Lab 3: Reaction Kinetics Part 1

Introduction

By now you should be familiar with balanced chemical equations. While these equations can be used to represent the 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 a drastically slow rate. Another reaction that is far less energetically favored may proceed at an explosively rapid rate. Understanding of a new field of study called kinetics is necessary to determine both the rate and the mechanism of a chemical reaction.

Background

The rate of 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 stuck behind a slow car, the rate of the slowest car determines the other rates.

If the slow step depends on a single species, the mechanism is relatively simple because you do not have to worry about the orientation of collisions. However, if the slow step of a reaction depends upon two species, then 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 with enough energy for bonds to break. Even if the collision occurs with the correct orientation, if the species have too little or too much energy, no reaction will take place.

The chances of all this happening if the reaction requires a collision involving more than two particles are remote. All three (or more) particles would have to arrive to exactly the same point in space at the same time, with everything lined up exactly right, and having enough energy to react. That is not likely to happen very often!

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

1. Chemical Nature of the reacting species
2. Concentration of reacting species
3. Temperature at which the reaction occurs
4. Surface area in heterogeneous reactions
5. Catalysis

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, the rate expression, or simple the ***rate law***. The rate law for a given reaction must be determined experimentally by running a series of reactions, with varying concentrations of each of the reactants, and measuring the rare of each reaction. By observing the magnitude of the change in the rate of the reaction (if any), it is possible to determine to the extent to which each reactant is involved in the rate expression. After careful experimentation, a rate law can be written for that reaction.

Consider the hypothetical reaction:

$aA + bB \rightarrow cC + dD$

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 concentration 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 and these are called "orders of reaction"**. These exponents may be zero (0), small whole numbers, or even fractions. Generally, a value of 0 is called *zeroeth order*, a value of 1 *first order*, and a value of 2 *second order.* The value, k, in the rate law expression is called the rate constant. The value of the rate constant is dependent upon all values that may affect the rate of a homogeneous reaction, *except* concentration.

Only once the rate law (with the orders for each reactant) are determined, can the rate be determined based on concentration. If the rate constant, k, and the orders are determined, you are able to find the rate of reaction, based on concentration. See the example"

Example:

a) You have determined the rate law for $aA + bB \rightarrow cC + dD$ as the following:

$$\text{Rate} = 0.1\,[A]^1[B]^2$$

If [A] = 0.1 M, and [B] = 0.5 M, what is the rate of reaction?

$\text{Rate} = (0.1)(0.1)^1(0.5)^2 = (0.1)(0.1)(0.25) = \mathbf{0.0025}$

b) If you were to double the starting concentrations of both A and B, what would the rate of reaction be?

$\text{Rate} = (0.1)(0.2)^1(1)^2 = (0.1)(0.2)(1) = \mathbf{0.02}$

The reaction rate is doubled, due to the doubling of the [A], but is *also* quadrupled due to the doubling of [B]. Since [B] is second order, that means that doubling the concentration actually quadruples the rate, as you need to square the larger concentration. Therefore, doubling the concentrations of both reactants doesn't simply double the reaction rate, it actually increases it by eight times.

The Reactions

(1) $3I^-_{(aq)} + H_2O_{2(aq)} + 2H_3O^+_{(aq)} \rightarrow I_3^-{}_{(aq)} + 4H_2O_{(l)}$

(2) $2S_2O_3^{2-}{}_{(aq)} + I_3^-{}_{(aq)} \rightarrow 3I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

(3) $I_3^-{}_{(aq)} + \text{Starch}_{(aq)} \rightarrow I_3^-{}_{(aq)} \bullet \text{Starch}_{(aq)}$ (Dark Blue)

The Experiment

In this experiment, you will determine the orders for reaction (1) above with respect to two of the reactants. Then you will determine the specific rate constant (k) the reaction. Finally, you will write the modified rate law expression for the reaction.

