Review of Diffusion

Fundamental process that controls the rate of the transformation - **diffusion**

Diffusion occurs to reduce the Gibbs free energy of the system

Diffusion can occur either down a concentration gradient OR even up the concentration gradient
Two types of diffusion mechanisms:
- Substitutional atoms diffuse by vacancy mechanism
-Interstitial atoms diffuse by forcing their way between the other larger atoms, i.e. interstitially

Vacancy mechanism of substitutional atom diffusion shown below:

For substitutional diffusion,

i) Atom should have sufficient vibrational energy ($\sim 3kT$) to force itself between the adjacent atoms = probability of jumping

ii) There has to be a vacancy site adjacent to the diffusing atom - depends on concentration of vacancies - depends on temperature
Interstitial diffusion involves interstitial sites

![Diagram of octahedral interstices in fcc and bcc crystal structures](image)

**Mechanism of interstitial diffusion:**

![Diagram of a (100) plane in an fcc lattice showing the path of an interstitial atom](image)

Typically an interstitial atom has vacant adjacent interstices, so interstitial diffusion is easier/faster as compared with substitutional diffusion.

Interstitial diffusion can be considered as a random jump process.

Example: consider a parent simple cubic lattice of A atoms. B atoms fit in the interstices without causing any appreciable distortion.

Assume that the solution of B in A is so dilute that every B atom has six possible vacant interstitial sites adjacent to it.

*Phase Transformations*
Concentration gradient of B atoms shown above
Consider the exchange of atoms between two adjacent atomic planes (1) and (2)
\( \Gamma_B = \text{random jump frequency of interstitial atom} \)
Plane (1) has \( n_1 \) atoms of B per unit area
Number of atoms that jump from plane (1) to (2) in 1 sec,
\[ \bar{J}_B = \frac{1}{6} \Gamma_B n_1 \]
\[
\bar{J}_B = \frac{1}{6} \Gamma_B n_2
\]
\[
J_B = \frac{1}{6} \Gamma_B (n_1 - n_2)
\]
\[
C_B(1) = \frac{n_1}{\alpha}, C_B(2) = \frac{n_2}{\alpha}
\]
\[
n_1 - n_2 = \alpha (C_B(1) - C_B(2))
\]
\[
C_B(1) - C_B(2) = -\alpha \frac{\partial C_B}{\partial x}
\]
\[
J_B = \left( -\frac{1}{6} \Gamma_B \alpha^2 \right) \frac{\partial C_B}{\partial x}
\]
\[
D_B = \frac{1}{6} \Gamma_B \alpha^2
\]
\[
J_B = -D_B \frac{\partial C_B}{\partial x}
\]

This is Fick’s first law of diffusion

D_B is the intrinsic diffusivity or diffusion coefficient of B and has units of m^2/sec

Typically D is considered independent of composition

Not always the case - e.g. carbon in fcc Fe at 1000°C for a solution containing 0.15 wt% C is \(2.5 \times 10^{-11}\) m^2/sec, increases to \(7.7 \times 10^{-11}\) m^2/sec for solution containing 1.4 wt% C (Why?)

Diffusion is also related to the random walk problem:

If the direction of jump for an atom is completely independent of the direction of the previous jump, then the case is termed a random walk problem.

Mathematically it can be shown that for an atom on a random walk, after n random steps, each of length \(\alpha\), the net displacement is

\[
r = \frac{\alpha}{\sqrt{n}}
\]

\[
n = \Gamma t, r = \frac{\alpha}{\sqrt{\Gamma t}}
\]

\[
r = \frac{2.4}{\sqrt{D t}}
\]
Effect of temperature - thermal activation on diffusion

Diffusion is a thermally activated process
Atoms are vibrating about their mean positions - occasionally a particularly violent oscillation will displace an interstitial atom to an adjacent vacant interstitial site - during this process lattice distortion is caused as shown below

\[ \Delta G_m \text{ is the activation energy for diffusion to take place} \]

Jump frequency \( \Gamma_B \),

\[ \Gamma_B = z \nu \exp \left( - \frac{\Delta G_m}{RT} \right) \]

