PRE LAB ASSIGNMENT - EXPERIMENT 6

1. In a reaction involving the iodination of acetone, the following initial concentrations were present in the reaction mixture:

acetone (0.8 mol/L), H^+ (0.2 mol/L), I_2 (0.004 mol/L)

At a particular temperature it took 240 s for the colour of the I_2 to completely disappear. If the reaction is zero order in I_2, how long would it take for the iodine to completely disappear if the initial iodine concentration was 0.008 mol/L and all the other conditions remained the same?

2. A 1.5×10^{-5} M aqueous iodine solution had an absorbance of 0.348 for a 1 cm path length at a wavelength of 350 nm. Calculate the value of the molar absorption coefficient, ε, for iodine at this wavelength.

3. What do you think are the major sources of error in this lab?

EXPERIMENT 6

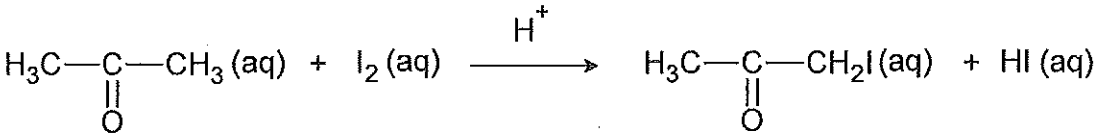
THE RATE OF IODINATION OF ACETONE

Objective

To determine orders of reaction, rate constant and activation energy of a reaction.

Introduction

In this experiment, you will study the reaction between acetone and iodine to produce iodoacetone:



Acetone iodoacetone

The rate of the above reaction depends upon the hydrogen ion concentration, which is a catalyst in this reaction, as well as the concentrations of the two reactants, and so the rate law is:

$$\text{rate} = k[\text{acetone}]^a[I_2]^b\,[H^+]^c$$

It just so happens that the reaction is **zero order with respect to iodine** (the value of b = 0) and the aim of the first part of the experiment is to determine the values of a and c. You will then have the overall rate law and can calculate the value of rate constant, k, at room temperature. The aim of the second part of the experiment is to determine the temperature dependence of k and to calculate the energy of activation, E_a, for the reaction.

Iodine is actually not soluble in pure water (why?) but in the presence of potassium iodide, KI, it reacts with the iodide ion, I^-, to form the triiodide ion, I_3^-, which is very soluble in water. However, for simplicity we will still refer to it as I_2 (aq). Because iodine has a distinctive yellow-orange colour in dilute solution, the progress of the reaction can be followed visually by observing the disappearance of the yellow colour as the iodine is consumed. When the yellow colour disappears, the reaction is over. As mentioned already, this reaction is **zero order with respect to iodine** which means that the rate of reaction does not depend on the iodine concentration at all. So, if we perform a series of experiments in which the iodine concentration is **much lower** than the acetone and hydrogen ion concentrations, the following points apply:

a) The rate of reaction will be independent of the iodine concentration and will remain effectively constant during the time of reaction because the other reactant concentrations will not change significantly.

b) Because the iodine is coloured we can determine the rate of reaction by monitoring how the absorbance changes with time using a spectrophotometer.

The triiodide ion absorbs strongly in the ultraviolet region and has a λ_{max} = 352 nm. However the absorption peak runs well into the visible region and a convenient wavelength to measure absorbance for this experiment is at 480 nm. At this wavelength absorbance values during the experiments will be typically less than 1.0 and Beer's law is obeyed well under these conditions. Beer's law shows that the absorbance, A, at a given wavelength, is proportional to the concentration of the absorbing species, c, and the pathlength, b, of the light beam through the sample:

$$A \propto bc$$

If we apply a proportionality constant, called the molar absorption coefficient, symbol ε (epsilon), we obtain the familiar form of Beer's law:

$$A = \varepsilon bc$$

Because we ultimately want to relate the absorbance to the concentration of the iodine our first task is to measure the absorbance for each of a set of standard solutions of iodine of varying concentrations. If we plot absorbance (A) against concentration (c) then, according to the above equation, it should give a straight line with slope equal to εb. Given that b, the pathlength, is set by the cuvette as 1 cm, the value of ε can then be determined.

