Big Idea #4

Kinetics
Factors Affecting Reaction Rate

Collision theory states that reactants must collide in the correct orientation and with enough energy for the molecules to react; changing the number of collisions will affect the reaction rate.

Factors that Affect Reaction Rate

- **State of reactants**
  - Rate increases as state changes from solid $\rightarrow$ gas as increased molecular movement allows for more opportunity for collision.
  - Greater surface area of solids will increase rate as more reactant is exposed and able participate in collisions.

- **Temperature** - more kinetic energy leads to more successful collisions between molecules.

- **Concentration** – more reactants $\rightarrow$ more collisions.

- **Use of a catalyst** – affect the mechanism of reaction leading to faster rate.

Rate is the change in concentration over time $\Delta[A]/t$.

LO 4.1: The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction.
Factors Affecting Reaction Rate

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Factors that Affect Reaction Rate:

- **State of reactants**: Rate increases as state changes from solid \( \rightarrow \) gas as increased molecular movement allows for more opportunity for collision.
- **Greater surface area of solids**: Will increase rate as more reactant is exposed and able to participate in collisions.
- **Temperature**: More kinetic energy leads to more successful collisions between molecules.
- **Concentration**: More reactants \( \rightarrow \) more collisions.
- **Use of a catalyst**: Affect the mechanism of reaction leading to faster rate.

\[ \Delta [A]/t \]

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Factors Affecting Reaction Rate

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Factors that Affect Reaction Rate:

1. **State of reactants**
   - Rate increases as state changes from solid → gas as increased molecular movement allows for more opportunity for collision.

2. **Greater surface area of solids** will increase rate as more reactant is exposed and able to participate in collisions.

3. **Temperature**
   - More kinetic energy leads to more successful collisions between molecules.

4. **Concentration**
   - More reactants → more collisions.

5. **Use of a catalyst**
   - Affect the mechanism of reaction leading to faster rate.

LO 4.1: The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction.

\[ \frac{\Delta [A]}{t} \]

1 point is earned for a valid explanation.
Determining Rate Order

- Rate law for a reaction has the form: $rate = k[A]^m[B]^n$... (only reactants are part of the rate law)
- Exponents ($m$, $n$, etc.) are determined from examining data, not coefficients:

$$for \ A + B \rightarrow C$$

<table>
<thead>
<tr>
<th>Trial</th>
<th>Initial $[A]$ (mol/L)</th>
<th>Initial $[B]$ (mol/L)</th>
<th>Initial Rate (mol/(L•s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.100</td>
<td>0.002</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>0.100</td>
<td>0.002</td>
</tr>
<tr>
<td>3</td>
<td>0.200</td>
<td>0.200</td>
<td>0.004</td>
</tr>
</tbody>
</table>

- The overall rate expression for the reaction is $rate = k[B]$.
- $k$ is the rate constant and is determined experimentally by plugging in data into the rate expression.

**Plot to create a straight line graph:**

- Zeroth Order
  - $[A]/\text{Time}$
  - Slope = $-k$
- First Order
  - $\ln[A]/\text{Time}$
  - Slope = $-k$
- Second Order
  - $1/[A]/\text{Time}$
  - Slope = $k$

LO 4.2: The student is able to analyze concentration vs. time data to determine the rate law for a zeroth-, first-, or second-order reaction.
Half-life (First Order)

- Time needed for the concentration of reactant to reach half its initial value
- Time to reach half concentration is dependent on $k$, not initial concentration
- Half life remains constant in a first order reaction

**Example:** when $t_{1/2} = 30$ sec, the concentration is halved each 30 seconds

\[
\ln [A] = -kt + \ln [A]_0
\]

\[
\ln \left(\frac{[A]_0}{2}\right) = -kt + \ln [A]_0
\]

\[
\ln [A]_0 - \ln 2 = -kt + \ln [A]_0
\]

\[
\ln [A] - \ln [A]_0 - \ln 2 = -kt
\]

\[
-\ln 2 = -kt
\]

\[
\ln 2 = kt
\]

\[
t_{1/2} = \frac{\ln 2}{k}
\]

The first order half life equation is derived from the first order integrated rate law

The first order half life equation is derived from the first order integrated rate law

Initial Conditions (12 molecules)  After 30 seconds (6 molecules)  After 60 seconds (3 molecules)

Source

LO 4.3: The student is able to connect the half-life of a reaction to the rate constant of a first-order reaction and justify the use of this relation in terms of the reaction being a first-order reaction.
Collision Theory and Reaction Mechanisms

- In a successful collision
  - Molecules have enough energy to overcome $E_a$.
  - Molecules collide with proper orientation to break the bonds.

- In a Mechanism
  - The rate law of any elementary reaction can be written from its stoichiometry.
  - The rate law of the slow step is the rate law of the overall reaction.

- The larger the rate constant, the larger the percentage of molecules having successful collisions.

