

Experiment 4

Chemical Kinetics – Effect of Temperature – The Arrhenius Equation

Introduction:

In the previous experiment we were interested in determining the rate equation for the reaction of potassium permanganate with oxalic acid. You should have found that the reaction was first order in permanganate and first order in oxalate thus giving a rate equation:

$$\text{Rate} = k[\text{KMnO}_4][\text{H}_2\text{C}_2\text{O}_4]$$

We can now focus our attention on the effect that temperature has on the speed of a chemical reaction. As noted in the introduction to experiment three: a temperature increase generally increases the rate of a chemical reaction. A daily observation of this is in preparing foods; we generally heat foods when preparing them to eat and freeze them for long term storage. For many chemical reactions a general rule of thumb is that the rate of a chemical reaction doubles with every 10°C temperature increase. Why is this?

Effect of Temperature on the Speed of a Chemical Reaction:

On the molecular level, the determining factor of the speed of a chemical reaction is the collisions between molecules. The more frequently they collide, the greater the likelihood that a reaction will take place. This is not a bad starting premise for understanding a chemical reaction. Let's now just look at what happens to the permanganate molecule in its reaction with oxalic acid. It goes from MnO_4^- to Mn^{2+} . This seemingly involves bond breakage which must require energy. Thus, is not sufficient that the molecules just collide, but they must collide with sufficient energy such that the reaction may occur. This energy barrier that must be overcome is called the **Activation Energy**. By increasing the temperature one not only increases the number of collisions but one also increases the energy of the collisions and thus a greater probability that some of those collisions have sufficient energy to overcome this barrier. There is another factor that comes into play called the orientation factor, though it is not very important in this reaction. This factor takes into account the number of collisions that occur at the correct location to effect breakage of the desired bond. A rather bizarre way to understand this is that throwing a stone at a window with sufficient force to break it does not ensure breaking the window if your aim is suspect!!

In 1889, Svante Arrhenius, demonstrated that the rate constant of a chemical reaction varies with temperature according to the equation

$$k = Ae^{-E_a/RT}$$

- k: rate constant
- A: Preexponential term, a factor that includes collision frequency and orientation.
- E_a : Activation energy.
- R: Ideal Gas Constant (in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
- T: Temperature (in K)

If we know take the natural log of the above equation:

$$\ln k = \ln A - (E_a/RT)$$

by just rewriting this slightly differently we get:

$$\ln k = (-E_a/R)(1/T) + \ln A$$

which is in fact the equation of a straight line that relates the **natural logarithm of k** to the **inverse of the temperature**. Thus if one were to plot **ln k vs 1/T**, one should obtain a straight line with a negative slope. The slope of this line is equal to **- E_a/R** and the intercept **ln A**.

This is the heart of this experiment. Using a very similar technique to the last experiment, you will determine k at four different temperatures and by doing the appropriate plot determine the activation energy for this reaction.

Experimental Procedure

Important Notes:

- The following procedure should be done, in duplicate, at four different temperatures. The temperatures should be monitored carefully and if the temperature increases or decreases during the reaction then the average of the starting temperature and the final temperature should be taken as the reaction temperature.
- In order to achieve thermal equilibrium, the Erlenmeyer Flask and the 15 cm test tube should be placed in the water bath for at least five minutes before mixing.

Suggested Temperatures:

We are aiming to run this experiment at 0, 10, 20 and 30°C. To make water baths at these temperatures you will have to mix ice and water, in the plastic containers provided, for the 0, 10 and 20°C water bath. The 30°C water bath may be obtained by heating water gently in a 400mL beaker to ~32°C and then transferring this to the plastic container. Obtaining the suggested water bath temperature is not critical, so long as you know and record the actual temperature and that you obtain an ~ 10°C difference for each bath.

Determining the Activation Energy

1. Using a buret place 20mL of ~0.5M $\text{H}_2\text{C}_2\text{O}_4$ in an Erlenmeyer Flask and 10mL of ~0.02M KMnO_4 in a 15cm test tube.
2. Place both vessels in your water bath and let them sit there for five minutes. Take care that the test tube does not topple over in the bath. Your test tube holder may come in handy here! This is also a good time to set up your second trial at this temperature.
 - If you are doing the reaction at ~0°C then a single determination is enough. The reaction at this temperature takes ~28 minutes to complete.
3. Mix the reactants and record the time it takes for the solution again to go yellow/brown. Don't forget to swirl the contents regularly.
4. Repeat the procedure with another sample at this temperature.
5. Using the average time, determine k at this temperature.
6. Repeat this procedure for the other suggested temperatures.
7. When complete, determine the Activation Energy by plotting $\ln k$ v $1/T$. (Remember, temperature must be in Kelvin).

Write-Up:

In this experiment you are going to write up a complete record of the experiment.

Objective: Give a short objective of the experiment.

Procedure: Write a brief procedure.

Data Collection: Should consist of a table similar to:

KMnO₄	H₂C₂O₄	Temp.	Reaction Time Trial 1	Reaction Time Trial 2	Av. Time
mL	mL	°C	s	s	s

Calculations:

Make sure that:

1. You show sample calculation on determining the rate: $\text{Rate} = [\text{KMnO}_4]/t$
2. Show a sample calculation on how you determined k:
 $k = \text{Rate}/([\text{KMnO}_4][\text{H}_2\text{C}_2\text{O}_4])$

3. Tabulate your results similar to:

T °C	T K	1/T 1/K	k	Ln k

4. Draw a good graph (**it should occupy the whole page**) and from the slope determine E_a . The graph may be drawn using "real" graph paper or by using a graphing program such as Excel.

Discussion:

A brief comment on the magnitude of E_a should be given paying attention to its magnitude and a comparison between it and typical bond energies. (Remember these from chem 111.)