In the next part of the experiment you will start with a set of concentrations of iodine, acetone and hydrogen ions, and measure the rate of reaction by collecting absorbance/time data. Using the value of ε determined in the first part of the experiment allows conversion of the absorbance/time data into the rate of reaction, with units of mol/L.s. Then, keeping the concentrations of two of the reactants the same as in the first experiment, you double the initial concentration of the third reactant, and determine

the rate again. By determining how the rate changes compared to the original reaction we will be able to determine the order with respect to this particular reactant. By repeating the procedure you can find the orders of all the reactants (you can also confirm that the reaction is zero order in iodine). Once you have the values of a, b and c, you can insert them into the rate equation and obtain a value for the rate constant, k.

The aim of the final part of the experiment is to determine the activation energy of the reaction. You will need to repeat one of the trials at least at two other temperatures, one above room temperature and one or more below room temperature. Then the previously determined rate law to determine the values for k at the new temperatures and then use the Arrhenius equation:

$$k = A\, e^{-E_a/RT}$$

In the above equation k is the rate constant, A is the Arrhenius pre-exponential factor (same units as k), E_a is the activation energy (in units of kJ/mol), R is the gas constant (8.314 kJ/K.mol) and T is the temperature (in Kelvin) . Taking the natural logarithm on each side of the equation then gives:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

The above equation is of the general form y = mx + b. Therefore, if you plot ln k against 1/T, the slope of the line is – Ea/R and the y-intercept is equal to ln k.

Experimental Procedure

Part A. Determination of the Absorption Coefficient for the Absorbance at a Wavelength of 480 nm

1. Turn on the Spectronic 20 spectrophotometer at least 15 minutes before making measurements to ensure that the bulb has ample time to warm up.

0.001 ? mol/L

2. Obtain about 150 mL of the 0.0100 M I_2 (aq) solution in a 250-mL beaker.

3. Rinse a burette with a little of the iodine solution. Run some through the tap. Repeat. Finally charge the burette with the solution. Now obtain five 100-mL volumetric flasks and dispense the following volumes into the flasks:

Flask Number	Volume of I_2 (aq) (mL)	Final Concentration of I_2 (aq) (M)
1	2.00	0.00020
2	4.00	0.00040
3	8.00	0.00080
4	12.00	0.0012
5	16.00	0.0016

4. Use the wavelength selector on the Spectronic 20 to select a wavelength of 480 nm. Obtain two matching cuvettes and fill one with deionized water. Use the deionized water as a blank to set the absorbance at zero. Instructions for doing this are given in Appendix 1.

5. Now take the other cuvette and rinse it twice with the most dilute standard I_2 (aq) solution. Finally fill the cuvette with the solution and measure its absorbance. Proceed to the next standard by emptying the cuvette and rinsing it twice with the new solution. Read the absorbance. Repeat this sequence until all of the standards have been measured. Record your measurements in a neat table.

Part B. Determination of the Rate Law.

Draw 50 mL of each of the following into separate 100-mL beakers.

1. 4 mol/L acetone
2. 1 mol/L HCl

Cover them with watch glasses to help prevent evaporation

For **trial 1**:

1. Have the spectrophotometer ready and set at zero absorbance with the blank.

2. Pipette 5 mL of the acetone solution and 5 mL of HCl (aq) into a clean dry 125-mL Erlenmeyer flask.

3. Into a clean dry 50-mL Erlenmeyer flask pipette 5 mL of the 0.010 M I_2 (aq) and add 10 mL of deionized water from a burette.
4. Have a thermometer ready and then pour the entire contents of the 50-mL flask into the 125-mL flask and briefly swirl to ensure thorough mixing. Measure and record the temperature of the solution then **quickly** proceed to the next step.

5. Rinse the other cuvette with a little of the reaction solution and fill about 2/3 full. Place the cuvette in the spectrophotometer.

6. Carefully record the absorbance of the solution at 15 second intervals until the absorbance approaches zero.

For the other **trials** (**2** to **4**) repeat steps 1 to 6, adjusting the reagent volumes accordingly.

Trial #	Temp (°C)	Volume of acetone (aq) (mL)	Volume of HCl (aq) (mL)	Volume of d.H2O (mL)	Volume of I_2 (aq) (mL)
1		5	5	10	5
2		10	5	5	5
3		5	10	5	5
4		10	10	0	5

20 mL
∴ allow 30 mL/group

Part C Measurement of the Rate at Different Temperatures and the Determination of the Activation Energy, E_a.

Results from Part B will allow the determination of the rate law and the value of the rate constant at room temperature. In order to obtain the Arrhenius parameters, E_a and A, the value of the rate constant must be determined at different temperatures. This

part is the most difficult one to obtain good results from because the main problem is maintaining the chosen temperature while making absorbance measurements. Inevitably the samples will change temperature while they are being measured in the spectrophotometer but as long as enough measurements can be made in a short time the change will be small and we can use an average temperature without introducing much of an error.

