

THE KINETICS OF THE IODINATION OF ACETONE

This experiment involves two parts: the first is to determine the reaction orders for acetone and hydrogen ion using the method of initial rates. The second involves using the Arrhenius equation to find the activation energy and frequency factor for the reaction. **You will be assigned either a reaction mixture (1, 2 or 3) from Part 1 or a specific temperature from Part 2 to investigate. Class data will be used for complete analysis.**

PART 1 DETERMINATION OF REACTION ORDERS

Theory of Reaction Rates

The rate of a chemical reaction depends upon many factors, such as concentration of reactants, temperature, and the presence of a catalyst. The rate of a reaction is usually dependent on the concentration of reactants. The rate decreases as concentration decreases. We can write a rate law equation to show this relationship. The rate law equation relates the rate of a reaction to the concentration of each reactant. Consider the general reaction below:



The small letters represent the stoichiometric coefficients. We can express the general rate of reaction in terms of the disappearance of the reactants or appearance of the products.

$$\text{rate of reaction} = \text{rate} = -\frac{\Delta[A]}{\Delta t} \text{ or } -\frac{\Delta[B]}{\Delta t} \text{ or } \frac{\Delta[C]}{\Delta t} \text{ or } \frac{\Delta[D]}{\Delta t} \quad (2)$$

Here $\Delta[A]$ is the change in the molar concentration of reactant A over time, Δt . The reaction rate will have units of M/time. By convention, the minus sign for reactants ensures a positive value for the rate since a change in concentration of a reactant with time, $(\Delta[A]/\Delta t)$, is a negative value.

An **empirical formula** (rate law equation or rate equation) has been found from experiment that relates rate to the concentration of each reactant at any time in the reaction. The **rate law equation** has the form

$$\text{rate} = k[A]^m[B]^n \quad (3)$$

In the rate law equation, $[A]$ and $[B]$ are the molarities of each reactant in the balanced equation at some time t . Here k is the rate constant (depends only on temperature), and m and n are the orders of the reaction with respect to A and B. **Important: m and n are not related to the stoichiometric coefficients in the balanced equation! Reaction orders must be determined by experiment!** Reaction orders are usually integers of value 0, 1, or 2. The rate constant, k , is also determined by experiment.

Method of Initial Rates

One method of determining the reaction orders (and rate constant) for a chemical reaction is through the method of **initial rates**. In this method an experiment is performed where the rate of reaction is measured **at the beginning of the reaction** under a known set of initial concentrations for each reactant. A second experiment is then performed where the concentration **of only one reactant is changed** (usually doubled or halved) and the rate of reaction is again measured. By comparing how the rate of reaction changes as the concentration of one reactant is changed the value of the reaction order can be determined for that reactant. For example consider the following simple rate law equation:

$$\text{rate} = k[A]^n \quad (4)$$

The value of n will determine how the reaction rate changes as the concentration of A changes. If $n = 0$, a zero order reaction, then changing the concentration of A will have no effect on the rate since $[A]^n$ will always equal 1, therefore $\text{rate} = k$ at all times. As we change the initial concentration of A in an experiment we will see no change in the reaction rate for a zero order reactant. Now, if $n = 1$, a first order reaction, then $\text{rate} = k[A]$. If $[A]$ is doubled in an experiment we should see the reaction rate double as well. What will happen to the reaction rate if $n = 2$, a second order reaction, if $[A]$ is doubled? You should convince yourself that the reaction rate increases by a factor of $2^2 = 4$.

Determining the Rate Constant

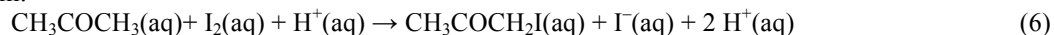
Once the reaction orders have been determined the rate constant can be calculated from the measured rate and the initial reactant concentrations. Consider an experiment where the rate depends on reactants A and B with reaction orders of n and m as in equation 3. For a set of initial concentrations, $[A]_0$, and $[B]_0$, the initial reaction rate is measured. Rearranging equation 3 we have

$$k = \frac{\text{rate}}{[A]_0^n [B]_0^m} \quad (5)$$

Where $[A]_0$ and $[B]_0$ are the initial concentrations of A and B and n and m are found from previous experiments.

