

Iodine Clock Reaction – Determination of the Rate Expression

Objective: To study the rate of the iodine clock reaction and determine how changes in the reactant concentrations and changes in temperature affect the rate of this reaction.

Concept to be Tested: Reaction rate depends upon the concentrations of reactants and upon temperature.

Text References: McMurray and Fay: Chapter 12.1-12.11

Laboratory Techniques References: *General Laboratory Procedures* use of an ice bath.

Introduction

You are familiar with balanced chemical equations. While these can be used to represent a material and energy balance of a particular reaction, they provide virtually no information about the mechanism or rate of the reaction. A reaction may be highly favored energetically and yet proceed at an imperceptibly slow rate. Another reaction that is far less favored may proceed at an explosively rapid rate.

The rate of the reaction depends upon its reaction mechanism. The reaction mechanism is the step or series of steps (pathway) by which the reactants form products. The overall reaction cannot proceed faster than the slowest step in the pathway. A good analogy is that the average rate of traffic in a traffic jam proceeds at the rate of the slowest car. If this slow step is a single species falling apart the mechanism is relatively simple because you do not have to worry about the orientation of collisions. This type of reaction is a simple first order reaction.

The term *species* is a useful term to represent any sort of particle you like – this could be a molecule, ion, free radical, reactant, and/or intermediate involved in the reaction.

If the slow step of a reaction depends upon two species, it is pretty obvious that they can only react together if they come into contact with each other. They first have to collide, and then they *may* react.

Why "*may* react"? It isn't enough for the two species to collide – they have to collide with the correct orientation, and they have to collide with enough energy for bonds to break. Even if the collision occurs with the correct orientation, if the species have too little energy or too much, no reaction will take place.

(The chances of all this happening if your reaction needed a collision involving more than two particles are remote. All three (or more) particles would have to arrive at exactly the

same point in space at the same time, with everything lined up exactly right, and having enough energy to react. That's not likely to happen very often!)

Reaction rates are important in everyday life and in industrial applications. In industry, time is money and if you know the rate expression, you can speed up the overall reaction. While this might not be foremost in your mind, the rate at which a pill gets rid of a headache or the symptoms of a cold or the flu also follow a rate expression, as does the duration of the effectiveness of that remedy.

Human metabolism tends to follow first order kinetics. This doesn't mean that you are stuck waiting for the medicine to finally work; you can speed up the delivery. Liquids provide fastest relief; pills and caplets are slowest with powders being in between the two. Some manufacturers are now providing a rapid dissolving form of their product to speed up the onset their effectiveness. Even then, you can still speed time to onset of relief two ways. Taking the medicine with caffeine tends to cut the time until relief of symptoms in half. Excedrin[®] has used this for years while touting fastest relief. Caffeine causes vasodilatation in all but the cranial blood vessels and helps speed circulation. You can also cut the time to onset of relief in half by taking the medication with a hot beverage (even plain water). And yes, a hot caffeinated beverage works over twice as fast.

The rate of a chemical reaction is affected by a variety of factors:

1. Chemical nature of the reacting species – the chemical structure and composition of the reacting substances govern how fast a reaction takes place
2. Concentration of reacting species – this can be molarity or partial pressure, an increase in the number of reacting species in a given volume results in an increase in collisions with sufficient energy and correct orientation which increases the rate
3. Temperature at which the reaction occurs – (do not confuse this with the position of the equilibrium) in general an increase in temperature increases both the number of collisions and the colliding species which have sufficient energy for reaction
4. Surface area in heterogeneous reactions – species involved in heterogeneous reactions can react only where the two phases touch; small particles have a large surface area when compared to larger particles
5. Catalysts – catalysts alter the mechanism of the reaction; these interact with the reactants to provide a new pathway which has reactions with lower activation energies (meaning a higher percentage of the reacting species have sufficient energy to react)

The relationship between the rate of a chemical reaction and the concentration of the reactants, if all other factors are held constant, is called the rate law expression, or rate expression, or simply the rate law. The rate expression for a given reaction must be determined experimentally by running a series of reactions, varying the concentration of each of the reactants (individually), and measuring the rate of each reaction. By

observing the magnitude of the change in the rate of the reaction (if any), it is possible to determine how each reagent is involved in the rate expression. After careful experimentation, a rate expression (rate law) can be written for that reaction.