Where \( z \) is the coordination number and \( \nu \) is the frequency of oscillation of the atoms

\[ D_B = \left[ \frac{1}{6} \alpha^2 z \nu \exp \left( \frac{\Delta S_m}{R} \right) \right] \exp \left( - \frac{\Delta H_m}{RT} \right) \]

\[ D_B = D_{B0} \exp \left( - \frac{Q_{ID}}{RT} \right) \]

Fig. 2.6  Interstitial atom, (a) in equilibrium position, (b) at the position of maximum lattice distortion. (c) Variation of the free energy of the lattice as a function of the position of interstitial. (After P.G. Shewmon, in *Physical Metallurgy, 2nd edn.*, R.W. Cahn (Ed.), North-Holland, Amsterdam, 1974.)
\[
\log D = \log D_0 - \frac{Q}{2.3RT}
\]

![Graph showing logarithmic relationship between \(D\) and \(1/T\).](image)

**Fig. 2.7** The slope of \(\log D\) v. \(1/T\) gives the activation energy for diffusion \(Q\).

**Steady-state diffusion:** concentration at any point does not change with time

Steady-state is reached when the concentration gradient everywhere is constant

Consider a thin-walled vessel, of thickness \(l\), containing hydrogen gas

Assuming the hydrogen outside (in atmosphere) is \(\sim 0\), the gas from inside the container diffuses outside till a steady-state is reached

\[
\frac{\partial C}{\partial x} = \frac{0 - C_H}{l}
\]

\[
J_H = \frac{D_H C_H}{l}
\]

**Non Steady-state diffusion:** Most real life situations, steady-state conditions are not achieved and the concentration varies as a function of both distance and time - Fick’s first law cannot be applied
Consider a concentration gradient as shown above.

Flux of atoms into plane (1) is \( J_1 \) and flux of atoms leaving plane (2) is \( J_2 \). Net accumulation of atoms within the volume \( A \delta x \) is proportional to \( J_1 - J_2 \).

\[
\delta C_B = \frac{(J_1 - J_2) A \delta t}{A \delta x}
\]

\( J_2 = J_1 + \frac{\partial J}{\partial x} \delta x \)

\( \delta t \to 0 \),

\[
\frac{\partial C_B}{\partial t} = - \frac{\partial J_B}{\partial x} \quad \text{Fick’s second law}
\]

\[
\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left( D_B \frac{\partial C_B}{\partial x} \right) = D_B \frac{\partial^2 C_B}{\partial x^2}
\]
Solution of diffusion equations: carburizing of steel
Increase the carbon concentration in the surface layers of steel for obtaining a harder and more wear resistant surface
Surface concentration of carbon maintained at a constant value by controlling the chemistry of a gas mixture containing CH₄ (or CO).
Concentration profiles of carbon obtained after different times shown below:

Analytical expression for these profiles can be obtained by solving Fick’s second law using boundary conditions, \( C(x=0) = C_S \) and \( C(x=\text{infinity}) = C_0 \)

\[
C = C_S - (C_S - C_0) \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
\]

\[
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2)dy
\]
erf(0.5) \sim 0.5, therefore, to determine the thickness of layer where the carbon concentration is midway between C_S and C_0 is

$$erf\left(\frac{x}{2\sqrt{Dt}}\right) = 0.5 = \frac{x}{2\sqrt{Dt}}$$

$$x = \sqrt{Dt}$$

Depth of any iso-concentration line is proportional to $\sqrt{Dt}$

Substitutional diffusion:
Atom can only jump if there is a vacancy in an adjacent site
Self-diffusion is the simplest form of substitutional diffusion - atom jumping substitutionally within the lattice of the same atom
Usually measured by introducing an isotope A* into A lattice - but they are identical in terms of jump frequency

$$D_A^* = D_A = \frac{1}{6} \alpha^2 \Gamma$$

Strictly speaking the above is based on the assumption that each jump is uncorrelated with the previous jump - holds good for interstitial diffusion but may not be the case for substitutional - Why?
Reason: In case of substitutional, if atom has jumped into vacant adjacent site, the subsequent jump of highest probability is back into the same vacant site - no net diffusive flux

