# STUDY OF THE RATE OF ELECTROLYTIC OXIDATION OF Mn(II) To Mn(III) AND ITS REACTION WITH THIOSULPHATE USING FERROIN AS INDICATOR

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The rate of electrolytic generation of Mn(III) in sulphuric acid medium and the shelf life of the so prepared solution have been studied. The prepared solution has been successfully used to standardise a method for the determination of thiosulphate potentiometrically, with Mn(III) as self indicator and ferroin as external indicator. The method reported here is convenient, practical, accurate and can be used for routine work also.

### INTRODUCTION

Since manganese (II) is highly stable in neutral or acidic aqueous solutions, all its compounds are strong oxidants in acidic media [1]. Disproportionation is greatly responsible for the deterioration of the stability of the manganese (III) solutions forming stable complexes with manganese (III) or by increasing the concentration of manganese (II) or of hydrogen ions [1].

$$2Mn^{3+} + 3H_2O \rightarrow Mn^{2+} + MnO(OH)_2 + 4H^+$$

Although diphosphate, phosphate and fluoride have often been used as complexing agents, yet in a number of cases the complexing properties of acetic, sulphuric and various polyaminocarboxylic acids have also been pressed into effect [2].

Manganese (III) usually oxidises many inorganic substances fast in direct titrations, whereas the oxidation of organic compounds is often slow [2]. Hence in the latter cases an excess of the reagent is usually added to increase the rate of the reaction and to make unambiguous, stoichiometric and quantitative studies so that the excess of the reagent is back titrated to determine its exact consumption.

Keeping in view the high redox potential value of about +1.4V of the system,

$$Mn^{3+} + e^- \rightarrow Mn^{2+}$$

Mn(III) has been made use of in the present work [1]. Although the determinations of a variety of inorganic and organic substances has already been carried out using manganese (III) as volumetric titrant [1, 2], yet in the present investigations its usefulness has been extended through the study of the rate of electrochemical generation of its diphosphate complex in sulphuric acid, stability of the diphosphate complex, introduction of Ferroin [1-10] phenanthroline iron (II) salt] (Ferroin) as a new redox indicator in its investigations on redox studies and the standardisation of a method for the determination of thiosulphate. Some of the results of these investigations have been reported in this work.

### EXPERIMENTAL

*Reagents:* In all these studies the water means double distilled water if not otherwise mentioned:

Manganese (II) sulphate. A 1.0M aqueous solution of manganese (II) sulphate  $(MnSO_4)$ . HO<sub>2</sub>) was prepared by dissolving 169.02 g of the substance (Merck) in one litre of water.

Sodium pyrophosphate (anhydrous). A 1.0 M solution of sodium pyrophosphate was prepared by dissolving 266.0 g of the substance (Merck) per litre.

Potassium dichromate. A 0.01N standard aqueous solution was prepared by dissolving 1.226 g of the substance (GR – Merck) in 250.0 ml of water.

Ferrous sulphate. Approximately 0.1 N solution of ferrous sulphate was prepared by dissolving 0.695 g of  $FeSO_4$ .  $7H_2O$  (GR-Merck) in 250 ml of water in which 5 ml of concentrated  $H_2SO_4$  (GR-Merck) was already added and the solution so prepared was standardised according to the conventional method.

Diphenylamine. A 1.0% solution in concentrated sulphuric acid was used during these studies.

Ferroin. A  $1_{40}$  M Ferroin solution (Merck) was used as redox indicator.

Sodium thiosulphate. A 0.1N aqueous solution of sodium thiosulphate was prepared by dissolving 12.409 g

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of  $Na_2S_2O_3.5H_2O$  (Merck) in 500 ml of water. The solution was standardised according to the conventional method.

*Iodine solution.* 20 g of the iodate free KI(Merck) are dissolved in 35 ml of water to which 12.7 g of iodine (Merck) was added and the solution was made to one litre which was standardized against  $As_2O_3$  [2]. All other reagents used were either of A.R. Grade or of equivalent purity.

Apparatus. Electroanalyser of Hungarian make, with 5 Amps current passage capacity-double unit fitted also with voltmeter, range 0-10V and interchangeable polarity, was used for the generation of Mn(III). All other glassware used was officially calibrated and of A grade.

**Preparation of manganese (III) diphosphate complex in** sulphuric acid. Of the three methods for the preparation of manganese (III) i.e. chemical oxidation of manganese (II) by reagents with high redox potential, dissolution of solid compound of manganese (III) diphosphate and electrochemical oxidation preparation, the last one was used in these studies [2]. The apparatus used for the purpose has been described above. A small rectangular glass cell of 200 ml capacity and the electrodes were of 2 cm<sup>2</sup> carbon disc.

The preparation of the solution was according to the known method using manganese (II) diphosphate [2]. During these studies electrolysis was carried out at 0.1,0.2

and 0.3A. The media employed for this preparation were 10, 15 and 20N  $H_2SO_4$ . The titre of the prepared Mn(III) solution was determined with the help of standard ferrous sulphate solution using diphenylamine as indicator [1].

Shelf Life of manganese (III) diphosphate solution. The finally prepared solution of manganese (III) diphosphate in 10 and 15N  $II_2SO_4$  through electrolysis was divided into two parts, one of which was kept at 20° while the other was kept at 30° The shelf-life of both of these was determined after regular intervals of time.