Consider the hypothetical reaction

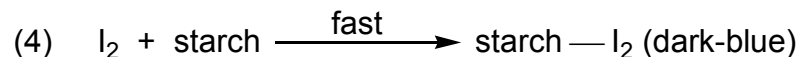
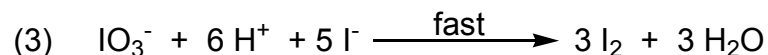
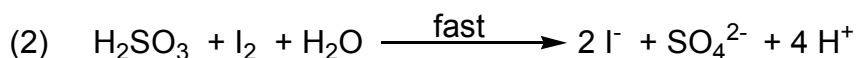
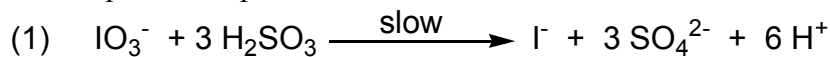


The rate law expression for this forward reaction is

$$\text{rate} = k[A]^x[B]^y$$

Note that the powers, x and y , to which the concentrations of the reactants, A and B , are raised are not necessarily the same as the stoichiometric coefficients, a and b , for these reactants. The values of x and y must be determined experimentally. These exponents may be zero (0), small whole numbers, or even fractions. The value, k , in the rate law expression is called the **specific rate constant**. The value of the specific rate constant is dependent upon all values that may affect the rate of a homogeneous reaction *except* concentration.

The reaction to be examined today in the laboratory consists of a series of individual steps. The most important steps are outlined below:



The reaction mechanism is very complex. Fortunately the very first step shown here is the rate-determining step. Step 4 shown here is the step that produces the final color indicating that the reaction is completed. It is the appearance of this color you will be timing. Even traces of I_2 will cause this colored complex to form.

Iodate ion, IO_3^- , reacts both with H_2SO_3 to form iodide ion, I^- , and with iodide ion to produce I_2 . Of key importance in the reaction today, H_2SO_3 reacts very rapidly with I_2 to produce iodide ion. The colored complex cannot appear until all of the H_2SO_3 has been consumed.

The Experiment

In the experiment today, you will determine the rate expression and the order of this reaction. Then you will determine the specific rate constant for your reaction. Finally you will also observe the effect that changing the temperature produces in the rate of your reaction.

$$\text{rate} = k[\text{IO}_3^-]^x[\text{H}_2\text{SO}_3]^y$$

To do this it will be necessary to observe the rate at several different concentrations. Fortunately, the endpoint of the reaction is an easily observed dark-blue (almost black) solution of the starch-iodine complex. The simplest method of measuring these rates is to run the reaction at several different concentrations of iodate ion, IO_3^- , while holding the

H₂SO₃ concentration constant. This should be sufficient to determine the order of IO₃⁻ (the exponent) in the rate expression. Then a second group of reactions will be run in which the IO₃⁻ concentration is held constant and the H₂SO₃ concentration is changed. This will allow the “order” of H₂SO₃ in the reaction. Taken together, the overall rate expression can be determined. Since the order and the time required for the reaction are known for one reaction, using the concentrations of the two solutions and the time, it will be possible to calculate the specific rate constant, *k*, for the reaction.

Example. The table contains data collected for following reaction was run at 50 °C.



Use this data to determine the rate expression for the reaction.

