Ye Olde Chemical Kinetics of the Iodination of Acetone Molecule

I. Introduction

Chemical reactions are most often thought about and discussed in terms of the starting reagents and end products: Molecule A reacts and turns itself into Molecule B. This is all well and good. However, it overlooks a long and rich story surrounding collisions between the molecules, intermediate compounds, and the thermal energy landscape provided by solvent molecules. All of this long story is studied in the field of **Chemical Kinetics**. This Chem 112 Experiment provides modest exposure to that enormous field.

To begin, the field of Chemical Kinetics is a complex, diverse, and at the same time very intriguing branch of science. Here is why. The modern day chemist is rather adept at predicting the product(s) of a chemical reaction. And the chemist is equally skilled at identifying chemical reaction products so as to verify or disprove someone's predictions. The chemist is very knowledgeable about reactants and products in equilibrium states.

Accurate predictions of the **rate**--the measure of how fast or slowly a given chemical reaction will take place--are another story altogether. On this account, the chemist's expertise is surprisingly and sadly sparse. This is in spite of a century of experimental and theoretical progress in the field of Chemical Kinetics.

Making accurate predictions about chemical reaction rates is tough sledding for the chemist for more than one reason. Let us explore why.

First, the typical chemical reaction is predicated on a **collision** between two molecules, for example, Molecule A and a solvent molecule. For the typical reactive molecule in liquid environment, the collision rate is on the order of 10^{12} per second. This means that Molecule A experiences a trillion *opportunities* to transform itself into something else (Molecule B) every second. This is a lot of opportunities for change! Yet if the multitudinous opportunities were the only facet of the story, virtually all chemical reactions would occur sooner than quicker. For consider a 1.00 mole sample of reactive molecules, each one of which experiences 10^{12} binary collisions per second. The **total number of collisions per second** is given by:

$$6.02 \times 10^{23} \times 10^{12} \text{ collisions per second} \times (1/2).$$

The "1/2" is needed because it takes two molecules to effect a binary collision, say, between Molecule A and a solvent molecule such as water. Needless to say, the typical liquid sample sustains a very large number of reaction opportunities each second. If the majority of opportunities were successful in forming products--B molecules--then chemical reaction rates would be astronomically fast.

The experimental facts are otherwise. Lucky for everybody, the vast majority of chemical reactions take place extraordinarily slowly. The reactive Molecule A has frequent opportunities to change itself into Molecule B. But the overwhelmingly majority of opportunities prove unsuccessful. The molecule collides frequently, but with no chemical side effects.

Why do the vast majority of collisions result in no reaction? The oversimplified answer is because (lucky for the chemist) the vast majority of molecules are inherently stable objects. The chemical bonds which hold the atoms in Molecule A together are typically of energy 100 kilojoules per mole. By contrast, the typical collision energy is only about 3 kilojoules per mole. Accordingly, the collision energy is insufficient for causing a "crack" in one or more of Molecule A's chemical bonds. If such a crack would ever take place, then Molecule A would become very reactive instantly, as the octet rule (among other things) is no longer satisfied.

Chemical reactions are predicated on collisions; hence no collisions, no reactions. But the collisions that can result in reactions are rare events. How rare? *Very* occasionally a violent collision takes place involving Molecule A with energy approaching that of one or more chemical bonds. The collision energy is then absorbed by all parties, but in such a way that causes a chemical bond in Molecule A to fracture. To be more quantitative, if the fracture energy--the time-honored name is the **activation energy** E_a--is 100 kilojoules per mole, and Molecule A's collision rate is 10^{12} per second, then the number of collisions per second that *actually give birth to Molecule B* at room temperature are approximately:

$$10^{12} \text{ x } \exp[-E_a / RT]$$

$$= 10^{12} \text{ x } \exp[-100{,}000 / (8.3 \text{ x } 294)].$$

$$= 10^{12} \text{ x } 1.6 \text{ x } 10^{-18}$$

The result is a very small number and provides a telling fact of chemical life. The chemist learns that Molecule A indeed has a trillion or so opportunities to change into B every second. But it can take over 600,000 seconds before such a transformation takes place. To beat the drum yet again on the most important points of this section:

(1) Chemical Reactions require collisions--most often binary ones.

