

## Kinetics Notes #1

**Kinetics** refers to the speed or rate of a chemical reaction.

### Factors that Influence the Rates of Chemical Reactions

1. Physical State

- Solids having greater surface area will react faster. Airborne sawdust burns fast!

2. Concentration of Reactants

- Increased concentration generally means a faster reaction

3. Temperature

- Increased temperature generally makes reactions go faster
- Rule of Thumb: Increase temperature by 10°C, double the rate of a reaction.

4. Catalyst

- These substances speed up a chemical reaction without being consumed in the reaction.
- “Start with 5 grams of a catalyst, you’ll have 5 grams of the catalyst after the reaction.”

5. Inhibitor

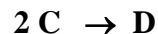
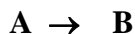
- These substances slow down the rate of a reaction.
- Good examples include food preservatives which slow down the rate of food spoilage.

### Reaction Rates

Refers to the change in the concentration (Molarity) of a reactant or of a product per unit time.

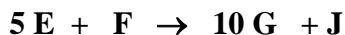
### Comparisons of Rates of Disappearance of Reactants and Formation of Products

Consider these balanced equations:



Rate that **A** disappears = Rate that **B** appears

**C** disappears \_\_\_\_\_ faster than **D** forms



**G** forms \_\_\_\_\_ faster than **E** disappears.

**E** disappears \_\_\_\_\_ faster than **J** forms.

## Rate Law (“Rate Expression”)



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

Where  $k$  = **rate constant** that is specific to a given reaction at a certain temperature

Values of  $x$  and  $y$  must be determined experimentally.

$x$  and  $y$  ARE NOT BASED ON THE COEFFICIENTS IN AN EQUATION.

## Kinetics Notes #2

### Reaction Mechanisms

Process by which a reaction occurs “We know the starting materials and the products, but how did this happen?”

### Elementary Steps:

Reactions that occur in one single step, one collision.



Rate Law comes directly from the coefficients in elementary step reactions!

### Rate Laws for Elementary Steps

If we know a reaction is an elementary step, we get its rate law directly from the coefficients in the balanced elementary step equations.

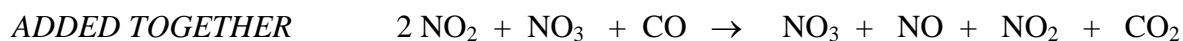
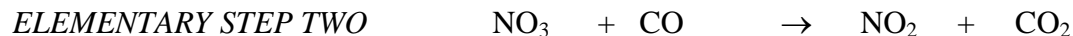
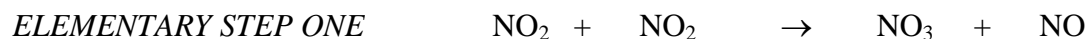
<u>Molecularity</u>	<u>Elementary Step</u>	<u>Rate Law</u>
Unimolecular	$\text{A} \rightarrow \text{Products}$	$k[\text{A}]$
Bimolecular	$\text{A} + \text{A} \rightarrow \text{Products}$	$k[\text{A}][\text{A}]$ or $k[\text{A}]^2$
Bimolecular	$\text{A} + \text{B} \rightarrow \text{Products}$	$k[\text{A}][\text{B}]$
Termolecular	$\text{A} + \text{A} + \text{A} \rightarrow \text{Products}$	$k[\text{A}][\text{A}][\text{A}]$ or $k[\text{A}]^3$
Termolecular	$\text{A} + \text{A} + \text{B} \rightarrow \text{Products}$	$k[\text{A}]^2[\text{B}]$
Termolecular	$\text{A} + \text{B} + \text{C} \rightarrow \text{Products}$	$k[\text{A}][\text{B}][\text{C}]$

### Multi-Step Mechanisms

Reactions that are not elementary steps occur by a sequence of elementary steps.



This overall process occurs in 2 elementary steps (two separate collisions are needed)

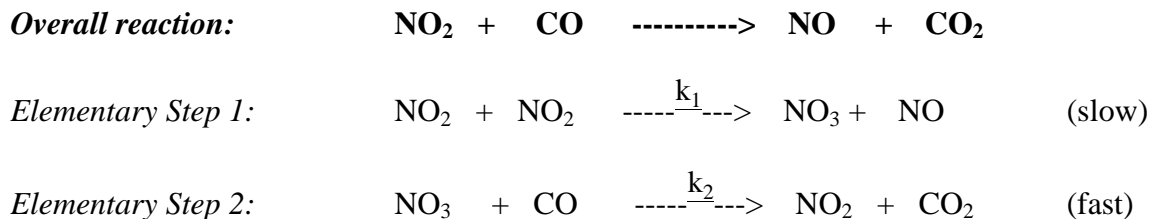


Notice that  $\text{NO}_3$  does not appear in the starting materials or in the product of the overall reaction. Therefore,  $\text{NO}_3$  is called an **intermediate**.

### Rate Laws for Multi-Step Mechanisms (Pouring Water through Series of Funnels)

- Where is the “slow” step in the elementary step sequence?
- Slow step is called the **rate-determining step**. This step dictates the rate of the overall reaction

Consider the following example.



$k_2 \gg k_1$  The intermediate  $\text{NO}_3$  formed in Step 1 is instantly consumed in Step 2 as fast as it forms.

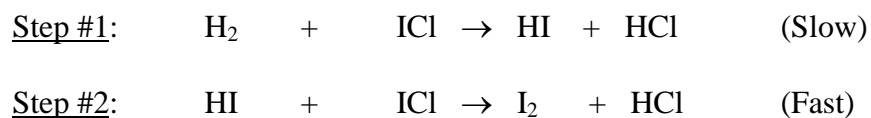
Step 1 is the rate-determining step. Therefore, Overall Rate =  $k_1 [\text{NO}_2]^2$

IF the overall reaction were an elementary step, we would predict a different rate law.  
We would have predicted: Overall Rate =  $k [\text{NO}_2][\text{CO}]$

The overall reaction is balanced as written, but this overall rate does NOT match experimental observations, so it is NOT CORRECT.

### Practice Problem:

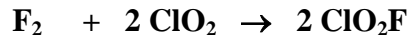
1. The following mechanism has been proposed for the gas phase reaction of  $\text{H}_2$  with  $\text{ICl}$



- Write the balanced equation for the overall reaction. \_\_\_\_\_
- Identify any intermediates in the proposed mechanism. \_\_\_\_\_
- What is the rate law for the overall reaction?

## Practice Problems: Multi-Step Mechanisms with Intermediates

Consider the following chemical reaction.



The following data about the reaction shown above were obtained from three experiments:

Trial	[F <sub>2</sub> ]	[ClO <sub>2</sub> ]	Rate of Formation of ClO <sub>2</sub> F (M sec <sup>-1</sup> )
1	0.010	0.10	2.4 x 10 <sup>-3</sup>
2	0.010	0.40	9.6 x 10 <sup>-3</sup>
3	0.020	0.10	4.8 x 10 <sup>-3</sup>

Based on the experimental data, what is the rate law for this reaction?

$\text{F}_2 + 2 \text{ClO}_2 \rightarrow 2 \text{ClO}_2\text{F}$	<b>How? What's the mechanism?</b>
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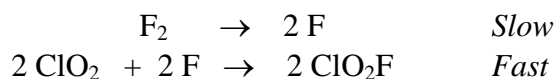
Two different reaction mechanisms have been proposed for this overall process.

Which mechanism is consistent with the experimental data?

Make sure that **no intermediates are present in your final rate laws.**

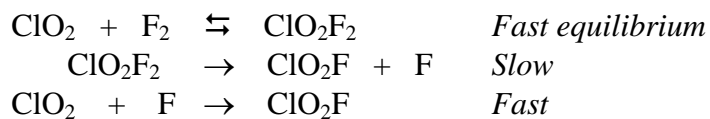
Proposed Mechanism #1:

PREDICTED RATE LAW



Proposed Mechanism #2:

PREDICTED RATE LAW



Consider the following chemical reaction:  $2A + B \rightarrow C + D$

The following data about the reaction shown above were obtained from three experiments:

Trial	[A]	[B]	Rate of Formation of C ( $M \text{ min}^{-1}$ )
1	0.10	0.10	$1.1 \times 10^{-3}$
2	0.10	0.40	$4.4 \times 10^{-3}$
3	0.30	0.10	$9.9 \times 10^{-3}$

Based on the experimental data, what is the rate law for this reaction?

$2A + B \rightarrow C + D$	How? What's the mechanism?
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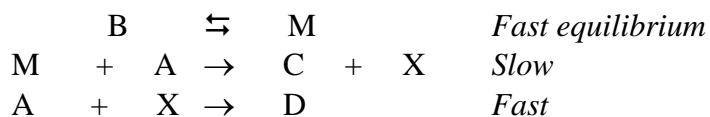
Three different reaction mechanisms have been proposed for this overall process.

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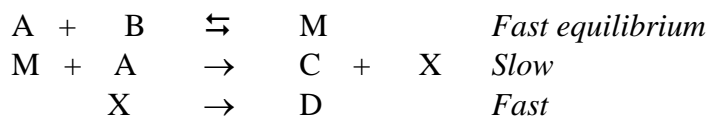
Proposed Mechanism #1:

PREDICTED RATE LAW



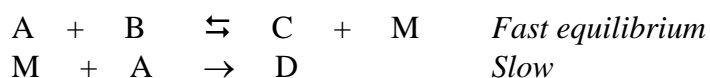
Proposed Mechanism #2:

PREDICTED RATE LAW



Proposed Mechanism #3:

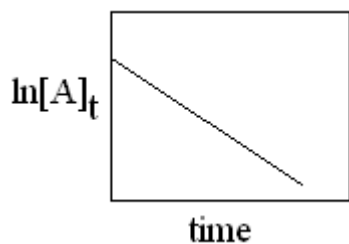
PREDICTED RATE LAW



**Kinetics Notes #3**  
**Integrated Rate Laws & Reaction Profiles**

**First-Order Reactions**

$$\ln[A]_t - \ln[A]_o = -kt$$



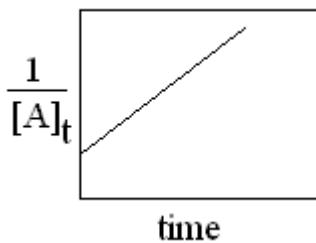
if reaction is first-order, this graph will be a straight line  
**slope** = -k      **y-intercept** =  $\ln[A]_o$

**First-Order Half-Life**

$$t_{1/2} = \frac{0.693}{k}$$

**Second-Order Reactions**

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$



if reaction is second-order, this graph will be a straight line  
**slope** = k      **y-intercept** =  $\frac{1}{[A]_o}$

**Second-Order Half-Life**

$$t_{1/2} = \frac{1}{k[A]_o}$$

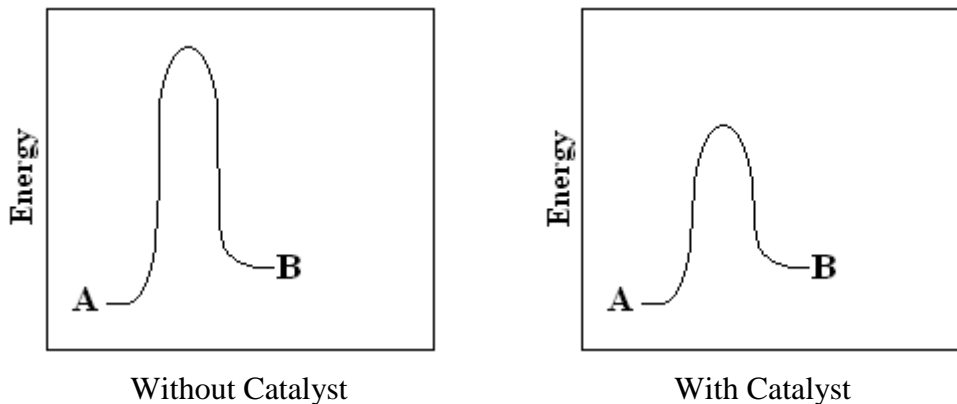
### Collision Model:

- Molecules must collide to react
- Higher temperatures mean faster molecular motion and more collisions
- Orientation factor: Molecules must line up properly for reactions to occur.

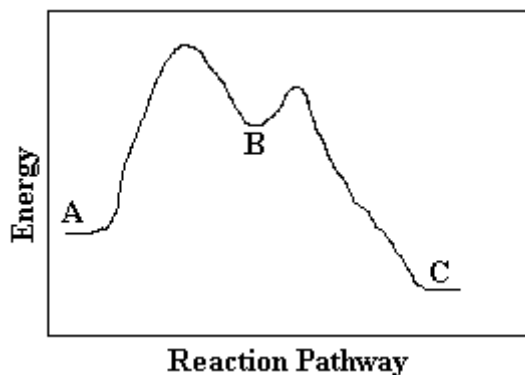
### Activation Energy

- Molecules must possess a certain minimum amount of energy in order to react.
- Catalysts make reactions go faster by decreasing the activation energy for a reaction.

### Reaction Profiles



Answer the following questions based on the reaction profile shown below.



- Label the intermediates (I) that are formed in the reaction  $A \rightarrow C$ .
- Label the transition states (TS) that are shown.
- Label the Activation Energies (AE) associated with the steps  $A \rightarrow B$  and  $B \rightarrow C$ .
- Which step  $A \rightarrow B$  or  $B \rightarrow C$  is faster? Explain.