

Module-5

Diffusion

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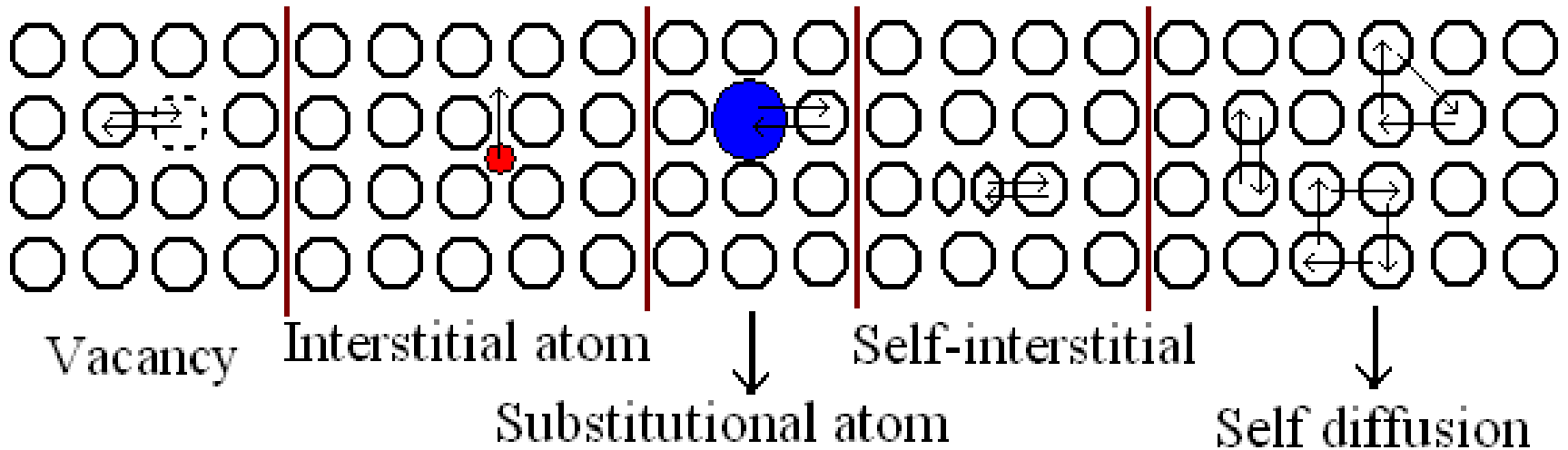
Diffusion phenomenon

- *Definition* – Diffusion is the process of mass flow in which atoms change their positions relative to neighbors in a given phase under the influence of thermal and a gradient.
- The gradient can be a compositional gradient, an electric or magnetic gradient, or stress gradient.
- Many reactions in solids and liquids are diffusion dependent.
- Diffusion is very important in many industrial and domestic applications.

E.g.: Carburizing the steel, annealing homogenization after solidification, coffee mixing, etc.

Diffusion mechanisms

- From an atomic perspective, diffusion is a step wise migration of atoms from one lattice position to another.
- Migration of atoms in metals/alloys can occur in many ways, and thus corresponding diffusion mechanism is defined.



Diffusion mechanisms (contd...)

- Most energetically favorable diffusion mechanism is vacancy mechanism. Other important mechanism is interstitial mechanism by which hydrogen/nitrogen/oxygen diffuse into many metals.
- In ionic crystal, Schottky and Frankel defects assist the diffusion process.
- When Frenkel defects dominate in an ionic crystal, the cation interstitial of the Frenkel defect carries the diffusion flux. If Schottky defects dominate, the cation vacancy carries the diffusion flux.
- In thermal equilibrium, in addition to above defects, ionic crystal may have defects generated by impurities and by deviation from stoichiometry.

