

## Chapter 19a : Reaction Rates and Equilibrium

### Part 1 - Notes: Introduction to Rates

**Objectives:** Explain what is meant by “rate of reaction.”  
Identify, define, and explain: rate, collision theory, activation energy, activated complex, and transition state.  
Draw and interpret a graph showing the progression of a reaction.  
Draw and interpret a graph showing the rate of a reaction.

**Text Reference:** Section 19.1 – pages 533-536

#### **Initial Questions**

Sometimes we wish to speed up a reaction and make it happen faster. Why would we want this?

Sometimes we wish to slow down a reaction and make it happen slower, why would we want this?

#### **Chemical Kinetics:**

**What is a rate?** A **rate** is . . .

Consider a car traveling at a constant speed. If it travels 50 km in 30 minutes, its rate would be . . .

But you get into a car not traveling any speed. You need to press on the accelerator to get the car to start moving. If you travel a total distance of 90 miles and the whole trip takes you 2 hours, your **average** speed is . . .

When you look at the speedometer in your car, you get the . . .

Sometimes you need to know the speed at a given instant, but most of the time in chemistry, you are looking at how the speed is changing over a short period of time or you want the average speed. If you choose a very short period of time, your average speed approximates the instantaneous speed.

How would you use a graph to interpret the rate (or speed) of a reaction?

If speed is constant . . .

If speed is not constant because of acceleration or deceleration: . . .

If the line is horizontal . . .

#### **Reaction Rates**

Balanced equations do not tell the whole story of a reaction. The key to the way in which reactions take place lies on the path between the initial reactants and the final products. This is the key that enables scientists to increase the efficiency of reactions. Primary goal of a scientist who studies reaction rates is to explain and describe macroscopic observations on the rates of reactions at the microscopic level in terms of atoms, molecules, and ions.

How would you measure the rate at which a reaction proceeds?

Let's consider a reaction:  $\text{Mg(s)} + 2 \text{HCl(aq)} \rightarrow \text{H}_2\text{(g)} + \text{MgCl}_2\text{(aq)}$

How would you measure the rate at which this reaction proceeds?

Why would you choose this?

Time (min)	Volume of H <sub>2</sub> (g) in (mL)	Change in H <sub>2</sub> for the <i>segment</i>	Rate of H <sub>2</sub> produced for the <i>segment</i> (mL/min)	Rate of H <sub>2</sub> produced for the <i>whole reaction</i>
0.0	0.0	0.0	0.0	0.0
3.0	13.1			
6.0	30.8			
9.0	41.6			
12.0	47.3			
15.0	48.5			

What would a *Volume versus time* graph look like for this reaction?

The reaction did not proceed at a constant rate throughout the experiment.

Changes in either the reactant or the product over a given amount of time may be studied.

What can you say about the rate of production of hydrogen gas compared to rate at which the magnesium is used?

When the production or use of a gas is monitored, there are two things which may be measured: the volume or the pressure.

**Volume:**

**Pressure:**

The rate may also be determined by measuring the change in . . .

***Some more key terms:***

**Isothermal:**

**Isobaric:**

**Isochoric:**

How does a reaction happen?

Does every collision make a reaction happen?

**Activation energy:**

If all reactions require an input of energy to “go,” why do exothermic reactions happen at all?

## Chapter 19a : Reaction Rates and Equilibrium

### Part 1 - Assignment: Introduction to Rates

1. A friend tells you that you can recognize a fast reaction because it produces more product than a slow reaction. What other factors must be included to make this a correct statement?
2. Explain how you can tell from a plot of product concentration versus time – without actually calculating reaction rates – whether the reaction rate is increasing, decreasing, or remaining constant.
3. What reactant or product would you choose to measure in order to determine the rate of this reaction:  $\text{Zn(s)} + 2 \text{HCl(aq)} \rightarrow \text{H}_2\text{(g)} + \text{ZnCl}_2\text{(aq)}$ ? Explain how you would measure the substance you chose.
4. At 20.°C, a small strip of magnesium reacts with 3.0 M hydrochloric acid to produce 0.00050 mole of  $\text{H}_2$  gas in 20. seconds.
  - a. What is the rate of this reaction in mol/minute?
  - b. Suppose 6.0 M hydrochloric acid is substituted for the 3.0 M acid. Predict whether the new rate of reaction will be faster or slower than before.
5. Refer to the data in question 4 to answer these questions.
  - a. How much magnesium reacts to form 0.00050 mol of hydrogen gas?
  - b. How many moles of hydrochloric acid (HCl) react to form 0.00050 mol of hydrogen gas?
  - c. What would be the rate of disappearance of the magnesium metal? Of the hydrochloric acid in mol/second?
6. Iodine-137 is a radioactive substance that has been used medically to detect whether the thyroid is functioning normally. Over a four day period, a 100.-mg sample of this isotope decays at an average rate of 7.3 mg/day. What mass of I-137 has decayed after *exactly* 4 days?

