Today

Review Transition State Theory

Arrhenius Theory

Kinetic Mechanisms
Why does a reaction follow a particular rate law?
What is actually happening in the reaction?

Arrhenius Law

The rate constant $k$ is a function of temperature

$$k = A \ e^{-E_a/RT}$$

Temperature

pre-factor

barrier

The higher the temperature the more molecules that have enough energy to make it over the barrier

Let's make a new Equation

$$k = A \ e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

Let's look at two temperatures

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

Subtract to get a new equation that doesn't have $A$

$$\ln(k_2/k_1) = \frac{-E_a}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$
The activation energy for this reaction is?

A. $-1.2 \times 10^4$ K
B. $1 \times 10^5$ J mol$^{-1}$
C. $1.2 \times 10^4$ J mol$^{-1}$
D. $1 \times 10^5$ K
E. $-1 \times 10^2$ kJ mol$^{-1}$

Slope = $-\frac{\Delta \ln(k)}{\Delta(1/T)} = -1.2 \times 10^4$ K

Slope = $-\frac{E_a}{R}$

$E_a = -8.314$ J K$^{-1}$ mol$^{-1} \times (-1.2 \times 10^4$ K) = $1 \times 10^5$ J mol$^{-1}$

Why are reactions faster at higher temperatures?

More molecules have sufficient energy to get over the barrier. BIG EFFECT

More molecules have collisions (but this is a very small effect) that is ignored in Arrhenius view of transition state theory.
Why is something first order? second order?

Because of the number of molecules involved in the "key" (slowest) step in the reaction.

We need to think about what is actually happening. This is the mechanism of the reaction.

Nonsense "real world" example:

student + quiz + TA  $$\rightarrow$$  happy student with quiz turned in
student + TA + quiz  $$\rightarrow$$  student with quiz + TA
student with quiz  $$\rightarrow$$  student with completed quiz
student with completed quiz + TA  $$\rightarrow$$  happy student with quiz turned in

Imagine step one was very slow (we passed out preprinted bubble sheets in alphabetical order checking ID before handing you the quiz).

Rate dominated by "handing" out the quiz.

What controls the rate of this reaction?

What we want. All steps to be fast except step 2. Then the rate is dominated by step 2. However step 1 still matters.
Nonsense "real world" example

student + quiz + TA  →  happy student with quiz turned in

student + TA + quiz  →  student with quiz + TA

student with quiz  →  student with completed quiz

student with completed quiz + TA  →  happy student with quiz turned in

dominated by step 3. You need to have your quiz notarized before turning it in.

All three steps matter

Principles of Chemistry II

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H₂(g) + Br₂(g) → 2HBr(g)

What actually happens?
Does a H₂ and a Br₂ molecule collide and react?
Does something else happen?

Step 1  Br₂ ↔ 2Br  intermediates
Step 2  Br + H₂  →  HBr + H
Step 3  H + Br₂  →  HBr + Br
Step 4  2Br  →  Br₂

Overall  H₂(g) + Br₂(g) → 2HBr(g)

Which Step Matters?

The rate is dominated by the slowest step
this is called the "rate limiting step"

Br₂ ↔ 2Br  slow
Br + H₂  →  HBr + H  fast
H + Br₂  →  HBr + Br  fast
2Br  →  Br₂  fast

As soon as some Br is formed it reacts very rapidly through the other step.
The rate is dominated by "waiting" for step 1

With this mechanism what is the predicted rate law?

Br₂ ↔ 2Br  slow
Br + H₂  →  HBr + H  fast
H + Br₂  →  HBr + Br  fast
2Br  →  Br₂  fast

What molecules are reactants in the slow step?

only one molecule of Br₂

Therefore rate = k[Br₂]
What if this was the mechanism?

\[
\begin{align*}
\text{Br}_2 &\underset{\text{fast}}{\longrightarrow} 2\text{Br} \\
\text{Br} + \text{H}_2 &\underset{\text{slow}}{\longrightarrow} \text{HBr} + \text{H} \\
\text{H} + \text{Br}_2 &\underset{\text{fast}}{\longrightarrow} \text{HBr} + \text{Br} \\
2\text{Br} &\underset{\text{fast}}{\longrightarrow} \text{Br}_2
\end{align*}
\]

rate = \(k[\text{Br}][\text{H}_2]\)

Can't have Br in the rate law, it is an intermediate.

where did the Br come from?

