

# Determination of a Rate Law by the Method of Initial Rates

## Assignment & Report Guidelines

**READING** Experiment – Lab Handout Download

*Chemistry*, 5<sup>th</sup> or 6<sup>th</sup> ed. by Silberberg: Sections 16.1-16.3

**PRE-LAB** Begin the prelab on a new page of your laboratory notebook. **ALL elements of the pre-lab MUST be completed before an experiment is started.** The COPY page from your notebook will be collected as you enter the lab. The original pages must stay in your notebook.

### Heading

- Title of experiment and number, your name, the dates of the experiment.

### Purpose & Balanced Equation

- Briefly & specifically explain the purpose of the experiment.
- In context, provide the balanced chemical equation for the specific reaction we are studying. A net ionic equation is acceptable. Include state symbols for all species.

### Data Table

- Copy Table 1 into your notebook, including a proper title. On a NEW page, prepare a table recording each quantity you will measure in the lab.

(Do *not* turn in with the prelab, however, it may be checked off before you begin.)

### Answers to Pre-Lab Questions

- Answer the questions directly on the handout pages. For #1A, prepare an appropriate graph to determine the order. You may prepare either on graph paper or using graphing software. Create your graph individually. Turn in a hardcopy of the graph with your prelab assignment.

## **LAB REPORT**

*Begin the lab report section on a new page of the lab notebook. **The discussion and conclusion sections should be word-processed.** Other parts of the report - calculations, etc. may be typed or written in the lab notebook.*

### **Heading**

- Title of experiment and number, your name, your lab partner's name(s) if applicable, the dates of the experiment.

### **Data / Observations / Results**

- ORIGINAL QUALITATIVE & QUANTITATIVE DATA (signed data pages from your lab notebook).
- **Reminder:** Record ALL data directly in your lab notebook.

*Note: Provide context for each statement or calculation, with proper labels. Please do not use the numbers on a step in the procedure as a label.*

### **Calculations / Data Analysis / Results**

*Show complete calculations for the following quantities. Use proper format for labeling and showing calculations in a formal report):*

- Provide full calculations for one trial in the experiment, including labeling each calculation and showing formulas, substitutions, and units.
- Additional trial calculations may be carried out using Microsoft Excel or other spreadsheet software if you choose (highly recommended). Data and results of the calculations should be presented in an appropriate table either prepared with a spreadsheet or word processor, or neatly written in the lab notebook.
- Calculations / Data Analysis / Results as described in the Procedure section.

### **Discussion – Theory / Results / Error Analysis**

*In this section, you will explain the experiment, evaluate and discuss your results, and analyze error.*

- Briefly summarize the experiment. Be sure to explain the process and theory of the initial rates experiment that we carried out, including how each order was determined and what functions the sodium thiosulfate and the starch served. Provide other information needed to understand the process carried out in the lab and you analysis.
- Evaluate your results. Are the orders you determined reasonable? Discuss errors or problems with our assumptions that could lead to deviations from expected results. Discuss your k values and its standard deviation. How precise were your data?

### **Conclusions**

*Your conclusion should include:*

- A clear statement of the rate law for the experiment observed, including the k' value with units.

### **Answers to the Post-Lab Question:**

Consider the reaction studied in this experiment. It is an oxidation-reduction reaction. Write the  $\frac{1}{2}$ -reactions for this overall reaction.

# Determination of a Rate Law by the Method of Initial Rates

## BACKGROUND

In this experiment, a quantitative statement as to *how* changes in reactant concentrations affect reaction rate is expressed in an experimentally derived rate law.

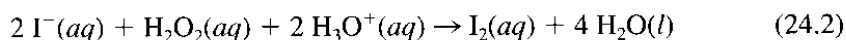
To assist in understanding the relationship between reactant concentration and reaction rate, consider the general reaction,  $A_2 + 2 B_2 \rightarrow 2 AB_2$ . The rate of this reaction is related, by some exponential power, to the concentration of each reactant. For this reaction, we can write the relationship as

$$\text{rate} = k [A_2]^p [B_2]^q \quad (24.1)$$

This expression is called the **rate law** for the reaction. The value of  $k$ , the reaction **rate constant**, varies with temperature but is independent of reactant concentrations.

The superscripts  $p$  and  $q$  designate the **order** with respect to each reactant and are *always* determined experimentally. For example, if doubling the molar concentration of  $A_2$  while holding the  $B_2$  concentration constant increases the reaction rate by a factor of 4, then  $p = 2$ . In practice, a large excess of  $B_2$  makes an insignificant change in its concentration during the course of the reaction; therefore, the change in reaction rate results from the more significant changes in the smaller amounts of  $A_2$  in the reaction. An experimental study of the kinetics of any reaction involves determining the values of  $k$ ,  $p$ , and  $q$ .

