pentachloride. Sulfur dioxide was evolved to a slight extent when the tubes were opened. The supernatant liquid consisted chiefly of the excess of thionyl chloride and phosphorus trichloride, but in addition sulfur monochloride also was detected. It was thought that the oxidizing action of the excess of thionyl chloride on the phosphorus trichloride had proceeded according to the equation

$$3PCl_3 + 4SOCl_2 = 3PCl_5 + 2SO_2 + S_2Cl_2,$$

which is quite different from that given by Michaelis. However, it is certain that reaction does not follow the above equation quantitatively, inasmuch as in every case decomposition of the liquid contents of the tubes by means of water gave appreciable quantities of hydrogen sulfide, indicating that to some extent at least, reaction follows the equation given by Michaelis.

Summary.

Thionyl and sulfuryl chlorides react with sulfur at temperatures from 150° to 180° with formation of sulfur dioxide and sulfur monochloride. Under similar conditions both reagents react with phosphorus, either red or yellow, with the formation of phosphorus trichloride. Prolonged heating tends to cause the trichloride to become pentachloride, but the reaction is far from complete even after heating for several hours at 160° to 180°.

NEW BRUNSWICK, N. J.

[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY, THROOP COLLEGE OF TECHNOLOGY, NO. 4.]

THE USE OF METALLIC SILVER AS A REDUCING AGENT IN THE VOLUMETRIC ESTIMATION OF IRON.

BY GRAHAM EDGAR AND A. R. KEMP.

Received March 16, 1918.

I. Purpose of the Investigation.

Several investigators have studied the reaction between metallic silver and solutions of ferric salts, and have shown that it proceeds to an equilibrium, in which at room temperature a considerable concentration of ferric salt is usually present. This fact apparently renders silver unsuitable as a reducing agent for the quantitative estimation of iron. However, if the silver-ion concentration in the solution is reduced (*e. g.*, by precipitation) the equilibrium may be shifted until only inappreciable quantities of ferric iron remain in the solution. Thus Hoenig[1] has shown that in the presence of a sufficient concentration of hydrochloric acid, ferric chloride may be reduced to the ferrous state by metallic silver with sufficient completeness to permit the quantitative estimation of the iron by titration with potassium permanganate after filtering off the silver chloride and the excess of silver.

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[1] *Z. anal. Chem.*, **54**, 441 (1915).

In the present investigation the reaction between metallic silver and solutions of ferric sulfate in the presence of sulfuric acid and a soluble thiocyanate has been studied. The results show that the reduction of the ferric iron is sufficiently complete for the purposes of quantitative analysis, and that the reaction may serve as the basis of a procedure for the estimation of iron which is rapid and accurate, and which possesses certain other advantages over many standard procedures.

II. Experimental.

Materials.—The silver used in these experiments was in some cases prepared electrolytically by a method previously described[1] and in other cases by reduction of ammoniacal silver nitrate solution by tartaric acid or cuprous chloride. It was in all cases given a preliminary purification by boiling it with dilute sulfuric acid, filtering, and washing it thoroughly.

The solutions of ferric sulfate and potassium permanganate were carefully standardized, and proper precautions of measurement, such as the use of calibrated burets, and correction of end points, were observed throughout.

Technique and Results. Procedure 1.—After a series of preliminary experiments a number of quantitative determinations were carried out as follows: A measured volume of standard ferric sulfate solution, containing 0.05 to 0.20 g. iron, was acidified with 3 cc. conc. sulfuric acid (sp. gr. 1.84), diluted to about 75 cc., and treated with about 3 g. metallic silver. The mixture was heated to boiling in a small flask and boiled gently until the solution became nearly colorless (usually one or two minutes). To the boiling solution was then added, drop by drop, sufficient ammonium thiocyanate solution (about 0.5 *N*) to precipitate all of the silver dissolved in the reaction and give a small excess.[2] The solution was then boiled gently until it became perfectly colorless (usually not more than a minute or two), cooled under the tap or allowed to stand until cool, filtered, and the residue washed thoroughly with cold water. To the filtrate was added a little ferric sulfate solution and then enough dilute silver nitrate solution to discharge the red color of ferric thiocyanate. The mixture was then titrated with 0.1 *N* potassium permanganate solution, without filtering off the

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[1] Edgar, This Journal, 38, 1297 (1916).

