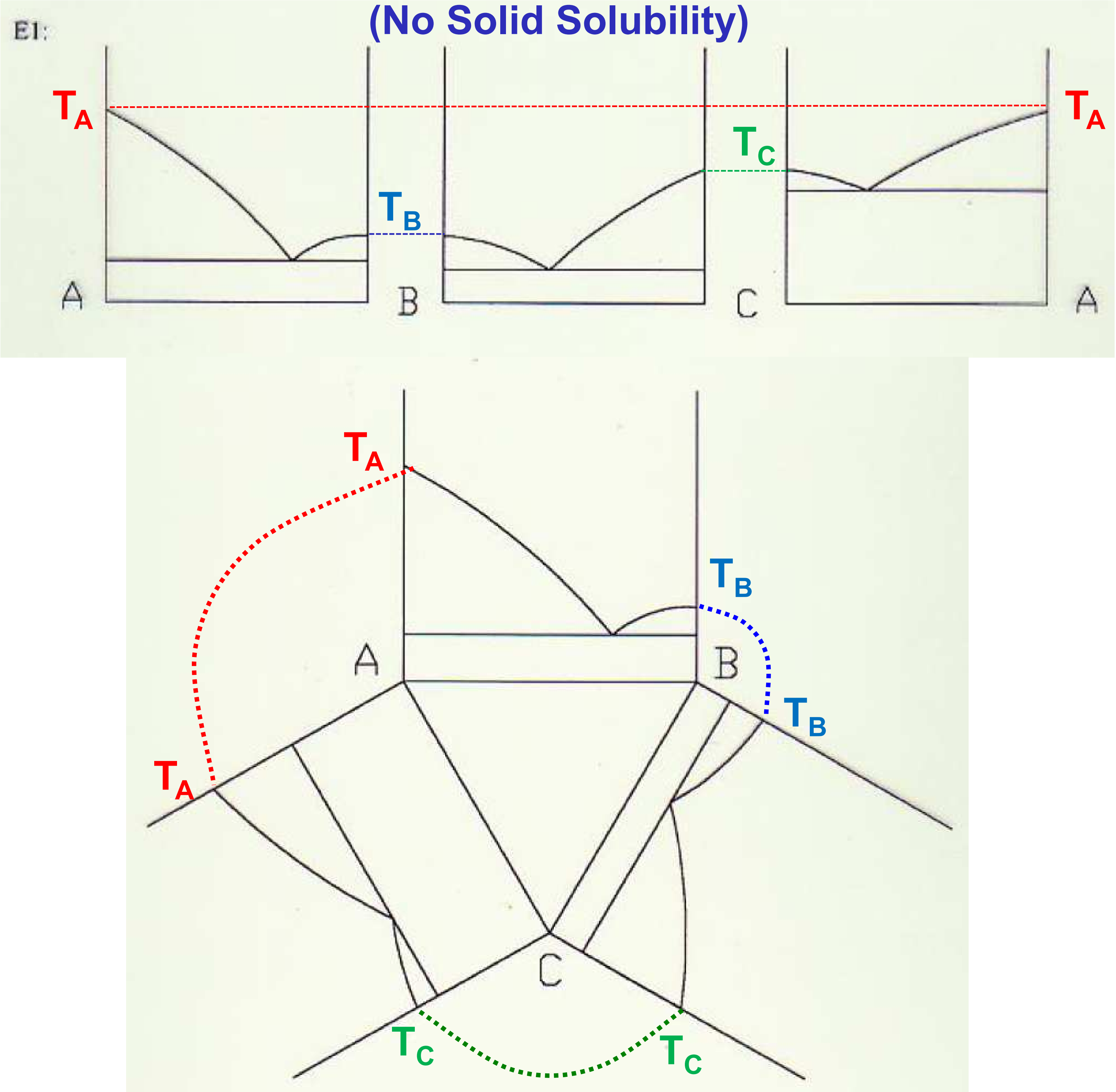
$$\boxed{L = \alpha + \beta + \gamma}$$

A liquid phase solidifies into three separate solid phases

Made up of three binary eutectic systems, all of which exhibit no solid solubility

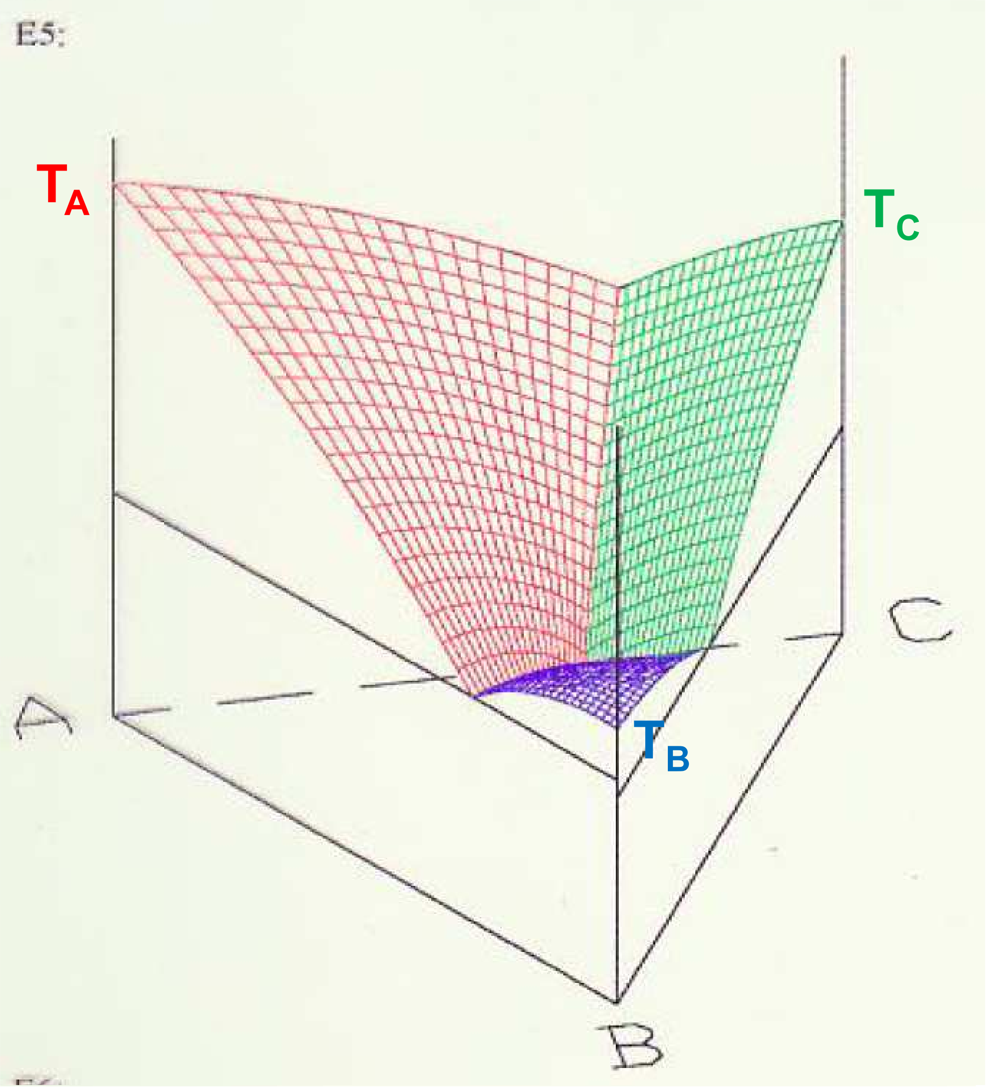
Ternary Eutectic System

(No Solid Solubility)

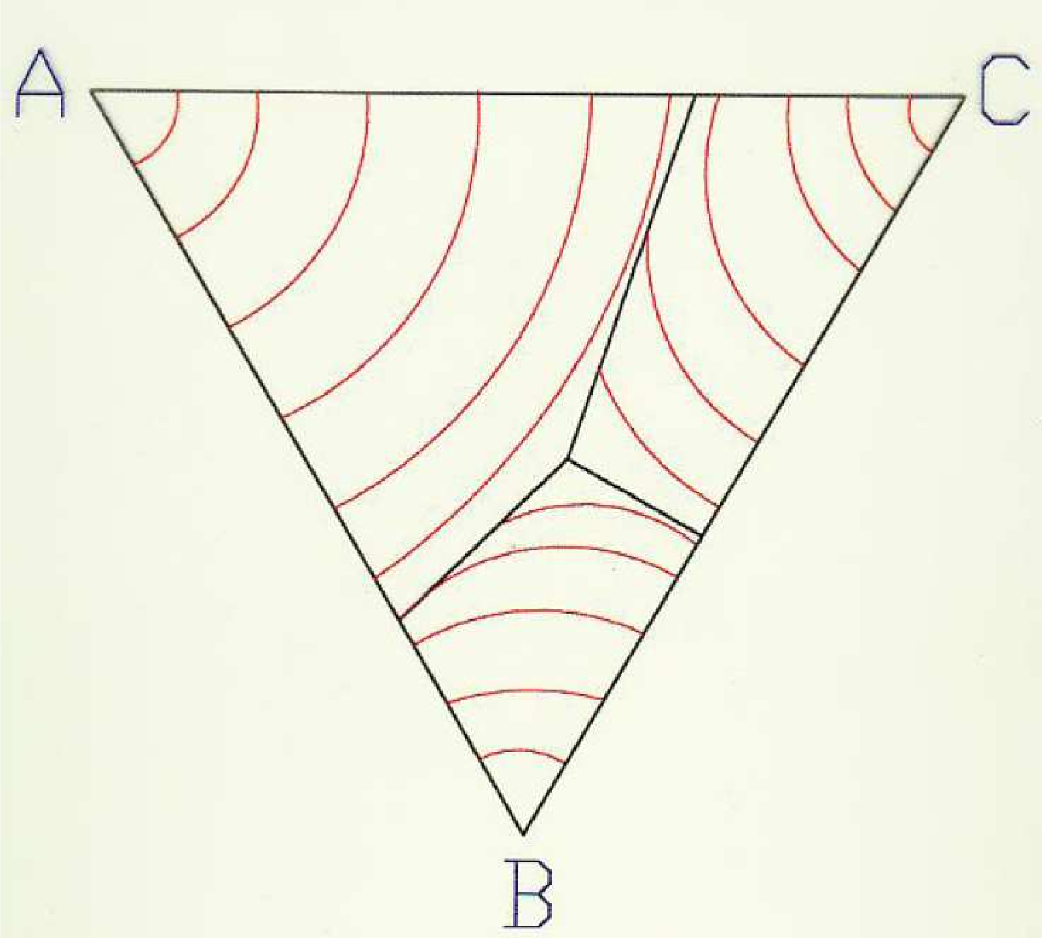


Ternary Eutectic System

(No Solid Solubility)

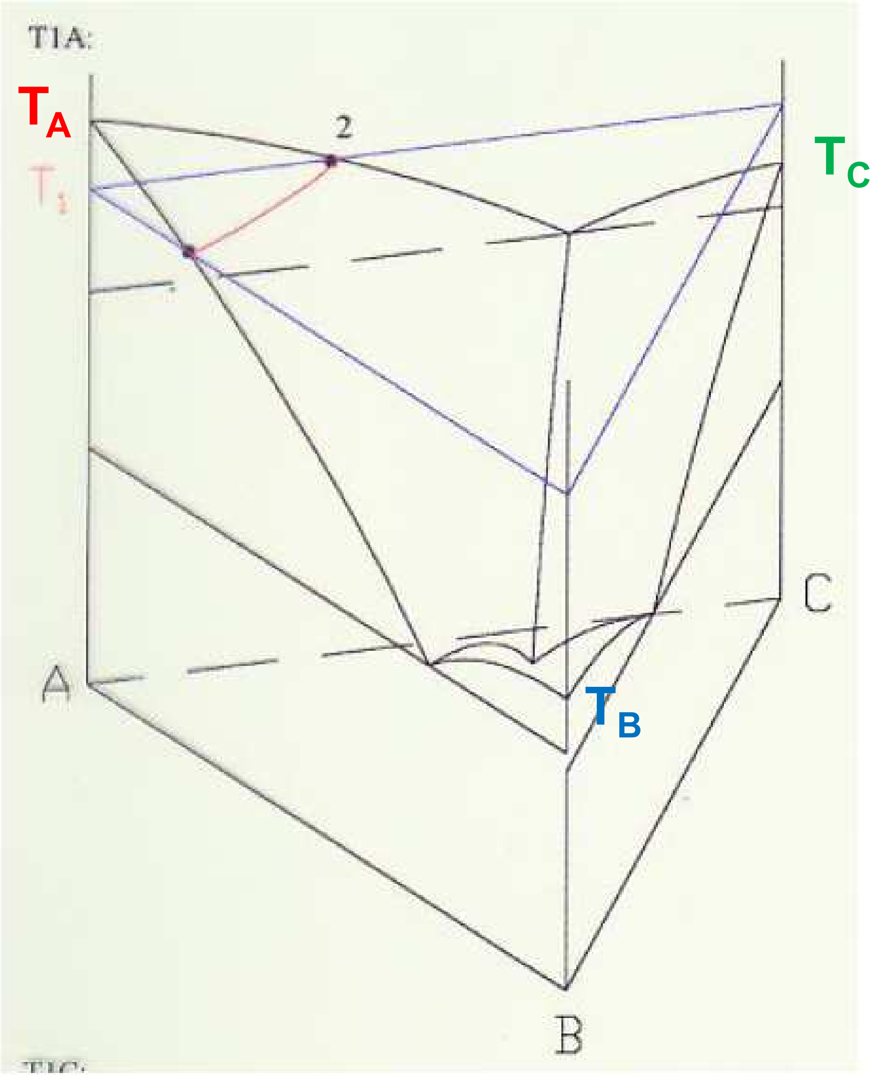


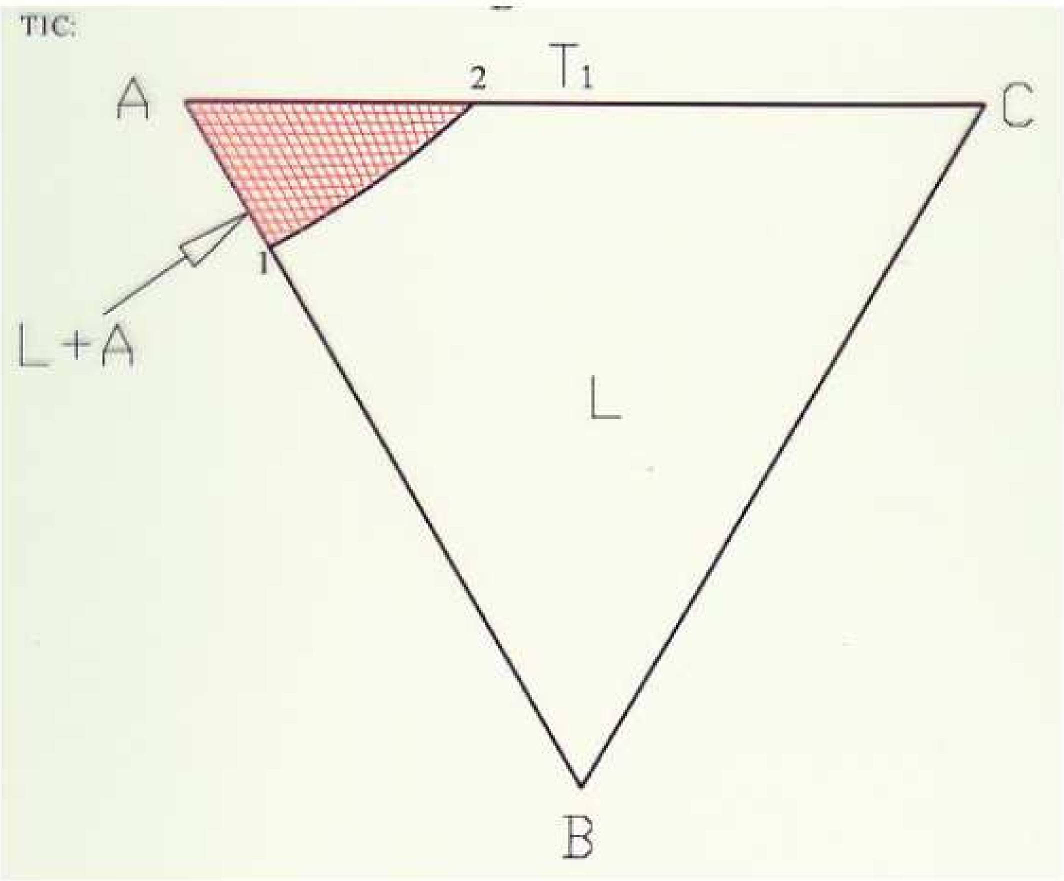
Liquidus projection



Ternary Eutectic System

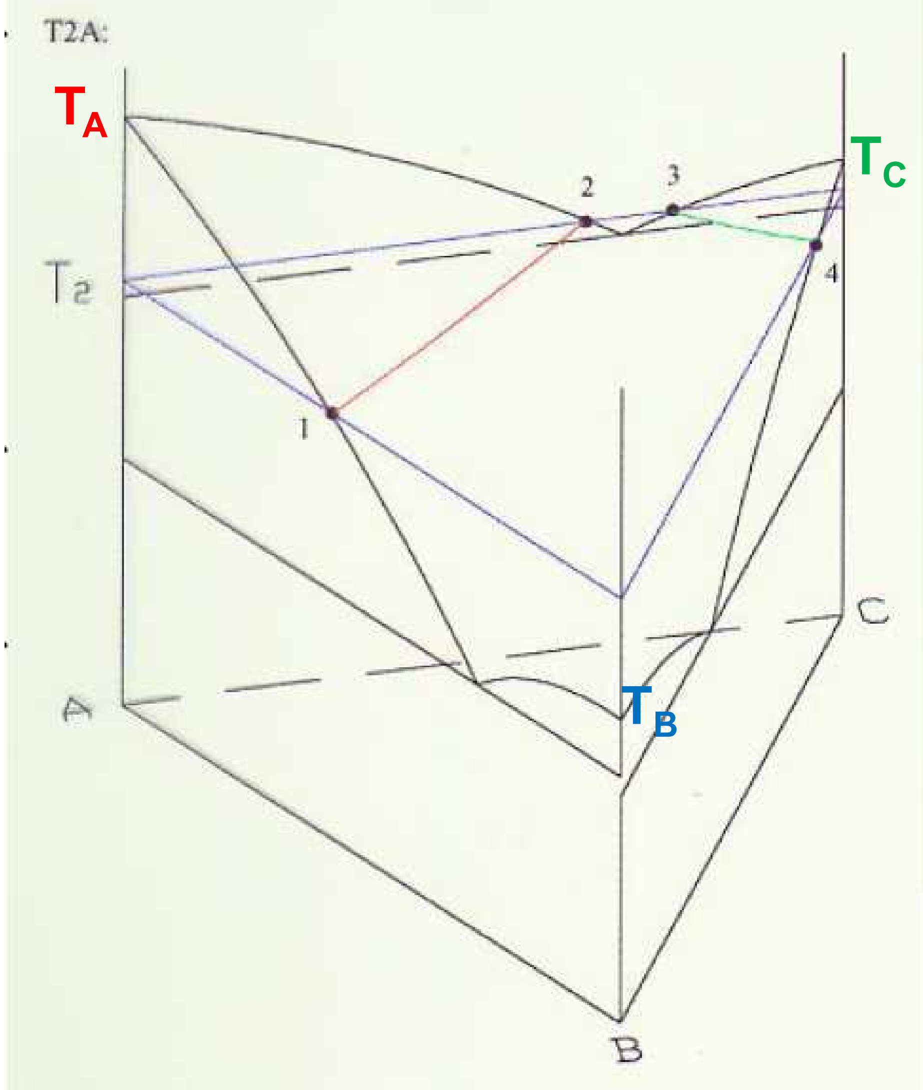
(No Solid Solubility)

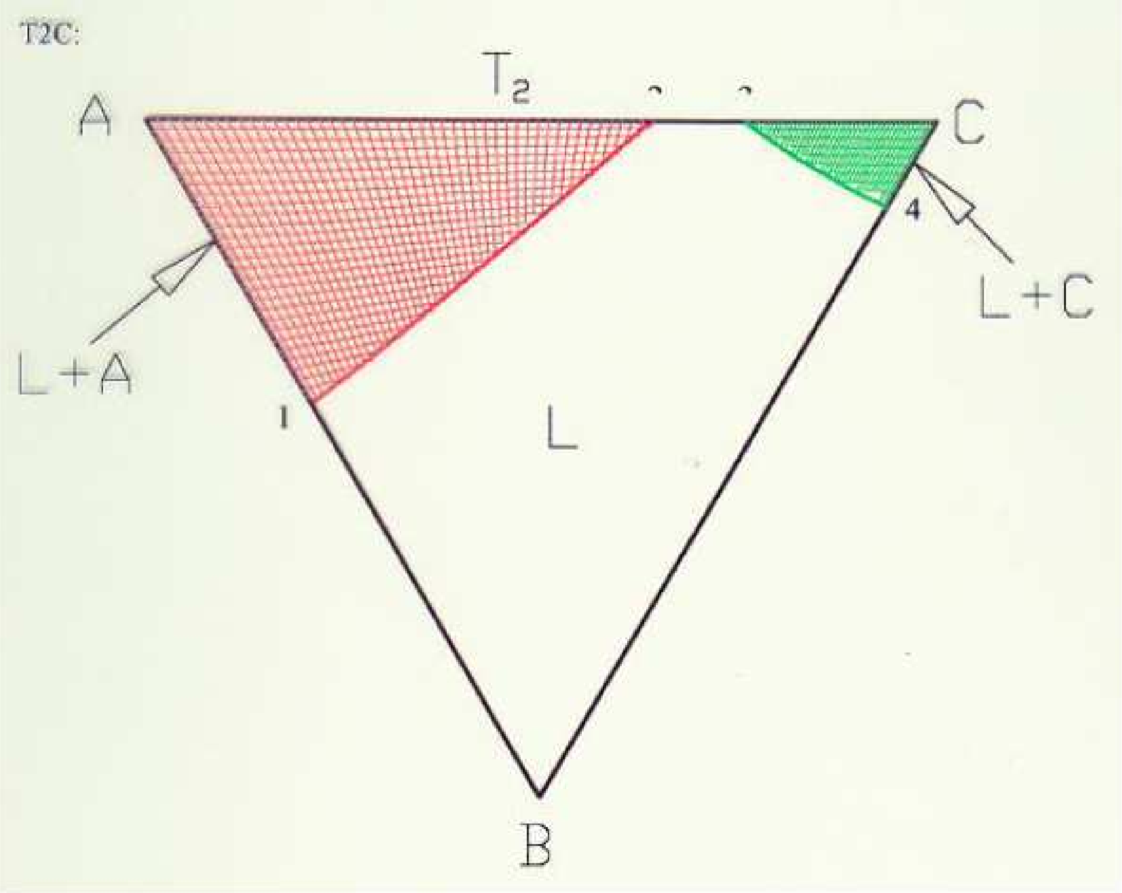




Ternary Eutectic System

(No Solid Solubility)





Ternary Eutectic System

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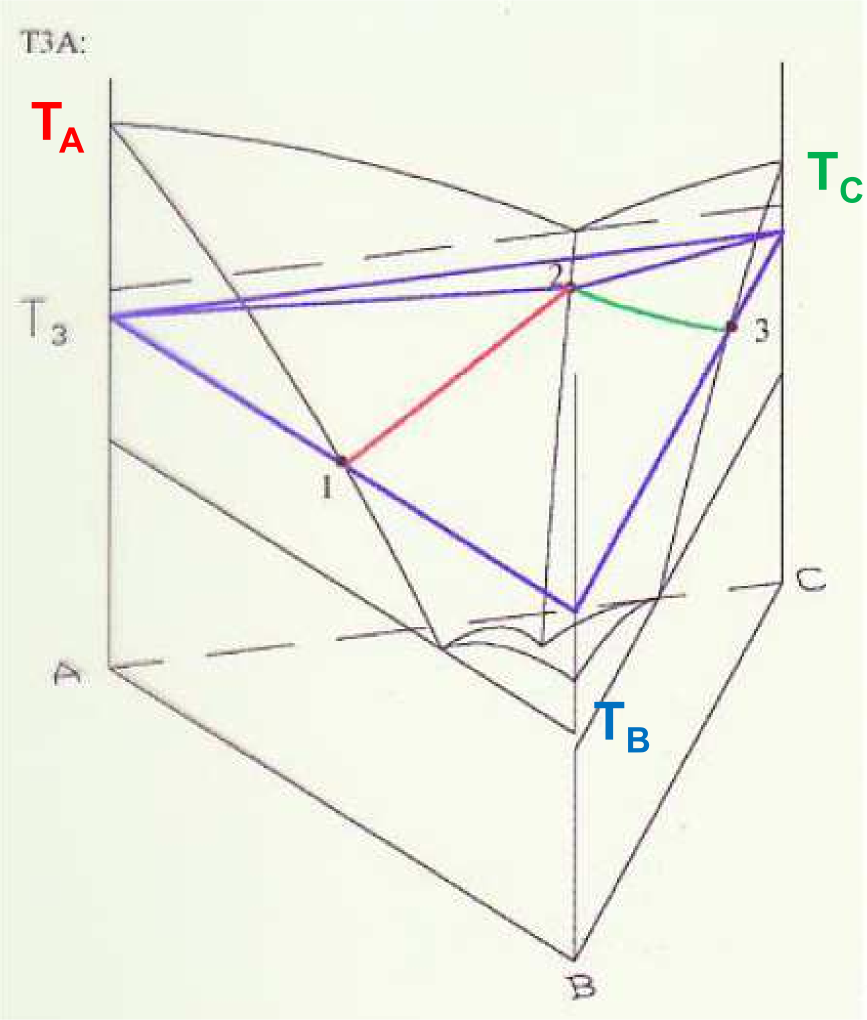
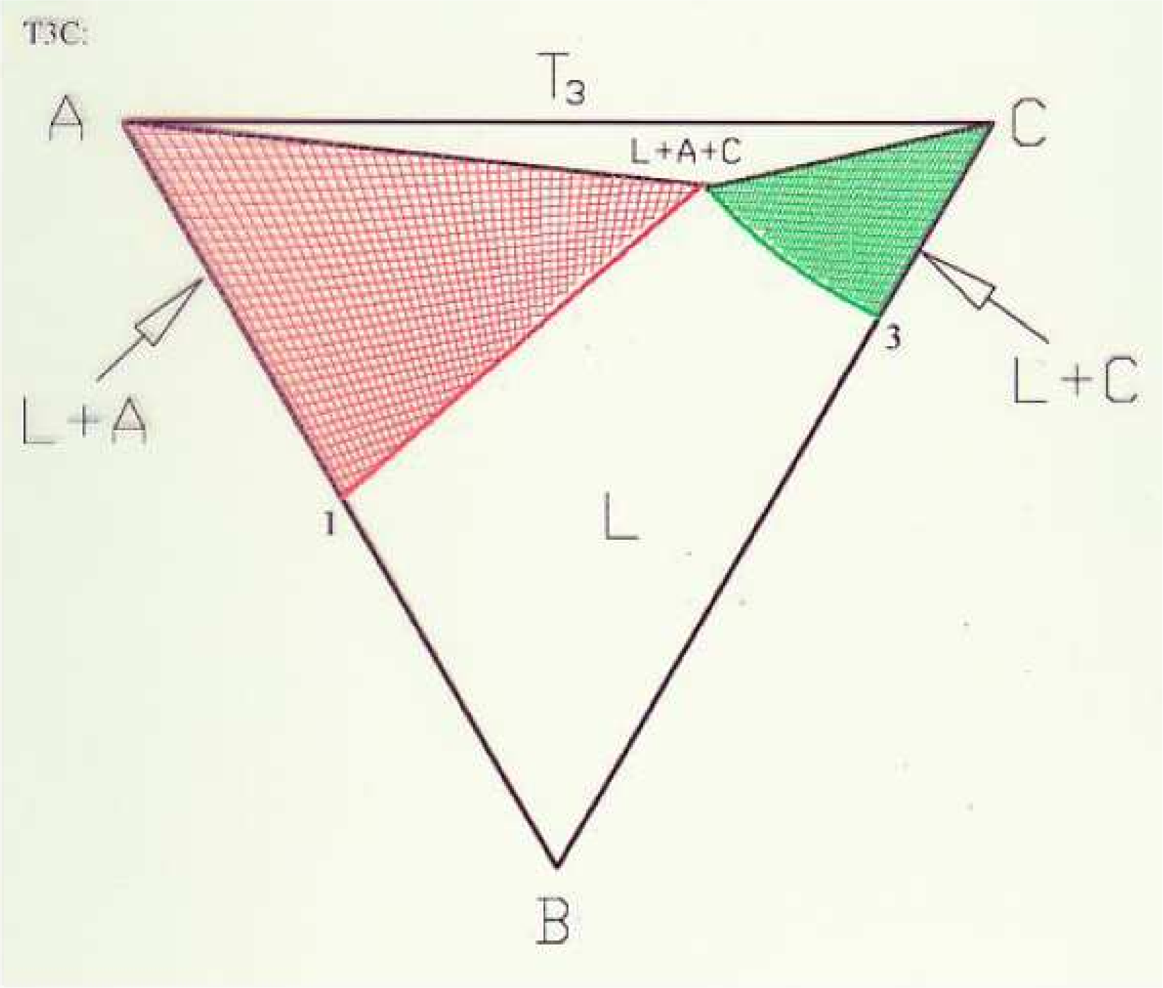
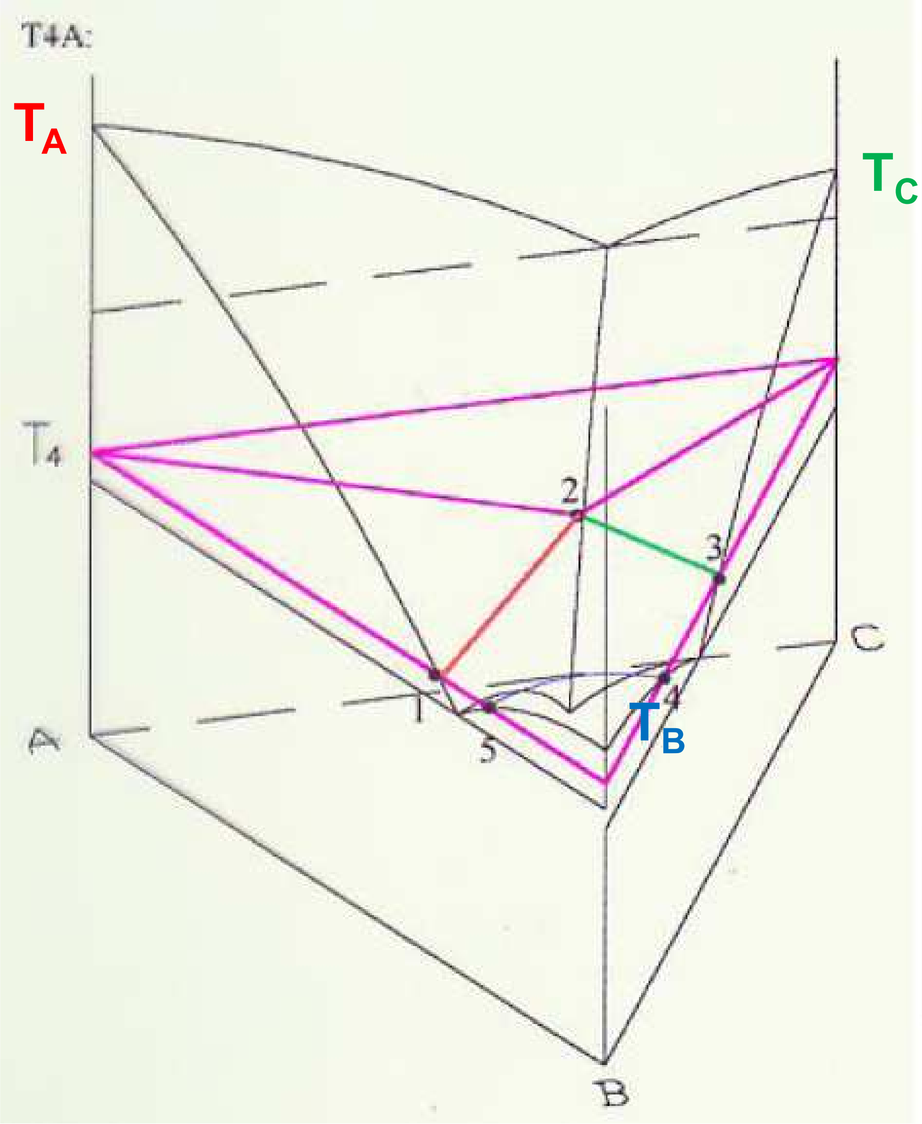
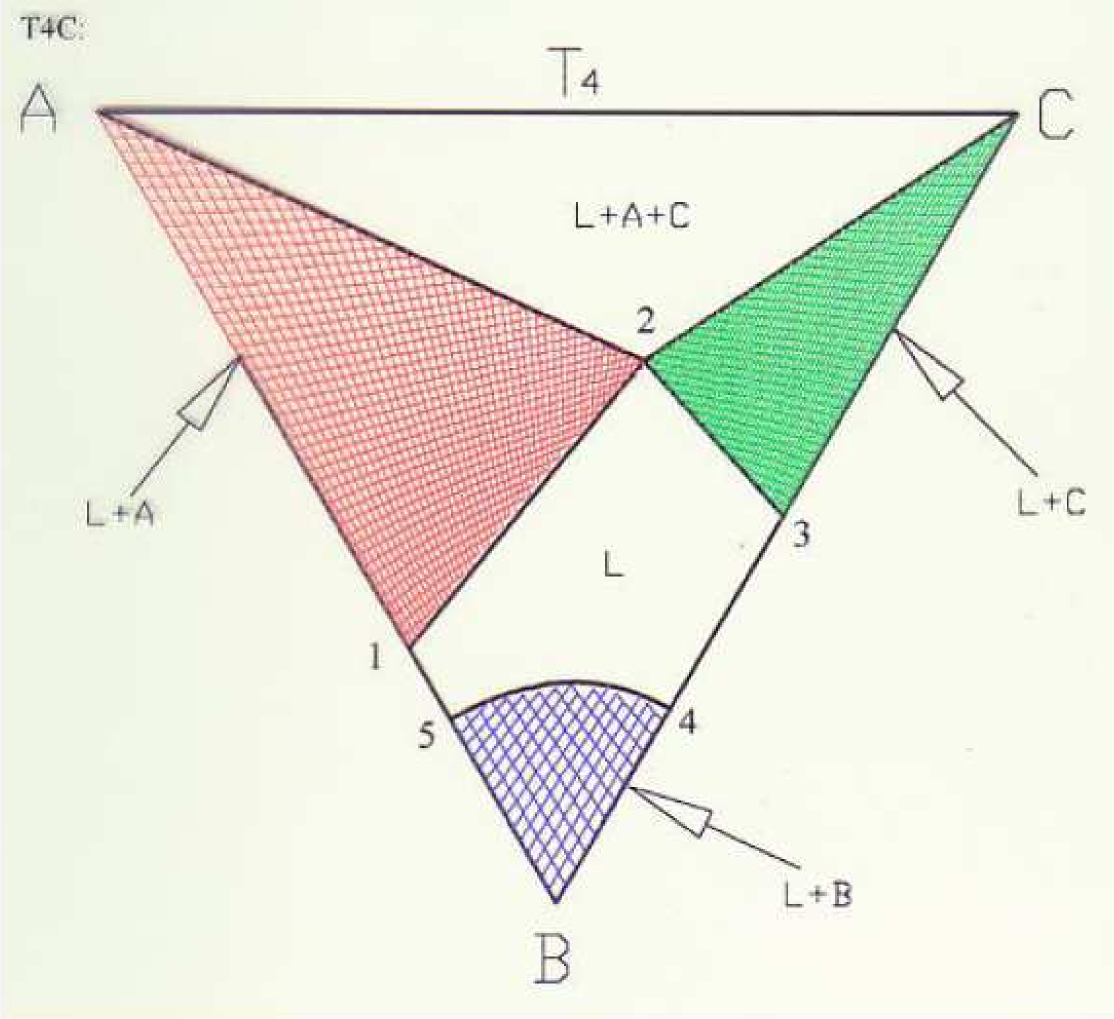




Ternary Eutectic System

(No Solid Solubility)





