

Chapter 12 – Kinetics (pages 527-566) **READ THEM!!!!**

Chemical Kinetics:

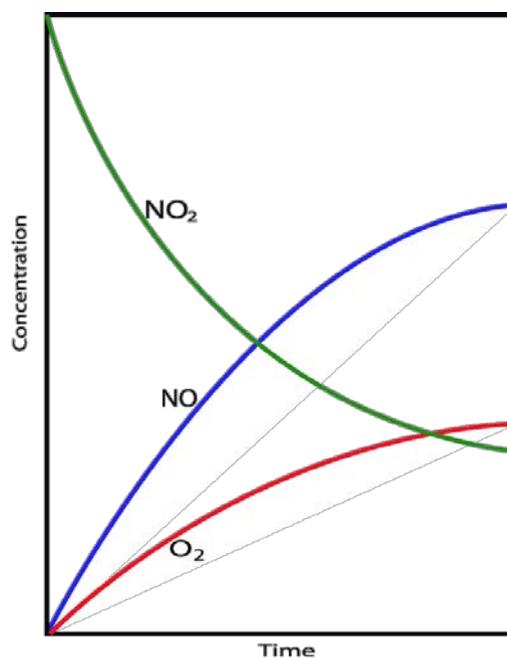
12.1 Reaction Rate: Change in concentration of a reactant or product per unit time.

$$\text{Rate} = \frac{\text{concentration of A at } t_2 - \text{concentration of A at } t_1}{t_2 - t_1} = \underline{\hspace{2cm}}$$

For this reaction: $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$

- As time goes on you **lose** NO_2 and **gain** NO and O_2 .
- At the beginning the concentration of NO_2 is higher, so the reaction rate is faster. As time goes on you lose NO_2 as it changes to product, so the reaction slows down.
- If you graph the data (Figure 12.1 page 529) in your notes and create a best fit curve for all 3 chemicals it would look like this. **Note as NO_2 decreases NO and O_2 appears.**

Time (sec)	NO_2 (M/L)	NO (M/L)	O_2 (M/L)
0	.0100	0	0
50	.0079	.0021	.0011
100	.0065	.0035	.0018
150	.0055	.0045	.0023
200	.0048	.0052	.0026
250	.0043	.0057	.0029
300	.0038	.0062	.0031
350	.0034	.0066	.0033
400	.0031	.0069	.0035



- Rate of consumption of NO_2 = rate of production of NO = 2(rate of production of O_2)

$$\text{Rate} = \frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t} = 2 \left(\frac{\Delta[\text{O}_2]}{\Delta t} \right)$$

- _____ are taken over long intervals
- _____ are determined by finding the slope of a line tangent to the curve at any given point because the rate can change over time
- **We will learn to use both.**

Reaction Rate:

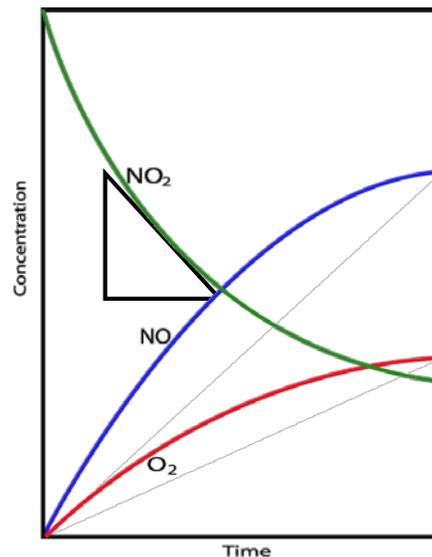
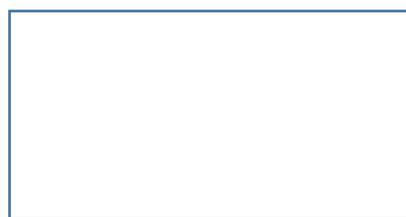
1. Can measure disappearance of _____
2. Can measure appearance of _____
3. Are proportional stoichiometrically
4. Are equal to the _____ to that point
5. Change as the reaction proceeds,
if the rate is _____

6. $\frac{\Delta[NO_2]}{\Delta t} \neq \text{constant}$

- Average slope method



- Instantaneous slope method.



- How to get the average reaction rate from the table and from the graph.

