SCH4U1
ER09

Name:
Date:

The Rate Law and Reaction Mechanisms

The rate law equation provides a quantitative description about how the concentration of reactants (in the gas or aqueous state) affects the rate of reaction. These relationships are usually determined by experiment. In some reactions, the reactant concentration does not appear to affect the rate at all. These "zero order" reactants are difficult to rationalize by the collision theory, which tells us that higher reactant concentrations should lead to more collisions and hence a faster rate. The existence of zero order reactants can be understood by examining reaction mechanisms.

One-Step (Elementary Step) Reactions

One step reactions cannot be explained in terms of simpler steps since they involve the direct collision of reactant. In these reactions, the order of each reactant is determined by the coefficient of each reactant. Since a coefficient cannot be zero, there cannot be a zero order reactant in an elementary step.

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)} \qquad r = k[Ag^+][Cl^-]$$

Multi-Step Reactions

Many chemical reactions we study actually occur as a series of simpler steps. A reaction mechanism is simply the series of elementary steps by which the overall reaction occurs. Consider the experimentally determined rate law equation for this reaction:

$$NO_{2\,(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2\,(g)} \qquad r = k[NO_2]^2[CO]^0$$
$$\therefore\ r = k[NO_2]^2$$

Since the rate law equation does not include [CO], this reactant must be zero order. This means that it must be a multi-step reaction. This reaction has been studied and is thought to involve two elementary steps:

Step 1: $NO_{2\,(g)} + NO_{2(g)} \rightarrow NO_{3\,(g)} + NO_{(g)}$ slow

Step 2: $NO_{3\,(g)} + CO_{(g)} \rightarrow NO_{2\,(g)} + CO_{2\,(g)}$ fast

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Net: $NO_{2\,(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2\,(g)}$

Note that the reaction intermediate NO_3 has been cancelled out when the equations are added. Since the **slowest** elementary step (called the **rate determining step**) is the only one that affects the overall reaction rate, only the reactants in this step will appear in the rate law equation for the overall reaction.

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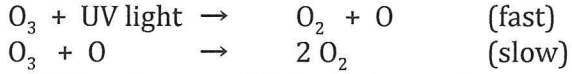
Reaction Mechanism - Worksheet

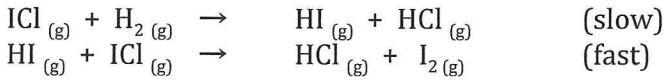
1. In the ozone layer, UV radiation is absorbed, converting ozone to oxygen gas. The proposed mechanism is shown below:



O_3 + UV light → O_2 + O (fast)
O_3 + O → $2\,O_2$ (slow)

a) Write the overall balanced equation.
b) What is the reaction intermediate?

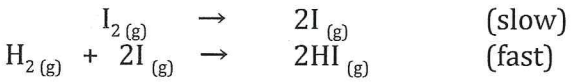
2. A proposed mechanism for the reaction between iodine chloride gas and hydrogen gas is shown below.



$ICl_{(g)} + H_{2\,(g)} \rightarrow HI_{(g)} + HCl_{(g)}$ (slow)
$HI_{(g)} + ICl_{(g)} \rightarrow HCl_{(g)} + I_{2\,(g)}$ (fast)

a) Write the balanced equation for the overall reaction.
b) What are the reactions intermediates (if any)?
c) The rate law equation was determined experimentally to be $r = k[ICl][H_2]^0$. Does the proposed mechanism above agree with the experimental results? If it does not agree, explain why not.

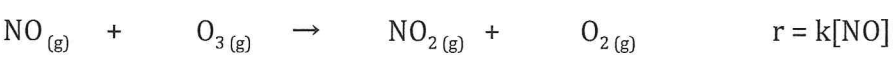
3. A two-step reaction is shown below.



$I_{2\,(g)} \rightarrow 2I_{(g)}$ (slow)
$H_{2\,(g)} + 2I_{(g)} \rightarrow 2HI_{(g)}$ (fast)

a) What is the overall reaction?
b) What are the reaction intermediates (if any)?
c) What step would you expect to be the rate-determining step?
d) Write the rate law equation if the proposed mechanism is correct.

