Topic 2.4:
• Mass transport: diffusion.
DEFINITION OF DIFFUSION

**Diffusion (transport phenomena):** mechanisms by which material is transported through the material.

*Diffusion in solids* ⇒ movement of atoms within a solid ⇒ The thermal vibrations in solids permit movement of some atoms ⇒ Phenomena that need thermal activation

**Diffusion:** movement of atoms through the material.
DIFFUSION is **RAPID** in...
- Open crystalline structures
- Materials with low $T_m$
- Increasing the $T$

DIFFUSION is **SLOWER** in...
- Compact crystalline structures
- Materials with high $T_m$
- Covalent materials
- Large species
What is necessary for diffusion?

**EMPTY SITE**

**ENERGY**

Mechanisms of diffusion

**Vacancies**

**Interstitials**

**DIFFUSION MECHANISMS**
DIFFUSION MECHANISMS

**Self-diffusion**: atoms exchanging positions are of the same type (pure metals)

![Diagram showing self-diffusion process]

Potential Energy of atoms as a function of their position
Atoms movement

1) $\Delta E_{\text{thermal}}$ to overcome $E_{\text{activation}}$

2) Displacement of vacancies or defects. Vacancies are defects in equilibrium and are always present.

As $T \uparrow$ $\Rightarrow$ $\{\uparrow$ [defects] $\uparrow$ $E_{\text{thermal}} \leftrightarrow E_{\text{act}}\} \Rightarrow \uparrow$ diffusion

VACANCY DIFFUSION
ACTIVATION ENERGY

- When $T_{\text{melting}} \uparrow \Rightarrow E_{a} \uparrow$
- Given that if $T_{m} \uparrow \Rightarrow E_{\text{bond}} \uparrow$

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Temperature (°C)</th>
<th>Crystal structure</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>419</td>
<td>HCP</td>
<td>91.6</td>
</tr>
<tr>
<td>Aluminium</td>
<td>660</td>
<td>FCC</td>
<td>165</td>
</tr>
<tr>
<td>Copper</td>
<td>1083</td>
<td>FCC</td>
<td>196</td>
</tr>
<tr>
<td>Nickel</td>
<td>1452</td>
<td>FCC</td>
<td>293</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2600</td>
<td>BCC</td>
<td>460</td>
</tr>
</tbody>
</table>
Atoms in interstitial positions are displaced to other interstitial positions **without displacing** permanently any atoms of the matrix.

The atoms that diffuse interstitially are small with respect to the matrix (i.e.: in metals: C, H, O, N)

**Interstitial diffusion**:  
- Has $E_a < \text{Diffusion of Vacancies}$  
- It is more rapid  
- There are many more interstitial sites than vacancies
STEADY STATE DIFFUSION : Fick's 1st law

The rate at which the atoms diffuse in a material can be measured by a diffusion flux, $J$, defined as the number of atoms that passing through a plane of unit area per unit time.

$\delta C/\delta x =$ concentration gradient in x direction (at/m³ or kg/m³)

$D =$ diffusivity or diffusion coefficient (m²/s)

$J = n^o \text{ atoms (or mass) per unit surface and time along distance } x \ (\text{at/m}^2\text{s or kg/m}^2\text{s})$

$Fick\text{'s 1st Law}$

$J = -D \frac{\delta C}{\delta x}$

Units of diffusion: $m^2/s$
**Steady state conditions:** The concentration of solute atoms at any point does not change with time. 
The diffusion flux does not change with time

\[
\frac{\partial J}{\partial t} = 0
\]

It is created putting in contact 2 materials with different composition. \( J \) at a \( T \) is constant only if the compositions are constant on each side \( \Rightarrow \) if the composition gradient is constant
STEADY STATE DIFFUSION: example

Example: Diffusion of inert gas through a layer of Pd. H₂ Purification

\[ J = -D \frac{\Delta C}{\Delta x} \]

Determine the thickness of a plate of Pd with transversal area of 0.2m² so that it can purify \( 1.733 \cdot 10^{-3} \) kg/h of hydrogen, if the hydrogen concentration at the side of high pressure of the plate is 1.5 kg/m³ and at the side of low pressure is 0.3 kg/m³. The diffusion coefficient of hydrogen in Pd is \( 1 \cdot 10^{-8} \) m²/s.

