

Oxalate complexes of iron



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In coordination chemistry there are different types of ligands. Monodentate ligands donate only one lone pair to the metal ion. Bidentate ligands donate two pairs of electrons such as the oxalate ligands which can bind at two sites with the metal ion, thus a coordination number of three ligands around one metal ion. Oxalate has four oxygens with each having a lone pair but it only uses two lone pairs to form a coordination compound. There are also multidentate ligands such as the EDTA which donate more than two pairs of electrons. Oxalate is can be regarded as a chelating agent. This means that two or more bonds are being broken so that the ligand would be separated from the metal. These chelating ligands provide more stability to the complex than those with monodentate ligands. 1

The potassium trioxalatoferrate (III) trihydrate and the iron (II) oxalate have a stereochemistry of an octahedral. The oxalate ion is a weak field ligand according to the spectrochemical series. The Fe^{2+} has 6 electron in its d orbitals while Fe^{3+} would have 5 electrons. The unpaired electrons of the iron (III) would have a high spin and so behave paramagnetically.

Fe^{2+} and Fe^{3+} electrons can either distribute themselves either in a low spin or a high spin arrangement.

An example of the arrangement which is more favoured according to Hund's rule

3d 4s 4p

3d 4s 4p

Iron can accept 6 pairs of electrons because the orbitals are hybridised in a way to produce 6 orbitals of equal energy.

A redox titration is a type of reaction which is based on redox equations between the analyte and the titrant. Reduction-oxidation reactions are reactions where one of the component is being oxidized such as iron (II) to iron (III) thus becoming more positively charged while the other is being reduced thus it is gaining electrons and will become less positive in its nature.

Potassium permanganate has the formula of MnO_4^- which can be reduced to Mn^{2+} in reducing conditions. This is an oxidizing agent.

In this experiment the iron (II) oxalate and potassium trioxalatoferrate(III) trihydrate were analysed. Then these two salts were analyzed for their iron and oxalate content and also the empirical formula of each salt was determined.

Apparatus: Pasteur pipette, weighing boat, spatula, watch glass, measuring cylinder stirring rod, Buchner funnel, stopper, heating mantle, balance, beakers, thermometer, filter paper, ice-salt bath, flasks.

Chemicals:

Chemical

Brand

Grade

Ferrous ammonium sulfate

GPR

Aldrich

Oxalic acid dihydrate

GPR

N/A

2M sulphuric acid

GPR

BDH

Acetone

GPR

BDH

Iron(II) oxalate

GPR

N/A

Potassium oxalate monohydrate

GPR

BDH

Hydrogen peroxide

GPR

BDH

Ethanol

GPR

BDH

Potassium permanganate

GPR

BDH

Zinc

GPR

Carlo Erba

Method:

Experiment A: Preparation of Iron(II) Oxalate

15g of ferrous ammonium sulphate were dissolved in 50cm³ of warm water which has been acidified with 2M sulphuric acid (1cm³).

75cm³ of 10% oxalic acid solution was added with rapid stirring. The mixture was heated gently to the boiling point and then the yellow precipitate of ferrous oxalate was allowed to settle.

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The precipitate was removed by filtration on a Buchner funnel.

It was washed thoroughly with hot water and then with acetone.

The product was allowed to dry on the funnel under suction and weighed.

The product was used for the next section.

Experiment B: Preparation of potassium trioxalatoferrate(III)Trihydrate

3. 25g of ferrous oxalate was suspended in a warm solution of potassium oxalate (5g in 15cm³ water.

15cm³ of 20vol hydrogen peroxide was added from a burette whilst the solution was stirred continuously and maintained at 40°C. The solution contained the precipitate of ferric hydroxide.

This was removed by heating the solution to boiling.

10cm³ of 10% oxalic acid and then a further small amount of oxalic acid was added dropwise until the precipitate just dissolved.

During the addition of oxalic acid, the solution was maintained near the boiling point.

The hot solution was filtered.

15cm³ of ethanol was added to the filtrate, any crystals that were formed by gentle heating were re-dissolved and put in a dark cupboard to crystallise.

