MERCUROUS NITRATE AS A REDUCTIMETRIC REAGENT

I. STOICHIOMETRY OF THE REACTION

by

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Mercurous nitrate was first advanced as a reagent for the direct titration of ferric iron by BRADBURY AND EDWARDS¹. It has a marked advantage over the other two reagents (stannous chloride and titanous chloride), which have been used for the same purpose, in that the reagent is stable. It does not reduce the ferric ion unless thiocyanate ion is present in excess; hence the reduction only takes place when complex ferric thiocyanate is formed. The presence of thiocyanate has a further advantage in providing an indication of the end-point of the reaction, which is taken as the disappearance of the blood-red colour. The mercurous nitrate is dissolved in 0.8N nitric acid.

BRADBURY AND EDWARDS made only a very limited examination of the reagent. The stoichiometry of the reaction was checked by standardising the ferric solution by the iodometric method of MOHR, and the mercurous nitrate by both the calomel method, and by a new method involving titration with standard iodine. When the solution of ferric iron was then titrated with mercurous nitrate, good agreement with the expected values was found. However, the titrations were only carried out at one level and under very restricted conditions, 10 ml of an approximately 0.1M ferric alum solution being titrated with approximately 0.1Mmercurous nitrate. Before the method could be adopted for general purposes, it would be necessary to know whether or not the reaction is stoichiometric over a much wider range of concentrations. BRADBURY AND EDWARDS noted that sulphuric and nitric acids had no marked interference on the titration, but hydrochloric acid in excess of 0.1M caused high titration values. This is the only reference made to interference by other ions apart from divalent manganese, which is without effect.

There is little further information in the later literature. BELCHER AND SPOONER² used the method for the indirect determination of pyritic sulphur in coal, but first separated the iron, together with other trivalent metals, by precipitation. 0.02M solutions of mercurous nitrate were used, but were evaluated against a standard solution of iron, and no check on the stoichiometry at this level was *References p. 267*.

made. They observed, however, that the titration could be done in open conical flasks, and the stoppered bottles used by BRADBURY AND EDWARDS were unnecessary.

The only two further references we could find dealing with the use of this reagent, provided no further information regarding the stoichiometry of the reaction and interfering substances, but concerned themselves solely with the determination of iron in pharmaceutical syrups³ and coal ash⁴.

PUGH⁵ later recommended the use of mercurous perchlorate. He used volumes containing ferric alum more in accordance with those usually employed in titrimetric analysis, *i.e.*, 100-200 ml. PUGH claimed that the reaction was not stoichiometric at the dilutions he used, and it was necessary to standardise empirically. He confirmed that moderate amounts of sulphuric acid and nitric acid had no effect, but hydrochloric acid much above 0.1M in concentration yielded high results. PUGH stated that the effect of high acidity could be eliminated by partial neutralization. This might be so in the case of sulphuric and nitric acids, but is hardly credible in the case of hydrochloric acid since it would seem to be the chloride ion which interfered. Obviously chloride ion cannot be eliminated by merely neutralising hydrochloric acid. PUGH also recommended heating to 60° -70° C near the end-point, otherwise several minutes had to be allowed between drop additions. No systematic examination of interfering ions was made.

It seemed to us that a detailed systematic examination of the stoichiometry of this reaction, and of possible interferences was long overdue. Moreover, it seemed likely that by a very simple modification to the procedure, mercurous nitrate might be used for the determination of many other ions besides iron. Any substance which is capable of oxidising ferrous iron at room temperature might be titrated, by adding to it thiocyanate in excess and a small quantity of a solution containing ferrous iron. The ferrous ion would be oxidised to yield the blood red ferric thiocyanate, but on titration with mercurous nitrate would be reduced back to the ferrous state. Further oxidation would then take place and the process would be repeated until all the oxidising agent was consumed. The amount of mercurous nitrate consumed should be equivalent to the amount of oxidising agent originally present.

In the present paper a detailed study of the stoichiometry of the reaction has been made. Later papers will deal with the determination of ions other than ferric iron.