Application of the Theory: The Iodination of Acetone

In this lab we will study the iodination of acetone. This is a simple reaction where a single hydrogen atom on acetone is replaced by an iodine atom:



The reaction requires the presence of hydrogen ions (acidic conditions) to take place. The hydrogen ion act as a catalyst and influence the reaction rate. Without the hydrogen ions the reaction rate is exceedingly slow. The rate law for this reaction is

$$\text{rate} = k[\text{Ac}]^m [\text{H}^+]^n [\text{I}_2]^p \quad (7)$$

Where Ac = acetone. From previous studies it has been determined that the rate of reaction is zero order with respect to iodine, $p = 0$. Thus, equation 7 can be rewritten as

$$\text{rate} = k[\text{Ac}]^m [\text{H}^+]^n \quad (8)$$

We will use the method of initial rates to determine the reaction order for both acetone and the hydrogen ion. Once they are known we will be able to find the value of the rate constant, k , for the reaction at various temperatures.

Key Experimental Design Concept

To make the reaction rate independent of time for hydrogen and acetone we set the iodine as the limiting reactant and provide a large excess of acetone and hydrogen ions. Recall from equation 8 that the reaction rate will change as the concentration of acetone and hydrogen ion change. **If the initial concentrations of acetone and hydrogen ion are much greater than iodine, ($[\text{Ac}]_0$ and $[\text{H}^+]_0 \gg [\text{I}_2]_0$), then as the reaction proceeds the concentrations of acetone and hydrogen ion will not change appreciably during the reaction.** From equation 8 we then have the following since the order for iodine is zero:

$$\text{rate} = k[\text{Ac}]_0^m [\text{H}^+]_0^n; \text{ Let } k' = k[\text{Ac}]_0^m [\text{H}^+]_0^n \text{ (all constants over time); so } \text{rate} = k' \quad (9)$$

The constant k' is called a pseudo (false) rate constant since it is the product of the true rate constant, k , and the initial concentrations of any reactants that do not change over time, namely acetone and hydrogen ions. This does not imply the reaction rate no longer depends upon the acetone and hydrogen ion concentrations: **what we have done is removed the time dependence of the reaction rate with respect to the acetone and hydrogen ion concentrations.**

A graph of iodine concentration versus time should therefore be linear since the rate of reaction is constant at k' . Thus, the loss of the reactant iodine over time will appear to follow zero order kinetics, $\text{rate} = k'[\text{I}_2]^0 = k'$. From the zero-order integrated rate law:

$$[\text{I}_2]_t = -k't + [\text{I}_2]_0 \quad (10)$$

Here k' is interpreted as the pseudo zero-order rate constant. To measure the rate of reaction we take advantage of the fact that iodine, I_2 , is yellow in solution while acetone and hydrogen ion are colorless. The products of the iodination reaction (refer to equation 7) are also colorless. As the reaction proceeds the mixture will change from yellow to colorless. To measure the reaction rate we time how long it takes for the solution to become colorless after all the reactants have been mixed. This time corresponds to the complete reaction (100%) of the limiting reactant iodine. From equation 2 the reaction rate can now be written as

$$\text{rate} = -\frac{\Delta[\text{I}_2]}{\Delta t} = -\frac{[\text{I}_2]_{\text{final}} - [\text{I}_2]_{\text{initial}}}{\Delta t} = -\frac{0 - [\text{I}_2]_0}{\Delta t} = \frac{[\text{I}_2]_0}{\Delta t} = k' \quad (11)$$

Thus, we can measure the zero-order pseudo rate constant, k' , by measuring the time required to consume all the iodine initially present in each reaction mixture.

