

Chemical Kinetics: Reaction Rates

Minneapolis Community and Technical College
C1152 v.1.16



I. Introduction

The Reactions

Question #1: Will a given chemical reaction occur?

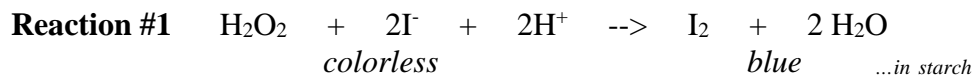
This question is very important especially if a reaction's products promise new lifesaving drugs, stronger synthetic plastics or alternative fuels. The answer to this question is the focus of chemical thermodynamics and enthalpy and entropy considerations.

However, in this experiment, you will study a reaction that is *known to occur* in hopes of answering a second, important question:

Question #2: How fast does the reaction occur and in what way (if any) does it depend on the concentrations of the reactants?

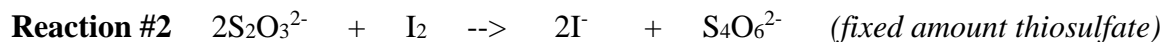
Such things are very important from a practical point of view since a reaction may be totally worthless if it requires many years to produce significant amounts of product.

Fortunately, the reaction studied in this experiment proceeds quickly enough for us to perform it many times within a reasonable amount of time. The reaction, shown below, involves hydrogen peroxide and its reaction with iodide and hydrogen ions to form molecular iodine and water.



Aqueous starch, also present in the reaction vessel, turns the solution blue the moment molecular iodine (I_2) concentrations increase. (Produced by the reaction: $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$, it is the I_3^- product and its reaction with starch that creates the blue color) Unfortunately, we can't get much useful information about the reaction's rate by simply mixing the reactants. The reaction will produce enough I_2 (I_3^-), even in its early stages, to quickly turn the solution blue regardless of whether the reaction is fast or slow.

A second reaction, occurring in the same container, is utilized in such a way that reaction rate information can be obtained.



The reaction utilizes thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ions to convert (or reduce) molecular iodine into the iodide ion (I^-). This process keeps the I_2 concentration at zero and thus keeps the solution from turning blue. However, when all of the thiosulfate is used up, reaction #2 no longer occurs permitting I_2 concentrations to quickly build and turn the solution blue.

In this experiment you will perform the above reaction sequence several times under different but carefully controlled conditions. However, in all cases, the amount of thiosulfate ($\text{S}_2\text{O}_3^{2-}$) is *always the same* and is the limiting reactant. How quickly the thiosulfate is consumed determines how quickly the solution turns blue. If a reaction mixture takes more time to turn blue, it is because the reaction is relatively slow (low reaction rate) requiring more time to use up the available thiosulfate. A fast reaction uses up thiosulfate more quickly and turns blue in less time.

Consider the analogous pie-eating contest (cartoon above). One way to organize such an event is to give each participant the same number of pies to eat (i.e. $\text{S}_2\text{O}_3^{2-}$). The fastest contenders finish with the pies in less time than those whose rate is slower. An individual whose *rate is twice as fast* finishes her pies in *half the time* as someone else. At the end of the race you might even see a few contestants turn blue (or green)!

Reaction Rates

The rate of a chemical reaction often depends upon the concentrations of the reactants. In this experiment, the reactants are hydrogen peroxide, iodide and hydrogen ions (Reaction #1). Mathematically, the rate of the reaction is related to these concentrations via the following rate equation:

$$\text{Rate} = k_T [\text{H}_2\text{O}_2]^x [\text{I}^-]^y [\text{H}^+]^z$$

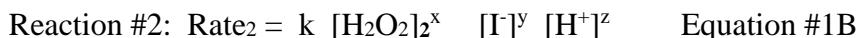
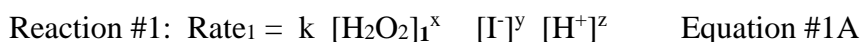
In this equation, k_T is the temperature dependent reaction rate constant, $[H_2O_2]$, $[I^-]$, $[H^+]$ are the molar concentrations of the three reactants, and x , y & z are exponents to be determined. When a reactant's concentration doesn't affect the reaction rate the reaction is referred to as "zeroth order" in that reactant (i.e. the exponent is a zero). Similarly, reactions found to depend directly or upon the square of a reactant's concentration are said to be "first order" or "second order" respectively (i.e. the exponent is a 1 or 2).

The **overall reaction order** is obtained by adding the exponents of the individual reaction orders. For example, if the rate equation is known to be $Rate = k_T [A]^1 [B]^1 [C]^2$ we would say that the reaction is **first order in A**, **first order in B** and **second order in C**. The overall reaction order is easily calculated by adding $1 + 1 + 2 = 4$. That is, the reaction is **4th order overall**.

Your goal in today's experiment is to determine the reaction orders, x , y and z , for all three reactants

Consider a reaction known to be second order in some reactant (exponent is 2). Tripling the concentration of the reactant will increase the rate of the reaction by a factor of $3^2 = 9$. That is, the reaction proceeds at 9x the rate as before the concentration was changed. Naturally, 9x the rate means the reaction is finished in $1/9^{\text{th}}$ of the original time.

