재료상변태

Phase Transformation of Materials

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박은수

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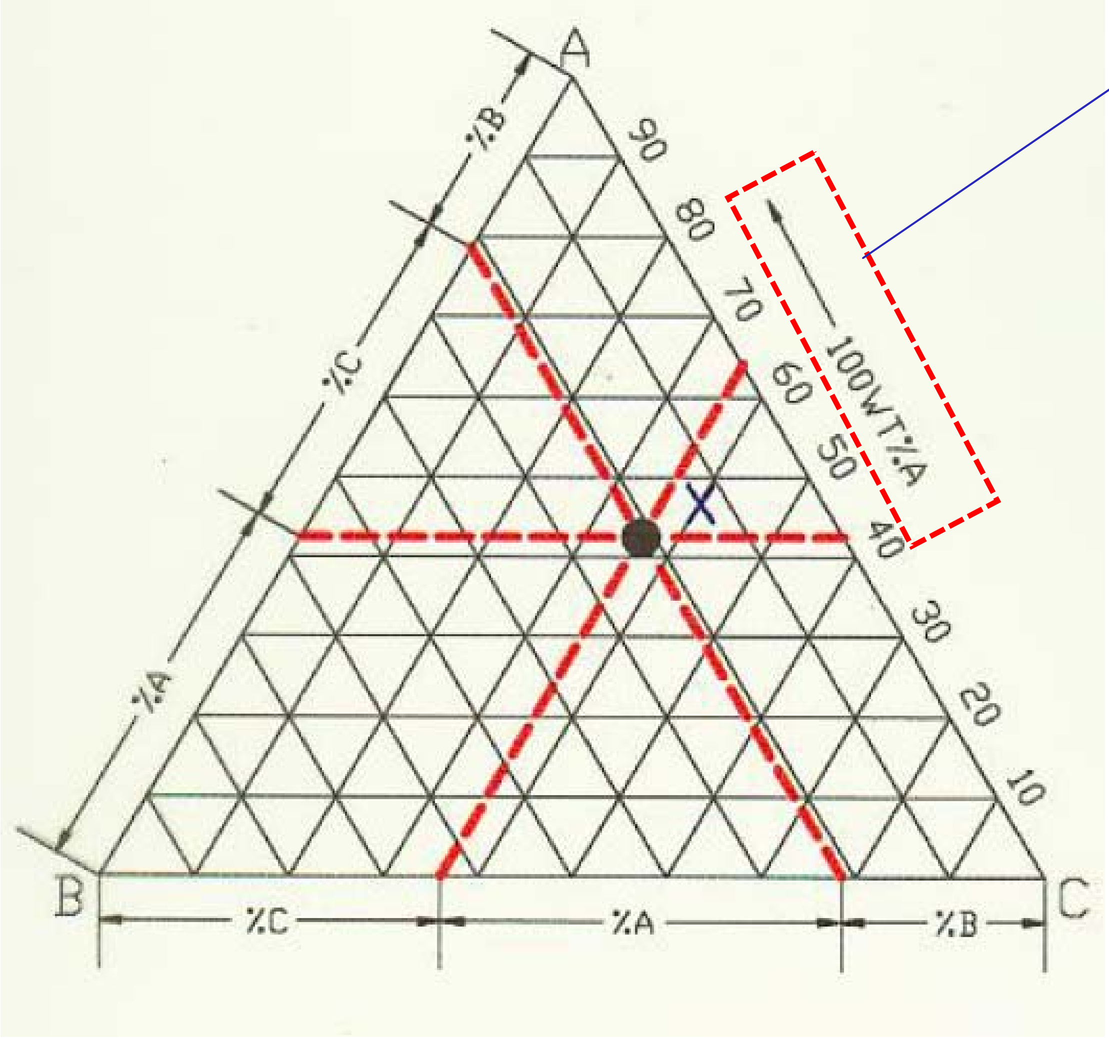
Contents for previous class

- **Effect of Temperature on Solid Solubility** $X_B^e = A\exp\left\{-\frac{Q}{RT}\right\}$
- **Equilibrium Vacancy Concentration** $X_V^e = \exp\frac{-\Delta G_V}{RT}$
- **Influence of Interfaces on Equilibrium**

  $\Delta G = \frac{2\gamma V_m}{r}$ Gibbs-Thomson effect
- **Gibbs-Duhem Equation:** **Be able to calculate the change in chemical potential that result from a change in alloy composition.**
- **Ternary Equilibrium: Ternary Phase Diagram**

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 %”.

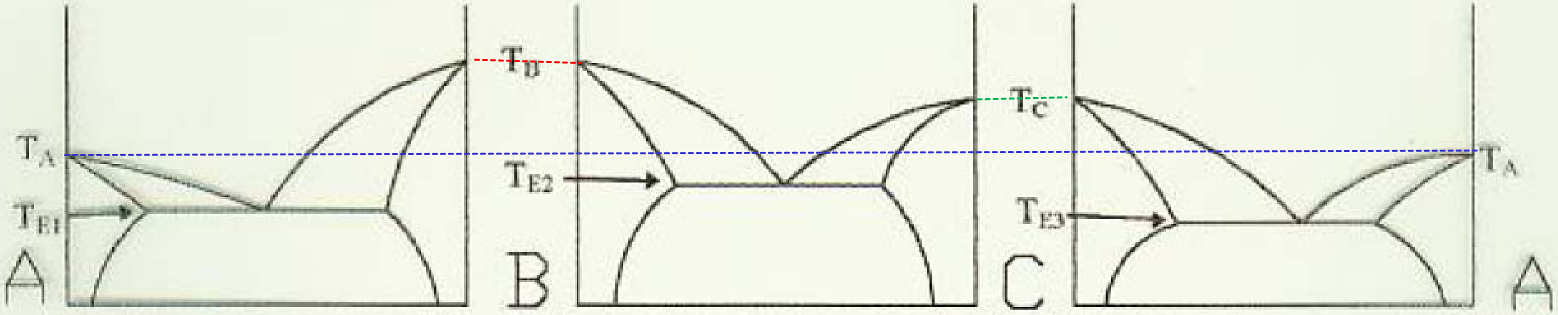
$X_A+X_B+X_C = 1$

Used to determine the overall composition

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

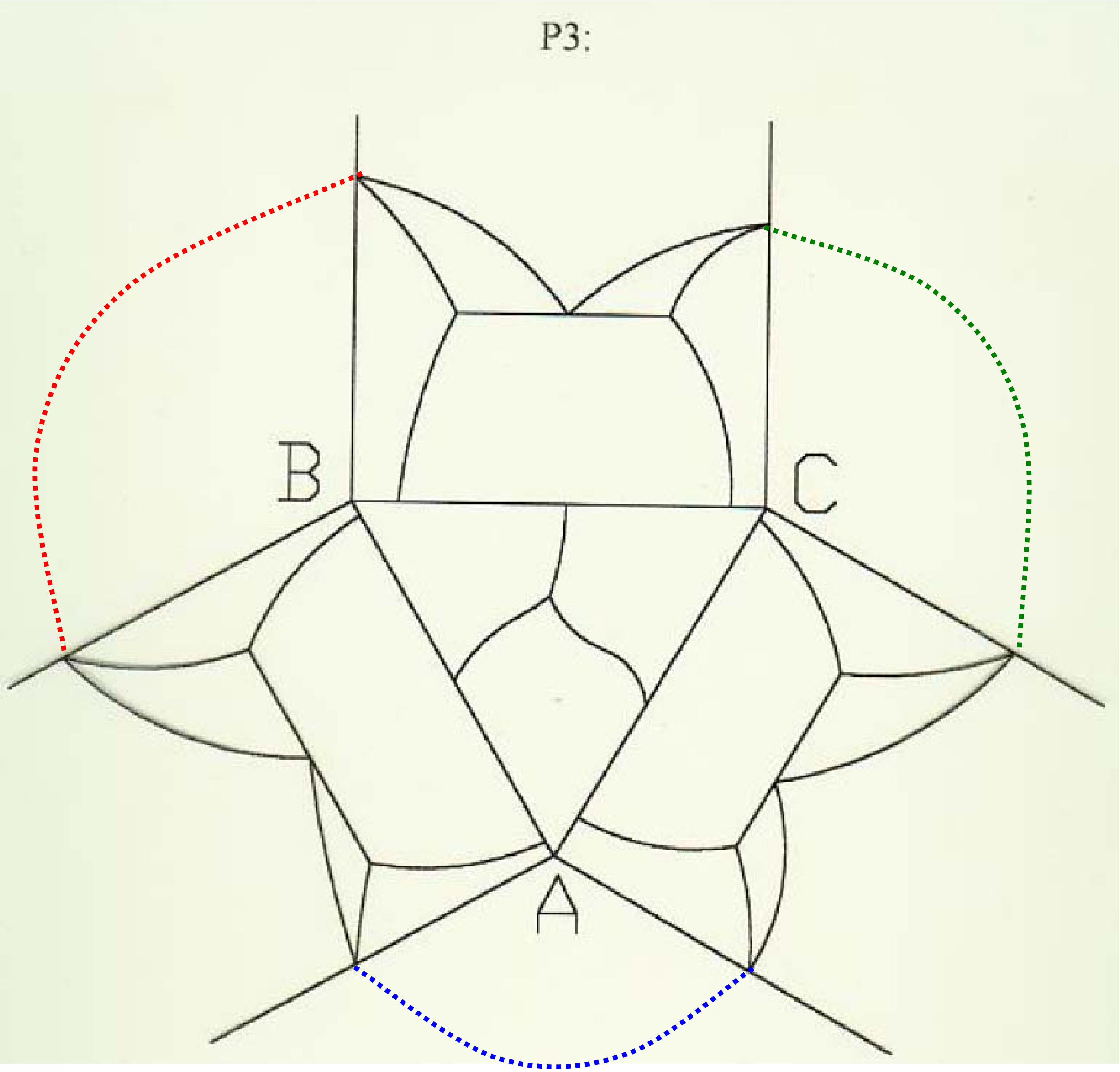
T_{E1}: Eutectic Temperature Of A-B

T_{E2}: Eutectic Temperature Of B-C

T_{E3}: Eutectic Temperature Of C-A

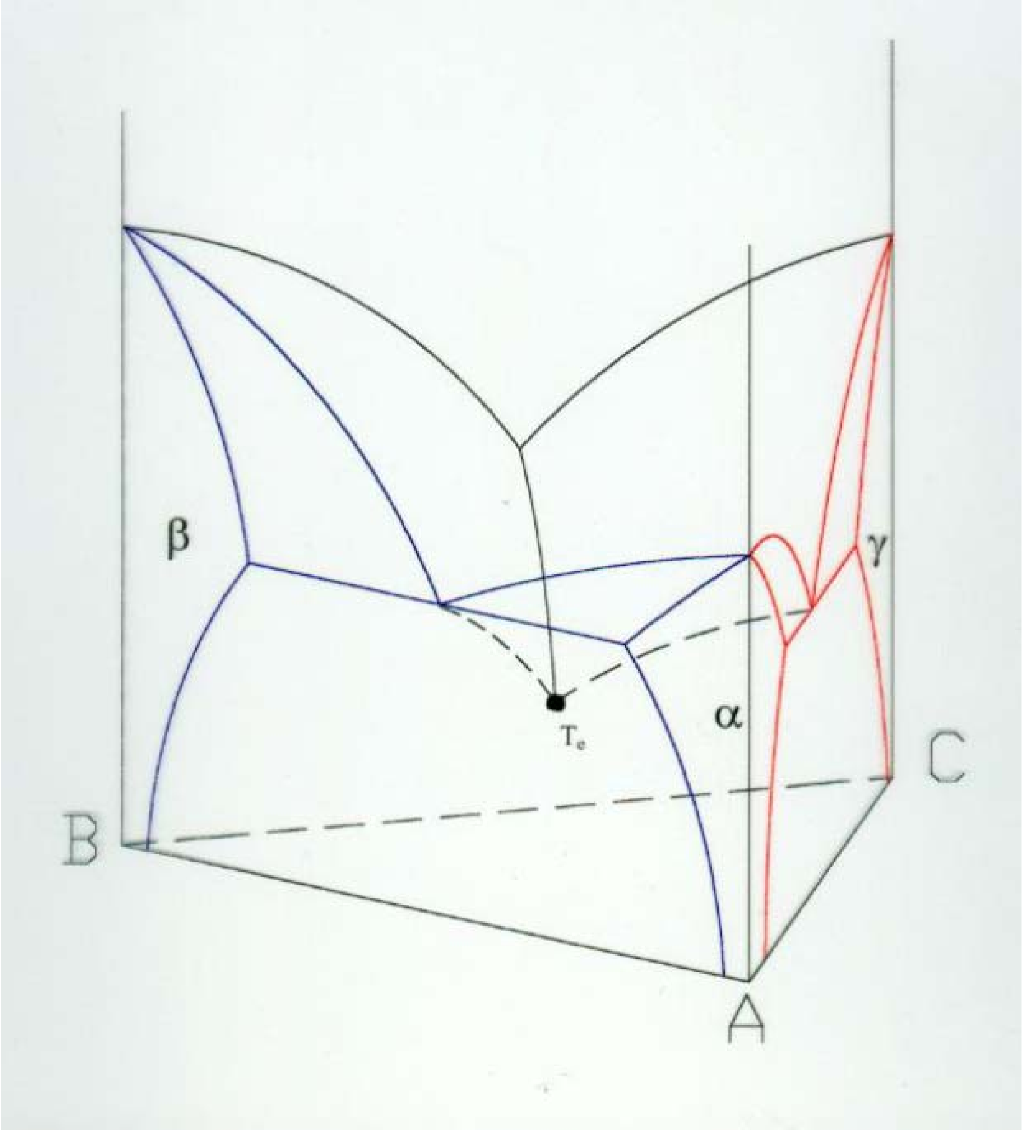
Ternary Eutectic System

(with Solid Solubility)

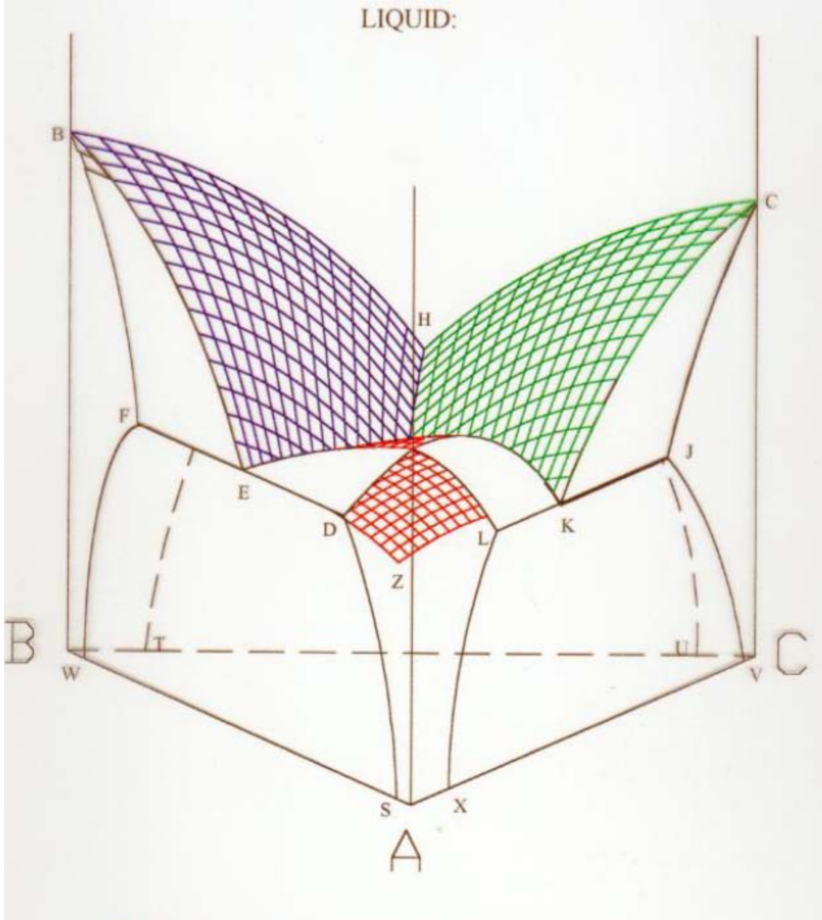


Ternary Eutectic System

(with Solid Solubility)



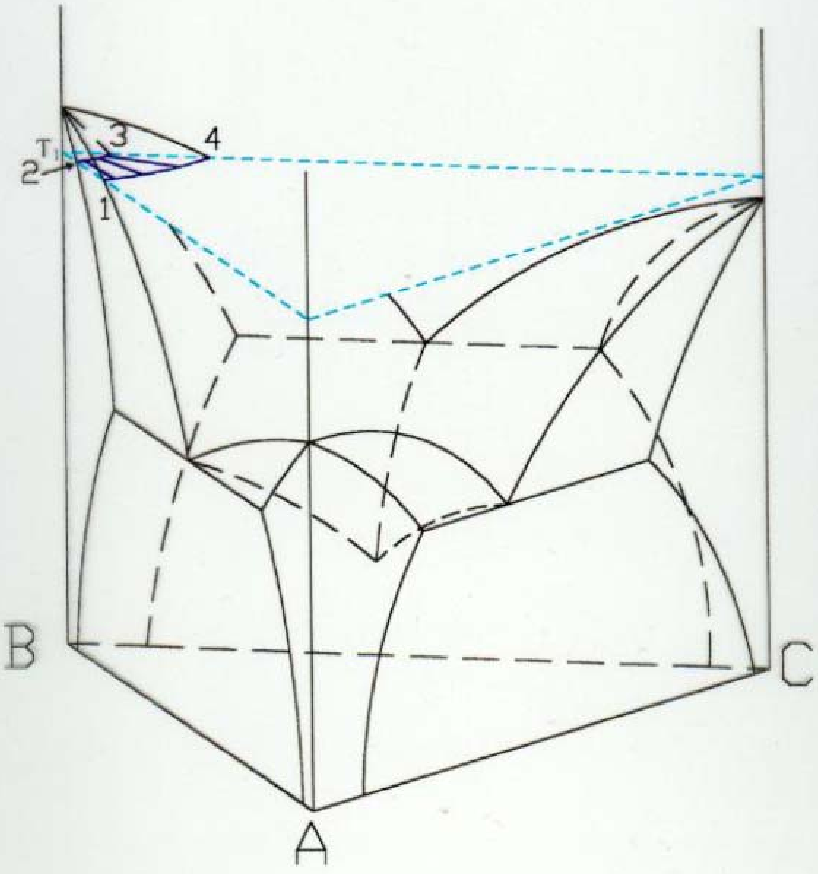
Main outline of Ternary Phase Diagram with Ternary Eutectic (T_e) and Solid Single Phase Regions Shown



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

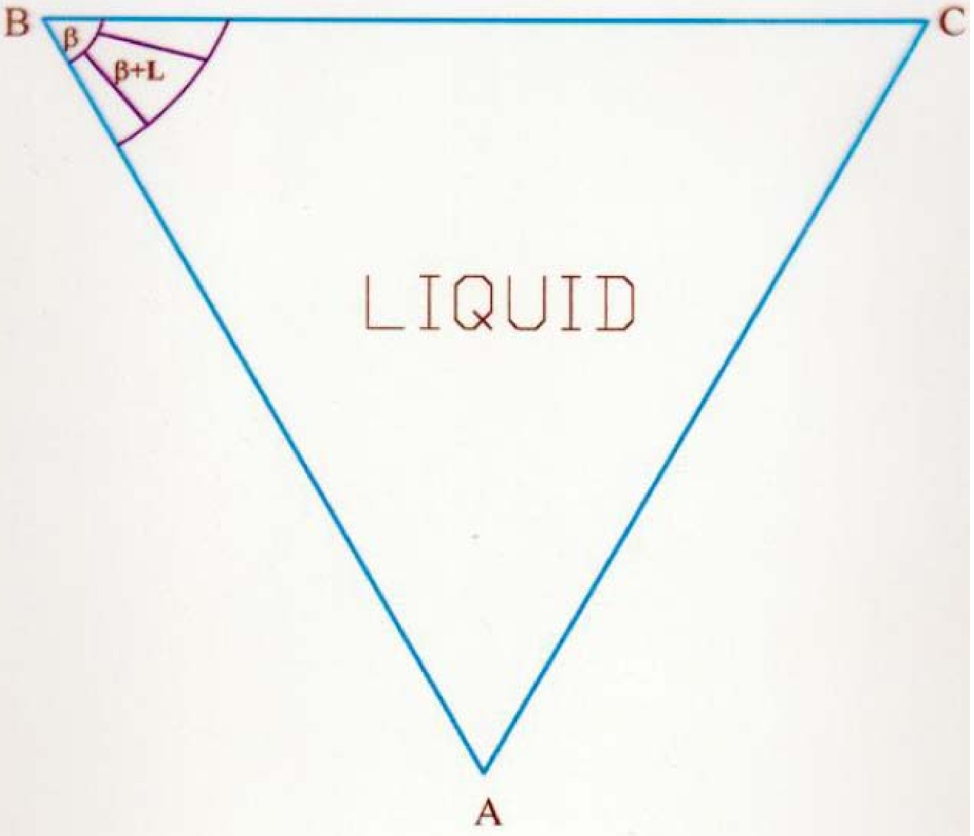
Ternary Eutectic System

(with Solid Solubility)



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

T1B:

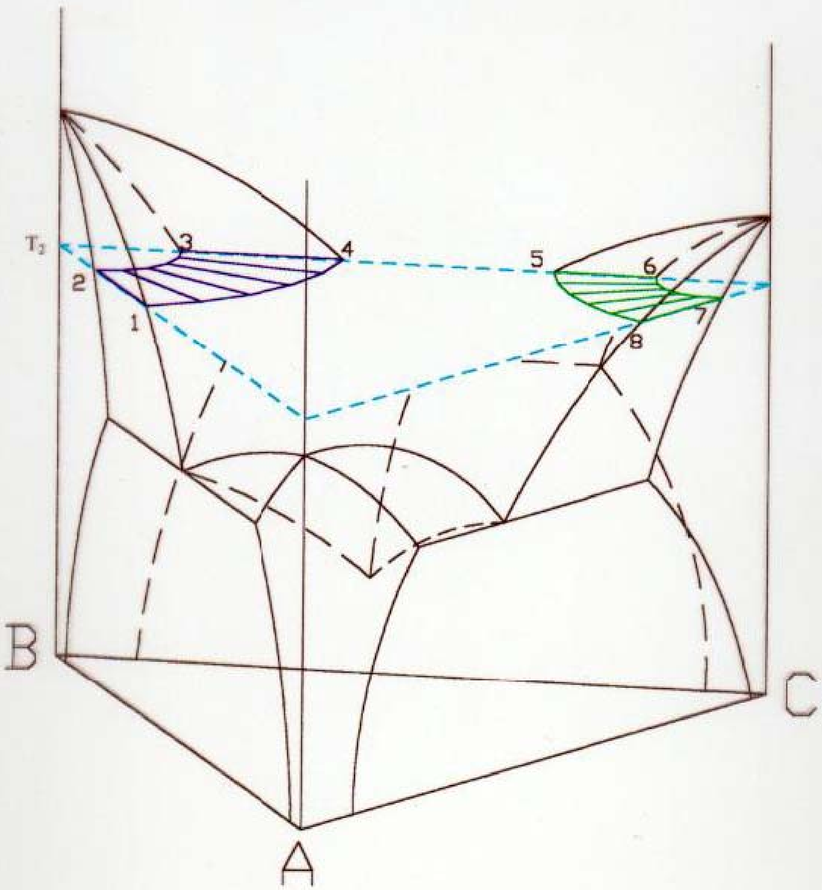


Isothermal Section At $T=T_1$

Ternary Eutectic System

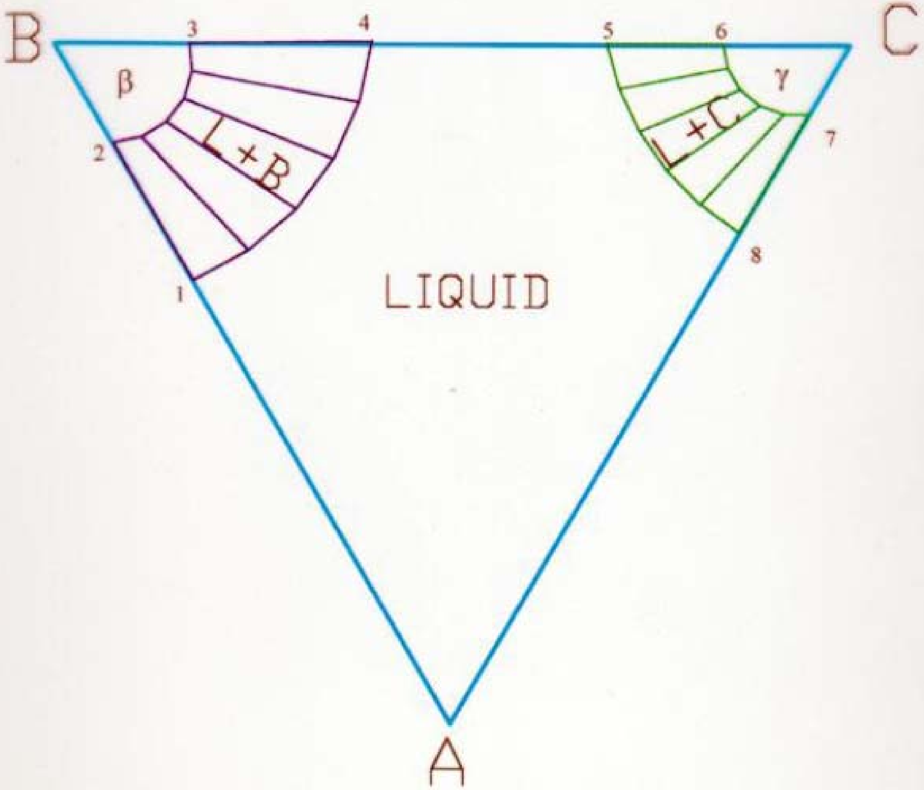
(with Solid Solubility)

T2A



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

T2B

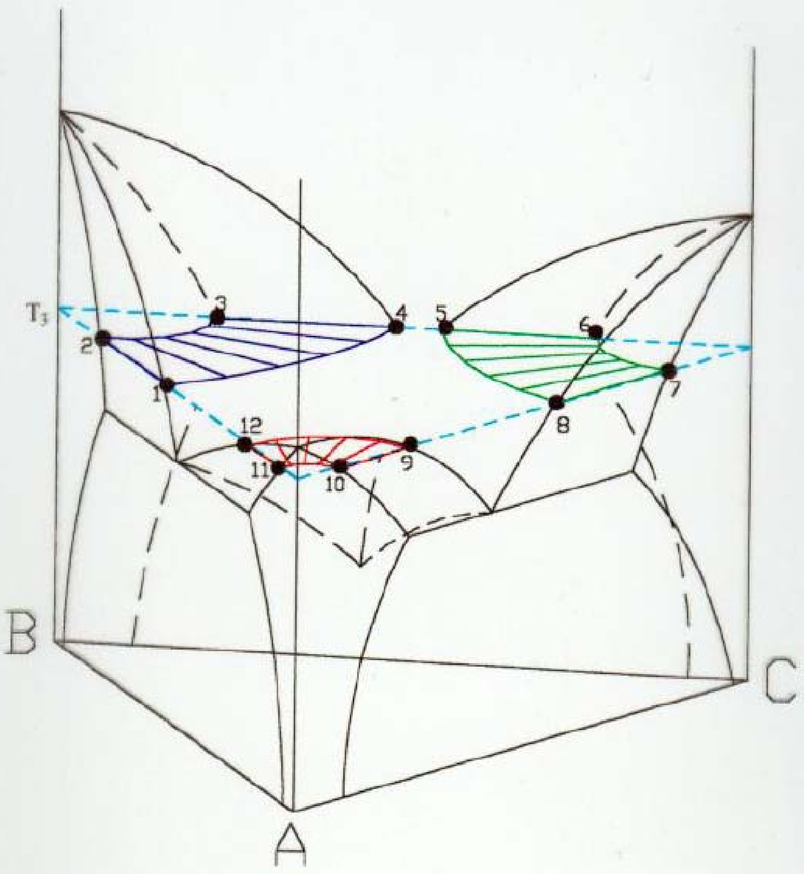


Isothermal Section At $T = T_2$

Ternary Eutectic System

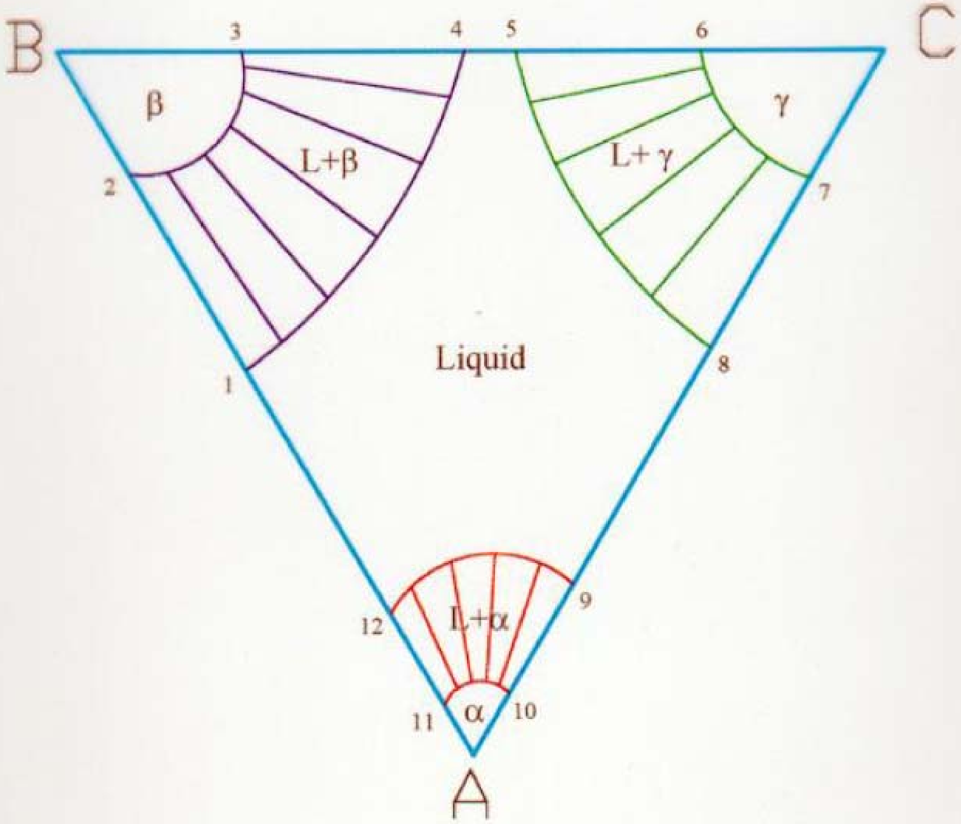
(with Solid Solubility)

T3A:

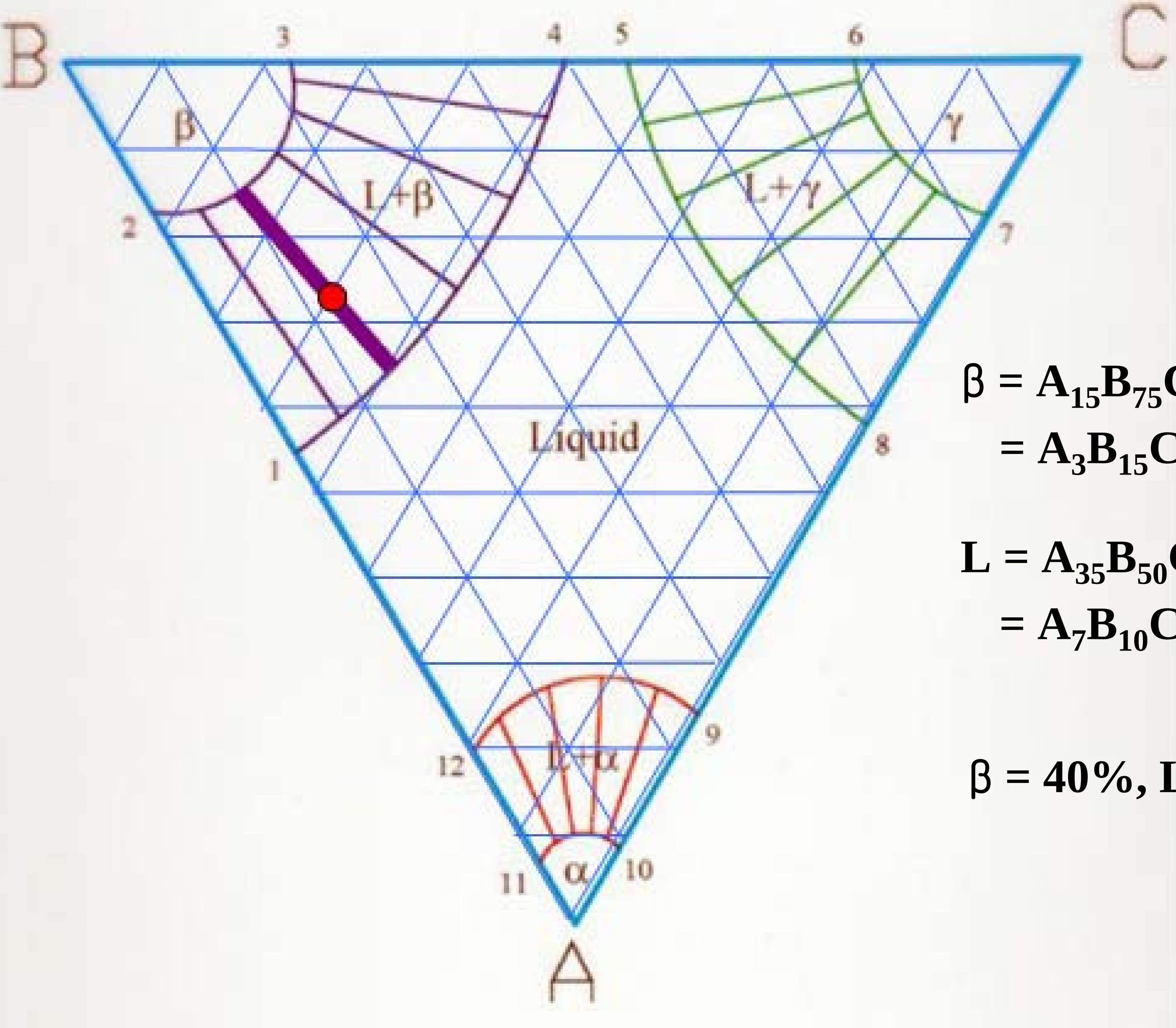


Temperature Slice At $T_3 < T_A$, T_B, T_C, But $T3 > T_{E1}$, T_{E2}, T_{E3}

T3B



Isothermal Section At $T = T_3$



$\beta = A_{15}B_{75}C_{10}$

$= A_3B_{15}C_2$

$L = A_{35}B_{50}C_{15}$

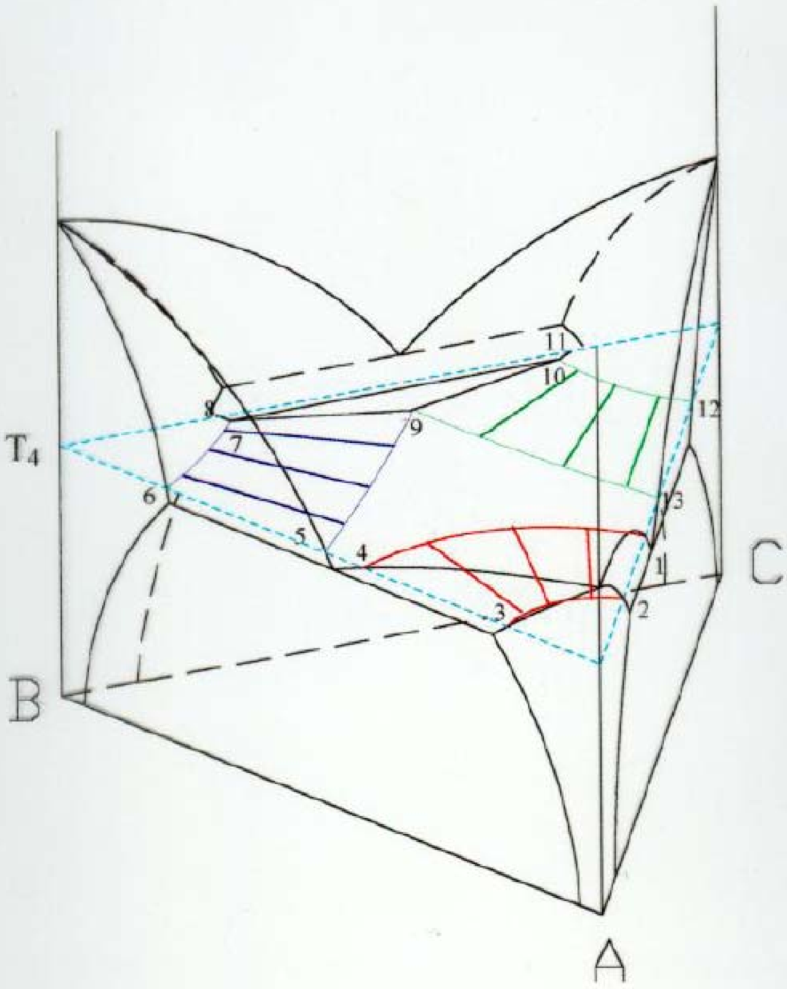
$= A_7B_{10}C_3$

β = 40%, L=60%

Ternary Eutectic System

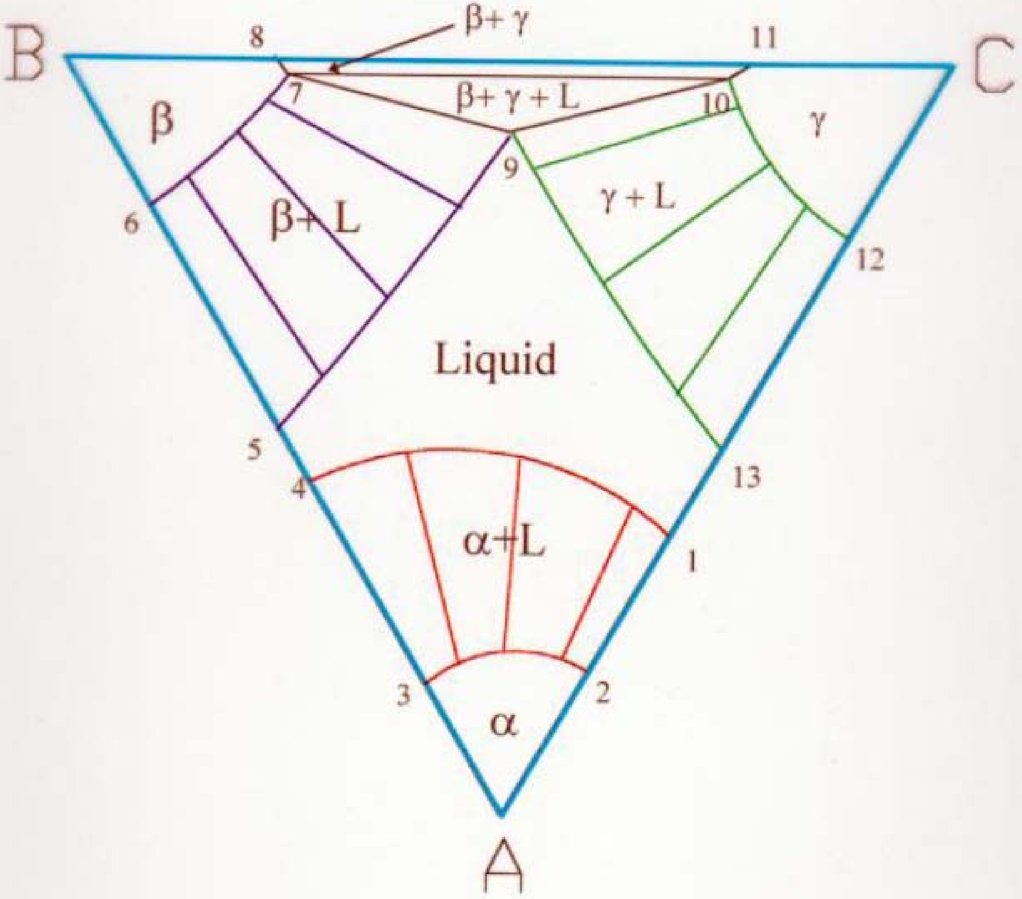
(with Solid Solubility)

T4A:



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

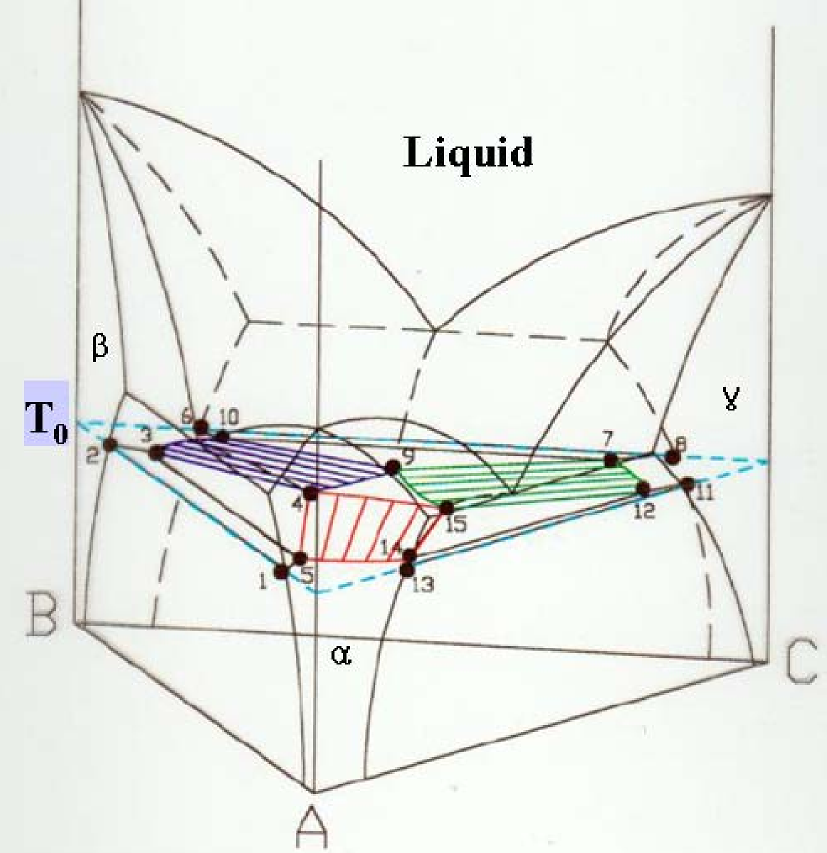
T4B:



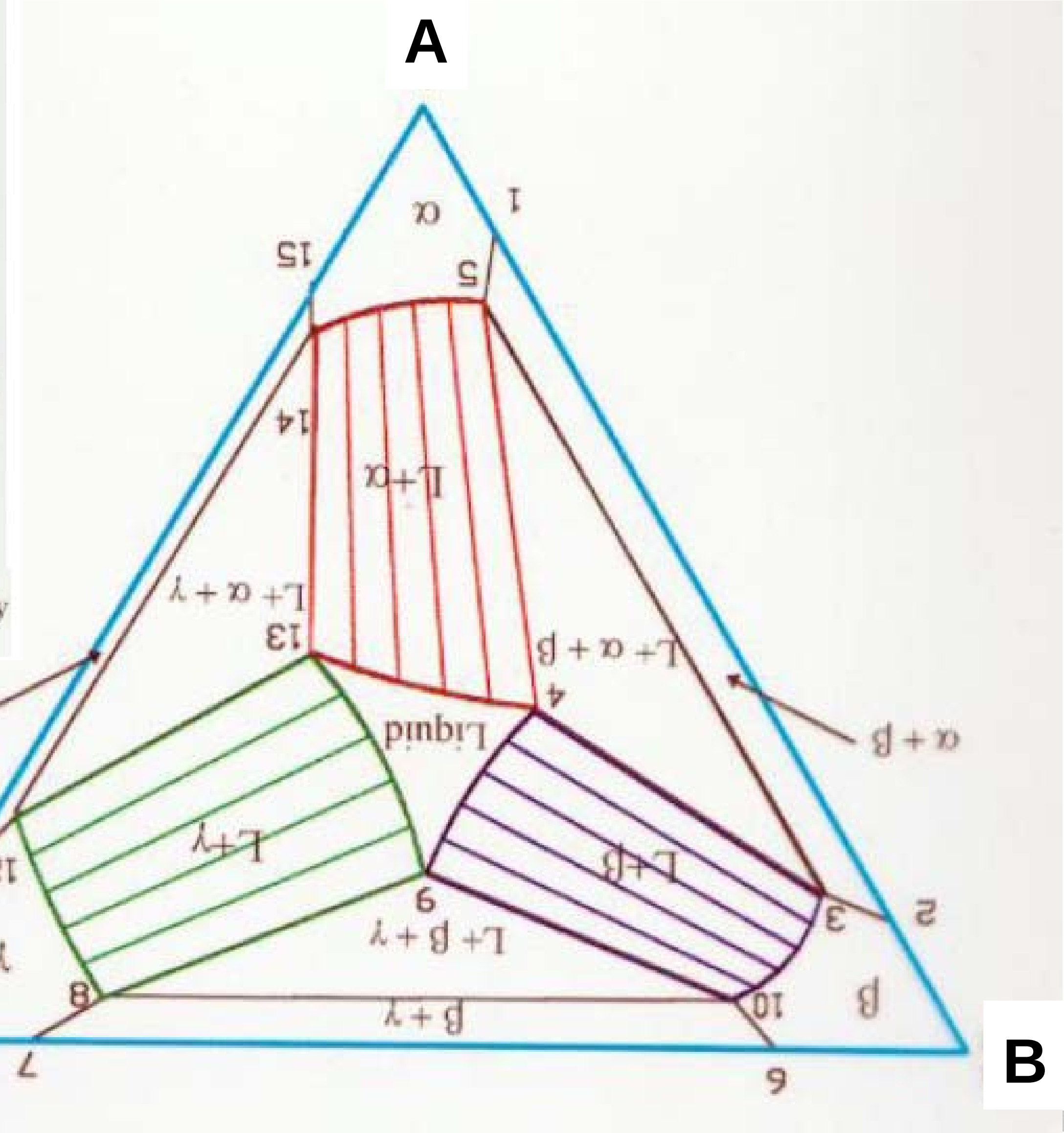
Isothermal Section At $T = T_4$

Ternary Eutectic System

(with Solid Solubility)



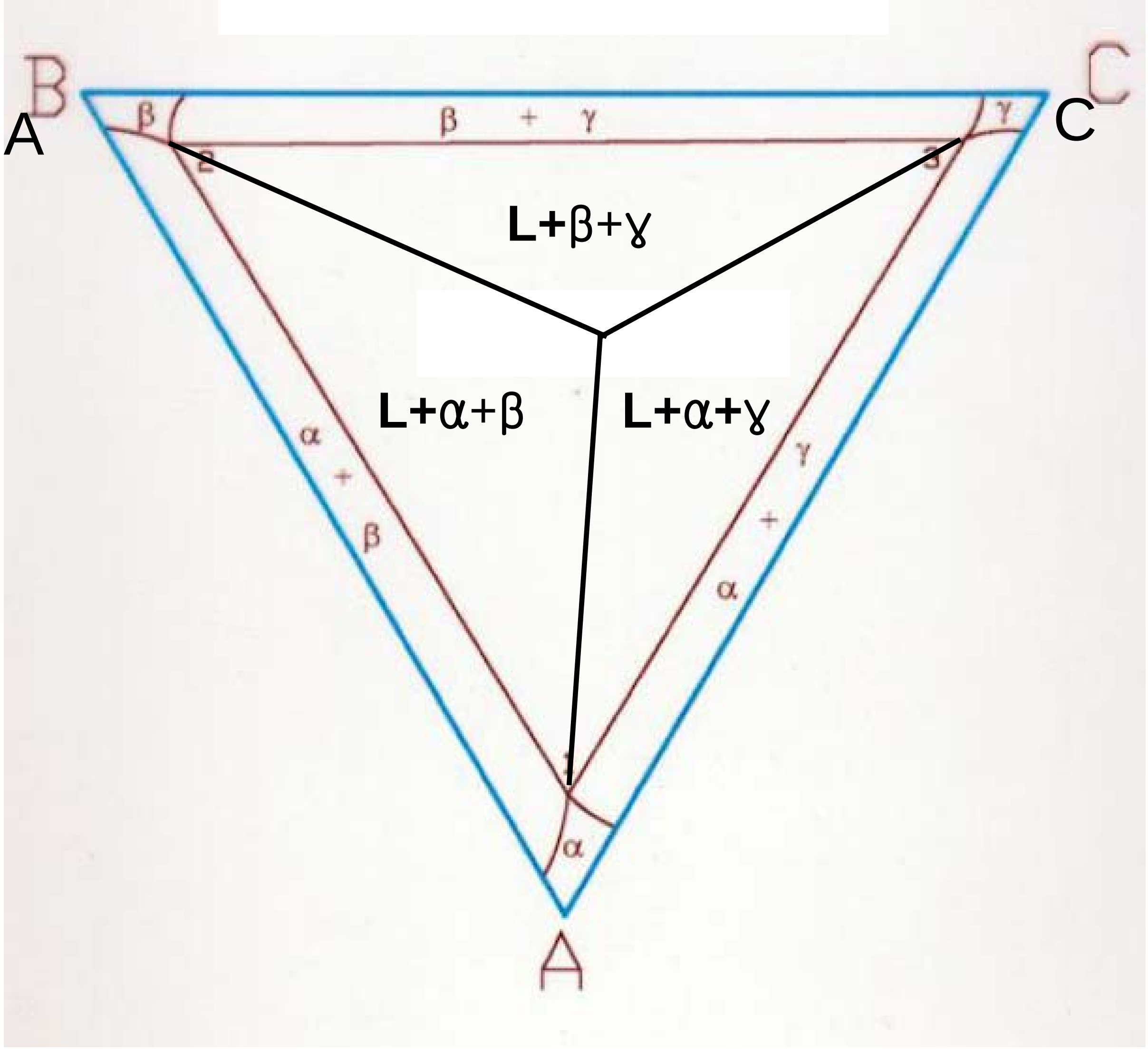
Temperature Slice Below All Binary Eutectics But, Above The Ternary Eutectic



Ternary Eutectic System

(with Solid Solubility)

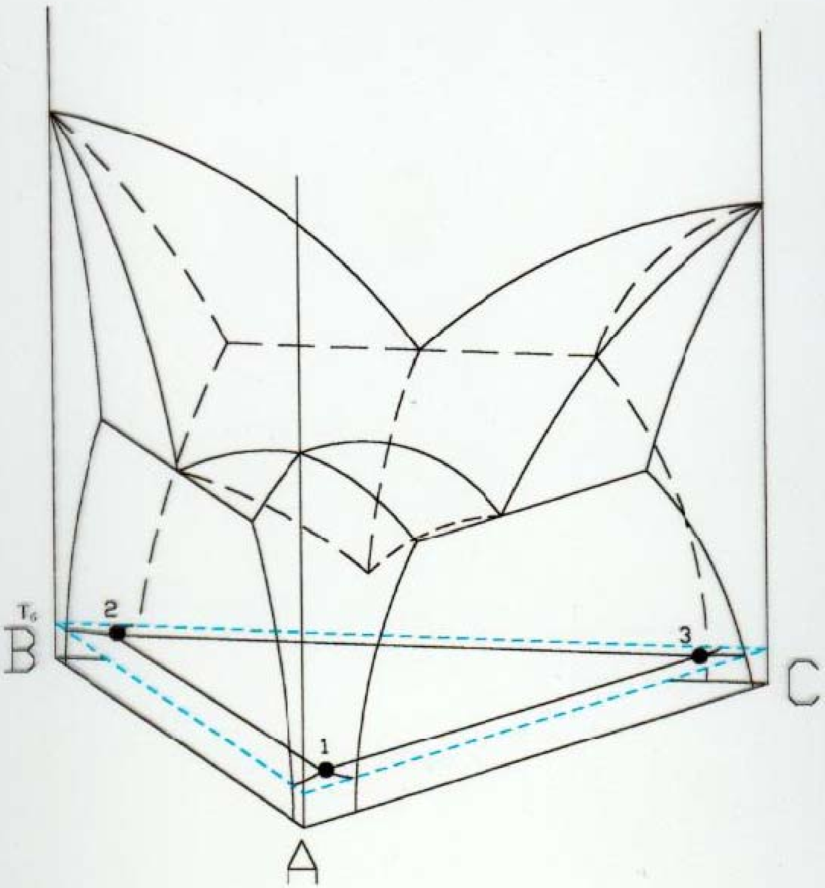
T= ternary eutectic temp.



Ternary Eutectic System

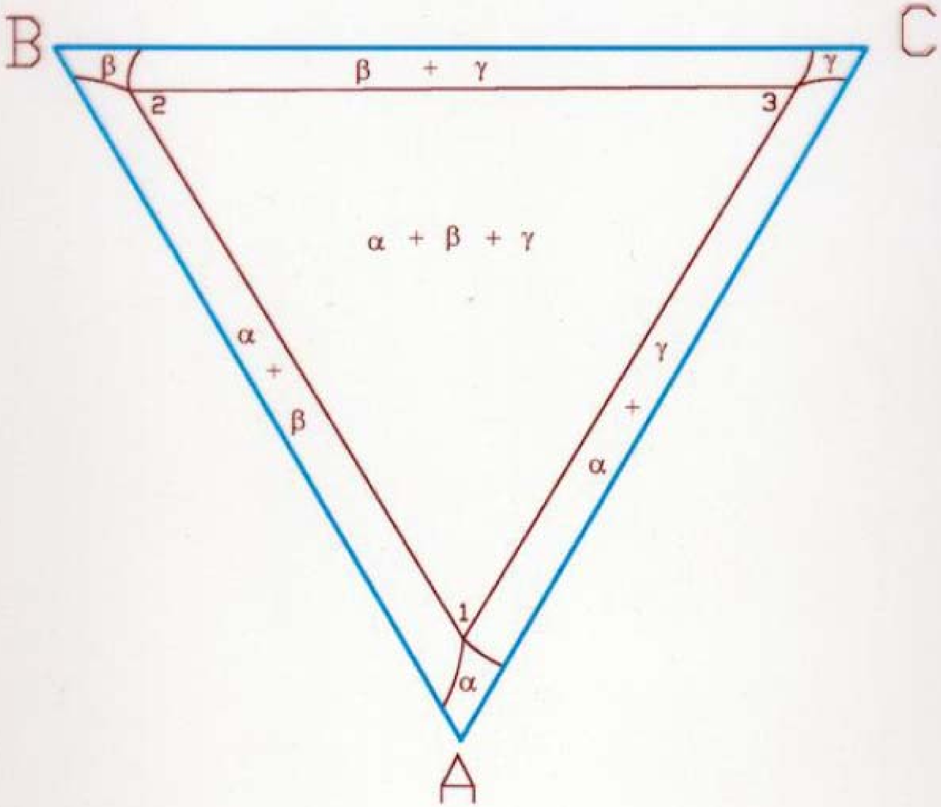
(with Solid Solubility)

T6A:



Temperature Slice at $T_6 < T_E$

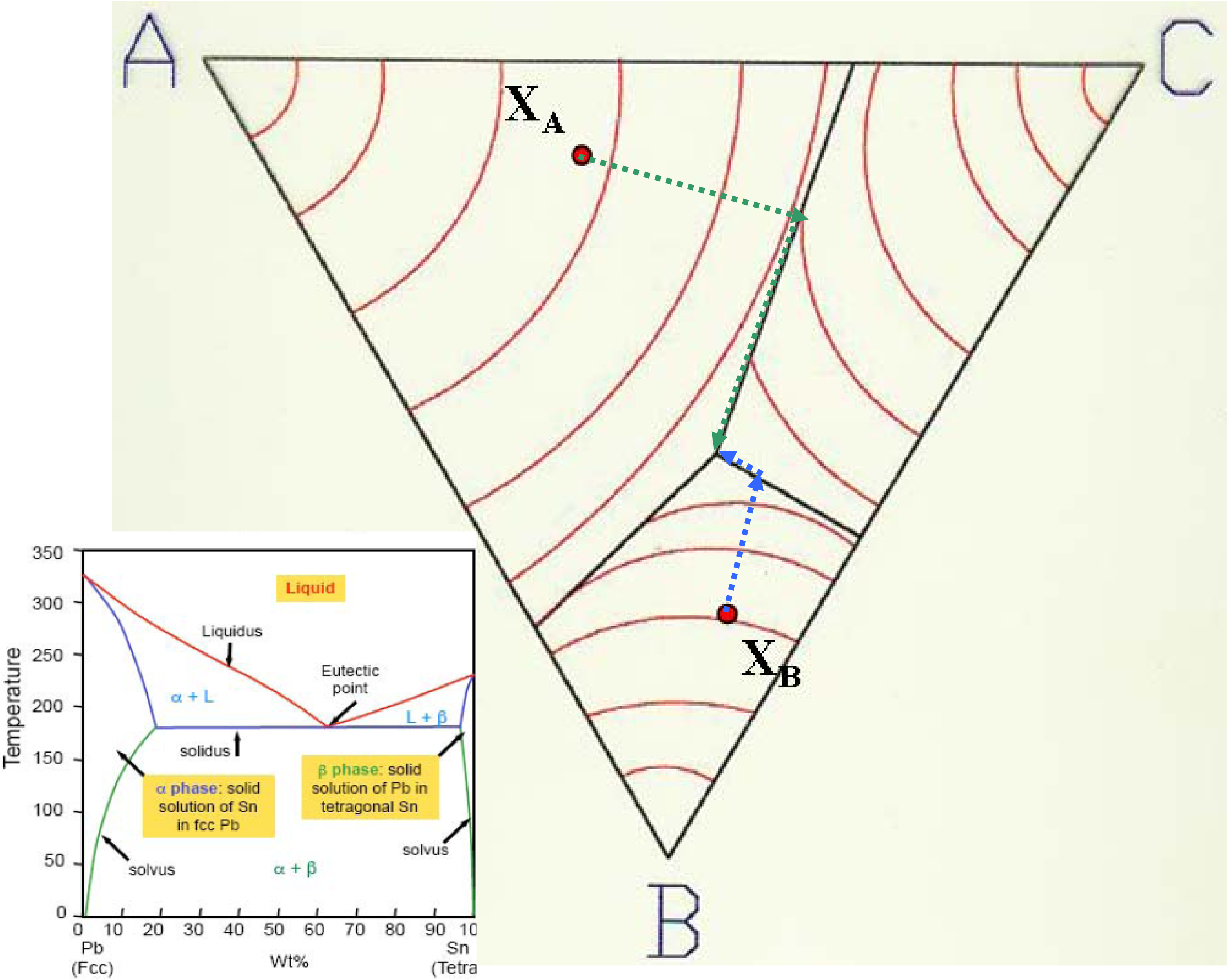
T6B:



Isothermal Section At $T=T_6$

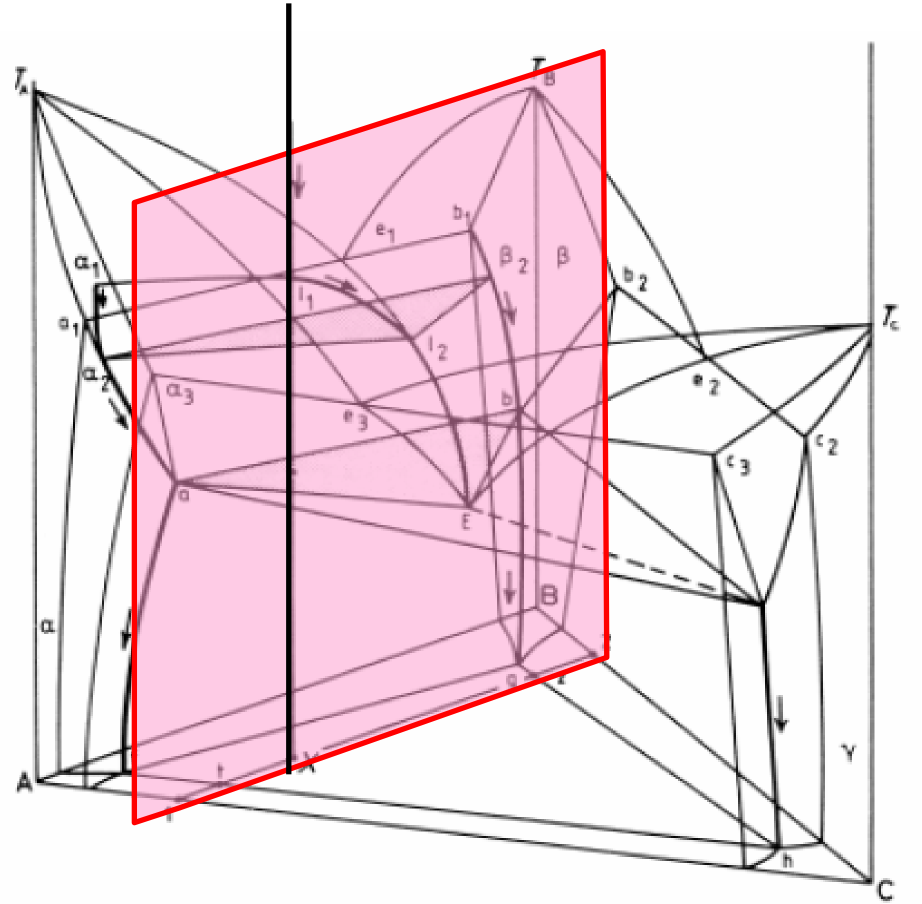
정해솔 학생 제공 자료 참조: 실제 isothermal section의 온도에 따른 변화

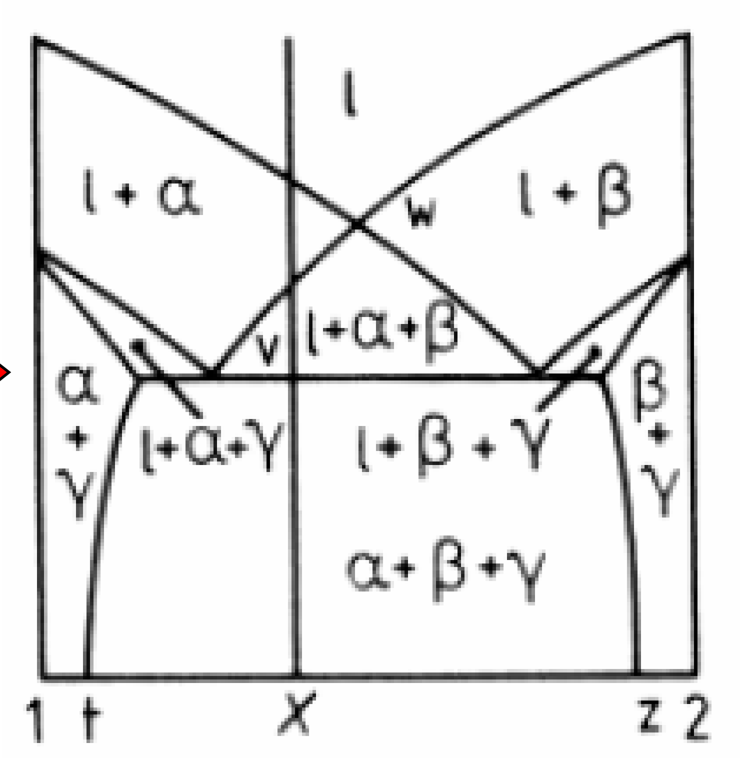
http://www.youtube.com/watch?v=yzhVomAdetM


A
C
B
X_A
X_B
Liquid
Liquidus
Eutectic point
α + L
L + β
solidus
α phase: solid solution of Sn in fcc Pb
β phase: solid solution of Pb in tetragonal Sn
solvus
solvus
α + β
Temperature
350
300
250
200
150
100
50
0
0
10
20
30
40
50
60
70
80
90
10
Pb (Fcc)
Wt%
Sn (Tetra

Ternary Eutectic System

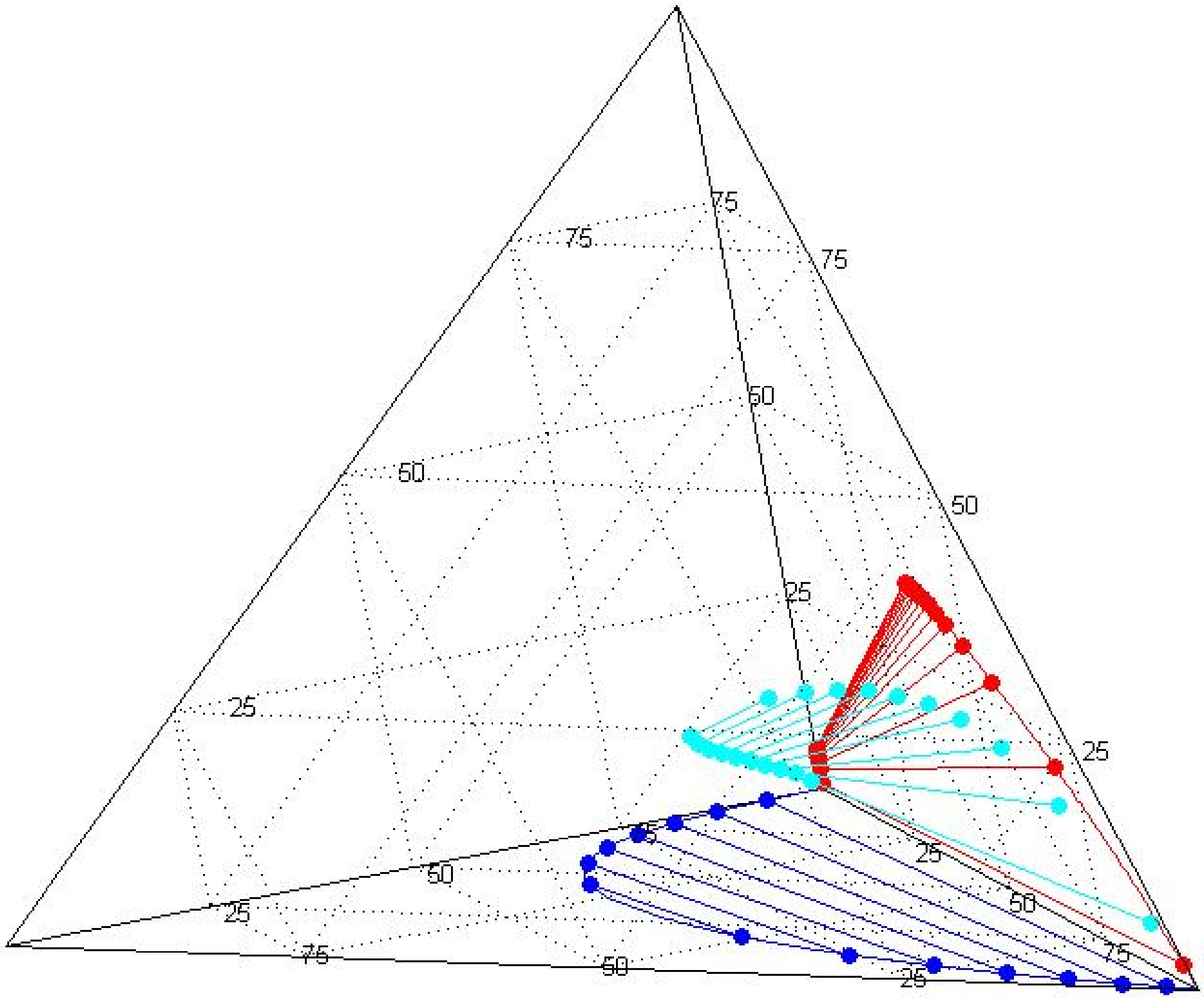
Solidification Sequence





2 상영역에서 수직 단면이 tie line과 불일치하므로 다른 온도에서 평형상만 나타내고 조성은 표시할 수 없음.

Quarternary의 평형상태를 기하학적으로 표시한 그림.



4성분원소들 가운데서 임의의 3성분의 농도가 독립적으로 변할 수 있는 함수이므로 여러가지 조성의 Quarternary alloy은 공간적으로 표시된다. 3원계의 조성은 정4면체의 면상에, 그리고 4원계 합금의 조성은 정4면체의 내부공간에 표시된다. 합금의 조성은 정4면체의 기하학적성질에 의하여 결정된다. 4원계에서 상조성을 결정하기 위하여 lever rule을 이용한다. 4원합금의 변태행정을 고찰할 때 정4면체안의 추상적인 4차원투영을 이용한다.

Contents in Phase Transformation

상변태를
이해하는데
필요한 배경

- **(Ch1) 열역학과 상태도: Thermodynamics**
- **(Ch2) 확산론: Kinetics**
- **(Ch3) 결정계면과 미세조직**

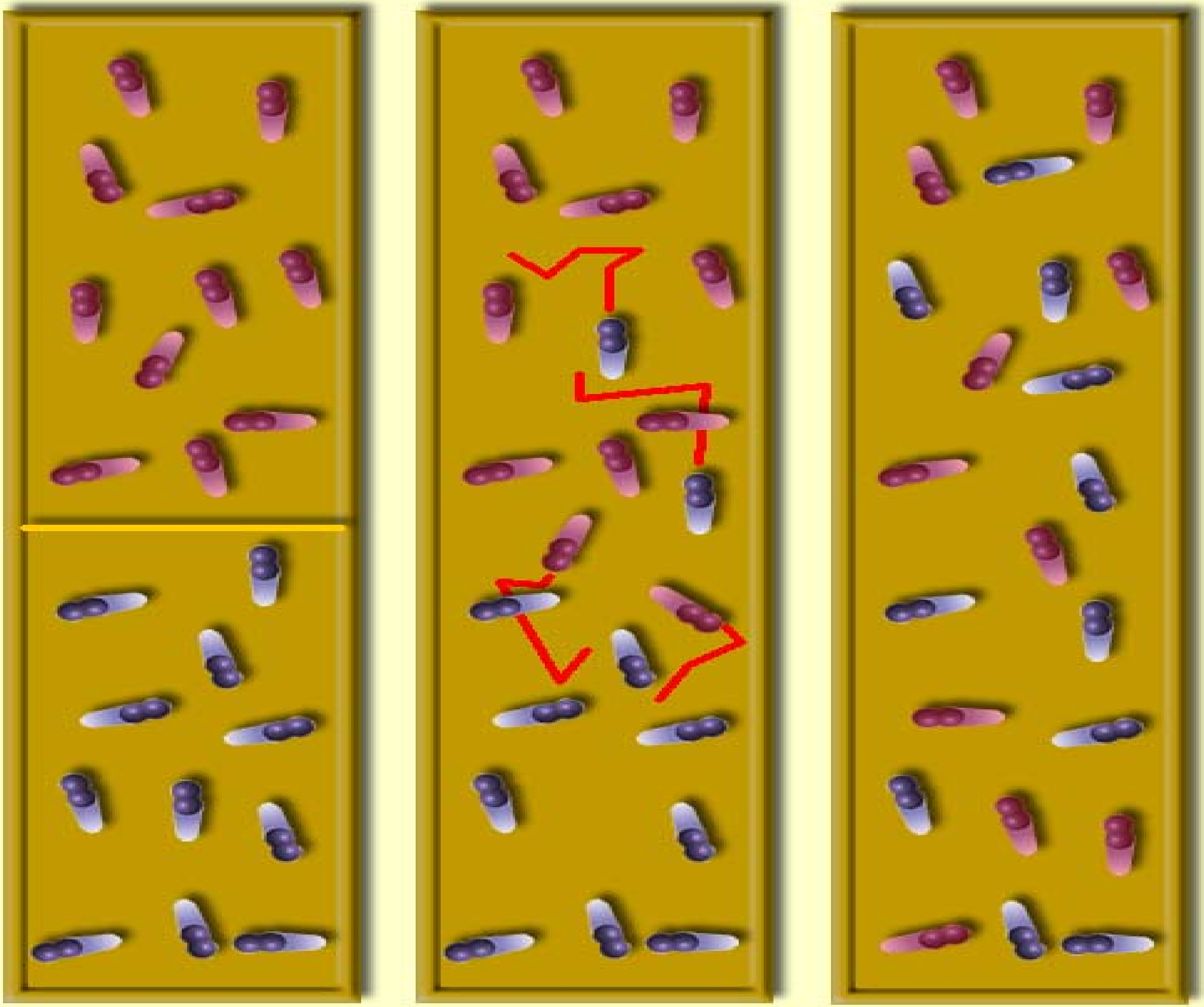
대표적인 상변태

- **(Ch4) 응고: Liquid → Solid**
- **(Ch5) 고체에서의 확산 변태: Solid → Solid (Diffusional)**
- **(Ch6)고체에서의 무확산 변태: Solid → Solid (Diffusionless)**

Contents for today’s class

- Diffusion
- Interstitial Diffusion – Fick’s First Law
- Effect of Temperature on Diffusivity
- Nonsteady-state diffusion – Fick’s Second Law

Diffusion



Mechanism of Solid-State Diffusion

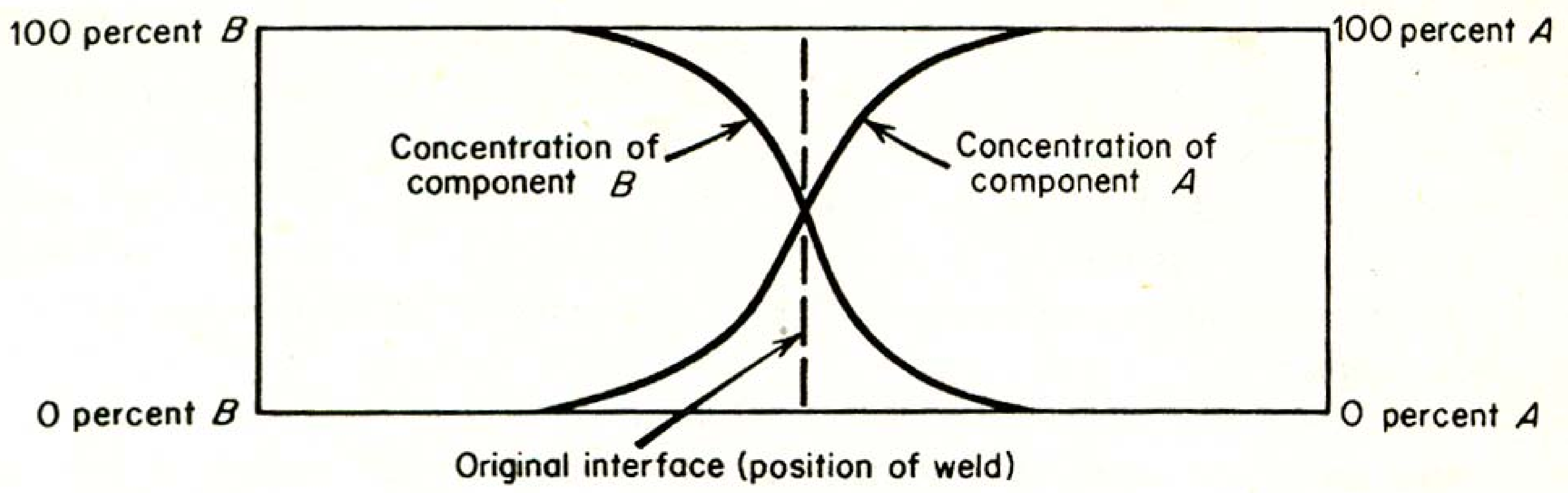
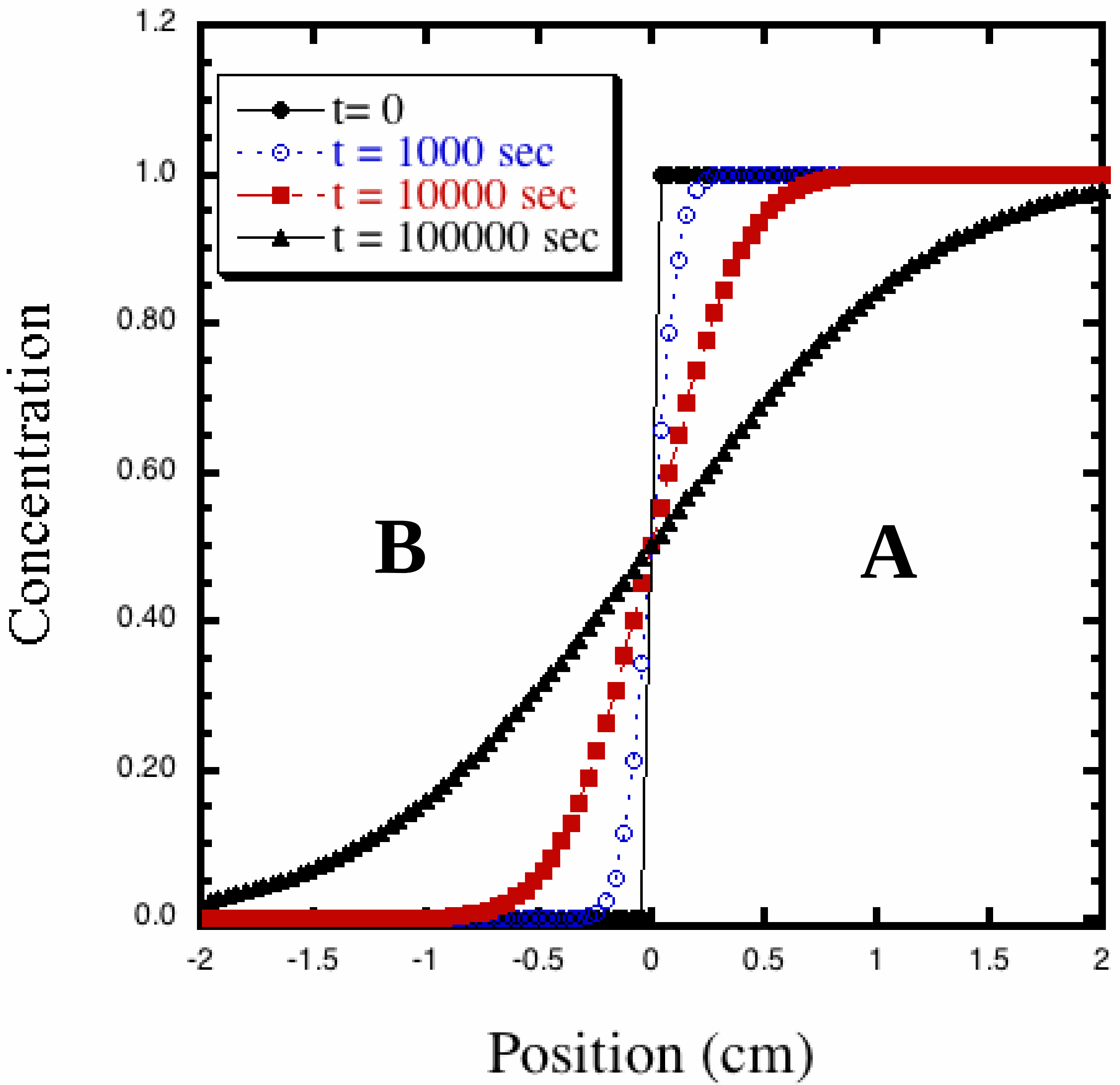


Fig. 10.6 Curves showing concentration as a function of distance along a diffusion couple. Curves of this type are usually called *penetration curves.*

R.E. Reed-Hill, Physical Metallurgy Principles



t= 0
t = 1000 sec
t = 10000 sec
t = 100000 sec
B
A
Concentration
Position (cm)
1.2
1.0
0.80
0.60
0.40
0.20
0.0
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2

Diffusion

Movement of atoms to reduce its chemical potential μ.

Driving force: Reduction of G

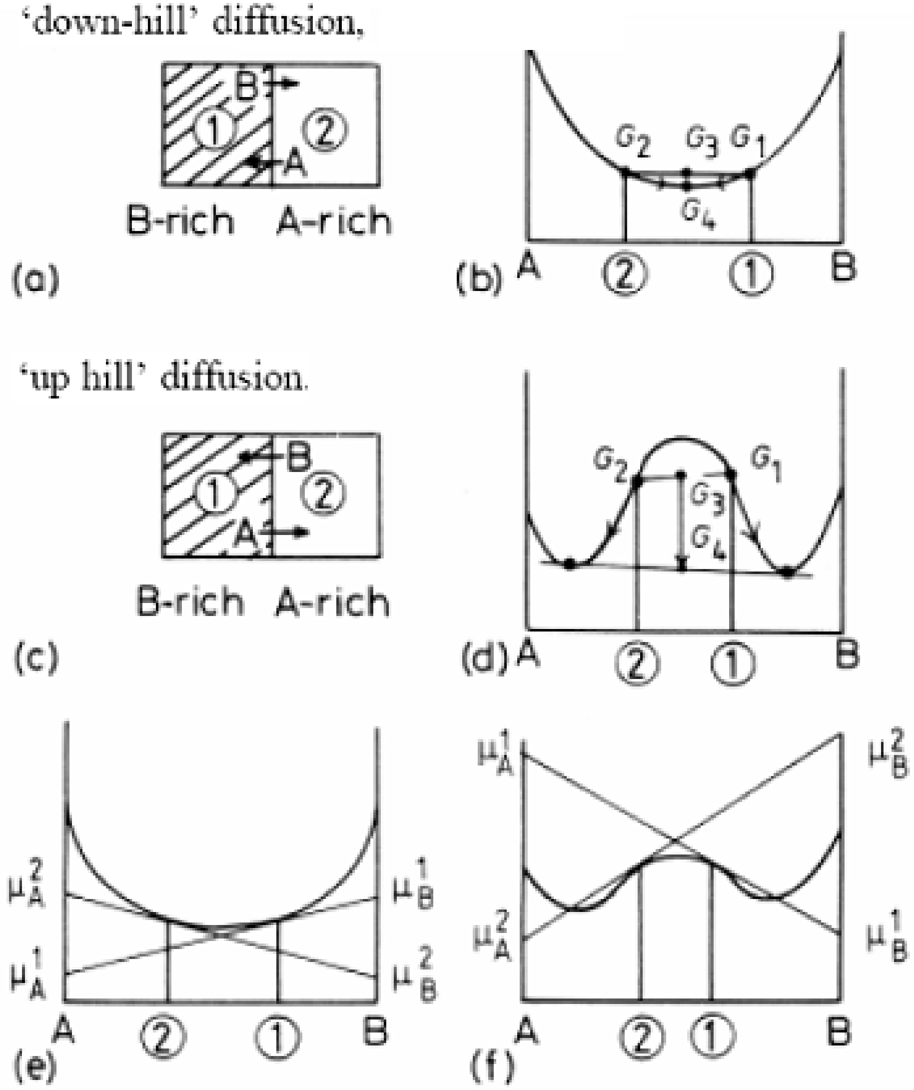
Down-hill diffusion

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

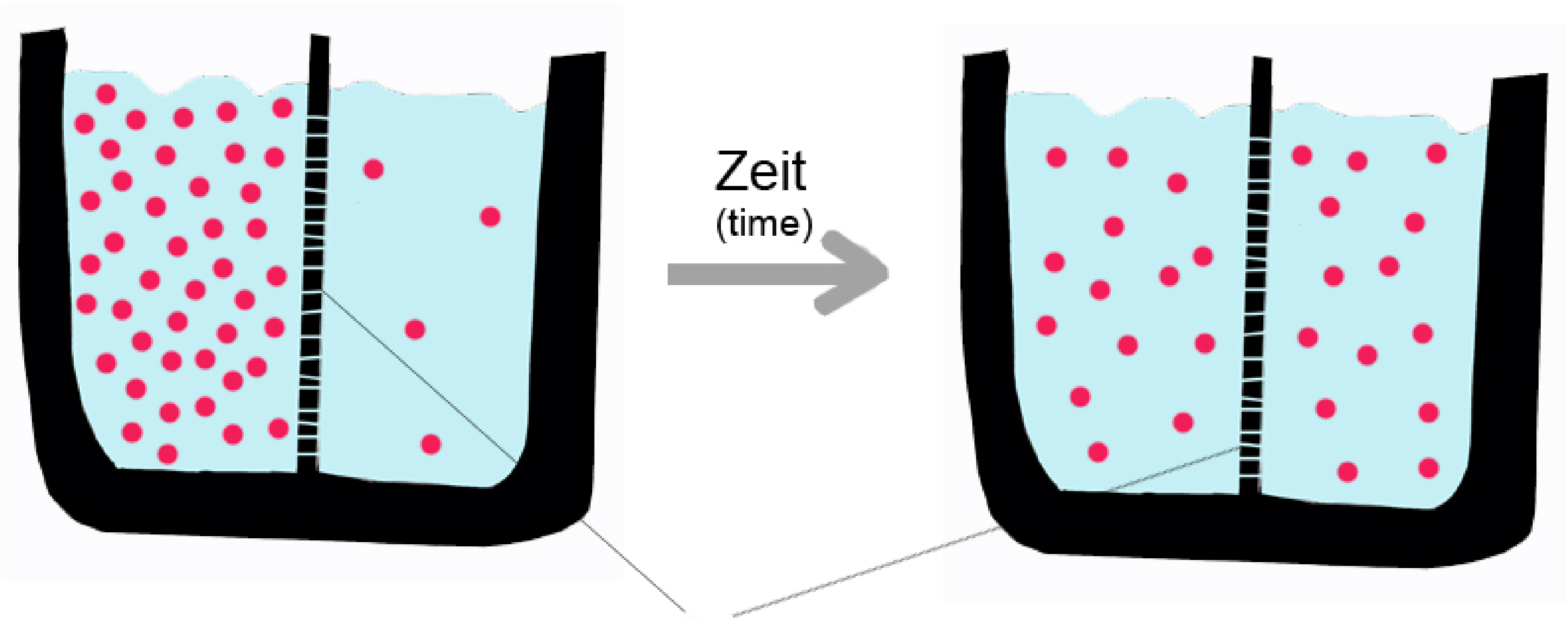
Up-hill diffusion

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

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



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



Zeit
(time)

semipermeabel

Diffusion

Movement of atoms to reduce its chemical potential μ.

Driving force: Reduction of G

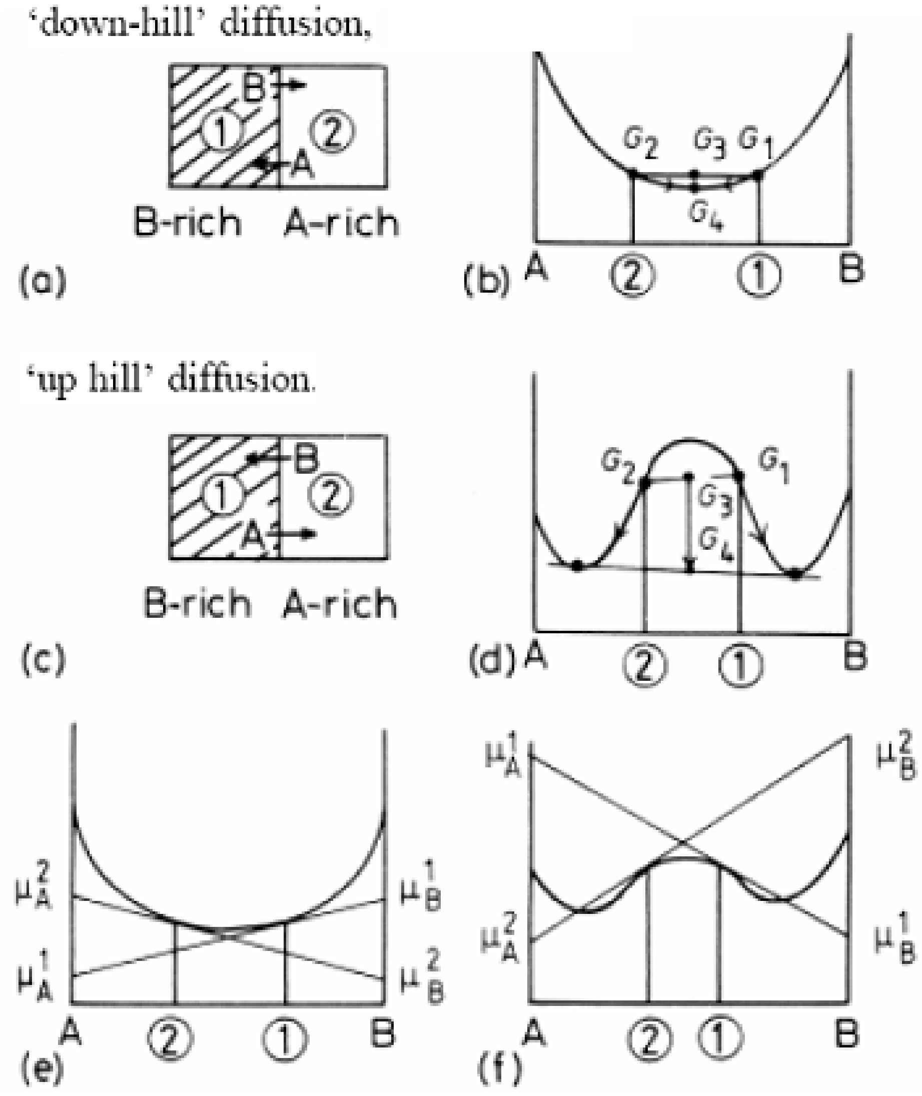
Down-hill diffusion

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

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



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

Phase separation in metallic glasses

$Nd_{60}Al_{10}Co_{30}$

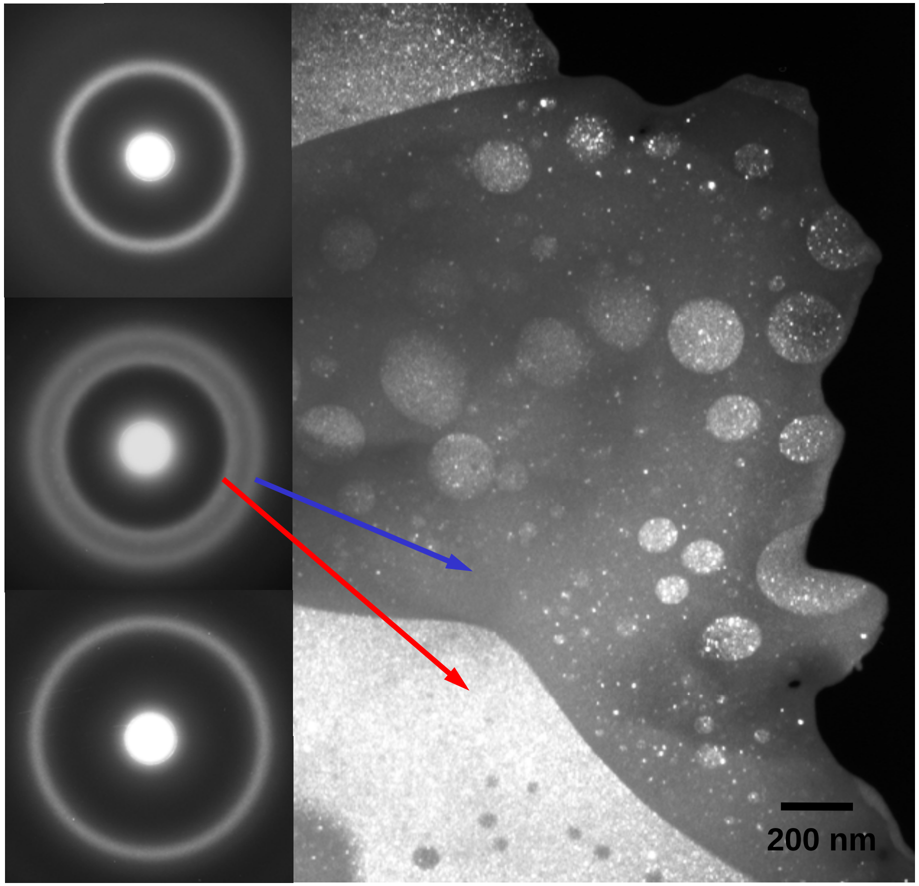
2.91 Å

$Nd_{30}Zr_{30}Al_{10}Co_{30}$

2.37 Å, 2.99 Å

$Zr_{60}Al_{10}Co_{30}$

2.40 Å



TEM results for $Nd_{30}Zr_{30}Al_{10}Co_{30}$ alloy

Diffusion

Diffusion : Mechanism by which matter transported through matter

What is the driving force for diffusion?

⇒ a concentration gradient (x)

⇒ a chemical potential (o)

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

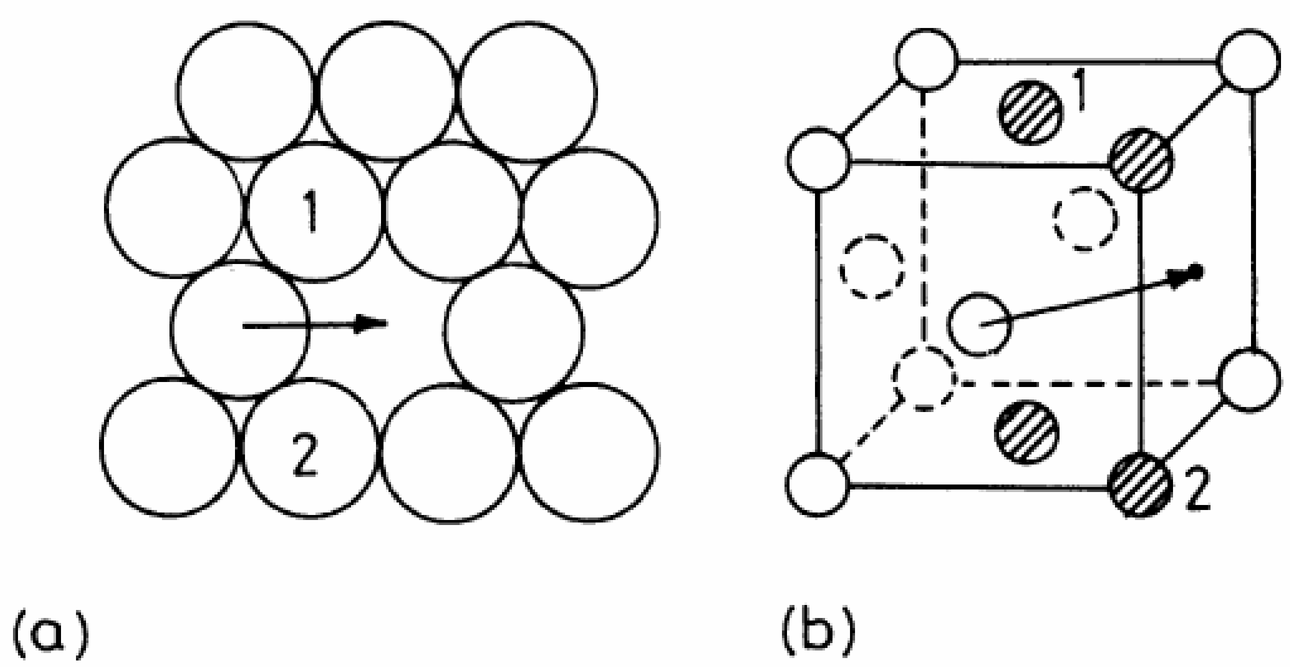
Atomic mechanisms of diffusion

Substitutional vs. Interstitial diffusion

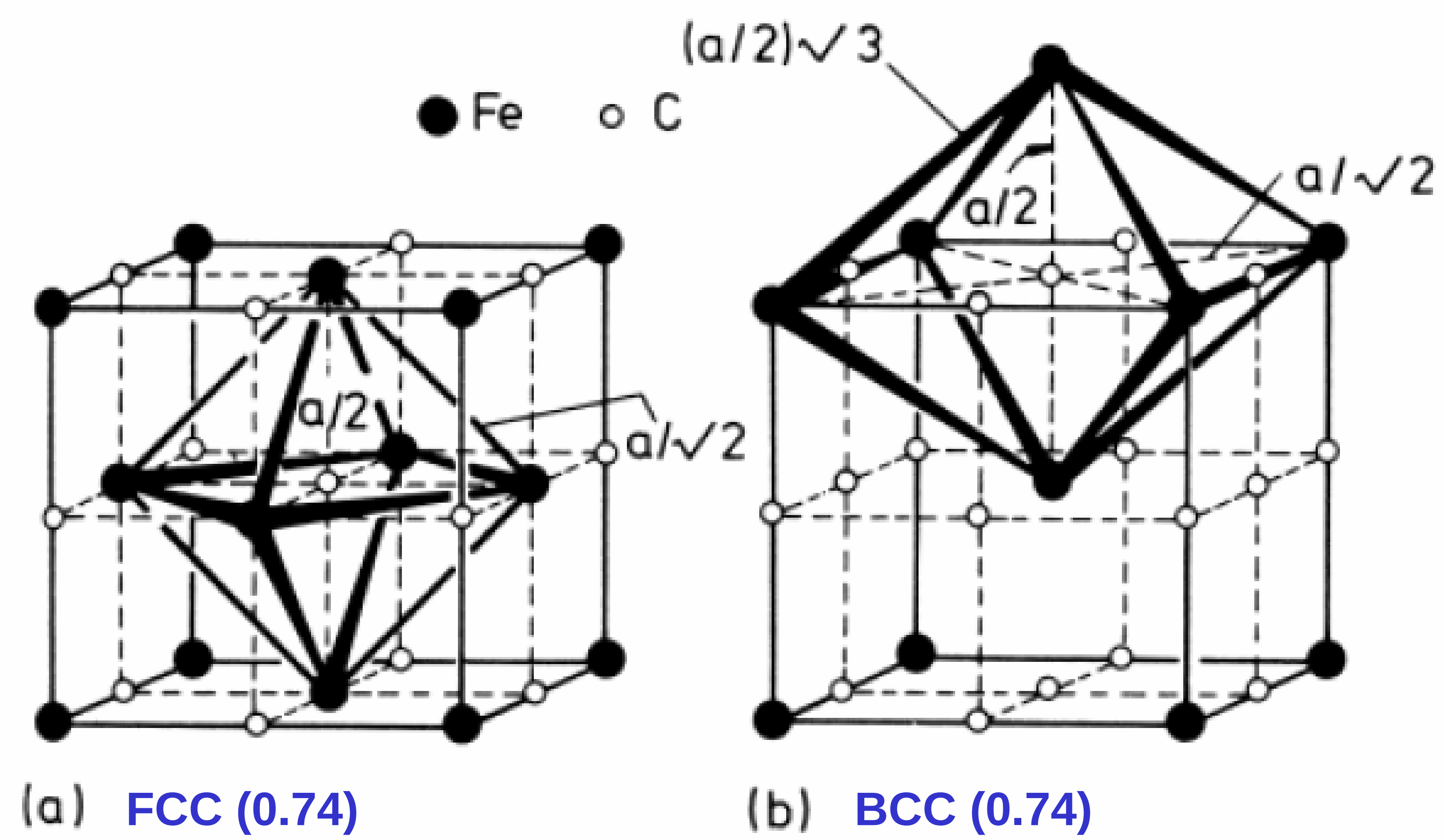
The mean vibrational energy is **3kT**, therefore the amplitude of thermal oscillation of an atom increases markedly with temperature. If a neighboring atom site is vacant, then the oscillation atom can change site with a certain probability (**atom jumping**). The probability consists of creation of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

Substitutional diffusion

FCC



Interstitial diffusion

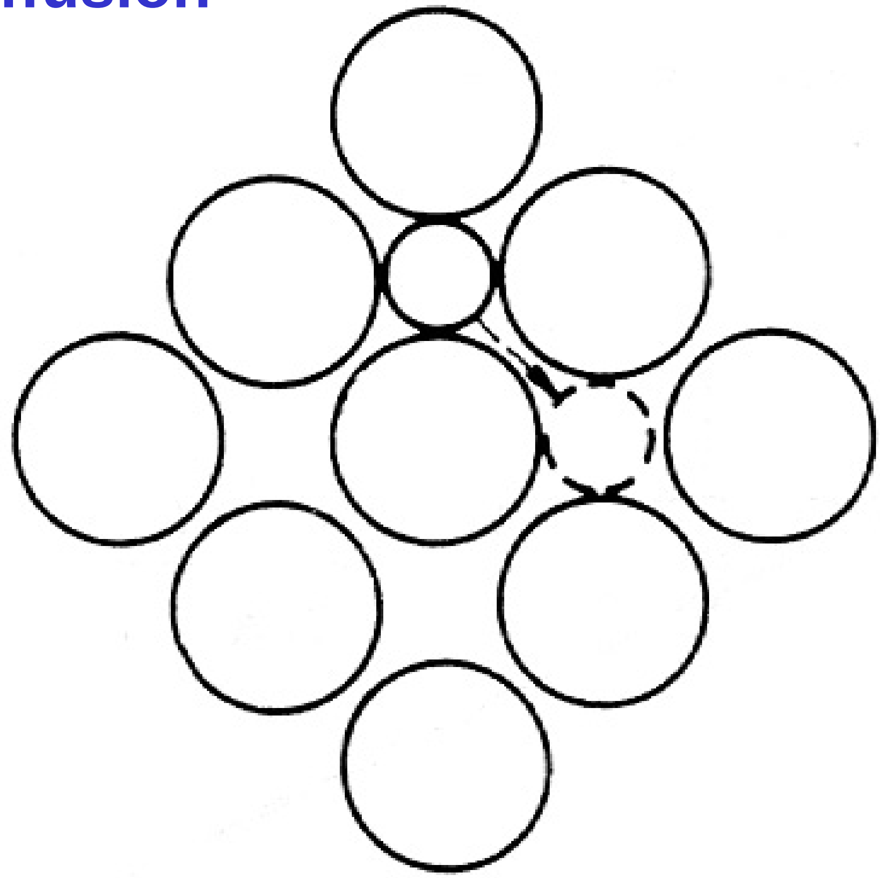


FCC (0.74)

BCC (0.74)

Fig. 2.3 (a) Octahedral interstices (0) in an fcc crystal. (b) Octahedral interstices in a bcc crystal. (After P. Haasen, *Physical Metallurgy*, Cambridge University Press, Cambridge, 1978.)

Interstitial diffusion



How interstitial diffusion differs from substitutional diffusion?

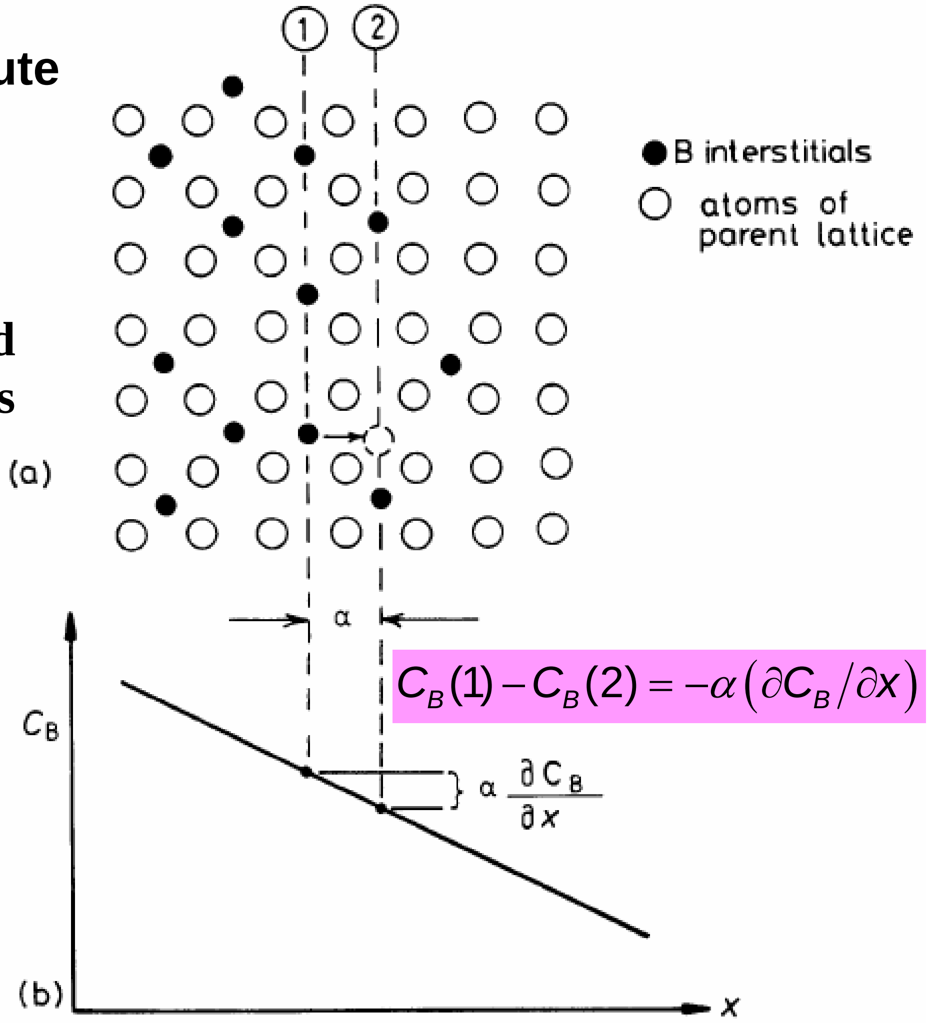
Interstitial diffusion

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.

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

J_B : 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



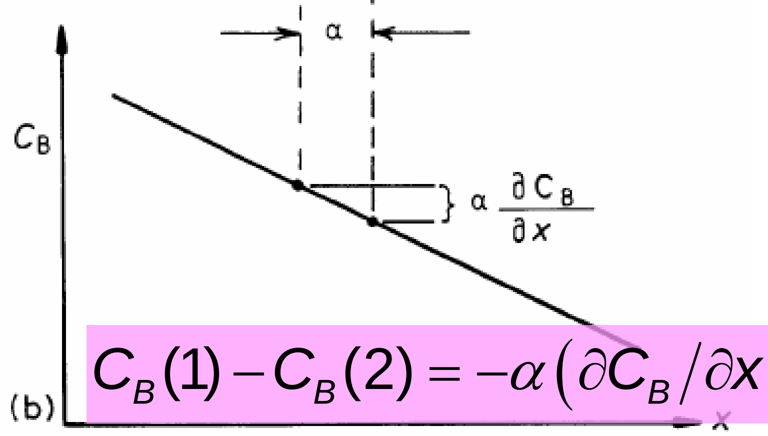
$C_B(1) - C_B(2) = -\alpha\left(\partial C_B/\partial x\right)$

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

Fick's First Law of Diffusion

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

α: Jump distance



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

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

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

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

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

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 at 1000oC.

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

lattice parameter of γ-Fe : ~0.37 nm

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

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

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

If the crystal structure is not cubic, then the probability of jump is anisotropic. 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,

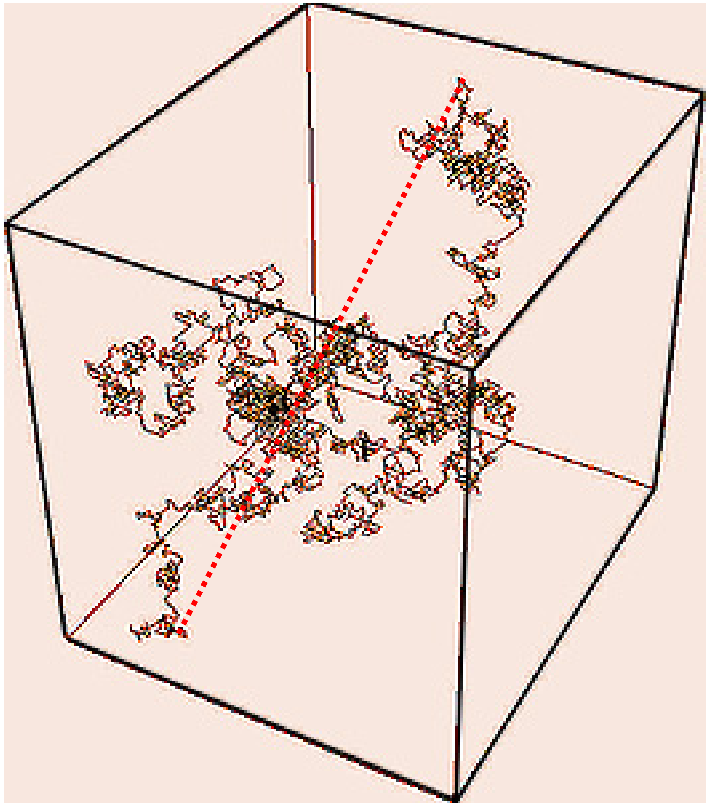
D_c = 2.5 x 10^{-11}m^{2}s^{-1}, when C_c = 0.15 wt%

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

$$\boxed{C_c \uparrow \rightarrow D_C \uparrow}$$

For random walk in 3 dimensions,
after n steps of length α

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



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

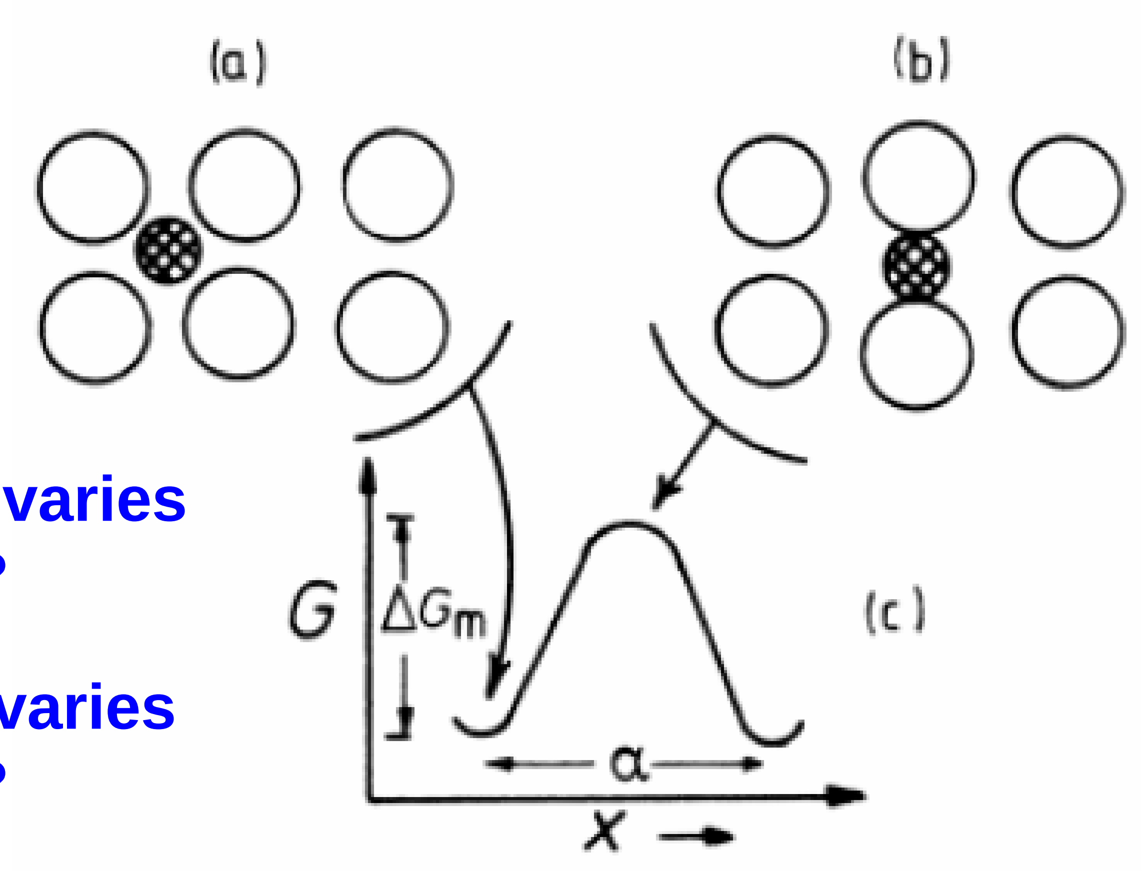
$$D_B = \frac{1}{6}\Gamma_B\alpha^2$$

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

In 1 s, each carbon atom will move a total distance of ~ 0.5 m
→ a net displacement : ~ 10 μm.

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. (After P.G. Shewmon, in *physical Metallurgy, 2nd edn.*, R.W. Cahn (Ed.), North-Holland, Amsterdam, 1974.)

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

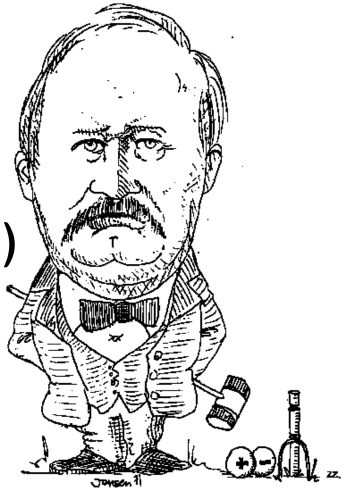
$$\left\{ \Delta G_m = \Delta H_m - T\Delta S_m \quad , \quad D_B = \frac{1}{6}\Gamma_B \alpha^2 \right\}$$

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

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

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

(Arrhenius-type equation)



Temperature Dependence of Diffusion

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

How to determine Q_{ID} experimentally?

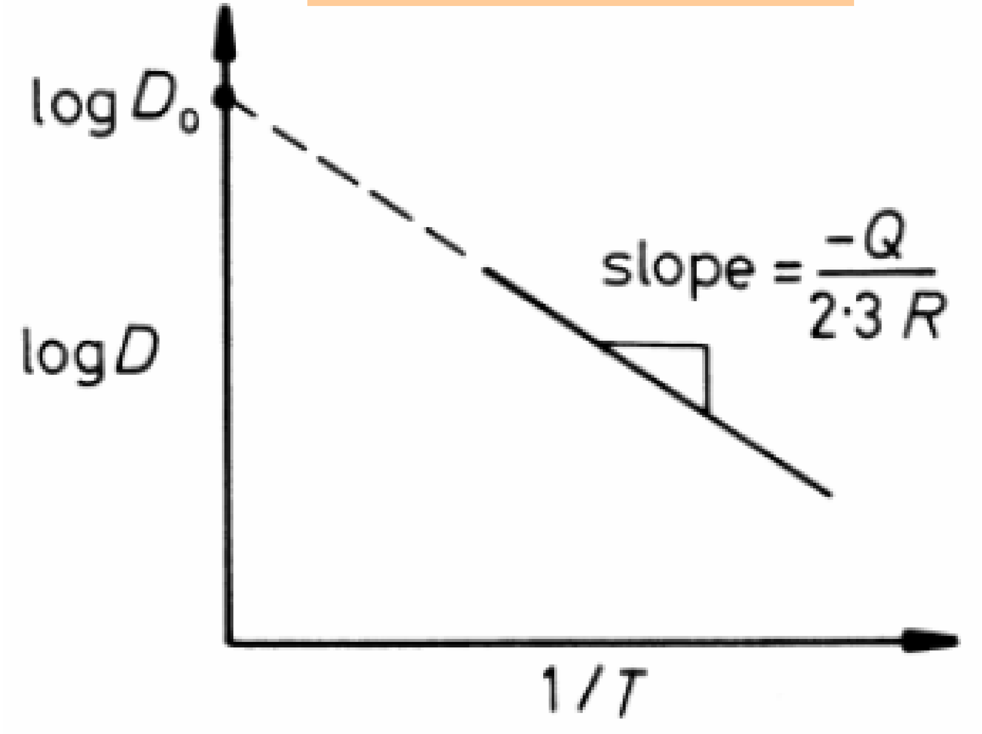


Fig. 2.7 The slope of log D v. 1/T gives the activation energy for diffusion Q.

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

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