

Lecture 2 **"Diffusion"**

Diffusion in solids

The movement or jumping of atoms, within the solid is called diffusion. As the temperature is increased, the increased energy permits the atoms to vibrate into greater or shorter interatomic distances.

The activation energy for diffusion (Q) (cal /mole, J/atom or eV/ atom) depends upon the following factor:

- 1- Atomic size → Greater the atomic size → higher Q
- 2- Bond strength → Greater the bond strength of solid → higher Q
- 3- Diffusion mechanism → Vacancy diffusion mechanism needs higher Q than that for interstitial diffusion mechanism

Classification of diffusion

- 1- Self-diffusion: The movement of atoms through their structure is called self-diffusion. This type was studied experimentally by adding a trace of radioactive isotopes of Ni, into a normal Ni.
- 2- Inter-diffusion: The movement of atoms in two different metals from both sides into each other is called inter-diffusion. The inter-diffusion is observed in binary metal alloys such as Cu- Ni system.
- 3- Grain boundary diffusion: The movement of atoms along the grain boundaries of a material is called grain boundary diffusion.
- 4- Surface diffusion: The movement of atoms along the surface of material is called surface diffusion. The diffusion process is governed by two laws derived by Fick in 1880.

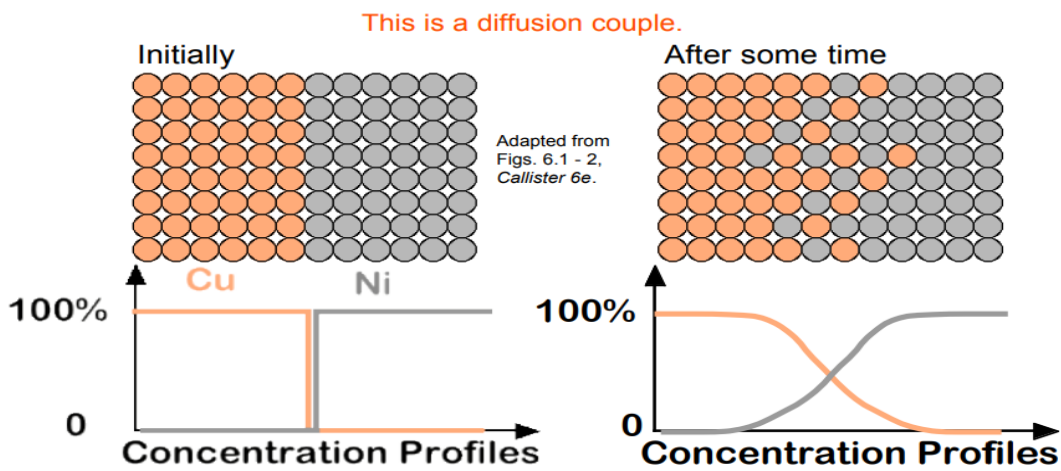
Diffusion - Mass transport by atomic motion

Mechanisms

- Gases & Liquids – random (Brownian) motion
- Solids – vacancy diffusion or interstitial diffusion

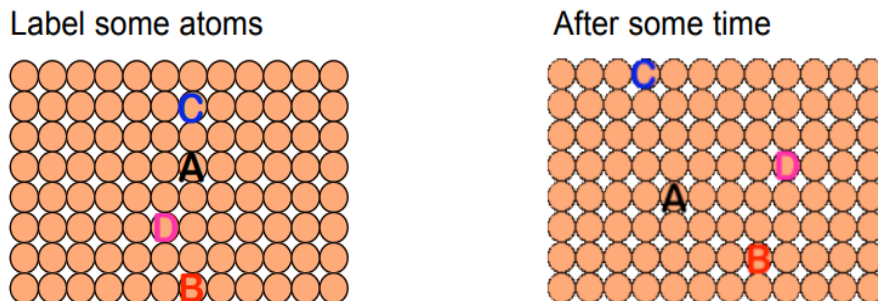
Inter-diffusion

- **Interdiffusion:** In alloys, atoms tend to migrate from regions of large concentration.