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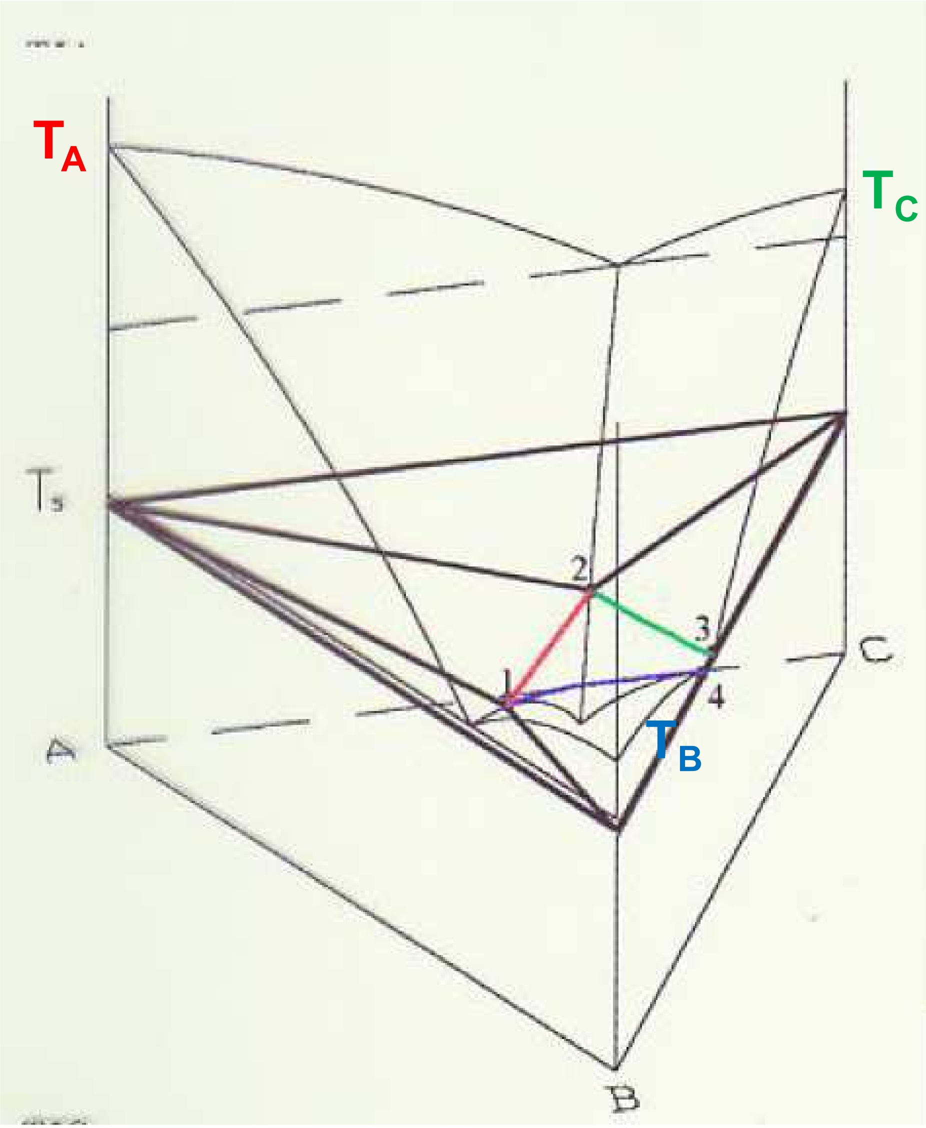
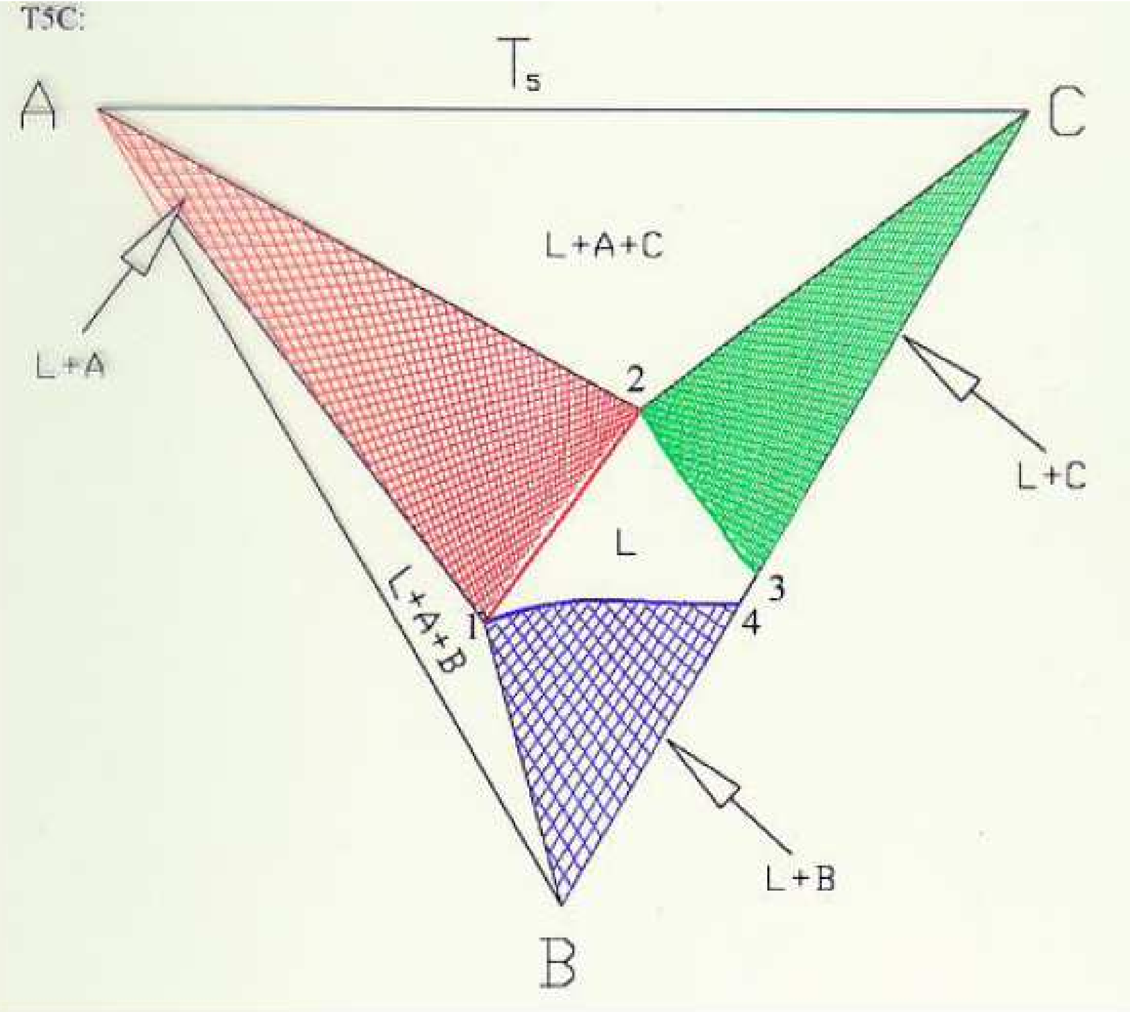
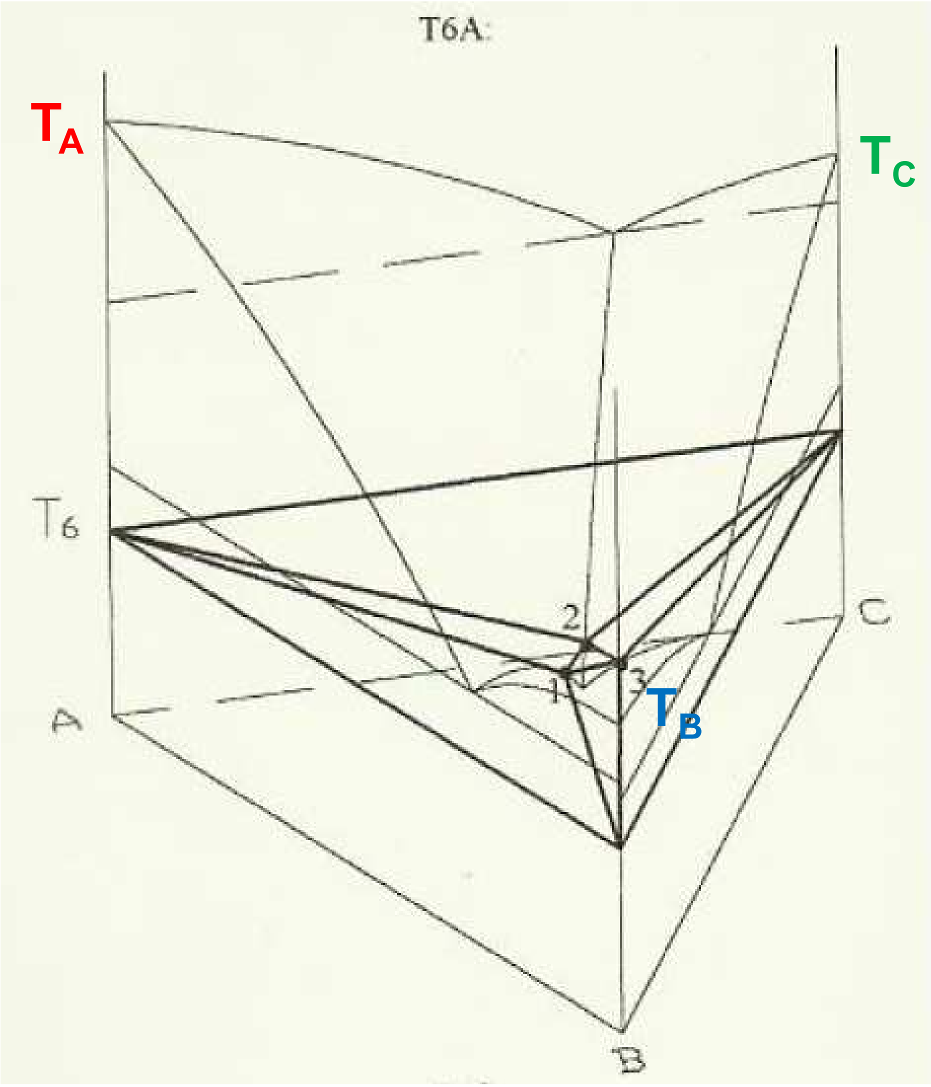
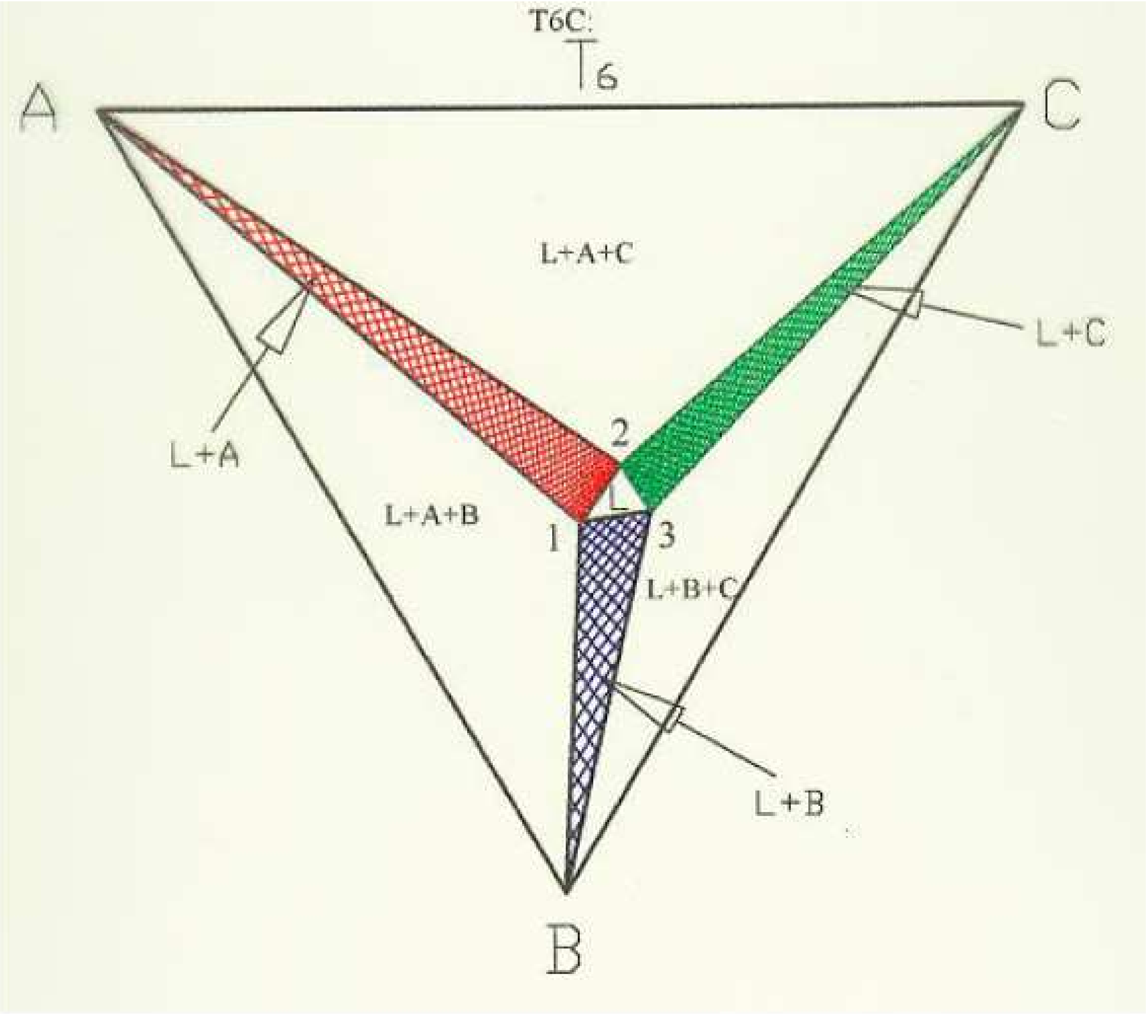




Ternary Eutectic System

(No Solid Solubility)

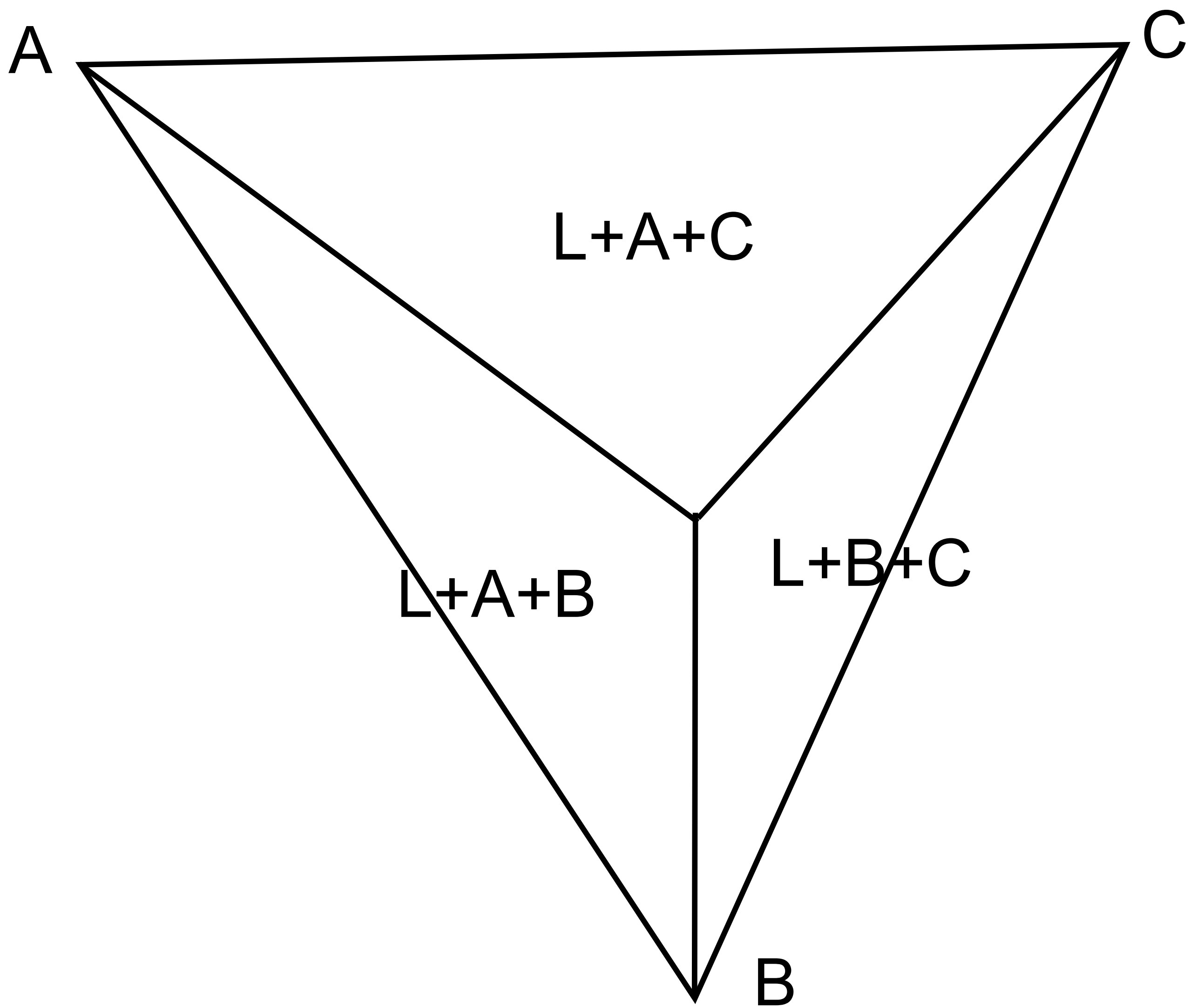




Ternary Eutectic System

(No Solid Solubility)

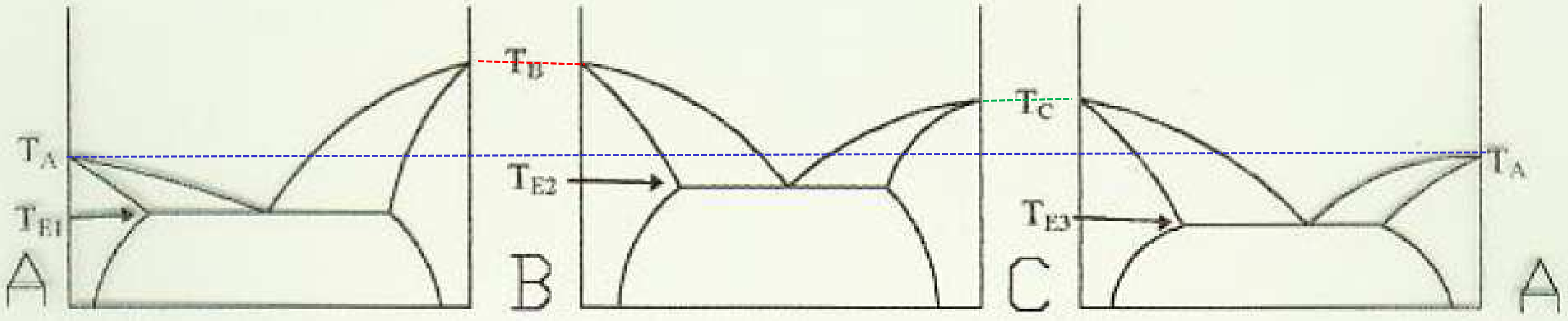
T= ternary eutectic temp.



Ternary Eutectic System

(with Solid Solubility)

P1:



T_A: Melting Point Of Material A

T_B: Melting Point Of Material B

T_C: Melting Point Of Material C

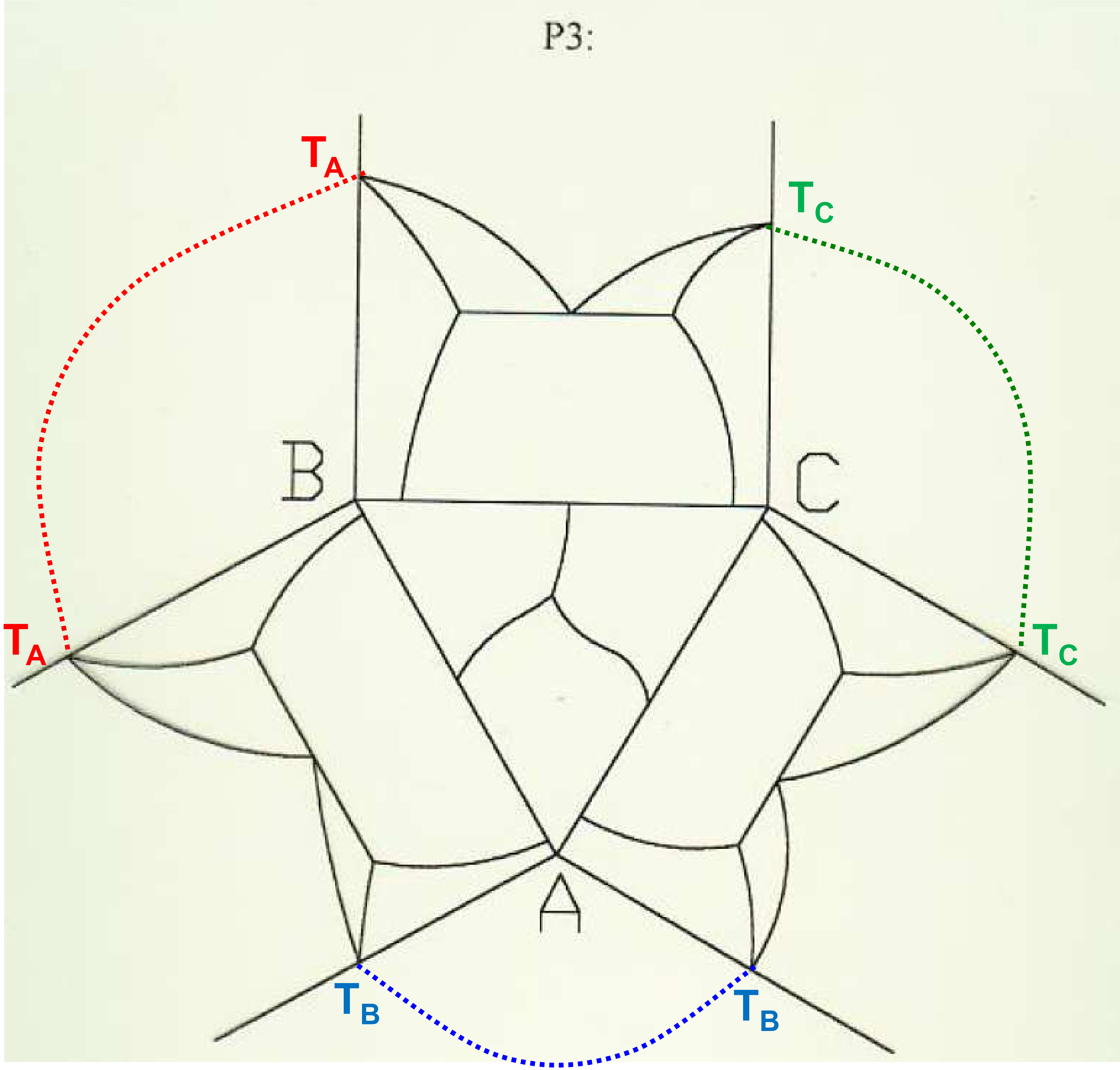
T_{E1}: Eutectic Temperature Of A-B

T_{E2}: Eutectic Temperature Of B-C

T_{E3}: Eutectic Temperature Of C-A

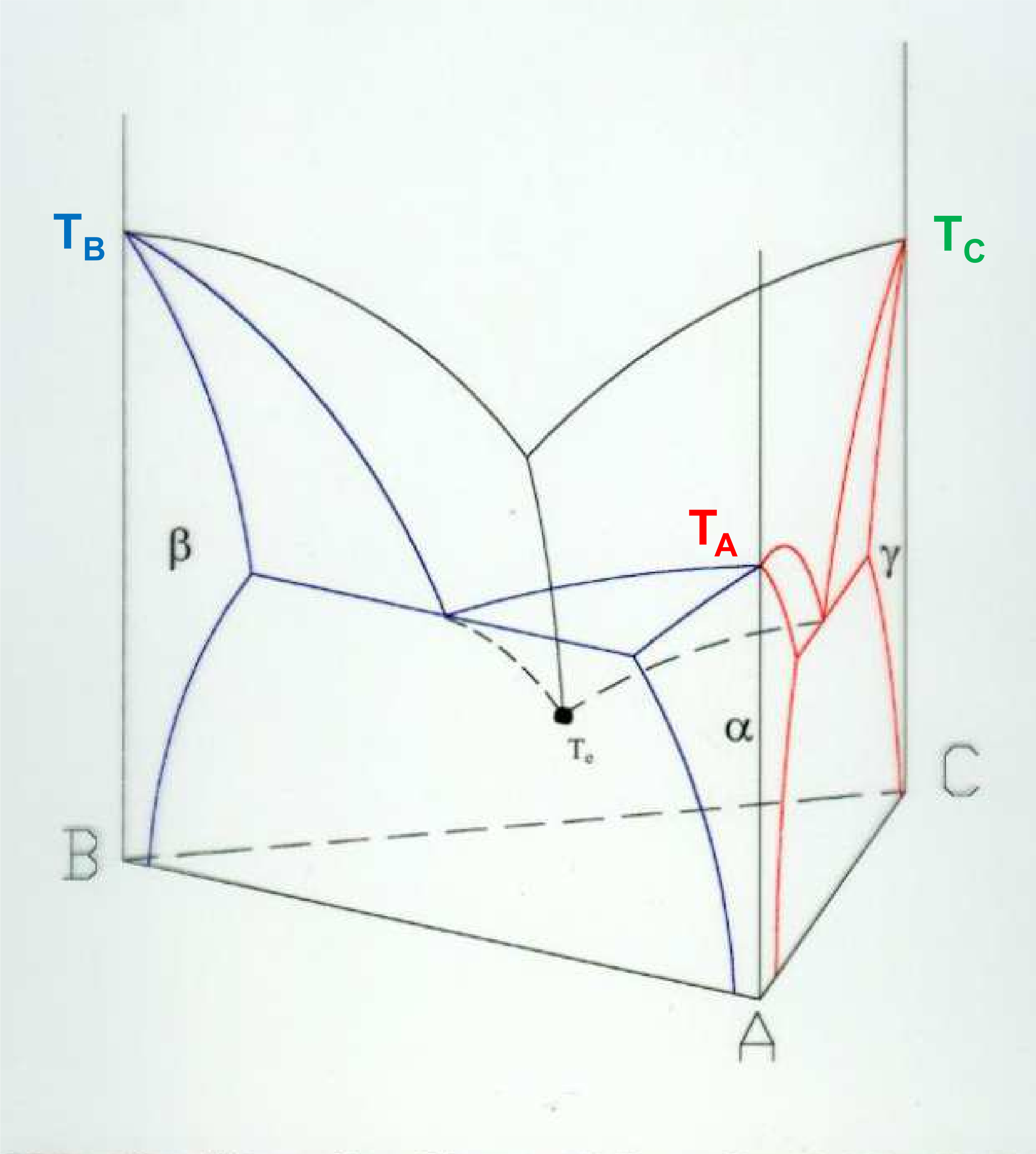
Ternary Eutectic System

(with Solid Solubility)

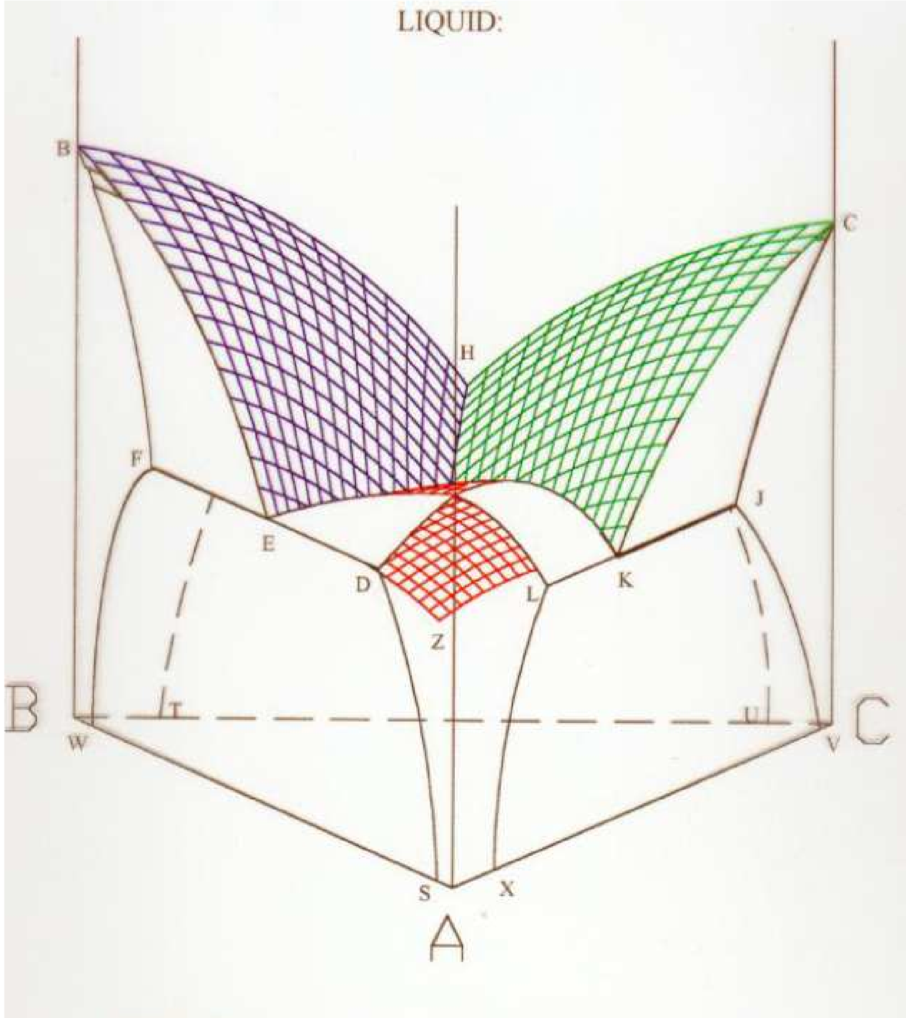


Ternary Eutectic System

(with Solid Solubility)



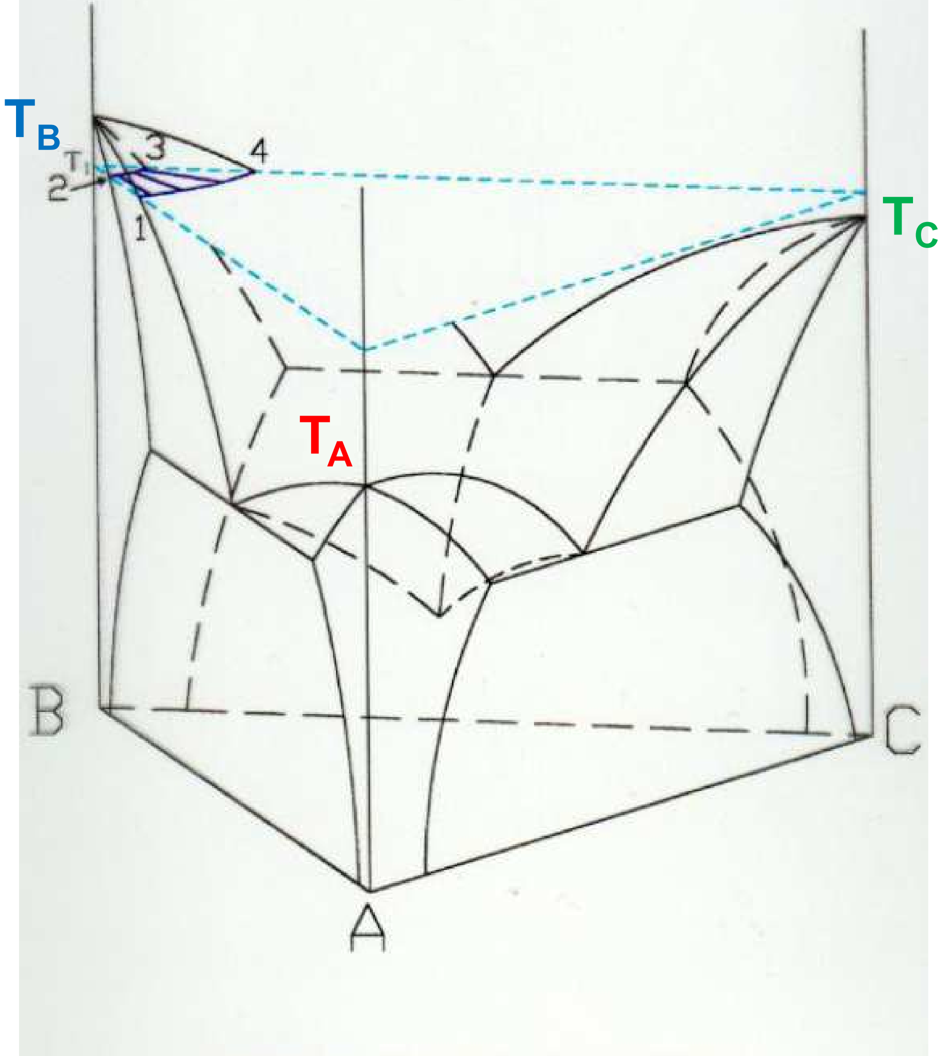
Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown



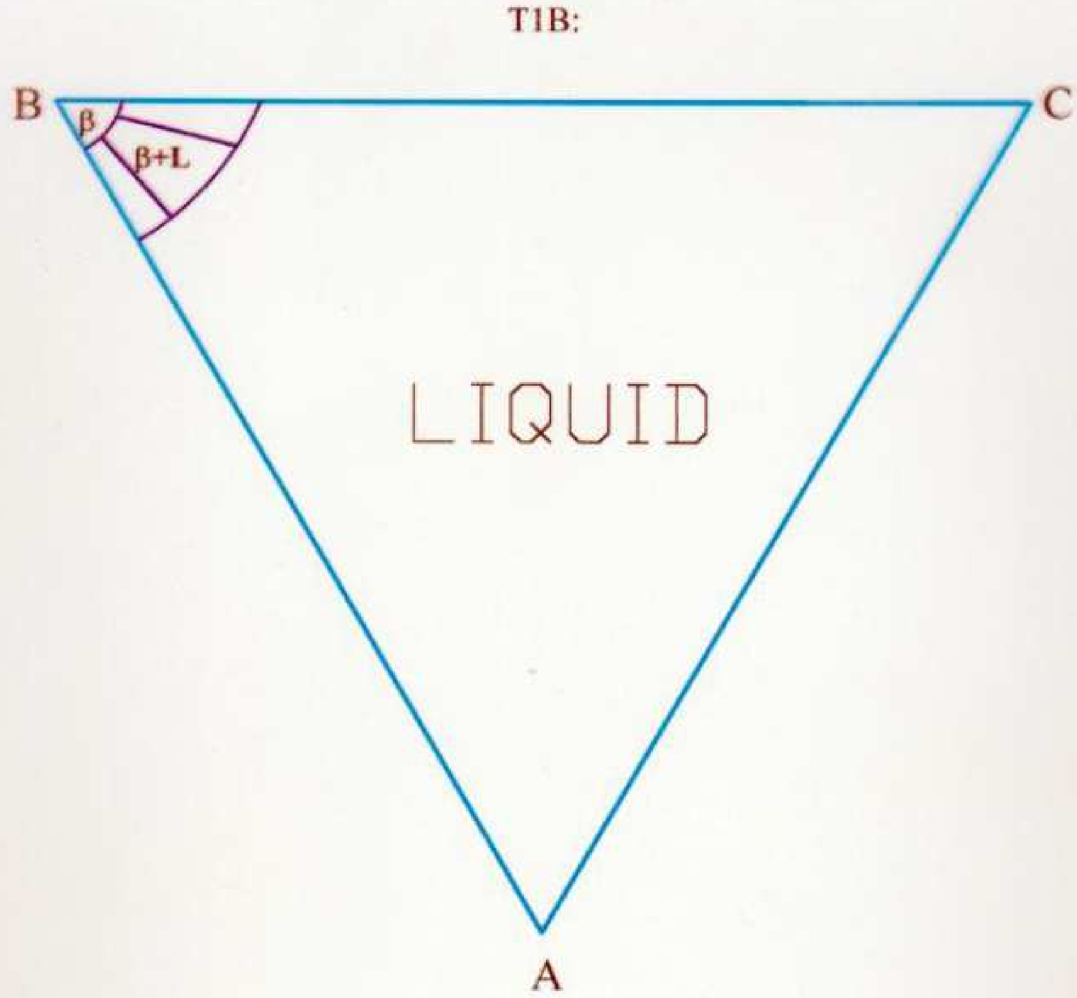
All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System

(with Solid Solubility)



Temperature Slice At $T_1 < T_B$, But $>T_A$, T_C

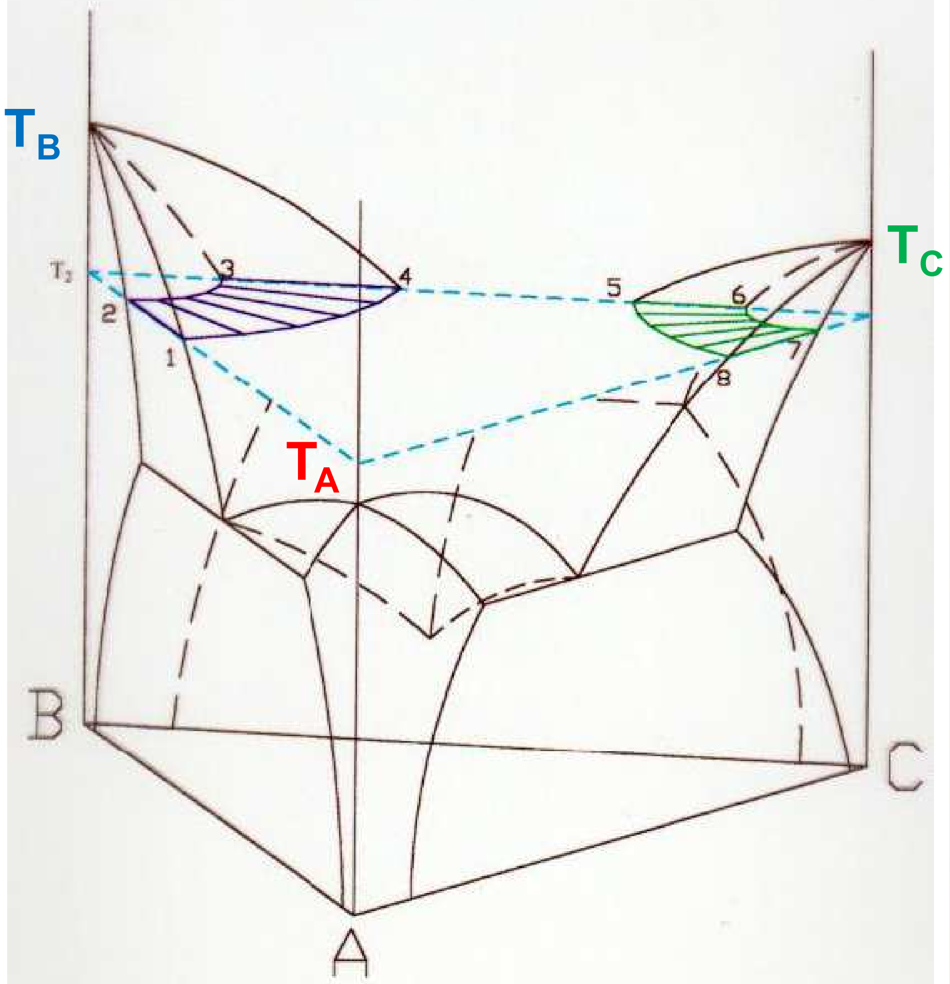


Isothermal Section At $T=T_1$

Ternary Eutectic System

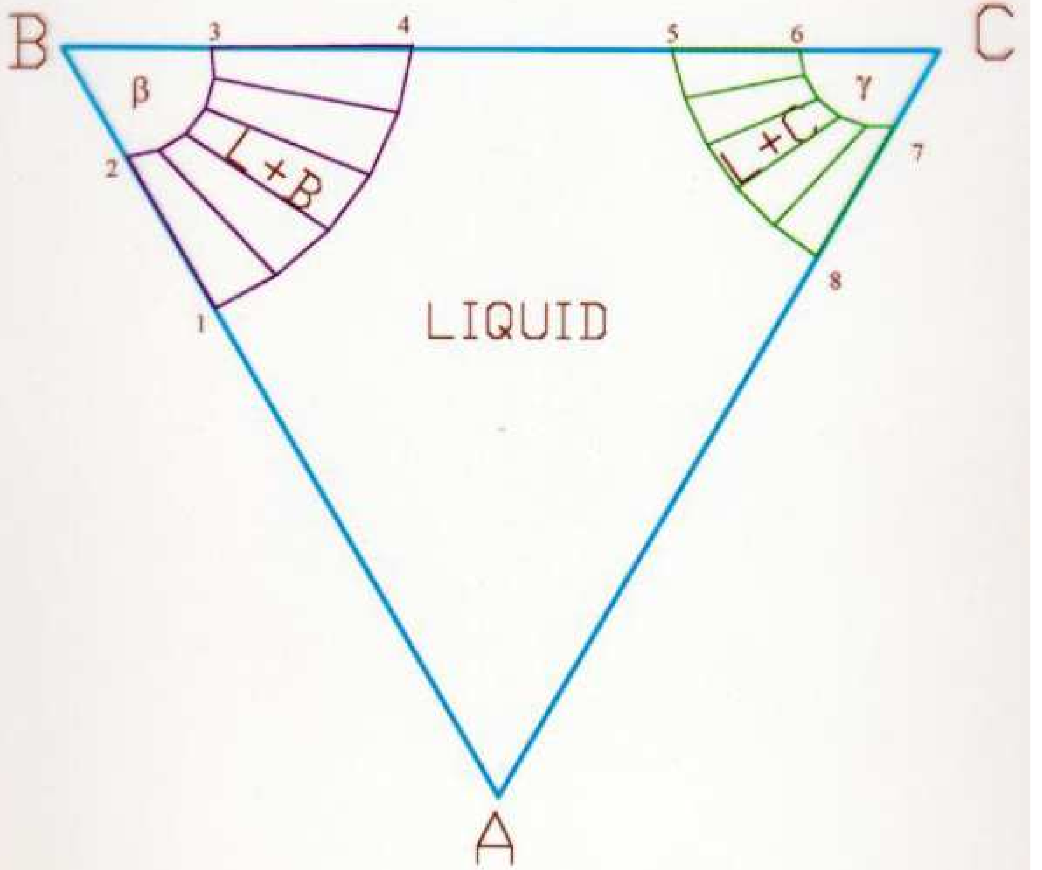
(with Solid Solubility)

