
Experiment #4 – Chemical Kinetics: The Iodination of Acetone

The rate at which a chemical reaction occurs depends on several factors: the nature of the reaction, the concentrations of the reactants, the temperature, and the presence of possible catalysts. All of these factors can markedly influence the observed rate of reaction.

In this experiment, we will study a reaction which, in the vicinity of room temperature, proceeds at a relatively easily measured rate.

For a given reaction, the rate typically increases with an increase in the concentration of any reactant. For the reaction $aA + bB \rightarrow cC$, the rate can be expressed by the following equation, which is called the rate law,

$$\text{rate} = k[A]^m[B]^n \quad (1)$$

where m and n are generally, but not always, integers, 0, 1, 2 or possibly 3; $[A]$ and $[B]$ are the initial concentrations of A and B (ordinarily in moles per liter); and k is the specific rate constant for the reaction. The numbers m and n are called the orders of the reaction with respect to A and B. If m is 1 the reaction is said to be first order with respect to the reactant A. If n is 2 the reaction is second order with respect to reactant B. The overall order is the sum of m and n . In this example, the reaction would be third order overall.

The rate of reaction is also significantly dependent on the temperature at which the reaction occurs. An increase in temperature increases the rate, an often cited rule being that a 10 °C rise in temperature will double the rate. This rule is only approximately correct; nevertheless, it is clear that a rise of temperature to say 100 °C could change the rate of a reaction appreciably.

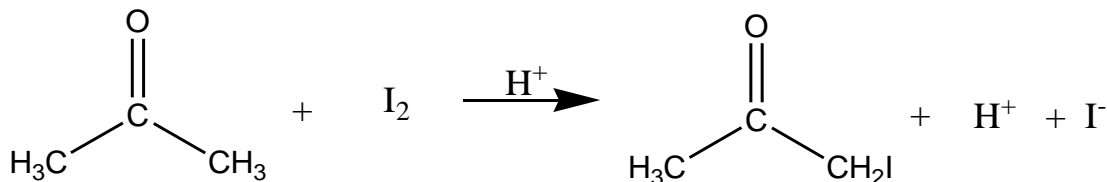
As with the concentration, there is a quantitative relationship between reaction rate and temperature. This relation is based on the idea that in order to react, the reactant species must have a certain minimum amount of energy present at the time the reactants collide in the reaction step. This amount of energy, which is typically furnished by the kinetic energy of the species present, is called the activation energy of the reaction.

The equation relating the rate constant, k , to the absolute temperature, T , and the activation energy, E_a , is

$$\ln k = \frac{-E_a}{RT} + \text{constant} \quad (2)$$

where R is the gas constant (8.314 Joules/mole K for E_a in Joules per mole). By measuring k at different temperatures we can determine graphically the activation energy for a reaction.

In this experiment, we will study the kinetics of the reaction between iodine and acetone in aqueous solution:



The rate of this reaction is expected to depend on the concentration of hydrogen ion in the solution, a catalyst, as well as the concentrations of the two reactants. By Equation 1, the rate law for this reaction is

$$\text{rate} = k [\text{acetone}]^m [\text{H}^+]^n [\text{I}_2]^p \quad (3)$$

where **m**, **n**, and **p** are the orders of the reaction with respect to **acetone**, **hydrogen ion**, and **iodine**, respectively, and *k* is the rate constant for the reaction.

The rate of this reaction can be expressed as the (small) change in the concentration of I_2 , $\Delta[\text{I}_2]$, divided by the time interval, Δt , required for the change:

$$\text{rate} = \frac{-\Delta[\text{I}_2]}{\Delta t} \quad (4)$$

The minus sign is to make the rate positive ($\Delta[\text{I}_2]$ is negative). Ordinarily, since rate varies as the concentrations of the reactants according to Equation 3, in a rate study it would be necessary to measure (directly or indirectly) the concentration of each reactant as a function of time; the rate would typically vary markedly with time, decreasing to very low values as the concentration of at least one reactant becomes very low. This makes reaction rate studies relatively difficult to carry out and introduces mathematical complexities that are difficult for beginning students to understand.