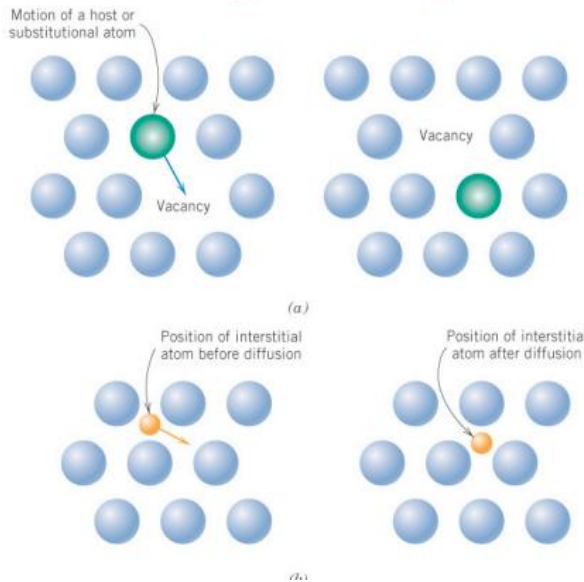
Self-diffusion

- **Self-diffusion:** In an elemental solid, atoms also migrate.



Substitution-diffusion: vacancies and interstitials

- applies to substitutional impurities
- atoms exchange with vacancies
- *rate* depends on (1) **number of vacancies**;
(2) **activation energy to exchange**.



Number (or concentration*)
of Vacancies at T

$$c_i = \frac{n_i}{N} = e^{-\frac{\Delta E}{k_B T}}$$

• $k_B T$ gives eV

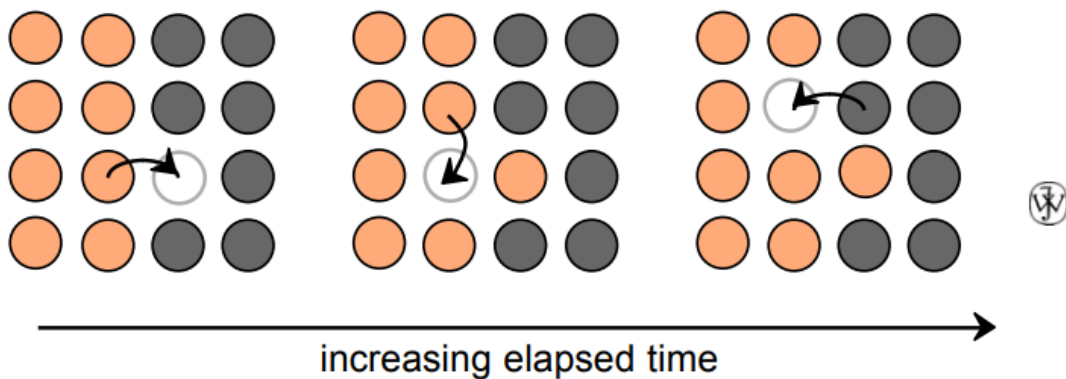
* see web handout for derivation.

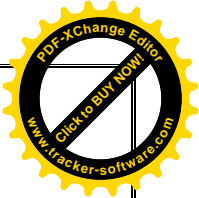
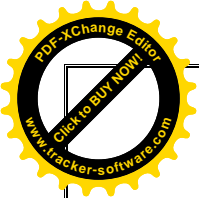
ΔE is an **activation energy**
for a particular process
(in J/mol, cal/mol, eV/atom).

Substitution-diffusion

Vacancy Diffusion:

- applies to substitutional impurities
- atoms exchange with vacancies
- *rate* depends on (1) **number of vacancies**;
(2) **activation energy to exchange**.





