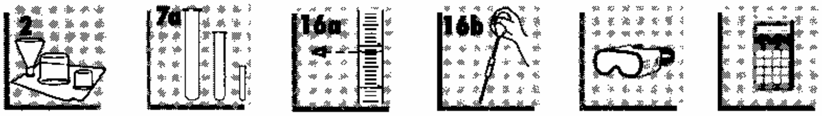
Determination of a Rate Law by the Method of Initial Rates

OBJECTIVES

- To determine the rate law for a chemical reaction
- To utilize a graphical analysis of the experimental data

TECHNIQUES

The following techniques are used in the Experimental Procedure



INTRODUCTION

The rate of a chemical reaction is affected by a number of factors, most of which were studied in Experiment 23. The rate of a reaction can be expressed in a number of ways, depending on the nature of reactants being consumed or the products being formed. The rate may be followed as a change in concentration (mol/L) of one of the reactants or products per unit of time, the volume of gas produced per unit of time (Figure 24.1), or the change in color (percent transmittance) per unit of time, just to cite a few examples.

Changing the temperature of the reaction system or the concentration of a reactant is a common procedure for changing reaction rate; neither affects the "chemistry" (referred to as the mechanism) of the reaction. The presence of a catalyst does affect the mechanism of a reaction and is commonly used in the chemical industry.

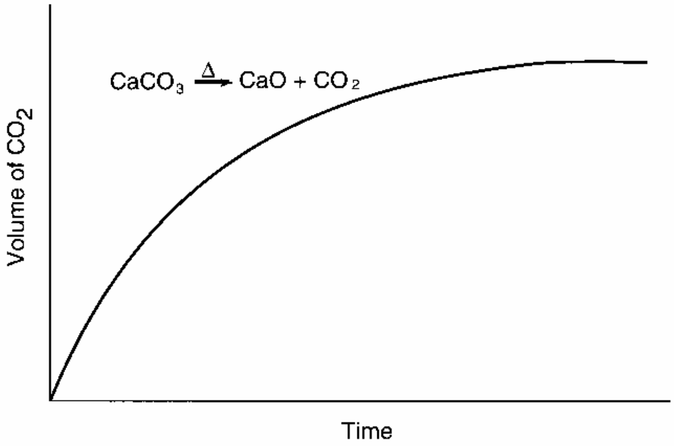


Figure 24.1 The rate of thermal decomposition of calcium carbonate is determined by measuring the volume of evolved carbon dioxide gas versus time.

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

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

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

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.[1] When these reactants are mixed, hydrogen peroxide slowly oxidizes iodide ion to elemental iodine, I_2.

$$2\ I^-(aq) + H_2O_2(aq) + 2\ H_3O^+(aq) \rightarrow I_2(aq) + 4\ H_2O(l) \qquad (24.2)$$

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

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

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.)

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

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

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.

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

$$\text{rate} = k'\,[I^-]^p \bullet c \qquad (24.5)$$

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

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[1] Your laboratory instructor may substitute $K_2S_2O_8$ for H_2O_2 for this experiment. The equation for the reaction is

$S_2O_8^{2-}(aq) + 2\ I^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + I_2(aq)$

[2] In general, a combined solution of H_2O_2 and I^- is only very slightly acidic and the acidity changes little during the reaction. Therefore, the buffer solution may not be absolutely necessary for the reaction. However, to ensure that change in H_3O^+ concentrations is *not* a factor in the reaction rate, the buffer is included as a part of the experiment.

In logarithmic form, Equation 24.5 becomes

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

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

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

C equals $\log k' + \log c$ or $\log k' + \log [\mathrm{H_2O_2}]^q$.

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

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

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 I^- and $\mathrm{H_3O^+}$ concentrations essentially constant during each trial. Under these conditions the logarithmic form of the rate law (Equation 24.4) becomes

$$\begin{aligned} \log(\text{rate}) &= q \log [\mathrm{H_2O_2}] + C' \\ y &= mx + b \end{aligned} \qquad (24.8)$$

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

A second plot, log (rate) versus log $[\mathrm{H_2O_2}]$, produces a straight line with a slope equal to q, the order of the reaction with respect to the molar concentration of hydrogen peroxide.

