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FROM THE

KENT CHEMICAL LABORATORY

OF

YALE UNIVERSITY

EDITED BY

FRANK AUSTIN GOOCH

Professor of Chemistry in Yale University

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RESEARCH PAPERS

FROM THE

KENT CHEMICAL LABORATORY OF YALE UNIVERSITY

RESEARCH PAPERS

I

THE DETERMINATION OF TELLURIUM BY PRECIPITATION AS THE IODIDE.

By F. A. GOOCH and W. C. MORGAN.*

It was known to Berzelius that hydriodic acid and tellurous acid interact with the formation of tellurium tetraiodide, which is converted by water into an oxyiodide and by excess of an alkaline iodide into a soluble double salt. Wheeler † has shown that the double salt which is formed when tellurous iodide is boiled in a strong solution of potassium iodide in dilute hydriodic acid is definite and has the constitution represented by the formula $2KI \cdot TeI_4 \cdot 2H_2O$. We have observed, however, that when potassium iodide is added to a cold solution of tellurous acid containing at least one-fourth of its volume of strong sulphuric acid, no tendency toward the formation of a double salt becomes apparent until the potassium iodide amounts to more than enough to convert all the tellurous acid present into the tetraiodide according to the equation,

$$H_2TeO_3 + 4H_2SO_4 + 4KI = TeI_4 + 4KHSO_4 + 3H_2O.$$

The tellurium tetraiodide which is thus formed is extremely insoluble in sulphuric acid of the strength mentioned, though soluble in excess of potassium iodide, and acted upon by water with the formation of tellurium oxyiodide and hydriodic acid. It is produced at first in the condition of a finely divided dark brown precipitate which upon agitation of the liquid containing it gathers in curdy masses and settles, leaving the

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* From Am. Jour. Sci., ii, 271.

† Am. Jour. Sci., xlv, 267.

supernatant liquid clear. By taking advantage of this tendency to curd it is possible to determine without great difficulty the exact point during the gradual addition of potassium iodide when the precipitation of the tellurium iodide is complete, and we have been able to found upon this property a very simple titrimetric method for the direct determination of small amounts of tellurium.

In our test experiments we used tellurium dioxide prepared by oxidizing presumably pure tellurium with nitric acid and igniting the residue at a low red heat. Weighed amounts of the oxide thus prepared were dissolved in Erlenmeyer beakers in a very little of a strong solution of potassium hydroxide, and dilute sulphuric acid was added carefully until the tellurous acid which was precipitated upon the neutralization of the alkaline hydroxide was just redissolved. To this solution sulphuric acid of half-strength was added in such amount that the solution finally obtained, after adding the aqueous solution of potassium iodide subsequently, should still contain at least one-fourth of its volume of strong sulphuric acid. The Erlenmeyer beaker was placed upon a pane of window glass supported upon strips of wood about 1 cm. above the level of the work table, which was covered with white paper. A solution of approximately decinormal potassium iodide free from iodate and carefully standardized in terms of iodine by a method described in a former paper from this laboratory * was introduced gradually from a burette into the middle of the Erlenmeyer beaker. As the drops of the potassium iodide touched the liquid the precipitation formed at the centre and travelled in rings toward the outer walls of the beaker. When the liquid became so opaque that the effect of the potassium iodide was distinguished with difficulty, the beaker was rotated and the curdled precipitate permitted to settle, and then the process of titration was continued as before. We experimented with amounts of tellurium dioxide varying from approximately 0.025 grm. to 0.1 grm., the latter quantity being as large as can be handled with accuracy without intermediate removal of the

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* Am. Jour. Sci., xxxix, 188. Volume I, p. 1.

precipitate by filtration. With an Erlenmeyer beaker 10 cm. in diameter across the bottom and a final volume of liquid amounting to not more than 100 cm³, we were able to follow the precipitation most easily.

The results of a series of determinations made according to the method described and recorded in the following table are closely accordant, and, in close agreement with the theory of the process if the atomic weight of the tellurium which we used is taken as 127. We feel justified in taking this number as the atomic weight of our tellurium, because the mean result of twelve oxidations by standard potassium permanganate of tellurium dioxide, prepared similarly to that which we used and from the same lot of material, and the mean result of twelve reductions by hydrobromic acid of the telluric acid thus produced,* point to this figure.

Final volume.	Strongest H_2SO_4 present.	Iodine value of KI used.	TeO_2 taken.	TeO_2 found.	Error.
cm³	cm³	grm.	grm.	grm.	grm.
50	17	0.0706	0.0228	0.0221	0.0002–
50	17	0.0764	0.0244	0.0289	0.0005–
50	17	0.1591	0.0496	0.0499	0.0003+
60	17	0.1655	0.0517	0.0519	0.0002+
60	17	0.1578	0.0498	0.0494	0.0004–
80	80	0.1591	0.0498	0.0499	0.0001+
100	30	0.3179	0.1001	0.0997	0.0004–
100	80	0.3186	0.1008	0.0999	0.0009–
100	30	0.3208	0.1011	0.1005	0.0006–
100	30	0.3208	0.1010	0.1005	0.0005–

From these results it is obvious that the method, which is very rapid, is accurate.

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* Am. Jour. Sci., xlviii, 377, 378. Volume I, pp. 279, 281.

II

ON THE APPLICATION OF CERTAIN ORGANIC ACIDS TO THE ESTIMATION OF VANADIUM.

BY PHILIP E. BROWNING AND RICHARD J. GOODMAN.*

IN a former paper† by one of us a method for the determination of vanadium was described in which tartaric acid was used to reduce vanadic acid to the condition of the tetroxide. The method may be briefly outlined as follows:

Measured and weighed portions of a solution of ammonium vanadate, the standard of which had been determined by the evaporation and ignition of definite portions, were treated with tartaric acid in excess and boiled, when the appearance of the deep blue color indicated the reduction to the condition of the tetroxide. After cooling, the solution was neutralized with potassium bicarbonate and a moderate excess of that reagent added. To the alkaline solution an excess of a standard solution of iodine was added and the whole allowed to stand about one hour, when no further bleaching of the iodine was noticed. The excess of iodine was then destroyed with a standard solution of arsenious oxide, starch was added, and the blue color obtained with a few drops of the iodine solution. The total amount of iodine used, less the amount equivalent to the arsenious oxide solution used, is the amount necessary to oxidize the vanadium from the condition of the tetroxide to that of the pentoxide, from which, according to the following equation, can be calculated the amount of vanadium present:

$$V_2O_4 + I\text{-}I + H_2O = V_2O_5 + 2HI.$$

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* From Am. Jour. Sci., ii, 355.

† Zeitschr. anorg. Chem., vii, 158.

‡ These determinations are best made in small Erlenmeyer beakers, closed with paraffin-coated corks while standing with iodine.

The work to be described in this paper is in part an application of the work described in the paper above mentioned to a series of determinations of vanadium in the presence of molybdenum and tungsten. The solution of vanadium used was one of ammonium vanadate, and the standard was determined by evaporating and igniting, in the presence of a drop of nitric acid, measured and weighed portions, the mean of closely agreeing results being taken as the standard. Our first series of determinations was by the method previously described, that being the natural starting-point for the work contemplated. The results follow in the table:

Exp.	V_2O_5 taken.	V_2O_5 found.	Error.	Tartaric acid.
	grm.	grm.	grm.	grm.
(1)	0.1621	0.1618	0.0003−	2
(2)	0.1620	0.1624	0.0004+	2
(3)	0.1614	0.1622	0.0008+	2
(4)	0.1619	0.1606	0.0013−	1
(5)	0.1604	0.1597	0.0007−	2
(6)	0.1618	0.0615	0.0003−	3
(7)	0.1298	0.1305	0.0007+	1
(8)	0.1294	0.1297	0.0003+	1
(9)	0.1618	0.1618	0.0000±	2
(10)	0.2588	0.2575	0.0013−	3
(11)	0.2722	0.2726	0.0004+	2
(12)	0.3273	0.3269	0.0004−	2

We next tried the effect of treating a solution of sodium tungstate in the same manner. We found that after the boiling with tartaric acid, neutralizing, adding iodine and allowing to stand as before, the amount of free iodine present, as shown by the amount of arsenious oxide solution necessary to destroy it was the same as that originally added, showing that no reduction had taken place. Accordingly a series of determinations of vanadium in the presence of tungsten was made which is recorded in the next table.

The results show that vanadium may be easily determined by this method in the presence of tungsten without any evident interfering action on the part of the latter element.

When the same method of treatment was applied in the presence of molybdenum in the form of ammonium molybdate,

Exp.	V_2O_5 taken.	V_2O_5 found.	Error.	Sodium tungstate.	Tartaric acid.
	grm.	grm.	grm.	grm.	grm.
(1)	0.1618	0.1615	0.0003–	1	3
(2)	0.1615	0.1606	0.0009–	1	3
(3)	0.1618	0.1624	0.0006+	1	3
(4)	0.1619	0.1624	0.0005+	1	3
(5)	0.1627	0.1623	0.0004–	1	3
(6)	0.1621	0.1624	0.0003+	1	4
(7)	0.2587	0.2574	0.0013–	1	4
(8)	0.2587	0.2589	0.0002+	1	4

the majority of the determinations gave large plus errors, and a few experiments made with the molybdate alone seemed to show a noticeable reduction of the molybdic acid. In the following table the results are tabulated. In experiments (3), (4) and (5) the mixtures were not boiled with tartaric acid, but warmed on a steam bath, with, however, no very apparent prevention of the reducing action.

Exp.	V_2O_5 taken.	V_2O_5 found.	Error.	Ammonium molybdate.	Tartaric acid.
	grm.	grm.	grm.	grm.	grm.
(1)	0.1620	0.1790	0.0170+	1	2
(2)	0.1624	0.1619	0.0005–	1	2
(3)	0.1294	0.1416	0.0122+	1	2
(4)	0.1296	0.1361	0.0065+	1	2
(5)	0.1291	0.1312	0.0021+	1	2
(6)	0.1293	0.1324	0.0031+	1	2
(7)	0.1636	0.1760	0.0124+	1	2
(8)	0.1640	0.1724	0.0084+	1	2
(9)	0.1622	0.1624	0.0002+	1	3
(10)	0.1622	0.1632	0.0010+	1	3
(11)	0.1619	0.1879	0.0260+	1	3
(12)	0.1292	0.1360	0.0068+	1	3
(13)	0.1860	0.1917	0.0057+	1	3
(14)	0.3274	0.3733	0.0459+	1	4
(15)	0.2324	0.2383	0.0059+	1	4

We next tried the action of tartaric acid upon the vanadium solution in the cold and found that the reduction could be carried on to completion under these conditions if the tartaric acid was in large excess, the time sufficient, and the volume of the solution small. The following series was made to determine these points:

Exp.	V_2O_5 taken.	V_2O_5 found.	Error.	Time.	Tartaric acid.	Total vol.
	grm.	grm.	grm.	days.	grm.	cm^3
(1)	0.1646	0.1649	0.0008+	1	4	25
(2)	0.1640	0.1606	0.0034–	1	4	65
(3)	0.1298	0.1264	0.0029–	2	3	55
(4)	0.1638	0.1628	0.0005–	2	4	65
(5)	0.1293	0.1288	0.0005–	3	2.5	50
(6)	0.1298	0.1299	0.0001+	8	2.5	50
(7)	0.1295	0.1279	0.0016–	8	8	55
(8)	0.1617	0.1597	0.0020–	4	2	70
(9)	0.1623	0.1622	0.0001–	4	8	80

Solutions containing sodium tungstate and ammonium molybdate were allowed to stand from one to four days with varying amounts of tartaric acid without giving any evidence of reduction.

In the series which follows may be seen the results of a

Exp.	V_2O_5 taken.	V_2O_5 found.	Error.	Ammonium molybdate.	Sodium tungstate.	Time in days.	Total volume.	Tartaric acid.
	grm.	grm.	grm.	grm.	grm.		cm^3	grm.
(1)	0.1552	0.1558	0.0006+	. .	. .	1	25	5
(2)	0.1289	0.1301	0.0012+	. .	. .	1	25	5
(3)	0.2583	0.2587	0.0004+	. .	. .	1	50	5
(4)	0.1293	0.1299	0.0006+	1	. .	1	25	6
(5)	0.2582	0.2591	0.0009+	1	. .	1	50	6
(6)	0.2582	0.2588	0.0006+	1	. .	1	50	5
(7)	0.1297	0.1308	0.0011+	1	. .	1	25	5
(8)	0.1291	0.1289	0.0002–	. .	1	1	25	6
(9)	0.2582	0.2568	0.0014–	. .	1	1	50	5
(10)	0.1293	0.1299	0.0006+	1	1	1	25	8
(11)	0.2582	0.2579	0.0003–	1	1	1	50	5
(12)	0.1550	0.1538	0.0012–	. .	. .	2	25	5
(13)	0.1556	0.1545	0.0011–	. .	. .	2	25	5
(14)	0.1289	0.1296	0.0007+	. .	. .	2	25	5
(15)	0.1549	0.1527	0.0022–	0.5	. .	2	25	5
(16)	0.1553	0.1548	0.0005–	1	. .	2	25	5
(17)	0.1556	0.1554	0.0002–	1	. .	2	25	5
(18)	0.1293	0.1310	0.0017+	1	. .	2	25	6
(19)	0.1295	0.1299	0.0004+	. .	1	2	25	6
(20)	0.1298	0.1289	0.0004–	1	1	2	25	7
(21)	0.1298	0.1301	0.0008+	. .	. .	8	25	5
(22)	0.1289	0.1299	0.0010+	0.5	. .	8	25	5
(23)	0.1298	0.1292	0.0001–	1	. .	8	25	7
(24)	0.1556	0.1567	0.0011+	1	. .	8	80	5
(25)	0.1291	0.1289	0.0002–	1	1	8	25	7
(26)	0.1550	0.1557	0.0007+	. .	. .	4	25	5
(27)	0.1554	0.1557	0.0003+	1	. .	4	25	5
(28)	0.1556	0.1557	0.0001+	0.5	. .	4	25	5

number of determinations of vanadium in the presence of molybdenum and tungsten made in the cold and allowed to stand from one* to four days. It will be noticed that the results on standing one day with five grams of tartaric acid are for the most part satisfactory, and an increase in the length of time does not cause any apparent reduction of the molybdenum.

Friedheim † has shown that vanadium is reduced from the condition of the pentoxide to that of the tetroxide by boiling with oxalic acid. The reduction is so complete that he has developed a method for the estimation of vanadium upon this reaction and shows that it may be applied in the presence of molybdenum and tungsten, the acids of these elements not being reduced by the oxalic acid. When the vanadic acid is reduced the oxalic acid is oxidized and a definite amount of carbon dioxide evolved according to the reaction.

$$V_2O_5 + H_2C_2O_4 = V_2O_4 + H_2O + 2CO_2.$$

This carbon dioxide Friedheim conducts by an appropriate form of apparatus into potassium hydroxide and weighs. From this weight the amount of vanadic acid originally present may be readily calculated.

We have applied the method of oxidation with standard iodine described in the tartaric acid process to the residue after boiling with oxalic acid. The method of treatment was identical with that outlined at the beginning of this paper. The results which follow in the table are for the most part satisfactory and the method is certainly more easily applied than Friedheim's process, the potassium hydroxide absorption apparatus being unnecessary.

Having applied successfully both tartaric acid and oxalic acid in the manner described, the action of citric acid applied in the same manner suggested itself as a fitting conclusion to the study of the action of this class of organic acids. In this

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* Some of the determinations designated in the table as having stood one day in reality stood only about fifteen hours, from 6 P. M. to 9 A. M.

† Zeitschr. anorg. Chem., i, 312.

Exp.	V_2O_5 taken.	V_2O_5 found.	Error.	Oxalic acid.	Ammonium molybdate.	Sodium tungstate.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1806	0.1803	0.0003–	1	. .	. .
(2)	0.1950	0.1955	0.0005+	1	. .	. .
(3)	0.1959	0.1955	0.0004–	1	. .	. .
(4)	0.1950	0.1959	0.0009+	1	. .	. .
(5)	0.1954	0.1977	0.0023+	1	. .	. .
(6)	0.1956	0.1960	0.0004+	1	. .	. .
(7)	0.1956	0.1964	0.0008+	1	. .	. .
(8)	0.1956	0.1957	0.0001+	1	. .	. .
(9)	0.3900	0.3899	0.0001–	2	. .	. .
(10)	0.3897	0.3917	0.0020+	2	. .	. .
(11)	0.3903	0.3905	0.0002+	2	. .	. .
(12)	0.1954	0.1959	0.0005+	2	1	. .
(13)	0.1957	0.1960	0.0003+	2	1	. .
(14)	0.1954	0.1961	0.0007+	2	1	. .
(15)	0.1806	0.1818	0.0012+	3	. .	. .
(16)	0.1807	0.1827	0.0020+	3	. .	. .
(17)	0.1809	0.1803	0.0006–	3	1	. .
(18)	0.1956	0.1961	0.0005+	3	. .	1
(19)	0.3611	0.3617	0.0006+	5	. .	. .
(20)	0.3616	0.3626	0.0010+	5	1	. .

case, as in the others, the reduction of the vanadic acid is easily and quickly effected, but the oxidation with the iodine is slower than in the presence of alkaline oxalates and tartrates. In the case of oxalic acid on standing about fifteen minutes with the excess of iodine, when tartaric acid has been used, the bleaching of the iodine continues from thirty to forty-five minutes, but in the presence of the alkaline citrate the time required is fully an hour. A large excess of tartaric or oxalic acids does not seem to materially affect the results, but in the use of citric acid it is advisable to avoid a large excess, which tends to give high results. Accordingly in the following series of experiments it will be noticed that the amounts of citric acid do not exceed two grams except where ammonium molybdate or sodium tungstate are present, when the ammonium or sodium base combines with part of the free acid. The results follow, on p. 10.

The mode of proceeding in the estimation of vanadium by the use of either tartaric, oxalic, or citric acid may be briefly summarized as follows: To a solution of a vanadate with or without a tungstate or molybdate, add approximately one

Exp.	V_2O_4 taken.	V_2O_5 found.	Error.	Citric acid.	Ammonium molybdate.	Sodium tungstate.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1956	0.1956	0.0000	1	. .	. .
(2)	0.3905	0.3921	0.0016+	2	. .	. .
(3)	0.1960	0.1960	0.0000	1	. .	. .
(4)	0.1953	0.1960	0.0007+	1	. .	. .
(5)	0.2088	0.2082	0.0006–	2	. .	. .
(6)	0.2100	0.2098	0.0002–	2	. .	. .
(7)	0.2092	0.2107	0.0015+	1	. .	. .
(8)	0.2092	0.2107	0.0015+	2	. .	. .
(9)	0.2096	0.2082	0.0014–	2	0.5	. .
(10)	0.2099	0.2116	0.0017+	3	0.5	. .
(11)	0.2095	0.2101	0.0006+	2	. .	0.5
(12)	0.2099	0.2095	0.0004–	8	. .	0.5

gram of the acid for every tenth of a gram of substance to be determined. Heat the solution to boiling, except in case tartaric acid be present with molybdic acid, when digestion for from fifteen to twenty-four hours in the cold should be substituted. To the cold liquid add about five grams of potassium bicarbonate for every gram of acid used. Add iodine in slight excess and set aside until no further bleaching is noticeable. Destroy the excess of iodine with arsenious oxide solution, add starch, and titrate back with standard iodine. The total amount of iodine used less the equivalent of the arsenious oxide is the measure of the oxidation.

We have found it of advantage, when starting with a new solution of the vanadate, to make one determination roughly and to get from this rough determination the proportions of acid and iodine to be used in the determinations to follow. Large amounts of the acid and a large excess of the iodine have been employed in many determinations without any apparent unfavorable effect upon the results. The tendency, however, under these circumstances is toward plus errors, which may be avoided by following the above directions.

