2021 Fall

“Phase Transformation *in* Materials”

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Contents for previous class:

- **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) $T\uparrow$ ➡ $X_B^e\uparrow$ **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 $\Delta G_0 = -V\Delta G_V + A\gamma + V\Delta G_s$

: 변태를 위한 전체 구동력/핵생성을 위한 구동력은 아님

⇕ **Chapter 5.1**

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)

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

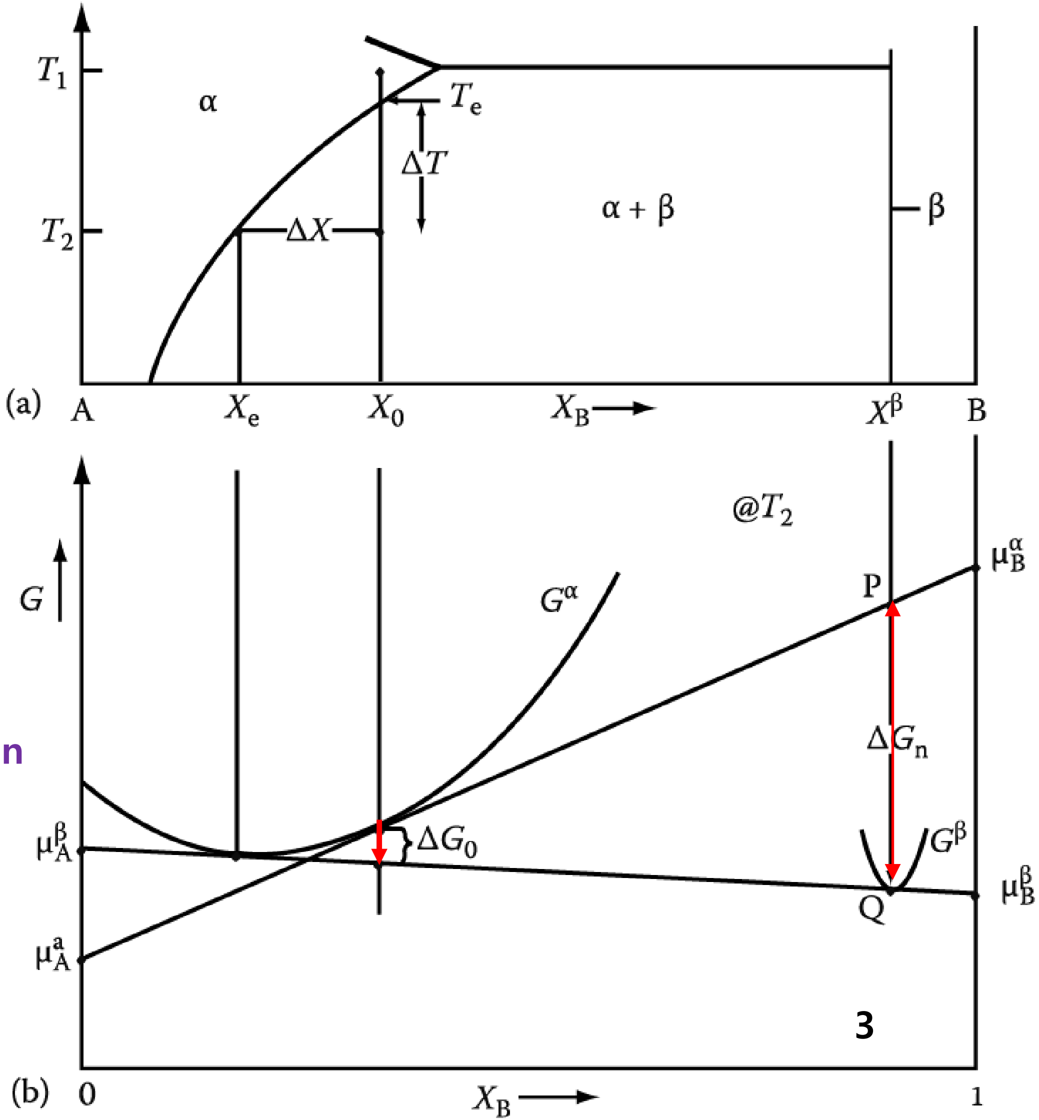
: driving force for β precipitation

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



Contents for today's class

- Ternary Phase Diagram
- Measurement of multi-component phase diagram
- Computation of Phase Diagram

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

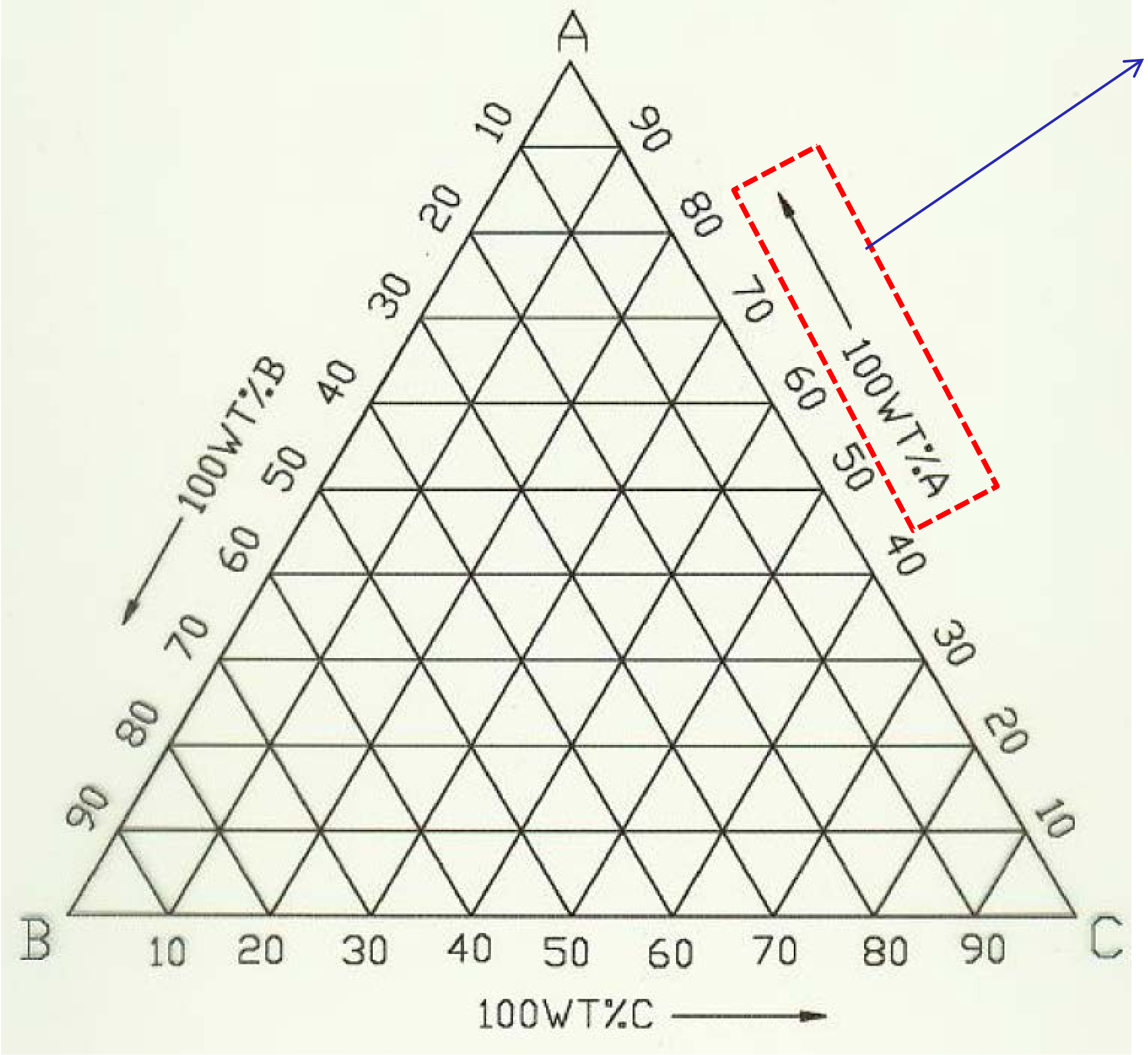
For C = 3, the maximum number of phases will co-exist when F = 0

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.

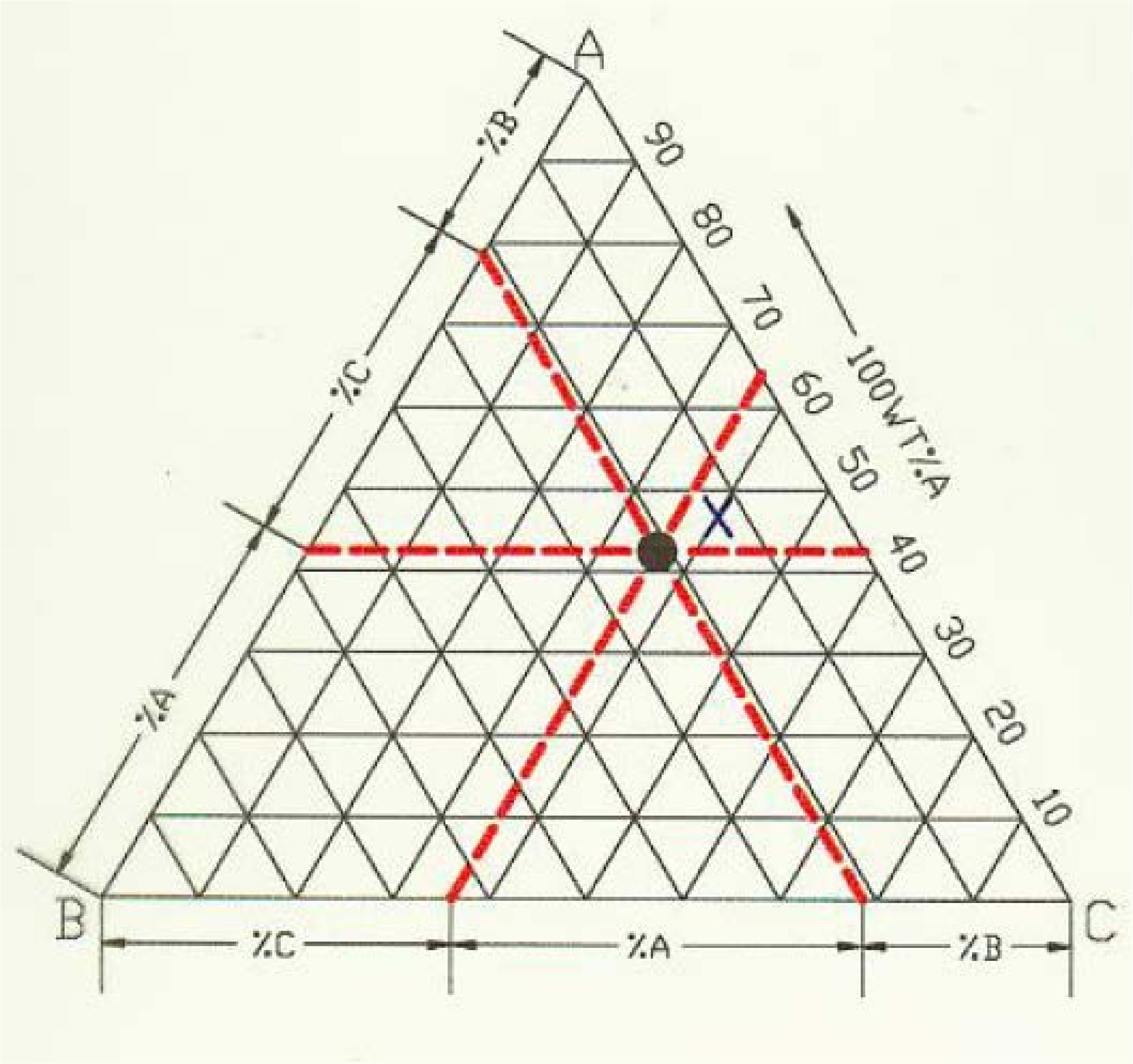


Concentration can be expressed as either “wt. %” or “at.% = molar %”.

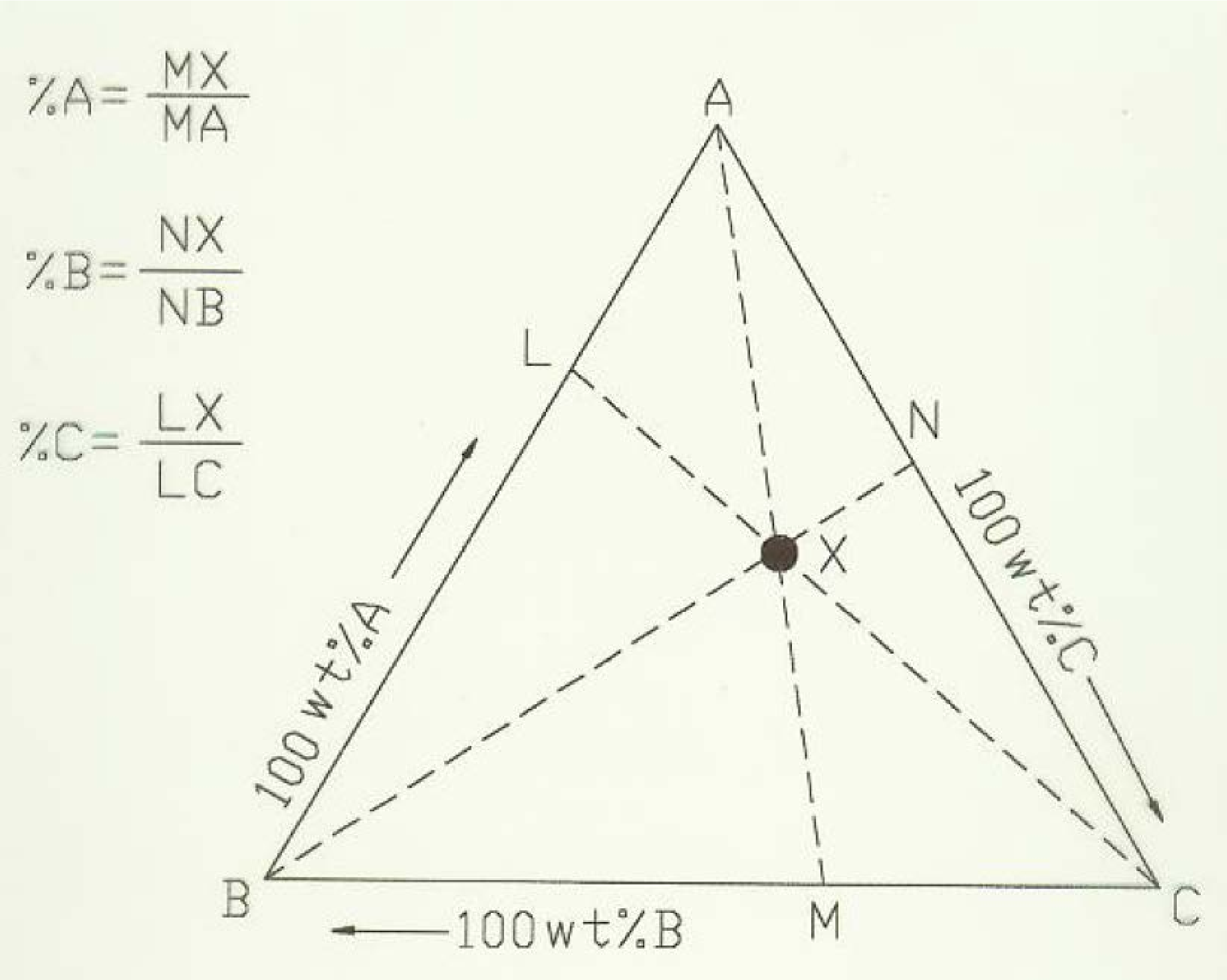
$$X_A+X_B+X_C = 1$$

Used to determine the overall composition

Overall Composition



Overall Composition



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

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

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

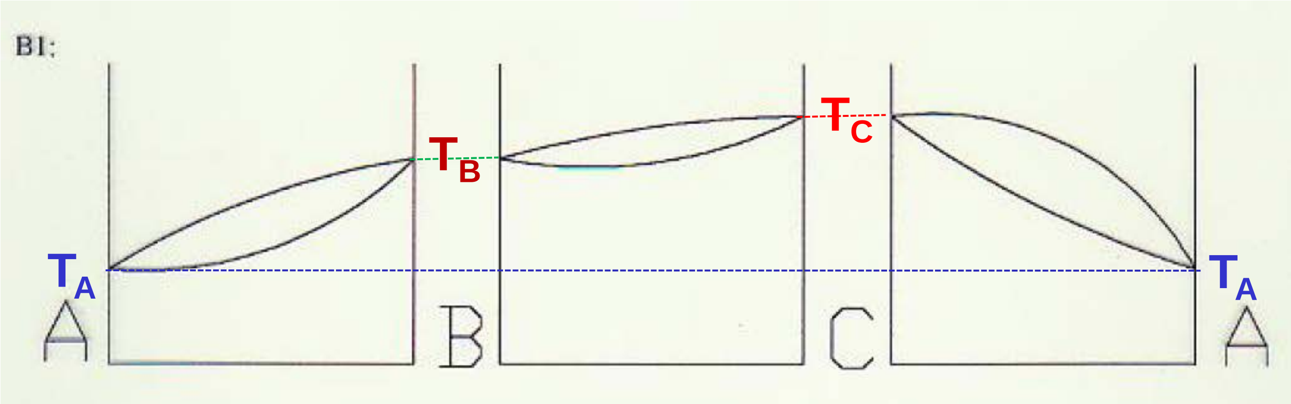
Ternary Isomorphous System

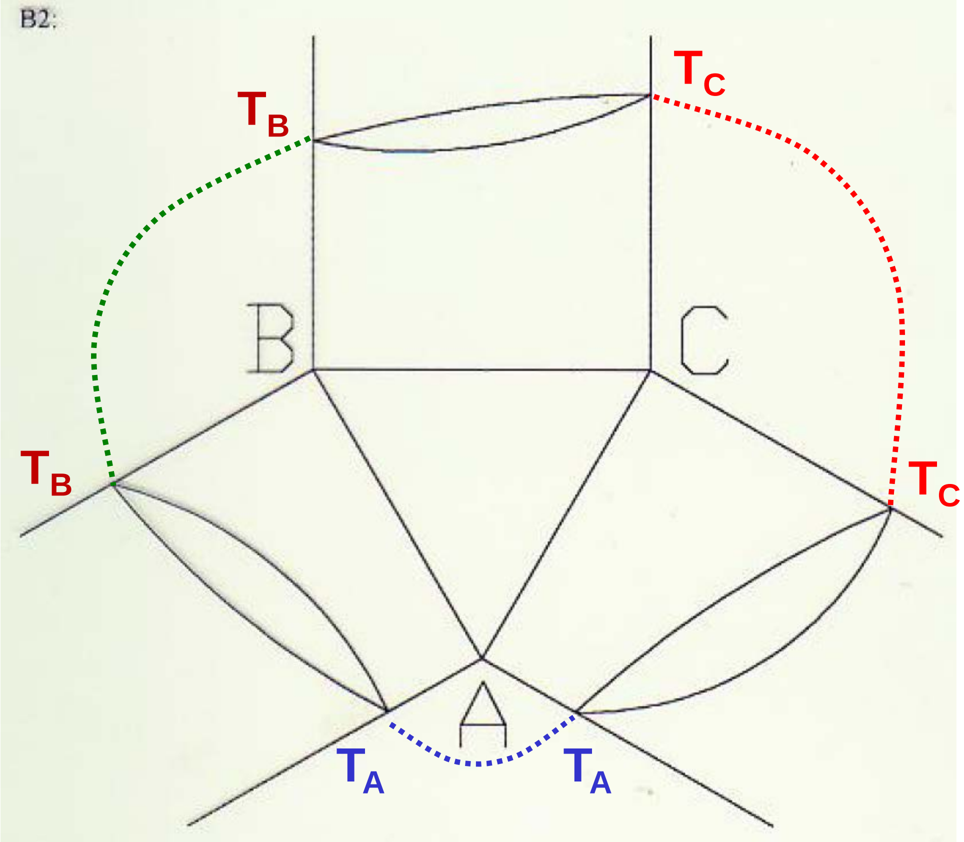
Isomorphous System: A system (ternary in this case) that has only one solid phase. All components are totally soluble in the other components. The ternary system is therefore made up of three binaries that exhibit total solid solubility.

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

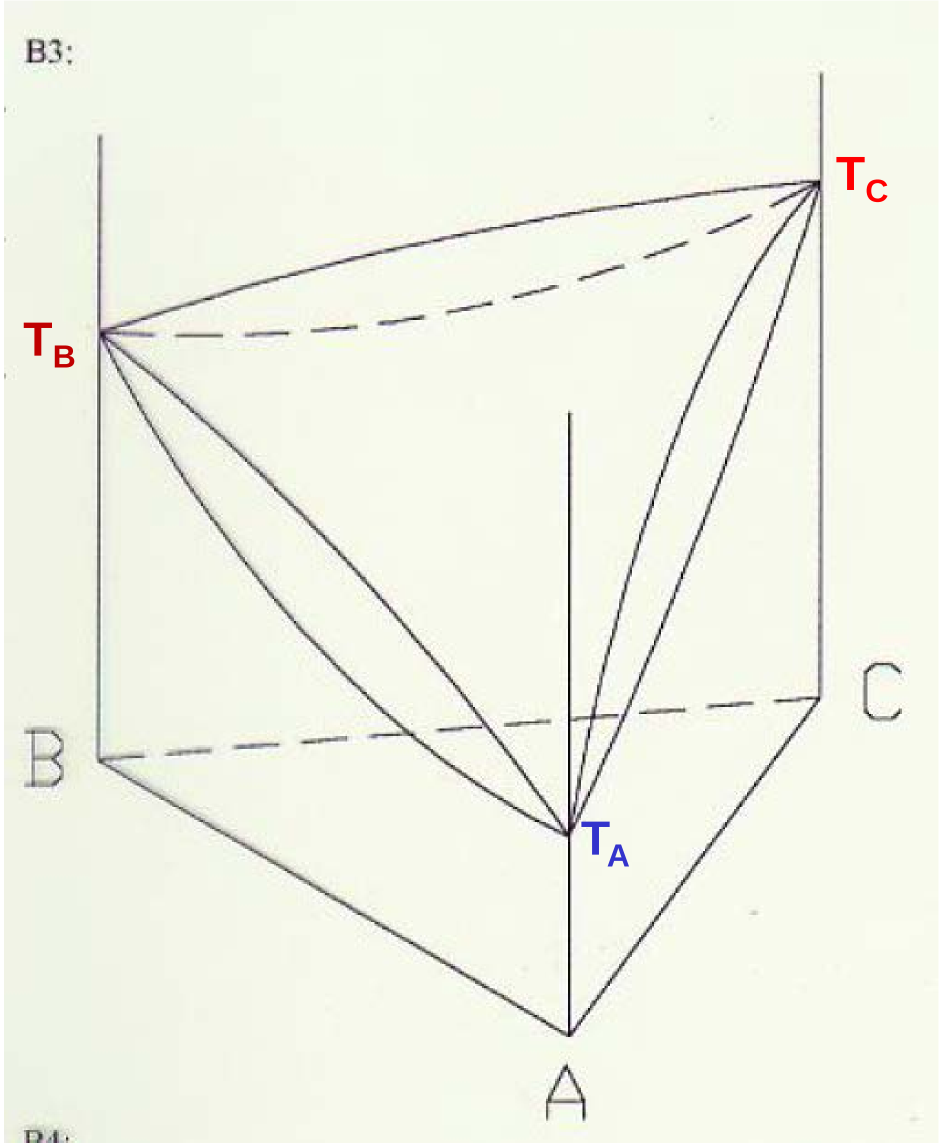
The Solidus Surface: A plot of the temperatures below which a (homogeneous) solid phase forms for any given overall composition.

