

CHAPTER 4 DIFFUSION IN SOLIDS

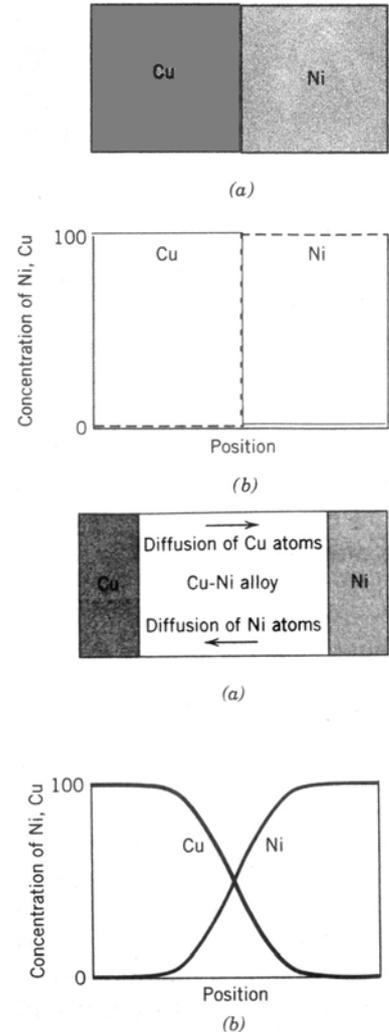
4.1 INTRODUCTION

In the previous chapters we learnt that any given atom has a particular lattice site assigned to it. Aside from thermal vibration about its mean position on the crystal lattice, the atom was assumed not to move. In actual fact, however, the atoms do have more freedom and they move from one lattice to another. This movement or migration of atoms is called *diffusion*. In short, diffusion is a physical process involving shifts of atoms and molecules to new positions.

Diffusion is fundamental to phase changes and is important in heat treatments. It is basic to many processes such as case hardening of steel production of strong bodies by sintering powders, homogenization of castings, and other industrial operations.

The phenomenon of diffusion may be demonstrated with the use of a diffusion couple, which is formed by joining bars of two different metals together so that there is intimate contact between the two faces; This is illustrated for copper and nickel in figure 4.1.

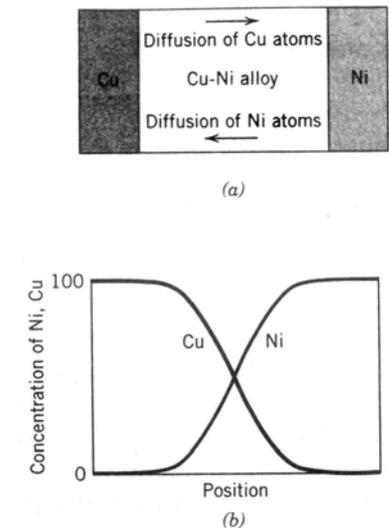
Fig 4.1 (a) A copper-nickel diffusion couple before a high-temperature heat treatment. (b) Concentration of copper and nickel as function of position across the couple.



This couple is heated for an extended period at an elevated temperature (but below melting point of both metals), and cooled to room temperature. Chemical analysis will reveal a condition similar to that represented in figure 4.2 (a) namely, pure copper and nickel at the two extremities of the couple, separated by an alloyed region. Concentrations of both metals vary with positions as shown in figure 4.2 (b). This result indicates that copper atoms have migrated or diffused into the nickel, and that nickel has diffused into copper.

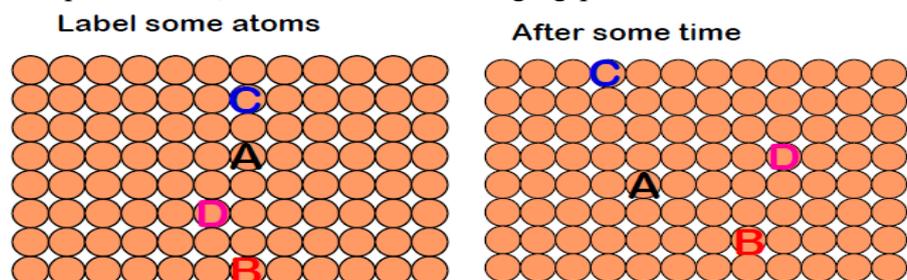
This process whereby atoms of one metal diffuse into another, is termed **interdiffusion**, or **impurity diffusion**.

Fig 4.2 (a) A copper nickel diffusion couple after high temperature heat treatment, showing the alloyed diffusion zone. (b) Concentration of copper and nickel as a function of position



Interdiffusion may be observed as changes in concentration which occur over time, as in the example for Cu-Ni diffusion couple. There is a net drift or transport of atoms from high to low-concentration regions.

Diffusion also occurs for pure metals, but all atoms exchanging positions are of the same type; this is termed **self-diffusion**. Of course, self diffusion is not normally subject to observation by noting compositional change, because in pure metals all atoms are alike.



Self Diffusion

4.2 DIFFUSION MECHANISMS

From an atomic perspective, diffusion is just the step wise migration of atoms from lattice site. In fact, the atoms in solid materials are in constant motion, rapidly changing positions. In order to make such a move two conditions must be met

1. There must be an empty adjacent site, and
2. The atom must have sufficient energy to break bonds with its neighbour atom and then cause some lattice distortion during the displacement. This energy is vibrational in nature and increases with rising temperature.

There are two important mechanisms by which atoms or ions can diffuse.