III

THE DETERMINATION OF OXYGEN IN AIR AND IN AQUEOUS SOLUTION.

By D. ALBERT KREIDER.*

While there is little to be hoped for by way of improvement in the accuracy of present known methods for the determination of oxygen in the air, some choice as to manipulation may nevertheless be desirable, and a process which is not limited wholly to the methods and apparatus of ordinary gas analysis will doubtless often be found serviceable.

The very satisfactory results which I have obtained in the determination of perchlorates by the action of the liberated oxygen upon hydriodic acid through the medium of nitric oxide† has led me to test this action upon the oxygen of the air, where only the smaller amount of oxygen and its greater dilution with nitrogen might be expected to be unfavorable. However, with the apparatus and manipulation herein described it will be seen that the method affords a means for the determination of the oxygen of the air or of dissolved oxygen with ease and rapidity and with sufficient accuracy for all practical purposes.

The method in brief is simply the conducting of a known volume of air through a strong solution of hydriodic acid in the presence of nitric oxide; subsequently neutralizing the acid with potassium bicarbonate and titrating the liberated iodine with standard decinormal arsenic solution from which the equivalent volume of oxygen is readily calculated. By several simple devices, to be described, all calculations may be done away with and the percentage of oxygen seen imme-

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* From Am. Jour. Sci., ii, 361.

† Am. Jour. Sci., l, 287. Volume I, p. 316.

diately by the volume of arsenic solution required for the titration.

The volume of oxygen found by means of the arsenic solution is, of course, under the standard conditions of temperature and pressure (0° and 760 mm.), and it is therefore essential either to calculate this volume into that which it would occupy under the conditions of the experiment or to reduce to the standard conditions of temperature and pressure the volume of air taken. The latter plan is the more satisfactory since by Lunge's ingenious device* the reduction can be readily effected without any calculation and independently of changing temperature and pressure. For my purpose the following arrangement of two burettes answered admirably. One burette graduated to 120 cm^3 contained over mercury the same volume of moist air which 100 cm^3 of air at 0° and 760 mm. would occupy under the given conditions, this standard being very carefully determined. By means of a T-tube this standard burette was placed between and in connection with the burette in which the volume of air to be analyzed was measured, and a movable reservoir of mercury. Both burettes were firmly fastened to a movable iron rod and the zero marks accurately adjusted to the same level. By drawing into the measuring burette a volume of air greater than that required — for which purpose a small bulb was attached to the lower end of the burette, and then by raising the reservoir of mercury, compressing the air in the standard tube to the 100 cm^3 mark, at the same time allowing the excess of air to escape from the measuring burette, exactly 100 cm^3 of air under the standard conditions of temperature and pressure was obtained. To facilitate the adjustment, two strips of wood were fastened to the rubber connection by means of screw pinch-cocks in such a way that by closing one pinch-cock the flow of mercury from the reservoir could be shut off, and then by gradually tightening the other pinch-cock the mercury would be forced out of the rubber, and thus an easy and accurate adjustment to the 100 cm^3 mark be secured.

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* Zeitschr. angew. Chem., 1890, 139.

The apparatus in which the action of the oxygen upon hydriodic acid was effected consisted of a 300 cm^3 bulb pipette, both ends of which were cut off short and sealed to glass stop-cocks. The tube from one of the stop-cocks was cut off short after being tapered and constricted so as to hold a rubber connector tightly, while the tube from the other stop-cock was left sufficiently long to reach to the bottom of a 500 cm^3 Erlenmeyer beaker. These tubes are preferably of about 3 mm. bore, since for the several connections all air may be expelled from tubes of this size by displacement with water. In order to expel all air from the flask, instead of passing a current of carbon dioxide as was done in the determination of perchlorates, time was saved by first filling the flask with water, which was then displaced by pure carbon dioxide (prepared as described below) and the flask subsequently exhausted, which was accomplished instantaneously by the device described in the article on perchlorates. The required amounts of potassium iodide solution, hydrochloric acid and nitric oxide were drawn in in the order named, after which the measured volume of air was gradually admitted while the bulb was constantly agitated so as to keep the hydriodic acid continually renewed along the surface of the bulb. The shaking was continued for a minute or two until the action was completed, when a dilute solution of potassium bicarbonate was admitted. The carbon dioxide liberated forces the liquid from the bulb into a beaker which contains bicarbonate in amount sufficient, as previously determined, to neutralize all the acid taken. When the exit is too slow more bicarbonate may be admitted through the other stop-cock, and after neutralization has been completed the bulb may be washed out without any danger from the admission of air.

All the water employed, both for the solution of potassium iodide and for the various connections, was free of oxygen. It was prepared by filling a three-liter flask with distilled water and boiling until the volume of the liquid was reduced about one-third, when the flask was closed by a doubly perforated rubber stopper and fitted as a wash bottle. By means of the tube which reached below the surface of the water, pure carbon dioxide was passed through while the water was still boiling, which together with the escaping steam was sure to expel all oxygen. Then the heat was removed and the current of carbon dioxide continued until the boiling ceased, when the escape tube was closed by a piece of rubber tubing and screw pinch-cock. As the water cooled it was well shaken while still in connection with the carbon dioxide generator, and thus became saturated with the gas, which was then pumped in under considerable pressure by the little hand pump described in a previous paper from this laboratory. By this means the water could be drawn as needed without the introduction of any air. The escape tube was provided with a rubber tube and screw pinch-cock, and a long, slender nozzle which could be inserted into the tubes of the absorption apparatus. A bottle thus charged sufficed for all the determinations and required only an occasional supply of carbon dioxide when large draughts of water were required for making the potassium iodide solution.

The potassium iodide solution was made up to contain one gram of the salt in thirty cubic centimeters of water, and was contained in convenient form in an ordinary wide-mouthed bottle fitted as a wash bottle, and graduated approximately for each thirty cubic centimeters' volume — the amount usually taken. The potassium iodide was weighed into the bottle, which was then closed and all air expelled by a current of carbon dioxide, when the desired amount of water, free of oxygen, was drawn in, and attachment again made with the carbon dioxide generator. After allowing the gas to pass for several minutes the exit was closed and the gas pumped in by the little hand pump. Inasmuch as this solution, when it was used, was drawn into an exhausted bulb, the bottle could be emptied without ever exposing its contents to the air.

Nitric oxide was generated very satisfactorily according to Professor Gooch's method — by the action of nitric acid upon globules of copper in a Kipp generator. When the nitric acid is diluted with an equal volume of water the evolution of the gas is sufficiently rapid without the application of heat, but contamination by the higher oxide is more likely. However, since it is necessary, in order to be certain of purity, to pass the gas through an acidified solution of potassium iodide before applying it to the determination of oxygen, whatever higher oxide may be present will be reduced. By passing the gas, as it issued from the generator, through a set of Geisler bulbs containing an acidified solution of potassium iodide and washing with potassium iodide solution, the perfectly purified gas was obtained. Theoretically, only a small amount of the nitric oxide is required for the transference of the oxygen to the hydriodic acid, but when too little is taken the action is very slow. On the other hand, too large an amount relieves the vacuum to such an extent as to interfere with the introduction of the air. A little device to measure the volume of gas taken was therefore attached to the generator. It consisted of a tube filled with water and roughly graduated for every five cubic centimeters, so attached to the generator that the gas would enter by displacement of the water, which would descend to a lower bulb, and as the gas was withdrawn the water would again take its place. Fifteen cubic centimeters of the gas was found a convenient and satisfactory amount for the analysis.

Carbon dioxide was generated in a Kipp generator, the acid and marble of which had been previously boiled and contained a little cuprous chloride. To remove a trace of reducing matter which the gas was found to contain, it was first passed through a solution of iodine and washed with potassium iodide.

For the titration a decinormal solution of arsenious oxide (4.95 grms. to the liter) was employed: 1 cubic centimeter being equal to 0.559846 cm^3 of oxygen at 0° and 760 mm. when the weight of a liter of oxygen at 0° and 760 mm. is taken as 1.42895 grm. When the volume of air taken is 100 cm³ under standard conditions of temperature and pressure, as obtained by Lunge's device, the following table, calculated for the volume of oxygen equivalent to the volume of arsenic solution, shows directly the percentage of oxygen corresponding to the reading of the burette. The correction necessary for the fraction of a tenth of a cubic centimeter of the arsenic solution is obtained with sufficient accuracy by simply multiplying by 0.005.

Relation of Arsenic to Oxygen.

$\frac{n}{10}As_2O_3$.	Oxygen equivalent at 0° and 760 mm.	Correction for 0.01 cm³ $\frac{n}{10}As_2O_3$.
cm³	cm³	
37.0	20.714	0.005
37.1	20.770	
37.2	20.826	
37.3	20.882	
37.4	20.938	
37.5	20.994	
37.6	21.050	
37.7	21.106	
37.8	21.162	
37.9	21.218	
38.0	21.274	

Table I shows the results obtained in a series of determinations. Experiments (1) to (11) inclusive were made upon portions of air collected over water on March 28, measured in an ordinary gas burette and reduced to the standard conditions of temperature and pressure. The remainder of the determinations were made upon air collected on April 8, each portion having been measured in the apparatus described, for the reduction to standard conditions.

No correction was found necessary for the blank determinations, since when boiled water was used the solution was only faintly colored with iodine, which requires only a drop of arsenic solution to bleach it. As is evident from the table, the determinations according to this method are not reliable beyond 0.05 per cent, but for practical purposes this is sufficiently accurate. For the sake of comparison two determinations by

TABLE I.

Exp.	Volume of Air reduced to 0° and 760 mm.	$\frac{n}{10}As_2O_3$ required.	Volume of Oxygen found at 0° and 760 mm.	Per cent of Oxygen in Air.
	cm³	cm³	cm³	
(1)	91.18	34.06	19.07	20.91
(2)	91.73	34.47	19.30	21.04
(3)	90.84	34.25	19.17	21.11
(4)	90.60	34.20	19.16	21.13
(5)	86.06	32.55	18.22	21.17
(6)	85.96	32.40	18.14	21.10
(7)	86.49	32.53	18.21	21.06
(8)	87.85	33.00	18.47	21.03
(9)	44.17	16.60	9.29	21.04
(10)	44.11	16.70	9.35	21.19
(11)	44.54	16.80	9.41	21.12
(12)	100.00	37.44	20.96	20.96
(13)	100.00	37.54	21.01	21.01
(14)	100.00	37.50	20.99	20.99
(15)	100.00	37.57	21.03	21.03
(16)	100.00	37.47	20.97	20.97
(17)	100.00	37.50	20.99	20.99

the pyrogallic acid method were made upon a portion of the same air used in the last experiments, the results being 20.93 and 20.88 per cent respectively. While the pyrogallic acid method is capable of much greater accuracy when applied in Hempel's improved apparatus, in ordinary burettes it will probably not yield more closely agreeing results than the above method.

Determination of dissolved Oxygen. — A determination of oxygen dissolved in water can be completed by the above method in about ten minutes by means of the apparatus illustrated by the accompanying figure.

FIG. 17.

The apparatus consisted of a flask of about 300 cm³ capacity, into the bottom of which was sealed a stop-cock with a long exit tube. Upon the neck was cut the fiducial circle *c* and immediately above this stop-cock *e* was sealed as shown. The neck of the flask was drawn out and sealed to stop-cock *d* and the bulb, *a*, of about 30 cm³ capacity blown in it. The capacity of the apparatus between stop-cock, *b*, and the fiducial mark, *c*, was carefully determined.

The manipulation for the determination of dissolved oxygen was as follows: The flask was held in the position shown by a clamp fastened to a movable support. Stop-cock *b* being closed, the water was admitted through *e* and the air allowed to escape through *d* until the level of water was that indicated by the line *f*. (When the water to be examined is not saturated with air, the flask must first be filled with carbon dioxide and the water entered by replacement of that gas.) With *d* closed, sufficient water was allowed to escape through *b* to bring the surface to *e*, which was then closed. The nitric oxide generator was then attached to *d*, and by opening *b* the gas was allowed to replace the water until the meniscus coincided with *c*, when *d* was closed and the generator disconnected. Two cubic centimeters of strong hydrochloric were introduced through *e* by expelling nitric oxide through *d*, in which a drop of water formed an effective trap to prevent the entrance of air. Then the potassium iodide was admitted in the same way. The solution of iodide for this purpose was free of oxygen and contained one gram in three cubic centimeters. It was kept under pressure of carbon dioxide in the bottle previously described, and by means of a long nozzle could be conducted to the bottom of *eh* and thus be admitted with but momentary and slight contact with the air. The tube *eh* contained approximately three cubic centimeters. With all the stop-cocks closed, the flask was inverted several times and thoroughly shaken, at the same time washing out the ends of the stop-cocks with distilled water. After again placing the apparatus in its position, enough potassium bicarbonate solution was admitted through *e* to expel all the nitric oxide through *d*; the bulb, *a*, holding sufficient of the bicarbonate to neutralize all the acid taken. The bicarbonate being heavier quickly diffuses through the contents of the flask and neutralizes the acid; *d* and *e* are kept closed for a minute with *b* open so as to allow sufficient of the liquid to escape into a beaker containing some bicarbonate to provide space for the carbon dioxide evolved. Then the flask is washed out and its contents titrated with arsenic.

The bleaching, by the aid of starch for the final reaction, can be accurately read to a single drop Usually the reading was verified by adding a drop of $\frac{n}{10}$ iodine solution, which produced the characteristic color.

Table II gives the results of a series of determinations.

TABLE II.

Volume of Water taken.	Temperature.	As_2O_3 required.	Volume of Oxygen dissolved in 1000cm³ of water at 760 mm.
cm³	° C.	cm³	cm³
314.63	20	3.42	6.04
314.63	20	3.45	6.09
314.63	20	3.40	6.00
314.63	20	3.41	6.02
314.63	20	3.43	6.05
314.63	20	3.40	6.00
314.63	20	3.36	5.98
314.63	20	3.40	6.00
314.63	20	3.40	6.00
314.63	20	3.50	6.18
314.63	20	3.38	5.96
314.63	20	3.40	6.00

The mean of these determinations gives 6.022 cm³ of oxygen as the amount dissolved in distilled water at 20° C. and 760 mm., and while some of the determinations vary considerably from this mean, as a whole they are fairly accordant. This method, moreover, is applicable to carbonated water.

IV

A METHOD FOR THE SEPARATION OF ALUMINUM FROM IRON.

BY F. A. GOOCH AND F. S. HAVENS.*

OF the well-known methods for the separation of aluminum from iron — by the action, for example, of an alkaline hydroxide in aqueous solution or by fusion of the mixed oxides in potassium or sodium hydroxide; by reduction of the iron oxide to the metal by heating in hydrogen, with the subsequent solution of the metallic iron in hydrochloric acid; by boiling the nearly neutral solution of the salts of aluminum and iron with sodium thiosulphate either with or without sodium phosphate; by acting with hydrogen sulphide or ammonium sulphide upon solutions of the salts containing also an ammoniacal citrate or tartrate — no single process can be said to be ideal as regards directness, rapidity and accuracy of working. We have deemed it not superfluous, therefore, to attempt the utilization of a reaction which should apparently be capable of effecting directly and quickly the separation of aluminum from iron under conditions easily attainable.

It is known † that the hydrous aluminum chloride $AlCl_3.6H_2O$ is very slightly soluble in strong hydrochloric acid, while ferric chloride, on the other hand, is extremely soluble in that medium. It is this difference of relation of which we wished to take advantage.

It appeared at the outset that crude aluminum chloride could be freed from every trace of a ferric salt by dissolving it in the least possible amount of water, saturating the cooled solution with gaseous hydrochloric acid, filtering upon asbestos

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* From Am. Jour. Sci., ii, 416.

† Gladysz, Ber. Dtsch. chem. Ges., xvi, 447.

in a filtering crucible or cone, and washing the crystalline precipitate with the strongest hydrochloric acid. Aluminum chloride prepared in this way gave no trace of color when dissolved in water and tested with potassium sulphocyanide. The correlative question as to how much aluminum chloride goes into solution under the conditions was settled by taking a portion of the pure aluminum chloride, dissolving it in a very little water, diluting the solution with strong hydrochloric acid, saturating the cooled liquid with the gaseous acid, filtering on asbestos, precipitating by ammonia the aluminum salt in the filtrate and weighing the ignited oxide.

From 10 cm^3 of such a filtrate we obtained in two determinations 0.0022 grm. and 0.0024 grm. of the oxide, the mean of which corresponds to 23 parts of the oxide or 109 parts of the hydrous chloride in 100,000 parts of the strong hydrochloric acid. This degree of solubility, though inconsiderable when the objective point is the preparation of the pure salt of aluminum, is obviously incompatible with the attainment of quantitative accuracy in the retention of the aluminum. We have found, however, that various mixtures of anhydrous ether and the strongest hydrochloric acid can be used satisfactorily as solvents for the iron chloride, while the aluminum chloride is insoluble to a very high degree in a mixture of hydrochloric acid and ether taken in equal parts and thoroughly saturated with gaseous hydrochloric acid at the atmospheric temperature. We found that 50 cm^3 of the solution of aluminum chloride, obtained by mixing about 0.1 grm. of the hydrous chloride (dissolved in 2 cm^3 of water) with the mixture of pure, specially prepared aqueous hydrochloric acid and ether in equal parts and again saturating the liquid at 15° C. with gaseous hydrochloric acid, left upon evaporation and ignition 0.0004 grm. in each of two experiments — results which indicate a maximum solubility corresponding to 1 part of the oxide or approximately 5 parts of the chloride in 125,000 parts of the equal mixture of ether and aqueous hydrochloric acid of full strength.

Pure aqueous hydrochloric acid of full strength mixes perfectly with its own volume of anhydrous ether, but it is a curious fact that the addition to this mixture of any very considerable amounts of a solution of ferric chloride in strong hydrochloric acid determines the separation of a greenish oily ethereal solution of the ferric salt upon the surface of the acid. The addition of more aqueous acid does not change the conditions essentially, but more ether renders the acid and the oily solution completely miscible. The ferric chloride seems to abstract ether from the ether-acid mixture and, then dissolved in the ether, remains to some extent immiscible with the aqueous acid thus left until the addition of more ether restores to the mixture that which was taken from it by the ferric chloride. Our experiments show that, while for the separation of insoluble aluminum chloride from certain small amounts of soluble ferric chloride the mixture of the strongest aqueous hydrochloric acid and ether in equal parts serves a most excellent purpose, when larger amounts of ferric chloride are to be dissolved ether must be added proportionately in order to prevent the separation of the ethereal solution of ferric chloride from the rest of the liquid.

Great care was taken to insure the purity of the aluminum chloride used in the test experiments. The so-called pure chloride of commerce was dissolved in the least possible amount of water and this solution was treated with a large volume of strong hydrochloric acid. The chloride thus obtained, free from iron, but possibly contaminated (as we found by experience) with some alkaline chloride, was dissolved in water and converted by ammonia to the form of the hydroxide, which was thoroughly washed and dissolved in hot hydrochloric acid of half-strength. From this solution, after cooling, gaseous hydrochloric acid precipitated the hydrous chloride in pure condition. The chloride thus prepared was dissolved in water and the strength of the solution was determined by precipitating the hydroxide from definite portions, and weighing the ignited oxide in the usual manner.

In the experiments recorded in Table I, measured portions of the standardized solution were submitted to the treatment

TABLE I.