4. Consider the following reaction that occurs in the atmosphere on a smoggy day:

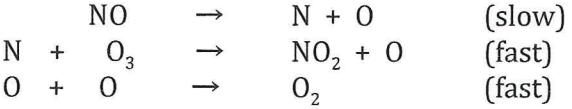


$NO_{(g)} + O_{3\,(g)} \rightarrow NO_{2\,(g)} + O_{2\,(g)}$ $\quad r = k[NO]$

Which of the following mechanisms is consistent with this rate law? Explain.

a) NO + O_3 → NO_2 + O_2 (slow)

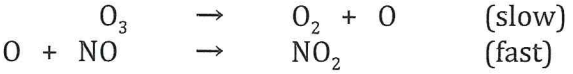
b)



NO → N + O (slow)
N + O_3 → NO_2 + O (fast)
O + O → O_2 (fast)

NO + O_3 → NO_2 + O_2 (overall)

c)



O_3 → O_2 + O (slow)
O + NO → NO_2 (fast)

NO + O_3 → NO_2 + O_2 (overall)

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REACTION MECHANISM TUTORIAL

http://www.youtube.com/watch?v=Bu_f-UkMAio&feature=related

Example 1:

Complex Overall Reaction: $2O_3 \rightarrow 3O_2$

Copy out
Elementary Steps:

Reaction Intermediate(s) are_____, _____

What is the **Catalyst** in the above mechanism? _____

Example 2:

Step 1	**$2NO \rightarrow N_2O_2$**	**(slow)**
Step 2	**$N_2O_2 + H_2 \rightarrow N_2O + H_2O$**	**(fast)**
Step 3	**$N_2O + H_2 \rightarrow N_2 + H_2O$**	**(fast)**

Complex Overall Reaction:

Reaction Intermediate(s) are : _____, _____

Catalyst: ___none____
* since there is not a substance that is consumed in step 1 and produced in the last step.

Which step above is the rate determining step? _____

The Rate Law is dependent on the rate determining step. If you are given the reaction mechanism then determining the rate law is simple. The coefficients of the reactants in the slow step are the actual exponents in the rate law.

Therefore the rate law for the above reaction is

r =

Name:_____ Date: _____

REACTION MECHANISM TUTORIAL

Sketch the Illustration of the Energy Diagram Depicting the Reaction Mechanism in Example 2.

Read Summary pg 396

Do # 1, pg 396
2 pg 390
2,3 pg 391
5 pg 397

Chemistry 12
Worksheet 1-3 - Reaction Mechanisms

1. It is known that compounds called ***chlorofluorocarbons*** (C.F.C.s) (eg. $CFCl_3$) will break up in the presence of ultraviolet radiation, such as found in the upper atmosphere, forming single chlorine atoms:

$$CFCl_3 \rightarrow CFCl_2 + Cl$$

The Cl atoms then react with Ozone (O_3) as outlined in the following mechanism.

Step 1: $Cl + O_3 \rightarrow ClO + O_2$

Step 2: $ClO + O \rightarrow Cl + O_2$ *(single "O" atoms occur naturally in the atmosphere.)*

a) Write the equation for the ***overall reaction***. (Using steps 1 and 2)

_____

b) What is the ***catalyst*** in this reaction? _____

c) Identify an ***intermediate*** in this reaction _____

d) Explain how a *small* amount of chlorofluorocarbons can destroy a *large* amount of ozone.

_____

_____

e) What breaks the bond in the $CFCl_3$ and releases the free Cl atom?

_____

2. Given the following mechanism, answer the questions below:

Step 1: $O_3 + NO \rightarrow NO_2 + O_2$ (slow)

Step 2: $NO_2 + O \rightarrow NO + O_2$ (fast)

a) Give the equation for the ***overall reaction***.

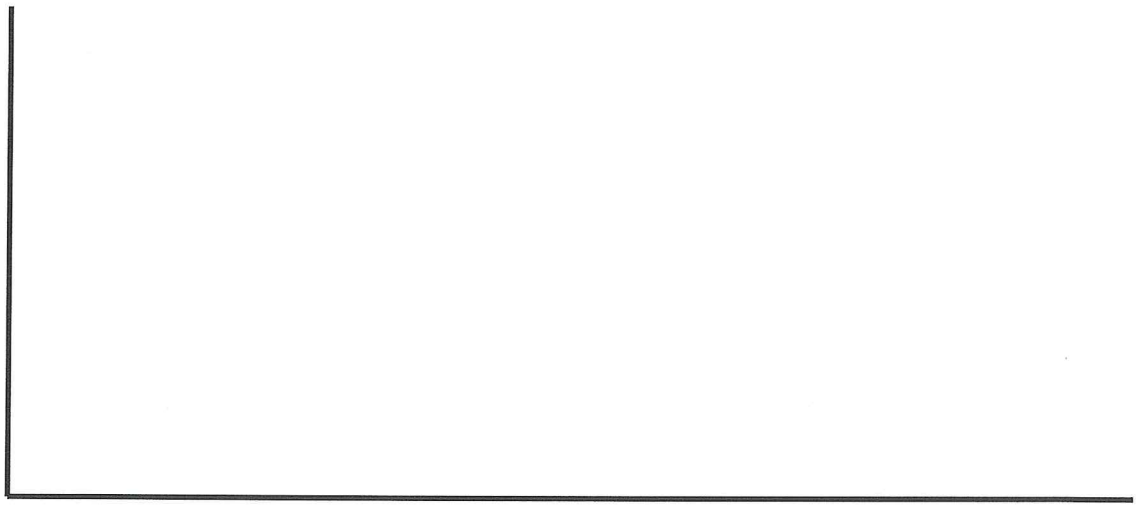
_____

b) What could the ***catalyst*** be in this mechanism? _____

c) What is an ***intermediate*** in this mechanism? _____

d) Given that the **uncatalyzed** overall reaction is a ***slow exothermic*** reaction, draw a *potential energy graph* which shows the possible shape of the curve for the ***uncatalyzed*** reaction. On the same graph, show a possible curve for the ***catalyzed*** reaction.

