

SYNTHESIS & ANALYSIS OF A COMPLEX IRON SALT

INTRODUCTION

Transition metal ions react with charged or neutral **ligands, L**, (e.g. Cl^- or H_2O) to form **complex ions**. Iron in the +3 oxidation state can form **octahedral complexes** with up to 6 unidentate ligands surrounding a central metal ion (Figure 1). The ligands act as **Lewis bases**, donating at least one pair of electrons to the Fe^{3+} ion. Oxalate ion, $\text{C}_2\text{O}_4^{2-}$, acts as a **chelating bidentate ligand**, donating 2 electron pairs from 2 oxygen atoms to the transition metal center, Fe^{3+} (Figure 2). During the first week of this experiment a coordination compound with the formula $\text{K}_x\text{Fe}_y(\text{C}_2\text{O}_4)_z \cdot n\text{H}_2\text{O}$ will be synthesized. A **coordination compound** typically contains a *complex ion* (with ligands bound to a central metal cation), counter ions, and, sometimes, waters of hydration. During the second week the empirical formula of the coordination compound will be determined (i.e., the values of x, y, z, and n) by redox titration and gravimetric analysis.

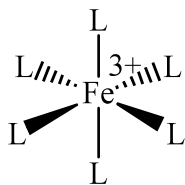


Figure 1. Octahedral Fe^{3+} complex surrounded by unidentate ligands, L (e.g., Cl^- , NO_2^- , H_2O , or NH_3). Each L donates 1 e^- lone pair forming a bond to Fe^{3+} .

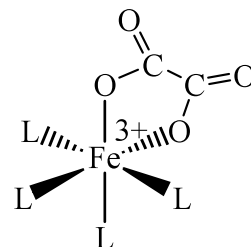


Figure 2. Octahedral Fe^{3+} complex with 1 bidentate oxalate ligand, $\text{C}_2\text{O}_4^{2-}$, which donates 2 e^- lone pairs to form 2 bonds.

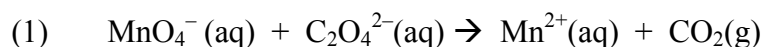
The first week synthesis of the iron complex begins with Mohr's salt: $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The salt is dissolved in water and the solution is kept at a low pH by addition of sulfuric acid to prevent the formation of rust colored iron oxides and hydroxides. Oxalate ions are added in the form of oxalic acid and potassium oxalate. The oxalate will replace some or all of the water and sulfate ligands coordinated to the iron (II) ion and a yellow solid forms. The bright yellow precipitate is filtered from solution, washed to remove impurities, and treated with 3% hydrogen peroxide to *oxidize* the iron to the +3 state. Although the solution is heated slightly to increase

the rate of oxidation, the addition of peroxide is done slowly to prevent the heat sensitive peroxide from decomposing before reacting with all of the iron (II) in solution. All the Fe^{2+} must be oxidized to Fe^{3+} . Complex ions that form with the Fe^{3+} have a different number of oxalate groups than those that form with Fe^{2+} . Empirical formula determination is difficult with a mixture of the two complex ions.

At this point, the Fe^{3+} complex ion combines with a potassium counter ion leading to the formation of the coordination compound: $\text{K}_x\text{Fe}_y(\text{C}_2\text{O}_4)_z \cdot n\text{H}_2\text{O}$. Since this salt is less soluble in alcohol than in water, 95% ethanol is added to the solution and a green crystalline solid begins to precipitate from solution within 2-3 days. The solution must be stored in the dark during crystallization because visible light will reduce Fe^{3+} to Fe^{2+} .

During the second week, the crystallized salt will be analyzed to determine the mass percent of oxalate ion. Additional data will be provided to calculate the mass percent of iron, water and potassium so the empirical formula can be determined.

The mass percent oxalate ion in the salt will be determined by titration with a standardized KMnO_4 solution according to the unbalanced reaction below:

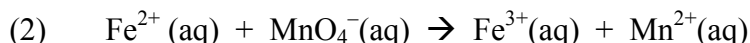


Since aqueous solutions of permanganate ion are not stable over a long period of time, the exact concentration of KMnO_4 must be determined by titration with a known amount of a primary standard salt such as sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$. After KMnO_4 has been standardized, the complex iron salt can be titrated to determine its oxalate content. The solutions containing $\text{C}_2\text{O}_4^{2-}$ and Mn^{2+} ion are colorless; the MnO_4^- solution is a deep purple color. Therefore, the titrated solution will remain colorless until all the oxalate salt is consumed in the reaction. The endpoint corresponds to the appearance of the first permanent pink color due to the presence of excess unreacted permanganate ion. The rate of the reaction is very slow at room temperature so the solution must be heated to 80°C to observe the color change in "real time". Often, at the beginning of the titration, the purple color of the KMnO_4 does not disappear for 30-60 seconds because the reaction has an intermediate that must form before the reaction goes to completion.