\[ \frac{\Delta C}{\Delta x} = \frac{C_{\text{ext}} - C_{\text{int}}}{x_1 - x_2} \]

The total mass of purified hydrogen depends on the flow of atoms that have passed through the Pd plate surface:

\[ \text{flux} = \frac{\text{mass}}{\text{area} \cdot \text{time}} \Rightarrow J = \frac{1.733 \cdot 10^{-3}}{0.2} = \frac{8.65 \cdot 10^{-3}}{0.2} \frac{kg}{m^2 h} = 2.4 \cdot 10^{-5} \frac{kg}{m^2 s} \]

\[ J = -D \frac{\delta C}{\delta x} \approx -D \frac{(C_a - C_b)}{\Delta x} = 1.0 \cdot 10^{-8} \frac{(1.5 - 0.3)}{\Delta x} = 2.4 \cdot 10^{-6} \text{kg m}^{-2} \text{s}^{-1} \Rightarrow \Delta x = 5 \text{mm} \]
NON-STEADY STATE DIFFUSION: Fick's 2\textsuperscript{nd} law

For the majority of materials ⇒ diffusion is \textit{non-steady state (transient)}: The concentration of solute atoms at any point of the material changes with time.

Non stationary state ⇒ The substances come to an end through extinction

\[
\frac{\delta C_x}{\delta t} = \frac{\delta}{\delta x} \left( D \frac{\delta C}{\delta x} \right)
\]

The diffusion flux and concentration gradient at some particular point in the solid vary with time, resulting in net accumulation or depletion of diffusing species.
**NON-STEADY STATE DIFFUSION : Fick's 2\textsuperscript{nd} law**

**HYPOTHESIS:** if $D \neq f(C)$ i.e. diffusion coeff. is independent of composition (there is no interaction between diffusing atoms)

\[
\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2}
\]

Rate of composition change \hspace{1cm} = \hspace{1cm} DIFFUSIVITY $\times$ Rate of composition gradient change

**For Boundary conditions:**

$t=0$, $C=C_0$ at $0 \leq x \leq \infty$.

$t>0$, $\rightarrow C=C_s$ at $x=0$ (surface concentration cnt.)

$\rightarrow C=C_0$ at $x=\infty$

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

$C_x$ = concentration at a distance $x$ after time $t$

$Erf$ = Gaussian error function
Example: diffusion of a gas (with constant surface concentration) in the interior of a semi infinite solid (carbon diffusion in steel, saturation of a metal with atmospheric gases)

\[ \frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \]

\[ z \quad \text{erf} (z) \quad z \quad \text{erf} (z) \]
\[
\begin{array}{cccc}
0.00 & 0.0000 & 0.70 & 0.6778 \\
0.01 & 0.0113 & 0.75 & 0.7112 \\
0.02 & 0.0226 & 0.80 & 0.7421 \\
0.03 & 0.0338 & 0.85 & 0.7707 \\
0.04 & 0.0451 & 0.90 & 0.7969 \\
0.05 & 0.0564 & 0.95 & 0.8209 \\
0.10 & 0.1125 & 1.00 & 0.8427 \\
0.15 & 0.1680 & 1.10 & 0.8802 \\
0.20 & 0.2227 & 1.20 & 0.9103 \\
0.25 & 0.2763 & 1.30 & 0.9340 \\
0.30 & 0.3286 & 1.40 & 0.9523 \\
0.35 & 0.3794 & 1.50 & 0.9661 \\
0.40 & 0.4284 & 1.60 & 0.9763 \\
0.45 & 0.4755 & 1.70 & 0.9838 \\
0.50 & 0.5205 & 1.80 & 0.9891 \\
0.55 & 0.5633 & 1.90 & 0.9928 \\
0.60 & 0.6039 & 2.00 & 0.9953 \\
0.65 & 0.6420 & & \\
\end{array} \]