[2] With moderate quantities of iron (0.1 to 0.2 g.) the presence of an excess of ammonium thiocyanate is usually indicated by the appearance of a faint red color of ferric thiocyanate, persisting through the solution for a short time. With smaller quantities of iron the equilibrium shifts so rapidly, as the silver ion is precipitated by the ammonium thiocyanate, that this color is not always apparent. If there is any doubt as to the presence of an excess of ammonium thiocyanate a small drop of the solution may be removed on the end of a glass rod and tested with ferric chloride solution. A considerable excess of ammonium thiocyanate may be added without interfering with the accuracy of the determination, but it is undesirable, since this excess must be precipitated later by silver nitrate.

silver thiocyanate, to the first persistent faint pink color. The results are given in Table I. They will be discussed below.

TABLE I.

Fe taken. Gram.	0.1 N $KMnO_4$. Cc.	Fe found. Gram.	Error. Gram Fe.
0.0526	9.42	0.0526	0.0000
0.0548	9.86	0.0550	0.0002
0.0688	12.32	0.0688	0.0000
0.1381	24.73	0.1381	0.0000
0.1381	24.74	0.1381	0.0000
0.1385	24.76	0.1383	0.0002
0.1243	22.27	0.1244	0.0001
0.1243	22.28	0.1244	0.0001
0.1317	23.54	0.1314	0.0003
0.1317	23.60	0.1318	0.0001
0.1976	35.40	0.1977	0.0001
0.1976	35.35	0.1974	0.0002
0.1976	35.35	0.1974	0.0002
0.1317[1]	23.60	0.1318	0.0001
0.1317[2]	23.60	0.1318	0.0001
0.1263[3]	22.63	0.1263	0.0000

The above experiments were selected purely at random from about three times the number of similar determinations.

Procedure 2.—A second series of determinations was made by a different method. A measured portion of ferric sulfate solution was acidified with about 3 cc. concentrated sulfuric acid, diluted to a volume of about 75 cc., and treated with 3 to 5 g. silver and with ammonium thiocyanate solution in excess of that necessary to precipitate the silver dissolved in the reaction. The dark red solution was then shaken in the cold until it became perfectly colorless (usually 3 to 12 minutes). It was then filtered, and the filtrates treated with silver nitrate and titrated with potassium

TABLE II.

Expt. No.	Fe taken. Gram.	0.1 N $KMnO_4$. Cc.	Fe found. Gram.	Error. Gram Fe.
1[4]..........	0.0658	11.80	0.0658	0.0000
2[4]..........	0.1317	23.61	0.1318	0.0001
3[4]..........	0.1976	35.39	0.1977	0.0001
4[4]..........	0.1976	35.37	0.1976	0.0000
5[5]..........	0.0658	11.77	0.0657	0.0001
6[5]..........	0.1263	22.64	0.1264	0.0001
7[5]..........	0.1263	22.63	0.1263	0.0000
8[5]..........	0.1976	35.36	0.1975	0.0001
9[5]..........	0.1317	23.60	0.1318	0.0001

[1] 5 cc. H_2SO_4 (sp. gr. 1.8) added.

[2] 10 cc. H_2SO_4 (sp. gr. 1.8) added.

[3] Ag spiral made from Ag wire was used. Time, 30 min.

[4] 3–5 g. Ag used. Shaken in cold. Time of reaction 3–12 min.

[5] 3–5 g. Ag used. Heated on water bath and shaken. Time 3–12 min.

permanganate as in the first procedure. The results of these experiments are given in Table II. In a few of the experiments the procedure was varied somewhat, and where this was done a note describes the changes made.

