

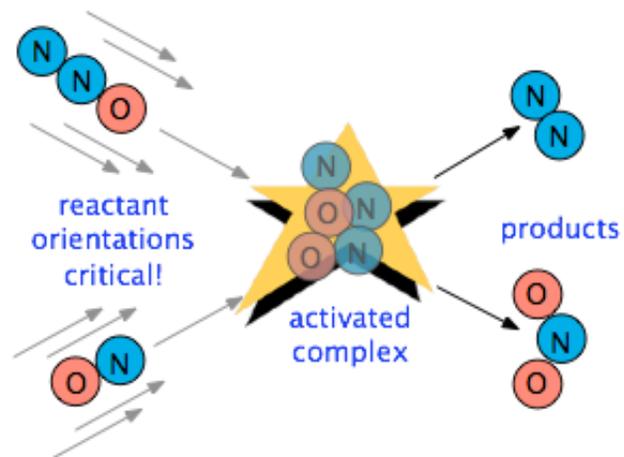
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# Big Idea #4

# Kinetics

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# 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*

Rate is the change in concentration over time

$$\Delta[\mathbf{A}] / t$$

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 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

[Video](#)

■ 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



# Factors Affecting Reaction Rate

1)

## 2016 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS



2. A student designs an experiment to study the reaction between  $\text{NaHCO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . The reaction is represented by the equation above. The student places 2.24 g of  $\text{NaHCO}_3$  in a flask and adds 60.0 mL of 0.875 M  $\text{HC}_2\text{H}_3\text{O}_2$ . The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.
- (a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.
- (b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.
- (c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

 $\Delta[\text{A}] / t$ 

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.



# Factors Affecting Reaction Rate

1)

## 2016 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS

- (c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

As the reaction proceeds, both reactants are consumed and their concentrations decrease. Collisions between reactant particles become less likely as their concentrations decrease, thus the reaction rate slows.

1 point is earned for a valid explanation.

reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

$$\Delta[A] / t$$

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.

# + Determining Rate Order

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



When [A] is doubled, the rate do not change, so the reaction is zero order with respect to A

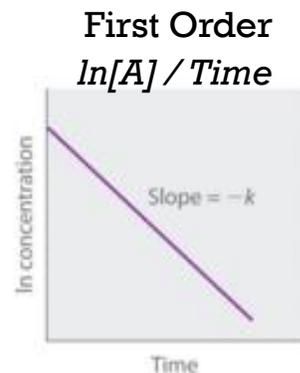
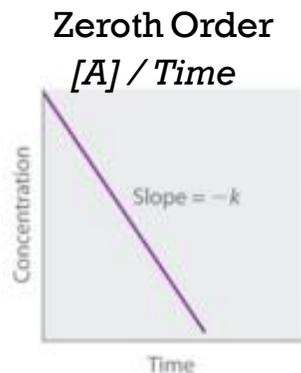
Trial	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate (mol/(L•s))
1	0.100	0.100	0.002
2	0.200	0.100	0.002
3	0.200	0.200	0.004

When [B] is doubled, the rate doubles, so the reaction is first order with respect to B

[Video](#)

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

## Plot to create a straight line graph:



The first and second order integrated rate laws can be found on the Kinetics section of the AP Equations Sheet

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)

$$\ln[A] = -k t + \ln[A]_0$$

$$\ln \frac{[A]_0}{2} = -k t + \ln[A]_0$$

$$\ln[A]_0 - \ln 2 = -k t + \ln[A]_0$$

$$\ln[A]_0 - \ln[A]_0 - \ln 2 = -k t$$

$$-\ln 2 = -k t$$

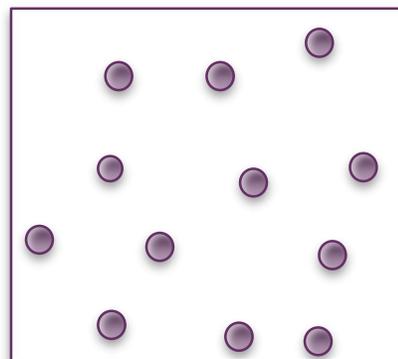
$$\ln 2 = k t$$

$$t_{1/2} = \frac{\ln 2}{k}$$

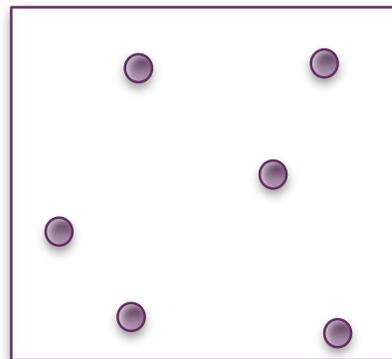
The first order half life equation is derived from the first order integrated rate law