The iodination of acetone is a rather atypical reaction in that it can be very easily investigated experimentally. First of all, iodine has color so that one can readily follow changes in iodine concentration visually. A second and very important characteristic of this reaction is that it turns out to be zero-order in I_2 concentration. This means (see Equation 3) that the rate of the reaction does not depend on $[\text{I}_2]$ at all as $[\text{I}_2]^0 = 1$ no matter what the value of $[\text{I}_2]$ is as long as it is NOT zero.

Since the rate of reaction does not depend on $[\text{I}_2]$, we can study the rate by simply making I_2 the limiting reagent present in a large excess of acetone and H^+ ion. We then measure the time required for a known initial concentration of I_2 to be completely used up. If both acetone and H^+ are present at much higher concentrations than that of I_2 , their concentrations will not change appreciably during the course of the reaction, and the rate will remain, by Equation 3, effectively constant until all the iodine is gone, at which time the reaction will stop. Under such circumstances, if it takes *t* seconds for the color of a solution having an

initial concentration of I_2 equal to $[I_2]_{\text{initial}}$ to disappear, the rate of reaction, by Equation 4, would be:

$$\text{rate} = \frac{-\Delta[I_2]}{\Delta t} = \frac{[I_2]_{\text{initial}} - 0}{t - 0} = \frac{[I_2]_{\text{initial}}}{t} \quad (5)$$

Although the rate of the reaction is constant during its course under the conditions we have set up, we can vary it by changing the initial concentrations of acetone and H^+ ion. If, for example, we should double the initial concentration of acetone over that in Mixture 1, keeping $[H^+]$ and $[I_2]$ at the same values they had previously, then the rate of Mixture 2 would, according to Equation 3, be different from that in Mixture 1:

$$\text{rate 2} = k [2A]^m [H^+]^n [I_2]^p \quad (6a)$$

$$\text{rate 1} = k [A]^m [H^+]^n [I_2]^p \quad (6b)$$

Dividing the first equation by the second, we see that the k 's cancel, as do the terms in the iodine and hydrogen ion concentration, since they have the same values in both reactions, and we obtain simply

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{[2A]^m}{A^m} = 2^m \quad (6)$$

Having measured both rate 2 and rate 1 by Equation 5, we can find their ratio, which must be equal to 2^m . We can then solve for m using logarithms and so find the order of the reaction with respect to acetone:

$$\log(\text{rate 2}/\text{rate 1}) = \log 2^m = m \log 2 \quad (7)$$

By a similar procedure we can measure the order of the reaction with respect to H^+ ion concentration and also confirm the fact that the reaction is zero-order with respect to I_2 . Having found the order with respect to each reactant, we can then evaluate k , the rate constant for the reaction.

The experiment goals include the determination of the orders m and n , the confirmation of the fact that p , the order with respect to I_2 , equals zero, and the evaluation of the rate constant k for the reaction at room temperature. You will be furnished with standard solutions of acetone, iodine, and hydrogen ion, and with the composition of the solutions that will give a reasonable rate.

The final part of the experiment is to study the rate of this reaction at different temperatures in order to find its activation energy. This is done by studying the rate of reaction in one of the mixtures at room temperature and at two other temperatures, one above and one below room temperature. Knowing the rates, and hence the k 's, at the three temperatures, you can solve for E_a , the energy of activation, by plotting $\ln k$ vs. $1/T$. The slope of the resultant straight line, by Equation 2, is $-E_a/R$.

Procedure

Select two regular test tubes; when filled with distilled water, they should appear to have identical color when you view them down the tubes against a white background. One test tube will be the reaction test tube and the other will be the reference test tube. For the reference, add 5 mL of D.I. water to a test tube and set aside for comparison later.

