**LAB 11: Reaction Order and Rate Laws**

**Pre-Lab**

**\*Come to class with the pre-lab completed and be ready to begin the lab.**

**1. Explain how different factors will affect rates of reaction.**

**2. What is the difference between zero, first, and second orders of reaction?**

**3. What are the steps for determining the rate law? Give some detail here.**

**4. What is the general idea of the lab?**

**5. Give a brief description of what you are required to do in this lab, based off of the procedure.**

**Introduction:**

 In this laboratory activity, the effect of reactant concentration on the rate of the reaction between sodium thiosulfate and hydrochloric acid will be studied. The data will then be used to determine the order of each reactant and the rate law for the reaction.

**Background - Reaction Rates:**

The rate of a chemical reaction is a measure of how fast the reaction occurs. Some chemical reactions occur as soon as the reactants come into contact with each other. Two examples of this type of fast reaction are acid-base reactions or the decomposition of hydrogen peroxide with a catalyst. Other chemical reactions may take years to occur such as the oxidation of iron. Fast or slow processes can be made to occur faster or slower, depending on the reaction conditions. Some of the factors that affect the reaction rate are the nature of the reactants, temperature, surface area, concentration, and the addition of a catalyst.

All rates are measured in terms of the time it takes to complete an event. For example, a car may travel at a rate of 60 miles/hour, a manufacturing plant may produce cars at the rate of 10 cars/day, or a potter may make eight pieces of pottery/week. Each of these rates tells how much time it takes to travel 60 miles, produce 10 cars, or make eight pieces of pottery. In a chemical reaction, the event that is completed is the conversion of reactants to products. A chemical reaction rate is measured in terms of the rate of disappearance of reactants and appearance of products. The reaction is completed when all of one or more reactants have been consumed and converted products. One way to determine the rate of a chemical reaction is to measure the time from when the reactants are mixed (the start) to when at least one of the reactants has been completely consumed (the end). Some reactions have no convenient visual way to identify the end of the reaction, so advanced instrumentation is needed to monitor the reaction in progress. However, other reactions, such as the one in this laboratory activity, do have convenient ways to identify the end of the reaction such as a color change or precipitate formation.

***Reaction Order and Rate Laws***

The overall rate of a chemical reaction may depend on the concentrations of one or more of the reactants or it may be independent of the reactant concentrations. Exactly how the rate depends n reactant concentration is expressed in and equation called a *rate law.* For a general chemical equation, such as

 A+B → C (1)

the general rate law would be written as

 Rate=*k* [A]*n*[B]*m* (2)

where *k* is the rate constant, [A] and [B] are the molar concentrations of each of the reactants, and *n* and *m* are exponents that determine how the rate depends on the reactant concentrations. The rate constant and the exponents *n* and *m* must be determined experimentally—they cannot be determined simply by looking at the balanced chemical equation. The rate constant for a reaction does not depend on the reactant concentrations, but does depend on temperature. The exponents *n* and *m* give the order of the reaction. The above reaction is said to be *n*th order in A and *m*th order in B. The overall reaction order is obtained by taking the sum *n* + *m*. generally, the exponents *n* and *m* are positive whole numbers; however, they may contain fractions or even be negative numbers.

 Because the exponents *n* and *m* vary from reaction to reaction, rate laws for different reactions take on different forms. The chemical equations and their experimentally determined rate laws listed in Table 1 can be compared to illustrate this fact.

|  |  |  |
| --- | --- | --- |
| **Reaction #** | **Overall Chemical Equation** | **Rate Law** |
| Reaction #1 | 2NO(g) + O2(g) → 2NO2(g) | Rate = *k* [NO]2[O2] |
| Reaction #2 | H2(g) + Br2(g) → 2HBr(g) | Rate = *k* [H2][Br]1/2 |
| Reaction #3 | NO2(g) + CO(g) → NO(g) + CO2(g) | Rate = *k* [NO2]2 |
| Reaction #4 | 2N2O5(g) → 4NO2(g) + O2(g) | Rate = *k* [N2O5] |
| Reaction #5 | NO2(g) + O3(g) → NO3(g) + O2(g) | Rate = *k* [NO2][O3] |

**Table 1.**

From the equations in Table 1, several important points about rate laws can be made.

**1).** The orders of each reactant in the rate law determine how the rate changes as the

 concentration of each reactant changes.