PART 2: DETERMINATION OF THE ACTIVATION ENERGY

THEORY OF REACTION ENERGETICS

Activation Energy

Molecules require some minimum energy to react. This energy barrier to initiate a reaction is called the **activation energy**, E_a . Figure 1 shows the activation energy profile for the reaction of NO_2 and CO (to give NO and CO_2). If the activation energy is small, then the kinetic energy needed to overcome the barrier is low. At room temperature a high proportion of the molecules will have sufficient energy to react and the reaction rate is fast. Conversely, if the activation energy is large then at room temperature few molecules will have sufficient kinetic energy to overcome the barrier and the reaction rate is slow. The maximum in the **potential energy diagram** (energy curve) is called the **transition state**. Enough energy has been added to initiate the bond breaking process while the bond forming process has also begun. As the new bonds form energy is released until the product state is formed.

Temperature Effects on Reaction Rates

Temperature has a great effect on reaction rates. As temperature increases the fraction of collisions with enough kinetic energy to overcome the activation energy increases. Thus more collisions have the minimum energy to overcome the activation energy, hence a greater reaction rate. As a rule-of-thumb, for every 10°C increase in temperature the reaction rate will double.

Effect of Molecular Orientation on Reaction Rates

Not only must molecules have a minimum kinetic energy to react they also must come together in the correct orientation. The orientation during the collision of the molecules will determine if the correct bonds will begin to break. If the orientation of the molecules is not correct, the molecules will simply bounce off each other and no reaction will take place. As shown in figure 1 one of the O atoms of NO_2 must collide with the carbon atom of CO . This orientation dependence is called the **steric factor** for the reaction.

The Arrhenius Equation

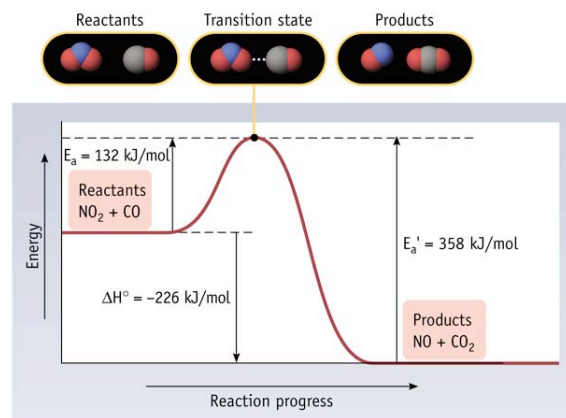
The activation energy, steric factor and temperature dependence of the reaction rate are summarized by the **Arrhenius equation**:

$$k = Ae^{\frac{-E_a}{RT}} = Af \quad (12)$$

Where k is the rate constant for the reaction (in our experiment, k^*), A is the frequency factor, E_a is the activation energy, and T is the temperature. The frequency factor, A , is related to the number of collisions with the correct orientation to react. R is the universal gas constant, $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$. The frequency factor has the same units of the rate constant and can be interpreted as the number of collisions per unit time per unit molarity of reactants. This is typically a large number, 10^8 or greater. The quantity $f = e^{\frac{-E_a}{RT}}$ is interpreted as **the fraction of collisions having at least the minimum energy for reaction**. This value is always significantly less than one, 10^{-10} or even smaller. The Arrhenius equation is valuable since we can use it to determine A , and E_a for a reaction by measuring the rate constant as a function of temperature. Finally, using the properties of logarithms we have an equation for a straight line from the Arrhenius equation.

$$\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A) \quad (13)$$

Figure 1. Reaction Coordinate Diagram for a Simple Reaction



The reaction of NO_2 and CO (to give NO and CO_2) requires an activation energy of 132 kJ/mol . The reverse reaction (for $\text{NO} + \text{CO}_2 \longrightarrow \text{NO}_2 + \text{CO}$) requires 358 kJ/mol . The net enthalpy change for the reaction of NO_2 and CO is -226 kJ/mol .

