VI. Diffusion in Solids

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Examples

• Ink in water

• Biology

• Smell

Transpiration
Definition

Diffusion: The dispersal of material by random atom or molecular movement from regions of high concentration to those of lower concentration.

The result of diffusion is to decrease the concentration non-uniformity.
Ni-Cu alloy

Ni in Cu

Cu in Ni

x = 0

concentration

0

100

t = 0

t = \infty

t = t_1
Diffusion Mechanism

Vacancy diffusion

Interstitial diffusion
Activation Energy

$$\Delta G = \Delta H - T\Delta S$$

Vibration frequency: $v$

Nearest neighbor sites: $z$

Jump Frequency:

Interstitial diffusion

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\Delta H_m \gg T\Delta S_m$$

$$\Gamma =$$

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

Vacancy diffusion

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

- Applies to substitutional impurities
- Atoms must hop to open vacancy
- Rate depends on probability of overcoming migration activation energy, $Q_m$
  \[ p_Q = B \exp(-H_m/kT) \]
  And
  \[ p_v = N_v/N = \exp(-H_v/kT) \]
  - Probability of a vacancy
  - Here is Diffusion Coefficient is:
  \[ D = D_0 \exp(-H_d/kT) \]
  where $H_d = H_m + H_v$
Interstitial Diffusion

- Applies to interstitial impurities (tend to be low concentration)
- Most interstitial sites are not occupied
- More rapid than vacancy diffusion
- Activation energy involves overcoming the migration activation energy, $H_m$.
- Rate is defined by the Diffusion Coefficient
  \[ D = D_0 \exp\left(-\frac{H_d}{kT}\right) \]

where $D_0$ is a pre-exponential factor (m$^2$/s) and $H_d = H_m$
## Data

### Interstitial diffusion in Fe

<table>
<thead>
<tr>
<th>solute</th>
<th>$\Delta H_m$(kJmol$^{-1}$)</th>
<th>$D_0$(10$^{-6}$m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>84</td>
<td>2.0</td>
</tr>
<tr>
<td>N</td>
<td>76</td>
<td>0.3</td>
</tr>
<tr>
<td>H</td>
<td>13</td>
<td>0.1</td>
</tr>
</tbody>
</table>

### Self-diffusion data for metals

<table>
<thead>
<tr>
<th>metal</th>
<th>$T_m$(K)</th>
<th>$Q$ (kJmol$^{-1}$)</th>
<th>$D_0$ (10$^{-6}$m$^2$s$^{-1}$)</th>
<th>$D(T_m)$ (10$^{-12}$m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>933</td>
<td>142</td>
<td>170</td>
<td>1.9</td>
</tr>
<tr>
<td>Cu</td>
<td>1356</td>
<td>200</td>
<td>31</td>
<td>0.59</td>
</tr>
<tr>
<td>Ni</td>
<td>1726</td>
<td>279</td>
<td>190</td>
<td>0.65</td>
</tr>
<tr>
<td>$\gamma$-Fe</td>
<td>1805</td>
<td>284</td>
<td>49</td>
<td>0.29</td>
</tr>
</tbody>
</table>

![Diagram](image)
Other Diffusion Mechanisms

- Direct exchange
- Zener ring
Fick’s First Law

\[ n_2 = n_1 + a \frac{dn}{dx} \quad \nu: \text{Jump Frequency} \]

\[ \tau = \frac{1}{\nu} : \text{average time if atom stay at the lattice site} \]

**Jump Frequency along x direction**:

\[ J = J_{1\rightarrow 2} - J_{2\rightarrow 1} \]

\[ J = a \left( \frac{1}{6\tau} n_1 - \frac{1}{6\tau} n_2 \right) \]

\[ = -a^2 \frac{1}{6\tau} \frac{dn}{dx} \]
Geometric Factor and Diffusion Coefficient

\[ J = -D \frac{dn}{dx} \]
\[ J = J_{1\rightarrow2} - J_{2\rightarrow1} \]

\[ D = \alpha \frac{a^2}{\tau} \]

- Lattice parameter
- Average stay time at interstitial site
- Diffusion constant
- Geometric factor

Einstein formula

\[ D = \frac{1}{6} \frac{1}{\tau} \lambda^2 \]

\( \lambda \): jump distance

Simple cubic

- \( \lambda = a \)
- \( \alpha = \frac{1}{6} \)

FCC

- \( \lambda = \frac{\sqrt{2}}{2} a \)
- \( \alpha = \frac{1}{12} \)

BCC

- \( \lambda = \frac{\sqrt{3}}{2} a \)
- \( \alpha = \frac{1}{8} \)
Steady State Diffusion

Steady state: the state where the concentration profile does not change with time, which means at any time the concentration at certain spot in space is a constant.

**Fick’s first law:**

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

n: number density
Fick’s Second Law
Diffusion into a Semi-infinite Solid

$t \leq 0$, before diffusion start

$n(x) = n_0, \ 0 \leq x \leq \infty$

$t > 0$, diffusion start

$n(x=0) = n_s, \ n(x = \infty) = n_0$

Solution to the Fick’s second law

$$\frac{n_x(t) - n_0}{n_s - n_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

, erf: Gaussian error function

Fixed surface concentration.
Error function \[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-\xi^2} d\xi \]
Hydrogen gas purification can be achieved by pass mixed gas through palladium sheet. Assume the there is a hydrogen purification system with cross-sectional area of 0.2m², the palladium film thickness is 10mm hydrogen concentration on the two sides are 3kg/m³ and 0.5kg/m³. If the room temperature hydrogen diffusion coefficient in Pd is $1.0 \times 10^{-15}$ m²/s and the activation energy is 27.8kJ/mol. Calculate the pure hydrogen generation speed (kg/hour) when the system works at 500°C.
I. What we know:

- $C_1 = 3\text{kg/m}^3$, $C_2 = 0.5\text{kg/m}^3$
- Palladium film thickness $d=10\text{mm} = 0.01\text{m}$
- Diffusion area $A=0.2\text{m}^2$
- $D @ 300K = 1.0 \times 10^{-11}\text{m}^2/\text{s}$
- $Q_d = 27.8\text{kJ/mol}$

Calculate how much hydrogen can diffuse through in 1 hour at 500°C.
Diffusion into a Semi-infinite Solid

II. Calculate the carburizing time to achieve 0.45 wt% C at a position of 2mm into a 0.2 weight percent steel. Sample was maintained at 1000°C with 1.3 wt% carbon atmosphere.
Diffusion Coefficient and Thermally Activated Process

Thermally activated processes: The processes have exponentially increasing rates versus temperature.

Vacancy formation, electrical conductivity, creep and diffusion are thermally activated processes.

\[ D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \]

- \( D_0 \): temperature independent parameter (m\(^2\)/s).
- \( Q_d \): activation energy for diffusion (J/mol).
- \( R \): gas constant 8.31 J/mol\( \cdot \)K
- \( T \): absolute temperature
**Arrhenius Plot**

\[ rate = C \exp\left(-\frac{Q}{RT}\right) \]

\[ \log(rate) = \log(C) - \frac{Q}{RT} \]

Arrhenius Plot: \( \log(\text{rate}) \) vs. \( \frac{1}{T} \)

From the slope the thermal activation energy can be calculated
Diffusion and Temperature

$D$ has exponential dependence on $T$

\[
D \propto \exp \left( \frac{-\Delta F}{RT} \right)
\]

Graph showing diffusion coefficients for various elements in different phases of iron at different temperatures. The graph illustrates that diffusion coefficients are higher for interstitial sites compared to substitutional sites, with specific examples given for carbon in different phases of iron and aluminum in aluminum.