7. Suppose a thin sheet of zinc containing 0.2 moles of the metal is completely converted in air to ZnO in one month. What is the rate of this reaction?
8. In 60 seconds, 90 percent of 50 mL of a 3-percent solution of hydrogen peroxide decomposes at 20°C in the presence of a catalyst. If the rate of this reaction doubles for each 10-degree increase in temperature, how long might it take for the same amount of this solution to decompose at 40°C?
9. CO<sub>2</sub> reacts with water in animal cells according to the following:  $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$   
Without a catalyst, two molecules of CO<sub>2</sub> react with 2 molecules of H<sub>2</sub>O per minute when the temperature is 37°C. How many molecules of carbon dioxide will react in a single day? A single molecule of the enzyme carbonic anhydrase can catalyze  $3.6 \times 10^7$  molecules of carbon dioxide in one minute. How many molecules of carbon dioxide will react in one day, using one molecule of the enzyme?
10. How is the activation energy of a reaction like a wall or a barrier?

## Chapter 19a : Reaction Rates and Equilibrium

### Part 2 - Notes: Factors Affecting Reaction Rates

**Objectives:** Identify factors that can affect the rate of a reaction and recognize how a change in each factor can affect the rate of the reaction.  
Compare the rate of a reaction with and without a catalyst.  
Using the collision theory, explain how a chemical reaction is influenced by reaction conditions and why reaction rates change when reaction conditions change.  
Identify, define, and explain: catalyst, collision theory, inhibitor, and effective collision.

**Text Reference:** Section 19.1 – pages 536-538

#### *Collision Theory:*

Are all collisions going to lead to the formation of new products?

What is true of particles in order for a collision to be successful and form a new product?

According to the Collision Theory, the rate of a reaction depends upon two factors:

So, in order to speed up a reaction, you need to . . .

How do you increase the number of collisions?

**Answer:**

#### ***Effect of Surface Area***

The surface area of a solid affects both chemical and physical changes.

Smaller pieces of a solid react faster than larger pieces of the same solid because . . .

You can predict that increasing the surface area . . .

#### ***Collision Theory and Concentration***

If you increase the concentration of a reactant, you . . .

In a more concentrated solution, there are . . .

An increase in effective collisions, . . .

#### ***Nature of Reactants***

In general, reactions between *simple* ions, such as  $\text{Ag}^+$  or  $\text{Cl}^-$ , which combine in a one-to-one mole ratio, are almost instantaneous. Experimental measurements show that most of these reactions occur in about one-millionth of a second. On the basis of this and many other experiments, we can conclude that the nature of the reactants . . .

The differences in the reactants involved will cause . . .

### ***Effect of Temperature***

**\*\*\*For many reactions at room temperature, an increase in the temperature by 10 degrees (from about 293K to 303K) will *double* the rate of the reaction.**

Increasing the temperature . . .

Molecules move faster as their temperature increases, but not all the molecules will move at the same speed at the same temperature. In fact gas molecules at a specific temperature have a wide range of kinetic energies. A few of the molecules travel at very high speeds and have very high kinetic energies. If one of these high-speed molecules collides with another molecule, there is a greater chance that it will result in an effective collision.

***Question:*** What is the relationship between temperature of a molecule and its kinetic energy? Do all molecules at a particular temperature have the same kinetic energy?

***Answer:***

A chemical reaction takes place only if the two colliding molecules bring enough energy to the collision that a rearrangement of atoms occurs to form new molecules.

*Activation Energy =  $E_a$ :*

Let's examine the distribution of energy levels for molecules at two different temperatures,  $T_1$  and  $T_2$ . Note that at the ***higher temperature,  $T_2$*** , there are more molecules that have average kinetic energies equal to or greater than the activation energy than at the lower temperature level,  $T_1$ .

