The Synthesis of an Iron Oxalato Complex Salt

(The Student Friendly Version)

Introduction: In this experiment you will synthesize a compound that will contain the elements potassium, iron, carbon, hydrogen, and oxygen. Carbon and oxygen will be present in the form of oxalate ($C_2O_4^{-2}$) whereas hydrogen and oxygen will be present as H_2O. The final product may be given the following formula:

$$K_wFe_x(C_2O_4)_y \bullet \mathbf{z}\ H_2O$$

Your job is to synthesize the compound and then determine the simplest formula (find w, x, y, and z) using a variety of analytical techniques.

Experiment #1 – Synthesis of Complex

Purpose: In this experiment you will react an aqueous solution containing aqueous iron (III) chloride with an aqueous solution containing excess $K_2C_2O_4$ to produce the crystal $K_wFe_x(C_2O_4)_y \bullet \mathbf{z}\ H_2O$.

$$\mathbf{w}\ K^+(aq) + \mathbf{x}\ Fe^{+3}(aq) + \mathbf{y}\ C_2O_4^{-2}(aq) + \mathbf{z}\ H_2O(l). \rightarrow K_wFe_x(C_2O_4)_y \bullet \mathbf{z}\ H_2O(s)$$

Procedure:

- Obtain, in a clean 50mL beaker, 8.00 mL of stock solution containing 0.400 g $FeCl_3$/mL.
- Weigh 12.0 to 12.5g $K_2C_2O_4 \bullet H_2O$ into a clean dry 50 mL beaker. Add 20 mL of DI water to dissolve the $K_2C_2O_4 \bullet H_2O$. Heat on hot plate stirring constantly until all the $K_2C_2O_4 \bullet H_2O$ is completely dissolved.
- Carefully pour the hot solution into the beaker containing the $FeCl_3$ and stir. At this point, a green color should be detected.
- Cool the solution. Leave the beaker in a refrigerator over night. Crystals should form during this time.
- After giving the crystals ample time to form, carefully pour off (decant) and discard the solvent without removing any crystals.
- Filter the crystals by vacuum filtration using a Buchner funnel and a clean filter flask.
- Wash the crystals twice with ice water. Use less than 5 mL for each wash and work quickly to avoid the dissolving of your product with the wash water. Finally wash the crystals twice with 5 mL portions of acetone.
- Spread the crystals out in the bottom of a clean dry vial and store it in a dark spot.
- (NOTE: You need to have produced at least 3.5g or crystals to complete the series of experiments. Be sure to check your yield at this point to ensure you have enough. If not, repeat procedure above and synthesize more.)
- Let crystals dry overnight before continuing with experiment.

Experiment #2 – Preparation and Standardization of $KMnO_4$

Purpose: Potassium permanganate is a relatively inexpensive, intensely colored compound commonly used in laboratories as a powerful oxidizing agent. In this experiment, a 0.010 M $KMnO_4$ will be prepared. The $KMnO_4$ will be titrated against a known concentration of $C_2O_4^{-2}$ in order to standardize it (find the exact molarity). The following equation represents the titration you will be performing:

$$MnO_4^{-1} + C_2O_4^{-2} \rightarrow CO_2 + Mn^{+2}$$ (keep in mind this is an UNBALANCED equation)

In a later experiment, you will use the standardized $KMnO_4$ solution to determine the % oxalate in your crystal.
So why do we standardize the $KMnO_4$? The $KMnO_4$ we purchase from our chemical sources is not 100% pure, so we need to standardize it to determine how much MnO_4^{-1} is actually in our stock solution.

Procedure:

Preparation of $KMnO_4$

- Calculate the mass of $KMnO_4$ required to prepare 250 mL of a 0.010 M solution. Using a balance that measures to the 0.001g, weigh out the $KMnO_4$. Record the mass you use on your data table.
- Using distilled water, carefully transfer the $KMnO_4$ crystals into a 250 mL volumetric. Be sure to rinse off the weighing paper well to ensure the transfer of ALL crystals to the volumetric.
- Add DI water to bring the solution level to the calibration mark on the flask neck.
- Hold the stopper in place and mix the flask contents by inverting the flask and returning it to upright position at least 10 times.
- Transfer to an appropriate reagent bottle as indicated by your instructor. Be sure to rinse the bottle with three very small portions of $KMnO_4$ (1-2 ml each) before the transfer. Label the bottle with your period, table number, and your initials. Store out of the light or wrap bottle in foil.