1. Vacancy mechanism
2. Interstitial mechanism

Vacancy Diffusion:

In self-diffusion and diffusion involving substitutional atoms, an atom leaves its lattice site to fill a nearby vacancy (thus creating a new vacancy at the original lattice site). As diffusion continues, we have counter flows of atoms and vacancies, called vacancy diffusion. The number of vacancies, which increased as the temperature increases, helps determine the extent of both self-diffusion and diffusion of substitutional atoms.

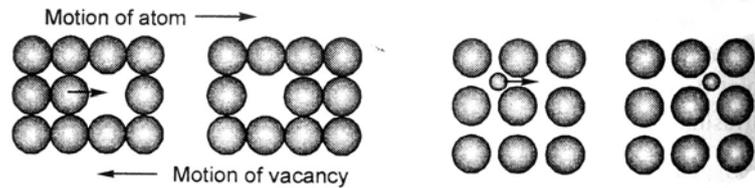


Fig 4.3 (a) Vacancy diffusion (b) interstitial diffusion.

Interstitial Diffusion:

When a small interstitial atom or ion is present in the crystal structure, the atom or ion moves from one interstitial site to another. No vacancies are required for this mechanism. Partly because there are many more interstitial site than vacancies, interstitial diffusion occurs more easily than vacancy diffusion. Interstitial atoms that are relatively smaller can diffuse faster.

Detailed theoretical calculations of the energy required for atomic motion to occur by mechanisms cited above show that diffusion by vacancy motion should predominate in pure metals and substitutional alloys. Many experiments bear out this choice. For one group of alloys, however, interstitial motion certainly predominates. This motion is the diffusion of small atoms dissolved in interstices in the parent crystal. Such alloys are called *interstitial alloys*.

Interstitial diffusion is normally more rapid than vacancy diffusion because: (1) interstitial atoms, being smaller, are more mobile; and (2) the probability of an empty adjacent interstitial site is greater than for a vacancy adjacent to a host (or substitutional impurity) atom.

4.3 Activation Energy (Q) for Diffusion

Energy is always required for atoms to move from one lattice position to another lattice position. To make the jump from one site to another site, an energy barrier must be overcome. *The energy required by the atom to overcome this energy barrier (Fig. 4.4) is called the activation energy of diffusion.*

In a vacancy mechanism, the energy is required to pull the atom away from its neighbours (Fig. 4.4). In the interstitial mechanism energy is required to force the atom into closer contact with

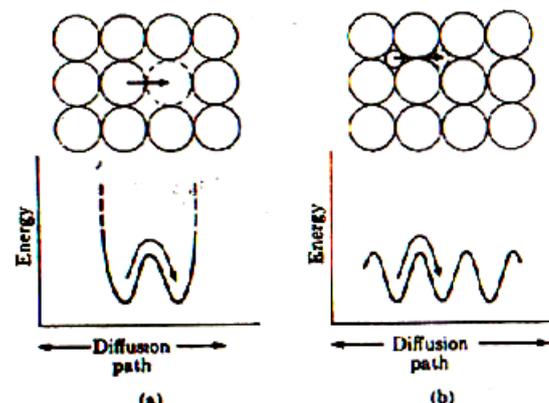


Fig 4.4 Atom movements and energy barrier
(a) Vacancy mechanism (b) Interstitial mechanism

neighbouring atoms as it moves along them (Fig. 4.4).

4.4 Diffusion Flux (J)

Diffusion is a time-dependent process- that is , the quantity of an element that is transported within another is a function of time. Diffusion flux indicates how fast the diffusion occurs (or the rate of mass transfer). **Diffusion flux** is defined as the mass (or, equivalently, the number of atoms) M diffusing through and perpendicular to a unit cross-sectional area of solid per unit of time.

If M = quantity diffused in kg or number of atoms
 A = area across which diffusion occurs, in m²

Then, $\frac{M}{A}$ = quantity diffused per unit area in Kg/m²

Let, t = time duration of diffusion, in seconds,

Then, J = quantity diffused/ unit area/ unit time.

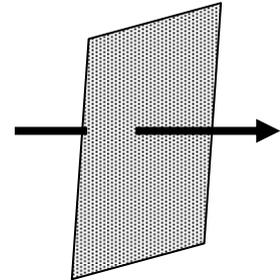
$$= \frac{M/A}{t}$$

i.e $J = \frac{M}{At}$ (4.1)

The unit of J are kg/m²-s or atoms/m²-s

In differential form, the above equation becomes,

$$J = \frac{1}{A} \cdot \frac{dM}{dt}$$



4.5 Steady-State diffusion

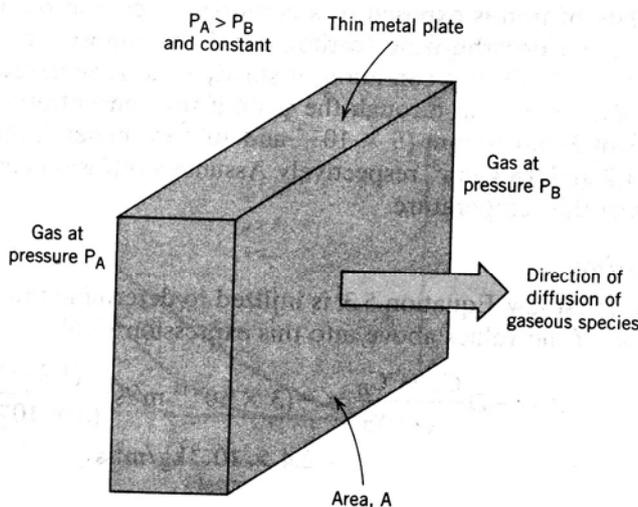
(S 09)

Steady-state diffusion is the situation wherein the rate of diffusion into a given system is just equal to the rate of diffusion out, such that there is no net accumulation or depletion of diffusing species--i.e., the diffusion flux is independent of time.

