ASSIGNMENT
STUDY ALL 4.4

DIFFUSION

Living things move

ATOMS ARE VERY SMALL THINGS, THEREFORE THEY MOVE WITH TEMPERATURE

Temperature > 0

Random walks jump around
(Drunk man) Example

T↑ = MORE JUMPS
GAS = CONSTANT JUMPS (PRESS)
LIQUIDS = FREQUENT JUMPS
SOLIDS = OCCASIONAL JUMPS

Solid diffusion
Modeling like atoms between two planes

• Pick 2 layers A and B and think A is solute in an environment of B

⇒ DEFINE \( c_A = \text{concentration} \)

\[
\begin{align*}
A & \xrightarrow{J_{12}} B \\
\text{If } c_2 > c_1 & \Rightarrow J_{21} > J_{12} \\
\text{If } c_2 < c_1 & \Rightarrow J_{21} < J_{12}
\end{align*}
\]

\[
J_{\text{total}} = -(c_2 - c_1) \cdot \frac{\text{flux}}{c} = -\Delta c
\]

Assumption

DF4
2) WHAT ABOUT $\Delta x$? FURTHER THEY ARE AND LESS LIKELY THEY JUMP! WHY?

$\Delta x$ SMALL $\Delta x$ BIG

$J_{21} > J_{12}$

$J_{tot} = \rightarrow$

$\Rightarrow J_{tot} \propto \frac{1}{\Delta x}$ ASSUMPTION

3) ATOMS TRY TO JUMP AT A FREQUENCY, THIS FREQUENCY DEPENDS ON TEMPERATURE

$\Rightarrow$

FICK'S LAW

$\bar{J} = D \left( \frac{-\partial c}{\partial x} \right)$

$\bar{J} = \frac{\# \text{ particles crossing}}{\text{UNIT AREA} \times \text{SECOND}}$

$J = [m^{-2}s^{-1}]$

$c = [\frac{1}{m^3}]$

$x = [m]$

$D = [m^2s^{-1}]$

$\Rightarrow c = \frac{1}{[m^3]}$

IDENTICAL TO HEAT FLUX \[ \Rightarrow \text{FLUX OF HEAT} \]

$\bar{J}_q = k \frac{\text{Temp.-Temp.}}{\Delta x}$

$= -k \frac{\partial T}{\partial x}$

SAME
TEMPERATURE DEPENDENCE?

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

\[ = D_0 \exp \left( \frac{-\Delta G}{kT} \right) \]

\( \Rightarrow \) log \( D \) vs \( 1/T \)

\( \Delta G = 0 \Rightarrow \frac{\partial C}{\partial x} = 0 \)

\( \Rightarrow J_{\text{tot}} = 0 \) \text{ (Correct)}

\( \begin{align*}
J_{\text{tot}} &= J_{22} - J_{21} = 0 \\
J_{22} &\rightarrow J_{21}
\end{align*} \)

Remember \( J > 0 \) if \( u \) same direction of \( z \)

IF \( T > 0 \& u \) always have stuff moving!!

But if \( \frac{\partial C}{\partial x} = 0 \) (homogeneous)

Then \( \Delta \) same amount goes right \& left

\( \Rightarrow \) overall \( = 0 \) \text{ (Ultra-Huge-Important)}
MECHANISM OF DIFFUSION IN COVALENT AND METALLIC CRYSTALS

EXAMPLE EXTRA CARBON IN STEEL, IMPURITY DIFFUSION!

IN SOLIDS WITH EXTRA INTERSTITIAL SPACE ALWAYS AVAILABLE

USUALLY ACTIVATION ENERGIES

\[ Q_v > Q_i \]

NEED ENERGY TO FORM VACANCY TOO!!

WHAT ABOUT WITHOUT IMPURITIES IN PURE SYSTEMS ATOMS DIFFUSE TOO!

IT'S SELF DIFFUSION

IN SOLID SOLUTIONS WITH DEFECTS THE DARK ATOM NEEDS HELP OF A VACANCY

\[ \Rightarrow \text{PROP DEPENDS ON CONCENTRATION OF VACANCIES} \]

\[ \Rightarrow \text{D(C)} \]

FIGURE 4.4-5 Diffusion of radioactive isotopes in a matrix of the same atomic species. Increasing time is indicated in (a), (b), and (c). With time the radioactive species diffuse into the surrounding material. By measuring the concentration profiles at different times, the tracer diffusion constant can be determined.