Procedure 3.—Since silver does not dissolve in the dil. sulfuric acid except by virtue of its reaction with the ferric salt, the amount dissolving should be a measure of the ferric salt present, and it should be possible to estimate the ferric salt by determining this dissolved silver. To ascertain whether or not this was feasible a number of determinations were made by Procedures 1 and 2, except that the ammonium thiocyanate and silver nitrate solutions were carefully standardized and carefully measured, and at the conclusion of the potassium permanganate titration[1] the excess of silver nitrate in the solution was determined by titration with standard ammonium thiocyanate, using ferric sulfate as indicator. From the total amounts of ammonium thiocyanate and silver nitrate solutions used, the silver dissolved in the reaction (and from it the ferric iron present) was calculated. The results obtained by this procedure were invariably slightly high when the reduction was carried out in boiling solution (as in Procedure 1), and these results are not tabulated. Where reduction was carried out in the cold (as in Procedure 2), results were obtained which agreed closely with the potassium permanganate titration, and with the true values. These results are given in Table III.

TABLE III.

Expt. No.	Fe taken. Gram.	0.1 *N* $KMnO_4$. Cc.	Fe found by $KMnO_4$. Gram.	0.1 *N* NH_4CSN.[2] Cc.	Fe found by NH_4CSN. Gram.
1..........	0.1317	23.58	0.1317	23.57	0.1316
2..........	0.1317	23.62	0.1319	23.62	0.1319
3..........	0.1317	23.58	0.1317	23.55	0.1315
4..........	0.1263	22.60	0.1262	22.62	0.1264
5..........	0.1263	22.63	0.1263	22.63	0.1263

All shaken in the cold with 3 g. Ag. Time 8–10 min.

Test Analyses of Iron Ores.—To test the applicability of these procedures to the analysis of iron ores determinations were carried out upon the Bureau of Standards' "Crescent Iron Ore," No. 26, and upon their "Sibley Iron Ore," No. 27. Weighed samples of the ores were treated with hydrochloric acid, filtered from the insoluble residue, the filtrate treated with 5 cc. of conc. sulfuric acid, evaporated to the fuming point and heated until all hydrochloric acid was expelled. The insoluble residue was decomposed with hydrofluoric acid and sulfuric acid and the solution added to the main portion. The resulting solution was then diluted to 75 cc., treated with 3 to 5 g. of silver, and analyzed according to the directions given above,

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[1] In an actual analysis the potassium permanganate titration may, of course, be omitted.

[2] After subtracting the cc. 0.1 *N* $AgNO_3$ used.

Procedure 1 being used in the case of the "Crescent" ore, and Procedure 2 in the case of the "Sibley" ore. The results are given in Table IV.

TABLE IV.

Sample, gram.	0.1 N $KMnO_4$, cc.	% Fe in sample.	B. of S. value.
"Crescent Iron Ore," B. of S. Sample No. 26.			
0.2019	21.19	58.59	...
0.3097	32.52	58.64	...
0.3039	31.85	58.52	...
	Average,	58.58	58.62
"Sibley Iron Ore," B. of S. Sample No. 27.			
0.3500	43.40	69.25	...
0.3526	43.73	69.25	...
0.3570	44.25[a]	69.22	...
0.3597	44.60[a]	69.24	...
	Average,	69.24	69.26

III. Discussion.

The results tabulated in Tables I, II, III, and IV, together with numerous other experiments not here recorded, lead to the following conclusions:

1—Metallic silver may be used to effect the complete reduction of ferric sulfate to ferrous sulfate, provided the silver dissolved in the reaction is precipitated by a thiocyanate. The resulting ferrous solution may be titrated with potassium permanganate, after filtering off the silver and then precipitating the excess of thiocyanate with silver nitrate solution. The titration measures very accurately the amount of iron present.