T2A



Temperature Slice At $T_2 > T_A$ But, $T_2 < T_B$, T_C

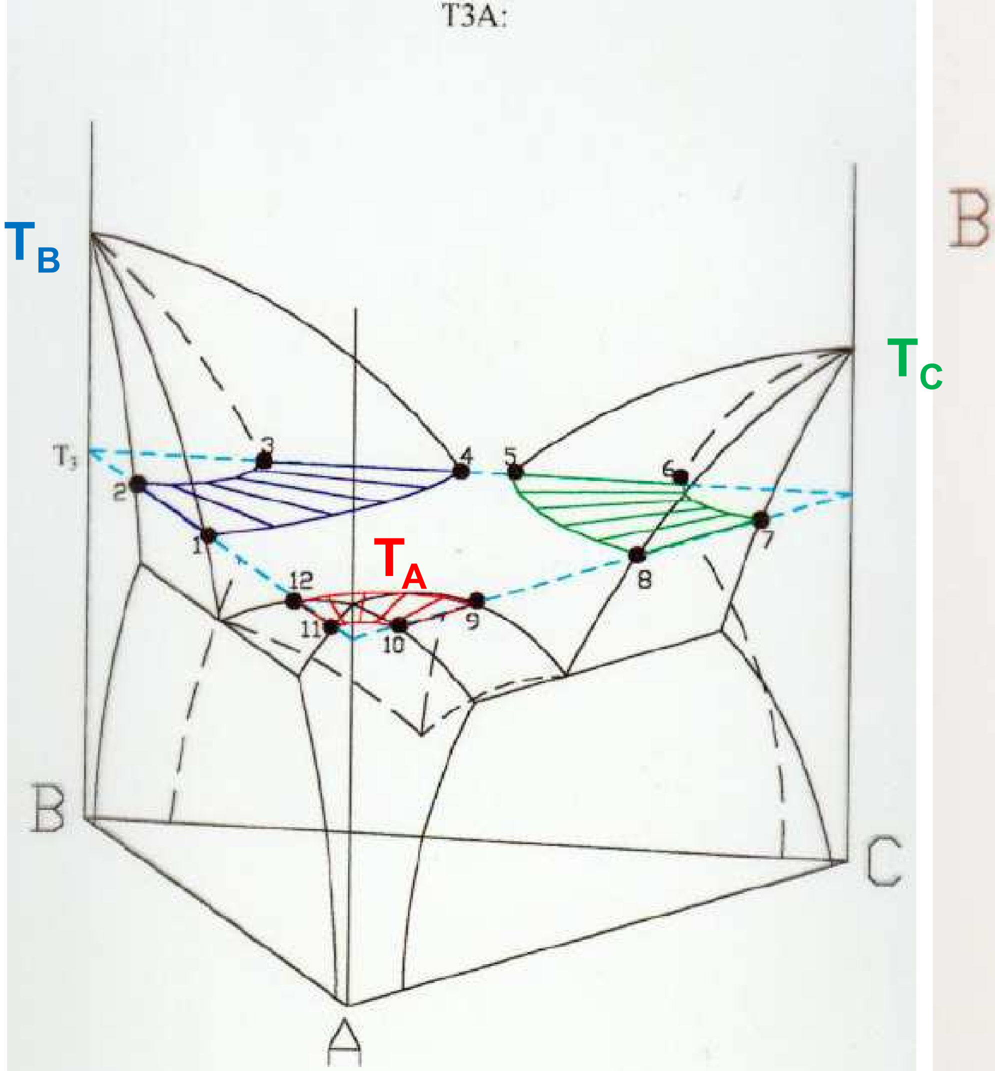
T2B



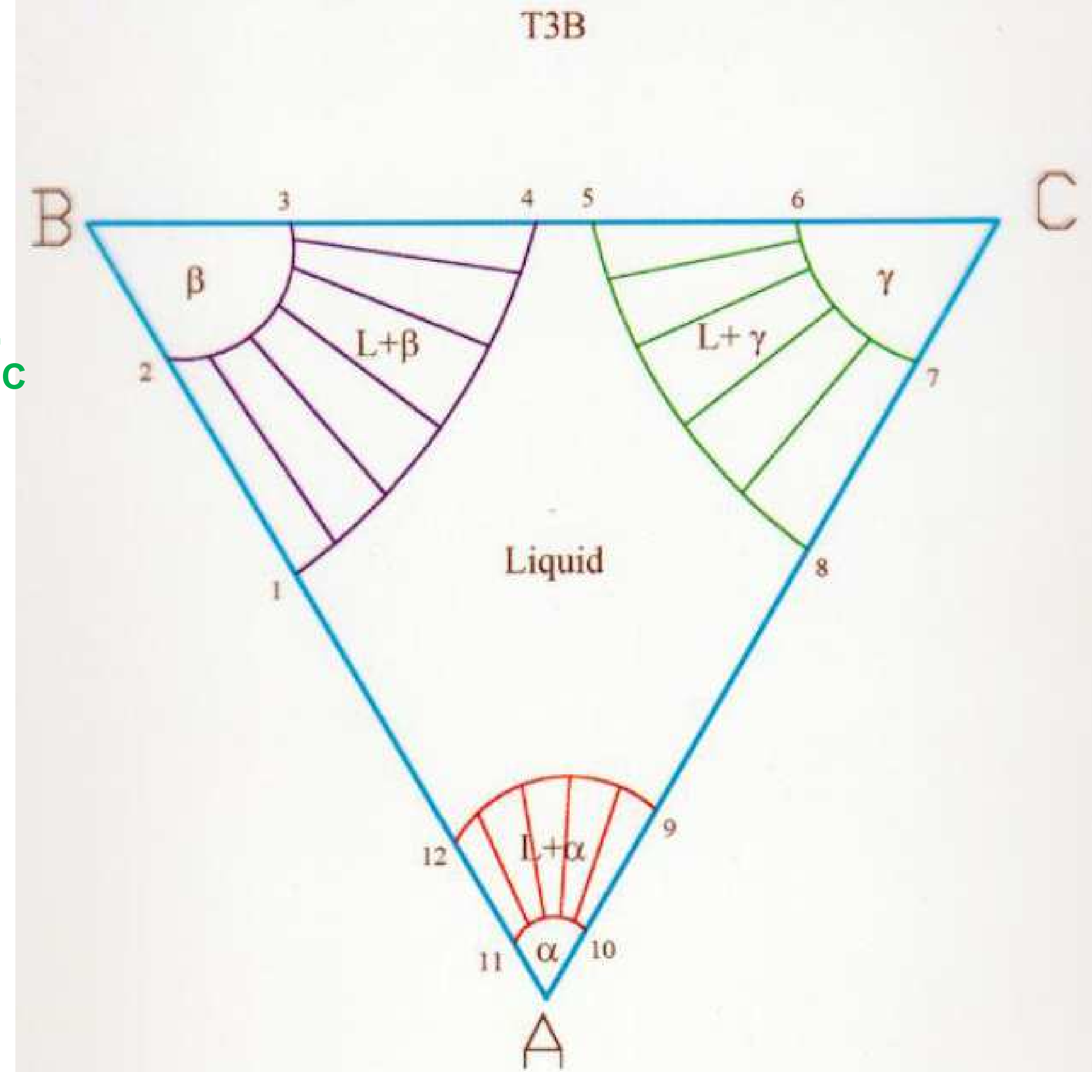
Isothermal Section At $T=T_2$

Ternary Eutectic System

(with Solid Solubility)



Temperature Slice At $T_3 < T_A, T_B, T_C$, But $T3 > T_{E1}, T_{E2}, T_{E3}$

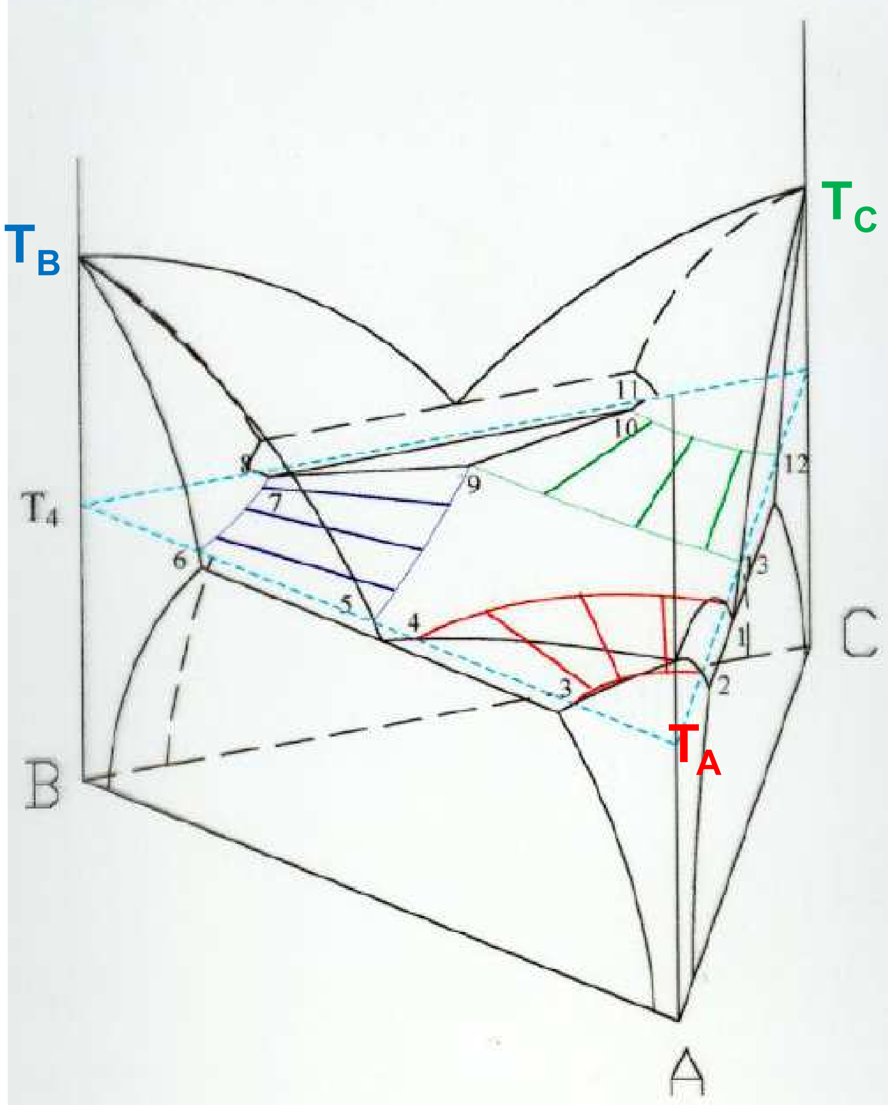


Isothermal Section At $T= T_3$

Ternary Eutectic System

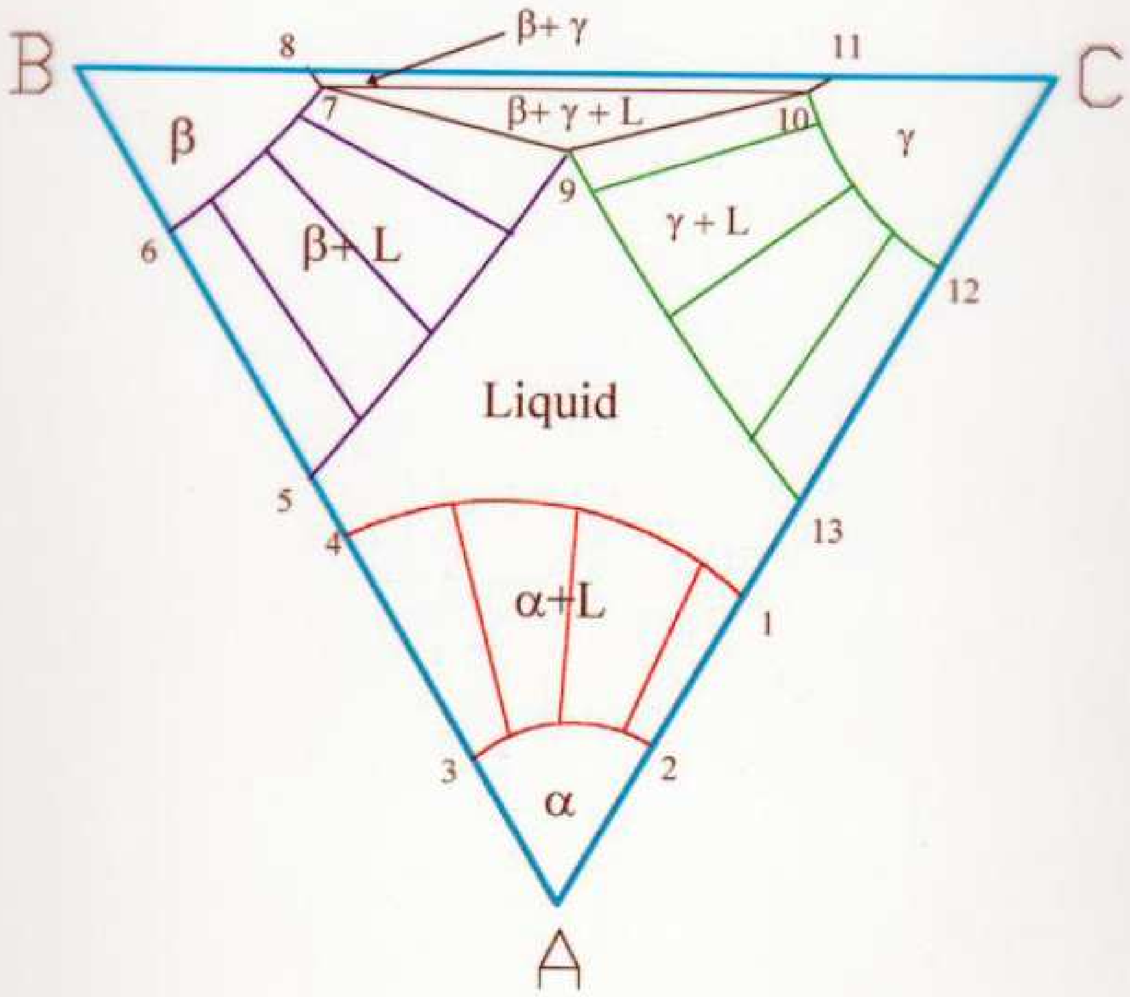
(with Solid Solubility)

T4A:



Temperature Slice At $T_4<T_{E2}$ And $T_4>T_{E1},T_{E3}$

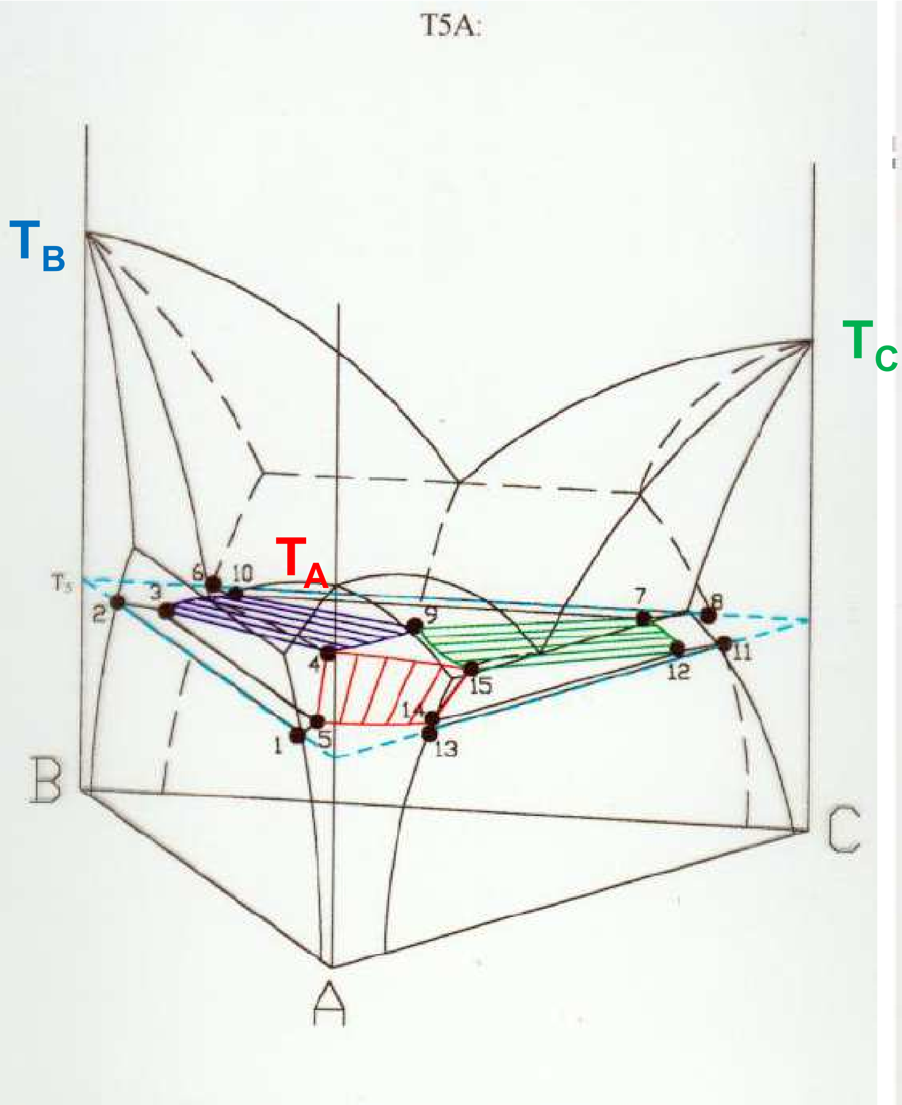
T4B:



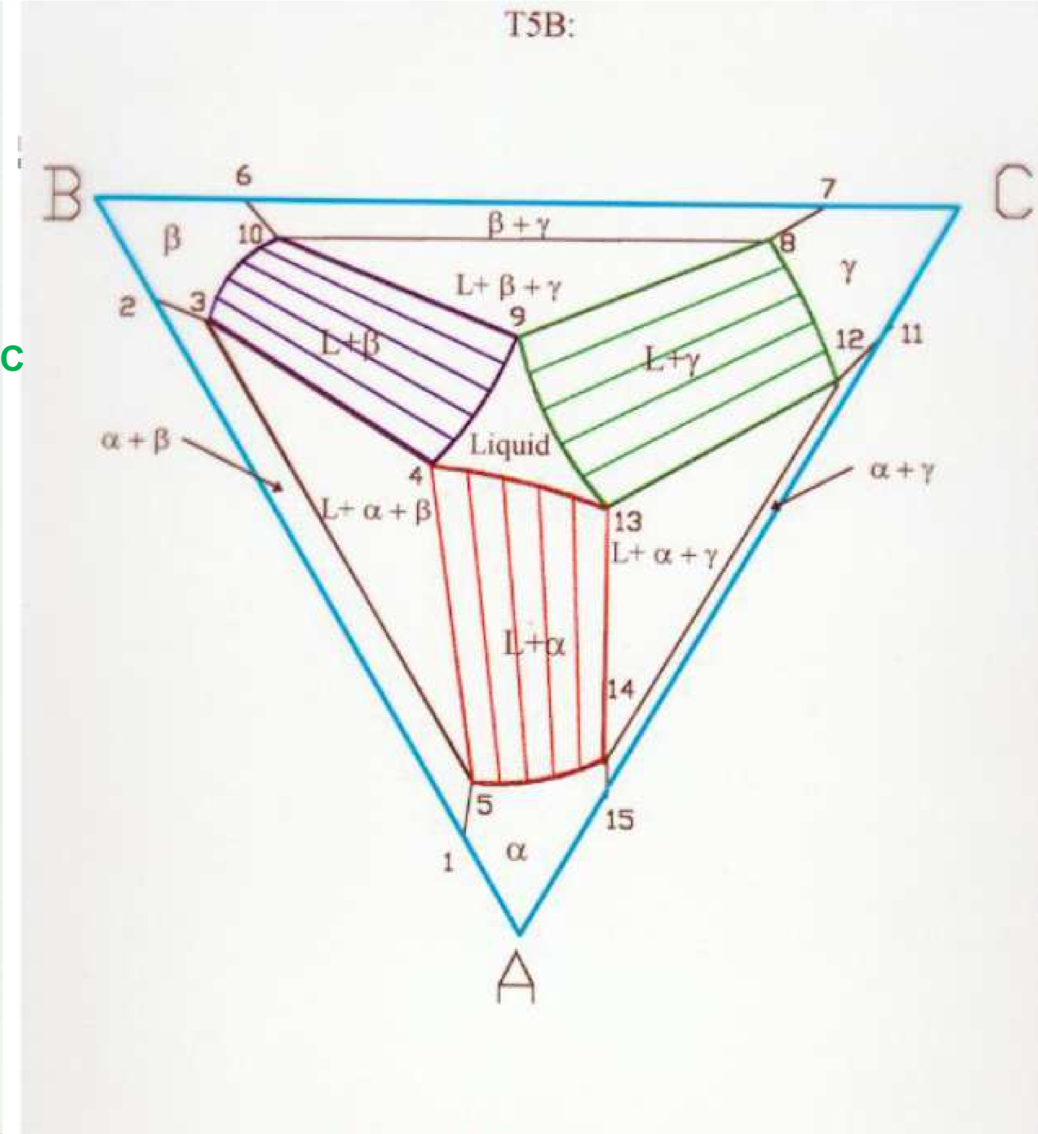
Isothermal Section At $T=T_4$

Ternary Eutectic System

(with Solid Solubility)



Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic

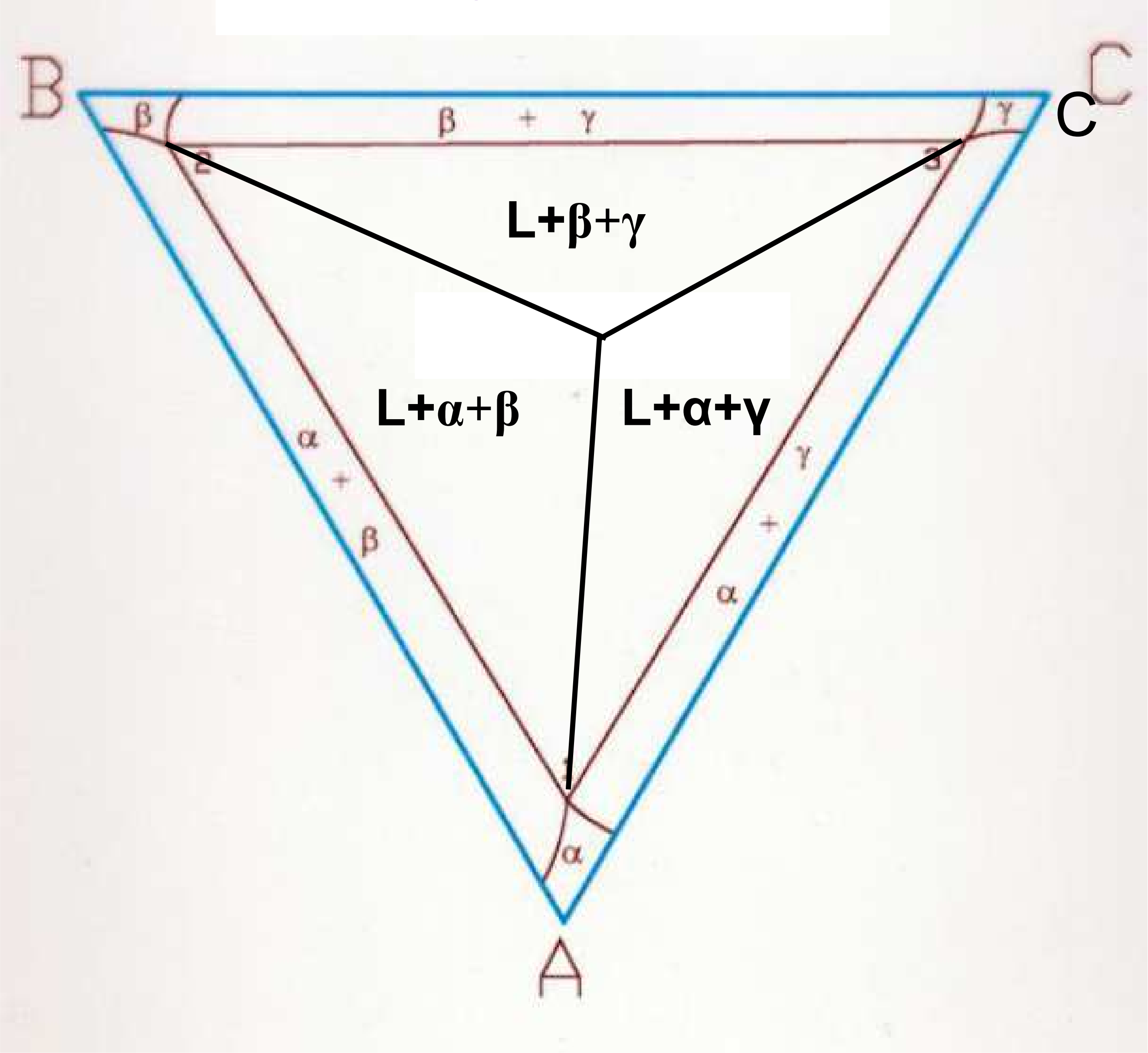


Isothermal Section At T=T$_5$

Ternary Eutectic System

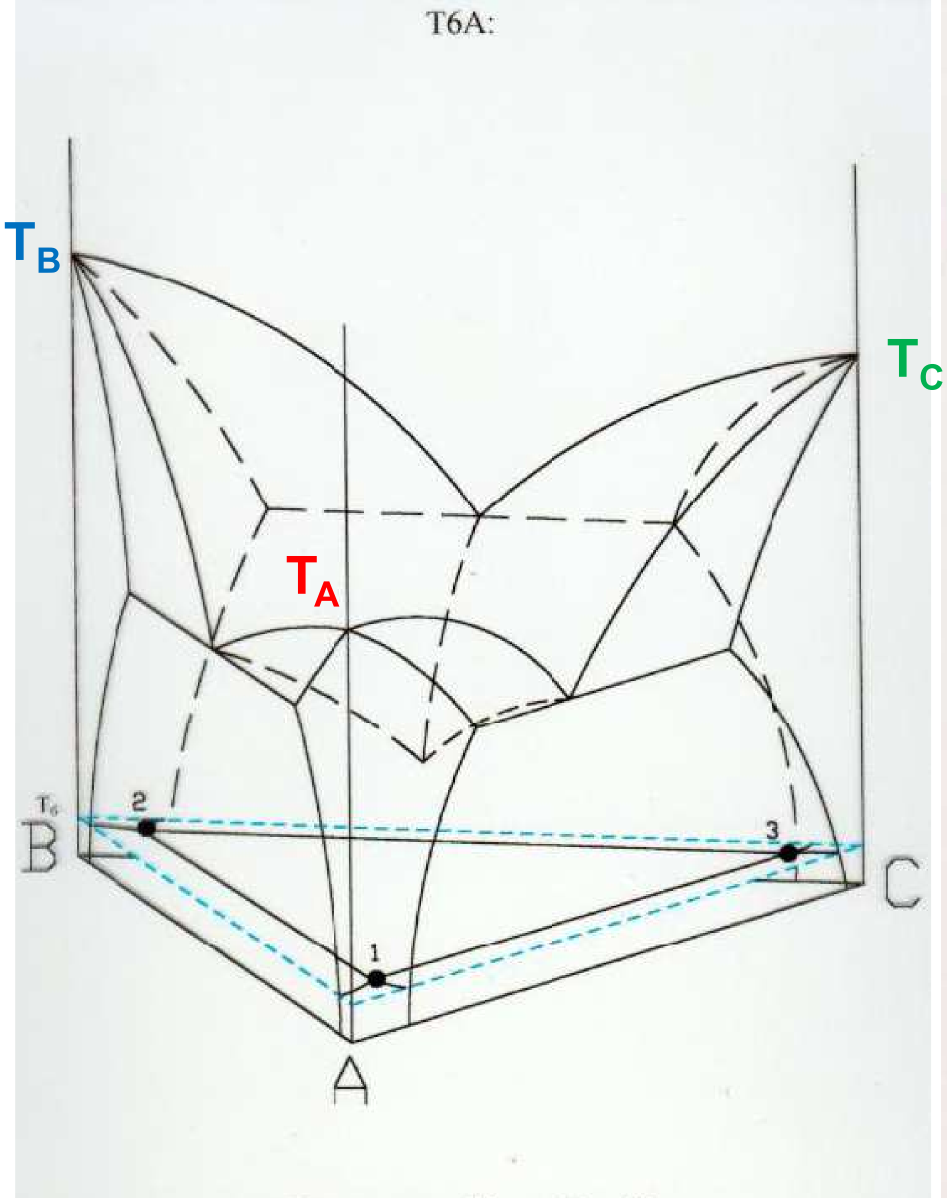
(with Solid Solubility)

T= ternary eutectic temp.

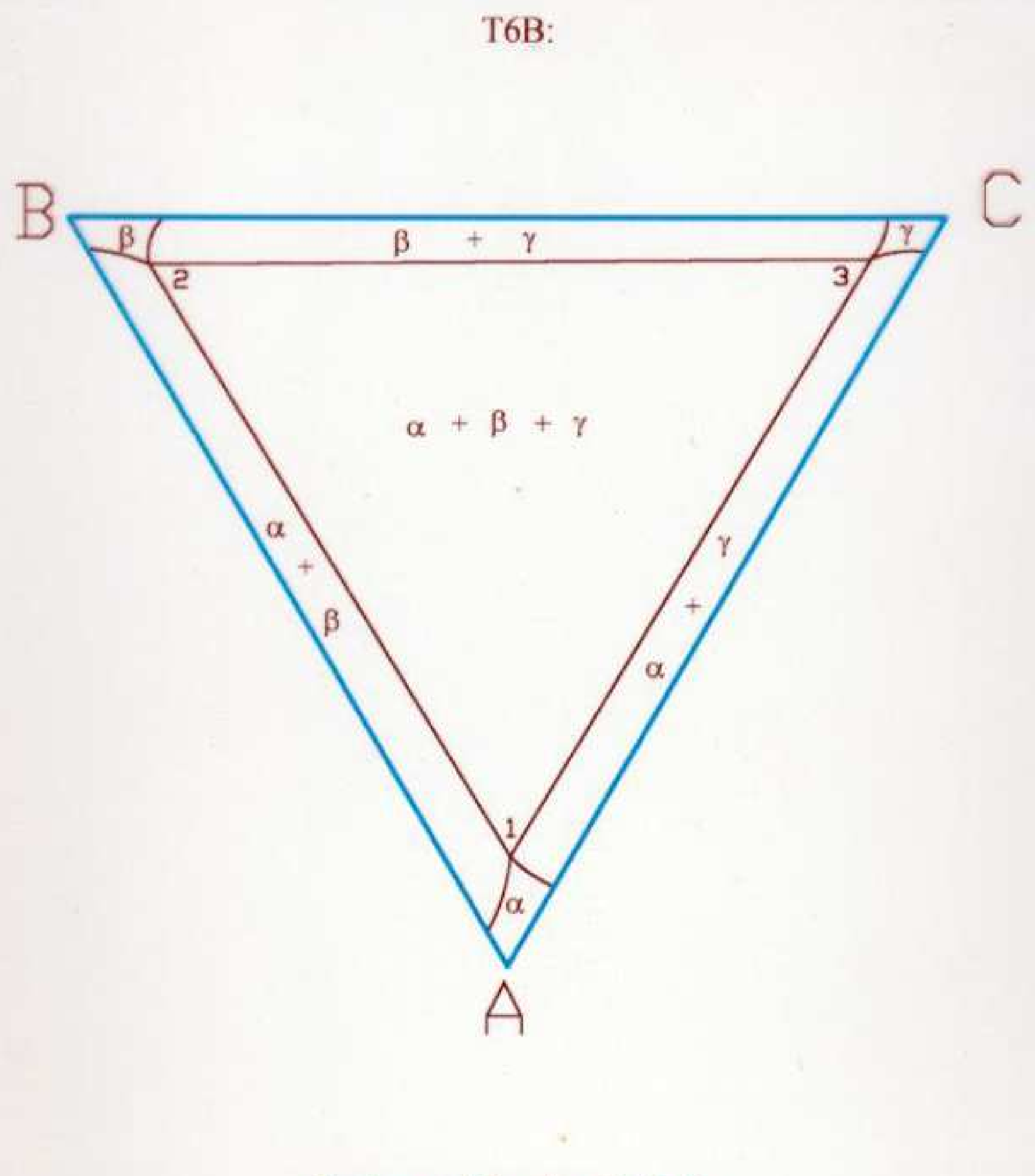


Ternary Eutectic System

(with Solid Solubility)



Temperature Slice at $T_6 < T_E$



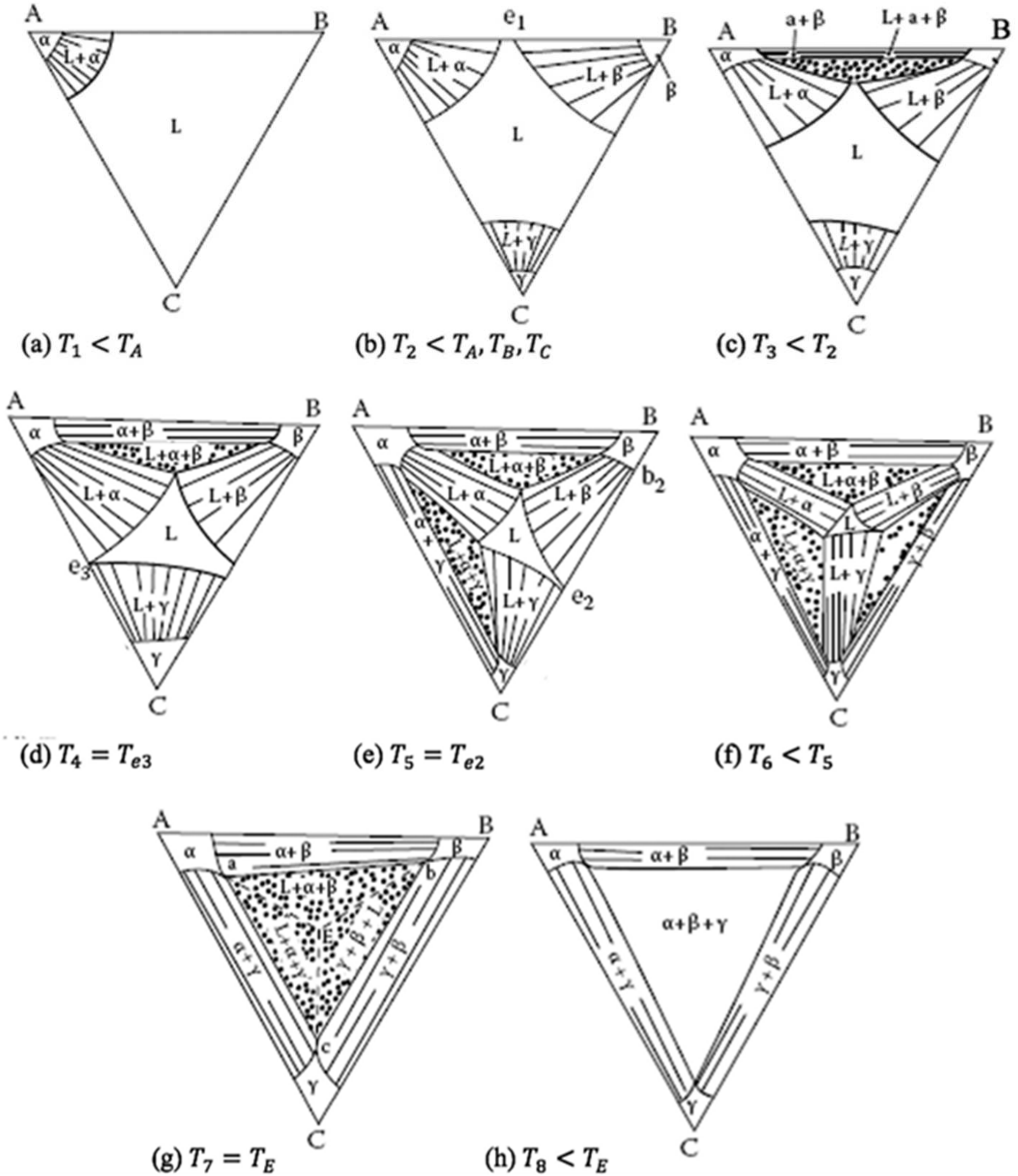
Isothermal Section At $T=T_6$

정해솔 학생 제공 자료 참조: 실제 isothermal section의 온도에 따른 변화

http://www.youtube.com/watch?v=yzhVomAdetM

Ternary Eutectic System (with Solid Solubility)

Fig. 1.42 Isothermal sections in a system showing a ternary eutectic at the temperature T_7=T_E. Binary eutectics are at e_1, e_2 and e_3.