DF4 SINCE ATOMS ARE IDENTICAL YOU CANNOT RECOGNIZE \Rightarrow NEED FOR COLOR!! \Rightarrow TAKE ISOTOPE
FIGURE 4.4-6 Self-diffusion coefficients for selected metals. The data were extrapolated to "infinite" temperature to demonstrate $D_0$. Data obtained from several sources.

TABLE 4.4-1 Diffusion coefficients for selected systems.

<table>
<thead>
<tr>
<th>Material</th>
<th>$D_0$ (m/s)</th>
<th>$Q$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-diffusion coefficients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>$4.32 \times 10^{-1}$</td>
<td>227</td>
</tr>
<tr>
<td>Cu</td>
<td>$2.00 \times 10^{-8}$</td>
<td>97</td>
</tr>
<tr>
<td>Ag</td>
<td>$4.03 \times 10^{-7}$</td>
<td>184</td>
</tr>
<tr>
<td>Au</td>
<td>$9.10 \times 10^{-8}$</td>
<td>283</td>
</tr>
<tr>
<td>Fe</td>
<td>$4.18 \times 10^{-5}$</td>
<td>283</td>
</tr>
<tr>
<td>Si</td>
<td>$1.10 \times 10^{-3}$</td>
<td>283</td>
</tr>
<tr>
<td>Fe in melt</td>
<td>$2.10 \times 10^{-4}$</td>
<td>283</td>
</tr>
<tr>
<td>Impurity diffusion coefficients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu in Ag</td>
<td>$1.40 \times 10^{-1}$</td>
<td>191</td>
</tr>
<tr>
<td>Cu in Al</td>
<td>$6.50 \times 10^{-1}$</td>
<td>325</td>
</tr>
<tr>
<td>Zn in Ag</td>
<td>$3.40 \times 10^{-1}$</td>
<td>174</td>
</tr>
<tr>
<td>Zn in Cu</td>
<td>$3.40 \times 10^{-1}$</td>
<td>191</td>
</tr>
<tr>
<td>Ni in Cu</td>
<td>$2.70 \times 10^{-1}$</td>
<td>256</td>
</tr>
<tr>
<td>Ni in Fe</td>
<td>$7.70 \times 10^{-1}$</td>
<td>280</td>
</tr>
<tr>
<td>Cu in BCC Fe</td>
<td>$2.00 \times 10^{-1}$</td>
<td>84</td>
</tr>
<tr>
<td>Cu in FCC Fe</td>
<td>$2.00 \times 10^{-1}$</td>
<td>147</td>
</tr>
<tr>
<td>Ni in Fe</td>
<td>$3.00 \times 10^{-1}$</td>
<td>78</td>
</tr>
<tr>
<td>Al in AlO</td>
<td>$2.5 \times 10^{-1}$</td>
<td>477</td>
</tr>
<tr>
<td>O in AlO</td>
<td>$2.0 \times 10^{-1}$</td>
<td>304</td>
</tr>
<tr>
<td>Mg in MgO</td>
<td>$3.9 \times 10^{-1}$</td>
<td>394</td>
</tr>
<tr>
<td>Al in MgO</td>
<td>$4.10 \times 10^{-1}$</td>
<td>844</td>
</tr>
<tr>
<td>Ni in NiO</td>
<td>$1.4 \times 10^{-1}$</td>
<td>207</td>
</tr>
<tr>
<td>O in SiO$_2$</td>
<td>$2.5 \times 10^{-1}$</td>
<td>187</td>
</tr>
<tr>
<td>Cu in polycryst. PET</td>
<td>$6.4 \times 10^{-1}$</td>
<td>187</td>
</tr>
<tr>
<td>CO in PE</td>
<td>$2.0 \times 10^{-1}$</td>
<td>8</td>
</tr>
<tr>
<td>CO in PVC</td>
<td>$4.2 \times 10^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>O in PET</td>
<td>$5.3 \times 10^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>O in PE</td>
<td>$6.3 \times 10^{-1}$</td>
<td>4</td>
</tr>
<tr>
<td>O in PVC</td>
<td>$6.2 \times 10^{-1}$</td>
<td>4</td>
</tr>
</tbody>
</table>
EXAMPLE 4.4-4

Explain each of these observations:

a. The activation energy for the diffusion of H in FCC iron is less than that for self-diffusion in FCC iron.

b. The activation energy for the diffusion of H in BCC iron is less than that for the diffusion of H in FCC iron.

2) **H SMALL ! FE BIG**

b) **BCC OPEN, FCC IS CLOSED PACKED**

**MECHANISM IN IONICS**

You have both ions jumping around!