C_t may be determined at any time and position if the parameters C_0, C_s and D are known.
### DIFFUSIVITY

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent Structure solvent</th>
<th>Diffusivity at 500°C m²/s</th>
<th>Diffusivity at 1000°C m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>Iron FCC</td>
<td>5 x10^{-15}</td>
<td>3 x10^{-11}</td>
</tr>
<tr>
<td>Carbon</td>
<td>Iron BCC</td>
<td>10^{-12}</td>
<td>2 x10^{-9}</td>
</tr>
<tr>
<td>Iron</td>
<td>Iron FCC</td>
<td>2 x10^{-23}</td>
<td>2 x10^{-16}</td>
</tr>
<tr>
<td>Iron</td>
<td>Iron BCC</td>
<td>10^{-20}</td>
<td>3 x10^{-14}</td>
</tr>
<tr>
<td>Nickel</td>
<td>Iron FCC</td>
<td>10^{-23}</td>
<td>2 x10^{-16}</td>
</tr>
<tr>
<td>Manganese</td>
<td>Iron FCC</td>
<td>3 x10^{-24}</td>
<td>10^{-16}</td>
</tr>
<tr>
<td>Silver</td>
<td>Silver (crystal)</td>
<td>-</td>
<td>10^{-12}</td>
</tr>
<tr>
<td>Silver</td>
<td>Silver (grain boundary)</td>
<td>10^{-11}</td>
<td>-</td>
</tr>
<tr>
<td>Carbon</td>
<td>Titanium HCP</td>
<td>3 x10^{-16}</td>
<td>2 x10^{-11}</td>
</tr>
</tbody>
</table>

*metastable phases*
FACTORS THAT INFLUENCE DIFFUSIVITY

a) Diffusion mechanism: Atom size
   C diffuses interstitially in Fe-γ
   Fe diffuses by vacancy diffusion in Fe-γ

b) Type of crystalline structure of the matrix lattice (solvent)
   \[ D_{(C \text{ in } Fe-\gamma, \text{ FCC})} = 5 \times 10^{-15} \text{ m}^2/\text{s} < D_{(C \text{ in } Fe-\alpha, \text{ BCC})} = 10^{-12} \text{ m}^2/\text{s} \]

   packing factor (BCC) < packing factor (FCC)
   \[ d_{\text{interatomic (BCC)}} > d_{\text{interatomic (FCC)}} \]

c) Type of imperfections or defects in the crystal:
   Open structures (more holes) \( \Rightarrow \uparrow D \)
   \[ D_{\text{surface}} > D_{\text{grain boundary}} > D_{\text{volume}} \]
FACTORS THAT INFLUENCE THE DIFFUSIVITY

d) Concentration of species that diffuse
When we ↑ the concentration of solute atoms we modify D.

e) Temperature
↑T ⇒ ↑D
Diffusion of atoms: when ↑ T, ↑ amplitude of vibration of atoms ⇒ greater probability of jump ⇒ D↑
D = f (T) Experimentally we find there is an Arrhenius type dependence:

\[
\ln(D) = \ln(D_0) - \frac{E_D}{R \cdot T}
\]

\[
D = D_0 e^{-\frac{E_D}{R \cdot T}}
\]

- Q/R

1/T

\[\text{D} = \text{diffusivity (m}^2/\text{s})\]
\[\text{D}_0 = \text{proportional coeff. (frequency factor)}\]
\[E_D = \text{activation energy necessary to produce the diffusive movement of 1 mol of atoms}\]
\[R = \text{gas constant}\]
\[T = \text{Temperature (K)}\]
Cementation of gears $\text{CH}_4 - \text{H}_2$

Fabrication of integrated circuits with Si wafers: diffusion of impurities.

Si powder nitriding: $\text{Si}_3\text{N}_4$

Diffusion soldering

Sintering
Case Hardening - Cementation (Interstitial diffusion) Diffusion of C atoms in the surface of a steel component.

The C atoms “block” the movement of dislocations, deform the lattice, make more difficult plastic deformation \(\Rightarrow\) **Hardening**
The excess of C in the surface leaves a state of residual stresses in **compression**