2—Three separate procedures may be employed by which iron may be estimated by means of the reaction. In Procedure 1 the ferric sulfate solution is heated at first with the silver alone, and the thiocyanate solution is added after a considerable portion of the iron is reduced. In Procedure 2 the reduction is carried out in the cold, and the thiocyanate is added at the beginning of the reaction. Procedure 3 differs from Procedure 2 only in the use of standard thiocyanate and silver nitrate solutions, which permits the estimation of the iron by means of these solutions instead of by potassium permanganate.

3—The time required for the estimation of iron by Procedure 1 is very short. The reduction is complete in 2 or 3 minutes, and the solution may be cooled, filtered and titrated in 5 to 10 minutes more. The reduction proceeds somewhat more slowly in the cold (Procedure 2), but even in this case it is usually complete in 4 to 12 minutes, which compares very favorably with the time required by almost any other standard method of

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[a] In these two determinations the residues of Ag and AgCNS were not thoroughly washed, and it was found that on further washing an amount of Fe was obtained which required 0.05 cc. of $KMnO_4$ to reoxidize it. This correction was applied in the results given above.

analysis. This is especially true when a considerable number of determinations are to be carried out at once.

4—Procedure 3 makes it possible to check the potassium permanganate titration by also estimating the silver dissolved in the reduction, or to determine iron by means of standard silver nitrate and ammonium thiocyanate alone. It may also serve, if desired, for the analysis of a solution containing both ferrous and ferric salts; for the results of the ammonium thiocyanate titration give the ferric iron present, while the potassium permanganate titration gives the total iron.

5—A distinct advantage of these methods over practically every other method for the reduction of ferric iron is that there is never any uncertainty as to whether the reduction is complete. The thiocyanate serves as a very sensitive indicator, and the disappearance of the red color of ferric thiocyanate gives an absolute indication that no ferric salt remains.

6—The reduced solution may be left in contact with the silver, without the slightest danger of reoxidation by the air for as long as 24 hours or more; for any ferric iron formed by atmospheric oxidation is at once reduced by the silver. This is especially advantageous where several determinations are being made at once, as there need be no hurry about filtering the solutions.

7—The statement is sometimes made that ferrous solutions even when cold, can not be filtered without undergoing appreciable oxidation. That this is incorrect is shown by the fact that the solutions in the above experiments, containing an excess of thiocyanate, remained perfectly colorless during the filtration, and for some time thereafter.

8—The presence of the precipitate of silver thiocyanate during the potassium permanganate titration does not influence the result, provided the solution is cold and the potassium permanganate is added at a reasonable rate. The pink color at the end point may fade out upon standing somewhat more rapidly than is the case with iron solutions alone; but there is not the slightest difficulty in obtaining a perfectly sharp end point. If the solution is warm, the potassium permanganate may act appreciably upon the silver thiocyanate and introduce error.

9—The accuracy of the results is practically independent of the amount of silver taken, its method of preparation, the amount of sulfuric acid used, and the excess of ammonium thiocyanate added, within rather wide limits. Thus the amount of silver was varied between 2 and 5 g., the sulfuric acid between 1 and 10 cc. of conc. acid in a volume of 75 cc., and in some cases nearly twice the necessary amount of ammonium thiocyanate was added, without any apparent effect upon the accuracy of the determination. The speed of the reaction, however, varies somewhat with the amount of silver added and its state of subdivision, the concentration of ferric sulfate, and the particular technique used. The directions given in the three procedures give perhaps the most convenient and satisfactory quantities of material and methods of operation; but they may be varied considerably, if desired.

10—A number of experiments were made to determine the effect of foreign substances upon the reaction. These experiments showed that hydrochloric acid in more than small amounts is apt to be acted upon by the permanganate under the conditions of the determination, and thus introduce error; nitric acid in small amount does not usually affect the determination unless Procedure 3 is being employed; it is best, however, to remove both of these acids by evaporation with sulfuric acid and heating. Molybdic acid is irregularly reduced and thus introduces error. Chromic acid is completely reduced, but if present in appreciable amount it uses up some permanganate. Vanadic acid is quantitatively reduced to the quadrivalent state, and may be corrected for. Titanium is not reduced at all.

