

## Chem 112 – Experiment 3 – Simulation – Chemical Kinetics

### Background

#### Chemical Kinetics

Different chemical reactions have different reaction rates. The chemical reaction that inflates a car airbag happens almost instantaneously. The reaction between the acid in rainwater and limestone that causes the weathering of marble statues takes place over centuries. There are many factors that affect the rates of reactions, including the concentration, temperature, and physical state of the reactants.

#### Reaction Rate

The rate of a chemical reaction is typically expressed as the change in concentration of a product or reactant per unit time. Reaction rates usually increase with temperature because increased kinetic energy increases the chance that the reaction will occur. Other factors, such as stirring, increasing surface area, and increasing the concentration of reactants can also increase the rate. Concentration is usually expressed in molarity (M) which is the number of moles of solute in exactly one liter of a solution.

$$M = \frac{\text{\# moles}}{V(L)}$$

Reaction rate depends on the amount of reactant present. A rate expression indicates the relationship between rate and the concentration of reactants. Consider a reaction with two reactants as shown below.



The rate expression for this reaction can be written in terms of any reactant or product as shown.

$$\text{rate} = \frac{-1}{a} \times \frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{-1}{b} \times \frac{\Delta[B]}{\Delta t}$$

$$\text{rate} = \frac{1}{c} \times \frac{\Delta[C]}{\Delta t}$$

$$\text{rate} = \frac{1}{d} \times \frac{\Delta[D]}{\Delta t}$$

The rate of a reaction can also be expressed by the rate law,

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

where k is the rate constant, [A] and [B] are the concentrations of the reactants, and x and y are the reaction orders with respect to each reactant. The values of x or y are typically whole numbers. Order is not dictated by the coefficients in the balanced equation but can be determined experimentally.

Consider reactant A in the reaction above. For a zero order reaction ( $x = 0$ ) with respect to A, the rate is independent of [A]. For a first order reaction ( $x = 1$ ) with respect to A, the rate is directly proportional to [A]. For a second order reaction ( $x = 2$ ) with respect to A, the rate increases as the square of [A].

The overall reaction order is the sum of the reaction orders with respect to each reactant. Assume that the reaction is first order with respect to A and second order with respect to B ( $x = 1$ ;  $y = 2$ ). The overall reaction order is 3 and the rate law is written as shown below.

$$\text{rate} = k[A][B]^2$$

### Determination of the Reaction Order and Rate Constant

The reaction order and the value of  $k$  can both be determined experimentally from measurements of the reaction rate. For a reaction with more than one reactant, reaction order is determined by varying the concentration of one reactant while holding the concentration of other reactants constant.

For example, if you vary [A] while holding [B] constant, the rate law given in the preceding section is written as shown.

$$\text{Rate} = k[A]^x \times c$$

where  $c$  is a constant that equals  $[B]^y$ .

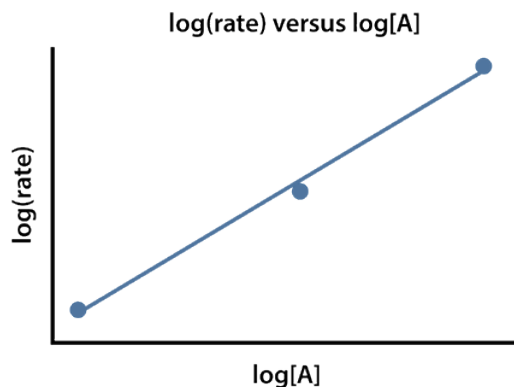
The expression can then be converted to logarithmic form as shown.

$$\log(\text{rate}) = \log k + x \log [A] + \log c$$

The constants  $\log k$  and  $\log c$  can be combined into a single constant,  $C$ , generating an equation for a straight line as shown.

$$\begin{array}{rcccc} \text{Log (rate)} & = & x \log[A] & + & C \\ y & = & mx & + & b \end{array}$$

Thus, the slope of a plot of  $\log(\text{rate})$  versus  $\log[A]$  equals  $x$  as shown in the figure below.

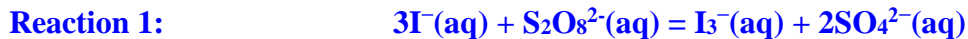


Similarly,  $y$  can be determined by varying [B] at constant [A]. Due to experimental error, the slope is often not an integer, but can typically be rounded to the nearest whole number value. Once the order of the reaction with respect to each reactant is known,  $k$  can be determined by rearranging the rate law as shown.

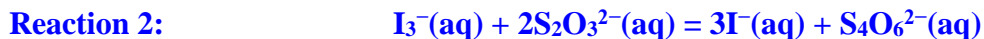
$$k = \frac{\text{rate}}{[\text{A}]^x[\text{B}]^y}$$

## About This Lab

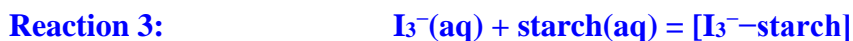
In this lab, you will measure the rate of the reaction between iodide ion ( $\text{I}^-$ ) and persulfate (peroxodisulfate) ion ( $\text{S}_2\text{O}_8^{2-}$ ).