- 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

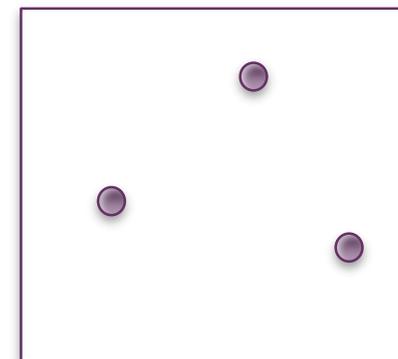
[Video](#)



Initial Conditions  
(12 molecules)



After 30 seconds  
(6 molecules)



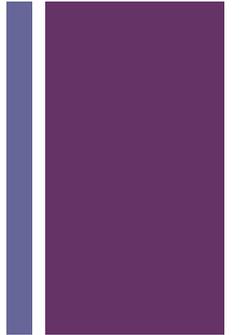
After 60 seconds  
(3 molecules)

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

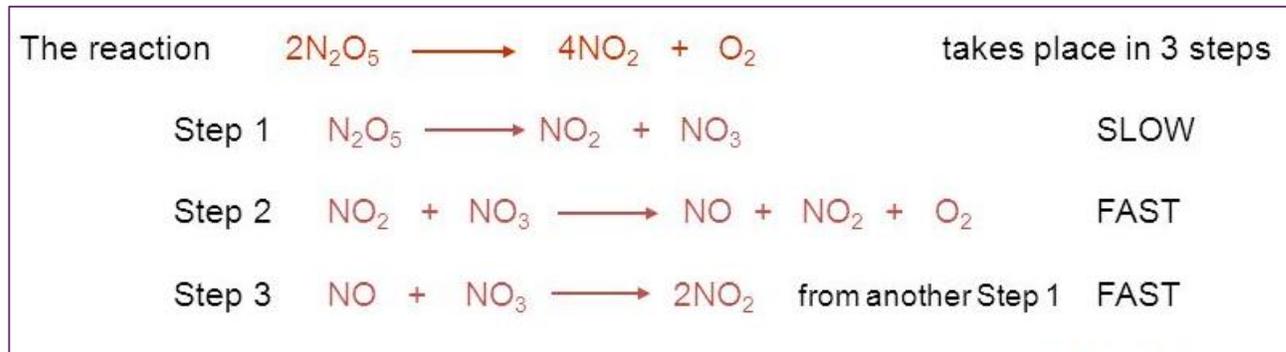
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- In a successful collision
  - Molecules have enough energy to overcome  $E_a$ .
  - Molecules collide with proper orientation to break the bonds.
- In a Mechanism
  - The rate law of any elementary reaction can be written from its stoichiometry.
  - 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.

[Video](#)

2)



Click here after you identify the rate determining step AND have written the rate law