Now consider two experiments, identical in every way except that the first uses a different concentration of hydrogen peroxide than the second. Their reaction rate equations can be written:



Note that k , $[I^-]^y$ and $[H^+]^z$ are the same in both equations. Thus, if we divide these two equations by one another the identical terms cancel out:

$$\frac{rate_1}{rate_2} = \frac{k \times [H_2O_2]_1^x \times [I^-]^y \times [H^+]^z}{k \times [H_2O_2]_2^x \times [I^-]^y \times [H^+]^z} = \frac{[H_2O_2]_1^x}{[H_2O_2]_2^x} \quad \text{Equation \#2}$$

or

$$\frac{rate_1}{rate_2} = \frac{[H_2O_2]_1^x}{[H_2O_2]_2^x} = \left(\frac{[H_2O_2]_1}{[H_2O_2]_2} \right)^x \quad \text{Equation \#3}$$

As mentioned earlier, the rate of reaction is inversely proportional to the time it takes for the reaction to occur (i.e. twice as fast \rightarrow half the time). Therefore, the above equation can be rewritten as:

$$\frac{t_2}{t_1} = \left(\frac{[H_2O_2]_1}{[H_2O_2]_2} \right)^x \quad \text{Equation \#4}$$

where t_1 and t_2 are the times required for the reaction mixture to turn blue.

Lastly, by taking the \log_{10} of both sides of this equation we can solve for "x":

$$x = \frac{\log\left(\frac{t_2}{t_1}\right)}{\log\left(\frac{[H_2O_2]_1}{[H_2O_2]_2}\right)} \quad \text{Equation \#5}$$

Thus, by performing two trials in which only the initial hydrogen peroxide concentrations are different, we can determine "x" by measuring the respective times for each trial and substituting these values into the equation above. Other reaction orders (y and z) for the other reactants are calculated in the same fashion.

Concentration considerations:

The initial concentrations of H_2O_2 , I^- and H^+ are not simply those that appear on their respective bottle labels. Mixing these liquids together produces dilution effects that decrease the effective concentrations of the three reactants. We need the post-dilution concentrations when we perform the calculations outlined above.

To do this, you will need to start with the concentrations obtained from the respective bottle labels. Note that because H_2O_2 constantly decomposing into O_2 gas and H_2O , the H_2O_2 concentration changes from day to day. Consequently, it is necessary to measure the H_2O_2 solution concentration prior to the start of lab and this number appears on the bottle label. Note that this number is probably not 0.800 M exactly. Use the bottle label concentration when performing your H_2O_2 dilution calculations.

In addition to bottle concentrations, you'll also need the total solution volume. In all trials, liquid amounts have been adjust to maintain 150 mL as the total volume and you should use this value for V_2 in the dilution equation below:

$$M_1 V_1 = M_2 V_2$$

Use this equation to calculate the new initial concentrations for I^- and H_2O_2 and report these values in a Table 2.

The H^+ concentrations are determined by a chemical buffer and this is something we'll study in great detail in Chapter 15. For this experiment, use the H^+ concentrations provided. Note that for solution #4, the H^+ concentration is **10X the H^+ concentration** for all other trials.

II. Prelab Exercise

Clearly answer these questions in INK in your lab notebook before coming to lab.

1. A reaction is known to be zeroth order in A, first order in B and second order in C.
 - a. Write out the reaction rate equation for this reaction.
 - b. How many times faster will the reaction occur if the concentration of A is doubled whilst keeping all other reactant concentrations constant?
 - c. How many times faster will the reaction occur if the concentrations of all reactants are doubled?
2. Catalysts:
 - a. What is the homogeneous catalyst used in this experiment?
 - b. How do you expect the catalyst to affect reaction *times*?
 - c. What's the difference between a heterogeneous and homogeneous catalyst?
3. A student prepares at test solution by combining **10.0 mL of "A"** with **20.0 mL of "B"**.

In a later experiment, the student recognizes the need to **change only one variable at a time** and so decides to **half the A concentration** whilst keeping the **"B" concentration constant**.

So, she correctly combines **5.0 mL of "A"**, **20.0 mL of "B"** and **5.0 mL of distilled water**.

Explain why the distilled water was needed.

III. Word Processed Report

Page 1: *Upper right hand corner Name, Lab section number and date*

Data tables: Obtain a copies of Data Tables 2 & 3 from the lab-handout web site and type in your values.

Page 2: Answers to the following questions.

1. Explain why it is important that the *total* solution volume be kept constant from one trial to another in these experiments.
2. Solutions 1 and 2 showed you how the H_2O_2 concentration can be used to control the reaction time.
 - a. Based on these your results for solutions 1 and 2, calculate the H_2O_2 concentration required to produce a 2000 second time delay for the reaction. (Show calculation)
 - b. Calculate the volume in mL of the stock H_2O_2 solution that would be required for this 2000 second experiment.
 - c. How many mL of H_2O would be required? (Show calculation)
3. Based on your values of x, y and z, how should the reaction rate be affected if all concentrations are doubled?
4. Chemists often claim that reaction rates roughly double for every additional 10°C .
 - a. How many times faster did the reaction rate increase in your experimental trial #6? (Show calculation)
 - b. Does this result support the chemist's claim?