At a higher temperature, the average speed of the molecules is greater, so more collisions involve energy greater than the activation energy that is needed for reaction. Because there are more effective collisions at higher temperatures, the rate of reaction is greater. How much the rate changes varies from one reaction to another.

### ***Catalysts***

Remember that in order for a reaction to occur, the colliding molecules must have high enough energy to overcome the  $E_a$ . If the activation energy is very high, then only a few collisions will have enough energy to react, and the reaction will be slow.

***Catalyst:***

The catalyst speeds the reaction by . . .

***Enzymes –***

*Chapter 19a : Reaction Rates and Equilibrium*  
*Part 2 - Assignment: Factors Affecting Reaction Rates*

1. One piece of zinc reacts with 6.00 M hydrochloric acid at 25°C. Another piece of zinc of equal size and shape reacts with 1.00 M hydrochloric acid at 25°C. Predict which reaction occurs at a faster rate. Why?
2. A chunk of zinc reacts with 1.00 M hydrochloric acid at 25°C. An equal mass of powdered zinc reacts with 1.00M hydrochloric acid at 25°C. Compare the reaction rates. Use collision theory to explain your answer.
3. Why does changing temperature affect the average kinetic energy of colliding reactant particles?
4. Does the decomposition of hydrogen peroxide take place faster when manganese dioxide is present or when manganese dioxide is absent?
5. Why is manganese dioxide referred to as a catalyst for the decomposition of hydrogen peroxide?
6. Hydrogen and iodine react at 400°C, according to the following equation: 
$$\text{H}_{2(g)} + \text{I}_{2(g)} \rightarrow 2 \text{HI}_{(g)}$$
How would the rate of reaction be affected by doing the following?
  - a. increasing the temperature
  - b. increasing the concentration of hydrogen
  - c. increasing the concentration of both hydrogen and iodine
  - d. adding a catalyst
7. Which will react faster, zinc and 3 M HCl or zinc and 1 M HCl? Why?
8. Use the collision theory to explain why increasing the concentration of HCl would cause an increase in the rate of its reaction with zinc.

9. Which will burn faster, a solid log, a split log, or wooden shavings?
10. You have a cube of zinc measuring 1000. cm on each edge.
- Calculate the surface area of the cube.
  - If the cube is cut into smaller cubes that are 10.0 cm on each edge, find the surface area of each cube, the total number of cubes, and the total surface area of all the cubes.
  - The cubes are then cut into cubes that are exactly 1 cm on each edge. Find the surface area of one of these cubes, the number of these cubes, and the total surface area of all the 1-cm cubes.
  - In which of the three forms described will the zinc react fastest with 1 M HCl? Explain your answer using the collision theory.
11. White phosphorus reacts rapidly with oxygen when exposed to air. What can you say about the magnitude of the activation energy for this reaction?
12. The metallic luster of fine copper wool doesn't readily change unless it is put into a crucible and heated at a high temperature. This causes the copper to darken as it reacts with oxygen. How, do you think, does the activation energy of this reaction compare with that of the phosphorus reaction described in question 11?
13. Which of the following statements is true:
- All chemical reactions can be sped up by increasing the temperature.
  - Once a chemical reaction gets started, the reactants no longer have to collide for products to form.
  - Enzymes are biological catalysts.

## Chapter 19a : Reaction Rates and Equilibrium

### Part 3 - Notes: Reaction Pathways and Mechanisms

**Objectives:** Demonstrate how the potential energy of the substances involved in a chemical reaction changes as the reaction progresses, using a graph.  
Define a reaction mechanism and explain how the rate-determining step of the mechanism affects the overall rate of the reaction.  
Given an energy diagram for a reaction, analyze the mechanism for the reaction.  
Identify, define, and explain: reaction mechanism, intermediate, elementary reaction, and transition state.

**Text Reference:** Section 19.5 – pages 566-569

*Exothermic Reaction:*                      General Equation:

- The total potential energy of the system is shown along the vertical axis.
- The horizontal axis is called the reaction coordination.
- The points along this axis represent different stages during the progress of the reaction.
- At each point, the inter-atomic distances of the interacting atoms change, and also the potential energy changes.

