2015 Fall

"Phase Transformation *in* Materials"

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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

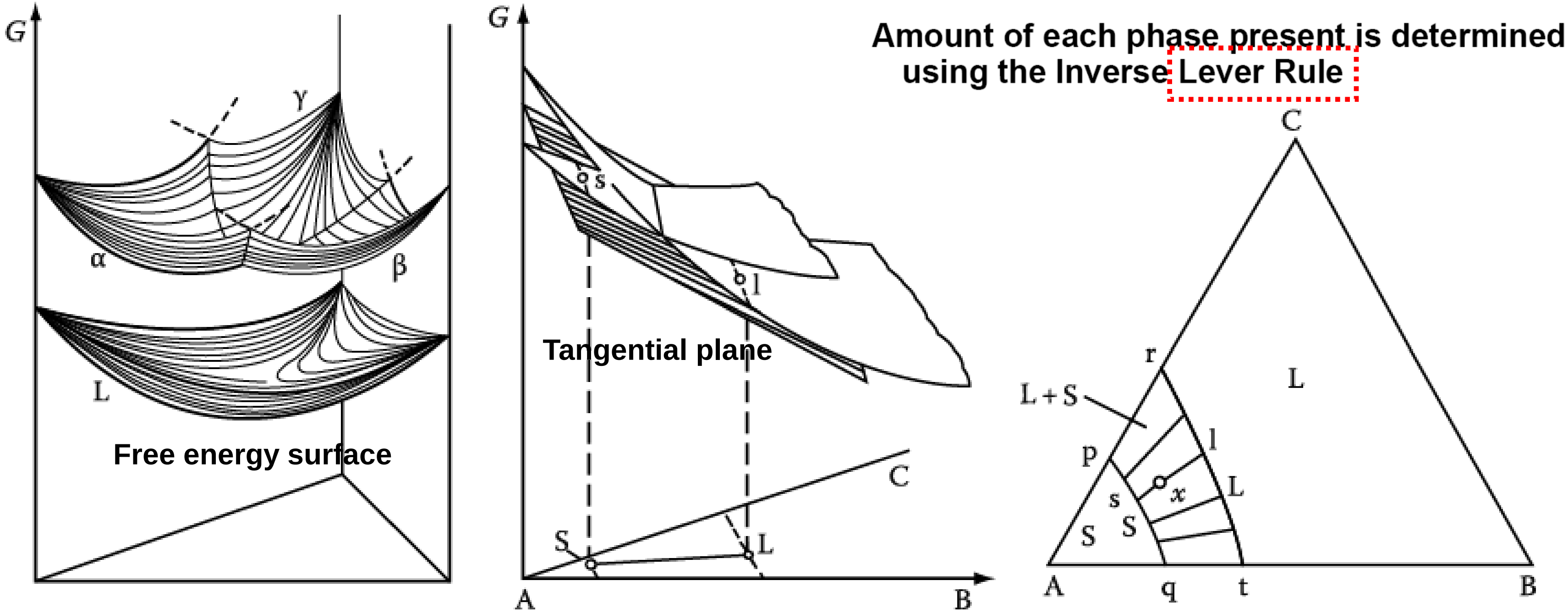


Fig. 1.41 (a) Free energy surface of a liquid and three solid phases of a ternary system.

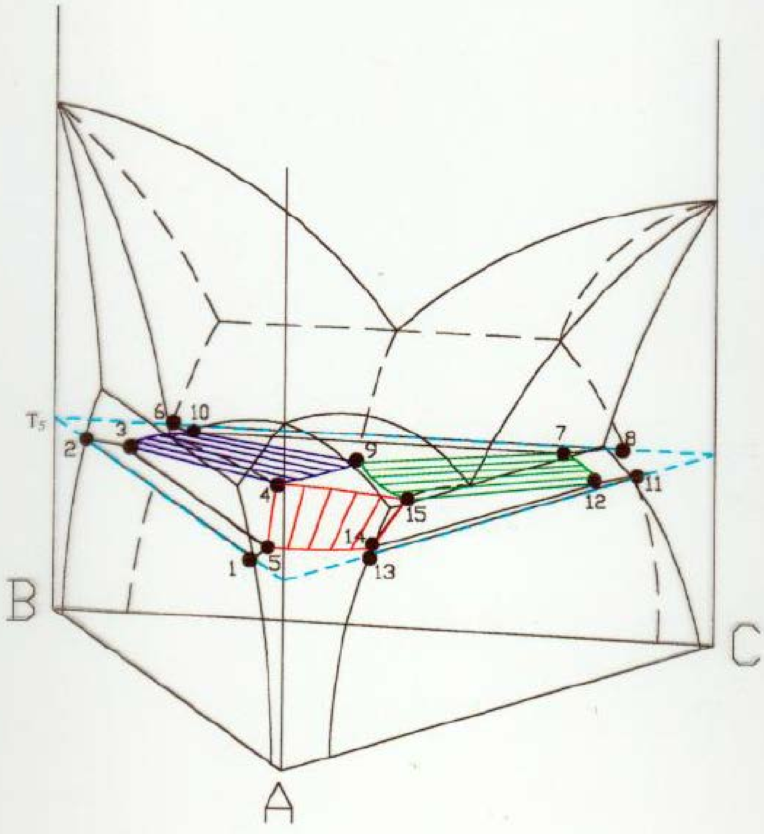
(b) A tangential plane construction to the free energy surfaces defined equilibrium between s and l in the ternary system

(c) Isothermal section through a ternary phase diagram

Ternary Eutectic System

(with Solid Solubility)

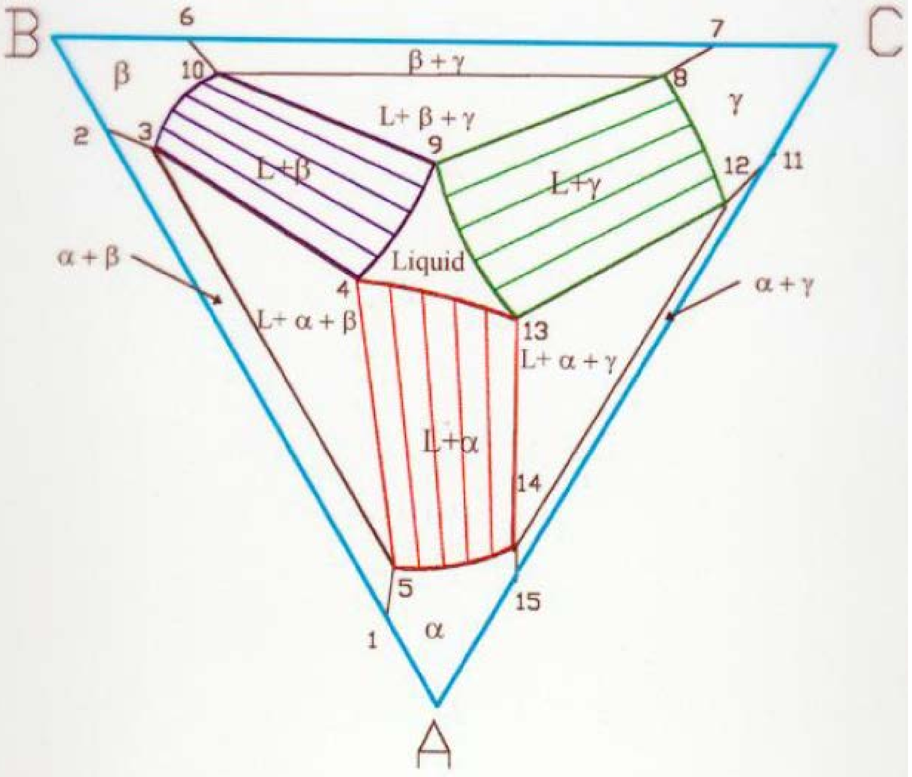
T5A:



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

T5B:

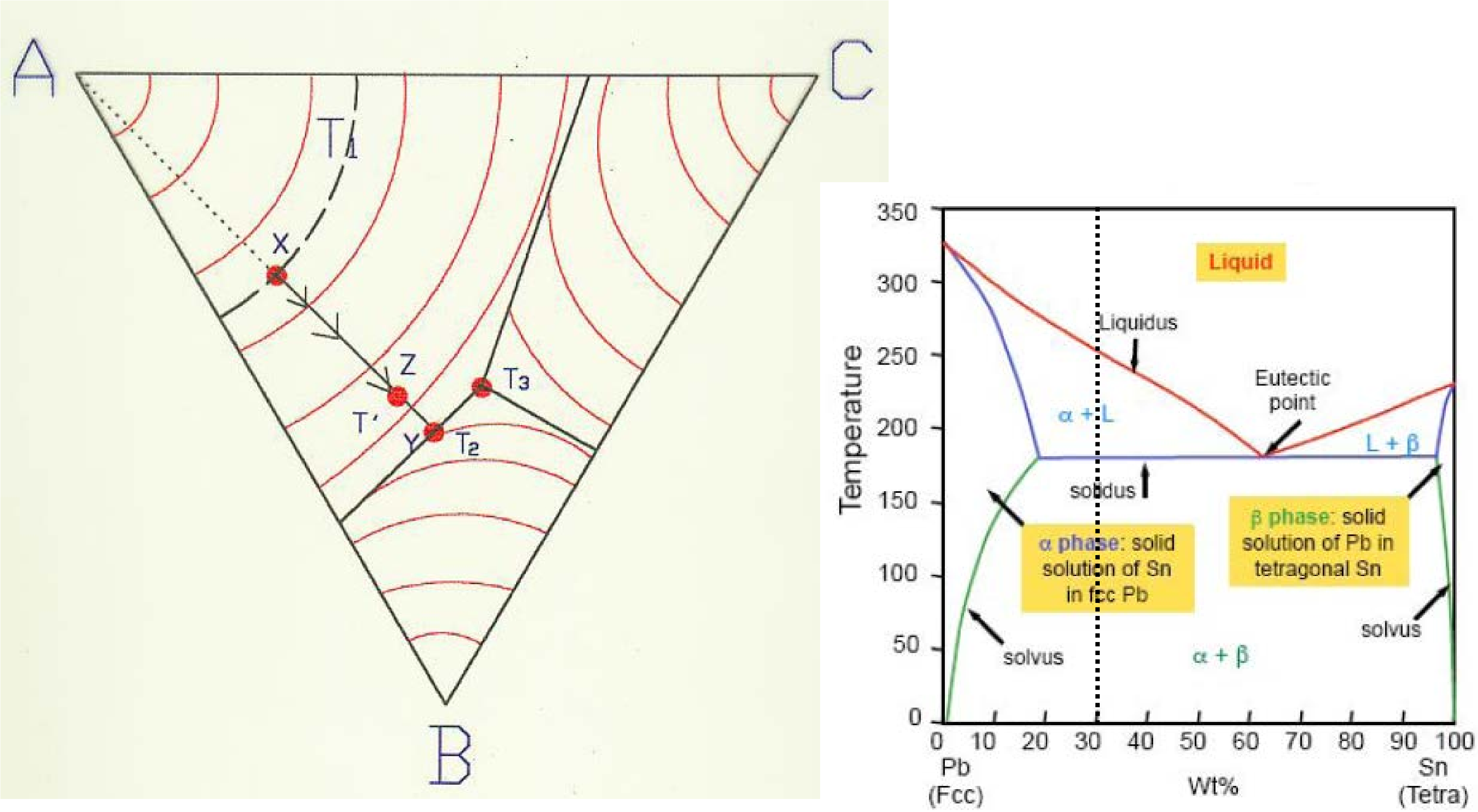
3 phases region: tie triangle



Isothermal Section At $T=T_5$

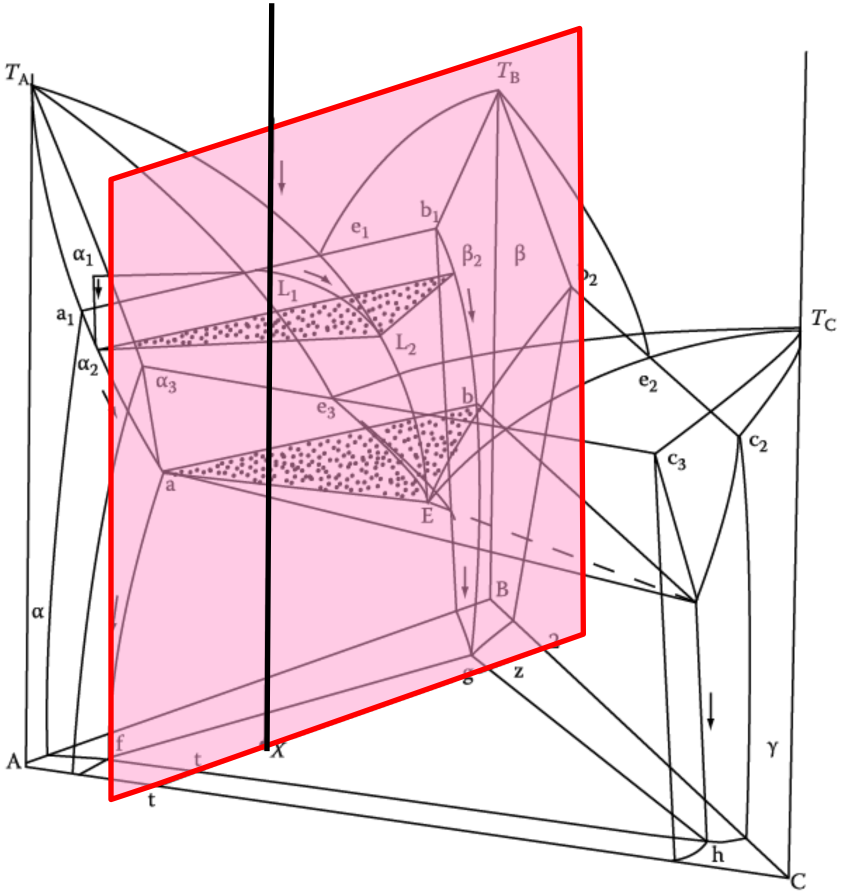
Ternary Eutectic System

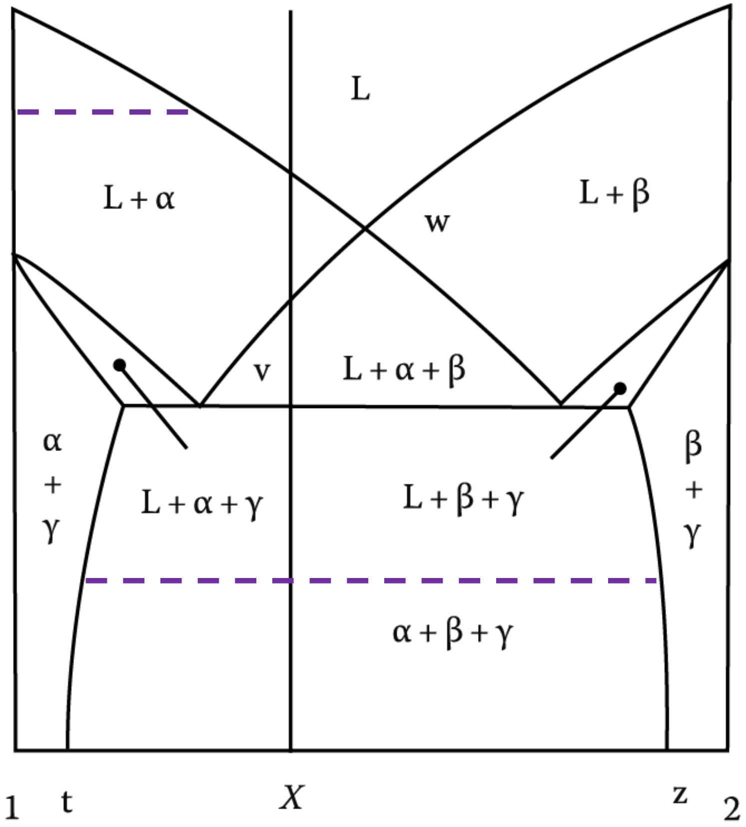
3) Solidification Sequence: liquidus surface



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

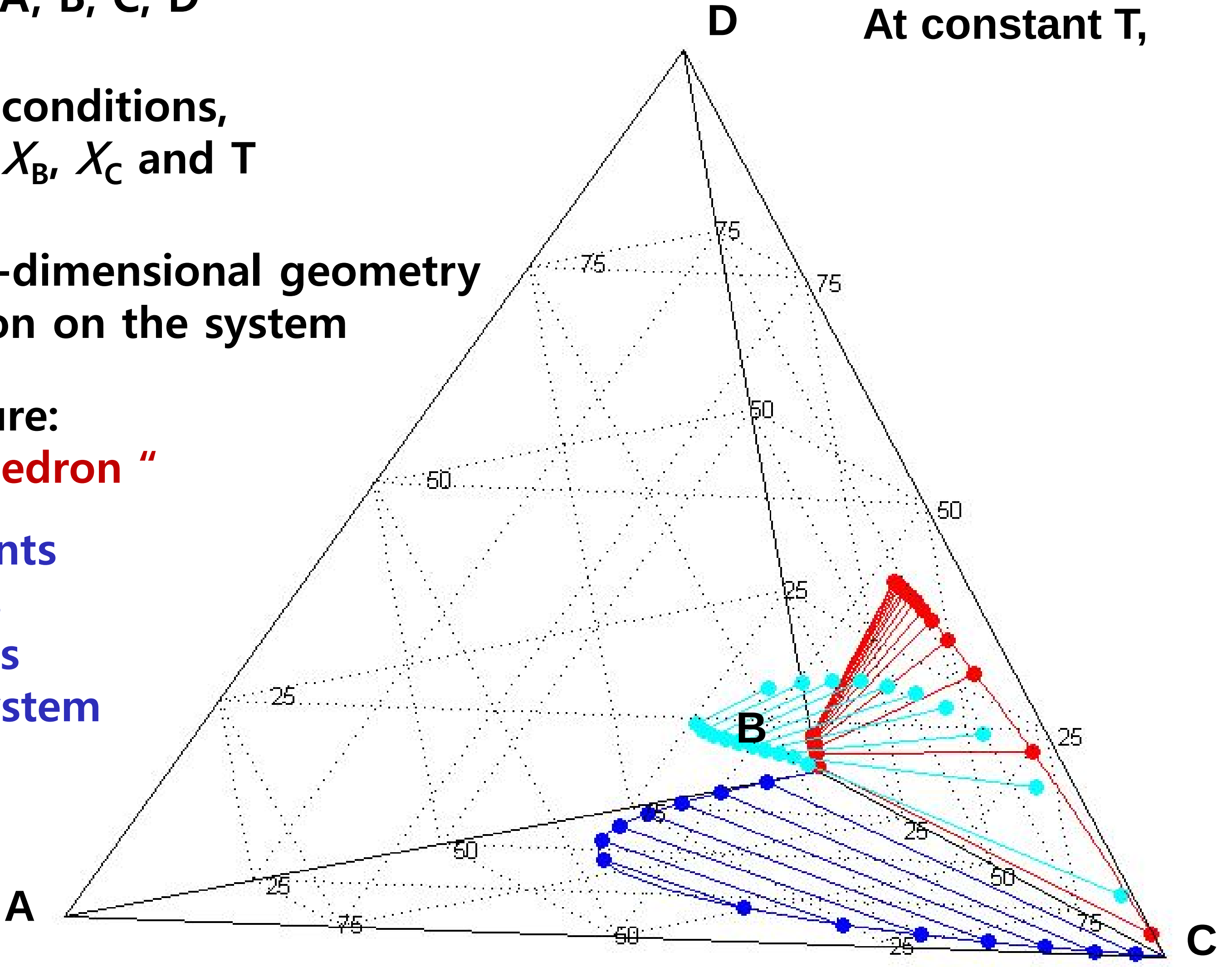
Assuming isobaric conditions,
Four variables: X_A, X_B, X_C and T

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

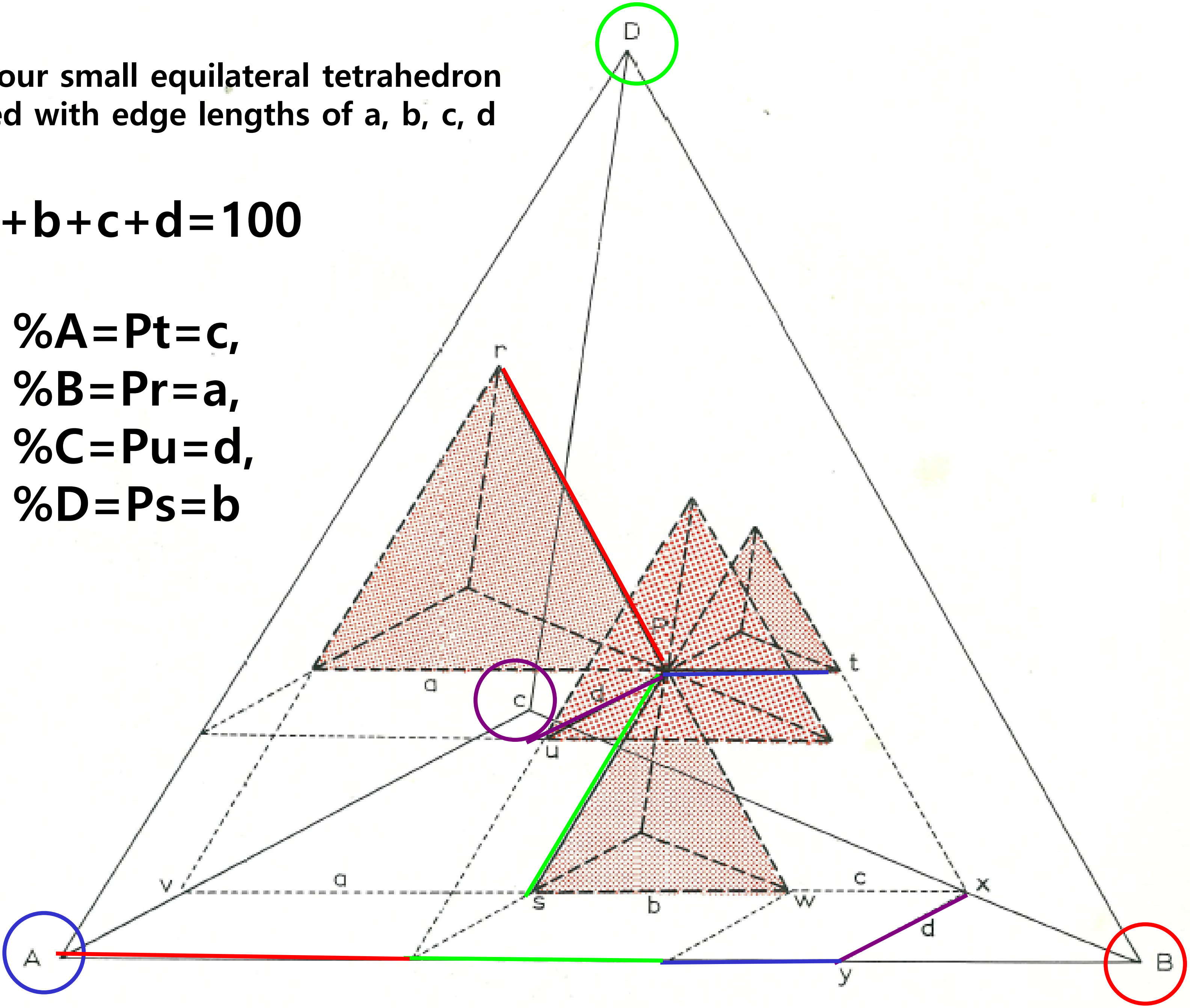


Fig. 247. Representation of a quaternary system by an equilateral tetrahedron.