Standardization of $KMnO_4$

- Preweigh between 0.12 and 0.13 g $Na_2C_2O_4$. Record the amount of $Na_2C_2O_4$ to the 0.001g. Be sure to transfer this value to your data table.
- Carefully transfer the $Na_2C_2O_4$ to a clean (but OK if it is wet) 250 mL beaker or erlenmeyer. Use a total of 50 mL of DI water to make the transfer, using a little bit of water at a time.
- Once all the $Na_2C_2O_4$ and the 50mL of water are in the flask/beaker add 6 mL of 6M sulfuric acid.
- Heat the solution in the flask to just below the boiling point and begin the titration at this temperature.
- While your solution is heating, rinse a clean buret a 3 times with a few mLs of $KMnO_4$. Expel any air trapped in the tip and take in initial buret reading. Record in data table.
- Titrate the warm solution to the first appearance of a faint pink that persists for about 30 seconds. If the temperature drops to less than 60℃, reheat until about 70 ℃ and add more $KMnO_4$ if necessary to reach the equivalence point. Record final volume.
- Repeat the procedure twice more with 2 other samples of $Na_2C_2O_4$.

- Once complete, immediately rinse out the burets with water numerous times. Do not leave the $KMnO_4$ in the buret for longer than one class period. It will stain the glass of the buret. If you find your burets are stained after the procedure, let your instructor know.

- If you need to finish your titrations at a later time, be sure to do so within two days because the $KMnO_4$ needs to be fresh for consistent results.

- Label your $KMnO_4$ bottle with the average molarity in your calculated results. Save and store the $KMnO_4$ for use in a future experiment.

Data for Experiment #2 – Preparation and Standardization of 0.010 M $KMnO_4$

I. Preparation of $KMnO_4$

Mass of $KMnO_4$ used _____

Volume of solution prepared _____

Apparent molarity based on mass of $KMnO_4$ used _____

II. Titration Results (data w/ ★ to be collected in the lab)

		1	2	3
1.	Trial number			
2.	Mass of $Na_2C_2O_4$ ★	_____	_____	_____
3.	Moles of $Na_2C_2O_4$	_____	_____	_____
4.	Moles of $C_2O_4^{-2}$	_____	_____	_____
5.	Mole ratio of $C_2O_4^{-2}$ / MnO_4^{-1} (found in balanced equation)	_____		
6.	Moles of MnO_4^{-1}	_____	_____	_____
7.	Initial buret reading ★	_____	_____	_____
8.	Final buret reading ★	_____	_____	_____
9.	Volume of $KMnO_4$ used	_____	_____	_____
10.	Molarity of $KMnO_4$ *	_____	_____	_____
11.	Average Molarity of $KMnO_4$ *	_____		
12.	Average Molarity of $KMnO_4$ (+/- 2δ)	_____		

III. Purity of Solid $KMnO_4$

13. Calculated avg. # grams of $KMnO_4$ in 250mL of sample _____
(Use the avg. molarity from step 11 to make determination)

14. Grams of $KMnO_4$ in original 250 ml (see above) _____

15. Percent purity (step13/ step 14 x 100) _____

Experiment #3 – Determination of % $C_2O_4^{-2}$ in $K_wFe_x(C_2O_4)_y \cdot z\ H_2O$

Purpose: The % oxalate will be determined by titrating a solution of known mass of the green crystals you synthesized with the 0.010 M $KMnO_4$ prepared and standardized in experiment #2. The mass and % of oxalate in a sample can be determined by using the volume of $KMnO_4$ to calculate the moles of $KMnO_4$ leading to the moles of $C_2O_4^{-2}$ which then can be converted to grams of $C_2O_4^{-2}$. Knowing the original mass of green crystals used, you can then determine mass % of $C_2O_4^{-2}$.

Procedure:

- Weigh your green crystals to the nearest 0.0001g so it falls somewhere between 0.120g and 0.130g. Record in your data table.
- Carefully transfer the measured crystals to a labeled flask for titrating. Use a total of 50mL of water in the transfer as you have done before.
- Add 6 mL of 6M sulfuric acid to your sample.
- Free iron ions can cause problems in detecting the proper equivalence point color, so add 1 mL of 85% phosphoric acid to the sample.
- Heat the solution to just below the boiling point as you did in the last experiment.
- While the solution is heating, rinse a clean buret with 3 small portions of your standardized $KMnO_4$. Fill the buret , expel air bubbles, and take an initial buret reading. Record in data table.
- Remove the flask from the heat source and titrate.
- Titrate the warm solution to the first appearance of a faint pink that persists for about 30 seconds. If the temperature drops to less than 60℃, reheat until about 70 ℃ and add more $KMnO_4$ if necessary to reach the equivalence point. Record final volume.
- Repeat the procedure again with another green crystal sample.
- Once complete, immediately rinse out the burets with water numerous times. Do not leave the $KMnO_4$ in the buret for longer than one class period. It will stain the glass of the buret. If you find your burets are stained after the procedure, let your instructor know.

