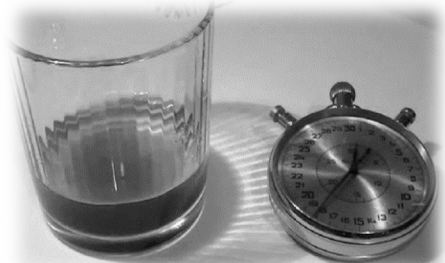# 2—A Kinetic Study of an Iodine Clock Reaction

Name: _____

Date: _____

Section: _____

Objectives
- Determine the order of the rate law (values of *m* and *n*) for an iodine clock reaction using the method of initial rates
- Determine the rate constant (*k*) of the same rate law
- Determine the energy of activation of the reaction

Pre-Laboratory Requirements
- Read Chapter 16.2 – 16.3 and 16.5 in Silberberg, with particular attention on "Determining Reaction Orders by Changing the Reactant Concentration" (pp. 507 – 510), "Determining the Rate Constant" (p. 6512), and Figure 16.13
- Review the instructional video on pipetting
- Pre-Lab Questions (if required by your instructor)
- Laboratory Notebook—prepared before lab (if required by your instructor)

Safety Notes
- Eye protection must be worn at all times

Discussion
This experiment will reinforce your knowledge of rates of chemical reactions, also known as chemical kinetics. Chemical kinetics governs the rates of many processes around us: For example, the combustion of sugars in our bodies occurs at a much slower rate than the combustion of gasoline in our cars; and we make use of kinetics when we slow down reactions that cause food to spoil by keeping it in the refrigerator or freezer. In chemistry, we study kinetics to determine a possible *reaction mechanism*, or what might be happening at the molecular level.

For the general reaction:

$$A + B \rightarrow \text{products}$$
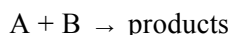
The rate law equation takes the form:

$$\text{Rate} = R = k[A]^m[B]^n$$

in which [A] and [B] are the concentrations in mol/L of species A and B, the exponents m and n are the orders of A and B, respectively, and k is the rate constant. The specific rate constant (k) is a proportionality constant that is a characteristic of every reaction at a specific temperature. The sum of the exponents m and n defines the order of the reaction.

The order of a reaction is a key indicator of its mechanism. The mechanism is the sequence of steps from reactants to products, or the pathway of the reaction. As mentioned in your lecture, the slowest step in the mechanism is said to be the *rate-controlling* or *rate-limiting* step and has a *molecularity* that must be equal to the order of the overall reaction. For example, if $m = 2$ and $n = 1$ in the rate law above, two molecules of A and one molecule of B are involved the transition state of the rate-limiting step. This provides valuable information on the reaction mechanism.

Rate laws must be determined by experiment; and you cannot predict them from the balanced overall equation, because the exponents m and n are not necessarily related to the coefficients of the reaction. The rate of reaction can be represented in terms of the increase in concentration of product (ΔC), divided by the time interval (Δt) required for the change (Silberberg, 3rd ed., p 501).

$$R = \frac{\Delta C}{\Delta t}$$

In this experiment, we will be determining the rate of a reaction by measuring how long (Δt) it takes to produce a certain concentration (ΔC) of our product. By varying the concentrations of A and B (part I), we can then determine the values of m and n, using the *Method of Initial Rates* (Silberberg, 3rd ed., pp 507 – 510). In this method, the rates are observed for a series of reaction mixtures in which the concentration of one reactant is changed while that of the other(s) is held constant. Once the values of m and n are known, we can calculate k (Silberberg, 3rd ed., p 512). By varying the temperature (part II), we can determine the activation energy, E_A (Silberberg, 3rd ed., Figure 16.13).

The reaction that you are going to study is that between the persulfate ion ($S_2O_8^{2-}$) and the iodide ion (I^-).

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-} \tag{1}$$

The generalized rate equation for this reaction is:

$$R = k \, [I^-]^m [S_2O_8^{2-}]^n$$

Reaction [1] proceeds at a rate that allows for convenient measurements of the rate equation. Rather than measuring the concentration of I_2 or SO_4^{2-} directly, we are going to add known amounts of $S_2O_3^{2-}$ ion to our reaction mixture, because it reacts instantaneously with I_2 according to the reaction equation:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \tag{2}$$

The iodine (I_2) produced in reaction [1] is absorbed immediately by reaction with thiosulfate ion as shown in reaction [2]. As long as any $S_2O_3^{2-}$ remains in solution, the concentration of I_2 is effectively zero. When all of the $S_2O_3^{2-}$ is used up, any additional I_2 that is made via reaction [1] will react with a starch indicator, which will then turn blue.

