Diffusion

- Mass transport by atomic motion

Mechanisms

- Gases & Liquids – random (Brownian) motion
- Solids – vacancy diffusion or interstitial diffusion

\[ D_{\text{gasses}} > D_{\text{liquids}} > D_{\text{solids}} \]
Interdiffusion: In an alloy, atoms tend to migrate from regions of high concentration to regions of low concentration.

Initially

After some time
Diffusion

- Self-diffusion: In an elemental solid, atoms also migrate.

Label some atoms

![Diagram showing self-diffusion](image)

After some time

Often self-diffusion can be best characterised by radioisotope-marking, since the atoms of different isotopes are virtually identical chemically. Radiation profiles are readily traceable in macroscopic samples.
Vacancy Diffusion:

- atoms exchange with vacancies
- applies to substitutional impurities atoms
- rate depends on:
  - number of vacancies
  - activation energy to exchange.
Diffusion Mechanisms

- Interstitial diffusion – smaller atoms can diffuse between atoms.

More rapid than vacancy diffusion!

Degree of interstitialcy – obvious definition…
Case Hardening:
- Diffuse carbon atoms into the host iron atoms at the surface.
- Example of interstitial diffusion is a case hardened gear.

Result:
The presence of C atoms makes iron (steel) harder.
Carburising of steel

Note: Distances in thousands of inch. Times in hours.
Carburising of steel

Fe₃C (cementite)

\( T(°C) \)

\( δ \)

\( γ \)

\( γ + L \)

\( L \)

\( L + \text{Fe}_3\text{C} \)

\( \gamma + \text{Fe}_3\text{C} \)

\( α \)

\( α + \text{Fe}_3\text{C} \)

\( 727°C = T_{\text{eutectoid}} \)

\( 1.4% \)

\( \text{Fe}_3\text{C} \text{ (cementite)} \)

\( C_o, \text{ wt}\% \text{ C} \)

\( \text{(Fe)} \)

\( \text{(austenite)} \)
Doping silicon with phosphorus for $n$-type regions:

Process:

1. Deposit P rich layers on surface.
2. Heat it.
3. Result: Doped semiconductor regions.

![magnified image of a Si chip](image)

- **light regions**: Si atoms
- **light regions**: Al atoms

0.5 mm
Diffusion

- How do we quantify the amount or rate of diffusion?

\[ J \equiv \text{Flux} \equiv \frac{\text{moles (or mass) diffusing}}{(\text{surface area})(\text{time})} = \frac{\text{mol}}{\text{cm}^2 \text{s}} \text{ or } \frac{\text{kg}}{\text{m}^2 \text{s}} \]

- Measured empirically
  - Make thin film (membrane) of known surface area
  - Impose concentration gradient
  - Measure how fast atoms or molecules diffuse through the membrane

\[ J = \frac{M}{At} = \frac{1}{A} \frac{dM}{dt} \]

\( M = \) mass diffused

\( J \propto \text{slope} \)
Steady-State Diffusion

Rate of diffusion independent of time
Flux proportional to concentration gradient = \( \frac{dC}{dx} \)

Fick’s first law of diffusion

\[
J = -D \frac{dC}{dx}
\]

\( D \equiv \text{diffusion coefficient} \)
\([D] = \text{m}^2/\text{s}\)

if linear
\[
\frac{dC}{dx} \approx \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1}
\]
Example: Chemical Protective Clothing (CPC)

- Methylene chloride is a common ingredient of paint removers. Besides being an irritant, it also may be absorbed through skin. When using this paint remover, protective gloves should be worn.

- If butyl rubber gloves (0.04 cm thick) are used, what is the diffusive flux of methylene chloride through the glove?

- Data:
  - diffusion coefficient in butyl rubber: $D = 110 \times 10^{-8}$ cm$^2$/s
  - surface concentrations: $C_1 = 0.44$ g/cm$^3$  
    $C_2 = 0.02$ g/cm$^3$
Example (cont).

- **Solution** – assuming linear conc. gradient

\[ J = - D \frac{dC}{dx} \approx -D \frac{C_2 - C_1}{x_2 - x_1} \]

Data:  
\[ D = 110 \times 10^{-8} \text{ cm}^2/\text{s} \]
\[ C_1 = 0.44 \text{ g/cm}^3 \]
\[ C_2 = 0.02 \text{ g/cm}^3 \]
\[ x_2 - x_1 = 0.04 \text{ cm} \]

\[ J = - (110 \times 10^{-8} \text{ cm}^2/\text{s}) \frac{(0.02 \text{ g/cm}^3 - 0.44 \text{ g/cm}^3)}{(0.04 \text{ cm})} = 1.16 \times 10^{-5} \text{ g/cm}^2\text{s} \]
Diffusion and Temperature

- Diffusion coefficient increases with increasing $T$.

\[
D = D_o \exp \left( - \frac{Q_d}{RT} \right)
\]

$D$ = diffusion coefficient [m$^2$/s]
$D_o$ = pre-exponential [m$^2$/s]
$Q_d$ = activation energy [J/mol or eV/atom]
$R$ = gas constant [8.314 J/mol-K]
$T$ = absolute temperature [K]
Diffusion and Temperature

