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Title: determination of the percentage of oxalate in iron (II) oxalate by redox titration

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Objective: to find out the percentage of oxalate in iron (II) oxalate by redox titration.

Introduction

Potassium manganate (VII) is not suitable for use as a primary standard as its solution decimoises in solution, especially in sunlight, and readuky oxidizes organic matter. Moreover, brown deposits of manganese (IV) oxide are often present in its solution. In fact, potassium manganate (VII), being not a primary standard, is usually standardized by standard solution of sodium thiosulphate.

Permanganate ion, MnO_4(aq), is a strong oxidant. Since permanganate ion is intensely coloured and its reduction product, $Mn2^+$(aq), is almost colourless, a self-indicating titration is possible. The addition of the first drop of permanganate solution in excess imparts a pink colour to the solution.

Potassium manganate(VII) reacts quantitatively with many reducing agents. Oxalates are readily determined by titration with standard potassium manganate (VII) in warm acidic solution: $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

In strongly acidic medium, permanganate undergoes a 5 electrons reduction to manganese(II) ion: MnO_4(aq) $+ 8H^+$(aq) $+ 5e^- \rightarrow Mn2^+$(aq) $+ 4H_2O$(aq)

Potassium permanganate does not oxides oxalates in cold solution. A temperature of about 70ºC is necessary to cause the reaction to occur rapidly.

If coloured or oxidized cations are present, the procedure will be more complicated. In this experiment, iron (II) ions in fact also participate in the redox reaction: $Fe^{2+} \rightarrow Fe^{3+} + e^-$
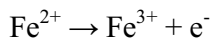
Procedures

1) Plastic bag with iron (II) oxalate crystal was provided.
2) The weigh of the plastic bag with crystal was taken.
3) Iron (II) oxalate crystal inside the plastic bag was put into a beaker.
4) The weigh of the plastic bag without crystal was taken.
5) About 150 cm^3 of 2M sulphuric acid was added to the beaker.
6) The reaction mixture was warmed over a heating machine with stirring until all the iron (II) oxalate crystal was dissolved and the solution became clear.
7) The reaction mixture was cooled to room temperature.
8) The reaction mixture was and washing were transferred to a 250 cm^3 volumetric flask.
9) The reaction mixture was diluted by adding distilled water to the graduation mark of the volumetric flask.

10) The volumetric flask was inverted for ten times to make sure that the solutions inside were well mixed.

11) 10 cm^3 of the diluted reaction mixture was transferred to a 250 cm^3 conical flask by a pipette.

12) The burette was filled with standard potassium manganate (VII) solution.

13) The initial reading on the burette was recorded.

14) The reaction mixture inside the conical flask was warmed over a heating machine to about 60°C before titration.

15) A few drops of standard potassium manganate (VII) solution was run out from the burette to the solution inside the conical flask with constant swirling until the solution became clear..

16) Standard potassium manganate (VII) solution was run out from the burette to the solution inside the conical flask until the solution change from pale yellow to permangent pale pink.

17) The final reading on the burette was recorded.

Data of results

Titration table of iron (II) oxalate solution against standard 0.02007M potassium manganate (VII) solution

	Trial	1st titration	2nd titration	3rd titration
Initial reading on the burette	6.7 cm^3	13.3 cm^3	10.1 cm^3	11.2 cm^3
Final reading on the burette	24.3 cm^3	30.6 cm^3	27.4 cm^3	28.5 cm^3
Volume of potassium manganate (VII)used	17.6 cm^3	17.3 cm^3	17.3 cm^3	17.3 cm^3

Average volume of potassium manganate (VII) solution used
= 17.3 cm^3
17.6 cm^{3}is rejected because this is just a trial.

Mass of plastic bag with iron (II) oxalate crystal is 3.773g
Mass of plastic bag without iron (II) oxalate crystal is 1.141g
Mass of iron (II) oxalate crystal = 3.773g – 1.141g
$$= 2.632g$$

Calculation

Percentage by mass of FeC_2O_4 in the sample

The equation of the reaction:

$3MnO_4^- + 24H^+ + 5FeC_2O_4 \rightarrow 3Mn^{2+} + 10CO_2 + 5Fe^{3+} + 12H_2O$

As 17.3 cm^3 of MnO_4^- is used,

no. of mole of $MnO_4^- = 0.02007$ x (17.3 ÷ 1000)

$= 0.000347211$ mol.

Mole ratio of MnO_4^- to $FeC_2O_4 = 3:5$

No. of mole of FeC_2O_4 (10 cm^3) = 0.000578685 mol.

No. of mole of FeC_2O_4 (250cm^3) = 0.000578685 x 25

$= 0.014467125$ mol.

Molar mass of $FeC_2O_4 = 143.8$

Mass of FeC_2O_4 in the sample = 143.8 x 0.014467125

$= 2.080372575$ g

Percentage by mass of FeC_2O_4 in the sample = (2.080372575 ÷ 2.632) x 100 %

$= 79.0$ %

Percentage of oxalate in the sample

Molar mass of $FeC_2O_4 = 143.8$

Molar mass of $C_2O_4 = 88$

Percentage of oxalate in the sample predicted from the formula:

$= (88 ÷ 143.8)$ x 100% = 61.2%

Mass of FeC_2O_4 in the sample = 88 x 0.014467125 = 1.273107g

Calculated percentage of oxalate in the sample = (1.273107 ÷ 2.632) x 100%

$= 48.4\%$

The chemical formula of the hydrated iron (II) oxalate

We assume all the impurity in the sample are water of crystallization, then the water of crystallization by mass in the compound is 21% and the chemical formula of hydrated iron (II) oxalate is known to be $FeC_2O_4。xH_2O$

Relative formula mass of $FeC_2O_4。xH_2O = 55.8 + 12x2 + 16x4 + (1x2 + 16)x$

$= 143.8 + 18\ x$

Relative molecular mass of water of crystallization = $18x$

$18x ÷ (143.8 + 18x) = 21 ÷ 100$

$1800x = 3019.8 + 378x$

$1422x = 3019.8$

$x = 2.124$

≈ 2

Therefore, the chemical formula of the hydrated iron (II) oxalate is $FeC_2O_4。2H_2O$.