Ternary Isomorphous System

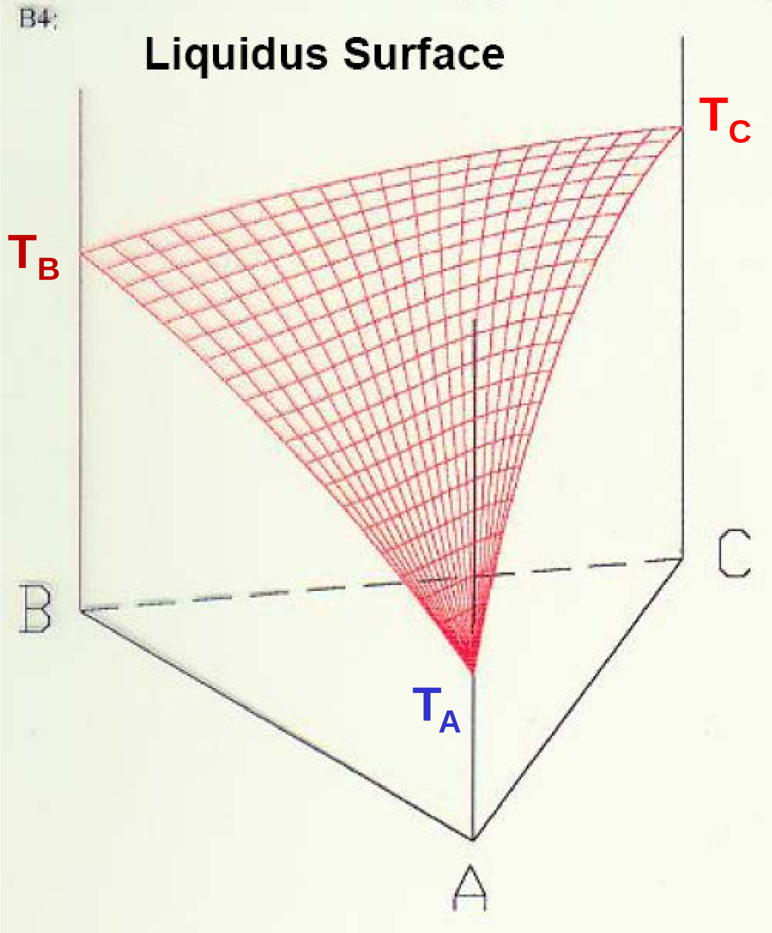


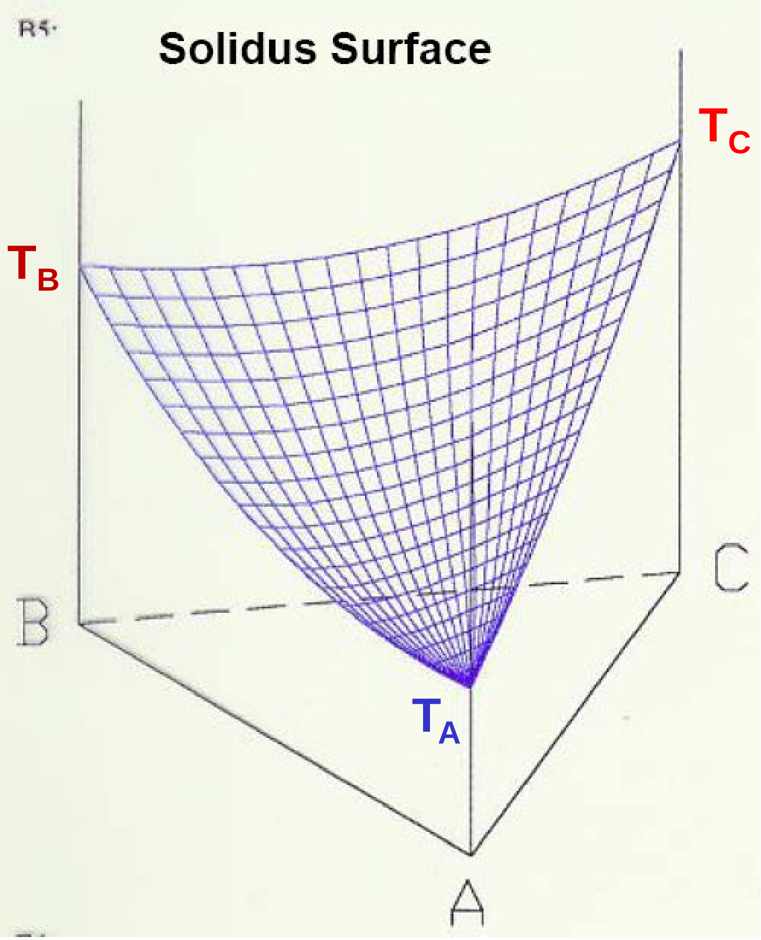


Ternary Isomorphous System

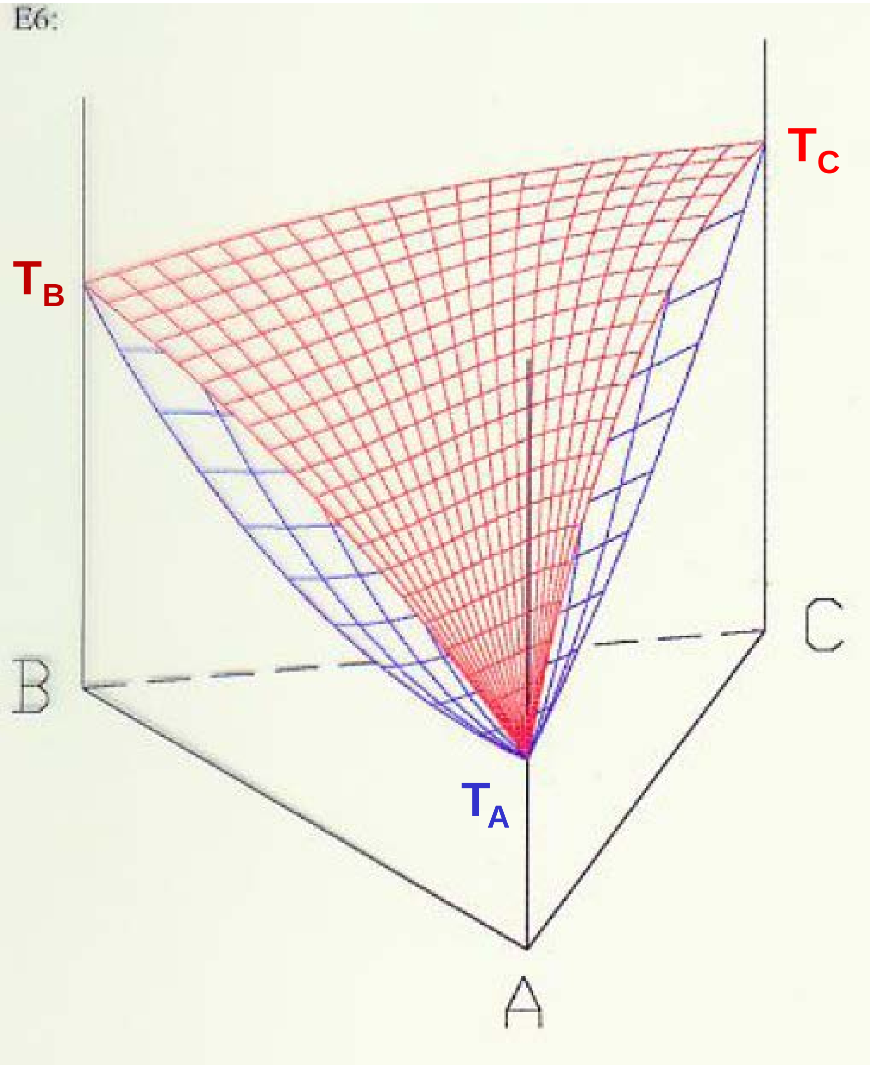


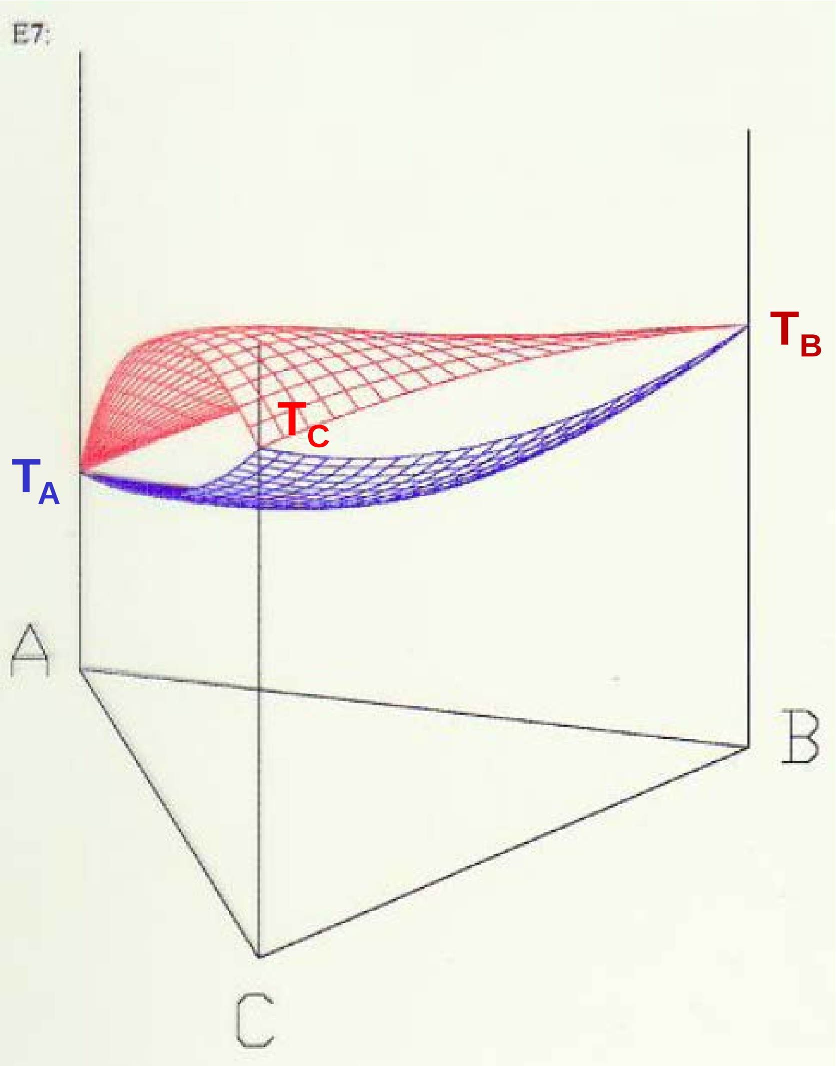
Ternary Isomorphous System


Liquidus Surface


Solidus Surface

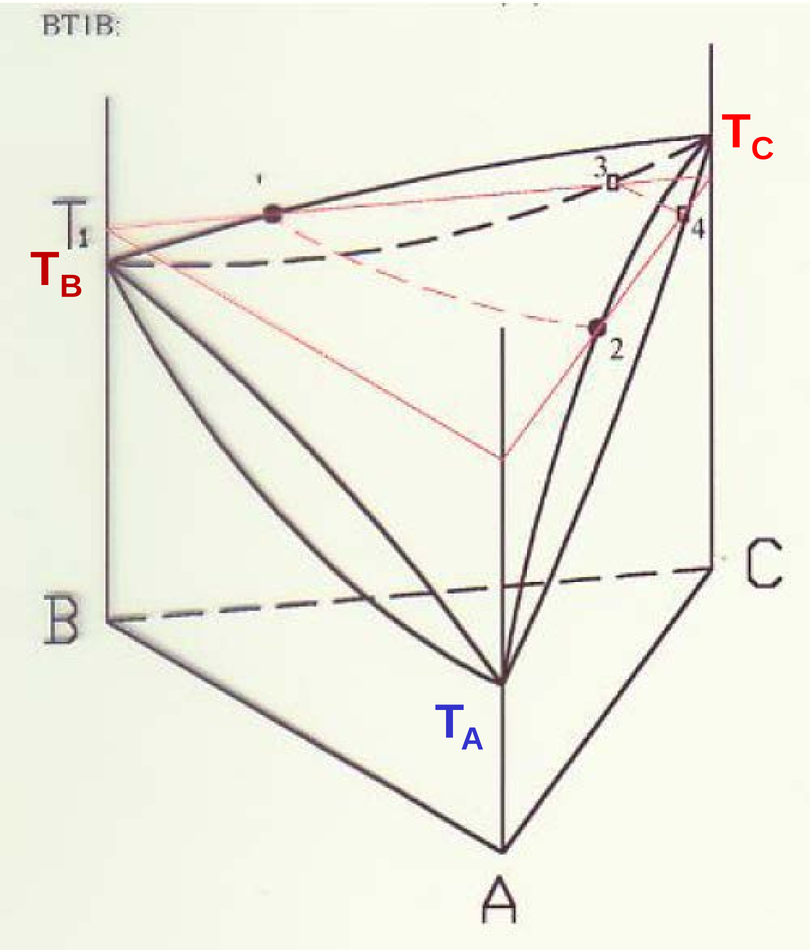
Ternary Isomorphous System

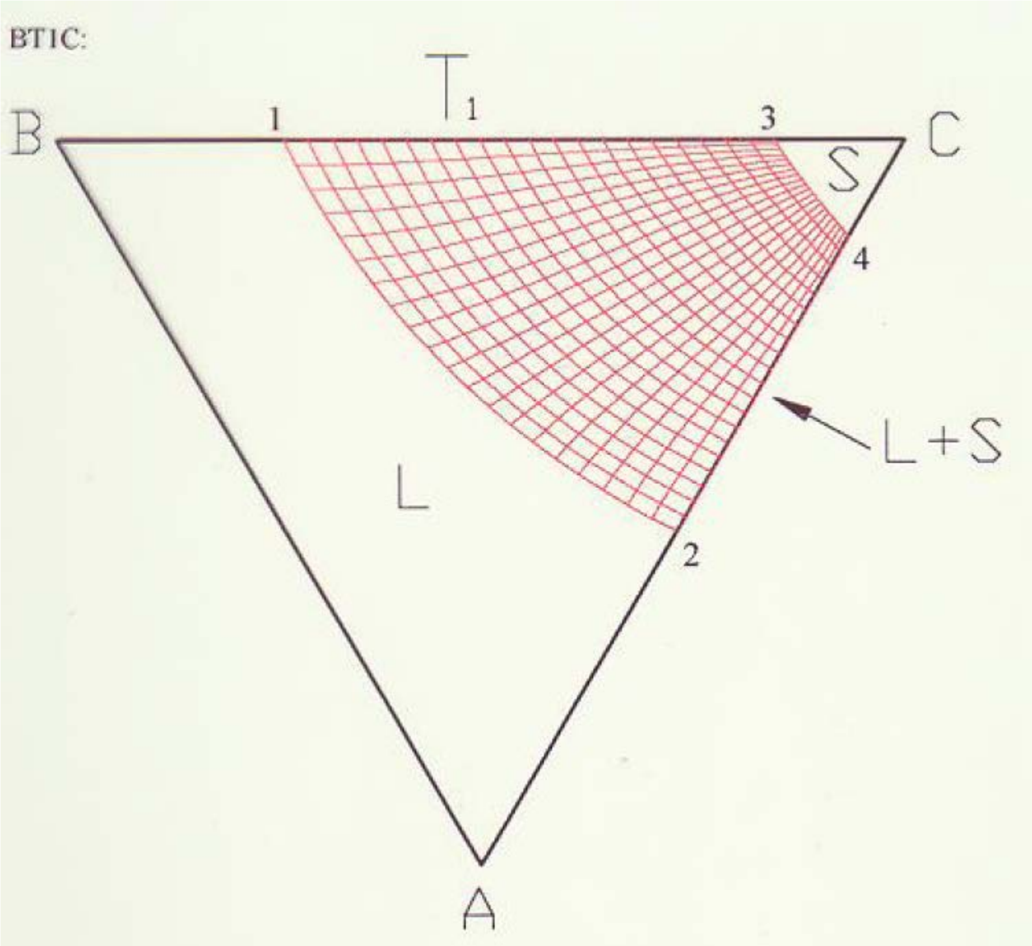




Ternary Isomorphous System

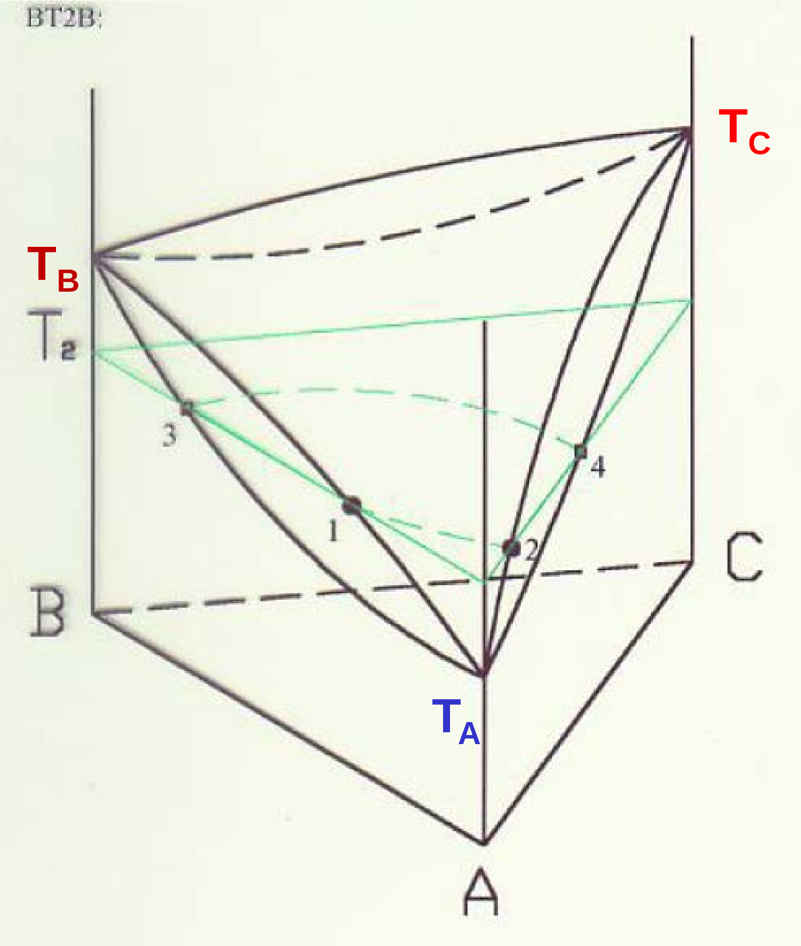
Isothermal section → $F = C - P$

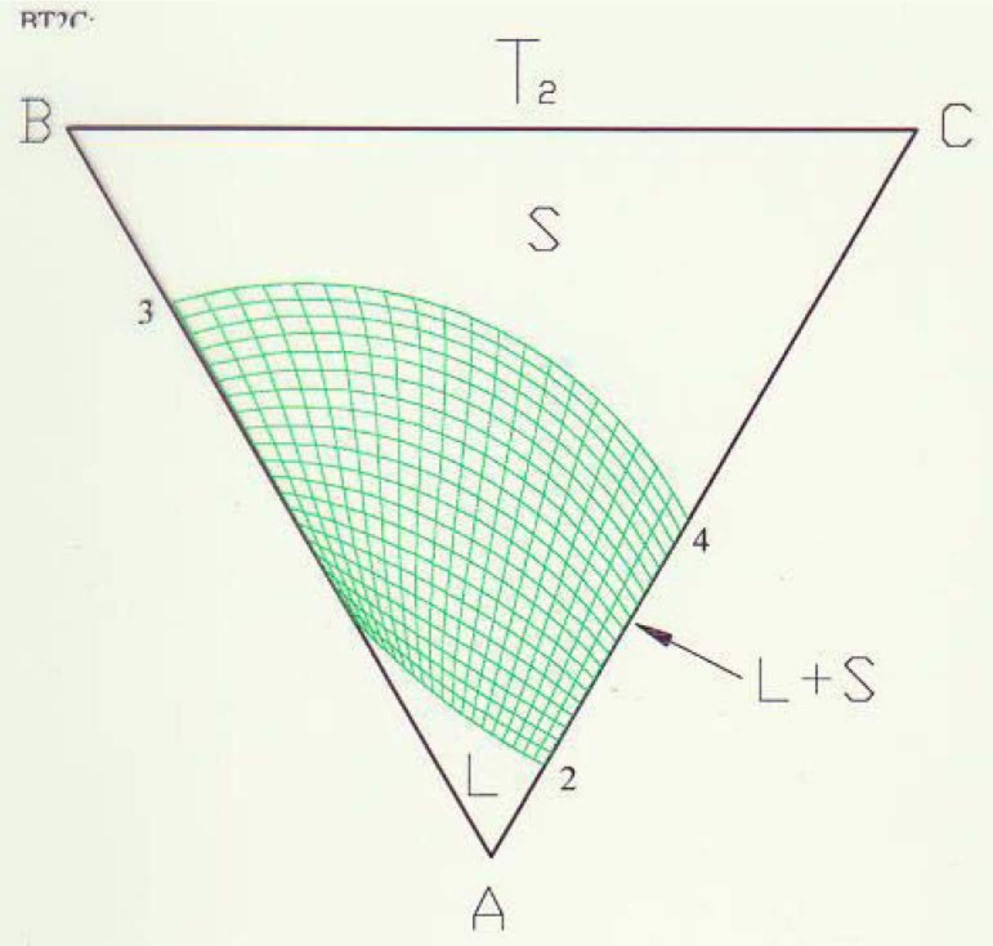




Ternary Isomorphous System

Isothermal section





Ternary Isomorphous System

Isothermal section → $F = C - P$

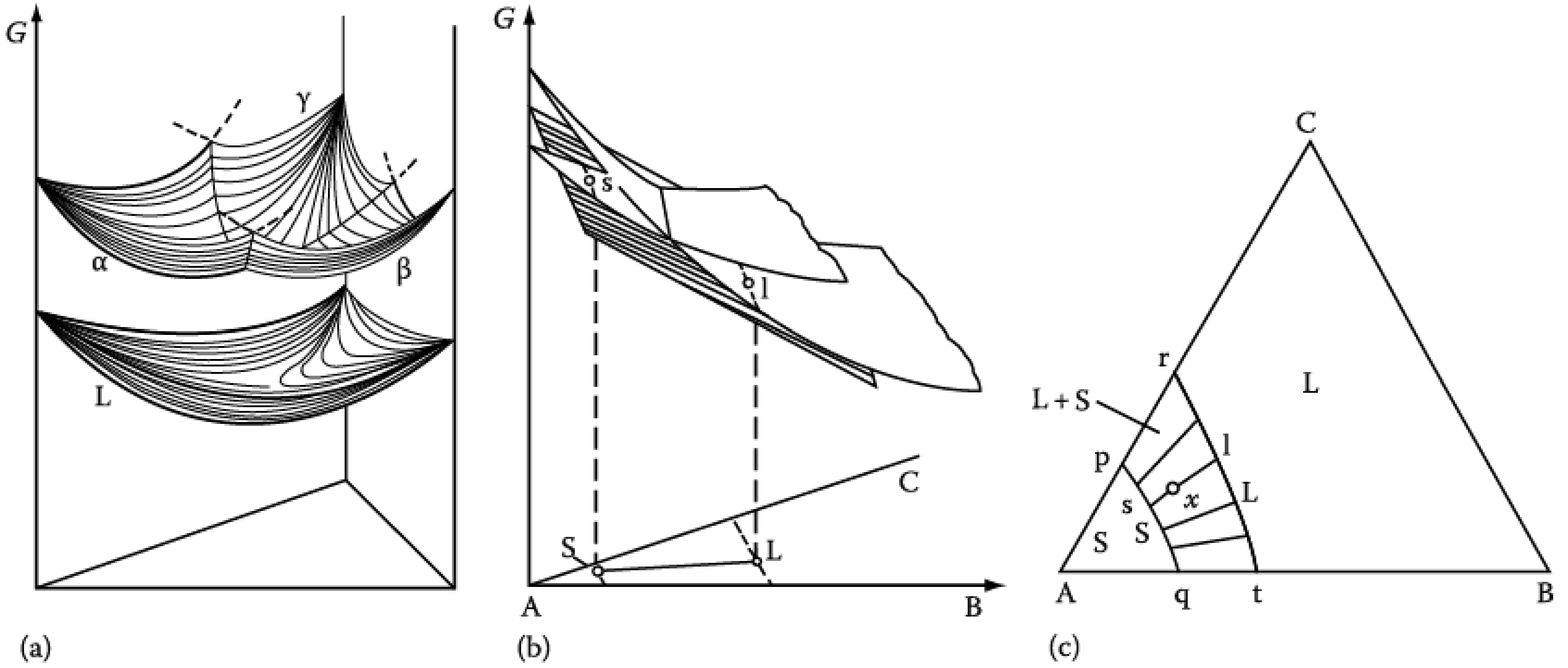


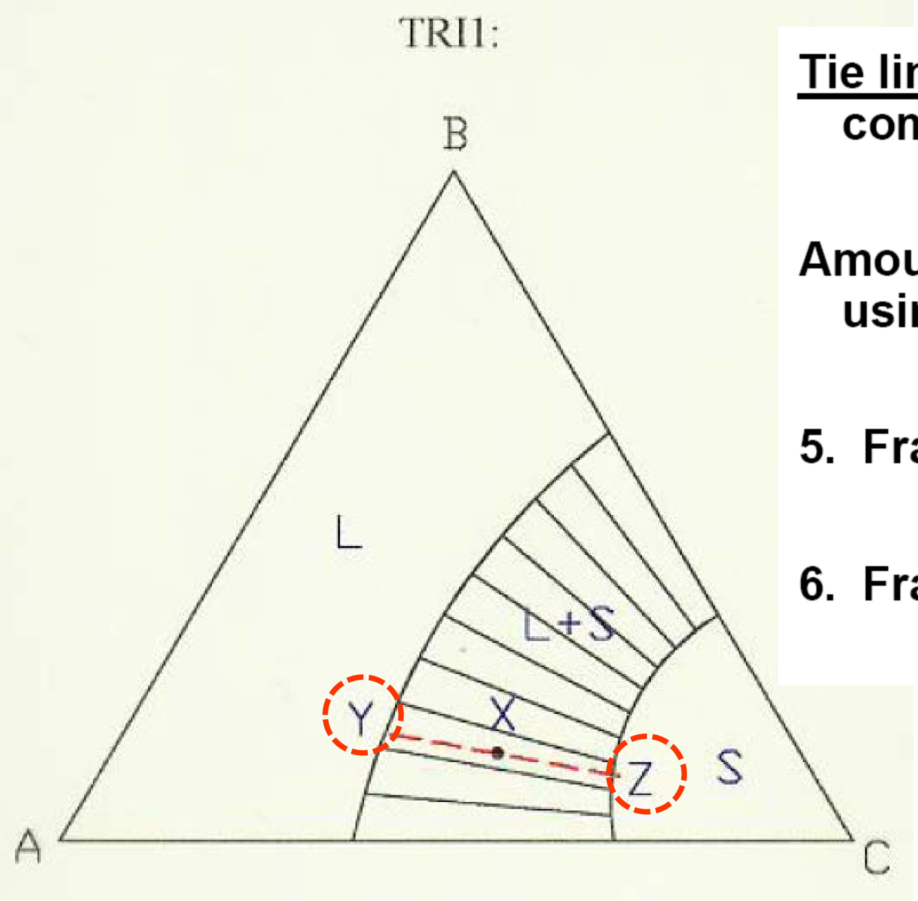
Fig. 1.41 (a) Free energy surface of a liquid and three solid phases of a ternary system.

(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:

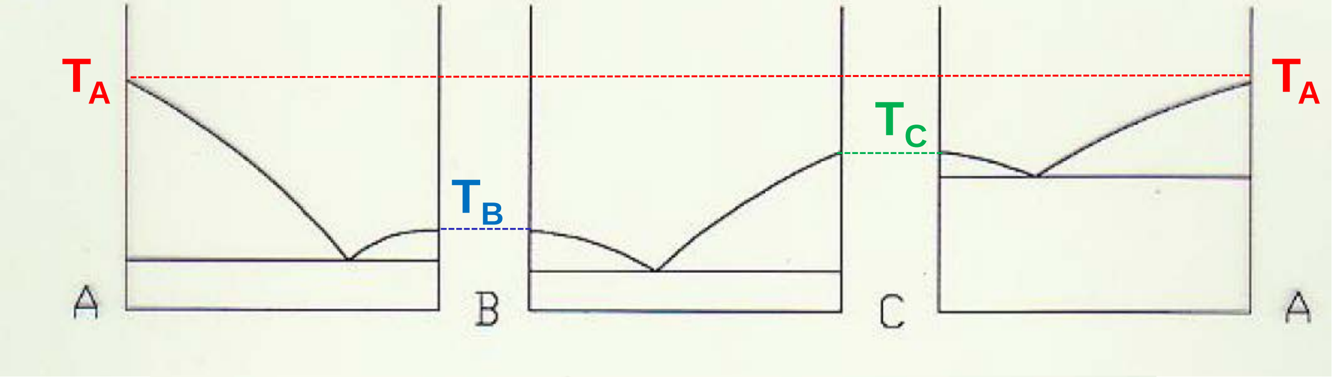
$$\boxed{L = \alpha + \beta + \gamma}$$

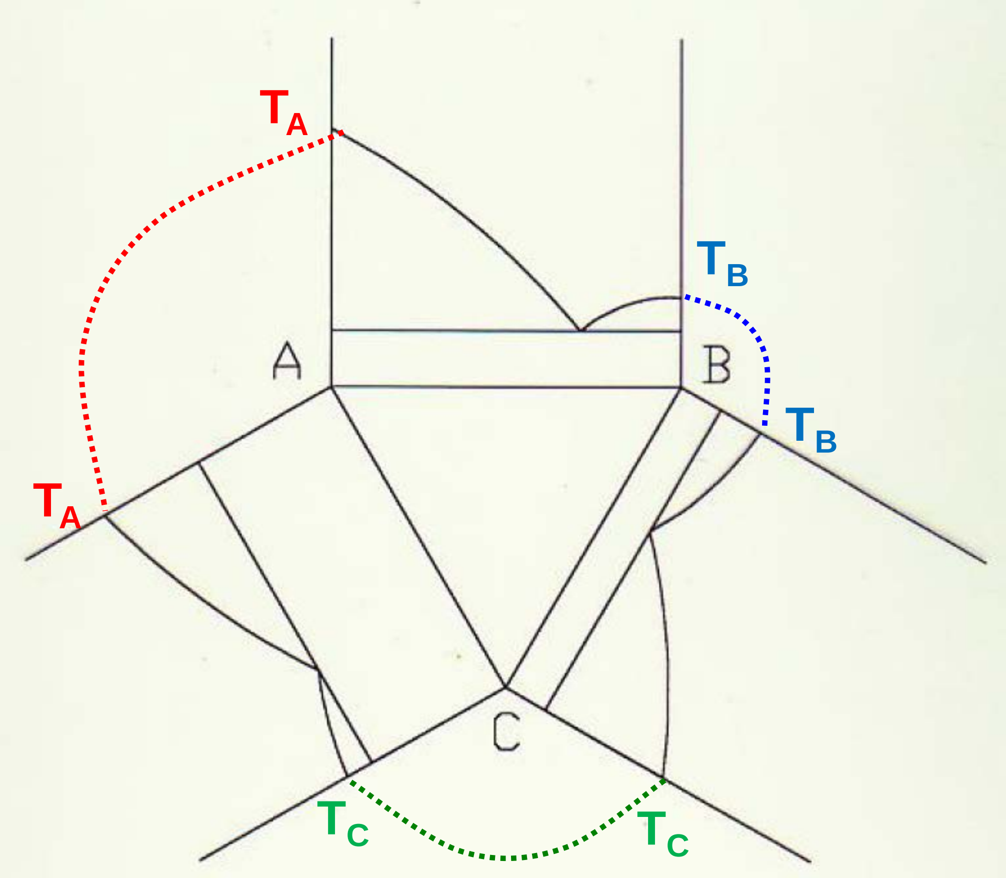
A liquid phase solidifies into three separate solid phases

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

Ternary Eutectic System

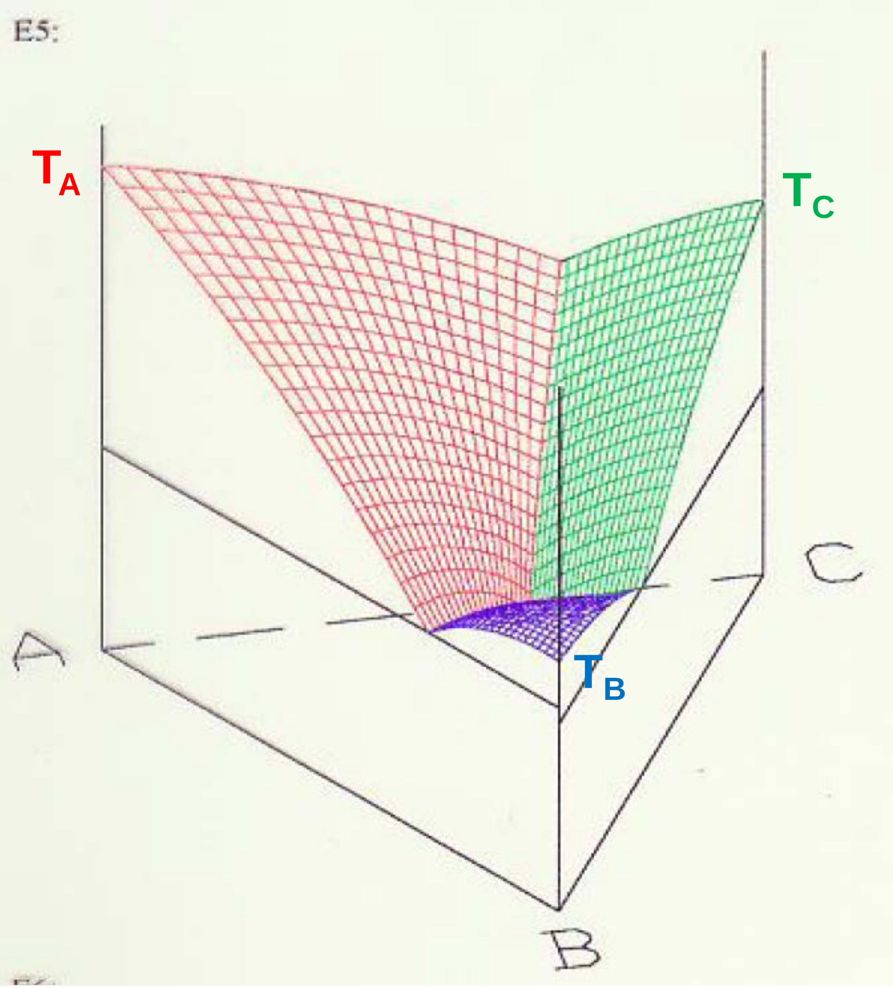
(No Solid Solubility)



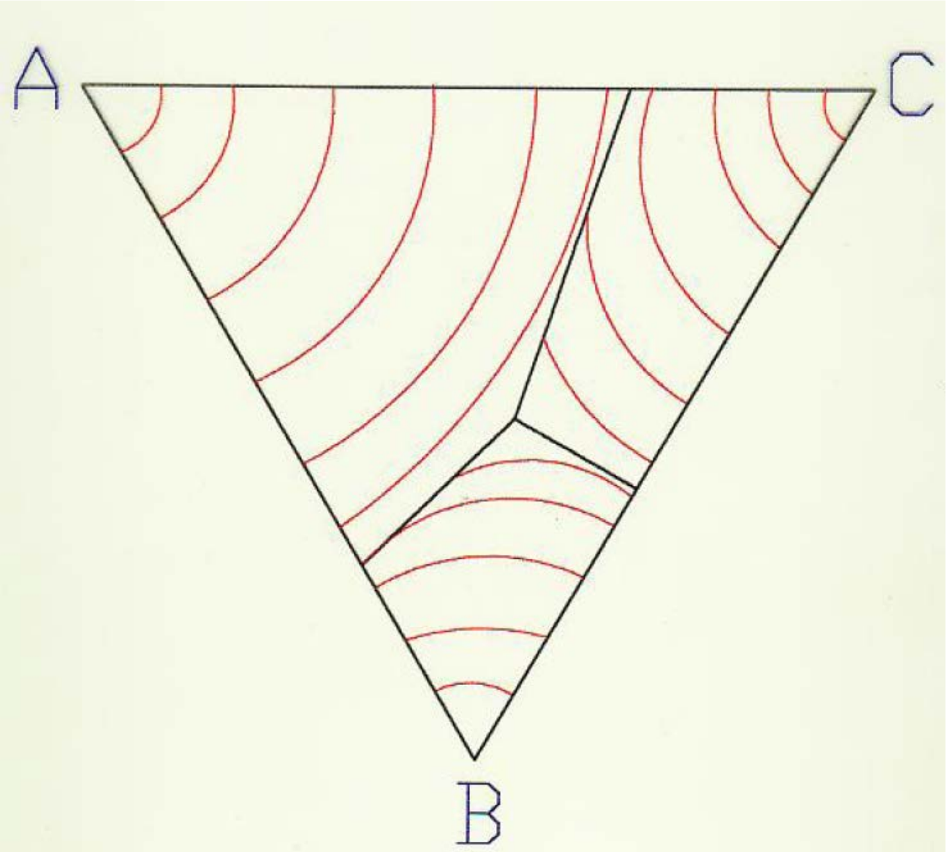


Ternary Eutectic System

(No Solid Solubility)

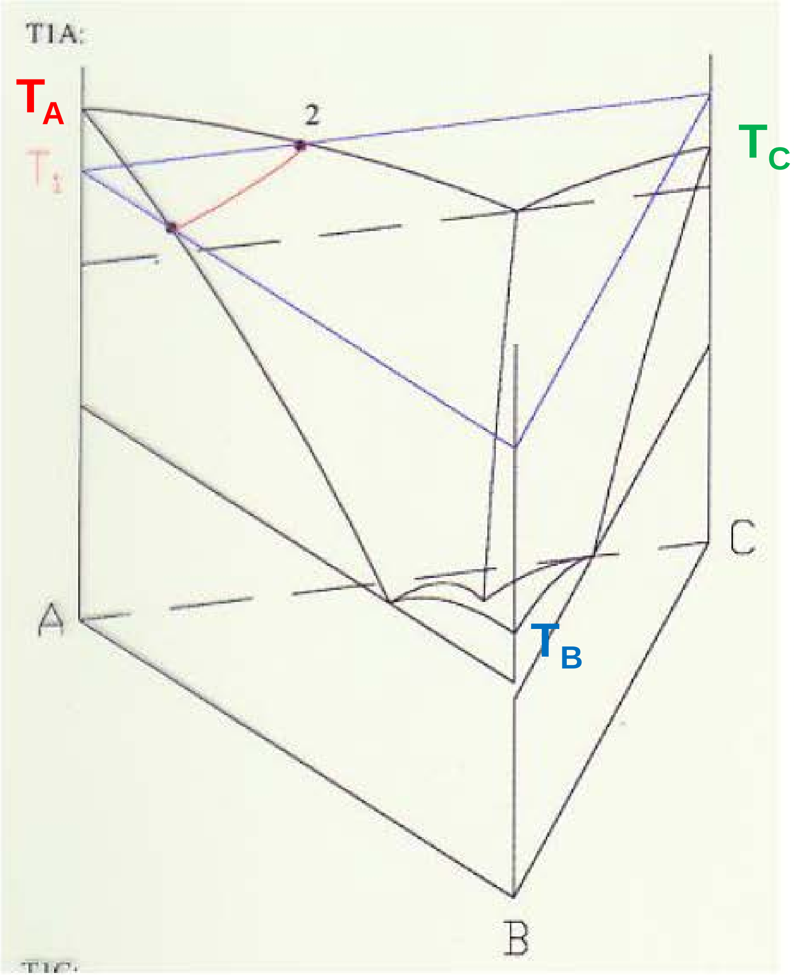


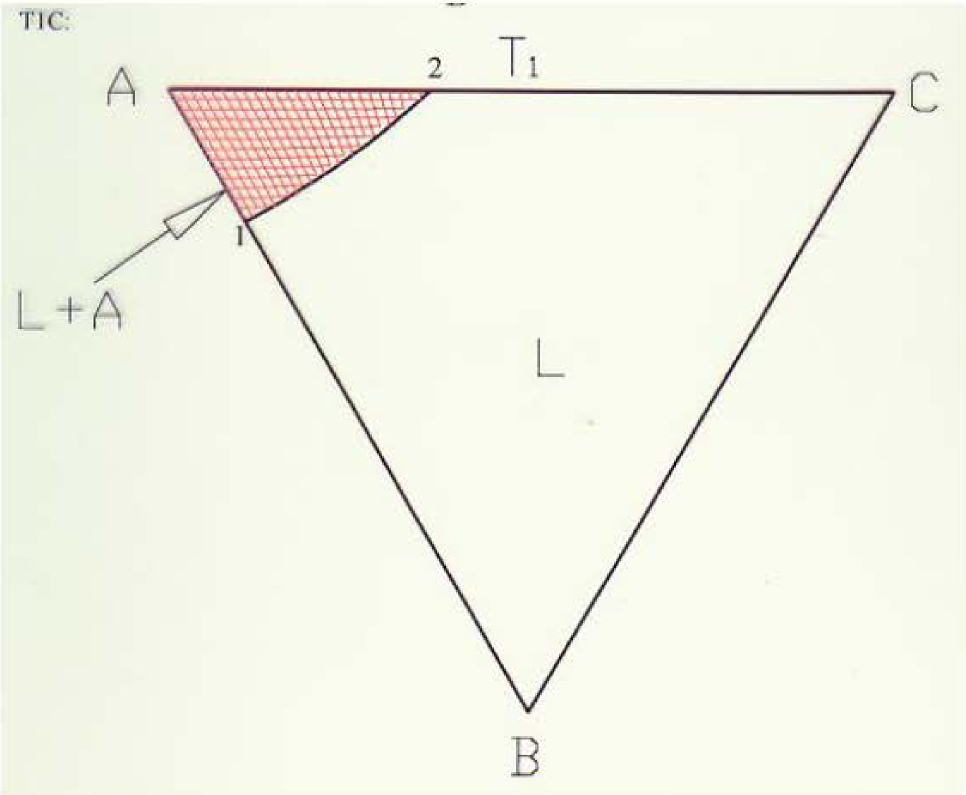
Liquidus projection



Ternary Eutectic System

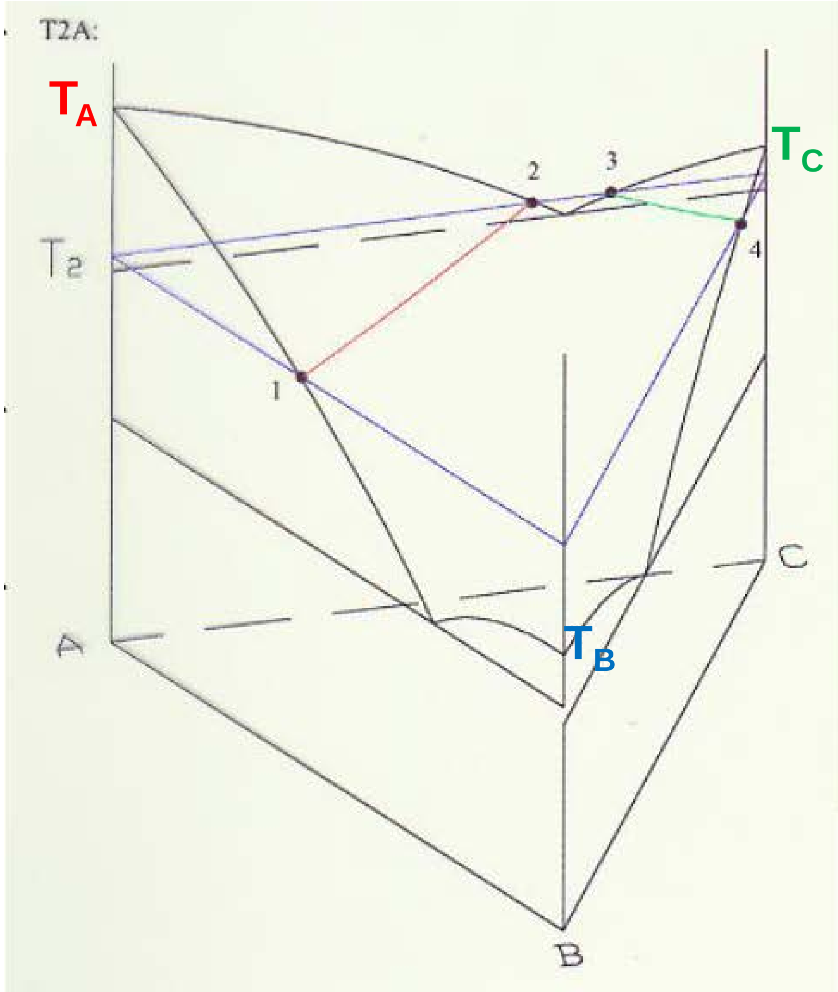
(No Solid Solubility)

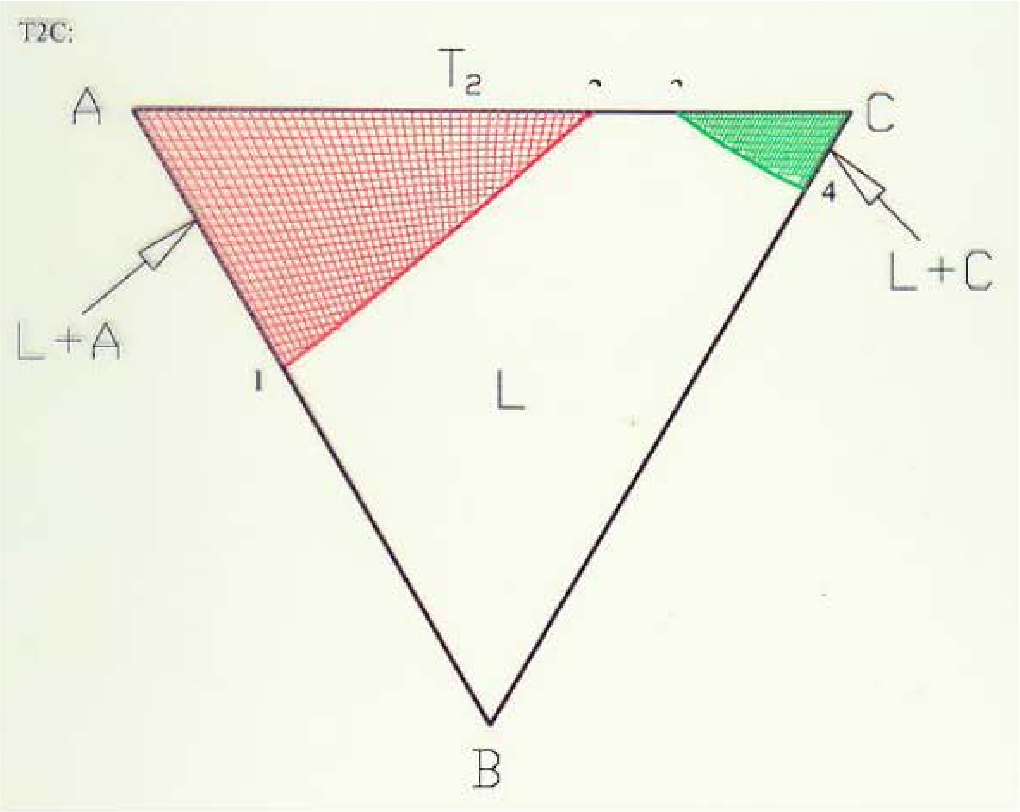




Ternary Eutectic System

(No Solid Solubility)





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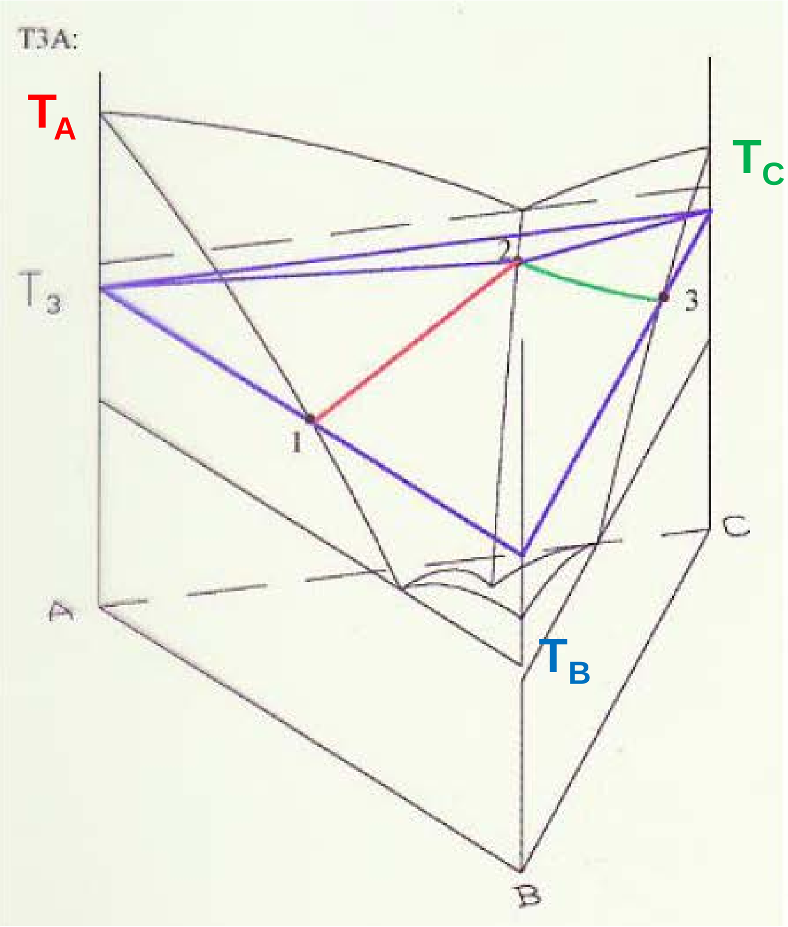

