

UWO **CHEM 1302**

Fall 2024, Chapter 16 Notes



Table of Contents

Chapter 16. Reaction Mechanisms and Arrhenius Equation

16.1. Chapter Intro

16.1. Collision Theory and Activated Complex Theory

16.1.1. 3 Necessary Steps For a Reaction to Occur

16.1.2. Collision Theory

16.1.3. Collision Theory Represented By A Graph

16.1.4. Transition State Theory

16.1.5. Additional Notes on the Arrhenius Equation

16.2. Arrhenius Equation

16.2.1. Arrhenius Equation

16.2.2. Example: Arrhenius Equation

16.2.3. Example: Arrhenius Equation

16.2.4. Practice: Arrhenius Equation

16.3. Measuring Ea Given a Graph

16.3.1. How Do We Measure Ea

16.3.2. Practice: Determining the Activation Energy

16.4. Enzymes

16.4.1. Catalysts

16.4.2. Enzymes

16.4.3. Example: Identifying a Catalyst Vs an Intermediate In a Mechanism

16.4.4. Example: Catalysts 2

16.5. Pre-Equilibrium

16.5.1. Pre-Equilibrium

16.5.2. Practice: Pre-Equilibrium

16.6. Reaction Mechanisms

16.6.1. Reactions Mechanisms – Elementary Reactions

16.6.2. Example: Reactions Mechanisms – Elementary Steps

16.6.3. Rate Determining Step Introduction

16.6.4. Example: Rate Determining Step

16.6.5. Practice: Rate of A Reaction

16.6.6. Practice: Reaction Coordinate Diagram

16.6.7. Practice: Mechanism

16. Reaction Mechanisms and Arrhenius Equation

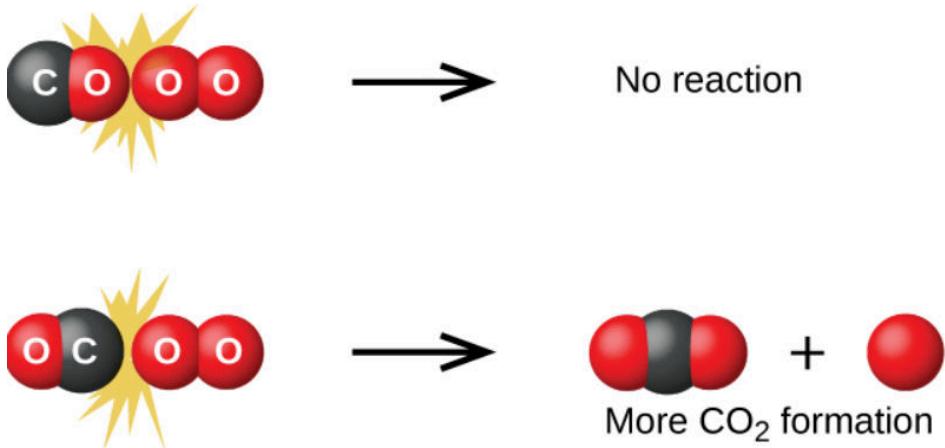
16.I

16.1 Collision Theory and Activated Complex Theory

16.1.1

3 Necessary Steps For A Chemical Reaction to Occur

- For now just focus on **understanding**, we will revisit this topic later in this lesson!
- 1) We need to have a **physical collision** between reactants and products
 - 2) Reactants need to collide with the **correct orientation**
 - 3) Reactants also need to have **sufficient energy** to overcome the energy barrier, called:

