

McGill **CHEM 120**

Winter 2025, Chapter 2 Notes



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2. Kinetics (Ch 17)

2.1 Introduction to Kinetics

2.1.1

Introduction to Kinetics

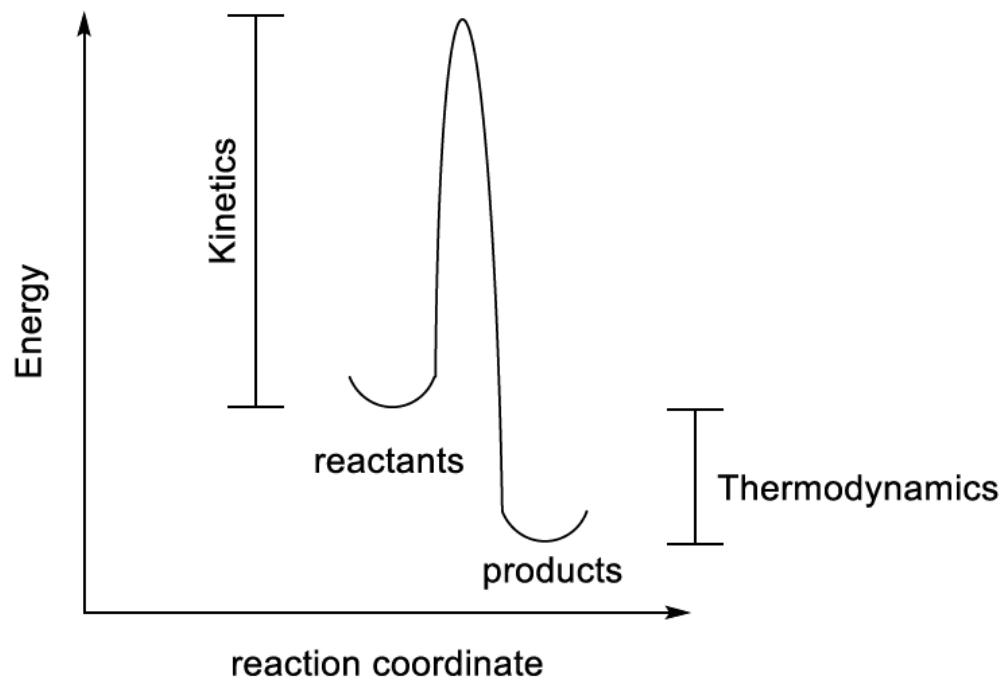
Kinetics: The study of the rates of chemical reactions

- While thermodynamics can tell us which reactions are possible (spontaneous or nonspontaneous) it cannot give us any information about how long the reaction will take.
- The most famous example of this is diamonds.



$$\Delta G < 0$$

- So if the reaction from diamond to graphite is spontaneous why do diamonds last forever?
- The rate of this reaction is so slow, that the Sun will become a red giant and consume the earth before any diamonds spontaneously change phase to graphite.



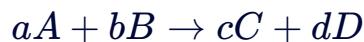
2.2

Rate of Reaction

2.2.1

Reaction Rates

- The reaction rate is a measure of the change in concentration of a reactant or product over time!
 - ex. In physics we know velocity= $\Delta d/t$, in chemistry, a reaction rate= $\Delta []/t$
 - The units of rate would be **M/s** where M=mol/L
- A general form of a **reaction rate** is shown below:



$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

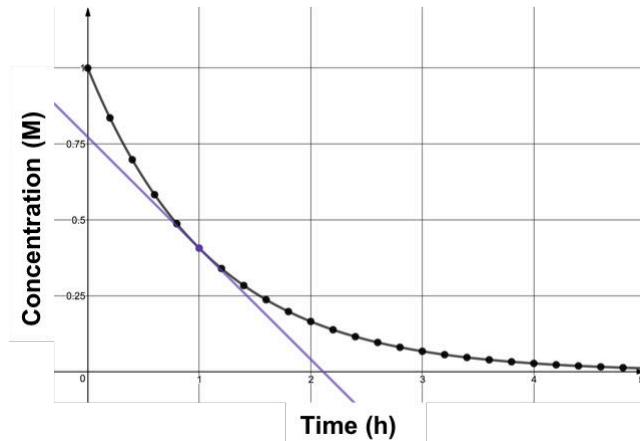
- As the reaction proceeds are we getting more/less of the reactant? _____ More/less of the product?
 - The **- sign** indicates that the concentration of reactants are decreasing (losing reactants as the reaction proceeds)
 - The **+ sign** indicates that the concentration of products is increasing (gaining product as the reaction proceeds)
-
- ****Rates must be determined through experimentation.**

Measuring Reaction Rates

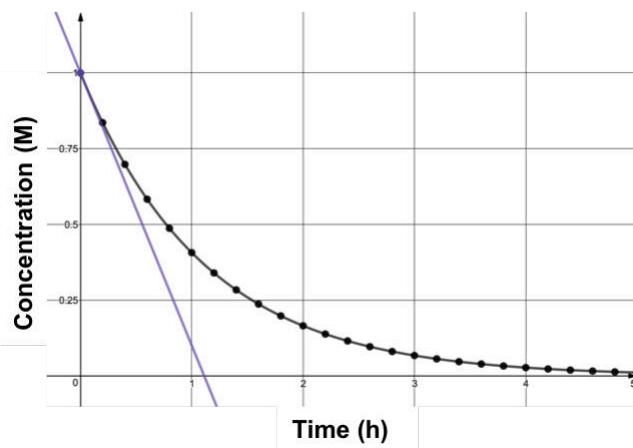
- Consider the reaction: $A \rightarrow B$
- The reaction rate can be measured using **any** substance in the reaction. **Reaction rate units are always M/s** (M stands for concentration, mol/L)

$$\text{Rate} = -\frac{\Delta [A]}{\Delta t} = \frac{\Delta B}{\Delta t}$$

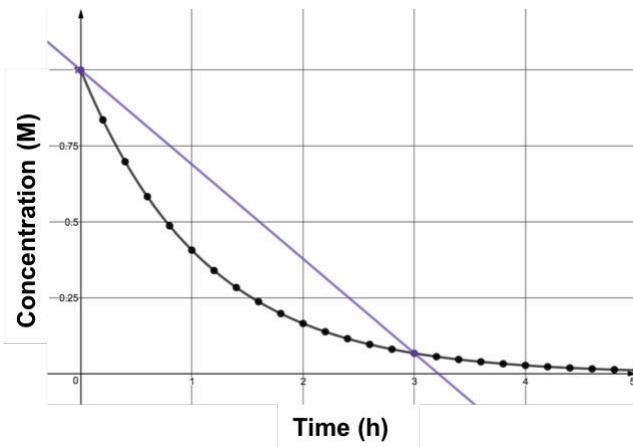
- Instantaneous rate:** the rate of reaction **at an instance in time** (the slope of the tangent line to a point in a concentration vs time graph)



- Initial rate** – instantaneous rate of a chemical reaction at $t = 0$, immediately after the reaction has begun



- **Average rate:** the rate of reaction **over a period of time** (the slope of the line connecting 2 points in a concentration vs time graph)



2.2.3

Practice: Rates of Reaction

If N_2 is consumed at 2 M/s, what is the rate of production of NH_3 and rate of consumption of H_2 in the reaction?