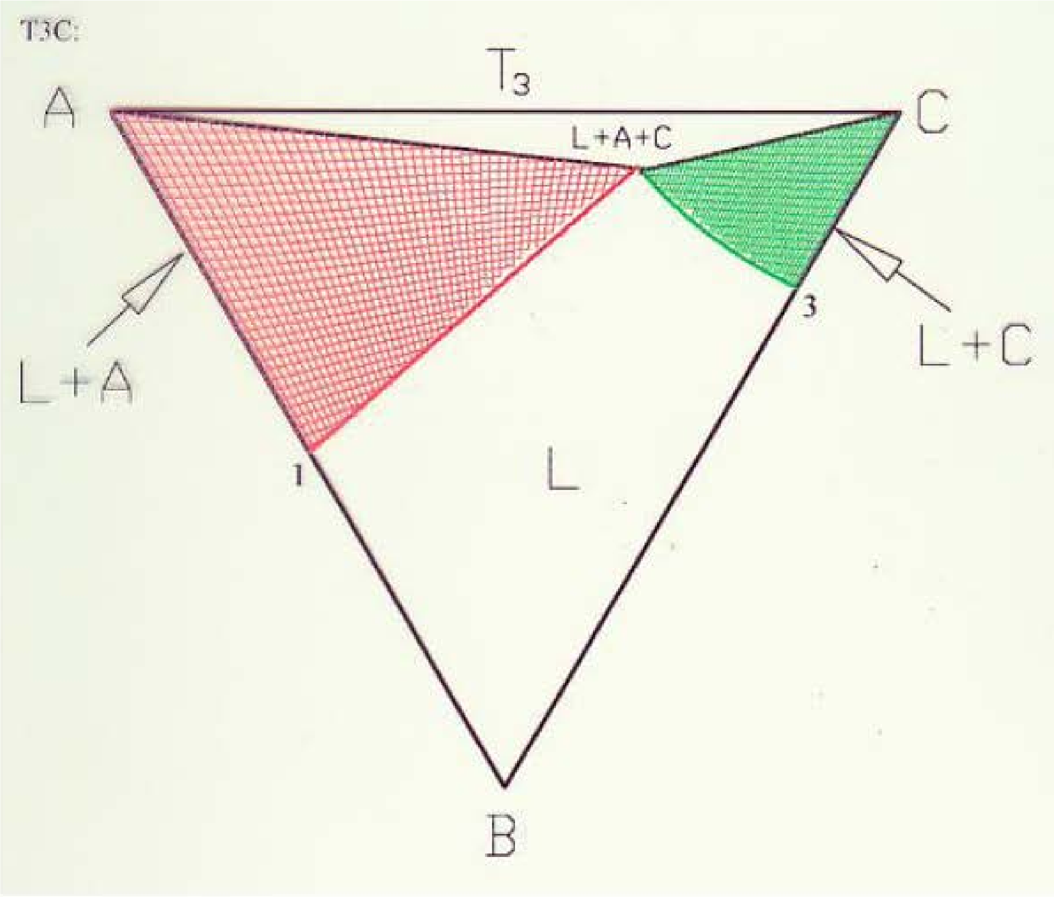

Ternary Eutectic System

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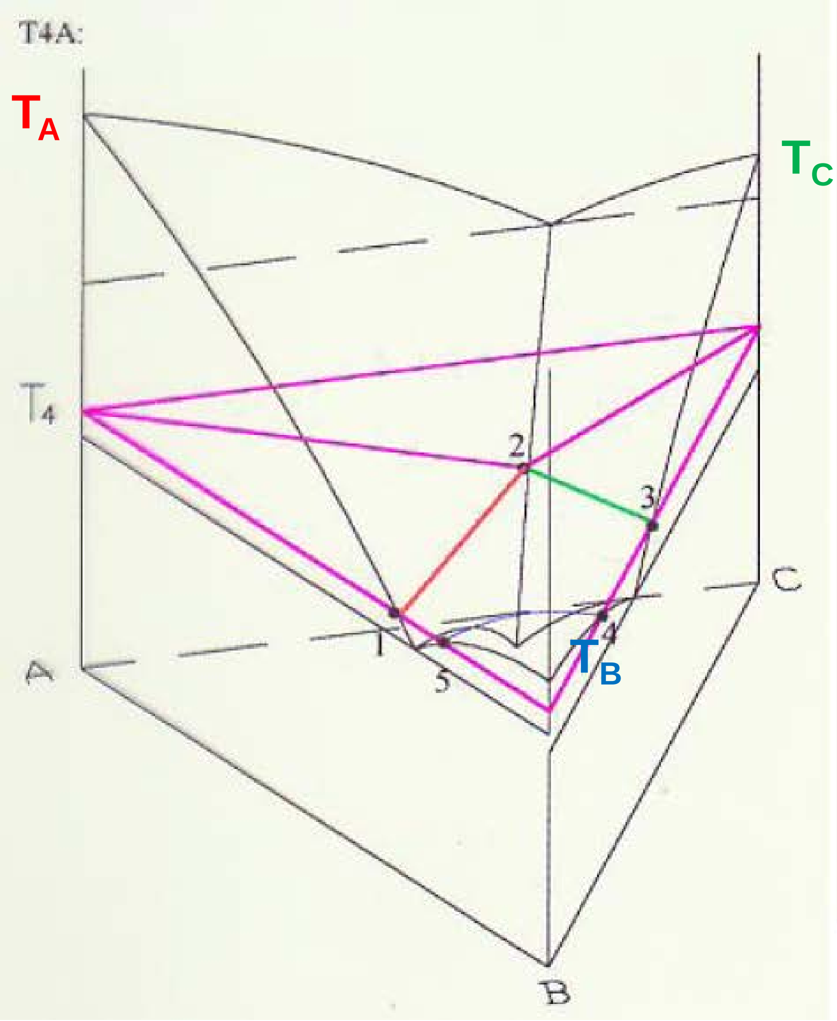
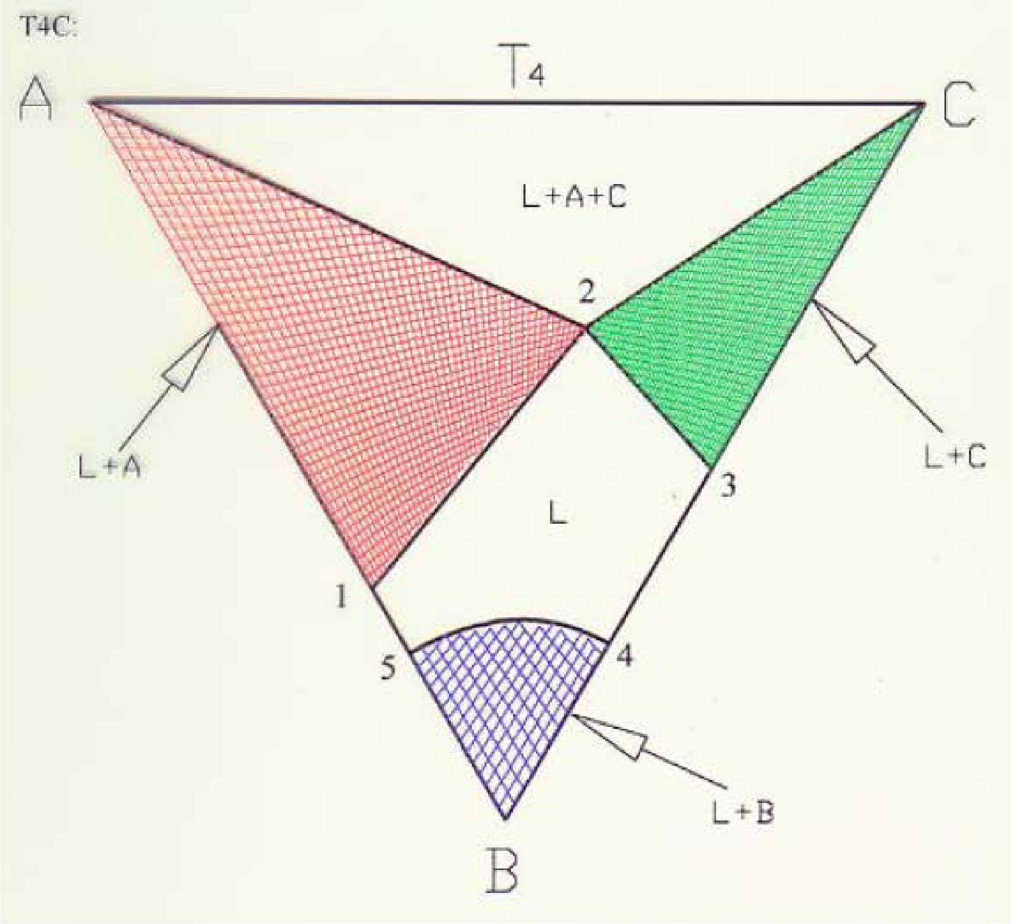
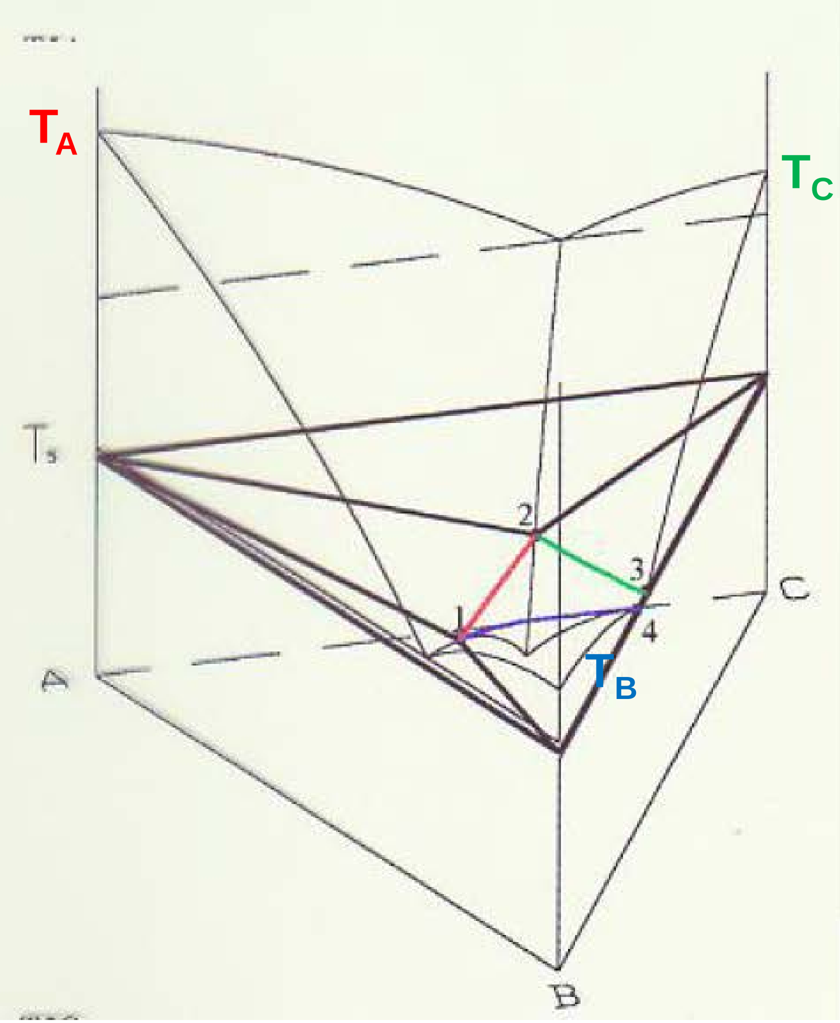
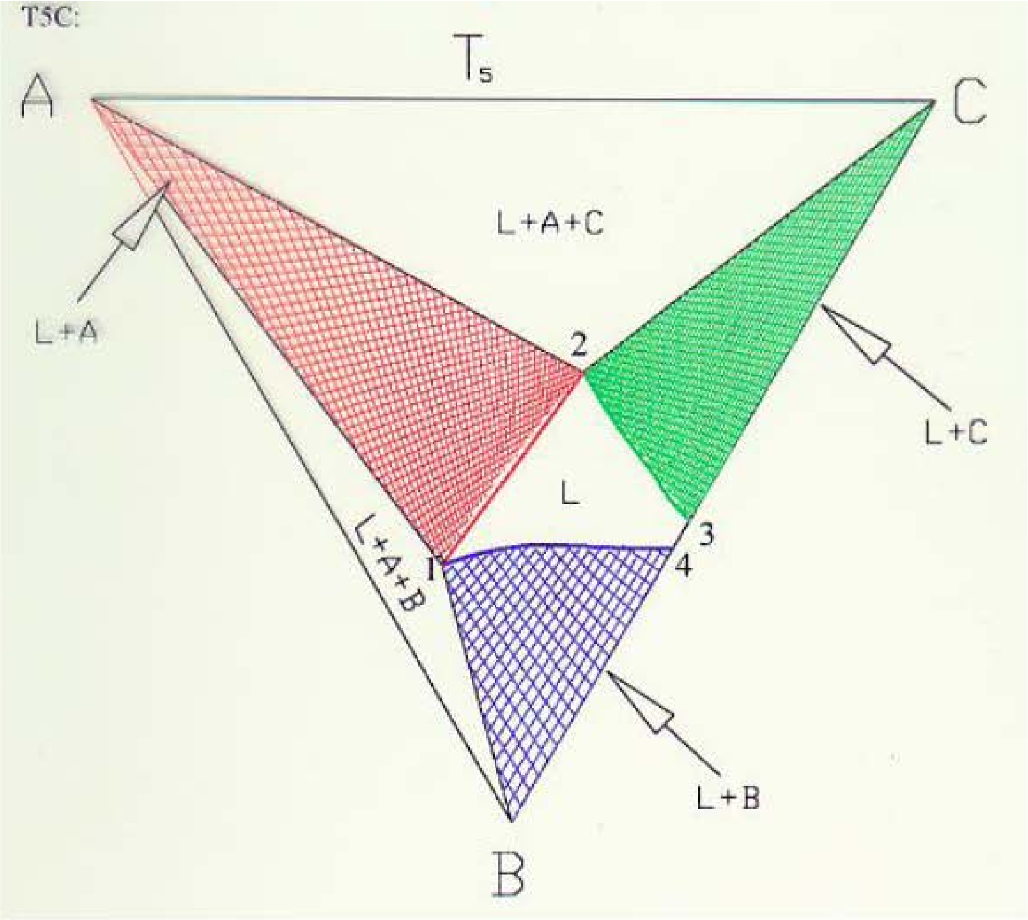




Ternary Eutectic System

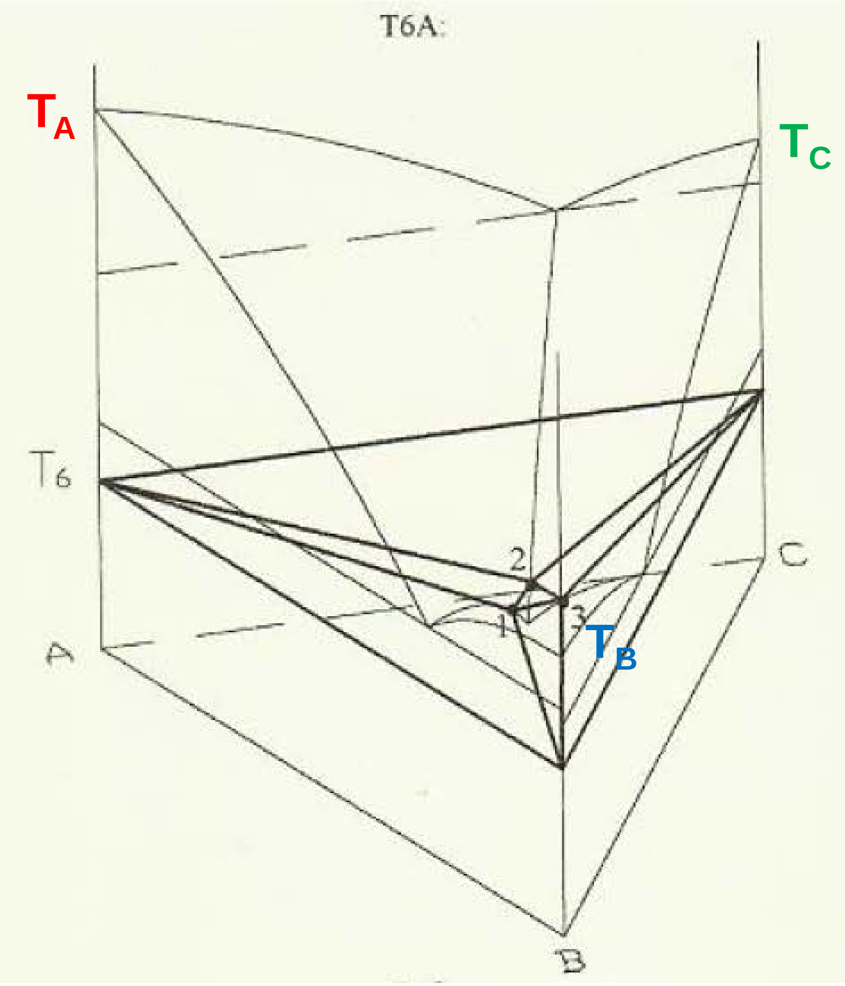
(No Solid Solubility)

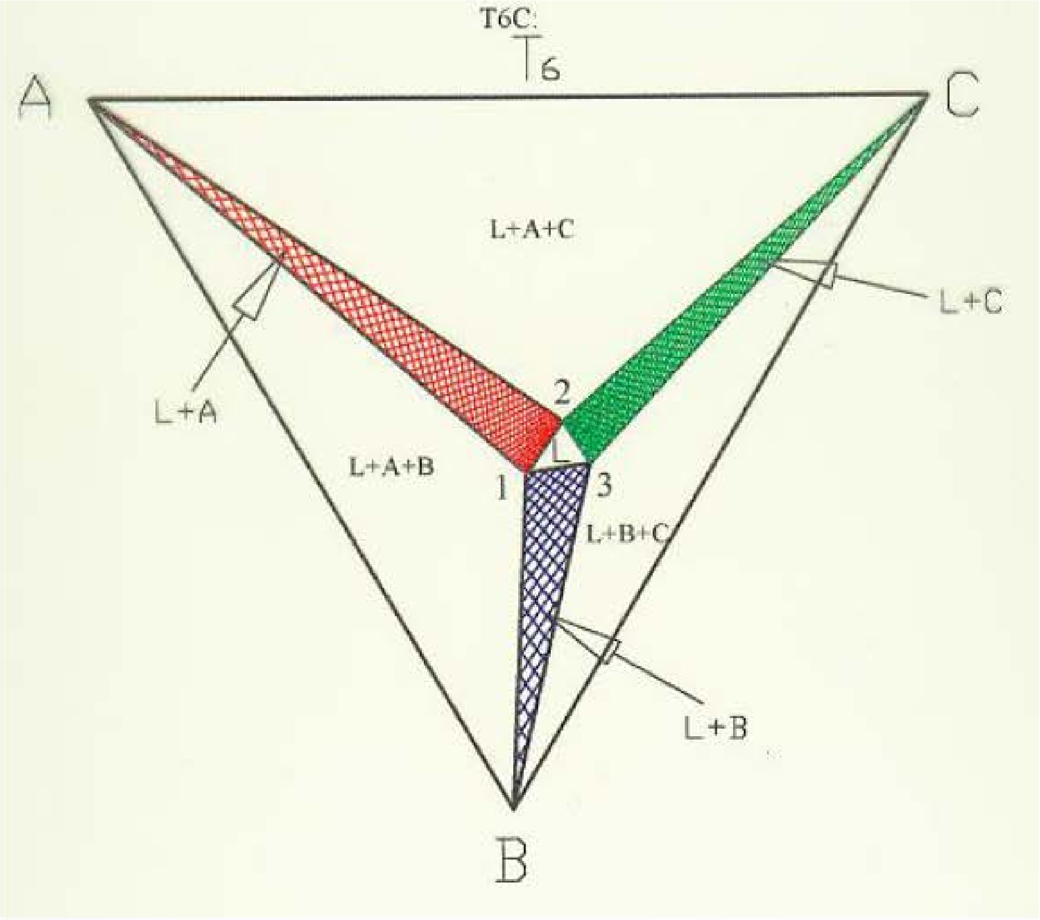




Ternary Eutectic System

(No Solid Solubility)

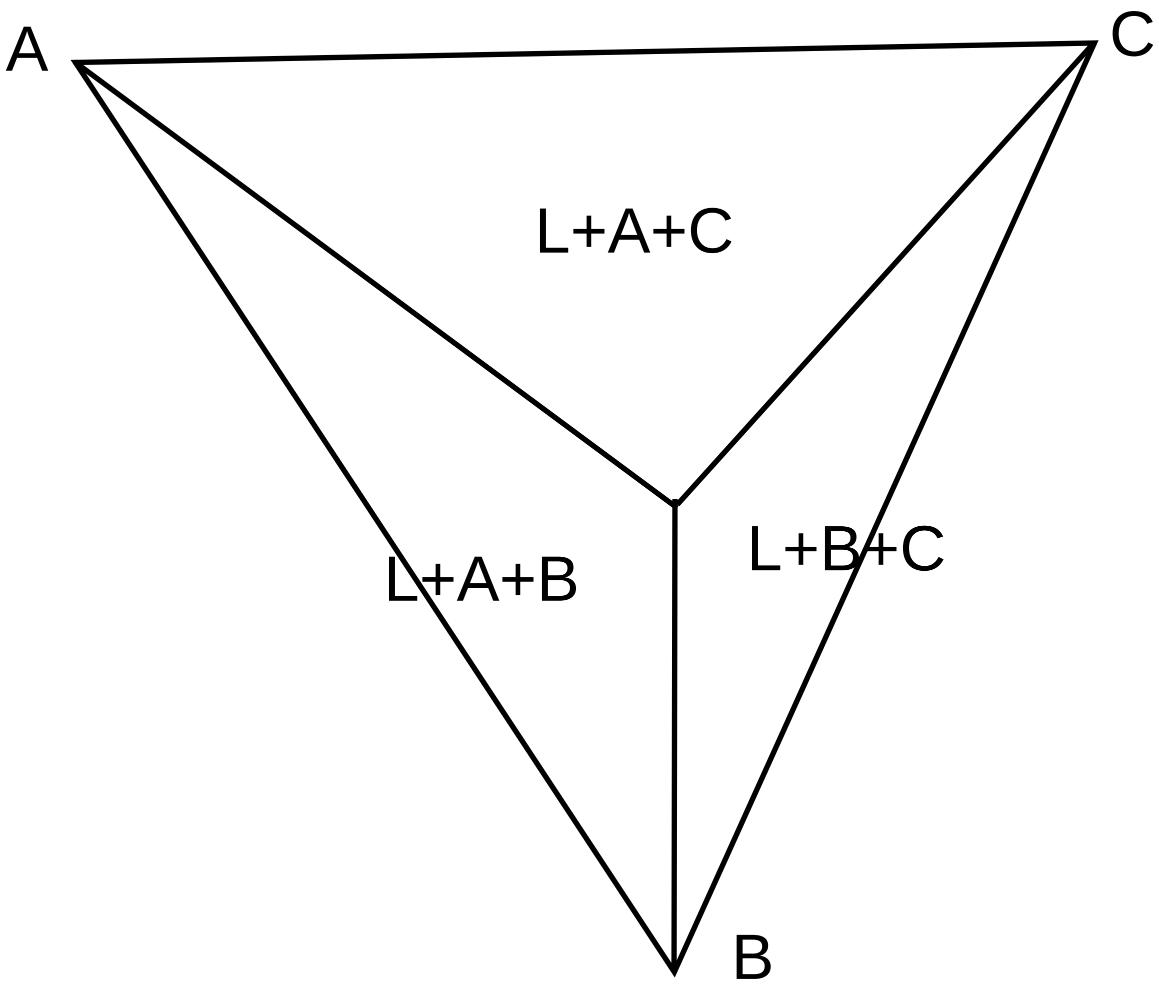




Ternary Eutectic System

(No Solid Solubility)

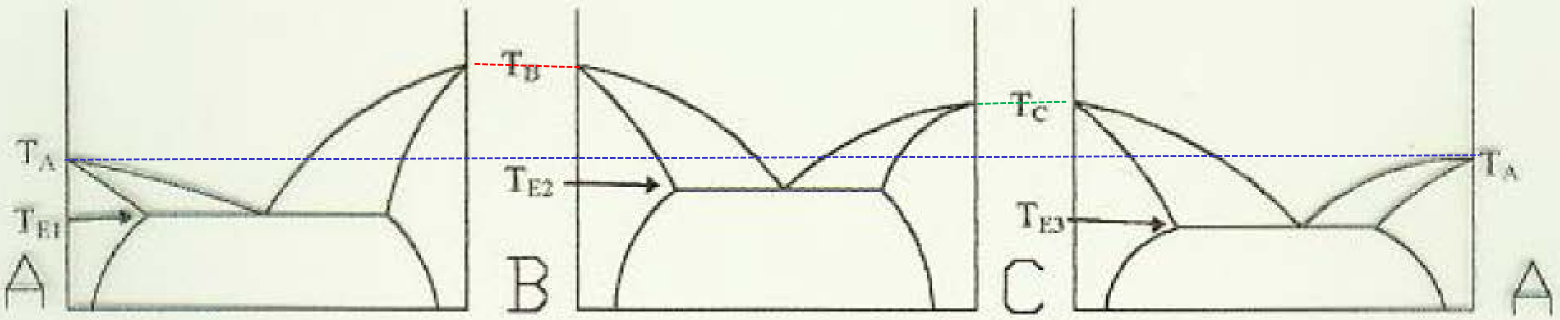
T= ternary eutectic temp.



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

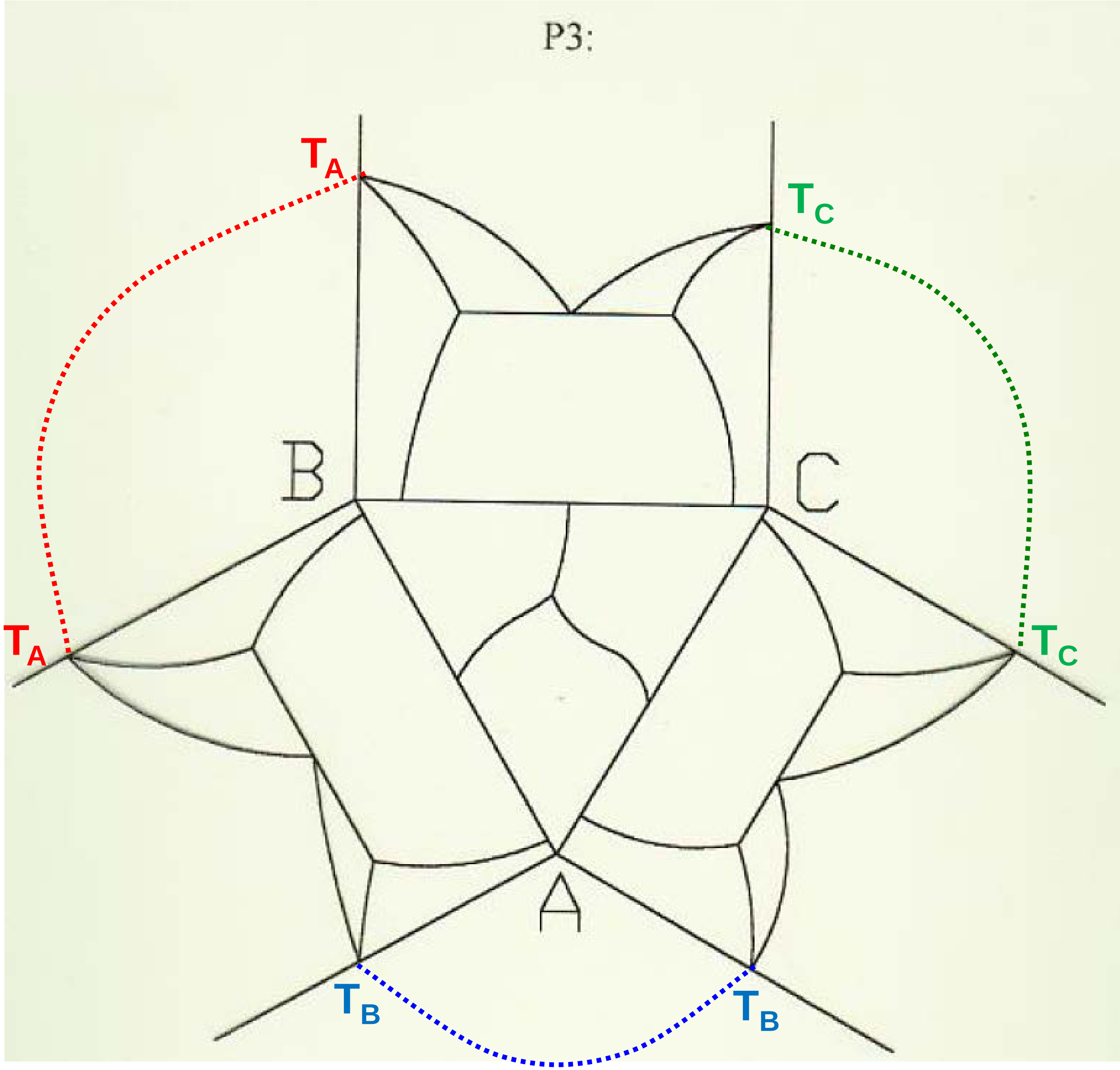
T_{E1}: Eutectic Temperature Of A-B

T_{E2}: Eutectic Temperature Of B-C

T_{E3}: Eutectic Temperature Of C-A

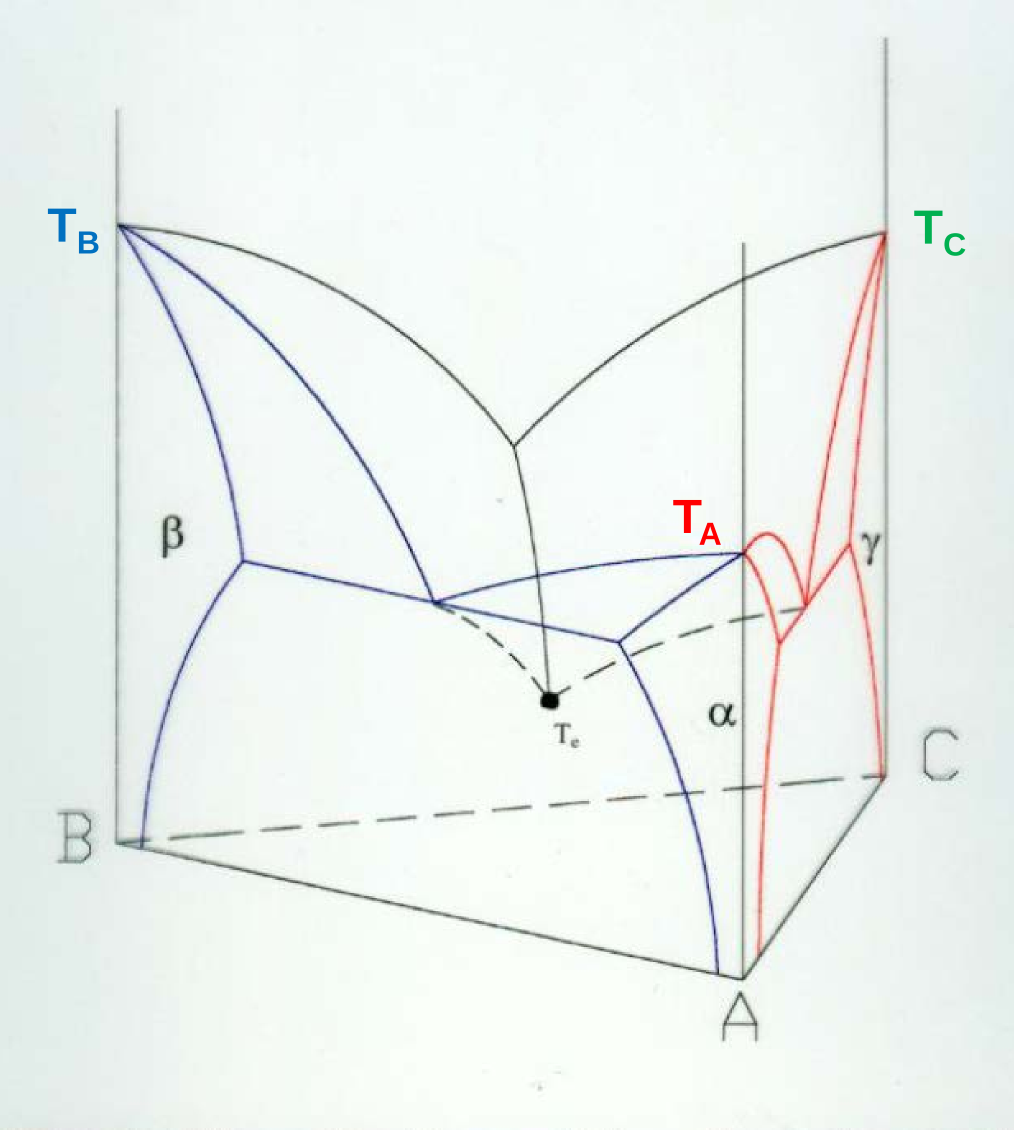
Ternary Eutectic System

(with Solid Solubility)

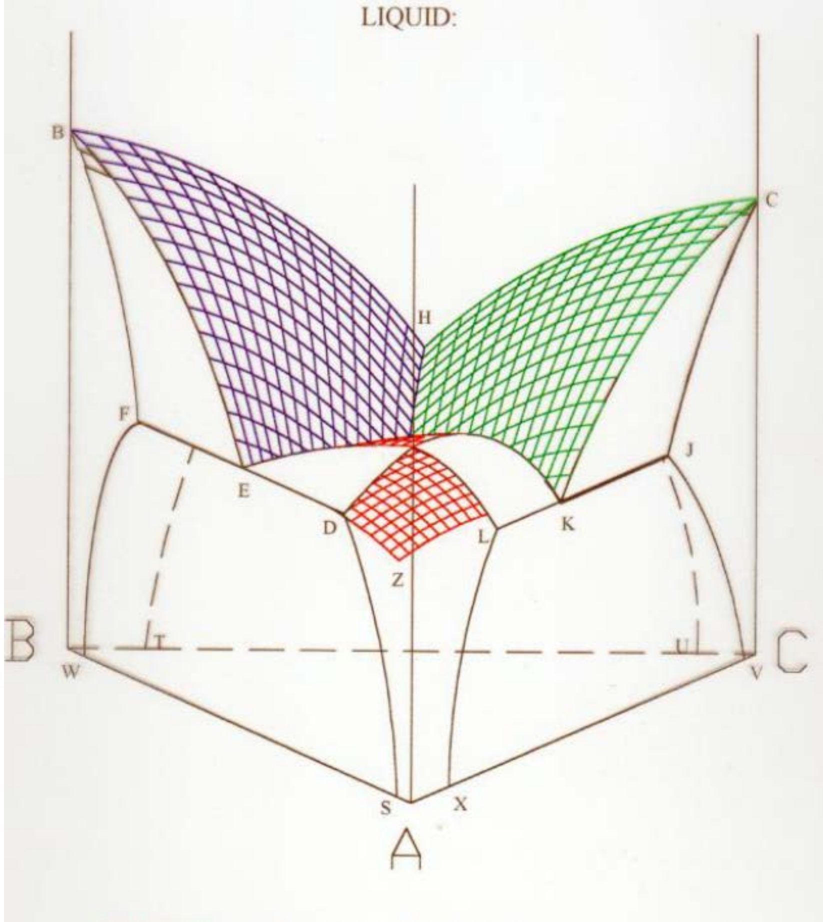


Ternary Eutectic System

(with Solid Solubility)



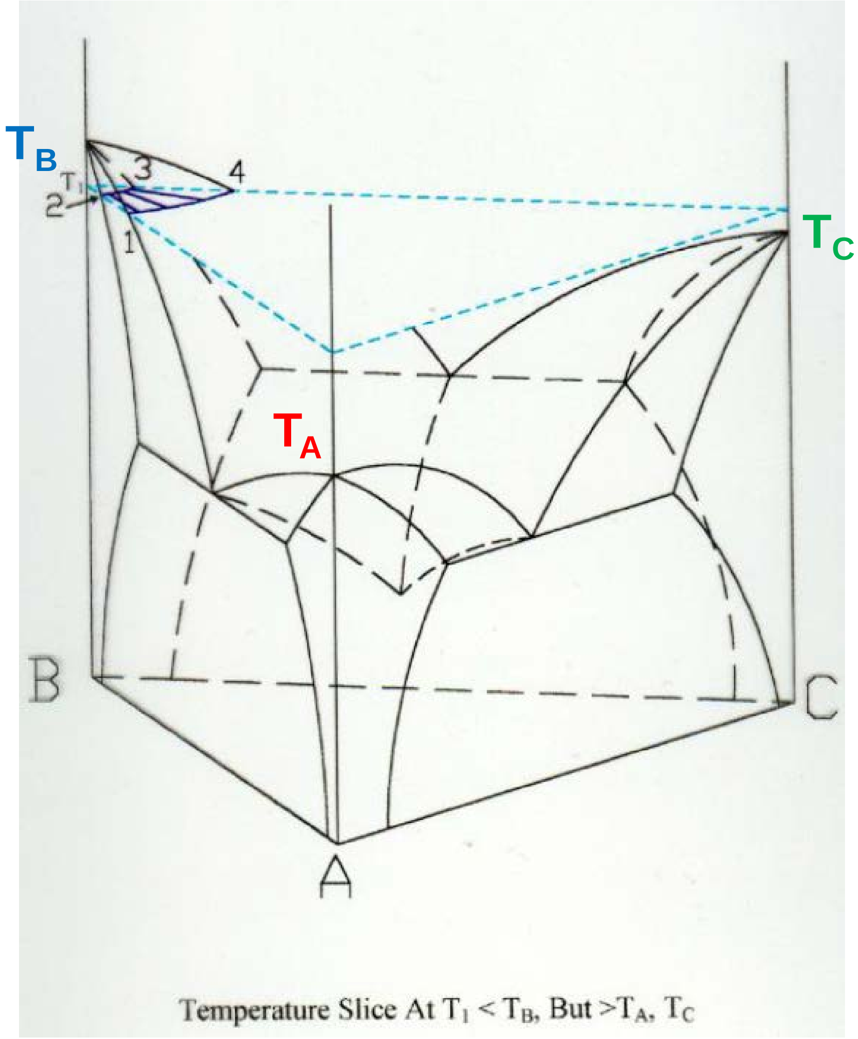
Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown



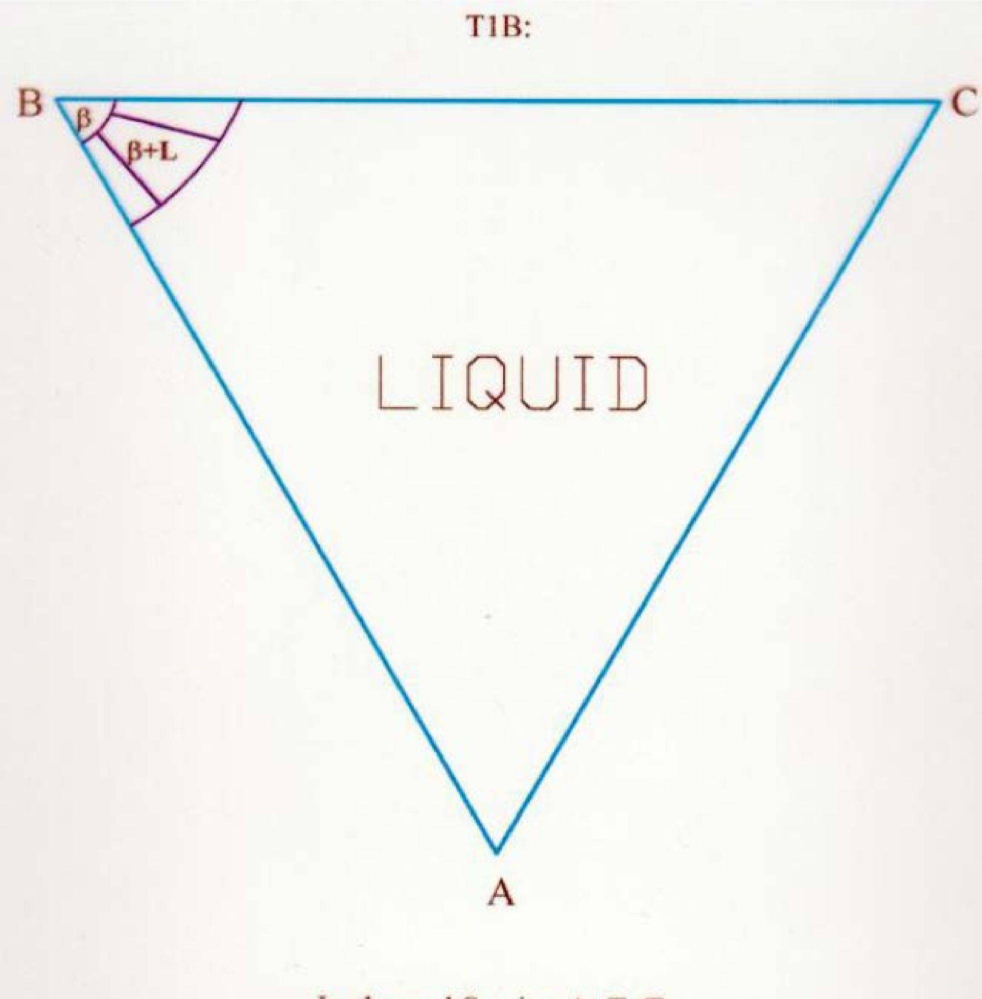
All Liquidus surfaces (α+L-Red, β+L-Purple, γ+L-Green)

Ternary Eutectic System

(with Solid Solubility)