(a) $T_1 < T_A$

(b) $T_2 < T_A, T_B, T_C$

(c) $T_3 < T_2$

(d) $T_4 = T_{e3}$

(e) $T_5 = T_{e2}$

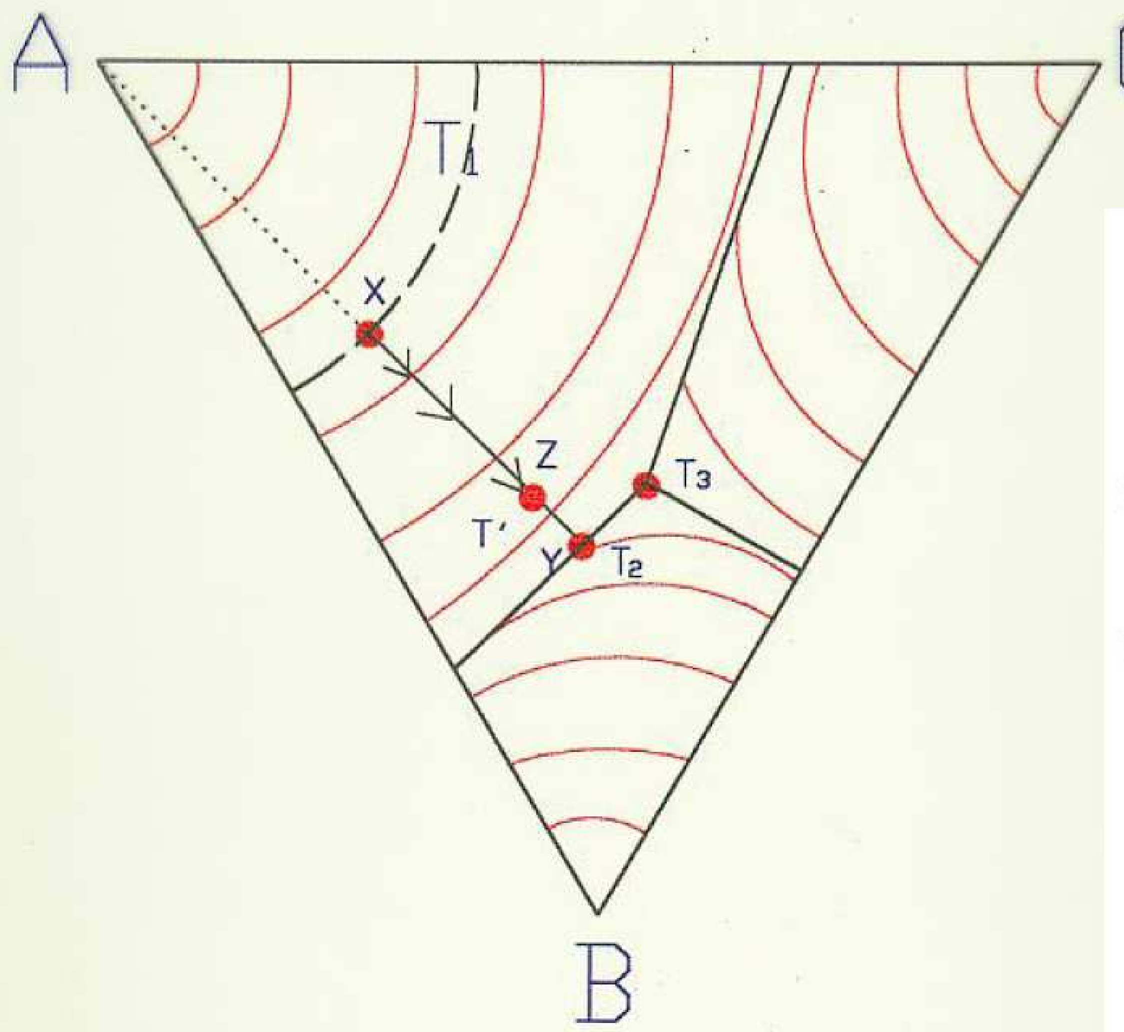
(f) $T_6 < T_5$

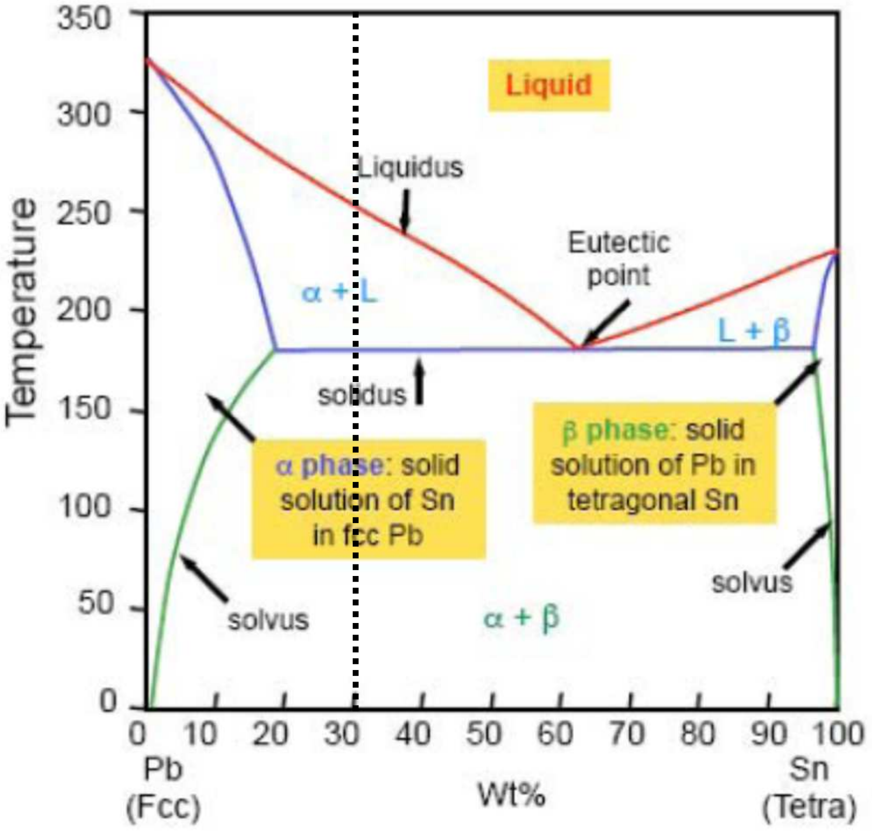
(g) $T_7 = T_E$

(h) $T_8 < T_E$

Ternary Eutectic System

3) Solidification Sequence: liquidus surface





Ternary Eutectic System

3) Solidification Sequence: liquidus surface

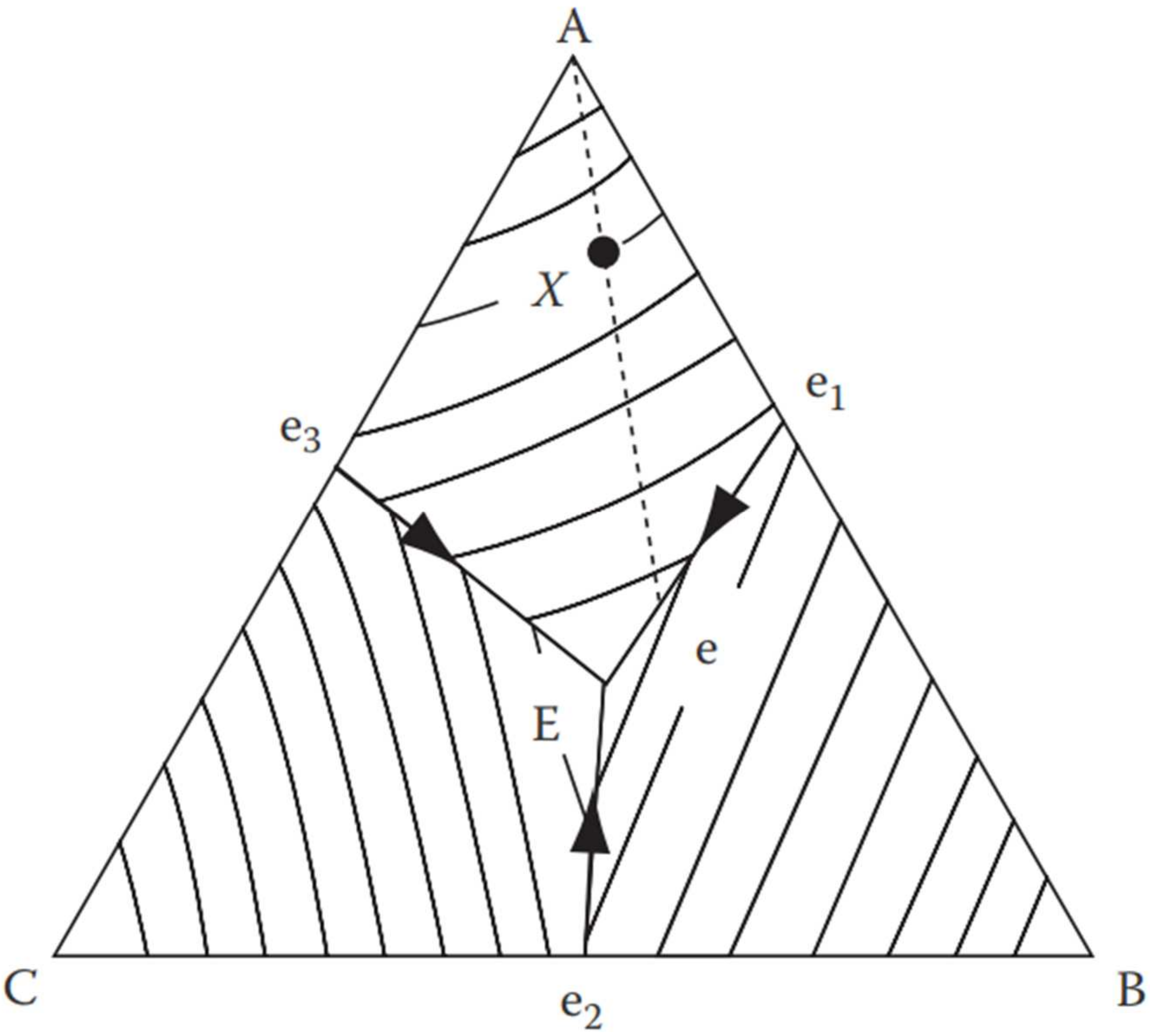
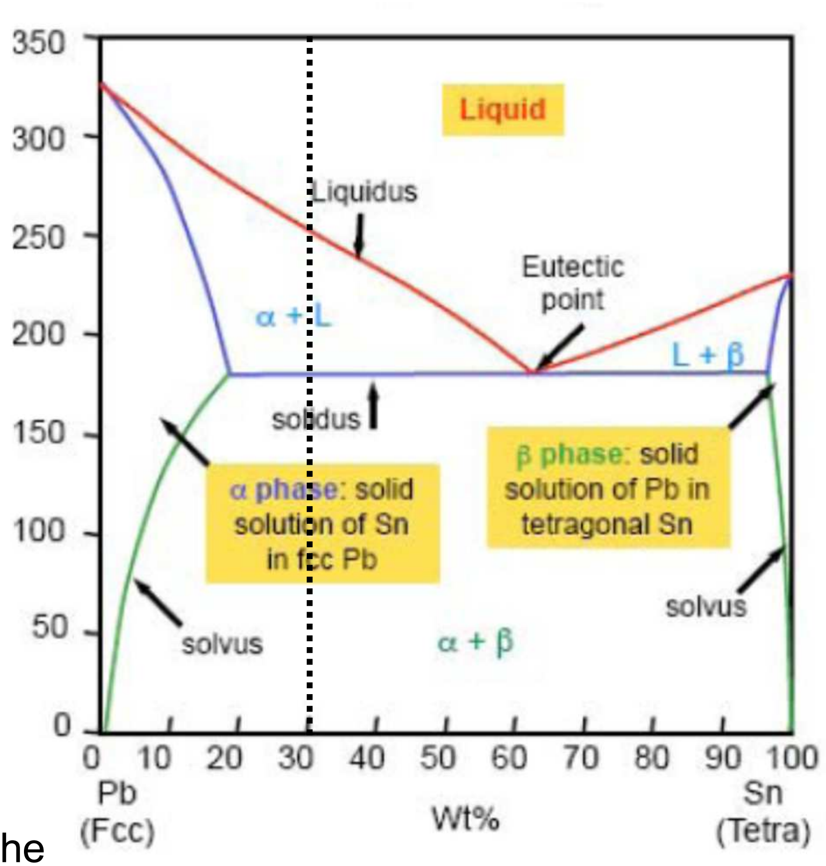
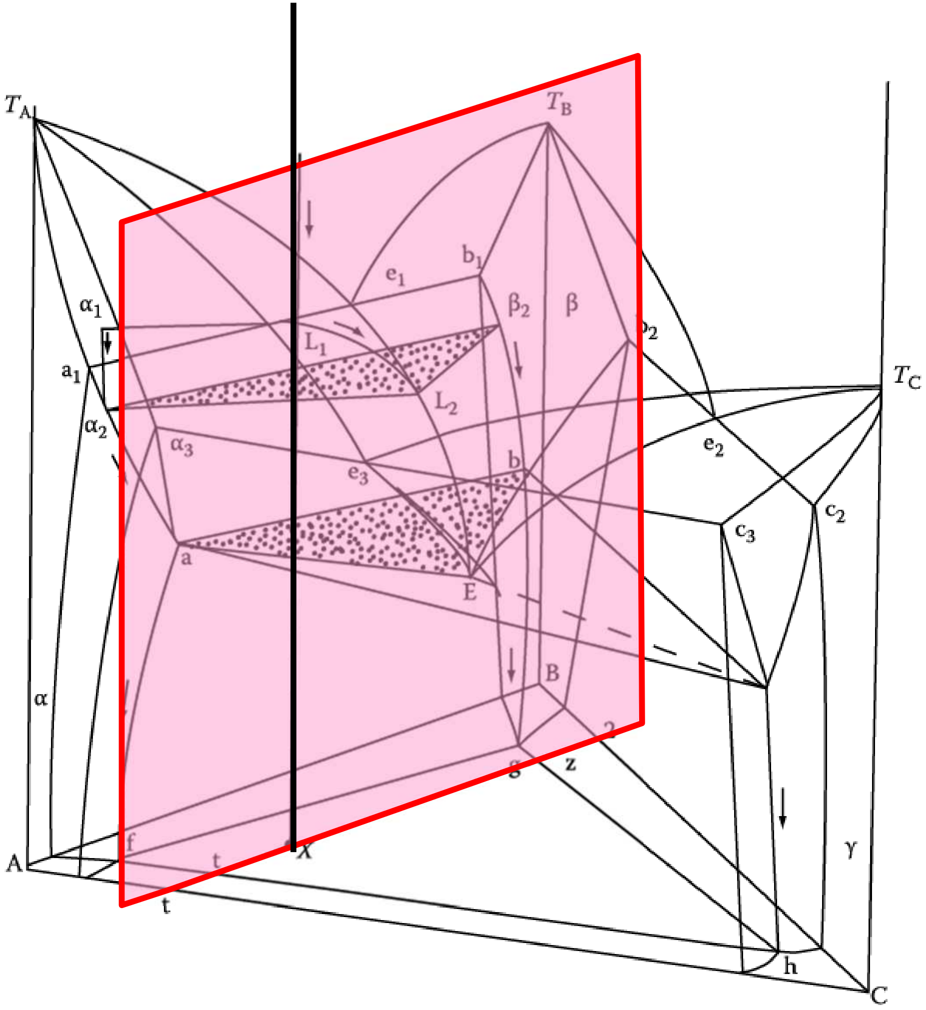


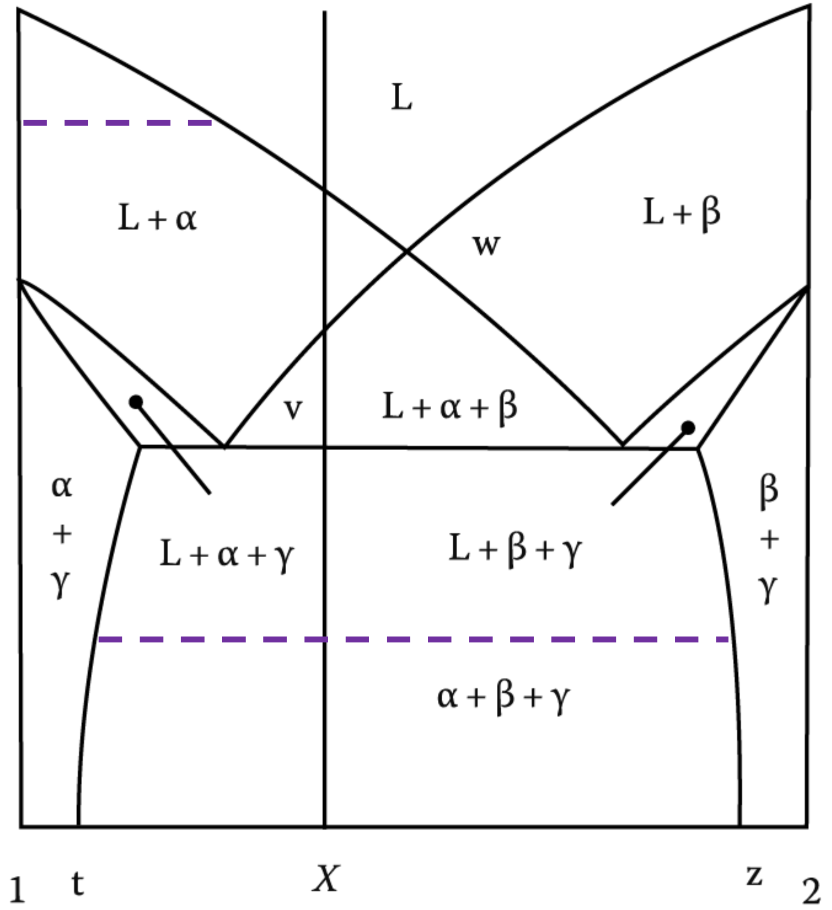
Fig. 1.43 A projection of the liquidus surfaces of Figure 1.4.2 onto the Gibbs triangle. Contour lines show equal temperatures decreasing from the corners. Binary eutectic points are at e_1, e_2 and e_3.



Ternary Eutectic System

* Vertical section





* The horizontal lines are not tie lines.
(no compositional information)

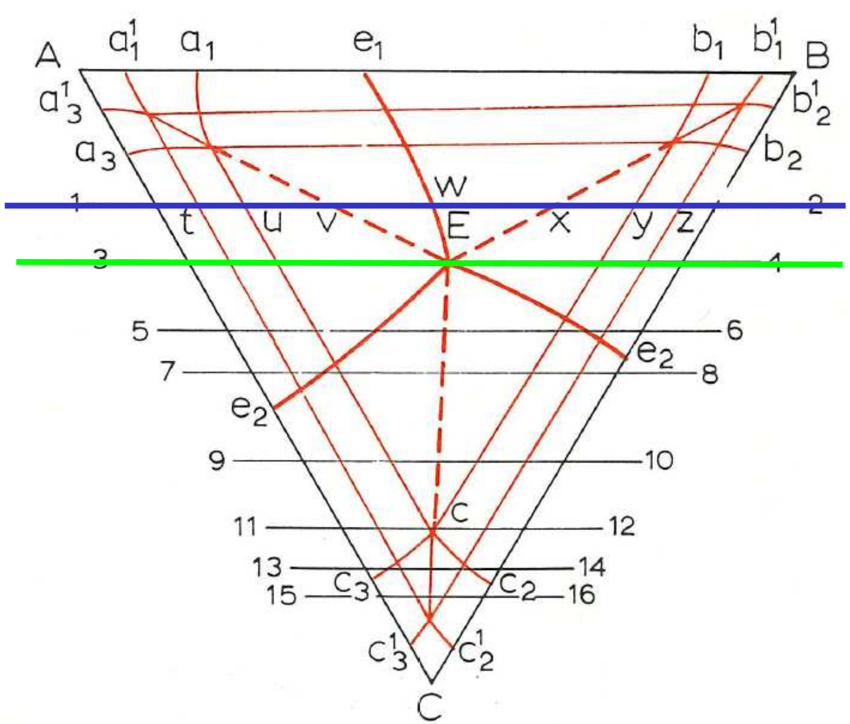
* Information for equilibrium phases at different tempeatures

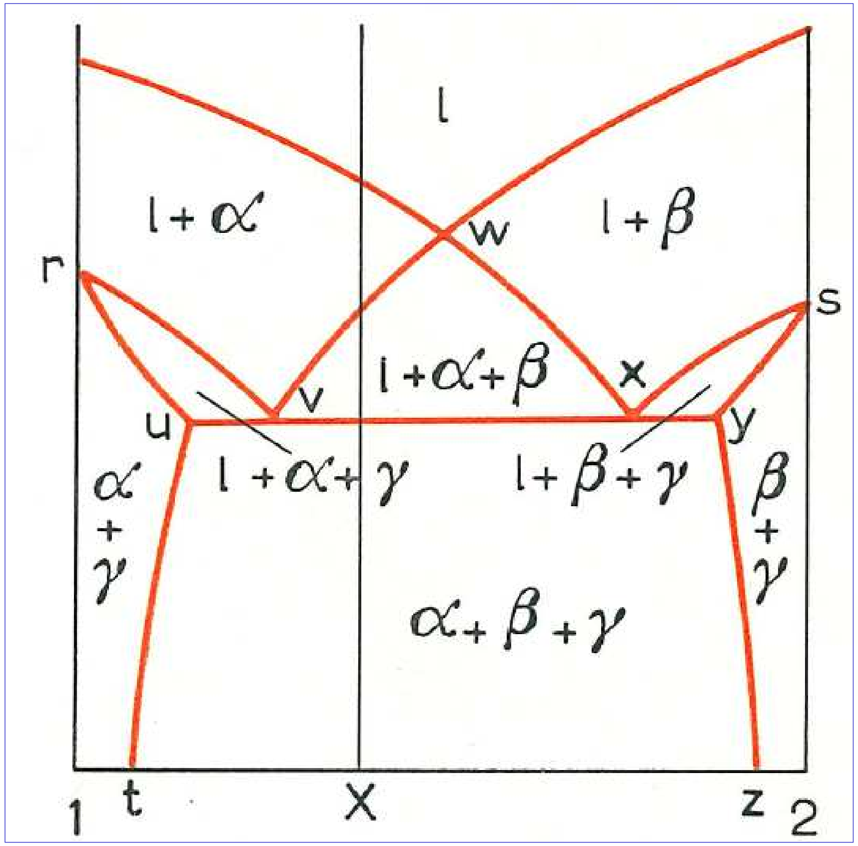
THE EUTECTIC EQUILIBRIUM

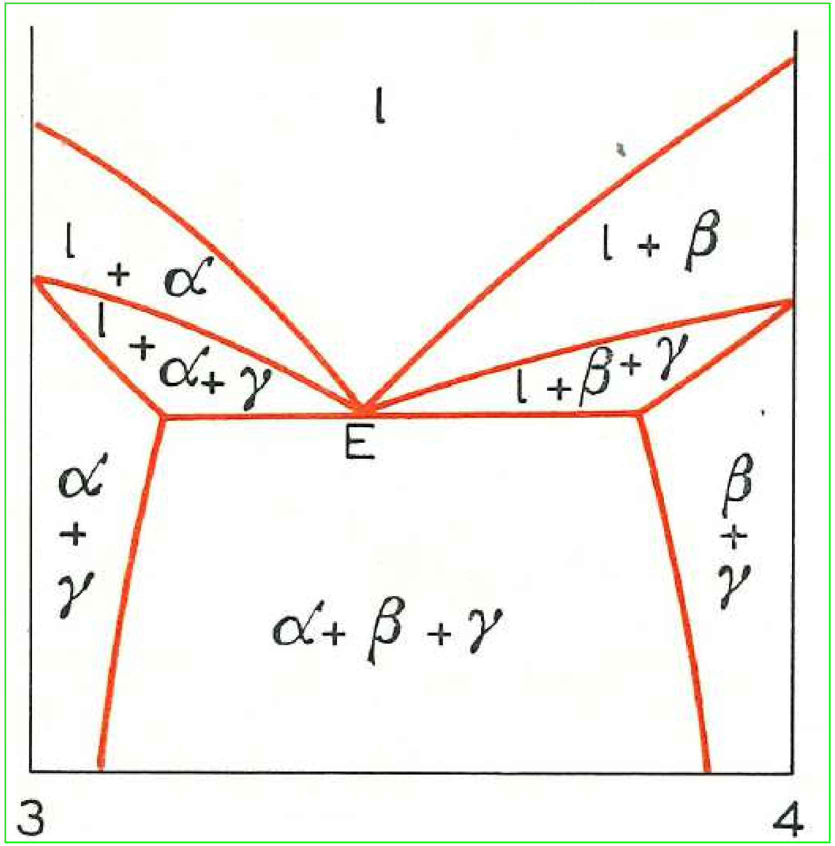
($l = \alpha + \beta + \gamma$)

Vertical section

Location of vertical section



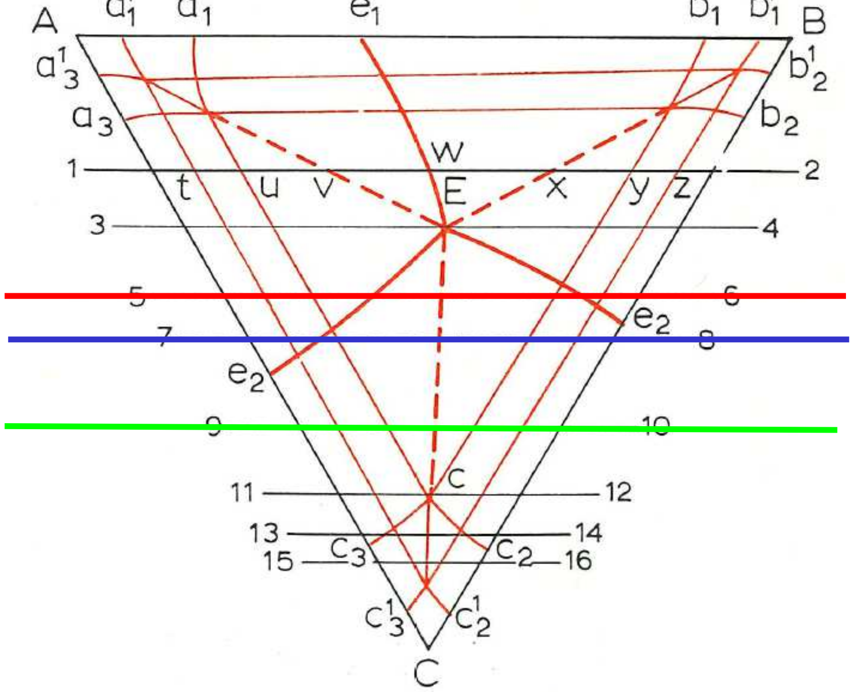


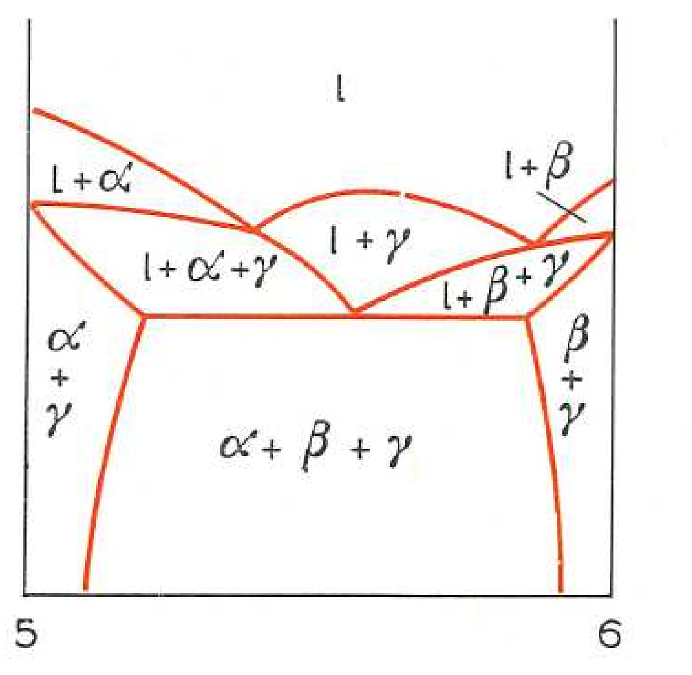


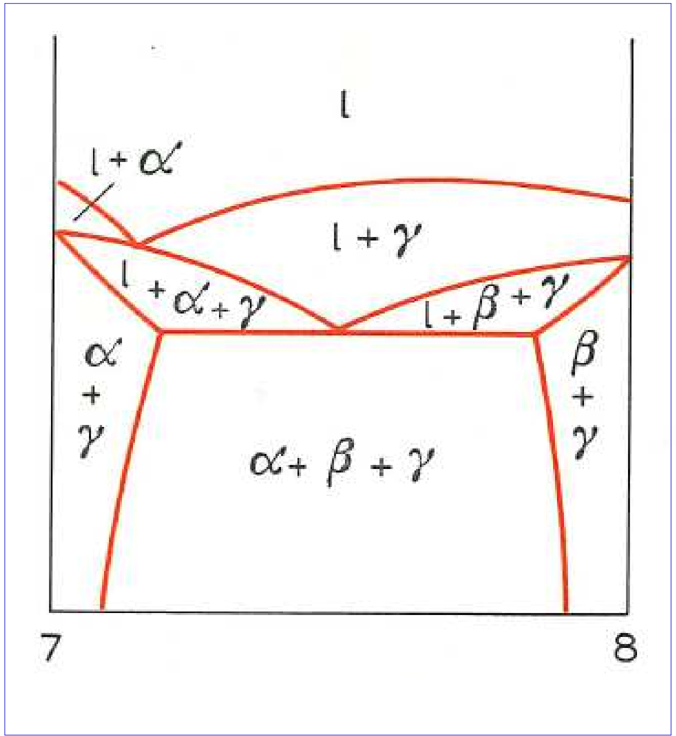
THE EUTECTIC EQUILIBRIUM (*l* = α + β + γ)

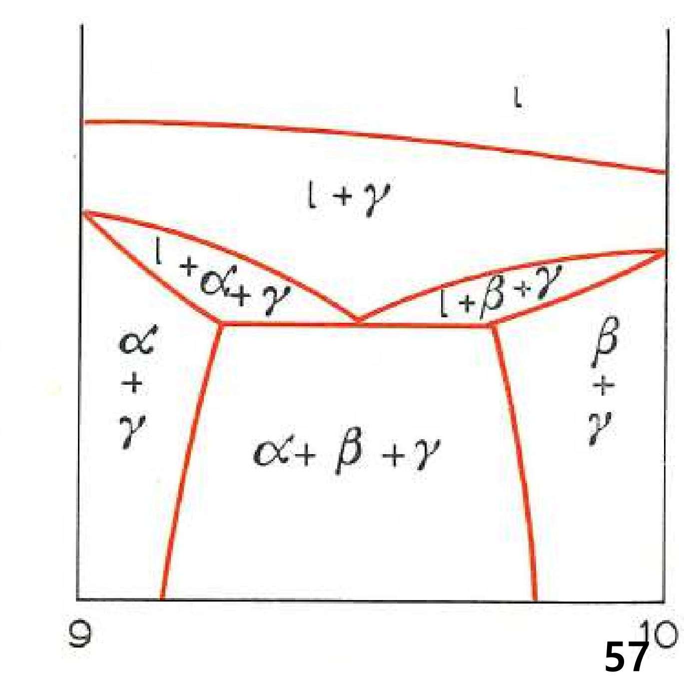
Vertical section

Location of vertical section





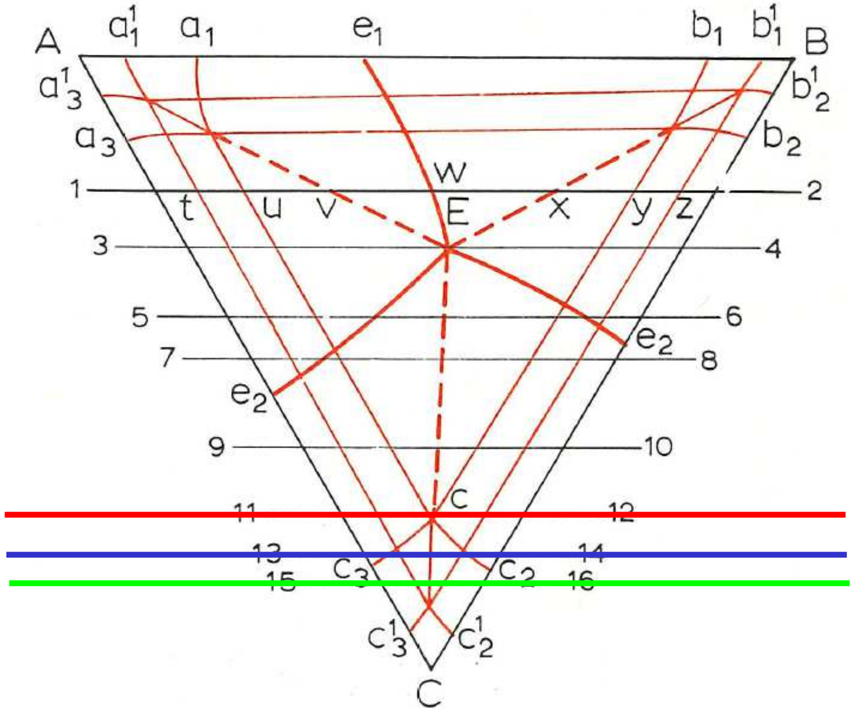


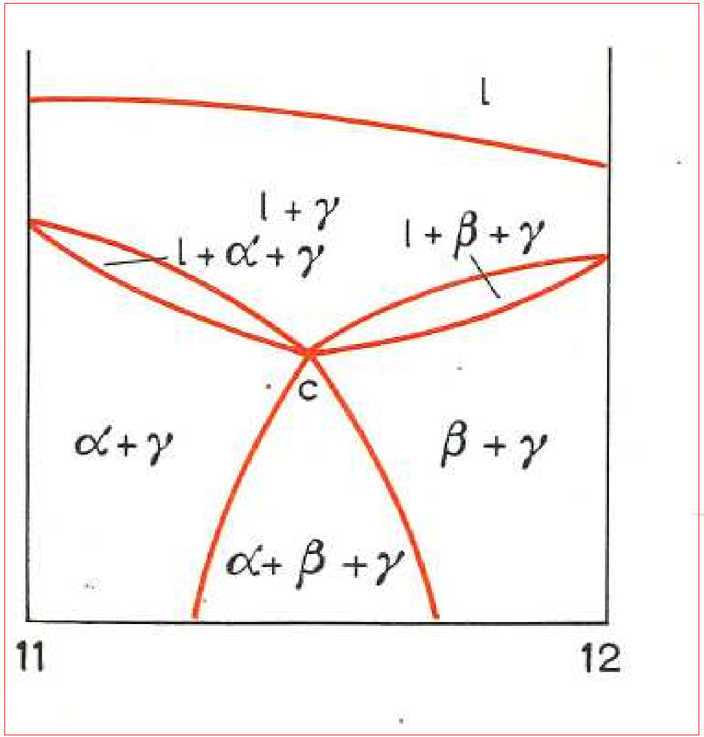


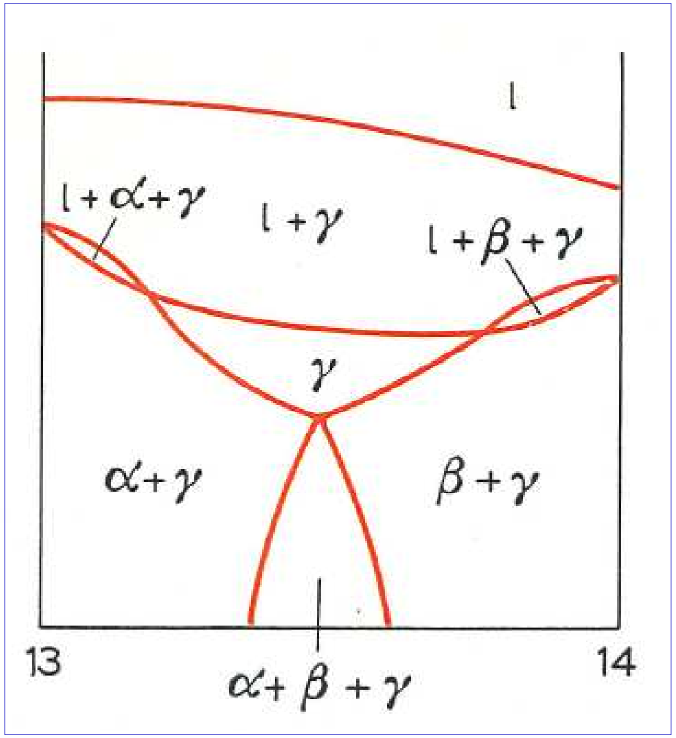
THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

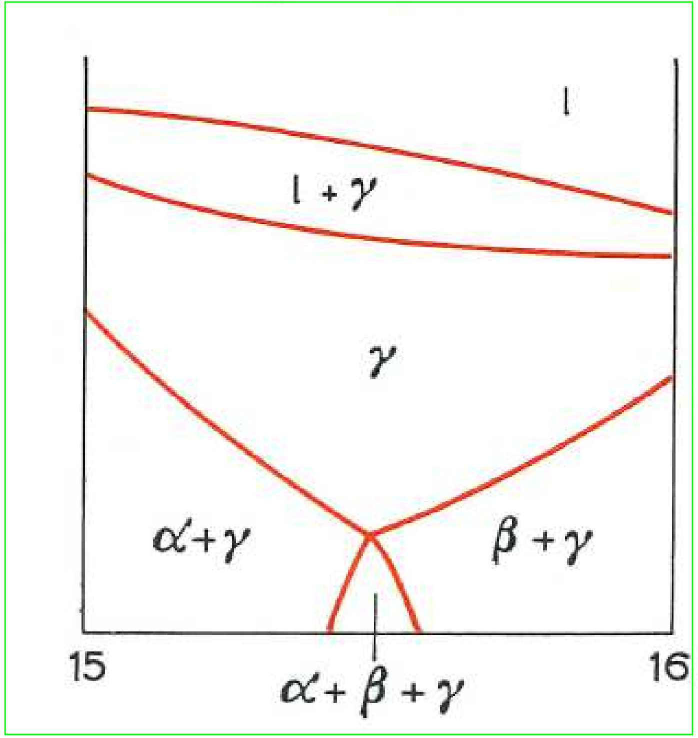
Vertical section

Location of vertical section



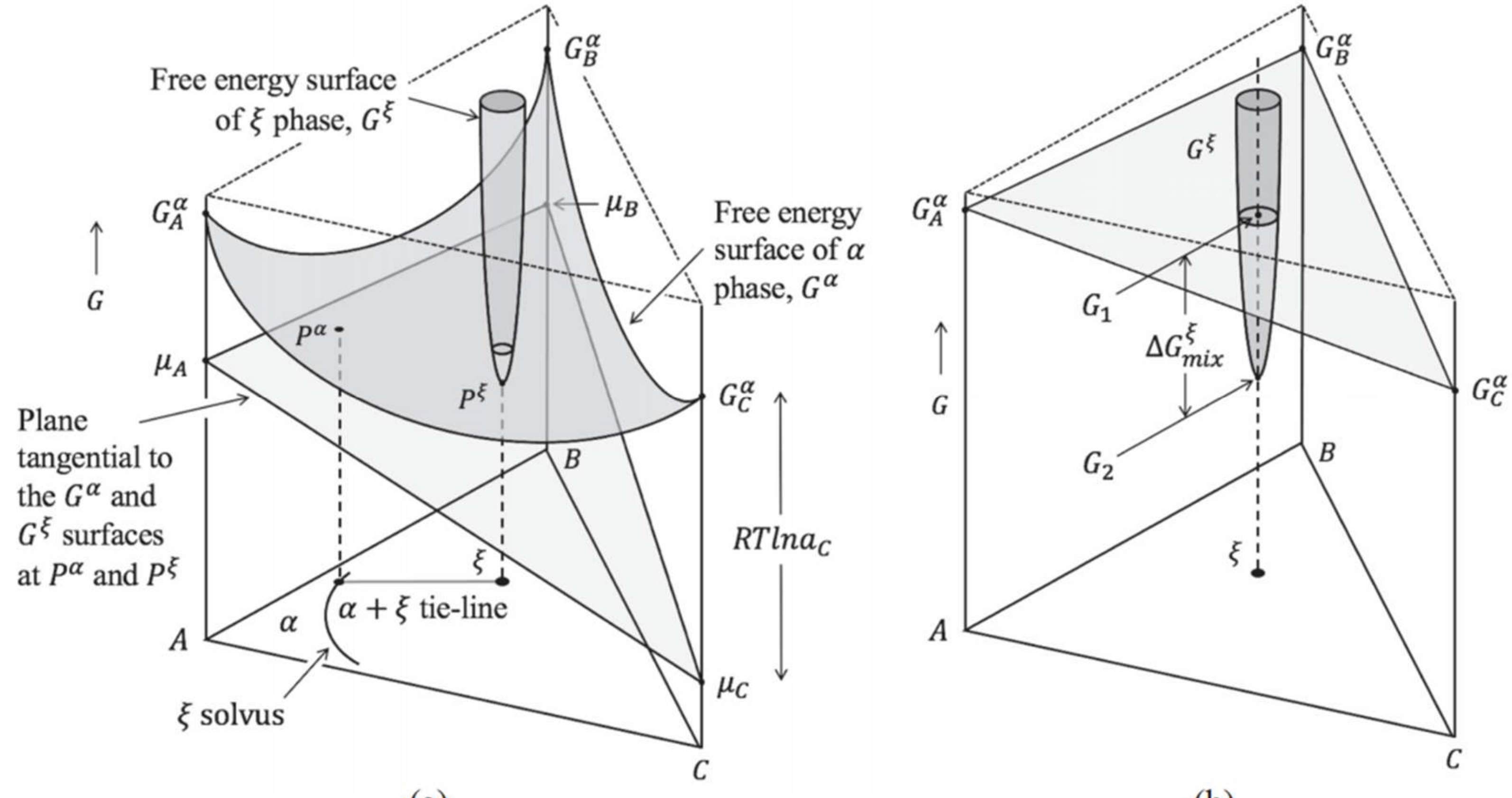






1.7.2 Solubility product

Metallic alloys are often based on small additions of sparingly soluble alloying elements to the host metal as in the case many aluminum alloys and steels, for example. Then, we are only interest in the one corner of the thermal phase diagram, and essential thermodynamic aspects of the alloy can be understood using the concept of the solubility product.



(a) (b)

FIGURE 1.45 (a) Illustration of how the solubility of a ternary compound, ξ, in the phase α depends on the relative positions of the molar free energy surfaces G^α and G^ξ. At the stoichiometric composition, $G^\xi < G^\alpha$. (b) X_A^ξ moles of α containing 100% A, X_B^ξ moles of α containing 100% B, and X_C^ξ moles of α containing 100% C in the unmixed condition have a total free energy G_1, which lies on the plane through G_A^α, G_B^α and G_C^α at the point corresponding to the composition X_A^ξ, X_B^ξ, X_C^ξ. When these are rearranged into the ξ crystal structure, the free energy decreases by ΔG_{mix} to G_2.