(2) The binary collisions are enormously frequent, but almost always occur with energy insufficient to fracture a chemical bond. The collision energy is dissipated in the collision neighborhood of the liquid with no effect on the integrity of any chemical bonds.

(3) But by no means are all collisions are alike. The collision energetics are inherently statistical--as with other molecular properties. A tiny fraction of collisions thus result in cracks of the chemical bond masonry. The fraction is estimated by the **Exponential Factor**

$$\exp[-E_a / RT]$$

It was the wisdom of folks like **Ludwig Boltzmann** and **Svante Arrhenius** who connected chemical reaction rates with activation energies. This was all accomplished toward the end of the nineteenth century. Thirty or so years later, Henry Eyring took the study of chemical reaction rates to a much higher level. Much more about this subject is presented in **Chapter Fifteen** of Kotz, Treichel, and Weaver.

II. The Reaction Between Acetone and Iodine Molecules in the Aqueous Phase

The simplest reactions are unimolecular: Molecule A reacts to form Molecule B. The next category up features two species expressed on the left-hand-side of the reaction arrow. For example, acetone (nail polish remover) reacts with iodine (low tech germicide) to give iodoacetone and iodide ion. There are some chemistry details: the reaction environment is enhanced in the presence of hydrogen ions. And all parties require a suitable solvent such as water molecules. The solvent molecules are not incidental to the transformations. Their critical role is to maintain a **high collision rate** (~ 10^{12} per second) for the reacting parties in a statistical manner that promotes chemical bond fractures.

The chemical reaction we will study in this experiment appears on the next page. As discussed in Chem 102, the **differential rate law** for this reaction is written as follows:

$$\text{reaction rate} = \text{moles per liter of chemical reactions per second}$$

$$= k\,[\text{ acetone}]^m\,[\,I_2\,]^n\,\,[\,H^+\,]^p$$

where k is the **reaction rate constant dependent on temperature**, and m, n, p are the **reaction order coefficients** for acetone, iodine, and hydrogen ion, respectively. The rate constant depends exponentially on temperature and can only increase with increasing temperature. By contrast, the order values are independent of temperature. For acetone, iodine, and hydrogen ions, the values of m, n, and p are the same for 0 C as they are for 100 C.

The big picture goal of this Chem 112 experiment is sketched in **Section I**: to gain some experience in the field of Chemical Kinetics. The more immediate goals in the three-hour lab surround the above reaction. They are to:

(1) Measure the **rate constant k** at two or more temperatures.

(2) Identify the **reaction order coefficients** for acetone, iodine, and hydrogen ion.

III. Experimental Procedure and Calculations

To begin, please put on safety glasses. Then every team should organize the following equipment needed for the experiment:

thermometer
beakers of volume ≥ 100 milliliters

watch glasses
graduated cylinder
Erlenmeyer flasks of volume ≤ 100 milliliters
small test tubes
stopwatch
hot plate

There should be office copy paper available in the lab. A sheet or two will assist in the experiment.

Then please apportion five to seven pages of your lab notebook for the data collection necessary to this experiment. Then please put on a pair of latex gloves.

Use three clean beakers to collect from the reagents stored in the hood:

50.00 milliliters of 4.0 molar aqueous acetone
50.00 milliters of 1.0 molar aqueous hydrochloric acid
50.00 milliliters of 0.0050 molar aqueous iodine

Please bend over backwards to avoid spilling. The acetone solution is harmful to all plastic and clothing--it will dissolve polyester fabrics outright. The hydrochloric acid poses all of the dangers of strong acid solutions. The iodine solution causes severe staining of both skin and clothing.

After bringing the reagents to the work area, please place watch glasses on the beakers. These are needed to retard evaporation. Please keep the watch glasses in place as much as possible during the experiment. To do otherwise greatly impacts the experimental results in a negative way.