**\[
\text{MgO} \rightarrow \text{D_{Mg}} \text{ and } \text{D_{O}}
\]**

Ions \(\rightarrow\) coulomb bonded, no free charge

\(\Rightarrow\) electrical conductivity is all given by ionic diffusion

\(\Rightarrow\) small conductivity, but I can get diffusion measuring conductivity!

**MECHANISM IN POLYMERS**

Polymer molecules \(\Rightarrow\) like spaghetti entangled moving worms!

Completely different mechanism

\(\Rightarrow D = D_0 e^{-Q/RT}\)

\(\Rightarrow D_0 \propto \frac{1}{N^2}\)

DFG
FIGURE 4.4-8
Diffusion coefficients of various organic molecules in natural rubber as a function of temperature. Note that at any given temperature, the smaller species diffuse more rapidly than the larger species.

BUT VERY FAST FOR IMPURITIES! NEED TO SEPARATE TWO ORGANIC SPECIES?

NEED TO TAYLOR PROPER LENGTH WHERE THE FIRST GOES THROUGH & THE SECOND DOES NOT!

WHAT ABOUT TIME EVOLUTION?

\[ J = -D \frac{\partial c}{\partial x} \]

but \[ J = \text{STUFF per unit second} \Rightarrow \frac{\partial c}{\partial t} \]

\[ \Rightarrow \frac{\partial c}{\partial t} \]

TAKE THE BOX!

DF7
IF $J_{out} \neq J_{in}$
SOMETHING
CHANGES INSIDE!!

PARTICLES DO NOT
GET DESTROYED $\Rightarrow$ CONC
CHANGES

$J_{out}(x+dx) = J(x+dx) = J(x) + \frac{\partial J}{\partial x} dx$  TAYLOR

$J_{in}(x) = J(x)$

$J =$ FLUX $\Rightarrow$ # PARTICLES FLOWING PER UNIT AREA PER UNIT SECOND

$\Rightarrow J_{in} \, dA \Rightarrow \# \text{ PART GETTING IN/UNIT SECOND}$

$\Rightarrow J_{out} \, dA \Rightarrow \# \text{ PART GETTING OUT/UNIT SECOND}$

$\Rightarrow (J_{out} \, dA) \Rightarrow \# \text{ PART DISAPPEARING INSIDE/UNIT SECOND}$

$(J_{in} - J_{out}) \, dA = \# \text{ PART INCREASING INSIDE PER UNIT SECOND}$

$\Rightarrow (J(x) - J(x) = \frac{\partial J}{\partial x}) \, dA = \frac{d}{dt} (C \, dA \, dx) = \frac{dN}{dt} \Delta t$

VOLUME DOES NOT
CHANGE IN TIME

$\Rightarrow \frac{d}{dt} (C \, dA \, dx) = \frac{dA \, dx}{dt} \frac{dc}{dt}$

$\Rightarrow \frac{\partial J}{\partial x} = \frac{dc}{dt}$

CONSERVATION OF PARTICLES
\[ J = -D \frac{\partial c}{\partial x} \]

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

Differential Equation
Need boundary conditions

Example: \( C \& FE \)

\[ C(x,t) = C_0 + [C_s - C_0] \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{D}t} \right) \right] \]

Carburization of steel
To make it wear resistant!

\[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-y^2} \, dy \]
DEPLETING SOURCE

\[ C(x,t) = \left( \frac{\beta}{2\sqrt{\piDt}} \right) \exp\left( -\frac{x^2}{4Dt} \right) \]

\( x_{\text{eff}} \) is where \( \text{shape is } \approx \frac{1}{3} \text{ of original} \)

\( x_{\text{eff}} \approx 2\sqrt{Dt} \)

**EFFECTIVE PENETRATION DISTANCE**

Plot \( x_{\text{eff}} \) where \( C(x_{\text{eff}},t) = \frac{C_0 + C}{2} \)

\[ \Rightarrow \text{FOR PLATE} \Rightarrow \frac{1}{2} - \text{erf} \left( \frac{2x_{\text{eff}}}{2\sqrt{Dt}} \right) \approx \text{erf}(0.5) \]

\[ \Rightarrow x_{\text{eff}} \approx \sqrt{Dt} ! \]

\( x_{\text{eff}} \approx 2\sqrt{Dt} \) for cylinders

\[ \text{erf}(z) \equiv \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-x^2} dx \]

\( \text{erf}(-z) = -\text{erf}(z) \)

\[ \lim_{z \to \infty} \text{erf}(z) \to 1 \]

\[ \text{erf}(z) \sim \frac{2}{\sqrt{\pi}} z \text{ for } z \approx 0 \]

\[ \text{erf}(\frac{z}{2}) \sim \frac{1}{2} \]

DF10