

# Material Science

## Prof. Satish V. Kailas

Associate Professor  
Dept. of Mechanical Engineering,  
Indian Institute of Science,  
Bangalore – 560012  
India

### Chapter 5. Diffusion

Diffusion is the process by which atoms move in a material. Many reactions in solids and liquids are diffusion dependent. Structural control in a solid to achieve the optimum properties is also dependent on the rate of diffusion.

Atoms are able to move throughout solids because they are not stationary but execute rapid, small-amplitude vibrations about their equilibrium positions. Such vibrations increase with temperature and at any temperature a very small fraction of atoms has sufficient amplitude to move from one atomic position to an adjacent one. The fraction of atoms possessing this amplitude increases markedly with rising temperature. In jumping from one equilibrium position to another, an atom passes through a higher energy state since atomic bonds are distorted and broken, and the increase in energy is supplied by thermal vibrations. As might be expected defects, especially vacancies, are quite instrumental in affecting the diffusion process on the type and number of defects that are present, as well as the thermal vibrations of atoms.

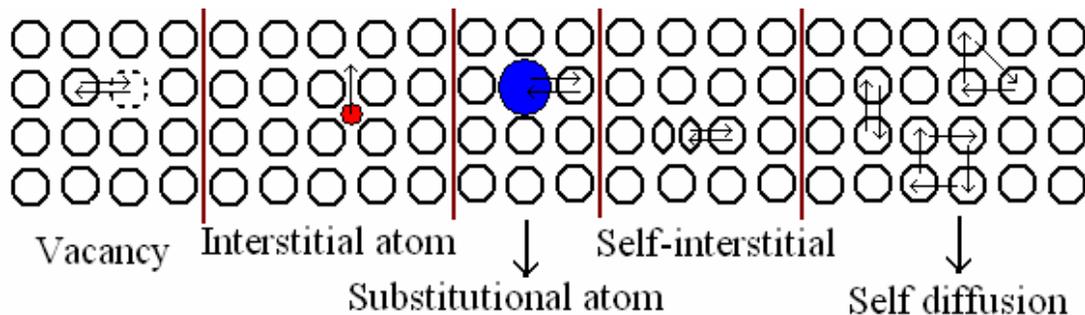
Diffusion can be *defined* as the mass flow process in which atoms change their positions relative to neighbors in a given phase under the influence of thermal and a gradient. The gradient can be a compositional gradient, an electric or magnetic gradient, or stress gradient. In this chapter we discuss diffusion because of concentration gradient only.

#### 5.1 Diffusion mechanisms, Steady-state and Non-steady-state diffusion

##### 5.1.1 Diffusion mechanisms

In pure metals self-diffusion occurs where there is no net mass transport, but atoms migrate in a random manner throughout the crystal. In alloys inter-diffusion takes place where the mass transport almost always occurs so as to minimize compositional differences. Various atomic mechanisms for self-diffusion and inter-diffusion have been proposed. *Figure-5.1* presents schematic view of different atomic diffusion mechanisms.

The most energetically favorable process involves an interchange of places by an atom and a neighboring vacancy – *vacancy diffusion*. This process demands not only the motion of vacancies, but also the presence of vacancies. The unit step in vacancy diffusion is an atom breaks its bonds and jumps into neighboring vacant site. In *interstitial diffusion*, solute atoms which are small enough to occupy interstitial sites diffuse by jumping from one interstitial site to another. The unit step here involves jump of the diffusing atom from one interstitial site to a neighboring site. Hydrogen, Carbon, Nitrogen and Oxygen diffuse interstitially in most metals, and the activation energy for diffusion is only that associated with motion since the number of occupied, adjacent interstitial sites usually is large. *Substitutional diffusion* generally proceeds by the vacancy mechanism. Thus interstitial diffusion is faster than substitutional diffusion by the vacancy mechanism. During *self-diffusion* or *ring mechanism* or *direct-exchange mechanism*, three or four atoms in the form of a ring move simultaneously round the ring, thereby interchanging their positions. This mechanism is untenable because exceptionally high activation energy would be required. A *self-interstitial* is more mobile than a vacancy as only small activation energy is required for self-interstitial atom to move to an equilibrium atomic position and simultaneously displace the neighboring atom into an interstitial site. However, the equilibrium number of self-interstitial atoms present at any temperature is negligible in comparison to the number of vacancies. This is because the energy to form a self-interstitial is extremely large.