Get average NO₂ rate from 0-400 sec

Get average NO rate from 50-200 sec

- If all the concentrations of the reactants and the products are known from 0 time to completion of the reaction, such as in the above example then the following rate laws are not needed. But many times it is hard to get this information, so the **differential rate law** and the **integrated rate law** are needed to calculate the reaction rates and reaction concentrations during a reaction.

- **Hwk: Read Ch 12.1 (p527-532)**

12.2 Rate Laws an Introduction:

Differential rate laws

The differential rate law is usually just called "the rate law."

Integrated rate laws

12.3 Determining the form of the rate law

Introduction to the Differential Rate Law (Rate Law)

- Shows the relationship between the initial concentration of the reactants and the reaction rate. (initial)
- *Example 1:* $2\text{NO}_{2(g)} \rightarrow 2\text{NO}_{(g)} + \text{O}_{2(g)}$

The differential rate law is:

- $[\text{NO}_2]$ = initial conc. of NO_2 in M (mol/L)
 - **k** is _____
-

It is determined by experimental data.

- **n** = _____ – a number that reflects how the concentration of the reactant affects the reaction rate. N can only be determined from experimental data and can have a value from 0 to infinity. We will use equations with an n as a whole number from 0 to 4. Most reactions have n values of 0, 1, or 2.
- *Example:* For this reaction $2\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \rightarrow \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

The differential rate law is:

Zero Order Rate Law

- If changing the concentration of the reactants has _____ on the reaction rate then **n = 0 and the reaction is called a** _____
- If the powers of all the reactants are added together and equal zero, then the reaction is called a **zero order reaction**. In the equation above, if $n = 0$ and $m=0$, then both the reactants are 0 order reactants and $n + m$ will = 0, and the reaction is a _____.

First Order Rate Law

- If changing the concentration of the reactants causes a corresponding change in the reaction rate ($2x = 2x$ rate. $\frac{1}{4}x$ conc. = $\frac{1}{4}x$ rate), then _____
- If the powers of all the reactants are added together and equal one, then the reaction is called a **first order reaction**.

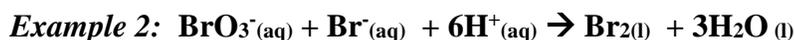
Second Order Rate Law

- If changing the concentration of the reactants causes _____ in the reaction rate
- ($2x$ conc. = $4x$ rate, $3x$ conc. = $9x$ rate, $\frac{1}{4}x$ conc. = $\frac{1}{16}x$ rate), then _____
- If the powers of all the reactants are added together and equal two, then the reaction is called a **second order reaction**.



If I tell you the reaction _____ to the conc. of NO_2 then NO_2 is a first order reactant and $n = 1$. Since it is the only reactant all the powers add up to 1, so it is a _____.

- The differential rate law is
- Rate = $k[\text{NO}_2]^n$ Therefore the Rate =

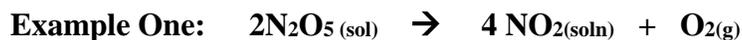


If I tell you the reaction varies directly proportionally to the conc. of BrO_3^- then BrO_3^- is a _____ reactant and $n = 1$. The reaction rate directly proportionally to the conc. of Br^- then Br^- is a _____ reactant and $m = 1$. When H^+ is doubled the reaction rate is 4x as fast, so H^+ is a _____ and $p = 2$. Since all the powers add up to 4 ($n + m + p$), the reaction is a _____.

- The differential rate law is :
- Rate = $k[\text{BrO}_3^-]^n [\text{Br}^-]^m [\text{H}^+]^p$

Writing Differential Rate Laws

- A differential rate law shows how varying the starting concentration of the reactants affects the initial reaction rate.



- The differential rate law is :

Exp	Init. Conc in M of N_2O_5	Initial Rate (mol/Lsec)
1	.90M	5.4×10^{-4} mol /L sec
2	.45M	2.7×10^{-4} mol /L sec

- Since the rate is cut in half when the concentration of N_2O_5 was cut in half, they are _____ . So N_2O_5 is a _____ order reactant.

Work:

- The order of the reaction is the sum of the powers so the **reaction order is** _____ .
- Get the rate constant k:** (use data either set)
- $k[\text{N}_2\text{O}_5]^n$

Data set from Exp. 1

Data set from Exp. 2

Rate = _____

Added question: Find the initial rate of the reaction if the initial concentration of N_2O_5 was .336M?