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

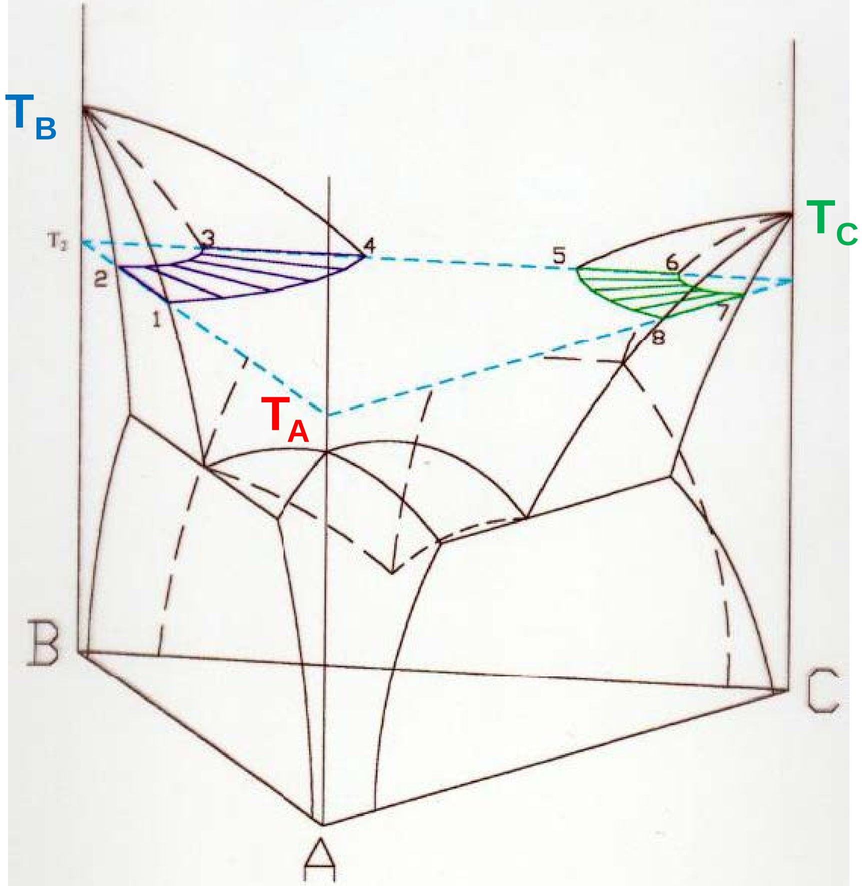


Isothermal Section At $T=T_1$

Ternary Eutectic System

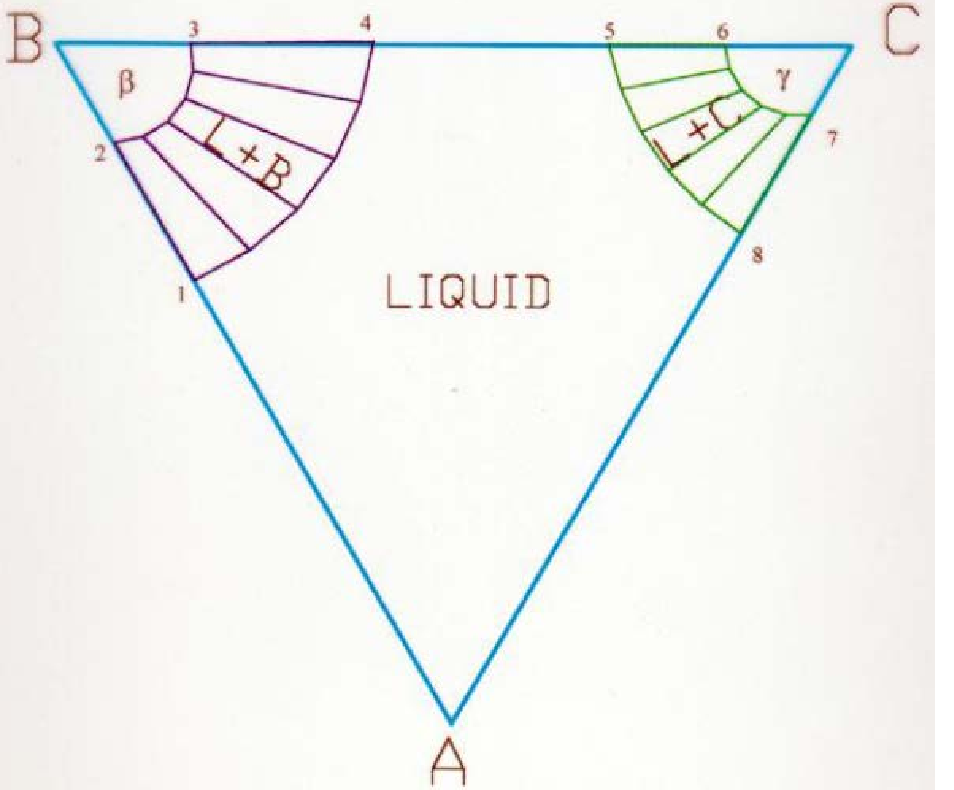
(with Solid Solubility)

T2A



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

T2B

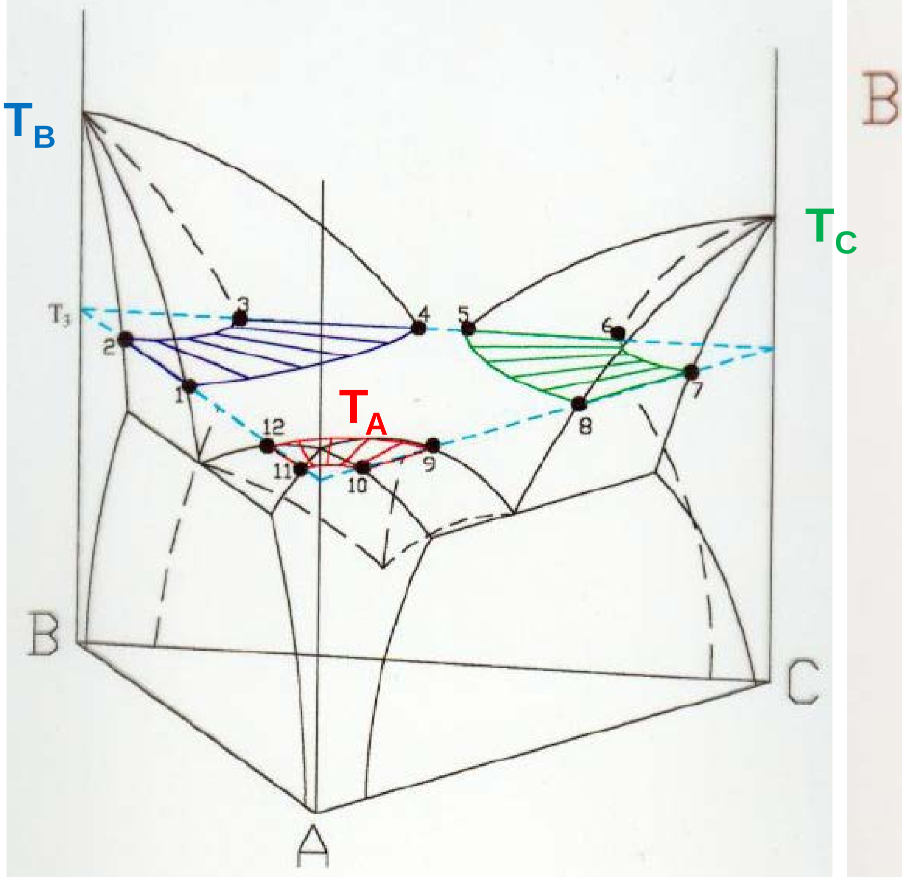


Isothermal Section At $T=T_2$

Ternary Eutectic System

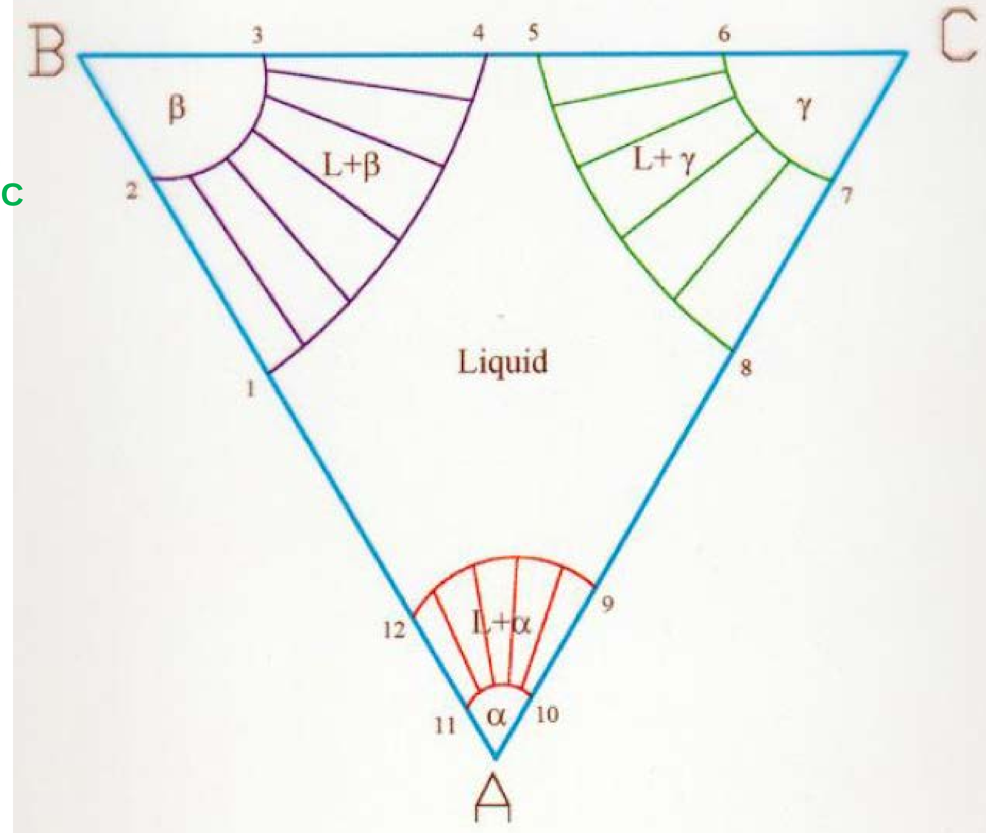
(with Solid Solubility)

T3A:



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

T3B

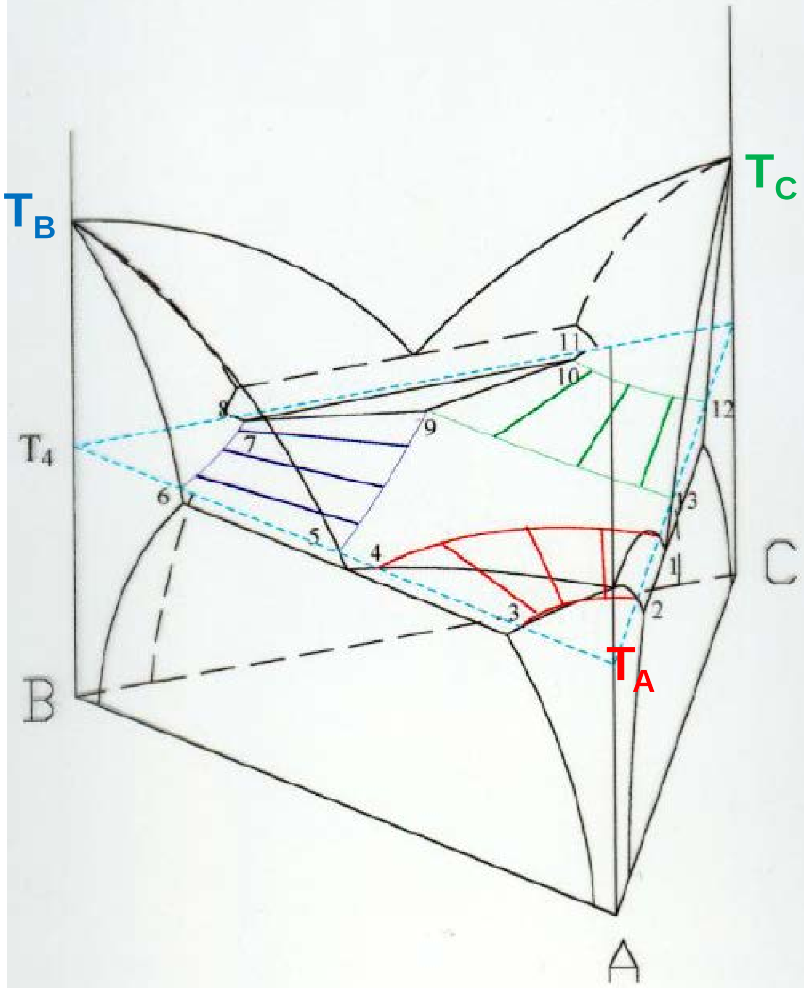


Isothermal Section At $T = T_3$

Ternary Eutectic System

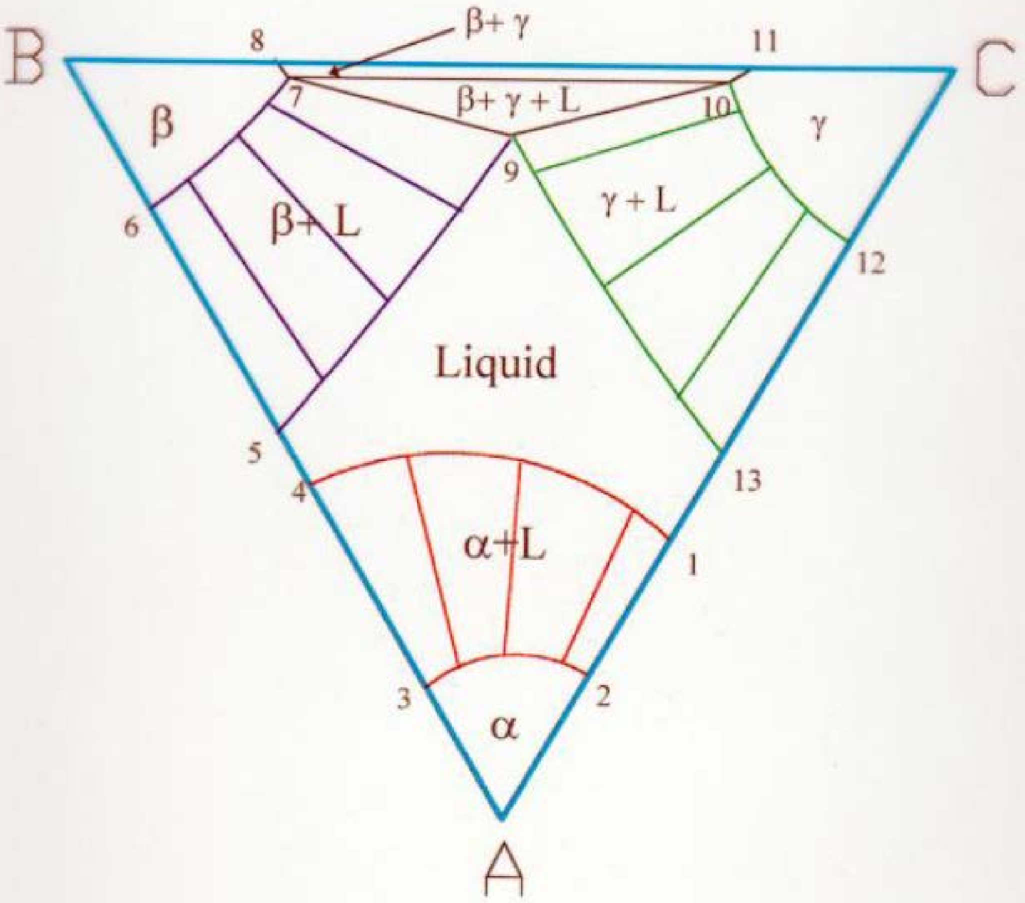
(with Solid Solubility)

T4A:



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

T4B:

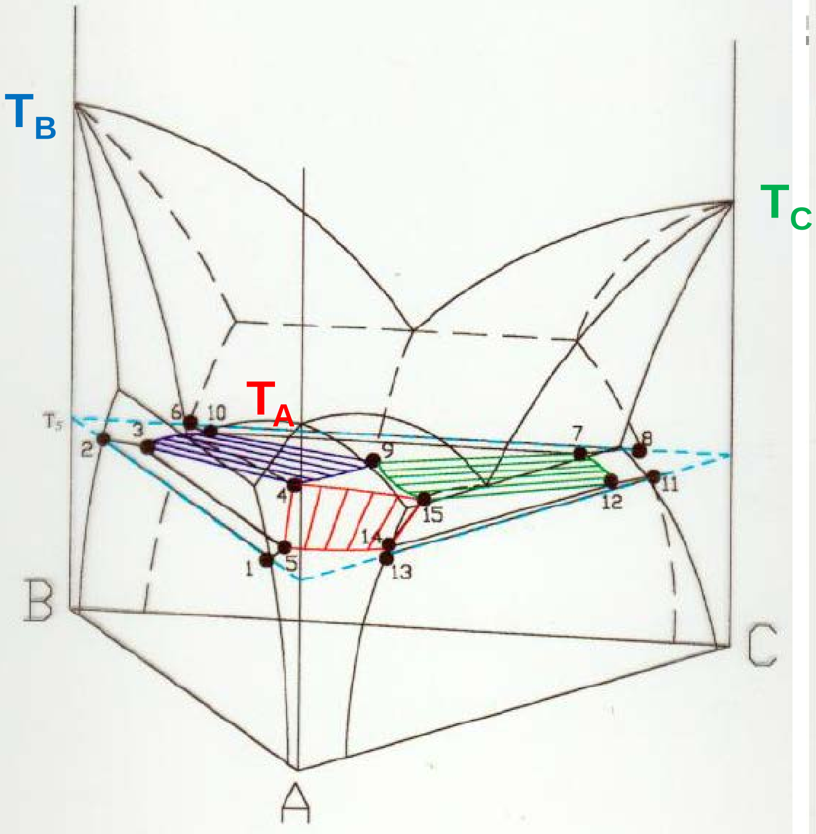


Isothermal Section At $T=T_4$

Ternary Eutectic System

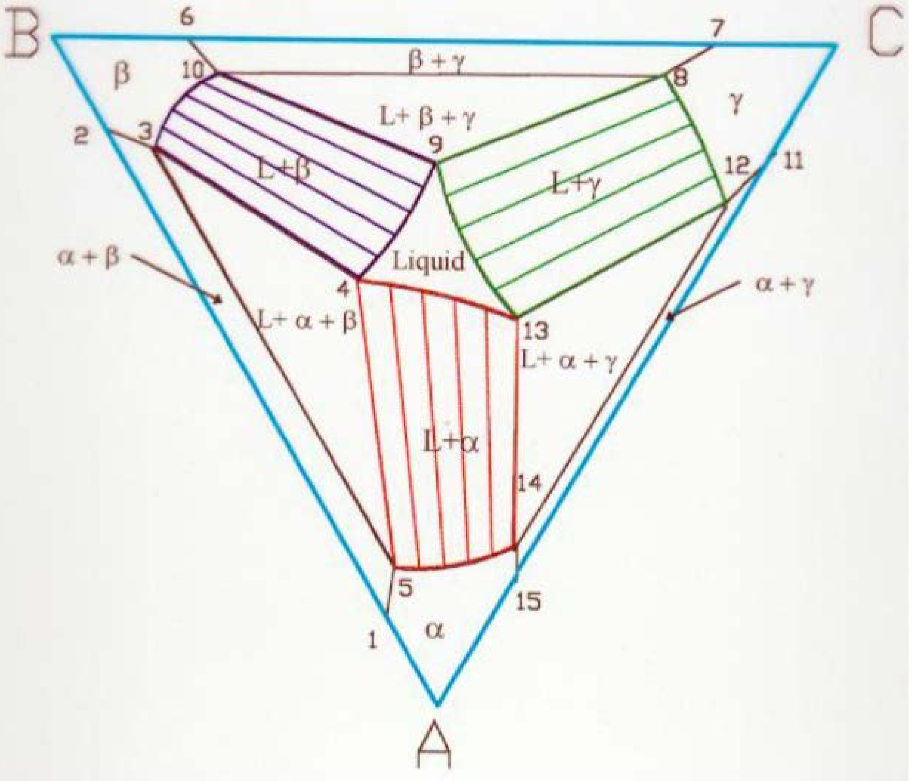
(with Solid Solubility)

T5A:



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

T5B:

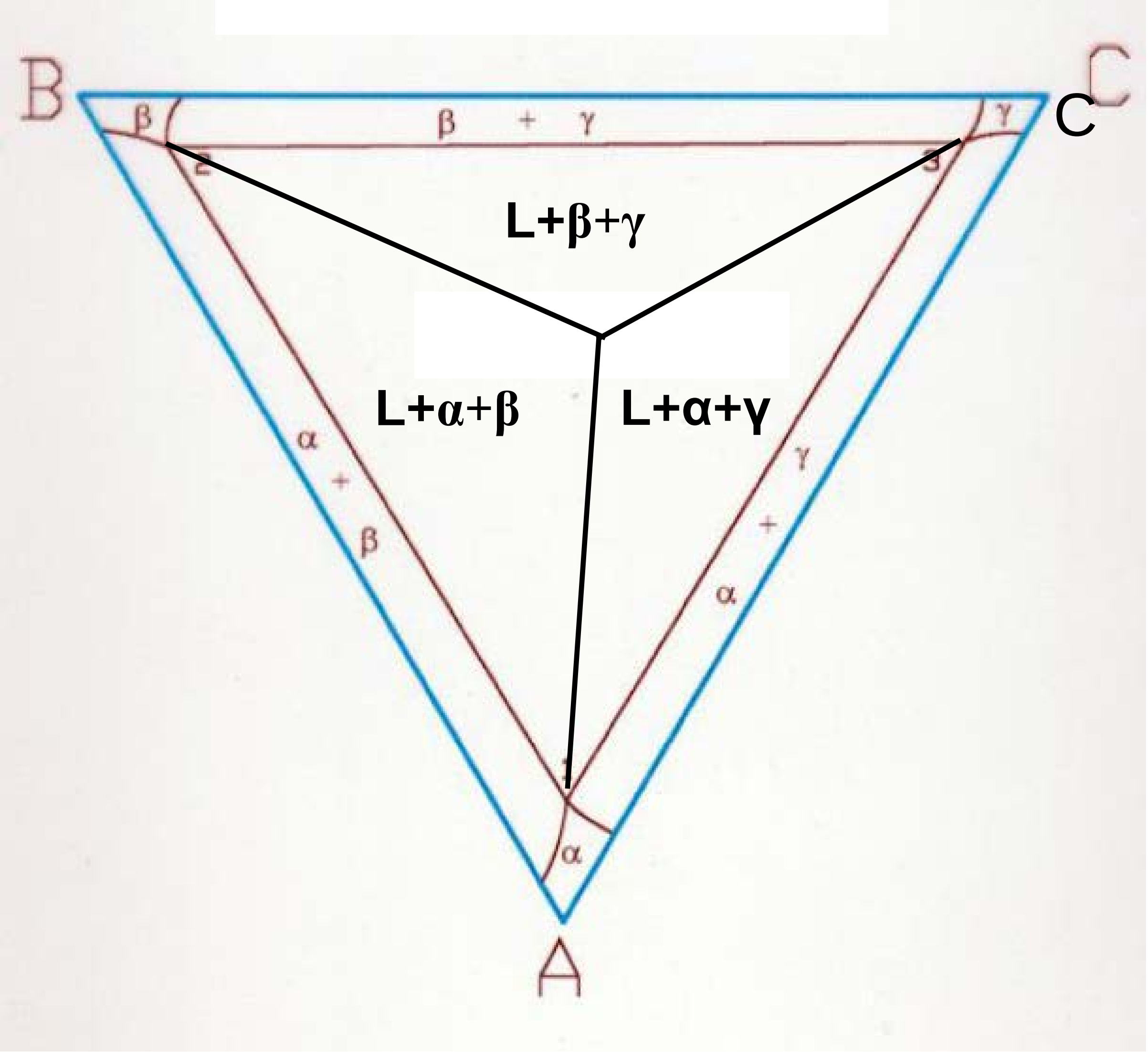


Isothermal Section At $T=T_5$

Ternary Eutectic System

(with Solid Solubility)

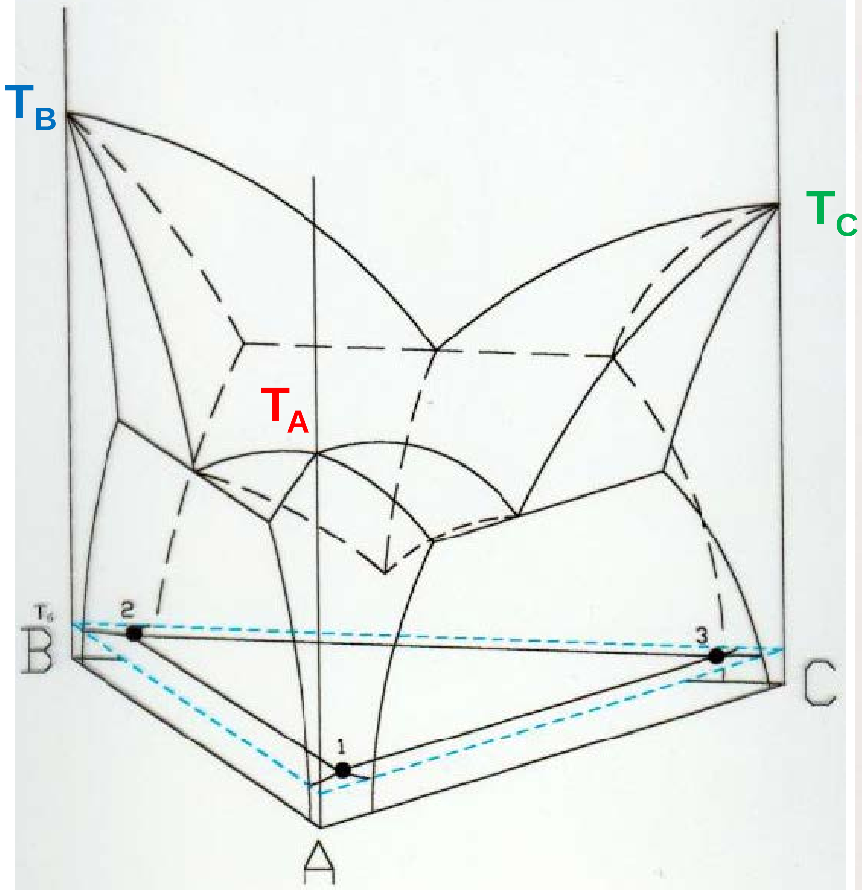
T= ternary eutectic temp.



Ternary Eutectic System

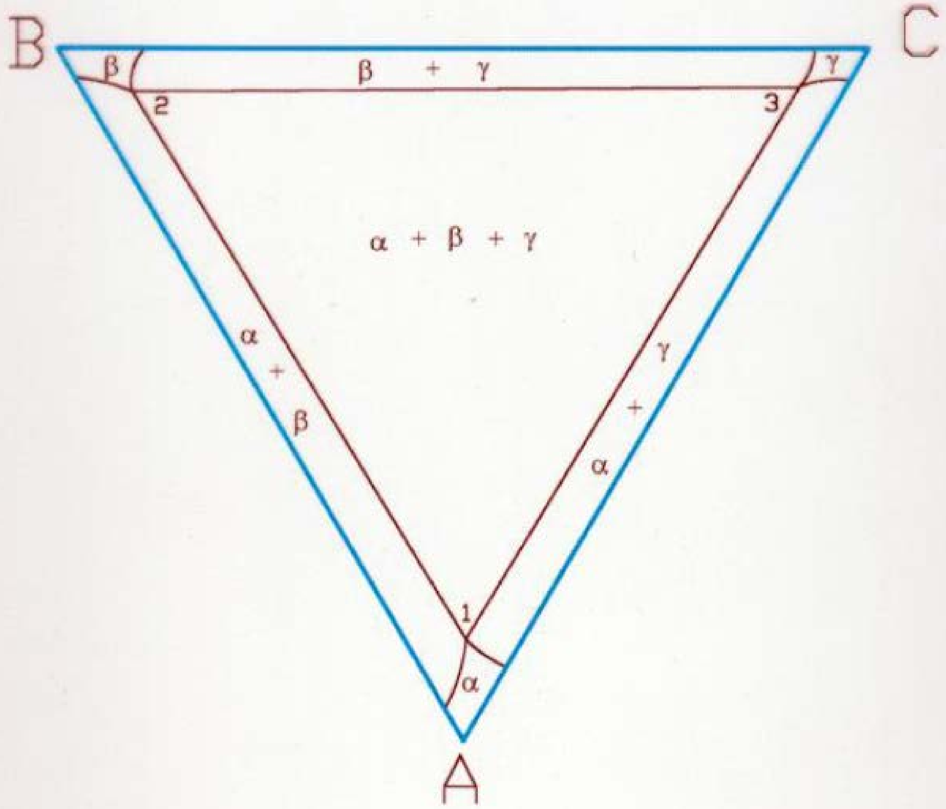
(with Solid Solubility)

T6A:



Temperature Slice at $T_6 < T_E$

T6B:



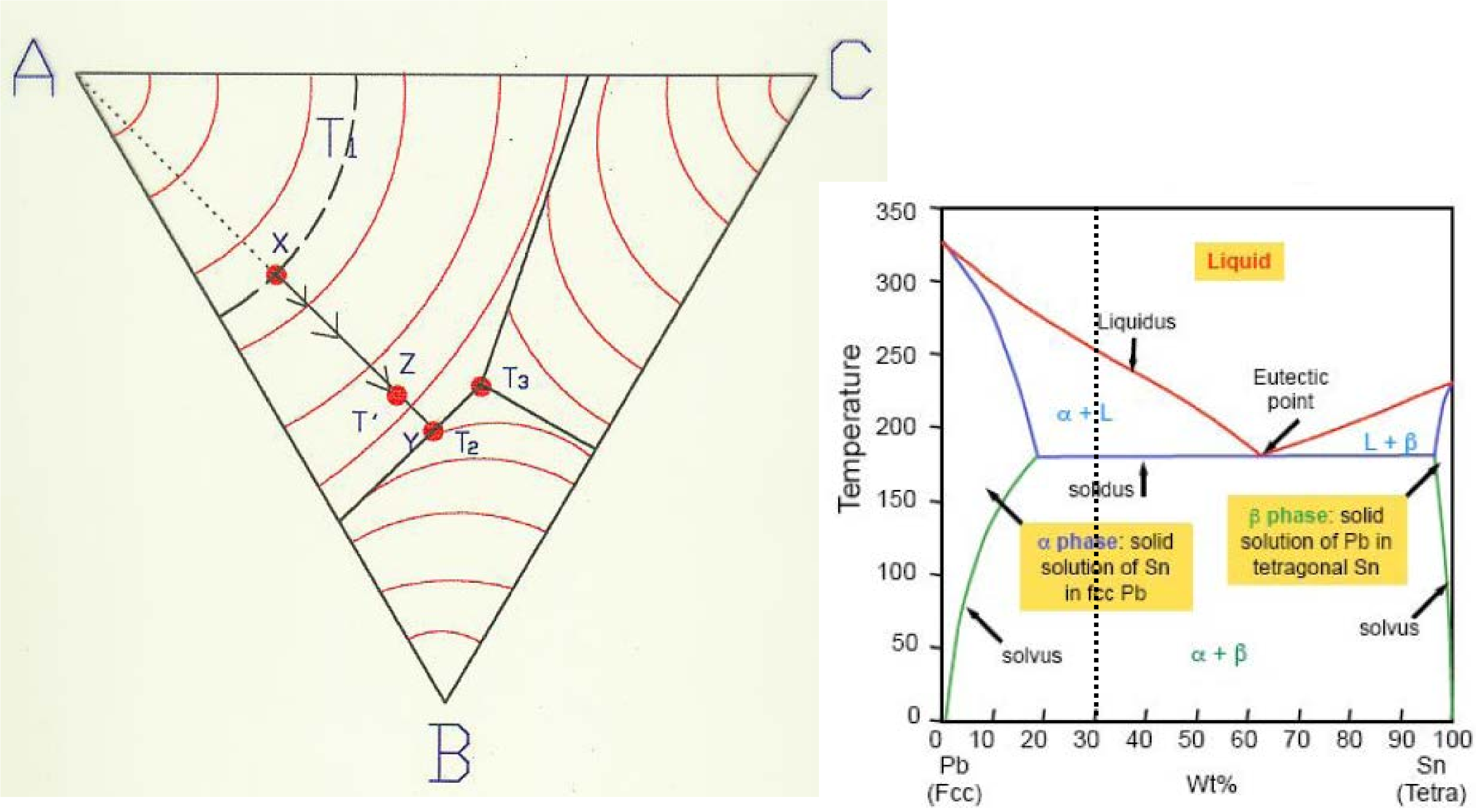
Isothermal Section At $T=T_6$

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

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

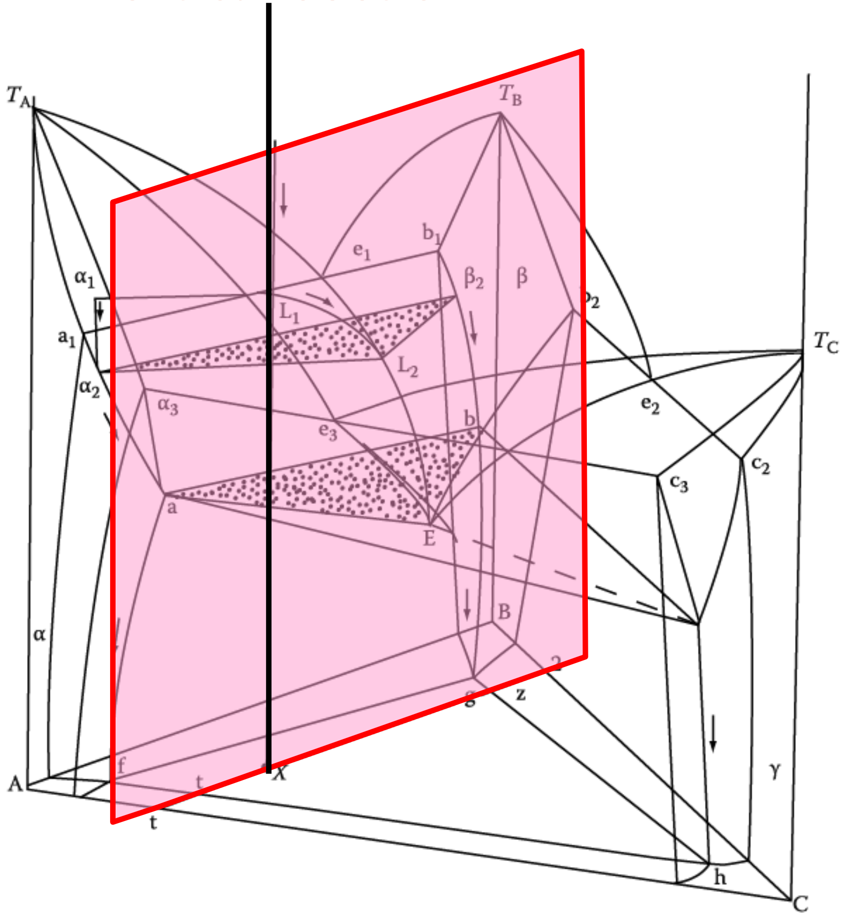
Ternary Eutectic System

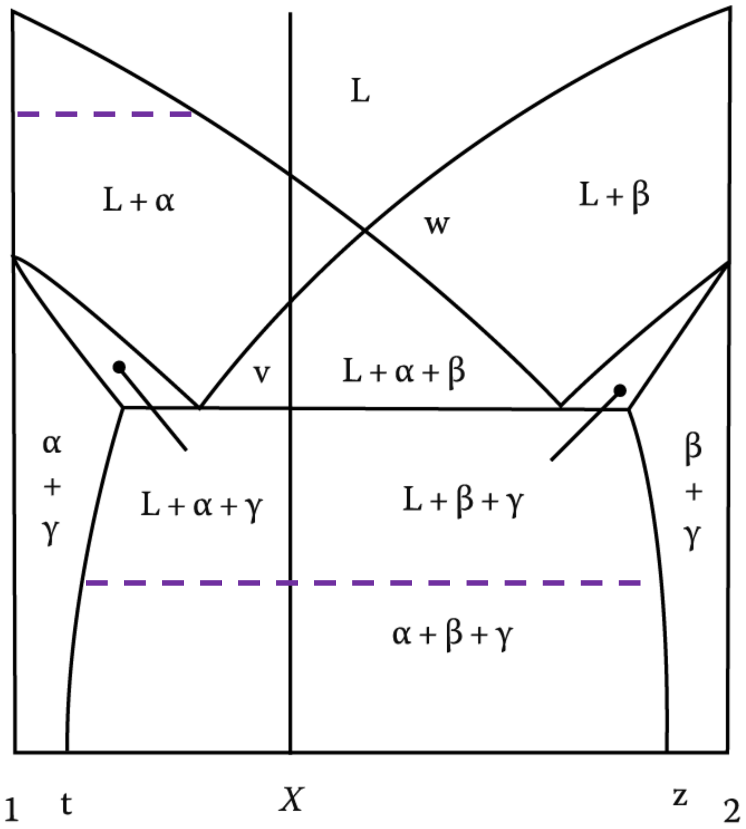
3) Solidification Sequence: liquidus surface



Ternary Eutectic System

* Vertical section





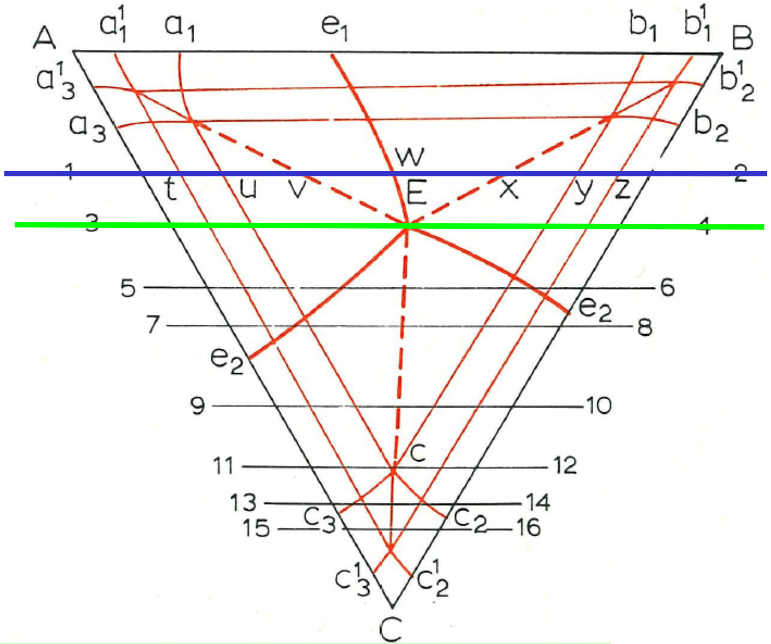
* The horizontal lines are not tie lines. (no compositional information)

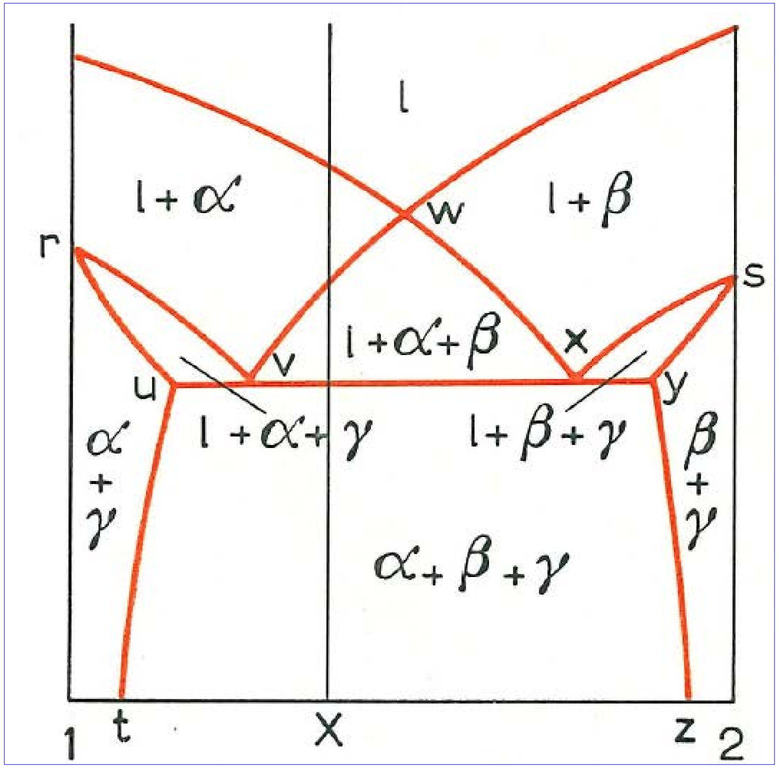
* Information for equilibrium phases at different tempeatures