Considering dilute compositions in the A-rich corner of the phase diagram, the activity of A in the α phase will be close to unity while the activites of the other components will be proportional to their concentrations:

$$a_B = \gamma_B X_B \text{ and } a_C = \gamma_C X_C$$

, where γ_B and γ_C are the constant activity coefficients of B and C in α.

$$\boxed{X_B^q \cdot X_C^r = K} \tag{1.69}$$

where, for a given temperature, K is a constant given by

$$K = \frac{\exp\left(\Delta G_{\text{mix}}^{\xi} / RT\right)}{\gamma_B \gamma_C}. \tag{1.70}$$

K is known as the solubility product and as $\Delta G_{\text{mix}}^{\xi} < 0$ it increases with increasing temperature. The equation can also be written in the form

$$\ln\left(X_B^p \cdot X_C^q\right) = \Delta H_{\text{mix}}^{\xi} / RT - \Delta S_{\text{mix}}^{\xi} / R - \ln\left(\gamma_B \gamma_C\right) \tag{1.71}$$

where $\Delta H_{\text{mix}}^{\xi}$ is the enthalpy of formation (a negative quantity) and $\Delta S_{\text{mix}}^{\xi}$ is the entropy of formation.

$$\boxed{\log_{10} K = \log_{10}\left(w_B^m \cdot w_C^n\right) = k_1 + \frac{k_2}{T}} \tag{1.72}$$

where w_B is the weight (or mass) percent of B and w_C is the weight percent of C in α in equilibrium with the compound $A_l B_m C_n$. The terms k_1 and k_2 are taken as constants that are obtained by fitting either experimental solubility data or thermodynamically calculated solubilities over the range of temperatures of interest. Equation 1.72 is an approximate representation of Equation 1.71 since the activity coefficients are not constants but functions of temperature.

1.7.2 Solubility product

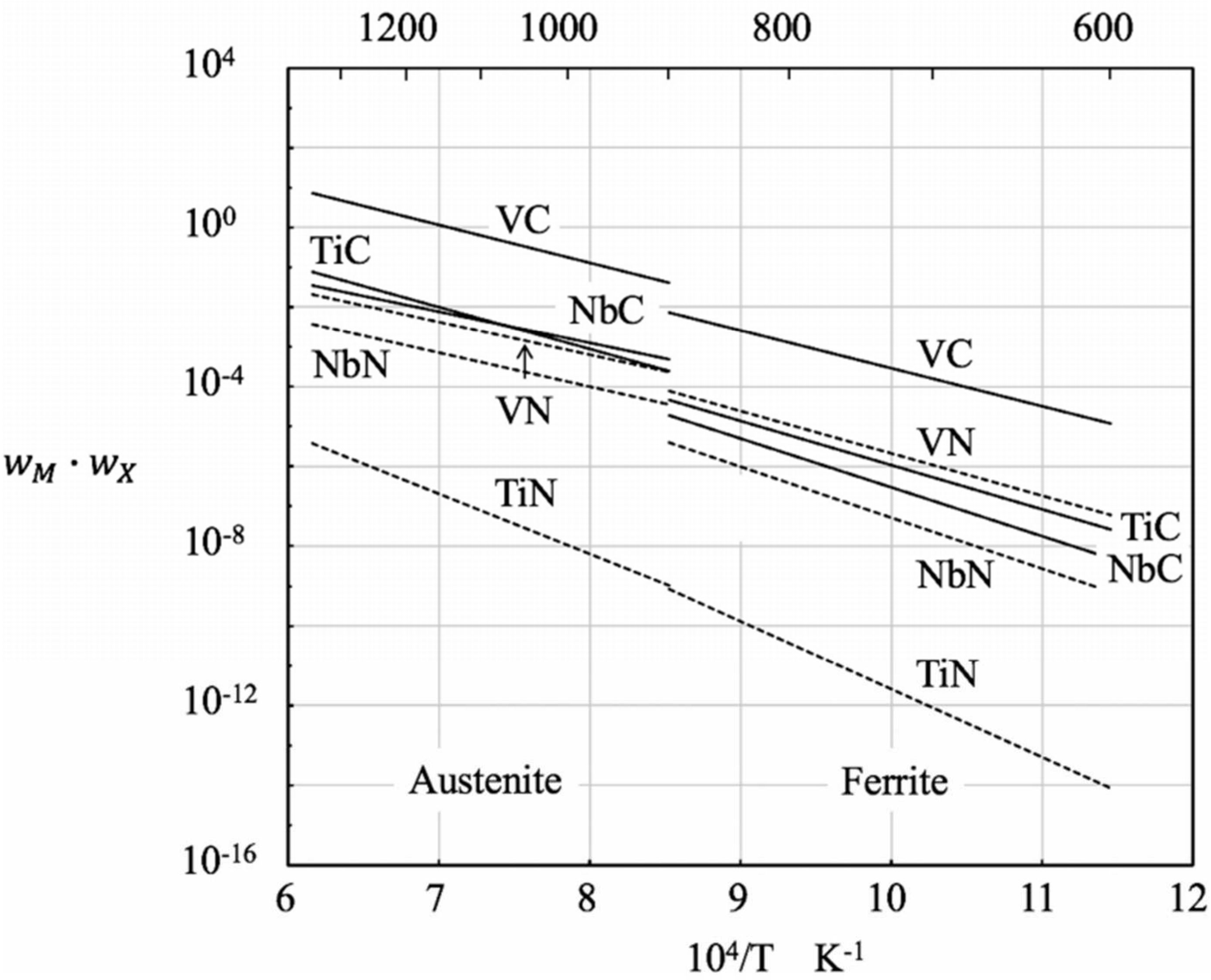


FIGURE 1.46 The effect of temperature on the solubility products of MX in austenite and ferrite in the systems Fe–M–X. Full lines are carbides, dashed line nitrides.

1.7.2 Solubility product

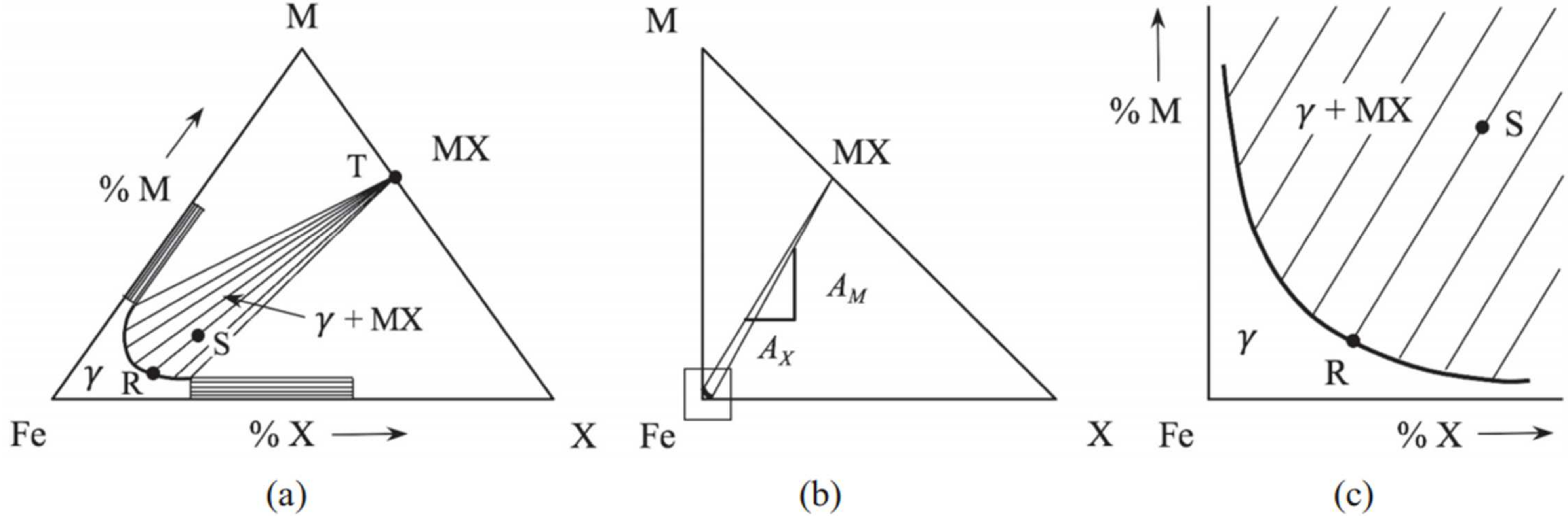


FIGURE 1.47 (a) Schematic of a ternary phase diagram for the system Fe–M–X at a temperature where austenite is stable. M represents V, Nb or Ti, and X represents C or N. Compositions are in wt.%. At equilibrium, the weight fraction of MX in alloy S is the ratio of the lengths RS/RT. (b) The same but using a right triangle and better drawn to scale. All $\gamma + MX$ tie-lines have a slope ≈ A_M / A_X. (c) An enlargement of the Fe corner.

Atomic weight

1.7.2 Solubility product

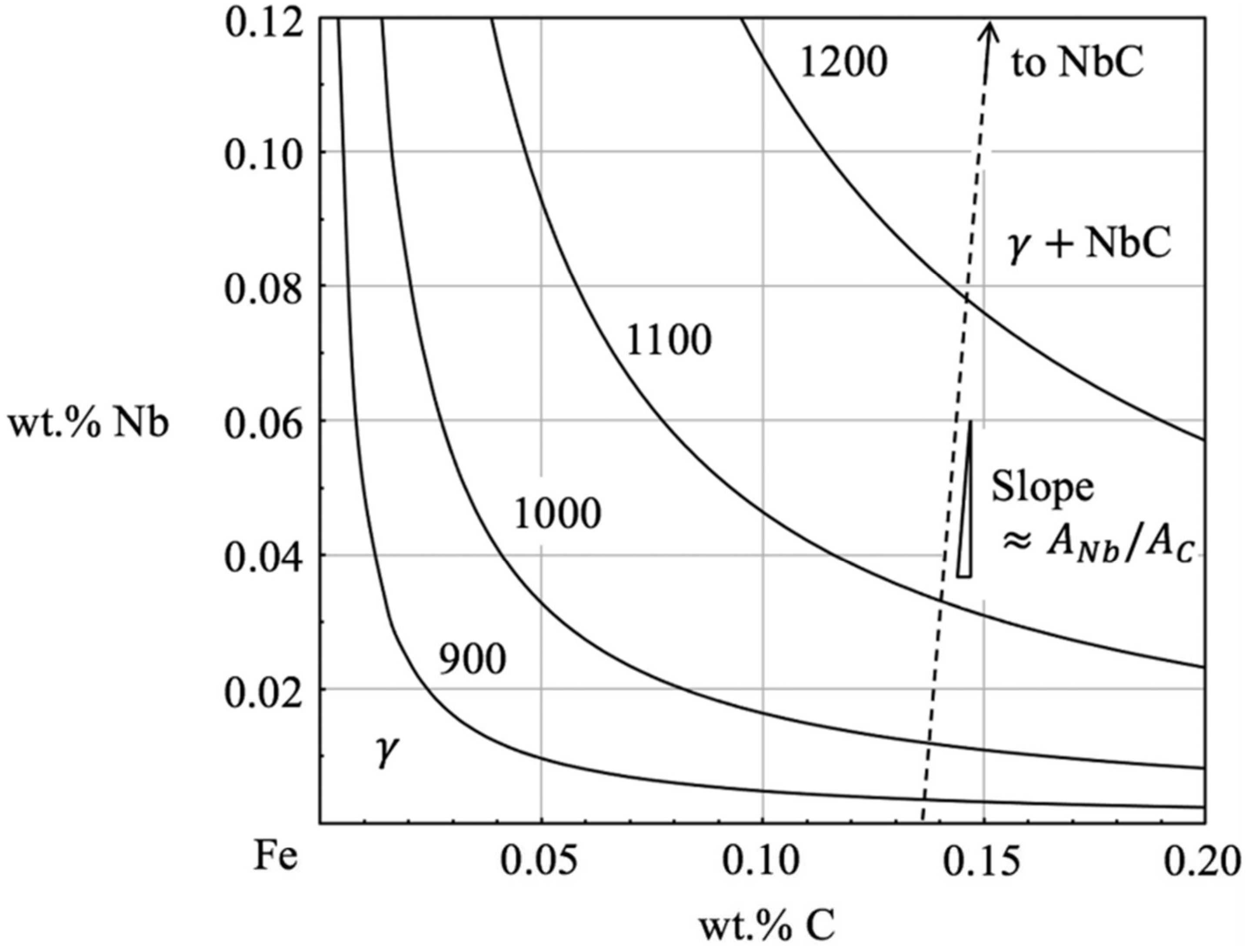


FIGURE 1.48 The effect of temperature in the range 900°C–1,200°C on the solvus for NbC in austenite (γ). Single-phase γ exists below the solvus and two-phase γ + NbC above the solvus. Tie-lines are not shown, but the dashed line shows their approximate slope.

< Quaternary phase Diagrams >

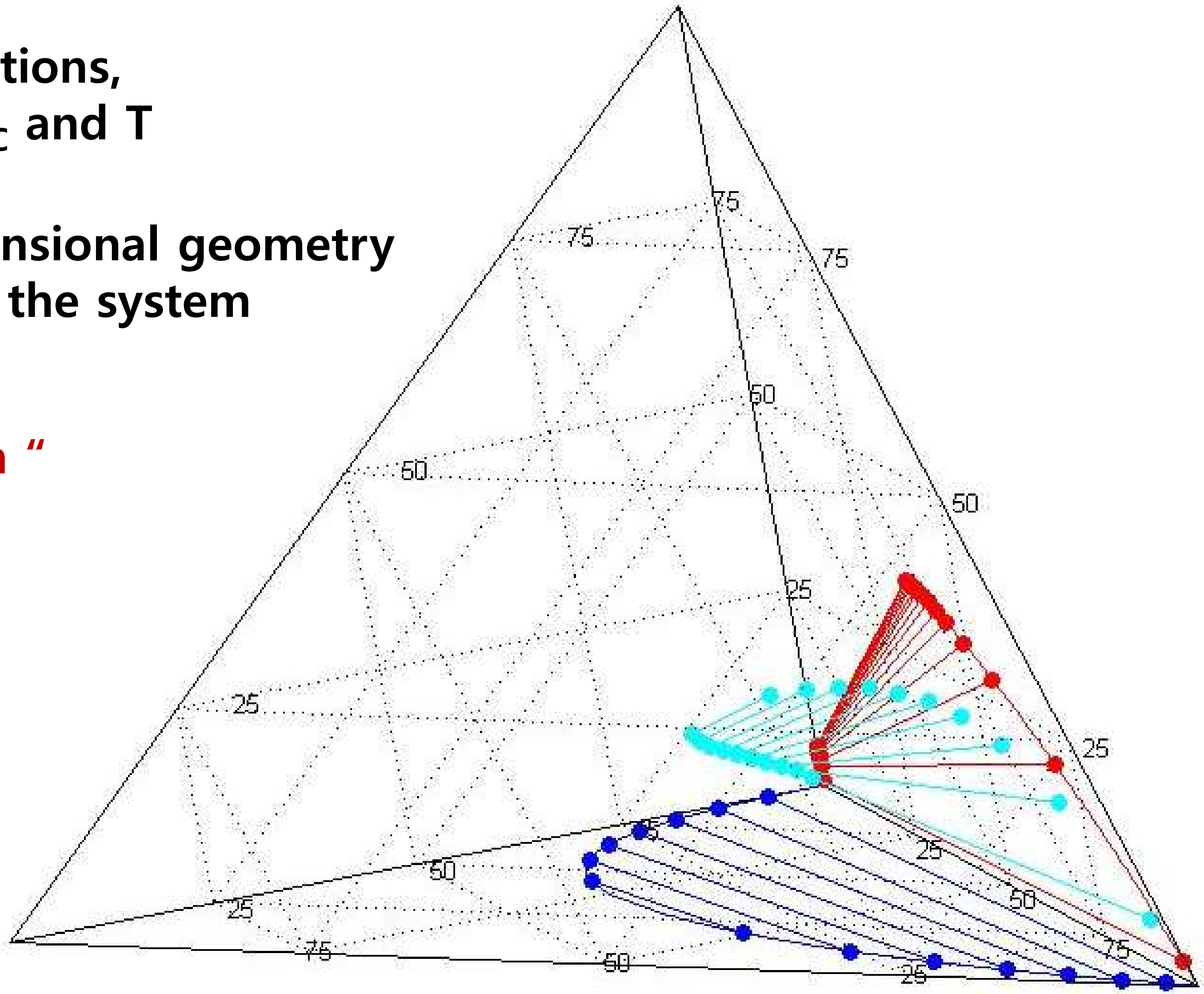
Four components: A, B, C, D

Assuming isobaric conditions,
Four variables: X_A, X_B, X_C and T

A difficulty of four-dimensional geometry
→ further restriction on the system

Most common figure:
“ equilateral tetrahedron “

4 pure components
6 binary systems
4 ternary systems
A quarternary system



* Draw four small equilateral tetrahedron
→ formed with edge lengths of a, b, c, d

$a+b+c+d=100$

%A=Pt=c,
%B=Pr=a,
%C=Pu=d,
%D=Ps=b

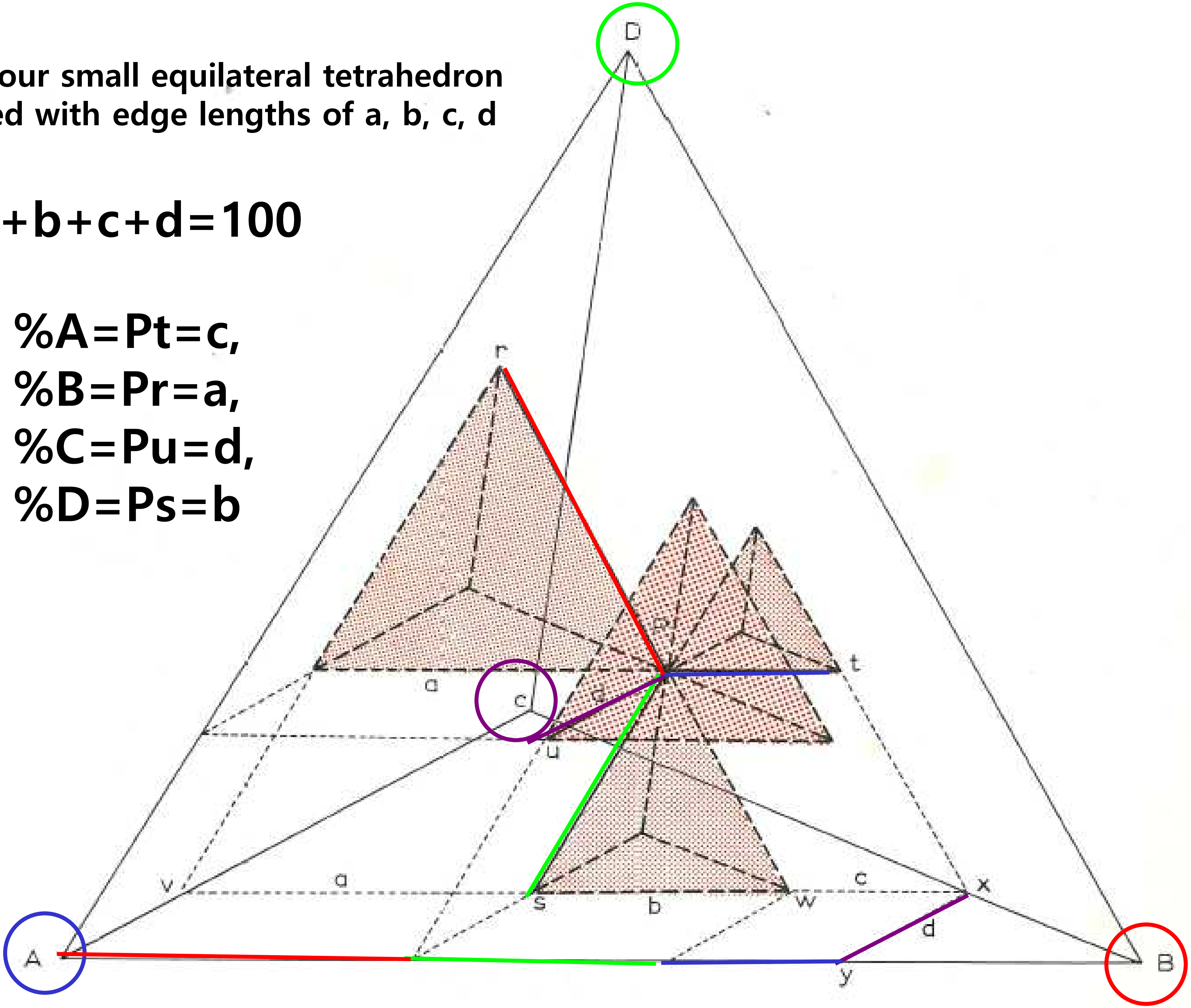


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

*** Incentive Homework 1**

Please submit ternary phase diagram model which can clearly express 3D structure of ternary system by October 18 in Bldg. 33-313.
You can submit the model individually or
with a small group under 2 persons.

*** Homework 1 : Exercises 1 (pages 59-61)**
by October 11 in Bldg. 33-313.

Good Luck!!

2023 Fall

“Phase Transformation *in* Materials”

2023.09.27.

Eun Soo Park

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

Contents for previous class

- **Ternary Equilibrium: Ternary Phase Diagram**

1) Gibbs Triangle

Used to determine the overall composition

$X_A+X_B+X_C = 1$

2) Isothermal section → $F = C - P$

2 phases region

Tie line: A straight line joining any two ternary compositions

Amount of each phase present is determined by using the Inverse Lever Rule

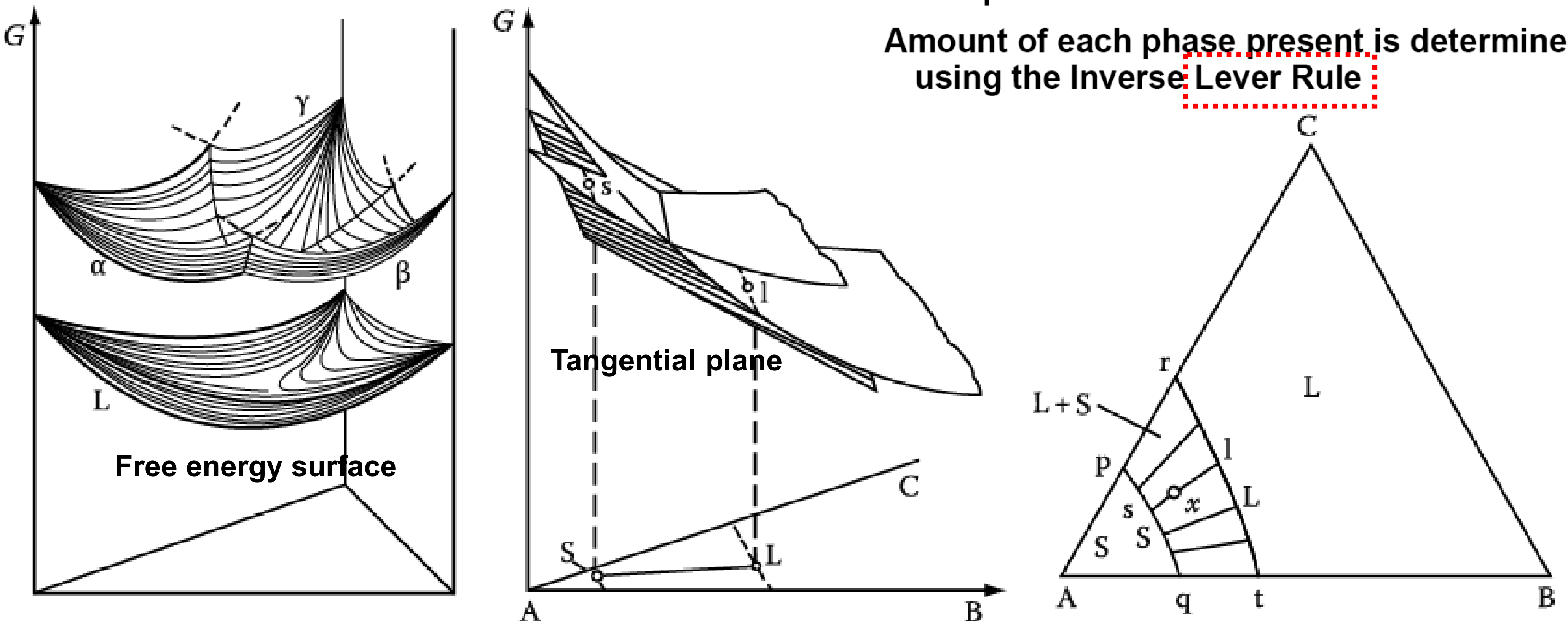


Fig. 1.41 (a) Free energy surface of a liquid and three solid phases of a ternary system.

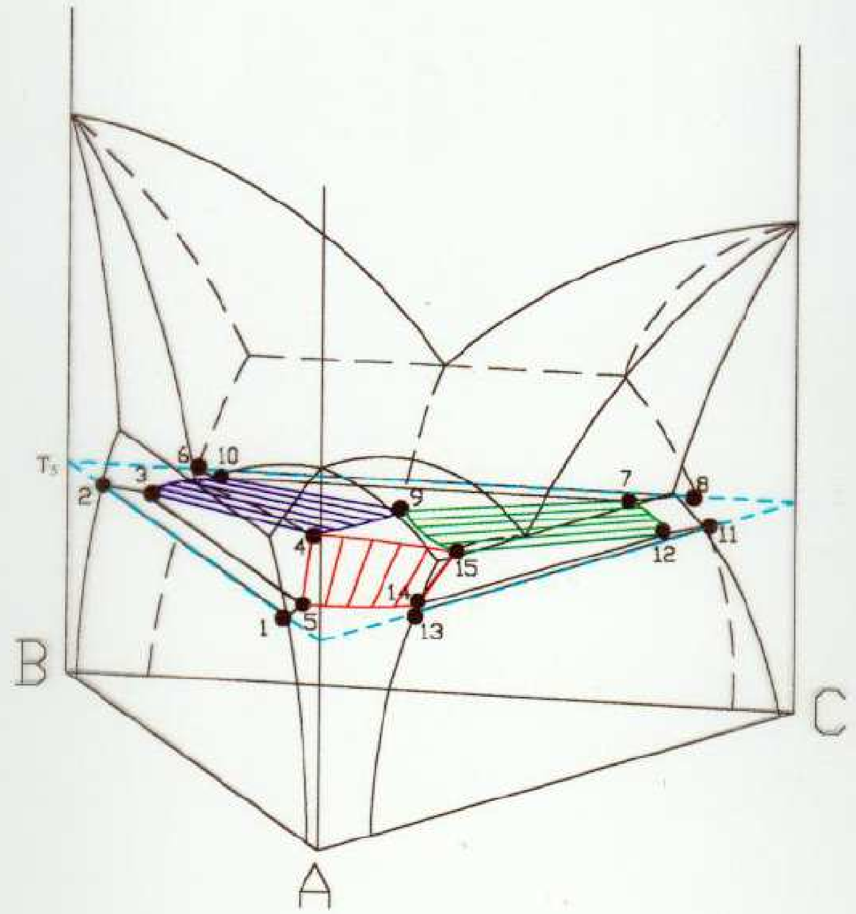
(b) A tangential plane construction to the free energy surfaces defined equilibrium between s and l in the ternary system

(c) Isothermal section through a ternary phase diagram

Ternary Eutectic System

(with **Solid Solubility**)

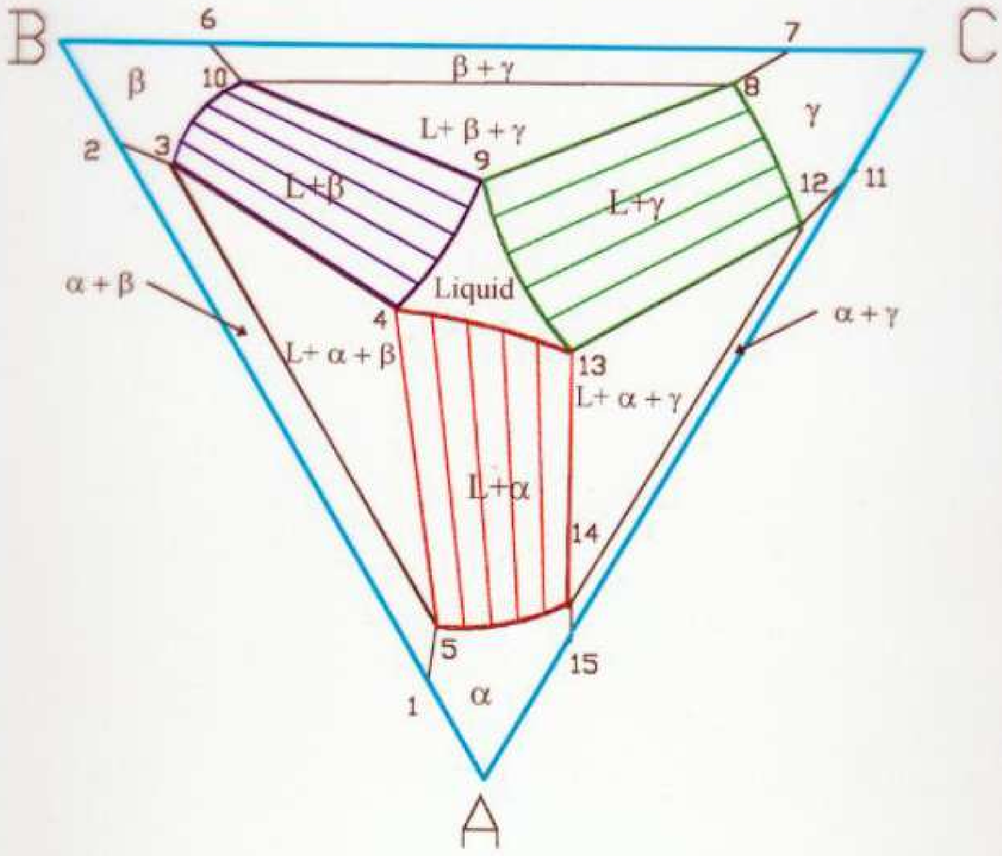
T5A:



Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic

T5B:

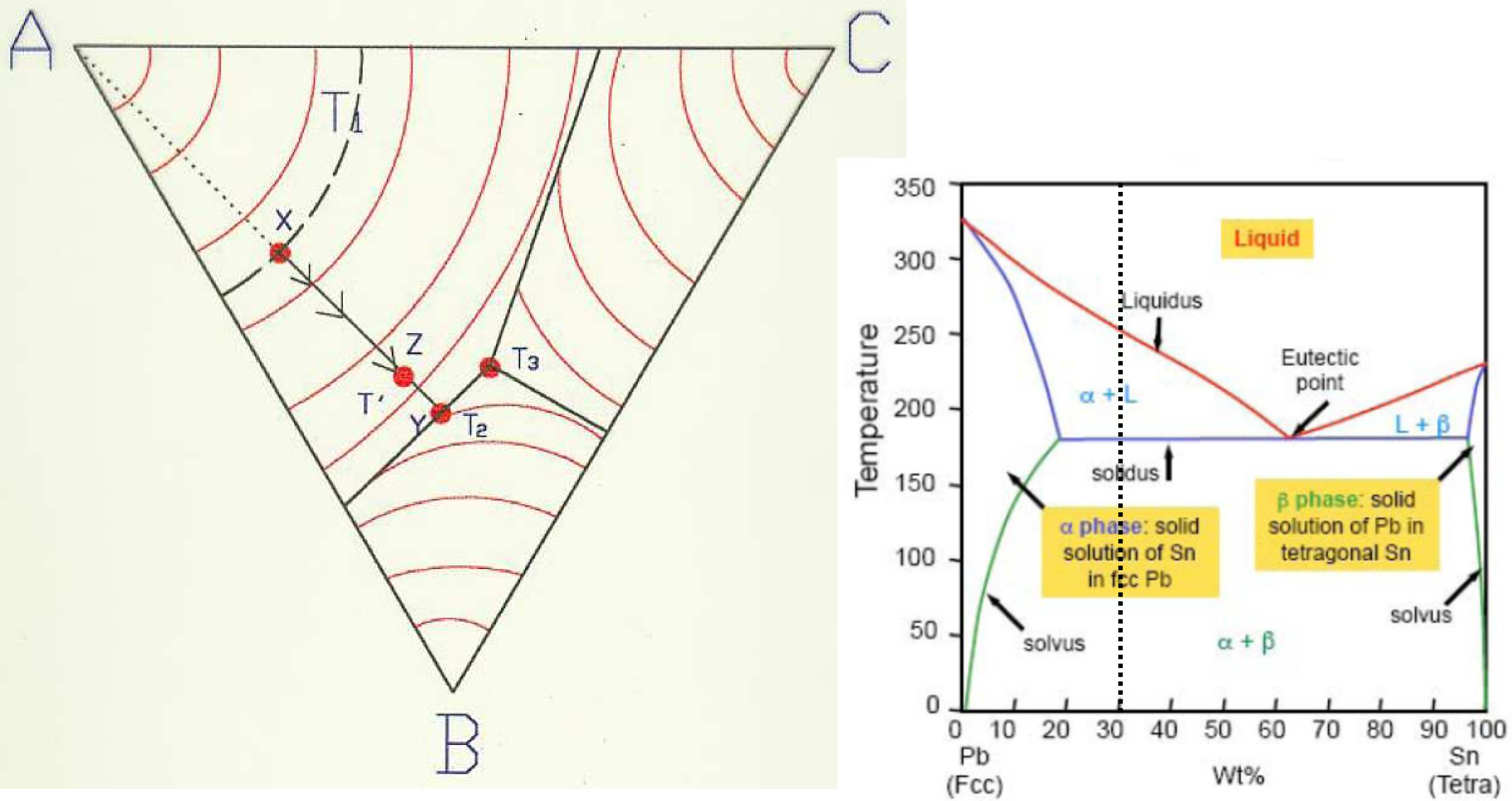
3 phases region: tie triangle



Isothermal Section At T=T$_5$

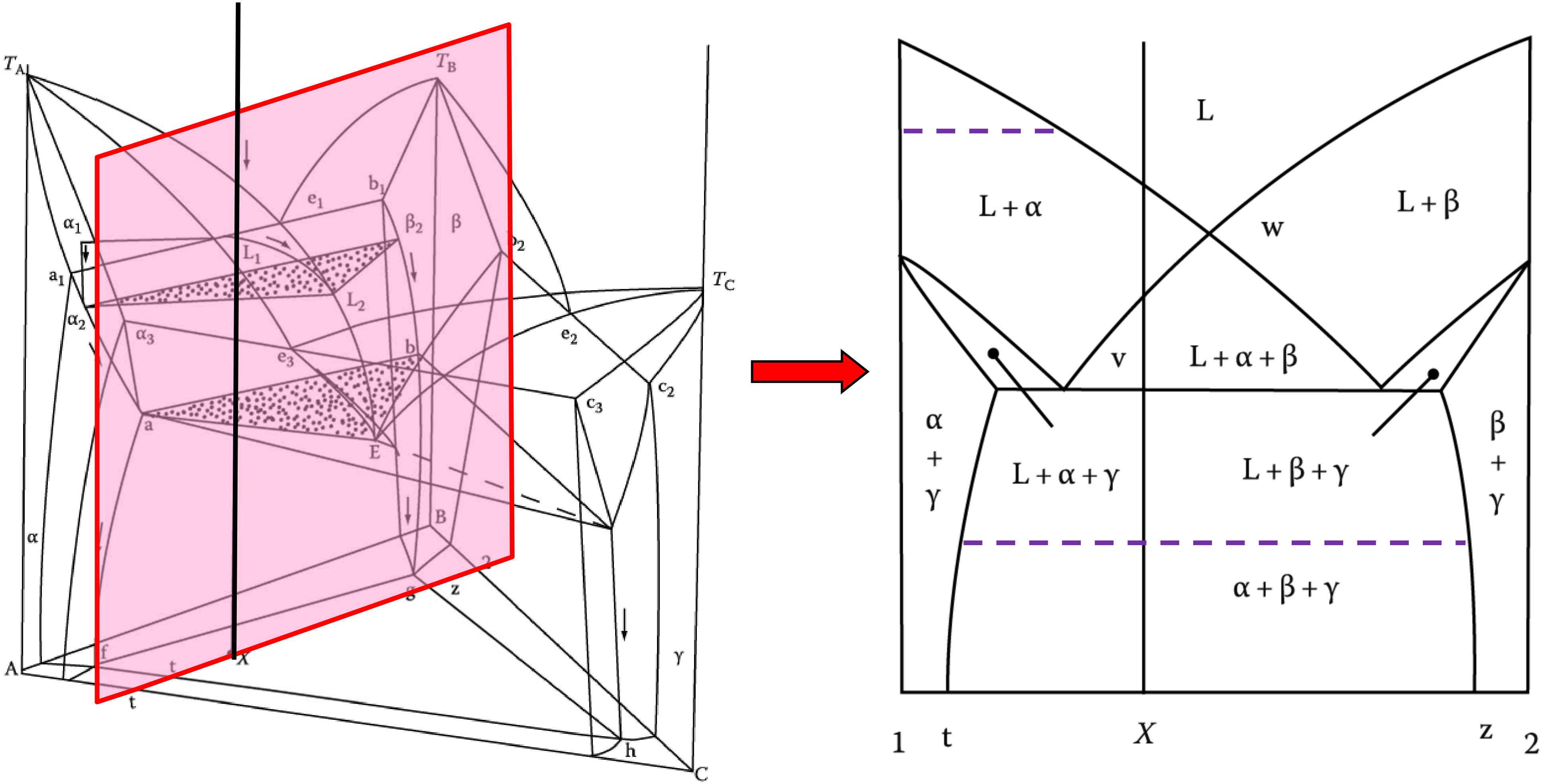
Ternary Eutectic System

3) Solidification Sequence: liquidus surface



Ternary Eutectic System

* Vertical section



* The horizontal lines are not tie lines.
  (no compositional information)

* Information for equilibrium phases
  at different temperatures

< Quaternary phase Diagrams >

Four components: A, B, C, D

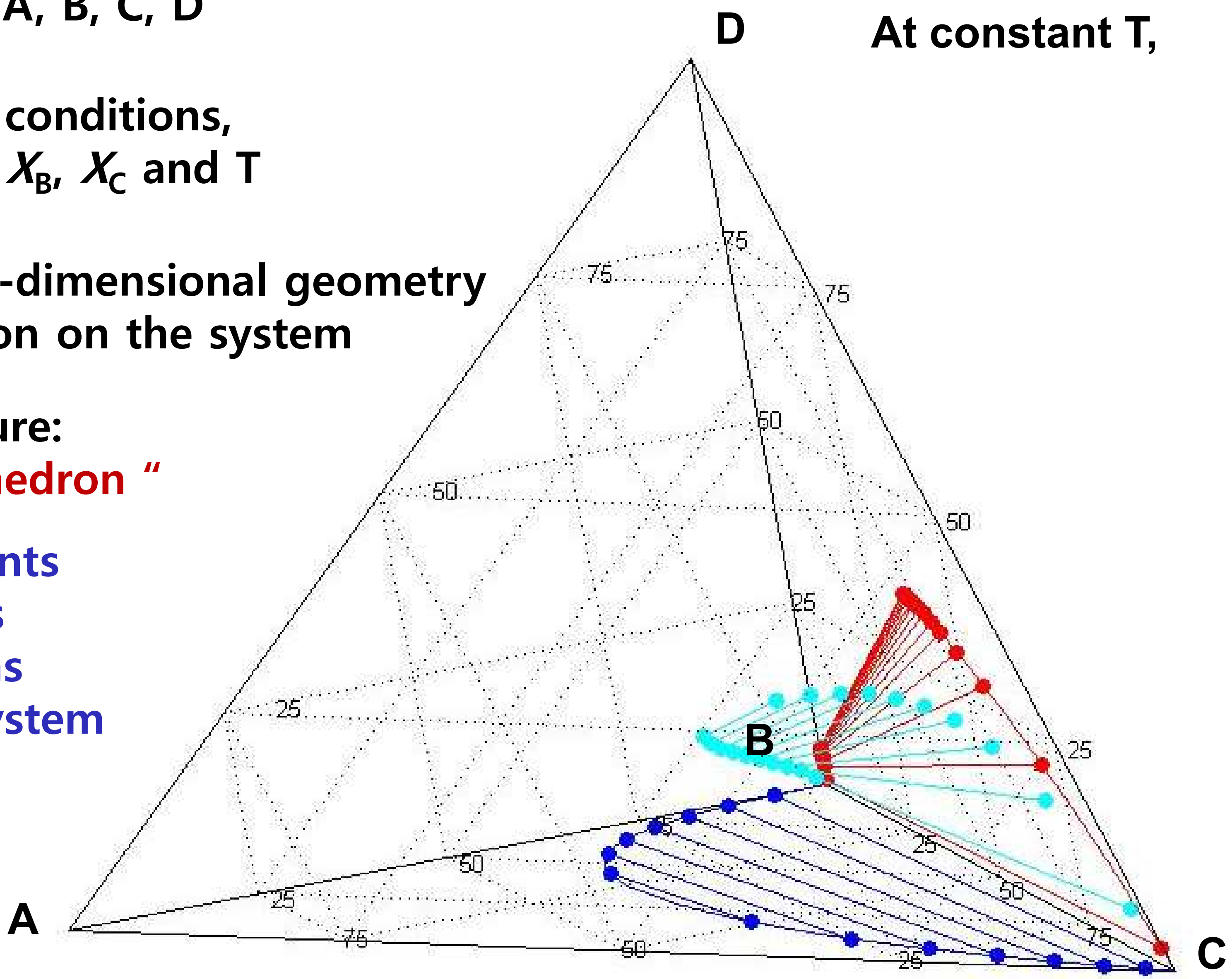
Assuming isobaric conditions,
Four variables: X_A, X_B, X_C and T