The height of the plateau at the left represents the total potential energy (or enthalpy) of the A<sub>2</sub> and B<sub>2</sub> molecules. Along this part of the path, the reactant molecules have kinetic energy but are so far apart that no potential energy changes occur.

When the A<sub>2</sub> and B<sub>2</sub> molecules are close enough for their electron clouds to exert a significant repelling effect, the molecules slow down, lose kinetic energy, and gain potential energy with an accompanying enthalpy increase. As kinetic energy is converted to potential energy, the curve shows a rise. From this point to the peak, the A-A bonds and the B-B bonds are lengthening and weakening as energy is absorbed. At the same time, new bonds are forming between A and B, a process in which energy is evolved. The continued rise of the curve shows that more energy is absorbed than liberated. At the peak where potential energy is a maximum, the activated complex is formed.

**Activated complex:**

The potential energy of the activated complex determines the activation energy for the reaction. From the figure, the activation energy of \_\_\_\_\_ kJ/mol is . . .

Activation energy always . . .

Once formed, the activated complex either . . .

From the peak down to the right plateau, A-A bonds and B-B bonds continue to lengthen, and the A-B bonds become shorter and stronger. Bond formation now predominates so that more energy is liberated than absorbed. The potential energy of the system decreases as the potential energy of the activated complex is converted into the kinetic energy of the product molecules. When the plateau of the right side is reached, all the potential energy of the complex has been converted to the kinetic energy of the products. The height of the right plateau represents the total potential energy (or enthalpy) of the products.

Fast Reactions versus Slow Reactions

It is observed that slow reactions generally have . . .

Endothermic Reactions versus Exothermic Reactions

An endothermic reaction always has a greater activation energy and a slower rate than the opposing exothermic reaction. Endothermic reactions have the opposite type of graph.

### Effects of Catalysts on Activation Energy

Increasing the temperature of a reaction system will usually increase the rate of the reaction, but it may also cause the decomposition of the reactants before the reactants can react. In addition, increased temperatures may result in the formation of unwanted (side) products. Catalysts may be used to increase the rate of a reaction while not causing either of these problems. In general, catalysts provide a new reaction path in which a different, lower-energy, activated complex can form. They lower the activation energy and thereby increase the rate of the reaction. Both the forward and the reverse reactions follow the same path. The activation energy is reduced to the same extent for both the forward and reverse reactions.

### **Reaction Mechanism**

#### *Elementary reaction:*

Most chemical reactions consist of a number of elementary reactions.

#### *Reaction Mechanism:*

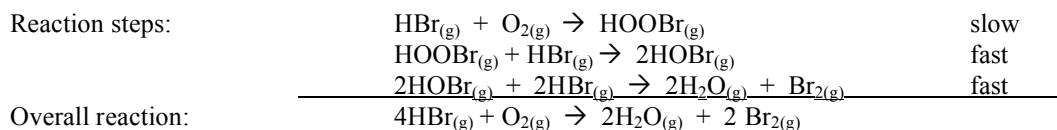
The reaction progress curve for a complex reaction consists of a number of hills and valleys. The hills correspond to the energy levels of the activated complexes. The valleys correspond to the energy levels of the intermediate products.

#### The acid-catalyzed decomposition of formic acid:

- The over-all reaction:  $\text{HCOOH} \rightleftharpoons \text{CO} + \text{H}_2\text{O}$
- The steps involved in the formation of the intermediate and the regeneration of the  $\text{H}^+$  ion catalyst are:
  - o  $\text{HCOOH} + \text{H}^+ \rightleftharpoons \text{HCOOH}_2^+$
  - o  $\text{HCOOH}_2^+ \rightleftharpoons \text{HCO}^+ + \text{H}_2\text{O}$
  - o  $\text{HCO}^+ \rightleftharpoons \text{H}^+ + \text{CO}$
- These three reactions constitute the reaction mechanism.

#### *Rate-determining step:*

- When a reaction is the result of a series of elementary processes, the *rate of the overall reaction is determined by the slowest reaction in the sequence.*
- You can control the rate of the overall reaction by . . .



If you want to increase the rate of the overall reaction, increasing the concentration of HOBr would not increase the rate of the reaction. You would need to increase the rate of HBr or the  $\text{O}_2$ .

## Chapter 19a : Reaction Rates and Equilibrium

### Part 3 - Assignment: Reaction Pathways and Mechanisms

The potential energy of substances involved in a reaction can be plotted versus the progress of the reaction, as the process moves from initial reactants, through activated complex, to final products. For the questions below, use the given information, draw the energy diagrams, and answer the questions.