Exp.	Al_2O_3 taken in solution as the chloride.	Al_2O_3 found.	Final volume.	Error.
	grm.	grm.	cm^3	grm.
(1)	0.0761	0.0746	50	0.0015–
(2)	0.0761	0.0745	50	0.0016–
(3)	0.0761	0.0741	50	0.0020–
(4)	0.0761	0.0734	50	0.0027–
(5)	0.0761	0.0756	50	0.0005–
(6)	0.0157	0.0149	45	0.0008–
(7)	0.0157	0.0147	40	0.0010–
(8)	0.0157	0.0144	45	0.0013–
(9)	0.0480	0.0481	30	0.0001+
(10)	0.0960	0.0957	30	0.0003–

with hydrochloric acid and ether. The essential thing in the process is to have at the end a mixture of the strongest aqueous hydrochloric acid with an equal volume of anhydrous ether saturated at a temperature of about 15° C. The most convenient way to secure these conditions seems to be to mix the aqueous solution of the aluminum salt with a suitable volume of the strongest aqueous hydrochloric acid — enough to make the entire volume something between 15 and 25 cm^3 — to saturate this mixture with gaseous hydrochloric acid while the liquid is kept cool by immersing the receptacle containing it in a current of running water, to intermix a volume of ether equal to the volume of the liquid, and finally, to treat the ethereal mixture once more with the gaseous acid to insure saturation. The precipitated crystalline chloride was collected upon asbestos in a perforated crucible, washed with a previously prepared mixture of hydrochloric acid and ether carefully saturated with the gaseous acid at 15° C., and either ignited after careful drying at 150° or redissolved in water, converted to the hydroxide by ammonia in the usual way and weighed as the oxide after filtration, washing, and ignition. In experiments (1) to (4) the precipitated chloride was ignited directly; in experiment (5) the ignition was made with great care in an atmosphere of superheated steam; and in experiments (6) to (10) the chloride was dissolved, precipitated as the hydroxide, and weighed as the oxide.

The experiments in which the chloride was converted to the hydroxide before ignition show upon the average an absolute loss of about 0.0006 grm.: the single experiment in which the ignition took place in steam shows about the same loss — 0.0005 grm.; while in those experiments in which the chloride was dried and then ignited directly, the average loss amounts to about 0.0020 grm. The error of the process which involves the precipitation of the aluminum as the hydroxide, falls within reasonable limits, but it is plain that the direct ignition of the chloride is liable to error, which may possibly be explicable as a mechanical loss occasioned by the too rapid evolution of the hydrochloric acid and water of crystallization, or, possibly, as the result of a very slight volatilization of the aluminum still holding chlorine in spite of the decomposing action of the water upon the chloride. In either case, it would seem to be reasonable to suppose that a layer of some easily volatilizable oxidizer placed upon the aluminum chloride might serve to obviate the difficulty — in the one case, by serving as a screen to diminish mechanical transportation of the non-volatile material; and in the other, by acting as an agent to promote the exchange of chlorine for oxygen on the part of the aluminum chloride.

We have tried, therefore, the expedient of covering the aluminum chloride before ignition with a layer of mercuric oxide, which of itself left no appreciable residue when it volatilized. The hydrous chloride was collected as usual upon the asbestos in a perforated crucible, dried for a half-hour at 150° C., covered with about 1 grm. of the pure mercuric oxide, gently heated with great care under a suitable ventilating flue, and finally ignited over the blast. The results are given below (see Table II).

It is obvious, therefore, that the precipitation of the crystalline hydrous aluminum chloride from solutions of the pure salt is perfectly feasible and very complete, when effected by aqueous hydrochloric acid and ether thoroughly saturated with the gaseous acid and kept cool; and that the conversion of the chloride into the weighable form of the oxide is best effected

TABLE II.

Exp.	Al_2O_3 taken in solution as the chloride.	Al_2O_3 found by ignition with HgO.	Final volume.	Error.
	grm.	grm.	cm^3	grm.
(1)	0.0761	0.0758	25	0.0003–
(2)	0.0761	0.0754	25	0.0007–
(3)	0.0761	0.0751	25	0.0010–

by ignition under a layer of mercuric oxide, or by dissolving it in water and precipitating it as the hydroxide to be afterward washed, dried, and ignited. Of the two methods the former is by far the more convenient.

The precipitation of the aluminum chloride in pure condition from solutions containing ferric chloride ought not, it would seem, to present any difficulty, providing only that the precaution is taken to have present a sufficient excess of ether. The question was put to the test of experiment with the results recorded in Table III.

TABLE III.

Exp.	Al_2O_3 taken in solution as the chloride.	Al_2O_3 found by ignition with HgO.	Fe_2O_3 present as chloride.	Final volume.	Error.
	grm.	grm.	grm.	cm^3	grm.
(1)	0.0761	0.0757	0.15	25–30	0.0004–
(2)	0.0761	0.0756	0.15	25–30	0.0005–
(3)	0.0761	0.0755	0.15	25–30	0.0006–
(4)	0.0761	0.0755	0.15	25–30	0.0006–

Measured portions of the standardized solution of aluminum chloride were evaporated nearly to dryness in a platinum dish, an amount of pure ferric chloride equivalent to about 0.15 grm. of the oxide was added in a very little water, 15 cm^3 of the mixture of strong hydrochloric acid and ether in equal parts were introduced, the liquid was saturated at 15° C. with gaseous hydrochloric acid (the dish being held in a convenient device for cooling it by running water), 5 cm^3 more of ether were added to secure complete miscibility of the solutions, and more gas passed to perfect saturation. The aluminum chloride was collected upon asbestos in a perforated crucible, washed with a mixture of ether and aqueous hydrochloric acid thoroughly saturated with the gaseous acid, dried at 150° C. for a half-hour, covered with 1 grm. of pure mercuric oxide, and ignited at first gently and finally over the blast.

The results show plainly a very satisfactory limit of error.

V

THE ESTIMATION OF MOLYBDENUM IODOMETRICALLY.

BY F. A. GOOCH.*

IN a former paper from this laboratory † several modes of applying hydriodic acid to the reduction of molybdic acid were studied. It was found, first, that the digestion process of Mauro and Danesi ‡ is of very limited applicability, owing to the fact that the reaction of reduction is reversible. Secondly, it appeared that the use of the same reaction by Friedheim and Euler § in a distillation process, so arranged that the iodine set free in the reduction might be caught in the distillate and titrated to serve as the measure of the reducing action, was not sufficiently regular because of inattention to minor details. It was shown that by taking care to adjust the conditions constant results might be obtained. Thirdly, the fact was developed that by simply boiling the solution under well defined conditions in an ordinary Erlenmeyer flask, partly closed by a simple trap, the reduction of the molybdic acid proceeded regularly, and that the addition of standard iodine to the solution made alkaline with sodium bicarbonate served to restore the original condition of oxidation of the molybdic acid. The results of this treatment were shown to be accurate.

In a recent paper ‖ Friedheim has seen fit to make our modifications of the distillation process the subject of attack. Friedheim's comments upon the third method discussed (as

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* From Am. Jour. Sci., iii, 237.

† Gooch and Fairbanks, Am. Jour. Sci., ii, 157. Volume I, p. 375.

‡ Zeitschr. anal. Chem., xx, 507.

§ Ber. Dtsch. chem. Ges., xxviii, 2066.

‖ Ber. Dtsch. chem. Ges., xxix, 2981.

well as upon a subsequent application of the process) * are evidently prompted wholly by personal opinion and demand no further attention. With reference to Friedheim's denial of the necessity of modification in the Friedheim and Euler treatment the case is different.

The process of Friedheim and Euler consists, it will be remembered, in treating the soluble molybdate, or the solution of molybdic acid in sodium hydroxide, with potassium iodide and hydrochloric acid in a Bunsen apparatus, boiling until the solution is of a clear green color, collecting the iodine distilled in potassium iodide, and titrating it with sodium thiosulphate. We found that the development of the green color was not a sufficient criterion of the exact reduction of the molybdic acid to the condition of the pentoxide and of the removal of the iodine which should be theoretically set free. To accomplish that end we found it safer and more convenient to start the distillation with a definite volume (40 cm^3) of liquid and boil until a definite volume (25 cm^3) was reached, care being taken with regard to the strength of acid and the excess of potassium iodide employed. Experience showed unmistakably that in order to avoid the decomposing action of the air upon the hot vaporous hydriodic acid in the retort, it was necessary to go beyond the measures advised by Friedheim and Euler (namely, to warm the retort and its contents slowly, heating to boiling only when the connecting tube was well filled with iodine vapor and the tendency toward back-suction of the liquid in the receiver began to appear) and to conduct the operation in a simple little apparatus (the retort holding about 100 cm^3) put together entirely with sealed and ground joints, as shown in the figure of the former paper, so arranged that a current of purified carbon dioxide could be passed through retort and receiver during the distillation. With this apparatus we were able to determine with accuracy the point of concentration at which the free iodine left the liquid, the molybdic acid having been converted to the con-

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* Am. Jour. Sci. ii, 181. Volume I, p. 391.

dition of the pentoxide. It was found that if dependence is placed upon the occurrence of the so-called clear green color of the liquid to determine the end of the distillation, it may frequently happen that free iodine remains in the residue. This takes place, it will be observed, in the atmosphere of carbon dioxide, so that the presence of the free iodine can by no possibility be attributed to the action of atmospheric air upon the hydriodic acid remaining after the distillation is complete. On the other hand, it appeared that, if the distillation is pushed too far, the molybdenum pentoxide may be still further reduced with consequent evolution of more than the expected amount of iodine. The attainment of an exact degree of reduction with the expulsion of the corresponding amount of iodine becomes, therefore, a matter of chance unless further precautions are taken. We found in our experiments that, if amounts less than 0.3 grm. of the molybdic acid are introduced in soluble form into the 100 cm^3 retort with a not too great excess of potassium iodide, and the 40 cm^3 of liquid so constituted that 20 cm^3 of it shall be water and 20 cm^3 the strongest hydrochloric acid, the reduction proceeds with a fair degree of regularity in the manner expected. We found it important to restrict the excess of potassium iodide so that it shall never exceed the theoretical requirement by more than 0.5 grm.

Our determinations with the pure molybdenum trioxide showed errors varying from 0.0010 grm. + to 0.0007 grm. −; the variations from theory in the experiments with ammonium molybdate ranged from 0.0011 grm. + to 0.0011 grm. −. If these results are compared with those given by Friedheim and Euler, the advantage is a little in favor of the latter; but a scrutiny of the figures given by Friedheim and Euler develops the fact that the apparent accuracy of their work is founded upon miscalculations. This fact was known to us at the time of our former writing, but we did not consider it essential then to make the matter public. The recent attack of Friedheim makes that course now necessary.

Herewith is reproduced a table of results obtained by Friedheim and Euler in the test of their method upon ammonium molybdate, shown by analysis to contain 81.49 per cent of molybdenum trioxide. The figures which are incorrect are enclosed in brackets:

ORIGINAL FIGURES OF FRIEDHEIM AND EULER.

Molybdate taken.	$Na_2S_2O_3$ used.		MoO_3 found.	Per cent of MoO_3 referred to molybdate taken.
grm.	cm³		grm.	
0.2674	30.8	1 cm³ = 0.00709 MoO_3.	0.2184	[81.71]
0.4418	50.8		0.3601	81.51
0.4075	[40.7]*		0.3317	81.40
0.3281	37.33	1 cm³ = 0.007086 MoO_3.	0.2644	[81.85
0.4340	49.43		0.3502	81.69
0.4098	46.63		0.3304	81.67
0.4305	49.08		0.3478	81.78]

Appended is a recalculation of the percentage of the trioxide found, with columns showing the percentage error and the error stated in fractions of a gram. Changes from the figures of Friedheim and Euler are in heavy-faced type.

RECALCULATION OF THE RESULTS OF FRIEDHEIM AND EULER.

Corrected per cent of MoO_3, found, referred to the molybdate.	Error in per cent of MoO_3 found compared with MoO_3 taken.	Error of MoO_3.
		grm.
81.68	0.23+	0.0005+
81.51	0.03+	0.0001+
81.40	0.12–	0.0004–
80.58	1.12–	0.0030–
80.69	0.99–	0.0035–
80.62	1.05–	0.0035–
80.79	0.86–	0.0030–

These figures of their own (properly calculated) are sufficient to show the inadequacy of the method of Friedheim and Euler. We ourselves were occasionally able to get results from the method of Friedheim and Euler quite as good as

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* Probably 46.7.

these; it must be said, however, that most of our results obtained by their unmodified method have been even worse than their own.

In another series of six determinations, in which molybdenum trioxide was the starting-point, Friedheim and Euler were more successful, the errors varying from 0.0006 grm. + to 0.0006 grm. —. Thus Friedheim and Euler establish by their own results the fact that the hitting of the right point at which to stop their process of boiling is a matter of chance. In spite of the probability that some of the iodine which they found in the receiver was liberated by atmospheric action, the fact remains that their results are in many cases very low. That is, they did not boil long enough.

The difficulty appears again in the modification of their method which Friedheim and Euler apply to the determination of molybdenum trioxide associated with vanadium pentoxide,* namely, the distillation with phosphoric acid and potassium iodide of the residue left after reducing the vanadium pentoxide by hydrochloric acid and potassium bromide, according to the method of Holverscheit. We reproduce the part of their table which refers to the determination of the molybdenum, adding, however, columns containing the errors and corrected percentages.

MoO_3 taken.	MoO_3 found.	Per cent MoO_3 F. and E.	Error.	Per cent MoO_3. Recalculated.
grm.	grm.		grm.	
0.15037	0.15005	99.79	0.00032—	99.79
0.16895	0.16879	99.90	0.00016—	99.90
0.17758	0.17729	99.84	0.00029—	99.84
0.24975	0.24962	99.95	0.00013—	99.95
0.33151	0.33607	[99.87]	0.00456+	**101.38**

Four of the five determinations are accurate, but the fact that all figures are carried out to the fifth decimal place does not keep three good-sized figures out of the error column for the fifth determination.

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* Ber. Dtsch. chem. Ges., xxviii. 2072.

It is hardly necessary, in the light of a comparison of the results of Friedheim and Euler with ours, to discuss further the unreliability of the unmodified process. The necessity of a proper control of the volume, strength of acid, and excess of potassium iodide, as well as proper protection from atmospheric oxidation, is real.

VI

THE APPLICATION OF IODIC ACID TO THE ANALYSIS OF IODIDES.

By F. A. Gooch and C. F. Walker.*

It has long been understood that iodic acid is easily and completely reduced by an excess of hydriodic acid with the liberation of iodine according to the equation:

$$HIO_3 + 5HI = 6I + 3H_2O.$$

To apply this reaction to the quantitative estimation of iodic acid, it is only necessary to add to the free iodic acid or soluble iodate an excess of a soluble iodide, to acidify — best with dilute sulphuric acid — and to titrate the iodine thus set free with sodium thiosulphate, one-sixth of the iodine found being credited to the iodic acid.

It has been shown recently by Riegler† that this reaction may be also applied to the quantitative estimation of iodides, the iodine set free upon the addition of a known excess of iodic acid to the iodide solution being removed by petroleum ether, and the residual iodic acid titrated directly with sodium thiosulphate.

The present investigation was undertaken to define more particularly the limit of applicability of the reaction and to establish, if possible, a direct method for the quantitative estimation of iodides, dependent upon the action of iodic acid or an iodate in the presence of free sulphuric acid, neutralization of the solution by means of an acid carbonate, and titration of the free iodine by arsenious acid — five-sixths of the iodine thus found being credited to the iodide to be estimated. It

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* From Am. Jour. Sci. iii, 293.

† Zeitschr. anal. Chem., xxxv, 305.

has been found that by fulfilling certain necessary conditions, the proposed method is entirely successful, so far as concerns the estimation of iodine in iodide solutions free from large amounts of chlorides or bromides.

In a system containing a considerable quantity of free iodine with variable amounts of the other reagents mentioned, as well as possible impurities, it is conceivable that secondary reactions may occur, depending largely on conditions of mass, time, and temperature, and of a sort likely to alter the amount of recoverable iodine, or to exert an excessive oxidizing influence on the arsenious acid finally titrated. It has been established by Schönbein, Lunge and Schloch, and others, that iodine forms compounds with the alkalies of the type R–O–I, and Phelps* has recently found that the formation of some such compound, accompanying the iodate naturally expected, is distinctly recognizable when iodine and barium hydroxide interact at ordinary temperatures. It has been shown, also, in a former paper from this laboratory† that free iodine or an iodide interacts very easily with iodic acid in the presence of dilute hydrochloric acid with the formation of iodine monochloride, according to the equations:

$$HIO_3 + 2I_2 + 5HCl = 3H_2O + 5ICl.$$
$$HIO_3 + 2KI + 5HCl = 3H_2O + 2KCl + 3ICl.$$

Moreover, organic compounds containing the groups $-I = O$ and $-I\begin{matrix}=O\\=O\end{matrix}$, in which iodine seems to be analogous to nitrogen, result in great variety from the oxidation of halogen substitution products. It would seem, therefore, that the formation of inorganic reduction products of iodic acid under the conditions likely to obtain in this analytical process might be by no means beyond the bounds of possibility.

A few simple qualitative tests to determine the possibility of interaction between small quantities of iodine and iodic acid alone met with negative results. Thus, a single drop of a decinormal solution of iodine, made as usual in potassium

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* Am. Jour. Sci., ii, 70. Volume I, p. 370.

† Roberts, Am. Jour. Sci., xlviii, 157. Volume I, p. 257.

iodide, gave when added to 10 cm^3 of decinormal iodic acid a distinctive color to chloroform. Similar results were obtained when the iodine was employed in aqueous solution in which there was no alkaline iodide. A few drops of an aqueous solution of iodine treated (in either order) with 10 cm^3 of a saturated solution of potassium bicarbonate and 10 cm^3 of decinormal iodic acid gave the same distinctive color to chloroform as came from the same amount of iodine in the absence of the iodic acid. So it appears that if in the system under consideration reactions do occur between iodic acid and iodine to alter the amount of iodine recoverable, such action is not appreciable between small amounts of these materials. This, however, does not preclude the possibility of perceptible changes under the mass-action of a large amount of iodine.

The reactions of hydrochloric acid, and probably of hydrobromic acid, in the presence of varying amounts of iodic acid, iodine, and iodide, as well as the reaction of the alkaline carbonate upon such mixtures are doubtless complex, more or less reversible, and dependent upon proportions and dilution. The tendency of the former reactions is toward the reduction of the molecule of iodic acid, and the formation of the chloride or bromide of iodine. Thus, Miss Roberts * demonstrated that a solution of hydrochloric acid, so dilute that by itself it is without effect on iodic acid, acts upon a mixture of iodic acid with either free iodine or an iodide to form iodine monochloride. The action of the acid carbonate upon the iodine chloride or bromide may produce a salt of the oxy-acids and free iodine.

The practical effects, under the conditions of analysis, of the reaction between iodine, iodic acid and the halogen acids in presence of sulphuric acid, and of reactions which may occur upon neutralization by an acid carbonate, were studied in detail in a number of experiments.

The preliminary experiments of Table I were made to bring out the effect of neutralizing with the acid carbonate and subsequently titrating with an alkaline arsenite a solution

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* Loc. cit.

TABLE I.

EFFECT OF THE CARBONATE.

[5 cm³ H_2SO_4 (1 : 3). Total volume of liquid, 250 cm³.]