A difficulty of four-dimensional geometry
→ further restriction on the system

Most common figure:
“ equilateral tetrahedron “

- 4 pure components
- 6 binary systems
- 4 ternary systems
- A quartернary system

At constant T,



* Draw four small equilateral tetrahedron
→ formed with edge lengths of a, b, c, d

$$a+b+c+d=100$$

$$\%A=Pt=c,$$
$$\%B=Pr=a,$$
$$\%C=Pu=d,$$
$$\%D=Ps=b$$

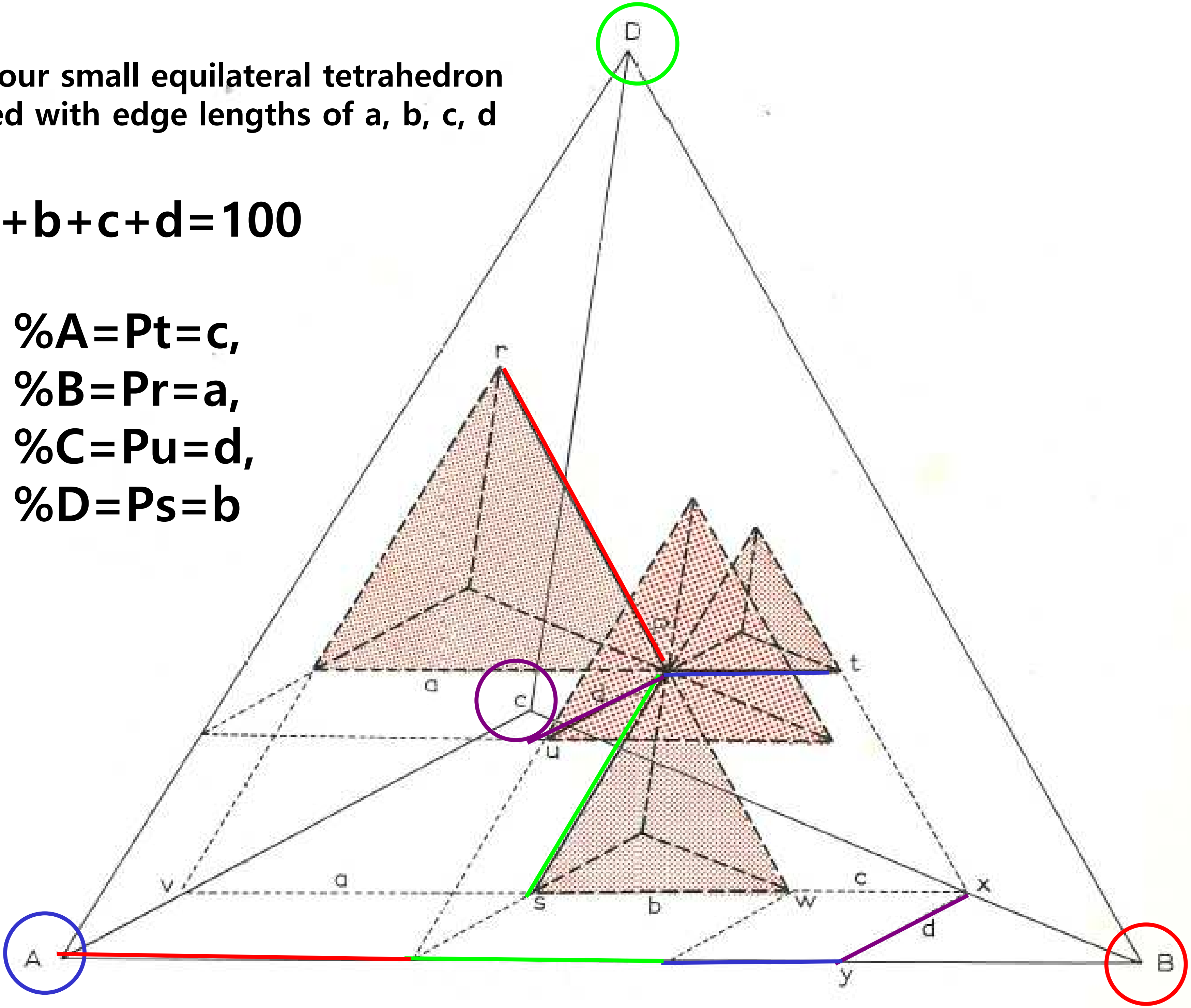
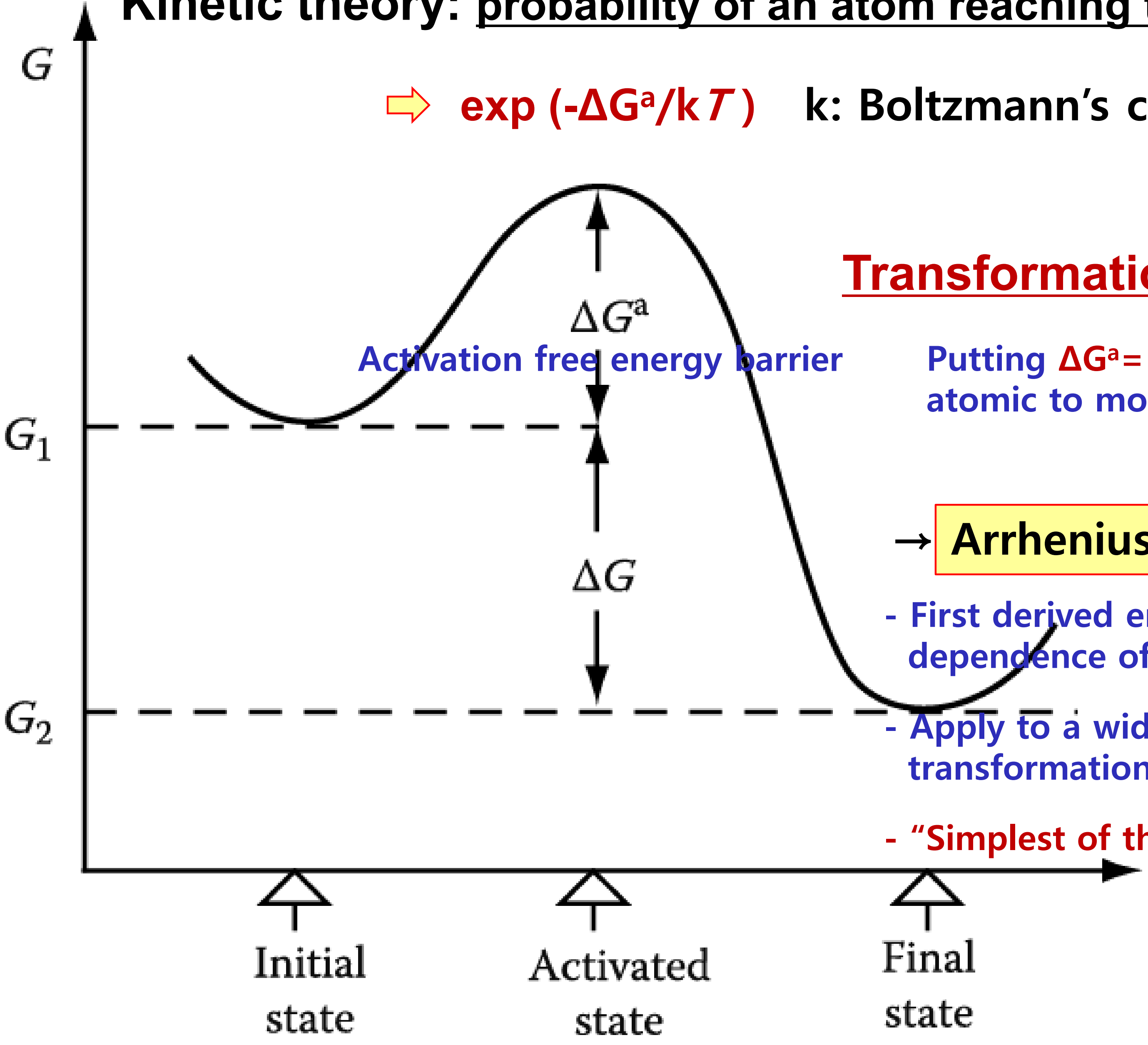


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

1.9 The kinetics of phase transformations

Kinetic theory: probability of an atom reaching the activated state

⇨ $\exp(-\Delta G^a/kT)$ k: Boltzmann's constant (R/N_a)



Activation free energy barrier

Transformation rate $\propto \exp(-\Delta G^a/kT)$

Putting $\Delta G^a = \Delta H^a - T\Delta S^a$ and changing from atomic to molar quantities

$\propto \exp(-\Delta H^a/RT)$

→ **Arrhenius rate equation**

- First derived empirically from the observed temp. dependence of the rate of chemical reactions
- Apply to a wide range of processes and transformation in metals and alloys
- "Simplest of these is the process of diffusion"

Contents in Phase Transformation

Background to understand phase transformation

- (Ch1) Thermodynamics and Phase Diagrams
- (Ch2) Diffusion: Kinetics
- (Ch3) Crystal Interface and Microstructure

Representative Phase transformation

- (Ch4) Solidification: Liquid → Solid
- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → Solid

Contents for today's class

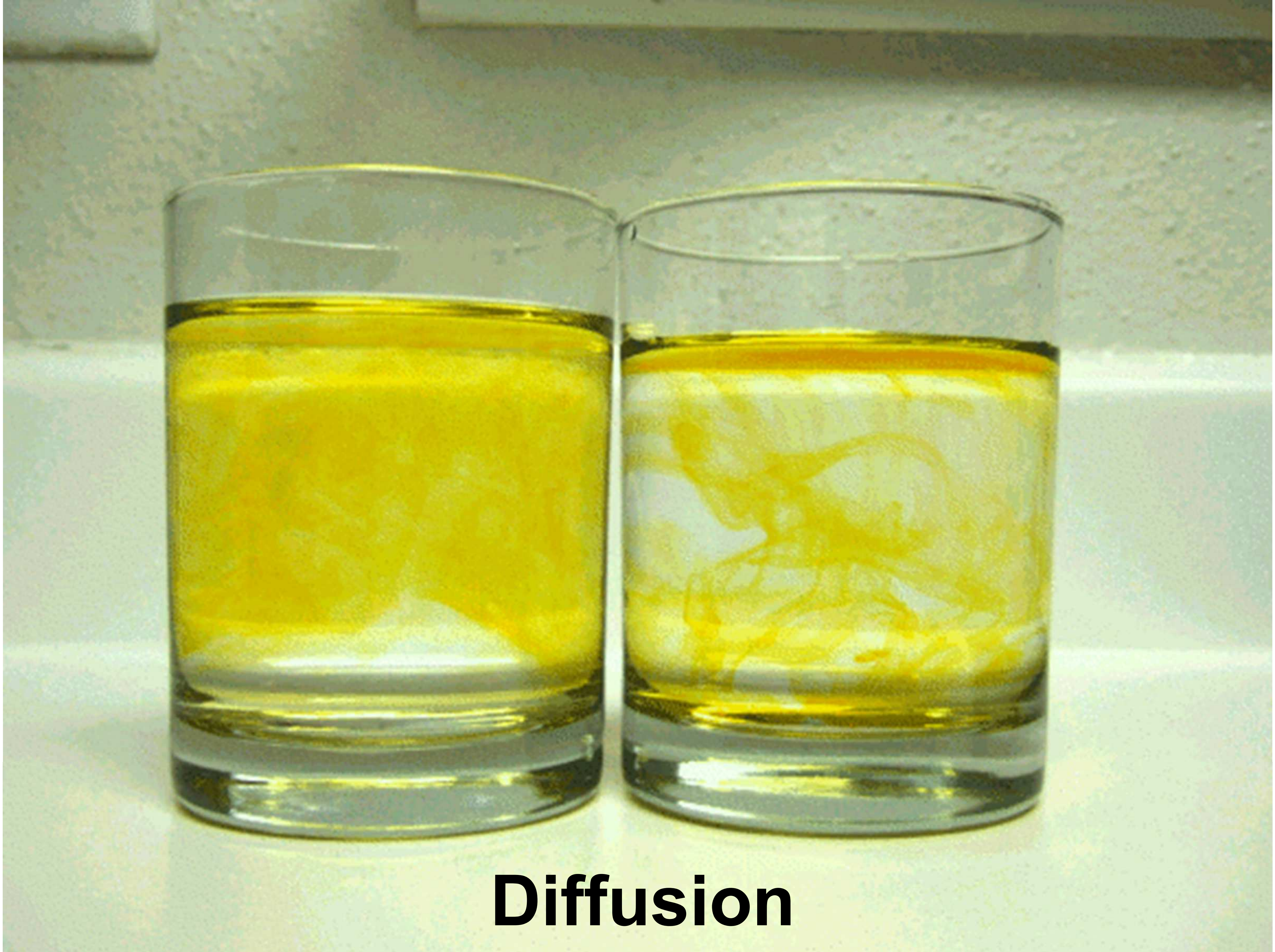
- Diffusion
- Interstitial Diffusion – Fick's First Law
  - Effect of Temperature on Diffusivity
  - Nonsteady-state diffusion – Fick's Second Law
- Solutions to the diffusion equations
- Substitution Diffusion
  1. Self diffusion in pure material
  2. Vacancy diffusion
  3. Diffusion in substitutional alloys

Q1. What is the driving force for diffusion?

⇒ **a concentration gradient (x)**

⇒ **a chemical potential gradient (o)**

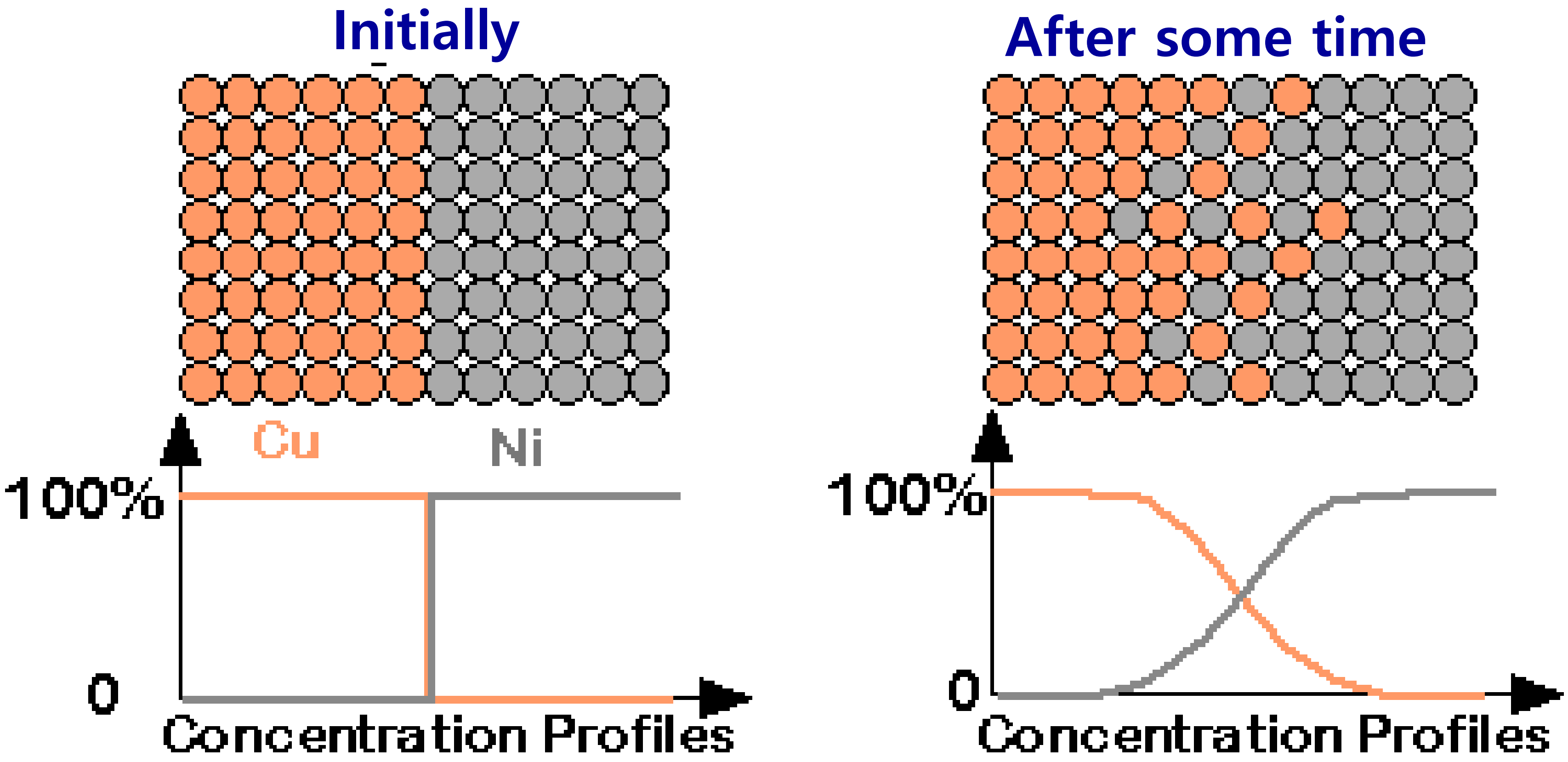
Diffusion ⇨ **Movement of atoms to reduce its chemical potential μ.**



Diffusion

Diffusion: THE PHENOMENON

- **Interdiffusion**: in a solid with more than one type of element (an alloy), atoms tend to migrate from regions of large concentration.



< Diffusion couple between Cu and Ni >

Mechanism of Solid-State Diffusion

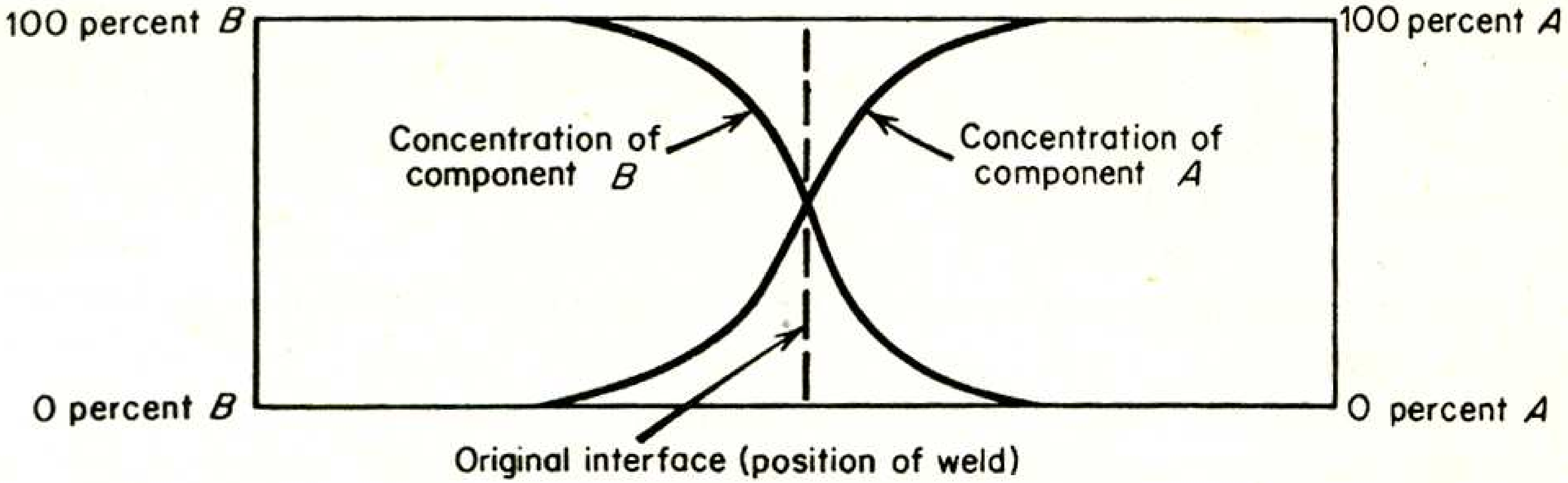


Fig. 10.6 Curves showing concentration as a function of distance along a diffusion couple. Curves of this type are usually called *penetration curves.*

Substitutional diffusion ⟺ **Interstitial diffusion**

R.E. Reed-Hill, Physical Metallurgy Principles

Diffusion : Movement of atoms to reduce its chemical potential μ.

Driving force: Reduction of G

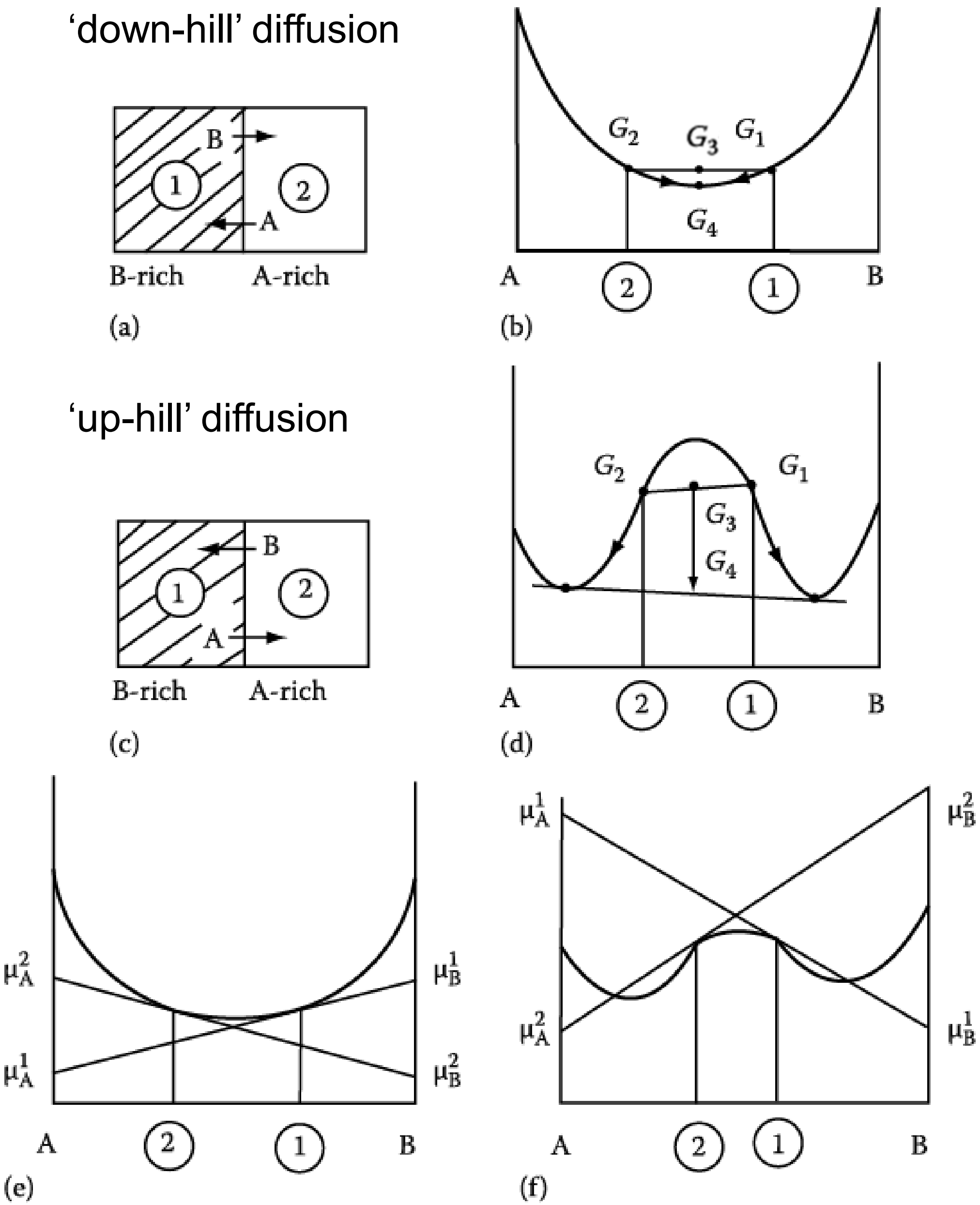
Down-hill diffusion

movement of atoms from a high concentration region to low concentration region.

Up-hill diffusion

movement of atoms from a low concentration region to high concentration region

$$\mu_A^1 < \mu_A^2$$
$$\mu_B^1 > \mu_B^2$$

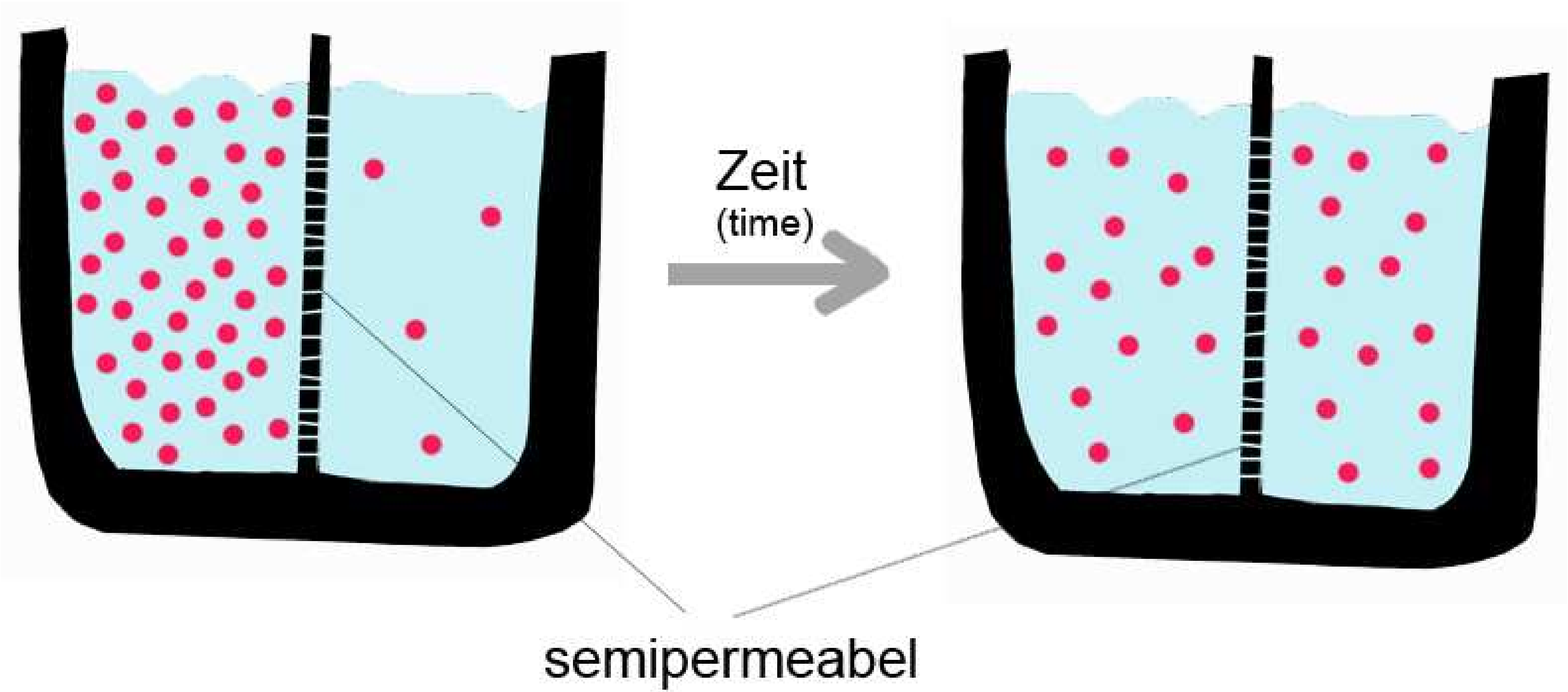


$$\mu_A^1 > \mu_A^2$$
$$\mu_B^1 < \mu_B^2$$

Fig. 2.1 Free energy and chemical potential changes during diffusion

Down-hill diffusion

movement of atoms from a high concentration region to low concentration region.



Diffusion

Movement of atoms to reduce its chemical potential μ.

Driving force: Reduction of G

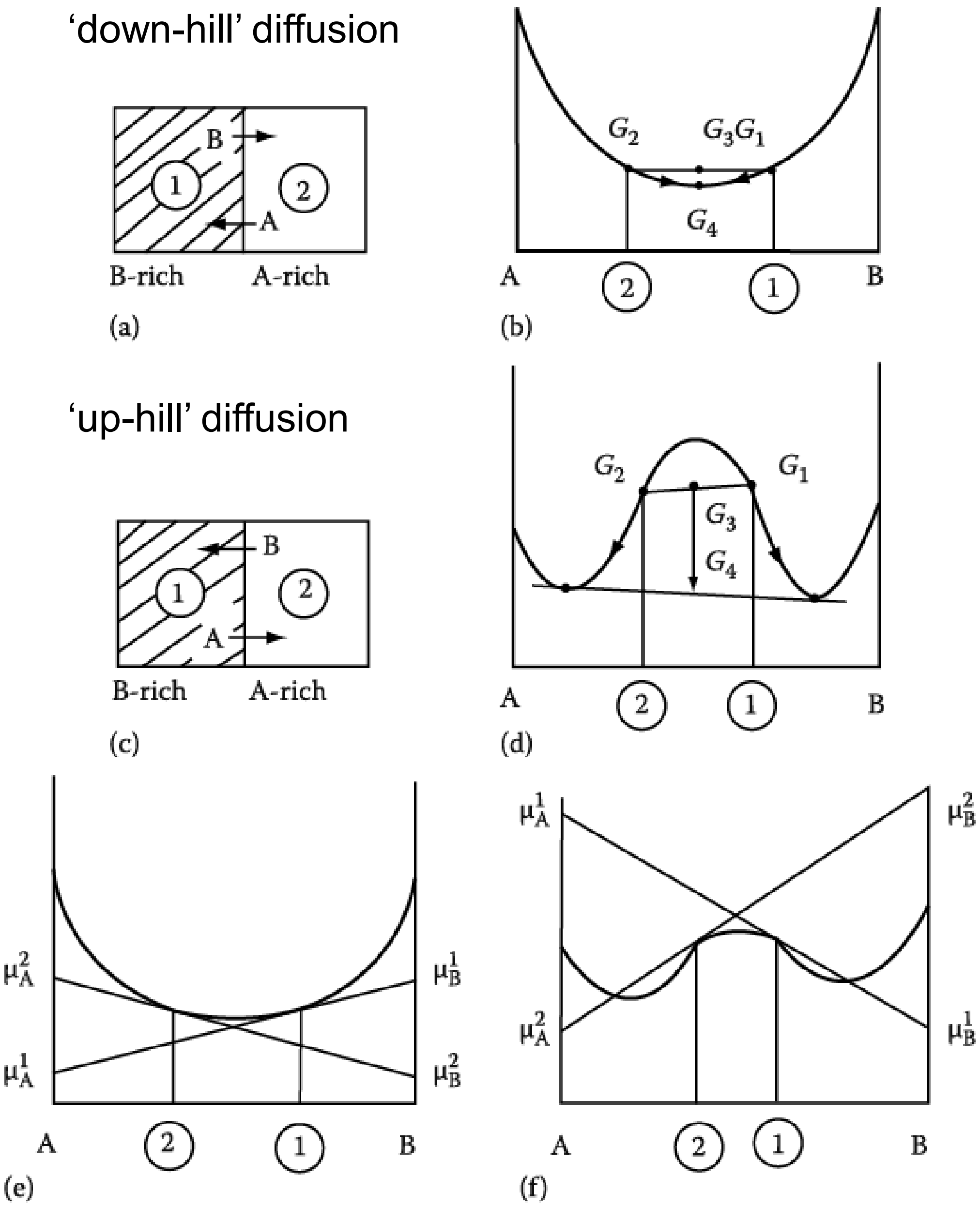
Down-hill diffusion

movement of atoms from a high concentration region to low concentration region.

Up-hill diffusion

movement of atoms from a low concentration region to high concentration region

$$\mu_A^1 < \mu_A^2$$
$$\mu_B^1 > \mu_B^2$$


'down-hill' diffusion

'up-hill' diffusion

$$\mu_A^1 > \mu_A^2$$
$$\mu_B^1 < \mu_B^2$$

Fig. 2.1 Free energy and chemical potential changes during diffusion

5.5.5 Spinodal Decomposition

Spinodal mode of transformation has no barrier to nucleation

: describing the transformation of a system of two or more components in a metastable phase into two stable phases

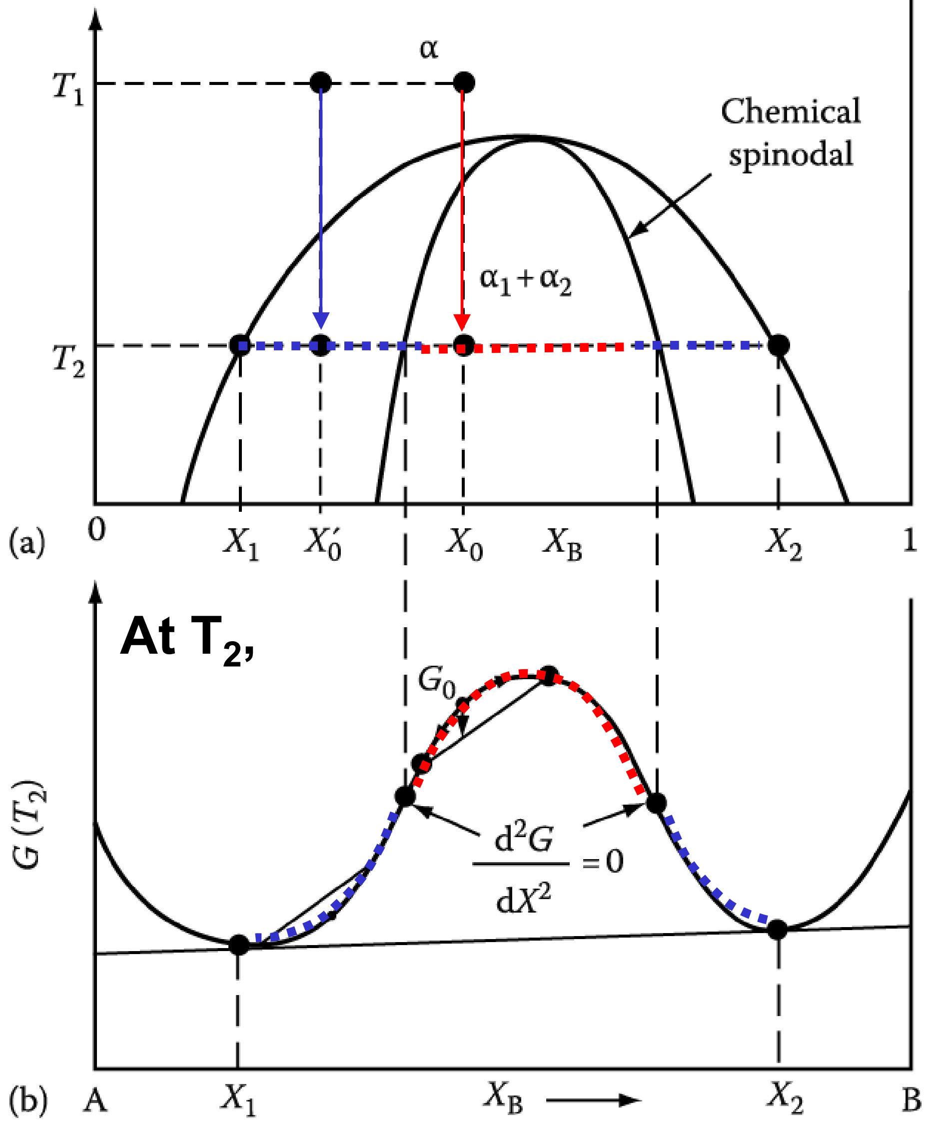


Fig. 5.38 Alloys between the spinodal points are unstable and can decompose into two coherent phasees α_1 and α_2 without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodal are metastable and can decompose only after nucleation of the other phase.

How does it differ between inside and outside the inflection point of Gibbs free energy curve?

1) Within the spinodal $\frac{d^2G}{dX^2}<0$

: phase separation by small fluctuations in composition/ "up-hill diffusion"

2) If the alloy lies outside the spinodal, small variation in composition leads to an increase in free energy and the alloy is therefore metastable.

The free energy can only be decreased if nuclei are formed with a composition very different from the matrix.

→ **nucleation and growth**

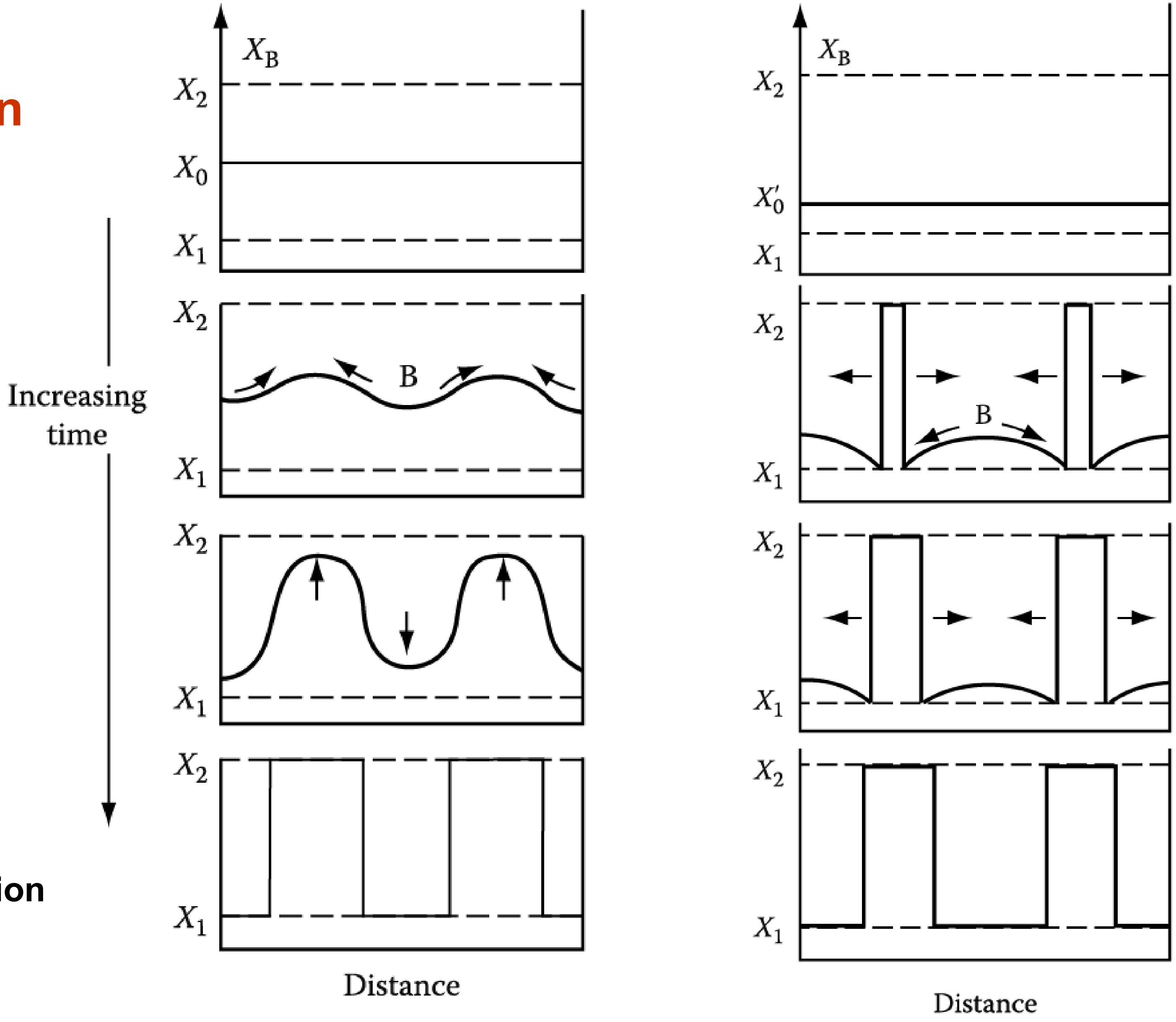
: "down-hill diffusion"

a) Composition fluctuations within the spinodal

b) Normal down-hill diffusion outside the spinodal

up-hill diffusion

down-hill diffusion



interdiffusion coefficient
D<0

Fig. 5.39 schematic composition profiles at increasing times in (a) an alloy quenched into the spinodal region (X_0 in Figure 5.38) and (b) an alloy outside the spinodal points (X_0' in Figure 5.38)

Diffusion

Diffusion : Mechanism by which matter transported through matter

What is the driving force for diffusion?

