Thermally Activated Processes

General Description of Activated Process:

Fig. 1.27: Tilting a filing cabinet from state $A$ to its edge in state $A^*$ requires an energy $E_A$. After reaching $A^*$, the cabinet spontaneously drops to the stable position $B$. $PE$ of state $B$ is lower than $A$ and therefore state $B$ is more stable than $A$.

Thermally Activated Processes

- Arrhenius Behavior -

Diffusion:

Fig. 1.28: Diffusion of an interstitial impurity atom in a crystal from one void to a neighboring void. The impurity atom at position $A$ must posses an energy $E_A$ to push the host atoms away and move into the neighboring void at $B$. 

Thermally Activated Processes
- Arrhenius Behavior -

- Diffusion:

- Temperature Plays a significant role in diffusion
- Temperature is not the driving force.
- **Remember:**

  \[ \text{DRIVING FORCE} = \text{GRADIENT of a FIELD VARIABLE} \]

- **Remember:** Driving force for diffusion is a difference in the chemical potential.

- **H ave**

  \[ \Delta \mu \neq 0 \text{ or } \nabla \mu \neq 0 \]

- **However:** Temperature increases the activity of a diffusing species.

  **Question:** What is the probability that an atom will diffuse?
  - Atoms are **Bosons**
  - Use **Maxwell-Boltzmann Statistics**!

\[
N(\varepsilon) d\varepsilon = f(\varepsilon) g(\varepsilon) d\varepsilon
= \frac{N e^{-\beta \mu} g(\varepsilon) d\varepsilon}{\int e^{-\beta \mu} g(\varepsilon) d\varepsilon}
= \frac{\text{No. Impurities with } E > E_A}{\text{Total No. of Impurities}}
= Ae^{-E_A/\beta}
\]

- **Question:** What is the probability that an atom will diffuse?

\[
\begin{align*}
\theta = 0^\circ & \quad \theta = 90^\circ \\
\theta = 180^\circ & \quad \theta = 270^\circ
\end{align*}
\]

**Fig. 1.29:** An impurity atom has four site choices for diffusion to a neighboring interstitial vacancy. After \( N \) jumps, the impurity atom would have been displaced from the original position at \( O \).

Diffusion:

- Frequency of Jump is proportional to the probability
- Coefficient of Diffusion is proportional to Jump Frequency

\[ v = V_0 f(E) \]
\[ D \propto v \propto A v_0 e^{-E/kT} \]

**Diffusivity or Diffusion Coefficient (Arrhenius Rate Equation):**

\[ D = D_0 e^{-E_a/(kT)} \]

- \( E_a \) is the activation energy for diffusion
- \( k_b T \) is the thermal energy
- \( D_0 \), the pre-exponential factor, contains a number of physical constants and properties including:
  - entropy of formation of the defect
  - attempt frequency for jumps into available neighboring sites
  - lattice constant
  - crystal structure dependence
Thermally Activated Processes
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**Diffusion:** Diffusivity or Diffusion Coefficient:

**Question:** How does one obtain:
- Activation energy
- Pre-exponential

\[ D = D_0 e^{-\frac{E_a}{k_B T}} \]

Linearize Diffusivity:
\[ \ln D = \ln \left( D_0 e^{-\frac{E_a}{k_B T}} \right) \]
\[ = -\frac{E_a}{k_B T} + \ln D_0 \]

Has form of Equation of a Line!
\[ y = mx + b \]
Thus:
\[ y = \ln D; \quad x = \frac{1}{T}; \quad m = -\frac{E_a}{k_B}; \quad b = \ln D_0 \]

Best way to calculate \( E_a \):
\[ m = \frac{\Delta y}{\Delta x} = \frac{\ln D_1 - \ln D_2}{\frac{1}{T_2} - \frac{1}{T_1}} \]

So:
\[ E_a = -k_B \cdot \text{slope} \]
\[ = -k_B \ln D_1/D_2 \cdot \frac{1}{T_1} - \frac{1}{T_2} \]