The combination of reactions [1] and [2] together with the starch indicator constitutes one type of *Iodine Clock Reaction*. The "clock" or color change indicated when enough iodine has been produced by reaction [1] to use up all of the $S_2O_3^{2-}$. A knowledge of the **original $S_2O_3^{2-}$ concentration** and the **stoichiometric ratio between I_2 and $S_2O_8^{2-}$** leads to **the quantity of $S_2O_8^{2-}$ that has reacted** when the blue color appears. Because one mole of I_2 reacts with 2 moles of $S_2O_3^{2-}$ during reaction [2], the quantity of I_2 produced at the time the blue color first appears (= t) is equal to one-half the initial quantity of $S_2O_3^{2-}$ (which is known).

$$\Delta C = [I_2]_{produced} = \tfrac{1}{2}[S_2O_3^{2-}]_{initial}$$

Since the initial concentration of $S_2O_3^{2-}$ is kept small in comparison with the quantities of I^- and $S_2O_8^{2-}$ used for reaction [1], the blue color will always appear before any appreciable quantity of $S_2O_8^{2-}$ is used up. Thus, the concentrations of reactants and the rate found in the rate equation for reaction [1] will remain essentially constant during the time interval over which the rate is measured. As a result, the reaction rate may be calculated as

$$Rate = R = \frac{\Delta C}{\Delta t} = \frac{\tfrac{1}{2}[S_2O_3^{2-}]_{initial}}{t} \qquad\qquad [3]$$

In Part I of this experiment, the study of reaction [1] will be conducted according to the conditions specified above and using the initial concentrations that can be found in Table 1. In each experiment, the initial concentration of $S_2O_3^{2-}$ will be the same, while the concentration of either I^- (Experiment 1) or $S_2O_8^{2-}$ (Experiment 3) is changed in comparison to Experiment 2. In this way the order of reaction [1] with respect to each reactant can be determined.

For example, to determine the value of m, measurements for Experiments 1 and 2 will be used. In these experiments, the concentration of $S_2O_8^{2-}$ is held constant. The rate laws for these experiments are:

$$Rate \text{ for Expt 1} = \frac{\tfrac{1}{2}[S_2O_3^{2-}]_{initial}}{t_1} = k\,[I^-]_1^m\,[S_2O_8^{2-}]_1^n \qquad\qquad [4]$$

$$Rate \text{ for Expt 2} = \frac{\tfrac{1}{2}[S_2O_3^{2-}]_{initial}}{t_2} = k\,[I^-]_2^m\,[S_2O_8^{2-}]_2^n \qquad\qquad [5]$$

in which $[I^-]_1^m$ and $[S_2O_8^{2-}]_1^n$ are the initial concentrations of I^- and $S_2O_8^{2-}$ in experiment 1; the rate law for experiment 2 uses similar notation. Because $[S_2O_3^{2-}]$ and $[S_2O_8^{2-}]$ are held constant in experiments 1 and 2 and because k is a constant at a given temperature, $\tfrac{1}{2}[S_2O_3^{2-}]_{initial}$, $[S_2O_8^{2-}]^n$, and k cancel out when dividing equation [5] by equation [4] to yield

$$\frac{1/t_2}{1/t_1} = \frac{[I^-]_2^m}{[I^-]_1^m} \qquad \text{which can be rewritten as} \qquad \frac{t_1}{t_2} = \left(\frac{[I^-]_2}{[I^-]_1}\right)^m \qquad [6]$$

Substituting in the times and initial concentrations for experiments 1 and 2 allows equation [6] to be solved for m, as in the problem on page 509 of Silberberg, 3rd ed. If, as a result of doubling the concentration of I^-, the rate also doubles, we know that $m = 1$. If the rate change is measureable but increased by not exactly double (or by four times if $m = 2$), we can conclude that m is not an integer. Under these circumstances, the order m may be calculated by taking the log of both sides.

A similar approach may be taken for determining the value of *n* by comparing the rates of experiments 2 and 3, dividing the rate law for Expt 2 by that for Expt 3.

In Part II, the effect of temperature on the rate of reaction [1] will be studied. With the same set of concentrations, the reactions will be carried out at several temperatures in addition to room temperature. From these results and a graph based on equation [7], the *activation energy* (E_A) for the reaction may be determined.

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \qquad\qquad [7]$$

$$y = \quad m\ x \ + \ b$$

In equation [7], *k* is the rate constant at each of the different temperatures, E_A is the activation energy in J/mol, *R* is the gas law constant (8.314 J/molK), and *T* is the absolute temperature in Kelvin. The value of *k* can be calculated via the rate law equation [5], using the measured time *t* and the initial concentrations of the reactants: $[S_2O_3^{2-}]$, $[I^-]$, and $[S_2O_8^{2-}]$. Plotting ln *k* as a function of $1/T$, the activation energy can be obtained from the slope (= $-E_A/R$) of the resulting straight line, as shown in Figure 16.13 of the text (Silberberg, 3rd ed.)