1. Potential energy of reactants: 250kJ  
Potential energy of activated complex: 350 kJ  
Potential energy of products: 300 kJ

Is the reaction endothermic or exothermic?

What is the value of  $\Delta H$ ?

If a catalyst were added, what would happen to the diagram?

What would happen to the energies of the reactants, products, and activated complex?

Explain the effect on the rate of the reaction?

What is the activation energy of the reverse reaction?

2. Potential energy of reactants: 350 kJ  
Activation energy: 100 kJ  
Potential energy of products: 250 kJ

Is the reaction endothermic or exothermic?

What is the value of  $\Delta H$ ?

What is the activation energy of the reverse reaction?

What is the potential energy of the activated complex?

If the concentration of the reactants were increases, what would happen to the energies of the reactants, products, and activated complex and to the rate of the reaction?

3. Potential energy of the products: 200 kJ  
Potential energy of activated complex: 400 kJ  
 $\Delta H$ : +150 kJ

Is the reaction endothermic or exothermic?

What is the potential energy of the reactant?

What is the activation energy of the forward reaction?

What is the activation energy of the reverse reaction?

4. Sketch the potential energy curve and label all parts:  $A + B \rightarrow C + D$   
 $\Delta H = -35$  kJ; activation energy for the forward process is 25 kJ  
What is the activation energy of the reverse reaction?

## Chapter 19a: Reaction Rates and Equilibrium

### Part 4 - Notes: Reaction Mechanisms

**Objectives:** See objectives from lesson 3.

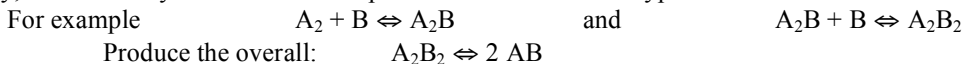
Given an energy diagram for a reaction, analyze and explain the energy and progress of the reaction.

**Text Reference:** See pages from lesson 3.

A **net reaction** such as  $A_2 + 2B \rightleftharpoons 2 AB$  often consists of a number of steps. Short-lived intermediates may be formed by some steps and consumed in other steps.



Evidently, we can always subdivide the steps further and introduce hypothetical intermediates.



If the concentration of the hypothetical intermediate is too small and the lifetime too short to allow experimental observation, the introduction of the hypothetical intermediate is of no consequence for the agreement between the model and the experimental results, but the introduction of the hypothetical intermediate is not necessarily sensible.

This leads to the introduction of the concept of the **elementary step**. A step in a reaction mechanism is elementary if it is the most detailed, sensible description of the step. More specifically, *elementary steps* are a series of simple reactions that represent the progress of the overall reaction at the molecular level. A step that consists of a sequence of two or more elementary steps is a **composite step**. The description of a net reaction as a sequence of elementary steps is the **mechanism** for the reaction. The most important aspect of a reaction mechanism is the reaction rate. Even if we have reliable data for the overall rate reaction over a large range of reaction conditions we may be unable to distinguish between two very different reaction mechanisms.

If a step in a mechanism is an elementary reaction or not depends on how detailed the available information is. The reaction mechanism deduced from a few, crude measurements of the reaction rate may consist of a small number of elementary steps. If then we decide to investigate the reaction through quantum chemical calculations, we will most likely find that many of these steps are in fact composite.

*Requirements for the reaction mechanism:*

- Any reactant for the stoichiometric reaction is on the left-hand side in one or more reaction steps. Any product is on the right-hand side of one or more elementary steps.
- The stoichiometric reaction is a linear combination of the elementary steps. Each elementary step enters into the linear combination with a weight, which is the stoichiometric number for the reaction.
- The reaction enthalpy of each step is moderate. (This rule is approximate due to the actual reaction enthalpy.)
- For any step, the number of reactants and product molecules, as well as the number of bonds broken or formed, is small. (This is approximate due to the actual activation entropy.)

*Complications in the reaction mechanism:*

- The reaction does not necessarily consist of a sequence of consecutive steps.
  - o There may be parallel steps that convert the same reactant into the same product via different paths.
  - o A dead end intermediate may be formed by a reaction and consumed in the reverse of this reaction.
  - o A number of steps may form a loop.
- The mechanism may contain intermediates, which are not present in the net reaction. The mechanism may even contain intermediates that have not been observed experimentally.
- Changing the reaction by adding a fast step in series or a slow step in parallel may not have any detectable consequence.
- Very different reaction mechanisms may predict the same overall reaction rate.