* **Zero Order.** If a reactant has an order of zero, the rate is independent of the concentration of that reactant, and that reactant does not appear in the rate law (because anything raised to the zeroth power is one). For example, in Reaction #3, the order of CO is zero and hence [CO] does not appear in the rate law. Because [CO] does not appear in the rate law, it cannot affect the rate. This means that increasing or decreasing the concentration of a reactant which has an order of zero does not affect the rate of the reaction.
* **First Order**. When a reactant is first order, the reactant will appear in the rate law and have an exponent of 1. For example, in reaction #5, both NO2 and O3 have an order of 1. Increasing the concentration of NO2 or O3 increases the rate and decreasing the concentration of NO2 or O3 decreases the rate. If the concentration of NO2 is doubled, for instance, the rate will also double, if the concentration of O3 is halved, the rate will also be cut in half. Hence, the rate is directly proportional to any reactant that is first order.
* **Second Order.** For reactants that are second order, they will appear in the rate law as the concentration of the reactant squared. For example, in Reaction #1, [NO] appears in the rate law and is squared. hence NO has an order of 2. As a result, if the concentration of NO is doubled, this will cause the rate to increase by a factor of 4.

**2).** The orders *n* and *m* in the rate law are not necessarily the same as the coefficients in the

 balanced chemical equation. For example, in Reaction #2, the exponent for [Br2] is 1/2,

 while its coefficient is 1. Similarly, reaction #3 is second order in NO2 and zeroth order in

 CO, while both of their coefficients in the balanced chemical equation are 1.

**3).** Reactants can be fractional exponents, even though they are generally positive whole

 numbers. For example, Reaction #2 is half order in Br2. This means that if the

 concentration of Br2 is doubled, the rate increase by 21/2 or √2.

**4).** The overall reaction order is the sum of the individual reactant orders. For example, in

 Reaction #1, the order with respect to NO2 is 2 and the order with respect to O2 is 1.

 Therefore, the overall reaction order is 2 + 1 = 3.

**5).** The units for the rate in the rate law will always be the same, while the units on the rate

 constant and the reactant concentrations raised to their powers vary from rate law to rate

 law.

* Reaction rates are expressed in sec-1 (1/sec).
* The units for each reactant’s concentration depend on the exponent, or order of the reactant. The concentration is always expressed in terms of Molarity, or moles/liter. But, if a reactant has an order of 2 for a given rate law, such as NO2 in Reaction #3, then that reactant’s concentration will have units of (moles/liters)2.
* The units on the rate constant *k* must give the correct units for the rate (sec-1) when multiplied by the reactant concentrations. The units for the rate constant will be the same in reactions with the same overall reaction order, but different between two reactions with different overall reaction orders. To see why, look at Reactions #3 and #5. Both have an overall reaction order of 2 even though they have different forms for the rate law. In Reaction #3, the units for [NO2]2 are (moles/liter)2. In Reaction #5, the units for [NO2][O3]are (moles/liter) × (moles/liter) = (moles/liter)2. In each case, because the overall reaction order is 2, the units for the reactant concentration part of the rate law are the same, (moles/liter)2. The units for the rate constant for reactions with an overall reaction order of 2 must therefore be liters2/(moles2∙sec).

**Determining a Rate Law**

To determine a rate law for a reaction, the following procedure may be followed. First, one reactant’s concentration is held constant while the second reactant’s concentration is varied. For each reaction, the reaction time is measured and recorded. Then, the first reactant’s concentration is varied while the second reactant’s concentration is held constant.

Again, the reaction time for each reaction is measured and recorded. The reaction rate for each reaction is calculated by taking the inverse of the reaction time. The data is then analyzed to determine the order of each reactant and the rate law.

The steps below outline the procedure to estimate the rate law for the reaction between nitric oxide and oxygen gas.

 2NO(g) + O2(g) → 2NO2(g) (3)

 Rate = *k* [NO]*n*[O2]*m* (4)

The following is a sample set of data that was obtained by performing the reaction five times and varying the concentrations of the reactants as indicated. In each case, the reaction time was measured, then inverted to find the reaction rate.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Trial #** | **[NO]** | **[O2]** | **Reaction Time (sec)** | **Reaction Rate (sec-1)** |
| 1 | 0.02 | 0.01 | 35.7 | 0.028 |
| 2 | 0.02 | 0.02 | 17.5 | 0.057 |
| 3 | 0.02 | 0.04 | 8.8 | 0.114 |
| 4 | 0.04 | 0.02 | 4.4 | 0.227 |
| 5 | 0.01 | 0.02 | 71.4 | 0.014 |