(i) High Temperature Trial (Trial #5)

For the higher temperature trial use the water bath which will be set to a temperature of 38 °C. Rather than collect absorbance data at set time intervals use the **split function on the stopwatch** to note the time at which the absorbance passes a particular value on the readout.

1. Take a 125-mL Erlenmeyer flask and into it pipette 5 mL of the acetone solution and 5 mL of the HCl (aq) solution. Add 30 mL of deionized water, seal the flask with a rubber stopper and place it in the water bath.

2. Pipette 10 mL of the I_2 (aq) solution into another 125-mL Erlenmeyer flask, stopper, and also place it in the water bath.

3. After about ten minutes pour the contents of the second Erlenmeyer into the first, swirl, note the temperature of the solution and proceed **immediately** to the next step.

4. Use the reaction solution to rinse the cuvette, discard the solution and then fill again to about two-thirds full. Place the cuvette in the spectrophotometer and collect time/absorbance data as quickly as possible using the **split function on your stopwatch**. Try to collect a reasonable number of measurements within about two minutes. As soon as you stop recording data **note the temperature** of the solution remaining in the flask. For calculation purposes use an average of the final and initial temperatures.

(ii) Low Temperature Trial (Trial #6)

For the low temperature run an additional problem is that that the cuvette tends to fog up rapidly when cooled, leading to inaccurate absorbance measurements. To solve this problem the cuvette needs to be treated with the **anti-fogging solution**

supplied. Apply the solution to the outside of the cuvette and wipe of the excess with a tissue.

1. Take a 125-mL Erlenmeyer flask and into it pipette 20 mL of the acetone solution and 20 mL of the HCl (aq) solution. Seal the flask with a rubber stopper and place it in the ice-water bath.

2. Pipette 10 mL of the I_2 (aq) solution into another 125-mL Erlenmeyer flask, stopper, and also place it in the ice-water bath.

3. After about ten minutes pour the contents of the second Erlenmeyer into the first, swirl thoroughly, note the temperature of the solution and proceed **quickly** to the next step.

4. Use the reaction solution to rinse the cuvette, discard the solution and then fill again to about two-thirds full. Place the cuvette in the spectrophotometer and collect time/absorbance data as quickly as possible using the **split function on your stopwatch**. Try to collect at least five measurements within about two minutes. As soon as you stop recording data **note the temperature** of the solution remaining in the flask. For calculation purposes use an average of the final and initial temperatures.

5. Discard the solution from the cuvette and rinse it with more solution from the reaction flask and then fill it about two thirds full again. Put the cuvette back in the spectrometer, note the temperature of the solution in the flask and again collect absorbance data for around two minutes, noting the temperature again at the end of this period. Again use the average temperature for calculations.

6. If the solution still hasn't turned colourless it may be possible to obtain a third set of measurements at a slightly higher temperature.

Guide to Calculations
Part A

1. Use the absorbance/concentration data to construct a graph of absorbance, A, against the concentration of iodine. Draw the best-fit straight line through the data points and calculate the slope of the line.

2. The slope of the line is equal to εb so ε = slope/b. The units of ε are L/mol.cm.

Part B

1. For each run construct a plot of absorbance against time and draw the best-fit straight line through the data points.

2. The slope of the line = ΔA/Δt. Convert to a rate of reaction, in units of mol/L.s, by using Beer's law:

$$\frac{\Delta[I_2]}{\Delta t} = \frac{\Delta A/\varepsilon b}{\Delta t}$$

3. Calculate the initial concentrations of acetone and HCl in trials 1 to 4 using the dilution equation: $M_1V_1 = M_2V_2$

4. Use the data for the trials1 to 3 to determine the orders with respect to acetone and HCl and determine the overall rate law for the reaction.

5. Use the rate law to determine the value of the rate constant.

6. Show that the data from trial 4 agrees with the determined rate law.

Part C

1. Use the absorbance/time data to determine the rates of reaction for each of the trials at various temperatures.

2. For each trial use the rate of reaction and the rate law to calculate the value of the rate constant at the various temperatures.

3. Construct an Arrhenius plot of ln k against 1/T remembering to use the Kelvin temperature in your calculations.

4. Draw a best-fit straight line through the points on the Arrhenius plot. Use the slope of the line to determine E_a and the y-intercept to determine A.