In this experiment the rate law for the reaction of hydrogen peroxide,  $H_2O_2$ , with potassium iodide, KI, is determined.<sup>1</sup> When these reactants are mixed, hydrogen peroxide slowly oxidizes iodide ion to elemental iodine,  $I_2$ .



The rate of the reaction, governed by the molar concentrations of  $I^-$ ,  $H_2O_2$ , and  $H_3O^+$ , is expressed by the rate law,

$$\text{rate} = k [I^-]^p [H_2O_2]^q [H_3O^+]^r \quad (24.3)$$

When the  $[H_3O^+]$  is greater than  $1 \times 10^{-3}$  mol/L, the reaction rate is too rapid to measure in the general chemistry laboratory; however, if the  $[H_3O^+]$  is *less than*  $1 \times 10^{-3}$  mol/L, the reaction proceeds at a measurable rate. An acetic acid–sodium acetate **buffer** maintains a nearly constant  $[H_3O^+]$  at  $1 \times 10^{-5}$  mol/L during the experiment.<sup>2</sup> As  $H_3O^+$  ion does not affect the reaction rate at this lower concentration, the rate law for the reaction becomes

$$\text{rate} = k' [I^-]^p [H_2O_2]^q \quad (24.4)$$

where  $k' = k [H_3O^+]^r$ .

In this experiment we will determine  $p$ ,  $q$ , and  $k'$  for the hydrogen peroxide–iodide ion system. Two sets of experiments are required: One set of experiments is designed to determine the value of  $p$  and the other to determine the value of  $q$ .

*Rate constant: a proportionality constant relating the rate of a reaction to the initial concentrations of the reactants*

*Order: the exponential factor by which the concentration of a substance affects reaction rate*

*Buffer: a solution that resists changes in acidity or basicity in the presence of added  $H^+$  or  $OH^-$  (Buffer solutions are studied in Experiment 25.)*

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### Determination of $p$ , the Order of the Reaction with Respect to Iodide Ion

In the first set of experiments, the effect that iodide ion has on the reaction rate is observed in several kinetic trials. A “large” excess of hydrogen peroxide in a buffered system maintains the  $H_2O_2$  and  $H_3O^+$  concentrations essentially constant during each trial. Therefore, for this set of experiments, the rate law, Equation 24.4, reduces to the form

$$\text{rate} = k' [I^-]^p \cdot c \quad (24.5)$$

$c$ , a constant, equals  $[H_2O_2]^q$ .

In logarithmic form, Equation 24.5 becomes

$$\log(\text{rate}) = \log k' + p \log [\text{I}^-] + \log c \quad (24.6)$$

Combining constants, we have the equation for a straight line:

$$\begin{aligned} \log(\text{rate}) &= p \log [\text{I}^-] + C \\ y &= mx + b \end{aligned} \quad (24.7)$$

$C$  equals  $\log k' + \log c$  or  $\log k' + \log [\text{H}_2\text{O}_2]^q$ .

Therefore, a plot of  $\log(\text{rate})$  versus  $\log [\text{I}^-]$  produces a straight line with a slope equal to  $p$ , the order of the reaction with respect to the molar concentration of iodide ion.

In the second set of experiments, the effect that hydrogen peroxide has on the reaction rate is observed in several kinetic trials. A "large" excess of iodide ion in a buffered system maintains the  $\text{I}^-$  and  $\text{H}_3\text{O}^+$  concentrations essentially constant during each trial. Under these conditions the logarithmic form of the rate law (Equation 24.4) becomes

$$\begin{aligned} \log(\text{rate}) &= q \log [\text{H}_2\text{O}_2] + C' \\ y &= mx + b \end{aligned} \quad (24.8)$$

$C'$  equals  $\log k' + \log [\text{I}^-]^p$ .

A second plot,  $\log(\text{rate})$  versus  $\log [\text{H}_2\text{O}_2]$ , produces a straight line with a slope equal to  $q$ , the order of the reaction with respect to the molar concentration of hydrogen peroxide.

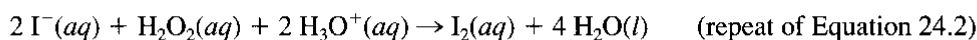
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### Determination of $q$ , the Order of the Reaction with Respect to Hydrogen Peroxide

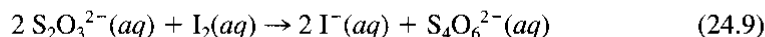
To follow the progress of the rate of the reaction, two solutions are prepared:

- Solution A: a diluted solution of iodide ion, starch, thiosulfate ion ( $\text{S}_2\text{O}_3^{2-}$ ), and the acetic acid–sodium acetate buffer
- Solution B: the hydrogen peroxide solution

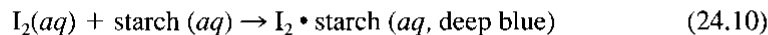
When Solutions A and B are mixed, the  $\text{H}_2\text{O}_2$  reacts with the  $\text{I}^-$  (Equation 24.2).