2) The reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ takes place in 3 steps

<table>
<thead>
<tr>
<th>Step 1</th>
<th>$N_2O_5 \rightarrow NO_2 + NO_3$</th>
<th>SLOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 2</td>
<td>$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$</td>
<td>FAST</td>
</tr>
<tr>
<td>Step 3</td>
<td>$NO + NO_3 \rightarrow 2NO_2$ from another Step 1</td>
<td>FAST</td>
</tr>
</tbody>
</table>

Click here after you identify the rate determining step AND have written the rate law
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<table>
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<tr>
<th>Step</th>
<th>Reaction</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$N_2O_5 \longrightarrow NO_2 + NO_3$</td>
<td>SLOW</td>
</tr>
<tr>
<td>2</td>
<td>$NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$</td>
<td>FAST</td>
</tr>
<tr>
<td>3</td>
<td>$NO + NO_3 \longrightarrow 2NO_2$</td>
<td>from another Step 1</td>
</tr>
</tbody>
</table>

The rate determining step is STEP 1. Rate = $k [N_2O_5]$

LO: 4.4: Connect the rate law for an elementary reaction to the frequency/success of molecular collisions, including connecting the frequency and success to the order and rate constant.
Successful and Unsuccessful Molecular Collisions

Assume that all of these curves show the distribution of molecular speeds for the same substance.

![Graph showing molecular speed distribution](image)

**Question:** Which curve indicates the particles most likely to produce collisions that result in a chemical change? Justify your selection.

LO 4.5: The student is able to explain the difference between collisions that convert reactants to products and those that do not in terms of energy distributions and molecular orientation.

**Click here after you have chosen the correct curve and justified your answer.**
Successful and Unsuccessful Molecular Collisions

Assume that all of these curves show the distribution of molecular speeds for the same substance.

3) Curve D because a larger number of its particles have higher kinetic energies, and so are more likely to overcome the activation energy barrier when they collide.

Question: Which curve indicates the particles most likely to produce collisions that result in a chemical change? Justify your selection.

LO 4.5: The student is able to explain the difference between collisions that convert reactants to products and those that do not in terms of energy distributions and molecular orientation.
In order for both Reaction A and Reaction B to proceed in the forward direction at the same rate, which reaction would need to be at the higher temperature? Justify your choice.

LO 4.6: The student is able to use representations of the energy profile for an elementary reaction (from the reactants, through the transition state, to the products) to make qualitative predictions regarding the relative temperature dependence of the reaction rate.
In order for both Reaction A and Reaction B to proceed in the forward direction at the same rate, which reaction would need to be at the higher temperature? Justify your choice.

The greater the activation energy, the slower the reaction. Since Reaction A has a greater activation energy, it should be slower than Reaction B at the same temperature. To bring its rate up to that of Reaction B would require increasing its temperature. Important note: It does not matter at all, in answering this question, that Reaction A is endothermic and Reaction B is exothermic.

LO 4.6: The student is able to use representations of the energy profile for an elementary reaction (from the reactants, through the transition state, to the products) to make qualitative predictions regarding the relative temperature dependence of the reaction rate.
A reaction and its experimentally determined rate law are represented above. A chemist proposes two different possible mechanisms for the reaction, which are given below.

<table>
<thead>
<tr>
<th>Mechanism 1</th>
<th>Mechanism 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_2 \rightarrow 2X$</td>
<td>$X_2 \rightarrow 2X$</td>
</tr>
<tr>
<td>$(\text{slow})$</td>
<td>$(\text{slow})$</td>
</tr>
<tr>
<td>$X + Y_2 \rightarrow XY_2$</td>
<td>$X + Y_2 \rightarrow XY + Y$</td>
</tr>
<tr>
<td>$(\text{fast})$</td>
<td>$(\text{fast})$</td>
</tr>
<tr>
<td>$X + XY_2 \rightarrow X_2Y_2$</td>
<td>$X + XY \rightarrow X_2Y$</td>
</tr>
<tr>
<td>$(\text{fast})$</td>
<td>$(\text{fast})$</td>
</tr>
<tr>
<td>$X_2Y + Y \rightarrow X_2Y_2$</td>
<td>$X_2Y + Y \rightarrow X_2Y_2$</td>
</tr>
<tr>
<td>$(\text{fast})$</td>
<td>$(\text{fast})$</td>
</tr>
</tbody>
</table>

Based on the information above, which of the mechanisms is/are consistent with the rate law? List the intermediates in each mechanism:
5) \( \text{X}_2 + \text{Y}_2 \rightarrow \text{X}_2\text{Y}_2 \)  \quad \text{rate} = k[\text{X}_2] \\

A reaction and its experimentally determined rate law are represented above. A chemist proposes two different possible mechanisms for the reaction, which are given below.