The crystals were collected by filtration on a Buchner funnel.

These were washed with an equivolume mixture of ethanol and water and finally with acetone.

This was dried, weighed and the product kept in the dark.

Experiment C: The analysis of the products for iron and oxalate

Iron(II) oxalate

0.3g of oxalate was dissolved in 25cm³ of 2M sulphuric acid. The solution was heated to 60°C and titrated with 0.02M standard potassium permanganate solution until the first permanent pink colour was observed.

2g of zinc dust were added to the solution and boiled for 25 minutes.

It was filtered through the glass wall and the residual was washed with 2M sulphuric acid.

The washings were added to the filtrate and this was titrated with a solution of standard potassium permanganate

The percentages of iron, oxalate, water of crystallisation in the product and the empirical formula were determined.

Potassium trioxalateoferrate(III) trihydrate

0.2g of the complex were dissolved in 25cm³ 2M sulphuric acid. This was titrated with 0.02M standard potassium permanganate solution until the first permanent pink colour was observed.

2g of zinc dust were added to the solution and boiled for 25 minutes.

This was filtered through a glass wool and the residual was washed with 2M sulphuric acid.

The washings were added to the filtrate and this was titrated with a solution of standard potassium permanganate.

The percentage of iron and oxalate in the complex was determined.

These were compared to the theoretical values.

Results:

Experiment A:

Ferrous oxalate: 7. 478g

Experiment B

Potassium oxalate: 5. 058g

Potassium trioxalatoferrate(III) hydrate: 6. 019g

Ferrous oxalate: 3. 273g

Experiment C:

Iron oxalate: 0. 301g

Volume of potassium permanganate

Initial

Final

Titre value

Volume of potassium permanganate after adding zinc

Initial

Final

Titre value

Potassium trioxalatoferrate(III) trihydrate: 0. 200g

Volume of potassium permanganate

Initial

Final

Titre value

Volume of potassium permanganate after adding zinc

Initial

Final

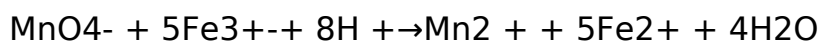
Titre value

Calculation:

Iron(II) oxalate

Iron(II) and oxalate is oxidized by permanganate to Iron(III) and carbon dioxide

Iron(III) is reduced by zinc to Iron(II)