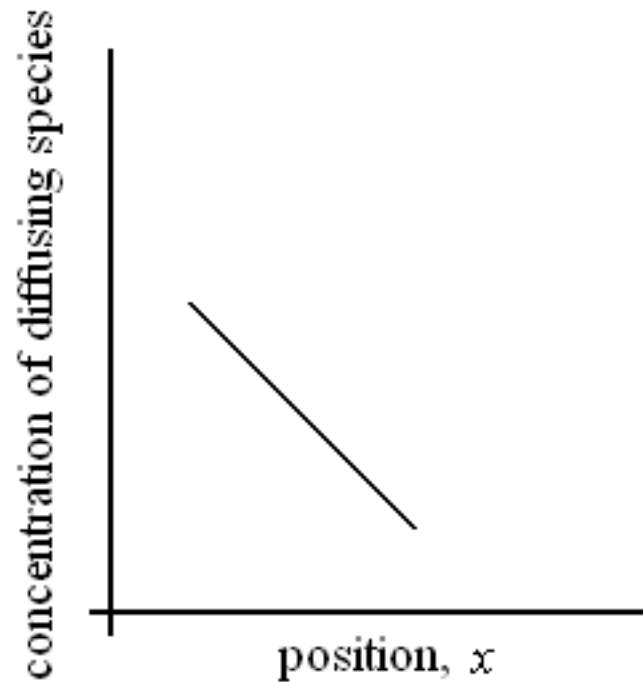
Diffusion mechanisms (contd...)

- Diffusion that occurs over a region is volume diffusion.
- Diffusion can occur with aid of linear/surface defects, which are termed as short-circuit paths. These enhances the diffusivity.
- However, diffusion by short-circuit paths (e.g.:dislocaions, grain boundaries) is small because the effective cross-sectional area over which these are operative is small.
- Diffusion can occur even in pure metals that is not noticeable. Diffusion that occurs in alloys which is noticeable called *net diffusion* as there occurs a noticeable concentration gradient.

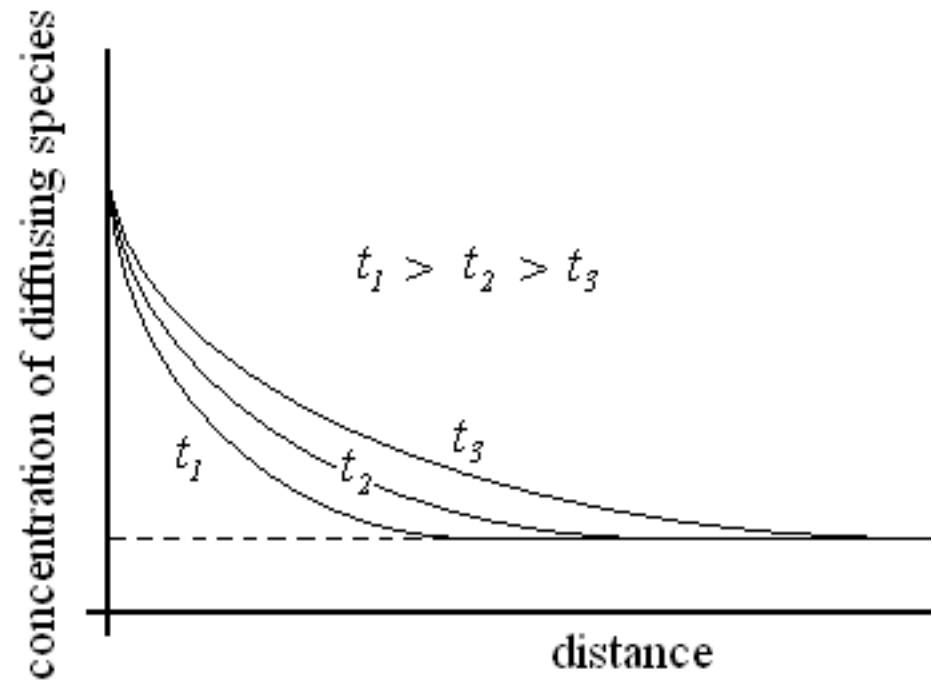
Diffusion – time function?

- Steady-state and Non-steady-state diffusion processes are distinguished by the parameter – diffusion flux, J .
- Flux is defined as number of atoms crossing a unit area perpendicular to a given direction per unit time.
- Thus flux has units of atoms/m².sec *or* moles/m².sec.
- If the flux is independent of time, then the diffusion process is called steady-state diffusion. On the other hand, for non-steady-state diffusion process, flux is dependent on time.

Diffusion – time function? (contd...)