In redox titrations, solvent impurities act as reducing or oxidizing agents requiring the addition of more titrant. To correct for this a **blank** containing only the solvent must be titrated. The "corrected volume" is equal to the volume of KMnO_4^- required to titrate oxalate ion in solvent minus the volume required to titrate the solvent alone. (Important note: The amount needed to titrate the blank is often only one or two drops of KMnO_4^- .)

The ferric ion, Fe^{3+} , is released into solution when permanganate ion reacts with oxalate ion and destroys the complex ion. The liberated Fe^{3+} ion is reddish colored and can interfere with observation of the faint pink titration endpoint. To eliminate the color interference, a small amount of concentrated phosphoric acid is added to the solution. The phosphate ion reacts with Fe^{3+} to yield a colorless complex ion, $\text{Fe}(\text{PO}_4)_2^{3-}$, eliminating the reddish-brown color of Fe^{3+} from solution.

To determine the mass percent of iron, Fe(III) must first be reduced to Fe(II) by exposure to sunlight or by reaction with Al metal. The resulting Fe^{2+} ion is then titrated with a standardized KMnO_4 solution according to the unbalanced equation below:



The mass percent of water is determined by gravimetric analysis. A known mass of the complex salt containing water is weighed, heated and reweighed. The weight of water is the mass difference between the hydrous and anhydrous forms of the salt.

The mass percent of potassium in the salt is determined by difference using the experimentally determined masses of iron, oxalate and water and the mass of the complex iron salt.

SAFETY PRECAUTIONS

Safety goggles, aprons, and gloves must be worn in lab at all times. **Oxalate** is very toxic via oral and inhalation routes and severe kidney damage is possible if oxalate salts are taken internally. Oxalate compounds can be absorbed through the skin; wear gloves and wash affected areas with cold water. 6 M **sulfuric acid** is very corrosive and can cause severe burns. Wear gloves when handling these compounds and wash any affected areas thoroughly with cold water. **Ethanol** and **acetone** are flammable and harmful by inhalation, ingestion, and when in contact with skin. Any container holding either liquid should be capped when not in use to prevent evaporation of the solvents, as they are harmful when inhaled. Ethanol/acetone solutions must be placed in appropriate waste bottles and can NEVER be poured down the drain. **H₂SO₄** and concentrated **H₃PO₄** are corrosive acids; wash all affected areas thoroughly with cold water. Acetone and alcohol are flammable reagents; extinguish any open flames or spark sources in the lab. **KMnO₄** is a very strong oxidizing agent; do NOT pour any permanganate solutions into the ORGANIC collection bottles. Permanganate solutions can stain skin and clothing. Report all spills, accidents, or injuries to your TA.

Before starting the experiment, the TA will ask you to do a quick demonstration or talk-through one of the following:

- 1) How to use the heating and stirring on a hot plate? What does a stir bar look like?
- 2) Titration: How to properly fill a buret?
- 3) Titration: How to read the volume amount on a buret?
- 4) How to reduce the sodium bisulfite?
- 5) How to neutralize the solution?

Make sure you watch the videos on the course website and read the documents to prepare. These demonstrations will be done every week. Everyone will have presented at least one topic by the end of the quarter. The demonstrations should be short (>1 min) and will be graded.

PROCEDURE***Week 1:******Part A. Gravimetric Analysis of $K_xFe_y(C_2O_4)_z \cdot nH_2O$***

Using a grease pen or labeling tape, put your name on a scintillation vial. Measure and record its mass. Obtain ~0.100 g of $K_xFe_y(C_2O_4)_z \cdot nH_2O$ that was made by students in a previous quarter. Record the exact mass and appearance of the crystals. Place the container with crystals in the oven for at least one hour. Carefully remove from the oven and place in a desiccator until cooled to room temperature and then record the mass. If the mass continues to decrease, place the container with crystals back in the desiccator.

Part B. Synthesis of $K_xFe_y(C_2O_4)_z \cdot nH_2O$

Work in pairs and in the fume hood. *Safety goggles, aprons, and gloves must be worn in lab at all times.* Place ~2.5 grams of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 10 mL of DI water, and a stir bar in a 100-mL Erlenmeyer flask. Add 2-3 drops of 6M H_2SO_4 and warm the mixture gently to dissolve the iron salt. Stir in 13 mL of 1M $H_2C_2O_4$ and gently heat in a water bath the mixture to its boiling point. A thick yellow precipitate of iron (II) oxalate, FeC_2O_4 , should form. **STIR CONTINUOUSLY WHILE HEATING GENTLY** to prevent splattering. (Caution - uneven heating can also cause the beaker to crack or break.)