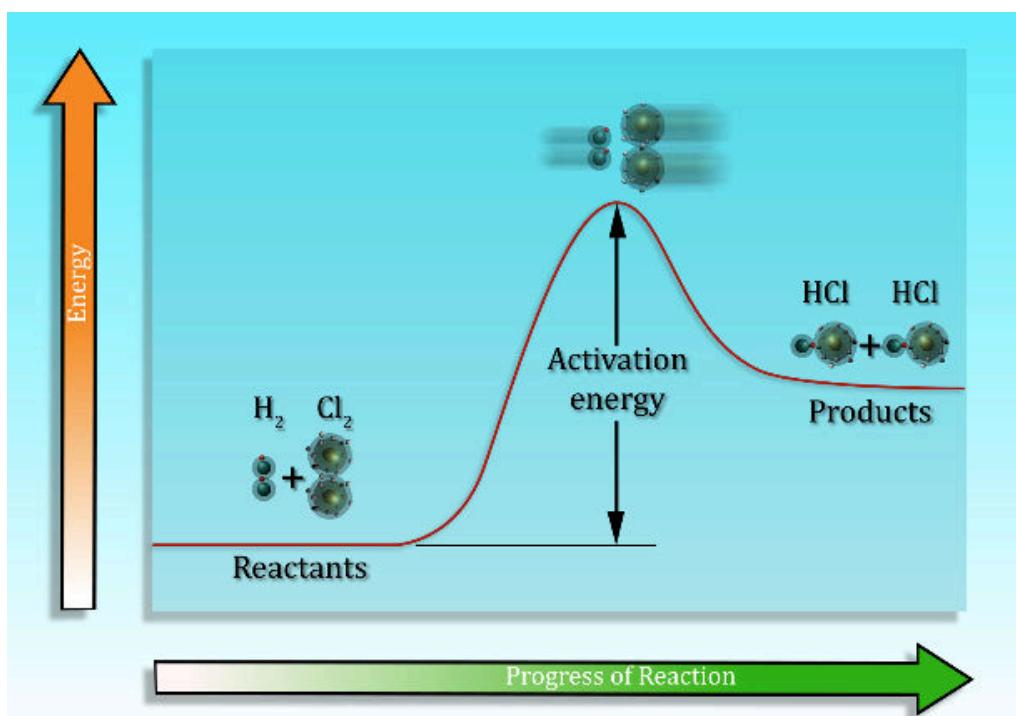


Collision Theory

Collision theory has to do with the 3 necessary steps for a reaction to occur that we looked at earlier:

Recall:

- 1) We need to have a **physical collision** between reactants and products
- 2) Reactants need to collide with the **correct orientation**
- 3) Reactants also need to have **sufficient energy** to overcome the energy barrier, called activation energy



Collision Theory: according to this theory, a reaction only occurs when 2 particles collide with the correct orientation and with sufficient energy to overcome the activation energy barrier

$$\text{Rate} = \text{frequency of collisions} \times \text{fraction of collisions that are effective}$$

- This shows that if we can increase the frequency of collisions, it results in an (increase/decrease) in rate: _____

- It also shows that if we increase the fraction of collisions that are effective, it results in an (increase/decrease) in rate: _____

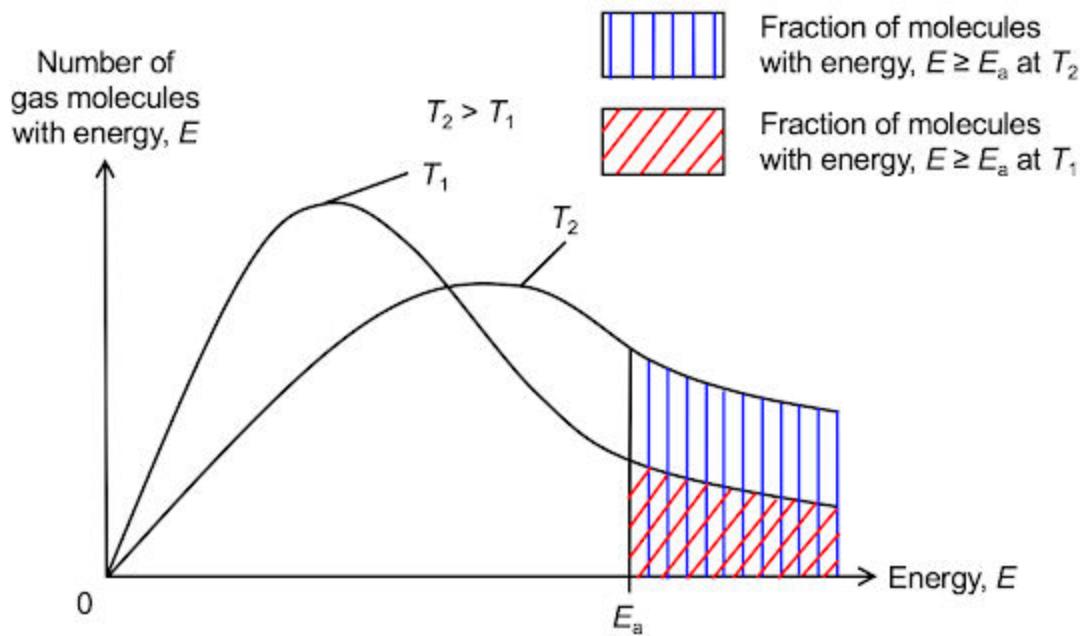
Understanding Activity:

Fill in the following table with the factors that affect rate (nature of reactant, concentration of reactant, surface area, catalyst, temperature)

Hint: One factor increases both the frequency of collisions and fraction of effective collisions!