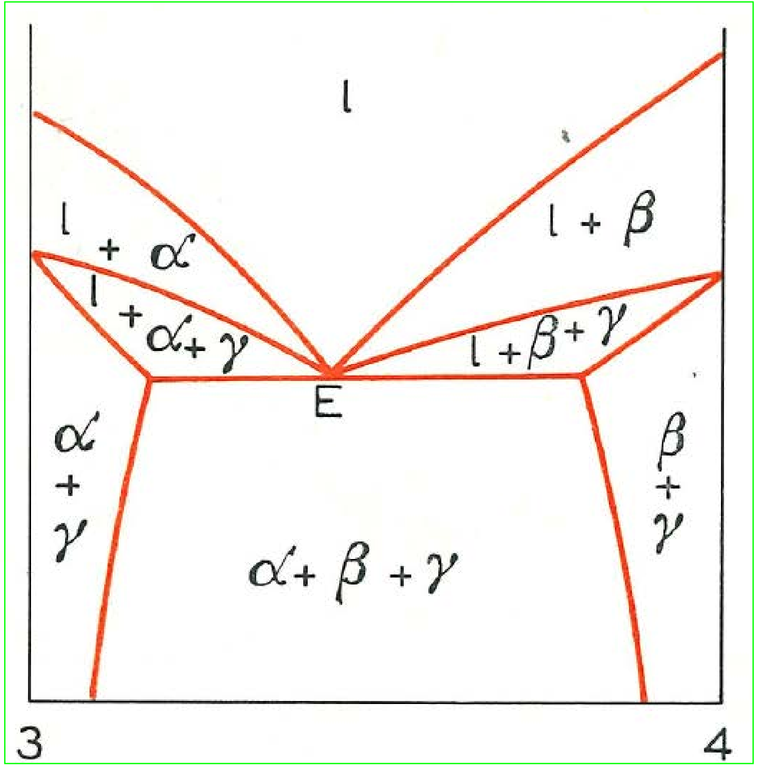
10.1. THE EUTECTIC EQUILIBRIUM
($l = \alpha + \beta + \gamma$)

Vertical section

Location of vertical section



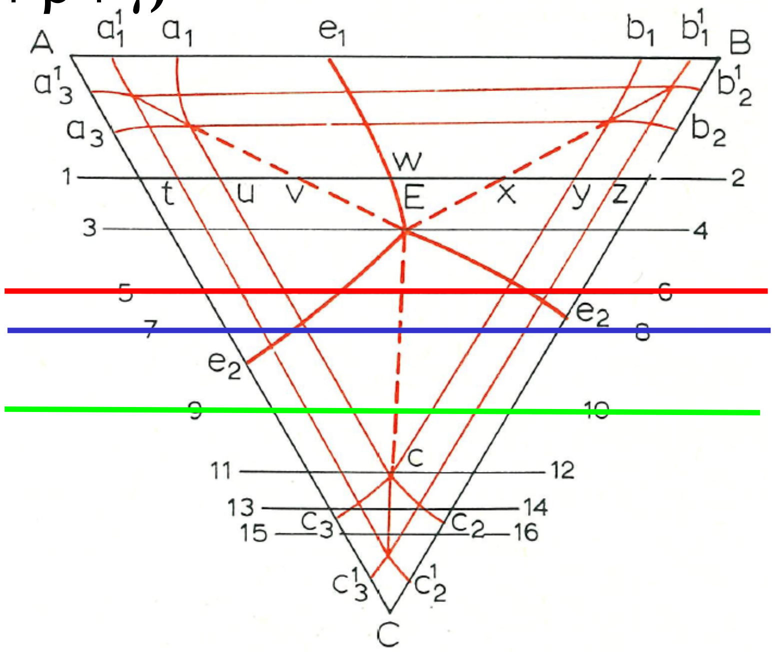


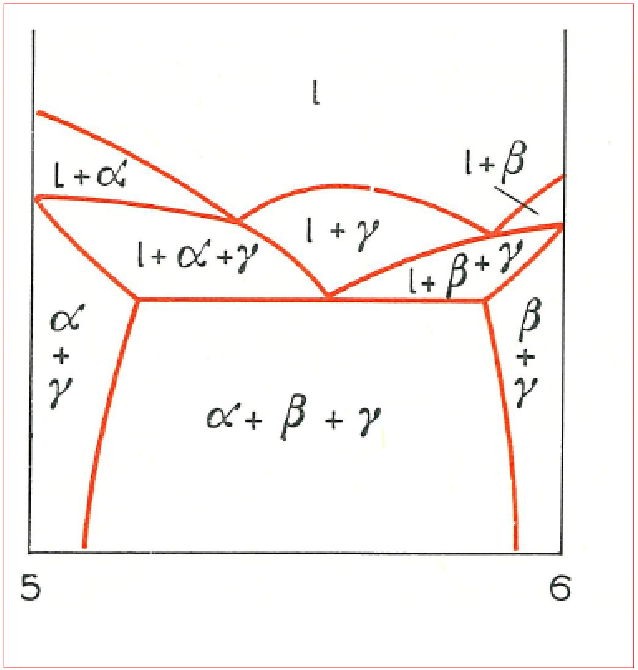


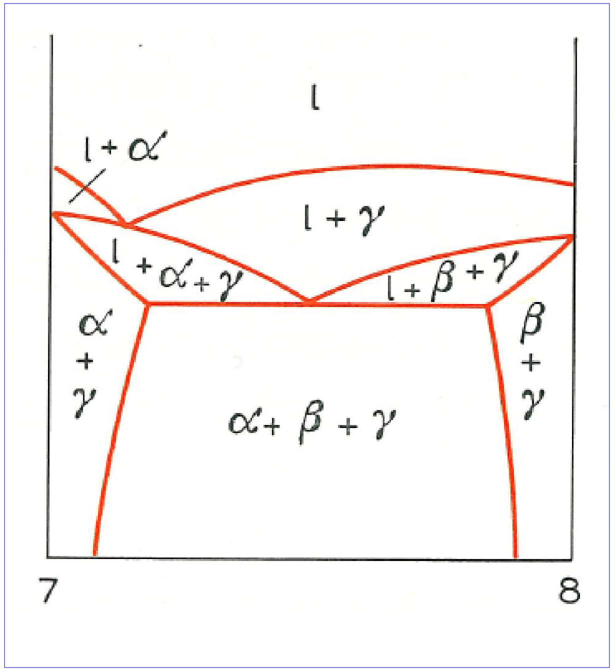
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

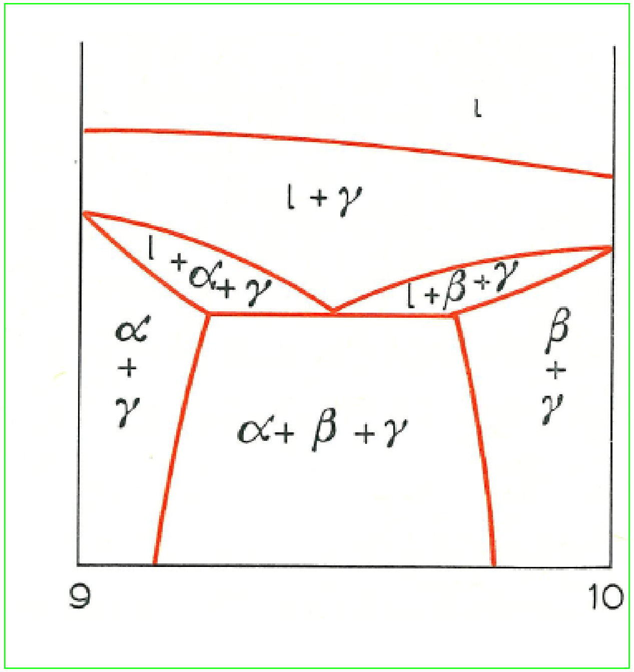
Vertical section

Location of vertical section





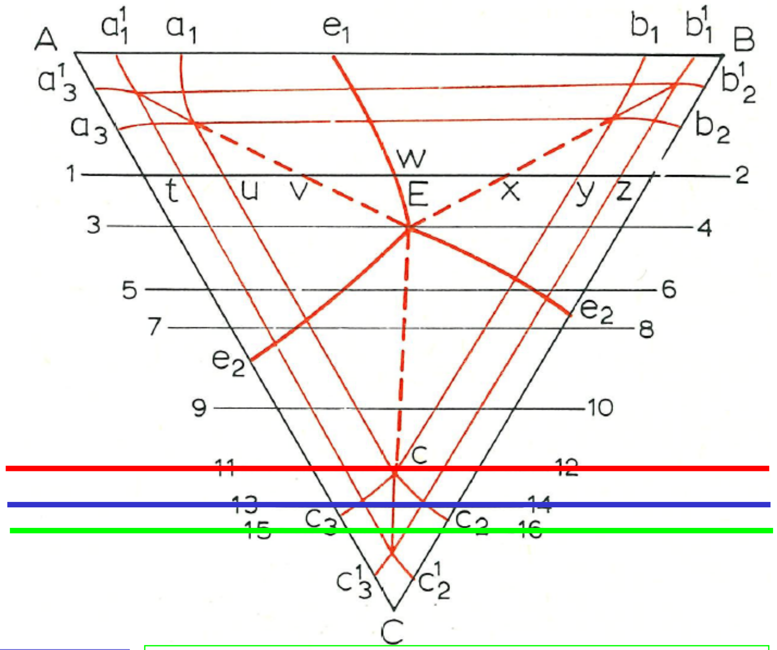


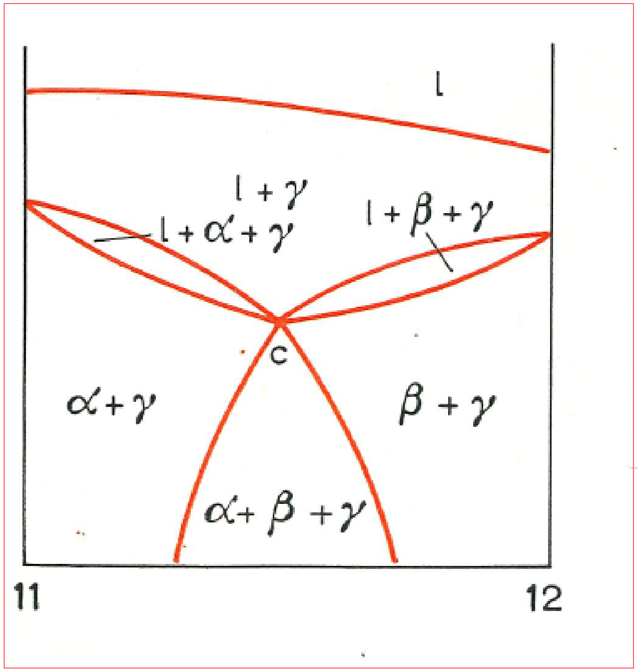


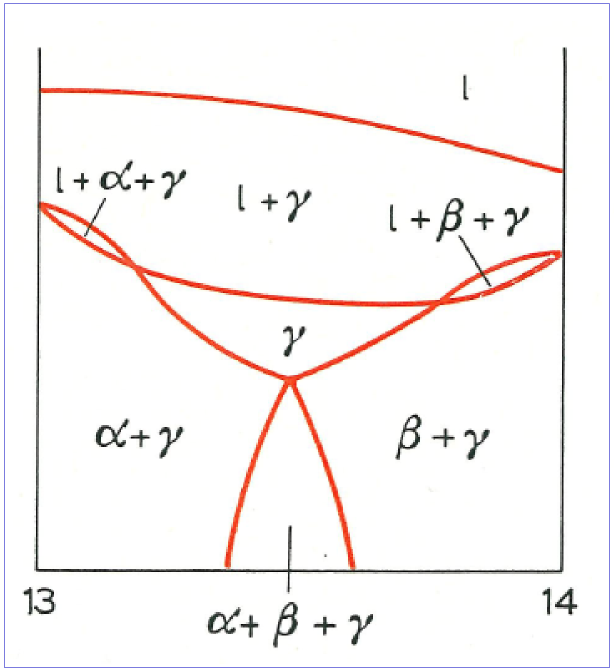
10.1. THE EUTECTIC EQUILIBRIUM ($l = \alpha + \beta + \gamma$)

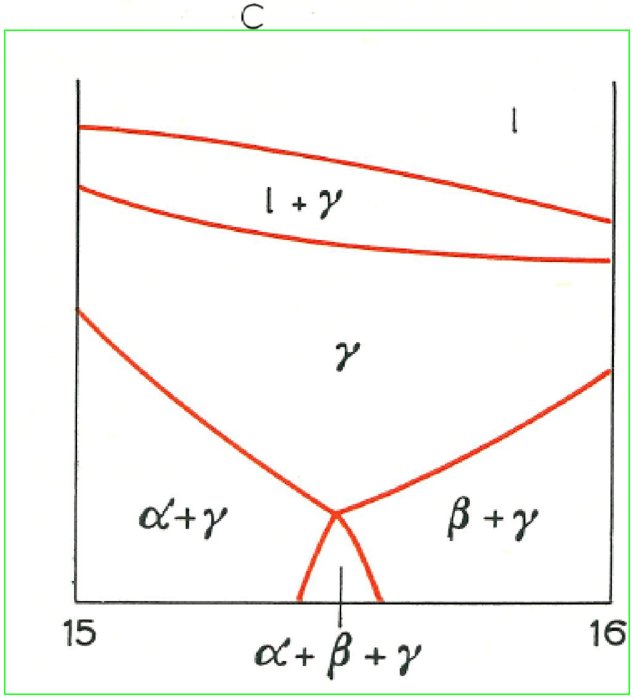
Vertical section

Location of vertical section









< Quaternary phase Diagrams >

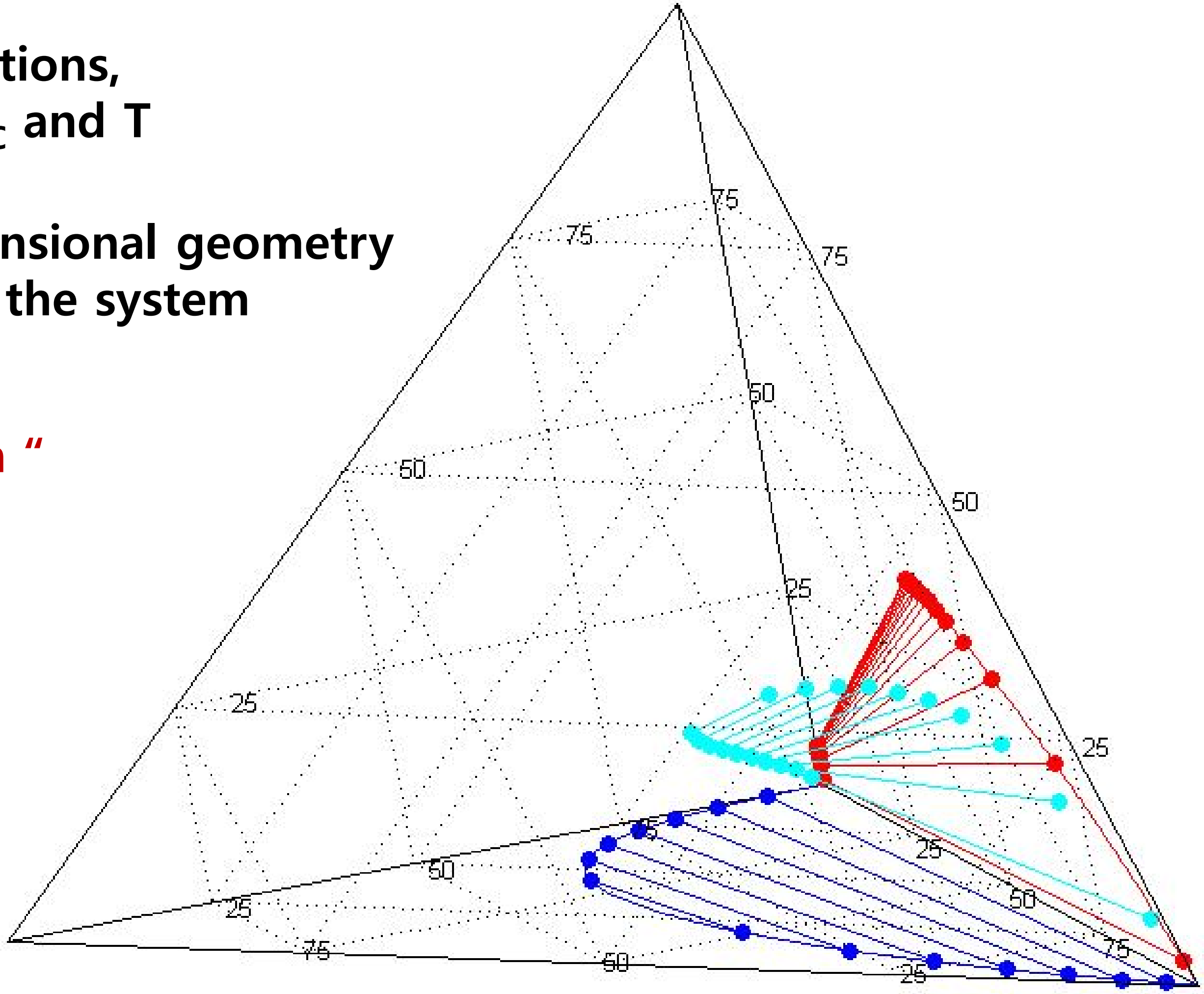
Four components: A, B, C, D

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

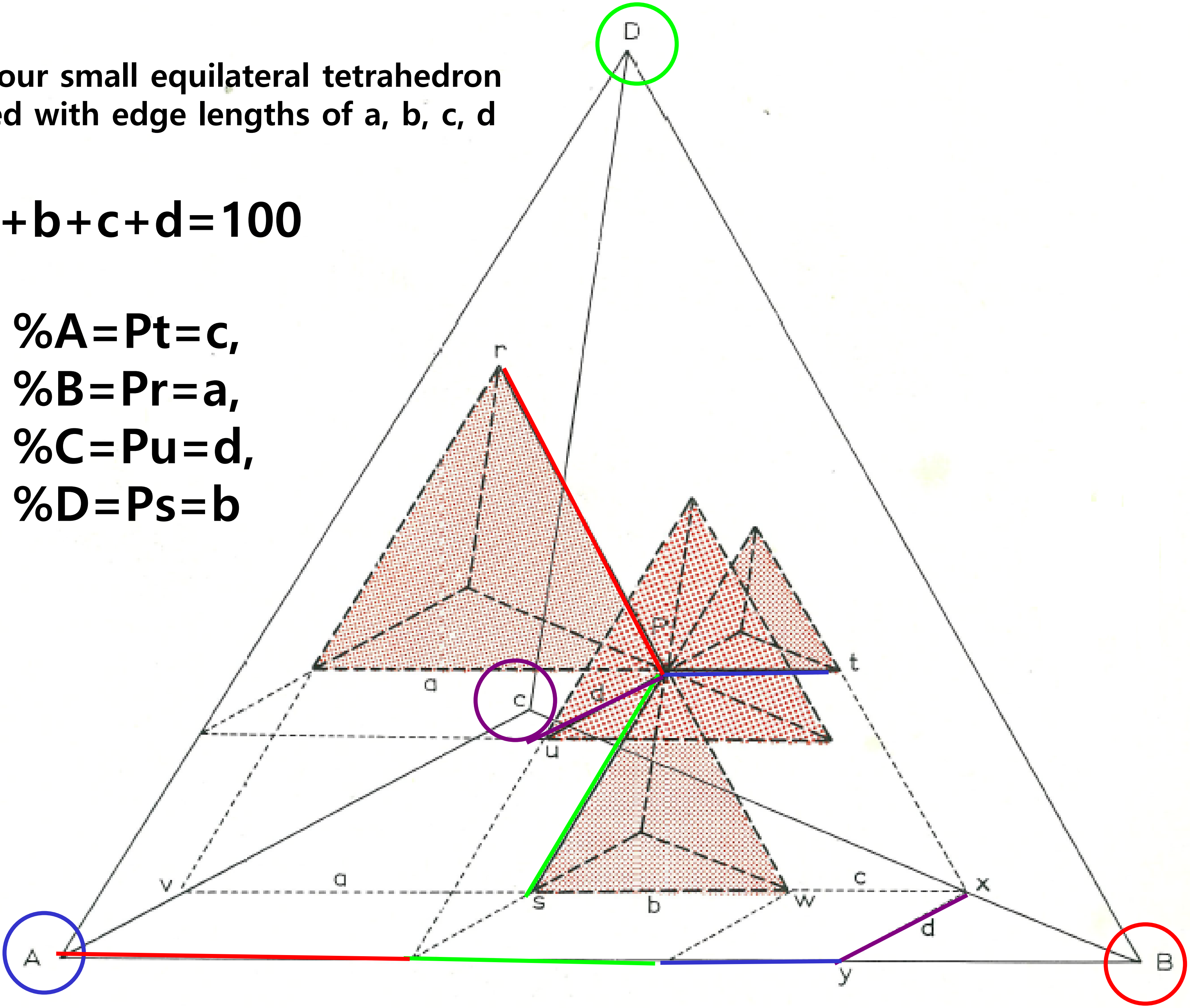
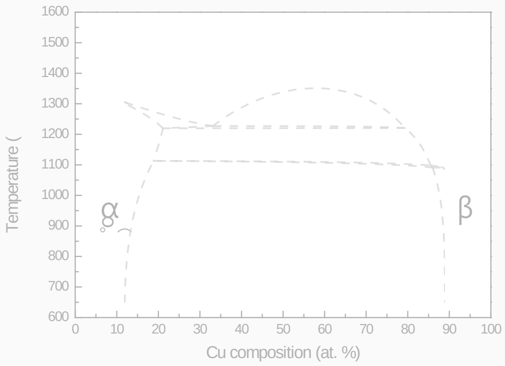


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

Q2: “Measurement of multi-component phase diagram”?

Construction of pseudo-binary phase diagram for multi-component alloy system

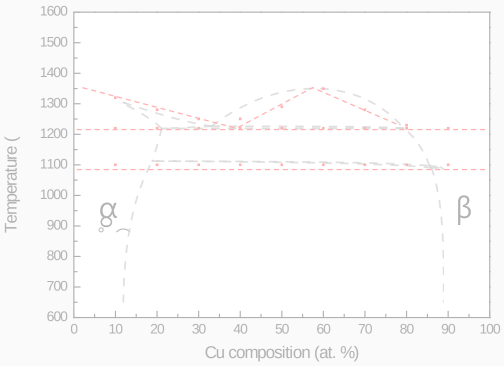


Thermodynamic calculation

- Expecting approximation of phase diagram

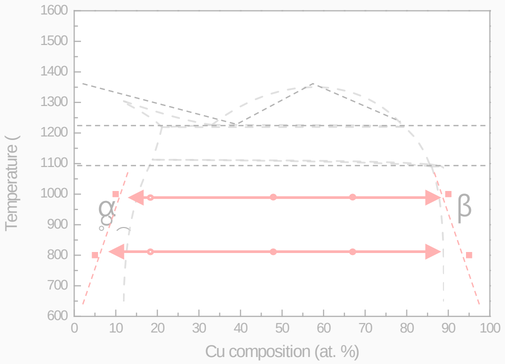
X-ray diffraction

- Determination of phases



TGA/DSC

- Finding out temperatures of phase transformations
- Confirming invariant reaction points

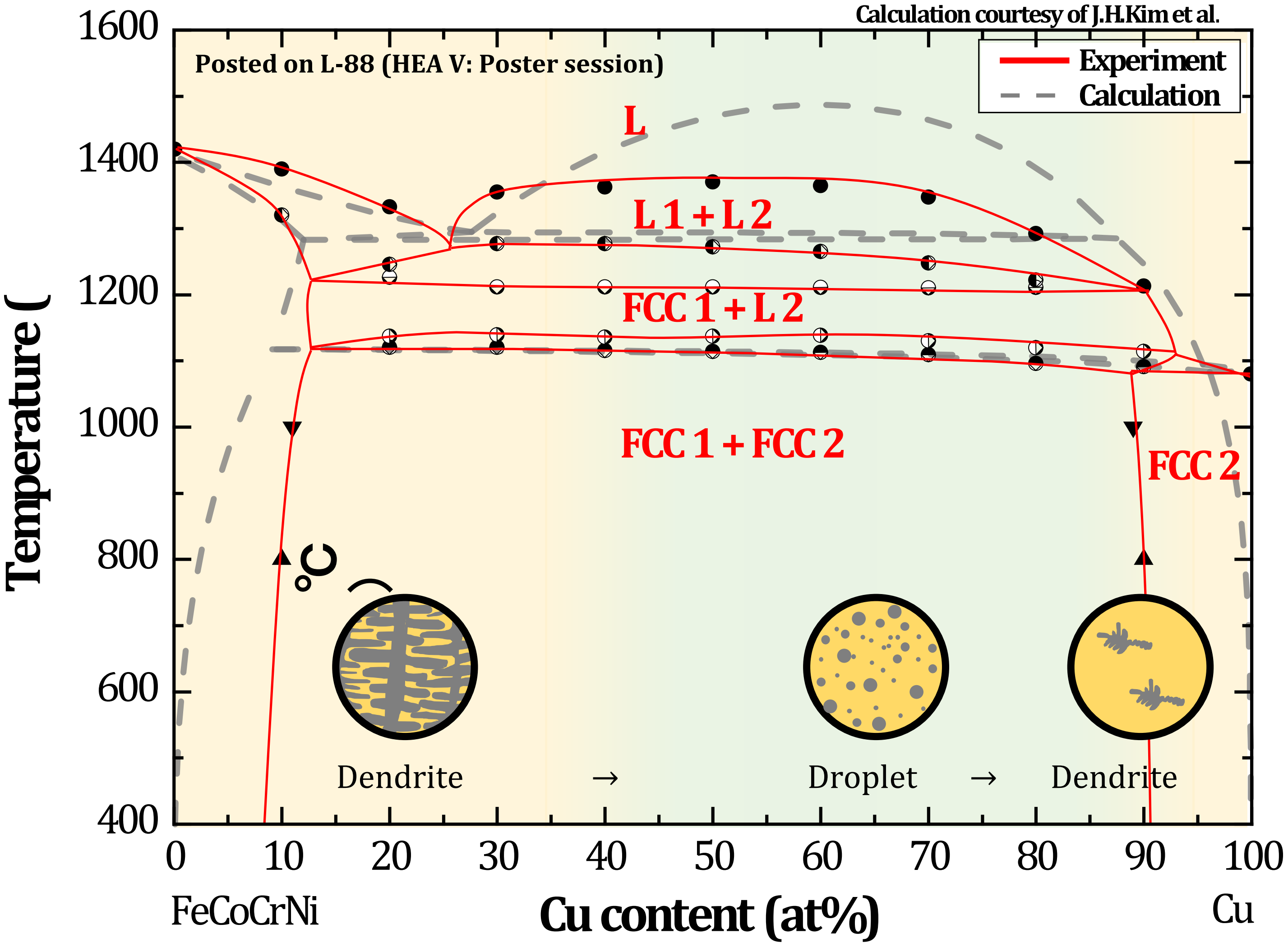


FE-EPMA

- Investigation of equilibrium composition at each temperature

➤ Phase diagram was expected to optimize composition and microstructure of phase separating HEA

Pseudo-binary phase diagram of PS-HEA



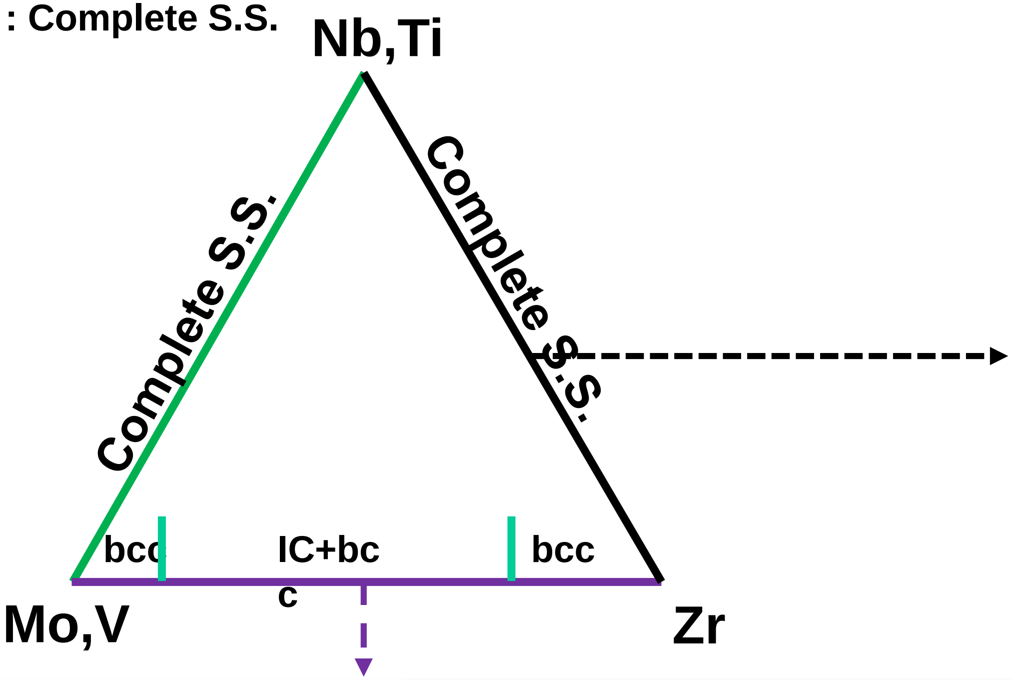
- Pseudo-binary system between FeCoCrNi and Cu shows monotectic reaction having liquid separation region.

MoVNbTiZr: Construction of pseudo-ternary phase diagram

Mo, V, Nb, Ti : Complete S.S.

V-Zr, Mo-Zr

Ti-Zr, Nb-Zr



Nb,Ti

Complete S.S.

Complete S.S.

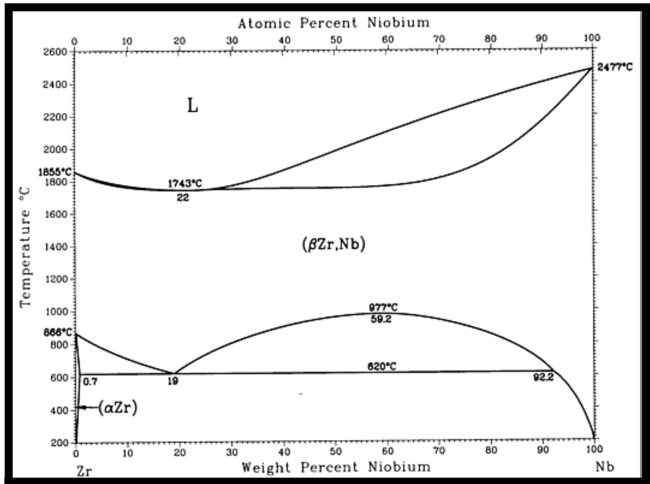
bcc

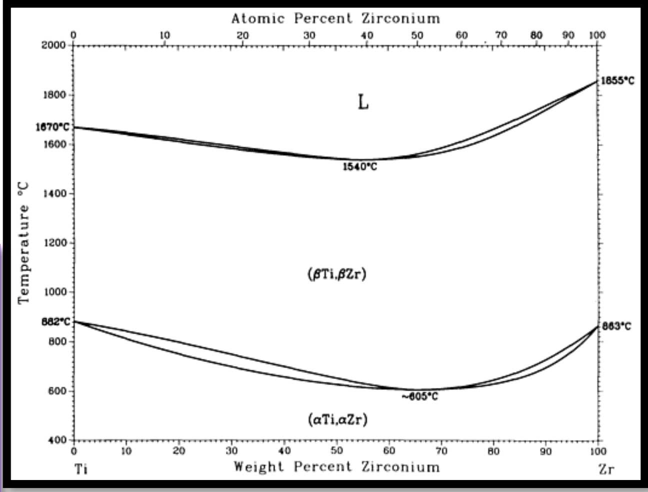
IC+bcc

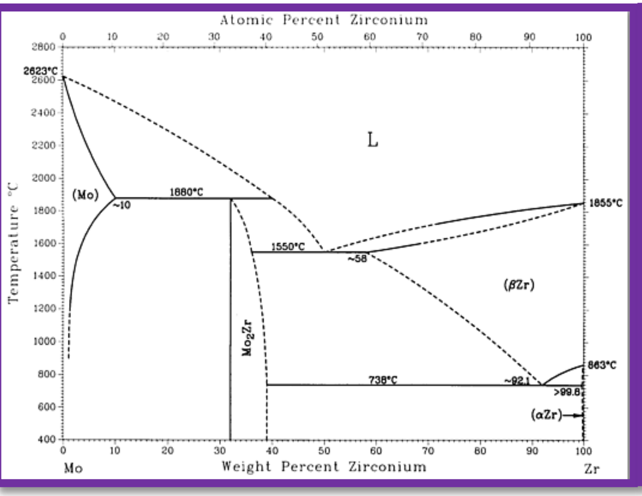
bcc

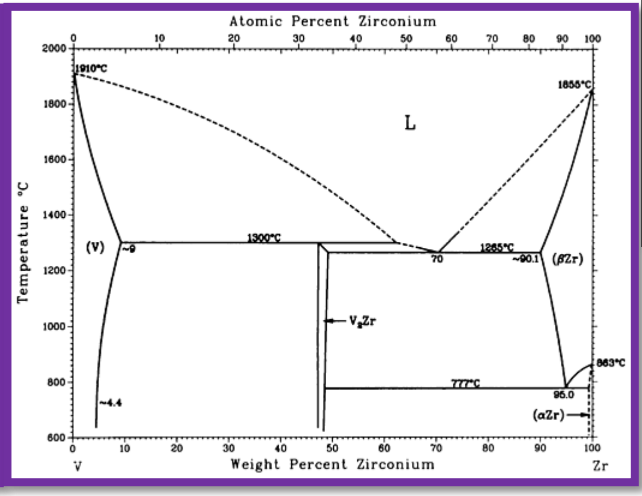
Mo,V

Zr

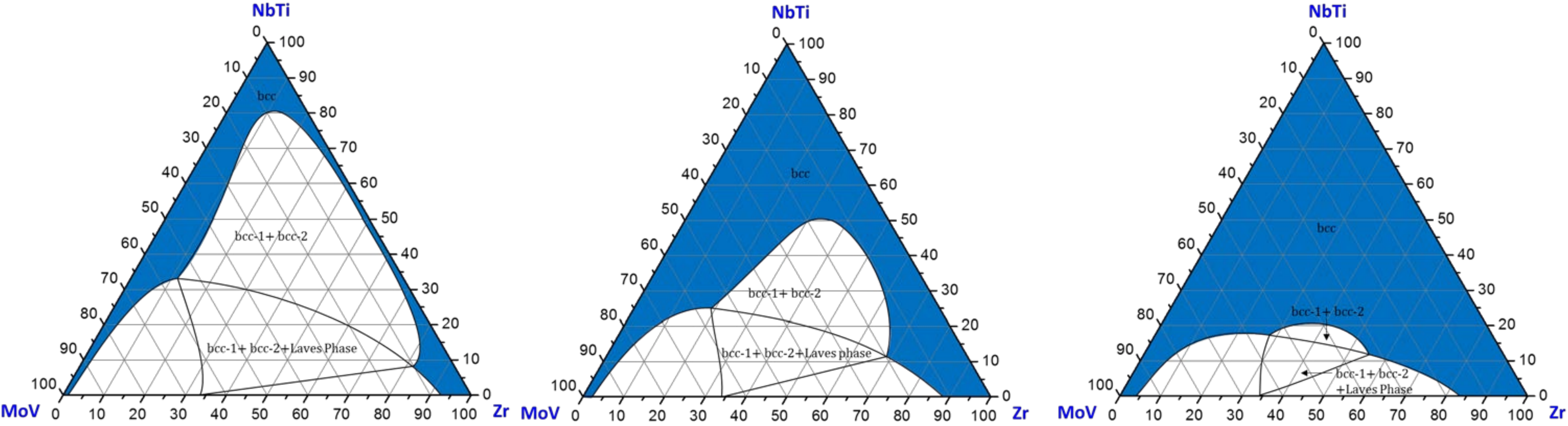








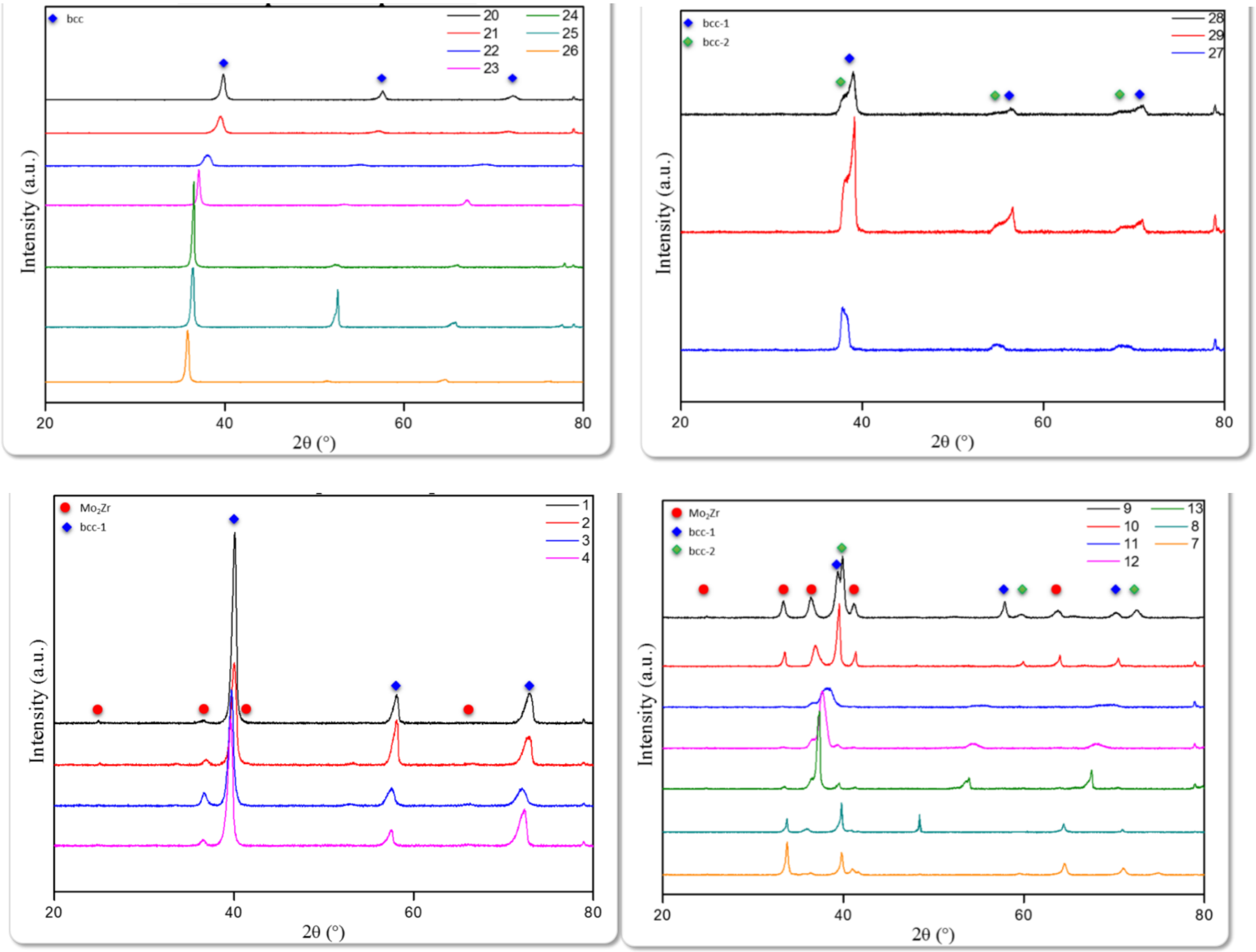
TiNbMoVZr: Construction of pseudo-ternary phase diagram



1100K 1300K 1500K

Calculated pseudo-ternary isothermal sections of the MoNbTiVZr system

MoVNbTiZr: Construction of pseudo-ternary phase diagram



X-ray diffraction analysis of the as-cast samples

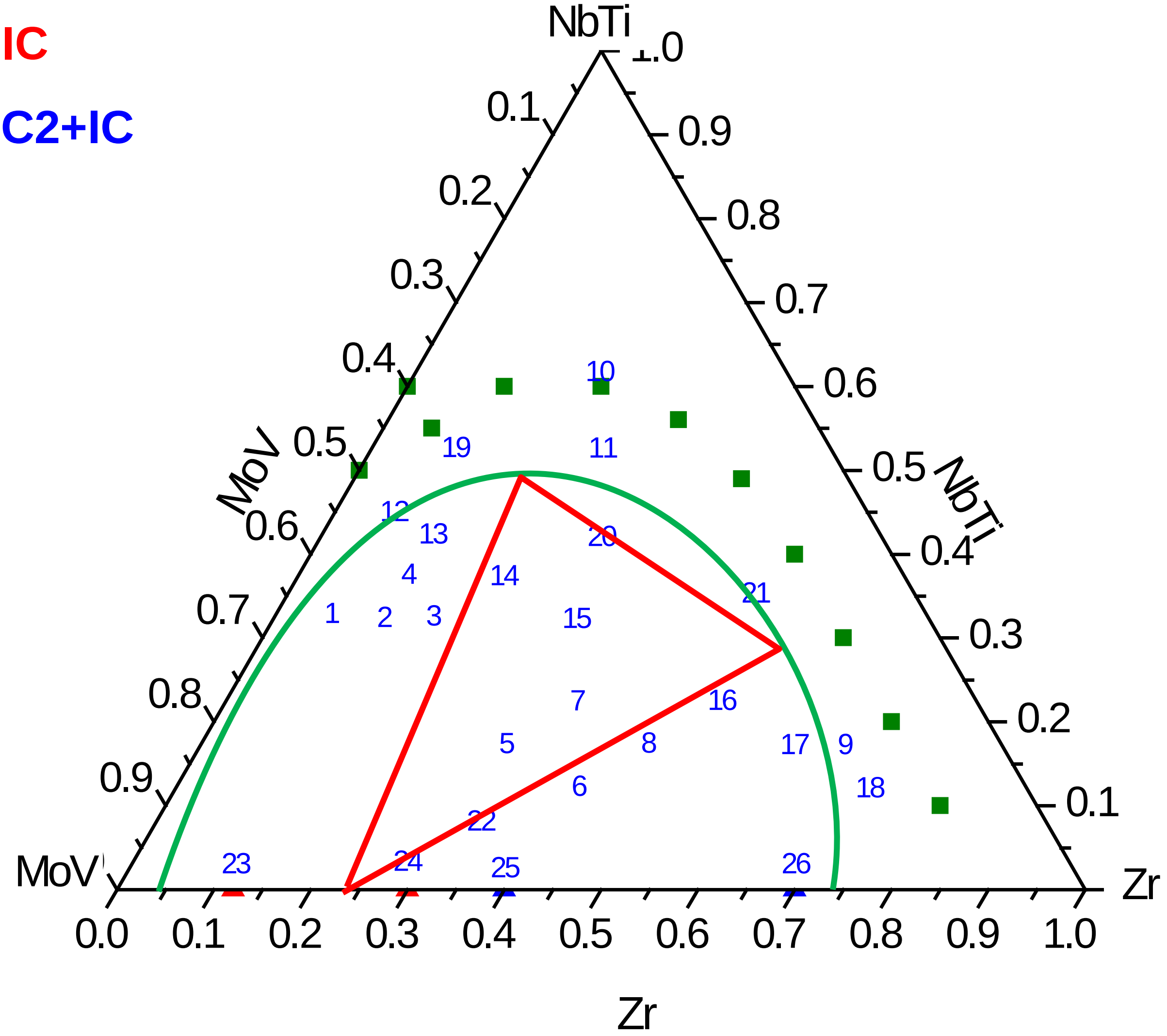
Construction of pseudo-ternary phase diagram

BCC1+BCC2+IC

BCC1+IC / BCC2+IC

BCC1+BCC2

Single BCC



Find single phase region without intermetallic compounds

Q3: “Computation of Phase Diagram”?