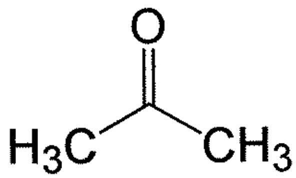
The First Experiment/Chemical Kinetics Measurement

Please combine and thoroughly stir the following in an Erlenmeyer flask:

4.00 milliliters of the acetone solution
4.00 milliliters of the HCl solution
4.00 milliliters of the iodine solution
8.00 milliters of distilled water

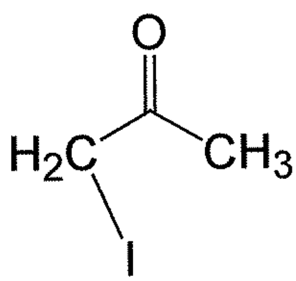
Add the iodine solution last. Upon combining the reagents, start timing with the stopwatch. Also measure the temperature of the solution. Please swirl or gently shake the solution continuously. Parafilm can be used to retard evaporation of the reaction mixture.

The solution will evidence a color due to the iodine molecules. This color is more pronounced to one's eyeballs if the Erlenmeyer flask is placed on or near a piece of office copy paper. The solution color will persist until *all* of the iodine has reacted with the acetone. Refer



$+ \ I_2 \quad + \ H^+ \longrightarrow$

Acetone



$+ \ I^- \quad + \ H^+$

Iodoacetone

again to the reaction specified in **Section II**. The products of the reaction are iodoacetone and iodide are both colorless; the hydrogen ions (and spectator chloride ions) impart no color during the experiment.

Importantly, please record the number of seconds for the iodine color to persist.

Calculate the concentrations in moles per liter of the acetone, iodine, and hydrochloric acid in the Erlenmeyer flask *upon mixing*. Note that these concentrations will be less than those of the pure reagents stored in the hood.

Divide the calculated iodine concentration by the number of seconds. This is the measured **reaction rate**. This quantity in moles per liter per second is the important result of the first experiment.

The Second Experiment/Chemical Kinetics Measurement

Please combine and thoroughly stir the following in an Erlenmeyer flask:

2.00 milliliters of the acetone solution
4.00 milliliters of the HCl solution
4.00 milliliters of the iodine solution
10.0 milliliters of distilled water

Add the iodine solution last. Upon combining the reagents, start timing with the stopwatch as in the first experiment. Measure the temperature of the solution. It needs to be the same as in first experiment! Please swirl or shake the solution continuously. Parafilm can be used as in the first experiment.

The second experiment features the same players as the first. Thus the color will persist until of the iodine has reacted with the acetone.

As in the first experiment, please record the number of seconds for the iodine color to persist.

Calculate the concentrations in moles per liter of the acetone, iodine, and hydrochloric acid in the Erlenmeyer flask *upon mixing*. These concentrations will of course be less than those of the pure reagents stored in the hood.

Very Importantly: the computed concentration of the acetone should be one-half of that employed for the first experiment. The concentrations of the HCl and iodine should be otherwise the same as in the first experiment.

After the color has died away, divide the calculated iodine concentration by the observed number of seconds. This is the measured **reaction rate** for the second experiment. This is *one of two results* of the second experiment.

Now aim for the reaction order (the second result) affiliated with the acetone. The acetone concentration employed for the second experiment is half that used for the first experiment. We appeal to the following chemical kinetics criteria:

If the reaction rate measured for Experiment II is **the same** as that measured for Experiment I, then the acetone order is **zero.**

If the reaction rate measured for Experiment II is **one-half** that measured for Experiment I, then the acetone order is **one.**

If the reaction rate measured for Experiment II is **one-fourth** that measured for Experiment I, then the acetone order is **two.**

Use the above criteria and the experimental results to determine the reaction order for acetone. This is the value of **m** used in the differential rate law.