- The differential rate law is :

Exp	BrO_3^{1-}	Br^{1-}	6H^+	Reaction rate in M/sec (mol/Lsec)
1	.10M	.10M	.10M	8.0×10^{-4} mol /L sec
2	.20M	.10M	.10M	1.6×10^{-3} mol /L sec
3	.20M	.20M	.10M	3.2×10^{-3} mol /L sec

4	.10M	.10M	.20M	3.2×10^{-3} mol /L sec
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- Since the rate is cut in half when the concentration of N_2O_5 was cut in half, they are _____ . So N_2O_5 is a _____ **order reactant**.
- The order of the reaction is the sum of the powers so the **reaction order is** _____.

Reactant orders: (by looking at the data and math) **You must show work!!!**

Differential rate law: (partial)

Reaction Order:

Rate constant k:

Differential rate law:

Question: Get the initial reaction rate if the initial concentrations are $[BrO_3^-] = .38M$, $[Br^-] = .26M$ and $[H^+] = .19M$



- The differential rate law is :

Exp	Init. Conc in M of N_2O_5	Initial Rate (mol/Lsec)
1	.020M	1.5×10^{-3} mol /L sec
2	.032M	1.5×10^{-3} mol /L sec
3	.016M	1.5×10^{-3} mol /L sec

Reactant orders: (by looking at the data and math) **You must show work!!!**

Differential rate law: (partial)

Reaction Order:

Rate constant k:

Differential rate law:

Question: Get the initial reaction rate if the initial concentrations are $[N_2O] = .14M$

*****Practice AP Question 2010*****

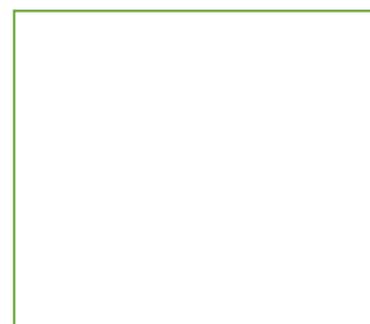
Ch 12 Hwk Set 1 due next Tuesday

Introduction to the Integrated Rate Laws

- The process can get complicated, so we will only use reactions with 1 reactant or reactions with more than one reactant but only 1 of the reactants determines almost 100% of the reaction rate.
- For the introduction we will use the generic equation _____

Zero Order Rate Law

- From experimental data if the graph of conc. Vs time is a straight line:
- $[A]_0 = [A]$ at time = _____
- Then it is a _____
- This is a **zero order reaction** because the same amount of A is lost every second, (same slope all the way down – constant rate)
- **The changing concentration of A, [A] has no effect on the reaction rate.**
- The formula for a straight line is _____



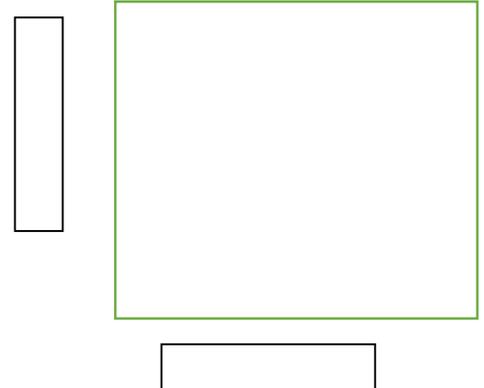
- In the graph $y = [A]$ $m = \text{slope} = -k$ $x = t$ (time) $b = y\text{-intercept} = [A]_0 = [A]$ at time = 0

- Therefore $y = mx + b$ becomes: _____
- Therefore $y = mx + b$ becomes: _____
- This is the integrated rate law for a _____
- It can be used to get concentration of A at any time during the reaction
- The differential rate law is :

- It gives the starting reaction rate as a function of the starting concentration

First Order Rate Law

- From experimental data if the graph of conc. Vs time is a gradual smooth curved line:
- Graph of _____
- This is a _____
- The concentration of A is directly proportional to the reaction rate.
- If [A] is down to 1/2 what it was, then the reaction rate is down 1/2.
- If [A] is down 1/4 what it was then the reaction rate is down 1/4.



