Kinetics of Hydrogen Peroxide

Objectives

In this experiment you will determine the rate law for the reaction between hydrogen peroxide and potassium iodide.

Introduction

When hydrogen peroxide is added to a solution of potassium iodide, the iodide ion is slowly oxidized to iodine according to the equation:

$$H_2O_{2(aq)} + 2\,I^-_{(aq)} + 2\,H^+_{(aq)} \rightarrow I_{2(aq)} + 2\,H_2O_{(l)} \qquad \text{Equation 1}$$

The reaction is faster in the presence of acid, provided that the concentration of hydrogen ion is greater than about 1.00×10^{-3} M. If the acidity is less than this, the effect of hydrogen ion is negligible. The purpose of this experiment is to determine the rate law for the reaction at low acidity, with the presumption that the reaction rate can be expressed in the form:

$$R = k[H_2O_2]^a[I^-]^b \qquad \text{Equation 2}$$

Here k is the rate constant and the exponents ‘a’ and ‘b’ have certain (integer) values. The task is to determine the numerical values of k, ‘a’, and ‘b’.

The reaction is carried out in a solution that has a low and constant acidity due to the presence of an acetate-acetic acid buffer, where the concentration of the hydrogen ion is constant at about 2.00×10^{-5} M.

The reaction with which we are concerned is one in which an equilibrium mixture will result if the concentration of the product, iodine, is allowed to build up. If our measurements are to be made on the actual rate of the forward reaction, rather than on the net difference between forward and reverse rates, it is essential that the reverse reaction be suppressed completely, e.g., by removing the iodine as quickly as it is formed. This is easily done by adding sodium thiosulfate. Thiosulfate does not react at a measurable rate with any of the other chemical species in the solution, but it does react rapidly and completely with iodine, according to the equation:

$$I_{2\,(aq)} + 2\,S_2O_3{}^{2-}{}_{(aq)} \rightarrow 2\,I^-_{(aq)} + S_4O_6{}^{2-}{}_{(l)} \qquad \text{Equation 3}$$

As long as excess thiosulfate is present in the solution, no free iodine can accumulate, and the net forward reaction will not be slowed down.

An additional and helpful consequence of the thiosulfate-iodine reaction is that the concentration of iodide ion in the solution remains at its original value. Even though the peroxide-iodide reaction uses up iodide ion, the thiosulfate immediately returns the iodine to the iodide ion form. As long as there is excess thiosulfate ion present, there is no change in the molarity of the iodide ion.

The addition of thiosulfate also facilitates accurate measurement of the rate at which the peroxide iodide reaction takes place. Suppose that a small, known amount of thiosulfate is added to the original mixture of peroxide and iodide. Iodine is produced slowly by the primary reaction and immediately reacts with the thiosulfate. The solution remains colorless. Ultimately all the thiosulfate will be used up; then the yellow color of free iodine is seen in the solution. The color is further enhanced by addition of starch, resulting in the formation of a blue-black starch-iodine complex. The color change is sharp, and the time elapsed is determined by timing with a stopwatch.

We know how many moles of the thiosulfate have reacted and how long it took for them to react. We also know the stoichiometry's of the thiosulfate-iodine and peroxide-iodide reactions from equations 1 and 3, so we can determine how many moles of peroxide were reduced in the known interval of time. Consequently the average rate (moles of H_2O_2 per L•s) at which the reaction proceeds during this period can be calculated.

In general, as the reaction proceeds, the consequent reduction in the concentrations of the reactants produces a slowing in the rate of the reaction. In the present case, however, the amount of thiosulfate added to the reaction mixture is sufficiently small so that no significant change in the concentrations of the reactants takes place during the period in which the measurement of the rate is made. Consequently the average rate determined for this period can be taken as a satisfactory approximation to the reaction rate corresponding to the initial reaction concentrations.

Acknowledgement

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Experimental Procedure

In quantitative work with hydrogen peroxide, cleanliness is critical, since many common substances catalyze the decomposition of hydrogen peroxide.

Prepare Solutions and Time Reactions

Table 1. Volume of Chemicals for Preparing the Five Test Solutions

Solution Number	**Volumes (in mL)**						
	Buffer	**0.300 M KI**	**Starch**	**0.0200 M $Na_2S_2O_3$**	**Deionized Water**	**0.100 M H_2O_2**	**Total Volume**
1	5.00	5.00	1.00	5.00	64.0	20.00	100.0
2	5.00	5.00	1.00	5.00	74.0	10.00	100.0
3	5.00	5.00	1.00	5.00	79.0	5.00	100.0
4	5.00	3.00	1.00	5.00	81.0	5.00	100.0
5	5.00	1.50	1.00	5.00	82.5	5.00	100.0

1. Label two clean dry 150 mL (or larger) beakers for solution (1) and solution (2). Also, label two smaller clean dry beakers or large test tubes appropriately for the peroxide portions of these two solutions.