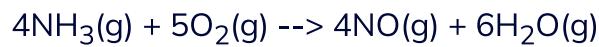


Rate of production of NH_3 (ans in M/s)

Rate of consumption of H_2 (ans in M/s)

2.2.4

In the following reaction the average rate of formation of NO(g) is 1.12 mol/Ls. If 2 minutes passes, what is the concentration of O₂(g) that is consumed?



1.4 M/s

1.68x10² M

2.7x10² M

2.8 M/s

2.3

The Rate Law

2.3.1

Rate Laws

- We can use initial reaction rates (using initial concentrations of reactants) to get an expression of the reaction rate called the **rate law**.



$$\text{rate} = k[A]^x[B]^y$$

WIZE CONCEPT

It's important to be able to recognize the rate law!

- The rate law only includes reactants/products: _____
- k* is the rate constant**

WATCH OUT!

We use x and y here because **x and y are NOT the coefficients in the balanced equation!**

$$\text{overall reaction order} = x + y$$

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)

- We will take a look at both of these ways to figure out the order of the reaction next!

2.3.2

Determine the order of each reactant and the overall order for the following rate laws.

1. $v = k[\text{NO}][\text{C}]^2$

2. $v = k[\text{O}_3]^1$

3. $v = k[\text{O}_2]^{1/2}[\text{CH}_4]$

4. $v = k$

Determining the Rate Law from Experimental Data

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

a) We could determine the reaction order from experimental data

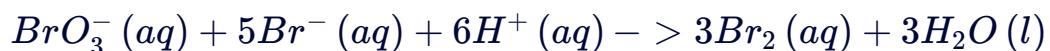
OR

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



This method of finding the rate law is found on tests quite often!

Part 1: Use the rate data provided to determine an experimental rate law for the following reaction:



Trial	[BrO ₃ ⁻] (M)	[Br ⁻] (M)	[H ⁺] (M)	Initial Rate (M/s)
1	0.1	0.1	0.1	8.0x10 ⁻⁴
2	0.2	0.1	0.1	1.6x10 ⁻³
3	0.2	0.2	0.1	3.2x10 ⁻³
4	0.1	0.1	0.2	3.2x10 ⁻³

1) We'll write the general rate law expression:

2) Let's figure out what x would be (exponent for BrO_3^-):

(it doesn't matter which exponent we choose to solve for first!)

3) Let's figure out what y would be (exponent for Br^-):

4) Let's figure out what z would be (exponent for H^+):

5) Finally, we can write out the completed rate law:

Part 2: What is the overall reaction order?

Part 3: What is the rate constant?

To find k we can just substitute data in directly from the table with the experimental data.
We need the **completed rate law** and we can **choose any trial** to take #s from (choose the trial with the lowest numbers for easier calculations!)

Here we'll use trial 1:

According trial 1, rate= 8.0×10^{-14} , $[\text{BrO}_3^-] = 0.1\text{M}$, $[\text{Br}^-] = 0.1\text{M}$, $[\text{H}^+] = 0.1\text{M}$

Now rearrange to solve for k (the rate constant)!

What about the units for k?

Recall rate has units: _____

And concentration has units: _____

Part 4: If we were asked to solve for the rate but were given k and the reactant concentrations for a trial, how would we do that?

Shortcut to Find Units of k Quicker

For 0th order: k has units $M \cdot s^{-1}$

For 1st order: k has units s^{-1}

For 2nd order: k has units $M^{-1} \cdot s^{-1}$

Recognize a pattern?

What would the units for k be for a 3rd order reaction?

In summary, units of k will be: $M^{1-n} \cdot s^{-1}$

Low yield:

What if the answer options don't have M but instead have moles and L?

What would the units be for a 2nd order reaction for example?

Well $M = mol/L$

So for a 2nd order reaction, we know the units would be $M^{-1} \cdot s^{-1}$

This is the same as writing: $\frac{1}{M \cdot s}$

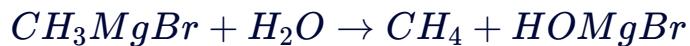
Now let's substitute M for mol/L:

$$\frac{1L}{mol(s)}$$

Which could be written as: $L \cdot mol^{-1} \cdot s^{-1}$

2.3.5

Use the rate data provided to determine an experimental rate law for the following reaction. Solve for the rate constant, k, as well.



Run	$[CH_3MgBr]_0$	$[H_2O]_0$	initial rate
1	1.0 M	1.0 M	0.0045
2	2.0 M	1.0 M	0.0091
3	2.0 M	2.0 M	0.0183

rate=k[H₂O] where k is 0.009/Ms

rate=k[CH₃MgBr][H₂O] where k is 0.009/Ms

rate=k[CH₃MgBr][H₂O] where k is 0.0045/Ms

rate=k[CH₃MgBr][H₂O]² where k is 0.0045/Ms

2.3.6

The following data was gathered for the reaction:



Initial [A] (M)	Initial [B] (M)	Initial [D] (M)	Initial Rate (M/s)
1.0	1.0	1.0	3.5×10^{-2}
0.5	0.5	1.0	4.4×10^{-3}
2.0	1.0	1.0	7.0×10^{-2}
0.5	0.5	2.0	4.4×10^{-3}
1.0	2.0	1.0	1.4×10^{-1}

Find the rate law exponents and the rate constant for this reaction. Report your exponents as integers and your rate constant as a decimal to two significant figures without units in the answer field.

$$v = k[A]^x[B]^y[D]^z$$

x

y

z

k

2.3.7

The reaction $A + 2B \rightarrow$ products was found to follow the rate law: $\text{rate} = k[A]^2[B]$. Predict by what factor the rate of reaction will increase when the concentration of A is doubled, the concentration of B is tripled, and the temperature remains constant.

5

6

12

18

none of these

2.3.8

Suppose a gas-phase reaction has the rate law, $\text{rate} = k[\text{A}][\text{B}]^2$. Which of the following could be the units for the rate constant, k ?