To determine the reaction orders it will be necessary to observe the reaction rate at several different concentrations. Fortunately, the end point of the reaction is an easily observed by a dark-blue (almost black) solution of the starch-iodine complex. As stated in the Background, the rate law of reaction (1) is dependent on the molar concentrations of the reactants and the rate law can be expressed as the following:

$$\text{Rate} = k[I^-]^p[H_2O_2]^q[H_3O^+]^r$$

In today's experiment, the reaction will be carried out in an acetic acid-sodium acetate buffer solution. As a result, the concentration of $[H_3O^+]$ will remain constant. This constant concentration of $[H_3O^+]$ can be combined with the rate constant (k) to generate a new modified rate law expression:

$$\mathbf{Rate = k' \; [I\text{-}]^p \; [H_2O_2]^q}$$

In this modified rate law expression, $k' = k*[H_3O^+]^r$. Your goal for the day is to determine the effect that changing the concentrations of $[I^-]$ and $[H_2O_2]$ have on the rate of reaction. Using this information you will be able to calculate the values for the reaction orders "p" and "q". You will *not* determine the order r for $[H_3O^+]$.

The simplest method of measuring these rates is to run the reaction at several different concentrations of I^- while holding the concentration of H_2O_2 constant. The collected data will be used to determine the order of "p". Then a second group of reactions will be run in which the $[H_2O_2]$ is changed and the $[I^-]$ is held constant. This data will enable us to calculate the order of "q". Taken together, the overall rate expression can be determined. Since the order and the time required for reaction completion are known for each reaction, using the concentration of any two solutions and the time for that combination makes it possible to calculate the rate constant, k', for the reaction.

Determining Concentrations After Dilution

It would be prudent to add a brief review of the calculation for molarity of a solution since this is critical in your data analysis. You must calculate the initial concentration of each of your reactants 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 reactant that you added to the test tube and that the final solution volume is **10mL**.

Example: You mixed 3.0 mL of 0.1M H_2O_2 with 4.0 mL of water, 1.0 mL Buffer, 1.0 mL of 0.3 M KI solution and 1.0 mL of $Na_2S_2O_3$ solution. What is the new concentration of I^- and H_2O_2?

Total Volume = 3.0 mL + 4.0 mL + 1.0 mL + 1.0 mL + 1.0 mL = 10.0 mL

$M_1V_1 = M_2V_2$

H_2O_2: 0.01 M x 3.0 mL = M_2 x 10.0 mL

M_2 = (0.01 x 3.0)/(10.0) = **0.003 M** H_2O_2

I^-: 0.03 M x 1.0 mL = M_2 x 10.0 mL

M_2 = (0.03 x 1.0)/(10.0) = **0.003 M** I^-

Analysis of Kinetic Data to Determine Reaction Rate

When we consider rate in our everyday lives we usually think about things like how fast we are driving our cars. We have a speedometer that tells us our rate (miles per hour); however we can also calculate the rate if we know how many miles were traveled and how many hours it took. For example, while driving on 1-70 from Kansas City to St. Louis I pass exit 28 at 10:00am, and hit exit 58 at 10:30am. In order to calculate my rate, I do the following:

Miles: Exit 28 to Exit 58: 58-28 = 30 miles

Time: 10:00am to 10:30am = 30 mins = 0.5hrs

Rate = Miles/hr = 30miles/0.5hrs = 60mph

In a chemical reaction, we look at rate in a similar way but instead of looking at distance covered over time we look at ***the amount of product produced over time***. For example, for the reaction of:

$$aA \rightarrow bB$$

the rate could be represented by the increase in concentration of B produced per unit of time.

$$\text{Rate} = \Delta[B]/\Delta t$$

We are going to be analyzing reaction (1) in this week's experiment; i.e. how much I_3^- is produced per unit of time.

$$\text{Reaction (1) } 3I^-_{(aq)} + H_2O_{2(aq)} + 3H_3O^+_{(aq)} \rightarrow I_3^-{}_{(aq)} + 4H_2O_{(l)}$$

$$\textbf{Rate} = \boldsymbol{\Delta[I_3^-]/\Delta t}$$

We chose I_3^- because once it is produced it will react with $S_2O_3^{2-}$ consuming it (reaction (2)).