#### **RESULTS AND DISCUSSION**

The previously employed method for the electrolytic generation of Mn(III) (2) yielded a very slow rate of oxidation of Mn(II) to Mn(III); hence sulphuric acid within the range from 1 to 20 N was used and the current intensity was kept at 0.1,0.2 and 0.3 amp: for each concentration of the acid. The oxidation process started immediately when the current was switched on. The solution colour turned brownish red.

As shown in Table 1, the rate of oxidation of Mn(II) increased with the increase in the current intensity and the time, but more so in the case of  $15N H_2SO_4$ . At the same

Medium 10N H2SO4 Current = 0.1 Amp. 24 72 2 48 120 168 182 Time (hours) 0.00012 0.0069 0.0155 0.0345 Concentration of Mn(III) 0.0221 0.0422 0.0455 (N) Current = 0.2 Amp. 2 48 72 120 182 24 168 Time (hours) 0.0010 Concentration of Mn(III) 0.0010 0.0222 0.0284 0.0428 0.0511 <del>0</del>.0540 (N) Current = 0.3 Amp 120 182 Time (hours) 2 24 48 72 168 0.0150 0.0320 Concentration of Mn(III) 0.0385 0.0455 0.0520 0.0566 0.0566 (N)  $15N H_2SO_4$  Current = 0.1 Amp 48 72 120 168 182 Time (hours) 2 24 Conceptration of Mn(III) 0.00145 0.0220 0.0301 0.0382 0.0496 0.0560 0.0566 (N) Current = 0.2 Amp Time (hours) 2 24 48 72 120 168 182 Concentration of Mn(III) 0.0226 0.0359 0.0422 0.0455 0.0535 0.0566 0.0566 (N) Current intensity = 0.3 Amp. 2 24 48 72 120 168 182 Time (hours) 0.0292 0.0452 0.0502 0.0555 0.0566 Concentration of Mn(III) 0.0386 0.0566 (N)

Table 1. Showing the rate of electrolytic generation of Mn(III) in 10 and 15N H<sub>2</sub>SO<sub>4</sub> (volts = 2.0)

Table 2. Showing the stability of the Mn(III) solutions prepared in 10 N and  $15N H_2SO_4$ 

		Mn(III) solution kept at		
Medium	Time	30°	20°	
	(hours)	(N)	(N)	
10N H <sub>2</sub> SO <sub>4</sub>	0	0.0388	0.0388	
	24	0.0270	0.0273	
	48	0.0221	0.0242	
	96	0.0125	0.0160	
	120	0.0107	0.0141	
	170	0.0087	0.0119	
15N H <sub>2</sub> SO <sub>4</sub>	0	0.0388	0.0388	
	24	0.0275	0.0280	
	48	0.0268	0.0275	
	96	0.0262	0.0270	
	120	0.0255	0.0263	
	170	0.0250	0.0260	

According to the Table 2, the rate of decrease of Mn(III) concentration is greater at higher temperature  $(30^{\circ})$  than at low temperature  $(20^{\circ})$  both in 10N and 15N H<sub>2</sub>SO<sub>4</sub>. But the decrease in the normality of Mn(III) in 10N H<sub>2</sub>SO<sub>4</sub> is more than in 15N H<sub>2</sub>SO<sub>4</sub> both at 20° and 30°

The determination of thiosulphate was carried out in  $10N H_2SO_4$  as medium using Mn(III) as self-indicator, Ferroin as external indicator and potentiometrically. From the results of these studies as reported in Table 3, it is obvious that thiosulphate can be easily determined within the range from 0.09 to 1.20 mg with a maximum error of -1.67% potentiometrically, -2.0% in case of Mn(III) as self indicator and -0.83% in case ferroin is used as indicator. The reaction proceeds very fast and one titration could be completed within 3-5 min. Therefore, any of the reported methods is quite convenient to follow the determination of thiosulphate. Even in case of the potentiometric end-point method the potential stabilisation is quite fast after each addition of the titrant.

Table 3. Showing the results of determination of thiosulphate in 10N H<sub>2</sub>SO<sub>4</sub> medium

Thiosulphate taken (mg)	Thiosulphate found potentiometrically (mg)	Error Th wi (%)	niosulphate found th Mn(III) as self- indicator (mg)	Ептот (%)	Thiosulphate found with ferroin as indicator (mg)	Error (%)
1.20	1.18	-1.67	1.18	-1.67	1.19	-0.83
0.60	0.59	-1.66	0.59	-1.66	0.60	± 0.00
0.50	0.50	±0.00	0.49	-2.00	0.50	±0.00
0.21	0.21	± 0.00	0.21	± 0.00	0.21	± 0.00
0.16	0.16	± 0.00	0.16	± 0.00	0.16	±0.00
0.10	0.10	± 0.00	0.10	± 0.00	0.10	± 0.00
0.09	0.09	± 0.00	0.09	± 0.00	0.09	± 0.00

time it was clear that after 120 hr of electrolysis time, the rate of oxidation of Mn(II) and the concentration of the solutions were almost equal with respect to Mn(III) content whether it is 10N or  $15N H_2SO_4$  or the current intensity is 0.3 Amp in the case of 10 N sulphuric acid or 0.1,0.2 or 0.3 Amp in the case of 15N sulphuric acid.

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