$\text{M}\cdot\text{s}^{-1}$



$\text{mol}^{-2}\cdot\text{s}^{-1}$



$\text{L}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$



$\text{L}^{-2}\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$



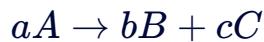
2.4

Integrated rate Laws

2.4.1

Integrated rate Laws

- gives [] of reactants and products at any time after the start of the reaction
- By integrating general rate equations we can obtain integrated rate laws. These laws allow us to predict the concentration of a species over the entire course of a reaction.
- The general form of the 0th, 1st, and 2nd order integrated rate laws are on your formula sheet and are also shown below. These equations are applied to a system which depends on the concentration of one species [A].
- Note your formula sheet has assumed that a = 1. Be very careful that if a does not equal 1 you remember to include it.



$$[A] = [A]_0 - kt \quad 0^{th}$$

$$\ln [A] = \ln [A]_0 - kt \quad 1st \text{ (linear form)}$$

$$[A] = [A]_0 e^{-kt} \quad 1st \text{ (exponential form)}$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad 2nd$$

[A] is the concentration of a species at time, t.

[A]₀ is the initial concentration.

t is time in seconds!

- In order to determine if a reaction is 0th 1st or 2nd order in a substrate, scientists can plot [A] vs t
 - in 0 order: [A] decreases in a linear fashion as t increases, slope=-ak (show how!)

-
- in 1st order: $[A]$ decays exponentially with t , larger k will result in _____ (slower/faster) decay, and _____ (shorter/longer) half life (see half life equation for 1st order to help: 1st order: $t_{1/2}=\ln 2/ak$)
 - but if you plot $\ln[A]$ vs t you will get a linear decline in $[A]$ as t increases (this is how you can confirm it is 1st order!)
 - this linear plot also has slope= $-ak$
 - for 2nd order: if we plot $1/[A]$ vs t we get a straight line with slope= ak

2.4.2

For each of the above integrated rate laws determine what will need to be plotted in order to obtain a straight line graph. What is the significance of the slope and y intercept? Remember that a straight line has the formula $y = mx + b$

0th order:

1st order:

2nd order:

2.4.3

N_2O_4 decomposes to NO_2 in a first order process with a rate constant of 0.0007 s^{-1} . How long will it take for 75% of a sample of N_2O_4 to decompose?

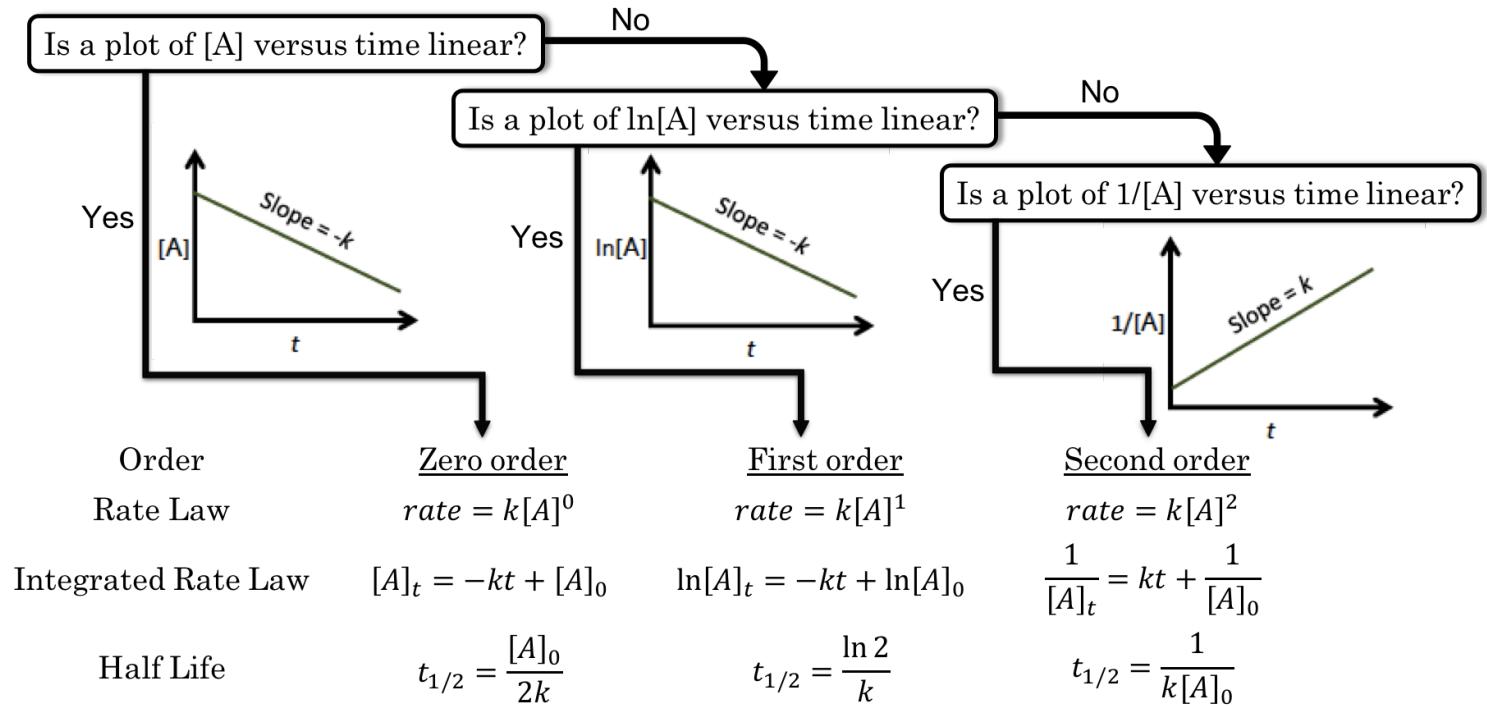
200 seconds

1200 seconds

33 minutes

60 minutes

2.4.4



2.4.5

First Order Reactions

- For first-order reactions, the differential rate law is:

$$\text{Rate} = k[A]^1 = k[A]$$

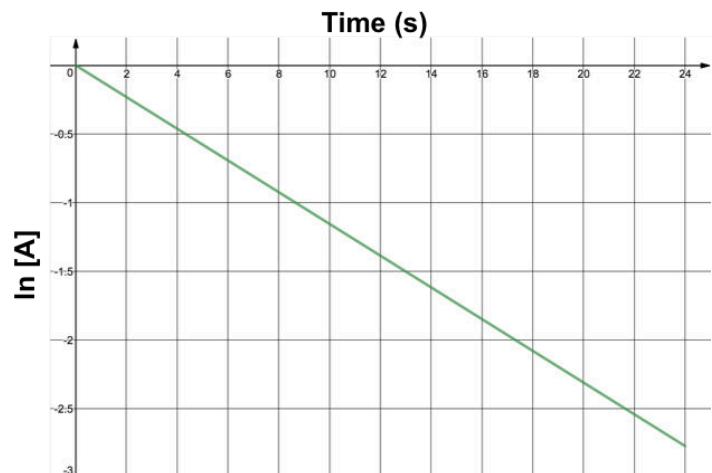
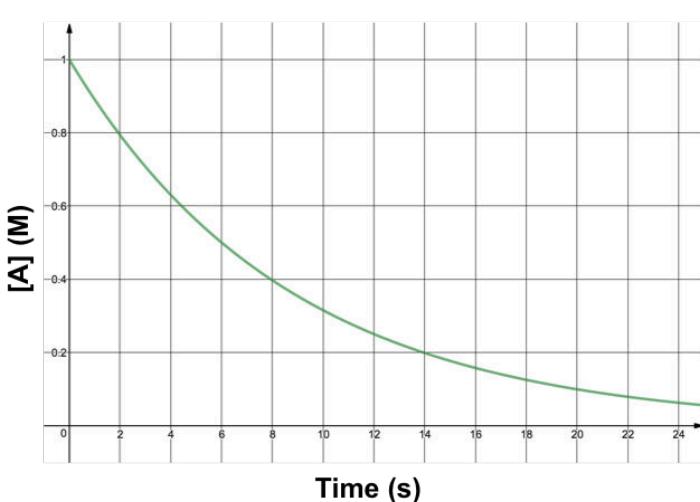
- The integrated rate law for a first-order reaction is:

