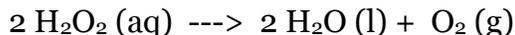


Lab: Kinetics of the Pt-catalyzed Decomposition of Hydrogen Peroxide

Name _____

A popular brand of contact lens solutions uses hydrogen peroxide as a disinfectant. The lenses are lowered into a chamber that contains the peroxide solution. The decomposition is catalyzed by the use of a platinum-coated disc and occurs as follows:



The bubbling action of the oxygen produced also helps to remove any excess proteins built up from daily wear.

According to the manufacturer, the level of hydrogen peroxide has dropped to a “safe” level (60 parts of peroxide per million parts of solution) after a period of 6 hours. At this point, the contact lens are sitting in an oxygenated solution of water mostly free of hydrogen peroxide.

Purpose

Part 1: Determine the order of reaction and the value of the rate constant using the method of initial rates.

Part 2: Using the correct integrated rate law, determine the “safe” reaction time.

Procedure/Data/Results

Part 1:

Use the pressure probe to study the rate of reaction.

In this part of the experiment you will use the gas pressure sensor to document the progress of the reaction as it occurs in a closed system.

As the reaction proceeds, the amount of oxygen gas (and thus the pressure) will continue to increase. You will use this data to determine the rate of reaction with respect to the loss of hydrogen peroxide.

You will collect pressure data for four different concentrations of H_2O_2 (aq) for a period of 100 seconds per trial.

Solution Preparation Information

Trial #	[H_2O_2]	Volume of 3.0% H_2O_2 (aq)	Volume of distilled water
1	0.88 M	20 mL	0 mL
2	0.66 M	15 mL	5 mL
3	0.44 M	10 mL	10 mL
4	0.22 M	5 mL	15 mL

Plug in the pressure sensor. Choose “DataQuest”. Make sure that the sensor is set up to collect 1 sample for a period of 100 seconds. (Use “Time Graph.” The time between samples should be 1 second. The experiment length should be 100 seconds.) Alternatively, you can use the default setting for the gas pressure sensor and just press STOP once 100 seconds have elapsed.

Once the data has been collected for a trial, select the **linear** portion of the graph and perform a linear regression to determine the initial rate of reaction.

The slope of this line will be the initial rate of reaction with respect to an increase in pressure due to oxygen **production** (kPa/second). You will then need to transform that rate to express it in terms of the **loss** of moles of hydrogen peroxide per Liter of solution per second. A formula is provided on the next page to help you with that transformation. Record your results in the table on the next page.

Room Temperature: _____ degrees Celsius = _____ Kelvins

Volume of Oxygen Gas Produced: 0.035 L (The test tubes we are using hold 0.020 L of solution and the remaining “air” space in the test tube and the pressure sensor tubing is equal to 0.035L.)

Reaction Rate (M H₂O₂ / s) =

$$\frac{\left(\frac{?kPa}{s}\right)\left(\frac{1.00atm}{101.3kPa}\right)(volume\ O_2\ in\ Liters)}{(0.08206\ \frac{LO_2 \cdot atm}{molO_2 \cdot K})(Temp\ In\ Kelvins)} \times \frac{2mol\ H_2\ O_2}{1mol\ O_2}$$

0.020L solution

Trial #	[H ₂ O ₂]	Initial Rate of Reaction (kPa/s)	Initial Rate of Reaction (M H ₂ O ₂ /s)
1	0.88 M		
2	0.66 M		
3	0.44 M		
4	0.22 M		

Now create a new “Lists & Spreadsheet” page.

Input the following information:

Initial Rate of Reaction (M H₂O₂/s)

Suggested variable : **R** in column A

Concentration of H₂O₂

Suggested variable : **C** in column B

Create new columns which transform the data:

natural log of the initial rate of reaction Suggested variable : **lnR** in column C

natural log of the concentration Suggested variable : **lnC** in column D

Create a “Data & Statistics” page.

Graph **lnR** on the y-axis. Graph **lnC** on the x-axis. You should get a straight-line graph. The slope of this straight line (ln Rate vs. ln Concentration) is equal to the reaction order.

Explanation of why this works:

Rate law for the decomposition of hydrogen peroxide:

$$\text{Rate} = k [\text{H}_2\text{O}_2]^a$$

Taking the natural log of both sides yields a new equation:

$$\ln(\text{Rate}) = \ln(k [\text{H}_2\text{O}_2]^a)$$

Another way to write this same equation is:

$$\ln(\text{Rate}) = a \cdot \ln[\text{H}_2\text{O}_2] + \ln(k)$$

This equation has the same form as:

$$y = m x + b$$

So, when ln(Rate) is graphed on the y-axis and ln[H₂O₂] is graphed on the x-axis, the slope is equal to the reaction order (a).

