EXPERIMENT **4**

"IF IT WERE DONE...THEN 'TWERE WELL IT WERE DONE QUICKLY"

CHEMICAL KINETICS

Techniques

- rate measurement
- order determination from graphs
- graphing
- complex formation
- use of spectrophotometers

MSDS available for

- sodium EDTA, $Na_2C_{10}H_{14}N_2O_8 \cdot 2\ H_2O$ (aq)
- chromium nitrate, $Cr(NO_3)_3 \cdot 9\ H_2O$ (aq)

Principles

- instantaneous reaction rate
- order of the reaction
- complexation
- absorbance
- spectrophotometry

Recommended Advanced Reading

- **Chapters 14,18 in Petrucci,Herring,Madura,Bissonnette's General Chemistry,10th Ed.**

INTRODUCTION

The beginning

This experiment is designed to introduce you to kinetics and the use of a spectrophotometer. In today's session you will work with your partner to:

- prepare a reaction mixture at different pH levels.
- observe the formation of a coloured complex over a period of time.
- determine the progression of the reaction using the ability of the coloured complex to absorb light of certain intensity.
- plot the measured absorbances as a function of the time of reaction.
- determine the instantaneous rate of reaction at a fixed pH using the above graph.
- plot the calculated rate as a function of the concentration.
- determine the partial order of the reaction with respect to one of the reactants.
- Show that the reaction generally follows pseudo first-order kinetics.

This is a general overview of what you will be accomplishing in this experiment.

EXPERIMENT 4: *Chemical Kinetics*

Introduction

"*The reactants in a reaction are a lot like money in my pocket: the more there are, the faster it goes!!*"

How Fast are Chemical Reactions?

The speeds of chemical reactions vary tremendously, from very fast reactions, such as explosions, to very slow reactions, such as the conversion of diamond to graphite at room temperature. The usefulness of a reaction depends very much on its rate. A reaction may give you the products you want, but if it takes years to do so, it isn't much help! Chemical kinetics is the study of the factors that control the rates of reactions and the mechanisms by which the reactions occur. One of these factors is the concentration of the reactants. This experiment is designed to investigate the way in which the rate of a chemical reaction depends on the concentration of the reactants. This particular characteristic is known as the ***order of the reaction***.

Rate of a Reaction

The rate of a chemical reaction is proportional to the product of the concentrations of the reacting species, each raised to a power. The power indicates the order of the reaction with respect to each individual reactant. For example, in a reaction such as

$$A + B \rightarrow P \qquad [1]$$

the ***rate*** can be expressed as

$$\text{Rate} \ \alpha \ [A]^n [B]^m \qquad [2]$$

or, removing the proportionality sign and forming an equation, we get

$$\text{Rate} = k \ [A]^n [B]^m \qquad [3]$$

where k, the proportionality constant, is called the ***rate constant***. The concentration of the reactants is expressed in mol L^{-1}, or M.

The rate can also be determined graphically. If the concentration, or a value reflecting the concentration, is plotted

as a function of time, then an ***instantaneous rate*** can be determined at any time by taking the slope of the tangent at that time. This method is more approximate.

Order

In Equation [3], the exponents, n and m, refer to the ***order*** of the reaction with respect to the reactants [A] and [B] respectively. The sum, n + m, gives the **total order** of the reaction. The order of a reaction **must** be determined experimentally, and cannot be deduced from the stoichiometric equation of the reaction. For simple reactions, the order is usually one or two, but many chemical reactions that look simple are actually complex and the order may be fractional or inverse.

There are several methods for determining the order of a reaction. The method used in this experiment involves the measurement of the appearance of a coloured species as time progresses. The absorbance is then plotted as a function of time for different values of one of the reactants. This method may be applied to any reaction and, in its simplest form, involves the measurement of the change in rate of reaction with time.

Concept of the Experiment

At a pH of 4, when a solution of a chromium (III) salt is added to a solution containing an excess of EDTA [ethylene (dinitrilo)tetraacetate] at room temperature, no reaction appears to occur.[1] However, as time progresses, the green-grey colour of the original solution is replaced by the distinct purple colour that is characteristic of the chromium (III)-EDTA complex. Formation of the complex involves a number of slow steps, the first being first-order with respect to chromium (III) and inversely proportional to the concentration of hydrogen ion. In reality, this slow rate is unexpected given that the value for the formation constant of the complex is so high. The colour perceived is actually a mixture of several intermediates. At a wavelength of 545 nm, the complex that will be studied has the highest absorbance. Changes in the pH or the wavelength at which the measurement is made will cause the final result of the experiment to be quite different. It is interesting to note that

pH is commonly found to have an effect on the kinetics of aqueous reactions, even when the exact mechanism is unknown.