For each trial, add the specified volumes of 1.0 M HCl, 4.0 M acetone, and water from the provided burets directly into the clean, dry reaction test tube. Swirl the test tube to mix the reagents.

Noting the time, add the iodine solution into the test tube using the appropriate pipet and quickly swirl the test tube or stir with a CLEAN, DRY STIRRING ROD to thoroughly mix the reagents. The reaction mixture will appear yellow because of the presence of the iodine, and the color will fade slowly as the iodine reacts with the acetone. Look down the reacting test tube side-by-side with the reference test tube toward a well-lit piece of white paper, and note the time the color of the iodine just disappears. Measure the temperature of the mixture in the test tube after the reaction is complete.

Repeat the experiment using the reacted solution as the reference instead of distilled water. The amount of time required in the two runs should agree within 20 seconds. Use this same reference test tube for all the remaining mixtures.

Carry out the remaining reaction mixtures twice with each of the indicated compositions (including your own mixture composition); the times should not differ by more than 15 seconds for the same mixture. The temperature must remain relatively constant, within two degrees of that in the initial run.

Calculate the new initial (diluted) concentrations for the reactants ($M_1V_1 = M_2V_2$) and the rates of the reaction. The rate of the reaction equals the initial concentration of I_2 in the reaction mixture divided by the average elapsed time. Since the reaction is zero-order in I_2 , and since both acetone and H^+ ion are present in great excess, the rate is constant throughout the reaction and the concentrations of both acetone and H^+ remain essentially at their initial values in the reaction mixture.

Calculate the order with respect to each reactant for this reaction. Then determine the value of the rate constant, k , from the rate law (3) using your reactant orders, the calculated concentrations, and rate data for each of the mixtures you studied. If the temperatures at which the reactions were run are all within two degrees, k should be about the same for each mixture.

Using your own mixture values, predict how long it will take for the I_2 color to disappear. Calculate the predicted reaction rate using the rate law with your average k value, your calculated orders, and the initial concentrations for your mixture. Then calculate the predicted time using equation 5. Compare your measured time for this reaction with your predicted time.

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Reaction data from mixture D at three temperatures has been provided for you to determine the energy of activation for the reaction using Equation 2.

Data and Calculations

Table 1. Reactant Volumes and Reaction Times

Mixture	Volume (mL) of:				Time of reaction (sec)			Temp
	4.0 M acetone	1.0 M HCl	0.0050 M I ₂	H ₂ O	1 st run	2 nd run	Ave time	°C
A	1.00	1.00	1.00	2.00				
B	2.00	1.00	1.00	1.00				
C	1.00	2.00	1.00	1.00				
D	1.00	1.00	0.50	2.50				
Your Mixture*								

*Note: Must add up to 5.0 mL; water is not required.

Table 2. Initial Concentration and Rate of Reaction

Mixture	[acetone] _{ini}	[H ⁺] _{ini}	[I ₂] _{ini}	Rate = [I ₂] _{ini} / (ave time)
A				
B				
C				
D				
Your Mixture*				

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Part A: Reactant Order Determination

Calculate the value of m (order with respect to acetone) to TWO decimal places. This means you have to use logarithms. Show calculations. Then round off to the nearest integer to get the true value for m.

m = _____ (2 decimal places)

m = _____ (nearest integer)

Calculate the value of n (order with respect to the H⁺):

n = _____ (2 decimal places)

n = _____ (nearest integer)

Calculate the value of p (order with respect to the I₂):

p = _____ (2 decimal places)

p = _____ (nearest integer)

Write the overall rate law: _____

Part B: Determination of the Rate Constant, k

Given the values of m, n, and p, calculate the rate constant k (**with correct units**) for each mixture by simply substituting those orders, the initial concentrations, and the observed rate from the Table 2 above into Equation 3.

Table 3. Rate Constant, k

Mixture	A	B	C	D	average	Units of k
k						

Show calculations for k value of Mixture A:

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Part C: Prediction of Reaction Rate in Your Mixture

Initial concentrations (from Table 2):

[acetone]_{ini} _____ M [H⁺]_{ini} _____ M [I₂]_{ini} _____ M

Calculate the predicted rate based on your determined rate law in Part A as well as your average rate constant (from Part B).