Procedure

Part I: Dependence of Reaction Rate on Concentration

These three experiments are to be carried out at room temperature.

The volumes of the KI, KCl, $(NH_4)_2S_2O_8$, $(NH_4)_2SO_4$ and $Na_2S_2O_3$ solutions should be measured with a pipet. The KCl and $(NH_4)_2SO_4$ solutions are used rather than water in diluting to a constant volume so that the total ionic strength of the reaction mixture, *which has some effect on the reaction rate*, can be kept approximately constant. Use clean, dry, **labeled** medium-sized test tubes to obtain 7-8 mL of each solution to take back to your lab bench.

Table 1. Quantities of reactants used at room temperature

	Volume of Reactant (mL)		
Reactant	Experiment 1	Experiment 2	Experiment 3
0.200 M KI	1.00	2.00	2.00
0.200 M KCl	1.00	0	0
0.100 M $(NH_4)_2S_2O_8$	2.00	2.00	1.00
0.100 M $(NH_4)_2SO_4$	0	0	1.00
0.005 M $Na_2S_2O_3$	1.00	1.00	1.00

1. For experiment 1, pipet the specified volumes of 0.200 M KI and 0.200 M KCl solutions into a 50 mL beaker, which will be used as the reaction vessel.
2. Pipet 1.00 mL of 0.005 M $Na_2S_2O_3$ into this beaker and add 2 drops of starch solution.
3. Insert a thermometer into the reaction vessel.

4. Pipet the specified volumes of 0.100 M $(NH_4)_2S_2O_8$ and 0.100 M $(NH_4)_2SO_4$ into a separate 50 mL beaker.
5. Record the initial temperature of the solution.
6. Observe the time (or start a stopwatch) when pouring the persulfate solution from the beaker into the reaction vessel. (*Pour the solution back and forth to mix thoroughly.*)
7. Record the time required to turn the solution blue. (*Constant observation is necessary because the blue color will appear suddenly.*)
8. Rinsing the beakers thoroughly between experiments, repeat Experiment 1 until two elapsed times are within 5 seconds of each other.
9. Repeat steps 1 through 8 for Experiment 2, using the reactant quantities in Table 1 (which does not include KCl).
10. Repeat steps 1 through 8 for Experiment 3, using the reactant quantities in Table 1 (which does not include KCl).

Temperature = _____ °C = _____ K

Expt	Initial [I⁻]	Initial [S₂O₈²⁻]	Elapsed Time (s)	Reaction Rate (M/s)	Average Rate (M/s)
1a	_____	_____	_____	_____	
1b	_____	_____	_____	_____	_____
2a	_____	_____	_____	_____	
2b	_____	_____	_____	_____	_____
3a	_____	_____	_____	_____	
3b	_____	_____	_____	_____	_____

For the reaction orders below, give the actual number obtained, unless it is within 5% of a whole number (in which case give the integer).

Order of reaction with respect to I⁻   _____

Order of reaction with respect to $S_2O_8^{2-}$ _____

Overall order of reaction   _____

Part II: Dependence of Reaction Rate on Temperature

You will be carrying out reaction [1] at the temperatures specified in Table 2. You will be using **the same concentrations as in experiment 2 of Table 1.**

Table 2. Iodine Clock Reaction and Temperature

Experiment	Temperature (^{o}C)
2	Room temperature
4	About 10° above room temperature
5	About 10° below room temperature
6	About 0 ^{o}C

1. Experiment 2 (room temperature) has already been carried out in Part 1.
2. For experiment 4, make the solutions as you did in experiment 2 in Part 1. Prior to mixing, heat the beakers in a warm water bath while keeping track of the temperature with a thermometer. When the temperature on the thermometer reaches about 10 ^{o}C above room temperature, mix the solutions and record the time it takes until color change
3. For experiments 5 and 6, use the same technique as in experiment 4 while using an ice bath rather than a warm water bath
4. *Be sure to* **record the times of mixing and when the color change occurs, along with the temperature at the time of the color change.**

Experiment	Temp (K)	1/T	Elapsed Time (s)	k	ln k
2	_____	_____	_____	_____	_____
4	_____	_____	_____	_____	_____
5	_____	_____	_____	_____	_____
6	_____	_____	_____	_____	_____

Using Excel, plot ln k vs. 1/T and add a trendline for these four data points. Be sure to have Excel show the equation for the trendline and the R^2 value on the graph, and include the fully labeled graph with your report.

Slope of trendline (from graph) _____

Calculated value of E_A (kJ/mol) _____