$D$ has exponential dependence on $T$

$D \propto e^{-E_a/kT}$

$D$ (m$^2$/s)

$10^{-8}$

$10^{-14}$

$10^{-20}$

$T$ (°C)

1500

1000

500

300

$1000K/T$

$D_{\text{interstitial}}$  $D_{\text{substitutional}}$

C in $\gamma$-Fe  Al in Al

C in $\alpha$-Fe  Fe in $\alpha$-Fe

Fe in $\gamma$-Fe

$D$ transform data

$\ln D$  $1/T$

Temp = $T$
Example: At 300°C the diffusion coefficient and activation energy for Cu in Si are

\[ D(300^\circ\text{C}) = 7.8 \times 10^{-11} \text{ m}^2/\text{s} \]
\[ Q_d = 41.5 \text{ kJ/mol} \]

What is the diffusion coefficient at 350°C?

\[
\ln D_2 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_2} \right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R} \left( \frac{1}{T_1} \right)
\]

\[
: \quad \ln D_2 - \ln D_1 = \ln \frac{D_2}{D_1} = - \frac{Q_d}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]
Example (cont.)

\[ D_2 = D_1 \exp \left[ -\frac{Q_d}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] \]

\[ D_2 = (7.8 \times 10^{-11} \text{ m}^2/\text{s}) \exp \left[ \frac{-41,500 \text{ J/mol}}{8.314 \text{ J/mol-K}} \left( \frac{1}{623 \text{ K}} - \frac{1}{573 \text{ K}} \right) \right] \]

\[ D_2 = 15.7 \times 10^{-11} \text{ m}^2/\text{s} \]
Non-steady State Diffusion

- The concentration of diffusing species is a function of both time and position \( C = C(x,t) \)
- In this case *Fick’s Second Law* is used

Fick’s Second Law

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]
Non-steady State Diffusion

- Copper diffuses into a bar of aluminum.

B.C. at \( t = 0 \), \( C = C_o \) for \( 0 \leq x \leq \infty \)

at \( t > 0 \), \( C = C_S \) for \( x = 0 \) (const. surf. conc.)

\[ C = C_o \text{ for } x = \infty \]
**Solution:**

\[ C(x,t)-C_o \over C_s-C_o = 1-\text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \]

\( C(x,t) = \text{Conc. at point } x \text{ at time } t \)

\( \text{erf}(z) = \text{Gaussian error function} \)

\[ = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} \, dy \]

\[ \tau = \frac{(\Delta x)^2}{16D} \]

Characteristic diffusion time necessary to penetrate an infinite slab of thickness \( \Delta x \), for about 0.5% concentration threshold.
Non-steady State Diffusion

- Sample Problem: An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.

- Solution: use equation

\[
\frac{C(x, t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)
\]
Solution (cont.):

\[
\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)
\]

- \( t = 49.5 \text{ h} \) \( x = 4 \times 10^{-3} \text{ m} \)
- \( C_x = 0.35 \text{ wt\%} \) \( C_s = 1.0 \text{ wt\%} \)
- \( C_o = 0.20 \text{ wt\%} \)

\[
\frac{C(x,t) - C_o}{C_s - C_o} = \frac{0.35 - 0.20}{1.0 - 0.20} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - \text{erf}(z)
\]

\[
\therefore \text{erf}(z) = 0.8125
\]
We must now determine from table the value of $z$ for which the error function is 0.8125.

<table>
<thead>
<tr>
<th>$z$</th>
<th>erf($z$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.7970</td>
</tr>
<tr>
<td>0.95</td>
<td>0.8209</td>
</tr>
<tr>
<td>$z$</td>
<td>0.8125</td>
</tr>
</tbody>
</table>

$z = 0.93$

Now solve for $D$

$\frac{z - 0.90}{0.95 - 0.90} = \frac{0.8125 - 0.7970}{0.8209 - 0.7970}$

$D = \frac{x^2}{4z^2t}$

$D = \frac{x^2}{4z^2t} = \frac{(4 \times 10^{-3} \text{ m})^2}{(4)(0.93)^2(49.5 \text{ h})} \frac{1 \text{ h}}{3600 \text{ s}} = 2.6 \times 10^{-11} \text{ m}^2/\text{s}$
To solve for the temperature at which $D$ has above value, we use a rearranged form of

$$D = D_o \exp\left(-\frac{Q_d}{RT}\right)$$

for diffusion of C in FCC Fe

$D_o = 2.3 \times 10^{-5}$ m$^2$/s  \hspace{1cm} Q_d = 148,000 J/mol

$$T = \frac{Q_d}{R(\ln D_o - \ln D)}$$

$$T = \frac{148,000 \text{ J/mol}}{(8.314 \text{ J/mol-K})(\ln 2.3 \times 10^{-5} \text{ m}^2/\text{s} - \ln 2.6 \times 10^{-11} \text{ m}^2/\text{s})}$$

$$T = 1300 \text{ K} = 1027^\circ \text{C}$$