<Computation of Phase Diagram>

In the phase diagram, we found many differences between the predicted values and the experimental results! Therefore, it is necessary to calibrate the G value!

i) Pure Stoichiometric Substances

Original Calculation of Enthalpy & Entropy

$$H = H^{\mathrm{ref}} + \int_{T_{\mathrm{ref}}}^{T} C_p \, dT$$

$$S = S^{\mathrm{ref}} + \int_{T_{\mathrm{ref}}}^{T} \frac{C_p}{T} \, dT$$

Enthalpy and Entropy is State Function!
Substract Initial state to final state,
Integral of dH/dT, dS/dT

Debye Suggest Heat Capacity as a function of T!

$$C = D\left(\frac{\Theta}{T}\right)$$

Here, θ : Debye Temperatrue $= \dfrac{h\omega_D}{2\pi k}$

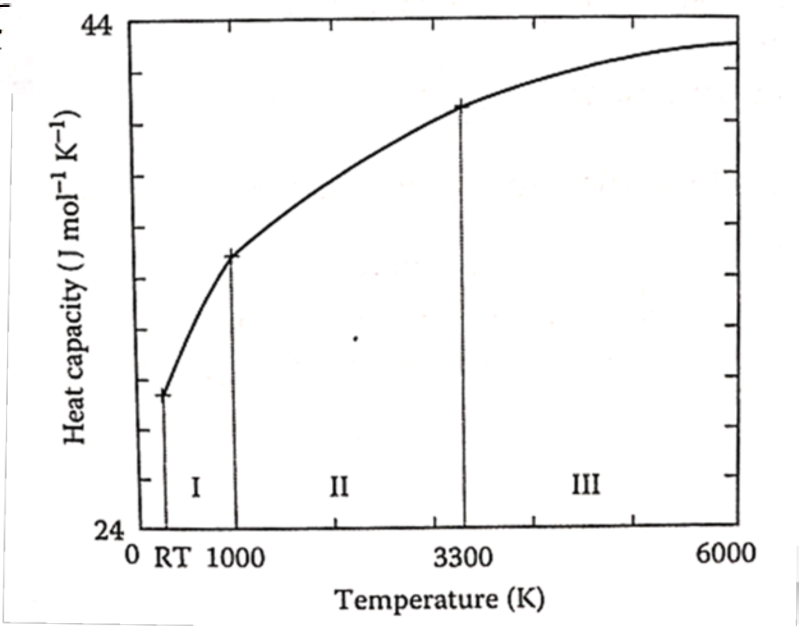
ω_D : Debye Frequency
(Maximum Frequency of lattice vibration)

After Mayer Kelley, more accurate to experiment result of specific heat capacity at Cp

$$C_p = C_1 + C_2 T + C_3 T^2 + \frac{C_4}{T^2}$$

➡

$$\boxed{G = C_1 + C_2 T + C_3 T \ln(T) + C_4 T^2 + C_5 T^3 + \frac{C_6}{T}}$$



$$G_m = G_{\text{lattice}} + G_{\text{magnetic}} + G_{\text{pressure}}$$

considering contribution of lattice & magnetic & pressure

<Magnetic Contribution>

$$G_{\text{magnetic}} = RTf\left(\frac{T}{T_c}\right)\ln(\beta+1)$$

Tc = Curie temperature
(to lose magnetic property)

β : magnetic moment per atom

f structure-dependent function of T

<Pressure Contribution>

$$G_{\text{pressure}} = V^0 \exp\left[\int_{298}^{T}\alpha(T)\mathrm{d}T\right]\frac{[1+nK(T)P]^{(1-(1/n))}-1}{(n-1)K(T)}$$

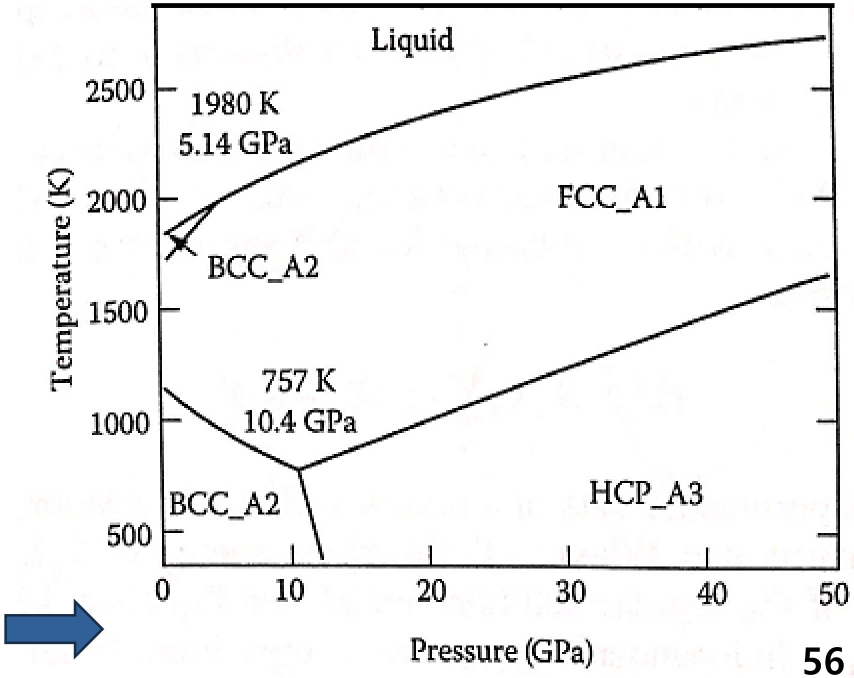
$$K(T) = K_0 + K_1T + K_2T^2$$

α(T) = thermal expansion of volume

$$= A_0 + A_1T + A_2T^2 + \frac{A_3}{T^2}$$

n is pressure derivative of bulk

This polynomial Function fit into real graph!



ii) Calculating G for Solid Solution

- Consider only **substitutional** solid solution.
- Binary ideal solution : $G^{id} = x_A G_A + x_B G_B + RT(x_A \ln x_A + x_B \ln x_B)$

⬇

- Multi-component ideal solution : $G^{id} = \sum X_i G_i + RT \sum X_i \ln(X_i)$
- Since $G = G^{id} + G^{ex}$, need calculation of $\boldsymbol{G^{ex}}$ for **G**

Method of Redlich & Kister

- Calculation of **ternary system** using thermodynamic data from **binary system**
  - Binary system : $G^{ex}_{AB} = x_A x_B \sum L^{(i)}_{AB} (X_A - X_B)^{(i)}$

L^{0}_{AB} independent of x_j
$L^{i\neq 0}_{AB}$ dependent of x_j

  - Ternary system : $G^{ex}_{ABC} = G^{ex}_{AB} + G^{ex}_{BC} + G^{ex}_{CA}$
- Use experimental value of ternary solid solution
  - Add $x_A x_B x_C L^{0}_{ABC}$ to the G^{ex}_{ABC} term for correction
  - Further correction → use expansion of the expression

$$x_A x_B x_C [L^{(0)}_{ABC} + \frac{1}{3}(1 + 2x_A - x_B - x_C) L^{(1)}_{ABC}$$
$$+ \frac{1}{3}(1 + 2x_B - x_A - x_C) L^{(1)}_{BCA} + \frac{1}{3}(1 + 2x_C - x_B - x_A) L^{(1)}_{CBA}]$$

Further multi-component system

- Quaternary system → need thermodynamic data from ternary system to calculate.
- Some data of ternary system is not available
- Database of quaternary system is not yet established
- Still, it is possible to calculate by correction using

  $x_A x_B x_C x_D L_{ABCD}^{(0)}$ term to G^{ex}

Homework1 :

Please explain more detail how to calculate multi-component phase diagram reflecting excess Gibbs energy (within 5 pages PPT)

*** Incentive Homework 1**

Please submit ternary phase diagram model which can clearly express 3D structure of ternary system by October 15 in Bldg. 33-313.
You can submit the model individually or
with a small group under 2 persons.

*** Homework 2 : Exercises 1 (pages 61-63)**

Good Luck!!

2021 Fall

"Phase Transformation *in* Materials"

2021.10.04.

Eun Soo Park

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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

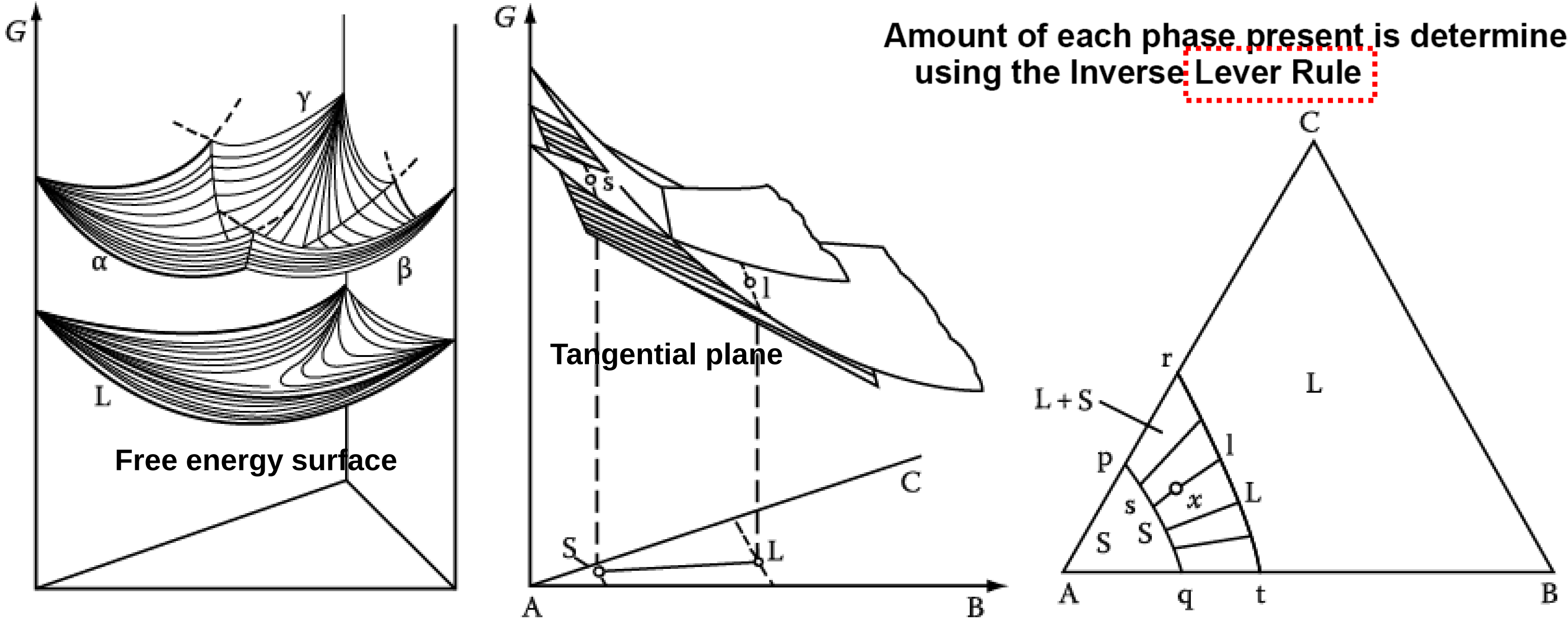
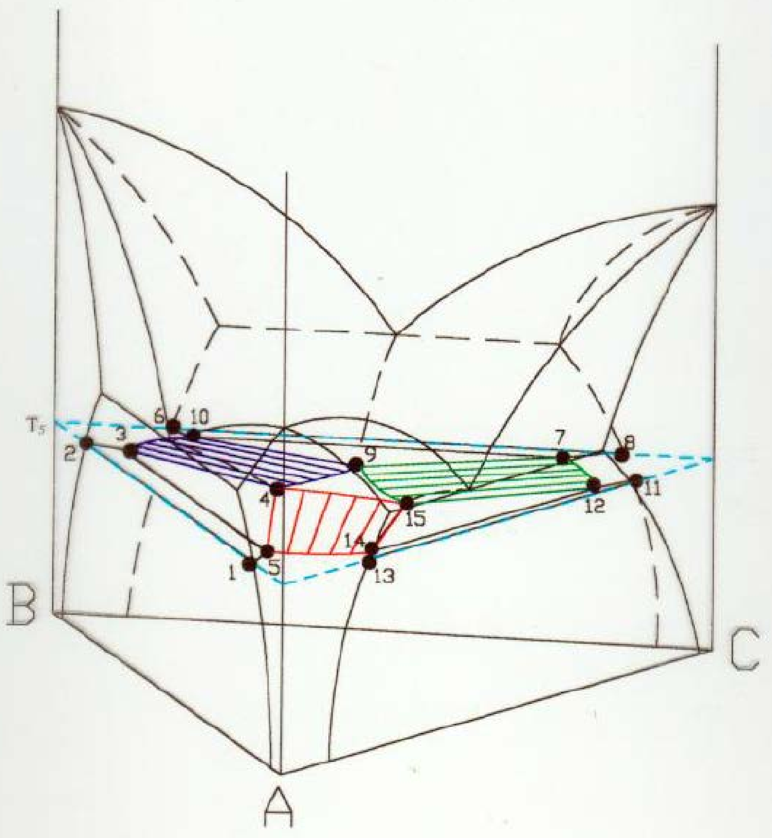


Fig. 1.41 (a) Free energy surface of a liquid and three solid phases of a ternary system. (b) A tangential plane construction to the free energy surfaces defined equilibrium between s and l in the ternary system (c) Isothermal section through a ternary phase diagram

Ternary Eutectic System

(with Solid Solubility)

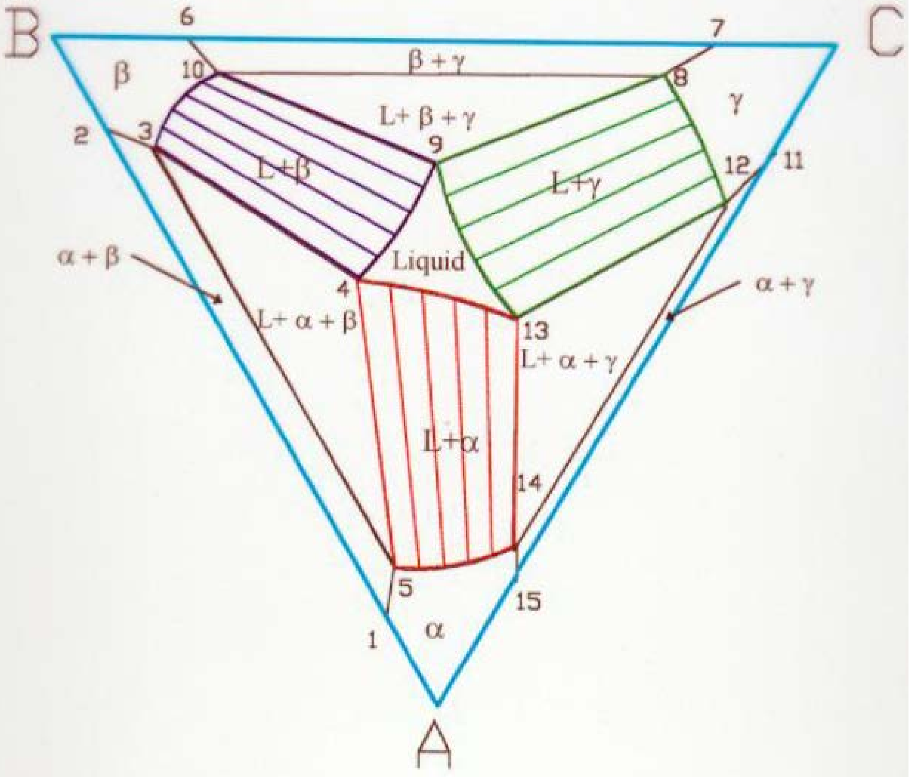
T5A:



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

T5B:

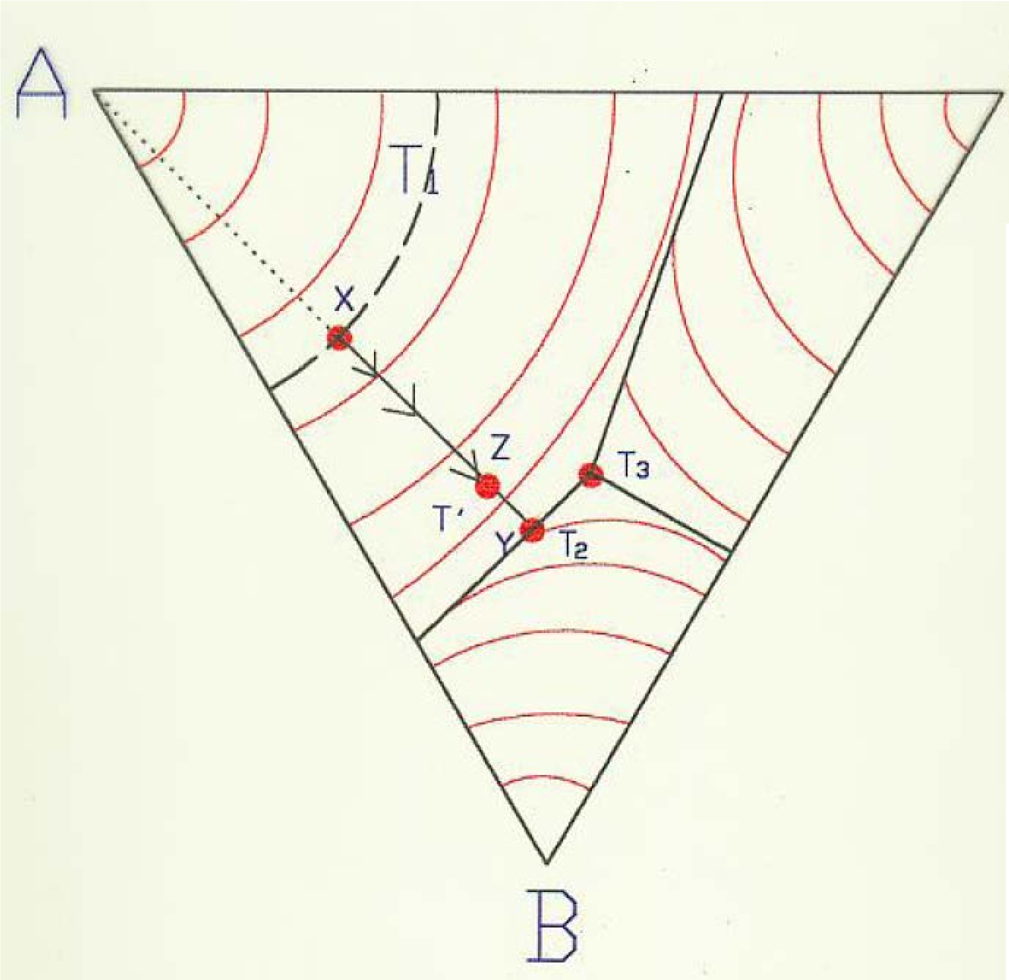
3 phases region: tie triangle

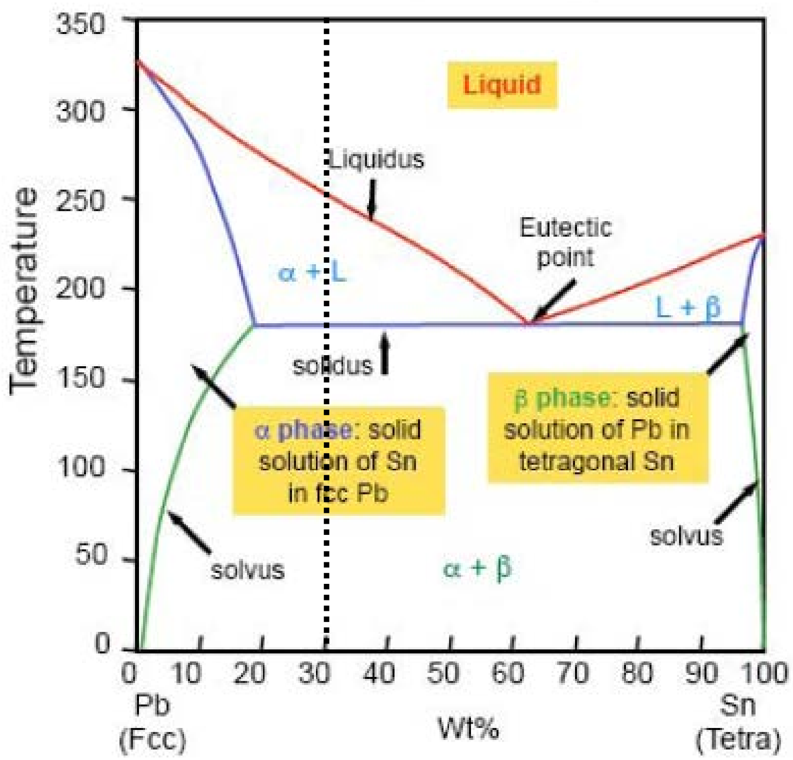


Isothermal Section At T=T$_5$

Ternary Eutectic System

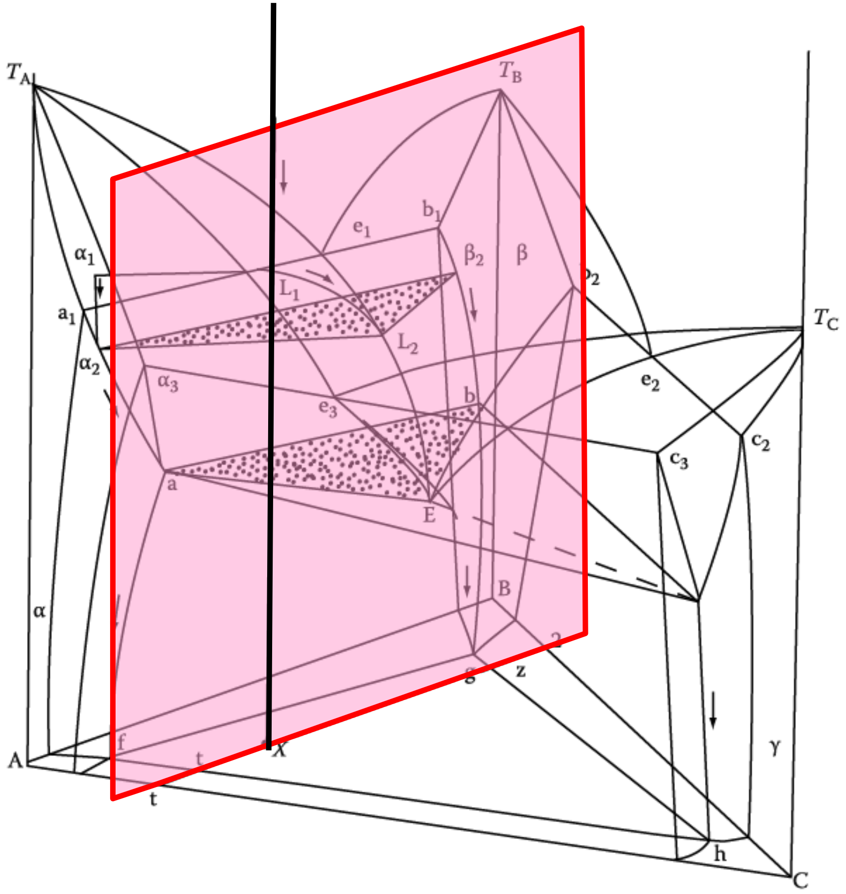
3) Solidification Sequence: liquidus surface

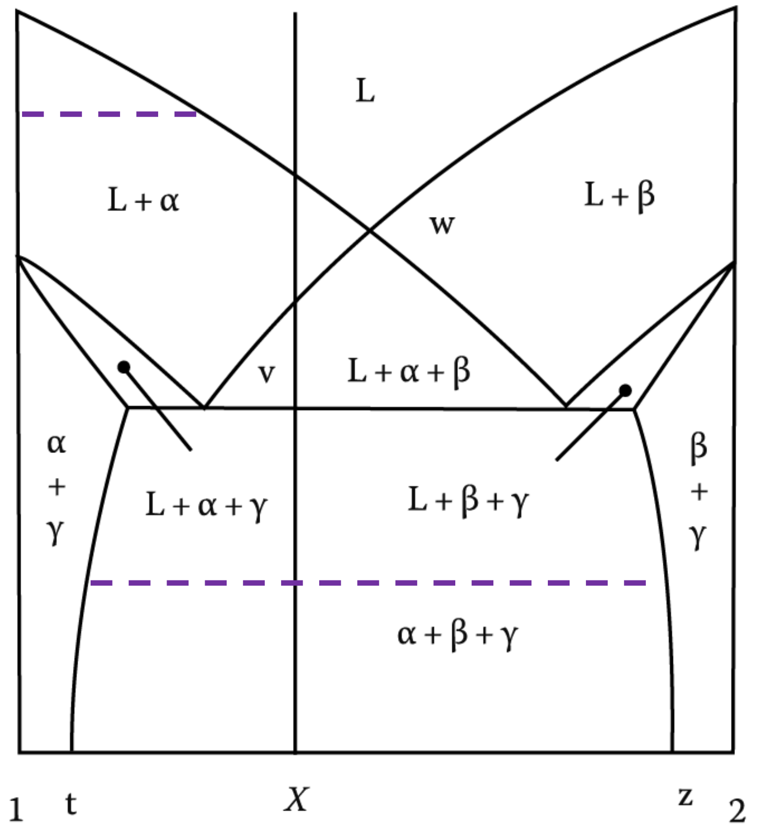




Ternary Eutectic System

* Vertical section





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

* Information for equilibrium phases
  at different temperatures

< Quaternary phase Diagrams >

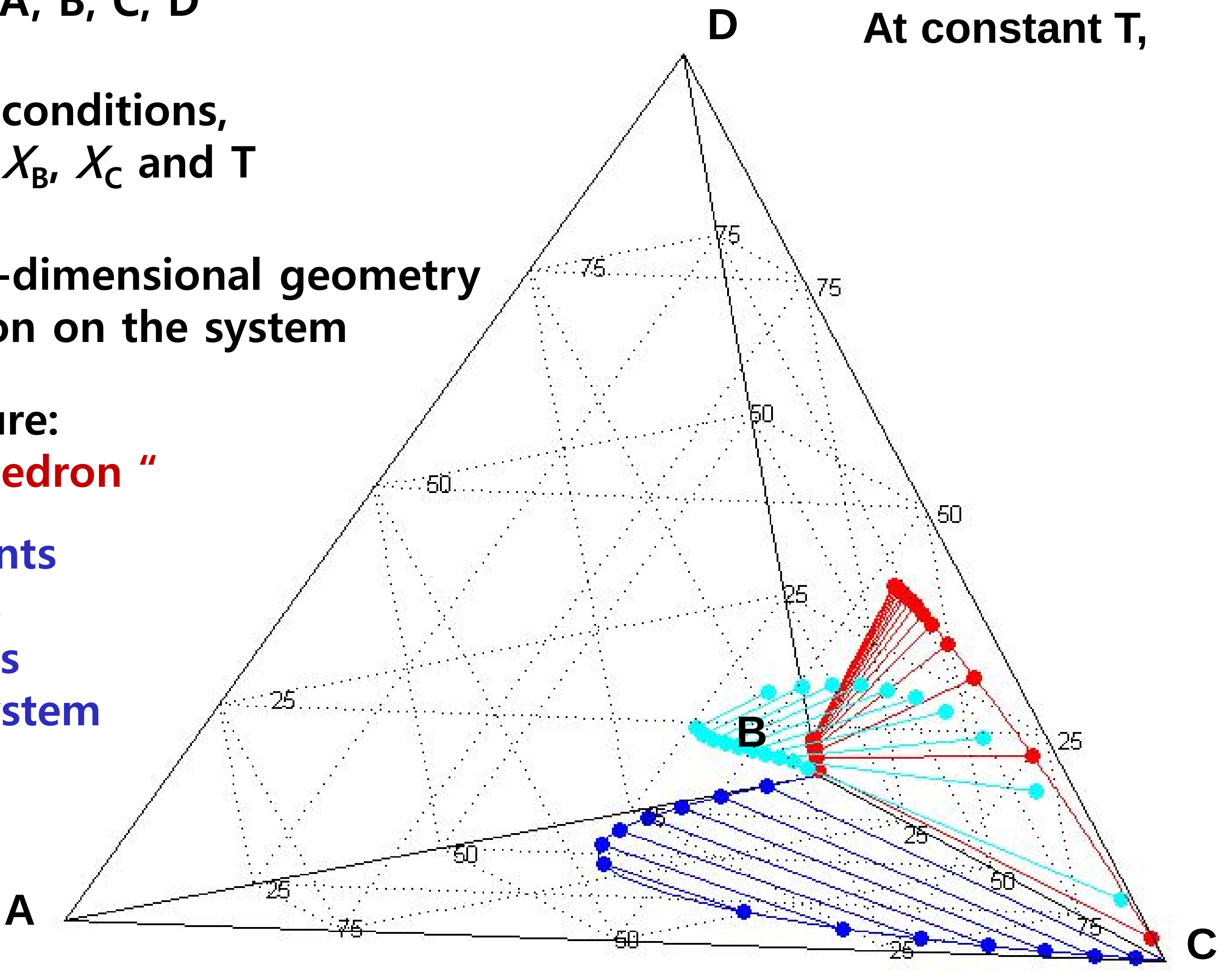
Four components: A, B, C, D

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 quarternary 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

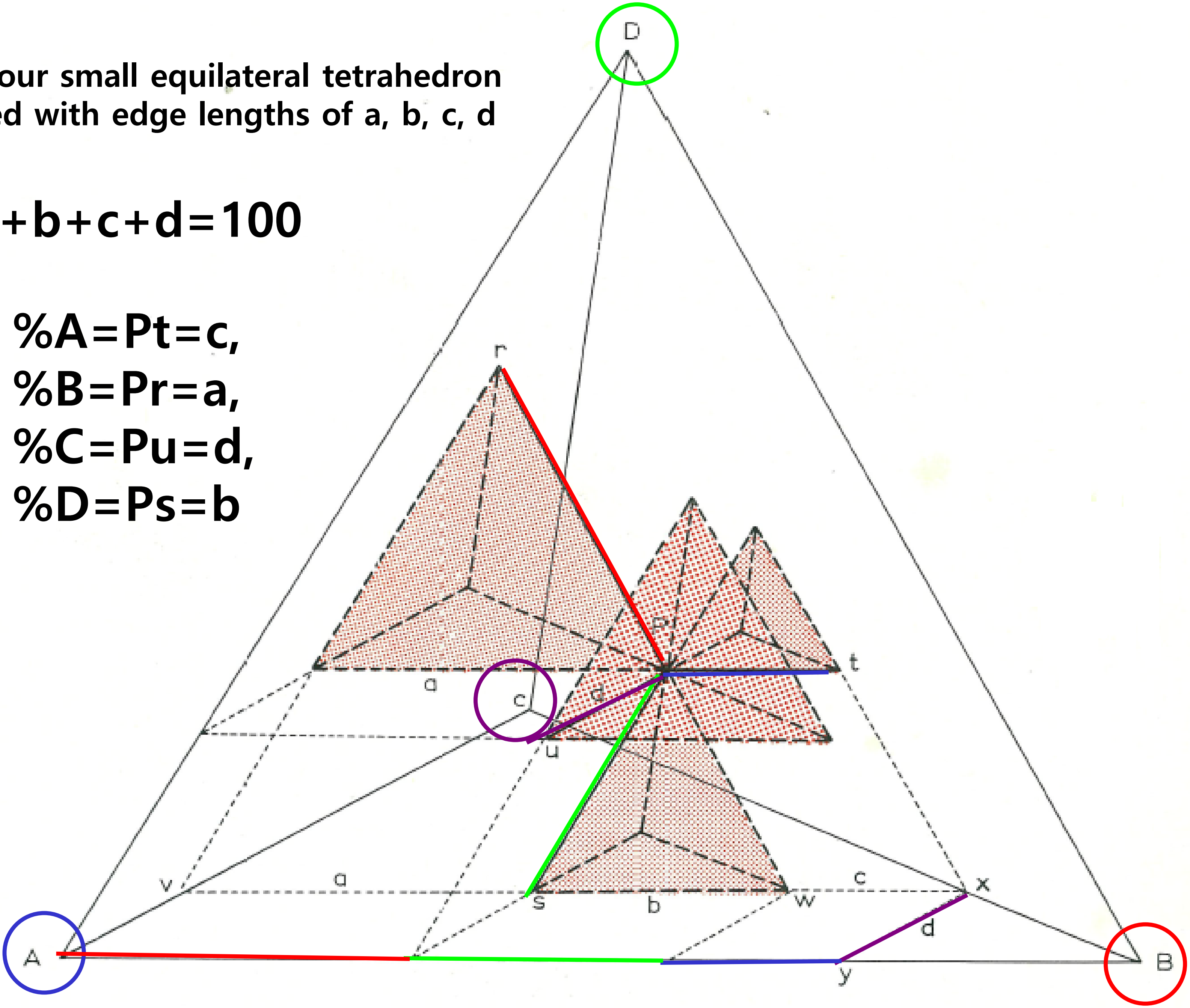
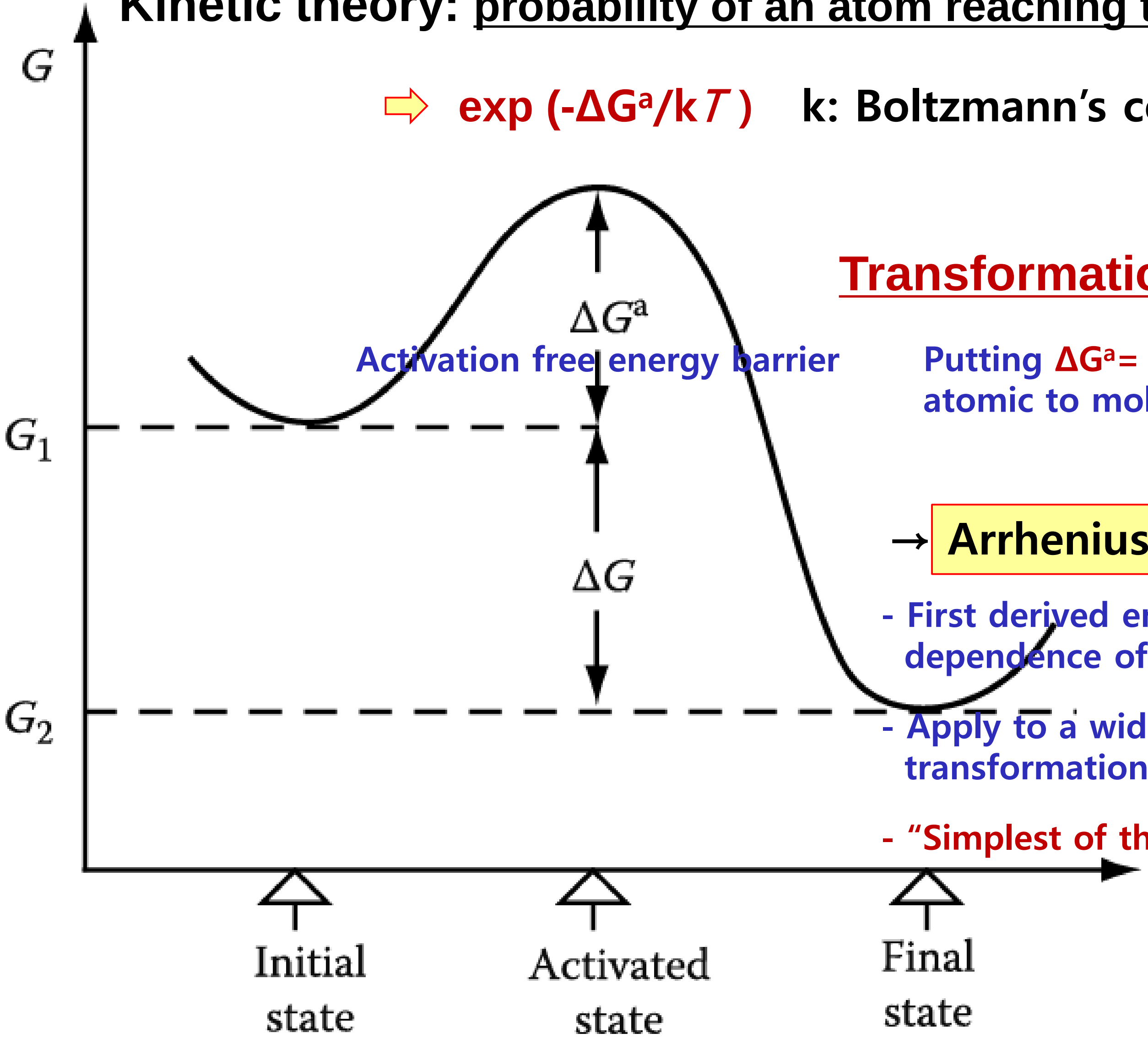


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

1.10 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)

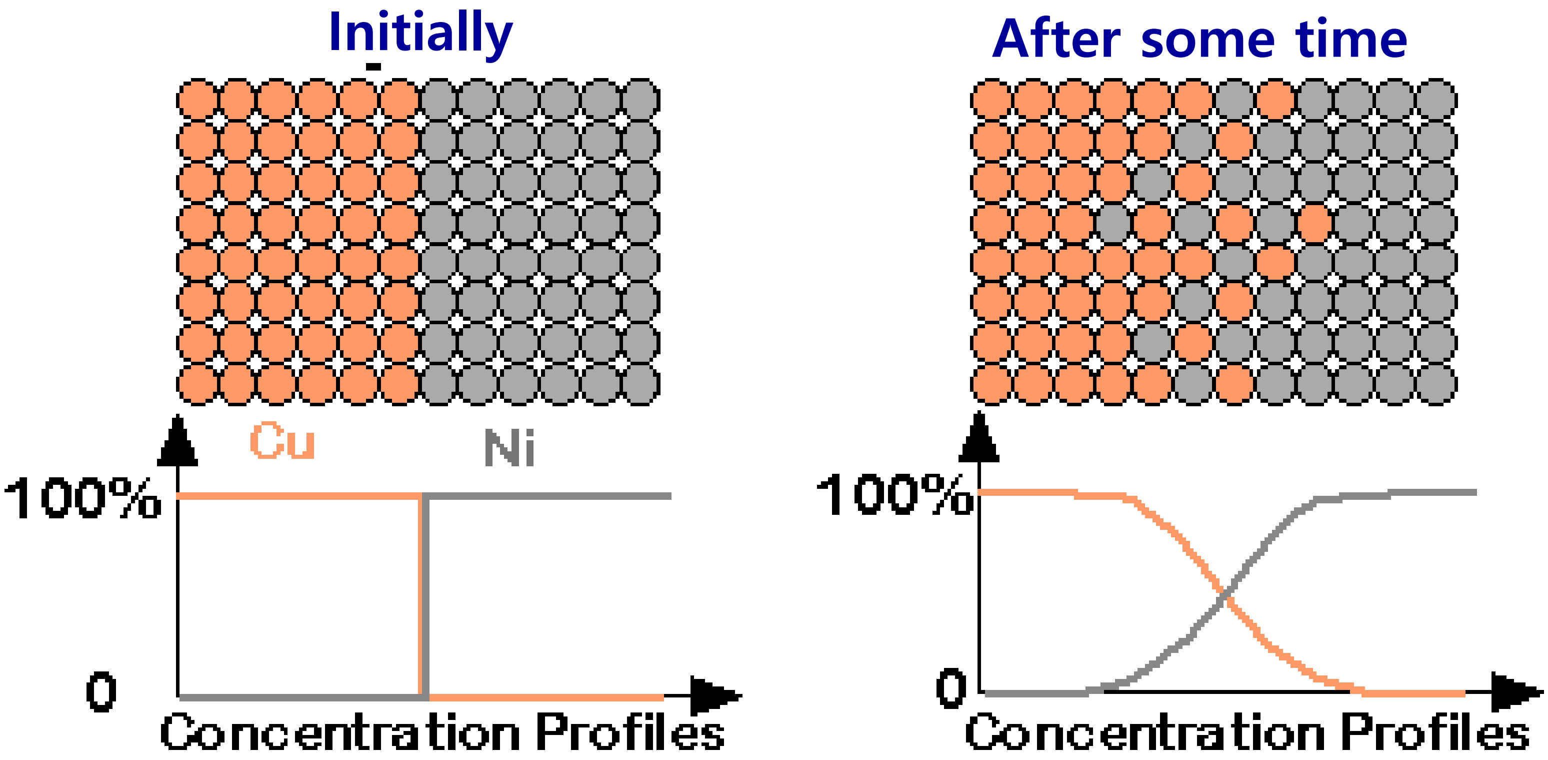
⇒ a chemical potential gradient (o)

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.