Trial	Conc. A (M)	Conc. B (M)	Reaction Time (sec)
1	0.001	0.100	36
2	0.002	0.100	18
3	0.003	0.100	12
4	0.001	0.050	72
5	0.001	0.200	18

The first part of the problem calls for “puzzle skills.” You need to compare the rates of the reaction when the concentration of one of the reactions is held constant. In this particular example, the concentration of B is held constant at 0.100 M for trials 1, 2, and 3. Since the concentration of B is the “same,” the changes in the concentration of A must be the only thing affecting the rate of the reaction.

You will initially be measuring the time required for the reaction. The actual “rate” of the reaction is inversely proportional to the time required (rate is proportional to 1/time) or rate \propto 1/time.

In Trial 1, the reaction time is 36 seconds. In Trial 2, the concentration of A is doubled (from 0.001 M to 0.002 M) at this time the time required for reaction is cut in half so the rate must be twice as fast **or doubling the concentration of A doubles the rate of the reaction.** In Trial 3, the concentration of A is three times greater than that in Trial 1 and the time required for reaction is one-third that required for Trial 1 so the rate is three times faster **or tripling the concentration of A triples the rate.**

By observation of the time required, the reaction is first order in A so:

$$\text{rate} = k[A]^1[B]^y$$

or $\text{rate} = k[A][B]^y$

Now since the order of A in the reaction has been determined, you can set about determining the order of B. Again you will use the data. In this case Trial 1, 4, and 5 are used. The concentration of A is constant 0.001 M in these three trials while the concentration of B changes.

In Trial 1, the reaction time is 36 seconds. In Trial 4, the concentration of B has been cut in half and the reaction time doubles. For the reaction time to double, the rate must have also been cut in half **or cutting the concentration in half cuts the rate of the reaction in half**. (Alternately, starting with Trial 4 and an initial concentration of B is 0.050 M, in Trial 1, the concentration of B is doubled and the reaction time is cut in half or **doubling the concentration doubles the rate of reaction**. It depends upon how you wish to analyze the data and what is easiest for you to see.) In Trial 5 the concentration of B is double what it was in trial 1 and the reaction time is cut in half **or doubling the concentration doubles the rate**.

Again by observation, the reaction is first order in B so:

$$\text{rate} = k[A][B]$$

Unfortunately, the data that you collect in the lab will probably not be this easy to analyze. Most of the data you see on exams and in examples has been “cleaned up” so that you can deduce most orders of reaction simply by observation and comparison of rates. In the lab, changes in temperature, trace contaminants, subtle mistakes in mixing or in concentration of solution combine with other less obvious variables to produce data that may not lend itself to this superficial examination. Therefore an old tried and true method is often called into play – graphical analysis of the data. With the advent of graphing calculators, this method has almost been forgotten. Because of the limited time in lab, you will collect only a few data points. Graphing is the most reliable method for analysis of this limited data. There is an excellent source of graph paper available on the web at http://www.mathematicshelpcentral.com/graph_paper.htm. There is also an excellent free-ware Graph Paper Printer Program created by Phillipe Marquis (no license fee required) available on this site. The program allows you to customize your own graph paper. The graphs in this discussion and in the lab report were generated using this program.

Graphical Analysis. The vast majority of reactants follow zero, first or second order kinetics. In all cases **time is plotted on the x-axis** and **concentration in some form is plotted on the y-axis**. The concentration of a given reactant is plotted three (3) different ways:

1. the simple concentration, $[A]$ – a straight line resulting from the plot of concentration, $[A]$, versus time indicates a **zero-order** reaction. The slope of the line is equal to $-k$.
2. the natural log of the concentration, $\ln[A]$ – a straight line resulting from the plot of $\ln[A]$ versus time indicates a **first-order** reaction. The slope of this line is equal to $-k$.
3. the reciprocal of the concentration, $1/[A]$ – a straight line resulting from the plot of $1/[A]$ versus time indicates a **second-order** reaction. The slope of this line is equal to k (**not** $-k$).

Again this is best demonstrated with an example using data generated with N_2O_5 .