$$2S_2O_3^{2-}{}_{(aq)} + I_3^-{}_{(aq)} \rightarrow 3I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$

Once all of the $S_2O_3^{2-}$ is consumed then any additional I_3^- produced will make a complex with the starch in solution, and create a dark blue color (reaction (3)).

$$I_3^-{}_{(aq)} + \text{Starch}_{(aq)} \rightarrow I_3^-{}_{(aq)} \bullet \text{Starch}_{(aq)} \text{ (Dark Blue)}$$

As a result the **$\Delta[I_3^-]$ will be equal ½ the starting concentration of $S_2O_3^{2-}$.** You can see the calculation of this change in concentration in the "Calculations" section of this experiment, below. We will track the time for $\mathbf{S_2O_3^{2-}}$ to disappear by using a stopwatch and waiting for the blue color to appear**. Δt is equal to time from mixing to the color change.** Once both of these values are determined, you can solve for the rate of a specific trial.

Graphical Analysis of Kinetic Data to Determine Reaction Orders

A vast majority of reactions follow zero, first, or second order kinetics, which was mentioned in the "Background" section. In order to determine the reaction order for each species in this experiment, we need to consider the overall rate law. Recall that it is the following:

$$\textbf{Rate} = k' [I^-]^p [H_2O_2]^q$$

There are three unknowns in this equation (k', p, q). As discussed in "The Experiment" section, we can simplify the rate law by holding the concentration of H_2O_2 constant, while varying the concentration of I^- (i.e. Trials 1-4 in the "Procedure" section) to determine the value of p.

$[H_2O_2]$ = Constant

$[H_2O_2]^q$ = $[\text{Constant}]^q$ = Constant

k' = constant

As a result when the concentration of H_2O_2 is constant the rate law expression is

Rate = k'' $[I^-]^p$

This can be simplified to isolate the reaction order "p" by using the laws of logarithms.

log (xy) = log x + log y and log x^y = y log x

log (Rate) = p log $[I^-]$ + log k''

This **log (Rate) = p log $[I^-]$ + log k''** is an equation of a line y = m x + b where the slope of the line is equal to the order with respect to the iodide ion.

Therefore, to find the value of p: *Plot Log $[I^-]$ (x-axis) Vs Log(Rate) (y-axis) for Trials 1-4 and determine the slope.*

To find the value of q, you would hold the concentration of I^- constant, while varying the concentration of H_2O_2 (i.e. Trials 1, 5, 6, and 7 in the "Procedure" section).

Therefore, to find the value of q: *Plot Log $[H_2O_2]$ (x-axis) Vs Log(Rate) (y-axis) for Trials 1,5,6,7 and determine the slope.*

You have now been shown how to determine the values for diluted concentrations of I^- and H_2O_2 for each trial and the Rate for each trial. Using that information, you were able to determine the overall reaction orders p and q.

Analysis of Kinetic Data to Determine the Rate Constant (k')

In order to find the value of the rate constan,t k', you need to rearrange the rate law expression. With all of the calculations that you have done in the previous three sections, you know the rate, the concentrations of the reactants and the reaction order for each trial. You can use the data from ***any*** trial to calculate k'. The value for k' should be the same for every trial, as the rate constant is specific *for a reaction*, and is independent of starting concentrations.