Initially

After some time

< Diffusion couple between Cu and Ni >

Mechanism of Solid-State Diffusion

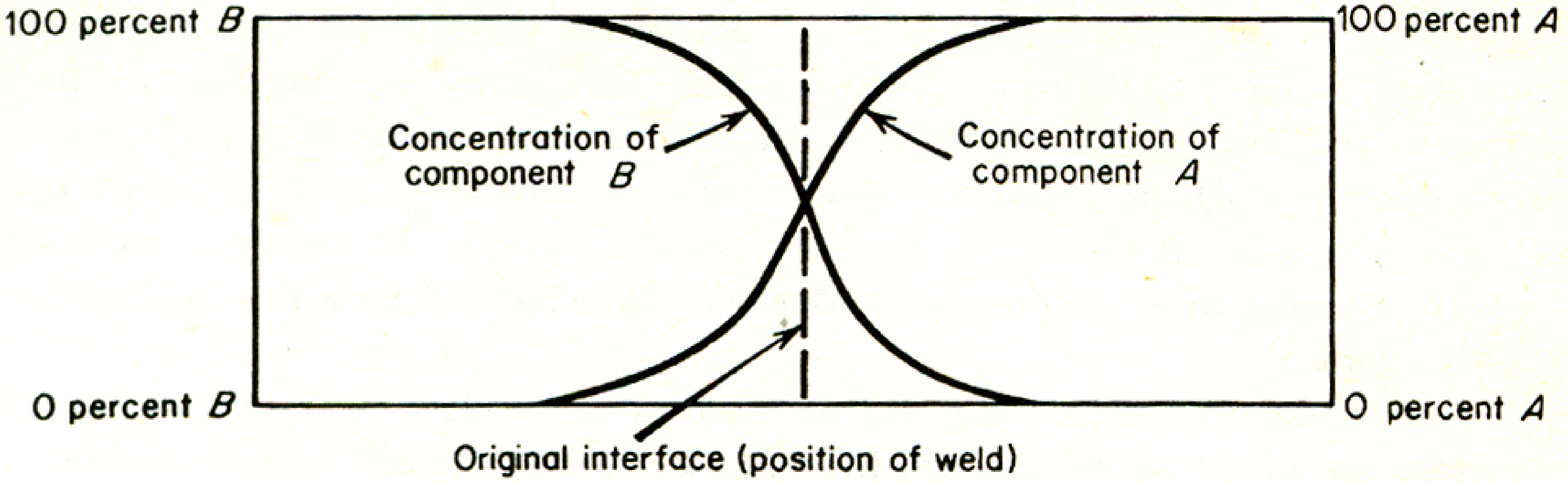


Fig. 10.6 Curves showing concentration as a function of distance along a diffusion couple. Curves of this type are usually called *penetration curves.*

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

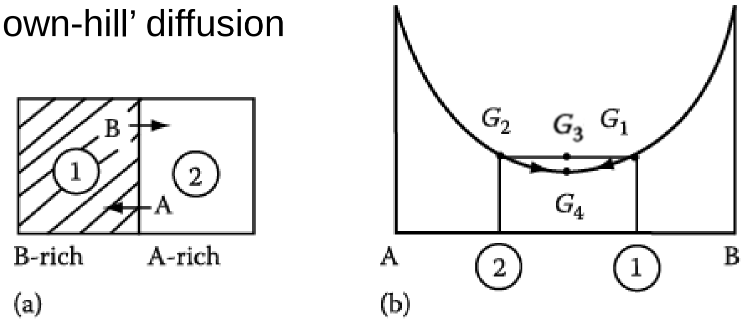
Down-hill diffusion

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

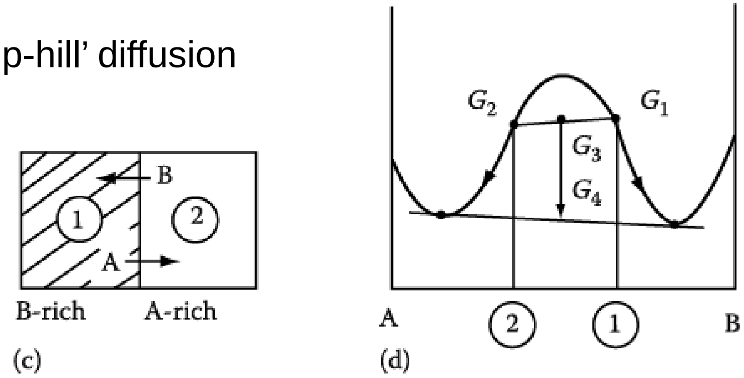
Up-hill diffusion

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

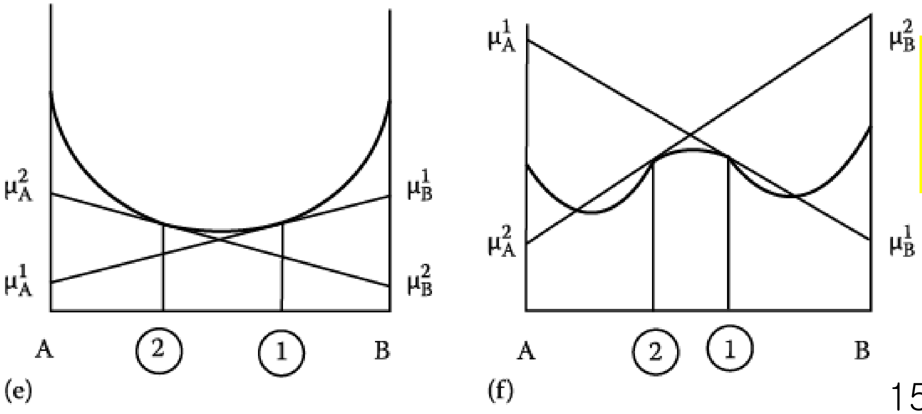
‘down-hill’ diffusion



‘up-hill’ diffusion



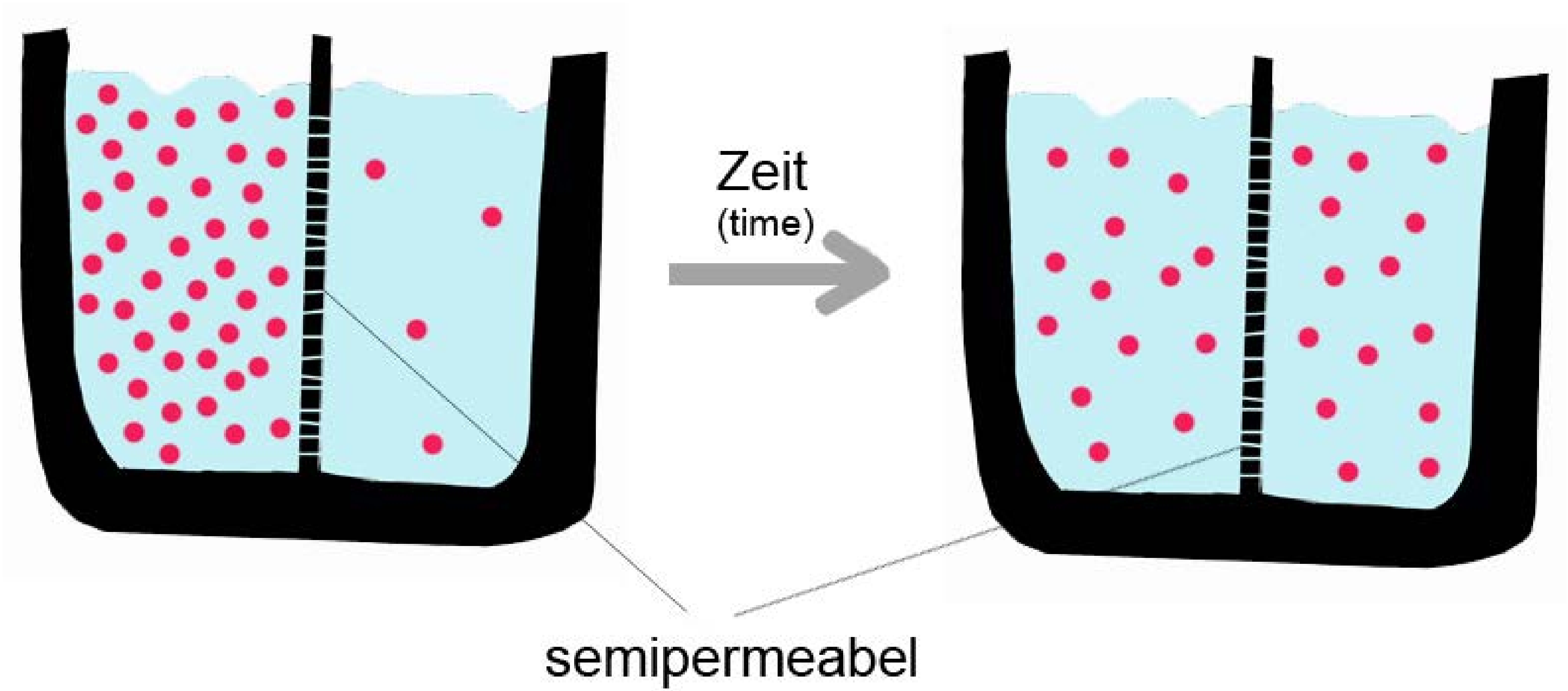
$$\mu_A^1 < \mu_A^2$$
$$\mu_B^1 > \mu_B^2$$



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

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

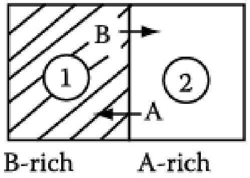
Down-hill diffusion

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

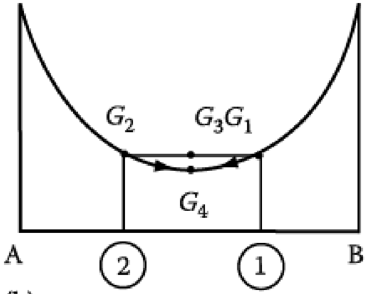
Up-hill diffusion

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

‘down-hill’ diffusion

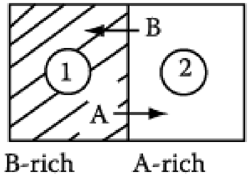


(a)

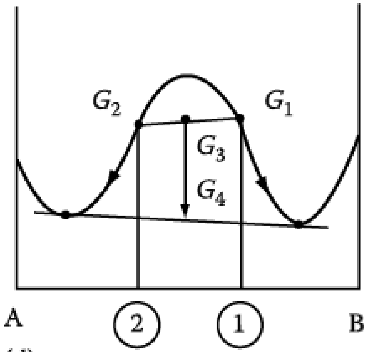


(b)

‘up-hill’ diffusion

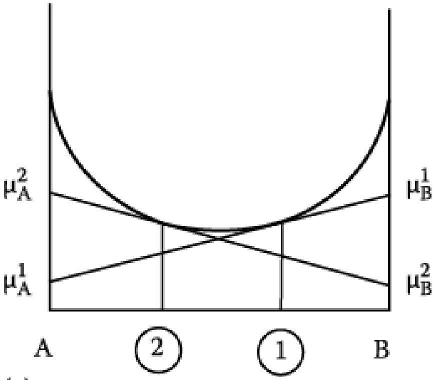


(c)

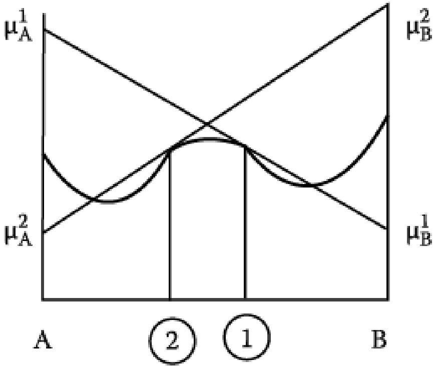


(d)

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



(e)



(f)

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

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

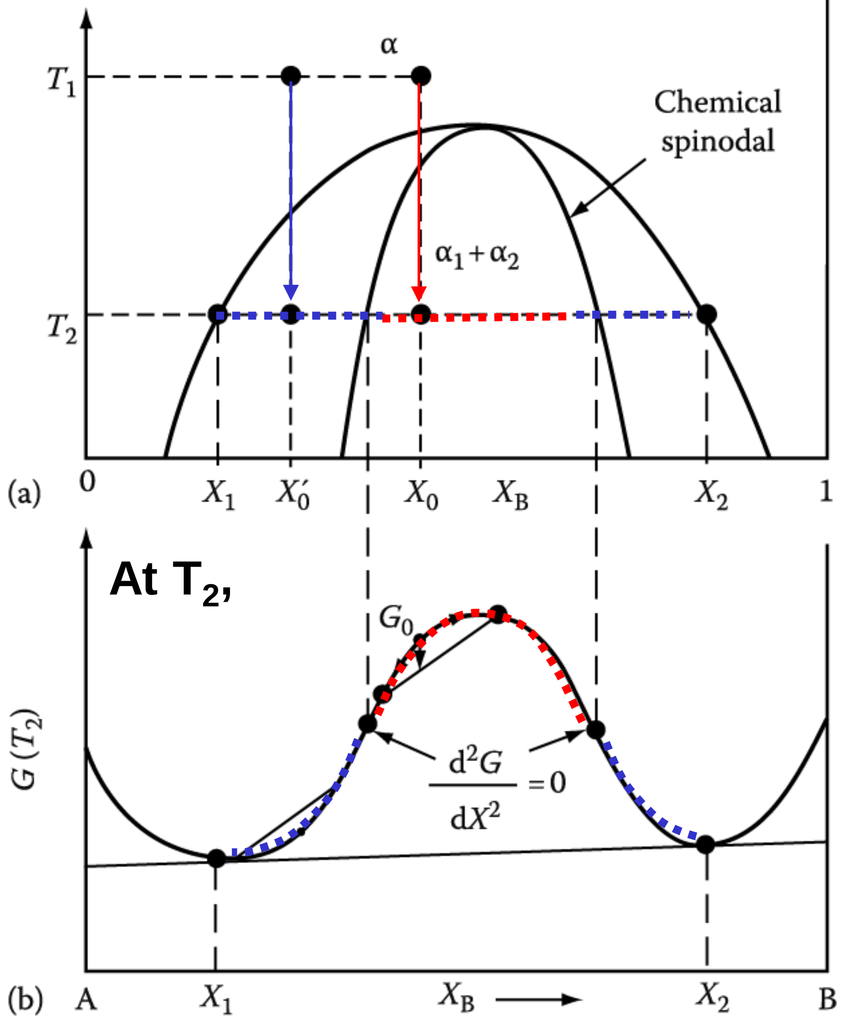


Fig. 5.38 Alloys between the spinodal points are unstable and can decompose into two coherent phasees α_1 and α_2 without overcoming an activation energy barrier. Alloys between the coherent miscibility gaps and the spinodal are metastable and can decompose only after nucleation of the other phase.

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

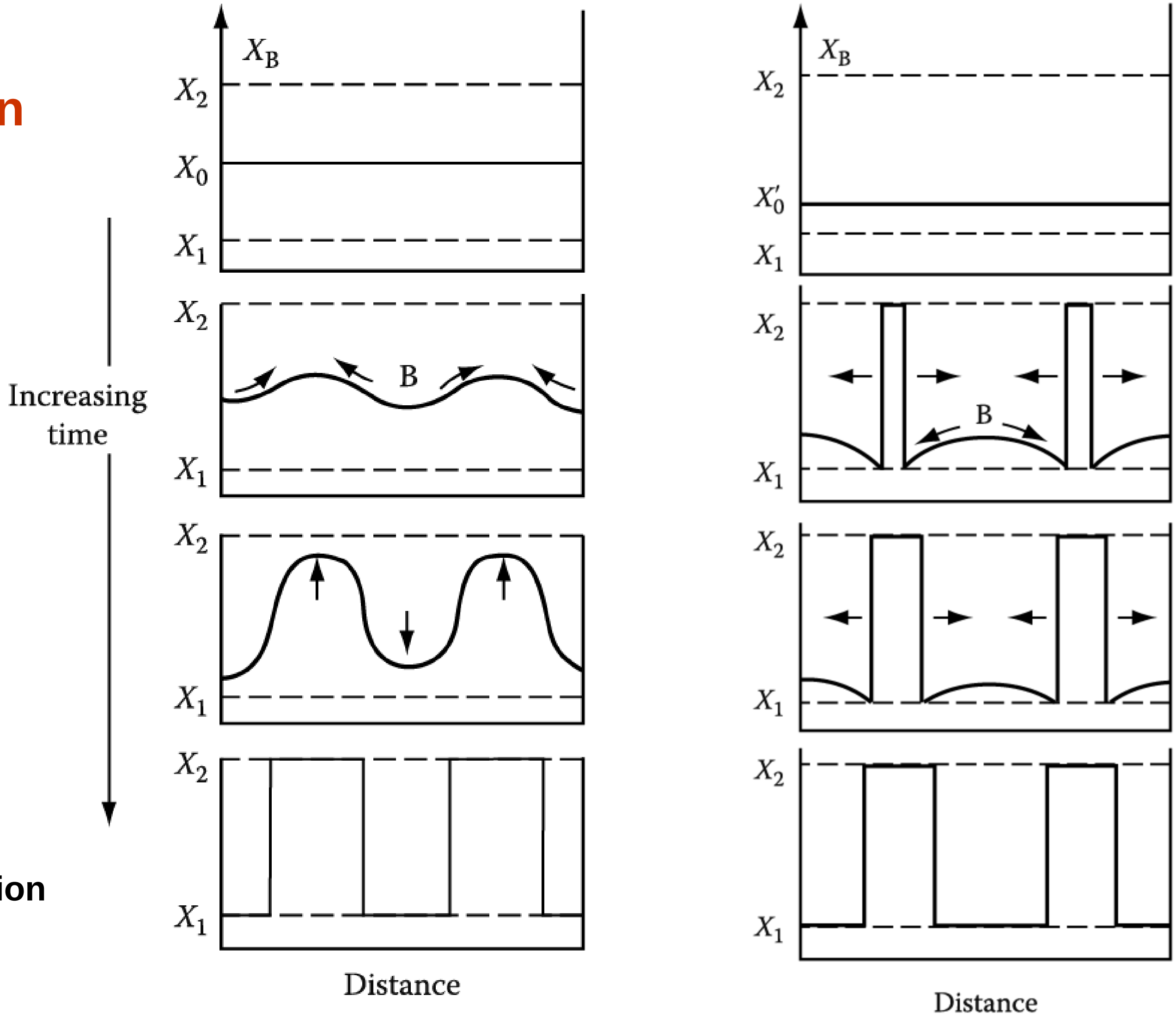
: "down-hill diffusion"

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 & 5.40 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?

⇒ a concentration gradient (x)

⇒ 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

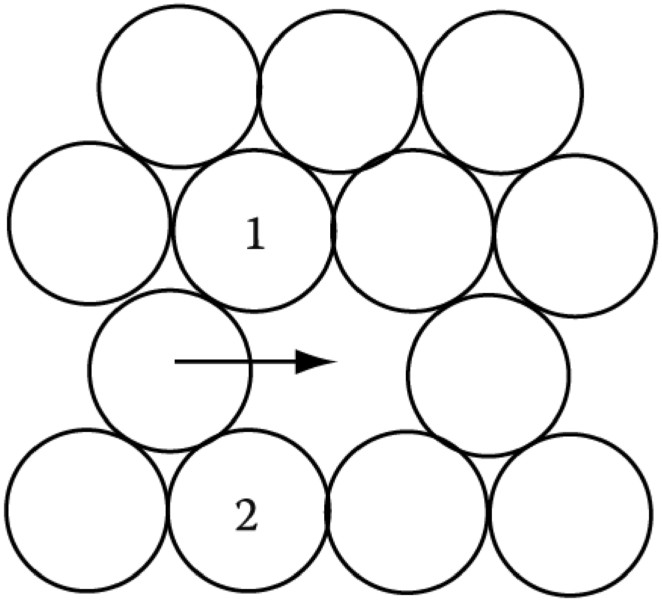
$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

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.

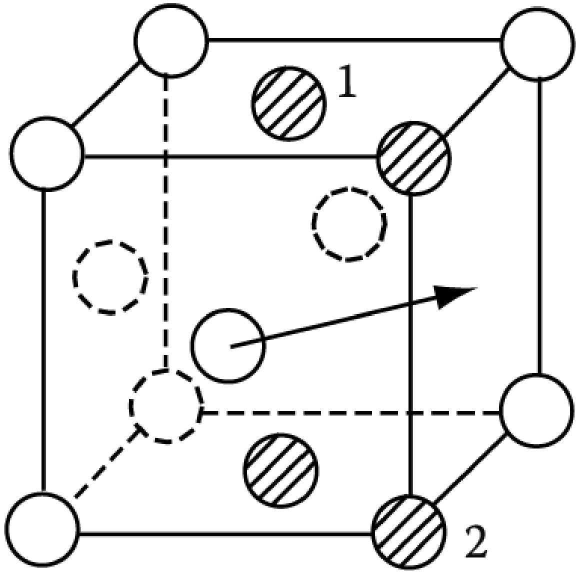
Substitutional vs. Interstitial diffusion

Substitutional diffusion



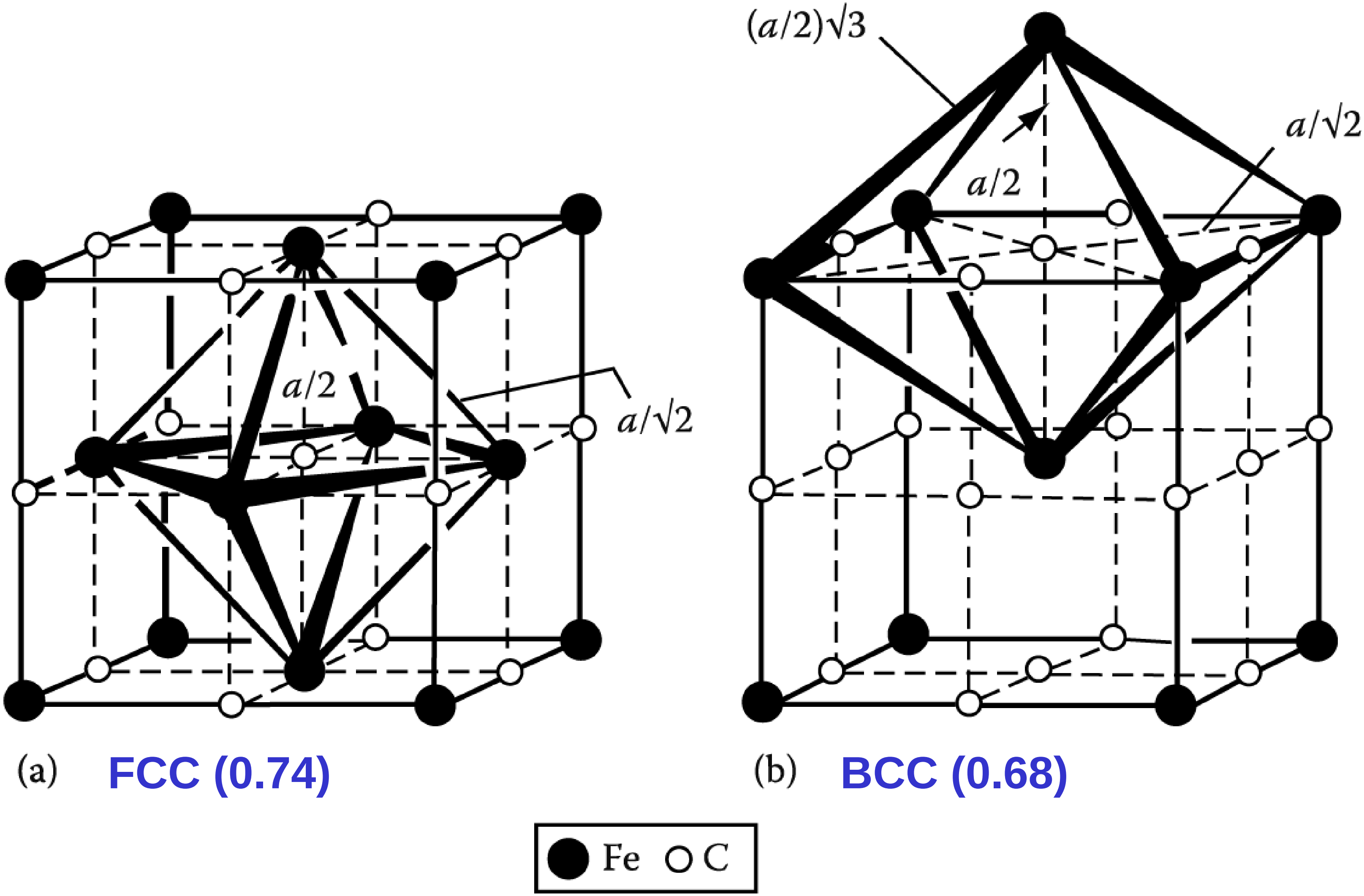
(a) **# of vacant site**

FCC



(b)

Interstitial diffusion

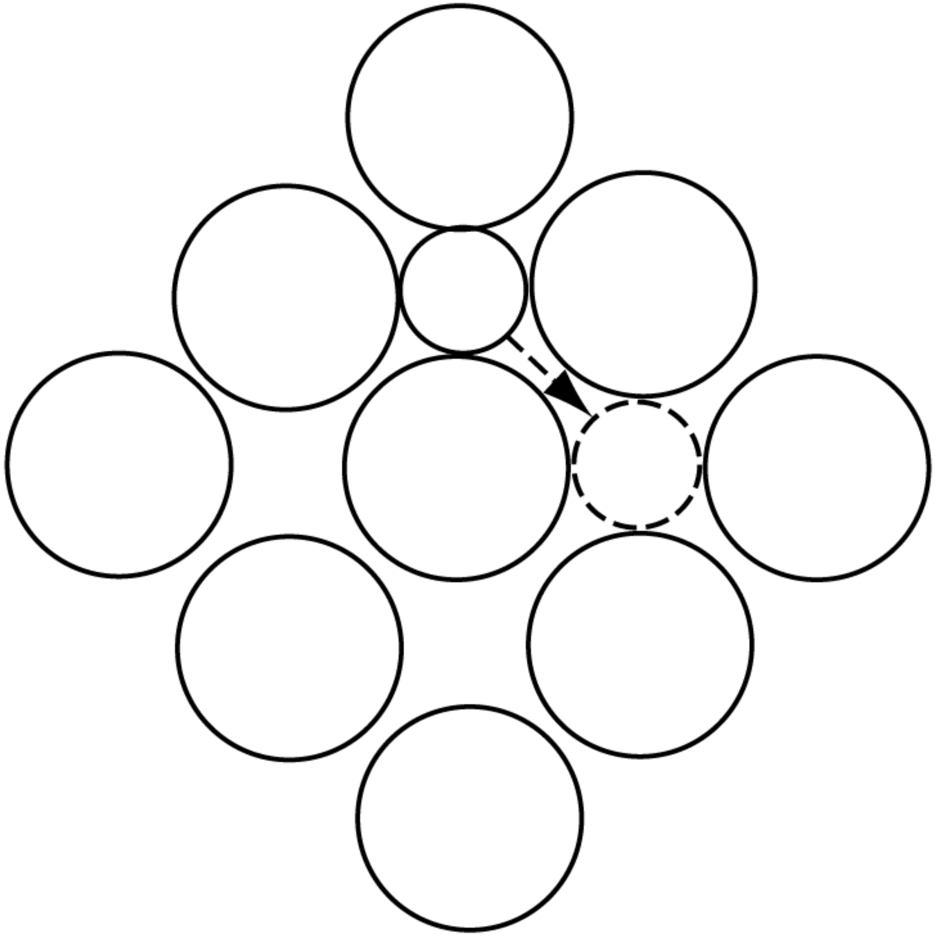


(a) **FCC (0.74)**

(b) **BCC (0.68)**

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

Interstitial diffusion



How interstitial diffusion differs from substitutional diffusion?

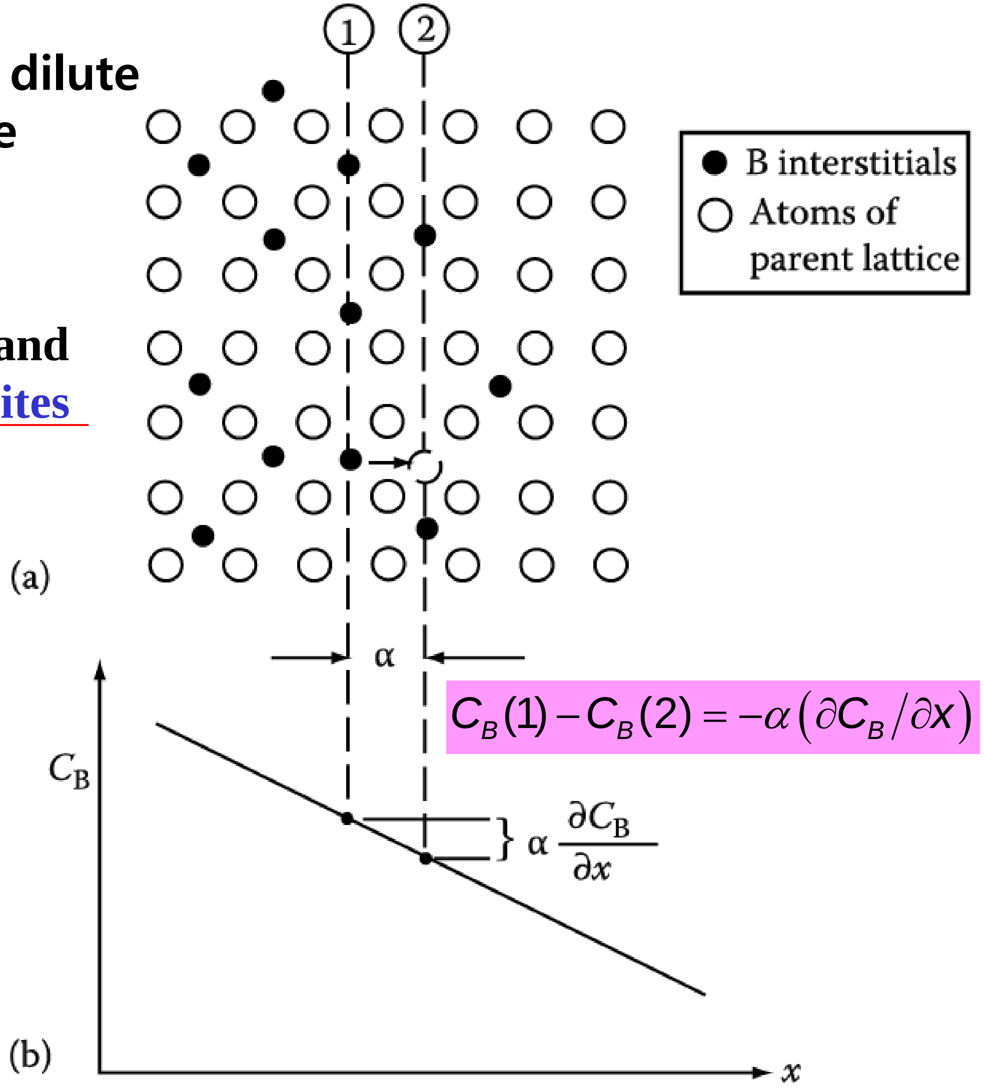
Interstitial diffusion

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.

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

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



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

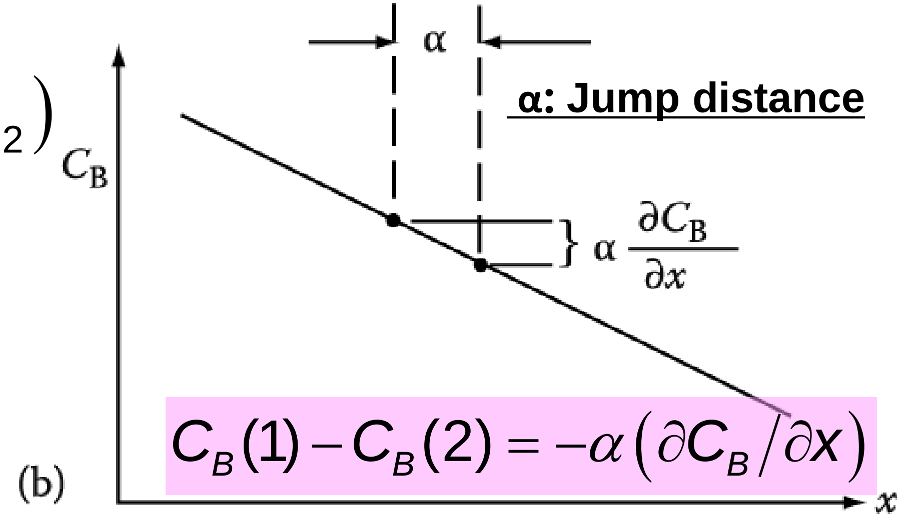
Fig. 2.5 Interstitial diffusion by random jumps in a concentration gradient.

Fick's First Law of Diffusion

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

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

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



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

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

(atoms m^{-2} s^{-1})

➡ **Concentration varies with position.**

D$_B$: Intrinsic diffusivity or
Diffusion coefficient of B

⇒ **depends on microstructure of materials**

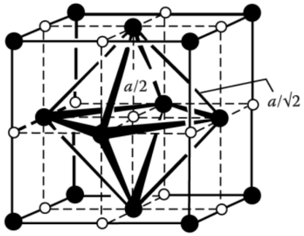
Magnitude of D in various media

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^{2}s^{-1}, when C_c = 0.15 wt%

D_c = 7.7 x 10^{-11}m^{2}S^{-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?