Potential
Energy



Progress of Reaction

3. Consider the following mechanism:

Step 1: $H_2O_2 + I^- \rightarrow H_2O + IO^-$ *(slow)*

Step 2: $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$ *(fast)*

a) Give the equation for the overall reaction.

_____

b) What acts as a ***catalyst*** in this mechanism? _____

c) What acts as an ***intermediate*** in this mechanism? _____

4. What is meant by the ***rate determining step*** in a reaction mechanism? _____

_____

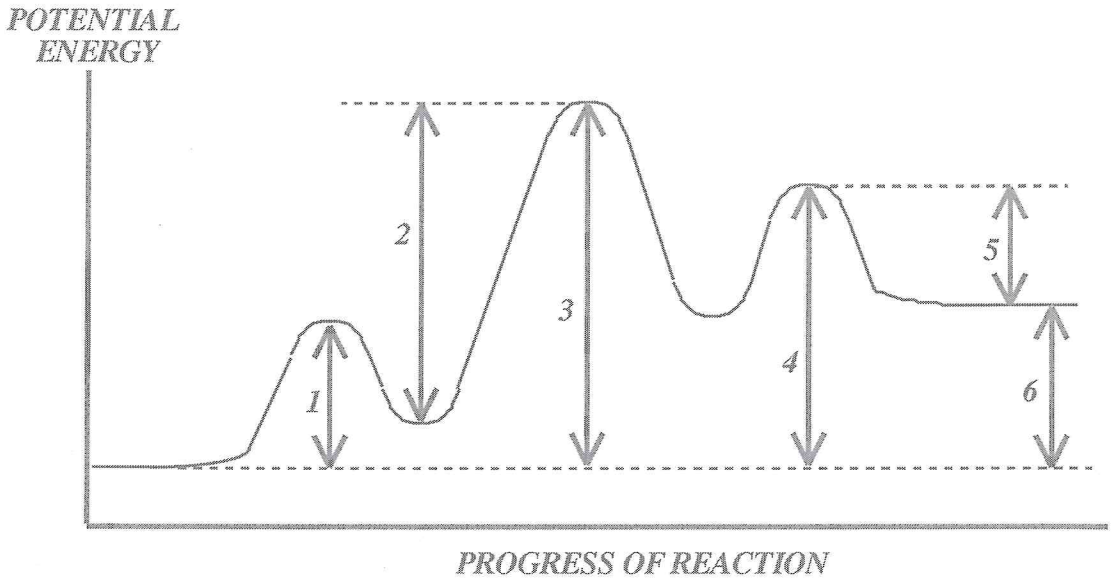
5. What is meant by a ***reaction mechanism***? _____

_____

6. How are reaction mechanisms determined? _____

_____

7. Given the following *Potential Energy Diagram* for a 3 step reaction, answer the questions below it:



a) Which arrow indicates the *activation energy* for the *first* step of the reverse reaction?

_____

b) Which arrow indicates the *activation energy* for the *first* step of the forward reaction?

_____

c) Which arrow indicates the *activation energy* for the *second* step of the forward reaction?

_____

d) Which arrow indicates the *enthalpy change* (ΔH) *or* "*enthalpy change*" for the *overall* **forward** reaction? _____

e) Which arrow indicates the *enthalpy change* (ΔH) *or* "*enthalpy change*" for the *overall* **reverse** reaction? _____

f) Which arrow indicates the *activation energy* for the ***overall*** forward reaction?

_____

g) Which step would be the ***rate determining step*** in the *forward* reaction? _____

h) In a dashed line or another colour sketch a possible curve that would represent the route for the ***uncatalyzed*** *overall reaction*. Label this on the graph.

8. Given the reaction:

$$4HBr + O_2 \rightarrow 2H_2O + 2Br_2$$

a) Would you expect this reaction to take place in a single step? _____

Why or why not? _____

b) This reaction is thought to take place by means of the following mechanism:

Step 1: $HBr + O_2 \rightarrow HOOBr$ (slow)

Step 2: $HBr + HOOBr \rightarrow 2HOBr$ (fast)

Step 3: $2HBr + 2HOBr \rightarrow 2H_2O + 2Br_2$ (fast)

c) Identify the two ***intermediates*** _____

d) A catalyst is discovered which increases the rate of *Step 3*. How will this affect the rate of the *overall reaction*? _____

Explain your answer. _____

_____

e) A catalyst is discovered which increases the rate of *Step 1*. How will this affect the rate of the *overall reaction*? _____

Explain your answer. _____

_____

f) Which step has the greatest ***activation energy***? _____

g) How many "bumps" will the potential energy diagram for the reaction mechanism have?