Exp.	I (in KI) taken.	$KHCO_3$ in excess.	I found.	Error.
	grm.	cm³	grm.	grm.
(1)	0.0713	Very small.	0.0707	0.0006–
(2)	0.0715	Very small.	0.0710	0.0005–
(3)	0.0718	10	0.0710	0.0008–
(4)	0.0710	10	0.0706	0.0004–
(5)	0.0723	10	0.0717	0.0006–
(6)	0.0713	20	0.0709	0.0004–
(7)	0.0718	20	0.0709	0.0004–
(8)	0.3565	Very small.	0.3560	0.0005–
(9)	0.3568	Very small.	0.3561	0.0007–
(10)	0.3567	10	0.3563	0.0004–
(11)	0.3596	10	0.3588	0.0008–
(12)	0.3565	10	0.3565	0.0000
(13)	0.3572	20	0.3560	0.0012–
(14)	0.3567	20	0.3569	0.0002+

containing sulphuric acid and a considerable amount of free iodine. The danger of mechanical loss of iodine during the effervescence accompanying neutralization, as well as by spontaneous volatilization from the surface during the process of titration, was minimized by effecting the neutralization in the trapped Drexel washing-bottle to be described later, and making the titration in the same tall washing cylinder without transfer. To varying amounts of a recently standardized decinormal solution of iodine were added successively 5 cm³ of dilute sulphuric acid and varying amounts of potassium bicarbonate in excess of that necessary to neutralize the free acid, decinormal arsenious acid in slight excess of the iodine, 5 cm³ of starch emulsion, and decinormal iodine to coloration, the total volume of the liquid being not greater than 250 cm³. The results show plainly that while the loss, mechanical or otherwise, in the treatment of reasonably large amounts of fairly concentrated iodine is perceptible, it is still well within permissible limits (amounting to a little less than 0.0005 grm. in the mean), and obviously independent of the excess of the carbonate in the solution, and of the amount of free iodine present.

TABLE II.

EFFECT OF DILUTION.

Exp.	KI taken.	KI found.	Error.	Approximate volume upon addition of H_2SO_4.	Volume H_2SO_4 (1 : 3) used.
	grm.	grm.	grm.	cm^3	cm^3
(1)	0.0772	0.0768	0.0004–	150	5
(2)	0.0772	0.0765	0.0007–	150	5
(3)	0.1544	0.1546	0.0002+	150	5
(4)	0.1544	0.1541	0.0003–	150	5
(5)	0.3087	0.3090	0.0003+	150	5
(6)	0.3087	0.3088	0.0001+	150	5
(7)	0.3859	0.3864	0.0005+	150	5
(8)	0.3859	0.3860	0.0001+	150	5
(9)	0.0772	0.0754	0.0018–	300	5
(10)	0.0772	0.0757	0.0015–	300	5
(11)	0.1543	0.1532	0.0011–	300	5
(12)	0.1544	0.1524	0.0020–	300	5
(13)	0.0772	0.0744	0.0028–	500	5
(14)	0.0772	0.0737	0.0035–	500	5
(15)	0.1544	0.1521	0.0023–	500	5
(16)	0.1544	0.1512	0.0032–	500	5
(17)	0.3859	0.3827	0.0032–	500	5
(18)	0.3859	0.3831	0.0028–	500	5
(19)	0.0772	0.0744	0.0028–	500	10
(20)	0.0772	0.0757	0.0015–	500	10
(21)	0.3859	0.3828	0.0031–	500	10
(22)	0.3859	0.3827	0.0032–	500	10

In the experiments of Table II the proposed process of analysis was tested upon potassium iodide taken by itself in varying amounts of a $\frac{1}{40}$ normal solution and carefully standardized by the method formerly elaborated in this laboratory.* The apparatus employed was a Drexel washing-bottle of 500 cm^3 or 1000 cm^3 capacity, according to requirements, with stop-cock and thistle-tube fused to the inlet tube and a Will and Varrentrapp absorption trap sealed to the outlet, as shown in the accompanying figure. The iodide for the test was drawn from a burette into the bottle and carefully washed down, and potassium iodate in excess of the amount theoretically necessary (namely,

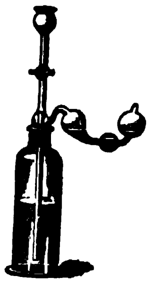

FIG. 18.

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* Gooch and Browning, Am. Jour. Sci., xxxix, 188. Volume I, p. 1.

5 cm^3 of a 0.5 per cent solution for every portion of 20 cm^3 of the iodide solution), was added and the volume of the liquid was adjusted to the volume at which it was desired that the iodic and hydriodic acids should react. The stopper with the thistle-tube and trap was now placed on the bottle and the trap was half filled by means of a pipette with a 5 per cent solution of potassium iodide. Five centimeters of dilute (1:3) sulphuric acid were added through the thistle-tube and washed down; the stop-cock was closed, and the solution gently agitated, if necessary, to insure a complete separation of iodine. Potassium bicarbonate in saturated solution to an amount about 10 cm^3 in excess of that required to neutralize 5 cm^3 of dilute (1:3) sulphuric acid, was poured into the thistle-tube, and allowed to flow into the bottle slowly enough to avoid a too violent evolution of gas. The stop-cock was closed and the solution agitated by giving to the bottle a rotary motion, at the same time keeping the bottom pressed down upon the work-table, to prevent a possible splashing of the iodide out of the trap into the yet acid solution. When the neutralization of the solution had been completed, the bottle was shaken until the last trace of violet vapor was absorbed in the liquid. The greater part of the solution in the trap was then run back into the bottle, the stopper removed, and the tube and trap carefully washed, the washings being added to the bulk of the solution. Decinormal arsenious acid was introduced from a burette to the bleaching point, 5 cm^3 of starch emulsion were added, and the solution was titrated back with decinormal iodine (usually only a few drops) to coloration.

Blank tests made upon a solution obtained by mixing the maximum amount of the iodate with 5 cm^3 of dilute sulphuric acid (1 : 3), neutralizing as usual with potassium bicarbonate, adding the iodide from the trap and 5 cm^3 of starch emulsion, showed that a single drop of iodine was invariably sufficient to bring out the starch blue. Occasionally it was found that the mixture, particularly when chlorides or bromides were present, of itself developed a trace of color, but by no means a reading tint. A correction of the one drop of iodine necessary to bring out the color reaction in the blanks, was applied uniformly in the analytical process.

The number of centimeters of decinormal arsenious acid required to bleach the free iodine, multiplied by 0.01383 (log. $\bar{2}$.140822) gives the number of grams of potassium iodide taken for analysis, being equivalent to five-sixths of the iodine liberated in the solution.

From these results it appears that the degree of dilution of the solution at the time when the mixed iodide and iodate are acidified has an important influence on the completeness of the reaction. Thus, the mean error of the determinations in which the volume at the time of the reaction did not exceed 150 cm³ was practically nothing, while the errors at volumes of 300 cm³ and 500 cm³ amounted to 0.0016 grm. and 0.0028 grm. respectively. It is obvious that the doubling of the amount of sulphuric acid used in acidifying does not increase the amount of iodine liberated at the highest dilution. The plain inference is that the interaction between the iodide and iodate should be brought about in a volume of liquid not much exceeding 150 cm³.

In the following series of experiments, recorded in Table III, the effect of the introduction of a chloride or bromide

TABLE III.

Effect of Chloride and Bromide.

Exp.	KI taken.	KI found.	Error.	NaCl taken.	KBr taken.
	grm.	grm.	grm.	grm.	grm.
(1)	0.0772	0.0795	0.0023+	0.2	. .
(2)	0.0772	0.0784	0.0012+	0.2	. .
(3)	0.0771	0.0823	0.0052+	0.5	. .
(4)	0.0773	0.0819	0.0046+	0.5	. .
(5)	0.1544	0.1588	0.0044+	0.5	. .
(6)	0.1544	0.1590	0.0046+	0.5	. .
(7)	0.0772	0.0802	0.0030+	. .	0.2
(8)	0.0773	0.0853	0.0080+	. .	0.2
(9)	0.0772	0.0873	0.0101+	. .	0.5
(10)	0.0772	0.0861	0.0089+	. .	0.5
(11)	0.1544	0.1646	0.0102+	. .	0.5
(12)	0.1543	0.1626	0.0083+	. .	0.5

into the iodide (before the iodate is added) was studied. The volume of the liquid at the time of acidifying was fixed at 150 cm^3 approximately, and 5 cm^3 of the dilute sulphuric acid (1 : 3) were used. The mode of procedure was otherwise similar to that of the foregoing series.

The influence of sodium chloride and potassium bromide in increasing the amount of iodine liberated is plain. The increase comes without doubt from the iodate, and is doubtless due to the formation of iodine chloride or bromide, during the acidifying, by the interaction of the free iodine, the iodic acid, and the hydrochloric or hydrobromic acid, according to the reactions previously discussed. It is plain, therefore, that the value of the process in the determination of iodine in an iodide is restricted of necessity to those cases in which it is known that chlorides or bromides are not present to

TABLE IV.

ANALYSIS OF PURE POTASSIUM IODIDE.

Exp.	KI taken.	KI found.	Error.
	grm.	grm.	grm.
(1)	0.0814	0.0816	0.0002+
(2)	0.0814	0.0813	0.0001–
(3)	0.0814	0.0805	0.0009+
(4)	0.0815	0.0809	0.0006–
(5)	0.0814	0.0808	0.0006–
(6)	0.0814	0.0806	0.0008–
(7)	0.0814	0.0812	0.0002–
(8)	0.1628	0.1624	0.0004–
(9)	0.1628	0.1617	0.0011–
(10)	0.1628	0.1621	0.0007–
(11)	0.1628	0.1619	0.0009–
(12)	0.1628	0.1624	0.0004–
(13)	0.1628	0.1621	0.0007–
(14)	0.1628	0.1626	0.0002–
(15)	0.2442	0.2451	0.0009+
(16)	0.2442	0.2442	0.0000
(17)	0.2442	0.2439	0.0003–
(18)	0.3256	0.3258	0.0002+
(19)	0.3256	0.3256	0.0000
(20)	0.3256	0.3258	0.0002+
(21)	0.3256	0.3272	0.0016+
(22)	0.3256	0.3256	0.0000
(23)	0.4071	0.4076	0.0005+
(24)	0.4071	0.4080	0.0009+
(25)	0.4071	0.4073	0.0002+

any considerable extent. For determining the standard of a solution of nearly pure potassium iodide, employed in so many laboratory processes, it should find useful application.

In Table IV are comprised a number of experiments made exactly like those which seemed to give the best results in the series of Table II. The iodide and an excess of iodate (5 cm^3 of the 0.5 per cent solution to every 20 cm^3 of $\frac{N}{10}$ iodide) were made to interact in a volume of about 150 cm^3, 5 cm^3 of sulphuric acid (1 : 3) were used to bring about the reaction, 10 cm^3 of potassium bicarbonate were added after the neutralization of the sulphuric acid was complete, and the free iodine was estimated by titrating decinormal arsenious acid, the manipulation being like that previously described in detail.

The average result of a series of several determinations in which a great excess (0.1 grm.) of potassium iodate was used, proved to be practically identical with that of a similar series in which only a small excess of the iodate was employed, so that it appears to be unnecessary in any practical work to restrict the amount of iodate below the amount necessary to decompose the maximum quantity of potassium iodide which we have handled, namely, 0.4 grm.

It appears that for the estimation of iodine in a soluble iodide free from notable amounts of chlorides or bromides, this method, depending as it does upon a single standard solution, is simple, fairly accurate, and rapid.

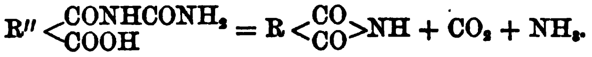
VII

THE ACTION OF UREA AND PRIMARY AMINES ON MALEIC ANHYDRIDE.*

By FREDERICK L. DUNLAP and ISAAC K. PHELPS.

In a former article,† a method was described by one of us for obtaining imides by the action of urea on the anhydrides of dibasic acids. It was shown that the formation of imides by the interaction of urea and anhydrides was to be explained by the addition of the urea and the anhydrides to form an acid, which when heated, decomposed with the formation of the imide, carbon dioxide and ammonia. These reactions can be shown by the following equations:

$$R'' <\substack{CO \\ CO}> O + NH_2CONH_2 = R'' <\substack{CONHCONH_2 \\ COOH}.$$



$$R'' <\substack{CONHCONH_2 \\ COOH} = R <\substack{CO \\ CO}> NH + CO_2 + NH_3.$$

In some cases this intermediate product, formed by the addition of the reacting substances, was readily isolated, and upon heating to certain temperatures, it was found that this addition-product decomposed with the formation of the imide.

It was found, in particular, that maleïc anhydride formed an addition-product with urea, and we hoped to obtain the unknown imide of maleïc acid by the decomposition of this addition-product.

Maleüric Acid. — When equal molecules of maleïc anhydride and urea are heated to 100°–105° C. in an oil-bath, the mixture melts, and if this temperature is maintained for a short time,

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* From Am. Chem. Jour., xix, 492.

† Am. Chem. Jour., xviii, 332. Volume I, 355.

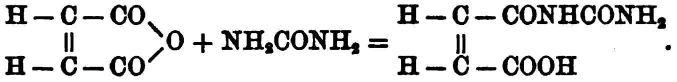
the liquid solidifies. This product was purified by crystallization from alcohol, and when pure was perfectly white and melted at 167.5°–168° with decomposition. Upon analysis the following results were obtained:

0.2148 gram substance gave 0.2968 gram CO_2 and 0.0751 gram H_2O.

	Calculated for $C_5H_6O_4N_2$.	Found.
C	37.97	37.69
H	3.80	3.88

Maleüric acid is soluble in hot water and alcohol, fairly insoluble in cold and insoluble in chloroform, benzene, ligroïn, carbon disulphide, acetone, and ether.

Its formation and structure are shown in the following equation:



$$\left.\begin{array}{l} H-C-CO \\ \quad \Vert \\ H-C-CO \end{array}\right\rangle O + NH_2CONH_2 = \begin{array}{l} H-C-CONHCONH_2 \\ \quad \Vert \\ H-C-COOH \end{array}.$$

No difficulty was expected in the formation of the imide of maleïc acid, either from the maleüric acid, or by the direct heating of maleïc anhydride and urea; for, in the cases already studied,* the reaction ran with great smoothness and ease. But, for some unknown reason, the imide of maleïc acid could not be obtained — at least in quantities for complete identification. A great many experiments were carried out under varying conditions, but only under one set of conditions could any product be isolated, and then unfortunately the yield was so distressingly small that the study of the compound had to be abandoned. When equal molecules of maleïc anhydride and urea are heated in a boiling-flask, at first slowly, and finally at the full heat of a Bunsen burner, a vigorous evolution of carbon dioxide and ammonia took place, and a small amount of a dark-colored distillate was obtained, which on cooling solidified and gave a melting-point of 130.5° after crystallization from anhydrous acetone. This same crystalline

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* Loc. cit.

product was also obtained on distilling the maleüric acid. In both cases a large amount of carbonaceous residue remained in the boiling-flask.

Although the method of formation of this compound is exactly parallel to that employed in the preparation of succinimide,* yet the identity of this product cannot be regarded as established until sufficient quantities of it have been prepared to subject it to elementary analysis.

The Action of Primary Amines on Maleïc Anhydride.

Anschütz† in 1889 published a method by which anilic acids could be very easily prepared by dissolving molecular quantities of aniline and the anhydride of dibasic acids in dry chloroform, when after standing for a short time the anilic acid crystallized out. Following out this line and method of formation, suggested by Anschütz's work, some derivatives of maleïc acid have been prepared and studied.

p-Tolylmaleämic Acid.—Molecular proportions of maleïc anhydride and *p*-toluidine were dissolved in dry chloroform, and upon mixing these two solutions, there immediately separated out a light yellow precipitate. After standing for a time to insure the complete precipitation of the product, it was filtered off and purified by crystallization from alcohol, from which it separated in lemon-yellow needles. The pure product melted at 201°, with evolution of gas. It is readily soluble in ether, acetone, and hot alcohol, but insoluble in benzene, ligroïn, carbon disulphide, chloroform and water. Upon analysis the following results were obtained:

0.2072 gram substance gave 0.4881 gram CO_2, and 0.1068 gram H_2O.

	Calculated for $C_{11}H_{11}O_3N$.	Found.
C	64.39	64.24
H	5.37	5.73

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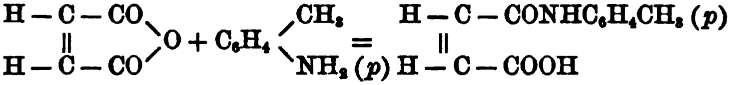
* Loc. cit.

† Ber. Dtsch. chem. Ges., xx, 3214.

The structure and mode of formation of this *p*-tolylmaleämic acid may be seen from the following equation:



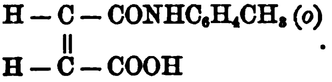
$$\begin{array}{l}H-C-CO\\ \quad\Vert\\ H-C-CO\end{array}\!\!\!>O+C_6H_4\!\!<\!\!\begin{array}{l}CH_3\\ \\ NH_2\,(p)\end{array}=\begin{array}{l}H-C-CONHC_6H_4CH_3\,(p)\\ \quad\Vert\\ H-C-COOH\end{array}$$

o-Tolylmaleämic Acid. — This acid was prepared similarly to the *p*-tolylmaleämic acid, using molecular proportions of maleïc anhydride and *o*-toluidine. The product was purified by crystallization from alcohol, from which it separated in bunches of thick light yellow prisms. When pure it melted at 117.5°–118°. It is readily soluble in acetone, and in alcohol; sparingly soluble in chloroform, and insoluble in ligroïn, carbon disulphide, benzene, water, and ether. Analysis gave the following results:

0.2124 gram substance gave 0.4993 gram CO_2, and 0.1146 gram H_2O.

	Calculated for $C_{11}H_{11}O_3N$.	Found.
C	64.39	64.12
H	5.37	5.99

It has the structure represented by the formula



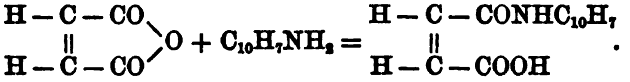
$$\begin{array}{l}H-C-CONHC_6H_4CH_3\,(o)\\ \quad\Vert\\ H-C-COOH\end{array}.$$

β-Naphthylmaleämic Acid. — When molecular quantities of *β*-naphthylamine and maleïc anhydride were mixed in dry chloroform solution they reacted and united as readily as did the *o*- and *p*-toluidines and the anhydride. Almost immediately a yellow crystalline precipitate separated out. This, after standing a short time, was filtered off and crystallized from alcohol. It separated from alcohol in small bright yellow needles, which, when pure, melted at 200° with evolution of gas. It is soluble in acetone and alcohol, but insoluble in ether, carbon disulphide, chloroform, benzene, ligroïn, and water. Analysis gave the following results:

0.2033 gram substance gave 0.5226 gram CO_2 and 0.0948 gram H_2O.

	Calculated for $C_{14}H_{11}O_3N$.	Found.
C	69.71	70.11
H	4.56	5.18

This addition-product is obviously formed as follows:



a-Naphthylamine appears also to be added readily to maleïc anhydride, but the product has not been submitted to analysis.

VIII

THE SEPARATION OF ALUMINUM AND BERYLLIUM BY THE ACTION OF HYDROCHLORIC ACID.

BY FRANKE S. HAVENS.*

IN a former paper † a method was described for the determination of aluminum in the presence of iron, based upon the fact that the hydrous aluminum chloride $AlCl_3 . 6H_2O$ is practically insoluble in a mixture of strong hydrochloric acid and anhydrous ether saturated with hydrochloric acid gas, while the ferric chloride is entirely soluble in that medium.

The work to be described in this paper is an extension of this process to cover the separation of aluminum from beryllium, with the subsequent determination of the beryllium by weighing as the oxide after conversion to the nitrate and ignition.

The aluminum chloride solution was prepared by dissolving the so-called pure aluminum chloride of commerce in as little water as possible, precipitating and washing free from iron with strong hydrochloric acid, dissolving the chloride thus obtained in water, precipitating the hydroxide by ammonia, washing the precipitate free from all alkalies, and redissolving it in hot hydrochloric acid. From this solution, after cooling, gaseous hydrochloric acid precipitated the pure hydrous chloride. This prepared chloride was dissolved in water and the solution standardized by precipitating with ammonia the hydroxide from weighed portions and weighing as the oxide. The solution of beryllium used was made by dis-

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* From Am. Jour. Sci., iv, 111.