The Third Experiment/Chemical Kinetics Measurement

Please combine and thoroughly stir the following in an Erlenmeyer flask:

4.00 milliliters of the acetone solution
2.00 milliliters of the HCl solution
4.00 milliliters of the iodine solution
10.0 milliliters of distilled water

Upon combining the reagents, start timing with the stopwatch as in the previous experiments. Measure the temperature of the solution. It needs to be the same as in previous two experiments. As per usual, please swirl or shake the solution continuously. Parafilm is also helpful here.

The same reaction is taking place as before. The color will persist until of the iodine has reacted with the acetone.

Please record the number of seconds for the iodine color to persist.

Calculate the concentrations in moles per liter of the acetone, iodine, and hydrochloric acid in the Erlenmeyer flask *upon mixing*.

Importantly: the concentration of the hydrochloric acid should be one-half of that employed for the first experiment. The concentrations of the acetone and iodine should be otherwise the same as in the first experiment.

After the color has died away, divide the calculated iodine concentration by the observed number of seconds. This is the measured **reaction rate** for the third experiment. As in the second experiment, this is *one of two results*.

Now aim for the reaction order affiliated with the hydrogen ions. The hydrogen ion concentration employed for the third experiment is half that used for the first experiment. We appeal to the same criteria applied to acetone. Accordingly...

If the reaction rate measured for Experiment III is **the same** as that measured for Experiment I, then the hydrogen ion order is **zero**.

If the reaction rate measured for Experiment III is **one-half** that measured for Experiment I, then the hydrogen ion order is **one**.

If the reaction rate measured for Experiment II is **one-fourth** that measured for Experiment I, then the hydrogen ion order is **two**.

Use the above criteria and the experimental results to determine the reaction order for hydrogen ions. This is the value of **n** used in the differential rate law.

The Fourth Experiment/Chemical Kinetics Measurement

Please combine and thoroughly stir the following in an Erlenmeyer flask:

4.00 milliliters of the acetone solution
4.00 milliliters of the HCl solution
2.00 milliliters of the iodine solution
10.0 milliliters of distilled water

Upon combining the reagents, start timing with the stopwatch as in all the previous experiments. Measure/verify the temperature of the solution. It needs to be the same as in previous three experiments. As always, please swirl or shake the solution continuously. Parafilm is again recommended to retard evaporation.

The iodine and acetone will react with one another--eventually. The color will persist until all of the iodine has reacted.

Please record the number of seconds for the iodine color to persist.

Calculate the concentrations in moles per liter of the acetone, iodine, and hydrochloric acid in the Erlenmeyer flask *upon mixing*.

Importantly: the concentration of the iodine should be one-half of that employed for the first experiment. The concentrations of the acetone and hydrochloric acid should be otherwise the same as in the first experiment.

After the color has vanished, divide the calculated iodine concentration by the observed number of seconds. This is the measured **reaction rate** for the fourth experiment. As in the second and third experiments, this is *one of two results*.

Now aim for the reaction order affiliated with the iodine molecules. The iodine concentration employed for the fourth experiment is half that used for the first experiment. We appeal to the following criteria:

If the reaction rate measured for Experiment IV is **the same** as that measured for Experiment I, then the iodine order is **zero**.

If the reaction rate measured for Experiment III is **one-half** that measured for Experiment I, then the iodine order is **one**.

If the reaction rate measured for Experiment II is **one-fourth** that measured for Experiment I, then the iodine order is **two**.

Use the above criteria and the experimental results to determine the reaction order for iodine. This is the value of **p** used in the differential rate law.

***

Now perform **Experiments Five, Six, Seven, and Eight**. They are operationally identical to **Experiments I - IV**. The primary objectives are to measure the reaction rate orders m, n, and p a **second time** for the acetone, iodine, and hydrogen ions, and to obtain additional data for the reaction rate constant value at room temperature.

***

At this juncture, please refer again to the **differential rate law**:

$$\text{reaction rate} = \text{moles per liter of chemical reactions per second}$$

$$= k\,[\text{ acetone}]^{m}\,[\,I_2\,]^{n}\,\,[\,H^{+}\,]^{p}$$

At this point in the lab, the reaction rate will have been measured eight times. The reaction orders m, n, and p will have been identified and verified.