To prevent an equilibrium (a back reaction) from occurring in Equation 24.2, thiosulfate ion is added to the system for the purpose of removing  $\text{I}_2$  as it is formed:



As a result, iodide ion is regenerated in the reaction system; this maintains a constant iodide ion concentration during the course of the reaction until the thiosulfate ion is consumed. When the thiosulfate ion has completely reacted in solution, the  $\text{I}_2$  combines with starch, forming a deep blue  $\text{I}_2 \cdot \text{starch}$  complex. Its appearance signals a length of time for the reaction (Equation 24.2) to occur, and the length of time for the disappearance of the thiosulfate ion.



The time required for a quantitative amount of thiosulfate ion to react is the time lapse for the appearance of the deep blue solution. During that period a quantitative amount of  $\text{I}_2$  is generated; therefore, the rate of  $\text{I}_2$  production (mol  $\text{I}_2$ /time), and thus the rate of the reaction, is affected *only* by the initial concentrations of  $\text{H}_2\text{O}_2$  and  $\text{I}^-$ .

Therefore, the rate of the reaction is followed by measuring the time required to produce a preset number of moles of  $\text{I}_2$ , *not* the time required to deplete the moles of reactants.

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### Observing the Rate of the Reaction

# Determination of a Rate Law by the Method of Initial Rates

## PROCEDURE

Table 1 summarizes the volumes required for trials 1-12. **Copy Table 1 into your lab notebook. Prepare a Data & Results Table to summarize the data and results of calculations described below. This should be done prior to lab.**

*Note:* All trials will be carried out in 150-mm test tubes.

1. *Preparation of solution A:* Pipette the listed volumes for the various solutions into a clean, dry test tube. Add the starch from a dropper. Prepare all of solution A for trials 1-6 at the same time.
2. *Preparation of solution B:* Pipette the indicated volume of 0.10 M H<sub>2</sub>O<sub>2</sub> into a *small* container (10-mL beaker). Prepare just before use in each trial.
3. Prepare to time the reaction. Place a piece of white paper behind the test tube rack so that you can easily see the color change.
4. Add solution B rapidly to the test tube with solution A for the trial. **START TIME** immediately. *Stopper the tube and invert twice (only 2 times!).* Remove the stopper and place into the test tube rack.
5. The change to a deep purple color will be sudden. Be prepared! **STOP TIME** when the blue color appears.
6. Record the time in seconds. Measure and record the temperature of the reaction mixture.
7. Repeat steps 2-6 for the additional kinetic trials.
8. Repeat steps 1-7 above for trials 7-12
9. Run a Trial “Zero” that is just like trial #1, but excludes the thiosulfate solution. This should help to illustrate dramatically the effect of the thiosulfate on the reaction mixture.

## DATA ANALYSIS & RESULTS

*Note:* Consider the volume of the drops in the calculation of the initial volumes of the reactants.  
1 drop  $\approx$  0.05 mL

10. Calculate the moles of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions consumed in each trial. From the stoichiometry of the reaction, calculate the moles of I<sub>2</sub> consumed by the reaction with the thiosulfate. Based on the moles I<sub>2</sub> and the total volume of the solution, calculate  $\Delta[I_2]$ .

*Note:* These values are the same for each trial and serve as the “clock” – when the moles of I<sub>2</sub> produced exceeds the stoichiometric ratio to the thiosulfate, it will complex with the starch to give the deep blue color of the starch-iodine complex.

11. Calculate the initial rate of the reaction for each trial with the equation: 
$$\text{rate} = \frac{\Delta[I_2]}{\Delta t}$$
 where  $\Delta t$  is the elapsed time in seconds (s).
12. Calculate the  $\log(\text{rate})$  for each trial.
13. For each trial, calculate the initial concentrations of hydrogen peroxide [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> and iodide [I<sup>-</sup>]<sub>0</sub> as well as  $\log[H_2O_2]_0$  and  $\log[I^-]_0$ .

**Note:** You will be making two separate determinations of the order for each reactant – one by the primary method used in lecture, and one by the graphical method described in the background of the experiment. If your data are consistent, you should arrive at the same order by both methods.