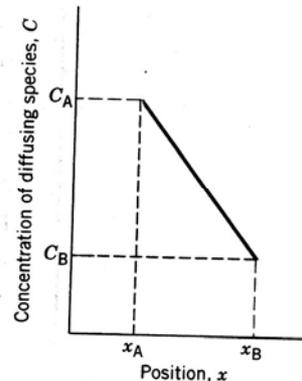
If the diffusion flux J (rate of mass transfer) doesn't change with time, then a steady state condition exists. Under steady state diffusion, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction.

Mathematically, $J \neq f(x,t)$

One common example of steady-state diffusion is the diffusion of atoms of a gas through a metallic plate for which the concentration (or pressures) of the diffusing species on both surface of the plate are held constant. This is schematically represented in figure.



(a)



(b)

When the concentration (c) versus position (or distance) within the solid (x) is plotted, the resulting curve is called *concentration profile*. The slope at a particular point on this curve is the concentration gradient.

$$\text{Concentration gradient} = \frac{dC}{dx}$$

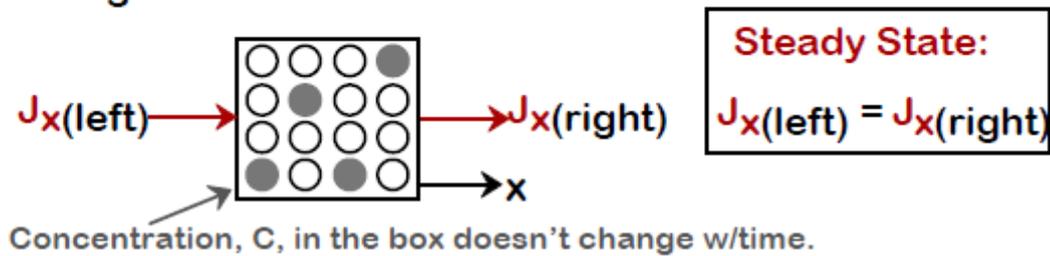
In steady-state flow, concentration profile is linear, and hence it can be written as,

$$\text{Concentration gradient} = \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

- Where C_A = concentration at point A
- C_B = Concentration at point B
- x_A = distance to point A
- x_B = distance to point B

Normally, (in diffusion problems) concentration is expressed in kg/m³ or g/cm³

- **Steady State:** the concentration profile doesn't change with time.



One practical example of steady-state diffusion is found in the purification of hydrogen gas. One side of a thin sheet of palladium metal is exposed to the impure gas composed of hydrogen and other gaseous species such as nitrogen, oxygen, and water vapour. The hydrogen selectively diffuses through the sheet to the opposite side, which maintained at a constant and lower hydrogen pressure.

4.6 FICK'S FIRST LAW

The mathematics of steady-state diffusion in a single (x) direction is relatively simple, in that the flux is proportional to the concentration gradient through the expression

$$\mathbf{J} = -D \frac{dC}{dx} \dots\dots\dots(4.2)$$

The constant of proportionality **D** is called the **diffusion coefficient, (Diffusivity)** which is expressed in m²/s.

The negative sign in this expression indicates that the direction of diffusion is from a high to a low concentration. Equation 4.2 is sometimes called Fick's first law.

Sometimes the term driving force is used in the context of what compels a reaction to occur. For diffusion reactions, several such forces are possible; but when diffusion is according to Equation 4.2, the concentration gradient is driving force.

Diffusion coefficient varies with the nature of the solute atoms, with the nature of the solid structure, and with changes in temperature. Some reasons for variations are: (1) higher thermal energies and therefore, greater probabilities of being activated over the energy barrier (see Section) between atoms; (2) carbon has a



Adolf Fick

higher diffusion coefficient in iron than does nickel in iron because the carbon atom is small one; (3) copper diffuses more readily in aluminum than in copper because the Cu-Cu bonds are stronger than Al-Al bonds as evidenced by their melting temperature; (4) atoms have higher diffusion coefficients in bcc iron than in fcc iron because the former has a lower atomic factor (0.68) versus 0.74); (5) the diffusion proceeds more rapidly along grain boundaries because this is a zone of crystal imperfections.

Nernst - Einstein Relation (S 2011)

Nernst-Einstein relation is a mathematical expression showing the relationship between diffusion coefficient and mobility of the diffusing element, and is given by

$$D_s = u \frac{RT}{N_A}$$

D_s = Diffusion coefficient

u_s = mobility of diffusing element

N_A = Avagadro's number.

EXAMPLE PROBLEM

[W 05, W 11]

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 position of 5 and 10 mm (5×10^{-3} and 10^{-2} m) beneath the carburizing surface are 1.2 and 0.8 kg/m^3 , respectively. Assume a diffusion coefficient of $3 \times 10^{-11} \text{ m}^2/\text{s}$ at this temperature.

Solution

It is given that steady state condition prevails. Hence we apply Fick's first law.

