

Iron compounds in two oxidation states

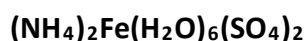
A. Syntheses

Iron(II) and iron(III) as their hexaaqua complex ions are part of two series of so-called double salts:

The alums have the general formula $M(I)M(III)(H_2O)_6(SO_4)_2 \cdot 6H_2O$, where M(I) is a not too small cation like K^+ or NH_4^+ and M(III) is a not too big cation like Al^{3+} , Ga^{3+} , V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} and Co^{3+} .

The Tutton salts have the general formula $M(I)_2M(II)(H_2O)_6(SO_4)_2$, typically with the same M(I) cations and the M(II) cations being Mg^{2+} , V^{2+} , Fe^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} .

Here the ammonium salts in both series are prepared with iron in its two typical oxidation states as sources of pure hexaaqua ions.



1. A tiny little of commercial iron(II) sulphate heptahydrate is dissolved in 2 dr. of hydrochloric acid (0.1 M) and to the solution is added 1 dr. of potassium thiocyanate (1 M) and 5 dr. of 3-methylbutanol. An impure compound gives a red upper layer.
2. 5 g of commercial iron(II) sulphate heptahydrate is dissolved in an absolute minimum of water (appr. 25 ml) at room temperature and 0.5 g of pure iron-powder is added, followed by as much concentrated sulphuric acid (18 M) as to make the solution 0.5 M in sulphuric acid. After a couple of minutes the excess iron is removed with a magnetic rod (teflon) - if necessary the solution is filtered (use filtering paper). To the filtrate is slowly added an equal volume ethanol while stirring. The crystals are separated using a glass filter funnel and is finally washed with ethanol.
3. The purified iron(II) sulphate is dissolved in 10 ml of slightly acidified (with sulphuric acid) water which has been boiled to remove air and then cooled to 60 °C. 2.5 g of ammonium sulphate is added and the temperature kept at 60 °C while it dissolves. The solution is then left at room temperature (or a little less). The crystals are separated by filtration and washed by covering them by a thin layer of ice-cold water, which is sucked off as far as possible. The moist crystals are dried in the air. A little of the moist product is dissolved in a few drops of hydrochloric acid (0.1 M) and to the solution is added 1 dr. of potassium thiocyanate (1 M) and 5 dr. of 3-methylbutanol. A pure compound gives a colourless upper layer.
4. Record mass of dry product: _____ g
Calculate the yield (in % of theoretically possible) _____ %

$\text{NH}_4\text{Fe}(\text{H}_2\text{O})_6(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

- 12 g of commercial iron(II) sulphate heptahydrate is dissolved in 25 ml of boiling sulphuric acid (1 M). In the fume cupboard 2.5 ml of concentrated nitric acid (14 M) is added dropwise and the mixture is slowly heated with stirring on a hot plate until boiling. Heating is continued until a lively redox reaction is observed. The solution should in the end be yellow.
- To 1 dr. of the solution is added 10 dr. of water and 1 dr. of potassium hexacyanoferrate(III) (0.1 M). A blue colour indicates the presence of iron(II). If iron(II) is detected another 1 ml portion of concentrated nitric acid is added and the solution heated and test for iron(II) performed as before.
- With the oxidation complete, the solution is boiled for additional 5 minutes and 3.5 g of ammonium sulphate is added. The total volume is adjusted with water to around 30 ml and the solution is left for slow crystallisation at 5°C. The crystals are separated by filtration and washed by covering them by a thin layer of ice-cold water, which is sucked off as far as possible. The moist crystals are carefully wiped with tissue and further dried in the air.
- Record mass of dry wiped _____ and product: _____ g
Calculate the yield (in % of theoretically possible) _____ %

B. Redox potentials

Objectives: Conditions of electrochemical measurements with electrodes. Standard potential as a function of ligand.

- Record the temperature.
 - Prepare stock solutions from dry solids:
 - 100 ml 0.01 M solution of hexaaquairon(II) (freshly prepared from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)
 - 100 ml 0.01 M solution of hexaaquairon(III) in 0.10 M in nitric acid (freshly prepared from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$),
1. Check of electrode setup and measurement of standard potential of the hexaaquairon(III)/(II)-couple:
 - Prepare 10-15 ml of solutions containing iron(III) and iron(II) in the exact ratios 1:2, 1:1 and 2:1, and measure the potential on a gold electrode (against a suitable reference electrode – calomel or silver chloride or mercurous sulphate. Enter name of reference electrode used in last column and its E°_{ref} (for table values see below)
 - Record numbers in column 2 .

Potential/ mV	at an Au-electrode	$E^\circ - E^\circ_{\text{ref}}$	E°	Ref-electrode
Fe(III)/Fe(II) ratio				name:
2:1				
1:1				
1:2				

- Calculate $E^\circ - E^\circ_{\text{ref}}$ from the three measurements from the Nernst equations. Enter calculated values in column 3.
 - Finally calculate E° for the hexaaquairon couple. Enter calculated values in column 4.
2. Standard potential of the tris(2,2'-bipyridine)iron(III)/(II)-couple:
- Prepare 10 ml of a 1:1 mixture of the two stock solutions and add 65 mg of solid 2,2'-bipyridine.
 - Record the potential using the same electrodes as above (only against one reference electrode): _____ mV
 - Calculate the standard potential for the tris(1,2'-bipyridine)iron couple:
_____ mV
3. Stability of tris(2,2'-bipyridine)iron(III):
- Which of the two oxidation states is stabilised most by coordination of 2,2'-bipyridine?
 - Look up – in SCDB - $\log\beta_3(\text{Fe}(\text{bipy})_3^{2+})$ at 25 °C and $I=0.1$ and calculate $\log\beta_3(\text{Fe}(\text{bipy})_3^{3+})$ on the basis of standard potentials found above

Table values: E° / mV for standard reference electrodes (25 °C) relative to Standard Hydrogen Electrode:

Name	Formula	Inner liquid	$E^\circ_{\text{ref}}/\text{mV}$	Inner liquid	$E^\circ_{\text{ref}}/\text{mV}$
Calomel	Hg_2Cl_2	1 M KCl	281	KCl saturated	244
Mercurous sulphate	Hg_2SO_4	1 M H_2SO_4	615	K_2SO_4 saturated	640
Silver chloride	AgCl	1 M KCl	237	KCl saturated	199