**KINETICS:** Diffusion and "Chemical Reactions:
Thermally Activated Processes

- We will use Si as an example of a system with various diffusion mechanisms.
- Two types of diffusion mechanisms:
  - Direct diffusion mechanisms: diffusion without the aid of point defects.
    - Interstitial diffusion
  - Indirect diffusion mechanisms: diffusion with the aid of point defects

\[ A_s + V \rightleftharpoons AV \quad \text{Vacancy mechanism} \]
\[ A_s + I \rightleftharpoons AI \quad \text{Interstitial mechanism} \]
\[ A_s + I \rightleftharpoons A_s \quad \text{Kick-out mechanism} \]
\[ A_s \rightleftharpoons A_s + V \quad \text{Dissociative (Frank-Turnbull) mechanism} \]
KINETICS: Diffusion and "Chemical Reactions:" Thermally Activated Processes

- Chemical reaction causes a change in concentration, \( C_I \), of interstitials

\[
A_i + l \leftrightarrow Al
\]

\[
\frac{\partial C_I}{\partial t} = k_f C_{Al} - k_r C_I C_A
\]

- For the equation that describes the total kinetics, that is, the total change in the concentration of \( C \), or \( C_{total} \):

\[
\frac{\partial C_{total}}{\partial t} = \frac{\partial C_{diff}}{\partial t} + \frac{\partial C_{reac}}{\partial t}
\]

Arrhenius behavior is observed in many areas of science

- Conduction in solids
Extra notes for those that are interested

- Other Examples of Arrhenius Rate Behavior:
  - Much of Kinetics shows this behavior
    - Carrier concentration and conduction in semiconductors and insulators
    - Mass Transport
    - Defect Formation
    - Rates of Chemical Reactions (Coefficient of Reaction Rate)
    - Creep Rate
    - Dislocation motion

Carrier Concentration in Semiconductors:
**Thermally Activated Processes**

- **Arrhenius Behavior** -

**Carrier Concentration:**

\[ n = n_e e^{-E_e / k_B T} \]

Intrinsic carrier concentration as a function of 1/T (Arrhenius plot).

**Carrier Conductivity in insulators:**

\[ \sigma \propto e^{-E_f / k_B T} \]

\[ \sigma = \sigma_0 e^{-E_f / k_B T} \]

Fig. 2.28: Conductivity vs reciprocal temperature for various low conductivity solids. (PVC = Polyvinyl chloride; PVAc = Polyvinyl acetate.) Data selectively combined from numerous sources.

SiO₂ Growth Kinetics Models: Deal-Grove Model

\[ B = C_1 e^{-E_1/k_B T} \] (oxidant diffusion)

\[ \frac{B}{A} = C_2 e^{-E_2/k_B T} \] (interface reaction rate)

<table>
<thead>
<tr>
<th>Ambient</th>
<th>B</th>
<th>B/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry O₂</td>
<td>( C_1 = 7.72 \times 10^5 \mu^3 \text{ hr}^{-1} )</td>
<td>( C_2 = 6.23 \times 10^5 \mu^3 \text{ hr}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( E_1 = 1.23 \text{ eV} )</td>
<td>( E_2 = 2.0 \text{ eV} )</td>
</tr>
<tr>
<td>Wet O₂</td>
<td>( C_1 = 2.14 \times 10^5 \mu^3 \text{ hr}^{-1} )</td>
<td>( C_2 = 8.95 \times 10^5 \mu^3 \text{ hr}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( E_1 = 0.71 \text{ eV} )</td>
<td>( E_2 = 2.05 \text{ eV} )</td>
</tr>
<tr>
<td>H₂O</td>
<td>( C_1 = 3.86 \times 10^5 \mu^3 \text{ hr}^{-1} )</td>
<td>( C_2 = 1.63 \times 10^5 \mu^3 \text{ hr}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( E_1 = 0.78 \text{ eV} )</td>
<td>( E_2 = 2.05 \text{ eV} )</td>
</tr>
</tbody>
</table>

Plots of \( B \) & \( B/A \) using values in table.

Chemical Vapor Deposition (CVD)

\[ J_{\text{sil}} = J_1 = -D_{\text{gas}} \frac{\partial C}{\partial x} \]

\[ J_{\text{surf}} = J_2 = k_s C_s \]

\[ J_{\text{rxn}} = J_2 = \frac{D_{\text{gas}}}{\delta_y} \left( C_{\text{gas}} - C_{\text{surf}} \right) \]

\[ = h_y \left( C_{\text{gas}} - C_{\text{surf}} \right) \]