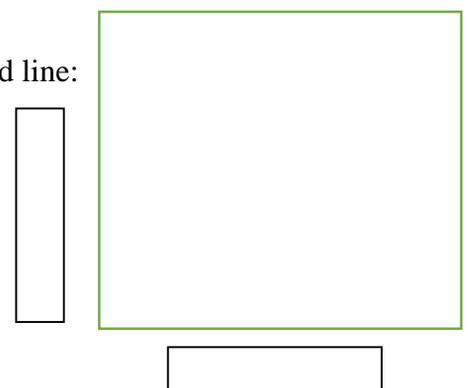
➤ In order to write a formula for the curve that is useful, we need to find out what to do to the conc. of [A] to make the graph a straight line. By trial and error we find that if we plot the

From experimental data if the graph of the $\ln[A]$ vs time is a straight line:

- In the graph $y = \ln [A]$ $m = \text{slope} = -k$ $x = t$ (time) $b = y \text{ intercept} = \ln [A]_0$ ($\ln [A]$ at $t = 0$)
- Therefore $y = mx + b$ becomes: _____
- This is the integrated rate law for a _____

Second Order Rate Law

- From experimental data if the graph of conc. vs time is a steeper curved line:
- Graph of _____
- This is a _____
- Need a straight line graph



- The concentration of A is directly proportional to the reaction rate.
- If [A] is down to ½ what it was, then the reaction rate is down ½.
If [A] is down ¼ what it was then the reaction rate is down ¼.
- In order to write a formula for the curve that is useful, we need to find out what to do to the conc. of [A] to make the graph a straight line. By trial and error we find that if we plot the

- From experimental data if the graph of the $\ln[A]$ vs time is a straight line:

Summary of Rate Laws: [A] is concentration and t is time

- If a [A] vs. t graphed gives a straight line, then: _____
- If a $\ln[A]$ vs. t graphed gives a straight line, then:

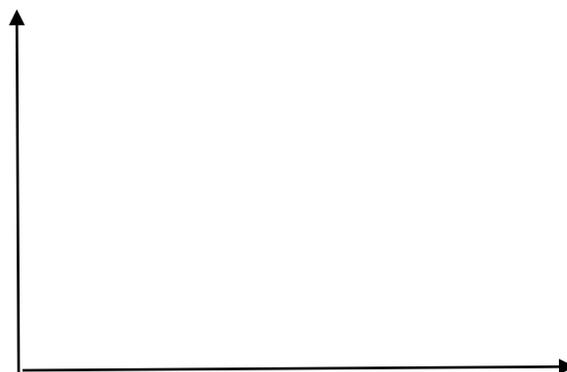
- If a $1/[A]$ vs. t graphed gives a straight line, then:

Order of reaction	What gives a straight line	Integrated rate law	Differential Rate law
0	[A] vs t		Rate = $k[A]^0$
1		$\ln[A] = -kt + \ln[A]_0$	
2	$1/[A]$ vs t	$1/[A] = kt + 1/[A]_0$	

Writing Integrated Rate Laws:

Problem 1 (Zero Order)

<u>[N₂O]</u>	<u>t (sec)</u>
.0800	0
.0725	5
.0650	10
.0575	15
.0500	20
.0425	25
.0350	30



▪ Since _____ gives a straight line, it is a **zero order reaction**

▪ So the integrated rate law is

Get k

▪ k is the slope of the line, so you make a triangle on the graph and get the slope or just plug into the integrated rate law.

▪ Differential rate law. Rate = _____ (zero order reaction)

Half Life Reactions (Example 1)

➤ The time for half of the reactant to be used up. The **differential rate** is only for starting concentrations, so we must use the **integrated rate law**:

$$t = \text{_____} = \text{half life}$$

Find the concentration of [N₂O] at 50 sec

Problem 2 (First Order)

If you plot _____ vs time gives you a straight line

- Integrated Rate Law:
- Differential Rate Law:



Find k when you start with a .1000M of $[\text{N}_2\text{O}_5]$ and after 400sec the concentration of $[\text{N}_2\text{O}_5]$ is .00625M

Hint: Use the diff. Rate law to find the units of k

Integrated Rate Law:

Differential Rate:

Half Life Reactions (Example 2)

- The time for half of the reactant to be used up. The **differential rate** is only for starting concentrations, so we must use the **integrated rate law**:

Use the k you calculated before to find the half-life $\ln [(1/2) .1000] = - (6.931 \times 10^{-3} \text{ s}^{-1})t + \ln [.1000]$

Get the $[\text{N}_2\text{O}_5]$ after 10 min (600sec)

Get the reaction rate if $[\text{N}_2\text{O}_5]$.560M is made

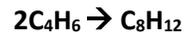
Problem 3 (Second Order)

If you graph the $[C_4H_6]$ vs time you will get a curved line.