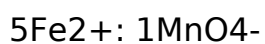


Iron

$$0.02 \text{ moles} = 1000 \text{ cm}^3$$

$$? 17.2 \text{ cm}^3$$

$$3.44 \times 10^{-4} \text{ moles}$$

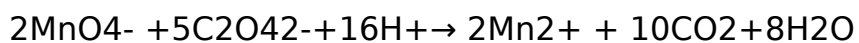


$$1.72 \times 10^{-3} : 3.44 \times 10^{-4} \text{ moles}$$

$$1 \text{ mole} = 56 \text{ g}$$

$$1.72 \times 10^{-3} \text{ moles} = ? 0.096 \text{ g}$$

Oxalate

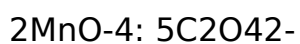


$$52.4 \text{ cm}^3 - 17.2 \text{ cm}^3 = 35.2 \text{ cm}^3$$

$$0.02 \text{ moles} = 1000 \text{ cm}^3$$

$$? 35.2 \text{ cm}^3$$

$$7.04 \times 10^{-4} \text{ moles}$$



$$7.04 \times 10^{-4} : 1.76 \times 10^{-3}$$

1mole= 88g

1. 76×10^{-3} moles = ? 0.155g

Empirical formula

$0.096\text{g} + 0.155\text{g} = 0.251\text{g}$

$0.301\text{g} - 0.251\text{g} = 0.05\text{g}$

1mole= 18g

? = 0.05g

2. 78×10^{-3} moles

1.72×10^{-3} moles 1.76×10^{-3} moles 2.78×10^{-3} moles

1.72×10^{-3} moles 1.72×10^{-3} moles 1.72×10^{-3} moles

1 1.02 ~ 1 1.6 ~ 2

FeC₂O₄. 2H₂O

% of iron, oxalate and water of crystallisation in Iron(II) oxalate

Theoretical

Fe C₂O₄ 2H₂O

56g 88g 36g

180g 180g 18

31% 49% 20%

Experimented

Fe C₂O₄ 2H₂O

0.096g 0.155g 0.05g

0.301g 0.301g 0.301g

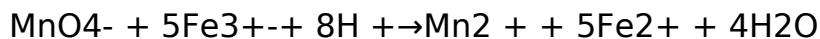
31.89% 51.5% 16.6%

Potassium trioxalatoferrate(III) trihydrate

Oxalate is oxidized by permanganate to carbon dioxide

Iron(III) is reduced by zinc to Iron(II)

Iron



0.02 moles = 1000 cm³

? 4.1 cm³

8.2 × 10⁻⁵ moles

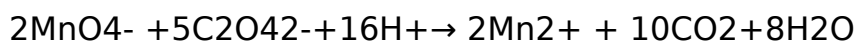
5Fe²⁺: 1MnO₄⁻

4.1 × 10⁻⁴ moles: 8.2 × 10⁻⁵ moles

1 mole = 56g

4.1 × 10⁻⁴ moles = 0.023g

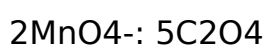
Oxalate



0.02 moles = 1000 cm³

? 26.4 cm³

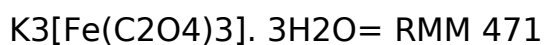
5.28 × 10⁻⁴ moles



5.28 × 10⁻⁴ : 1.32 × 10⁻³ moles

1 mole = 88g

1.32 × 10⁻³ moles = ? 0.116g



% of iron and oxalate in potassium trioxalatoferrate(III) trihydrate

Theoretical



120 56 264 36

471 471 471 471

25.48% 11.9% 56% 7.64%

Experimented



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0. 023 0. 116

0. 2 0. 2

11. 5% of iron in potassium trioxalatoferrate(III) trihydrate 58% of oxalate in potassium trioxalatoferrate(III) trihydrate

Precautions:

The crystals were scraped from the filter paper which could lead to inaccurate filtration.

The temperature of the solution was kept above 60°C during the titration of iron oxalate against potassium permanganate.

Titration apparatus was washed accordingly; Pipette and burette were washed first with water and then with the solution. Flasks were washed with water only.

It was made sure that the burette was not leaky since it would affect the final result.

The product of potassium trioxalatoferrate(III) trihydrate was put in a dark cupboard since it is photosensitive causing loss of product.

A heating mantle was used instead of a bunsen burner because ethanol is flammable.

When the ethanol was added to the filtrate in part B the solution was left to cool down since if the ethanol was added to the hot filtrate the ethanol could have evaporated.

Sources of error:

Glassware that was not calibrated properly could be a source of error

The crystals were not dried completely and so would lead to higher weight.

Loss of the product due to transferring from the balance to the flask, due to air currents and unsteady movements.

The color of the end point could be misleading as different people have different sensitivity to colors.

Hydrogen peroxide could decompose in light and so the oxidation of iron (II) and iron (III) would not be completed.

Permanganate solution when allowed to stand in burette can undergo partial decomposition to MnO₂.

Difficult in seeing the measurements on the burette because of the dark violet produced by the permanganate solution

Ferric ion is reddish brown which could have interfered with the observation of the faint pink titration endpoint.

Discussion:

Preparation of iron(II) oxalate

When oxalic acid is added to the mixture of ferrous ammonium sulphate in water and acidified with 2M of sulphuric acid, ions would form in solution.

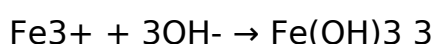
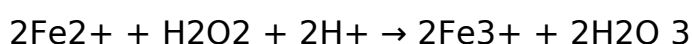


When adding oxalic acid to the solution oxalate ion forms which then reacts with the iron(II) forming the iron(II) oxalic acid which is the product. This is the yellow precipitate which is removed by precipitation on a Buchner funnel. It is then washed with water and acetone to remove impurities.