Fick's first law, is given by

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

D = diffusion coefficient = $3 \times 10^{-11} \text{ m}^2/\text{s}$

$$\frac{dC}{dx} = \text{Concentration gradient} = \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$

C_A = Concentration in side A = 1.2 kg/m^3

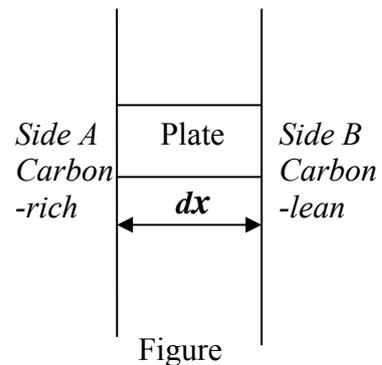
C_B = Concentration in side B = 0.8 kg/m^3

x_A = distance to point A = $5 \times 10^{-3} \text{ m}$

x_B = distance to point B = $10 \times 10^{-3} \text{ m}$

Substituting values we get

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



4.7 Effect of Temperature (Arrhenius Equation)

By experiments it has been observed that diffusion rate increases with temperature.. For example, for the self diffusion of Fe into α -Fe, the diffusion coefficient D increases approximately six orders of magnitude (from 3.0×10^{-21} to $1.8 \times 10^{-15} \text{ m}^2/\text{s}$) in rising temperature from 500 to 900°C (see Table at the end of the chapter).

The temperature dependence of the diffusion coefficient (D) is given by

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (4.6)$$

$$= D_0 e^{\left(-\frac{Q}{RT}\right)}$$

Where,

D_0 = A temperature-independent pre-exponential (m^2/s)

Q = The activation energy for diffusion (J/mol, Cal/mol or eV/atom)

R = The gas constant,

= 8.314 J/mol-K,

= 1.987 Cal/mol,

= 8.62×10^{-5} eV/atom K

T = Absolute temperature (K)

The activation energy may be thought of as that energy required to produce the diffusive motion of one mole of atoms. Large activation energy results in a relatively small diffusion coefficient. Table also contains a listing of D_0 and Q_d values for several diffusion systems

Taking natural logarithms of equation 4.6 yields

$$\ln D = \ln D_0 - \frac{Q}{R} \left(\frac{1}{T}\right) \quad (4.7)$$

Or in terms of logarithms to the base 10

$$\log D = \log D_0 - \frac{Q}{2.3R} \left(\frac{1}{T}\right) \quad (4.8)$$

Since D_0 , Q , and R are all constant, equation 4.8 takes on the form of an equation of a straight line.

$y = b + mx$

Where, y and x are analogous, respectively, to the variables $\log D$ and $1/T$. Thus, if $\log D$ is plotted versus the reciprocal of the absolute temperature, a straight line should result, have slope and intercept of $-Q/2.3 R$ and $\log D_0$, respectively.

Table

Diffusing Species	Host Metal	$D_0(\text{m}^2/\text{s})$	Activation Energy Q		Calculated Value	
			kJ/mol	eV/atom	$T (^{\circ}\text{C})$	$D (\text{m}^2/\text{s})$
Fe	α -Fe (BCC)	2.8×10^{-4}	251	2.60	500	3.0×10^{-21}
					900	1.8×10^{-15}
Fe	γ -Fe (FCC)	5×10^{-5}	284	2.94	900	1.1×10^{-17}
					1100	7.8×10^{-16}
C	α -Fe	6.2×10^{-7}	80	0.83	500	2.4×10^{-12}
					900	1.7×10^{-10}
C	γ -Fe	2.3×10^{-5}	148	1.53	900	5.9×10^{-12}
					1100	5.3×10^{-11}
Cu	Cu	7.8×10^{-5}	211	2.19	500	4.2×10^{-19}
Zn	Cu	2.4×10^{-5}	189	1.96	500	4.2×10^{-18}
Al	Al	2.3×10^{-4}	144	1.49	500	4.2×10^{-14}
Cu	Al	6.5×10^{-5}	136	1.41	500	4.1×10^{-14}
Mg	Al	1.2×10^{-4}	131	1.35	500	1.9×10^{-13}
Cu	Ni	2.7×10^{-5}	256	2.65	500	1.3×10^{-22}

Problem

Given an activation energy of $Q = 142 \text{ KJ/mol}$, for the diffusion of carbon in FCC and an initial temperature of 1000°K , find the temperature that will increase the diffusion coefficient by a factor 10. [$R = 8.314 \text{ J/mol.K}$], Will you use a high temperature? [S '05, 8M]

Solution

$$\begin{aligned} Q &= \text{Activation energy} \\ &= 142 \text{ kJ/mol} = 142 \times 10^3 \text{ J/mol} \\ T_1 &= \text{initial Temperature} \\ &= 1000 \text{ K} \end{aligned}$$

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

$$\begin{aligned} D &= \text{Diffusion coefficient} \\ D_0 &= \text{proportionality constant} \\ R &= \text{The gas constant, } = 8.314 \text{ J/mol.K} \\ T &= \text{Temperature in K} \end{aligned}$$

$$\text{Now, For initial condition we have } D_1 = D_0 \exp\left(-\frac{Q}{RT_1}\right) \dots\dots\dots(1)$$

$$\text{For Final condition we have } D_2 = D_0 \exp\left(-\frac{Q}{RT_2}\right) \dots\dots\dots(2)$$

$$\frac{(1)}{(2)} \Rightarrow \frac{D_1}{D_2} = \frac{\exp\left(-\frac{Q}{RT_1}\right)}{\exp\left(-\frac{Q}{RT_2}\right)}$$

$$\text{But } D_2 = 10 D_1$$

$$\text{Substituting values } \frac{D_1}{10D_1} = \frac{\exp\left(-\frac{142 \times 10^3}{8.314 \times 1000}\right)}{\exp\left(-\frac{142 \times 10^3}{8.314 \times T_2}\right)}$$

$$\text{Solving we get } T_2 = 1062 \text{ K}$$

Hence if we use a temperature of 434.29 K the diffusion coefficient becomes 10 times higher.

