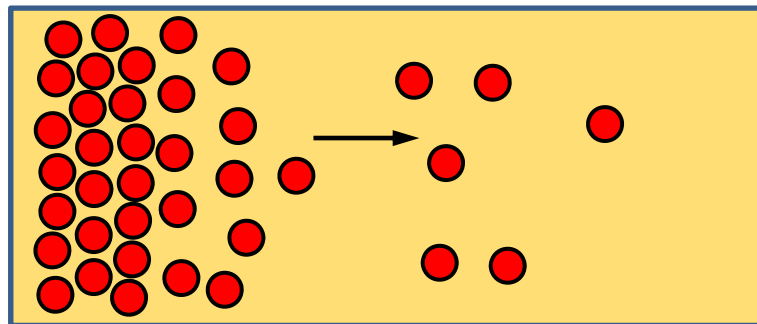


Diffusion

Diffusion Phenomena

- Diffusion is a process of mass transport by atomic movement under the influence of thermal energy and a concentration gradient.
- Atoms move from higher to lower concentration region.
- If this movement is from one element to another e.g. Cu to Ni, then it is termed *inter-diffusion*. If the movement is within similar atoms as in pure metals, it is termed *self-diffusion*.

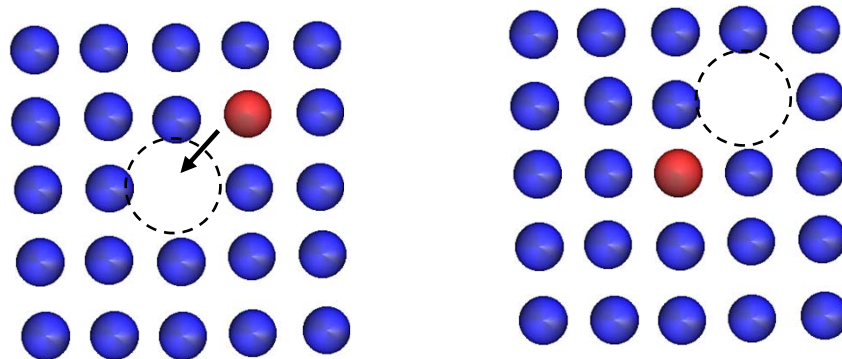


Diffusion Mechanism

- Diffusion of atoms involves movement in steps from one lattice site to the another. An empty adjacent site and breaking of bonds with the neighbor atoms are the two necessary conditions for this.

Vacancy Diffusion

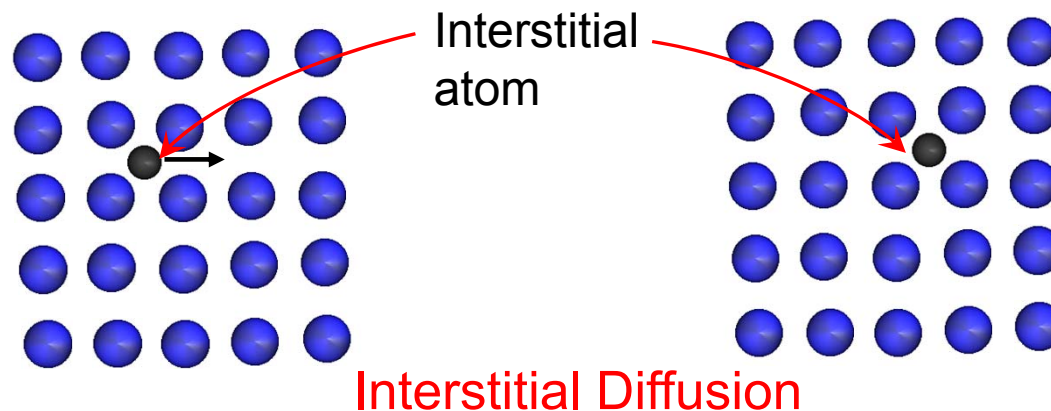
- This mechanism involves movement of atoms from a regular lattice site to an adjacent vacancy. Since vacancy and atoms exchange position, the vacancy flux is in the opposite direction.