# Collision Theory and Reaction Mechanisms

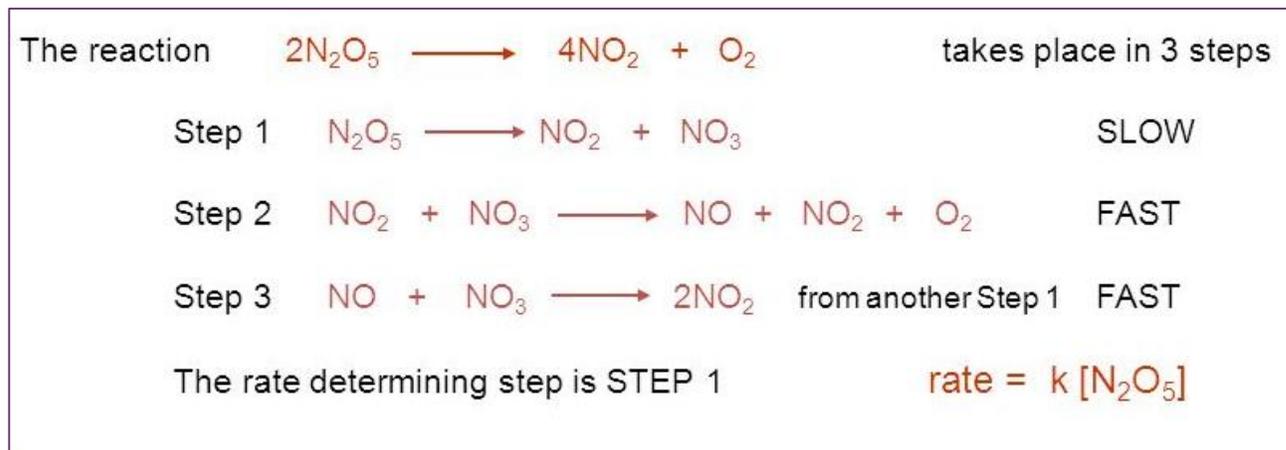
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[Video](#)

2)

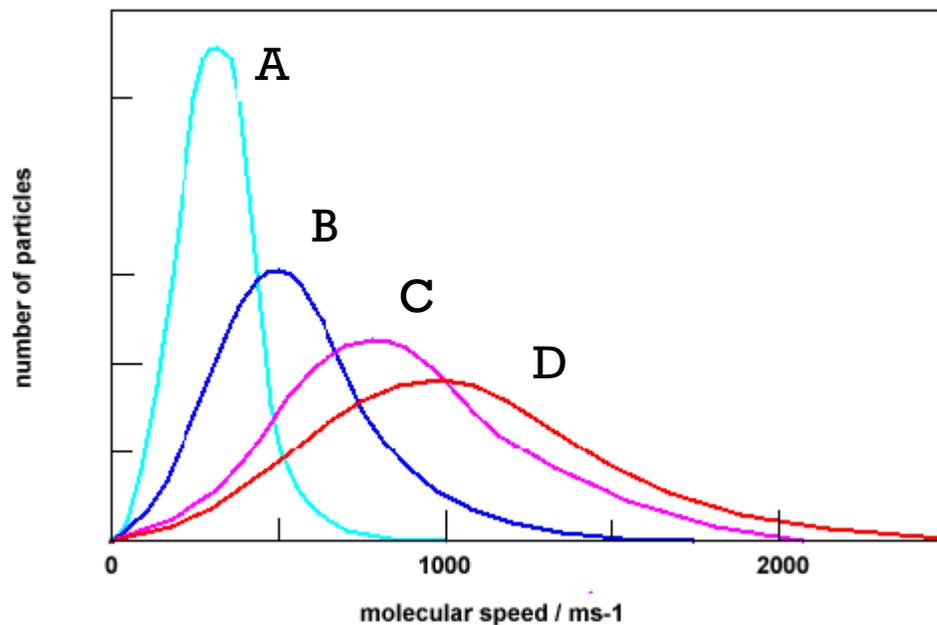


LO: 4.4: Connect the rate law for an elementary reaction to the frequency/success of molecular collisions, including connecting the frequency and success to the order and rate constant.



# Successful and Unsuccessful Molecular Collisions

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



3)

[Video](#)

Click here after you have chosen the correct curve and justified your answer.