Predicted rate: _____ M/sec

Calculate the predicted *time* (in seconds) for reaction based on [I₂]_{ini} and the value for the predicted rate above using:

$$\text{Rate} = [\text{I}_2]_{\text{ini}} / (\text{time})$$

Predicted time: _____ sec

Observed average time for reaction _____ sec (from Table 1 above)

Calculate the percent difference between the observed and predicted times below:

% difference: _____

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Part D: Energy of Activation Determination**PROBLEM SET – Use provided data below**

Fill Table 4 below.

Table 4. Reaction Rate Data for Mixture **D**.

Temp (°C)	Temp (Kelvin)	Time (sec)	Rate = $[I_2]_{ini} / (\text{time})$ (<i>NOTE: Use $[I_2]_{ini}$ from Mixture D</i>)
10.		208	
22		93	
40.		28	

Fill Table 5 below by calculating the rate constant at each temperature using rate from Table 4 above, initial concentrations for Mixture D (Table 2) and your experimentally determined rate law (from Part A).

Table 5. Calculated Values for Arrhenius Plot

Temperature	k	ln k (<i>y-axis</i>) (two decimal places)	1 / T (<i>x-axis</i>) (Kelvin ⁻¹)
10 °C			
22 °C			
40 °C			

Construct an Arrhenius plot by graphing ln k vs. 1 / T. Find the slope of the best fitting (straight) line through the points. Show your calculations below: Alternatively, you can use MS Excel to construct your graph; write the trendline equation below.

Slope = _____ OR Trendline Equation (MS Excel): _____

From Equation 2, we see that the slope = $-E_a / R$ where $R = 3.814 \text{ J / mol K}$. Use this relationship to calculate the value of E_a :

 $E_a = \text{_____ kJ / mol}$

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Pre-Lab Questions: The Iodination of Acetone

1. In a reaction involving the iodination of acetone, the following volumes were used to make up the reaction mixture.

1.0 mL 4.0 M acetone + 1.0 mL 1.0 M HCl + 1.0 mL 0.0050 M I₂ + 2.0 mL H₂O

- a. Calculate the initial (diluted) concentration of acetone in the reaction mixture.

[acetone]_{ini} = _____

- b. Calculate the initial (diluted) concentration of the hydrogen ion, H⁺, in the reaction mixture.

[H⁺]_{ini} = _____

- c. Calculate the initial (diluted) concentration of iodine, I₂, in the reaction mixture.

[I₂]_{ini} = _____

2. Using the reaction mixture in Problem 1, a student found that it took 300 seconds for the color of the I₂ to disappear.

- a. What was the rate of the reaction?

rate = _____

- b. Given the rate from Part a and the initial concentrations of acetone, H⁺ ion, and I₂ in the reaction mixture, write Equation 3 as it would apply to the mixture.

rate =

- c. What are the unknowns that remain in the equation in Part b?

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3. A second reaction mixture was made up in the following way:

2.0 mL 4.0 M acetone + 1.0 mL 1.0 M HCl + 1.0 mL 0.0050 M I₂ + 1.0 mL H₂O

a. What were the initial concentrations of acetone, H⁺ ion, and I₂ in the reaction mixture?

[acetone]_{ini} _____ M; [H⁺]_{ini} _____ M; [I₂]_{ini} _____ M

b. It took 140 seconds for the I₂ color to disappear from the reaction mixture when it occurred at the same temperature as the reaction in Problem 2.

What was the rate of the reaction? _____

Write Equation 3 as it would apply to the second reaction mixture:

rate =

c. Solve for the value of m, the order of the reaction with respect to acetone. (Use the logarithm method and calculate the value of m to two decimal places and then round to the nearest integer.)

m = _____ (2 decimal places)

m = _____ (nearest integer)