Filter the yellow solid from solution. Wash the solid with two separate 8-mL portions of hot DI water to remove the impurities. Pour the acidic filtered liquid and washings into the appropriate waste container in the hood. Scrape the yellow solid from the filter paper back into the small, 100-mL flask and add 5 mL of 2M $K_2C_2O_4$ solution. Heat gently to 40°C in a water bath. Then **SLOWLY ADD** 9 mL of 3% H_2O_2 while stirring the mixture continuously. A reddish-brown precipitate of iron (III) oxide (rust) may appear.

Heat the mixture to boiling on a hot plate in a water bath and add 3 mL of 1M $H_2C_2O_4$ rapidly while stirring. Add an **ADDITIONAL** 1-mL of 1 M $H_2C_2O_4$ **SLOWLY** in a dropwise fashion. A clear green solution should result. If the solution does not turn green or if solid particles are still present, add a few additional drops of 1M $H_2C_2O_4$. Filter if necessary. Remove the solution from the hot plate and cool. Add 5 mL of 95% ethanol to the cooled clear green solution. If a solid appears, dissolve it by gently warming the mixture on a hot plate **IN THE**

HOOD.

Use masking tape and label a plastic container with your name, date, TA's name and contents ($K_xFe_y(C_2O_4)_z \cdot nH_2O$ in ethanol). Transfer the solution to the container, cover it, and give it to your TA to store in a dark locker for your next lab period. The light-sensitive complex will crystallize from solution in a few days.

(Note: If you were not able to synthesize the complex iron salt in a previous experiment you should skip part A and go to part C. Borrow crystals from a labmate.)

Week 2:

Part C: Preparation of the Dried Salt

Use vacuum filtration to separate the crystals from solution. Wash the green crystals in the Buchner funnel with small quantities of 1:1 (by volume) ethanol and water solution and follow with small amounts of acetone to remove impurities and excess oxalate ion. Dry the crystals by continuing to draw air through the filter cake in the funnel for about 10 minutes. Pour the green alcohol/acetone filtrate solution into the waste bottles. After taking the mass of the dried green crystals, transfer them to a scintillation vial wrapped with Al foil (to avoid slow decomposition of the complex iron salt caused by exposure to light). Label the scintillation vial with your name, date, contents ($K_xFe_y(C_2O_4)_z \cdot nH_2O$), and mass.

Standardization of $KMnO_4$ Solution. Done by the Stockroom.

Record the mass of $Na_2C_2O_4$ and the volume of $KMnO_4$ solution from the label on the $KMnO_4$ solution; you will need it for your post-lab calculations.

The procedures followed by the stockroom personnel: An acidic solution of sodium oxalate ($Na_2C_2O_4$) was prepared by dissolving ~0.100 g of $Na_2C_2O_4$ in 150 mL of 1.0 M H_2SO_4 in a 250 mL Erlenmeyer flask. The resulting solution was heated to 80°C and then titrated with the ~ 30 mL of $KMnO_4$ solution until the first appearance of a permanent faint pink color. A "blank" containing 150 mL of 1.0 M H_2SO_4 was also titrated. After titration was completed, the titrated solutions and remaining $KMnO_4$ were neutralized according to the instructions in

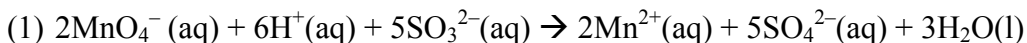
Part D.

Part D: Analysis of Oxalate Ion in the Complex Iron Salt

(Do not begin part D until all the green filtrate solutions from Part C have been removed from the lab by the stockroom staff.) Weigh approximately 0.1 g of the complex iron salt and record its mass to the milligram. Dissolve the salt in 10-mL of 6 M H₂SO₄ in a small beaker. Pour the acid solution carefully into 75 mL of DI water in a 250 mL Erlenmeyer flask and add 1-mL of concentrated H₃PO₄. Heat the solution to 80°C, stirring gently with a magnetic stir bar. Titrate the heated solution with KMnO₄ until the appearance of the first permanent faint pink color, recording the initial and final volumes of KMnO₄ used. *Repeat this titration at 2-3 more times.* Perform a blank titration on the same volumes of DI water, 6M H₂SO₄ and concentrated H₃PO₄ used to titrate the iron salt. When finished, pour all titrated solutions and any KMnO₄ remaining in your buret into a 1000 mL beaker. Rinse the buret and buret tip with a small amount of DI water and add the rinse water to the beaker. No pink color should be left in the buret when finished.