Data for Experiment #3 – Determination of % $C_2O_4^{-2}$ in $K_wFe_x(C_2O_4)_y \cdot z\,H_2O$

Molarity of standardized $KMnO_4$ _____

Trial #	1	2
1. Mass of sample	_____	_____
2. Initial buret reading	_____	_____
3. Final buret reading	_____	_____
4. mL $KMnO_4$ required	_____	_____
5. moles of $KMnO_4$ added	_____	_____
6. Mole ratio of $C_2O_4^{-2}$ / MnO_4^{-1} (found in balanced equation)	_____	
7. Moles of $C_2O_4^{-2}$ in sample	_____	_____
8. Mass of $C_2O_4^{-2}$ in sample	_____	_____
9. Percent of $C_2O_4^{-2}$ in sample	_____	_____
10. Average percent $C_2O_4^{-2}$	_____	

Experiment #4 – Standardization of NaOH

Purpose:
Since solid NaOH rapidly absorbs both H_2O and CO_2,, a solution of exact molarity cannot be prepared by weighing the solid and diluting to volume. Instead you must prepare a solution of approximately the desired concentration, and find its exact concentration by titrating it against a standard substance. The standardized NaOH will then be used in experiment #5 to determine %K and Fe in your crystal.

Procedure:

Preparation and Standardization of approximately 0.10 M NaOH

- Clean a 0.5 L bottle and rinse with distilled water.
- Measure approximately 2.0 g of NaOH, and dilute to about 0.5 liter with freshly distilled water and mix well.
- Obtain a sample of KHP(short for $KHC_8H_4O_4$) which has been dried in an oven and stored in a desiccator, and use a sensitive balance to accurately weigh 0.4 to 0.6 g onto a piece of waxed weighing paper. Wash the KHP into an Erlenmeyer flask using distilled water from a wash bottle. Add about 40 mL of distilled water and swirl until completely dissolved.
- Clean a buret, rinse with a small amount of distilled water, and three times with small portions (about 7 mL) of your NaOH solution, and then fill the buret with your NaOH solution. Open the stopcock briefly and allow the solution to fill the buret tip.
- Add 3 drops of phenolphthalein solution to the acid in the flask and then titrate with the NaOH solution until the first trace of pink color persists for 15 seconds. Remember to constantly swirl the flask, and to rinse the walls of the flask with water before you reach the end point. Record the volume of NaOH used, estimating to the nearest 0.01 mL.
- Repeat two more times. If you use slightly more acid each time, the second and third titrations will be much more rapid than the first because you will know how much NaOH you can safely add before you get close to the end point.
- Calculate the molarity of your NaOH solution.

Data for Exp. #4 – Determination Standardization of 0.10M NaOH

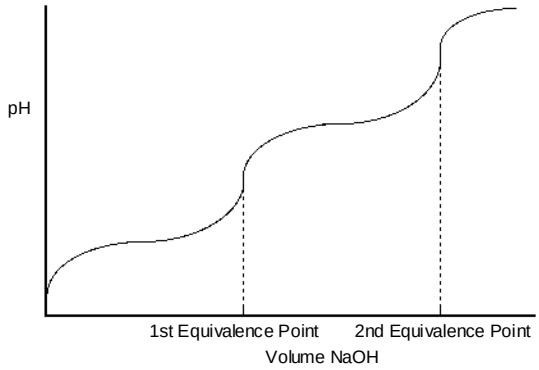
	Trial 1	Trial 2	Trial 3
mass of KHP	_____	_____	_____
moles of KHP = Moles H^+	_____	_____	_____
initial volume of NaOH	_____	_____	_____
final volume of NaOH	_____	_____	_____
volume of NaOH added	_____	_____	_____
moles of NaOH present	_____	_____	_____
concentration of NaOH (M)	_____	_____	_____
average concentration		_____	
2 standard deviations (2σ)		_____	

(If a titration falls out of the +/- 2σ range, drop that value and re-average. Be sure to indicate any drop of data in your lab report with a justification.)