Dinitrogen pentoxide, N_2O_5 , is an important nitrogen repository in the upper atmosphere. Its decomposition and subsequent reaction with chloride ion is suspected of having a significant impact upon the growth of the hole in the ozone layer. As a result, quite a bit of research has been directed at determination of the mechanism involved in this decomposition.

Example 1. Data for the decomposition of N_2O_5 in a solution at 45°C are as follows:

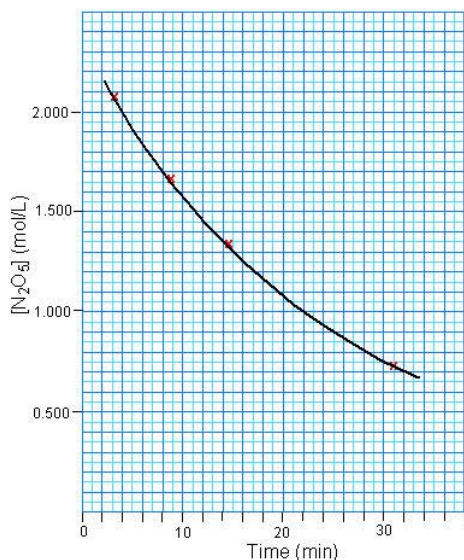
$[\text{N}_2\text{O}_5]$ (mol/L)	Time (min)
2.08	3.07
1.67	8.77
1.36	14.45
0.72	31.28

This data is sufficient for the first graph, however it is easiest to first calculate the other “values” of this concentration that will also be plotted.

$[\text{N}_2\text{O}_5]$ (mol/L)	$\ln[\text{N}_2\text{O}_5]$	$1/[\text{N}_2\text{O}_5]$	Time (min)
2.08	0.734	0.481	3.07
1.67	0.513	0.599	8.77
1.36	0.307	0.735	14.45
0.72	-0.328	1.389	31.28

Now plot each “concentration” versus time.

A quick reminder here, when setting up the scale for your x - and y -axes try to make the scale as large as possible (within reason). Maximizing the size of your graph makes it much easier to see whether the line you plot is straight or curved. Scrunching your data into a minimum size maximizes plotting error and ruins your efforts.



This plot of $[\text{N}_2\text{O}_5]$ versus time produces a curved line. Therefore the order of the reaction **is not zero-order**.

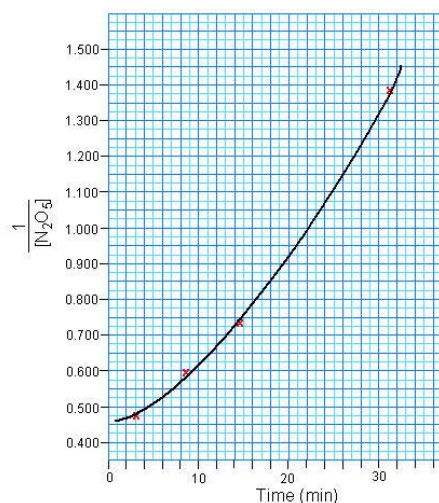


The plot of $\ln[\text{N}_2\text{O}_5]$ versus time produces a straight line. This reaction *is* **first-order**. The slope of the line will be equal to $-k$.

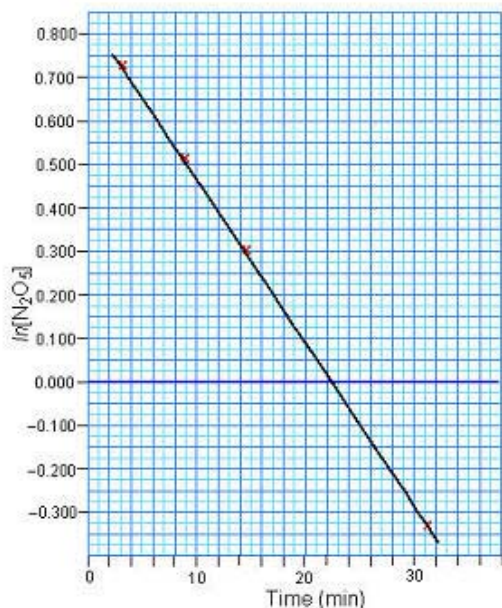
Notice that the points do not *exactly* fall on the line but it is very easy to draw a straight line that fits this data.