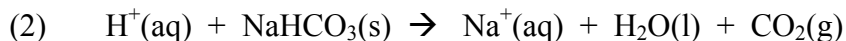
Part E: Reducing the Solution

IN THE HOOD, slowly mix sodium bisulfite (NaHSO₃) *solution* into the beaker containing the titrated solutions and leftover KMnO₄ until the mixture turns clear and colorless (3). Do not go on to the next step until the solution is completely colorless!



Part F: Neutralizing the Solution

The colorless mixture will be very acidic. To neutralize it, place about ½ inch of *solid* NaHCO₃ in the bottom of a clean 1000 mL beaker, add water until it barely covers the NaHCO₃, stir to make a slurry. Now slowly pour the solution from the first 1000 mL beaker into the bicarbonate slurry and stir. When foaming stops, check the solution with pH paper. If pH = 7, pour the neutralized solution into a collection bottle in the hood. If the pH of the solution is less than 7, prepare a new slurry and neutralize the solution again in the same manner.



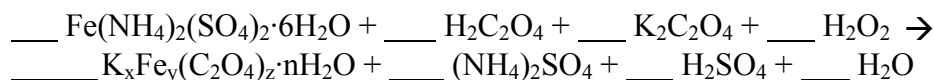
Be sure to clean your lab table, glassware and buret thoroughly before leaving lab. Return the test tube containing unused crystals to the TA before leaving lab.

CALCULATIONS

1. Determine the KMnO_4 concentration from the mass of $\text{Na}_2\text{C}_2\text{O}_4$ and volume of KMnO_4 solution used by the stockroom in standardization.
2. Using the standardized concentration of KMnO_4 and your own data from Part D, calculate the mass percent of oxalate ion in the complex iron salt. For the calculations below, you may average the mass percents or use the result that gives the most reasonable result.
3. Find the mass percent of water in the complex iron salt using the data from Part A.
4. Because of time constraints, the following data has been collected for you. In a previous experiment, 0.800 g of the green complex iron salt was placed in an Erlenmeyer flask and heated with concentrated sulfuric acid until all oxalate ion was destroyed (CO_2 , SO_2 and H_2O are formed). Ferric ion (Fe^{3+}) remained in solution and was reduced to Fe^{2+} by reaction with Al wire. The ferrous ion (Fe^{2+}) was then titrated with KMnO_4 solution according to equation (2) and 32.60 mL of 0.0100 M permanganate solution was required to reach the endpoint. The blank required 0.03 mL of the permanganate solution. Find the mass % of iron in the complex salt.
5. With the mass percent of Fe, oxalate ion, and water (calculated above); find the mass percent of potassium ion in the complex iron salt by difference.
6. From your data, find the empirical formula of the complex iron salt, $\text{K}_x\text{Fe}_y(\text{C}_2\text{O}_4)_z \cdot n\text{H}_2\text{O}$ using the mass percent of potassium, iron, oxalate and water.

7. For the empirical formula found in the question above, determine if the cationic and anionic charge balance to give a neutral ionic compound. If the empirical formula does not, suggest a new empirical formula based on the iron salt being neutral and having the iron to oxalate ratio used in the Computational Study assignment. (Note: You will not be able to determine the value of “n”.)

8. Insert the values from the question above for x, y, z, & n into $K_xFe_y(C_2O_4)_z \cdot nH_2O$ and provide the correct coefficients to balance the following equation:



(*Hint:* Remember H_2O_2 , an oxidizing agent, was used in the synthesis, so you’ll need to do a redox balance. Start with just the iron ions, balance the reaction, and then add the full formulas.)

9. Using the balanced equation just found and the mass of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ recorded at the beginning of last week’s experiment determine the percent yield of $K_xFe_y(C_2O_4)_z \cdot nH_2O$.

10. If you had to suggest a new empirical formula explain the possible errors that may have occurred using the following questions as a guide. (Not every question necessarily needs to be answered. You just need to indicate where the error was made, what kind of error it was, and how it could be avoided in the future.)

- What modifications could be made to the procedure to better account for random (indeterminate) errors?
- List three potential systematic (instrumental, methodological, or personal) errors that could be made in this experiment. (Note: Be specific, systematic errors are in the details. For example, losing your solution because you knocked over the cuvette is not a systematic error – it’s a gross one.)
- Did any gross errors occur? Did you mess up? Did the equipment or instrumentation fail?