* Incentive Homework 1

Please submit ternary phase diagram model which can clearly express 3D structure of ternary system by October 17 in Bldg. 33-313.
You can submit the model individually or
with a small group under 3 persons.

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

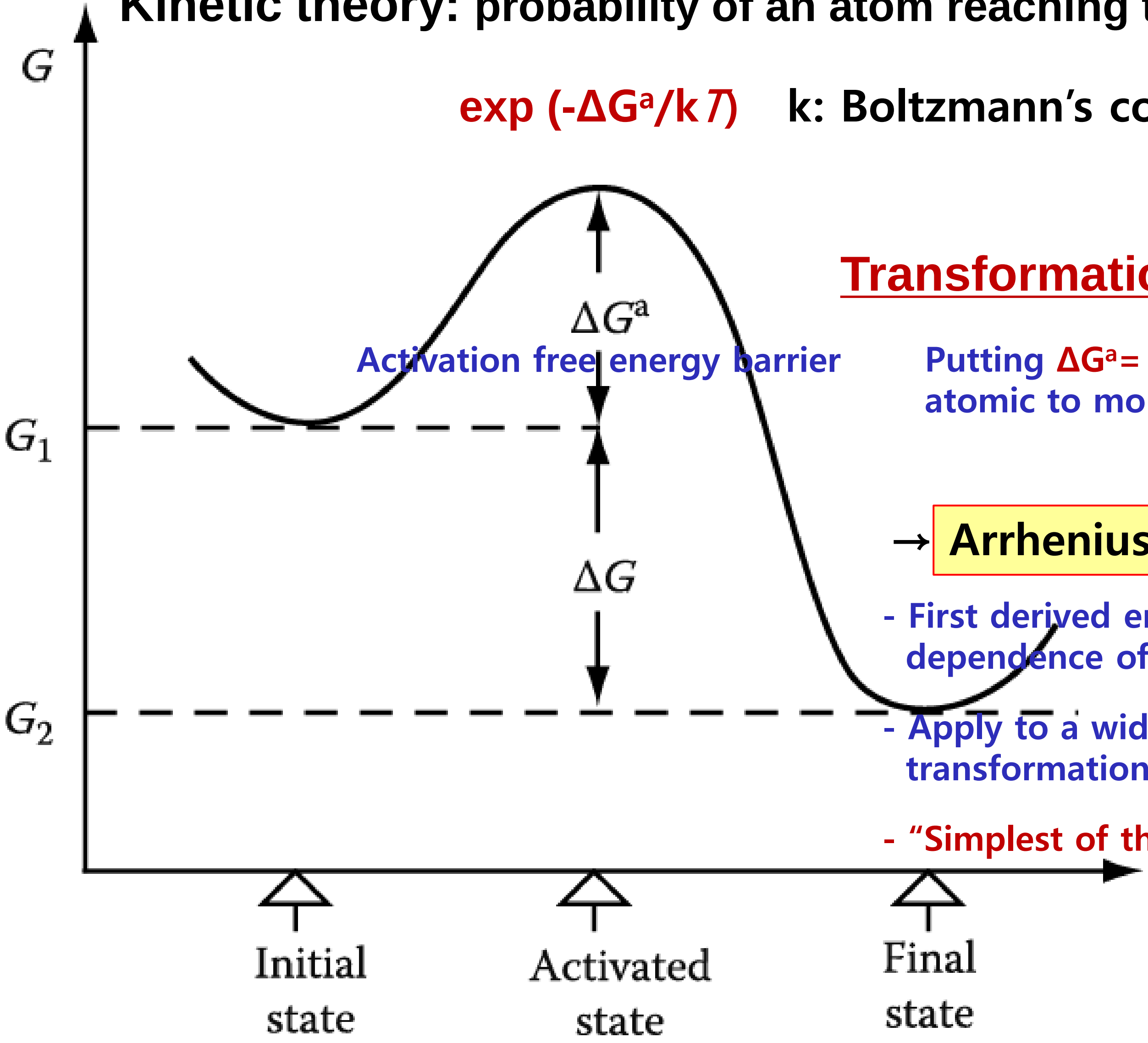
until the start of PTM class at 7th October.

Good Luck!!

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

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

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

Q. What is the driving force for diffusion?

⇒ **a concentration gradient (x)**

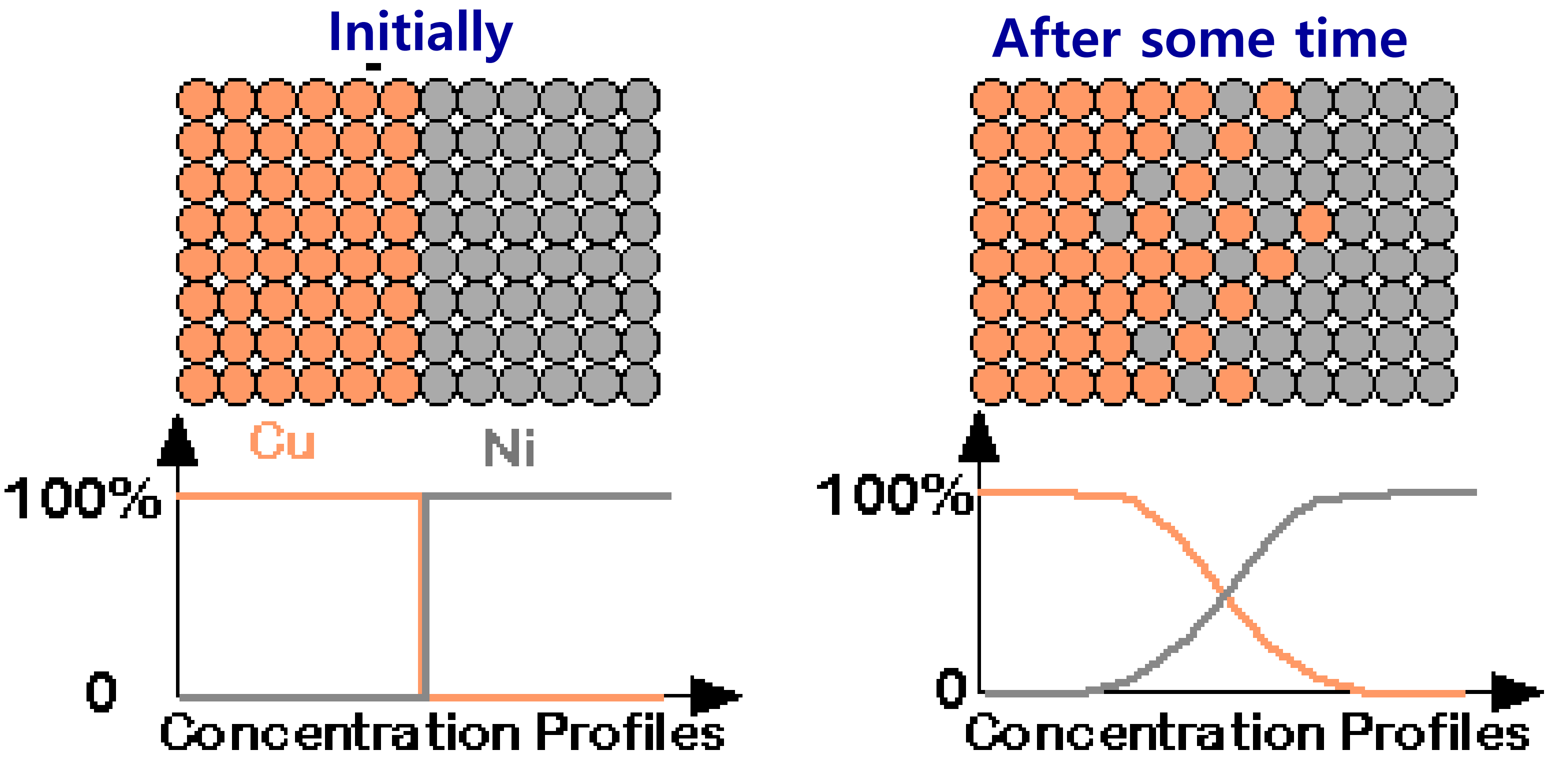
⇒ **a chemical potential gradient (o)**

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

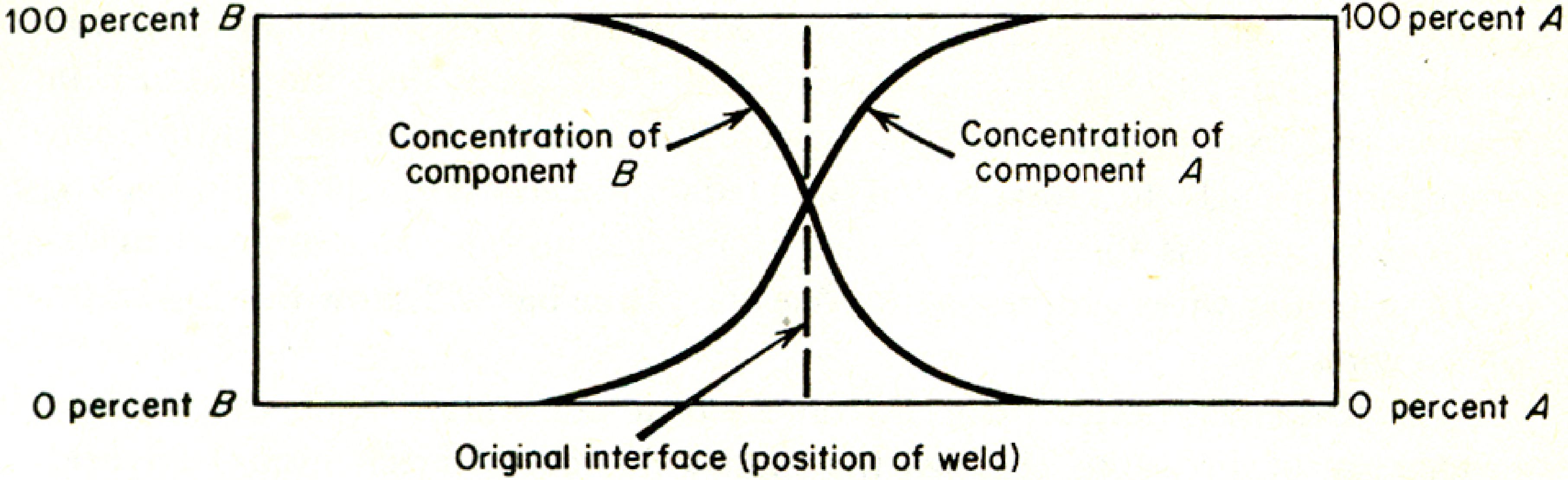


Fig. 10.6 Curves showing concentration as a function of distance along a diffusion couple. Curves of this type are usually called *penetration curves.*