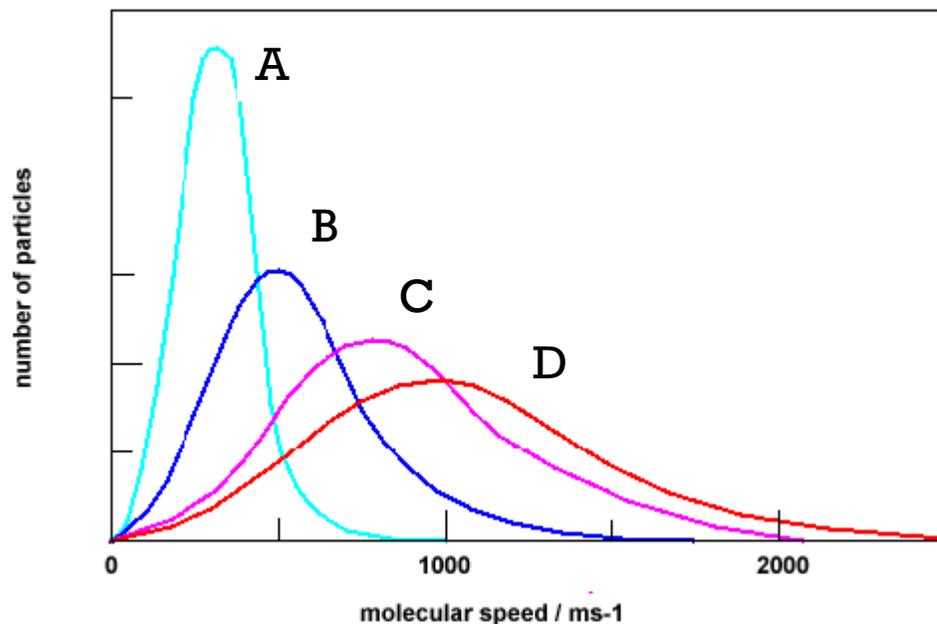
Question: Which curve indicates the particles most likely to produce collisions that result in a chemical change? Justify your selection.

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.



# Successful and Unsuccessful Molecular Collisions

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



3)

[Video](#)

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.

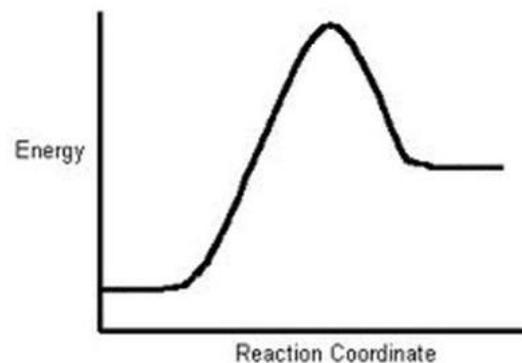
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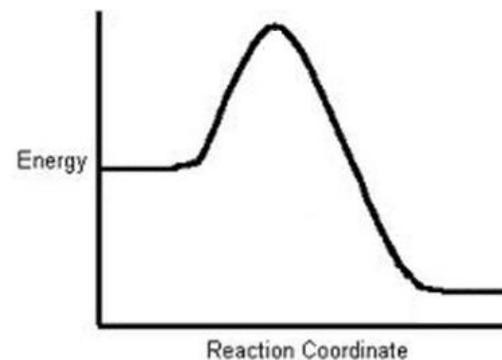
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# Temperature and Reaction Rate

[Source](#)



4)



[Video](#)

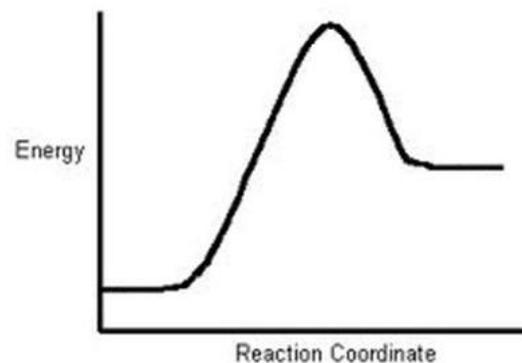
In order for both Reaction A and Reaction B to proceed in the forward direction at the same rate, which reaction would need to be at the higher temperature? Justify your choice.