$$D_A = f \frac{1}{6} \alpha^2 \Gamma, f < 1$$

Phase Transformations
However, it has been determined that in real systems $f \sim 1$
Atom can jump into adjacent vacant site provided it has sufficient thermal energy to overcome the activation barrier $\Delta G_m$
Probability of successful jump is $\exp\left(-\frac{\Delta G_m}{RT}\right)$ provided adjacent site is vacant - not often the case!
Probability that adjacent site is vacant = $zX_V$
Since, $\nu$ is the frequency of oscillation of the atoms, jump frequency,

$$\Gamma = \nu zX_V \exp\left(-\frac{\Delta G_m}{RT}\right)$$

$$X_V = \exp\left(-\frac{\Delta G_V}{RT}\right)$$

$$D_A = \frac{1}{6} \alpha^2 z \nu \exp\left(-\frac{\Delta G_m + \Delta G_V}{RT}\right)$$

$$D_A = \frac{1}{6} \alpha^2 z \nu \exp\left(\frac{\Delta S_m + \Delta S_V}{R}\right) \exp\left(-\frac{\Delta H_m + \Delta H_V}{RT}\right)$$

$$D_A = D_0 \exp\left(\frac{-Q_{SD}}{RT}\right)$$

$$D_0 = \frac{1}{6} \alpha^2 z \nu \exp\left(\frac{\Delta S_m + \Delta S_V}{R}\right)$$

$$Q_{SD} = \Delta H_m + \Delta H_V$$

For a given crystal structure and bond type, $Q/RT_m$ is roughly constant, $Q$ is proportional to the melting point
Rationale: higher the bond strength, higher the melting point, higher the values of $\Delta H_m$ and $\Delta H_V$, diffusion is more difficult
Vacancy diffusion:
Jumping of atoms into vacant sites can be considered as the jump of vacancy in the opposite direction
However, unlike atomic jumps, vacancy jumps always have adjacent atomic sites to jump into
Therefore, vacancies can be considered to have their own diffusion coefficient given by,

\[ D_V = \frac{1}{6} \alpha^2 \Gamma_V \]

\[ D_A = \left[ \frac{1}{6} \alpha^2 z V \exp \left( \frac{\Delta S_m}{R} \right) \right] \exp \left( -\frac{\Delta H_m}{RT} \right) \]

\[ D_V = D_A / X_V \]

Diffusion in substitutional alloys:

In case of self-diffusion all atoms are considered identical - so equal probability of any atom to jump into adjacent vacant site
Not so for alloy diffusion containing multiple species
Rate at which solvent (A) or solute (B) move into a vacant site is not equal - each species (A and B) have their own intrinsic diffusivity (\( D_A \) or \( D_B \))

A and B atoms moving at different rates through the same lattice, occupy the same type of lattice positions - \emph{induces a motion of the lattice through which A and B are diffusing}

\[ J_A = -D_A \frac{\partial C_A}{\partial x} \]

\[ J_B = -D_B \frac{\partial C_B}{\partial x} \]

Relative to the lattice

Across a given lattice plane
A and B blocks welded together to form a diffusion couple
Annealed at high temperature - concentration gradient results as shown above
Assume that the atoms per unit volume is constant for any composition,
\( C_0 = C_A + C_B \)
\[
\frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x}
\]
\[
J_A = -D_A \frac{\partial C_A}{\partial x} = D_B \frac{\partial C_A}{\partial x}
\]
\( D_A > D_B \)
\[
|J_A| > |J_B|
\]

**Flux of \( J_A \) means reverse flux (\( -J_A \)) of vacancies in opposite direction**

**Similarly, \( -J_B \) flux of vacancies**

**Net vacancy flux,**
\[
J_V = -J_A - J_B
\]
\[
J_V = (D_A - D_B) \frac{\partial C_A}{\partial x}
\]

*Fig. 2.15* Interdiffusion and vacancy flow. (a) Composition profile after interdiffusion of A and B. (b) The corresponding fluxes of atoms and vacancies as a function of position \( x \). (c) The rate at which the vacancy concentration would increase or decrease if vacancies were not created or destroyed by dislocation climb.