_____

h) Which step is called the ***rate determining step*** in this mechanism? _____

i) In order to have successful collisions, the colliding particles must have **both** the proper amount of *energy* and the proper _____

j) On the set of axes below, draw the shape of the curve you might expect for the reaction in this question. The overall reaction is *exothermic*! Make sure you get the "bumps" the correct relative sizes.

Potential Energy

Progress of Reaction

9. The equation for an ***overall*** reaction is:

$$I^- + OCl^- \rightarrow IO^- + Cl^-$$

a) The following is a proposed *mechanism* for this reaction. One of the species has been left out. ***Determine what that species is and write it in the box.*** Make sure the *charge* is correct if it has one!

Step 1: $OCl^- + H_2O \rightarrow HOCl + OH^-$ (fast)

Step 2: $I^- + HOCl \rightarrow IOH + Cl^-$ (slow)

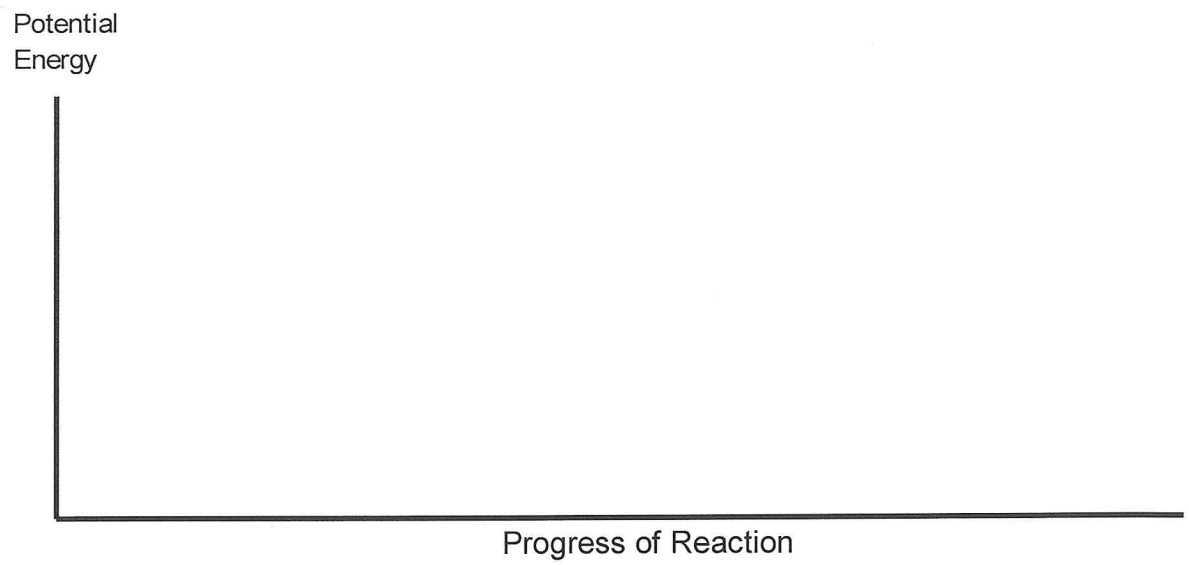
Step 3: $IOH + OH^- \rightarrow \square + H_2O$ (fast)

b) Which species in the mechanism above acts as a ***catalyst***? _____

c) Which three species in the mechanism above are ***intermediates***? _____

d) Step _____ is the ***rate determining step.***

e) On the set of axes below, draw the shape of the curve you might expect for the reaction in this question. The overall reaction is *endothermic*! Make sure you get the "bumps" the correct relative sizes.



10. Given the following steps for a mechanism:

Step 1: $Br_2 \rightarrow 2Br$ *(fast)*

Step 2: $Br + OCl_2 \rightarrow BrOCl + Cl$ *(slow)*

Step 3: $Br + Cl \rightarrow BrCl$ *(fast)*

a) Write the equation for the ***overall reaction***.

_____

b) A substance is added that *decreases* the *activation energy* for step ***1***. Will this speed up, slow down, or have no effect on the rate of the overall reaction?_____

Give a reason for your answer. _____

c) Is there a ***catalyst*** in this mechanism? _____. If so, what is it? _____

d) Is there an ***intermediate*** in this mechanism?_____. If so, what is it? _____

e) Which step is the ***rate determining step***? _____