**Figure-5.1:** Diffusion mechanisms.

Diffusion in most ionic solids occurs by a vacancy mechanism. In ionic crystals, Schottky and Frenkel defects assist the diffusion process. When Frenkel defects (pair of vacancy-interstitial) dominate in an ionic crystal, the cation interstitial of the Frenkel defect carries the diffusion flux. If Schottky defects (pair of vacant sites) 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. Thus imperfections in ionic materials that influence diffusion arise in two ways: (1) intrinsic point defects such as Frenkel and schottky defects whose number depends on temperature, and (2) extrinsic point defects whose presence is due to impurity ions of different valance than the host ions. The former is responsible for temperature dependence of diffusion similar to that for self-diffusion in metals, while the latter result in a temperature dependence of diffusion which is similar to that for interstitial solute diffusion in metals.

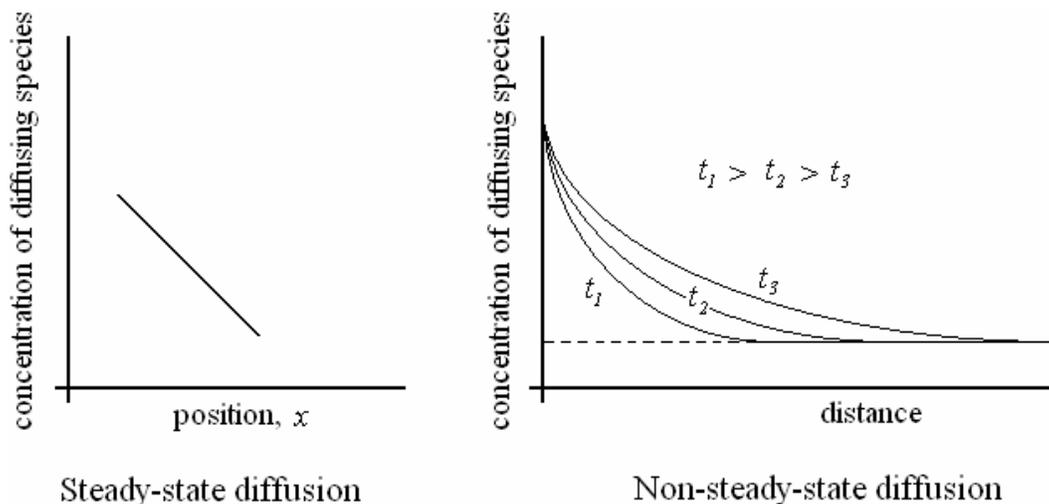
For example:  $\text{Cd}^{+2}$  cation in NaCl crystal will result in a cation vacancy. As Schottky defects form easily in NaCl crystal and thus cation vacancies carry the diffusion flux, even small fraction of  $\text{Cd}^{+2}$  increases the diffusivity of NaCl by several orders. Excess  $\text{Zn}^{+2}$  interstitials present in a non-stoichiometric ZnO compound increase the diffusivity of  $\text{Zn}^{+2}$  ions significantly. It is same with non-stoichiometric FeO.

In addition to diffusion through the bulk of a solid (volume diffusion), atoms may migrate along external or internal paths that afford lower energy barriers to motion. Thus diffusion can occur along dislocations, grain boundaries or external surfaces. The rates of diffusion along such *short-circuit paths* are significantly higher than for volume diffusion. However, most cases of mass transport are due to volume diffusion because the effective cross-sectional areas available for short-circuit processes are much smaller than those for volume diffusion.

There is a difference between diffusion and net diffusion. In a homogeneous material, atoms also diffuse but this motion is hard to detect. This is because atoms move randomly and there will be an equal number of atoms moving in one direction than in another. In inhomogeneous materials, the effect of diffusion is readily seen by a change in concentration with time. In this case there is a *net* diffusion. Net diffusion occurs because, although all atoms are moving randomly, there are more atoms moving away from regions where their concentration is higher.

### 5.1.2 Steady-state diffusion

Diffusional processes can be either steady-state or non-steady-state. These two types of diffusion processes are distinguished by use of a parameter called flux. It is defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time. For steady-state diffusion, flux is constant with time, whereas for non-steady-state diffusion, flux varies with time. A schematic view of concentration gradient with distance for both steady-state and non-steady-state diffusion processes are shown in *figure-5.2*.



**Figure-5.2:** Steady-state and Non-steady-state diffusion processes.

Steady-state diffusion is described by Fick's first law which states that flux,  $J$ , is proportional to the concentration gradient. The constant of proportionality is called diffusion coefficient (diffusivity),  $D$  ( $\text{cm}^2/\text{sec}$ ). Diffusivity is characteristic of the system and depends on the nature of the diffusing species, the matrix in which it is diffusing, and the temperature at which diffusion occurs. Thus under steady-state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction. For the one-dimensional case, *Fick's first law* is given by

$$J_x = -D \frac{dc}{dx} = \frac{1}{A} \frac{dn}{dt}$$

and

$$J_x \neq f(x, t)$$

where  $D$  is the diffusion constant,  $dc/dx$  is the gradient of the concentration  $c$ ,  $dn/dt$  is the number of atoms crossing per unit time a cross-sectional plane of area  $A$ . The minus sign in the equation means that diffusion occurs down the concentration gradient. Although, the concentration gradient is often called the *driving force* for diffusion (but it is not a force in the mechanistic sense), it is more correct to consider the reduction in total free energy as the driving force.

