Mechanism, Molecularity, and Elementary Steps

Mechanism of a reaction is the elucidation of detailed individual steps that can be established.

\[
\begin{align*}
\text{H} & \quad \text{I} \\
\text{H} & \quad \text{I} \\
\text{H} & \quad \text{I}
\end{align*}
\]

Approaching \quad Colliding \quad Separating

\[
\begin{align*}
\text{H}_2 + \text{I}_2 & \rightarrow 2\text{HI} \\
\text{HO}_2 & \rightarrow \text{H} + \text{O}_2
\end{align*}
\]

proved to be elementary, bimolecular

\[
\begin{align*}
\frac{d\xi}{V} &= -kC_{\text{HO}_2} \\
\text{First order, unimolecular process}
\end{align*}
\]

If an elementary step involves two molecules of a reactant

\[
\begin{align*}
2\text{A} & \rightarrow \text{Products} \quad \text{rate} = k C^2_{\text{A}} \\
\text{A} + \text{B} & \rightarrow \text{Products} \quad \text{rate} = k C_{\text{A}} C_{\text{B}} \\
\text{A} + \text{B} + \text{C} & \rightarrow \text{Products} \quad \text{rate} = k C_{\text{A}} C_{\text{B}} C_{\text{C}}
\end{align*}
\]
Unimolecular Decomposition:

\[
\begin{align*}
A & \quad \rightarrow \quad \text{Products} \\
A + A & \quad \xrightarrow{k_1} \quad A^* + A \\
A^* + A & \quad \xrightarrow{k_{-1}} \quad A + A \\
A^* & \quad \rightarrow \quad \text{Products}
\end{align*}
\]

Lindemann Mechanism

Rate determining step?

\[
\frac{dC_A}{dt} = -k_2C_{A^*}
\]

**Steady State Approximation:** if \(A^*\) does not accumulate, then

Rate of formation of \(A^*\) = rate of consumption of \(A^*\)

\[
i.e. \quad \frac{dC_{A^*}}{dt} = 0 = k_1C_A^2 - k_{-1}C_A C_{A^*} - k_2C_{A^*}
\]

\[
C_{A^*} = \frac{k_1C_A^2}{k_{-1}C_A + k_2}
\]
\[
\frac{dC_A}{dt} = -k_2 C_A^*
\]

\[
C_A^* = \frac{k_1 C_A^2}{k_{-1} C_A + k_2}
\]

\[
:\text{if } k_{-1} C_A \ll k_2 \text{ Second Order}
\]

\[
\frac{dC_A}{dt} = -\frac{k_1 k_2 C_A^2}{k_{-1} C_A + k_2}
\]

\[
:\text{if } k_{-1} C_A \gg k_2 \text{ First Order}
\]
Relaxation Methods to study equilibria:

Let the system be at equilibrium \( A + B \rightleftharpoons C \)

\[
\frac{d(\xi/V)}{dt} = k_f C_A C_B + (-k_r C_c)
\]

\[
\frac{d(\xi/V)}{dt} = k_f \left( C^o_A - \frac{\xi}{V} \right) \left( C^o_B - \frac{\xi}{V} \right) + \left[ -k_r \left( C^o_C + \frac{\xi}{V} \right) \right]
\]

If the temperature is increased by \( \sim 10^\circ C \), in few µs, then equilibrium is destroyed and concentrations start to change.

\[
\Delta C_t = \Delta C_{eq} \ e^{-\kappa t}
\]

\[
\kappa = k_f \left( C_{A, eq} + C_{B, eq} \right) + k_r
\]

Measure \( \kappa \) at various values of \( (C_{A, eq} + C_{B, eq}) \) to calculate \( k_f \) and \( k_r \)
Rate constants for some fast reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_f/(\text{L mol}^{-1} \text{ s}^{-1})$</th>
<th>$k_r/(\text{L mol}^{-1} \text{ s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$</td>
<td>$1.4 \times 10^{11}$</td>
<td>$2.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{OH}^- + \text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}_2\text{O}$</td>
<td>$3.4 \times 10^{10}$</td>
<td>$6 \times 10^{5}$</td>
</tr>
</tbody>
</table>
In-Class Assignment: April 16/02

Derive the integrated rate expression for:

a. First order reaction
   \[ \text{A} \rightarrow \text{Products} \]

b. Second order reaction
   \[ \text{A} \rightarrow \text{Products} \]

c. Second order reaction
   \[ \text{A} + \text{B} \rightarrow \text{Products} \]
Temperature and the rate of a reaction:

Arrhenius Equation \( k = Ae^{-E^*/RT} \)

- \( A \) = Frequency factor
- \( E^* \) = Activation Energy
- \( k \) = Rate constant at temperature ‘\( T \)’
- \( R \) = Gas Constant

\[
\log_{10} k = \log_{10} A - \frac{E^*}{2.303RT}
\]

Theoretical basis for this equation will be presented later.
Activated complex is a structure that has the energy of the TS
Catalyst is neither consumed nor created in the reaction.
-- participates
-- regenerated

\[ S + C \xrightleftharpoons[k_{-1}]{k_1} SC \]

\[ SC \xrightarrow{k_2} \text{Products} \]

\[ \frac{\partial[S]}{\partial t} = \dot{\vartheta} = k_2 [SC] \]

\[ \dot{\vartheta}_o = \text{initial rate} \]

\[ [P] \quad t \]