[Click here to see answer and justification.](#)

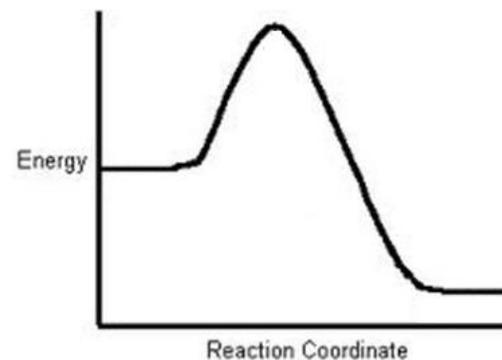
LO 4.6: The student is able to use representations of the energy profile for an elementary reaction (from the reactants, through the transition state, to the products) to make qualitative predictions regarding the relative temperature dependence of the reaction rate.



# Temperature and Reaction Rate



4)



[Video](#)



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.

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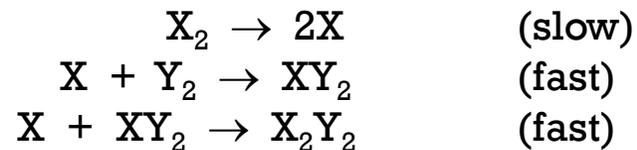
# Reaction Mechanisms



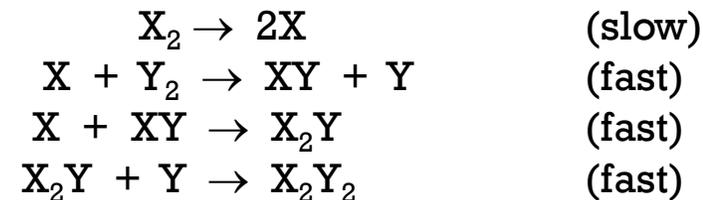
A reaction and its experimentally determined rate law are represented above. A chemist proposes two different possible mechanisms for the reaction, which are given below.

[Video](#)

## Mechanism 1



## Mechanism 2



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

[Click here to see answer and justification.](#)

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.

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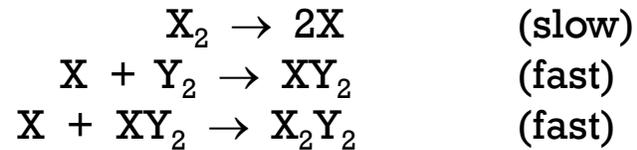
# Reaction Mechanisms



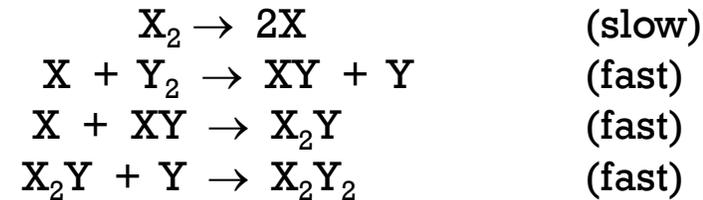
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[Video](#)

## Mechanism 1



## Mechanism 2



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: X, XY<sub>2</sub>. Intermediates in mechanism 2: X, XY, Y, X<sub>2</sub>Y

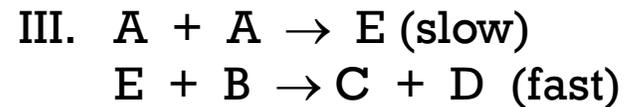
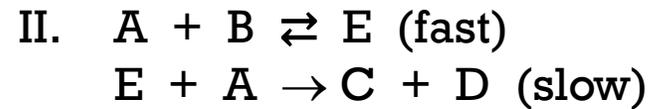
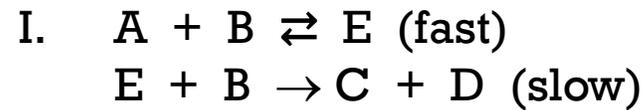
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# Reaction Mechanisms

6)

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



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

[Video](#)

Click here to see answer and justification.

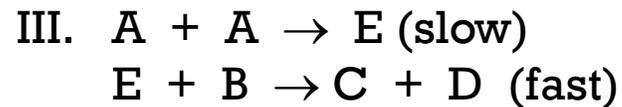
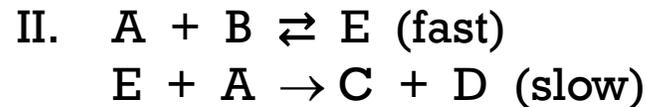
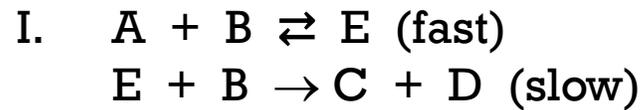
LO 4.7 The student is able to evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate.