Preparation of Potassium Trioxalatoferrate(III) Trihydrate

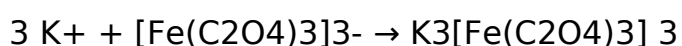
When potassium oxalate is added to the ferrous oxalate an orange intermediate complex would be formed. During the preparation of Potassium trioxalatoferrate (III) trihydrate the iron(II) in the iron(II) oxalate have to be oxidized to Iron(III). This is done by an oxidizing agent which in this case hydrogen peroxide is used. A brown precipitate of Iron(III) hydroxide would form



This could be removed by excess heating. 10% oxalic acid was added and so the oxalate ion could coordinate around the iron(III) metal forming a complex of $\text{Fe}(\text{C}_2\text{O}_4)_3$. A green solution would form in this stage. The following net equation would take place converting the iron(III) oxalate to trioxalatoferrate(III) ion.



The trioxalatoferrate(III) salt is soluble in water and would not precipitate out from an aqueous solution. Ethanol which is a less polar than water is added so that the salt would precipitate out since it is less soluble in ethanol. The precipitation is added by leaving the mixture overnight so that the salt would precipitate. This is placed in the dark because light would reduce the Iron(III) to Iron(II)



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Analysis of the products for iron and oxalate

In the last part of the experiment the percentage of iron, oxalate and water of crystallisation was found by titration of the iron(II) oxalate with potassium permanganate which is the titrant. The volume of potassium permanganate needed to react with the known volume of analyte was found. The titration was marked when a faint pink colour appeared. This is the Mn^{2+} which serves as its own indicator to show when the titration is ready. In the first part the oxalate and iron(II) are both oxidized to Iron(III) and carbon dioxide. Zinc is added which acts as a reducing agent which reduces the iron(III) back to iron(II).

When titrating the potassium permanganate with the potassium trioxalatoferrate(III) trihydrate salt, a faint pink colour is observed when the stoichiometric point has been reached thus titration would be completed. In the first part the oxalate only is oxidized to carbon dioxide since iron(III) is

already in its oxidized form. When zinc dust is added to the Iron (III) it is reduced to its reduced form iron(II).

The solution would remain colourless until all the oxalate salt is used. The solution is heated to 60°C since if the reaction takes place at room temperature it would be too slow.

The oxidation of the oxalate anion which is an organic chelating agent, does not take place very easily. In the presence of a metal ion, the rate of reaction increases since the oxidation would be kinetically more favourable when forming an intermediate metal chelate. In this experiment this type of intermediate had formed during the conversion of the oxalate ion to carbon dioxide by the permanganate ion. The permanganate ion is reduced to a lower oxidation state by taking an electron from the oxalate and so the carbon carbon bond in the oxalate is broken forming carbon dioxide.

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From the results one could observe that the percentages of iron and oxalate in the theoretical yield which are 31% and 49% respectively are quite comparable to those percentages of the theoretical which are 31.89% and 51.5%. The theoretical percentage were brought by comparing the iron and oxalate to the RMM of the iron (II) oxalate. The theoretical % of water of crystallisation in this compound is 20% which resulted to be in close proximity to the experimented value that of 16.6%. When working the empirical formula of the oxalate iron an approximation was taken and so it was not very accurate. The ratio of 1.02 was rounded to 1 and the ratio of 1.

6 was rounded to 2 for the water of crystallisation in the salt to result in the empirical formula of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

When working the percentages of iron and oxalate in the potassium trioxalatoferrate(III) trihydrate the percentages were also very near to the theoretical value since the % of iron in the salt is 11.9% when working the theoretical and the experimented values were worked to be 11.5%. On the other hand, theoretically 56% of the trioxalatoferrate(III) trihydrate is oxalate and 58% oxalate in experimented value.

Conclusion:

One can conclude that the aims were reached. The preparation of these two compounds was done so that in the end the percentage of both iron oxalate in the iron(II) oxalate and the potassium trioxalatoferrate(III) trihydrate would be determined. The theoretical percentage of iron and oxalate of the theoretical were approximately very near those that were determined experimentally. The empirical formula of the iron(II)oxalate was also found to be $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$