Conclusion

The percentage of oxalate in iron (II) oxalate is 48.4% which is smaller than the predicted one.

Discussion

Precaution

1) Handle potassium permanganate with great care because it is toxic and irritation to skin

2) Handle manganese (IV) oxide with great care because it can cause serious eye injury, is a skin and inhalation irritant, and can be fatal if swallowed

Sources of error

1) KMnO4 is too reactive that light may induce the decomposition of KMnO4. It may lead to the error in accurate determination of the concentration of oxalate.

2) We may read the reading on the burette inaccurately as the deep color of permanganate makes the burette reading very difficult.

3) The iron (II) oxalate may not be warm enough to react with the potassium permanganate

Questions

1) Is the in iron (II) oxalate hydrated or anhydrous?

The iron (II) oxalate crystals is hydrated as we found that the percentage by mass of iron (II) oxalate in the sample is not one hundred percent, then there may be water of crystallization inside it.

2) The potassium manganate (VII) solution which filled the burette is deep in colour, then how to read the reading on the burette?

Put a finger or a piece of white paper behind the reading of the burette.

Study Questions

1) Why is it unnecessary to use redox indicator in this titration?

Permanganate ion is deep purple in colour, while other soluble manganese ion is different colour, like pale red or green. This titration gives an sharp end-point because the solution in the conical flask change from colourless to permanent pink at the end point due to the present of magnate (II) ions. Therefore redox indicator which gives a sharp end-point to the titration is unnecessary in this titration.

2) In this titration, no brown precipitate should appear in the conical flask. If it does, what would you do? Explain why you should do so.

The present of brown precipitate is due to the present of manganese (IV) oxide MnO_2. In the lack of acid, the reaction become

$3Fe^{2+} + MnO_4^- + 4H^+ \rightarrow 3Fe^{3+} + MnO_2 + 2H_2O$
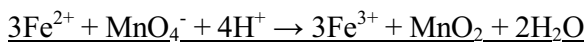
We can therefore add more sulphuric acid to the reaction mixture to dissolve manganese (IV) oxide and than reheat the solution.

3) It is suggested that the mixture in the flask must be thoroughly shaken during the titration. Explain.

The mixture in the conical flask must be thoroughly shaken during the titration to make sure that the solutions inside the flask are homogenous. Also to make sure that the pink colour discharged is permanent.

4) It is suggested that if the temperature of the oxalate solution fails appreciably during the titration, further heating will be necessary. What would happen if heating is insufficient?

Potassium manganate (VII) does not oxidize oxalates in cold solution. A temperature of about 70ºC is necessary to provide the activation energy for the reaction to proceed and to cause the reaction to occur rapidly.

5) Pipetting of 10 cm^3 of the oxalate solution must be done with special care. Why?

Iron (II) is not so stable. It will be oxidized by oxygen in air to give iron (III). If transferring of oxalate solution is not carried out immediately, Fe^{2+} will oxidized by oxygen in air to give Fe^{3+}.

6) The pink colour of potassium permanganate may not be immediately discharged in the initial stages of the titration. Why?

In the initial stage of the titration, only a small amount of Mn^{2+} is formed, therefore the pink colour of is covered by the large amount of green Fe^{2+} in the reaction mixture and we cannot see the pink colour in the initial stages of the titration. On the other hand, the reaction between MnO_4^- and FeC_2O_4 is slow and Mn^{2+} formed in the reaction mixture acts as a catalyst in the reaction. In the initial stages of the titration, only a small amount of Mn^{2+} is formed, therefore the reaction is slow and the Mn^{2+} is discharged at a slow rate and the colour of Mn^{2+} is covered by the green Fe^{2+}.

7) You are given a standard solution of potassium iodate, some solid potassium iodide, a bottle of dilute sulphuric acid and some starch indicator. Describe briefly how you could standardize a solution of sodium thiosulphate. You may assume that all common titration apparatus is available.

We can standardize sodium thiosulphate solution through titration of iodine with thiosulphate, therefore we need to prepare a standard iodine solution.

A standard iodine solution cannot be prepared directly by accurately weighing a certain amount of iodine, but it can be prepared by dissolving a known amount of pure potassium iodate solid into an acidic medium containing excess iodide.

We first dissolve weighed amount of KI into dilute sulphuric acid. The number of mole of it should be at least 5 times that of potassium iodate. After adding potassium iodate solution into acidified KI, iodine would be formed. Just use a small portion of the mixture and titrate with thiosulphate solution until the brown color nearly fade, then add starch solution and continue to titrate until the mixture becomes colourless. If Potassium iodate is in excess rather than KI, a slight addtion of KI to the resulting mixture would form a brown to dark brown mixture indicating that I_2 is formed.

End of Report