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What if this was the mechanism?

\[
\begin{align*}
\text{Br}_2 &\underset{\text{fast}}{\longrightarrow} 2\text{Br} \\
\text{Br} + \text{H}_2 &\underset{\text{slow}}{\longrightarrow} \text{HBr} + \text{H} \\
\text{H} + \text{Br}_2 &\underset{\text{fast}}{\longrightarrow} \text{HBr} + \text{Br} \\
2\text{Br} &\underset{\text{fast}}{\longrightarrow} \text{Br}_2
\end{align*}
\]

rate = \(k[\text{Br}][\text{H}_2]\)

You need 1/2 mole of \(\text{Br}_2\) to get one mole Br therefore.

rate = \(k[\text{Br}_2]^{1/2}[\text{H}_2]\)

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What is the rate law expected for the given mechanism?

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\begin{align*}
\text{NO}_2 + \text{NO}_2 &\longrightarrow \text{NO}_3 + \text{NO} \quad \text{slow} \\
\text{NO}_3 + \text{CO} &\longrightarrow \text{NO}_2 + \text{CO}_2 \quad \text{fast}
\end{align*}
\]

\[
\text{NO}_2 + \text{CO} \quad \longrightarrow \quad \text{NO} + \text{CO}_2 \quad \text{overall}
\]

A. rate = \(k[\text{NO}_2][\text{CO}]\)
B. rate = \(k[\text{NO}_3][\text{CO}]\)
C. rate = \(k[\text{NO}_2]^2[\text{CO}]\)
D. rate = \(k[\text{NO}_2]^2\)
E. rate = \(k[\text{NO}_2]^2[\text{NO}_3][\text{CO}]\)

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Mechanisms that involve products

\[
\begin{align*}
\text{Cl}_2 &\quad \text{Cl} + \text{Cl} \quad \text{fast} \\
\text{Cl} + \text{H}_2\text{S} &\quad \text{HCl} + \text{HS} \quad \text{fast} \\
\text{Cl} + \text{HS} &\quad \text{HCl} + \text{S} \quad \text{slow} \\
\text{Cl}_2 + \text{H}_2\text{S} &\quad 2\text{HCl} + \text{S}
\end{align*}
\]

rate = \(k[\text{Cl}][\text{HS}]\times \frac{[\text{Cl}][\text{H}_2\text{S}]}{[\text{HCl}][\text{HS}]}\times \frac{[\text{Cl}_2]}{[\text{Cl}]} = \frac{[\text{Cl}_2][\text{H}_2\text{S}]}{[\text{HCl}]}\)
Consider the following potential energy diagram.

Which arrow represents the activation energy?

1. a
2. c
3. b
4. f
5. d
6. c

Explanations:

The mechanism proposed for the oxidation of the iodide ion by the hypoiodite ion in aqueous solution is as follows:

1. \( \text{I}^- + \text{IClO} \rightarrow \text{ICl} + \text{O}_2 \) (slow)
2. \( \text{IClO} + \text{OH}^- \rightarrow \text{ICl} + \text{HO}_2^- \) (fast)
3. \( \text{HO}_2^- \rightarrow \text{HO}^- + \text{H}_2\text{O} \) (fast)

What is the rate law for the formation of HO\(_2\)\(^-\) implied by this mechanism?

1. \( \text{rate} = k \frac{[\text{IClO}]}{[\text{HO}_2^-]} \)
2. \( \text{rate} = k \frac{[\text{IClO}]}{[\text{HO}_2^-]^2} \)
3. \( \text{rate} = k \frac{[\text{HO}_2^-]}{[\text{IClO}]} \)
4. \( \text{rate} = k \frac{[\text{IClO}]}{[\text{HO}_2^-]} \)
5. \( \text{rate} = k \frac{[\text{IClO}]}{[\text{OH}^-]} \)