2. Prepare solutions in the appropriate beakers as accurately as possible by adding all components except the hydrogen peroxide in the volume indicated. The buffer, KI, starch, and $Na_2S_2O_3$ solutions will be obtained from stock bottles or burettes set up in the laboratory.

3. In the small clean, dry beaker or large test tube, obtain 20.00 mL of the 0.100 M hydrogen peroxide solution for solution (1) and 10.00 mL for solution (2) from the burette of H_2O_2.

4. When starting the reaction for solution (1), one student should be prepared to begin timing the moment the other student first adds the peroxide to the larger beaker for solution (1).

5. Then rapidly pour some of the mixed solution back and forth between the hydrogen peroxide container and the larger beaker several times to ensure that the entire 20.00 mL of H_2O_2 is well mixed into the solution in the larger beaker.

6. Once the solution is well mixed and most of it is in the larger beaker, place the beaker on a piece of white paper so that the color change may be observed easily. (Read through step 9 and start solution (2) as directed to manage the time it will take to complete the experiment.)

7. Watch solution (1) carefully for the appearance of a uniform color throughout the beaker. This should happen rather suddenly, and the time required should be measured to the nearest second. The first solution will require less than five minutes, possibly 2 or 3 minutes to change color.

8. When the color changes, be sure to record the minutes and seconds from the timer immediately.
9. After the first solution is in progress, mix solution (2) together in the same manner, ensuring thorough mixing, and place on a piece of white paper to observe the color change. This solution will take longer than solution (1). You must watch both solutions for the color change. If you waited, more than two minutes to read this direction wait for solution (1) to change color before starting solution (2).
10. After the first two solutions change color, and you have recorded the times; prepare the other three solutions in a similar manner. It is important that the temperature of the solutions be the same throughout the experiment. It is reasonable to expect that the temperature of the laboratory will not change significantly over the course of the experiment.
11. The third, fourth and fifth solution will take longer amounts of time to change color. While you are waiting for the color change, you should begin the calculations for the first solution. Be sure to keep an eye on the solutions.

Analysis Using the Initial Rates to Determine the Rate Equation

For all five solutions, calculate the molarity of sodium thiosulfate initially present, initial rate of reaction, the initial concentrations of H_2O_2 and I^-, determine the correct rate equation, and calculate the average rate constant for the reaction.

As discussed in the Introduction, the rate law for this reaction will have the general form:

$$R = k[H_2O_2]^a[I^-]^b \qquad \text{Equation 2}$$

One strategy for determining the values of a and b in this equation is to consider pairs of experiments in which the initial concentration of one reactant is held constant while the other is changed. The resulting difference in the rate allows us to solve for the exponent on the species that has a changing concentration.

Consider the following example:

For a reaction with a rate dependent on initial concentrations of X, Y and Z the rate equation is written:

$$= k\,[X\,]^a[Y\,]^b[Z\,]^c$$

Table 2. Sample Experiment Initial Concentrations and Rate

Experiment #	**1**	**2**	**3**
[X]i (M)	0.100	0.150	0.150
[Y]i (M)	0.200	0.200	0.250
[Z]i (M)	0.300	0.300	0.300
Rate(initial) (M/s)	9.78E-4	2.20E-3	4.29E-3

For trials 1 and 2, the initial concentration of X is changing while the other species are held constant. We can compare the rates as follows:

$$\frac{(initial\ rate)_{exp.1}}{(initial\ rate)_{exp.2}} = \frac{k\left[X_{exp.1}\right]^a\left[Y_{exp.1}\right]^b\left[Z_{exp.1}\right]^c}{k\left[X_{exp.2}\right]^a\left[Y_{exp.2}\right]^b\left[Z_{exp2}\right]^c}$$

Substitute the values into the above equation. Since *k* is a constant and the concentrations of Y and Z are the same in both experiments, we will see that most of these cancels out mathematically:

$$\frac{2.20E^{-3}\left(\frac{M}{s}\right)}{9.78E^{-4}\left(\frac{M}{s}\right)} = \frac{\cancel{k}[0.150\ M]^{a}\cancel{[0.200\ M]}^{b}\cancel{[0.300\ M]}^{c}}{\cancel{k}[0.100\ M]^{a}\cancel{[0.200\ M]}^{b}\cancel{[0.300\ M]}^{c}}$$