Problem

The diffusivity of silver atoms in solid silver metal is $1.0 \times 10^{-17} \text{ m}^2/\text{s}$ at 500°C and $7.0 \times 10^{-13} \text{ m}^2/\text{s}$ at 1000°C . Calculate the activation energy (joules/mole) for the diffusion of Ag in the temperature range $500\text{-}1000^{\circ} \text{C}$. (W '09, 4M)

Solution:

In general, diffusivity is given by

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

$$\begin{aligned} T_1 &= 500^{\circ} \text{C} = 500 + 273 = 773 \text{ K} \\ T_2 &= 1000^{\circ} \text{C} = 1000 + 273 = 1273 \text{ K} \\ R &= \text{Gas constant} = 8.31 \text{ J/mol K} \end{aligned}$$

$$\text{Now, } D_1 = D_0 \exp\left(-\frac{Q}{RT_1}\right)$$

$$D_2 = D_0 \exp\left(-\frac{Q}{RT_2}\right)$$

$$\frac{D_1}{D_2} = \frac{\exp\left(-\frac{Q}{RT_1}\right)}{\exp\left(-\frac{Q}{RT_2}\right)} = e^{-\left[\frac{Q}{RT_2} - \frac{Q}{RT_1}\right]} = e^{-\left[\frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]}$$

$$\Rightarrow \frac{7 \times 10^{-13}}{1 \times 10^{-17}} = e^{-\left[\frac{Q}{R}\left(\frac{1}{1273} - \frac{1}{773}\right)\right]}$$

$$\text{Or } 7 \times 10^4 = e^{-\left[\frac{Q}{R}\left(-5.08 \times 10^{-4}\right)\right]} = e^{-\left[\frac{Q}{R}\left(5.08 \times 10^{-4}\right)\right]}$$

$$\Rightarrow \log(7 \times 10^4) = \frac{Q}{R} (5.08 \times 10^{-4})$$

$$= \frac{Q(5.08 \times 10^{-4})}{8.314}$$

$$Q = \frac{11.6 \times 8.314}{5.08 \times 10^{-4}} = \mathbf{189800 \text{ J/mol}}$$

4.8 Factors Affecting Diffusivity

Diffusivity is affected by several factors. Important among them are

- (i) Temperature: With an increase in temperature, the diffusivity also increases. The increase is proportional to $e^{(-1/T)}$
- (ii) Melting point: The diffusivity and melting point of a solid are inversely proportional. The reason is that the solids with higher melting point require higher thermal energy to break the bonds. For example, take the case of Cu-Cu and Cu-Al diffusion. Melting points of Cu and Al are 1083°C and 657°C respectively. It means that Cu-Cu bonds are stronger than Al-Al bonds. That's why Cu atoms diffuse more easily in Al than in itself.
- (iii) Atomic packing factor: Highly packed crystals have low diffusivity. We know that APF for FCC and BCC structures are 0.74 and 0.68 respectively. Therefore FCC crystals have lower diffusivity than BCC crystals. That is why diffusion of carbon in BCC-iron (α -iron) is higher than its diffusion in FCC-iron (γ -iron).
- (iv) Crystal structure: A polycrystalline material shows higher diffusion than a single crystal material at lower temperature. It is due to longer grain boundaries in polycrystalline material which increases diffusion. However when lattice diffusion dominates at higher temperature, diffusivity becomes the same for polycrystalline and single crystal materials. The distorted crystals show higher diffusivity.
- (v) Atomic radius: Materials having smaller atomic radii exhibit higher diffusivity than those having larger atomic radii. For example, the radii of carbon and nickel atoms are 0.7 \AA and 12.5 \AA respectively. Thus a carbon atom is much smaller than the nickel atom. Hence diffusivity of carbon in iron is more than that of nickel in iron. This fact may be noticed in binary solutions where atomic radii of solute and solvent differ significantly. Reason of this situation is the occurrence of interstitial mechanism which requires lower activation energy than the vacancy mechanism.
- (vi) Grain Size: Fine grained materials have higher diffusivity than coarse grained materials. The reason may be attributed to grain boundaries. Diffusion through grain boundaries is faster, and fine grained materials have longer grain boundaries.
- (vii) Non-crystallinity: Gaseous molecules diffuse faster in non-crystalline structures due to presence of larger void space, as in polymers, or due to open network as in silicate.

Smaller molecules diffuse more rapidly. Use of plasticizer, and process of cross-linking have the effects of increasing and decreasing diffusivity respectively.

4.9 Non-steady-state Diffusion

Most practical diffusion situations are nonsteady-state ones. That is, the diffusion flux and the concentration gradient at some particular point in a solid vary with time, with a net accumulation or depletion of the diffusing species resulting.

4.8 Fick’s second law (S ’06, W 08)

Fick’s second law is an extension of the first law and is applicable to non-steady state conditions.

Here, at any given instant, the flux is not the same at different cross-sectional planes along the diffusion direction x.

Also, at the same cross-section, the flux is not the same at different times. Consequently, the concentration-distance profile changes with time.

Non-steady state flow is frequently met with practical application of the diffusion laws.

Consider an elemental slab of thickness Δx along the diffusion direction X.

Let the slab cross-section be perpendicular to X and its area be unity.

The volume of the slab is then Δx × 1 = Δx.