**Step 1. Determining the order with respect to O2.**

In the first three trials, the concentration of NO is constant while the concentration of O2 is varied. Therefore, any change in the rate will be solely due to the change in the concentration of O2. To determine the order with respect to O2, the [NO]*n* part of the rate law can be ignored because it does not vary. The rate constant *k* can also be ignored because it also does not vary. As a result, the only part of the rate law necessary for determining *m* is

 Rate ∝ [O2]*m* (5)

The symbol '∝' means “proportional to”. With this symbol, the goal is to find the factor by which [O2] is increased and the factor by which the rate is increased from one trial to the next. From the data table we see that as the concentration of O2 is doubled, the rate doubles also. The factors by which the concentration of O2 and the rate are increased are then inserted into the proportionality equation.

 2 ∝ [2]*m*  (6)

The exponent *m* is calculated such that the proportionality equation is satisfied. In this case, *m* must be 1 for the equation to be satisfied. This means that the reaction is first order in O2.

**Step 2. Determining the order with respect to NO.**

In trials 2, 4, and 5 the concentration of O2 is held constant while the concentration of NO is varied. Therefore, any change in the rate will be solely due to the change in the NO concentration. In the rate law, [O2]*m* and the rate constant *k* can be ignored because they do not vary. As a result, the part of the rate law necessary for determining *n* is

 Rate ∝ [NO]*n* (7)

Comparing trials 2, 4, and 5, it can be observed that as the concentration of NO is doubled, the rate increases by a factor of 4. Plugging these values into the proportionality equation gives

 4 ∝ [2]*n* (8)

The value of *n* must therefore be 2 satisfy the proportionality equation. This means that the reaction is second order in NO.

**Step 3. Determining the Rate Law.**

Plugging the orders for each reactant into the general rate law given in equation 4, the rate law for the reaction is determined to be:

 Rate = *k* [NO]2[O2] (9)**Experimental Overview**

In this laboratory experiment, experimental data will be used to determine the rate law for the reaction between hydrochloric acid, HCl, and sodium thiosulfate, Na2S2O3.

 2HCl(aq) + Na2S2O3(aq) → S(s) + SO2(aq) + H2O(l) + 2 NaCl(aq) (10)

To determine a rate law for this reaction, the following outline will be followed. First, the HCl concentration is held constant while the Na2S2O3 concentration is varied. For each reaction, the reaction time is measured and recorded. Then, the HCl concentration is varied while the Na2S2O3 concentration is held constant. Again, the reaction time for each reaction is measured and recorded. The reaction is timed by monitoring the appearance of the solid black product which is sulfur, S. As solid sulfur is formed, the reaction mixture will become dark and clouded with black precipitate. The reaction time will be measured by noting the time at which you can no longer see through the solution.

From the general form for a rate law given in equation 2, the general rate law for the reaction between HCl and Na2S2O3 is written as shown in equation 11.

 Rate = *k* [HCl]*n*[Na2S2O3]*m*  (11)

By determining how the reaction rate varies as the concentration of each reactant is varied, the orders *n* and *m*, and hence the rate law, will be determined.

**Chemical Concepts:**

* Kinetics
* Reaction order
* Rate laws
* Concentration vs. reaction rate

**Materials (for each lab group):**

|  |  |
| --- | --- |
| Hydrochloric acid solution, 1.0 M, 30 mL | Timer |
| Sodium thiosulfate solution, 0.30M, 30 mL | 3 mL syringe (2) |
| Distilled water | Beakers, 100 mL (3) labeled |
| Test tube rack | Black marker |
| 6 Test tubes, labeled |  |

**Safety Precautions:**

Hydrochloric acid solution is moderately toxic by ingestion and inhalation. It is corrosive to eyes and skin. Sodium thiosulfate is a body tissue irritant. The sulfur produced in this reaction has low toxicity, but may be a skin and mucous membrane irritant. Aqueous sulfur dioxide is generated in this reaction, which is a skin and eye irritant. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron.

**Procedure:**

**Pre-Lab Preparation**

1). Label one small beaker “HCl”. Add 30 mL of 1.0 M hydrochloric acid, HCl, solution to this beaker.

2). Label another small beaker “Na2S2O3”. Pour 30 mL of 0.30 M sodium thiosulfate,

 Na2S2O3, solution into this beaker.

3). Label a third small beaker “water”. Pour 25 mL of distilled or deionized water into this beaker.

4). A test tube rack with 6 labeled test tubes has been set up at the lab bench.