PROCEDURE

MATERIALS AND REAGENTS:

4.00 M acetone solution 1.00 M HCl(aq) 5.0x10⁻³ M I₂(aq) ice
600 mL beaker 2 Large test tubes LabQuest with temperature probe

SAFETY:

No open flames – 4 M acetone is flammable. Use only hot plates for heating the water baths.
1 M HCl(aq) is corrosive. Avoid contact with skin and eyes. If spilled, cleanup immediately.

PART 1 EXPERIMENTAL PROCEDURE – REACTION ORDERS

To find the reaction orders for acetone and hydrogen ion we will measure the rate of reaction using three different sets of initial concentrations. Table 1 gives the volumes of each reactant. As you can see in mixture 2 we have doubled the volume of acetone compared to mixture 1 and in mixture 3 we have doubled the volume of hydrogen ion (compared to 1). Copy this table into your notebook.

Table 1. Initial Reactant Volumes – COPY TO YOUR NOTEBOOK!

Mixture	4.00 M Acetone (mL)	1.00 M Hydrochloric acid (mL)	5.0x10 ⁻³ M Iodine (mL)	Deionized Water (mL)
1	1.0	1.0	1.0	2.0
2	2.0	1.0	1.0	1.0
3	1.0	2.0	1.0	1.0

Detailed Procedure

You may be assigned one mixture from Table 1 by your instructor. Repeat the procedure below at least three times for your mixture.

1. Wear safety glasses
2. Prepare a water bath as close to 25 °C as possible using a half-full a 600-mL beaker. Obtain two large test tubes.
3. Clean and dry the test tubes. Label them A, and B.
4. In test tube A pipette the required volumes of acetone and hydrochloric acid for your assigned mixture. Use Table 1 as a guide. In test tube B pipette the required volumes of iodine and water. Place the test tubes in the 25 °C water bath and allow to thermally equilibrate (about 5 minutes).
5. Remove test tubes A and B from the water bath. While watching the clock (or using a timer) pour the iodine (B) into the acetone/HCl mixture (A). Record the time if mixing or start a timer. To insure all the iodine is transferred, pour the entire mixture back-and-forth between the two test tubes several times. **Place the test tube with the reaction mixture back in the water bath.**
6. Insert a clean and dry stirring rod into the reaction mixture and stir gently while you observe the yellow color fade. Watching carefully record the time when the mixture becomes colorless.
7. Repeat steps 3 through 6 as time permits for your assigned reaction mixture.
8. Dispose of all waste in the appropriate waste container.

PART 2 EXPERIMENTAL PROCEDURE – ACTIVATION ENERGY

For the temperature dependence study **all groups will use mixture 2** from Table 1. Suggested temperatures are: 30, 20, 15 and 10 °C. Your instructor will assign you a single temperature for all your trials.

Repeat the procedure below at least three times (or as time allows) for your temperature.

1. Wear Safety Glasses
2. Prepare a water bath as close to your assigned temperature as possible using a half-full a 600-mL beaker. Obtain two large test tubes,
3. Clean and dry the test tubes. Label them A, and B.
4. In test tube A pipette the required volumes of acetone and hydrochloric **acid for mixture 2** from Table 1. In test tube B pipette the required volumes of iodine and water. Place the test tubes in the water bath and allow to thermally equilibrate (about 5 minutes).
5. Remove test tubes A and B from the water bath. While watching the clock (or using a timer) pour the iodine (B) into the acetone/HCl mixture (A). Record the time of mixing or start a timer. To insure all the iodine is transferred, pour the entire mixture back-and-forth between the two test tubes several times. **Place the test tube with the reaction mixture back in the water bath!**
6. Insert a clean and dry stirring rod into the reaction mixture and stir gently while you observe the yellow color fade. Watching carefully record the time when the mixture becomes colorless.
7. Repeat steps 3 through 6 for your assigned number of trials.
9. Dispose of all waste in the appropriate waste container.

PROCESSING THE DATA – FOLLOW THESE GENERAL GUIDELINES.