Under non-steady conditions,

$$\begin{aligned} \text{The flux entering the slab} &= J_x \\ \text{Flux generated in the slab} &= \frac{\partial J}{\partial x} \Delta x \\ \text{The flux leaving out of the slab} &= \text{flux entering} + \text{flux generated} \\ &= J_x + \frac{\partial J}{\partial x} \Delta x \end{aligned}$$

The rate of accumulation of the diffusing atoms within this elemental volume is = Flux entering – flux leaving.

$$\begin{aligned} &= J_x - (J_x + \frac{\partial J}{\partial x} \Delta x) \\ &= J_x - J_x - \frac{\partial J}{\partial x} \Delta x \\ &= -\frac{\partial J}{\partial x} \Delta x \dots\dots\dots(4.3) \end{aligned}$$

For a portion of slab with unit cross-sectional area and thickness Δx,

Rate of accumulation of atoms in the section of volume (Δx × 1)m³

$$\begin{aligned} &= \frac{\partial}{\partial t} (C \times \text{Volume}) \\ &= \frac{\partial}{\partial t} (C \Delta x) = \frac{\partial C}{\partial t} \cdot \Delta x \dots\dots\dots(4.4) \text{ (because unit area of cross section is considered.)} \end{aligned}$$

But equation (4.4) = (4.3)

$$\frac{\partial C}{\partial t} \cdot \Delta x = - \frac{\partial J}{\partial x} \Delta x$$

But we have $J = -D \frac{dC}{dx} \dots\dots\dots(4.2)$

Substituting,

$$\frac{\partial C}{\partial t} \cdot \Delta x = - \frac{\partial}{\partial x} \left(-D \frac{dC}{dx} \right) \Delta x$$

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

This equation is the **Fick’s second law** for unidirectional flow under non-steady state conditions, if D is independent of concentration.

In physical terms this relationship states that the rate of compositional change is proportional to the “rate of change” of the concentration gradient rather than to the concentration gradient itself.

Solution to the above differential equation (4.4) depends on boundary conditions imposed by problem of interest. One such practical case is case hardening.

Let us consider the case of a gas A diffusing into a solid B. As the time of diffusion increases the concentration of solute atoms at any point in the X direction will also increase.

If the diffusivity of gas A in solid B is independent of position, then the solution to Fick’s Second Law can be written as follows.

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \dots\dots\dots(4.5)$$

Where C_0 = the initial uniform concentration element in solid;

t = the time in seconds,

C_s = surface concentration of element in gas diffusing into the surface;

x = the distance from surface;

D = the diffusivity (diffusion coefficient) of diffusing solute element; in m^2/s

C_x , = the concentration of element at distance x from surface at time t ;

and

erf = error function which is a mathematical function existing by agreed definition and is used in solution of Fick’s Second Law.



Tabulation of Error Function Values

z	erf (z)	z	erf (z)	z	erf (z)
0	0	0.55	0.5633	1.3	0.9340
0.025	0.0282	0.60	0.6039	1.4	0.9523
0.05	0.0564	0.65	0.6420	1.5	0.9661
0.10	0.1125	0.70	0.6778	1.6	0.9763
0.15	0.1680	0.75	0.7112	1.7	0.9838
0.20	0.2227	0.80	0.7421	1.8	0.9891
0.25	0.2763	0.85	0.7707	1.9	0.9928
0.30	0.3286	0.90	0.7970	2.0	0.9953
0.35	0.3794	0.95	0.8209	2.2	0.9981
0.40	0.4284	1.0	0.8427	2.4	0.9993
0.45	0.4755	1.1	0.8802	2.6	0.9998
0.50	0.5205	1.2	0.9103	2.8	0.9999

Exercise

Consider the gas carburizing of a gear of 1020 steel at 927°C. Calculate the time in minutes necessary to increase the carbon content to 0.40 wt% at 0.50 mm below the surface. Assume that the carbon content at the surface is 0.90 wt% and that the steel has a nominal carbon content of 0.20 wt%. Given Diffusivity of C in Fe(γ) at 927°C, $D = 1.28 \times 10^{-11} m^2/s$ erf (z) = 0.7134, where $z = 0.755$ (S '07, 5M)

Solution

The solution of Fick's Second Law for gas and solid is applicable in this case. So we can use the following equation.

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

Given

Initial concentration, $C_0 = 0.20$

Surface concentration, $C_s = 0.90$

Duration of diffusion $t = ?$ to be found

At depth, $x = 0.5 \text{ mm} = 5.0 \times 10^{-4} \text{ m}$, Concentration $C_x = 0.40$

$D_{927^\circ\text{C}} = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$,

Substituting the above values in the equation, we get

$$\begin{aligned} \frac{0.40 - 0.20}{0.90 - 0.20} &= 1 - \operatorname{erf}\left[\frac{5.0 \times 10^{-4} \text{ m}}{2\sqrt{(1.28 \times 10^{-11} \text{ m}^2/\text{s})(t)}}\right] \\ \Rightarrow \frac{0.20}{0.70} &= 1 - \operatorname{erf}\left(\frac{69.88}{\sqrt{t}}\right) \\ \Rightarrow \operatorname{erf}\left(\frac{69.88}{\sqrt{t}}\right) &= 0.7143 \dots\dots\dots(1) \end{aligned}$$

Given that, $\operatorname{erf}(z) = 0.7134$, when $z = 0.755$.

This implies $\operatorname{erf}(0.755) = 0.7134 \dots\dots\dots(2)$

Equation (1) = (2)

Hence $\frac{69.88}{\sqrt{t}} = 0.755$.