Titration of varying amounts of ferric iron with mercurous nitrate dissolved in 5 per cent nitric acid

Amounts of ferric iron ranging from about 3 to 300 mg were titrated with solutions of mercurous nitrate of appropriate strength. As distinct from the procedure of BRADBURY AND EDWARDS the ferric iron solution was titrated in a volume of 100 ml instead of 10 ml. With 0.2M mercurous nitrate solutions References p. 267.

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the results were not in accordance with those required, but when more thiocyanate was added (30 ml) the reaction was stoichiometric. At all other dilutions the results indicated that the reaction was stoichiometric under the conditions used. The results of these titrations are summarised in Tables I-V. About 500 titrations were carried out altogether.

TITRATIONS WITH AN ACID SOLUTION OF MERCUROUS NITRATE TABLE I TABLE II

	-		
ml of 0.2 <i>M</i> Fe+ ³ solution	ml of 0.2M Hg+ solution	ml of 0.1 <i>M</i> Fe+ ³ solution	ml of o.1 <i>M</i> Hg+ solution
25.00	25.02	25.00	25.00
25.00	25.00	25.00	24.98
20.00	20.00	20.00	20.04
20.00	20.02	20.00	20.00
15.00	15.00	16.00	15 98
15.00	15.00	1500	15.00
10.00	10.02	10.00	10.00
10.00	10.00	10.00	10.00
5.00	5.02	5.00	5.02
TABL	E III	TABI	LE IV
ml of 0.05M Fe+8	ml of $0.05M$ Hg+	ml of 0.02M Fe+8	ml of 0.02M Hg+
solution	solution	solution	solution
25.00	24.08	25.00	25.00
25.00	25.00	25.00	25.00
20.00	20.00	20.00	10.08
20.00	20.00	20.00	20.00
15.00	15.02	15.00	15.00
15.00	15.00	15.00	1,500
10.00	9.96	10.00	0.08
10.00	10.00	10.00	10.02
5.00	5.02	5.00	5.00
······································	TAI	BLE V	
	ml of 0.01M Fe+ ⁸	ml of 0.01M Hg+	
	solution	solution	
	25.00	25.00	
	25.00	25.00	
	20.00	20.00	
	20,00	20.00	
	15.00	14.98	
	15.00	14.98	
	10.00	10.00	

10.00

4.98

10.00

5.00

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20.00

14.98

15.00

10.02

10.00

4.98

TITRATIONS WITH MERCUROUS PERCHLORATE

TABI		TAB	LE VII
ml of 0.2 <i>M</i> Fe+ ³ solution	ml of 0.2 <i>M</i> Hg+ solution	ml of 0.1 <i>M</i> Fe+ ³ solution	ml of 0.1M Hg+ solution
25.00	25.02	30.00	30.02
25.00	25.00	25.00	25.00
20.00	20.00	25.00	25.00
20.00	19.96	20.00	20.00
15.00	15.00	20.00	20.02
15.00	15.00	15.00	15.00
10.00	10.02	10.00	9.96
10.00	9.98	10.00	10.02
5.00	5.00	5.00	5.02
TABL	E VIII	TABI	LE IX
ml of 0.05 <i>M</i> Fe+ ³ solution	ml of 0.05M Hg+ solution	ml of 0.02 <i>M</i> Fe+ * solution	ml of 0.02 <i>M</i> Hg+ solution
25.00	25.00	25.00	24.98
25.00	25.00	25.00	25.02
20.00	20.04	20.00	20.00

20.00

15.00

15.00

10.00

10.00

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5.00

TADI D MIT

TABLE X

20.00

150.0

15.00

10.00

10.00

5.00

ml of 0.01 <i>M</i> Fe+ ³	ml of 0.01 <i>M</i> Hg+
	solution
25.00	25.00
25.00	25.00
20.00	19.98
20.00	20.00
15.00	15.02
15.00	15.00
10.00	10.00
10.00	10.00
5.00	4.98

An interesting phenomenon was observed during the course of this work. It was found that when the titrated solution was left in stoppered flasks, the bloodred colour re-appeared much more rapidly than when left in open flasks. After 5 hours the solution contained in a stoppered flask exploded, and brown nitrous References p. 267.