Part 1: Determination of Reaction Orders

1. The rate of reaction is calculated using equation 11 and the average reaction time and initial concentration of I₂.
2. By comparing the rates of reaction between the three mixtures you should be able to determine the reaction orders for acetone and hydrogen ion. Use the method of initial rates. Show your work on the report sheet.
3. Using eqn 5 calculate the rate constant for each mixture from the rate of reaction. What are the units of *k*? Enter the results of the calculation in the table. Is the rate constant the same between the three trials?

Part 2: The Temperature Dependence of the Rate Constant - Use Logger Pro for the following calculations.

1. From the class data for Part 2 calculate the rate of reaction (eqn 11) for each point. Remember all the data is from reaction mixture 2. You should have as many data points covering the temperature range from 30 °C down to about 10°C as possible. Don't forget to include the data for mixture 2 taken in Part 1.
2. Once the rate is calculated, calculate the rate constant using eqn 5, same as in Part 1, for each point.
3. Make a graph of natural log of the rate constant (y-axis) as a function of the inverse of the Kelvin temperature (x-axis).
4. Finally, make a linear fit function of $\ln(k) = (-E_a/R)(1/T) + \ln(A)$, where $\ln(A)$ is the y-intercept value and $(-E_a/R)$ is the slope of the line. R must have a value of 8.3145 with units of J/mol•K. From the fit A is the frequency factor and E_a is the activation energy.

REPORT SHEET: ACETONE KINETICS**PART 1**

Enter the following from the class experimental results and analysis. **Include any units missing in the column headings!**

Mixture	[Acetone] ₀ (M)	[H ⁺] ₀ (M)	[I ₂] ₀ (M)	Avg. time (s)	Reaction Rate	Rate constant, <i>k</i>	Avg. T (°C)
1							
2							
3							
						Average <i>k</i> & T	

Reaction orders from your analysis of Part 1 Data

Show your work for Acetone and H⁺

Acetone _____ H⁺ _____ I₂ _____ 0 _____

Questions on Part 1

- If the concentration of iodine is doubled in mixture 1 with the acetone and hydrogen ion remaining the same:
 - Will the reaction rate change? If so, by what factor?

 - Will the rate constant change? If so, by what factor?

 - How long would it take for this doubled concentration of iodine to become colorless?

PART 2: INCLUDE A COPY OF YOUR ARRHENIUS GRAPH, K VERSUS T.

1. From your Arrhenius graph, report your activation energy and frequency factor values to TWO significant figures with correct units.

activation energy _____ frequency factor _____

2. Calculate the fraction of collisions, f , that have enough energy to overcome the activation energy barrier at 25° C.

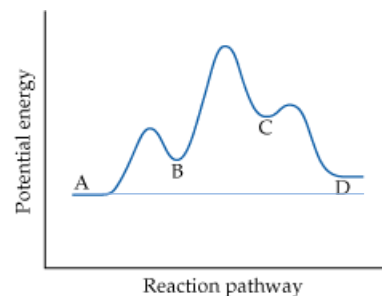
a) Multiply this by the frequency factor to obtain the rate constant at 25°C.

3. Calculate the temperature needed (in °C) to increase the rate constant by 10 times the value found at 25° C.

4. Find the rate constant at 5°C.

5. A catalyst is added at 25 °C. The rate constant increases by a factor of 132. What is the activation energy for the catalyzed reaction?

6. Based on the provided reaction profile diagram,
- How many intermediates are formed in the reaction $A \rightarrow D$? _____
 - How many transition states are there? _____
 - Which step ($A \rightarrow B$, $B \rightarrow C$, $C \rightarrow D$) is the fastest? _____
 - Draw a line on the graph showing the magnitude of the overall activation energy for $A \rightarrow D$.
 - Is the reaction $A \rightarrow D$ exothermic or endothermic? _____



7. Use the method of initial rates to find the orders for each reactant given:



Calculate the rate constant using trial 1 data.

Trial	[ClO ₂] (M)	[OH ⁻] (M)	Initial Rate (M/s)
1	0.060	0.030	0.025
2	0.020	0.030	0.0028
3	0.020	0.090	0.0083