Fick's first law gives the relation between the flux (the amount of substance flowing in unite time through unite surface area perpendicular to the flux, and the concentration gradient of the diffusing substance.

$$J = - D (\partial C / \partial X)$$

where:- J= the flux
 C= concentration perpendicular to the direction of flow.

($\partial C / \partial X$)= concentration gradient.

D= diffusion coefficient and it is a measure of the rate at which the system tends to eliminate the concentration difference (cm²/sec).

Fick's second law gives the relation between the concentration gradient and the rate of change of concentration caused by:- diffusion at a point in the system:-

$$\partial C / \partial t = D \partial^2 C / \partial X^2$$

The relationship between (D) and temperature:-

$$D = D_0 \exp -Q / RT$$

Where :- D₀ = frequency factor (cm²/sec).
 Q= activation energy of diffusion.
 R = gas constant (1.987 cal. mol/ °K) or (8. 314 J/ mol. °K)
 T = absolute temperature. (°K)

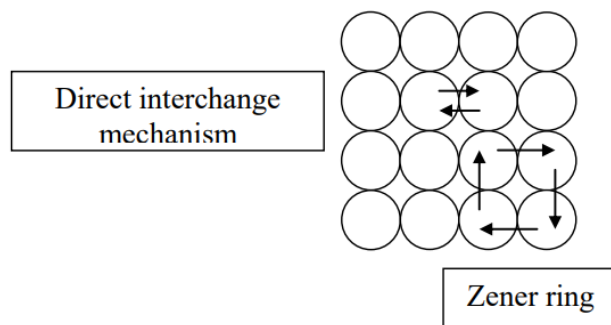
Factors affecting coefficients of diffusion:

- 1- Temperature: (D) increases exponentially with the increase in temperature.
- 2- Crystal structure: (D) is higher for those crystal structures that have low packing density.

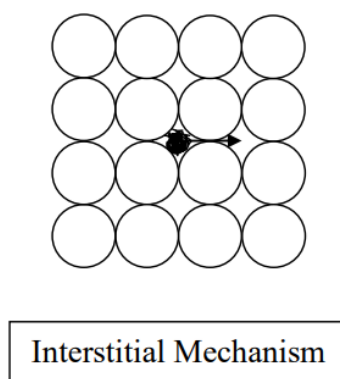
- 3- Atomic radius: (D) in a binary solution is higher if the atomic radii of the solute and solvent are different.
- 4- Melting temperature: (D) is higher for the solids having lower melting temperatures.
- 5- Grain size: (D) is higher for fine grain size materials than coarse grain size materials.

Diffusion Mechanisms:

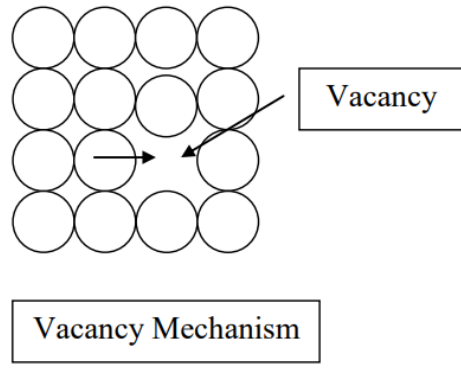
1- Direct Interchange Mechanism. Two atoms interchange their positions; this process requires a large amount of energy to distort the crystal as the atoms pass. The Zener Ring mechanism of diffusion avoids the problem of having the atoms squeeze past one another, it proposes that a ring of atoms (maybe 3 or 4) engages in a cooperative shift.



2- Interstitial Mechanism. This type of mechanism occurs in those binary metallic alloys whose atomic radii differ in size significantly, for example, the diffusion of carbon atoms in FCC or BCC iron takes place by interstitial mechanism. (The atomic radius of C atom is 0.077 nm while that of FCC iron is 0.127 nm).