† Gooch and Havens, Am. Jour. Sci., ii, 416. This volume, p. 20.

solving in water beryllium chloride found to be free from iron by the sulphocyanate test, and giving no precipitate when tested by the gaseous hydrochloric acid process to be described later on. This was standardized by precipitating with ammonia the hydroxide from weighed portions and weighing the ignited oxide in the usual manner.

In the experiments of Table I, weighed portions of the aluminum solution were mixed with portions of the beryllium chloride solution representing from 0.01 gram to 0.10 gram of the oxide, an equal volume of a mixture of strong hydrochloric acid and ether (taken in equal parts) was added to the solution of the mixed chlorides, and the whole was completely saturated with gaseous hydrochloric acid while kept at a temperature of about 15° C. by immersing the receptacle in running water. Ether was added, equal in volume to the aqueous aluminum and beryllium solutions originally taken, and the current of gas again turned on until saturation was complete. By this treatment there is present at the end of the saturation a volume of ether equal to that of the aqueous hydrochloric acid introduced and generated. The finely crystalline precipitate of aluminum chloride was caught on asbestos in a filter crucible washed with a previously prepared mixture of hydrochloric acid and ether in equal parts saturated at 15° C. with hydrochloric acid gas, and dried for half an hour at a temperature of 150° C. It was next covered with a layer of pure mercuric oxide, which had been tested and found to leave no residue on volatilizing,

TABLE I.

Exp.	Al_2O_3 taken in solution as the chloride.	Al_2O_3 found.	Final volume.	Error.
	grm.	grm.	cm^3	grm.
(1)	0.1046	0.1044	12	0.0002–
(2)	0.1046	0.1038	12	0.0008–
(3)	0.1067	0.1066	12	0.0001–
(4)	0.1071	0.1063	12	0.0008–
(5)	0.1059	0.1054	30	0.0005–

and the crucible was gently heated over a low flame under a ventilating hood and finally ignited over the blast.

From these results it is obvious that the aluminum chloride may be determined in the presence of beryllium chloride with reasonable accuracy.

The beryllium may be recovered in the filtrate from the aluminum chloride by precipitation with ammonia after nearly complete evaporation of the acid. It was found, however, upon trial that the conversion of the chloride to the oxide without precipitation and filtration may be easily accomplished by treatment with nitric acid and ignition. The results of Table II indicate this clearly. In these experiments weighed portions of the beryllium solution were evaporated just to dryness on a radiator, care being taken not to heat to the volatilizing point of the beryllium chloride, a few drops of strong nitric acid were added, the liquid was evaporated, and the residue heated — at first gently, to break up the nitrate safely and finally on the blast. It was found that this conversion of the beryllium to the nitrate can be carried on in platinum without attacking that metal appreciably, providing care be taken to remove thoroughly all excess of hydrochloric acid before the nitric acid is added to the dry residue.

TABLE II.

Exp.	BeO taken in solution as the chloride.	BeO found.	Error.
	grm.	grm.	grm.
(1)	0.0488	0.0481	0.0002–
(2)	0.0488	0.0483	0.0000
(3)	0.1076	0.1085	0.0009+

In Table III, (1)–(9), are given the results of experiments in which both the aluminum and the beryllium were determined — the former by precipitation as the hydrous chloride and weighing as the oxide after igniting with mercuric oxide: the latter by the conversion of the chloride, through the nitrate, into the oxide. In experiment (10) (made to get a comparison of the methods) the beryllium was recovered by precipitating the hydroxide with ammonia from the partially evaporated solution of the chloride after removing the aluminum.

In experiments (1) to (5), inclusive, the aluminum was determined exactly as previously described; in (6) and (7) the solutions (being originally larger) were concentrated by evaporation previous to the addition of the ether and hydrochloric acid mixture. In experiments (8), (9) and (10), the treatment was varied advantageously by saturating the aqueous solution directly with hydrochloric acid gas before adding an equal volume of ether, and completing the saturation.

TABLE III.

Exp.	Al_2O_3 taken in solution as the chloride.	Al_2O_3	Error.	Final volume.	BeO taken in solution as the chloride.	BeO found.	Error.
	grm.	grm.	grm.	cm^3	grm.	grm.	grm.
(1)	0.1059	0.1058	0.0001–	12	0.0198	0.0204	0.0006+
(2)	0.1053	0.1044	0.0009–	12	0.0194	0.0196	0.0002+
(3)	0.1065	0.1059	0.0006–	12	0.0197	0.0205	0.0008+
(4)	0.1068	0.1060	0.0008–	12	0.0199	0.0207	0.0008+
(5)	0.1049	0.1047	0.0002–	12	0.0198	0.0208	0.0010+
(6)	0.1060	0.1057	0.0003–	12	0.0977	0.0969	0.0008–
(7)	0.1064	0.1063	0.0001–	12	0.1085	0.1084	0.0001–
(8)	0.1046	0.1038	0.0008–	30	0.1083	0.1087	0.0004+
(9)	0.1051	0.1048	0.0003–	30	0.1071	0.1078	0.0007+
(10)	0.1076	0.1075	0.0001–	30	0.1086	0.1094	0.0008+

These results are plainly very good.

The manipulation of the process is not difficult. The gaseous hydrochloric acid is most conveniently produced by the well known method of treating with strong sulphuric acid in regulated current a mixture of strong aqueous hydrochloric acid and common salt. A platinum dish hung in an inverted bell-jar, provided with inlet and outlet tubes through which the current of water for cooling is passed, makes the best container for the solution to be saturated with the gas. It is advantageous to arrange the filtration upon asbestos so that the filtrate and washings may be caught directly in the crucible (placed under the bell-jar of the filter pump) in which the subsequent evaporation is to be effected. The heating of the strong acid solution must be gradual and conducted with care to prevent mechanical loss by a too violent evolution of the gaseous acid.

IX

THE TITRATION OF SODIUM THIOSULPHATE BY IODIC ACID.

By CLAUDE F. WALKER.*

This investigation was undertaken to determine the nature and limitations of the reaction between iodic acid and thiosulphuric acid, and to show the expediency of employing iodic acid in standard solution for the direct titration of sodium thiosulphate. Riegler† states that iodic acid is readily obtained in the pure state, that it may be accurately weighed out, and that a solution of it may be exactly made up to a desired strength and kept for a long time unaltered. He further states that when a solution of sodium thiosulphate is titrated with iodic acid the reaction takes place according to the equation,

$$6Na_2S_2O_3 + 6HIO_3 = 3Na_2S_4O_6 + 5NaIO_3 + NaI + 3H_2O,$$

under which circumstances no free iodine will be evolved until all the sodium thiosulphate has been oxidized to tetrathionate; the first drop of iodic acid in excess, however, will react with the sodium iodide that has been formed, and separate iodine, as shown by the equation,

$$5NaI + 6HIO_3 = 5NaIO_3 + 3H_2O + 3I_2,$$

thus furnishing an accurate means for determining the end point.

A careful repetition of the work of Riegler has shown that his conclusions are in a large measure erroneous. Thus, it has been found that the ordinary "chemically pure" iodic acid, purchased from reliable manufacturers, is likely to con-

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* From the Amer. Jour. Sci., iv, 235.

† Riegler, Zeitschr. anal. Chem., xxxv, 308.

tain more than the theoretical amount of iodine, due probably to the presence of the anhydride, although iodic acid can be safely employed for standardizing when it is made in the laboratory by dissolving the purified anhydride, crystallizing out the acid, and drying over sulphuric acid. Such a carefully prepared product, if used immediately, will be found to contain the theoretical amount of iodine. Riegler's proposed method of titration depends on two different reactions, and to insure the accuracy of the process these must be definite, complete and non-reversible under the conditions of analysis. Thus one molecule out of every six of iodic acid should be reduced by six molecules of thiosulphate, with the formation of a neutral mixture of iodide and iodate, free from other oxidizing or reducing substances. Under these circumstances it might be expected that iodine will be liberated by the first trace of iodic acid in excess. It has been found by investigation, however, that although the main reaction between iodic acid and sodium thiosulphate may result in the formation of sodium tetrathionate in the proportions given, there is nevertheless striking evidence of some other obscure action of the thiosulphate, which influences the reduction of the iodic acid in such a way as to make it impossible to calculate the analyses according to Riegler's reaction. Moreover, a peculiar "after-coloration" which invariably follows the first formation of the starch blue during the titration of one solution against the other, seems to point to the possibility that the reaction between the iodide and iodic acid is dependent, under these circumstances, on conditions of time and mass for its completeness. It is not impossible that some third compound of iodine unstable in its nature, may be formed as an intermediate product and thus delay the liberation of iodine. In consideration of the results that have been obtained it appears that Riegler's proposed process for standardizing sodium thiosulphate, as well as his related method for the analysis of iodides,* must remain impracticable unless they can be modified so as to do away with a number of sources of error.

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* Riegler, Zeitschr. anal. Chem., xxxv, 305.

The analyses of solutions of iodic acid, during the entire course of the work, was invariably performed by adding to the portion of the solution to be analyzed an excess of potassium iodide, acidifying with 5 cm^3 of dilute (1 : 3) sulphuric acid, and recovering the liberated iodine by directly titrating the acid solution with sodium thiosulphate, or by neutralizing with potassium bicarbonate in excess, and directly titrating the alkaline solution with arsenious acid. In the latter case the neutralization was performed in a trapped Drexel washing bottle such as has been described in connection with the analysis of iodides.* In either case one-sixth of the iodine recovered was calculated to iodic acid, according to the terms of the equation,

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

It follows from these proportions that to bring the analyses within the range of the decinormal solutions ordinarily employed, the iodic acid taken for analysis must be restricted to comparatively small amounts. In the present work it was found convenient to analyze the iodic acid in quantities not much exceeding one-tenth of a gram, in which case the variation in the results in the same series is found to be almost inappreciable. In both variations of the process one or two blank analyses were invariably made, by performing the operation as detailed, except that no iodic acid was employed, and the correction of one drop of iodine thereby shown to be necessary to bring out the starch blue was uniformly applied in the analytical work.

To determine whether or not the purity of the ordinary iodic acid is sufficient to admit of its direct application in standard solutions, a series of experiments was made. Two different samples of "chemically pure" iodic acid were used. The first was in coarse granular crystals, and the second was in the form of fine powder. Quantities of both of these were dried in a desiccator over sulphuric acid to constant weight. Neither sample lost weight appreciably when left

* Gooch and Walker, Am. Jour. Sci. iii, 293. This volume, p. 33.

for a considerable time on the scale pan. A third sample of iodic acid was prepared by dissolving a quantity of the purest obtainable iodic anhydride in water, and evaporating at ordinary temperature. The resulting crystalline mass was dried over sulphuric acid in a desiccator for one week, until it ceased to lose weight, when it was presumed to consist of the pure normal acid. Two presumably decinormal solutions of each of the first two samples, and one such solution of the third sample of iodic acid were made by weighing out 17.585 grms. and dissolving in exactly one liter of water at 15° C. Convenient portions of each of these solutions were analyzed in the manner described, with results shown in the following table, averaged from many determinations.

TABLE I.

ANALYSES OF APPROXIMATELY $\frac{N}{10}$ IODIC ACID.

Solution analyzed.	Sample used.	HIO_3 taken.	HIO_3 found.	Error.
		grm.	grm.	grm.
I	A	0.1055	0.1066	0.0011+
II	A	0.1055	0.1062	0.0007+
III	B	0.1055	0.1065	0.0010+
IV	B	0.1055	0.1073	0.0018+
V	C	0.1055	0.1058	0.0002–

These results show that while the deviation from the theoretical strength of the solution in the case of the acid prepared from the anhydride is hardly appreciable, and will not affect the accuracy of any work in which the solution may be applied as a means of standardization, the solutions made from the purchased product, on the other hand, contain a very appreciable amount of iodine in excess of the theoretical. That iodic acid is somewhat unstable at 30–40° C., gradually losing water with the formation of the anhydride,[*] is well known, and it is quite possible that to some such gradual change as this must be attributed the fact that the ordinary iodic acid cannot be safely employed as a means of standardization unless its purity be directly determined by analysis.

[*] Dammer, Anorg. Chem., i, 564.

To determine whether a solution of iodic acid, once prepared and standardized, will retain its strength for a long period of time, two such solutions were kept for four months (in the dark) and then again analyzed. The results (averages of several determinations), given in Table II, substantiate the observation of Riegler that a solution of iodic acid will remain of constant strength.

TABLE II.

CONSTANCY OF STRENGTH OF IODIC ACID SOLUTIONS.

Iodic acid solution.	First analysis. HIO_3 found.	Second analysis (after four months). HIO_3 found.	Variation.
	grm.	grm.	grm.
I	0.1078	0.1072	0.0001–
II	0.1049	0.1046	0.0003–

An approximately one-twentieth normal solution of "chemically pure" sodium thiosulphate was made and its exact strength ascertained by titrating it with standardized iodine. A series of analyses made by oxidizing the sodium thiosulphate to sulphate, and precipitating and weighing as barium sulphate, gave results identical with those obtained with iodine, proving that all the sulphur present in the solution was in the form of thiosulphate. According to Riegler's equation, sodium thiosulphate and iodic acid react molecule for molecule, and solutions of these substances should therefore require for their mutual saturation volumes inversely proportional to their concentration. It was found, however, that when the one-twentieth normal solution of sodium thiosulphate that has been described was titrated in the presence of starch emulsion with an approximately decinormal solution of iodic acid, prepared from the anhydride, a distinctly blue color was produced long before the theoretical amount of iodic acid had been added. It was further noticed that the end-point of the reaction was far from distinct, a faint tinge of blue at first being visible, then suddenly becoming deeper, and immediately reappearing when bleached with sodium thiosulphate. The deficiency in the amount of iodic acid actually required to produce the blue color was not lessened by introducing only three-fourths of the theoretical amount of iodic acid, and estimating the residual thiosulphate with iodine. It was found, however, that the addition of a considerable quantity of potassium iodide to the solution, either before or during the titration, had the marked effect of making the reaction sharp and distinct, entirely preventing the "after separation" of iodine, at the same time postponing the appearance of the starch blue until a quantity of iodic acid had been added considerably in excess of the theoretical. These experiments were repeated with entirely different reagents, and under varied conditions of concentration, the results in every case exactly confirming those already observed.

For the purpose of more particularly investigating this subject, there were prepared and standardized an approximately decinormal solution of sodium thiosulphate, and an approximately one-fiftieth normal solution of iodic acid. Measured portions of the sodium thiosulphate solution were titrated with the iodic acid in the presence of starch emulsion under varying conditions of mass, time and dilution.

To determine the variability of the end-point of the reaction when the titration was conducted as directed by Riegler, a series of experiments was made. Measured amounts of the sodium thiosulphate solution were drawn from a burette into an Erlenmeyer beaker of suitable capacity, the sides of the beaker were carefully washed down with a small amount of water, 5 cm^3 of starch emulsion were added, and the iodic acid was slowly dropped into the small bulk of acid and starch, with constant agitation of the mixture, until the first tint of blue coloration appeared. The results obtained are given in Table III.

These experiments indicate that the constancy of the end reaction in different titrations of equal volumes of the same solution depends to a certain degree on the volume of sodium thiosulphate taken. The results in the case of the maximum amounts vary within a range of 1.04 cm^3, which corresponds

TABLE III.

Variation of the End Reaction between $\frac{N}{10}$ Sodium Thiosulphate and $\frac{N}{50}$ Iodic Acid, in the absence of Potassium Iodide.

Exp.	$Na_2S_2O_3$ taken.	HIO_3 introduced.	Mean value.	Variation.
	cm³	cm³	cm³	cm³
(1)	6	28.13	28.32	0.19−
(2)	6	27.79		0.53−
(3)	6	28.03		0.29−
(4)	6	28.32		0.00
(5)	6	28.32		0.00
(6)	6	28.71		0.39+
(7)	6	28.83		0.51+
(8)	6	28.43		0.11+
(9)	4	18.94	18.68	0.26+
(10)	4	18.67		0.01−
(11)	4	18.50		0.18−
(12)	4	18.60		0.08−

to 0.0035 grm. of iodic acid, while the average variation is 0.25 cm³, corresponding to 0.0009 grm. The variation in the analyses of the smaller amounts is less, the range being 0.44 cm³, corresponding to 0.0015 grm., and the average variation being 0.13 cm³, or 0.0005 grm. The probable error which these irregularities would introduce in any series of practical analyses by this method is obviously greater than can ordinarily be permitted in iodometric work.

TABLE IV.

Variation of the End Reaction between $\frac{N}{10}$ Sodium Thiosulphate and $\frac{N}{50}$ Iodic Acid, in the Presence of Potassium Iodide.

Exp.	$Na_2S_2O_3$ taken.	HIO_3 introduced.	Mean value.	Variation.
	cm³	cm³	cm³	cm³
(1)	6	32.53	32.48	0.05+
(2)	6	32.45		0.03−
(3)	6	32.67		0.19+
(4)	6	32.37		0.11−
(5)	6	32.36		0.12−
(6)	6	32.50		0.02+
(7)	4	22.30	22.19	0.11+
(8)	4	21.98		0.21−
(9)	4	22.17		0.02−
(10)	4	22.30		0.11+

The experiments detailed in Table IV were performed exactly similarly to those of the last series except that two grams of potassium iodide were added to the sodium thiosulphate before the titration was commenced.

These experiments indicate plainly that in the presence of potassium iodide the end reaction of different titrations of equal volumes of the same solution is practically independent of the amount taken for analysis. The results in the case of the maximum amounts vary within a range of 0.31 cm^3, or 0.0011 grm. of iodic acid, while the average variation is 0.09 cm^3, corresponding to 0.0003 grm. The variation in the analyses of the smaller amounts is practically the same as that of the larger, the range being 0.32 cm^3, corresponding to 0.0011 grm., and the average variation being 0.11 cm^3, or 0.0004 grm. It is therefore evident that the presence of potassium iodide in the sodium thiosulphate to be titrated will bring the variation of the formation of the reading tint within permissible limits.

A series of experiments was made to determine the nature and effect of the "after coloration" observed to take place when a solution of sodium thiosulphate, free from potassium iodide, was titrated with iodic acid to blue coloration, and then bleached with sodium thiosulphate. The titrations were performed in the usual manner except that the volume was adjusted just before the addition of the iodic acid, and the iodine that was set free after the formation of the first reading tint was destroyed at fixed intervals with measured amounts of sodium thiosulphate. The results are given in Table V.

In the experiments with small volumes the evolution of iodine in any considerable quantity ceased after two or three hours, although the solution would become recolored as often as it was bleached for a number of days. The traces of iodine thus set free, however, were seldom equivalent to more than one or two drops of sodium thiosulphate. The larger volumes, however, continued to separate iodine in abundance for a very long time. The amount of iodine thus liberated after the first coloration evidently varies with the amount of iodic acid required for the titration, although not strictly proportional to

TABLE V.

Effect of Dilution and Lapse of Time on the "After Coloration."