$$[A] = [A]_0 e^{-kt}$$

- The integrated rate law can be rearranged to a standard linear equation format:

$$\begin{aligned}\ln[A] &= -kt + \ln[A]_0 \\ y &= mx + b\end{aligned}$$

- A plot of $\ln[A]$ versus t for a first-order reaction is a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$.



2.4.6

Second Order Reactions

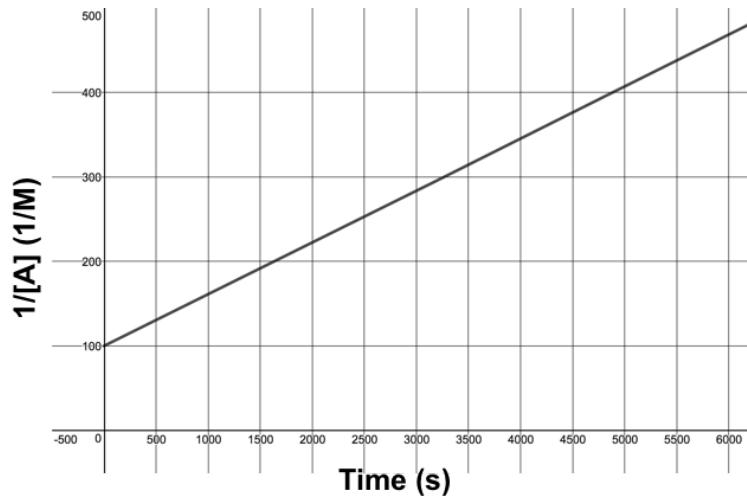
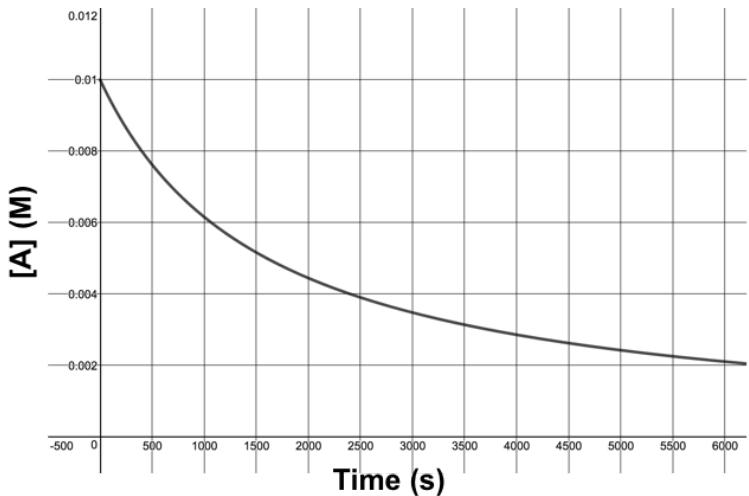
- For second-order reactions, the differential rate law is:

$$\text{Rate} = k[A]^2$$

- The integrated rate law for a second-order reaction has the form of the equation of a straight line:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$
$$y = mx + b$$

- A plot of $1/[A]$ versus t for a second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.



2.5 Half-lives for Various Orders

2.5.1

Half Life for Various Orders

Another important concept in kinetics is half-life, $t_{1/2}$. This is the time it takes for the concentration of a reactant to be cut in half.

$$\text{At } t_{1/2} : [A] = \frac{[A]_0}{2}$$

- Although it is fairly easy to derive the half-life equation from the integrated rate law we do not have to because it is given on the formula sheet and shown below.
- *If the stoichiometric coefficient of A, a, is not 1 we must include it with k in these equations just like the integrated rate laws!*

$$t_{1/2} = \frac{[A]_0}{2k} \quad 0^{th}$$
$$t_{1/2} = \frac{\ln 2}{k} \quad 1^{st}$$
$$t_{1/2} = \frac{1}{k[A]_0} \quad 2^{nd}$$

- we can see that for 1st order reactions, the half-life is independent of the initial concentration
- for radiocarbon dating, we also use first order kinetics, and can use another equation:

$$\frac{[At]}{[A_0]} = 0.5^{\frac{t}{t_{1/2}}}$$

[At]=concentration of substance at a particular time

[A₀]=initial concentration of substance

t=how much time has passed

t_{1/2}=half life

- note: if you use this equation, both t and t_{1/2} must have the same units!
- for 2nd order, t is inversely proportional to the initial concentration of the reactant
- and for the n order, t_{1/2} directly proportional to [A₀]¹⁻ⁿ

2.5.2

Americium-241 is a synthetic isotope made in nuclear reactors around the world. Chances are you have been in close proximity to this radioactive isotope thousands of time in your life because it is used in household smoke detectors. For a smoke detector to be functioning properly it needs more than 22mg of Americium-241. ^{241}Am is an alpha emitter whose decay obeys a first order rate-law (as do all nuclear decays) with a half-life of 432.6 years. If a typical smoke detector contains 25 mg of ^{241}Am , how long will the smoke detector last assuming the batteries are replaced regularly?

6 years

18 years

80 years

111 years

2.5.3

Americium-241 is a synthetic isotope made in nuclear reactors around the world. Chances are you have been in close proximity to this radioactive isotope thousands of time in your life because it is used in household smoke detectors. ^{241}Am is an alpha emitter whose decay obeys a first order rate-law (as do all nuclear decays) with a half-life of 432.6 years. What is the rate constant of its decay? How much ^{241}Am would remain of a 25mg sample if it were left for 300 years.