4- Vacancy Mechanism. The diffusion occurs because of the atoms jumping into the vacant sites, it may be noted that as the atoms move in one direction through the vacancy mechanism the vacancies move in the opposite direction.



Example:- Diffusion coefficient of Cu in Al needs to activation energy equal to $136 \times 10^3 \text{ J/mol}$, while the frequency factor is $0.84 \times 10^{-5} \text{ m}^2 / \text{sec}$.
 Determine :- 1- Diffusion coefficient at 130°C .
 2- Distance which Cu atoms can be diffused through one day according to the relation:- $X^2 = 4Dt$, Take $R = 8.314 \text{ J/mol}^\circ\text{K}$.

Solution:-

$$T = 130 + 273 = 403 \text{ }^\circ\text{K}$$

1- $D = D_0 \exp -Q/RT$

$$D = 0.854 \times 10^{-5} \exp (- 136 \times 10^3 / 8.314 \times 403)$$

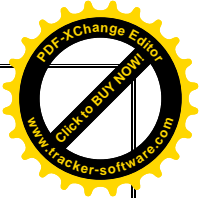
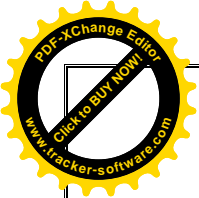
$$= 1.97 \times 10^{-23} \text{ m}^2/ \text{sec}.$$

2- $X^2 = 4Dt$

$$X^2 = 4 (1.97 \times 10^{-23} \text{ m}^2/ \text{sec}) (24 \times 60 \times 60) \text{ sec}$$

$$X^2 = 6.83 \times 10^{-18} \text{ m}^2$$

$$X = 2.61 \times 10^{-9} \text{ m} = 26.1 \text{ \AA}.$$



Diffusion Flux Computation

A plate of iron is exposed to a carburizing (carbon-rich) atmosphere on one side and a decarburizing (carbon-deficient) atmosphere on the other side at 700°C (1300°F). If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 and 10 mm (5×10^{-3} and 10^{-2} m) beneath the carburizing surface are 1.2 and 0.8 kg/m³, respectively. Assume a diffusion coefficient of 3×10^{-11} m²/s at this temperature.

Solution

Fick's first law, Equation 5.2, is used to determine the diffusion flux. Substitution of the values just given into this expression yields

$$\begin{aligned}
 J &= -D \frac{C_A - C_B}{x_A - x_B} = -(3 \times 10^{-11} \text{ m}^2/\text{s}) \frac{(1.2 - 0.8) \text{ kg/m}^3}{(5 \times 10^{-3} - 10^{-2}) \text{ m}} \\
 &= 2.4 \times 10^{-9} \text{ kg/m}^2 \cdot \text{s}
 \end{aligned}$$

Example 3: A sheet of steel 1.5 mm thick has nitrogen atmospheres on both sides at 1200°C and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is 6×10^{-11} m²/s, and the diffusion flux is found to be 1.2×10^{-7} kg/m²-s. Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is 4 kg/m³. How far into the sheet from this high-pressure side will the concentration be 2.0 kg/m³? Assume a linear concentration profile.

Solution

This problem is solved by using Equation 5.3 in the form

$$J = -D \frac{C_A - C_B}{x_A - x_B}$$

If we take C_A to be the point at which the concentration of nitrogen is 4 kg/m³, then it becomes necessary to solve for x_B , as

$$x_B = x_A + D \left[\frac{C_A - C_B}{J} \right]$$

Assume x_A is zero at the surface, in which case

$$\begin{aligned}
 x_B &= 0 + (6 \times 10^{-11} \text{ m}^2/\text{s}) \left[\frac{4 \text{ kg/m}^3 - 2 \text{ kg/m}^3}{1.2 \times 10^{-7} \text{ kg/m}^2 \cdot \text{s}} \right] \\
 &= 1 \times 10^{-3} \text{ m} = 1 \text{ mm}
 \end{aligned}$$