Exp.	$Na_2S_2O_3$ taken.	HIO_3 introduced.	$Na_2S_2O_3$ introduced.						Volume.
			15 m.	45 m.	1 h. 45 m.	2 h. 45 m.	20 h.	Total.	
	cm^3	cm^3	cm^3	cm^3	cm^3	cm^3	cm^3	cm^3	cm^3
(1)	6	27.68	0.25	0.18	0.08	0.00	0.03	0.49	50
(2)	6	27.70	0.20	0.10	0.03	0.03	0.08	0.39	50
(3)	6	28.17	0.16	0.10	0.08	0.01	none.	0.80	50
(4)	6	27.03	0.60	0.26	0.09	0.08	none.	0.98	150
(5)	6	27.60	0.98	0.28	0.06	0.04	0.04	1.35	150
(6)	6	28.60	1.34	0.46	0.17	0.03	0.14	2.14	200
(7)	6	28.85	1.20	0.50	0.28	0.06	0.27	2.81	200
(8)	6	31.68	1.46	0.74	0.10	0.21	0.23	2.74	250
(9)	6	29.90	1.04	0.60	0.23	0.15	0.46	2.48	250
(10)	6	36.09	1.60	1.23	0.63	0.84	0.18	3.98	300
(11)	6	37.59	1.65	1.38	0.72	0.27	0.10	4.07	800
(12)	6	37.23	1.92	1.05	0.64	0.33	*	. .	800

it. Both of these quantities increase at a regular rate with the volume of the solution.

To show with what accuracy the reaction between sodium thiosulphate and iodic acid may be applied to the direct estimation of one of these substances by the other, the averaged results of a large number of titrations are compared in Table VI. The operations were conducted as directed by Riegler, equal measured volumes of standardized sodium thiosulphate being titrated with iodic acid of known strength, in the presence of starch and under different conditions of time, dilution, and mass, the volume of iodic acid required to produced the blue coloration being in each case compared with the volume theoretically required by the terms of Riegler's equation.

These results show plainly that the amount of iodic acid required to decompose a given amount of sodium thiosulphate may be considerably above or below that required by the terms of Riegler's equation. Thus, with small volumes, and in the absence of potassium iodide, the thiosulphate is destroyed and the separation of iodine commences when only 93 per cent of the theoretical amount of acid has been titrated. At higher

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* No observation.

TABLE VI.

Titration of $\frac{N}{10}$ Sodium Thiosulphate with $\frac{N}{50}$ Iodic Acid.

Exp.	$Na_2S_2O_3$ taken.	HIO_3 used.	HIO_3 required by theory.	Error.	Error.	KI present.	Volume.
	cm³	cm³	cm³	cm³	per cent.	grm.	cm³
(1)	4	* 18.68	20.32	1.64–	8.0–	. .	50
(2)	6	28.32	30.48	2.16–	7.0–	. .	50
(3)	6	27.32	30.48	3.16–	10.0–	. .	150
(4)	6	28.78	30.48	1.75–	6.0–	. .	200
(5)	6	30.77	30.48	0.29+	0.01+	. .	250
(6)	6	36.97	30.48	6.49+	21.0+	. .	300
(7)	6	† 27.46	30.48	3.02–	10.0–	. .	50
(8)	6	26.15	30.48	4.33–	14.0–	. .	150
(9)	6	26.50	30.48	3.98–	13.0–	. .	200
(10)	6	28.16	30.48	2.32–	8.0–	. .	250
(11)	6	32.93	30.48	2.45+	8.0+	. .	300
(12)	4	* 22.19	20.32	1.87+	9.0+	2.0	50
(13)	6	32.48	30.48	2.00+	7.0+	2.0	50

dilutions the action is retarded, so that at 250 cm³ very nearly the theoretical amount of acid is required to produce the first blue color, and at 300 cm³ an excess of 21 per cent over the theoretical amount must be added. If the " after separation " of iodine is considered to be a measure of the excess of iodic acid, and if its amount is accordingly applied as a correction, it appears that for all volumes below 300 cm³ the original thiosulphate is completely destroyed when about 90 per cent of the theoretical amount of iodic acid has been added. The presence of potassium iodide in the system retards the action, so that at small volumes an excess of about 8 per cent of iodic acid must be added to completely destroy the thiosulphate and commence the separation of iodine. It is obvious from the preceding experiments that the reaction between iodic acid and sodium thiosulphate is so indefinite in its nature, and so dependent for completeness on conditions of time, dilution, and mass, that its direct application as a means of standardizing solutions must remain impracticable.

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* HIO_3 added to first blue color.

† Calculated by subtracting from the amount of iodic acid originally introduced, the volume of thiosulphate of equal strength required to bleach the solution after standing twenty hours.

the funnel tube and the mixture warmed again, when the oxidation of the oxalate was shown by the carbon dioxide evolved. The carbon dioxide was completely set free by the introduction of 10 cm^3 of sulphuric acid (1 : 4) and was driven completely to the absorption flask by boiling for five minutes. During the passage of the gas into the absorption flask, it was shaken frequently and was kept cool by standing in a dish of water and by pouring cold water over it from time to time. If, during the boiling, any fears are entertained as to the strength of the vacuum in the flasks, they may be easily allayed by opening momentarily the stop-cock of the funnel tube and noting the direction of the flow of water, contained in the funnel. After the boiling was ended, the atmospheric pressure was restored by allowing air, purified from carbon dioxide by passage through potash bulbs, to enter through the funnel tube of the boiling flask. Then the flasks were disconnected and the stopper of the absorption flask with its attachments was removed, the valve and its tube being carefully washed free from barium hydroxide. A second stopper, which was provided with a separating funnel, and a Will and Varrentrapp absorption apparatus, containing water to serve as a trap, was inserted into the mouth of the absorption flask and the emulsion brought to the boiling point. Decinormal iodine solution was then run in through the funnel tube in sufficient quantity to destroy the larger part of the excess of barium hydroxide and the emulsion brought to the boiling point again, after which iodine was again run in but this time to the permanent red color of the excess of free iodine. After cooling, this excess of iodine was determined by titration with decinormal arsenious acid solution. Thus, the excess of barium hydroxide taken being determined by the iodine lost, the barium hydroxide used, now in the form of carbonate, was known, from which the carbon dioxide which precipitated this carbonate, may be calculated.

The following results were obtained by this procedure.

TABLE I.

Exp.	Ammonium oxalate taken.	BaO_2H_2 taken.	BaO_2H_2 found.	CO_2 found.	CO_2 calculated.	Error on CO_2.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.2522	0.7267	0.1170	0.1565	0.1561	0.0004+
(2)	0.2542	0.7267	0.1118	0.1579	0.1574	0.0005+
(3)	0.5020	1.4535	0.2417	0.3110	0.3108	0.0002+
(4)	0.5058	1.3954	0.1753	0.3131	0.3131	0.0000±
(5)	1.0033	2.6168	0.1955	0.6218	0.6211	0.0002+
(6)	1.0003	2.5951	0.1836	0.6189	0.6192	0.0008–
(7)	1.0010	2.6163	0.2037	0.6192	0.6197	0.0005–

In experiments (5) and (6), a few drops of ammonia were added to the oxalate solution before running in the permanganate; in (3) and (7), the permanganate was treated to alkalinity with barium hydroxide; in the remaining experiments, (1), (2), and (4), the permanganate was slightly acid with the sulphuric acid used in its purification from carbon dioxide, as already described. The results obtained are good and it is plain that the oxidation proceeded regularly, whether the first action of the permanganate was in the alkaline or slightly acid solution.

Jones * has shown that formates may be determined volumetrically by titration with potassium permanganate in alkaline solution. In an attempt to determine formates by the process outlined above, the pure barium salt was used. This was prepared by treating the aqueous solution of formic acid with pure barium carbonate to neutrality and crystallizing the product. It was proved pure by ignition and weighing in the form of carbonate.

In making determinations of carbon in this formate, weighed portions were introduced into the boiling flask, together with sodium hydroxide solution, which was taken in such quantity as to more than neutralize the acid in the potassium permanganate. Naturally, the sodium hydroxide must be freed from carbonate — and this was effected by treatment with an excess of barium hydroxide and filtering. An excess

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* Amer. Chem. Jour., xvii, 539.

of potassium permanganate is then run into the flask and the solution heated to boiling. An excess of dilute sulphuric acid is introduced into the mixture and the carbon dioxide, thus set free, completely driven over to the absorption flask and determined as before. Table II shows results obtained by the process.

TABLE II.

Exp.	Barium formate taken.	BaO_2H_2 taken.	BaO_2H_2 found.	CO_2 found.	CO_2 calculated.	Error on CO_2.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.5001	0.9302	0.1745	0.1939	0.1935	0.0004+
(2)	0.5033	0.9012	0.1402	0.1953	0.1947	0.0006+
(3)	1.0002	1.6861	0.1793	0.3867	0.3870	0.0003−
(4)	1.0059	1.6279	0.1098	0.3897	0.3892	0.0005+
(5)	1.3750	2.2529	0.1820	0.5315	0.5320	0.0005−
(6)	1.5023	2.4419	0.1754	0.5816	0.5814	0.0002+

These results show plainly that the carbon of formic acid may be determined accurately by the method outlined.

It was found incidentally that ammonia cannot take the place of the sodium hydroxide in this process, probably because the ammonia volatilizes to the absorption flask during the boiling and is acted on by the iodine subsequently used and is thus registered as barium hydroxide.

It is a well-known fact that tartrates are oxidized by permanganates. I have found, however, that when tartaric acid is treated under the conditions of analysis outlined above in acid solution, the oxidation is incomplete; but that oxidation is complete if the tartrate is heated in a solution alkaline with sodium hydroxide and then acidified with sulphuric acid.

The tartrate used was a recrystallized tartar emetic, dried at 100° C. The following results were obtained with such a tartrate by this process.

It seems possible to draw the general conclusion from the results recorded that organic substances which are oxidized completely by the permanganate may be determined by the process outlined above. It will also be seen that the use of

TABLE III.

Exp.	Tartar emetic. taken.	BaO_2H_2 taken.	BaO_2H_2 found.	CO_2 found.	CO_2 calculated.	Error on CO_2.
	grm.	grm.	grm.	grm.	grm.	grm,
(1)	0.5051	1.2450	0.1709	0.2756	0.2751	0.0005+
(2)	0.5030	1.2226	0.1536	0.2743	0.2739	0.0004+
(3)	0.7509	1.7855	0.1401	0.4094	0.4091	0.0003+
(4)	0.7541	1.7430	0.1410	0.4111	0.4107	0.0004+
(5)	1.0018	2.8456	0.2187	0.5458	0.5456	0.0002+
(6)	1.0005	2.2485	0.1196	0.5451	0.5450	0.0001+

the rubber stopper in the boiling flask, with due care to prevent its contact with the solution, does not introduce an appreciable error.

Wanklyn and Cooper * and others have noted the fact that potassium permanganate, whether in acid or alkaline solution, will not oxidize all organic substances (acetates, for example), even at the boiling temperature. It is well known that a mixture of concentrated sulphuric and chromic acids has a much wider field of action in oxidizing organic compounds than the permanganate. With hopes of applying this reagent more widely to the determination of organic carbon, the experiments about to be recorded were tried.

Method of Oxidation by Chromic Acid.

A concentrated mixture of chromic and sulphuric acids, although a much more powerful oxidizer than potassium permanganate in aqueous solutions, fails to oxidize completely many organic compounds. Thus Cross and Higgin † have shown that carbohydrates are among the number of such organic substances; and later Cross and Bevan find that carbohydrates and many other substances are oxidized to a mixture of carbon dioxide and monoxide. Messinger ‡ has proved that carbon may be determined in organic compounds by passing the mixed products, resulting from the oxidation with chromic and sulphuric acids, through a short combustion tube,

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* Phil. Mag. (5), vii, 138.

† Jour. Chem. Soc., xli, 113.

‡ Ber. Dtsch. chem. Ges., xxiii, 2756.

filled with granular copper oxide and heated in a furnace—all of which facts have been confirmed in my own experience.

Ludwig* has observed that the contact of carbon monoxide with a mixture of chromic and sulphuric acids, especially when hot, results in the oxidation of that gas to carbon dioxide. This fact suggested the idea of substituting for the apparatus described above a new form, adapted to retain the first products of oxidation in prolonged contact with the oxidizing mixture. This apparatus, shown in the accompanying figure, by means of which, as the sequel shows, it has been found possible to extend the availability of the oxidizing mixture, is put together as follows: A thick-walled, round-bottomed flask of a liter's capacity, serving as an oxidizing chamber, is closed by a rubber stopper with two perforations, through one of which passes the tube of a separating funnel of about 100 cm^3 capacity. The tube of this funnel reaches nearly to the bottom of the flask and is drawn out at the lower end. A disc of platinum foil is hung in the neck of the flask, nearly closing it, and held in place by a platinum wire passing through the foil and tucked under the rubber stopper where the funnel tube enters. The second hole of the stopper is filled by the exit tube, a glass tube of 0.7 cm. internal diameter. This tube is expanded just above the stopper to a small bulb, which serves to prevent mechanical loss of the solid contents of the flask during the boiling, and is joined by means of a rubber connector (provided with a screw pinch-cock) to the inlet tube of the absorption flask, which is an ordinary 500 cm^3 round-bottomed flask. This flask is also closed by a rubber stopper with two perforations, through

Fig. 19.

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* Ann. Chem. (Liebig), clxii, 47.

one of which passes the inlet tube described above and through the other the exit tube, which is also enlarged to a small bulb just above the stopper and is closed by a rubber connector and screw pinch-cock. The glass ground stopper of the funnel tube is carefully cleaned and lubricated with a thick solution of metaphosphoric acid.

Instead of getting the vacuum by the water pump, it may be got almost as quickly and certainly more simply by boiling the water in the evolution flask and the barium hydroxide solution in the absorption flask at the same time — both flasks being connected, ready for making a determination. When steam issues in good quantity from the exit tube, the burner is removed from under the evolution flask, the attached pinch-cock closed, the burner under the absorption flask taken away, and the screw pinch-cock upon the exit tube quickly closed. The flasks are then allowed to cool.

In making a determination, the organic substance is weighed out in a counterbalanced bulb, so thin that it may be easily broken later and made with a wide mouth for convenience in introducing the solid substance. After the substance is weighed, the mouth of the bulb is sealed by heating in a small blow-pipe flame and the tube introduced into the evolution flask, together with an amount of pure potassium dichromate, which is known to be in excess of that required to oxidize the organic substance. The flasks are connected, as already described, with an appropriate amount of barium hydroxide solution in the absorption flask and 10 cm^3 of pure water in the evolution flask, and the vacuum is obtained (as described above) by boiling both flasks, the boiling being stopped when the water in the evolution flask has decreased to 2 or 3 cm^3. Naturally, this boiling must be so regulated as not to allow loss of the solid material in either flask. The vacuum obtained, the tube containing the organic substance is broken by shaking the flask, and 20 cm^3 of concentrated sulphuric acid, previously purified from organic material by heating to the fuming point with a few crystals of potassium dichromate, are run in through the funnel tube, when reduction of the chromic acid soon becomes evident. While still hot, the acid is shaken in the flask violently, the platinum foil hung in the neck serving to protect the rubber stopper. The flask is warmed to approximately 105° C., the highest temperature to which, as shown by Cross and Bevan,* a mixture of chromic and sulphuric acids may be safely heated without the disengagement of oxygen gas. Water is then run in until the crystals of chromic anhydride have disappeared and the danger of the evolution of oxygen is past. The solution is heated to its boiling point, care being taken that it shall not get under pressure, which can easily be observed by opening momentarily the stop-cock of the funnel tube and noting the direction of the flow of water, contained in the funnel. The flask is shaken and heated alternately for five minutes — a period of time which appears to be sufficient to bring about the oxidation of the small amount of carbon monoxide originally produced. Then more water (60–70 cm^3) is introduced through the funnel, and the stop-cock between the boiling and absorption flasks is opened, when the carbon dioxide enters the absorption flask, which is kept cool and shaken as before. The contents of the evolution flask are then heated to boiling

TABLE IV.

Exp.	Substance taken.	BaO_2H_2 taken.	BaO_2H_2 found.	CO_2 found.	CO_2 calculated.	Error on CO_2.
			Analysis of Ammonium Oxalate.			
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.5009	1.3584	0.1469	0.3097	0.3101	0.0004–
(2)	0.5006	1.8400	0.1308	0.3103	0.3099	0.0004+
(3)	0.5005	1.8400	0.1343	0.3094	0.3098	0.0004–
(4)	1.0002	2.5460	0.1347	0.6188	0.6192	0.0004–
(5)	1.0010	2.5192	0.1094	0.6185	0.6197	0.0012–
			Analysis of Cane Sugar.			
(1)	0.2001	1.3926	0.1905	0.3085	0.3088	0.0003–
(2)	0.2000	1.3926	0.1986	0.3077	0.3086	0.0009–
(3)	0.2001	1.8926	0.1857	0.8097	0.8088	0.0009+
(4)	0.2014	1.8400	0.1279	0.3111	0.3108	0.0003+

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* Jour. Chem. Soc., liii, 889.

and a slow current of air, freed from carbon dioxide by passing through potash bulbs, is allowed to enter through the funnel tube to keep the liquid from undue bumping. The boiling is continued for fifteen minutes, after which the excess of barium hydroxide is determined iodometrically and thus the carbon dioxide present estimated as before. Table IV shows results obtained by the treatment of crystallized ammonium oxalate and cane sugar, recrystallized from dilute alcoholic solution, in this manner.

The results are evidently very satisfactory.

The Determination of the Oxygen required to Oxidize an Organic Substance.

Several different methods have been proposed for estimating the oxygen present in organic substances, depending, in general, upon the determination of the oxygen which must be supplied to burn the substance to a known amount of carbon dioxide and water — thus discovering by difference the oxygen originally contained in the substance. Lavoisier is said to have measured directly the oxygen used in burning organic substances; Gay-Lussac and Thénard determined the oxygen used by measuring the amount of potassium chlorate reduced in burning the organic compound; Baumhauer[*] determined the oxygen used by measuring the volume of oxygen entering the combustion furnace and subtracting the measure of the gas coming from the combustion tube, which was set up according to the well known method for determining carbon and hydrogen; Stromeyer[†] determined the amount of copper reduced by the ignition of the substance in copper oxide; Ladenburg[‡] oxidized the substance by heating in a sealed tube with a known amount of iodic acid, determining at the end of the operation the amount of iodic acid left; Mitscherlich[§] has estimated the oxygen in organic substances directly by decomposing the substance by ignition in a stream of chlorine gas,

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[*] Ann. Chem. (Liebig), xc, 228.

[†] Ann. Chem. (Liebig), cxvii, 247.

[‡] Ann. Chem. (Liebig), cxxxv, 1.

[§] Ann. Phys. ccvi, 536 (1867).

estimating the oxygen content by determining the resulting carbon dioxide and monoxide.

As it has been shown in the work described that carbon may be determined in organic substances by oxidation with chromic and sulphuric acids without the evolution of oxygen gas, it would seem that the determination of the oxygen in the substance might be effected by determining the amount of chromic acid used in the operation, taking into consideration the products of combustion. This can be readily accomplished by taking a weighed amount of pure potassium dichromate as the oxidizing agent and determining, at the end of the operation, by treatment of the residue with hydrochloric acid, absorption of the chlorine evolved in an alkaline arsenite of known strength, and titration of the excess of that substance with decinormal iodine solution, the amount of chromic acid left.