Observing the Rate of the Reaction

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 ($\mathrm{S_2O_3^{2-}}$), and the acetic acid–sodium acetate buffer
- Solution B: the hydrogen peroxide solution

When Solutions A and B are mixed, the $\mathrm{H_2O_2}$ reacts with the I^- (Equation 24.2).

$$2\,\mathrm{I}^-(aq) + \mathrm{H_2O_2}(aq) + 2\,\mathrm{H_3O^+}(aq) \rightarrow \mathrm{I_2}(aq) + 4\,\mathrm{H_2O}(l) \qquad \text{(repeat of Equation 24.2)}$$

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 $\mathrm{I_2}$ as it is formed:

$$2\,\mathrm{S_2O_3^{2-}}(aq) + \mathrm{I_2}(aq) \rightarrow 2\,\mathrm{I}^-(aq) + \mathrm{S_4O_6^{2-}}(aq) \qquad (24.9)$$

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 $\mathrm{I_2}$ combines with starch, forming a deep blue $\mathrm{I_2}$•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.

$$\mathrm{I_2}(aq) + \text{starch}\,(aq) \rightarrow \mathrm{I_2} \bullet \text{starch}\,(aq, \text{deep blue}) \qquad (24.10)$$

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 $\mathrm{I_2}$ is generated; therefore, the rate of $\mathrm{I_2}$ production (mol $\mathrm{I_2}$/time), and thus the rate of the reaction, is affected *only* by the initial concentrations of $\mathrm{H_2O_2}$ and I^-.

Therefore, the rate of the reaction is followed by measuring the time required to produce a preset number of moles of $\mathrm{I_2}$, *not* the time required to deplete the moles of reactants.

Determination of a Rate Law by the Method of Initial Rates

PROCEDURE

Table 1 summarizes the volumes required for trials 1-12. 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_2O_2 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

10. Prepare a results table to summarize the data below.
11. Calculate the moles of $S_2O_3^{2-}$ ions consumed in each trial. From the stoichiometry of the reaction, calculate the moles of I_2 consumed by the reaction with the thiosulfate. We will designate this Δ(mole I_2). *These values are the same for each trial and serve as the "clock" – when the moles of I_2 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.*
12. Calculate the initial rate of the reaction for each trial with the equation: where Δt is the elapsed time.
$$rate = \frac{\Delta(mol\ \mathrm{I}_2)}{\Delta t}$$
13. Calculate the *log*(rate) for each trial.
14. For each trial, calculate the initial concentrations of hydrogen peroxide $[H_2O_2]_0$ and iodide $[I^-]_0$ as well as $log[H_2O_2]_0$ and $log[I^-]_0$.

    Note: Consider the volume of the drops in the calculation of the initial volumes of the reactants. 1 drop ≈ 0.05 mL

Prepare a data/analysis table that summarizes, for each trial, all of the measured and calculated values describe above.

Preliminary order determinations:

15. 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 $[H_2O_2]$.
16. 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:

17. Graph #1: Plot *log*$[I^-]_0$ (x-axis) vs. *log*(rate) (y-axis) for trials 1-6. Determine the slope of the line. The slope should be a good approximation of the order of the reaction for I^-.
18. Graph #2: Plot *log*$[H_2O_2]_0$ vs. *log*(rate) for trials 7-12. Determine the slope of the line. The slope should be a good approximation of the order of the reaction for H_2O_2.

RESULTS

19. State the differential rate law expression for the reaction of the iodide ion and hydrogen peroxide.
20. Calculate k′ for each of the seven trials and determine the average value. Calculate the standard deviation.

Table 1. Composition of Reaction Mixtures

	Solution A					Solution B
Trial	Buffer (0.5 *M* CH_3CO_2H / 0.5 *M* $NaCH_3CO_2$)	0.020 *M* $Na_2S_2O_3$	Starch	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	1.0 mL	*none*	6.0 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**:

   $3\,\mathbf{A} \rightarrow 2\,B + C$

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

   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.**

$[A]_0$ (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) 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).

C) Calculate k for each trial (show at least one calculation) and an average k value (including units).

D) Write the rate law expression with k and n substituted.

2. State the purpose of each of the following solutions in this experiment.

   A) Buffer solution

   B) Starch solution

   C) Sodium thiosulfate solution

   D) Deionized water

3. Consider the reaction studied in this experiment (Equation 24.2). It is an oxidation-reduction reaction. Write the ½-reactions for this overall reaction.

4. Write the equation for the reaction that serves as the "clock" for this reaction.