Experiment 1

Synthesis of an Iron Coordination Complex

Introduction:

The compound to be prepared is $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$. Its correct name is potassium tris(oxalato)ferrate(III) trihydrate. The components of this compound are K^+, Fe^{3+}, $C_2O_4^{2-}$, and H_2O. The ion $C_2O_4^{2-}$ is called the oxalate ion, and since there are three $C_2O_4^{2-}$ in the formula above, and iron is in the 3^+ state (indicated by the Roman numeral III), the complex ion in the square brackets has a 3^- charge, and thus three K^+ are required to balance the charge.

Preparation of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$:

During the first laboratory period, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ will be prepared. Ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$, is dissolved in a slightly acid solution, excess oxalic acid, $H_2C_2O_4$, is added, and the following reaction takes place:

$$Fe(NH_4)_2(SO_4)_2\cdot 6H_2O + H_2C_2O_4 \;=\; FeC_2O_4(s) + H_2SO_4 + (NH_4)_2SO_4 + 6H_2O(l) \qquad \text{Eq. 1}$$

FeC_2O_4 is a finely divided precipitate and tends to be colloidal. However, heating the solution causes it to coagulate and facilitates separating the precipitate from the solution.

Potassium oxalate is added to the FeC_2O_4 precipitate which produces a slightly basic solution for the oxidation of the ferrous ion to the ferric ion by hydrogen peroxide, H_2O_2. The following reaction takes place:

$$\begin{array}{lcll}
2Fe^{2+} & = & 2Fe^{3+} + 2e^- & (2e^-\text{ "lost"}) \\
H_2O + HO_2^- + 2e^- & = & 3OH^- & (2e^-\text{ "gained"}) \\
\hline
H_2O + HO_2^- + 2Fe^{2+} & = & 2Fe^{3+} + 3OH^- & (\text{net reaction}) \quad \text{Eq. 2}
\end{array}$$

Note that the FeC_2O_4 is the source of the Fe^{2+} in Equation 2.

The OH^- ion concentration of the solution is high enough so that some of the Fe^{3+} reacts with OH^- to form ferric hydroxide (brown precipitate) as follows:

$$Fe^{3+} + 3OH^- = Fe(OH)_3(s) \qquad \text{Eq. 3}$$

With the addition of more $H_2C_2O_4$, the $Fe(OH)_3$ dissolves and the soluble complex $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ is formed according to:

$$3K_2C_2O_4 + 2Fe(OH)_3(s) + 3H_2C_2O_4 = 2K_3[Fe(C_2O_4)_3]\cdot 3H_2O + 3H_2O \qquad \text{Eq. 4}$$

Alcohol is added to the solution to cause the complex iron salt to precipitate since it is less soluble in alcohol than in water.

The complexity of the series of reactions described in equations 1 - 4 may be greatly simplified by following the Fe^{2+}/Fe^{3+} ion throughout. One discovers that for every mole of $Fe(NH_4)_2(SO_4)_2]\cdot 6H_2O$ used as starting material, one mole of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ will be obtained as the final product.

$Fe(NH_4)_2(SO_4)_4\cdot 6H_2O + H_2C_2O_4$	=	FeC_2O_4 + ...etc.	(see Eq. 1)	($Fe^{2+} = Fe^{2+}$)
$FeC_2O_4 + K_2C_2O_4 + H_2O_2$	=	$Fe(OH)_3(s)$ + ...etc	(see Eq. 2 & 3)	($Fe^{2+} = Fe^{3+}$)
$Fe(OH)_3 + H_2O_2 + K_2C_2O_4$	=	$K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ + ..etc	(see Eq. 4)	($Fe^{3+} = Fe^{3+}$)

Experimental Procedure

Severe bumping can occur during the preparation of this complex, particularly in step 2.

Preparation of $K_3[Fe(C_2O_4)_3]\cdot3H_2O$:

The following is a generic procedure to synthesize the iron coordination complex. In your notebook you should write-up a procedure using a similar format that records the exact steps that you did in making your complex. You should record the quantities and volumes of the reagents that you used and not those given in the generic procedure below.

1. Using a top-loading balance, weigh about 5g of $Fe(NH_4)_2(SO_4)_2\cdot6H_2O$ in a 125-mL Erlenmeyer flask and record this weight on your data sheet. Dissolve this compound in 15mL distilled water and add 4-5 drops of 3M H_2SO_4.

2. Add 50mL ~0.5M $H_2C_2O_4$ to this solution and heat to boiling while stirring constantly to prevent bumping.

3. Remove the Erlenmeyer flask from the heat and allow the yellow precipitate of FeC_2O_4 to settle. Decant the supernatant liquid (pour the liquid away from the solid) and wash the precipitate using 20mL of hot distilled water. Swirl the mixture and allow the precipitate to settle; decant and repeat the washing once more.

4. Add 20mL of ~1M $K_2C_2O_4$ to the flask containing the precipitate, stir and heat to 40°C. While the temperature is at 40°C, *immediately* add 10mL of 6% H_2O_2 dropwise and stir continuously. Periodically check the temperature of the solution and make sure that it is at least 40°C (but not >50°C) during the addition of H_2O_2. (Some brown $Fe(OH)_3$ may precipitate at this time.)

5. Heat the resulting solution to boiling. Obtain 20mL of ~0.5M $H_2C_2O_4$ and add ~5mL of it all at once to the boiling solution. Stir continuously and add the last few mL dropwise while maintaining the temperature near boiling. The solution should turn clear green. If some brown residue remains, add an additional 1mL of $H_2C_2O_4$ dropwise, again while the solution is boiling, until the solution is clear green. However, if the residue that remains is yellow, it is probably unreacted FeC_2O_4, and more H_2O_2 should be added carefully. Consult your TA.

6. If the solution is cloudy, gravity filter it into a clean 125-mL Erlenmeyer. If it is clear, no filtration is necessary. Then, while swirling *constantly*, slowly add 15mL ethanol to the solution. Allow to cool, while an ice bath is prepared in a 400 mL beaker. Immerse the bottom portion of the flask in the ice bath and stir slowly until crystals begin to form. Stop stirring and allow the solution to stand in the ice bath for 20 minutes. A good crop of crystals should have formed before the solution is filtered. (Consult your TA if you are doubtful about quantity.)

7. Prepare a vacuum filtration apparatus.

8. Decant the supernatant liquid away from the green crystals which have formed in the flask and temporarily save the liquid in a beaker if the yield seems low. Consult with your TA before discarding this solution. With the aid of a glass rod, transfer the crystals to the Buchner funnel and apply suction for about 2 minutes.

9. Stop the suction and add 10mL of a 1:1 ethanol/water solution. Wait about 30 seconds and then apply suction for 2 minutes. Repeat this washing process. After this final wash, allow the suction to continue for a further two minutes.

10. Transfer the crystals to a ***preweighed**, labeled* dry sample vial. Discard the wash solutions.

Some Useful Molar Masses

$K_2C_2O_4$: 166.2 g.mol^{-1}

$Fe(NH_4)_2(SO_4)_2\cdot6H_2O$: 392.1 g.mol^{-1}

$K_3[Fe(C_2O_4)_3]\cdot3H_2O$: 491.1 g.mol^{-1}