An example of steady-state diffusion is provided by the permeation of hydrogen atoms through a sheet of palladium with different imposed hydrogen gas pressures on either side of the slab. This process has been used to purify the hydrogen gas as other gases like nitrogen, oxygen and water vapor cannot diffuse through palladium.

### 5.1.3 Non-steady-state diffusion

Most interesting cases of diffusion are non-steady-state processes since the concentration at a given position changes with time, and thus the flux changes with time. This is the case when the diffusion flux depends on time, which means that a type of atom accumulates in a region or is depleted from a region (which may cause them to accumulate in another region). *Fick's second law* characterizes these processes, which is expressed as:

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

where  $dc/dt$  is the time rate of change of concentration at a particular position,  $x$ . If  $D$  is assumed to be a constant, then

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

Solution to the above expression is possible when meaningful boundary conditions are specified. One common set of boundary conditions can be written as

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

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

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

And 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. Corresponding error function values for a variable are usually found from standard mathematical tables. The above equation demonstrates the relationship between concentration, position, and time. Thus the equation can be used to explain many practical industrial problems like corrosion resistance of duralumin, carburization and de-carburization of steel, doping of semi-conductors, etc.

## **5.2 Factors that influence diffusion and Non-equilibrium transformation & microstructure**

### **5.2.1 Factors that influence diffusion**

Ease of a diffusion process is characterized by the parameter  $D$ , diffusivity. The value of diffusivity for a particular system depends on many factors as many mechanisms could be operative.

Diffusing species: If the diffusing species is able to occupy interstitial sites, then it can easily diffuse through the parent matrix. On the other hand if the size of substitutional species is almost equal to that of parent atomic size, substitutional diffusion would be easier. Thus size of diffusing species will have great influence on diffusivity of the system.

Temperature: Temperature has a most profound influence on the diffusivity and diffusion rates. It is known that there is a barrier to diffusion created by neighboring atoms those need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion. Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature.

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

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. From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient. It can also be observed that there exists a linear proportional relation between  $(\ln D)$  and  $(1/T)$ . Thus by plotting and considering the intercepts, values of  $Q$  and  $D_0$  can be found experimentally.

Lattice structure: Diffusion is faster in open lattices or in open directions than in closed directions.

Presence of defects: As mentioned in earlier section, defects like dislocations, grain boundaries act as short-circuit paths for diffusing species, where the activation energy for diffusion is less. Thus the presence of defects enhances the diffusivity of diffusing species.

### ***5.2.2 Non-equilibrium transformation & microstructure***

During the processing of metallic materials, they are subjected to different conditions and thus transformation of its structure. During casting process, liquid metal is allowed to cool to become solid component. However, during cooling conditions can be such that they are in equilibrium or non-equilibrium state. Phases and corresponding microstructures, usually shown in a phase diagram, are generated during equilibrium solidification under the conditions that are realized only for extremely slow cooling rates. This is because with change in temperature, there must be readjustments in the compositions of liquids and solid phases in accordance with the phase diagram. These readjustments are accomplished by diffusional processes in both solid and liquid phases and also across the solid-liquid interface. But, it is well understood that diffusion is time-dependent phenomenon, and moreover diffusion in solid phases are much lower than in liquid phases, equilibrium solidification requires extremely longer times those are impractical. Thus virtually all practical solidification takes place under non-equilibrium conditions, leading to compositional gradients and formation of meta-stable phases.

As a consequence of compositional gradients during non-equilibrium cooling, segregation (concentration of particular, usually impurity elements, along places like grain boundaries) and coring (gradual compositional changes across individual grains) may occur. Coring is predominantly observed in alloys having a marked difference between liquidus and solidus temperatures. It is often being removed by subsequent annealing (incubation at relatively high temperatures that are close to lower solidus temperature, enhances diffusion in solids) and/or hot-working, and is exploited in zone-refining technique to produce high-purity metals. Segregation is also put to good use in zone refining, and also in the production of rimming steel. Micro-segregation is used to describe the differences in composition across a crystal or between neighboring crystals. On the other hand, macro-segregation is used to describe more massive heterogeneities which may result from entrapment of liquid pockets between growing solidifying zones. Micro-segregation can often be removed by prolonged annealing or by hot-working; but macro-segregation persists through normal heating and working operations.

In most situations cooling rates for equilibrium solidification are impractically slow and unnecessary; in fact, on many occasions non-equilibrium conditions are desirable. Two non equilibrium effects of practical importance are (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. These will be detailed in next chapters about phase transformation.

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