In order to ensure that the purple colour of the complex is the predominant colour perceived, the experiment will be performed under conditions where the pH ranges from 3.5 to 5.5. You will perform the same reaction with solutions at three different pH values (~4.0, ~4.5 and ~5.0) at room temperature. The results you obtain will be used to determine the partial order with respect to the Cr(III) ion.

Hypothetically, the rate expression for this reaction can be expressed in different forms, as shown:

$$Rate = -\frac{d[Cr(III)]}{dt} = +\frac{d[Cr(III)-EDTA]}{dt} = k[Cr(III)]^a[H^+]^b \qquad [4]$$

In order to simplify matters, the concentration of the EDTA is kept fairly high (0.1 M) with respect to the Cr(III) ion. The change in its concentration can thus be neglected in the rate expression, although some researchers have found that the rate was not dependent on the concentration of EDTA.

You will add a solution of Cr(III) ions to solutions of 0.1 M EDTA at three different pHs and monitor the increase in the concentration of the complex using a spectrophotometer. Since absolute rates for the reaction will not be measured, you will not need to measure concentrations or volumes exactly, nor will you need to run a blank.

Spectrophotometry

Spectrophotometry is the study of the interaction of electromagnetic radiation with matter. The two most commonly used terms when making spectrophotometric measurements are ***transmittance*** and ***absorbance***.

Transmittance is defined as the ratio of the intensity of light after it passes through the medium being studied (I) to the intensity of light before it passes through the medium (I_o).

$$T = I / I_o \qquad [5]$$

On the spectrophotometer, percent transmittance is used rather than transmittance.

$$\%T = I / I_o \times 100\% \qquad [6]$$

Absorbance is related to the transmittance as follows:

$$A = -\log T = -\log (I / I_o) \qquad [7]$$

Note that in Equation [7] it is the transmittance and not the percent transmittance that is used. Since you will be reading percent transmittance, it is necessary to convert it back to transmittance before determining the absorbance. Although most spectrophotometers have a scale for both percent transmittance and absorbance, the former is preferred. Percent transmittance is linear whereas absorbance follows a logarithmic scale. Hence it is more difficult to read the absorbance accurately on the spectrophotometer.

Spectrophotometry is an extremely powerful analytical tool that can be used to determine the concentration of fairly dilute solutions, as long as there is a species present that absorbs substantial quantities of light at a particular wavelength. Many such substances will absorb light over a range of wavelengths, but will absorb most strongly at a particular wavelength. In this experiment, the wavelength of maximum absorption is 545 nm. How, then, is the absorbance related to the concentration of the solution? The relation between absorbance and concentration is called the ***Beer-Lambert law*** and the equation for this relation is given below:

$$A = \varepsilon b c \qquad [8]$$

In this relation, A represents the absorbance, ε represents the molar absorptivity coefficient, b represents the path length and

c represents the concentration of the absorbing species in the solution. For a given substance that absorbs light, the molar absorptivity coefficient is a constant. Since you will be using the same cuvette to make all the measurements, the path length will also remain constant. Hence, Equation [8] shows that the absorbance is directly proportional to the concentration. In fact, in this experiment, we will use the absorbance value to represent the concentration of the absorbing species.

At the end of the experiment, you will heat the solution to 100°C for about 10 minutes in order to ensure that all the Cr(III) has reacted to form the coloured complex. This reading will give you a value of the absorbance at an infinite time, or A_∞. This reading represents the complete absence of Cr(III) ion, as it has all been converted to the Cr(III)-EDTA complex. We can use this value to find the amount of unreacted Cr(III) at any time according to the equation:

$$A_{Cr(III)} = A_\infty - A_t \qquad [9]$$

Thus, at time zero, we would find that we have only Cr(III) in solution and at time infinity, we would find we have no Cr(III), which is consistent with the physical reality of the experiment.

Determination of the Rate

If the values of $A_{cr(III)}$ are plotted as a function of time for the different pH values, a family of rate curves is obtained. These can be used to determine the partial order with respect to Cr(III) ion. On these plots, the instantaneous rate can be determined by taking the slope of the tangent at any point on the curve. As long as the concentration of the H^+ ion (pH) is maintained constant, only the concentration of the Cr(III) ion is changing and we should observe ***pseudo first-order kinetics***. What does this mean?