$\Rightarrow$ a concentration gradient (x)

$\Rightarrow$ a chemical potential gradient (o)

But this chapter will explain with "concentration gradients for a convenience".

(Down-hill diffusion)

Q2. Interstitial diffusion vs Substitutional diffusion

Fick's First Law of Diffusion

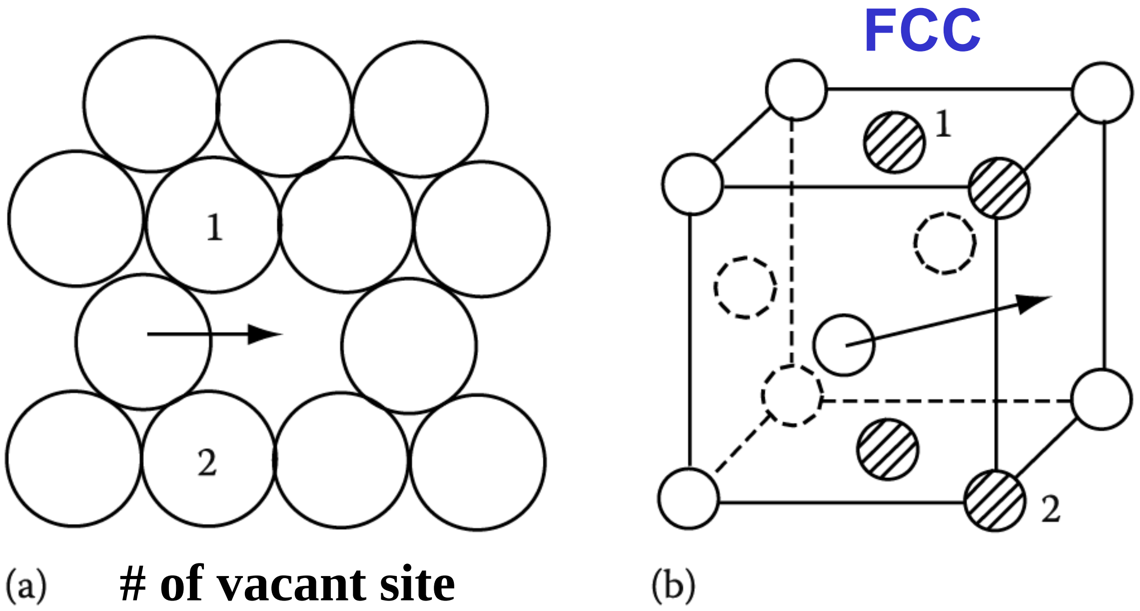
$$\boxed{J_B = -D_B \frac{\partial C_B}{\partial x}}$$

2.1 Atomic mechanisms of diffusion

The mean vibrational energy is **3kT**, therefore the amplitude of thermal oscillation of an atom increases markedly with **temperature**. If a neighboring atom site is vacant, then the oscillation atom can change site with a certain probability (**atom jumping**). The probability consists of **creation of the vacant site** and movement of a neighboring atom into the site.

Substitutional vs. Interstitial diffusion

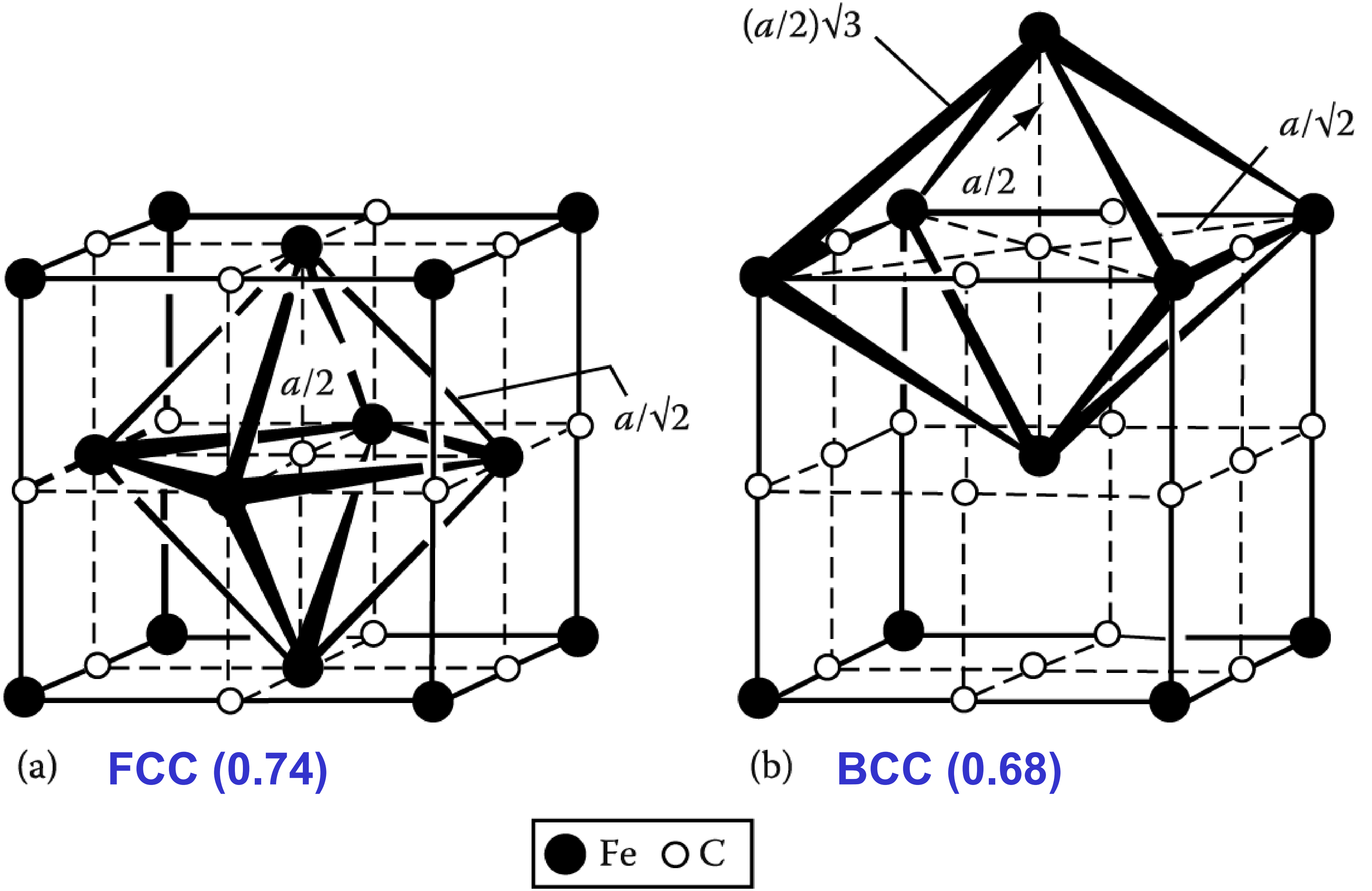
Substitutional diffusion



# of vacant site

Fig. 2.2 Movement of an atom into an adjacent vacancy in an fcc lattice. (a) A close-packed plane. (b) A unit cell showing the four atoms (shaded) which must move before the jump can occur.

Interstitial diffusion



(a) **FCC (0.74)**

(b) **BCC (0.68)**

Fig. 2.3 (a) Octahedral interstices (O) in an fcc crystal. (b) Octahedral interstices in a bcc crystal.

Interstitial diffusion

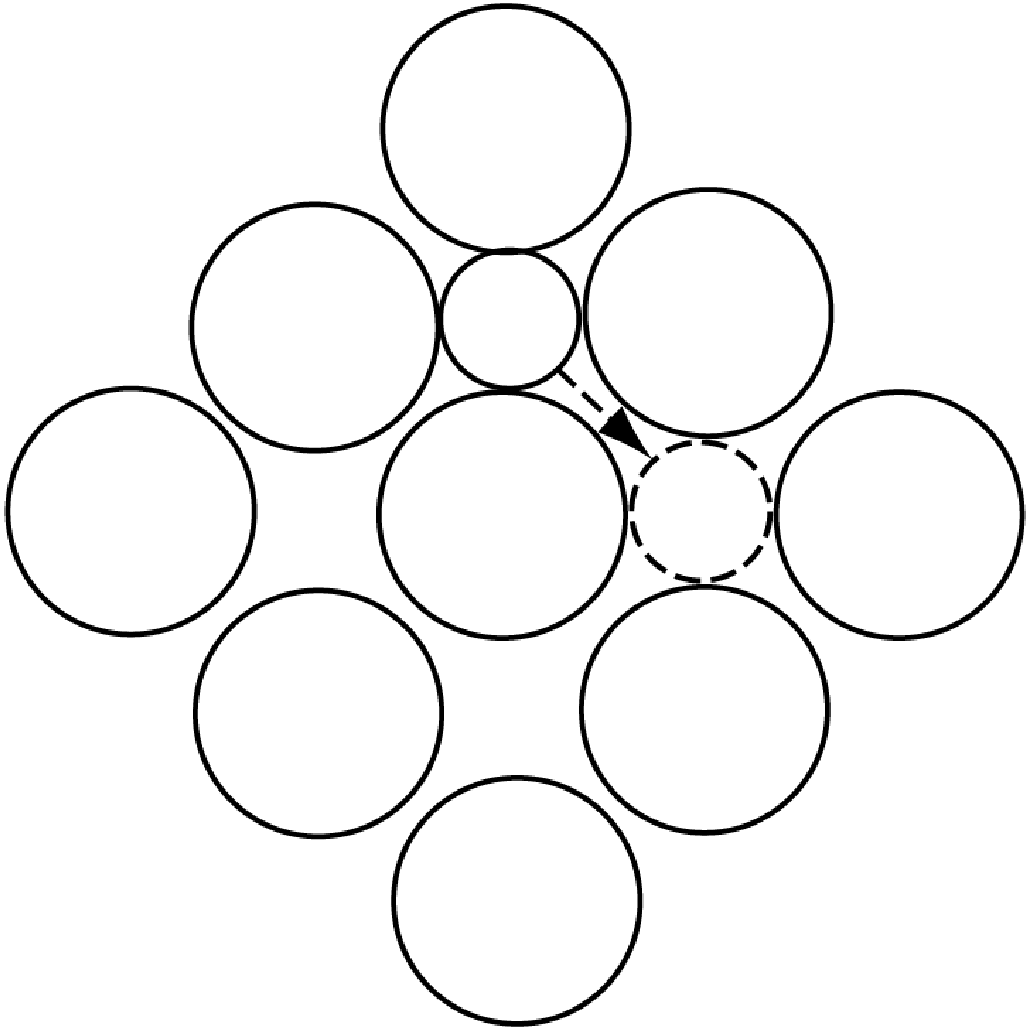


Fig. 2.4 A {100} plane in an fcc lattice showing the path of an interstitial atom diffusing by the interstitial mechanism.

How interstitial diffusion differs from substitutional diffusion?

2.2 Interstitial diffusion

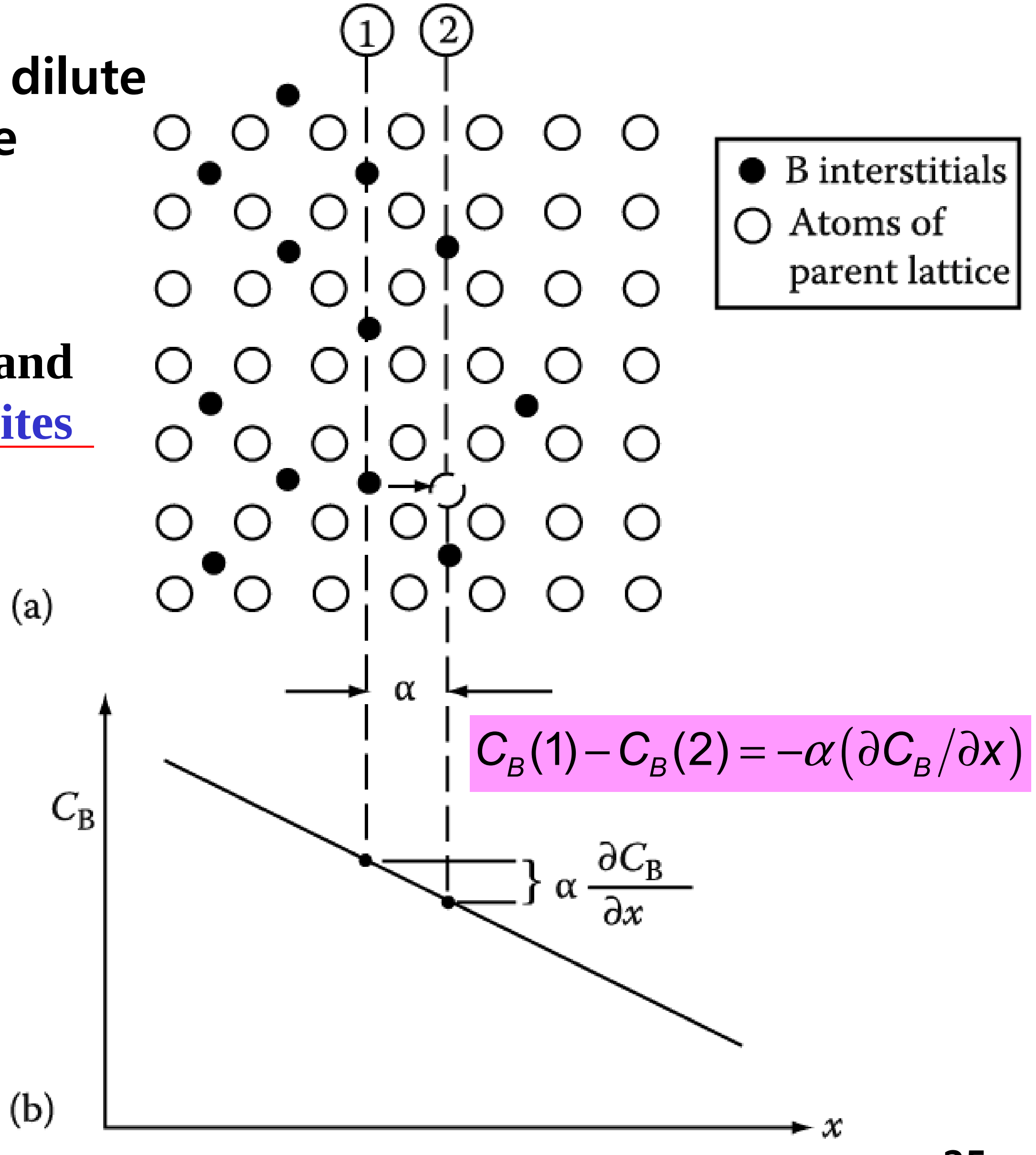
2.2.1

Random jump of solute B atoms in a dilute solid solution of a simple cubic lattice

Assume that there is no lattice distortion and also that there are always six vacant sites around the diffusion atom.

$$\boxed{J_B = \frac{1}{6}\Gamma_B n_1 - \frac{1}{6}\Gamma_B n_2}$$

J_B : Net flux of B atom
Γ_B : Average jump rate of B atoms
n_1 : # of atoms per unit area of plane 1
n_2 : # of atoms per unit area of plane 2



$$C_B(1) - C_B(2) = -\alpha\left(\partial C_B / \partial x\right)$$

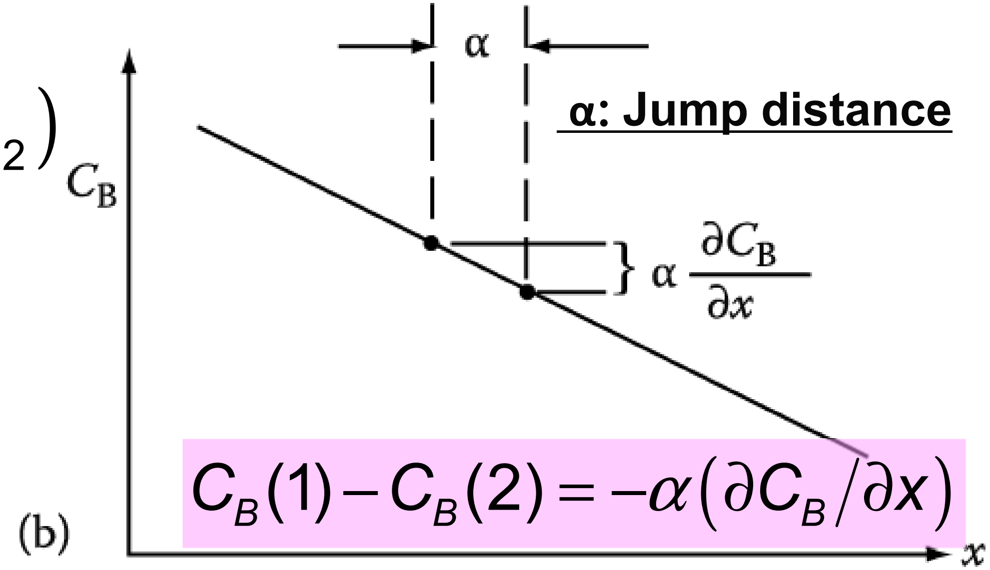
Fig. 2.5 Interstitial diffusion by random jumps in a concentration gradient.

Fick's First Law of Diffusion

$$J_B = \frac{1}{6}\Gamma_B n_1 - \frac{1}{6}\Gamma_B n_2 = \frac{1}{6}\Gamma_B\left(n_1 - n_2\right)$$

$$C_B(1) = n_1/\alpha,\ C_B(2) = n_2/\alpha$$

$$\left(n_1 - n_2\right) = \alpha\left(C_B(1) - C_B(2)\right)$$



$$C_B(1) - C_B(2) = -\alpha\left(\partial C_B/\partial x\right)$$

$$J_B = \frac{1}{6}\Gamma_B\left(n_1 - n_2\right) = -\left(\frac{1}{6}\Gamma_B\alpha^2\right)\frac{\partial C_B}{\partial x} = -D_B\frac{\partial C_B}{\partial x}$$

➡ Concentration varies with position. (atoms $m^{-2}\ s^{-1}$)

D_B: Intrinsic diffusivity or Diffusion coefficient of B

⇒ **depends on microstructure of materials**

Magnitude of D in various media

Gas : D ≈ 10^{-1} cm^2/s

Liquid : D ≈ 10^{-4} ~ 10^{-5} cm^2/s

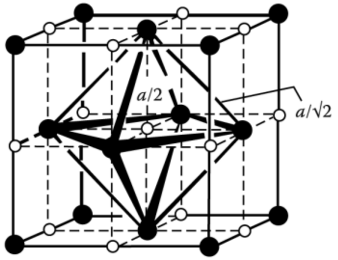
Solid : Materials near melting temp. D ≈ 10^{-8} cm^2/s

Elemental semiconductor (Si, Ge) D ≈ 10^{-12} cm^2/s

* Estimate the jump frequency of a carbon atom in γ-Fe (FCC) at 1000 °C.

$$D_B = \frac{1}{6}\Gamma_B \alpha^2$$

lattice parameter of γ-Fe : ~0.37 nm



$$\alpha = 0.37/\sqrt{2} = 0.26\,nm \qquad D_C = 2.5\times10^{-11}\,m^2 s^{-1}$$

$$\Gamma = 2\times10^{9}\ jumps\ s^{-1}$$

the vibration frequency of carbon : ~ 10^{13}

Only about one attempt in 10^4 results in a jump from one site to another.

*** If the crystal structure is not cubic, then the probability of jump is anisotropic (different α). For example the probability of jumps along the basal direction and the axial direction of hcp crystal are different.**

D_B, in general, is concentration-dependent.

For example, in γ-Fe at 1000 °C,

D_c = 2.5 x 10^{-11} m^2s^{-1}, when C_c = 0.15 wt%

D_c = 7.7 x 10^{-11} m^2S^{-1}, when C_c = 1.4 wt%

$$C_c \uparrow \rightarrow D_C \uparrow$$

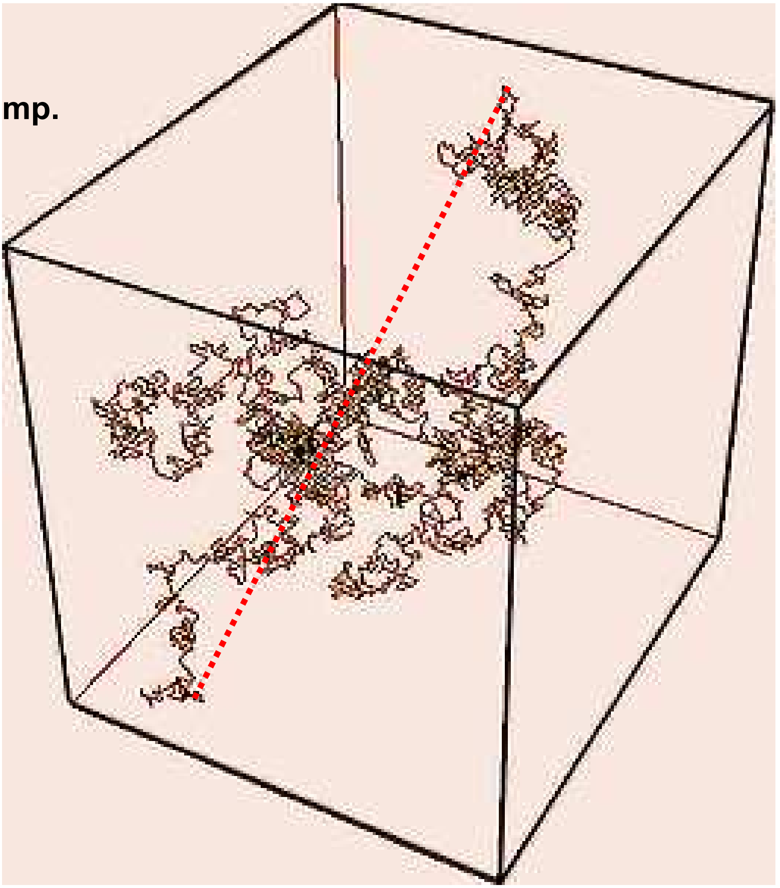
∵C atoms stain the Fe lattice thereby making diffusion easier as amount of strain increases.

Q3. What is the radial distance, r from the origin in random work?

$$\boxed{r = \alpha\sqrt{(\Gamma t)} = f(D) = 2.4\sqrt{Dt}}$$

For random walk in 3 dimensions,

The direction of each new jump is independent of the direction of the previous jump.



after n steps of length α

$$\rightarrow \alpha\sqrt{n}$$

Net distance from its original position

During random walk,
an atom will move in time (t)
a radial distance (r) from the origin

$$D_B = \frac{1}{6}\Gamma_B \alpha^2$$

$$\boxed{r = \alpha\sqrt{(\Gamma t)} = f(D) = 2.4\sqrt{Dt}} \because \Gamma = \frac{6D}{\alpha^2} \rightarrow r = \sqrt{6}\sqrt{Dt}$$

In 1 s, each carbon atom will move a total distance of ~ 0.5 m

→ a net displacement : ~ 10 μm.

⇨ **Very few of the atom jumps provide a useful contribution to the total diffusion distance.**

Q4. What is the effect of the temperature on diffusivity?

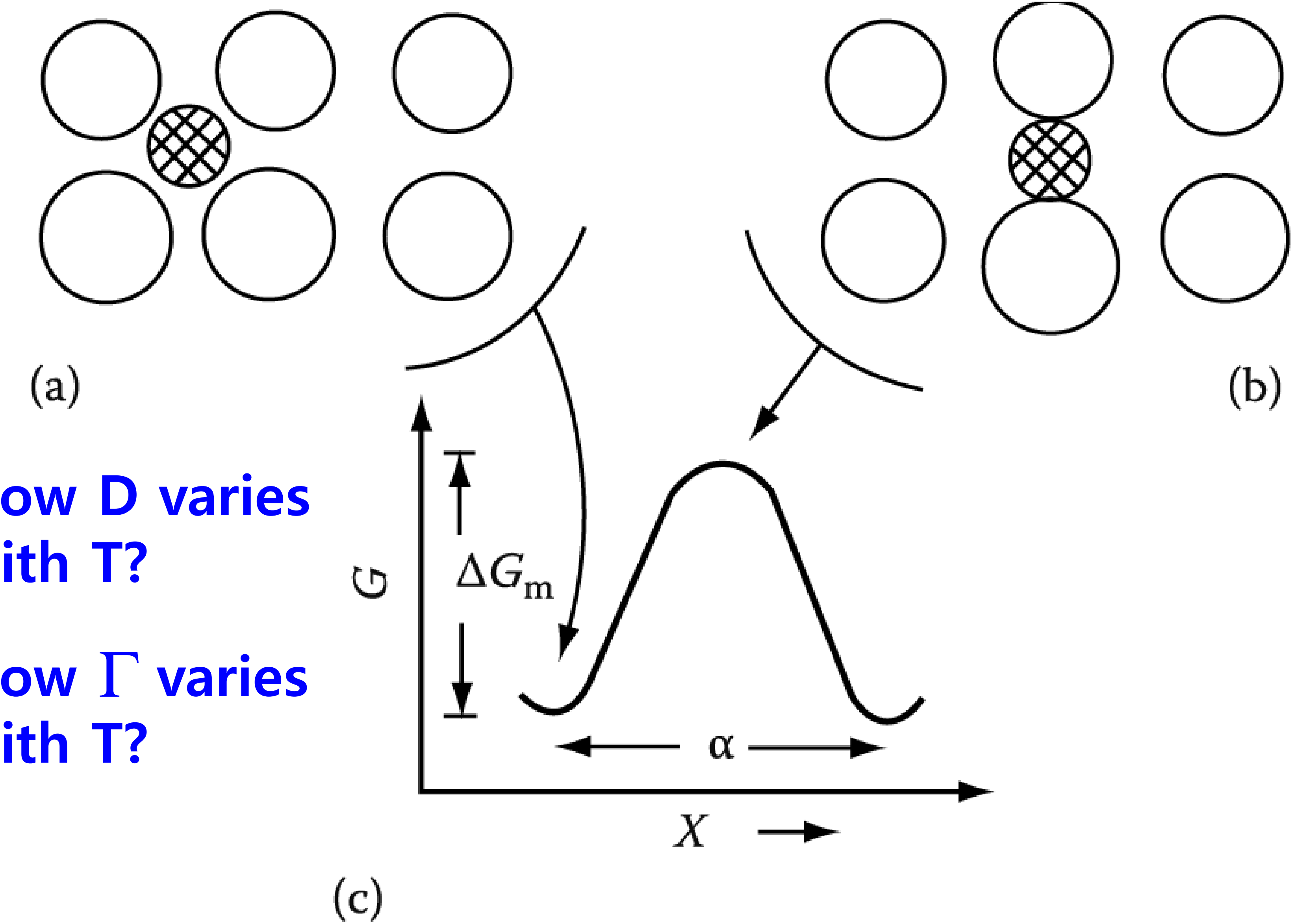
$$\boxed{D_B = D_{B0} \exp \frac{-Q_{ID}}{RT}}$$

(Arrhenius-type equation)

2.2.2

EFFECT OF TEMPERATURE on Diffusivity

Thermal Activation



How D varies with T?

How Γ varies with T?

Fig. 2.6 Interstitial atom, (a) in equilibrium position, (b) at the position of maximum lattice distortion. (c) Variation of the free energy of the lattice as a function of the position of interstitial.

Thermally activated process *jump frequency* Γ_B ?

$$\Gamma_B = Z\nu \exp\left(-\Delta G_m / RT\right)$$

Z : **nearest neighbor sites**

ν : **vibration frequency**

ΔG_m : **activation energy for moving**

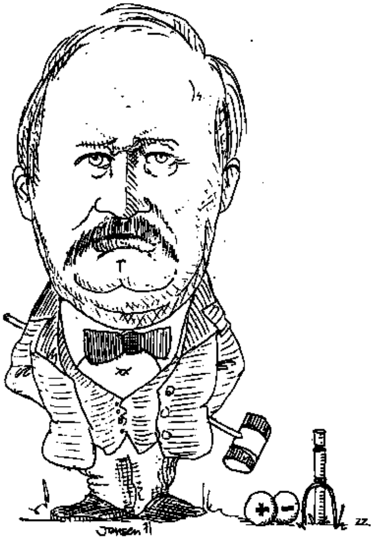
$$\left\{ \Delta G_m = \Delta H_m - T\Delta S_m \ , \ D_B = \frac{1}{6}\Gamma_B \alpha^2 \right\}$$

$$D_B = \left[\frac{1}{6}\alpha^2 Z\nu \exp\left(\Delta S_m / R\right)\right]\exp\left(-\Delta H_m / RT\right)$$

$$\Delta H_m \equiv Q_{ID}$$

$$\boxed{D_B = D_{B0} \exp\frac{-Q_{ID}}{RT}}$$

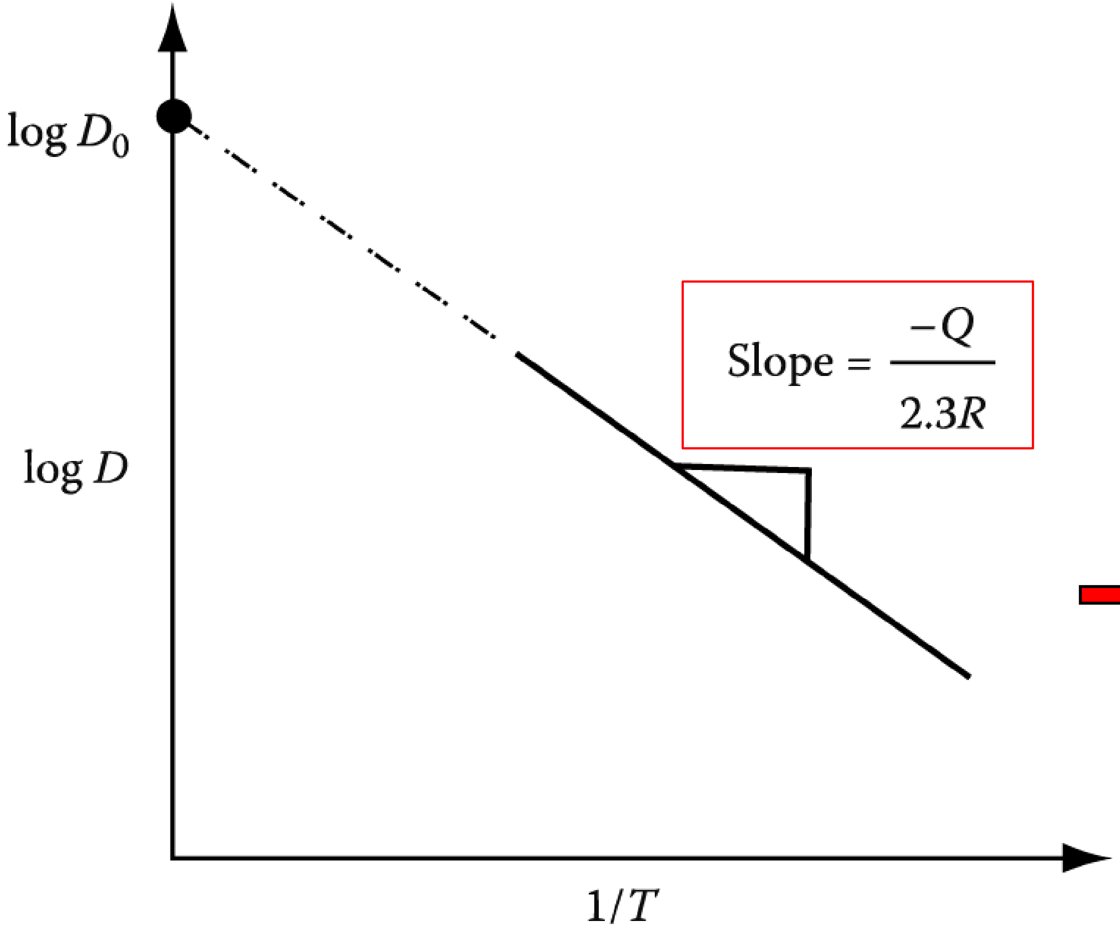
(Arrhenius-type equation)



Temperature Dependence of Diffusion

$$D_B = D_{B0} \exp \frac{-Q_{ID}}{RT}$$

How to determine Q_{ID} experimentally?



$$\log D = \log D_0 - \frac{Q}{2.3R}\left(\frac{1}{T}\right)$$

➡ *Therefore, from the slope of the D-curve in an log D vs 1/T coordinate, the activation energy may be found.*

Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

Q5. Steady state diffusion vs Non-steady state diffusion?

Fick's first Law

$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

Fick's Second Law

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

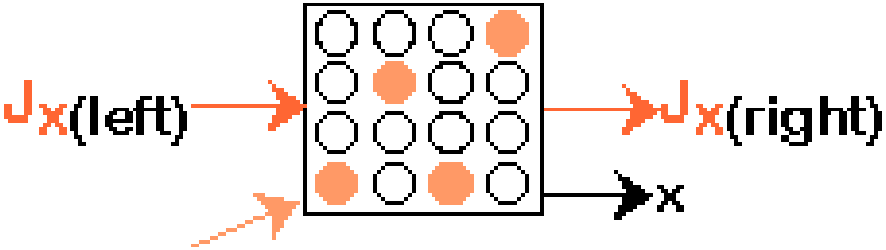
➡ **Concentration varies with "position"**

"Both position and time"

2.2.3

Steady-state diffusion

The simplest type of diffusion to deal with is when the concentration at every point does not change with time.



Concentration, C, in the box

Steady State

$J_{x\text{(left)}} = J_{x\text{(right)}}$

- Apply Fick's First Law:

$$J_x = -D\frac{dC}{dx}$$

If $J_{x\text{(left)}} = J_{x\text{(right)}}$, then

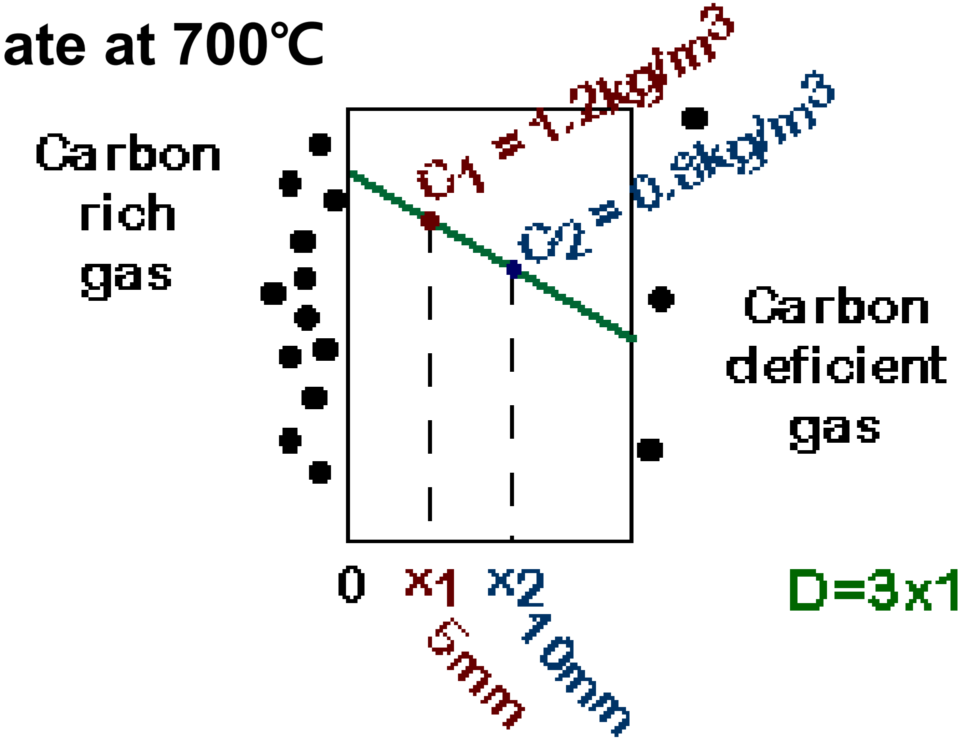
$$\frac{dC}{dx}_{\text{(left)}} = \frac{dC}{dx}_{\text{(right)}}$$

⇨ **the slope, dC/dx, is constant (does not vary with position)!**

Steady-state diffusion

The simplest type of diffusion to deal with is when the concentration at every point does not change with time.

- **Steel plate at 700℃**



$D=3\times10^{-11} m^2/s$

Q: How much carbon is transferring from the rich to deficient side?

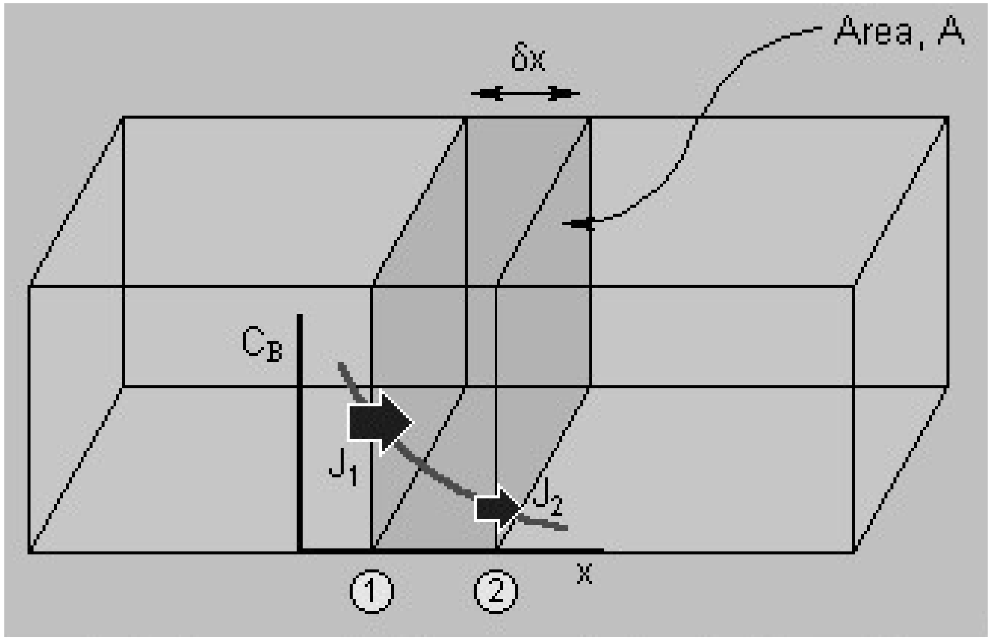
$$J=-D\frac{C_2-C_1}{x_2-x_1}=2.4\times10^{-9}\frac{kg}{m^2 s}$$

2.2.4

Nonsteady-state diffusion

In most practical situations steady-state conditions are not established, i.e. concentration varies with both distance and time, and Fick's 1st law can no longer be used.