Increase Collision Frequency	Increase in Fraction of Effective Collisions

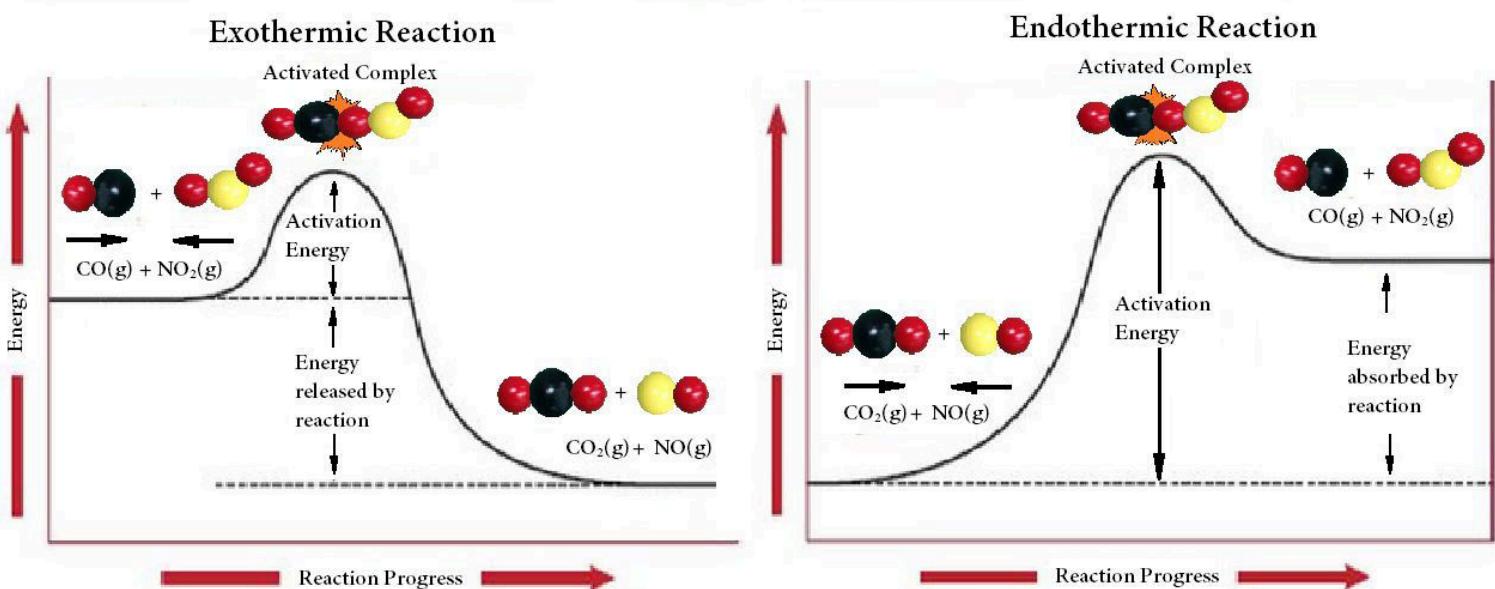
Collision Theory



- the fraction of molecules (f) that collide with a kinetic energy that is equal to or higher than E_a for a reaction is shown by the shaded areas under each curve
- the fraction increases as T increases

Transition State Theory

aka Activated Complex Theory



- **Activated Complex/Transition State=maximum energy**
 - Once energy has increased enough to reach this activated complex, energy then decreases as products are formed
 - Must have enough energy to overcome the activation barrier in order to react and form products!
- **Note: the activated complex cannot be isolated (it's hypothetical!)**
 - Transition state is a hypothetical state where we are halfway between reactants and products (bonds are about to be broken and formed)
- **The barrier height= E_a**
- **Catalysts only lower the energy of the transition state!**
- **A note on enthalpy:**
 - **$\Delta H > 0 = \text{endothermic}$** (energy needs to be added/absorbed for the reaction to occur)
 - **$\Delta H < 0 = \text{exothermic}$** (energy is released in the reaction)

Additional Notes on the Arrhenius Equation

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

Note that $e^{-E_a/RT}$ is between 0 and 1...

What happens when $E_a=0$? vs when E_a is a very large number (infinity)

$$k = \underline{\hspace{2cm}}$$

$$k = \underline{\hspace{2cm}}$$

What about when T is very low?

$$k = \underline{\hspace{2cm}}$$

(makes sense because there is no reaction at absolute 0)

vs when T is very high (infinity)

$$k = \underline{\hspace{2cm}}$$

$$A = p \times z$$

Where A is in the Arrhenius equation

p=orientation probability factor (in most cases it is between 10^{-6} and 1.

z=collision frequency (a measure of how easy molecules collide)

If there are more molecules then would z be a higher or lower #?

If the reactant molecules were very large, would they arrange themselves into the correct orientation more or less of the time compared to reactant molecules that were tiny?

What about if you had many reactants that needed to come together in one reaction, but in a different reaction only a couple of reactants need to come together to form products? Which reaction would have the correct orientation more of the time?

If we know rate of reaction= $k[A][B]$, where [A] and [B] are reactants in the RDS of the mechanism, and we know $k=Ae^{-E_a/RT}$ (Arrhenius),

then... rate of reaction= $Ae^{-E_a/RT}[A][B]$, we also know $A=pz$ so we could plug that in as well:

$$\text{rate of reaction}=(p)(z)e^{-E_a/RT}[A][B]$$

Based on this equation, we can see the 3 necessary components for a successful reaction where reactants are converted into products!

- 1) Molecules need to be **colliding** into one another (what will cause more collisions?)
- 2) Molecules need to be colliding in the **correct orientation**
- 3) While molecules are colliding in the correct orientation, they also need to have **enough energy** to overcome the energy barrier in order to form products

Only when we have all 3 of these factors do we have an effective collision and get products. The more of these effective collisions we have per second, the higher the rate of reaction!

16.2 Arrhenius Equation

16.2.1

Arrhenius Equation

- Rates of reaction are highly temperature dependent! Imagine the speed of ice melting at 0°C vs 40°C
- Svante Arrhenius discovered a simple equation that relates the rate of a chemical reaction to the temperature which it is performed at. The Arrhenius equation is shown below.