Steady-state diffusion



Non-steady-state diffusion

Steady-state diffusion

- Steady-state diffusion processes is characterized by Fick's first law, which states that diffusion flux is proportional to concentration gradient.
- The proportionality constant, D , is called diffusion coefficient or diffusivity. It has units as m^2/sec .
- For one-dimensional case, it can be written as

$$J_x = -D \frac{dc}{dx} = \frac{1}{A} \frac{dn}{dt} \quad J_x \neq f(x, t)$$

where D is the diffusion constant, dc/dx is the gradient of the concentration c , dn/dt is the number atoms crossing per unit time a cross-sectional plane of area A .

E.g.: Hydrogen gas purification using palladium metal sheet.

Non-steady-state diffusion

- Most interesting industrial applications are non-steady-state diffusion in nature.
- Non-steady-state diffusion is characterized by Fick's second law, which can be expressed as

$$\frac{dc}{dt} = -\frac{dJ}{dx} = \frac{d}{dx} \left(D \frac{dc}{dx} \right) \qquad \frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

where dc/dt is the time rate of change of concentration at a particular position, x .

- A meaningful solution can be obtained for the above second-order partial equation if proper boundary conditions can be defined.

Non-steady-state diffusion (contd...)

- One common set of boundary conditions and the solution is:

$$\text{For } t = 0, \quad C = C_0 \text{ at } 0 \leq x \leq \infty$$

$$\text{For } t > 0, \quad C = C_s \text{ at } x=0$$

$$C = C_0 \text{ at } x = \infty$$

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

where C_x represents the concentration at depth x after time t .

- The term *erf* stands for Gaussian error function, whose values can be obtained from standard mathematical tables.

E.g.: Carburization and decarburization of steel, corrosion resistance of duralumin, doping of semi-conductors, etc.

Influencing factors for diffusion

- Diffusing species: Interstitial atoms diffuse easily than substitutional atoms. Again substitutional atoms with small difference in atomic radius with parent atoms diffuse with ease than atoms with larger diameter.
- Temperature: It is the most influencing factor. Their relations can be given by the following Arrhenius equation

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

where D_0 is a pre-exponential constant, Q is the activation energy for diffusion, R is gas constant (Boltzmann's constant) and T is absolute temperature.

Influencing factors for diffusion (contd...)

- From the temperature dependence of diffusivity, it is experimentally possible to find the values of Q and D_0 .
- Lattice structure: Diffusivity is high for open lattice structure and in open lattice directions.
- Presence of defects: The other important influencing factor of diffusivity is presence of defects. Many atomic/volume diffusion processes are influenced by point defects like vacancies, interstitials.
- Apart from these, dislocations and grain boundaries, i.e. short-circuit paths as they famously known, greatly enhances the diffusivity.

Non-equilibrium transformation & microstructure

- Non-equilibrium transformation occurs, usually, during many of the cooling processes like casting process.
- Equilibrium transformation requires extremely large time which is in most of the cases impractical and not necessary.
- Alloy solidification process involves diffusion in liquid phase, solid phase, and also across the interface between liquid and solid.
- As diffusion is very sluggish in solid, and time available for it is less, compositional gradients develop in cast components.
- These are two kinds: coring and segregation.

Non-equilibrium transformation & microstructure

(contd...)

- Coring: It is defined as gradual compositional changes across individual grains.
- Coring is predominantly observed in alloys having a marked difference between liquidus and solidus temperatures.
- It is often being removed by subsequent annealing and/or hot-working.
- It is exploited in zone-refining technique to produce high-purity metals.
- Segregation: It is defined as concentration of particular, usually impurity elements, along places like grain boundaries, and entrapments.
- Segregation is also useful in zone refining, and also in the production of rimming steel.

Non-equilibrium transformation & microstructure

(contd...)

- *Micro-segregation* is used to describe the differences in composition across a crystal or between neighboring crystals.
- Micro-segregation can often be removed by prolonged annealing or by hot-working.
- *Macro-segregation* is used to describe more massive heterogeneities which may result from entrapment of liquid pockets between growing solidifying zones.
- Macro-segregation persists through normal heating and working operations.
- Two non equilibrium effects of practical importance:(1) the occurrence of phase changes *or* transformations at temperatures other than those predicted by phase boundary lines on the phase diagram, and (2) the existence of non-equilibrium phases at room temperature that do not appear on the phase diagram.