Simplified:

$$\frac{2.20E^{-3}\left(\frac{M}{s}\right)}{9.78E^{-4}\left(\frac{M}{s}\right)} = \frac{[0.150\ M]^{a}}{[0.100\ M]^{a}}$$

$$2.25 = 1.50^{a}$$

To solve for the exponent a, recall this property:

$$\log X^{y} = y \times \log X$$

Take the log of both sides and solve for a:

$$\log 2.25 \ = \ \mathrm{a} \times \log 1.50$$

$$0.352 = \ \mathrm{a} \times 0.176$$

$$\mathrm{a} = 2.00$$

To solve for other exponents in this example we would determine which trials to use to solve for b, however we would need more trials so that we could solve for b and c just the way we solved for a, the rate of X_{exp}.

When using experimental data, it is unlikely that all answers will be a decimal that can easily be changed into a whole number as in the example above. For the hydrogen peroxide, once you solve for the exponent with two sets of data, you will compare the answers for each exponent and determine the nearest whole number that agrees with each set.

Data and Observations

In a buffered solution, the rate of the reaction for the equation:

$$H_2O_{2(aq)} + 2\ I^-_{(aq)} + 2\ H^+_{(aq)} \rightarrow I_{2(aq)} + 2\ H_2O_{(l)}$$

is given (we shall assume) by an expression of the form:

$$R = \ k[H_2O_2]^{a}[I^-]^{b}$$

It is usually found that the exponents '**a**' and '**b**' in such rate expressions are **integers**. From the experimental data obtained it is possible to determine the values of '**a**' and '**b**' and to estimate the value of the rate constant, *k*. We will, however, assume values for '**a**' and '**b**' and evaluate the values of *k*. An approximate constancy of the values of *k* will show the correctness of our choice of '**a**' and '**b**'.

Reagent bottle [H_2O_2] = _______________

Add appropriate descriptive titles and units to the tables as needed.

Table 3 ____

Solution Number	**1**	**2**	**3**	**4**	**5**
Start time (min:sec)					
Time of color change (min:sec)					
Time interval, Δt (seconds)					

The table below will be filled in as you perform the calculations on the next page**.** Be sure to add units to the headings.

Table 4 ____

Δ [H_2O_2] ( )					
Rate = - $\frac{\Delta[H_2O_2]}{\Delta t}$ ( )					
Initial [H_2O_2] ( )					
Initial [I^-] ( )					

Calculations

Show the set up and answer with correct significant figures and units for each of the following for the first solution. Then complete the calculations for the rest of the solutions to fill in Table 4

1. Calculate the molarity of sodium thiosulfate initially present the solutions.
2. Using equations 1 and 3 to determine mole ratios, calculate the [H_2O_2] used up during the reaction in each case, this is the Δ[H_2O_2] for Table 4 which is a negative value.
3. Calculate the rate change for the peroxide by dividing the negative Δ[H_2O_2] by the Δt, record in Table 4.

4. Using the value supplied for the [H_2O_2] stock solution, calculate the molar concentrations of H_2O_2 initially present in each of the five solutions. Remember that in each case a volume of H_2O_2 was diluted to a total volume of 100.0 mL Record this information in Table 4. Be sure to use correct significant figures and units.
5. Calculate the molarity of iodide ion initially present in each solution and record this information in the Table 4. Be sure to use correct significant figures and units.

Analysis

Use the mathematical method with the data from the experiment, to determine the rate equation for the reaction of H_2O_2 with I^-, which has a rate equation of

$$R = k[H_2O_2]^a[I^-]^b$$

1. Identify the pairs of solutions that can be used to solve for a. Use the data from the experiment to solve for a. Check the work by using another pair to solve for a. Determine the whole number that agrees with both results.
2. Identify the pairs of solutions that can be used to solve for b. Use the data from the experiment to solve for b. Check the work by using another pair to solve for b. Determine the whole number that agrees with both results.
3. Now that the exponents in the equation are known, use the correct form of the rate equation to calculate the value of k. Show a sample calculation using the data from Solution 1 and report the value of k based on the results from Solutions 2-5 and the average in the table provided. Determine the units for k.
4. Write the rate law expression for this reaction, including the value of k with correct units. Identify the order of this reaction respect to [H_2O_2] and with respect to [I^-]. Determine the overall order of this reaction?