14.3 Activation Barrier to Reaction Process

Kinetic Molecular Theory and Collision Theory

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Activation energy

Reactants

Δ H (Enthalpy)

Products

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Chemical savvy says that reaction occurs when molecules or atoms come in contact (or collide together).

Some reactions are very fast:
\[ 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) \]

Others are very slow
\[ 4 \text{Fe}(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{Fe}_2\text{O}_3(\text{s}) \]

Reaction rate vs. Temp
In general, the rate of a reaction doubles for every 10° increase of the temperature.
Kinetic Molecular Theory

Kinetic Molecular Model

Collision Theory - explains factors which influence the speed of a chemical reaction?

Basic idea:

In a reaction, there must be a chemical changes

For chemical change to occur:
  Reactant bonds are broken
  Product bonds are formed

Factors influence reaction rate:

Rate →
Collision Frequency

1. Collision Theory - A collision must occur
   Collision frequency influence the rate of a reaction
   \[
   \text{rate} \propto \text{collision / time}
   \]

4 particle system
2 \(\bullet\) and 2 \(\square\)
\[\Rightarrow\] 4 collision
\(\bullet\) \[\leftrightarrow\] \(\square\) \[\leftrightarrow\] \(\bullet\)
Steric Factor

2. Orientation Factor - For collision to lead to products, the orientation of the molecules must be correct for bonds to break

\[ \text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2 \]
Activation Energy

KMT- According to the Kinetic Molecular Theory; any molecule in motion possesses kinetic energy \((1/2 \, mv^2)\). Faster the motion, the more likely reactants will fragment upon collision.

Consider the Car Analogy:
Cars will not disintegrate by itself. However at low speeds, collision between car will cause little to no damage. But at high speeds, there will be major damages.
**$E_{\text{act}}$ - Activation Energy**

If the k.E. is large enough, then upon collision molecules will vibrate so vigorously as to break bonds which can lead to new products.

Energetically, there must be some minimum collision energy that must be exceeded before a reaction occurs.

**Svante Arrhenius -**

Suggested that molecules must possess a minimum amount of K.E. in order to react. In other words, energy must be available to the reactant for the reaction to occur.

[Image of Svante Arrhenius]

SVANTE AUGUST ARRHENIUS

Stuff you should know: Terminology

**Chemical Specie**
- Energy reactant ($E_r$)
- Energy product ($E_p$)
- Energy intermediate
- Transition state energy

**Chemical Process**
- Energy of reaction ($\Delta H_{rxn}$)
- Activation Energy of the reaction ($E_{act}$)
- Activation Energy of the reaction forward direction ($E_{act \ f}$)
- Activation Energy of the reaction reverse direction ($E_{act \ r}$)

**Terminology**
- Reaction progression diagram
- Endothermic reactions
- Exothermic reactions
- Maxwell Boltzmann Plot
- Activated complex
- Transition state
- Intermediate
Consider the following reaction coordinate diagram in which NOCl is decomposed to NO and Cl₂.

The reactant NOCl has a certain initial energy. In order for products to form, an activation barrier must be overcome, this activation barrier is the energy of the transition state, or the activated complex.

\[E_a\] Activation Energy:
The minimum energy and conditions necessary for reactant to be converted to products.

Activated Complex - The intermediate specie that is formed or produced [intermediate].

In the end, the NO and Cl₂ products formed is more energetic than NOCl, the reaction is endothermic.

\[\Delta H (+)\]
Consider the reaction:

\[ \text{A}_{\text{(react)}} + \text{B}_{\text{(react)}} \rightarrow [\text{A} \cdots \text{B}]^* \rightarrow \text{AB (prod)} \]
Energy-Level Diagram:  
Exothermic Vs Endothermic

Consider the two reaction below. Each with two steps.  
Rxn A is exothermic, Rxn B is endothermic.

Note that in both examples, it is a two step reaction in which reactant converts to product. The faster step is the one with the lower $E_{\text{act}}$. The valley in the reaction coordinate correspond to a stable intermediate.
Reaction Rate and $E_{act}$

The rate of a reaction is directly correlated to the height of the activation barrier. The higher the $E_{act}$, the slower the reaction. Reactions with very small $E_{act}$ tend to go very fast.

In the reaction coordinate diagram:

- **Rxn A** is endothermic with a high $E_{act}$. This reaction is the slowest among the three examples.
- **Rxn B** is exothermic with a lower $E_{act}$, and it is faster than Rxn A.
- **Rxn C** is exothermic with a very low $E_{act}$. This reaction is very fast.

The number of molecules with the minimum kinetic energy large enough to initiate a reaction is related to temperature.
Recall from the gas laws that an energy profile for molecules can be describe by the Maxwell-Boltzmann distribution diagram.

As the temperature goes up, the population of molecules with more energy also increases.

The increase of temperature yields to more molecules exceeding the $E_{\text{act}}$, the minimum energy required to overcome the activation barrier for a reaction to occur.

$$E_{\text{act}} \propto e^{-E_a/RT}$$
Boltzmann Distribution and Rxn Coord. Diagram

The energy of a collection of reactants and the minimum energy necessary to overcome the activation barrier

An energy-level diagram of the fraction of collision reaching the activated state.

In either direction, the fraction of collisions exceeding $E_{\text{act}}$ is greater at higher temperatures.

In general, in an exothermic reaction at any temperature, the fraction of collision exceeding $E_{\text{act}}(f)$ is greater than the fraction exceeding $E_{\text{act}}(r)$.