Diffusion Mechanism

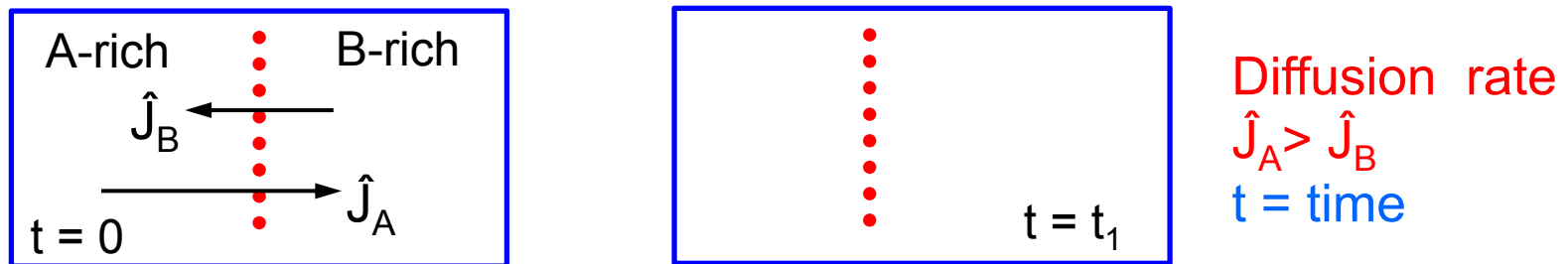
Interstitial Diffusion

- This mechanism involves migration of atoms from one interstitial site to a neighbouring empty interstitial site.
- This mechanism is more prevalent for impurity atoms such as hydrogen, carbon, nitrogen, oxygen which are small enough to fit in to an interstitial position.
- For substitutional diffusion atoms exchange their places directly or along a ring (ring diffusion mechanism).



Kirkendall Effect

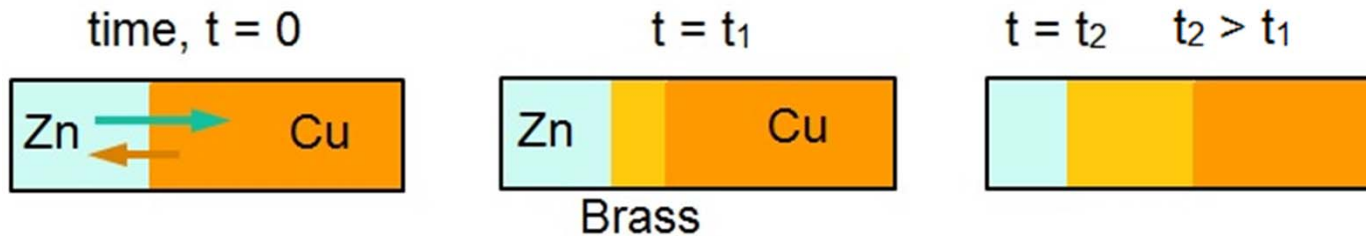
➤ If the diffusion rates of two metals A and B in to each other are different, the boundary between them shifts and moves towards the faster diffusing metal as shown in the figure.



- This is known as Kirkendall effect. Named after the inventor Ernest Kirkendall (1914 – 2005).
- It can be demonstrated experimentally by placing an inert marker at the interface.
- This is a direct evidence of the vacancy mechanism of diffusion as the other mechanisms do not permit the flux of diffusing species to be different.

Kirkendall effect

- Zn diffuses faster into Cu than Cu in Zn. A diffusion couple of Cu and Zn will lead to formation of a growing layer of Cu-Zn alloy (Brass).



- Same will happen in a Cu-Ni couple as Cu diffuses faster in Ni than vice versa.
- Since this takes place by vacancy mechanism, pores will form in Cu (of the Cu-Ni couple) as the vacancy flux in the opposite direction (towards Cu) will condense to form pores.