To find the slope of the graph (and thus the reaction order) and the correlation coefficient (r²), go back to the “Lists & Spreadsheet” page and perform statistical analysis on the two appropriate columns.

Report the slope and the correlation coefficient (r²) here:

Slope = _____

Correlation Coefficient (r²) = _____

Hopefully, you have now successfully determined if the reaction was a zero, first or second order decomposition.

Reaction Order (circle one):

zero

first

second

Now that you have determined the reaction order it's time to determine the rate constant.
 Since

$$\text{Rate} = k [\text{H}_2\text{O}_2]^a, \text{ it follows that } k = \text{Rate} / [\text{H}_2\text{O}_2]^a.$$

Since you have determined the value of "a" you can now solve for the rate constant for each trial of the experiment.
 Complete the following table .

Trial #	[H ₂ O ₂]	Initial Rate of Reaction (M H ₂ O ₂ /s)	rate constant (include units!)
1	0.88 M		
2	0.66 M		
3	0.44 M		
4	0.22 M		
average rate constant ----->			

Part 2:

Calculate the molarity of a hydrogen peroxide solution that would be 60.0 ppm.

$$\frac{? \text{ mol H}_2\text{O}_2}{\text{L solution}} = \frac{60.0 \text{ grams H}_2\text{O}_2}{1,000,000 \text{ grams solution}} \times \frac{\text{g sol'n}}{\text{mL sol'n}} \times \frac{\text{mL sol'n}}{\text{L sol'n}} \times \frac{\text{mol H}_2\text{O}_2}{\text{g H}_2\text{O}_2}$$

=

Now, using the correct **integrated** rate law, calculate the amount of time it would take for a hydrogen peroxide solution to go from it's starting point (3.0% or 0.88 M) to the manufacturer's "safe" ending point (60.0 ppm or ?M).

Work:

How does this time compare to the manufacturer's suggested wait time of 6 hours?

Integrated Rate Laws:

- zero order $[A] = - kt + [A]_{\text{initial}}$
- first order $\ln [A] = - kt + \ln[A]_{\text{initial}}$
- second order $1 / [A] = kt + 1 / [A]_{\text{initial}}$

Reference: *J. Chem. Educ.*, 2003, 80 (7), p 788

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Note1: The following procedure is one of two methods discussed in the article. (The other method involves using a gas buret with a leveling bulb to determine the volume of oxygen produced by the reaction under conditions of constant pressure and is a low-tech option if you don't have access to a pressure sensor.) You will note that this procedure is a more detailed discussion of the experiment than is given in my student handout. When I do this lab with students I simply discuss this procedure with them rather than giving it to them on paper. Also note that I use slightly different concentrations and do not have students use a buffer solution or a temperature bath. Students still generally get very good results without these modifications.

Note2: I have also included the instructor information from the lab which discusses equipment and reagents needed and potential sources of error.

-R. Lesniewski

Procedure: Measurement of the Pressure of Oxygen Evolved Under Conditions of Constant Volume

This method acquires the pressure of the oxygen evolved with a pressure sensor. The low-pressure sensor used in this experiment measures the difference between the pressure within the flask and the pressure of the lab. The partial pressure of the air and partial pressure of the water vapor within the flask are unchanged by the reaction and are assumed to equal to the pressure within the room. The sensor then measures the partial pressure of the oxygen generated by the reaction.

Prepare the solution to be studied and allow the solution to equilibrate with a constant temperature bath, if one is being used. Once the solution has reached a constant temperature and the AODisc® is prepared, place the disc in the solution, quickly stopper the flask and start to record data. Gently and consistently swirl the flask and collect pressure versus time until the partial pressure of oxygen has increased to about 8 kPa.

Prepare two samples of each of the four solutions in 125 mL or 250 mL Erlenmeyer flasks as is shown in the table below. The buffer is used to make sure that these solutions are at the same pH and that the pH of the reactant mixture remains relatively constant during the reaction. Care should be taken to ensure that each of these solutions is at the same temperature.

	Volume of H ₂ O ₂ (mL)	Volume of DI water (mL)	Volume of Buffer solution (mL)
Trial 1 (90%)	45	0	5
Trial 2 (75%)	37.5	7.5	5
Trial 3 (50%)	25	20	5
Trial 4 (25%)	12.5	32.5	5

During the first few minutes after placing a dry platinum-coated disc into the hydrogen peroxide solution, the rate of the decomposition of hydrogen peroxide actually increases. Eventually the rate of the reaction stabilizes, as the disc seems to become accustomed to the solution. The second identical solution for each trial is prepared to activate the platinum-coated disc in a solution that will not dilute the solution into which the disc is placed during the experiment.