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

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

- k is still the rate constant
- A is called the pre-exponential factor, it is unique for all reactions and is constant across all temperatures. It is related to the probability of a successful collision.
- T is temperature and R is the Gas constant
- E_a is the activation energy, which is shown below graphically

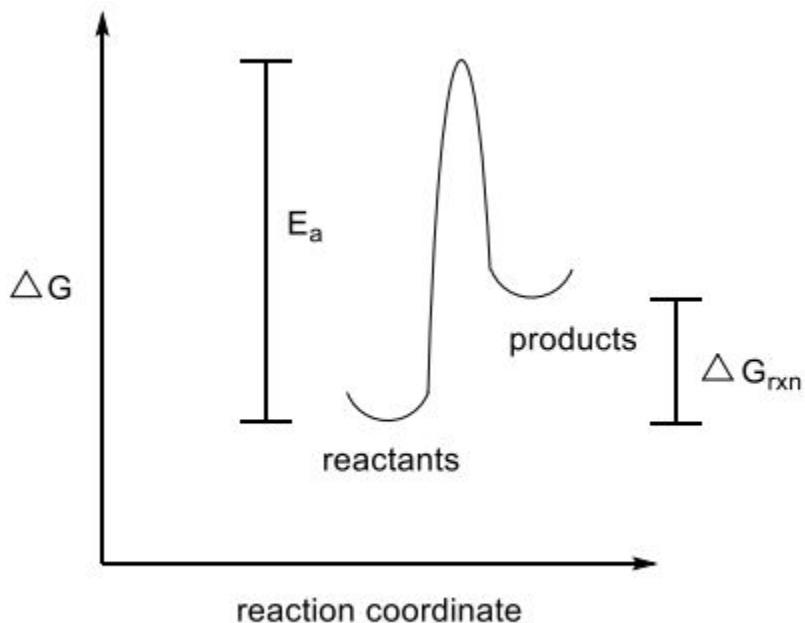


Figure 4.4.1 Reaction Coordinate Diagram

-
- Activation energy, E_a , is the amount of energy it takes to get to the products
 - The Arrhenius equation on its own is not very useful because of the pre-exponential factor A is difficult to calculate. However by dividing one rate by another and rearranging we end up with the following equation. Notice that A has been cancelled out and is no longer necessary.

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- We can use this equation to compare the rate of a reaction at two different temperatures.

16.2.2

- a. A chemical reaction increases its rate by a factor of 15 when it is warmed from room temperature to 100°C. What is the activation energy of this process? R=8.314J/Kmol

16.2.3

If the activation energy of a reaction is measured to be 59.6 kJ/mol, by what factor will the rate of this reaction be increased when the temperature is raised from 305 K to 405 K?

16.2.4

A Schiff base reaction between 3-propanone and aniline proceeds with rate constants of $0.0065 \text{ M}^{-1} \text{ s}^{-1}$ and $0.0084 \text{ M}^{-1} \text{ s}^{-1}$ at 30°C and 80°C respectively. Determine the activation energy and preexponential factor for this reaction.

16.3 Measuring Ea Given a Graph

16.3.1

How Do We Measure E_a

- If we take the Arrhenius equation and rearrange it into linear form we can use graphical methods to find an experimental activation energy, E_a .

$$k = Ae^{-\frac{E_a}{RT}}$$

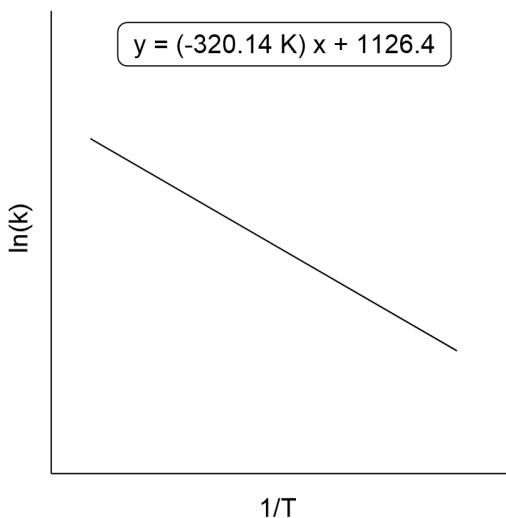
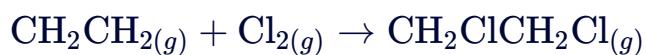
$$\ln(k) = -\frac{E_a}{R} \frac{1}{T} + \ln(A)$$

- If we plot $\ln(k)$ vs $1/T$ we can determine the activation energy of the reaction from the slope of the straight line.

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

16.3.2

Use the graph below to calculate the activation energy of the reaction below.