The plot of $1/[\text{N}_2\text{O}_5]$ versus time produces a curved line. The reaction *is not* **second-order** for $[\text{N}_2\text{O}_5]$.

Again while the points may not necessarily lie exactly on the curve, a curve is the *best fit* for the points plotted on your graph.



Now that you have established that the reaction follows **first-order** kinetics, it is possible to determine the specific rate constant, k , from the graph.



$$\text{Slope} = -k = \frac{(-0.328) - (0.734)}{(31.28 - 3.08) \text{ min}} = -3.74 \times 10^{-2} \text{ min}^{-1}$$

$$k = 3.74 \times 10^{-2} \text{ min}^{-1}$$

Since the rate of the reaction is simply the change in concentration divided by the change in time, simply choose two points along the line you have plotted. In the above example the initial and the final times and concentrations were chosen for this calculation.

Pseudo-First Order Reactions

Once a reaction mechanism is known (the order of the reaction determined), it is possible to manipulate the reaction. All rates are simply a change in concentration divided by the corresponding change in time, $\Delta[A]/\Delta t$. Consider a second-order reaction in which the rate expression is

$$\text{rate} = k[A][B]$$

If a reaction is run in which the concentration of B is made so large in comparison to [A] that over the course of the reaction [B] does not change significantly, then [B] is effectively removed from the rate expression. This produces a pseudo-first order rate expression:

$$\text{rate}' = k'[A]$$

It is very common to alter reaction conditions to force a reaction of this type (first order in two different reactants) to follow pseudo-first order kinetics. The plot of data from a pseudo-first order reaction gives a nice straight line just like a first order reaction does. However, for this *pseudo-first order* plot the slope is not equal to $-k$ but rather is equal to $-k([B]_0 - [A]_0)$ where $[B]_0$ is the initial concentration of [B] and $[A]_0$ is equal to the initial concentration of [A]. And since the initial concentrations of both [A] and [B] are known, the slope will have the correct units for a second order rate, $M^{-1}s^{-1}$. Remember, for this discussion [B] was arbitrarily chosen as the reactant present at high concentration (so its concentration didn't significantly change). The same would have been true had $[A]_0$ been very large in comparison to [B], only in that case the slope would have been equal to $-k([A]_0 - [B]_0)$.

Other Calculations

Most of the calculations needed have already been discussed; however it would be prudent to add a brief review of the calculation of molarity of a solution since this is critical in your data analysis. You must calculate the initial concentration of each of your reagents in the solution (at the moment of mixing). Treat this as a simple dilution

$$M_1V_1 = M_2V_2$$

You know the initial volume of reagent that you pipetted into the beaker; the final volume for all of the reactions is 100 mL.

Example 2. You mix 30 mL of 0.02 M KIO_3 with 20 mL of 0.01 M sulfite—starch solution in 50 mL of water. What is the initial concentration of the KIO_3 ?

$$\text{Total volume} = 30 \text{ mL} + 20 \text{ mL} + 50 \text{ mL} = 100 \text{ mL}$$

$$M_1V_1 = M_2V_2$$

$$0.02 \text{ M} \times 30 \text{ mL} = M_2 \times 100 \text{ mL}$$

$$M_2 = \frac{0.02 \text{ M} \times 30 \text{ mL}}{100 \text{ mL}} = 0.006 \text{ M}$$

Experimental Procedure

Obtain a clean 100 mL graduated cylinder, two (2) 10 mL volumetric pipettes and a pipet pump (two pumps if sufficient supplies are available), a hot plate stirring motor, a stir bar, a small beaker, three (3) 150- to 250-mL beakers, and a stopwatch.