11—Comparing briefly silver as a reducing agent for ferric sulfate with some other substances commonly employed, we may note the following facts: (*a*) Silver is readily obtained perfectly free from iron, which is never the case with zinc or aluminum. This renders blank determinations unnecessary. (*b*) It reduces vanadic acid definitely to the quadrivalent state, and does not reduce titanium at all, whereas zinc and aluminum reduce vanadic acid irregularly, and also reduce titanium. (*c*) It is much more rapid in its action and more certain in its results than such substances as sulfur dioxide and hydrogen sulfide. (*d*) By the use of the thiocyanate solution not only is the reaction brought to completion, but the point of complete reduction is sharply indicated by the color of the solution—an advantage over every other standard method.

12—Although metallic silver is somewhat expensive, it may be readily recovered from the residues of silver and silver thiocyanate by treatment with ammonium hydroxide and tartaric acid or cuprous chloride, and thus prepared for use again with very little trouble.

IV. Summary.

In this article has been described a new process for the volumetric estimation of iron, based upon the fact that ferric sulfate is reduced to ferrous sulfate by metallic silver in the presence of a thiocyanate. The reduced solution after filtration is treated with an excess of silver nitrate, and the ferrous iron is titrated with potassium permanganate (or if preferred the excess of silver nitrate may be titrated back with thiocyanate). Test analyses with known ferric sulfate solutions and with samples of iron ores standardized by the Bureau of Standards are presented which show that the method is one of high accuracy. The method has the advantages (1) that the thiocyanate serves to show when the ferric iron is completely reduced; (2) that silver, unlike zinc and aluminum, is ordinarily entirely free from iron, making blank determinations unnecessary; and (3) that silver does not reduce titanium at all, and reduces vanadium definitely to the quadrivalent state. The method is rapid in execution.

PASADENA, CAL.

NOTE.

Grinding Glass Tips for Drop-Weight Apparatus.—In order to make glass tips for use in "drop-weight" surface-tension measurements the usual procedure is to first grind the glass in a precision lathe until the cross section of the tube near the tip is a circle. This lateral surface is polished until it is smooth. It is then necessary to grind down the end of the tube until it is flat and the edges are sharp. In order to avoid chipping during the process various devices have been used. One of the most efficient of these methods previously used is that of imbedding the tip in a brass disc which is perfectly flat on the bottom. The hole through the brass is just a little larger than the glass tube. The latter is held in place by special wax which is melted, poured around the tube and allowed to harden. Glass tip and brass are then ground away simultaneously. However considerable trouble is experienced because particles of abrasive work into the wax around the edge of the tip. Fine glass and abrasive likewise work up into the small capillary opening and frequently become so tightly wedged into it that it is not possible to dislodge them without injury to the tip. When no supporting device is used for the tip while grinding the flat surface, lead glass is sometimes used because it is less easily splintered. However this kind of glass is often objectionable where it is necessary to seal the tip to another glass tube, as when an interface apparatus is to be made. It is also often desirable to use a glass which is not so easily attacked by strong reagents. Moreover, when viewed under the microscope a tip ground without having been inbedded in some supporting material not infrequently shows an imperfect edge.

To get around the use of the wax and in order to have a firm support for the tip edge during the grinding of the flat surface, the author has found Wood's metal or other similar low melting alloy to be admirable. Wood's metal melts at 65.5°; so that the glass will not be much heated by the molten alloy. The glass tube made ready for the final preparation of the face of the tip is supported in a vertical position with the tip against the flat bottom of a small cardboard box. The Wood's metal is melted in a test tube in a water bath and poured around the tip to a depth of about 10–15 mm. By raising and lowering the tube in the molten alloy or by applying a little suction to the tube the alloy is drawn a short distance into the capillary opening. Finally the tube is left with the tip against the bottom of the box until the alloy has solidified. When the paper is removed it is found that the tip is firmly imbedded in the alloy. Tube