Experiment #5 – Determination of the % of Potassium and Iron in $K_wFe_x(C_2O_4)_y \bullet z\ H_2O$ by Ion Exchange Chromatography

Purpose: This experiment involves determining both the % K and % Fe in a single titration after passing a solution containing a known mass of the complex salt down an ion exchange column.

Theory: As you run your sample through the column as indicated in the procedure below, the column will exchange out any +1 charged ion with a H^{+1} ion from its resin. Since K^{+1} is the only +1 ion in our crystal, we know that for every H^{+1} collected out of the column into our beaker, we left one K^{+1} behind. Therefore, the number of moles of H^{+1} in the beaker is equal to the number of moles of K^{+1} in the sample. Not only does, the H^{+1} run through the column, but so does the Fe^{+3}. Since Fe^{+3} is not attracted to this particular column NO exchange will occur there. The amount of H^{+1} and Fe^{+3} can be quantified by a titration with 0.1000 M NaOH creating a titration curve similar to the one pictured below.



Two titrimetric end points are obtained: the first after the addition of V1 mL of NaOH, and the second after the V2 mLs have been added. The first endpoint represents the complete neutralization of the H^{+1} and the second the completion of the precipitation of iron (III) hydroxide. Thus, V1 converted to liters represents the OH^{-1} necessary to neutralize the H^{+1} and V2-V1 converted to liters represents the OH^{-1} necessary to completely precipitate the $Fe(OH)_3$.

Procedure:

Column Separation

(be careful…you only have one shot at this)

- Turn the knob on the base of the column and let <u>one</u> drop out onto a piece of blue litmus paper and then close. Do NOT let the water level drop below that of the resin. (That would be VERY VERY bad.) Make sure your column pH is NOT acidic. Let your instructor know if that is the case.
- Weigh out about 0.16 g of your green salt to the nearest 0.0001 g in a 50mL beaker. Don't let the sample mass exceed 0.1650 g. Record the mass in your data table.
- Using a small graduated cylinder, measure out 4 mL of DI water and add this to the green salt. Swirl until all the salt is dissolved.
- Place a clean dry 150 mL collecting beaker under the ion exchange column and transfer your dissolved salt to the column. Open column and let run until the water level is just above the resin layer.
- Rinse the beaker you just emptied with 4 more mL of distilled water. Empty those contents into the column. Open column and again let run into collecting beaker until the water level is just above the resin layer.
- Repeat this procedure with 2 more 4mL water rinses.

Titration

You only get ONE shot at this so don't mess up! (No pressure-hee hee)

PROCEDURE

1. Obtain and wear goggles.

2 Place the beaker on a magnetic stirrer and add a stirring bar. If no magnetic stirrer is available, you need to stir with a stirring rod during the titration.

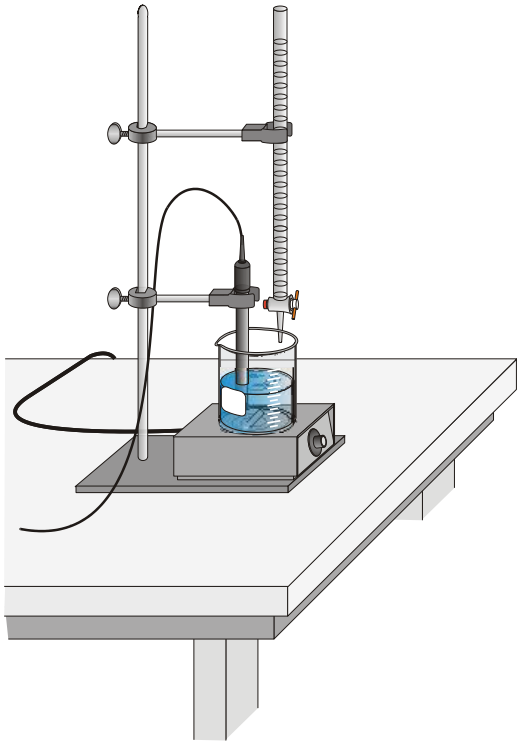


Figure 2

3. Connect the pH Sensor to LabQuest and choose New from the File menu. If you have an older sensor that does not auto-ID, manually set up the sensor.

4. Use a utility clamp to suspend a pH Sensor on a ring stand as shown in Figure 2. Position the pH electrode in the diprotic acid solution and adjust its position toward the outside of the beaker so that it is not struck by the stirring bar.