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

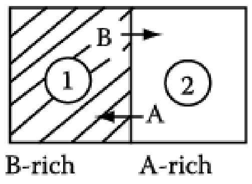
Down-hill diffusion

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

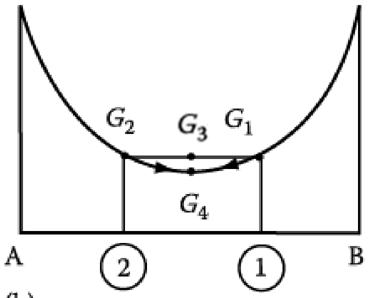
Up-hill diffusion

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

‘down-hill’ diffusion

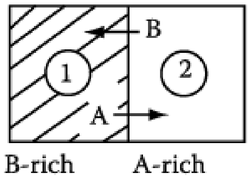


(a)

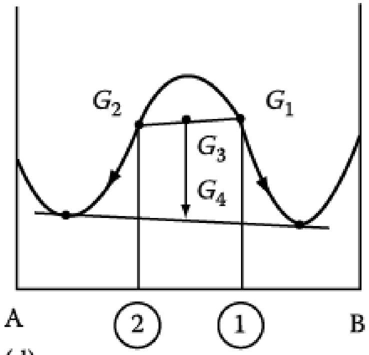


(b)

‘up-hill’ diffusion

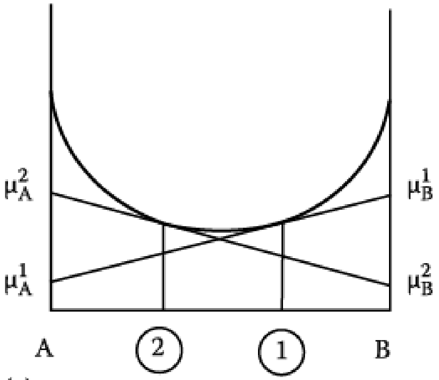


(c)

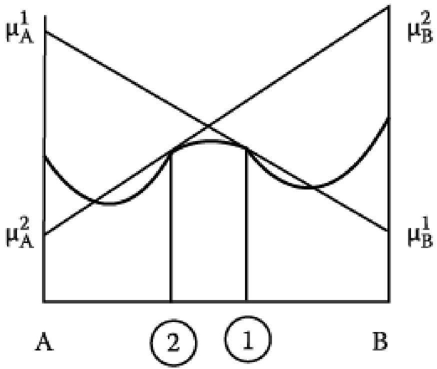


(d)

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



(e)

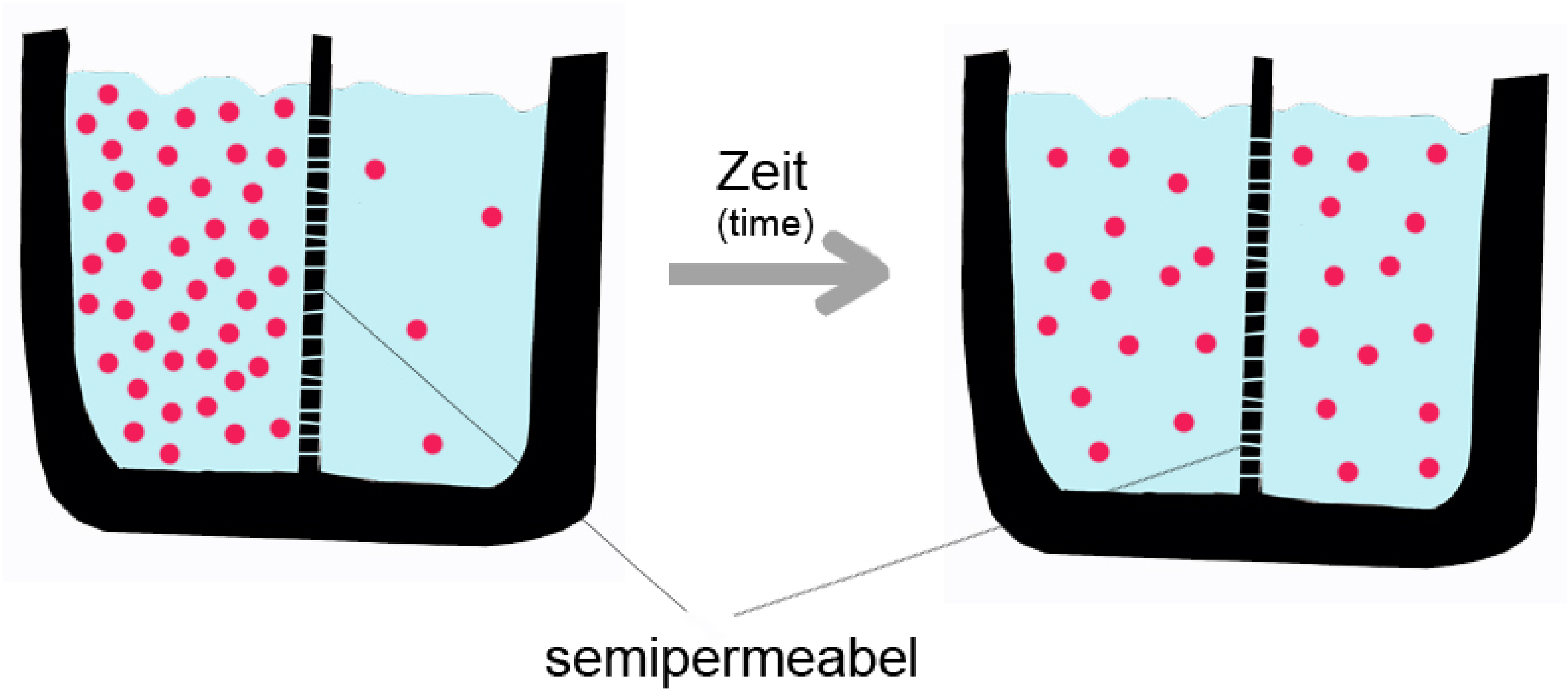


(f)

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

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

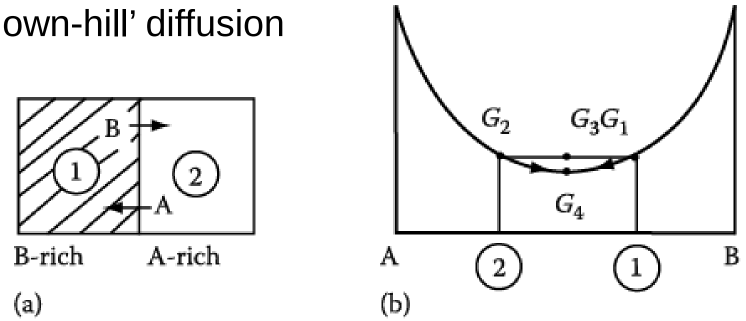
Down-hill diffusion

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

Up-hill diffusion

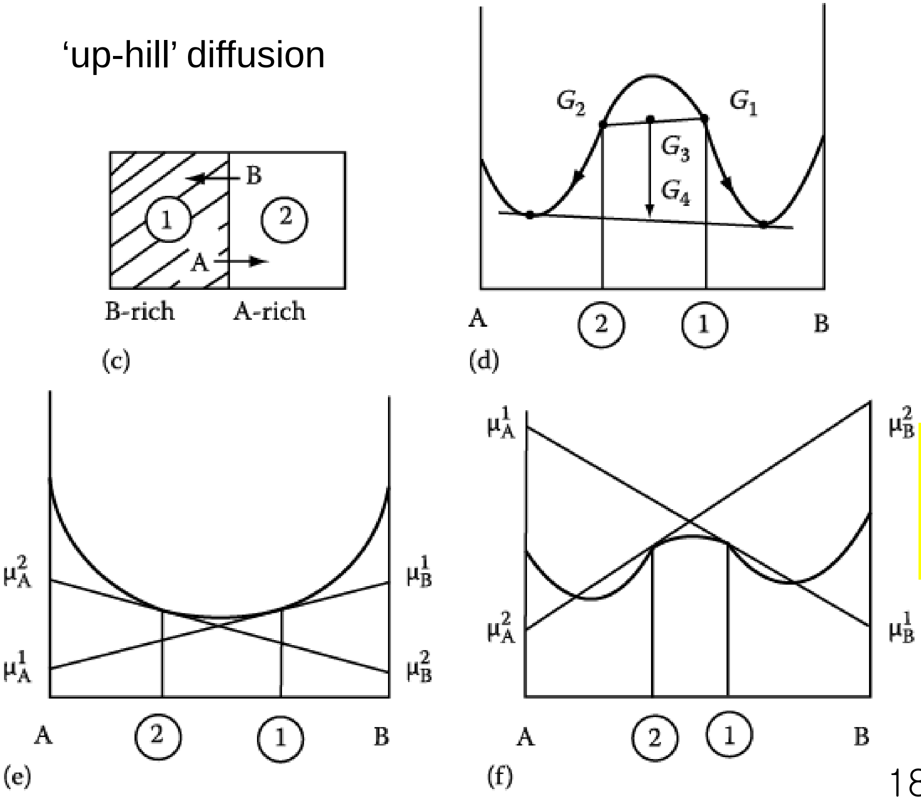
movement of atoms from a low concentration region to high concentration region

‘down-hill’ diffusion



(a) (b)

‘up-hill’ diffusion



(c) (d)

(e) (f)

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

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

Positive heat of mixing relation among constituent elements

- **Alloy design considering heat of mixing relation among constituent elements**

$\Delta H_{mix} \gg 0$ between A & B

⬇

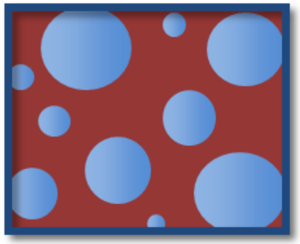
creates (meta)stable miscibility gap in limited composition range

⬇

Phase separation to A-rich & B-rich phase

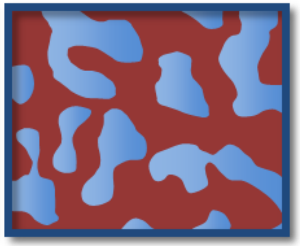
- **Different two-phase structure by initial composition before phase separation**

$C=C_1$



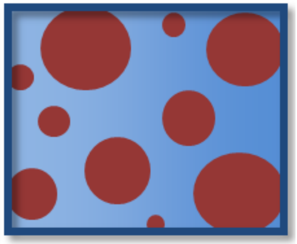
A-rich matrix
B-rich droplet

$C=C_2$

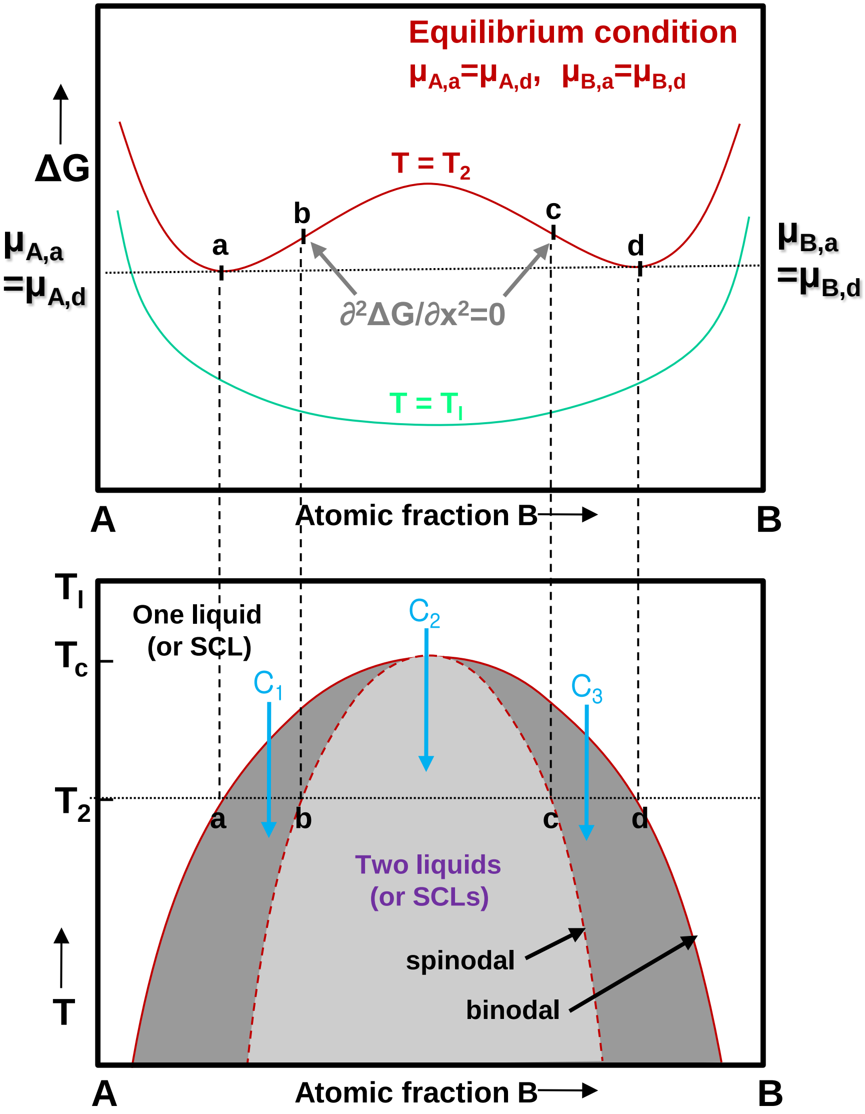


Interconnected
structure

$C=C_3$



B-rich matrix
A-rich droplet

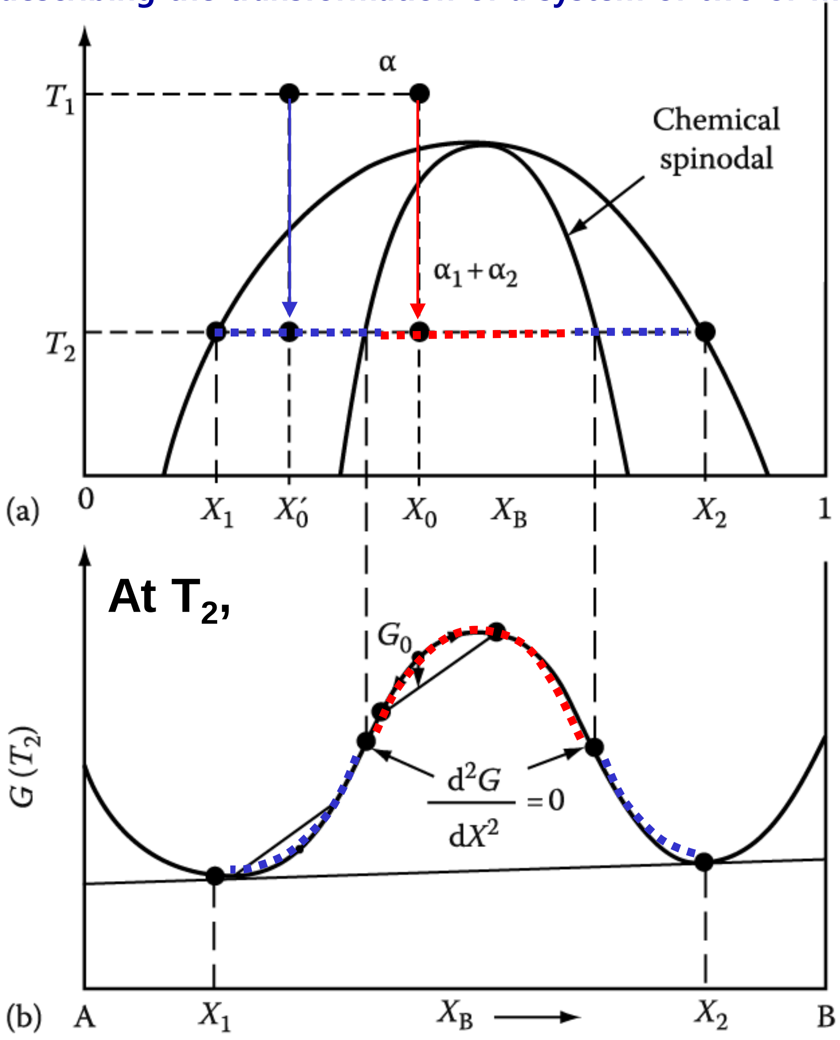


Nucleation and growth ↔ Spinodal decomposition without any barrier to the nucleation process

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



At T_2,

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.

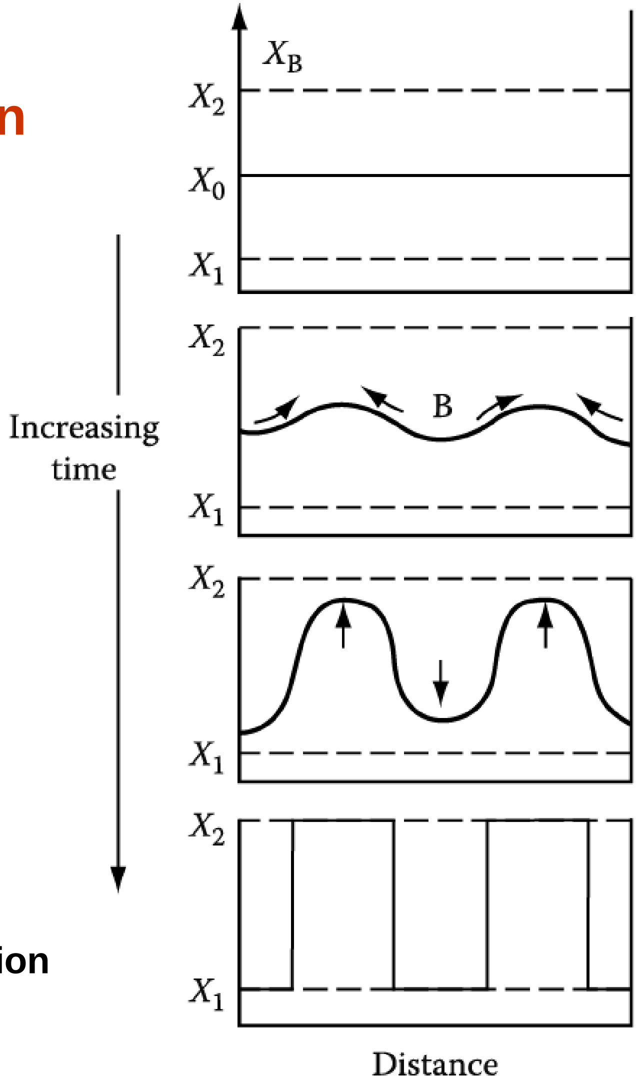
→ nucleation and growth

: "down-hill diffusion"

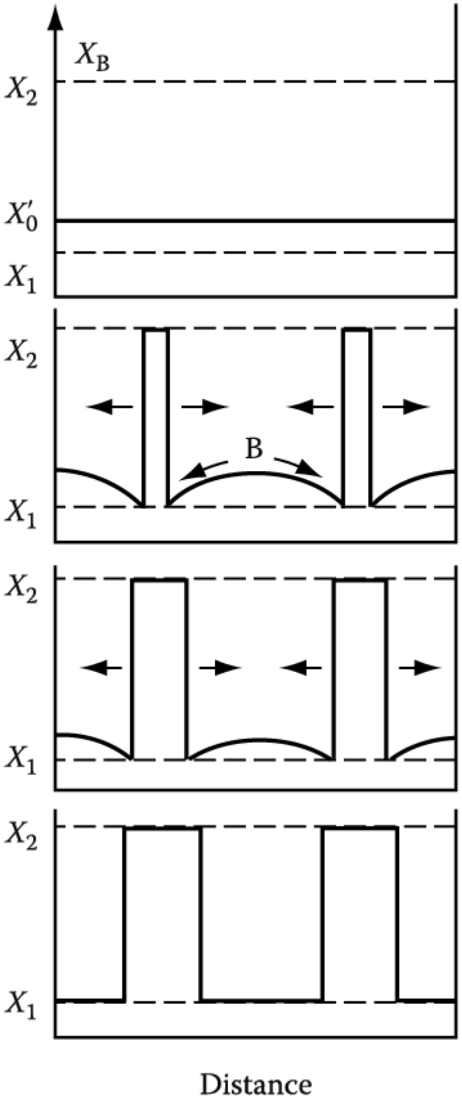
a) Composition fluctuations within the spinodal

b) Normal down-hill diffusion outside the spinodal

up-hill diffusion



interdiffusion coefficient D<0



down-hill diffusion

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)

Q. Interstitial diffusion vs Substitutional diffusion

Fick’s First Law of Diffusion

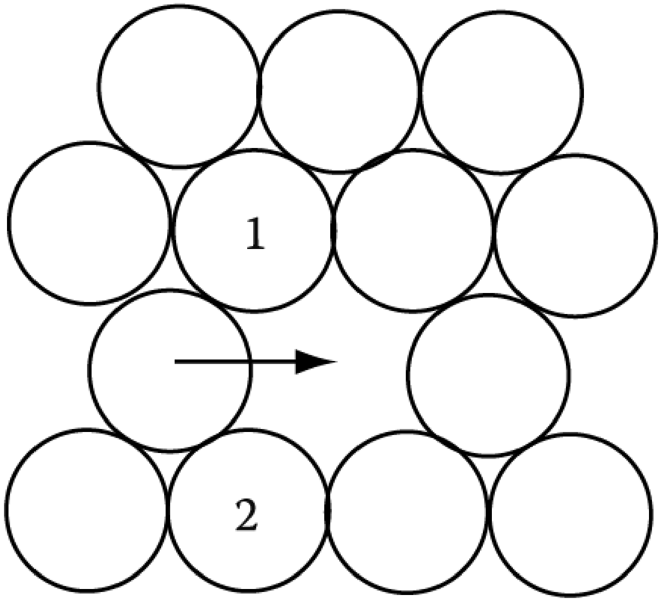
$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

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.

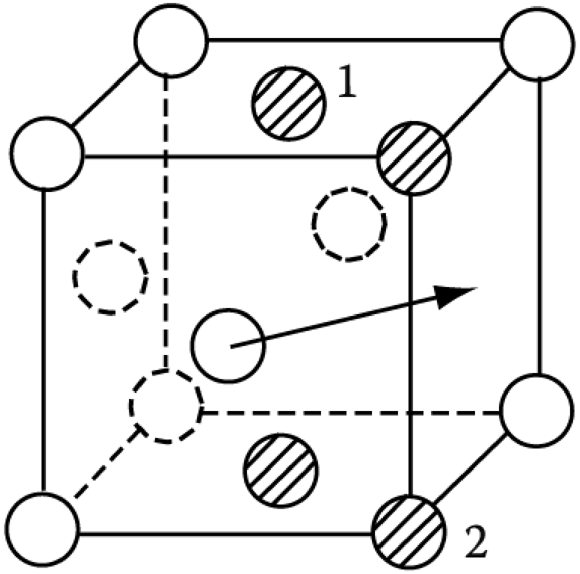
Substitutional vs. Interstitial diffusion

Substitutional diffusion



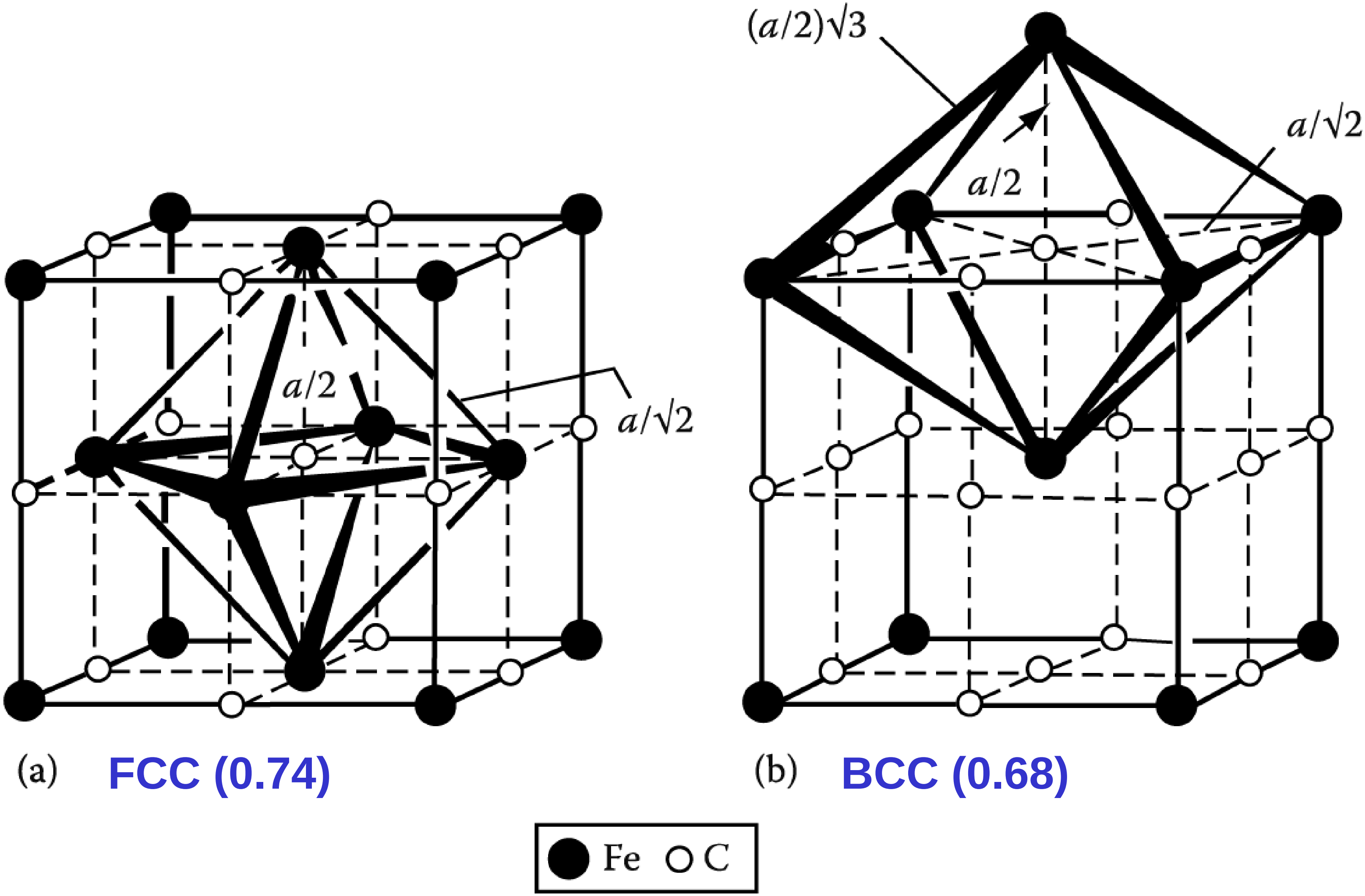
(a) **# of vacant site**

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.

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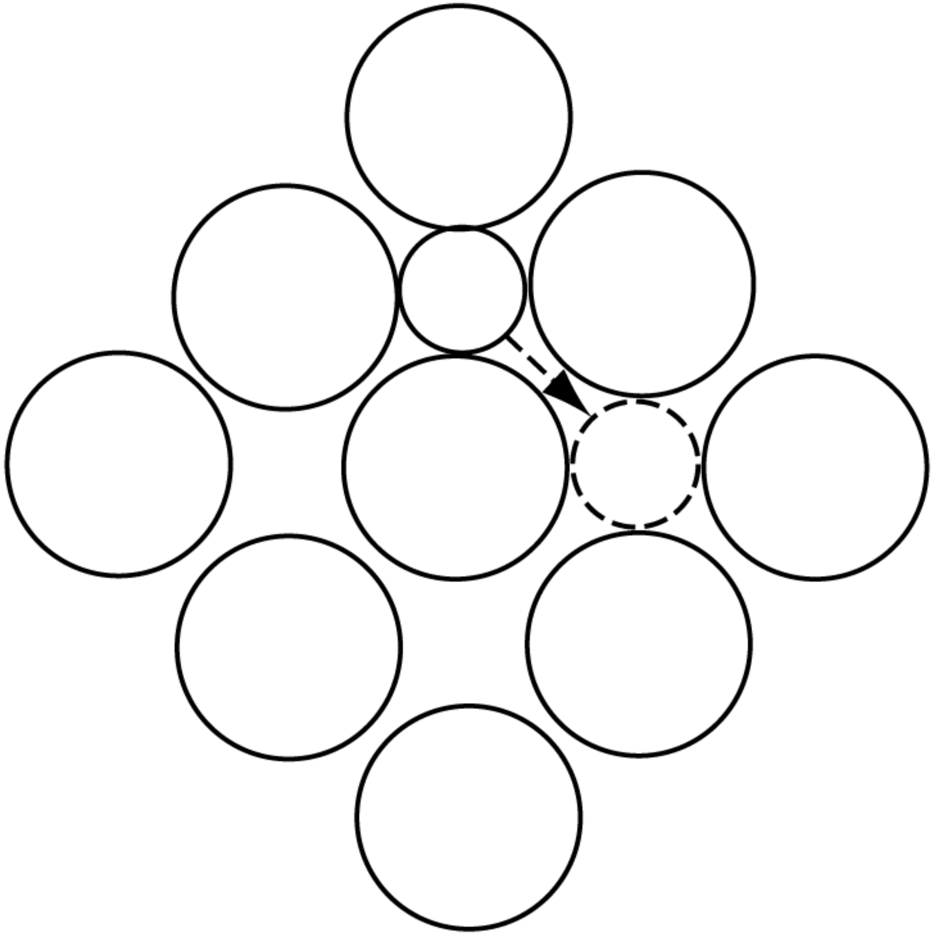
Interstitial diffusion



How interstitial diffusion differs from substitutional diffusion?

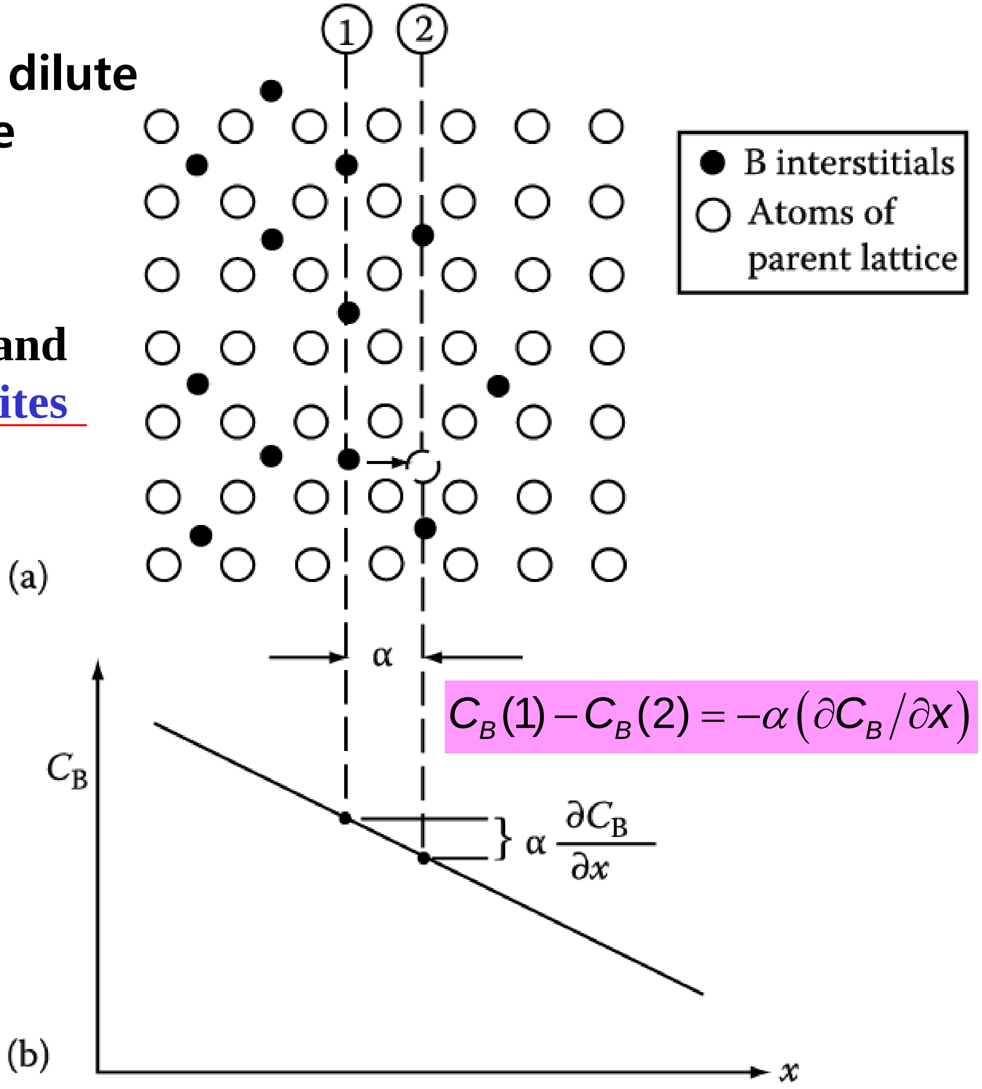
Interstitial diffusion

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



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

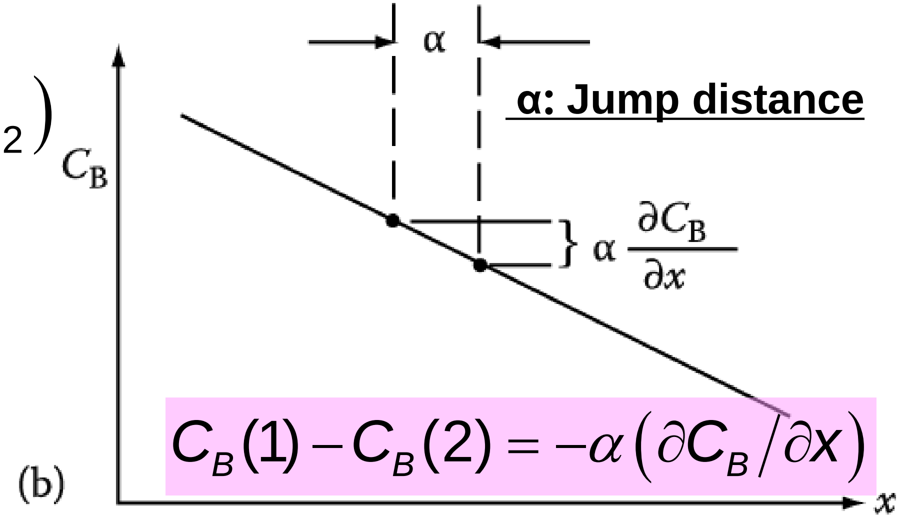
Fig. 2.5 Interstitial diffusion by random jumps in a concentration gradient.

Fick's First Law of Diffusion

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

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

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



α: Jump distance

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

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

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

➡ **Concentration varies with position.**

D_B: Intrinsic diffusivity or
Diffusion coefficient of B

⇒ **depends on microstructure of materials**

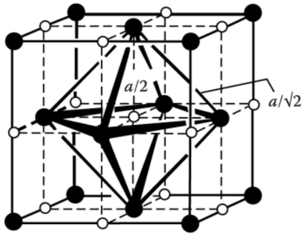
Magnitude of D in various media

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



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

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

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%

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

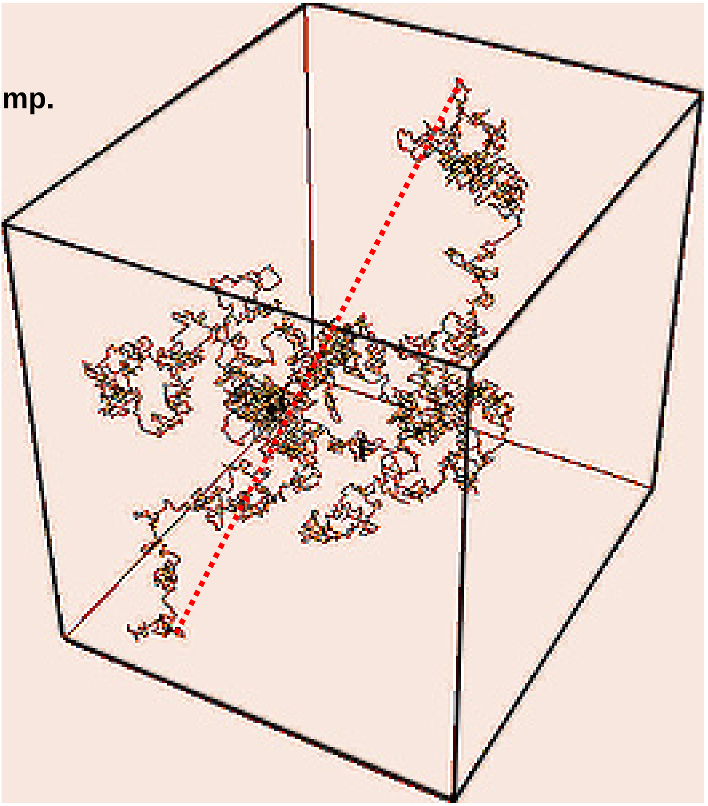
∵ C atoms stain the Fe lattice thereby making diffusion easier as amount of strain increases.

Q. 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.**

Q. 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?

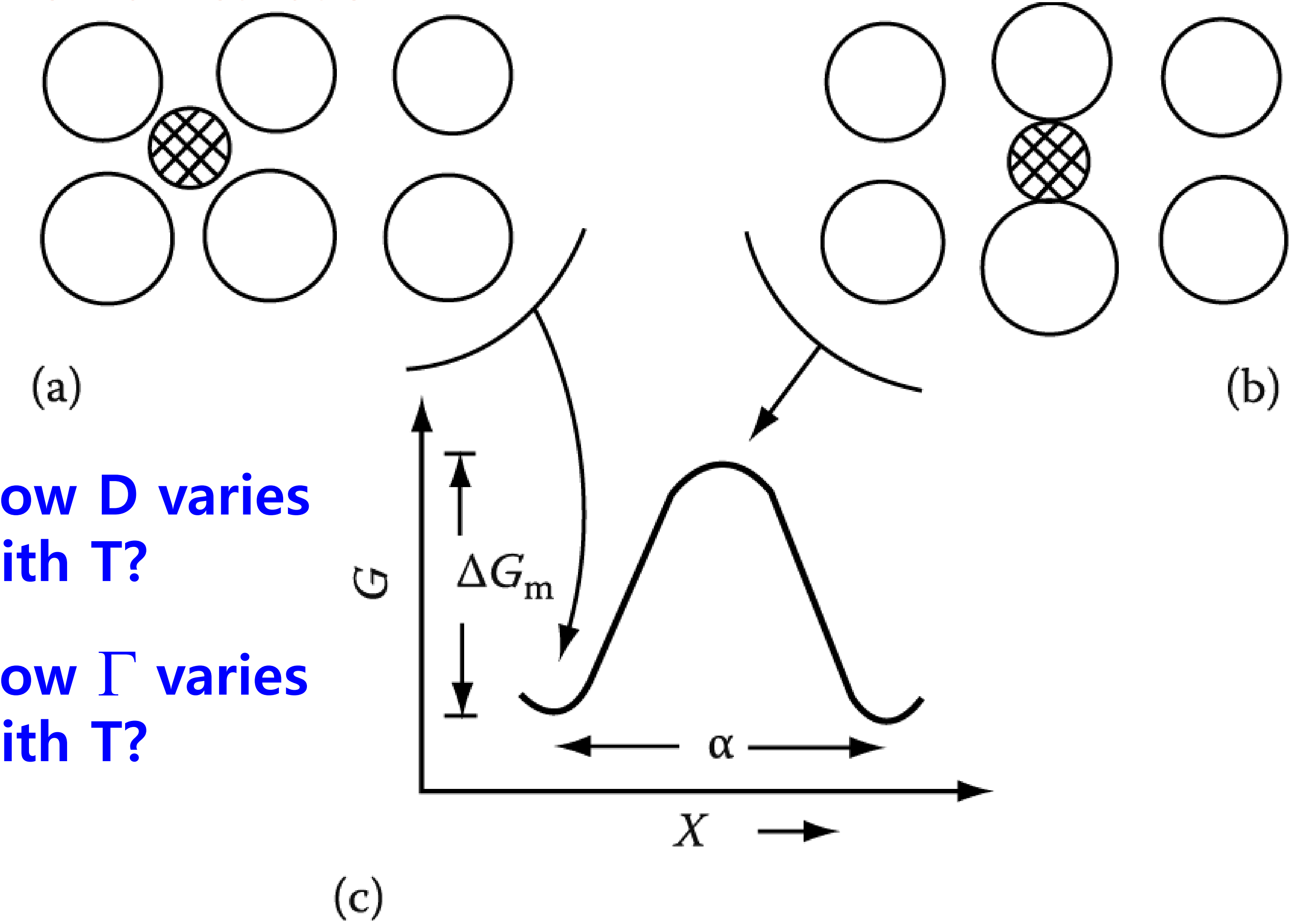


Fig. 2.6 Interstitial atom, (a) in equilibrium position, (b) at the position of maximum lattice distortion. (c) Variation of the free energy of the lattice as a function of the position of interstitial.

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**

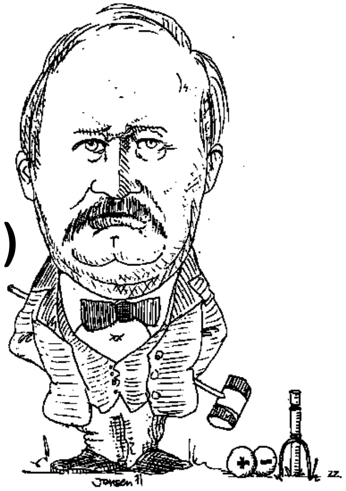
$$\left\{ \Delta G_m = \Delta H_m - T\Delta S_m \ , \ D_B = \frac{1}{6}\Gamma_B \alpha^2 \right\}$$

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

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

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

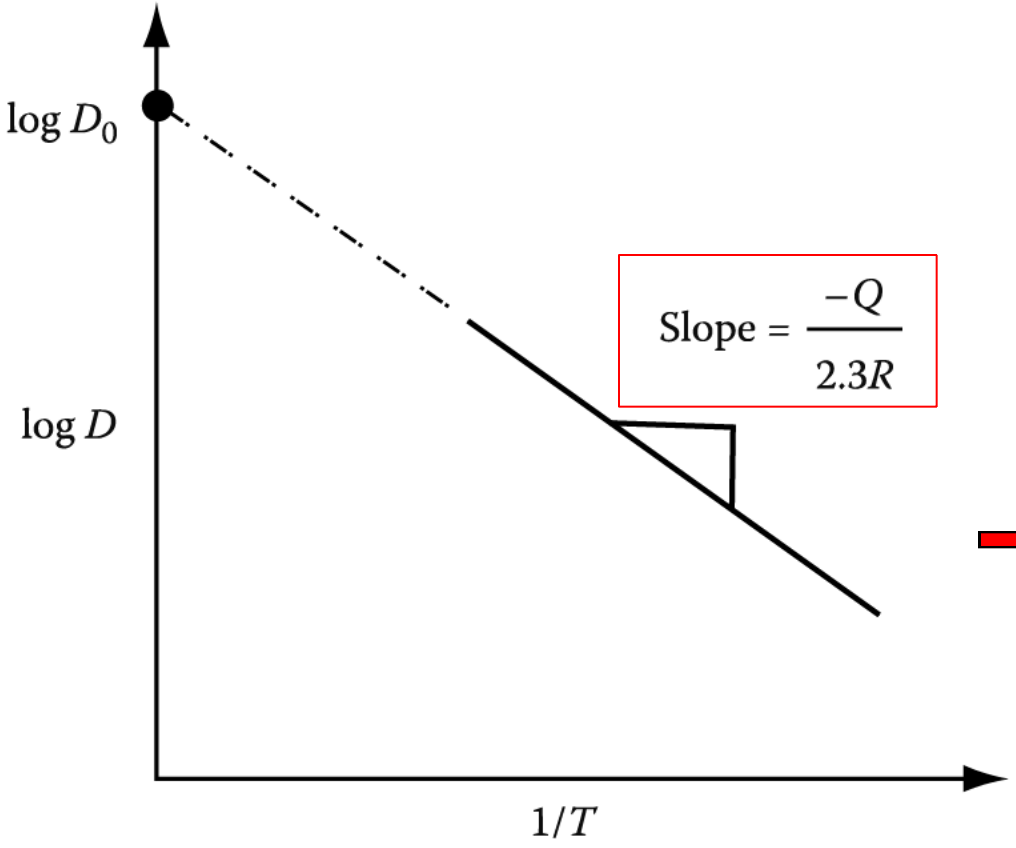
(Arrhenius-type equation)



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.

