Mr. Bracken
AP Chemistry

Name ___________________________
Period _____

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^{o}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:

A → B

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

2 C → D

C disappears _____ faster than **D** forms

5 E + F → 10 G + J

G forms _____ faster than **E** disappears.

E disappears _____ faster than **J** forms.

Rate Law ("Rate Expression")

A + B → C

$$\textbf{Rate} = \boldsymbol{k}\,[\textbf{A}]^{x}[\textbf{B}]^{y}$$

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.**

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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.

Elementary Step Reaction Example: $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

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.

Molecularity	**Elementary Step**	**Rate Law**
Unimolecular	$A \rightarrow$ Products	$k[A]$
Bimolecular	$A + A \rightarrow$ Products	$k[A][A]$ or $k[A]^2$
Bimolecular	$A + B \rightarrow$ Products	$k[A][B]$
Termolecular	$A + A + A \rightarrow$ Products	$k[A][A][A]$ or $k[A]^3$
Termolecular	$A + A + B \rightarrow$ Products	$k[A]^2[B]$
Termolecular	$A + B + C \rightarrow$ Products	$k[A][B][C]$

Multi-Step Mechanisms

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

Consider the following overall reaction: $\mathbf{NO_2 + CO \rightarrow NO + CO_2}$

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

ELEMENTARY STEP ONE $NO_2 + NO_2 \rightarrow NO_3 + NO$

ELEMENTARY STEP TWO $NO_3 + CO \rightarrow NO_2 + CO_2$

ADDED TOGETHER $2\,NO_2 + NO_3 + CO \rightarrow NO_3 + NO + NO_2 + CO_2$

Cancel out terms on both sides $NO_2 + CO \rightarrow NO + CO_2$

Notice that NO_3 does not appear in the starting materials or in the product of the overall reaction. Therefore, 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.

Overall reaction:	$\mathbf{NO_2 + CO}$	---------->	$\mathbf{NO + CO_2}$	
Elementary Step 1:	$NO_2 + NO_2$	$\xrightarrow{k_1}$	$NO_3 + NO$	(slow)
Elementary Step 2:	$NO_3 + CO$	$\xrightarrow{k_2}$	$NO_2 + CO_2$	(fast)

$k_2 >> k_1$ The intermediate 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 = $k_1 [NO_2]^2$

IF the overall reaction were an elementary step, we would predict a different rate law. We would have predicted: Overall Rate = $k [NO_2][CO]$

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 H_2 with ICl

Step #1:	H_2 + ICl	$\rightarrow$	HI + HCl	(Slow)
Step #2:	HI + ICl	$\rightarrow$	I_2 + HCl	(Fast)

(a) Write the balanced equation for the overall reaction. ________________________________

(b) Identify any intermediates in the proposed mechanism. ___________________________

(c) What is the rate law for the overall reaction?

Practice Problems: Multi-Step Mechanisms with Intermediates

Consider the following chemical reaction.

$$F_2 + 2\,ClO_2 \rightarrow 2\,ClO_2F$$

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

Trial	$[F_2]$	$[ClO_2]$	Rate of Formation of ClO_2F (M sec^{-1})
1	0.010	0.10	2.4×10^{-3}
2	0.010	0.40	9.6×10^{-3}
3	0.020	0.10	4.8×10^{-3}

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

$F_2 + 2\,ClO_2 \rightarrow 2\,ClO_2F$	**How? What's the mechanism?**

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

$F_2 \rightarrow 2\,F$ *Slow*

$2\,ClO_2 + 2\,F \rightarrow 2\,ClO_2F$ *Fast*

Proposed Mechanism #2: PREDICTED RATE LAW

$ClO_2 + F_2 \leftrightarrows ClO_2F_2$ *Fast equilibrium*

$ClO_2F_2 \rightarrow ClO_2F + F$ *Slow*

$ClO_2 + F \rightarrow ClO_2F$ *Fast*

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 min^{-1})
1	0.10	0.10	1.1×10^{-3}
2	0.10	0.40	4.4×10^{-3}
3	0.30	0.10	9.9×10^{-3}