How do we know the variation of C_B with time? → Fick's 2nd law



The number of interstitial B atoms that diffuse into the slice across plane (1) in a small time interval d*t* :

→ $J_1A\,dt$ Likewise : $J_2A\,dt$

Sine $J_2 < J_1$, the concentration of B within the slice will have increased by

Due to mass conservation

$$(J_1 - J_2)A\delta t = \delta C_B A\delta x \qquad \delta C_B = \frac{(J_1 - J_2)A\delta t}{A\delta x}$$

Nonsteady-state diffusion

$$J_2 = J_1 + \frac{\partial J}{\partial x}\delta x$$ **(δx is small)**

as δt → 0

$$\delta C_B = \frac{(J_1 - J_2) A\delta t}{A\delta x}$$

$$\boxed{\frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}}$$

substituting Fick's 1st law gives

$$J_B = -D\frac{\partial C_B}{\partial x}$$

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left(D_B \frac{\partial C_B}{\partial x}\right)$$

If variation of D with concentration can be ignored,

$$\boxed{\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}}$$

Fick's Second Law

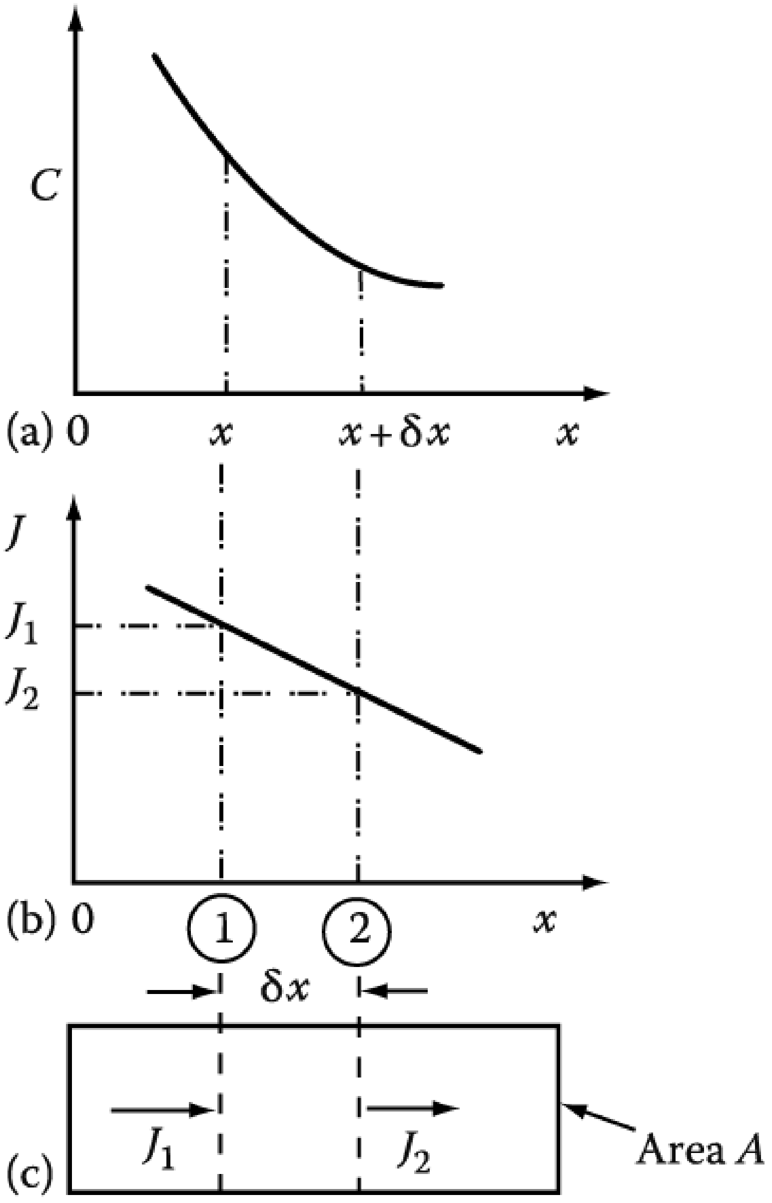
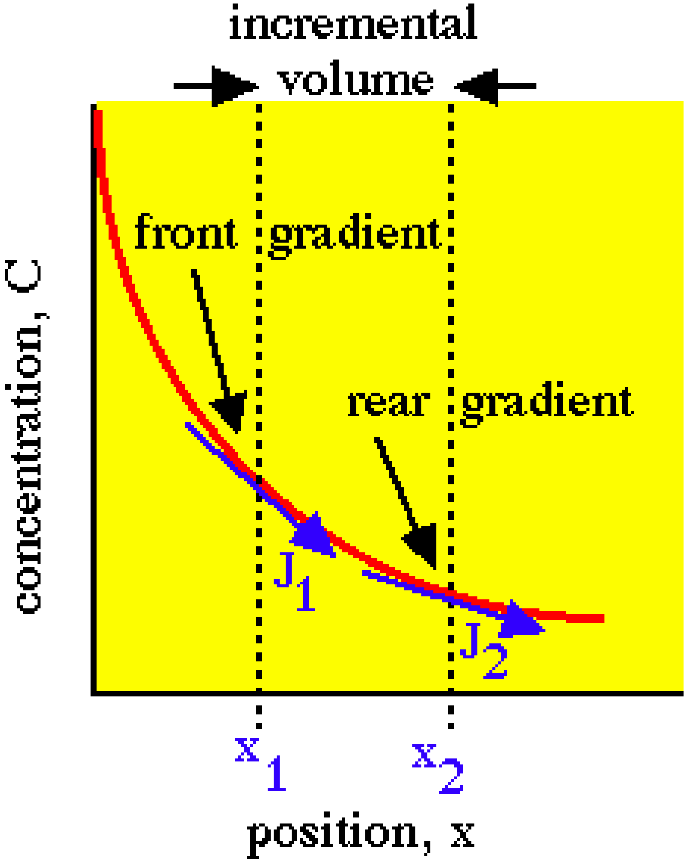


Fig. 2.8 The derivation of Fick's second law

Fick's Second Law

$$\boxed{\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}}$$

➡ **Concentration varies with time and position.**



$$\frac{\partial^2 C_B}{\partial x^2} = ?$$

Note that $\frac{\partial^2 C_B}{\partial x^2}$ is the <u>curvature</u> of the C_B versus x curve.

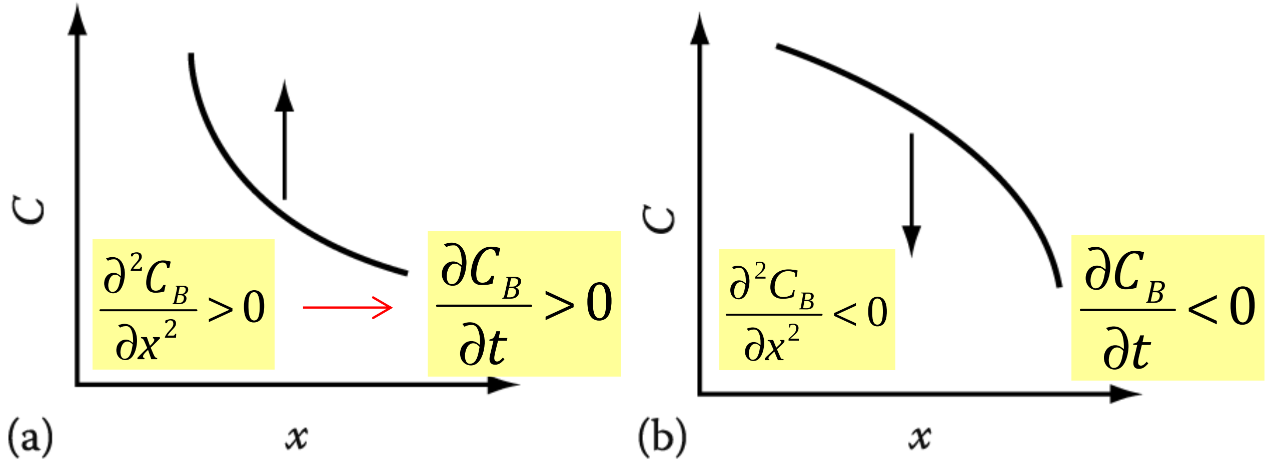


Fig. 2.9

All concentration increase with time

All concentration decrease with time

Q6. How to solve the diffusion equations?

: Application of Fick’s 2nd law

homogenization, carburization, decarburization, diffusion across a couple

2.2.5

Solutions to the diffusion equations (Application of Fick's 2nd law)

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

Ex1. Homogenization

of sinusoidal varying composition

in the elimination of segregation in casting

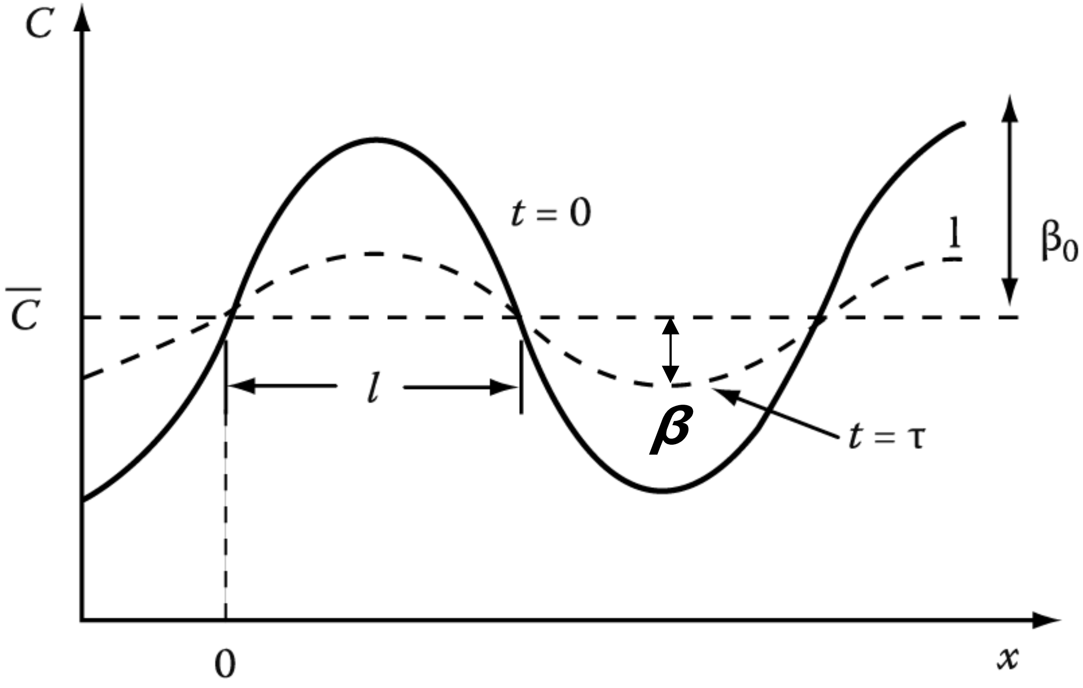


Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

Initial or Boundary Cond.?

$$C = \overline{C} + \beta_0 \sin\frac{\pi x}{l}$$ **at t=0**

$\overline{C}$: the mean composition

l : **half wavelength**

β_0 : the amplitude of the initial concentration profile

Rigorous solution of $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$ for $C(x,0) = \overline{C} + \beta_0 \sin\frac{\pi x}{l}$

Using a method of variable separation

Let $C = XT$ $\longrightarrow$ $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$

$$X\frac{dT}{dt} = DT\frac{d^2X}{dx^2}$$

$$\boxed{\frac{1}{DT}\frac{dT}{dt}} = \boxed{\frac{1}{X}\frac{d^2X}{dx^2}} \equiv -\lambda^2$$

$$\frac{1}{T}\frac{dT}{dt} = -\lambda^2 D$$

$$\frac{d\ln T}{dt} = -\lambda^2 D$$

$$T = T_0 e^{-\lambda^2 Dt}$$

$$\frac{d^2X}{dx^2} + \lambda^2 X = 0$$

$$X = A'\cos\lambda x + B'\sin\lambda x$$

$$\boxed{\mathrm{X}(\mathrm{x},0) \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l}}$$

$$\therefore C = (A\cos\lambda x + B\sin\lambda x)e^{-\lambda^2 Dt}$$

$$\therefore C = A_0 + \sum_{n=1}^{\infty}(A_n \sin\lambda_n x + B_n \cos\lambda_n x)$$

$$t = 0 \rightarrow C \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l} \qquad \lambda = \frac{\pi}{l}$$

$$;A_0 = \overline{C},\ B_n = 0,\ A_1 = \beta_0$$

$(\mathrm{A}_\mathrm{n} = 0$ for all others)

$$\therefore C \equiv \overline{C} + \beta_0 \sin\frac{\pi x}{l} e^{-\frac{t}{\boxed{l^2/\pi^2 D}}}$$

$$\boxed{C = \overline{C} + \beta_0 \sin\frac{\pi x}{l}\exp\left(\frac{-t}{\boxed{\tau}}\right)}$$

$$\tau = \frac{l^2}{\pi^2 D}$$ τ : relaxation time

$$\beta = \beta_0 \exp(-t/\tau) \quad at \quad x = \frac{l}{2}$$

Solutions to the diffusion equations

Ex1. Homogenization of sinusoidal varying composition in the elimination of segregation in casting

$$C = \bar{C} + \beta_0 \sin\frac{\pi x}{l} \quad \textbf{at t=0}$$

$$\boxed{C = \bar{C} + \beta_0 \sin\frac{\pi x}{l} \exp\left(\frac{-t}{\tau}\right)}$$

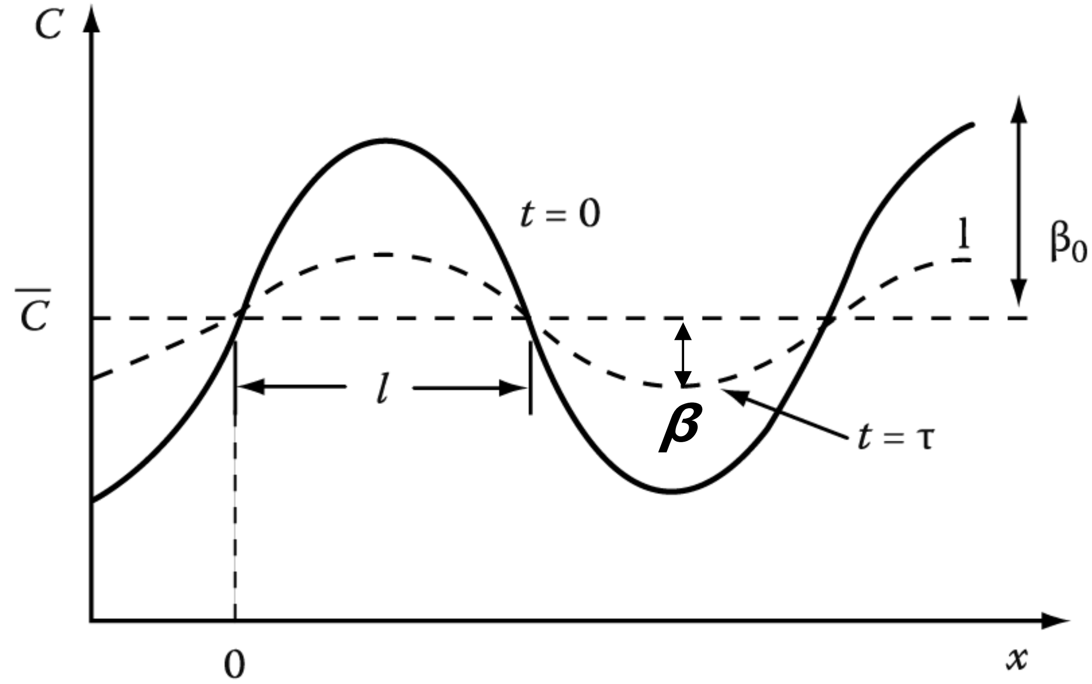


Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

$$\beta = \beta_0 \exp(-t/\tau) \quad at \quad x = \frac{l}{2}$$

Amplitude of the concentration profile (β) decreases exponentially with time, $C \Rightarrow \bar{C}$

$$\tau = \frac{l^2}{\pi^2 D} \qquad \tau : \text{relaxation time}$$

decide homogenization rate

The initial concentration profile will not usually be sinusoidal, but in general any concentration profile can be considered as the sum of an infinite series of sine waves of varying wavelength and amplitude, and each wave decays at a rate determined by its own "τ". Thus, the short wavelength terms die away very rapidly and the homogenization will ultimately be determined by τ for the longest wavelength component.

Solutions to the diffusion equations

Ex2. Carburization of Steel

The aim of carburization is to increase the carbon concentration in the surface layers of a steel product in order to achiever a harder wear-resistant surface.

1. Holding the steel in CH_4 and/or Co
   at an austenitic temperature.

2. By controlling gases the concentration
   of C at the surface of the steel can be
   maintained at a suitable constant value.

3. At the same time carbon continually
   diffuses from the surface into the steel.

Carburizing of steel

Depth of Carburization?

1) Specimen ~ infinitely long.
2) Diffusion coefficient of carbon in austenite increases with increasing concentration, but an approximate solution: Taking an average value

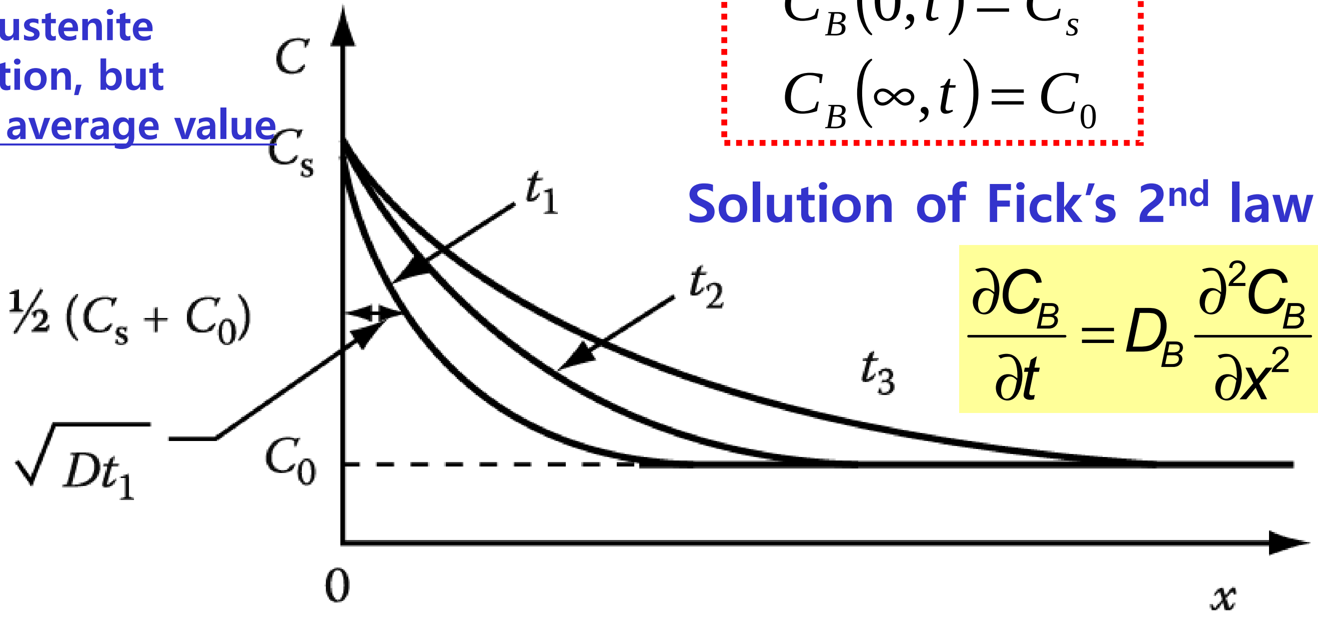
The error function solution:

$$\boxed{C = C_s - (C_s - C_0)\,erf\left(\frac{x}{2\sqrt{Dt}}\right)}$$

$$erf\,(Z) = \frac{2}{\sqrt{\pi}}\int_0^Z e^{-y^2}\,dy$$

* Concentration profile
: using boundary conditions

$$\boxed{\begin{aligned} C_B(0,t) &= C_s \\ C_B(\infty,t) &= C_0 \end{aligned}}$$



Solution of Fick's 2nd law

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

Fig. 2.11 Concentration profiles at successive times ($t_3>t_2>t_1$) for diffusion into a semi-infinite bar when the surface concentration Cs is maintained constant.

$$\frac{C_s - C}{C_s - C_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

erf(0.5)≈0.5

$$C = \frac{C_s + C_0}{2}$$

- Since erf(0.5)≈0.5, the depth at which the carbon concentration is midway between C_s and C_0 is given $(x/2\sqrt{Dt}) \cong 0.5$

that is $x \cong \sqrt{Dt}$ → **Depth of Carburization**

Error function

In mathematics, the error function (also called the Gauss error function) is a non-elementary function which occurs in probability, statistics and partial differential equations.

It is defined as:

$$\boxed{\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\,dt.}$$

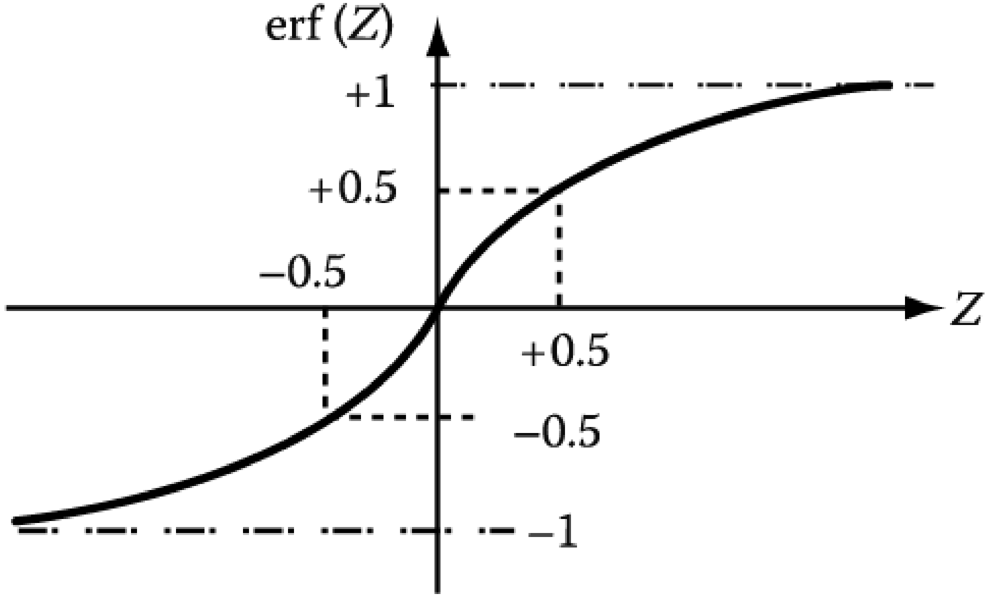
By expanding the right-hand side in a Taylor series and integrating, one can express it in the form

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{(2n+1)n!} = \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3} + \frac{x^5}{10} - \frac{x^7}{42} + \frac{x^9}{216} - \cdots \right)$$

for every real number x. **(From Wikipedia, the free encyclopedia)**

Error function

$$\operatorname{erf}(z)=\frac{2}{\sqrt{\pi}}\int_{0}^{z}\exp(-y^{2})dy$$



(a) Schematic diagram illustrating the main features of the error function.

Fig. 2.12

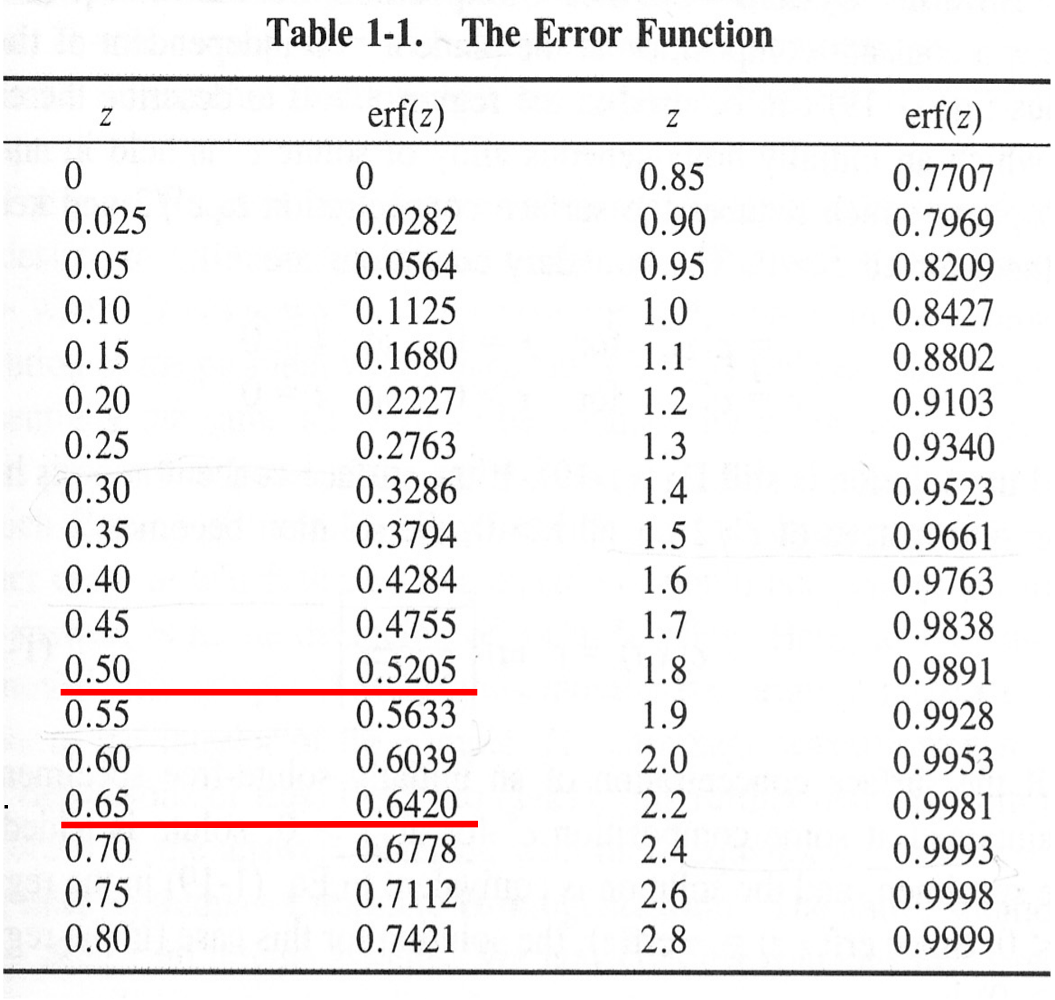


Table 1-1. The Error Function

z	erf(z)	z	erf(z)
0	0	0.85	0.7707
0.025	0.0282	0.90	0.7969
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3286	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

Carburizing of steel

Depth of Carburization?

1) Specimen ~ infinitely long.
2) Diffusion coefficient of carbon in austenite increases with increasing concentration, but an approximate solution: Taking an average value

* Concentration profile
: using boundary conditions

$$C_B(0,t) = C_s$$
$$C_B(\infty,t) = C_0$$

⇨ **Solution of Fick's 2nd law**

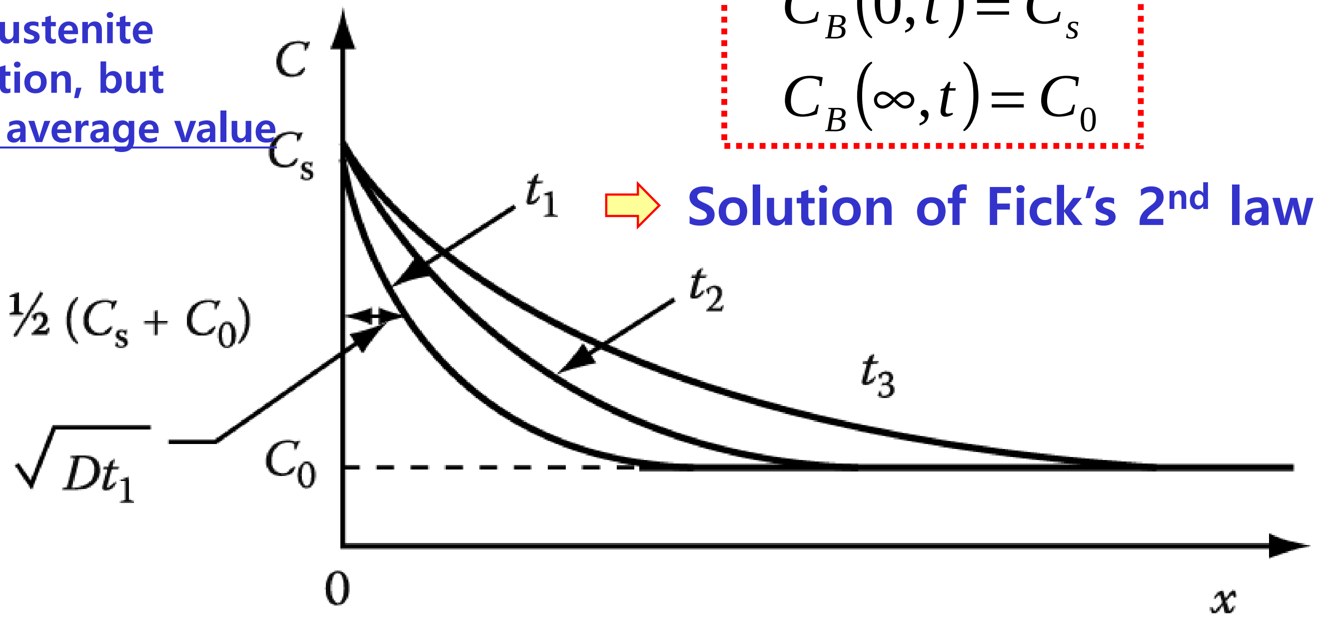


Fig. 2.11 Concentration profiles at successive times ($t_3>t_2>t_1$) for diffusion into a semi-infinite bar when the surface concentration Cs is maintained constant.

The error function solution:

$$C = C_s - (C_s - C_0)\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$erf(Z) = \frac{2}{\sqrt{\pi}}\int_0^Z e^{-y^2}\,dy$$

$$\frac{C_s - C}{C_s - C_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

erf(0.5)≈0.5

$$C = \frac{C_s + C_0}{2}$$

- Since erf(0.5)≈0.5, the depth at which the carbon concentration is **midway between C_s and C_0** is given $(x/2\sqrt{Dt}) \cong 0.5$

that is $x \cong \sqrt{Dt}$ → **Depth of Carburization**

Carburizing of steel

Thus the thickness of the carburized layer is $\cong \sqrt{Dt}$.

Note also that the depth of any is concentration line is directly proportion to $\sqrt{Dt}$, i.e. *to obtain a twofold increase in penetration requires a fourfold increase in time.*

(2배의 침투 깊이 → 4배의 시간)

Ex.3 Decarburization of Steel?

$$C = C_0 erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

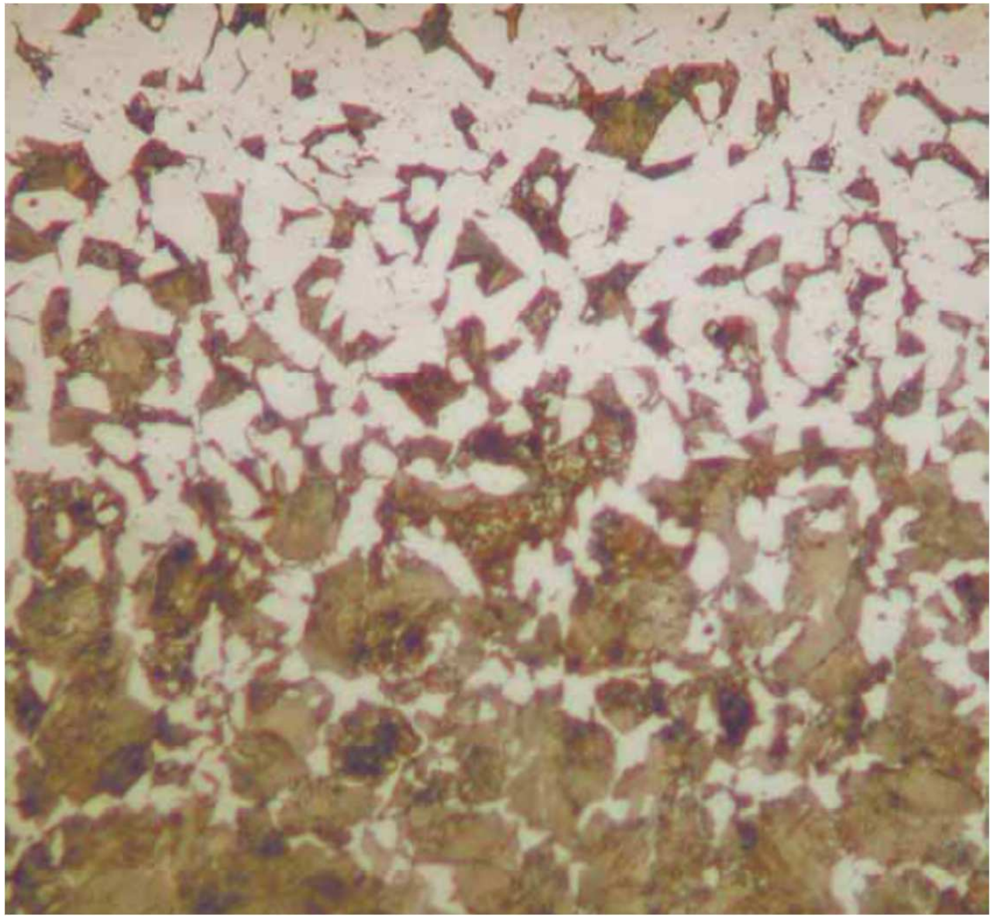
↕

$$C = C_s - (C_s - C_0) erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Carburization

$$erf(Z) = \frac{2}{\sqrt{\pi}} \int_0^Z e^{-y^2} dy$$

C_S = Surface concentration
C_0 = Initial bulk concentration



Solutions to the diffusion equations

Ex4. Diffusion Couple

Joining of two semi-infinite specimens of compositions C_1 and C_2 ($C_1 > C_2$)

Draw C vs. x with time t = 0 and t > 0.

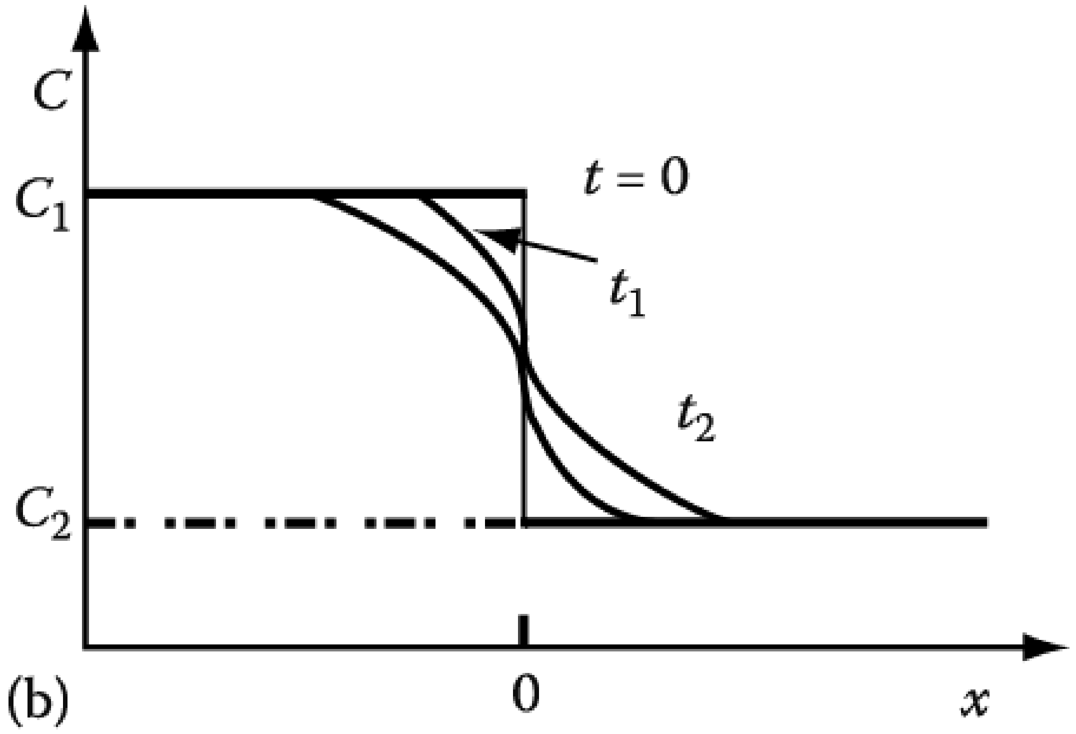


Fig. 2.12 (b) concentration profiles at successive times (t2>t1>0)
when two semi-infinite bars of different composition are annealed after welding.

Boundary conditions?

$$C = C_1 \quad t = 0, \; -\infty < x < 0$$

$$C = C_2 \quad t = 0, \; 0 < x < \infty$$

$$C = C_1 \quad x = -\infty, \; 0 < t < \infty$$

$$C = C_2 \quad x = \infty, \; 0 < t < \infty$$

$$\boxed{C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right) erf\left(\frac{x}{2\sqrt{Dt}}\right)}$$

The section is completed with **4 example solutions to Fick's 2nd law:** *carburisation, decarburisation, diffusion across a couple* and *homogenisation*.

The solutions given are as follows:

Process	**Solution**
Homogenization	$C = C_{mean} + \beta_0 \sin\left(\frac{\pi x}{l}\right) \exp\left(-\frac{t}{\tau}\right)$ C_{mean} = Mean concentration b_0 = Initial concentration amplitude l = half-wavelength of cells t = relaxation time
Carburization	$C = C_S - (C_S - C_0)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_S = Surface concentration C_0 = Initial bulk concentration
Decarburization	$C = C_0\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_0 = Initial bulk concentration
Diffusion Couple	$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right)\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ C_1 = Concentration of steel 1 C_2 = Concentration of steel 2

Contents for today's class

- **Diffusion** Movement of atoms to reduce its chemical potential μ.

  ⇨ driving force: Reduction of G

  Down-hill diffusion movement of atoms from a high C_B region to low C_B region.

  Up-hill diffusion movement of atoms from a low C_B region to high C_B region.

- **Interstitial Diffusion** / Substitution Diffusion

  - Steady-state diffusion– Fick's First Law

$$J_B = \frac{1}{6}\Gamma_B (n_1 - n_2) = -\left(\frac{1}{6}\Gamma_B \alpha^2\right)\frac{\partial C_B}{\partial x} = -D_B \frac{\partial C_B}{\partial x}$$

  ➡ Concentration varies with position. (atoms m^{-2} s^{-1})

  - Nonsteady-state diffusion – Fick's Second Law

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

  ➡ Concentration varies with time and position.

  - For random walk in 3 dimensions,

  after n steps of length α

$$r = \alpha\sqrt{(\Gamma t)} = f(D) = 2.4\sqrt{Dt}$$

- **Effect of Temperature on Diffusivity**

$$\log D = \log D_0 - \frac{Q}{2.3R}\left(\frac{1}{T}\right)$$