20.00

15.00

15.00

10,00

9.98

5.02

fumes were visible. The residual solution became colourless after standing open to the air for 2 min. It was found that all trace of thiocyanate ion had disappeared. Presumably on prolonged standing nitrous acid is formed, since the reaction occurs when the nitric acid has been freed from nitrogen oxides by bubbling air through the solution, and in any case there would be insufficient to react with the whole of the excessive amount of thiocyanate present. Nitrosyl thiocyanate, which is also blood-red in colour, is then produced. When the solution is allowed to stand in an open flask, the reaction takes place more slowly because most of the nitrogen oxides escape.

Titration of varying amounts of ferric iron with mercurous perchlorate

Varying amounts of ferric iron were also titrated using mercurous perchlorate. As with mercurous nitrate it was necessary to increase the thiocyanate concentration to obtain correct values when a 0.2M reagent was used. At all other dilutions the reaction was found to be stoichiometric. PUGH's recommendation that the solutions be heated to 60° to 80° C near the end-point was examined, but it was found that overheating, or heating too soon caused serious errors. It was found preferable to allow 15 sec between each addition over the last few drops. The results are summarised in Tables VI-X. About 400 titrations were carried out altogether.

Titration of varying amounts of ferric iron with mercurous nitrate dissolved in water

One advantage of mercurous perchlorate is that chlorides and bromides may be titrated with the same reagent⁶. Mercurous nitrate may be used similarly, ⁷,⁸ but only when considerably less acid is present than in the BRADBURY AND ED-WARDS reagent. Mercurous nitrate solutions of varying concentrations were prepared according to von ZOMBORY's method, and 3-300 mg amounts of ferric iron were titrated. It was not found possible to prepare a solution of mercurous nitrate more concentrated than 0.150M under these conditions.

The reactions with this reagent were found to be stoichiometric over the range of concentrations examined. Some of the results are included in Tables XI-XV. More than 300 titrations were carried out.

In all later investigations attention was confined to the BRADBURY-EDWARDS reagent. Mercurous perchlorate is more troublesome to prepare; and although von ZOMBORY's reagent may be used for the titration of halides it is less satisfactory than silver nitrate. Moreover, it may be desirable when large amounts of iron are to be determined, to use a more concentrated reagent than it is possible to obtain using von ZOMBORY's method of preparation.

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TITRATIONS WITH VON ZOMBORY'S MERCUROUS NITRATE REAGENT

TABLE XI		TABLE XII	
ml of 0.15 <i>M</i> Fe+ ³ solution	ml of 0.15 MHg+ solution	ml of 0.1 <i>M</i> Fe+3 solution	ml of o.rM Hg+ solution
25.00	25.00	25.00	25.02
25.00	25.00	25.00	25.00
20.00	20.02	20.00	19.88
20.00	20.00	20.08	20.00
15.00	15.00	15.00	15.00
15.00	14.98	15.00	15.00
10.00	10.04	10.00	10.00
10.00	10.00	10.00	9.98
5.00	4.98	5.00	5.00

TABLE XIII

TABLE XIV

ml of 0.05 <i>M</i> Fe+ ³ solution	ml of 0.05 M Hg+ solution	ml of 0.02 <i>M</i> Fe+3 solution	ml of 0.02M Hg+ solution
25.00	25.00	25.00	25.02
25.00	25.00	25.00	25.02
20.00	20.00	20.00	20,00
20,00	20.02	20.00	20.00
15.00	15.00	15.00	15.00
15.00	14.98	15.00	14.98
10.00	10.00	10.00	10.00
10.00	10.00	10,00	10.00
5.00	5.02	5.00	5.00

TABLE XV

ml of o.or <i>M</i> Fe+3 solution	ml of 0.01 <i>M</i> Hg+ solution
25.00	25.00
25.00	25.00
20.00	20.00
20.00	20.00
15.00	15.02
15.00	15.00
10.00	10.02
10.00	10.00
5.00	5.00

EXPERIMENTAL

Solutions required

Mercurous nitrate was prepared by weighing slightly more than the theoretical amount, and dissolving in 0.8N nitric acid. The solution was found to be stable indefinitely. Mercurous perchlorate and VON ZOMBORY'S mercurous nitrate reagent References p. 267.

were prepared according to the instructions in the original papers. The solutions were standardised by the calomel method, and corrections applied for the solubility. The iodimetric method of BRADBURY AND EDWARDS was also tried, but the results were variable.