According to Equation [4], the rate of this reaction should be dependent on [Cr(III)] as well as [H^+]. However, if we change both these concentrations at the same time, it is impossible to

determine whether any observed change in the rate is due to the change in [Cr(III)], the change in [H^+] or both. An analogy can be made to an athlete who is given a new power bar that is said to provide a huge energy boost and who is also provided with a new pair of running shoes. If the athlete wears the new shoes and eats the power bar and finds that there is a dramatic increase in performance, how can it be determined whether the power bar, the shoes or both were responsible for the improvement? The best option would be to try the power bar with the old running shoes and see what improvement resulted, then to try the new running shoes with the old diet and see the change. Similarly, in this experiment, to determine the effect of the H^+ ion, we would hold the concentration of Cr(III) constant and vary the pH. Since we are not concerned with the pH as much, we will not do this particular experiment. However, in order to determine the effect of [Cr(III)] on the rate, we will observe the rate as the [Cr(III)] changes while holding the pH value constant. Irrespective of the partial order with respect to H^+ (as long as we hold the pH constant), we will find that the order of the reaction is only "a", the partial order with respect to Cr(III). If it turns out that the rate is directly proportional to the [Cr(III)], (or that a = 1), we say that the reaction is exhibiting pseudo first-order behaviour.

In Equation [4], if we hold the [H^+] constant, the rate is proportional to k and is also proportional to $[Cr(III)]^a$. Remembering that k is a constant, we can take the logarithm of both sides of the equation. Rearranging the equation and remembering log rules, we find that

$$\text{Log Rate} = a \log [Cr(III)] + \log k \qquad [10]$$

Remembering that we are using $A_{Cr(III)}$ to represent [Cr(III)], the observance of pseudo first-order kinetics can be confirmed by plotting the logarithm of $A_{Cr(III)}$ as a function of time. A linear plot will confirm that the reaction is demonstrating pseudo first-order behaviour. The instantaneous rate is that shown in

Equation [4] and is simply the rate of change of the concentration of Cr(III) with time. Since we are using the absorbance to represent the concentration, the rate of change of the absorbance of Cr(III) also gives us the instantaneous rate. Once the instantaneous rate is known, a plot of the logarithm of the rate as a function of the logarithm of the concentration of the Cr(III) ion (or of log $A_{Cr(III)}$) can be made. The slope of this plot represents the partial order with respect to Cr(III) ion (as seen in Equation [10]).

[1] Hamm, R.C., J. Am. Chem. Soc., **75**, 5670 (1953).

(TTD) Things to Do

- Complete the prelab exercises before coming to the laboratory.
- Perform a series of reactions of Cr(III) ion with EDTA at different pH values.
- Determine the absorbance of these solutions over a period of 90 minutes.
- Determine the absorbance at time infinity.
- Make plots of $A_{Cr(III)}$ vs. time for the different pH values.
- Determine the instantaneous rate on 2 of the plots and use these values to make plots of log rate vs. log $A_{cr(III)}$.
- Determine the partial order with respect to Cr(III) ion and confirm that the reaction demonstrates pseudo first-order behaviour.
- Use safe laboratory procedures at all times.

Safety Precautions

1. **Wear approved eye protection at all times**.

2. Take care not to confuse the solutions. Make sure you check the reactant you are adding before preparing the mixture.

3. The solutions are slightly acidic. Use care when working with them.

PROCEDURE

Equipment and chemicals needed

Chemicals	*Equipment*
0.1 M EDTA solution	150 mL beaker
$Cr(NO_3)_3$ solution	transfer pipet
	50 mL grad. cylinder
	2 cuvettes with lids
	thermometer
	watch glass
	spectrophotometer
	watch with seconds hand
	water bath
	ruler, pencil, graph paper

Chemical Kinetics

Starting the experiment

Preparation for the Experiment

1. Obtain approximately 50 mL of the EDTA solution in a 50 mL beaker. At your bench, measure 50 mL of the solution using the 50 mL graduated cylinder. Transfer it to the 150 mL beaker. **NOTE the volume and pH value of the solution!**

2. Obtain the dropper bottle or pipet containing the Cr(III) ion solution.

3. Prepare a water bath using tap water. The temperature should be around 22 -25°C. Choose a temperature and

ensure that the water bath REMAINS at that temperature. Record the temperature of the bath.