# Reaction Mechanisms

6)

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



- 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  $[\text{E}] = K_{\text{eq}}[\text{A}][\text{B}]$ . This substitution gives us the desired rate law:  $\text{rate} = k'[\text{A}]^2[\text{B}]$

Video

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.



## Reaction Mechanisms and Energy Profiles – Practice Problem

7)

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.](#)



## Reaction Mechanisms and Energy Profiles – Practice Problem

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Draw and label axes for the energy profiles below.

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

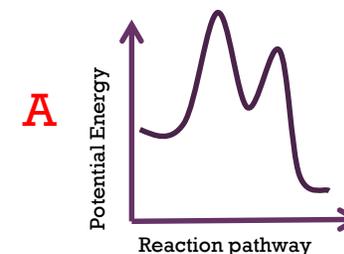
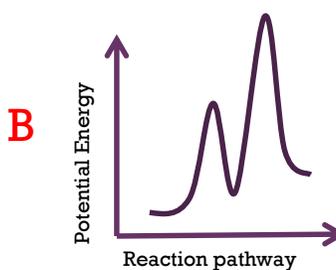
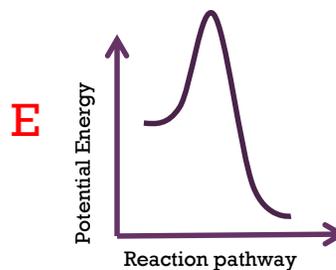
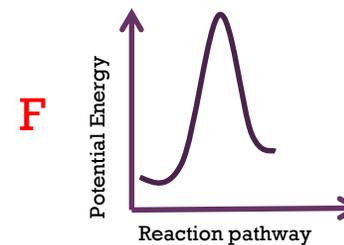
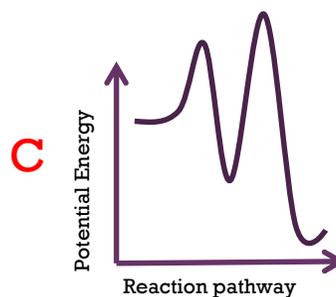
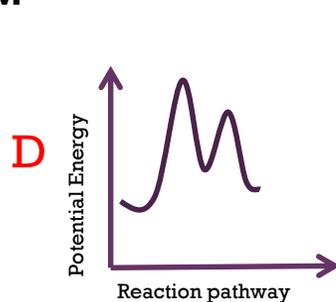
**B. endothermic reaction with a 2 step mechanism where the second step is slow**

**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.**

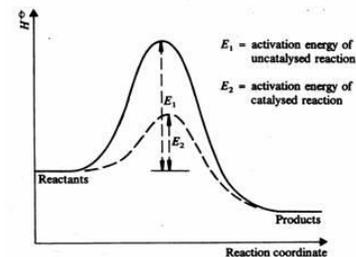
**F. endothermic reaction with a 1 step mechanism.**



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# Catalysts

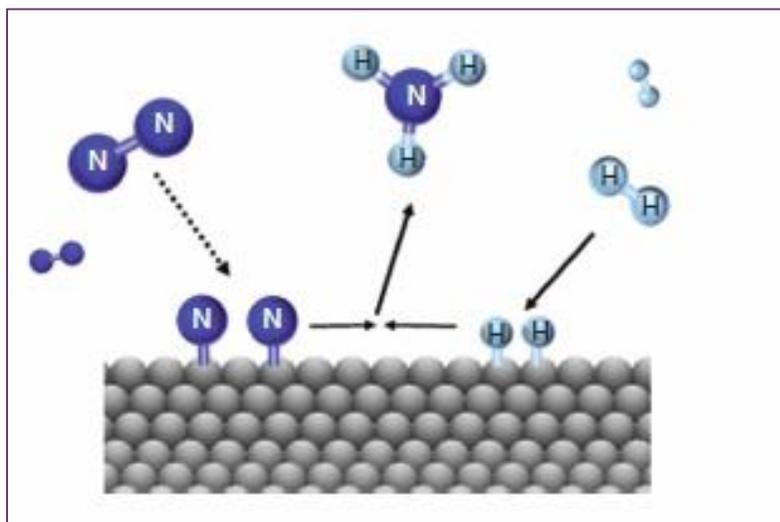
- A catalyst can stabilize a transition state, lowering the activation energy.
- A catalyst can participate in the formation of a new reaction intermediate, providing a new reaction pathway.