1.02 kJ/mol

1.55 kJ/mol

2.66 kJ/mol

3.17 kJ/mol

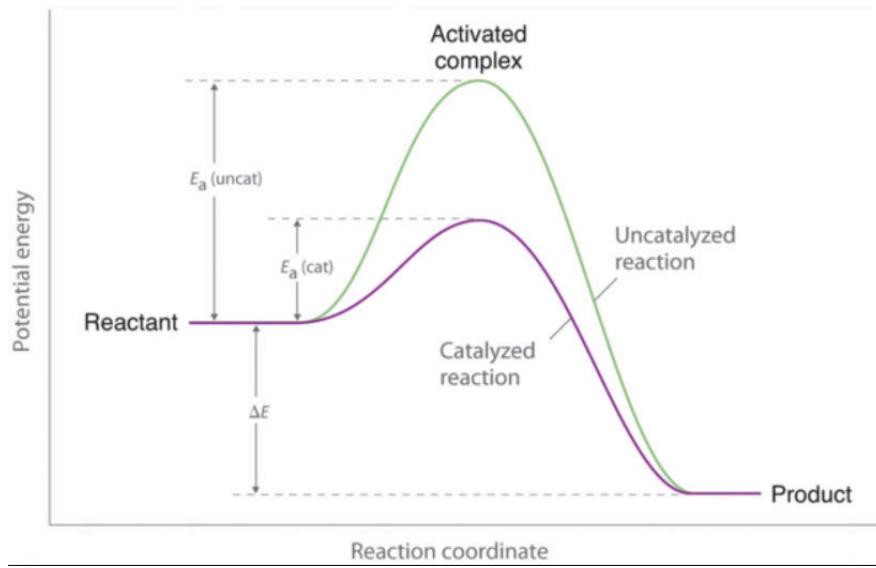
16.4 Enzymes

16.4.1

Catalysts

Catalysis General Information

- A catalyst is a species which is **not consumed** in the reaction but changes the **RATE** of the reaction
- A catalyst can increase the rate of a reaction by **lowering the activation energy**
 - **Activation Energy (E_a)**: Is the minimum amount of energy that the reacting species must possess to undergo the specified reaction.

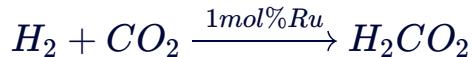


- Since the catalyst lowers E_a for a reaction, does it speed up just the forward, backward, or forward and backward reaction?
 - _____
- Will the equilibrium constant change when we add a catalyst?
 - _____
- Would the change in enthalpy be affected by a catalyst? If so, how? (Draw where we could see deltaH or deltaG on the above plot)

-
- • **This is a reminder that catalysts have to do with kinetics/thermodynamics: _____ so they don't affect equilibrium constants, Gibb's Free Energy, reaction enthalpy, equilibrium concentrations, etc, which have to do with kinetics/thermodynamics: _____

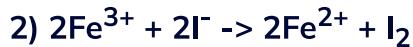
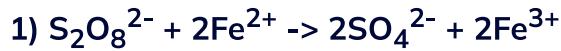
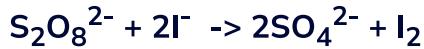
Catalysts Cntd.

- Simply put, a catalyst can affect kinetic parameters of a reaction such as rate and rate expression but cannot affect thermodynamic parameters such as ΔG , ΔH , ΔS , ΔE , and K .
- Catalysts are classified based on phase
 - If the catalyst is the same phase as the reactants the catalyst is said to be **homogenous**
 - If the catalyst is of a different phase than the reactants the catalyst is said to be **heterogeneous**
 - **main advantage of using a heterogeneous catalyst is that it can be easily separated from the reaction mixture**
- A huge advantage of catalytic reactions is that we can use very small amounts (loadings) of catalyst in a reaction because it is not consumed.



- Since the catalyst is not consumed in the reaction would you expect to see it in the overall balanced equation? _____
- Which elementary step in a mechanism would the catalyst be a part of (slow/fast)? _____
- If we were writing the rate of the overall reaction then, would the catalyst be written in that expression as well or not? _____

Identifying A Catalyst Vs An Intermediate In a Mechanism



WIZE CONCEPT

Intermediate: Produced in a step and then used up in another step; is not seen in the overall balanced equation

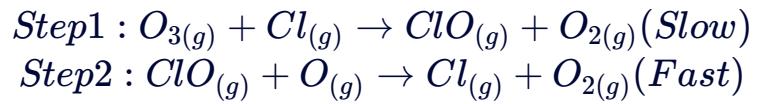
Catalyst: Not consumed in the reaction and is not changed permanently by the reaction.

Is there an intermediate in the above mechanism? If yes, what is it?

If there a catalyst in the above mechanism? If yes, what is it?

16.4.4

The decomposition of ozone ($O_{3(g)}$ + $O_{(g)}$ \rightarrow $O_{2(g)}$) is significantly sped up by the presence of chlorine in a two-step mechanism:



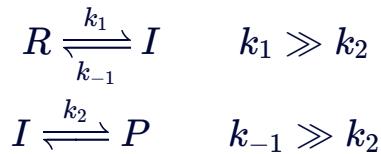
What is the role of chlorine in this reaction?