Fick's Law

Steady-state diffusion

- Steady-state diffusion is the situation when the diffusion flux is independent of time (e.g. diffusion of a gas through solid medium where concentration/pressure of the gas is kept constant at both the end).
- Fick's first law describes steady-state diffusion and is given by

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

Where, J is the diffusion flux or the mass transported per unit time per unit area and dC/dx is the concentration gradient. D is known as the diffusion coefficient.

Fick's Second Law

Non- Steady state diffusion

- In most practical situations, diffusion is non-steady state i.e. diffusion flux and concentration gradient varies with time.
- This is described by Fick's second law

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

- A solution to this equation can be obtained for a semi-infinite solid with the following boundary conditions.

For $t = 0$, $C = C_0$ at $0 \leq x \leq \infty$. For $t > 0$, $C = C_s$ (surface concentration) at $x = 0$ and $C = C_0$ at $x = \infty$

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

The more generalized form is $C_x = C(x, t) = A - B \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

Factors affecting Diffusion

Diffusing species

The magnitude of the diffusion coefficient, D , is an indication of the rate at which atoms diffuse. As the value of D is fixed for a given element in a given material, the extent of diffusion is first decided by the diffusing species itself.

Temperature

Temperature is a major factor which affects diffusion. Temperature dependence of the diffusion coefficient is expressed as

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

Where, D_0 is the pre-exponential factor and the Q is the activation energy for diffusion

Example

Ex.1. The carbon content of a steel at the **surface is 0.9%**. The steel is being carburized **at 927 °C**. The **nominal C content in the steel is 0.2%**. Calculate the time needed to increase the carbon content to 0.4% at 0.5 mm depth.
 $D = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$ at 927 °C.

Solution.
$$\frac{C_x - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \text{ ----- (1)}$$

$C_s = 0.9\%$, $C_o = 0.2\%$, $C_x = 0.4\%$, $x = 0.5 \text{ mm} = 5 \times 10^{-4} \text{ m}$
Substituting these values in equation (1)

$$\text{erf}\left(\frac{69.88}{\sqrt{t}}\right) = 0.7143 \quad \text{or} \quad \left(\frac{69.88}{\sqrt{t}}\right) = 0.755$$

$$t = 8567 \text{ s} = 143 \text{ min}$$

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Key words: Diffusion; Atomic diffusion; Fick's law of diffusion; Self-diffusion; Kirkendall effect; Diffusivity

Quiz

1. What is diffusion?
2. What are the two necessary conditions for diffusion to occur?
3. What are the mechanisms of diffusion?
4. What is self-diffusion?
5. What is steady state diffusion? Describe Fick's first law of diffusion.
6. What is Fick's second law of diffusion?
7. What is the effect of temperature on diffusion? How is the activation energy obtained?
8. What other factors affect diffusion rate in metals?
9. Give an example of an industrial process which uses diffusion.
10. Calculate the diffusivity of carbon in γ -Fe at 927 °C.
 $D_0 = 2 \times 10^{-5} \text{ m}^2/\text{s}$ and $Q = 142 \text{ kJ/mol}$

Quiz

11. The diffusivity of Ag atoms in Ag metal is $1.0 \times 10^{-17} \text{ m}^2/\text{s}$ at $500 \text{ }^\circ\text{C}$ and $7.0 \times 10^{-13} \text{ m}^2/\text{s}$ at $1000 \text{ }^\circ\text{C}$. Calculate the activation energy for diffusion of Ag atoms in the temperature range $500 - 1000 \text{ }^\circ\text{C}$.
12. A plain carbon steel (0.18% C) is to be carburized at $927 \text{ }^\circ\text{C}$. What is the time needed to make the carbon content 0.35% at a depth of 0.4 mm? Take C content at surface to be 1.15 wt%.
 $D = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$.
13. If the same steel is carburized for 7 hrs at $927 \text{ }^\circ\text{C}$ what will be the carbon content at a depth of 1mm from the surface?