4. At t=0, add the Cr(III) ion solution to the EDTA (See Table 1).

5. Swirl the beaker gently until the contents are well mixed. Fill a cuvette to the mark with the mixture and place the lid on the cuvette. Place BOTH the beaker AND the cuvette in the water bath. Cover the beaker with a watch glass to keep it from tipping over. Use a test tube rack to hold the cuvette (the solution level should be about 1 cm from the top of the cuvette).

6. You will be recording the % Transmittance values every 5 minutes. About 30 s before recording your % transmittance, remove the cuvette from the water bath.

7. Wipe the outside of the cuvette with a brown paper and then wipe carefully with a Kimwipe to remove any fingerprints or grease. Hold the cuvette by the lid ONLY.

8. The demonstrators have adjusted the machines. Simply open the holder door and place the cuvette in the slot **(the line on the cuvette should be aligned with the line on the holder)**.

9. At the 5 minute mark, note the value of the % Transmittance (linear scale). Record this value and the exact time.

10. Place the cuvette back into the test tube rack in the water bath.

Moving on!

11. Repeat Steps 6-10 until t = 100-120 minutes.

12. Once you have recorded the %T value at 100 or 120 minutes, remove the cuvette from the water bath and transfer it to one of the heated water baths that your demonstrator has prepared. Allow your solution to heat in the test tube rack for about 10 minutes.

13. Remove the cuvette from the hot water bath and allow it to cool in your previous water bath.

14. Measure the % T value for this solution once it has cooled.

15. Repeat Steps 1-14 with an EDTA solution of a different pH. (NOTE: You can start one solution and prepare the second solution immediately. You can stagger the start times by about 2-3 minutes and thus do two or more reactions simultaneously.)

Almost there!

16. By the end of the experiment, you should have completed measurements for solutions at 3 different pH values (~pH 4.0, ~pH 4.5 and ~pH 5.0).

Cleaning Up!

17. Discard all solutions down the drain, rinsing with plenty of water. Rinse all glassware thoroughly and return to its proper place. Return the cuvettes to your demonstrator.

18. Remember to get your raw data, written in PEN, signed by your TA and to attach this raw data to your report in order to receive a grade!

Table 1.

pH	4.0-4.2	4.5-4.7	5.0-5.2
No. of Drops of Cr(III) solution	7	6	5

Calculations

1. Convert all measurements of %T to A using Equations [5] and [6].

2. Calculate $A_{Cr(III)}$ for all values using Equation [9].

Graphs

1. Graph $A_{Cr(III)}$ as a function of time for all the pH values on one graph paper. Use different symbols for the different pH values.

2. Plot log $A_{Cr(III)}$ as a function of time on a separate graph paper. Is the plot linear? What does this tell you?

3. Using any two curves on Graph 1, approximate the instantaneous rate for every data point on each curve. In order to do this, we will make an estimation of the slope of the tangent at each point.

   For each point, choose a small interval on your x-axis (either 4 or 6 mm - this should represent 2-3 minutes on your time scale. The smaller the interval the better, but it should be measurable and should be centred around your point.) The Δy for the instantaneous rate will be approximated by the y value of your point. The Δx for the instantaneous rate will be approximated by the interval you have chosen (in time units).

   The instantaneous rate is simply $\Delta y/\Delta x$, which we will approximate as being $\mathbf{y/\Delta x}$. REMEMBER: although the slope is normally negative, the instantaneous rate is the NEGATIVE of the change in the concentration of Cr(III) with time!!!

4. Plot log Rate as a function of log $A_{Cr(III)}$ for each of the two curves separately but on one piece of graph paper. Determine the partial order with respect to the Cr(III) ion from the slope

of the lines. What are the values? Are they the same? Do you expect them to be?

Points to Ponder

- What are the sources of error inherent in the experiment? How does each source of error contribute to the result (ie. does it increase or decrease the value of the rate?)

- How important are volume and temperature measurements in this experiment? Why?

- Did you feel your data was reproducible?

- Why can we use the approximation that we make in Calculations 3? Justify it using your knowledge of kinetics…

- Can you make any predictions (guesses) as to the partial order with respect to the hydrogen ion? What information did you use to make this prediction?

Lab Report

- *Refer to page iii in the FYI section and the lab report section in experiment 1.*

- Make sure that your graphs occupy the majority of the graph paper, and that the graphs are titled, the axes are clearly labelled and the scale is appropriate. Overall, you should have 3 graphs.

- **ALL graphs must be made on millimetre x millimetre graph paper!!**