If you plot _____ vs time gives you a straight line

Therefore it is a second order reaction. (only 1 reactant so 2 order reactant).

- Integrated Rate Law:
- Differential Rate Law:



Find k when you start with a .0100M of $[C_4H_6]$ and after 6200sec the concentration of $[C_4H_6]$ is .00208M

Hint: Use the diff. Rate law to find the units of k

Integrated Rate Law:

Differential Rate:

Half Life Reactions (Example 3)

- The time for half of the reactant to be used up. The **differential rate** is only for starting concentrations, so we must use the **integrated rate law**:

Use the k you calculated before to find the half-life $1/[C_4H_6] = .06142t + 1/[C_4H_6]_0$

- Find the time for 25% of the $[C_4H_6]$ be gone:
- Get $[C_4H_6]$ after 1 hour (1 Hr = 3600 sec):
- Get reaction rate when $[C_4H_6]$ is .8052 M

✓ **Ch 12 Hwk 2:** Page 568-570 Problems 29, 31, 33, 35, 37, 39, 41

Helpful Hints to save you time: (33 second order, 35 This is zero order)

If the starting concentrations are not given, choose whatever you want. 1M is an easy # to use.

Reaction Mechanism:

The reaction mechanism is the _____ by which a chemical reaction occurs.

- The _____ of the elementary steps must give the overall balanced equation for the reaction
- The mechanism must agree with the experim

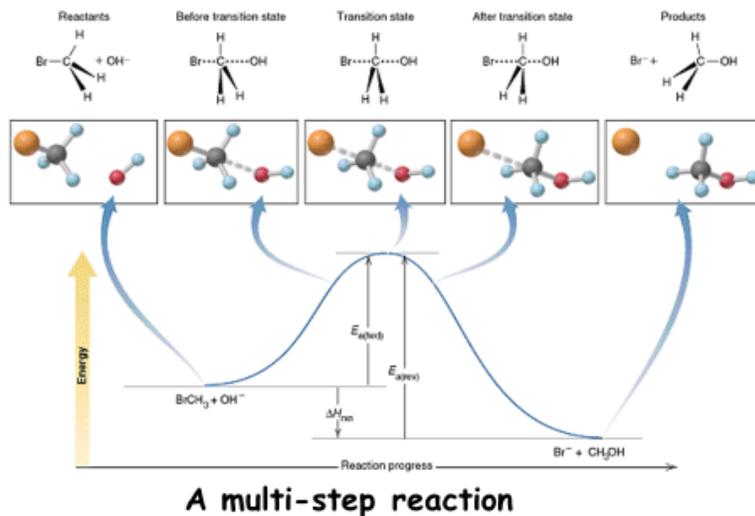
Rate-Determining Step:

In a multi-step reaction,

the slowest step is the rate-determining step.

It therefore determines the _____ of the reaction.

The *experimental rate law* must agree with the



Identifying the Rate-Determining Step: (Know)

For the reaction:



Which step in the reaction mechanism is the rate-determining (slowest) step?

Step # 1 _____

Step # 2 _____

_____ agrees with the experimental rate law

Identifying Intermediates:

Which species in the reaction mechanism are intermediates (do not show up in the final, balanced equation?)



Collision Model:

Key Idea: Molecules must collide to react. _____

- ✓ Collisions must have _____ to produce the reaction (must equal or exceed the activation energy).
- ✓ Colliding particles must be _____ to one another in order to produce a reaction.