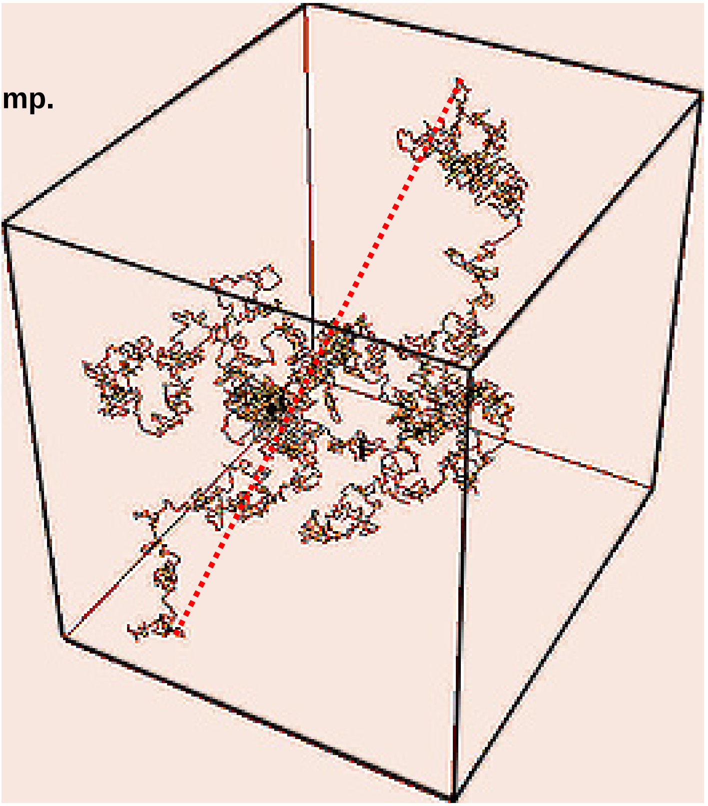
$$\boxed{r = \alpha\sqrt{(\Gamma t)} = f(D) = 2.4\sqrt{Dt}}$$

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.**

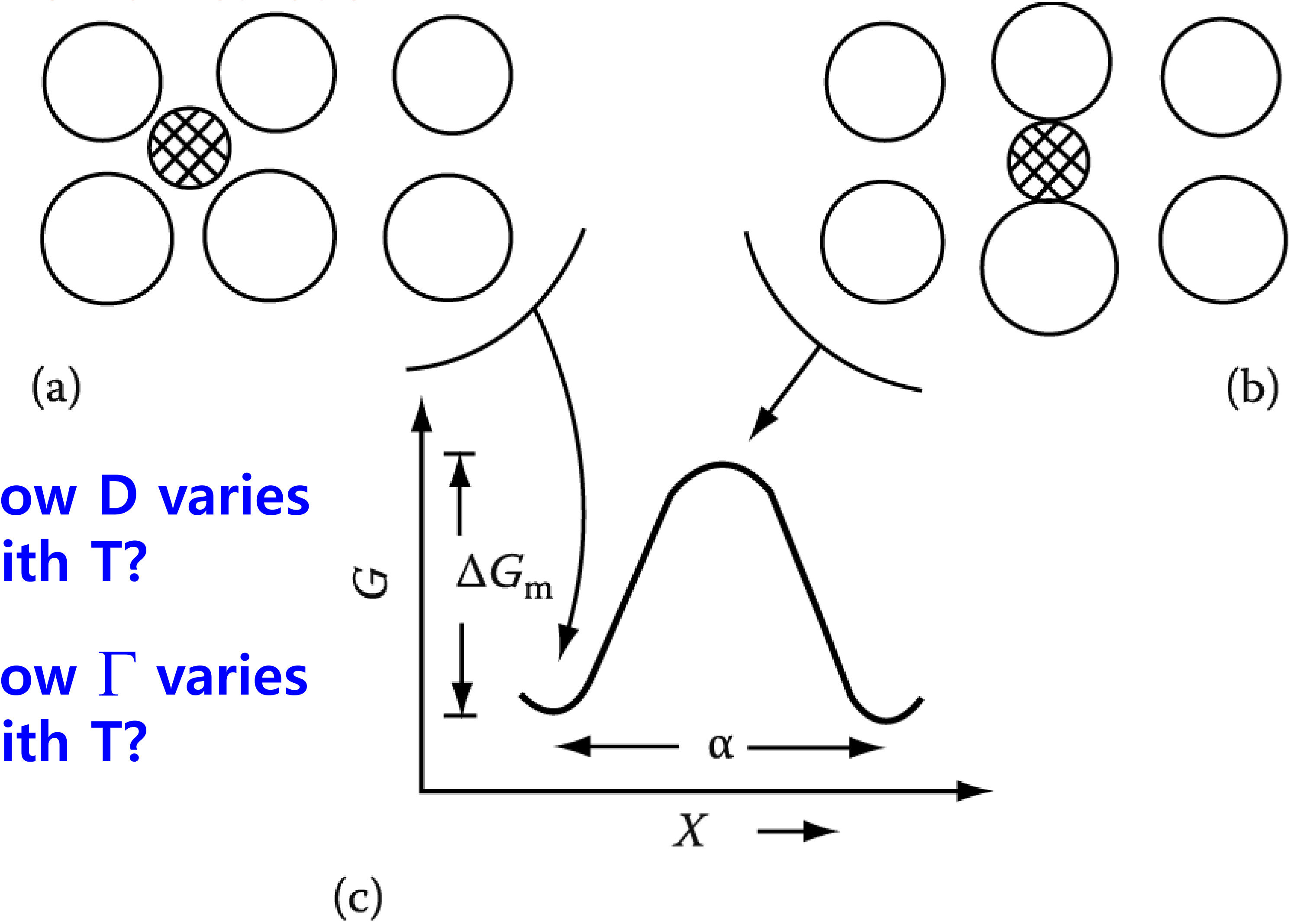
Q4. What is the effect of the temperature on diffusivity?

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

(Arrhenius-type equation)

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

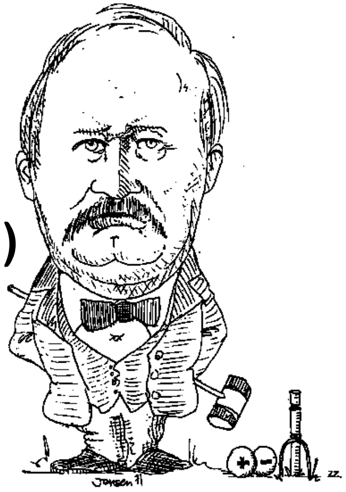
$$\left\{ \Delta G_m = \Delta H_m - T\Delta S_m \ , \ D_B = \frac{1}{6}\Gamma_B \alpha^2 \right\}$$

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

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

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

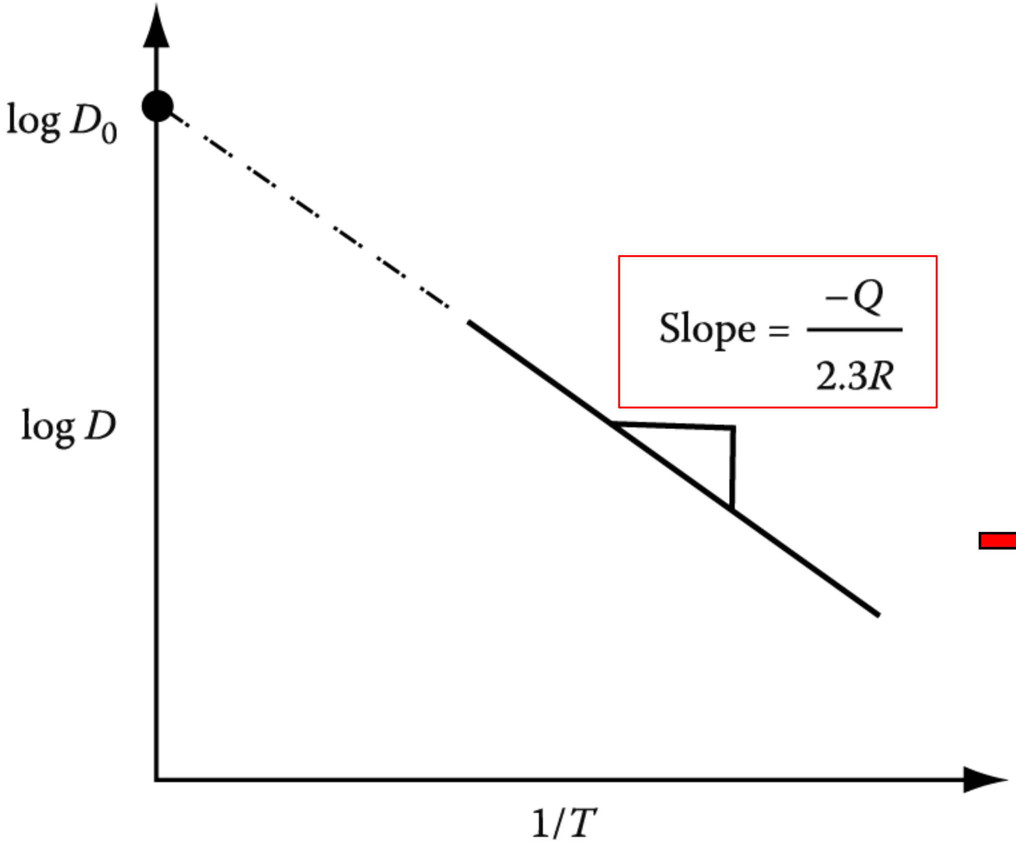
(Arrhenius-type equation)



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

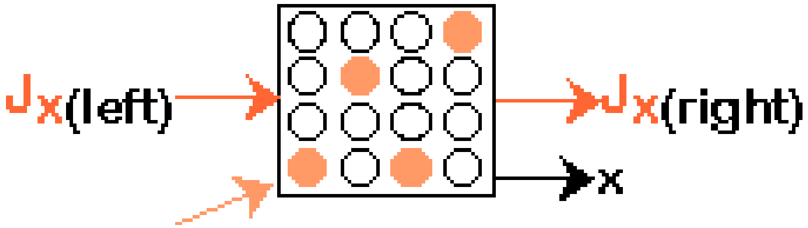
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

➡ **Concentration varies with "position"**

"Both position and time"

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

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

- **Apply Fick's First Law:**

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

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

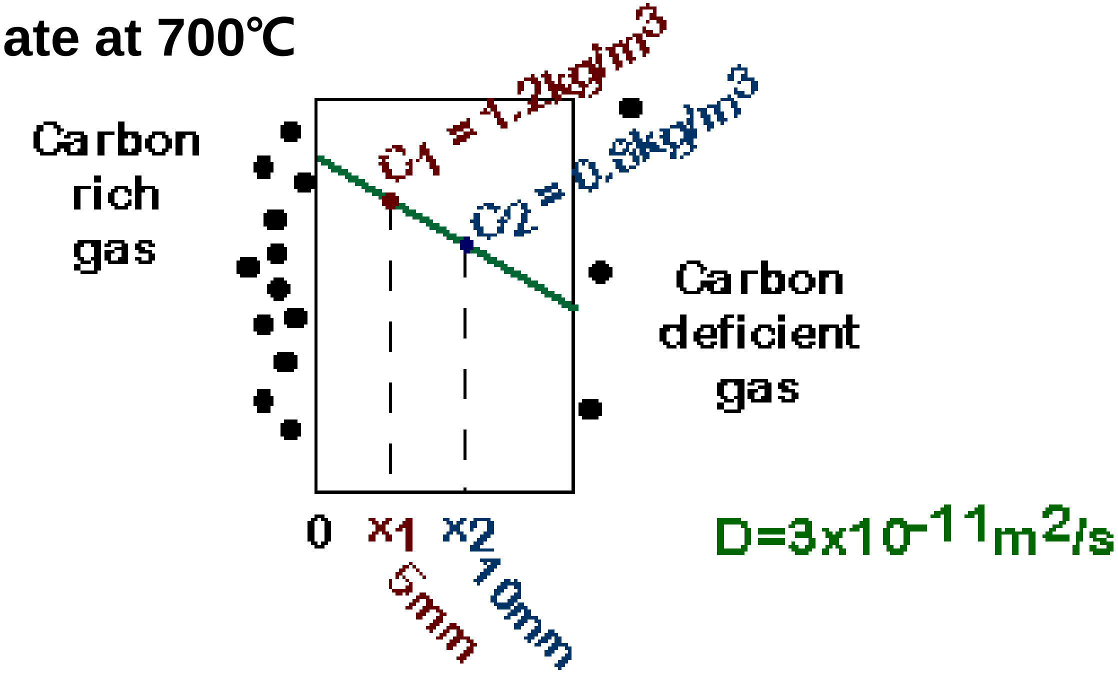
$$\frac{dC}{dx}_{(left)} = \frac{dC}{dx}_{(right)}$$

⇨ **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℃**



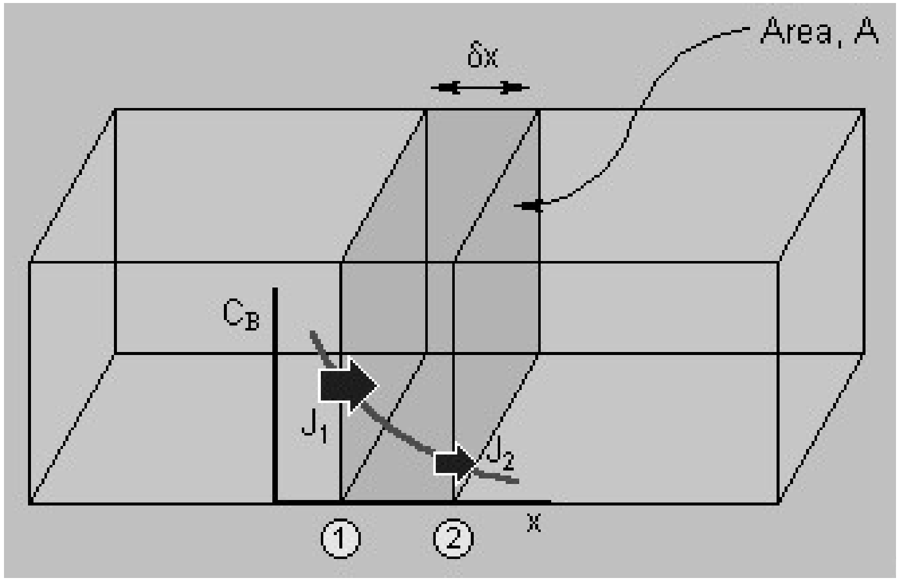
Q: How much carbon is transferring from the rich to deficient side?

$$J = -D\frac{C_2 - C_1}{x_2 - x_1} = 2.4 \times 10^{-9}\ \frac{kg}{m^2 s}$$

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

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

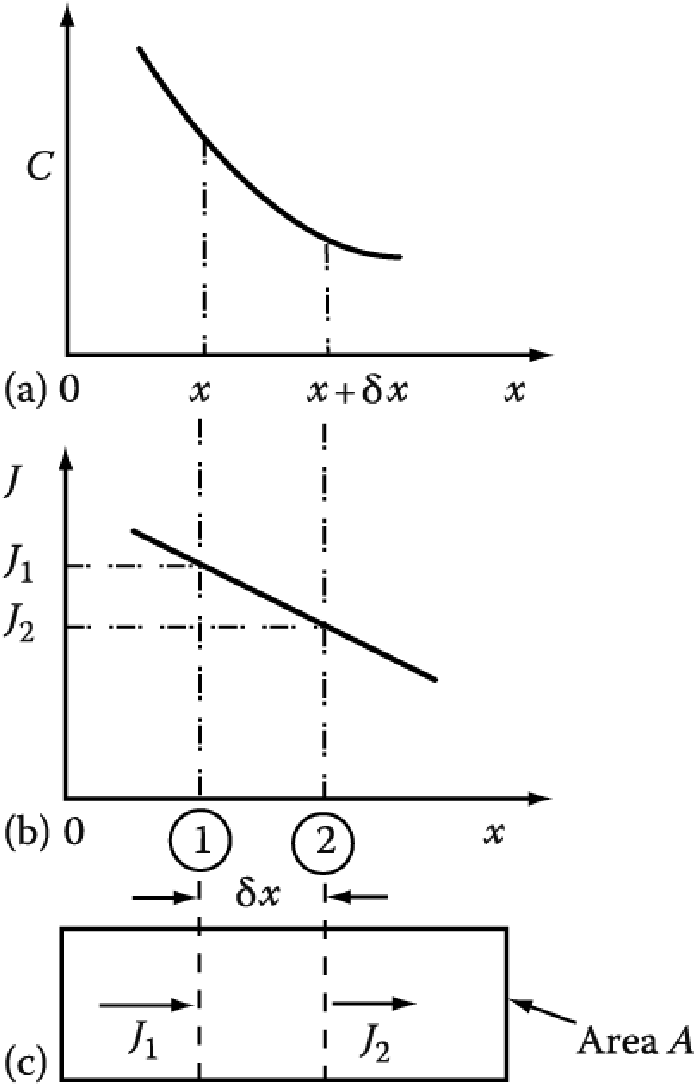
Nonsteady-state diffusion

$$J_2 = J_1 + \frac{\partial J}{\partial x}\delta x$$ **(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,

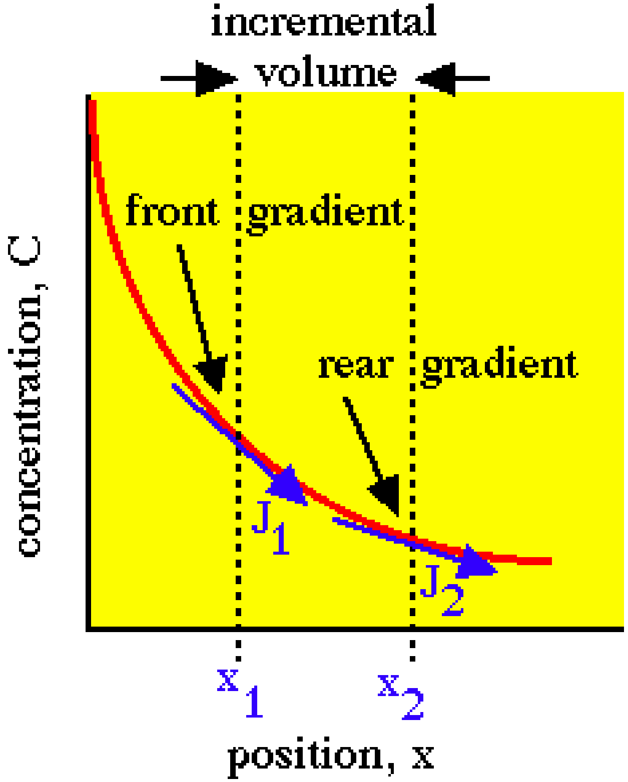
$$\boxed{\frac{\partial C_B}{\partial t} = D_B\frac{\partial^2 C_B}{\partial x^2}}$$

Fick’s Second Law

Fick's Second Law

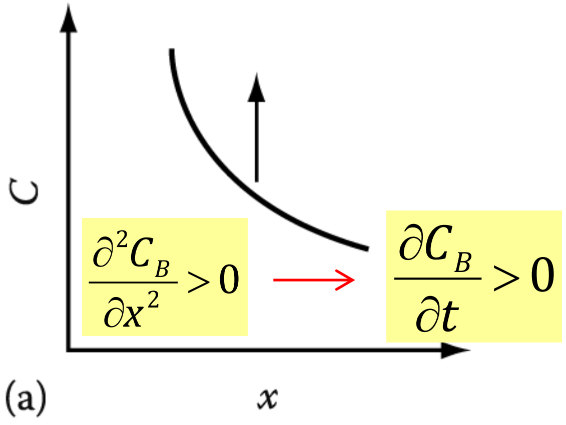
$$\boxed{\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}}$$

Concentration varies with time and position.



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

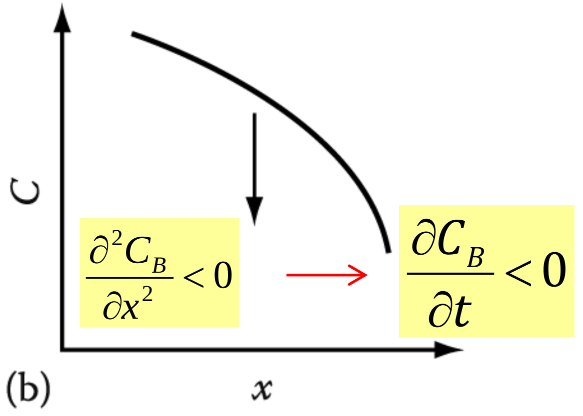
Note that $\frac{\partial^2 C_B}{\partial x^2}$ is the <u>curvature</u> of the C_B versus x curve.



$$\frac{\partial^2 C_B}{\partial x^2} > 0 \rightarrow \frac{\partial C_B}{\partial t} > 0$$

(a)

All concentration increase with time



$$\frac{\partial^2 C_B}{\partial x^2} < 0 \rightarrow \frac{\partial C_B}{\partial t} < 0$$

(b)

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

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

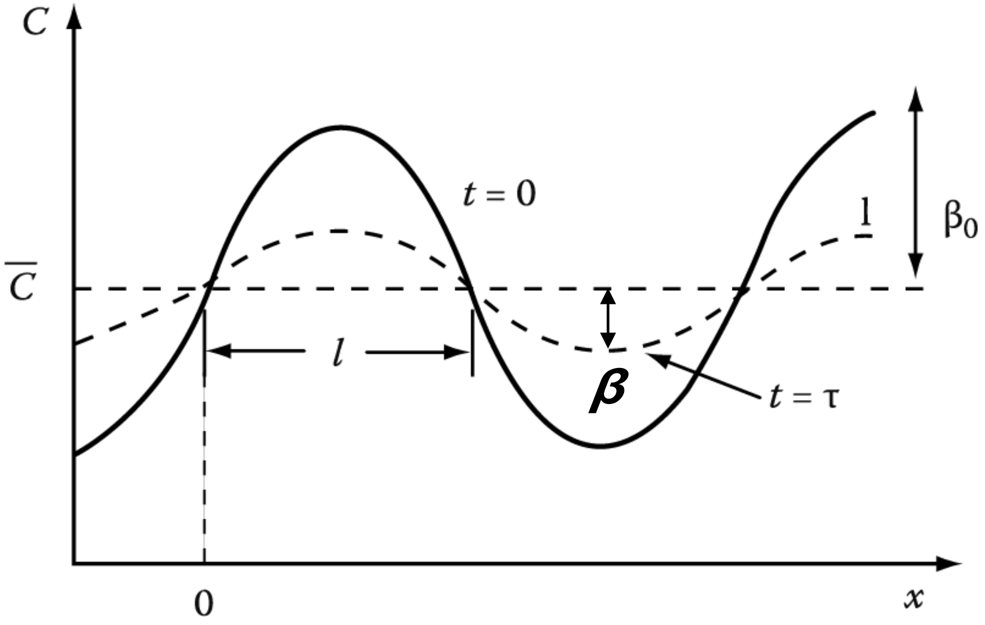


Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

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

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

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

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

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

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

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

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

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

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

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

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

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

($A_n = 0$ 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

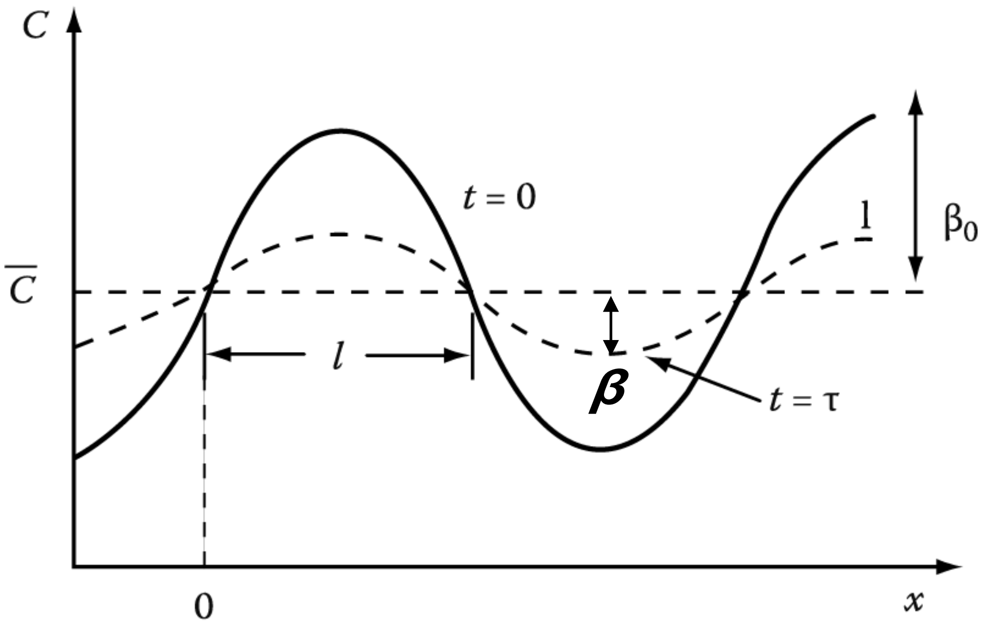


Fig. 2.10 The effect of diffusion on a sinusoidal variation of composition.

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

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

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

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

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

<u>decide homogenization rate</u>

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

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:

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

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

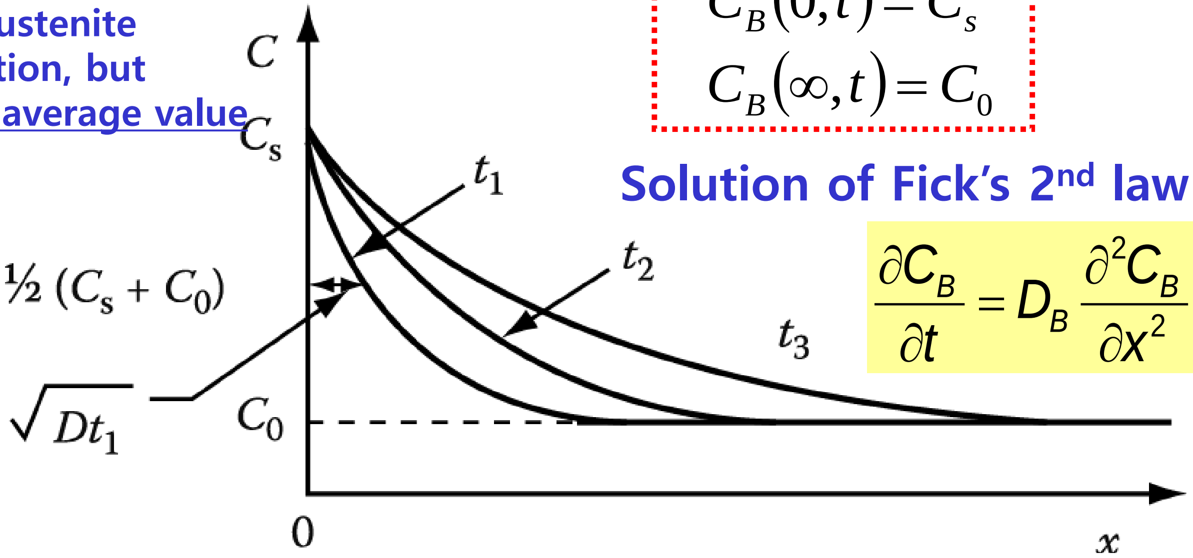


Fig. 2.11 Concentration profiles at successive times ($t_3>t_2>t_1$) for diffusion into a semi-infinite bar when the surface concentration Cs is maintained constant.

* Concentration profile : using boundary conditions

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

Solution of Fick's 2nd law

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

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

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:

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

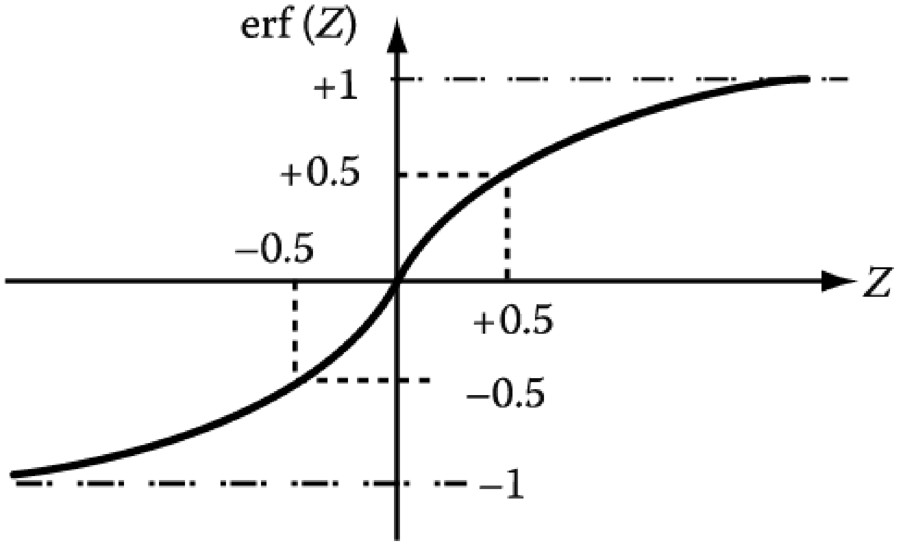
By expanding the right-hand side in a Taylor series and integrating, one can express it in the form

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

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

Error function

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{o}^{z} \exp(-y^2)\,dy$$



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

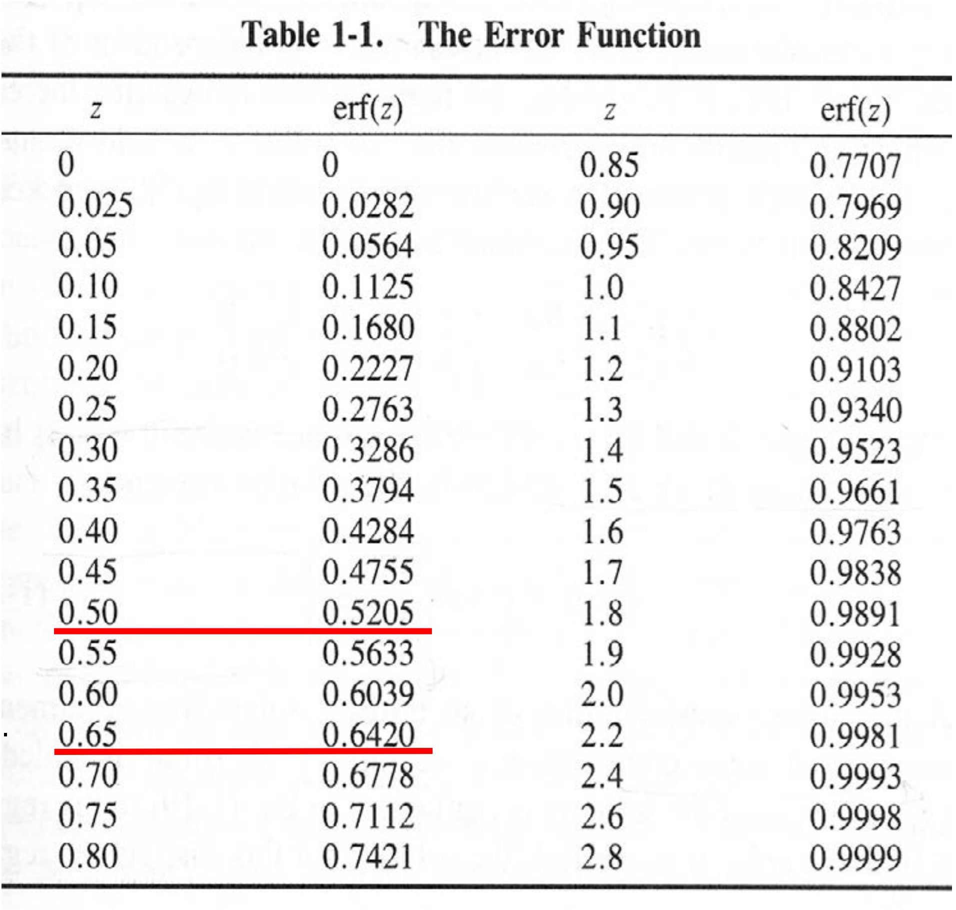


Table 1-1. The Error Function

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

The error function solution:

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

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

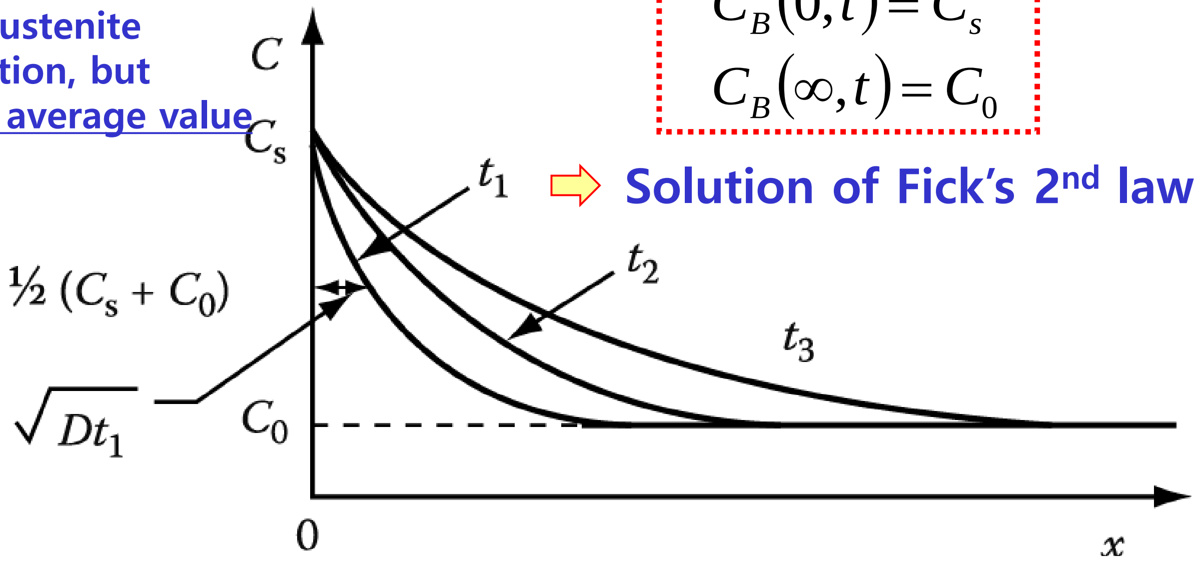


Fig. 2.11 Concentration profiles at successive times ($t_3>t_2>t_1$) for diffusion into a semi-infinite bar when the surface concentration Cs is maintained constant.

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

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**

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?

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

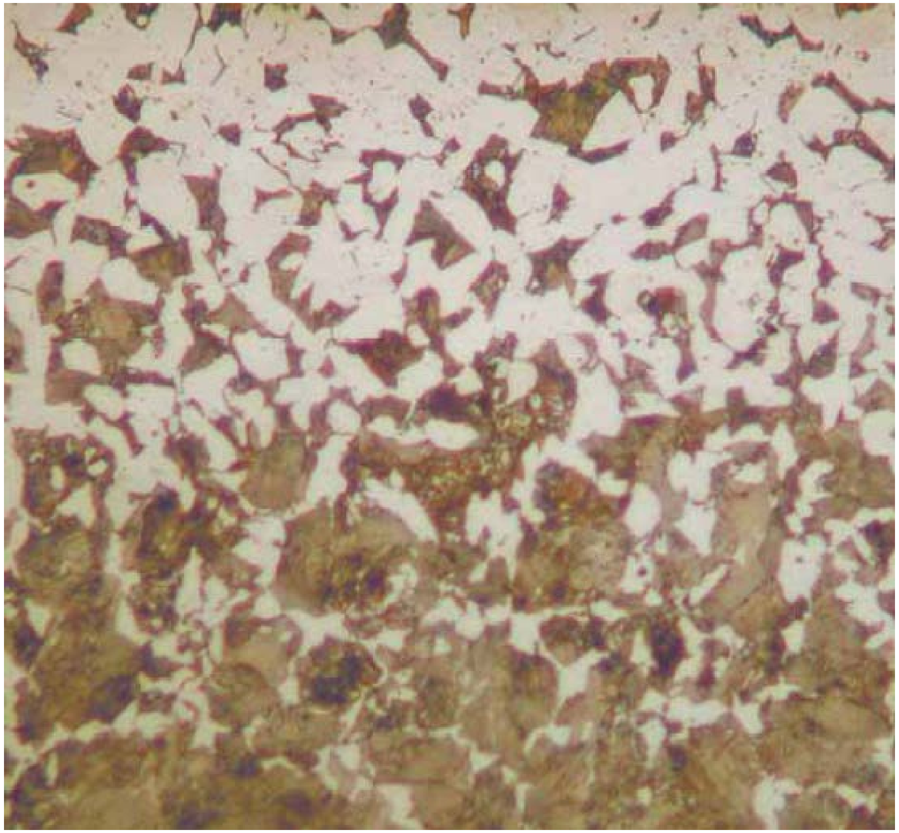
$$C = C_s - (C_s - C_0) erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

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.

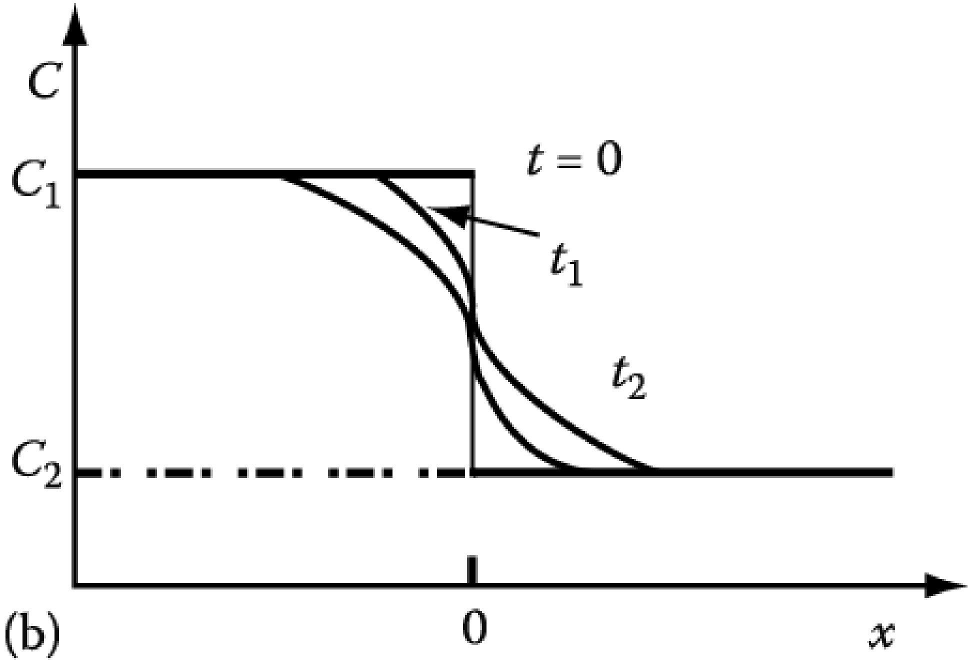


Fig. 2.12 (b) concentration profiles at successive times (t2>t1>0)
when two semi-infinite bars of different composition are annealed after welding.

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

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

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

  - Nonsteady-state diffusion – 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.**

  - For random walk in 3 dimensions,

  after n steps of length α

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

- **Effect of Temperature on Diffusivity**

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