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

$2A + B \rightarrow C + D$	**How? What's the mechanism?**

Three 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

$B \leftrightarrows M$ *Fast equilibrium*
$M + A \rightarrow C + X$ *Slow*
$A + X \rightarrow D$ *Fast*

Proposed Mechanism #2: PREDICTED RATE LAW

$A + B \leftrightarrows M$ *Fast equilibrium*
$M + A \rightarrow C + X$ *Slow*
$X \rightarrow D$ *Fast*

Proposed Mechanism #3: PREDICTED RATE LAW

$A + B \leftrightarrows C + M$ *Fast equilibrium*
$M + A \rightarrow D$ *Slow*

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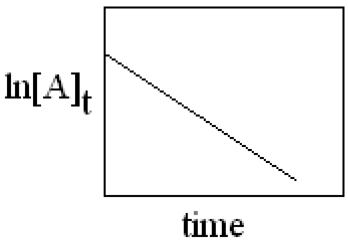
Kinetics Notes #3
Integrated Rate Laws & Reaction Profiles

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** = $\ln[A]_o$

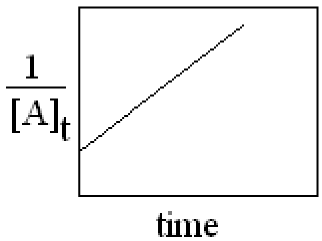
First-Order Half-Life

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

Half-life for first-order reaction is constant.

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

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

The half-life for a second-order reaction is not constant.

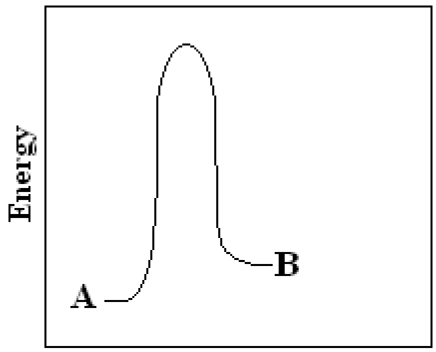
Collision Model:

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

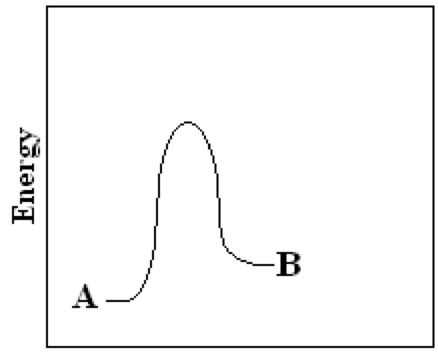
Activation Energy

- 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

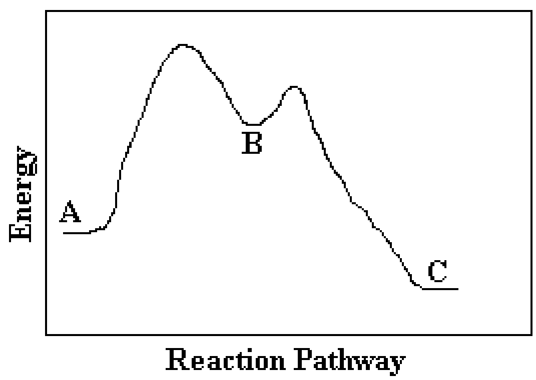


Without Catalyst



With Catalyst

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



(a) Label the <u>intermediates</u> (**I**) that are formed in the reaction A → C.

(b) Label the <u>transition states</u> (**TS**) that are shown.

(c) Label the <u>Activation Energies</u> **(AE)** associated with the steps A → B and B → C.

(d) Which step A→B or B→ C is faster? Explain.