**Rate-Determining Step – RDS (rate limiting step – RLS)**

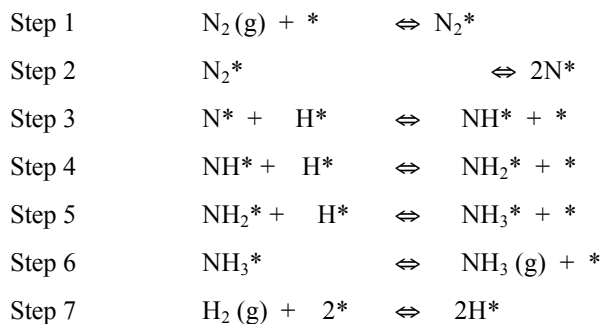
It is often the situation that most reaction steps in a mechanism are fast, while a single step is much slower than the others. In this situation, the slow step is called the rate-determining step as it determines the rate of the overall reaction. The principle that the slowest step determines the rate of the net reaction is very important and it is valid in many situations.

**Most Abundant Reaction Intermediate (MARI)**

In many reaction mechanisms there are several intermediates, but frequently the concentration of one of the intermediates is much larger than the concentration of the others. This intermediate is then called the **most abundant reaction intermediate**. The MARI determines the form of the rate expression.

### The Synthesis of Ammonia

Ammonia synthesis is one of the simplest catalytic reactions from a modeling viewpoint. It consists of seven steps that are not wholly sequential.



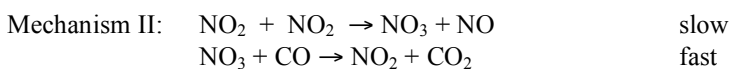
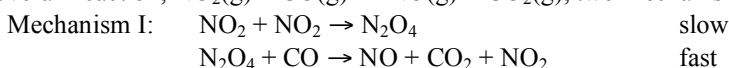
### NET

In this mechanism, the second step is known to be experimentally slow.

Try to find the algebraic sum of the above reactions and determine the net reaction for the synthesis of ammonia. What needs to be done to some of these steps?

### Question 1:

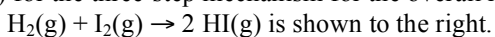
For the overall reaction,  $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$ , two mechanisms have been proposed.



Experimental facts include:  $\text{Rate} = k [\text{NO}_2]^2$ , and the detection of  $\text{NO}_3$ . Discuss the two mechanisms in terms of the experimental data.

### Question 2:

The activation energy reaction profile diagram (potential energy diagram) for the three-step mechanism for the overall reaction



Complete the table, based on the potential energy diagram:

	<i>Endothermic or Exothermic</i>	<i>Relative Rate</i>	<i>Equation for Reaction</i>
Step 1			
Step 2			
Step 3			

Chapter 19a : Reaction Rates and Equilibrium  
Part 4 - Assignment: Reaction Pathways and Mechanisms

- How does a catalyst affect the activation energy of a reaction?
- Does manganese dioxide *increase* or *decrease* the activation energy for the decomposition of hydrogen peroxide? Explain.
- What is a reaction mechanism?
- Suppose a reaction takes place according to this reaction mechanism:  
$$A + B \rightarrow C \quad \text{fast} \qquad A + C \rightarrow D \quad \text{slow}$$
Which is the rate determining step?
- If you want to increase the overall rate of the reaction, would you increase the concentration of A or of B? Explain.
- In this question, you will work with this hypothetical overall reaction:  
$$2 AB \rightarrow A_2 + B_2 + \text{energy}$$
Suppose this reaction has been found to take place in these two steps:  
$$2 AB \rightarrow A_2 + 2 B + \text{energy} \quad \text{slow} \qquad 2 B \rightarrow B_2 \quad \text{fast}$$
  - Show that by adding these two reactions, you obtain the overall reaction.
  - Which of these two steps in this reaction mechanism is likely to have the higher activation energy? Why?
- Hydrogen peroxide reacts with hydrogen ions and iodide ions according to the following reaction:  
(A)  $H^+ + I^- + H_2O_2 \rightarrow H_2O + HOI$   
A possible mechanism for this reaction is this:  
(B)  $H^+ + H_2O_2 \rightarrow H_3O_2^+ \quad \text{fast}$   
(C)  $H_3O_2^+ + I^- \rightarrow H_2O + HOI \quad \text{slow}$ 
  - Show that adding equation (B) and (C) gives equation (A).
  - How would you expect the rate to be affected if the concentration of  $I^-$  is doubled?
- In an important industrial process for producing ammonia, the overall reaction is as follows:  
$$N_{2(g)} + 3 H_{2(g)} \rightarrow 2 NH_{3(g)} + 100.3 \text{ kJ}$$
A yield of about 98% can be obtained at  $200^\circ\text{C}$  and 100 atm. The process makes use of a catalyst of finely divided iron oxides containing small amounts of potassium oxide and aluminum oxide.
  - Is the above reaction endothermic or exothermic?
  - How many grams of hydrogen must react to form 25 grams of ammonia?
  - Is it likely that the equation for the overall reaction represents the reaction mechanism? Explain.