Q. 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

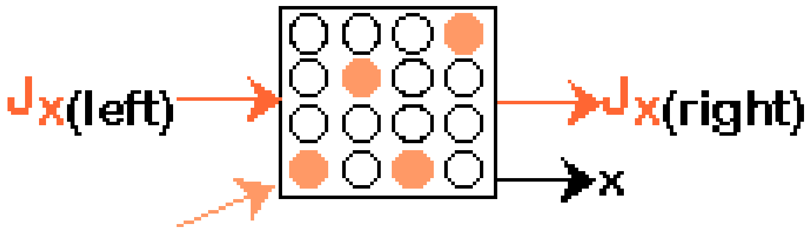
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

➡ **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.



Steady State

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

Concentration, C, in the box

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

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

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

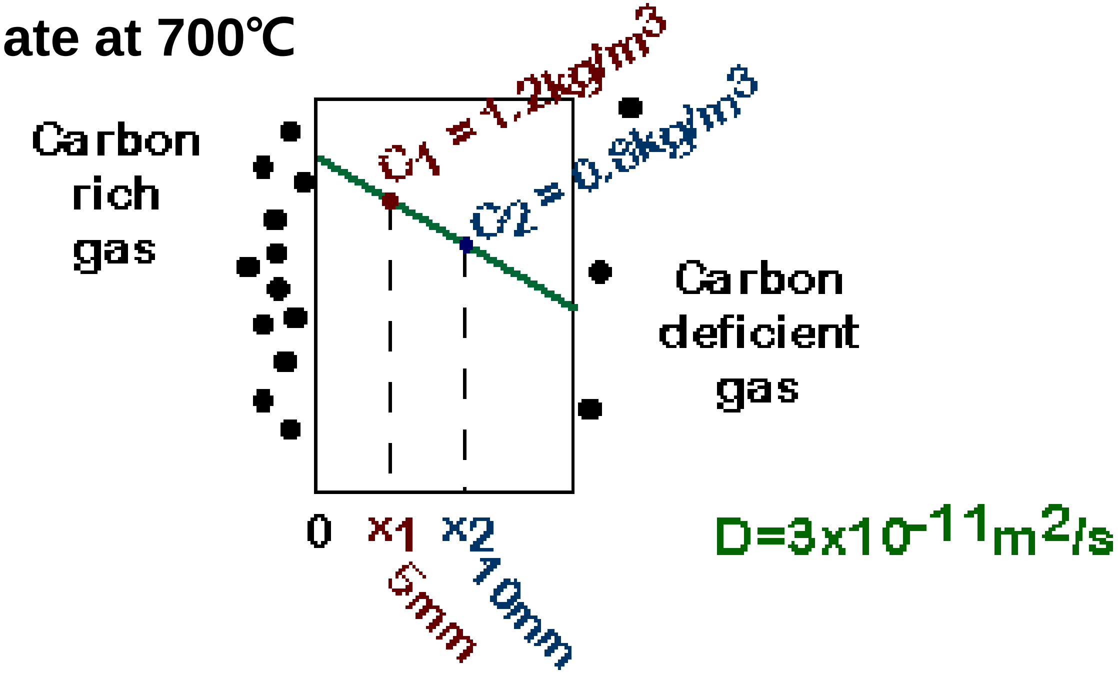
$$\frac{dC}{dx}_{(\text{left})} = \frac{dC}{dx}_{(\text{right})}$$

⇨ **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℃**



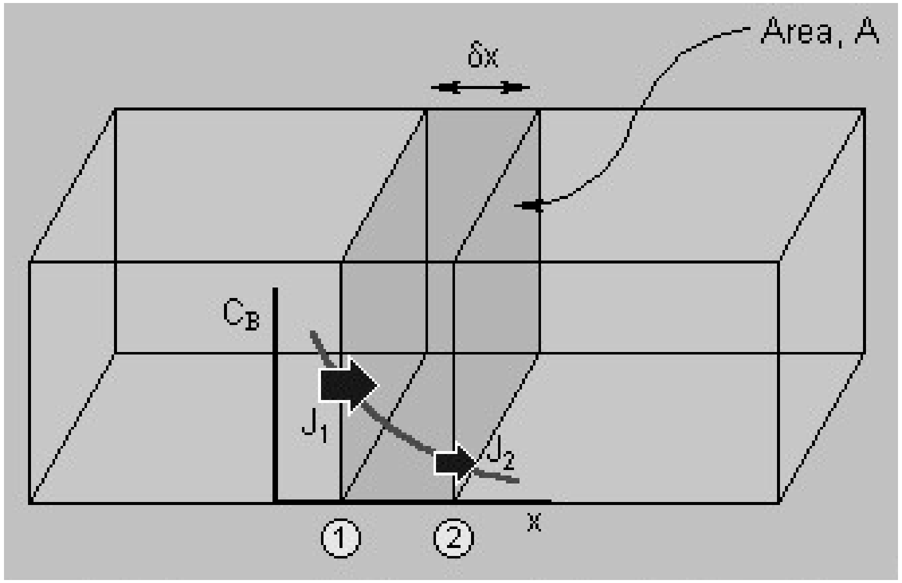
Q: How much carbon is transferring from the rich to deficient side?

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

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* :

→ $J_1 A\,dt$ Likewise : $J_2 A\,dt$

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

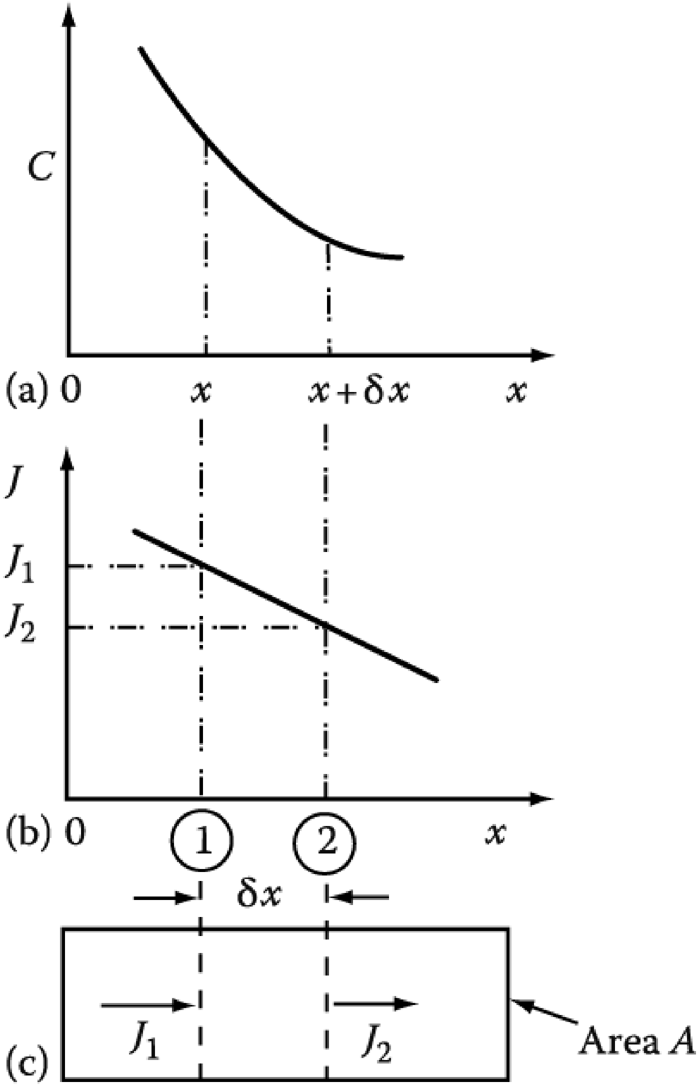
$$J_B = -D\frac{\partial C_B}{\partial x}$$

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

If variation of D with concentration can be ignored,

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

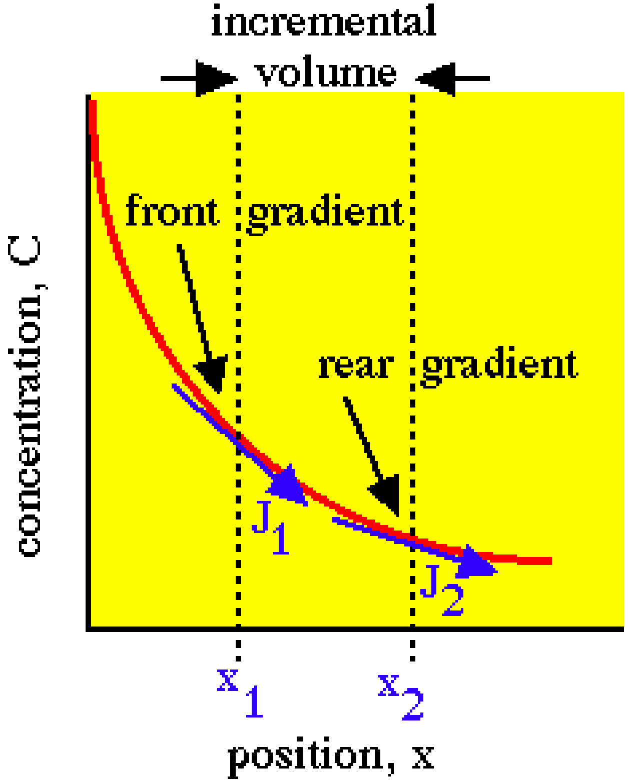
Fick's Second Law



Fick’s Second Law

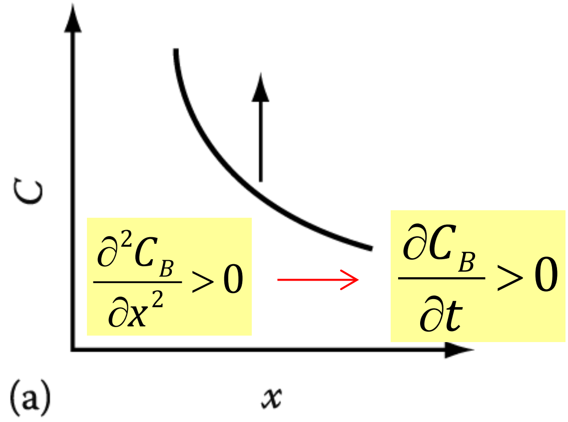
$$\boxed{\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}}$$

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



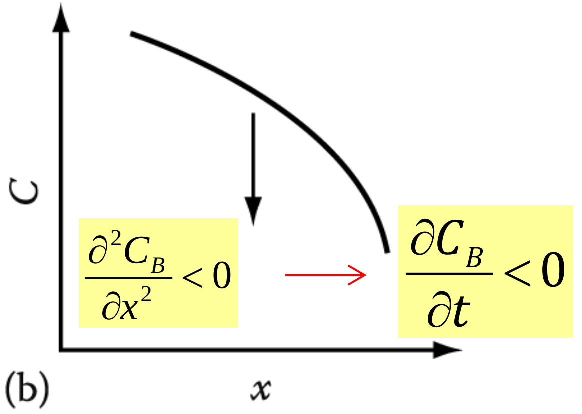
$$\frac{\partial^2 C_B}{\partial x^2} = ?$$

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



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

All concentration increase with time



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

All concentration decrease with time

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

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

➡ 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**

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