Lecture Notes CC: Chemical Kinetics II

1. Elementary steps in a chemical reaction

Unimolecular reaction

A --> B or A --> B+C

example: decomposition: N₂O₅ ---> NO₂ + NO₃

isomerization:

Concentration dependence: If I have more A, then more A will fall apart

first order in [A], rate = k[A]

Bimolecular reaction

A + B --> C or A + B --> C+D second order reaction (first order in [A] and [B])

example: NO + NO ---> N₂O₂

Concentration dependence: Need A and B to collide, so first order in [A] and [B]
second order overall
rate = k [A] [B]

it usually takes many collisions for a reaction to occur.

Termolecular reaction (rare, most single-step reactions are uni- or bi- molecular)

I (g) + I (g) + Ar --> I₂ (g) + Ar

Concentration dependence: Need all three to collide, rate = [I]² [Ar]
2. Multi-step reactions

Catalytic destruction of ozone (one of many pathways):

\[
\begin{align*}
Cl + O_3 & \rightarrow ClO + O_2 \\
ClO + O & \rightarrow Cl + O_2 \\
\hline
O_3 + O & \rightarrow 2 O_2
\end{align*}
\]

Cl is a catalyst, because it helps the reaction along, but is neither consumed nor produced in the reaction.

ClO is a reaction intermediate, because it exists only while the reaction is proceeding.

<table>
<thead>
<tr>
<th>amount of light from the sun</th>
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<tbody>
<tr>
<td>250 500 (\lambda) (nm)</td>
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Ozone Production

| Ozone blocking of UV radiation |

\[
\begin{align*}
2 \ [ Cl + O_3 & \rightarrow ClO + O_2 ] \\
2ClO + M & \rightarrow ClOOCl + M \\
ClOOCl + hv & \rightarrow ClOO + Cl \\
ClOO + M & \rightarrow Cl + O_2 + M \\
\hline
2 O_3 & \rightarrow 3 O_2
\end{align*}
\]

Chlorine resevoir

\[
Cl \leftarrow HCl, ClONO_2, ...
\]
Concept:

Consider the following biochemical reaction system:

\[ \text{sucrose} + \text{glycosidase} \rightarrow (\text{sucrose-glycosidase complex}) \]
\[ (\text{sucrose-glycosidase complex}) \rightarrow \text{glycosidase} + \text{fructose} + \text{glucose} \]

The enzyme glycosidase is:  
(a) an intermediate  (b) a catalyst

the (sucrose-glycosidase complex) is:  
(a) an intermediate  (b) a catalyst

3. Relation between kinetics and equilibrium

For an elementary (single-step) reaction:

\[ \text{A} + \text{B} \xrightleftharpoons[k_{\text{reverse}}]{k_{\text{forward}}} \text{C} + \text{D} \]

forward rate = \( k_{\text{forward}} \times [A][B] \)

reverse rate = \( k_{\text{reverse}} \times [C][D] \)

At equilibrium, the concentrations no longer change, so the forward and reverse rates are equal,

For a multi-step reaction:

\[ \text{Cl} + \text{O}_3 \xrightleftharpoons[k_1]{k_1} \text{ClO} + \text{O}_2 \quad K_1 = \frac{k_1}{k_1} \]

\[ \text{ClO} + \text{O} \xrightleftharpoons[k_2]{k_2} \text{Cl} + \text{O}_2 \quad K_2 = \frac{k_2}{k_2} \]

\[ \text{O}_3 + \text{O} \rightarrow 2 \text{O}_2 \quad K = \frac{(k_1k_2)}{(k_1k_2)} \]
4. Rate Limiting Step

Example 1: First elementary step is the slow (rate-limiting) step

Decomposition of H$_2$O$_2$, catalyzed by I$^-$

\[
\begin{align*}
H_2O_2 + I^- & \xrightleftharpoons[k_1]{k_2} H_2O + I^- \\
H_2O_2 + IO^- & \xrightarrow{k_2} H_2O + O_2 + I^-
\end{align*}
\]

\[
\begin{align*}
2 H_2O_2 & \rightarrow 2 H_2O + O_2
\end{align*}
\]

Example 2: Rate-limiting step is not first elementary step

\[
\begin{align*}
2NO & \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} N_2O_2 \quad \text{ (fast equilibrium)} \\
N_2O_2 + H_2 & \xrightarrow{k_2} N_2O + H_2O \quad \text{ (slow)}
\end{align*}
\]

\[
\begin{align*}
2NO + H_2 & \rightarrow N_2O + H_2O
\end{align*}
\]
Derive the rate law for the following reaction mechanism:

\[ \begin{align*}
I_2 & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I \\
H_2 + 2I & \overset{k_2}{\rightarrow} 2HI \\
\hline
H_2 + I_2 & \rightarrow 2HI
\end{align*} \]

Chlorine reacts with hydrogen sulfide in aqueous solution:

\[ \text{Cl}_2 (aq) + \text{H}_2\text{S} (aq) \rightarrow \text{S}(s) + 2\text{H}^+ (aq) + 2\text{Cl}^- (aq) \quad \text{rate} = k \left[ \text{Cl}_2 \right] \left[ \text{H}_2\text{S} \right] \]

Which of the following mechanisms is consistent with the observed reaction rate expression?

a) \( \text{Cl}_2 + \text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{Cl}^+ + \text{HS}^- \) (slow)
\[ \text{Cl}^+ + \text{HS}^- \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{S} \] (fast)

b) \( \text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+ \) (fast equilibrium)
\[ \text{HS}^- + \text{Cl}_2 \rightleftharpoons 2\text{Cl}^- + \text{S} + \text{H}^+ \] (slow)