Lindemann – Hinshelwood Mechanism

\[ A + A \rightarrow A^* + A \]

A* is collisionally activated with energy to form products

Given enough time, it forms products in a unimolecular process

\[ A^* \rightarrow \text{products} \]

Unless another collision removes the excess energy

\[ A^* + A \rightarrow A^* + A^* \]

leaving both with too little energy to decompose.
Lindemann – Hinshelwood Mechanism

Consider only one species A. This is easy to generalize.

\[ A + A \xrightarrow{k_a} A^* + A \]
\[ A^* + A \xrightarrow{k_a'} A + A \]
\[ A^* \xrightarrow{k_b} P \]

The rate law for formation of \( A^* \) is

\[ \frac{d[A^*]}{dt} = k_a [A]^2 - k_a' [A][A^*] - k_b [A^*] \]

And with ss approx

\[ [A^*] = \frac{k_a [A]^2}{k_b + k_a' [A]} \]

with the result

\[ \frac{d[P]}{dt} = k_b [A^*] = \frac{k_a k_b [A]^2}{k_b + k_a' [A]} \]
This is a reaction with indefinite order. However, if the rate for deactivation of \( A^\ast \) is much greater than the unimolecular decay, \( A^\ast \rightarrow P \), then \( k_a'[A^\ast][A] \gg k_b[A^\ast] \) or just \( k_a'[A] \gg k_b \), and we have that

\[
\frac{d[P]}{dt} = \frac{k_a k_b [A]}{k_a'} = k_{\text{eff}} [A] \quad \text{a pseudo first order reaction}
\]

Such a reaction goes from 2\(^{\text{nd}}\) order to 1\(^{\text{st}}\) order as the pressure increases. This is a very common gas phase mechanism, as collisions supply (take away) energy.

\[
A + B + M \rightarrow AB + M
\]
Lindemann – Hinshelwood Mechanism

\[ O + NO \rightleftharpoons NO_2^* \]

\[ NO_2^* + M \rightarrow NO_2 + M^* \]

Normally, bath gas dominates
From last time
\[
\frac{d[P]}{dt} = k[A] = \frac{k_a k_b [A]}{k_b + k_a' [A]} [A]
\]

Giving an effective 1\textsuperscript{st} order \(k\)
\[
k = \frac{k_a k_b [A]}{k_b + k_a' [A]}
\]

Rearranging,
\[
\frac{1}{k} = \frac{k_a'}{k_a k_b} + \frac{1}{k_a [A]}
\]
Lindemann - Hinshelwood Mechanism

\[(10^{-4} \text{ s}^{-1})/k\]

\[(10^{-3} \text{ mol dm}^{-3})/[A]\]
Catalysis:
Energy Profile for a Catalyzed Reaction

The catalyst is unchanged at the end if the reaction
Consider a reaction which utilizes a catalyst.

Which of the following statements is false?

A. The catalyst modifies $k_f$ and $k_r$.
B. The catalyst modifies $E_a$
C. The catalyst modifies $K_{eq}$
D. The catalyst modifies the net rate to products compared to that of the uncatalyzed reaction.

Let’s now look at a real catalytic process in our atmosphere.
Hydroxyl radical eats hydrocarbons in the atmosphere

\[ \cdot \text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO} \cdot \]

It looks like an elementary Rx, but it can be catalyzed by a single water molecule


\[ \cdot \text{OH} + \text{CH}_3\text{CHO}(\text{H}_2\text{O}) \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO} \cdot + \text{H}_2\text{O} \]

How??
Energy Profile for Water Catalyzed Reaction

\[ \cdot \text{OH} + \text{CH}_3\text{CHO(H}_2\text{O}) \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO}\cdot + \text{H}_2\text{O} \]

Energy Profile for Catalyzed Reaction
Chain Reactions

$$H_2 + Br_2 \rightarrow 2 \text{ HBr}$$

Observed Rate = \( \frac{k [H_2][Br_2]^{1/2}}{1 + [HBr]/m[Br_2]} \)

- \( Br_2 \rightarrow 2 \text{ Br} \) \quad \text{initiation}
- \( Br + H_2 \rightarrow \text{HBr} + H \) \quad \text{chain propagation}
- \( H + Br_2 \rightarrow \text{HBr} + Br \) \quad \text{chain propagation}
- \( H + HBr \rightarrow H_2 + Br \) \quad \text{inhibition}
- \( Br + Br \rightarrow Br_2 \) \quad \text{termination}
Chain Reactions

\[ H_2 + Br_2 \rightarrow 2 \text{ HBr} \]

Observed Rate = \[ \frac{k \ [H_2][Br_2]^{1/2}}{1 + [\text{HBr}]/m[Br_2]} \]

- \( Br_2 \rightarrow 2 \text{ Br} \) initiation: collisional or photolytic
- \( Br + H_2 \rightarrow \text{HBr} + H \) chain propagation
- \( H + Br_2 \rightarrow \text{HBr} + Br \) chain propagation
- \( H + \text{HBr} \rightarrow H_2 + Br \) inhibition
- \( Br + Br \rightarrow Br_2 \) termination
The Born Oppenheimer approximation:

- Generally a very accurate approximation, and one of the most important concepts in all of physical science.
- Without it, there would be no chemistry as we know it.
- B-O approximation allows the construction of potential energy surfaces for molecules (e.g., AB) and for reactions.
- Still too many nuclear degrees of freedom!
- Select only important ones