16.5 Pre-Equilibrium

16.5.1

Pre-Equilibrium

- when the rates of formation of the intermediate and its decay back into reactants are much faster than the rates of formation of products, you can assume that reactants and intermediates are in equilibrium throughout the course of the reaction=pre-equilibrium



The overall rate of reaction here is:

$$v_2 = k_2[I]$$

Write the rates of each elementary step:

- elementary step #1: $v_1 = k_1[R]$
- elementary step #1: $v_1' = k'[I]$
- elementary step #2: $v_2 = k_2[I]$

We also have **pre-equilibrium** here since R and I are in equilibrium throughout the reaction and $k_1 \gg k_2$

WIZE CONCEPT

Since the reactants and intermediate are in equilibrium, recall that for equilibrium we know:
the rate of the forward reaction=rate of the backward reaction

In this case: $k_1[R] = k'[I]$

Because of this we can write an expression $K = \frac{k_1}{k'} = \frac{[I]}{[R]}$

Now we can **solve for our intermediate (I):**

$$\frac{k_1[R]}{k'} = [I]$$

Now take the overall rate of reaction we have and plug in the expression for the intermediate:

$$v = v_2 = k_2[I]$$

$$v = v_2 = k_1 k_2 [R] / k'$$

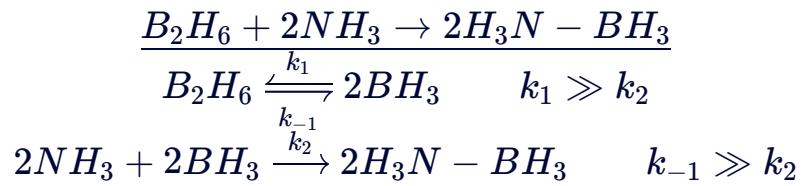
Could let $K = k_1 k_2 / k'$ to simplify it:

$$v(\text{overall}) = K[R]$$

This was much faster than standard state approximation! We got the same answer by using pre-equilibrium and we were able to do this because there was an equilibrium between the reactants and intermediate!

16.5.2

Write a rate law for the formation of NH_3BH_3 which involves only the concentration of reactants and rate constants.

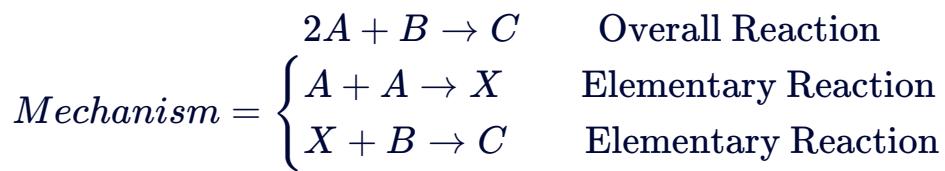


16.6 Reaction Mechanisms

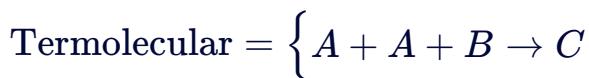
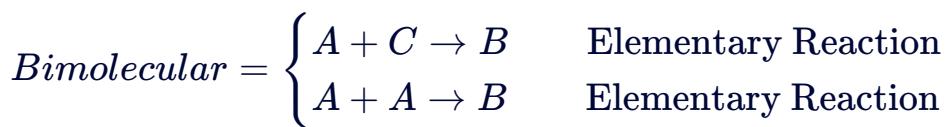
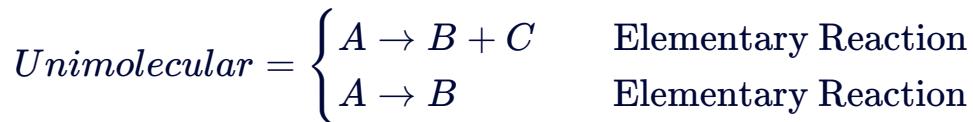
16.6.1

Reactions Mechanisms – Elementary Reactions

- All complex chemical reactions occur via a set of simpler reactions called elementary reactions.
- The summation of all these elementary reactions is referred to as the mechanism of the reaction.
- A mechanism tells us how a complex reaction occurs



- Elementary reactions can be classified based on the number of molecules which have to simultaneously collide. This is often referred to as molecularity.



The rate of an elementary reaction is quite simply expressed below.

$$v = k[A] \quad \text{Unimolecular}$$

$$v = k[A][B] \quad \text{Bimolecular}$$

$$v = k[A][B][C] \quad \text{Termolecular}$$

What about if we had an elementary reaction like this:

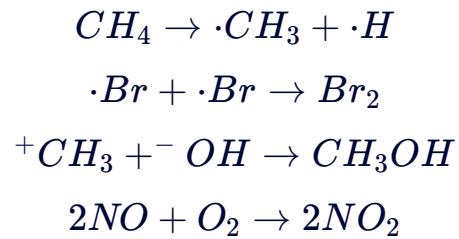


And what would the rate law look like for this elementary reaction?

Note: ONLY for elementary reactions can we use stoichiometry for rate laws

16.6.2

Example: Write out a general rate law for the following elementary reactions.