Solving we get $t = 8567\text{s} \cong 143 \text{ min}(\text{Ans})$

Problem

Describe Fick's second law of diffusion. The diffusion coefficients for copper in aluminium at 500°C and 600°C are $4.8 \times 10^{-14} \text{ m}^2/\text{s}$ and $5.3 \times 10^{-13} \text{ m}^2/\text{s}$, respectively. Calculate the time required at 500°C to produce diffusion depth equal to that at 600°C for 10 hr (S '11, 5M)

Solution

D = Diffusion coefficient of Copper INTO Aluminium

At 500°C , $D_{\text{Cu}} = 4.8 \times 10^{-14} \text{ m}^2/\text{s}$

At 600°C , $D_{\text{Cu}} = 5.3 \times 10^{-13} \text{ m}^2/\text{s}$

$t = 10 \text{ hrs}$

From the question it can be learnt that,

Copper diffuses into Aluminium.

First, it diffuses at 600°C for 10 hrs.

In the second case, diffusion takes place at temperature 500°C . (for an unknown time)

In both cases diffusion depth is same.

We need to find the time duration of diffusion at 500°C .

First lets find diffusion depth for the 500°C diffusion cases.

From Fick's second law,

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

Applying this expression for the case of 500⁰C diffusion

$$\frac{Cx - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{4.8 \times 10^{-14} \times t}}\right) \dots\dots\dots(1)$$

Applying the same equation for the case of 600⁰C diffusion,

$$\frac{Cx - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{5.3 \times 10^{-13} \times 10}}\right) \dots\dots\dots(2)$$

But for both cases concentration conditions are the same. Hence LHS of the above equations are equal.

Hence, $1 - \operatorname{erf}\left(\frac{x}{2\sqrt{4.8 \times 10^{-14} \times t}}\right) = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{5.3 \times 10^{-13} \times 10}}\right)$

Or,

$$\operatorname{erf}\left(\frac{x}{2\sqrt{4.8 \times 10^{-14} \times t}}\right) = \operatorname{erf}\left(\frac{x}{2\sqrt{5.3 \times 10^{-13} \times 10}}\right)$$

This implies,

$$\left(\frac{x}{2\sqrt{4.8 \times 10^{-14} \times t}}\right) = \left(\frac{x}{2\sqrt{5.3 \times 10^{-13} \times 10}}\right)$$

Or, $4.8 \times 10^{-14} \times t = 5.3 \times 10^{-13} \times (10 \times 3600)$

Since diffusion depth is also equal, the term ‘x’ in both sides gets cancelled.

$$\text{Or, } t = \frac{5.3 \times 10^{-13} \times (10)}{4.8 \times 10^{-14}} = \mathbf{11.45 \text{ hours}}$$

4.10 THE KIRKENDALL EFFECT (S '07, S 09)

In a binary solution of A and B, the rates at which A and B diffuse are not necessarily equal. Usually, the lower melting component diffuses much faster than the other. This leads to certain interesting effects as first observed by Kirkendall.

Inert markers (thin rods of a high melting point substances which is insoluble in the diffusion matrix) are placed at the weld joint of the couple, prior to the diffusion anneal. These markers are found to shift during the anneal in the same direction as the slower moving species. The extent of the shift is found to be proportional to the square root of the diffusion time. This kind of movement indicates that the net mass flow due to the difference in diffusivities is being compensated by a bulk flow of matter in the opposite direction within the diffusion zone. That is, lattice planes are created on one side of the diffusion zone, while they are destroyed on the other side, and the resulting bulk flow carries the markers along. Notice that the bulk flow occurs relative to the ends of the diffusion couple. It is quite a different phenomenon from the diffusion process itself. In many cases, porosity is observed on the lower-melting component side, indicating that the bulk flow does not fully compensate for the difference in diffusivities of the two species.

4.11 Applications of Diffusion

Diffusion refers to the net flux of any species, such as ions, atoms, electrons, holes, and molecules. The magnitude of this flux depends upon the initial concentration gradient and temperature.

The process of diffusion is central to a large number of today’s important technologies. There are following applications and technologies that depend on diffusion.

Carburization of steel: Steel is an alloy of iron and carbon. The maximum concentration of carbon in steel is less than 1.4%. Increasing the carbon content makes the material harder and brittle. But in some applications such as gears, hardening of the surface is necessary to improve its

wear resistance, without altering the properties of the bulk material. Surface hardening is done by making carbon diffuse up to a certain depth on the surface of steel. This process is called carburization. In carburization, a source of carbon, such as graphite powder or gaseous phase containing carbon, is diffused into steel components such as gears.

Doping of Semiconductors: Semiconductors (Si and Ge) are doped with trivalent or pentavalent impurities, to control their electrical properties. The doping is done by diffusion. The pure semiconductor crystal is exposed to dopant material in the gaseous form. The dopant atoms diffuse into the crystal. The concentration and the depth of penetration are controlled by temperature and the initial conditions.

Conductive Ceramics: Polycrystalline ceramics tend to be good insulators of electricity. Strong covalent and ionic bonds along with microstructural features are responsible for the poor electrical conductivity and, in fact, some are superconductors. Diffusion of ions, electrons, or holes also plays an important role in the electrical conductivity of many conductive Ceramics, such as partially or fully stabilized Zirconia (ZrO_2) or indium tin oxide (ITO). Lithium cobalt oxide ($Li Co O_2$) is an example of an ionically conductive materials are used for such products as oxygen sensors in cars, touch-screen displays, fuel cells, and batteries. The ability of ions to diffuse and provide a pathway for electrical conduction plays an important role in enabling these applications.