This is accounted for by the purple shade in the reaction coordinate diagram shown.

Once the temperature is raised for an exothermic reaction, however, the percentage increase of the product molecules overcoming the activation barrier is higher than that of the reactant and therefore $K_{\text{eq}}$ decreases and the reaction shifts to the left.

This is accounted for by the red shade in the reaction coordinate diagram shown. The % increase is greater for the product than the reactant as shown in the reaction coordinate diagram.
Boltzmann Distribution: Exothermic

Increasing the temperature for an exothermic reaction results in a greater proportion of molecules of the product exceeding the activation energy, therefore the rate \( r_{\text{rev}} \) becomes more significant than the rate \( f_{\text{for}} \).

The temperature increase is more significant for the product.
Boltzmann Distribution: Endothermic

Similarly, increasing the temperature for an endothermic reaction results in a greater proportion of molecules of the reactant exceeding the activation energy, therefore the rate forward becomes more significant than the rate reverse. The temperature increase is more significant for the reactant.

\[
\text{Endo: Rate}_f > \text{Rate}_r
\]
Maxwell-Boltzmann Distribution and Equilibrium

How does the Maxwell-Boltzman plot explain why the reaction favors the reactant for an exothermic reaction and why it favors the product for an endothermic reaction.

In general, a reaction is faster when the temperature is raised.
Arrhenius Equation

Savant Arrhenius (1889) -
Expressed the three factors responsible for a reaction into an equation (Arrhenius Equation).

Factors influence reaction rate:

Rate \rightarrow [\text{Collision} \cdot \text{Orientation} \cdot \text{Activation}] \rightarrow \text{frequency of molecules} \cdot \text{Energy}

A - pre-exponential term

\text{E}_{\text{act}} = e^{-\frac{E_a}{RT}}

therefore, \quad \text{Rate} = A e^{-\frac{E_a}{RT}} \cdot \text{[Conc}_{\text{(react)}]} = k \cdot [\text{Rct}]^x

Where,

K = A e^{-\frac{E_a}{RT}}

\ln K = \ln A - \frac{E_a}{RT}

\ln K = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A

\gamma \quad m \quad x \quad b
**Graphic Representation: Arrhenius Equation**

\[
\ln K = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A
\]

where,
- \(E_a\) - Activation Energy
- \(R = 8.314 \text{ J/mol} \cdot \text{K}\)
- \(T\) = Absolute Temp
- \(A\) = Collision freq. factor

Note that as the magnitude of \(E_{act}\) (↑), the \(K\) becomes **more negative**, or the rate constant is smaller. \(\ln K \propto -E_a \text{ (minus } E_a\) \)

The reaction rate decreases as the energy barrier increases
- \(E_{act}\) large, \(K\) also small
- \(E_{act}\) small, \(K\) also large

For a graph with 2 points:

\[
\ln \left(\frac{k'}{k}\right) = \frac{E_a}{R} \left[\frac{1}{T} - \frac{1}{T'}\right]
\]
Recall: Rate $\rightarrow$ [Collision frequency of molecules $\cdot$ Orientation $\cdot$ Activation Energy]

Increase rate by making collision effective via:
- Decrease $E_{\text{act}}$ for the reaction
- Increase the steric factor

Catalyst: A catalyst can serve this purpose in which an external chemical changes the reaction pathway without being consumed.

A catalyzed reaction proceeds by a different set of steps which involves lowering the $E_{\text{act}}$.

Results: Reaction proceeds at a faster forward rate.
Catalysis in action: Heterogeneous

In the combustion of gasoline, the reaction

\[ C_xH_x + N_2 + O_2 \rightarrow 2NO + CO + CO_2 + H_2O \]

In addition:

\[ O_2 \rightarrow 2NO_2 \text{ (g) (Smog)} \]

Clean air Act `75 Require minimum emission.

Possible Mechanism:

\[ 2NO + 2CO \rightarrow N_2 + 2CO_2 \]
Homogeneous Catalysis

Decomposition of Acetic Acid:

\[
R"COOR' \quad + \quad H_2O \rightarrow \quad RCOOH \quad + \quad R'OH \\
R"COOR' \quad + \quad H_2O \quad -H^+ \rightarrow \quad RCOOH \quad + \quad R'OH
\]

Note: The initial and final state (energies) are the same since the energies of compounds are state function. The catalyzed reaction has a lower overall \( E_{\text{act}} \).

The decomposition is catalyzed by acid.
Catalysis Review

Addition of catalyst Lowers the Eact for the forward and the reverse reaction.

Endothermic
a) Uncatalyzed
b) Catalyzed

Exothermic
a) Uncatalyzed
b) Catalyzed
In Class Exercise

Consider the following Reaction Coordinate Diagram.

Determine the following:

i) Steps in mechanism:
ii) $E_{\text{reactant}}$
iii) $E_{\text{product}}$

iv) $E_{\text{act}}^{\text{(forward)}}_1$

v) $E_{\text{act}}^{\text{(forward)}}_2$

vi) $E_{\text{act}}^{\text{(forward)}}_{\text{overall}}$

vii) $E_{\text{act}}^{\text{(reverse)}}_1$

viii) $E_{\text{act}}^{\text{(reverse)}}_2$

ix) $E_{\text{act}}^{\text{(reverse)}}_{\text{overall}}$

x) $E^+_1$, $E^+_2$, $E_{\text{int}}$, $\Delta H_{\text{rxn}}$