Rate Determining Step Introduction

- The rate determining step is the **slowest elementary step** in a reaction pathway.
- **This step determines the rate of the overall mechanism**
 - Let's think of an example to explain this. Let's say we need a lot of dishes washed! We get 3 students who start working together.
 - The first student is responsible for just getting the plate wet. You can imagine that the time this takes the first student for each plate is very little!
 - If this was a reaction: dry dirty dish \rightarrow wet dirty dish



- The second student is responsible for scrubbing the plates and adding soap. This student has to scrub until everything is cleaned.
- If this was a reaction: wet dirty dish \rightarrow wet clean dish



- Finally, the third student just needs to pat the front and back of the plate to dry it.
- If this was a reaction: wet clean dish \rightarrow dry clean dish



- Which student do you think would take the most amount of time per plate for their step?

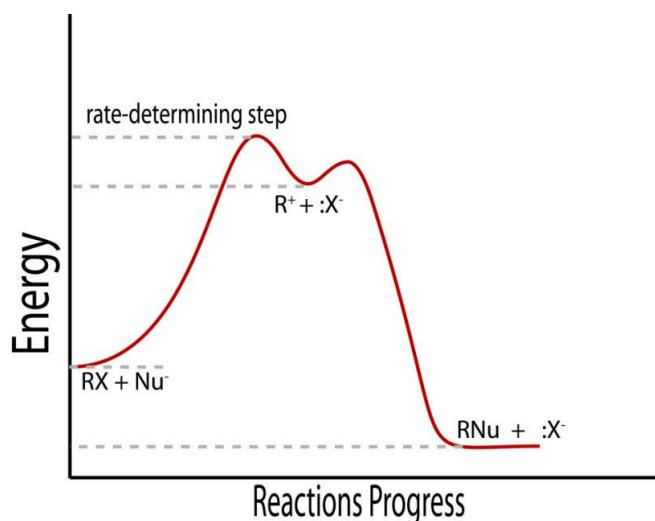
- This means that the rate of the overall process going from dry dirty dish -> dry clean dish is determined by which step? _____
- If we increase the rate of step 1 do you think that would affect the rate of the overall process?

- **The rate of the reaction is limited by the rate determining step.**
 - So if student 1 and 3 are both cleaning 1 plate/2 seconds but student 2 is cleaning 1 plate/30 seconds, the rate of the overall reaction would be 1 plate/30 seconds.
 - Reducing the time it takes for student 1 and 3 to 1plate/1sec does nothing to the RDS and so the overall process will still take 30 seconds/plate.
- Then how could we increase the rate of the reaction?
- In chemical reactions we use a **catalyst!** (*more on this later!)

Rate Determining Step

- The rate determining step is the **slowest elementary step** in a reaction pathway.
- This step determines the rate of the overall mechanism**

- Ea is higher/lower _____ for RDS
- Which is the RDS in the following diagram? _____



The reaction order can't be determined from the overall balanced equation

a) We could determine the reaction order from experimental data

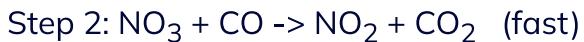
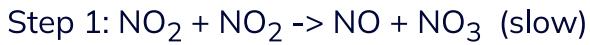
OR

b) We could determine the reaction order from a reaction mechanism (that shows elementary steps)

For the following mechanism, what is the rate for the overall reaction?



Mechanism:



i WIZE TIP

Since we will need the proper coefficients when figuring out the rate law, check to see if the equations are balanced!

1) What is the rate of each of the elementary steps?

i WIZE TIP

Here we can do this because it is clear that these are elementary steps (labelled Step 1 and 2). On your test don't assume you're looking at an elementary step unless it says so!

2) Which of these steps determines the rate of the overall reaction? _____

3) What is the rate of the overall reaction?

4) Are there any reaction intermediates? Where would we see these on the reaction coordinate diagram?

Do you think intermediates are easy/difficult to isolate? _____

5) What order is NO_2 ?

6) What order is CO?

7) Could I have found the rate law using this: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

8) Which of these steps would the catalyst act on?

9) If we looked at the reaction in reverse could we use the same catalyst or would we need a different one? (see reaction energy diagram for help!)

 WIZE CONCEPT

Coefficients from a balanced elementary step can be used to determine the rate law for only that step, whereas coefficients from the balanced RDS are used to get the rate law for the overall reaction!

 WIZE TIP

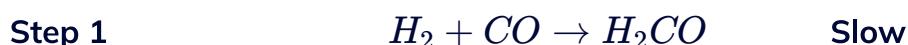
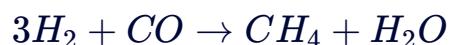
One last tip about mechanisms. In the above example, we have a balanced equation and then 2 elementary steps. Just note that the steps in a particular mechanism can't be proven, they can only be supported or refuted. You might get a question that gives you different pieces of info and asks which statement supports the mechanism.

For example, if the question said that increasing [CO] led to an increase in rate, would that support or refute the provided mechanism?

[CO] is not in the overall reaction rate law, so it shouldn't have an impact on the rate. Therefore, that piece of information refutes (or goes against) the mechanism that is provided!

16.6.5

Assume the following reaction occurs by the given reaction mechanism.



The rate law expression must be rate = _____.