Lattice Diffusion in Ionic Crystals: In ionic crystals, presence of point defects such as Schottky defect or Frenkel defect cause diffusion of the atoms within the lattice. The electrical conductivity in ionic crystals is directly proportional to the diffusion coefficient of the lattice atoms. The presence of point defects increases the ionic conductivity of ionic crystals because of diffusion.

Optical Fibers and Micro Electronic Components: Optical fibers made from silica (SiO_2) are coated with polymeric materials to prevent diffusion of water molecules. Water vapour has two related but separate effects on the performance of glass optical fibers. First, incorporation of water in the form of hydroxyl group (OH^-) increases optical losses. Second, water vapour attacks the glass surface, causing microcracks that lower the strength of glass. We capacitors and other components, to prevent diffusion of water vapour or other chemical that can deteriorate their performance.

Water and Air Treatment: In environmental engineering applications, such as the treatment of water or air, we are often interested in how certain ions or molecules diffuse through a filter or an ion exchange resin. In certain drug delivery applications, doctors and other health care professionals are interested in the diffusion of drugs or other biochemical molecules through small capillaries carrying blood.

Thermal Barriers Coatings for Turbine Blades: In an aircraft engine, some of the nickel superalloy- based turbine blades are coated with ceramic oxides such as yttria stabilized zirconia (YSZ). These ceramic coatings protect the underlying alloys from high temperatures; hence the name thermal barrier coatings (TBCs). The diffusion of oxygen through these ceramic coatings and the subsequent oxidation of the underlying alloy play a major role in determining the life time and durability of the turbine blades.

QUESTIONS

1. State Fick's law of diffusion. How can it help you in the problems of case hardening?
Given an activation energy of $Q = 142 \text{ KJ/mol}$, for the diffusion of carbon in FCC and an initial temperature of 1000°K , find the temperature that will increase the diffusion coefficient by a factor 10. [$R = 8.314 \text{ J/mol.K}$], Will you use a high temperature? [S '05, 8M]
2. 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 . If a condition of steady state is achieved, calculate the diffusion flux of carbon through the plate if the concentration of carbon at position of 5 mm and 10 mm beneath the carburizing surfaces are 1.2 and 0.8 Kg/m^3 . Assume a diffusion coefficient of $3 \times 10^{-11} \text{ m}^2/\text{s}$ at this temperature. How will you attempt the same problem, if non-steady state condition exists? (W 05, 6M)
3. State Fick's second law of diffusion. [S '06, 2M]
4. Differentiate between interstitial and vacancy diffusion. [S '06, 2M]
5. Briefly discuss Kirkendal effect with an example (S '07,3 M)
6. Consider the gas carburizing of a gear of 1020 steel at 927°C . Calculate the time (in minutes) necessary to increase the carbon content to $0.40 \text{ wt}\%$ at 0.50 mm below the surface. Assume that the carbon content at the surface is $0.90 \text{ wt}\%$ and that the steel has a nominal carbon content of $0.20 \text{ wt}\%$. Given: Diffusivity of C in Fe (γ) at 927°C , $D = 1.28 \times 10^{-11} \text{ m}^2/\text{s}$, if $\text{erf}(Z) = 0.7143$, $Z = 0.755$. (S '07,5M)
7. Explain why interstitial atoms such as C in Fe can diffuse more rapidly compared to vacancies (W 05, S '08, 2M)
8. State Fick's second law of diffusion. Describe how it affects heat treatment in carburization of low carbon steels. (W 08, 2+4M)
9. What is meant by the 'diffusivity'? What is steady state diffusion? How does it depend on temperature? (W 08, 2+2+2)
10. What is kirkendall effect? (S '09,2 M)
11. Explain steady state and non-steady state diffusion Derive Fick's law of diffusion (S '09,7)
12. The diffusivity of silver atoms in solid silver metal is $1.0 \times 10^{-17} \text{ m}^2/\text{s}$ at 500°C and $7.0 \times 10^{-13} \text{ m}^2/\text{s}$ at 1000°C . Calculate the activation energy (joules/mole) for the diffusion of Ag in the temperature range $500\text{-}1000^{\circ} \text{C}$. (W '09, 4 M)
13. Explain Arrhenius rate equation (W '09, 4 M)
14. Explain interstitial and vacancy diffusions. (S '10, 4M)
15. Explain Fick's law for non-steady state diffusions. (S '10, 4M)
16. Write notes on Fick's law of diffusion (W '10,5 M)
17. Mention and explain Nernst-Einstein relation in diffusion. (S '11, 5M)
18. Describe Fick's second law of diffusion. The diffusion coefficients for copper in aluminium at 500°C and 600°C are $4.8 \times 10^{-14} \text{ m}^2/\text{s}$ and $5.3 \times 10^{-13} \text{ m}^2/\text{s}$, respectively. Calculate the time required at 500°C to produce diffusion depth equal to that at 600°C for 10 hr (S '11, 5M)
19. Describe Fick's first law of diffusion. A plate of iron is exposed to a carburizing atmosphere on one side and a decarburizing atmosphere on the other side at 700°C . Under steady state conditions, calculate the diffusion flux of carbon through the plate, if the concentration of carbon at position of 5 mm and 10 mm beneath the carburizing surface are 1.2 kg/m^3 and 0.8 kg/m^3 , respectively. Assume a diffusion coefficient of $3 \times 10^{-11} \text{ m}^2/\text{s}$ at this temperature (W '11, 3+3M)
20. The diffusion coefficients for iron in nickel are given at following two temperatures.

T (K)	D (m^2/s)
1273	9.4×10^{-16}
1473	2.4×10^{-14}

Determine the values of D_0 and the activation energy Q_d

(S '12, 5M)