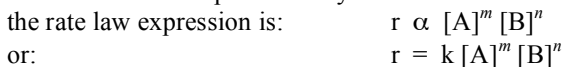
## Chapter 19a : Reaction Rates and Equilibrium

### Part 5 - Notes: Finding Reaction Rate Laws

**Objectives:** Interpret experimental rate data to deduce the rate laws for simple chemical reactions.  
Identify, define, and explain: rate law, rate constant, first-order reaction, and elementary reaction.

**Text Reference:** Section 19.5 – pages 566-469

The relationship between the rate of a reaction and the masses (expressed as concentrations) of reacting substances was recognized in 1864 by two Norwegian chemists, Cato M. Guldberg and Peter Waage. The relationship in their famous **Law of Mass Action** that states that *the rate of a chemical reaction is proportional to the product of the concentrations of the reactants*. For a general reaction between A and B represented by:



where [A] and [B] represent the molar concentrations of A and B,  $m$  and  $n$  are the powers to which the concentrations must be raised, and  $k$  is the a constant or proportionality known as the *rate constant*.

Data show that the rate constant is affected by concentration changes and the rate constant for a given reaction is dependent on the reaction conditions. The only valid way to obtain  $m$  and  $n$  is to use *experimental data*. They are derived by determining the effect of changing reactant concentration on the rate of the reaction. The exponents,  $m$  and  $n$ , may be zero, a fraction, or an integer. The sum of the exponents,  $m + n$ , on the concentration factors in the rate law equation, is called the **total reaction order**. For example, the experimentally derived rate law for the reaction:

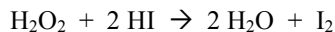


The reaction is second order, overall. That is, the sum of the exponents is  $1 + 1 = 2$ . That does NOT prove that the reaction is a *bimolecular elementary process* and that the product is formed by the collision of one  $\text{H}_2$  with one molecule of  $\text{I}_2$ .

Let's determine the exponents or  $m$  and  $n$  may be determined experimentally and let's write the rate law of some reactions using experimental data.

#### Example 1:

Use the following experimental data and the reaction:



Trial	[H <sub>2</sub> O <sub>2</sub> ]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 mol/L/s
2	0.10 M	0.20 M	0.0152 mol/L/s
3	0.20 M	0.10 M	0.0152 mol/L/s

Calculate (a) the rate law (b) the value of  $k$ , (c) the order of the reaction. Also (d) what is the rate of formation of the products if [A] is 0.25 M and [B] is 0.35 M.

#### Example 2:

For the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{g})$ , the following data were obtained.

Experiment	Initial [H <sub>2</sub> ]	Initial [I <sub>2</sub> ]	Initial rate of formation of HI
1	1.0 M	1.0 M	0.20 mol/L/s
2	1.0 M	2.0 M	0.40 mol/L/s
3	2.0 M	2.0 M	0.80 mol/L/s

- Write the rate law for this reaction and calculate the value of the rate constant.
- What would be the initial rate of formation of HI if the initial concentrations of  $\text{H}_2$  and  $\text{I}_2$  were each 0.50 M?
- What is the overall order of this reaction?

**Example 3:**

The reaction  $\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$  is run under carefully controlled conditions in the presence of an excess of acid. The following data is obtained.