$k[H_2]^2[CO]^2$

$k[H_2]^2[CO]$

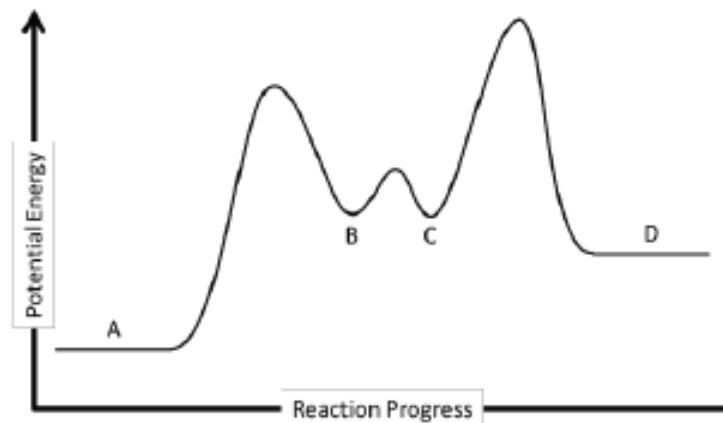
$k[H_2][CO]^2$

$k[H_2][CO]$

$k[H_2]^2[CO]^3$

16.6.6

Use the following reaction coordinate diagram to answer the following three questions.



Part 1

1) How many steps are there in this reaction?

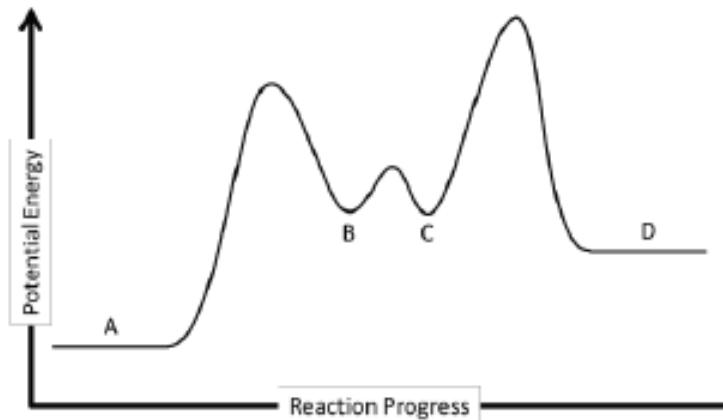
1

2

3

4

Use the following reaction coordinate diagram to answer the following three questions.



Part 2

How many parts of this diagram shows that intermediates are present?

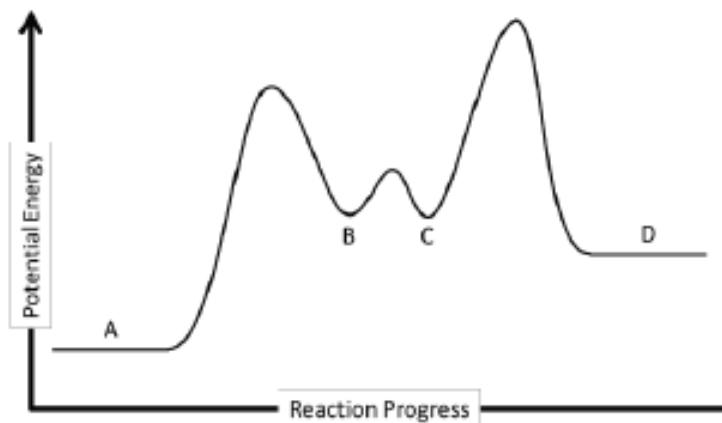
1

2

3

4

Use the following reaction coordinate diagram to answer the following three questions.



Part 3

How many transition states are present?

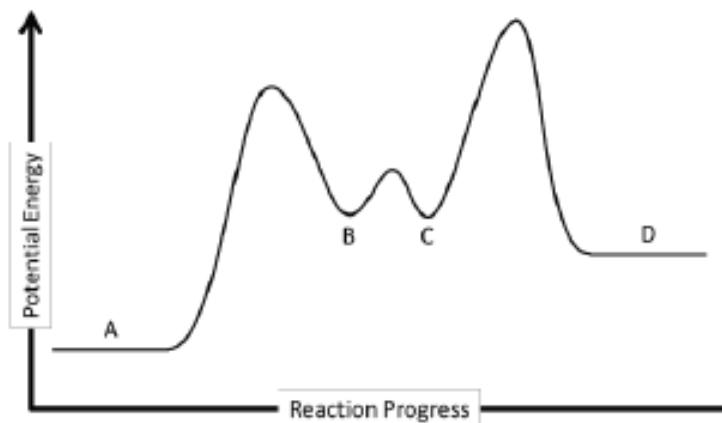
1

2

3

4

Use the following reaction coordinate diagram to answer the following three questions.



Part 4

Which step is the rate determining step?

1st

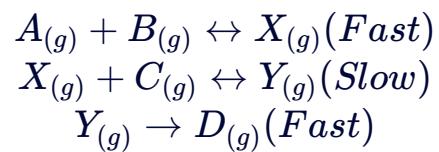
2nd class lovers

3rd

4th

16.6.7

The proposed mechanism for a reaction is:



- a. What is the overall reaction?
- b. Identify the intermediates, if any.