Factors Affecting Rate:

_____ always increases the rate of a reaction.

- Particles collide more frequently
- Particles collide more energetically

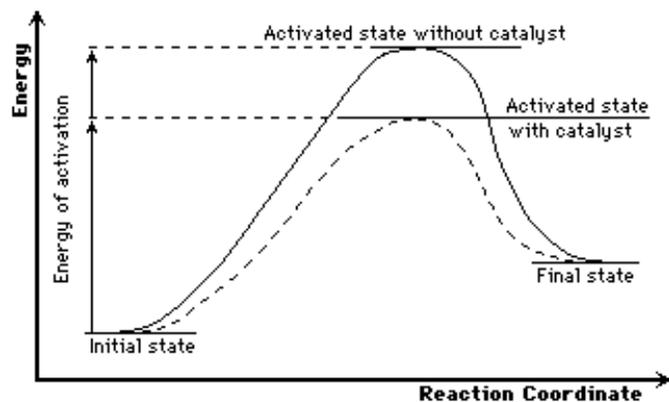
_____ increases the rate of a reaction.

_____ **USUALLY** increases the rate of a reaction.

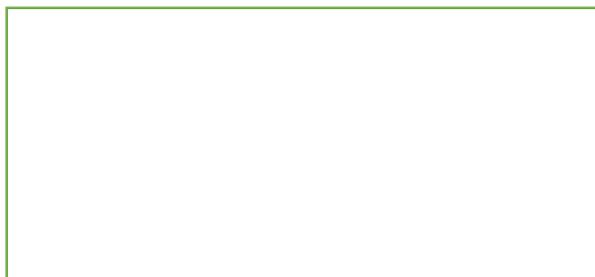
_____ which lower the activation energy by providing alternate pathways.

How Catalysts Work:

- ✓ Lowers the threshold energy for at least the _____ by making a new reaction mechanism.
- ✓ Does _____ the beginning reactants or end products
- ✓ Does make some new intermediate molecules
- ✓ Overall _____ for the reaction.
- ✓ Takes part in the reaction and changes some of the _____.
- ✓ Changes some of the intermediate E_a and ΔH 's but not the **overall ΔH**
- ✓ **Makes new intermediate molecules but never changes the starting reactants or the overall ending products.**
- ✓ Always changes the rate determining step
- ✓ **Is never used up, always comes back in a later step**
- ✓ Is called an enzyme in people and animals
- ✓ Is selective. Different substances are catalysts for different reactions.

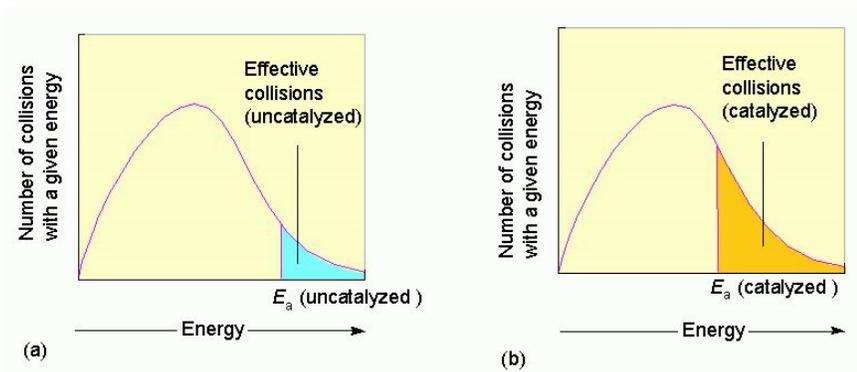


Catalysts speed up the rate determining step.



- _____ A large molecule (usually a protein) that catalyzes biological reactions.
- Homogeneous catalyst: Present in the same phase as the reacting molecules.
Ex: _____
- Heterogeneous catalyst: Present in a different phase than the reacting molecules.
Ex: _____

Catalysts Increase the Number of Effective Collisions:



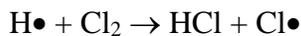
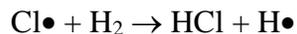
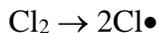
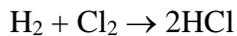
Arrhenius:

- Said that reaction rate should increase with temperature.
- At high temperature more molecules have the energy required to get over the barrier.
- The number of collisions with the necessary energy increases exponentially.
- There is an activation energy for each elementary step.
- Activation energy determines k.
- $k = Ae^{-(E_a/RT)}$
- **k determines** _____
- Slowest step (rate determining) must have the _____.

Chain Reaction: The Depletion of the Ozone Layer

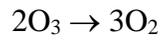
Part 1

- initiation steps
- propagation steps
- termination step

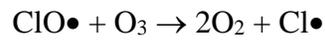


Cl• is a free radical

Part 2: Destruction of Ozone:



- initiation step
- propagation steps
- termination step



One Cl• _____