The iron solutions were prepared by dissolving the appropriate amounts of ierric alum in 0.2N nitric acid. They were standardised by the gravimetric method.

Ammonium thiocyanate solution was prepared by dissolving 40 g in water and diluting to roo ml.

Procedure

A suitable quantity of ferric alum solution was transferred to a conical flask, and a volume of 40 per cent ammonium thiocyanate solution added, depending on the amount of iron present. (10 ml is sufficient for amounts of iron up to 100 mg. For larger amounts more thiocyanate should be added, so that a further 10 ml is present for each extra 100 mg of iron. Excess of thiocyanate has no interfering effect.) The solution was then diluted with 0.8N nitric acid so that the volume at the end of the titration was approximately 100 ml. The solution was titrated immediately with standard mercurous nitrate until the blood-red colour faded to orange. The titration was then continued drop-wise, shaking well and allowing 15 sec between each drop until the last trace of orange colour disappeared. The rate of titration was not found to be critical until the orange colour appeared, but high results were obtained when the titration was done too quickly after this stage had been reached. Too rapid addition in the neighbourhood of the end-point is usually marked by a cloudiness of the solution, This cloudiness is due to unconsumed mercurous ions forming the difficultly soluble thiocyanate.

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SUMMARY

A study has been made of the stoichiometry of the reaction between an acid solution of mercurous nitrate and ferric iron in the presence of excess of thiocyanate ions. Amounts of iron between 3.0-300 mg were determined using solutions of mercurous nitrate of different concentrations. Under the conditions employed the reaction was found to be stoichiometric over this range. Mercurous perchlorate and an aqueous solution of mercurous nitrate were also examined. Their reactions were also found to be stoichiometric. There is little to choose between these reagents, but the acid solution of mercurous nitrate was considered to be the most convenient.

RÉSUMÉ

Les auteurs ont effectué une étude stoechiométrique de la réaction entre une solution acide de nitrate mercureux et de fer (III), en présence d'un excès d'ions thiocyaniques. Des quantités de fer de 3 à 300 mg ont été dosées en utilisant une solution de nitrate mercureux à diverses concentrations. Dans ces conditions, la réaction est stoechiométrique. Le perchlorate mercureux et une solution aqueuse de nitrate mercureux ont été également étudiés. Leurs réactions sont aussi stoechiométriques. Ces réactifs peuvent convenir, mais la solution acide de nitrate mercureux est la plus avantageuse.

ZUSAMMENFASSUNG

Die Stöchiometrie der Reaktion zwischen einer sauren Lösung von Mercuronitrat und dreiwertigem Eisen in Gegenwart eines Überschusses an Thiocyanationen Rejerences p. 267. wurde untersucht. Eisenmengen von 3-300 mg wurden mit Hilfe von Mercuronitrat-lösungen verschiedener Konzentration bestimmt. Unter diesen Bedingungen verläuft die Reaktion stöchiometrisch. Mercuroperchlorat und eine wässrige Lösung von Mercuronitrat wurden ebenfalls untersucht. Diese Reagentien reagieren ebenfalls stöchiometrisch mit dreiwertigem Eisen und können ebenfalls verwendet werden, doch ist die saure Mercuronitratlösung am geeignetsten.

REFERENCES

- F. R. BRADBURY AND E. G. EDWARDS, J. Soc. Chem. Ind., 59 (1940) 96 T.
 R. BELCHER AND SPOONER, Fuel, 20 (1941) 122.
 F. R. BRADBURY, K. C. CHATTERGEE AND E. G. EDWARDS, Quart. J. Pharmacol., 13 (1940) 297.
- Fuel Research Survey Paper. No. 50. D.S.I.R. p. 3.

- Fuel Research Survey Paper. No. 50. D.S.I.K. p. 3.
 W. Pugh, J. Chem. Soc., (1945) 588.
 W. Pugh, J. Chem. Soc., (1937) 1824.
 R. BURSTEIN, Z. anorg. allgem. Chem., 168 (1928) 325.
 L. VON ZOMBORY, Ibid., 184 (1929) 237.
 W. F. HILLEBRAND AND G. E. F. LUNDELL, Applied Inorganic Analysis, London, 1929, p. 175.

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