**Part A: Varying the Concentration of HCl**

1). Fill the 3-mL syringe up to the 2-mL mark with distilled water by submerging the syringe in the “water” beaker and drawing water into the syringe until the plunger is at the 2-mL mark. Make sure that there are no air bubbles in the syringe. (If the syringe has a tip cover, remove it before filling the syringe.)

2). Now submerge the syringe in the “HCl” beaker and draw 1 mL of HCl solution into the

syringe so that the plunger sits at the 3-mL mark.

3). Empty the syringe into the #3 test tube.

4). Follow the same filling and emptying procedure as outlined in Steps 1-3, but use the amounts of water and HCl solution indicated below for test tube #1 and #2. Fill the test tubes in reverse order (test tube #2 next, then test tube #1). By filling the syringe with the most dilute mixture first and working up to the most concentrated, the syringe does not need to be rinsed between fillings.

|  |  |  |
| --- | --- | --- |
| **Test tube** | **Volume Distilled Water (mL)** | **Volume HCl (mL)** |
| **1** | 0 | 3  |
| **2** | 1.5 | 1.5 |
| **3** | 2 | 1 |
| **4** | 0 | 3 |
| **5** | 1.5 | 1.5 |
| **6** | 2 | 1 |

5). **Switch to the other syringe** that will be used just with the sodium thiosulfate. Fill the 3-mL syringe to the 2-mL mark with the Na2S2O3 solution.

6). Prepare to start the timer.

7). Empty the syringe into test tube #1.

8). Time the reaction with a stopwatch or timer by measuring the time from which the solution was added until the black “+” sign can no longer be seen through the solution. Record the exact time in seconds in Data Table 1.

9). Repeat Step 5 for test tubes #2 and #3, adding 2 mL of the Na2S2O3 solution to each test tube. Carefully time each reaction with a stopwatch or timer by measuring the time from which the solution was added until the black “+” sign can no longer be seen through the solution. Record the exact time in seconds in Data Table 1

10). Repeat Steps 5-9 in test tubes #4-6 to obtain a second set of data.

11). Empty the six-test tubes into the collection container provided by your teacher.

12). Clean each of the test tubes with soap and water. Place the cleaned test tubes on the drying rack on the wall above the lab sink.

**Part B: Varying the Concentration of Na2S2O3**

1). Obtain a new set of marked test tubes for the second half of the experiment. Make sure that you have rinsed and dried each syringe in the lab area.

2). Fill the 3-mL syringe up to the 2-mL mark with distilled water by submerging the syringe in the “water” beaker and drawing water into the syringe until the bottom of the plunger is at the 2-mL mark. Make sure there are no air bubbles in the syringe.

3). Now submerge the syringe in the “Na2S2O3” beaker and draw 1 mL of the Na2S2O3 solution into the syringe so that the plunger sits at the 3-mL mark.

4). Empty the syringe into test tube #3 of the six-test tube set up. See Table 2 below.

5). Follow the same filling and emptying procedure as outlined in Steps 1 – 3 of Part A but use the amounts of water and Na2S2O3 solution indicated below for test tubes #1 and #2. Fill the test tubes in reverse order (test tube #2 next, then test tube#1). By filling the syringe with the most dilute mixture first and working up to the most concentrated, the syringe does not need to be rinsed between fillings.

|  |  |  |
| --- | --- | --- |
| **Test tube** | **Volume Distilled Water (mL)** | **Volume Na2S2O3 (mL)** |
| **1** | 0 | 3  |
| **2** | 1.5 | 1.5 |
| **3** | 2 | 1 |
| **4** | 0 | 3 |
| **5** | 1.5 | 1.5 |
| **6** | 2 | 1 |

5). **Switch to the other syringe** that will be used just with the hydrochloric acid. Fill the 3-mL syringe to the 2-mL mark with the HCl solution.

6). Prepare to start the timer.

7). Empty the syringe into test tube #1.

8). Time the reaction with a stopwatch or timer by measuring the time from which the solution was added until the black “+” sign can no longer be seen through the solution. Record the exact time in seconds in Data Table 2.

9). Repeat Step 5 for test tubes #2 and #3, adding 2 mL of the HCl solution to each test tube. Carefully time each reaction with a stopwatch or timer by measuring the time from which the solution was added until the black “+” sign can no longer be seen through the solution. Record the exact time in seconds in Data Table 2.

10). Repeat Steps 5-9 in test tubes #4-6 to obtain a second set of data.

11). Empty the six-test tubes into the collection container provided by your teacher.

12). Clean each of the test tubes with soap and water. Place the cleaned test tubes on the drying rack on the wall above the lab sink.