Importantly, use the experimental data to obtain eight values of the reaction rate constant k at room temperature. Compute the average and standard deviation. Assign the correct units to the rate constant k.

The Ninth Experiment/Chemical Kinetics Measurement

Please use the hot plate and a large-size beaker (250 - 500 milliliter) to prepare a water bath suitable for immersing an Erlenmeyer flask. Distilled water is unnecessary here for the beaker. Importantly, heat the water to a temperature between 36 and 40 C. The precise temperature is not that important, but the value must be measured and recorded via one's thermometer.

Then we attend to another reaction mixture that must be combined in an Erlenmeyer flask that has been warmed and thermally equilibrated with the above water bath. After equilibration, please combine and thoroughly stir the following in the flask:

2.00 milliliters of the acetone solution
4.00 milliliters of the HCl solution
8.00 milliliters of the iodine solution
6.00 milliliters of distilled water

After combining the reagents, immerse and hold the flask in the bath. Start timing with the stopwatch. Please swirl or shake the solution continuously. Parafilm will be advisable here both for retarding evaporation and for preventing water from the bath from mixing with the reagents.

We certainly know the drill by now. The color will persist until all of the iodine has reacted with acetone.

Please record the number of seconds for the iodine color to persist under the elevated temperature conditions.

Calculate the concentrations in moles per liter of the acetone, iodine, and hydrochloric acid in the Erlenmeyer flask *upon mixing*.

After the color has vanished, divide the calculated iodine concentration by the observed number of seconds. This is the measured **reaction rate** for the ninth/elevated temperature experiment.

Importantly: the order data from Experiments I - VIII enable calculation of the rate constant at the 40 C bath temperature. As described in Section II, the order-values are temperature independent. The new rate constant value is, however, the key objective of Experiment IX and is exponentially dependent on temperature. Please calculate this rate constant value. It is valid at the temperature of the warm water bath.

The Tenth and Final Experiment/Chemical Kinetics Measurement

Please use the large-size beaker (250 - 500 milliliters OK) to prepare a ice slush bath suitable for immersing an Erlenmeyer flask. Importantly, both ice and water must be combined to obtain a thermally effective bath at temperature 0 C.

Then we attend to the final reaction mixture that must be combined in an Erlenmeyer flask that has been equilibrated with the above water bath. After equilibration, please combine and thoroughly stir the following in the flask:

8.00 milliliters of the acetone solution
4.00 milliliters of the HCl solution
2.00 milliliters of the iodine solution

6.00 milliliters of distilled water

After combining the reagents, immerse and hold the flask in the ice/slush bath. Start timing with the stopwatch. Please swirl or shake the solution continuously as best as possible--this is a critical component for the low temperature experiment. Parafilm will be expendable as the evaporation is already retarded by the low temperature conditions. Please be careful, however, not to contaminate the reaction mixture with ice/additional water.

The color will persist until all of the iodine has reacted with acetone. Please record the number of seconds for the iodine color to persist under the low temperature conditions.

Calculate the concentrations in moles per liter of the acetone, iodine, and hydrochloric acid in the Erlenmeyer flask *upon mixing.*

After the color has vanished, divide the calculated iodine concentration by the observed number of seconds. This is the measured **reaction rate** for the tenth/low temperature experiment.

Importantly: the order data from Experiments I - VIII enable calculation of the rate constant at the 40 C bath temperature. The order values are temperature-independent as we know. The rate constant, however, is very dependent on temperature; its 0 C value is the objective of Experiment X. Please calculate this rate constant value.

***

We now have rate constant data at (hopefully!) three different temperatures. The room temperature values obviously have more currency because they were based on multiple measurements; this enabled computation of the average and standard deviation. Let us now aim for values of the activation energy via the following textbook formula:

$$\ln (k_1 / k_2) = (E_a / R) \; [(1 / T_1) - (1 / T_2)]$$

The above is basically the logarithmic version of Arrhenius Law. It applies to a set of two rate constant values k_1, k_2 determined at two **Kelvin-unit** temperatures T_1, T_2 .