**Preliminary order determinations:**

- Select two trials in which the  $[I^-]_0$  is constant between trials. Analyze the difference in the  $[H_2O_2]_0$  and the rate of reaction to make a preliminary determination of the order of the reaction for  $[H_2O_2]$ .
- Select two trials in which the  $[H_2O_2]_0$  is constant between trials. Analyze the difference in the  $[I^-]_0$  and the rate of reaction to make a preliminary determination of the order of the reaction for  $[I^-]$ .

**Graphical order determinations:**

- Graph #1: Plot  $\log[I^-]_0$  (x-axis) vs.  $\log(\text{rate})$  (y-axis) for trials 1-6. Prepare this graph by hand on a full page of graph paper. Determine the slope of the line using the equation: slope (m) =  $\Delta y/\Delta x$ . The slope should be a good approximation of the order of the reaction for  $I^-$ .
- Graph #2: Plot  $\log[H_2O_2]_0$  vs.  $\log(\text{rate})$  for trials 7-12. Prepare this graph using MS Excel or other graphing software. Determine the slope of the line using the linear regression feature. The slope should be a good approximation of the order of the reaction for  $H_2O_2$ .

**Rate law constant determinations:**

- Calculate  $k'$  for each of the **twelve** trials and determine the average value. Include correct units! Show a calculation for one trial. Summarize all twelve values in the data/results table. Calculate the standard deviation – SHOW WORK – calculation should be done by hand.
- State the differential rate law expression for the reaction of the iodide ion and hydrogen peroxide. Include the value and units of  $k$  substituted into the equation.

**Table 1.** Composition of Reaction Mixtures

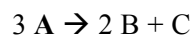
Trial	Solution A					Solution B
	Buffer: Mixture of 0.5 M $CH_3CO_2H$ & 0.5 M $NaCH_3CO_2$	0.020 M $Na_2S_2O_3$	Starch Solution	DI Water	0.30 M KI	0.10 M $H_2O_2$
1	1.0 mL	1.0 mL	5 drops	6.0 mL	1.0 mL	3.0 mL
2	1.0 mL	1.0 mL	5 drops	5.0 mL	2.0 mL	3.0 mL
3	1.0 mL	1.0 mL	5 drops	4.0 mL	3.0 mL	3.0 mL
4	1.0 mL	1.0 mL	5 drops	3.0 mL	4.0 mL	3.0 mL
5	1.0 mL	1.0 mL	5 drops	2.0 mL	5.0 mL	3.0 mL
6	1.0 mL	1.0 mL	5 drops	1.0 mL	6.0 mL	3.0 mL
7	1.0 mL	1.0 mL	5 drops	7.0 mL	2.0 mL	1.0 mL
8	1.0 mL	1.0 mL	5 drops	5.5 mL	2.0 mL	2.5 mL
9	1.0 mL	1.0 mL	5 drops	4.0 mL	2.0 mL	4.0 mL
10	1.0 mL	1.0 mL	5 drops	3.0 mL	2.0 mL	5.0 mL
11	1.0 mL	1.0 mL	5 drops	1.5 mL	2.0 mL	6.5 mL
12	1.0 mL	1.0 mL	5 drops	none	2.0 mL	8.0 mL
0	1.0 mL	none	5 drops	7.0 mL	1.0 mL	3.0 mL

**PRELAB QUESTIONS**

Name: \_\_\_\_\_

Please answer on this page and turn in with your prelab assignment.

1. The following data were collected in the disproportionation reaction of A:



The rate law for this reaction can be expressed as:  $\text{rate} = k[\text{A}]^n$

The indicator for this reaction will result in a color change from yellow to blue after 0.01 M of the A has reacted. **Each rate must, therefore, be calculated based on 0.01 M A reacting.**

$[\text{A}]_0$ (mol/L)	Time for color change (s)			
0.10	753			
0.20	264			
0.30	145			
0.40	98			
0.50	65			
0.60	53			

- A) Calculate the rate for each trial (show at least one calculation) and any other values necessary to graph the data by the method explained in the procedure.
- B) Prepare an appropriate graph to determine the order. You may prepare either on graph paper or using graphing software. Prepare your graph individually. Turn in a hardcopy of the graph with your prelab.
- C) Determine the order of the reaction in A (the value of n in the rate equation) from the graph. (*Hint:* Unlike many common reactions, it is not a whole number).
- D) Calculate k for each trial (show at least one calculation) and an average k value (including units).
- E) Write the rate law expression with k and n substituted.

2. State the purpose of each of the following solutions in this experiment. These should be short answers.

A) Buffer solution

B) Starch solution

C) Sodium thiosulfate solution

D) Deionized water

3. Write the equation for the reaction that serves as the “clock” for this reaction.