Rinse two of the beakers with distilled water and label them so that you can easily tell them apart. Place approximately 100 mL of Solution A, 0.02 M KIO₃, in one of the beakers and 100 mL of Solution B, 0.01 M H₂SO₃–starch solution, in the other beaker. You will also be using approximately 500 mL of distilled water during this experiment so you will need to begin with a nearly full wash bottle.

Part A.

If sufficient supplies are available, you may wish to obtain additional beakers so that you can have the next mixture prepared and ready to use when the reaction you are running is completed. Although not essential, this will dramatically reduce the time spent in the lab.

You will be running a series of trials in which the final volume will be 100 mL or very nearly 100 mL. In all cases you will be adding Solution A to a diluted mixture of Solution B. It will be important that you pipet Solution A into the small beaker. You will pour the measured volume of Solution A from this small beaker into the reaction mixture, this allows for a very rapid addition. You will need to begin timing the instant you add Solution A to the final mixture. Stop timing when the blue-black color appears in the solution. You may wish to place a piece of white paper on the stirring motor to help you visualize the instant the color first appears. Do not forget to record the time required for the reaction.

It is critical that you use volumetric pipettes to measure the quantities of both Solution A and B. It is critical that these volumes are precise and this level of precision is impossible to obtain using a graduated cylinder.

The general composition of the first five mixtures is shown here.

	Solution A (mL)	Solution B (mL)	Water (mL)
Mixture 1	10.00	10.00	80
Mixture 2	10.00	20.00	70
Mixture 3	10.00	30.00	60
Mixture 4	20.00	10.00	70
Mixture 5	30.00	10.00	60

Mixture 1: Using a clean 10.00 mL volumetric pipette transfer 10.00 mL of Solution A into the small beaker. Using a 100 mL graduated cylinder put 80 mL of distilled water into a clean beaker. Rinse and dry your stir bar and add this to the beaker, place this onto the stirring motor and begin stirring (**no heat is used for this series of mixtures**). Using the second clean 10.00 mL volumetric pipette transfer 10.00 mL of Solution B into the water. Now pour the beaker containing the 10.0 mL of Solution A into the mixture and immediately begin timing. (Do not worry if a little of Solution A is left in the beaker, since A, KIO_3 , is in excess – this will not produce a significant error into your measurements.) Stop the timing when the solution turns blue-black and record the time. Retrieve the stirring bar. The solution may safely be discarded down the drain. Rinse and dry both the stirring bar and the beaker.

Mixture 2: This is run in exactly the same manner as Mixture 1. Transfer 10.00 mL of Solution A into the small beaker. Using the graduated cylinder put 70 mL of distilled water into a clean beaker and add 20.00 mL of Solution B (two 10.00 mL transfers). Stir the mixture (stir bar) and rapidly add Solution A. Begin timing at the instant of addition and stop timing when the solution turns blue-black (record the time). Retrieve the stirring bar. The solution may safely be discarded down the drain. Rinse and dry both the stirring bar and the beaker.

Mixture 3: This is run in exactly the same manner as Mixture 1. Transfer 10.00 mL of Solution A into the small beaker. Using the graduated cylinder put 60 mL of distilled water into a clean beaker and add 30.00 mL of Solution B (three 10.00 mL transfers). Stir the mixture (stir bar) and rapidly add Solution A. Begin timing at the instant of addition and stop timing when the solution turns blue-black (record the time). Retrieve the stirring bar. The solution may safely be discarded down the drain. Rinse and dry both the stirring bar and the beaker.