<i>Trial</i>	<i>Initial</i> <i>[CH<sub>3</sub>COCH<sub>3</sub>]</i>	<i>Initial [I<sub>2</sub>]</i>	<i>Initial Rate</i>
1	0.100 M	0.100 M	$1.16 \times 10^{-7}$ mol/L/s
2	0.0500 M	0.100 M	$5.79 \times 10^{-8}$ mol/L/s
3	0.0500 M	0.500 M	$5.78 \times 10^{-8}$ mol/L/s

Write the rate law for the following reaction.

State the order of this reaction.

**Example 4:**

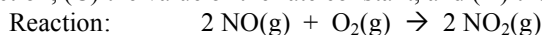
A sample of calcium has a mass of 0.750 g. This calcium is reacted with hydrochloric acid at 35°C and 1.25 atm. All of the hydrogen gas is generated in 3.75 minutes. Find the rate of hydrogen gas formation in mL/second.

## Chapter 19a : Reaction Rates and Equilibrium

### Part 5 - Assignment: Finding Reaction Rate Laws

Answer the following questions *on a separate sheet of paper*. Show all work required.

1. Nitrogen monoxide reacts with oxygen to produce nitrogen dioxide. Using the following data, calculate (A) the rate law expression, (B) the order of the reaction, (C) the value of the rate constant, and (D) the rate of the reaction if  $[\text{NO}] = 0.035$  and  $[\text{O}_2] = .025$ .



Trial	Initial [NO]	Initial [O <sub>2</sub> ]	Initial Rate
1	0.015	0.010	0.0041 mol/L/s
2	0.030	0.010	0.0164 mol/L/s
3	0.015	0.020	0.0082 mol/L/s

2. Use the following data to answer questions a – c for the reaction:  $4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{N}_2\text{O}_5(\text{g})$

Trial	Initial [NO <sub>2</sub> ]	Initial [O <sub>2</sub> ]	Initial Rate
1	0.025	0.011	$3.1 \times 10^{-4}$ mol/L/s
2	0.025	0.022	$6.2 \times 10^{-4}$ mol/L/s
3	0.050	0.011	$6.2 \times 10^{-4}$ mol/L/s

- Write the rate law expression for the reaction and determine the order of the reaction.
  - Calculate the rate constant.
  - Use the rate law expression and calculated value of  $k$  to compute the initial rate of formation of  $\text{N}_2\text{O}_5$  if the initial concentration of  $\text{NO}_2$  is 0.030 M and the concentration of  $\text{O}_2$  is 0.044 M.
3. Assume that  $\text{NO}(\text{g})$  and  $\text{H}_2(\text{g})$  react according to the rate law:  $\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$   
How does the rate change if:
- the concentration of  $\text{H}_2$  is doubled?
  - the volume of the enclosing vessel is suddenly halved?
  - the temperature is decreased?

For questions 4 – 7, refer to the following data which were taken for the reaction  $\text{A} + \text{B} + \text{C} \rightarrow \text{Products}$

Experiment	Initial [A]	Initial [B]	Initial [C]	Initial Rate
1	0.15	0.010	0.12	0.024 M/min
2	0.15	0.010	0.24	0.048 M/min
3	0.30	0.010	0.24	0.048 M/min
4	0.30	0.020	0.24	0.192 M/min

- What is the rate law?
- What is the value of the rate constant?
- What is the overall order of the reaction? What is the order of the reaction with respect to B?
- What is the rate when [A] is 0.20 M, [B] is 0.40 M, and [C] is 0.15 M?

For questions 8 – 10, refer to the following information.

For the hypothetical reaction:  $\text{A} + 2\text{B} + \text{C} \rightarrow \text{products}$ , the following data were taken:

Trial	Initial [A]	Initial [B]	Initial [C]	Initial rate
1	0.010 M	0.010 M	0.020 M	0.00012 M/s
2	0.020 M	0.010 M	0.020 M	0.00024 M/s
3	0.010 M	0.020 M	0.020 M	0.00048 M/s
4	0.020 M	0.010 M	0.010 M	0.00024 M/s

- What is the rate law for the reaction? What is the overall order of the reaction?
- What is the value for the rate law constant?
- What is the rate of the reaction if  $[\text{A}] = 0.025$ ,  $[\text{B}] = 0.015$ , and  $[\text{C}] = 0.030$ ?