Before acquiring data, activate the platinum-coated AODisc® for 30 minutes by placing the disc in one of the two samples of the trial 1 buffered hydrogen peroxide solution. Record the atmospheric pressure in the room from a barometer or from the instructor. Measure the temperature of the second trial 1 solution. Once the disc is prepared, place it into the second trial 1 hydrogen peroxide solution, stopper the flask and begin to record the pressure of oxygen generated while gently and consistently swirling the flask.

When the run is complete, place the platinum disc in one of the trial 2 solutions for 5 minutes to maintain the activation of the disc. Measure the temperature of the second trial 2 solution. Place the disc into the second trial 2 solution and measure the amount of generated oxygen as before. Repeat this procedure for trials 3 and 4.

Instructor Information

Equipment

- 8 Erlenmeyer flasks, 125 or 250 mL, per group
- One stopper with connections that allow it to be connected to the tubing that is in turn connected with the pressure sensor.
- One timing device per group. This can be as simple as a watch with a second hand.
- One water bath per group. This bath should be large enough to hold all of the flasks, so their temperature will be the same.
- One thermometer per group
- Some way to measure the atmospheric pressure for the class
- Low-pressure sensor (A sample rate of one or two pressure measurements per second was adequate. Any pressure sensor that can measure changes in pressure on the order of 0.1 kPa would be adequate.)

Reagents

- DI or distilled water
- One AOSEPT® disc. Any drug or grocery store should have this product for a small price. This disc is simply a plastic support coated with platinum black.
- About 100 mL of buffer solution per group. Approximately 800 mL of pH= 7.0 buffer can be prepared by adding 291 mL of 0.10 molar sodium hydroxide to 500 mL of 0.10 molar potassium dihydrogen phosphate, KH_2PO_4 . Adjust the final pH to 7.0 through small additions of either sodium hydroxide or potassium dihydrogen phosphate solutions. Alternatively, 0.1 molar solutions of 8 volumes dihydrogen phosphate and 3 volumes hydrogen phosphate salts can be prepared and mixed to give a solution that has a pH of approximately 7.0 as measured by a pH meter.
- About 500 mL of 3% hydrogen peroxide per group. This is easily purchased at any grocery or drug store.

Comments on Experiment

The reason for the activation of the discs is that when a dry disc is placed in a solution of hydrogen peroxide, the rate of the reaction increases over the first 20 minutes or so. It would probably be ok to use the same solution to initially activate the disc and to keep it moist between the runs. This would introduce a very small error in that the disc would be wet with a solution that is not at the same concentration as the solution into which it was being placed.

Measuring the volume of the flask should be done with the stopper on, and the volume should include the volume of the tubing up to the pressure sensor.

One error that is not discussed in the student handout is the pressure dependence of oxygen solubility in water. As the partial pressure of oxygen encountered by the solution during the run increases, the total amount of oxygen dissolved in the solution would also increase as described by Henry's law. The effect of this increase in solubility would be that the volume or pressure of oxygen measured would not be a true measure of the amount of the oxygen generated. Therefore, the measured rate would be slightly lower than the true rate. The error introduced by ignoring the small difference in the amount of oxygen measured and the true amount of oxygen generated is not significant.

The temperature dependence of oxygen solubility further complicates the picture because oxygen solubility decreases slightly as the temperature increases. Again, the amount of oxygen dissolved in solution relative the amount of generated oxygen is not significant.

A second error that is not discussed in the student hand out is that the vapor pressure of water is a colligative property. The vapor pressure of pure water that is subtracted from atmospheric pressure to obtain the partial pressure of oxygen is not the true vapor pressure of the solution. It is possible to use Raoult's Law to estimate the true vapor pressure given the solutions mole fraction. The mole fraction of the solution approximately 0.9 is close enough to unity to make this correction insignificant. As with the previous two errors it is felt by the authors that although the corrections for these errors is possible, it is not necessary or even helpful for general chemistry student understanding in this lab to attempt to include them.

Our most recent general chemistry laboratory section recently conducted this experiment. Their values for the rate constant at room temperature ranged ($N = 9$) from 0.00038 s^{-1} to 0.00077 s^{-1} giving a mean of 0.00058 s^{-1} and a standard deviation of 0.00015 s^{-1} . The safe reaction time for the average is 3.0 hours. Reducing the rate constant by two standard deviations increases the safe reaction time to 6.2 hours. Increasing the rate constant by two standard deviations reduces the safe reaction time to 2.0 hours. If one accepts these results as representative, the six hours recommended by CIBA appears adequate in almost all cases.