Mixture 4: This is run in exactly the same manner as Mixture 1. Transfer 20.00 mL of Solution A into the small beaker (two 10.00 mL transfers). Using the graduated cylinder put 70 mL of distilled water into a clean beaker and add 10.00 mL of Solution B. Stir the mixture (stir bar) and rapidly add Solution A. Begin timing at the instant of addition and stop timing when the solution turns blue-black (record the time). Retrieve the stirring bar. The solution may safely be discarded down the drain. Rinse and dry both the stirring bar and the beaker.

Mixture 5: This is run in exactly the same manner as Mixture 1. Transfer 30.00 mL of Solution A into the small beaker (three 10.00 mL transfers). Using the graduated cylinder put 60 mL of distilled water into a clean beaker and add 10.00 mL of Solution B. Stir the mixture (stir bar) and rapidly add Solution A. Begin timing at the instant of addition and stop timing when the solution turns blue-black (record the time). Retrieve the stirring bar. The solution may safely be discarded down the drain. Rinse and dry both the stirring bar and the beaker.

Part B. Temperature

You will observe the affect of temperature upon the rate of the reaction.

To conserve time, place approximately 100 mL of water into a clean beaker and begin heating it using the hot plate stirrer. You will need warm (*max. 50 °C*) water for the second trial. If the water begins to boil, remove the beaker from the hot plate and cool the contents by addition of more distilled water.

Trial 1. Using the 10.00 mL volumetric pipette transfer 10.00 mL of Solution A into the small beaker. Put approximately 100 mL of water into a beaker and add an ice-cube. While waiting for the water to chill, use the second 10.00 mL volumetric pipette to transfer 10.00 mL of Solution B into the reaction beaker. Use a thermometer to determine the temperature of the water. When the temperature has dropped below 5 °C use the 100 mL graduated cylinder and put 80 mL of the chilled water into the beaker containing the 10.0 mL of Solution B. Use the thermometer to stir the solution and record the temperature of this mixture. Now pour the beaker containing the 10.0 mL of Solution A into the mixture and immediately begin timing (use the thermometer to initially stir the mixture). Stop the timing when the solution turns blue-black (record the time). The solution may safely be discarded down the drain. Rinse and dry both the stirring bar and the beaker.

Trial 2. Using the 10.00 mL volumetric pipette transfer 10.00 mL of Solution A into the small beaker. Use the second 10.00 mL volumetric pipette to transfer 10.00 mL of Solution B into the reaction beaker. Use a thermometer to determine the temperature of the water you have been heating. When the temperature is between 40 °C and 50 °C use the 100 mL graduated cylinder and put 80 mL of the heated water into the beaker containing the 10.0 mL of Solution B. Use the thermometer to stir the solution and record the temperature of this mixture. Now pour the beaker containing the 10.0 mL of Solution A into the mixture and immediately begin timing. Stop the timing when the solution turns blue-black (record the time).

The blue-black starch iodine complex is **VERY** temperature sensitive and decomposes at temperatures over ~ 45 - 50 °C. If the temperature of the reaction is too hot, you **will not** see the complex but will begin to see the development of a brown color which is due to the formation of iodine. Stop timing if you see a yellow or brown color develop. Use this as the endpoint. Realize that your eyes are not as sensitive to formation of this faint color as they are to the intensely colored blue-black complex. So the actual time for the reaction to occur will be less than the time you measure.

Cleanup

All of the solutions used today may safely be discarded down the drain. Clean and dry the beakers and graduated cylinder and return them to storage. Rinse and dry the stirring bar and thermometer and return them to their appropriate storage areas. Return the stirring motor to its cabinet.

Safety

The solutions used in today's experiment are all considered to be irritants. If either solution is allowed to remain in prolonged contact with your skin, reddening and irritation of your skin will occur. These reagents are not environmental hazards and the solutions and the reaction mixture may safely be disposed of by pouring the solutions down the drain. Should you come in contact with either solution, rinse the affected area with water. Solution B contains sulfite, which could cause respiratory difficulties to some asthma sufferers if ingested. Wash your hands ***before*** leaving the laboratory.