To test the accuracy of the determination of chromic acid under these conditions of analysis, weighed portions of pure fused potassium dichromate were introduced into a Voit flask, whose outlet tube was sealed to the inlet tube of a Drexel wash bottle, the outlet of which, in turn, was sealed to a Will and Varrentrapp absorption apparatus. An amount of hydrochloric acid, more than enough to completely reduce the chromate (15–40 cm^3 of the strongest acid), was added with 20 cm^3 of strong sulphuric acid and the total volume made up to 120–140 cm^3 of liquid. The sulphuric acid used here was purified from carbonaceous matter (as in the carbon determination above) by heating with a few crystals of potassium dichromate, the excess of which was destroyed by holding the acid at the fuming point for about two hours, when a portion diluted with water gave no color with potassium iodide and starch paste. Pure arsenious oxide, in amount slightly in excess of that required to take up the oxygen to be given up by the chromate, was dissolved by the aid of heat in a solution of pure sodium hydroxide, taken in such quantity as to more than neutralize the arsenious acid and the hydrochloric acid used to reduce the chromate, and this solution was introduced into the Drexel wash bottle. The flask was then connected with the wash bottle, using a thick solution of metaphosphoric acid to lute the joint between the flask and its stopper. The absorption apparatus was charged with a dilute solution of sodium hydroxide. Carbon dioxide was generated in a Kipp generator by the action of hydrochloric acid on marble and purified from reducing matter by bubbling through a strong solution of iodine in potassium iodide and finally washed with a solution of potassium iodide alone. A slow stream of this purified carbon dioxide was allowed to enter the inlet tube of the Voit flask, the contents of which were then boiled. When concentration to a volume of 30–40 cm^3 was reached, the boiling was discontinued and, after cooling and disconnecting the flask, the contents of the receiver were made acid with sulphuric acid and then alkaline with acid potassium carbonate, and the excess of arsenite was determined by titration with decinormal iodine solution. Sometimes during the reduction of the chromic acid, the red fumes of the chlorochromic anhydride volatilized to the receiver; but since the chromic acid thus produced is reduced later by the arsenite,* this transfer is of no account in the working of the process. The following results were thus obtained.

TABLE V.

Exp.	$K_2Cr_2O_7$ taken.	As_2O_3 taken.	As_2O_3 found.	$K_2Cr_2O_7$ found.	Error on $K_2Cr_2O_7$.
	grm.	grm.	grm.	grm.	grm.
(1)	5.0002	5.1025	0.1144	4.9447	0.0555–
(2)	5.0018	5.0799	0.0526	4.9849	0.0169–
(3)	5.0005	5.0801	0.0582	4.9782	0.0223–
(4)	5.0013	5.0706	0.0908	4.9365	0.0648–

The cause of the error shown in these experiments was traced finally to too great concentration of the sulphuric acid in the process. When the boiling begins the chromate is reduced gradually and if the evaporation of the water is pushed too rapidly, the sulphuric acid may reach a strength

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* Browning Am. Jour. Sci., i, 35. Volume I, p. 344.

is oxidized vigorously by chromic and sulphuric acids, the gaseous acid is hardly attacked at the temperature used; naphthaline was also found to be volatilized, and hence not attacked, to such an extent as to render its determination by this process valueless.

XI

THE ESTIMATION OF MANGANESE AS THE SULPHATE AND AS THE OXIDES.

By F. A. GOOCH and MARTHA AUSTIN.*

The estimation of manganese by the conversion of salts of that element with volatile acids to the form of the anhydrous sulphate by the action of an excess of sulphuric acid, evaporation, and gentle heating was formerly a recognized procedure. On the authority of Rose,† however, this method was set aside on account of the supposed difficulty of removing the excess of acid without disturbing the composition of the normal salt. Thus, Oesten, working under Rose's direction, obtained, upon submitting the crystalline hydrous sulphate $MnSO_4 . 5H_2O$ to heat, results which may be summarized and compared with the results obtained by Rose's sulphide method (the ignition of the residue with sulphur in hydrogen) as follows:

$MnSO_4 . 5H_2O$ taken.	$MnSO_4$ found.	Theory.	Error.	MnS found.	Theory.	Error.
grm.	grm.	grm.	grm.	grm.	grm.	grm.
1.659	1.043‡	1.037	0.006+	0.597	0.595	0.002+
	1.023§		0.014–			
1.481	0.934‡	0.926	0.008+			
	0.905§		0.021–			
	0.725‖		0.201–			
1.430	0.880§	0.893	0.013–	0.509	0.512	0.003–

The residues remaining after the gentle ignition of the sulphate weighed apparently several milligrams more than should have been the case if the salt had been reduced to the normal anhydrous sulphate. At higher temperatures the sulphate

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* From Am. Jour. Sci., v, 209.

† Ann. Phys., clxxxvi, 125 (1860).

‡ Ignited gently. § Ignited at low red heat. ‖ Ignited at strong red heat.

turned brown and lost altogether too much weight. A comparison of the errors of the process in which the ignition was at low temperature with those of the sulphide process would seem to justify Rose's rejection of the former method for the latter. Upon recalculating these results, however, using atomic weights in use at present — viz.: Mn = 55, S = 32.06, O = 16 — it becomes plain that the errors of the two processes, as shown in Oesten's work, are not very different numerically, though with opposite signs.

$MnSO_4 . 5H_2O$ taken.	$MnSO_4$ found.	Theory.	Error.	MnS found.	Theory.	Error.
grm.	grm.	grm.	grm.	grm.	grm.	grm.
1.659	1.048	1.039	0.004+	0.597	0.599	0.002–
1.481	0.934	0.928	0.006+			
1.480				0.509	0.516	0.007–

The most uncertain element in these experiments is the difficulty, well-recognized at present, of getting the hydrous manganous sulphate, upon which the experiments were made, in a perfectly definite condition of hydration.

Volhard* subsequently studied the sulphate process, and showed that manganous sulphate may be dehydrated, separated from an excess of sulphuric acid, and brought into definite condition for weighing as the anhydrous salt by careful and protracted heating over a special device of his own — a ring burner enclosed in a sheet-iron casing. Thus, on evaporating and dehydrating a solution of pure neutral manganous sulphate, Volhard obtained the results recorded in the following statement:

Residue of $MnSO_4$ left by evaporation and dehydration .	0.1635
" after treatment with 3 drops of H_2SO_4 and heating 3 hours	0.1635
" after heating 2 hours	0.1638
" after treatment with 4 drops of H_2SO_4 and heating 2½ hours	0.1635
" after heating 3 hours	0.1635

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* Ann. Chem. (Liebig), cxcviii, 328.

Similar results were obtained on evaporating with sulphuric acid and igniting in like manner an aqueous solution of manganous chloride. Volhard's recommendation of the method has not secured for it the acceptance which its simplicity and exactness would seem to demand—possibly because the periods of ignition appear to be considerable and the manner of heating special.

In our own experiments with the sulphate process we have found that special apparatus is unnecessary, that the time of treatment may be short, and that the process is in every respect simple as well as very exact. We took for a starting point manganous chloride prepared in the manner to be detailed. An aqueous solution of the so-called pure manganous chloride of commerce was boiled with pure manganous carbonate (to throw out aluminum, iron, and chromium), filtered and precipitated with ammonium sulphide. The precipitate thus obtained was dissolved in a very slight excess of hydrochloric acid (to leave behind possible traces of nickel, cobalt, and copper), the solution was boiled to expel hydrogen sulphide and precipitated with sodium carbonate. The manganous carbonate thus thrown down was boiled repeatedly with successive portions of water, and washed until the washings were free from chloride. The greater part of this purified carbonate was dissolved in the least possible amount of pure hydrochloric acid, the reserved portion of the carbonate was added, the mixture was boiled, and the solution of the purified and neutral manganous chloride was filtered from the excess of undissolved carbonate. Definite portions of this solution were precipitated with silver nitrate, and from the weight of the silver chloride thus obtained the amount of manganous chloride present was calculated. Portions of the solution thus standardized were drawn, for our experiments, from a burette into a weighed platinum crucible, sulphuric acid was added in amount more than equivalent to the manganese, the solution was evaporated on the water-bath until the water was removed, and then, supported by means of a porcelain ring, or triangle, within a larger porcelain crucible used as a radiator so that the bottom and walls of the one were distant from the bottom and walls of the other by an interval of about 1 cm., the crucible was heated more strongly. The outer porcelain crucible may be heated over a good Bunsen flame to a red heat without risk of overheating the manganese sulphate within the inner crucible, and the ignition may proceed as rapidly as is consistent with the avoidance of mechanical loss by spattering. The results obtained by treatment of equal portions (50 cm^3) of the same solution are given, together with the results of standardizing the solution by precipitation with silver nitrate, in columns A of the following table. In the other columns are given comparative results got in the treatment of equal portions of several other solutions employed subsequently in other work.

Exp.	$MnSO_4$ calculated from AgCl found in 50 cm^3 of solution A.	Exp.	$MnSO_4$ found by treatment of 50 cm^3 of solution A with H_2SO_4.	Exp.	$MnSO_4$ found by treatment of 50 cm^3 of various solutions with H_2SO_4.					
	A.		A.		B.	C.	D.	E.	F.	G.
	grm.		grm.		grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.3518	(1)	0.3513	(1)	0.3100	0.3256	0.3534	0.3524	0.3355	0.5475
(2)	0.3512	(2)	0.3514	(2)	0.3104	0.3254	0.3543	0.3520	0.3357	0.5476
		(3)	0.3518	(3)	0.3096					

These results show plainly that the process of estimating manganese in the form of the anhydrous sulphate is both simple and accurate.

The estimation of manganese as the manganoso-manganic oxide Mn_3O_4, has been so frequently criticised unfavorably that the method may be said to have passed from very general use excepting in certain cases in which the directness of the process is a temptation to incur the risk of some uncertainty. The production of the other oxides of manganese in definite condition is thought to be even more uncertain. Manganese dioxide, MnO_2, begins, as Wright and Menke have shown * to

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* Jour. Chem. Soc., xxx, 775.

lose oxygen at a temperature (about 210° C.) to which the hydrated oxide must be heated to free it from water, or very nearly that at which the nitrate is converted into the dioxide; so that the chance of producing an undecomposed dioxide by the ignition of the hydrated dioxide (the form in which the dioxide generally appears in analytical processes), or of the nitrate, is small. Manganic oxide, Mn_2O_3, is produced, it is said, from the other oxides by ignition at a low red heat under the ordinary conditions. The manganoso-manganic oxide, Mn_3O_4, forms, presumably, when an oxide of manganese is submitted, under ordinary atmospheric conditions, to the high heat of the blast-lamp. If the proportion of oxygen in the surrounding atmosphere is reduced below the normal, the conversion of Mn_2O_3 to Mn_3O_4 goes on very easily, as Dittmar has shown,* at a temperature between the melting points of silver and aluminum, while if the proportion of oxygen in the surrounding atmosphere rises much above the normal, the reverse change, from Mn_3O_4 to Mn_2O_3 tends to take place at the same temperature. It is not surprising, in view of these phenomena, that the estimation of manganese as the oxide Mn_3O_4 should have fallen into disrepute; and yet, if the condition most favorable to the production of that oxide — a low proportion of oxygen in the surrounding air — can be maintained during the ignition, it is not impossible that the indications of the process might prove to be, under the conditions, reasonably accurate. Now, this may be exactly the condition of affairs when the ignition takes place ordinarily; for, if the products of combustion displace the ordinary air about the crucible, the proportion of oxygen about the oxide falls to a low limit. We have made the experiment of enclosing the ignited crucible within an inverted crucible, so that the products of combustion should be held immediately about and above the ignited oxide, but our experience has shown that the object in view is attained, apparently, quite as well when the ignition is so arranged that the crucible simply rests well within the upper part of the flame of a strong Bunsen

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* Jour. Chem. Soc., xvii, 294.

burner, or blast-lamp, in such manner that an oxidizing flame covers nearly the entire wall of the crucible.

In the following experiments we have put to the test this matter of getting definitely the different oxides of manganese. We started with a known amount of pure anhydrous sulphate, prepared from the pure chloride in the manner previously described. This sulphate was converted by ignition into the oxide — presumably the oxide Mn_3O_4 — the containing crucible being well within the upper flame of a powerful burner.

In the next step, this oxide was further oxidized by moistening it with nitric acid and heating the residue gently until the evolution of fumes ceased, the containing crucible being placed well above a porcelain crucible used as a radiator and heated so that only the bottom showed a faint red heat. In this process the attempt was made to arrest the ignition at the point where the anhydrous dioxide was produced. As the table shows, and as would be expected, this attempt was only occasionally and partly successful.

The residue of the last process was then submitted to a higher heat. The platinum crucible containing the oxide was placed within and touching the bottom of a larger porcelain crucible which was heated to redness. Under these conditions the temperature should not be too hot, and the products of combustion should naturally be thrown so far away from the oxide undergoing ignition that circumstances should be favorable for the formation of the oxide Mn_2O_3. The event proved that the attainment of the exact condition corresponding to the symbol Mn_2O_3 is a matter of some uncertainty.

Next, the oxide was subjected to the highest heat of a strong Bunsen burner (or in some cases, the broad flame of a blast lamp), the crucible being well surrounded by the products of combustion. The results of this treatment, it will be seen, agree, with a single exception out of ten experiments, reasonably well with the theory for Mn_3O_4.

By treating the final oxide with nitric acid and repeating the cycle of operations described, the observations of the phenomena were multiplied, until, finally, the oxide formed

$MnSO_4$ taken.	Exp.	MnO_2			Exp.	Mn_2O_3			Exp.	Mn_3O_4			Exp.	$MnSO_4$	
		Found.	Theory.	Error.		Found.	Theory.	Error.		Found.	Theory.	Error.		Found.	Error.
grm.		grm.	grm.	grm.		grm.	grm.	grm.		grm.	grm.	grm.		grm.	grm.
0.3712	. . .	. . . . .	. . . . .	. . . . . .	. . .	. . . . .	. . . . .	. . . . . .	(1)	0.1880	0.1876	0.0004+			
	(2)	0.2114	0.2138	0.0024—	(3)	0.1975	0.1954	0.0021+							
	(4)	0.2137		0.0001—	(5)	0.1959		0.0005+							
	(6)	0.2147		0.0009+	(9)	0.1986		0.0032+							
	(7)	0.2147		0.0009+	(10)	0.1957		0.0003+	(11)	0.1881		0.0005+			
	(8)	0.2138		0.0000											
	(12)	0.2145		0.0007+	(13)	0.1948		0.0006—	(14)	0.1877		0.0001+			
	(15)	0.2115		0.0023—	(16)	0.1939		0.0015—	(17)	0.1872		0.0004—			
	(18)	0.2158		0.0020+	(19)	0.1942		0.0012—	(20)	0.1899		0.0023+	(21)	0.3709	0.0003—
0.6436	. . .	. . . . .	. . . . .	. . . . . .	. . .	. . . . .	. . . . .	. . . . . .	(1)	0.3247	0.3252	0.0005—			
	(2)	0.3443	0.3707	0.0264—											
	(3)	0.3704		0.0003—	(4)	0.3372	0.3387	0.0015—	(5)	0.3245		0.0007—			
	(6)	0.3705		0.0002—	(7)	0.3367		0.0020—	(8)	0.3244		0.0008—			
	(9)	0.3597		0.0110—											
	(10)	0.3719		0.0012+	(11)	0.3369		0.0018—	(12)	0.3243		0.0009—			
	(13)	0.3729		0.0022+	(14)	0.3362		0.0025—	(15)	0.3244		0.0008—			
	(16)	0.3690		0.0017—	(17)	0.3366		0.0021—	. .	. .	. .	. .	(18)	0.6432	0.0004—
													(19)	0.6432	0.0004—
													(20)	0.6437	0.0001+

last was treated with sulphuric acid, ignited in the manner previously detailed, and weighed as the anhydrous sulphate, thus showing that no significant loss of material had taken place in the series of manipulations. The table comprises the results of these experiments. The numbers in parentheses indicate the order of treatment.

The inference is plain that the estimation of the manganese in the form of the manganoso-manganic oxide, Mn_3O_4, is by no means to be considered utterly untrustworthy when the process is conducted in the manner described, though it must be recognized that an irregular result may occur occasionally. The danger of accepting such an irregularity as a correct indication may be eliminated to a very considerable extent if the precaution is taken invariably to moisten the ignited oxide with nitric acid, and ignite again. The indications of harmonious results thus got may be taken with a fair degree of confidence. However, it is, in our judgment, by far the wiser and simpler plan to convert an oxide of manganese obtained in course of analysis into the sulphate and to weigh the manganese in that form.

XII

ON THE CONDITION OF OXIDATION OF MANGANESE PRECIPITATED BY THE CHLORATE PROCESS.

BY F. A. GOOCH AND MARTHA AUSTIN.*

HANNAY,† who was the first to propose the precipitation of manganese from its solution in nitric acid by the use of potassium chlorate, states that precipitation is complete, but that the oxide produced is not of constant composition. While, therefore, precipitation by this method serves an excellent purpose in separating manganese from other substances, it was Hannay's opinion that reliance cannot be placed upon the determination of the oxygen value of the oxide to estimate the manganese. Beilstein and Jawein,‡ who proposed the same method, subsequently, regarded the precipitate as the oxide MnO_2. Hannay's reaction was developed, independently, by Hampe § and Ford || into the method which is now known as the "chlorate process" for the estimation of manganese. The discussion of the exact condition of the precipitated oxide was very active ten years ago, and occasional echoes of it are heard at the present day; and yet, in all this discussion we find no account of an adequate test of the process upon an exact amount of a salt of manganese known to be pure. The discussion for the most part has centered about the degree of oxidation of the precipitate, but there is obviously another condition to be taken into account, viz.: the possibility of the mechanical inclusion of the comparatively insoluble chlorate in the precipitated oxide. As to the existence of the latter source of error we have had in the

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* From Am. Jour. Sci., v, 260.

† Jour. Chem. Soc., vol. xxxiii, 269.

‡ Ber. Dtsch. chem. Ges., xii, 1528.

§ Chem. Central-Blatt, 1885, 714.

|| Trans. Inst. Am. Min. Eng., ix, 347.

course of our work very strong affirmative evidence, the apparent condition of oxidation of the precipitate being sometimes so high as to be otherwise inexplicable. This difficulty does not occur, however, when a more soluble chlorate is chosen to do the work of oxidation, and we have found quite as convenient and much safer the substitution of sodium chlorate for the comparatively insoluble potassium chlorate. Besides, the rapidity with which the sodium chlorate is decomposed makes its use an advantage.

With regard to the completeness of the precipitation our experience has shown that with due precaution the method is practically perfect. Thus, after boiling manganous nitrate (free from chlorides and sulphates) with strong nitric acid (85 cm^3) and sodium chlorate (5 grm.) for five minutes, adding, subsequently, 15 cm^3 of the nitric acid and a few crystals more of the sodium chlorate, and discontinuing the heating as soon as the liquid again boils, the insolubility of the manganese is so great that no more than insignificant traces may be recovered from the filtrate after cooling, filtering upon asbestos and washing with water. The test for manganese in the filtrate and washings was made after evaporation and solution of the residue in distilled water by treating the hot solution with bromine and ammonia. In the first division of the table below are results obtained by treating the manganese

TABLE I.

$MnSO_4$ taken.	Mn found by KI treatment in filtrate.	Mn found by As_2O_3 treatment in filtrate.
grm.	grm.	grm.
0.3361	None.	. . . .
0.3361	None.	. . . .
0.3361	0.00006	. . . .
0.3361	0.00005	. . . .
0.3361	0.00002	. . . .
0.3361	0.00008	. . . .
0.3361	None.	. . . .
0.4128	. . . .	0.00003
0.4128	. . . .	0.00003
0.4128	. . . .	Trace.
0.4128	. . . .	Trace.

precipitated from the filtrate with potassium iodide and sulphuric acid, the iodine set free being determined by sodium thiosulphate. In the second series the precipitated manganese dioxide was reduced by a known amount of decinormal arsenious acid and the amount remaining unoxidized was estimated by titration with iodine in the presence of acid potassium carbonate.