$$\text{Rate} = k' [I^-]^p [H_2O_2]^q$$

$$k' = \frac{Rate}{[I-]^p[H2O2]^q}$$

Procedure

	Solution A					Solution B
Kinetic Trial	Deionized Water	Buffer	0.3 M KI	0.02M $Na_2S_2O_3$	Starch	0.1M H_2O_2
1	4.0 mL	1.0 mL	1.0 mL	1.0 mL	5 drops	3.0 mL
2	3.0 mL	1.0 mL	2.0 mL	1.0 mL	5 drops	3.0 mL
3	2.0 mL	1.0 mL	3.0 mL	1.0 mL	5 drops	3.0 mL
4	1.0 mL	1.0 mL	4.0 mL	1.0 mL	5 drops	3.0 mL
5	2.0 mL	1.0 mL	1.0 mL	1.0 mL	5 drops	5.0 mL
6	0.0 mL	1.0 mL	1.0 mL	1.0 mL	5 drops	7.0 mL
7	5.0 mL	1.0 mL	1.0 mL	1.0 mL	5 drops	2.0 mL

You will be running a series of trials in which the final volume will be 10.0 mL. In all cases you will be adding Solution B to Solution A (a mixture of deionized water, buffer, KI, $Na_2S_2O_3$, and starch). It is important that you *always* add Solution B *to* Solution A. Begin timing the instant you mix the solutions together. The general composition for each of the 7 trials is shown above.

Trial 1:

1. In a larger test tube labeled A1
   a. Using the burets placed around the room
      i. Add 1.0 mL of Buffer solution
      ii. Add 1.0 mL of 0.3M KI solution
      iii. Add 1.0 mL of 0.02 M $Na_2S_2O_3$
   b. Using a dropper add 5 drops of Starch solution (or scoop of starch powder as directed)
   c. Using a 10mL graduated cylinder add 4.0 mL of DI water
2. In a Second test tube labeled B1
   a. Using the burets placed around the room
      i. Add 3.0 mL of H_2O_2 solution

3. At your station pour B1 into A1 and start your timer.
    a. Make sure your solution is mixed well by placing a gloved thumb over the end of the test tube and inverting it once.
4. Once color appears stop the timer and record the value
5. Solutions can be placed in a satellite waste contain at your station before of being disposed of in you general waste container.

Trials 2-7:

Repeat the procedure as described in Trial 1 for remaining Trials but change the volumes of solutions as indicated in the table!

Calculations

Moles of I^-_3 Produced

Remember the I^-_3 is consuming the thiosulfate ion $S_2O_3^{2-}$ in the solution (reaction (2)). Once all of the $S_2O_3^{2-}$ ions are consumed the color change occurs. As a result the moles of I_3^- produced during this time period can be determined from the stoichiometric ratio of reaction (2), as shown below:

$$2S_2O_3^{2-}{}_{(aq)} + I_3^-{}_{(aq)} \rightarrow 3I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$

$$\frac{1.0\ mL\ Na2S2O3}{1}\left(\frac{1\ L}{1000\ ml}\right)\left(\frac{0.02\ moles\ Na2S2O3}{1\ L}\right)\left(\frac{1\ mole\ S2O3^{2-}}{1\ mole\ Na2S2O3}\right)\left(\frac{1\ mole\ I3-}{2\ moles\ S2O3^{2-}}\right) = 1.0x10^{-5} moles\ I_3^-\ produced$$

$$\Delta[I_3^-] = \frac{1.0x10^{-5} moles}{0.010\ L\ solution} = 0.0010M$$

Report Sheet

Please ensure that you document all of the values in **black** on your lab notebook page! These are numbers that you will enter into LabFlow's Data Report Sheet, and will be used to calculate the values in **red.**

	T1	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**
1. Time for Color Change (sec)							
[2] Moles S2O3^{2-} consumed (mol)							
[3] Moles I3- Produced (mol)							
[4] Concentration of I3- (Δ[I3-]) (M)							
[5] Rate of Reaction (Δ[I3-]/Δt) (M/sec)							
[6] Log(Rate)							
7. Volume of KI solution added (mL)							
[8] Concentration of I- after dilution [M]							
[9] Log [I-]							
10. Volume H2O2 solution added (mL)							
[11] Concentration of H2O2 after dilution [M]							
[12] Log of [H2O2]							

Determine k', the Specific Rate Constant for the reaction

	T1	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**
[13] Value of k'							
[14] Average Value of k'							