5.25 mg

12.98 mg

15.46 mg

24.11 mg

2.6 Arrhenius Equation

2.6.1

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

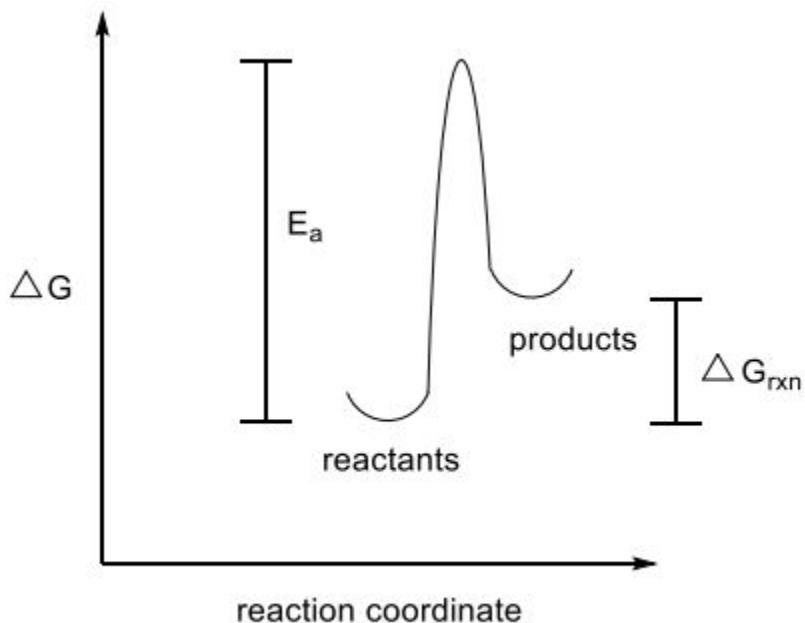


Figure 4.4.1 Reaction Coordinate Diagram

-
- 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.

2.6.2

- 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

2.6.3

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?

2.6.4

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.

2.7

Measuring Ea Given a Graph

2.7.1

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 .

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

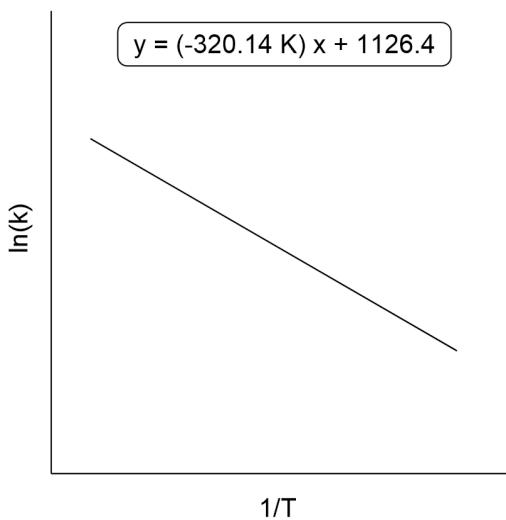
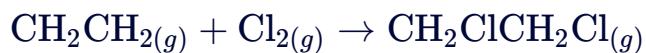
$$\ln(k) = -\frac{E_a}{R} \frac{1}{T} + \ln(A)$$

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

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

2.7.2

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

2.8

Collision Theory and Activated Complex Theory

2.8.1

3 Necessary Steps For A Chemical Reaction to Occur

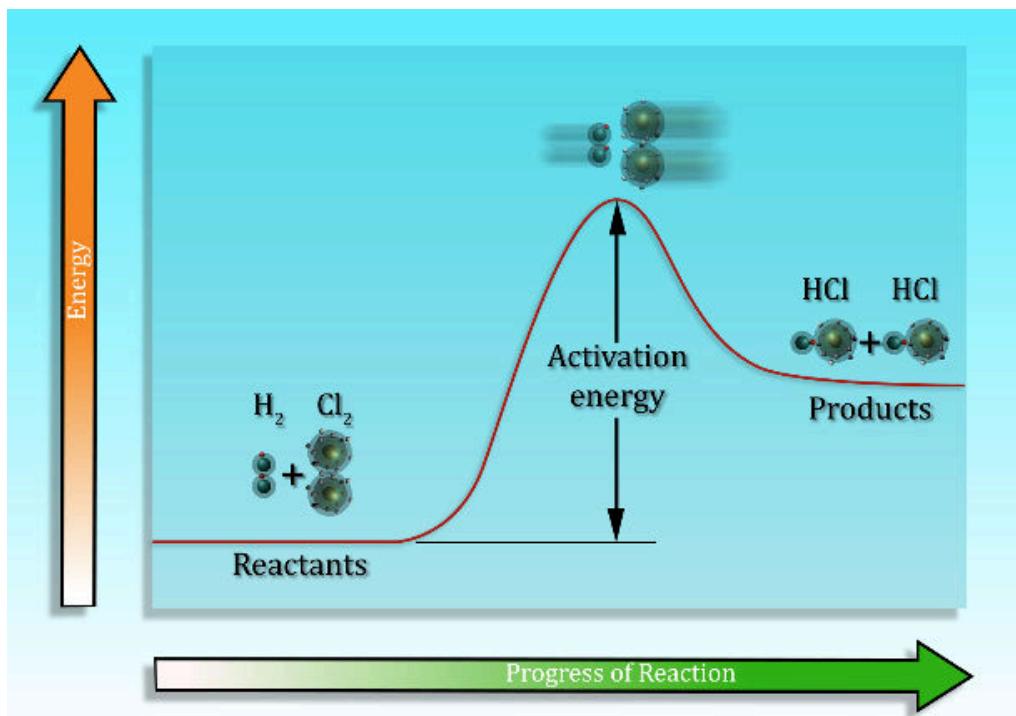
- For now just focus on **understanding**, we will revisit this topic later in this lesson!
- 1) We need to have a **physical collision** between reactants and products
 - 2) Reactants need to collide with the **correct orientation**

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: _____

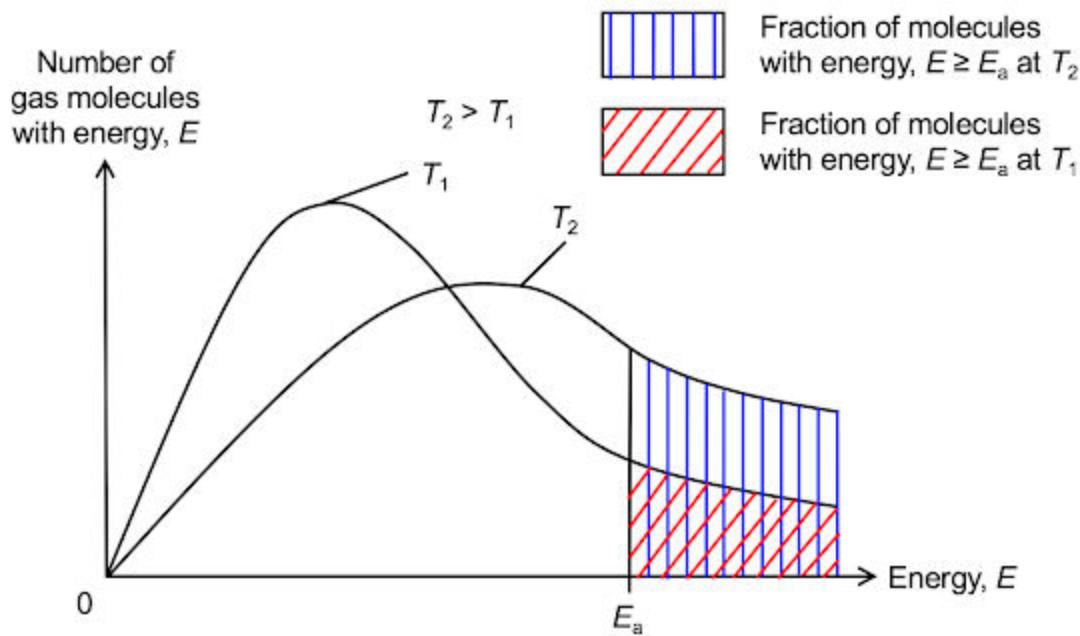
Understanding Activity:

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

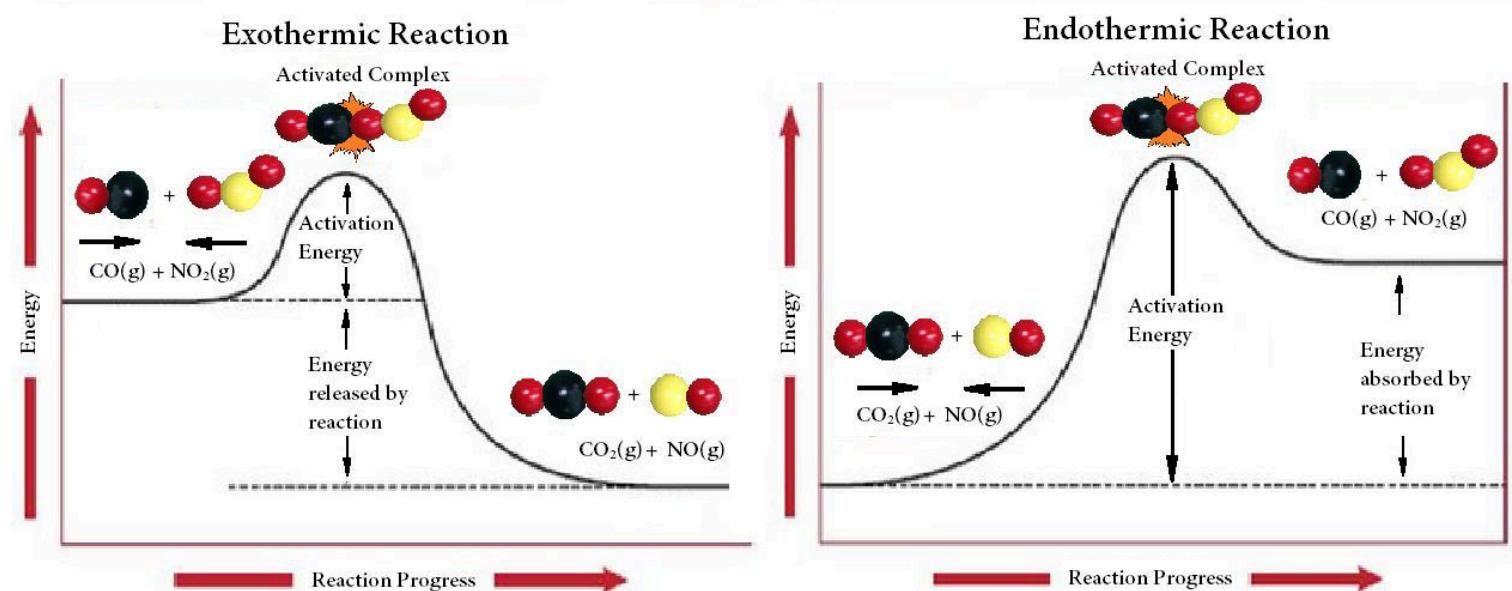
Collision Theory



- 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:**
 - **ΔH > 0 = endothermic** (energy needs to be added/absorbed for the reaction to occur)
 - **ΔH < 0 = exothermic** (energy is released in the reaction)



WIZE CONCEPT

Note that to increase the rate of the reaction we would LOWER the activation energy (reduce the energy barrier the reactant molecules need to get over)

What does this do to the transition state complex?

If we lower E_a , then the energy of the transition state complex is also LOWERED, making it MORE STABLE.

So know that **lowering E_a and stabilizing the transition state means the exact same thing**, and both would INCREASE the rate of the reaction.

Also note that changing the E_a and TS stability has no effect on thermodynamics! It only has to do with kinetics and the reaction rate!

Additional Notes on the Arrhenius Equation

Where $k=Ae^{-E_a/RT}$

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!

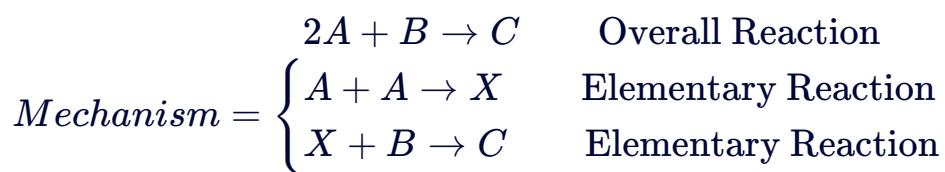
2.9

Reaction Mechanisms

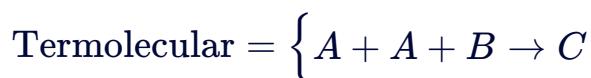
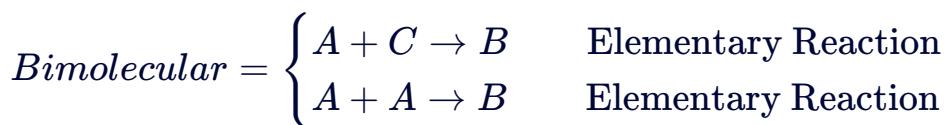
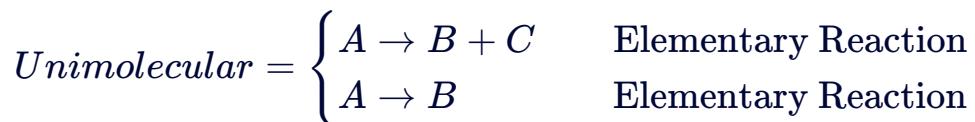
2.9.1

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:

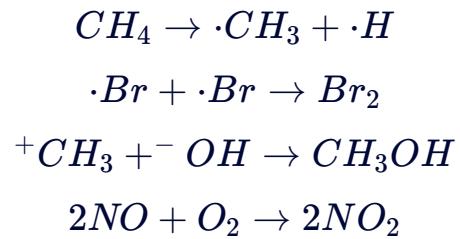


And what would the rate law look like for this elementary reaction?

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

2.9.2

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?