**Mechanism 1**

- \( \text{X}_2 \rightarrow 2\text{X} \) (slow)
- \( \text{X} + \text{Y}_2 \rightarrow \text{XY}_2 \) (fast)
- \( \text{X} + \text{XY}_2 \rightarrow \text{X}_2\text{Y}_2 \) (fast)

**Mechanism 2**

- \( \text{X}_2 \rightarrow 2\text{X} \) (slow)
- \( \text{X} + \text{Y}_2 \rightarrow \text{XY} + \text{Y} \) (fast)
- \( \text{X} + \text{XY} \rightarrow \text{X}_2\text{Y} \) (fast)
- \( \text{X}_2\text{Y} + \text{Y} \rightarrow \text{X}_2\text{Y}_2 \) (fast)

Based on the information above, which of the mechanisms is/are consistent with the rate law? List the intermediates in each mechanism:

**Answer:** Both are consistent. In both mechanisms, the molecularity of the slow, rate determining step is consistent with the rate law. Furthermore, the sum of the elementary steps for both mechanisms gives the overall balanced equation for the reaction.

**Intermediates in mechanism 1:** \( \text{X}, \text{XY}_2 \).  
**Intermediates in mechanism 2:** \( \text{X}, \text{XY}, \text{X}_2\text{Y} \)

**LO 4.7:** Evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate.
Reaction Mechanisms

The rate law for a reaction is found to be Rate = k[A]^2[B]. What is the intermediate? Which of the following mechanisms gives this rate law?

I. A + B ⇄ E (fast)
   E + B → C + D (slow)

II. A + B ⇄ E (fast)
   E + A → C + D (slow)

III. A + A → E (slow)
    E + B → C + D (fast)

A. I
B. II
C. III
D. Two of these

LO 4.7 The student is able to evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate.
The rate law for a reaction is found to be $\text{Rate} = k[A]^2[B]$. What is the intermediate? Which of the following mechanisms gives this rate law?

I. $A + B \rightleftharpoons E$ (fast)  
   $E + B \rightarrow C + D$ (slow)

II. $A + B \rightleftharpoons E$ (fast)  
    $E + A \rightarrow C + D$ (slow)

III. $A + A \rightarrow E$ (slow)  
     $E + B \rightarrow C + D$ (fast)

A. I  
B. II  
C. III  
D. Two of these

Answer: E is the intermediate. Only Mechanism II is consistent with the rate law. Whenever a fast equilibrium step producing an intermediate precedes the slow rate determining step and we want to remove the intermediate from the rate law, we can solve for the concentration of the intermediate by assuming that an equilibrium is established in the fast step. The concentration of the intermediate in the rate determining slow step can be replaced with an expression derived from the equilibrium constant $[E] = K_{eq}[A][B]$. This substitution gives us the desired rate law: $\text{rate} = k'[A]^2[B]$. 

LO 4.7 The student is able to evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate.
Draw and label axes for the energy profiles below.

A. exothermic reaction with a 2 step mechanism where the first step is slow.
B. endothermic reaction with a 2 step mechanism where the second step is slow.
C. exothermic reaction with a 2 step mechanism where the second step is slow.
D. endothermic reaction with a 2 step mechanism where the first step is slow.
E. exothermic reaction with a 1 step mechanism.
F. endothermic reaction with a 1 step mechanism.

Click here to see answer and justification.
Draw and label axes for the energy profiles below.

A. exothermic reaction with a 2 step mechanism where the first step is slow.

B. endothermic reaction with a 2 step mechanism where the second step is slow.

C. exothermic reaction with a 2 step mechanism where the second step is slow.

D. endothermic reaction with a 2 step mechanism where the first step is slow.

E. exothermic reaction with a 1 step mechanism.

F. endothermic reaction with a 1 step mechanism.
Catalysts

a. A catalyst can stabilize a transition state, lowering the activation energy.

b. A catalyst can participate in the formation of a new reaction intermediate, providing a new reaction pathway.

The rate of the Haber process for the synthesis of ammonia is increased by the use of a heterogeneous catalyst which provides a lower energy pathway.

\[ \text{N}_2(g) + 2\text{H}_2(g) \rightarrow \text{iron-based catalyst} + 2\text{NH}_3(g) \]
Catalysts provide alternative mechanisms with lower activation energy

a. In acid-base catalysis, a reactant either gains or loses a proton, changing the rate of the reaction.

b. In surface catalysis, either a new reaction intermediate is formed or the probability of successful collisions is increased.

c. In Enzyme catalysis enzymes bind to reactants in a way that lowers the activation energy. Other enzymes react to form new reaction intermediates.

Homogeneous catalysis of the decomposition of H₂O₂

LO 4.9 The student is able to explain changes in reaction rates arising from the use of acid-base catalysts, surface catalysts, or enzyme catalysts, including selecting appropriate mechanisms with or without the catalyst present.