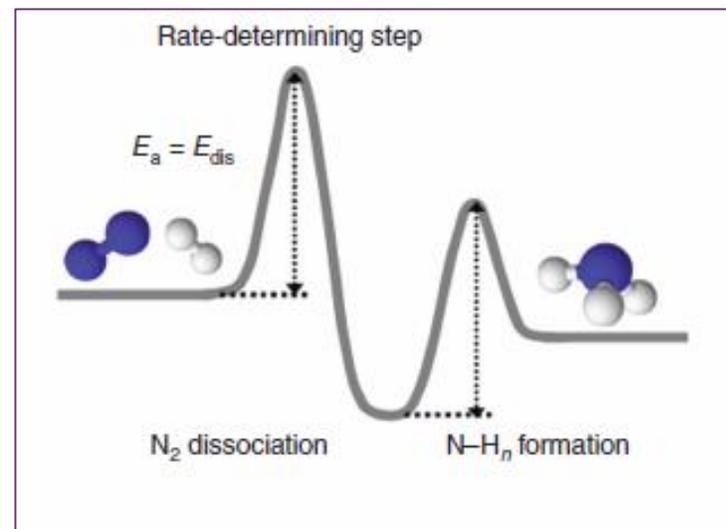
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[Video](#)

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.



Iron based catalyst



LO 4.8 The student can translate among reaction energy profile representations, particulate representations, and symbolic representations (chemical equations) of a chemical reaction occurring in the presence and absence of a catalyst.



# Catalysts

catalysts provide alternative mechanisms with lower activation energy

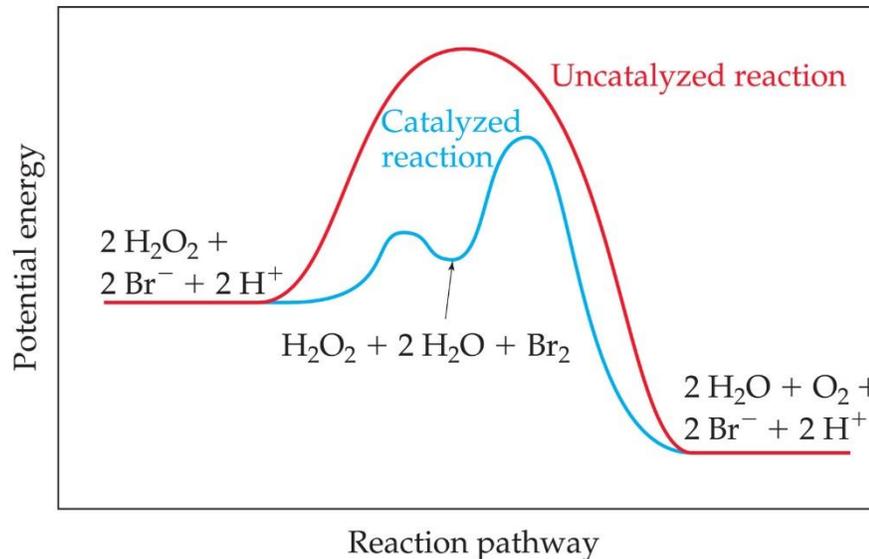
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- In acid-base catalysis, a reactant either gains or loses a proton, changing the rate of the reaction.
- In surface catalysis, either a new reaction intermediate is formed or the probability of successful collisions is increased.
- In Enzyme catalysis enzymes bind to reactants in a way that lowers the activation energy. Other enzymes react to form new reaction intermediates.

[Video](#)

Homogeneous catalysis  
of the decomposition of  $\text{H}_2\text{O}_2$



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.