5. Obtain a 50 mL buret and rinse the buret with a few mL of the ~0.1 M NaOH solution. Use a utility clamp to attach the buret to the ring stand as shown in Figure 2. Fill the buret a little above the 0.00 mL level of the buret. Drain a small amount of NaOH solution so it fills the buret tip *and* leaves the NaOH at the 0.00 mL level of the buret. Dispose of the waste solution in this step as directed by your teacher. **CAUTION:** *Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing.*

6. Set up the data-collection mode.

   a. On the Meter screen, tap Mode. Change the data-collection mode to Events with Entry.
   b. Enter the Name (Volume) and Units (mL). Select OK.

7. You are now ready to perform the titration. This process goes faster if one person manipulates and reads the buret while another person operates enters volumes.
   a. Start data collection.
   b. Before you have added any drops of NaOH solution, tap Keep and enter **0** as the buret volume in mL (using the numerical keyboard displayed on the screen). Select OK to store the first data pair for this experiment.
   c. Add the next increment of NaOH titrant (enough to raise the pH about 0.20 units). When the pH stabilizes, tap Keep and enter the current buret reading (to the nearest 0.01 mL). Select OK. You have now saved the second data pair for the experiment.
   d. Continue adding NaOH solution in increments that raise the pH by about 0.15 units and enter the buret reading after each increment. Your teacher will give you a clue as to the number of mLs at both equivalence points.
   e. Continue adding small increments until the pH no longer changes.

8. Stop data collection.

9. Examine the data on the displayed graph of pH *vs.* volume to find the *equivalence points*—that is the largest increase in pH upon the addition of 1 drop of NaOH solution. To examine the data pairs on the displayed graph, tap any data point. As you tap each data point, the pH and volume values are displayed to the right of the graph.

   Record the mL value at each equivalence point.

10. Dispose of the beaker contents as directed by your teacher. Rinse the pH Sensor and return it to the pH storage solution.

11. Clean your buret and invert. Clean and put all equipment back where it belongs.

Data for Exp. #5 – Determination of the % of Potassium and Iron in $K_wFe_x(C_2O_4)_y \cdot z\ H_2O$

1. Standardized Molarity of NaOH _____
2. Mass of Crystal Sample _____
3. V1 (Volume of NaOH required to reach 1st equivalence point) _____
4. Moles of NaOH _____
5. Moles of OH^- _____
6. Moles of H^+ _____
7. Moles of K^+ _____
8. Grams of K^+ _____
9. % K^+ in sample _____
10. V2 (Volume of NaOH required to reach 2nd equivalence point) _____
11. V2 - V1 (Volume of NaOH that reacted with Fe+3) _____
12. Moles of NaOH _____
13. Moles of OH^- _____
14. Moles of Fe^{+3} (YIKES…watch the mole ratio!) _____
15. Grams of Fe^{+3} _____
16. % Fe^{+3} in sample _____

Experiment #6 – Determination of % Water in $K_wFe_x(C_2O_4)_y \bullet z\ H_2O$

Purpose: In the next experiment you will determine the % water in the green crystal you produced. A hydrate contains water chemically bound in the solid state so that it is present in the compound in stoichiometric amounts. The percentage water will be determined by heating a weighed sample of the hydrate in an open container until all the water of hydration has been driven off. The loss in weight is equal to the mass of the water of hydration.

Therefore: % water of hydration = Mass lost/Mass of original x 100%

Procedure:

- Weigh 2 labeled evaporating dishes to the nearest 0.0001g.
- Add about 1g of your crystals to each of the dishes. Record the final mass of each dish after the addition of the crystal.
- Put both dishes in the oven overnight at about 110°C.
- The next day let cool in dessicator .
- Once cooled, weigh both dishes and record final weight.

Data for Exp. #6 – Determination of the % of Water $K_wFe_x(C_2O_4)_y \bullet z\ H_2O$

Sample #	1	2
1. Mass of dish and sample before heating	_____	_____
2. Mass of dish alone	_____	_____
3. Mass of unheated sample (#1-#2)	_____	_____
4. Mass of dish and sample after heating	_____	_____
5. Mass of water that left (#1-#4)	_____	_____
6. % of Water in Sample (#5/#3 x 100)	_____	_____

Final Calculations:

	K	Fe	$C_2O_4^{-2}$	H_2O
Percents				
Grams **(Assume 100 total)**				
moles				
moles/by smallest # of moles				
smallest mole ratio				

Final formula for the Crystal: