CHM 115 Lab 13

Kinetics: Concentration and Temperature Effects

Concentration Effect

The purpose of this experiment is to investigate the kinetics of the reaction

$$2\ H^+ + H_2O_2 + 2\ I^- \rightarrow I_2 + 2\ H_2O$$

The concentration of H^+ ion is held constant by using a buffer thus the $[H^+]$ term will not be included in the rate law, or in determining the rate constant. The rate of this reaction is measured by using the "clock reaction" $I_2 + 2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ I^-$

The clock reaction proceeds much faster than the reaction being studied, thus removing the I_2 as fast as it is produced. The $S_2O_3^{2-}$, present in a known amount, will react before any free I_2 is produced. The presence of free I_2 is detected by its reaction with the starch indicator to form a deep blue complex. Thus the rate of the reaction can be measured by timing the appearance of the starch-I_2 complex. While there is $S_2O_3^{2-}$ present, the concentration of the I^- remains essentially constant. Thus the rate of the reaction will be $\Delta[H_2O_2]/\Delta t$. Note that 1 mole of H_2O_2 reacts with 2 moles of I^- to produce 1 mole of I_2 which reacts with 2 moles of $S_2O_3^{2-}$. It is necessary to consider this stoichiometry to calculate the amount of H_2O_2 that reacts while the $S_2O_3^{2-}$ is present.

To determine the order of the reaction for each reactant, a series of reactions are run in which the concentration of only that reactant is varied. Then $\text{Rate} = k'[\ \ ]^n$, where k' includes all other reactants, and [ ] is the concentration of the reactant which is being varied. The logarithm of this expression is $\ln(\text{Rate}) = \ln(k') + n \ln[\ \ ]$. Thus a graph of ln (Rate) vs ln [ ] is a straight line which has a slope of n.

Procedure

Work with a partner. Each pair should obtain from the stockroom: 5 and 10 mL pipets, bulb and rack.

1. First the effect of the concentration of the I^- will be investigated. Label your four 250 mL Erlenmeyer flasks. Use the graduated cylinder to measure the deionized water indicated in the table below – add the water directly to the 250 mL Erlenmeyer flask. Pipet 5.0 mL of the $Na_2S_2O_3$ into the Erlenmeyer flask, followed by dispensing the appropriate amounts (indicated in the table below) of buffer, KI and starch directly from the auto-pipetters into the labeled Erlenmeyer flasks.

Flask	Deionized H_2O	Buffer	0.30 M KI	Starch	0.020 M $Na_2S_2O_3$	
1	129 mL	6 mL	2.0 mL	2 mL	5.0 mL	
2	127 mL	6 mL	4.0 mL	2 mL	5.0 mL	
3	123 mL	6 mL	8.0 mL	2 mL	5.0 mL	
4	115 mL	6 mL	16 mL	2 mL	5.0 mL	

Obtain about 125 mL (and only 125 mL) of the H_2O_2 solution in a clean *dry* 150 mL beaker. Record the exact concentration of the H_2O_2. 6.0 mL of the H_2O_2 is to be added to each flask. Use your graduated cylinder to measure 6.0 mL of the H_2O_2 into each of four small test tubes. The timing of the reaction begins with the addition of the H_2O_2. The H_2O_2 should be added quickly and the contents of the flask mixed well. Measure the time required for the reaction to consume the $S_2O_3^{2-}$.

2. Now the effect of the concentration of the H_2O_2 will be investigated. Rinse your four 250 mL Erlenmeyer flasks. Use the graduated cylinder to measure the deionized water indicated in the table below – add the water directly to the 250 mL Erlenmeyer flask. Pipet 5.0 mL of the $Na_2S_2O_3$ into the Erlenmeyer flask, followed by dispensing the appropriate amounts (indicated in the table below) of buffer, KI and starch directly from the auto-pipetters into the labeled Erlenmeyer flasks.

Flask	Deionized H_2O	Buffer	0.30 M KI	Starch	0.020 M $Na_2S_2O_3$	
1	128 mL	6 mL	6.0 mL	2 mL	5.0 mL	
2	125 mL	6 mL	6.0 mL	2 mL	5.0 mL	
3	119 mL	6 mL	6.0 mL	2 mL	5.0 mL	
4	107 mL	6 mL	6.0 mL	2 mL	5.0 mL	

This time the amount of H_2O_2 varies as follows:

Flask	H_2O_2
1	3.0 mL
2	6.0 mL
3	12 mL
4	24 mL

Use your graduated cylinder to measure the required amounts of peroxide. As before, measure the time required to consume the $S_2O_3^{2-}$.

3. Perform the necessary calculations and draw the required graphs to determine the order of the reaction with respect to peroxide, order with respect to iodide, and the rate constant for each trial.

Temperature Effect

In this experiment, you will measure the average rate of a redox reaction at several different temperatures, and then analyze the data to find the Arrhenius activation energy, E_a. The reaction is that between permanganate ion (MnO_4^-) and oxalate ion ($C_2O_4^{2-}$), where manganese is reduced from its purple +7 oxidation state to the pale pink +2 state. Progress of the reaction is monitored by watching the color change.

$$2\ MnO_4^-(aq) + 5\ C_2O_4^{2-}(aq) + 16\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 8\ H_2O(l)$$

The average rate will be defined as ($\Delta[MnO_4^-]/\Delta t$). The time taken for all of the permanganate ion to react is Δt and, since all of the permanganate has been used up when that time has elapsed, $\Delta[MnO_4^-]$ is equal to the initial permanganate concentration. A complication is that the reaction proceeds by way of a yellow intermediate, so the end point (the point at which the final time reading is made) will be when the purple color of the permanganate ion has just disappeared and the solution is pale yellow. When the average rate has been found for six different temperatures, a plot of the Arrhenius equation in the form $\ln(k) = -E_a/R*(1/T) + \ln(A)$, where $R = 8.314\ J\ K^{-1}\ mol^{-1}$, will yield the activation energy.

Note: The Arrhenius equation is $k = Ae^{-Ea/RT}$. You do not actually measure k, but we assume that since the concentration of reactants is the same at each temperature, the measured rate is k times a constant. Thus ln(rate) = ln(k) + ln(constant). Similarly, taking the log of the right-hand side, we get ln(A) - Ea/RT. Since ln(A) is also a constant, the overall equation becomes $\ln(k) = -E_a/R(l/T) +$ constant. You don't need to know the value of the constant to find the slope and evaluate E_a.

The temperatures used are **initial** temperatures, since we are not keeping the reaction mixtures in the water bath after mixing the reactants. Obviously the mixtures, other than the room temperature one, will cool some during the course of the reaction. For the purposes of this experiment, this factor is not critical, other than being aware of it.

Procedure:
Work in partners. Obtain a thermometer from the stockroom.

1. Obtain 35 mL (and only 35 ml) of each of the reagents required, 0.0050 M $KMnO_4$ and saturated oxalic acid, in *labeled* 50 mL beakers.

2. Determine the room temperature by examining the thermometer.

3. Use the graduated cylinder to measure 5.0 mL of 0.0050 M $KMnO_4$ solution into two of your large test tubes. Similarly measure 5.0 mL of saturated oxalic acid solution into two other large test tubes.

4. Set up a water bath in your 800 mL beaker. The beaker need be only about one-third full of water. Place your thermometer in the water. Place one test tube of each solution in the bath.

5. Begin *slowly* heating the bath to 10 degrees above room temperature.

6. Meanwhile, watching the time, pour the room-temperature tube of oxalic acid into the room-temperature test tube of potassium permanganate solution. Pour the solution back and forth twice to mix the solutions.

7. Note the exact time that the oxalic acid contacts the potassium permanganate solution. Use this as the initial time.

8. When the test tube has become yellow, with no hint of pink remaining, note the time. This value is the final time.

9. Place the test tube of reacted solutions in a 250 mL beaker so that you may observe any additional color change (Remember to record any observations in your notebook!)

10. Rinse out the empty tube from the room temperature trial. Measure 5.0 mL of 0.0050 M $KMnO_4$ solution into the tube. Measure 5.0 mL of oxalic acid solution into your remaining large test tube.

11. When the temperature of the water bath reaches 10°C above room temperature, record the temperature, remove the two tubes from the bath, mix and record the initial time as before. Place the newly-filled test tubes in the water bath and continue *slowly* heating to 20°C above room temperature; the temperature does not need not be exactly 20° C above room temperature, but record the experimental value.

12. Repeat the procedure, measuring times to disappearance of the purple MnO_4^- color at 30, 40, and 50 degrees above room temperature. (You will have to reuse your test tubes.)

13. Note any trend or pattern in your data; record this in your lab notebook. If one run does not fit the pattern, decide whether to repeat it or not.

14. Clean up.