Note that it does not matter which temperature, T_1 or T_2, is designated the higher temperature. It is instead crucial that the temperatures be paired correctly with the rate constant values k_1 and k_2.

Next importantly, one has obtained rate constant data at three different temperatures during this Chem 112 experiment. Three sets of {k, T} data enable three pairings in the log form of Arrhenius Law. Use these three pairings to obtain three values of the activation energy E_a in joules per mole. To that end, use the gas constant R value of 8.3 joules per

mole per Kelvin. Compute the average and standard deviation for this activation energy.

IV. Preliminary Report

Please complete the preliminary report sheet found on the last page of this handout. Each lab partner should complete his/her own sheet based on the team data. Turn in the preliminary report to the lab assistant before leaving.

V. Final Report

Please write a final report based on data recorded for this experiment. Each partner of a team must write and submit his/her own lab report. Each report must be typewritten; it should adhere to the following outline.

A. Introduction: Please describe the purpose of the experiment in your own words. Please write the chemical reaction being investigated and clearly delineate the quantitative objectives of the observations and measurements.

B. Experimental: Please briefly summarize the experimental method. Most importantly, please note any deviations from the procedure described in the handout.

C. Results: Please clearly present the results of ten experiments. A summary table will be very helpful here showing the reagent concentrations, temperatures, reaction times, and reaction rate values.

Please detail how each reaction order value m, n, and p was determined. Please write the differential rate law for the reaction.

Please note quantitatively the spread of observed room temperature k-values. How does the standard deviation compare to the average?

Please detail how each activation energy value was determined.
If three values were determined, how does the standard deviation compare to the average?

D. Discussion: Please discuss the significance of experimental results in your own words. What happened in the experiment that was expected? What happened that was surprising?

The order and rate constant measurements were based on observing color changes. Please note ambiguities in the experimental results.

The reaction involved breakage of an iodine-iodine and a carbon-hydrogen chemical bond. How does the measured activation energy compare with the bond energy values?

Please describe the next experiment that you would undertake in an investigation of acetone, iodine, and hydrogen ions. Please state the reasoning behind your choice of experiments.

Ye Olde Pre-Lab Assignment

1. The reaction between bromate ions and bromide ions in acid solution is written as follows:

$$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(liq)$$

A chemist performs four experiments with varying concentrations of the above reactants in order to measure the reaction rate four times. The initial concentrations (in moles per liter) and measured reaction rates (in moles per liter per second) are as follows:

Exp	**$[BrO_3^-(aq)]$**	**$[Br^-(aq)]$**	**$[H^+(aq)]$**	**Measured Rate**
1	0.10	0.10	0.10	8.15×10^{-4}
2	0.20	0.10	0.10	1.62×10^{-3}
3	0.20	0.20	0.10	3.21×10^{-3}
4	0.10	0.10	0.20	3.24×10^{-3}

a. What are the reaction rate orders for $BrO_3^-(aq)$, $Br^-(aq)$, and $H^+(aq)$?

b. What are four values of the rate constant k?

c. What is the average value of measured k?

d. What is the standard deviation of measured k?

2. A chemist combines 20.0 milliliters of 4.0 molar acetone, 20.0 milliliters of 1.0 molar hydrochloric acid, and 10.00 milliliters of 0.0050 molar iodine solution.

a. In the combined mixture, what are the initial concentrations of acetone, HCl, and iodine?

b. At room temperature, the chemist found that it took 180 seconds for the iodine color to disappear. What is the reaction rate in moles per liter per second?

Preliminary Report

Name:

Lab Partner's Name:

Lab Assistant's Name

	Temperature	Observed Reaction Time (sec)
Experiment One		
Experiment Two		
Experiment Three		
Experiment Four		
Experiment Five		
Experiment Six		
Experiment Seven		
Experiment Eight		
Experiment Nine		
Experiment Ten		