Page 3: Calculations: (Handwritten is acceptable)

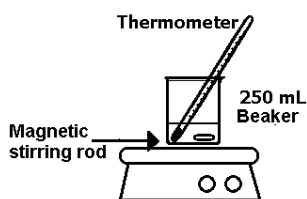
1. Show your H_2O_2 dilution calculations for Solutions 1 & 2
2. Show your calculations for x, y and z.
3. Provide x, y and z values with 4 decimal place accuracy.
4. Round off your x, y and z values to the nearest integer.
5. Write the complete rate equation using your integer values of x, y and z.

IV. Procedure

- You will be working with a partner today.
- Obtain ~40 mL of $\text{Na}_2\text{S}_2\text{O}_3$ solution in a clean, dry 50 mL beaker. You'll use this as a pipetting reservoir.
- Measure solution volumes carefully.
- Keep the temperature control in the off position until solution 6.
- Record the concentrations for all reactants as you find them on the bottle labels. This is especially important for H_2O_2 which decomposes. Its concentration won't be exactly 0.800 M.

Solution #1: (Two Trials)

A baseline for subsequent trial comparisons.



1. Add all liquids **except H_2O_2** in order from left to right on the solution preparation table (Below).
2. Reset the stopwatch. (*HINT: Practice using the stopwatch before you need it.*)
3. Steadily stir the solution at ~800 rpm using the magnetic stir plate/stir bar. Avoid splashing.
4. Measure the temperature of the mixture using an alcohol thermometer just before you add the H_2O_2 . Record this temperature in your lab notebook.
5. **Quickly pour** the H_2O_2 in the graduated cylinder into the reaction beaker while starting the stopwatch.
6. Stop timing when the solution abruptly turns blue.
7. Record the time in your lab notebook *and on the whiteboard* to the nearest tenth of a second.
8. Dispose of all waste solutions carefully in the lab sink.
9. Clean, rinse and shake off excess water and dry the 250 mL beaker.
10. **Repeat ONLY this trial a second time.** Results should agree to within a few seconds. If they don't, talk to your lab instructor before continuing.
11. Post your timing results on the blackboard.

Solutions 2, 3, 4, 5, and 6 require only one trial.

Please refer to Table 1 for the volume amounts required for each.

Solution #2: Half the H_2O_2 concentration.

Solution #3: Double the KI concentration.

Solution #4: $10 \times$ the H^+ concentration

Solution #5: The effect of a catalyst

Solution #6: 10°C temperature increase

1. Refer to the table below for volume amounts.
2. Warm the 250 mL beaker containing the mixture on a hot plate (stir and use very low setting).
3. When the temperature is approximately 10°C warmer than the original temperature remove the beaker from the hotplate and continue stirring on a second hotplate with the heat turned off.
4. Quickly add the H_2O_2 and start the stopwatch.
5. Record the time for the reaction.
6. Don't forget to record the high and low temperatures for the trial.

V. Data Tables: Cut and paste these data tables into your lab notebook using glue and transparent tape.

Table 1



Solution #	Temp (°C)	A Water (mL)	B 0.0500M Buffer (mL)	C 0.300 M HC ₂ H ₃ O ₂ (mL)	D 0.0500 M KI (mL)	E 1% Starch (mL)	F 0.0500 M Na ₂ S ₂ O ₃ (mL)	G 0.0100 M Mo(VI) Catalyst (mL)	H 0.800 M H ₂ O ₂ (mL)
		<i>100 mL grad cylinder</i>	<i>50 mL grad cylinder</i>	<i>@ buffer station</i>	<i>25 mL grad cylinder</i>	<i>5 mL grad cylinder</i>	<i>5 mL volumetric pipette</i>	<i>@ catalyst station</i>	<i>10 mL grad cylinder</i>
1	R.T.	75	30	0	25	5	5	0	10
2	R.T.	80	30	0	25	5	5	0	5
3	R.T.	50	30	0	50	5	5	0	10
4	R.T.	30	30	45	25	5	5	0	10
5	R.T.	70	30	0	25	5	5	5	10
6	R.T. + 10	75	30	0	25	5	5	0	10

Table 2



Bottle Concentrations (BEFORE dilution)			
	[I ⁻]	[H ₂ O ₂]	
Final Concentrations (AFTER dilution)			
<i>Use <u>excess significant figures</u> at all times unless asked to round.</i>			
Solution #	[I ⁻]	[H ⁺]	[H ₂ O ₂]
1		1.8×10^{-5}	
2		1.8×10^{-5}	
3		1.8×10^{-5}	
4		1.8×10^{-4}	
5		1.8×10^{-5}	
6		1.8×10^{-5}	

Table 3

Solution#	Trial 1		Trial 2	
	Temperature (°C)	Time (seconds)	Temperature (°C)	Time (seconds)
1				
2				
3				
4				
5				
6				