*Phase Transformations*
There is a net flux of vacancies across the diffusion couple as shown in the figure.

To maintain the vacancy concentration near equilibrium throughout the diffusion couple, vacancies have to be created on the B-rich side and then destroyed on the A-rich side.

Rate at which vacancies are created or destroyed at any point,

\[
\frac{\partial C_V}{\partial t} = - \frac{\partial J_V}{\partial x}
\]

Varies across the diffusion couple.

This net flux of vacancies leads to movement of the lattice.

Edge dislocations can act as effective sources or sinks for vacancies.

Vacancies can be absorbed by the extra half plane shrinking or plane can grow by emission of vacancies.

If this mechanism operates, then extra atomic planes will be added to B-rich side and removed from the A-rich side.

Consequently, lattice planes at the middle of the diffusion couple will be shifted to the left.

*Phase Transformations*
Velocity at which a given lattice plane moves can be related to the flux of vacancies crossing this plane, 
A is area of plane, moving with velocity \( v \), in time \( \delta t \) will sweep a volume of \( A \cdot v \cdot \delta t \cdot C_0 \) atoms 
Total number of vacancies crossing this plane = \( J_V \cdot A \cdot \delta t \) 
\[ J_V = v \cdot C_0 \]
\[ J_V = (D_A - D_B) \frac{\partial C_A}{\partial x} \]
\[ v = (D_A - D_B) \frac{\partial X_A}{\partial x} \]
Solving Fick’s second law for substitutional alloys 
Consider a thin slice of material \( \delta x \) at a distance \( x \) from one side of the couple

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*Fig. 2.18 A flux of vacancies causes the atomic planes to move through the specimen.*

*Fig. 2.19 Derivation of Fick’s second law for interdiffusion. (See text for details.)*

*Phase Transformations*
\[
\frac{\partial C_A}{\partial t} = - \frac{\partial J'_A}{\partial x}
\]

\[
J'_A = -D_A \frac{\partial C_A}{\partial x} + vC_A
\]

Flux of A atoms across a plane has two contributions:

(i) Usual diffusive flux

(ii) Flux \(vC_A\) due to the motion of the lattice

\[\nu = (D_A - D_B) \frac{\partial X_A}{\partial x}\]

\[J'_A = -(X_B D_A + X_A D_B) \frac{\partial C_A}{\partial x}\]

\[X_A = \frac{C_A}{C_0}, X_B = \frac{C_B}{C_0}\]

\[\tilde{D} = X_B D_A + X_A D_B \quad \text{Darken's equation}\]

\[J'_A = -\tilde{D} \frac{\partial C_A}{\partial x}\]

\[J'_B = -\tilde{D} \frac{\partial C_B}{\partial x} = \tilde{D} \frac{\partial C_A}{\partial x}\]

\[J'_A = -J'_B\]

Fick's second law becomes

\[
\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left( \tilde{D} \frac{\partial C_A}{\partial x} \right)
\]

Interdiffusion coefficient depends on the diffusivities of both B and A

*Phase Transformations*
Experimentally it is possible to determine the interdiffusion coefficient by determining the variation in $X_A$ and $X_B$ after annealing a diffusion couple at a certain temperature for a certain time - compare the analytical solutions of Fick’s second law with the measured compositional profile.

Determining the individual $D_A$ and $D_B$ are more challenging since these require knowledge of the velocity of the lattice during the diffusion process at a given point on the couple.

Experimentally the velocity of the lattice can be determined by inserting insoluble wires between the two diffusion blocks and annealing the diffusion couple - *Kirkendall effect*.

E.g. Insoluble Mo wires inserted between alpha brass (Cu-30wt %Zn) and pure Cu blocks, welded together and then annealed at certain temperature for certain time, the insoluble wires remain fixed to the lattice planes and their motion can be tracked.