To measure the rate of the reaction, you will measure the amount of  $\text{I}_3^-$  formed in a given amount of time. Then, in **reaction 2**, the  $\text{I}_3^-$  produced in **reaction 1** will react with the thiosulfate ion ( $\text{S}_2\text{O}_3^{2-}$ ) to re-form  $\text{I}^-$ .



The experiment is set up so that the concentration of  $[\text{S}_2\text{O}_8^{2-}]$  is significantly greater than the concentration of  $[\text{S}_2\text{O}_3^{2-}]$ . Thus, thiosulfate gets used up first. When all the thiosulfate is gone, only a small amount of persulfate has been used, so its concentration does not change appreciably during this part of the reaction. After all the thiosulfate is gone, triiodide begins to accumulate. Starch is often used in redox reactions as an indicator where triiodide is present, so the formation of triiodide is detected using starch. Triiodide forms a deep-blue complex with starch in the reaction below (**reaction 3**).



The starch-iodide complex has a blue-black color that can be observed visually. Because the color only forms after all thiosulfate has been used up, there is a lag between the start of the experiment and color formation. Reaction 2 and reaction 3 are fast relative to reaction 1, so the time it takes for color to form can be used as a clock to time reaction 1.

**The amount of triiodide formed** at the time the color change occurs can be **determined from the balanced chemical equation** for **reaction 2**. For two moles of thiosulfate reacted, one mole of triiodide is formed. Thus, the molar concentration of  $\text{I}_3^-$  formed and the rate of reaction ( $\Delta[\text{I}_3^-]/\Delta t$ ) can be calculated.

The value of **x** can be determined by **plotting log(rate)** versus **log $[\text{I}^-]$**  at constant  $[\text{S}_2\text{O}_8^{2-}]$ , and a **plot of log(rate)** versus **log $[\text{S}_2\text{O}_8^{2-}]$**  at constant  $[\text{I}^-]$  can be used to determine **y**. The values for **x** and **y** are used in the rate equation to determine the rate constant for the rate law.

$$\text{rate} = k[\text{I}^-]^x[\text{S}_2\text{O}_8^{2-}]^y$$

Finally, once you have determined the values of **x** and **y** you will solve the rate equation to determine the value of **k** for each experiment and then take the average of the five as the actual value of **k**

**Open the simulation by clicking on the virtual lab icon shown on the left on the Hayden-McNeil Web Site. The simulation will launch in a new window.**



**You may need to move or resize the window in order to view both the Procedure and the simulation at the same time.**

Follow the instructions in the Procedure to complete each part of the simulation. When instructed to record your observations, record data, or complete calculations, record them for your own records in order to use them later to complete the post-lab assignment.

## Procedure

1. Place **two 150 mL Erlenmeyer flasks** from the **Containers shelf** on the workbench. Double-click on the flasks to **label one flask “A” and the other “B”**. Obtain a **50 mL graduated cylinder** from the **Containers shelf**.
2. Place **two constant temperature baths** from the **Instruments shelf** onto the workbench.
3. **Set the temperature** on each bath to **21.5 °C**.
4. The contents of each flask will vary with each trial as indicated in the table below.

	<b>Flask A</b>			<b>Flask B</b>		
	Volume of 0.2 M potassium iodide (mL)	Volume of 0.2 M potassium nitrate (mL)	Volume of 0.2% starch (mL)	Volume of 0.2 M ammonium persulfate (mL)	Volume of 0.2 M ammonium sulfate (mL)	Volume of 0.01 M sodium thiosulfate (mL)
Exp 1	25	0	5	25	0	10
Exp 2	25	0	5	12.5	12.5	10
Exp 3	25	0	5	6.25	18.75	10
Exp 4	12.5	12.5	5	25	0	10
Exp 5	6.25	18.75	5	25	0	10

5. For Experiment 1, measure the indicated volume of each reagent from the Materials shelf using the appropriate graduated cylinder, then add to the appropriate flask.  
*Note: In a typical lab you would need a clean graduated cylinder for each solution. To save time and space on the workbench, the graduated cylinder is automatically cleaned for you so that it can be used multiple times.*
6. **Record the color** of the **initial solutions**.
7. Move **each flask into a water bath**.
8. **Pour the contents of flask B into flask A. Immediately** note the **time, including seconds**, from the **laboratory clock** or **other timing device**.
9. **Note the time elapsed** when the color first begins to change **from clear to black**. Record the time.
10. **Discard all materials in the waste**, then place the **containers in the sink**.
11. **Obtain two clean flasks and repeat steps 5–10 for Experiments 2–5**.
12. **Repeat the whole process one more time, recording the time for each experiment**. It is the **average of these two times** for each experiment that **you will use as the actual time**.
13. Clear the bench of all materials, containers, and instruments, then go to the **General Chemistry web site** and **download the Data file**, this when completed is the **report that you send to your TA**.