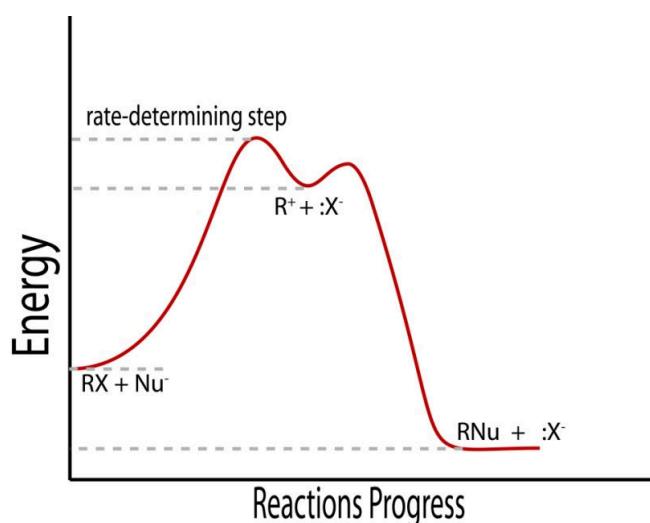
- This means that the rate of the overall process going from dry dirty dish -> dry clean dish is determined by which step? _____
- If we increase the rate of step 1 do you think that would affect the rate of the overall process?

- **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

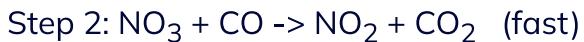
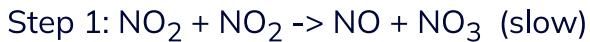
OR

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

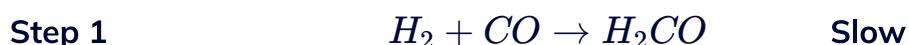
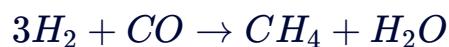
One last tip about mechanisms. In the above example, we have a balanced equation and then 2 elementary steps. Just note that the steps in a particular mechanism can't be proven, they can only be supported or refuted. You might get a question that gives you different pieces of info and asks which statement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

2.9.5

Assume the following reaction occurs by the given reaction mechanism.



The rate law expression must be rate = _____.

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

$k[H_2]^2[CO]$

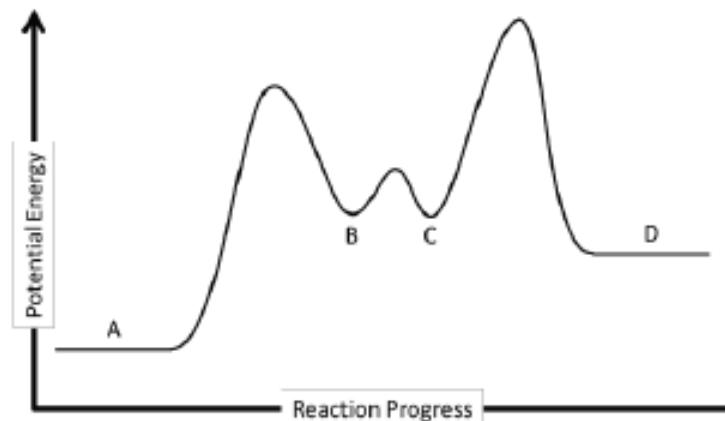
$k[H_2][CO]^2$

$k[H_2][CO]$

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

2.9.6

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



Part 1

1) How many steps are there in this reaction?

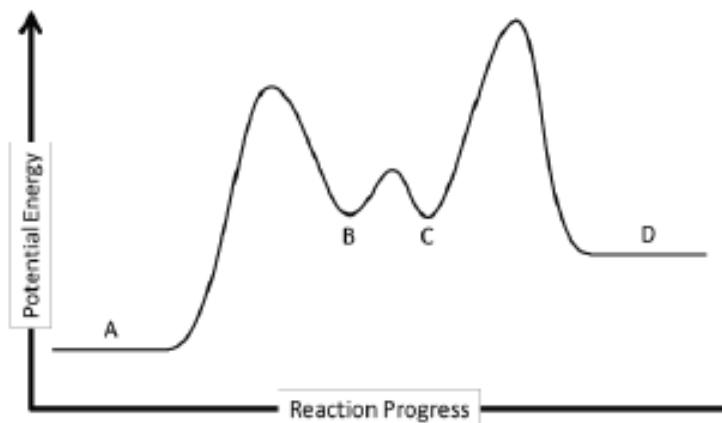
1

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?

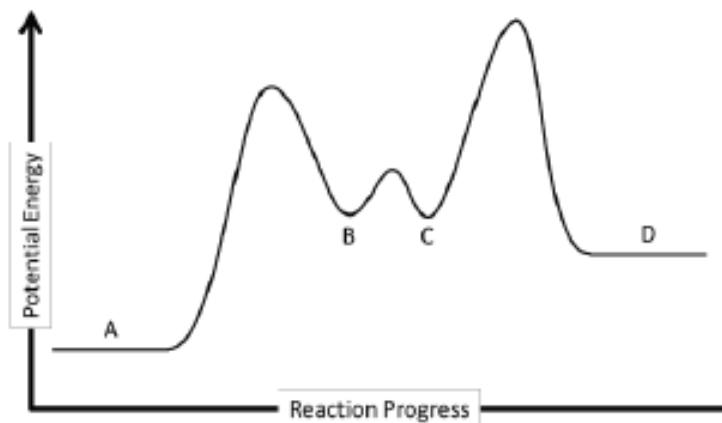
1

2

3

4

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



Part 3

How many transition states are present?

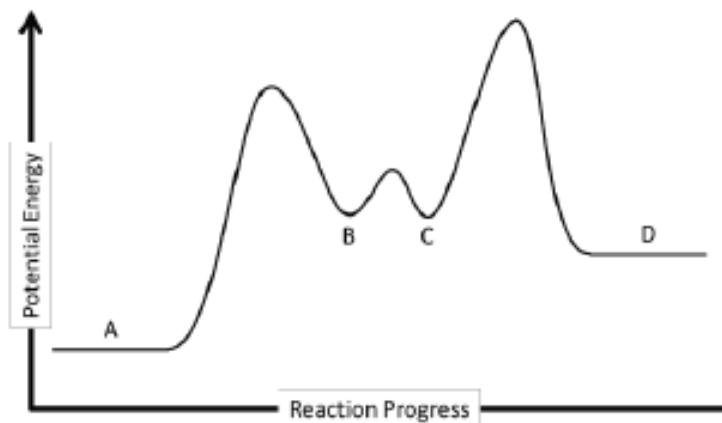
1

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

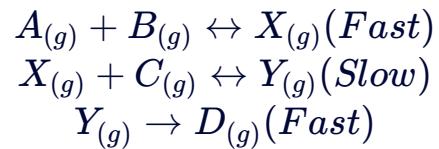
2nd class lovers

3rd

4th

2.9.7

The proposed mechanism for a reaction is:



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

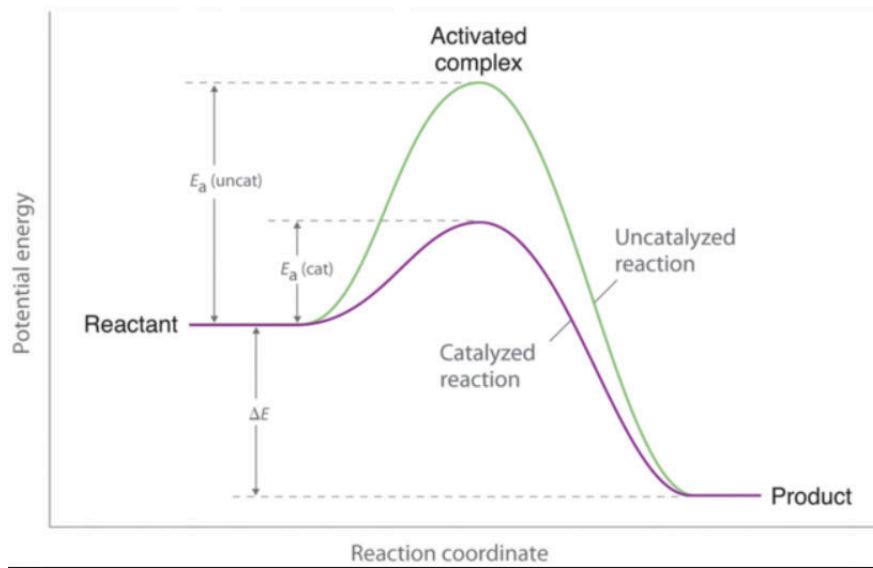
2.10 Enzymes

2.10.1

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.

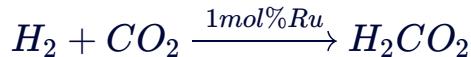


- Since the catalyst lowers E_a for a reaction, does it speed up just the forward, backward, or forward and backward reaction?
 - _____
- Will the equilibrium constant change when we add a catalyst?
 - _____
- Would the change in enthalpy be affected by a catalyst? If so, how? (Draw where we could see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

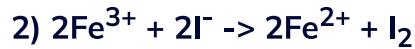
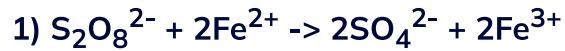
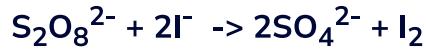
Catalysts Cntd.

- 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

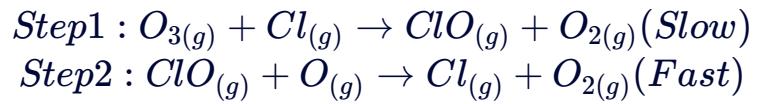
Catalyst: Not consumed in the reaction and is not changed permanently by the reaction.

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?

2.10.4

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?

2.11 Steady State Approximation

2.11.1

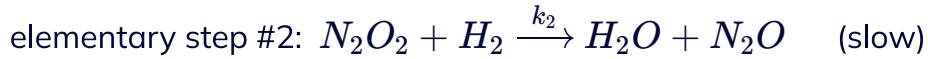
Steady State Approximation

- The steady state approximation assumes that after some time (an induction period) the **concentration of any intermediates is constant. ie. $d[I]/dt = 0$**
- Why is this useful? It allows us to express the rate of a reaction in terms of only reactants and products. We can then compare these results to experiment. An example is shown below.
- We can use this approximation if we are not told which step is slow or fast as well or if the steps have similar rates and one is not clearly the slow step or fast step!

2.11.2

Find a rate law for the following reaction using the provided mechanism which contains only reactants and rate constants.

You may use the steady state approximation for any intermediate.



Step 1: Figure out the rate of the overall reaction

Note: This is the same as saying find the formation of the product N_2O (or H_2O):

Hint: which step do we get this from??

$$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2]$$

Step 2: Look at the elementary steps to see if there are any intermediates.

Are there any intermediates here? _____

If so, what is it? _____

Step 3: Since there is an intermediate, we need to first write out the net rate of formation for the intermediate:

- to do this, it would help to first write out the rates of each elementary step!
- Note: For fast steps, write out the rate for the forward AND backward reaction. For slow steps the backward reaction can be ignored.
 - rate elementary step #1 (fwd): $v_1 =$ _____
 - rate elementary step #1 (bwd): $v_1' =$ _____
 - rate elementary step #2: $v_2 =$ _____

$$\frac{d[N_2O]}{dt} = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][H_2]$$

Step 4: Now we can make the steady state approximation by setting the net rate of formation of any intermediate equal to 0. Once we do this, we can now solve for our intermediate's concentration.

$$0 = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][H_2]$$

$$k_1[NO]^2 = k_{-1}[N_2O_2] + k_2[N_2O_2][H_2]$$

$$k_1[NO]^2 = [N_2O_2](k_{-1} + k_2[H_2])$$

$$[N_2O_2] = \frac{k_1[NO]^2}{(k_{-1} + k_2[H_2])}$$

Step 5: Now that we have an expression for the concentration of the intermediate $[N_2O_2]$ we can substitute it into the overall reaction rate expression/product formation expression:

$$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2]$$

$$\frac{d[N_2O]}{dt} = k_2 \frac{k_1[NO]^2}{(k_{-1} + k_2[H_2])} [H_2]$$

Step 6: Simplify the rate equation:

What is the rate law when H_2 is in vast excess?

- If H_2 is in vast excess then...

$$k_2[H_2] \gg k_{-1} \therefore k_{-1} + k_2[H_2] \approx k_2[H_2]$$

$$\frac{d[N_2O]}{dt} = k_2 \frac{k_1[NO]^2}{(k_2[H_2])} [H_2]$$

$$\frac{d[N_2O]}{dt} = k_1[NO]^2$$

What about if we weren't told anything was in excess?

- We want to try and simplify the denominator... $k' + k_2[H_2]$
- Which is bigger, k' or k_2 ? _____
- Since _____ is so much bigger: $k' \sim k' + k_2[H_2]$
- Our simplified rate expression becomes...

$$\frac{d[N_2O]}{dt} = k_2 \frac{k_1[NO]^2}{k' + k_2[H_2]} [H_2]$$

$$\frac{d[N_2O]}{dt} = k_2 \frac{k_1[NO]^2}{k'} [H_2]$$

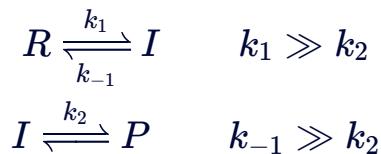
rewritten: $\frac{d[N_2O]}{dt} = \frac{k_1 k_2 [NO]^2 [H_2]}{k'}$

2.12 Pre-Equilibrium

2.12.1

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!

2.12.2

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