It will be seen that in no case did the manganese which escaped precipitation — that which corresponded to the iodine freed or the arsenious acid oxidized — exceed 0.0001 grm. Plainly this modified method of handling the chlorate process may be trusted to precipitate the manganese with gratifying rapidity and approximation to completeness. Our experience has shown plainly that prolonged boiling results in a considerable loss of manganese (from 0.0010 — 0.0030 grm.). This we think is due to the solvent effect of the lower oxides of nitrogen naturally produced (as is always the case in boiling nitric acid) after the chlorine dioxide has been thoroughly expelled. An excess of the chlorate at the end of the boiling seems to be essential and a slight yellow color in the solution, due to chlorine dioxide, is a favorable indication rather than the reverse. We find it best to filter the undiluted nitric acid, under pressure, upon asbestos on a perforated cone with a filtering surface of about 40 cm^2. The dilution of the nitric acid before filtration tends to produce some solubility of the manganese, and the loss then introduced, though trifling if the filtration is rapid, may be considerable if the process of filtration is prolonged, as is the case in the method approved by the "Verein der deutschen Eisenhütteleute." *

Our experiments upon the chlorate process have been made with manganous chloride prepared as detailed in a former paper, viz.: by boiling manganous chloride with manganous carbonate, precipitating the filtered solution with ammonium sulphide, dissolving the washed manganous sulphide in dilute hydrochloric acid, precipitating the solution thus obtained with sodium carbonate (after boiling out hydrogen sulphide), dis-

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* Von Reis, Zeitschr. angew. Chem., 1891, 376.

solving the greater part of the manganous carbonate (thoroughly washed by repeatedly boiling it in successive portions of water) in the least amount of hydrochloric acid, and boiling the solution thus obtained with the remainder of the pure carbonate and filtering. The standard of the solution thus prepared, neutral and probably very pure, was fixed by evaporating definite portions with sulphuric acid and weighing the residue as the normal sulphate in accordance with the procedure outlined in a former paper.*

Any method, by means of which the oxidizing power of the higher oxygen compounds of manganese is discoverable, may, obviously, be employed to determine the condition of the manganese precipitated in this chlorate process. Convenient processes for the determination of the available oxygen in the higher oxides of manganese are the iodometric methods of Bunsen and Pickering. Bunsen's method is applicable to any of the higher oxygen compounds of manganese — though somewhat inconvenient because it involves the distillation of the chlorine liberated by the action of strong hydrochloric acid upon the substance and its collection in potassium iodide, the iodine thus set free being estimated by standard thiosulphate. According to Pickering's† method the higher oxide is treated immediately with potassium iodide and hydrochloric acid and the iodine liberated is estimated by sodium thiosulphate. Plainly, the latter method is limited to the treatment of the less refractory or more finely comminuted oxides, and it fails in the presence of ferric salts and all other substances capable of liberating iodine from the acidified iodide.

Still another general iodometric method for determining the oxygen value of the higher oxides of manganese is suggested by Deshayes's titration of permanganic acid in nitric acid by means of standard arsenious acid.‡ Our experience in following out this idea shows that the precipitated oxides of manganese, as well as the soluble permanganate, may be easily reduced with the aid of gentle heating by arsenious acid in

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* Am. Jour. Sci., v, 209. This volume, p. 77.

† Jour. Chem. Soc., xxxvii, 128.

‡ Bull. Soc. Chim., xxix, 541.

the presence of sulphuric acid, and that the determination of the excess of arsenious acid by titration with iodine after neutralization of the free sulphuric acid by an alkaline carbonate gives exact data for estimating the oxidizing power of the manganese compound. We found, however, that if the iodine is allowed to come into contact with the manganous carbonate thrown down by the alkaline carbonate, as is inevitable for at least short intervals during the titration of the arsenious acid in presence of the floating carbonate, the danger arises of more or less reoxidation of the manganous carbonate by the iodine and the consequent introduction of error. Fortunately the difficulty may be obviated by adding to the solution, while still acid, enough tartaric acid or alkaline tartrate to prevent the precipitation of the manganese in the subsequent neutralization by the bicarbonate.

Confining our attention to the last two simpler iodometric methods — the reduction of the higher oxide by an acidified iodide on the one hand and by arsenious acid on the other — we made, first, some experiments to determine the accuracy with which manganese may be thus estimated. We used for the manganese compound of known oxidizing power a solution of potassium permanganate filtered carefully through asbestos and standardized against ammonium oxalate which had been found to be the exact equivalent of a specially prepared lead oxalate. For each experiment a definite portion of this solution was drawn from a burette and treated with a solution of pure manganous sulphate until the color of the permanganate had vanished, thus precipitating a hydrous oxide approximating quite closely probably to the condition of oxidation of the dioxide, but containing at all events, whatever its actual composition might be, the exact amount of available oxygen originally in the permanganate. In the experiments of the following table this precipitate was treated with a solution of potassium iodide (6 grm.) and tartaric acid (10 grm.), by which the freshly prepared hydrate is dissolved quite as well as by the iodide and hydrochloric acid of Pickering's original method and with less risk of evolution of iodine outside the main reaction. From the iodine found by titration with this sulphate we have calculated the weight of manganese dioxide which would liberate it; and a comparison of this value with the amount of the dioxide theoretically precipitated by the interaction of the known permanganate and the sulphate, upon the assumption that two molecules of the former throw down five molecules of the hydrated dioxide, should disclose the error of the analytical process when applied to the estimation of manganese dioxide. In all probability the assumption that it is the dioxide that is precipitated, and which afterwards acts upon the iodide, is not quite true under the conditions, since the precipitation takes place in presence of an excess of a manganous salt; but for our purpose it does not matter, since we are in effect simply dealing with the oxidizing power of a known amount of permanganate.

TABLE II.

Mn theoretically precipitated by $KMnO_4$ as MnO_2.	Mn in MnO_2 corresponding to iodine found.	Error of the analytical process (applied to MnO_2) in terms of Mn.
grm.	grm.	grm.
0.1351	0.1347	0.0004–
0.1351	0.1347	0.0004–
0.1351	0.1350	0.0001–
0.1351	0.1353	0.0002+
0.1351	0.1358	0.0007+
0.1351	0.1353	0.0002+

Thus, it is obvious that the mean error of the results is practically inconsiderable, varying between extremes of – 0.0004 grm. and + 0.0007 on 0.1351 grm. of manganese dioxide.

In the experiments of Table III the precipitated oxide was treated with an excess of a standard arsenious acid solution and 5 cm^3 of sulphuric acid of half strength, and the whole was heated until the manganese dioxide was dissolved. To this liquid was added tartaric acid (10 grm.) to prevent the precipitation of the manganese and the oxidation by iodine in the subsequent titration, the acid was neutralized by acid potassium carbonate, and the arsenic still remaining in the arsenious condition titrated by standard iodine.

TABLE III.

Mn precipitated by action of $KMnO_4$ on $MnSO_4$ as MnO_2.	Mn in MnO_2 corresponding to As_2O_3 oxidized.	Error of the process in terms of Mn.
grm.	grm.	grm.
0.1392	0.1396	0.0004–
0.1109	0.1117	0.0008–
0.1112	0.1117	0.0005–
0.1109	0.1117	0.0008–
0.1109	0.1117	0.0008–
0.1117	0.1125	0.0008–

It is clear that either of these methods of reduction, the action of an acidified iodide or that of arsenious acid, is capable of yielding fairly accurate indications when we have to deal with a pure salt of manganese. When, however, the manganese is associated with a considerable amount of iron, as is frequently the case, it becomes a matter of necessity to separate the manganese before attempting its estimation. For this purpose the "chlorate process" is by far the simplest of those generally used, and though it has been the subject of much discussion, it is at present the method of separation most widely used by practical chemists, whether the final estimation of the manganese is made gravimetrically as in Ford's process, or volumetrically, as in the methods of Volhard, Williams, or Pattinson.

Definite portions of the solution of pure manganous chloride were drawn from a burette into an Erlenmeyer flask of 300 cm^3 capacity, evaporated to dryness, precipitated by the "chlorate process" with the modifications given in detail above. The oxide, after careful washing, was returned with the asbestos to the flask and treated by one or other of the methods to be described. It was either treated with potassium iodide (5 grm.) and sulphuric acid (10 cm^3) of half strength, the iodine set free being estimated by thiosulphate; or it was heated with an excess of standard arsenious acid and 10 cm^3 of sulphuric acid of half strength, and after cooling, adding 5 grm. of the Rochelle salt and neutralizing with acid potassium carbonate, the arsenious acid remaining unoxidized was estimated with standard iodine. In Table IV are given the results obtained in this work.

TABLE IV.

Mn taken in the form of manganous chloride.	Mn found upon the hypothesis that MnO_2 is precipitated.	Error.	Mn found in the filtrate after evaporation and treatment with bromine and ammonia.
By Reduction with Potassium Iodide.			
grm.	grm.	grm.	grm.
0.1225	0.1183	0.0042–	0.00006
0.1225	0.1177	0.0048–	Trace.
0.1225	0.1180	0.0045–	0.00008
0.1225	0.1169	0.0056–	Trace.
By Reduction with Arsenious Acid.			
0.1222	0.1189	0.0033–	Not determined.
0.1222	0.1191	0.0031–	Not determined.
0.1222	0.1199	0.0023–	Not determined.
0.1222	0.1200	0.0022–	Not determined.
0.1222	0.1186	0.0036–	None.
0.1222	0.1187	0.0035–	0.0001
0.1222	0.1189	0.0033–	0.0002
0.1222	0.1194	0.0028–	Trace.
0.1222	0.1205	0.0017–	0.0001

The results show plainly that, while the manganese is so completely precipitated in the chlorate process of oxidation when properly conducted that only insignificant traces may escape, the condition of oxidation cannot be taken to be that of the dioxide. The average error thus put upon the determination of the manganese known to be present is more than 2 per cent. It follows, as a matter of course, that the indications of any process which rests upon the assumption that the oxygen value of the manganese compound precipitated in the chlorate process corresponds to that of the dioxide must of necessity be erroneous. If, therefore, the chlorate method is to be employed for the separation of the manganese, it is obvious that precautions must be taken to secure a definite condition of oxidation of the manganese before processes which depend upon the oxygen value of the higher oxide may be applied to the estimation of that element. The process which in our hands seems to give the oxide in definite condition is based upon the observations of Wright and Menke * that a dilute solution of potassium permanganate acting in excess, at 80° C., in the presence of zinc sulphate, and in thorough mixture upon manganous sulphate, yields an oxide which, though combined with alkali, holds the oxygen exactly in the proportion corresponding to the dioxide. Three-fifths of the manganese in such a precipitate represents the amount of that element originally present in the manganous salt. In the following table are given the results of experiments in which manganese was determined iodometrically after the interpolation of the permanganate treatment.

In these experiments a solution of manganous chloride of known strength was drawn from a burette, evaporated to dryness in a small beaker, heated with nitric acid until there was no evidence of the presence of nitrogen oxides. Strong nitric acid was poured in until the volume was 85 cm^3, sodium chlorate (5 grm.) was added carefully, the liquid was boiled five minutes, more nitric acid (15 cm^3) and a few crystals of the chlorate were introduced, and the solution brought to boiling temperature again. After cooling, the liquid was filtered on asbestos and washed with water, and the oxide upon the asbestos and walls of the beaker was dissolved in 2 cm^3 of hydrochloric acid. After diluting a little the solution was evaporated with 5 cm^3 of strong sulphuric acid until no more hydrochloric acid remained. The solution of manganous sulphate (not exceeding 0.5 grm. of the salt), very nearly neutralized by potassium carbonate, was mixed with a solution of zinc sulphate (2 grm.) and a freshly and carefully filtered dilute solution of potassium permanganate (1.5 grm. of the salt); the liquid, amounting now to about

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* Jour. Chem. Soc., xxxvii, 36.

500 cm^3, was heated to 80° C., and acid potassium carbonate added, in quantity a little more than enough to neutralize the remnant of the acid present. The precipitate was collected upon asbestos, and after careful washing was returned to the flask in which the precipitation had been made. The oxygen value of the oxide was determined by one or other of the methods described. In the one case the flask was fitted with a paraffined stopper having two bores, one holding a Will and Varrentrapp absorption apparatus (in which a solution of potassium iodide dissolved any escaping iodine), the other a small separating funnel. Sulphuric acid and potassium iodide in solution were run in through the funnel, the iodine set free was titrated with thiosulphate — the amount of manganese being reckoned from the iodine set free. The results of this work follow in the first part of Table V. In the second case the dioxide obtained in the manner described above was reduced by warming gently with a decinormal solution of arsenious acid. After cooling, and neutralizing with acid

TABLE V.

Mn taken in the form of chloride.	Mn found upon the hypothesis that MnO_2 is the oxide finally obtained.	Error.
By Reduction with Potassium Iodide.		
grm.	grm.	grm.
0.0643	0.0637	0.0006–
0.0643	0.0642	0.0001–
0.0643	0.0642	0.0001–
0.0651	0.0651	0.0000
0.1125	0.1121	0.0004–
0.1125	0.1121	0.0004–
0.1125	0.1120	0.0005–
0.1214	0.1206	0.0008–
0.1214	0.1207	0.0007–
0.1214	0.1223	0.0009+
0.1214	0.1214	0.0000
By Reduction with Arsenious Oxide.		
0.1213	0.1212	0.0001–
0.1213	0.1201	0.0012–
0.1213	0.1203	0.0010–
0.1213	0.1208	0.0005–

potassium carbonate in the presence of Rochelle salt, the excess of the arsenious acid was estimated with iodine in the presence of starch. The estimation by this method gave the results recorded in the second part of Table V.

These results show plainly, that if the precautions to which attention has been directed are taken, viz.: dilution of the solution and heating to 80° C., presence of zinc sulphate, and (most essential of all) the almost complete neutralization of free acid before the addition of the potassium permanganate, the manganese dioxide precipitated by the chlorate process from pure manganous nitrate may subsequently, after reduction, be brought by the permanganate treatment so nearly to the full degree of oxidation represented by the symbol MnO_2, that the amount of manganese originally treated may be calculated with a very fair degree of accuracy from the oxygen value of three-fifths of the oxide found. We do not recommend this procedure as a rapid analytical method; our purpose is accomplished when the fact is brought plainly to view that the oxide precipitated by the chlorate process is not the dioxide, but that it may be made such by subsequent treatment.

XIII

ON THE ESTIMATION OF MANGANESE SEPARATED AS THE CARBONATE.

BY MARTHA AUSTIN.*

THE estimation of manganese precipitated as the manganous carbonate, when that salt is obtained by the action of sodium or potassium carbonate, has been regarded as very undesirable for the reasons that, even if the conditions of the precipitate is such that it does not run through the filter, the manganous carbonate can never be freed entirely from alkaline salt, and that the conversion of the carbonate to the manganoso-manganic oxide — the form in which it is customary to weigh — is too uncertain. It had been supposed, also, that the presence of ammoniacal salts (as well as of carbonic acid) causes solution of the manganous carbonate, until the work of Guyard (Hugo Tamm) † showed that when the precipitation is accomplished by ammonium carbonate, even in the presence of ammonium chloride, complete separation of the manganese is possible. No data are given by Guyard to show the completeness of the separation of the manganese by this process; but Fresenius ‡ examined the method and speaks favorably of it. In this process the main difficulty of the older method of estimation as the carbonate — viz., the inclusion of the alkaline salt — is avoided. We know now how to avoid the difficulty in the way of weighing as the oxide by converting that substance to the form of the sulphate, as shown in a former paper. §

For a careful study of the separation of manganous carbonate by Guyard's method a solution of pure manganous chloride was prepared and standardized as the anhydrous sulphate in

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* From Am. Jour. Sci., v, 382.

† Chem. News, xxvi, 87.

‡ Zeitschr. anal. Chem., xi, 290.

§ Am. Jour. Sci., v, 209. This volume, p. 77.

the manner detailed in the paper to which reference has been made above. A definite volume of the manganous chloride was carefully drawn into a platinum dish and diluted to a volume of 200 cm^3. To the solution heated to 100° C. ammonium chloride (about 10 grm.) was added and ammonium carbonate in excess. The solution was kept warm until the precipitate subsided, and then was filtered off on asbestos on a perforated crucible under pressure. The presence of ammonium chloride is necessary to insure such a condition of the precipitate that it will not run through the felt.

Inasmuch as the precipitate was collected under conditions which readily permit an attempt to weigh as the carbonate, a trial of that method was made incidentally. The event proved, as Rose * has stated previously, that when the carbonate is gently heated, evolution of carbon dioxide and oxidation of the residue begins before the water is thoroughly removed; for, though nearly all the results are above the theory, the solution of the residue in hydrochloric acid indicated plainly the presence of a small amount of a higher oxide of manganese. In the following table are found the results of a series of experiments in which the attempt was made to weigh first as carbonate and again after strong ignition — well within the oxidizing flame of a powerful burner † — as the manganoso-manganic oxide. The application of the bromine test to the hot ammoniacal filtrate showed that in every one of these experiments, the precipitation of the manganese in the form of the carbonate had been complete.

$MnCl_2$.	MH_4Cl.	$MnCO_3$			Mn_3O_4		
		Found.	Theory.	Error.	Found.	Theory.	Error.
cm^3	grm.	grm.	grm.	grm.	grm.	grm.	grm.
50	10	0.2685	0.2680	0.0005+	0.1770	0.1776	0.0006–
50	10	0.2704		0.0024+	0.1788		0.0012+
50	10	0.2710		0.0080+	0.1770		0.0006–
50	10	0.2720		0.0040+	0.1774		0.0002–

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* Annal Phys. Chem., lxxxiv, 52.

† Am. Jour. Sci., v, 209. This volume, p. 82.

As shown in this table, weighing as the carbonate is out of the question; the errors of the process when the residue is ignited in the manner described to form the manganoso-manganic oxide are much smaller though rather variable. The estimation of manganese as the anhydrous sulphate had given in the work to which reference has been made results agreeing so much more closely than could be obtained by any other procedure, that the attempt was made to estimate the amount of manganese precipitated as the manganese carbonate by converting it first to the oxide, then to the sulphate. A given weight of sulphate was precipitated as the manganous carbonate, after the employment of all the precautions mentioned previously in this paper, and then filtered off on ashless filter paper. After washing thoroughly with hot water, the filter was burned, the residue ignited for the condition of the manganoso-manganic oxide and weighed as such. Then the oxide was converted to the sulphate by heating with three or four drops of concentrated sulphuric acid. The agreement of the results as shown in the following table is considerably better.

Exp.	MH_4Cl.	Mn_3O_4			$MnSO_4$		
		Found.	Theory.	Error.	Found.	Theory.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	10	0.2463	0.2478	0.0015–	0.4903	0.4905	0.0002–
(2)	10	0.1110	0.1121	0.0011–	0.2225	0.2219	0.0006+
(3)	10	0.1584	0.1581	0.0003+	0.3126	0.3128	0.0002–
(4)	10	0.1672	0.1699	0.0027–	0.3355	0.3364	0.0009–

By treatment of the filtrates of (1), (2), and (3) with bromine and ammonia at boiling temperature no manganese was found. In the filtrate from number (4) by the same treatment, a small amount of manganese dioxide was precipitated, which when heated with concentrated sulphuric acid gave 0.0006 grm. of manganous sulphate; and, hence, the error in that determination is really 0.0003 grm. on the sulphate. The slightly larger deficiency recorded in the table was probably due to imperfect filtering.

It seems to be evident that Guyard's method of separation of manganese as the manganous carbonate, when handled with precautions, gives complete separation of that element. It must be recognized clearly, however, that the precipitation should be made in the presence of a considerable amount of ammonium chloride, and that great care must be used in the filtering and washing of the finely divided precipitate. It is altogether preferable to weigh in the condition of the sulphate.

XIV

THE ACTION OF CARBON DIOXIDE ON SOLUBLE BORATES.

BY LOUIS CLEVELAND JONES.[*]

IN a process for the separation and estimation of boric acid devised by Morse and Burton,[†] the liberation of carbonic, silicic, and boric acids from a mixture of inorganic salts is effected by the action of sulphuric acid, using tropæolin *OO* as an indicator of acidity. In the solution thus prepared, containing in free condition only carbonic, silicic and boric acids. the silicic acid is dehydrated and made insoluble by anhydrous copper sulphate. The boric acid is then extracted with absolute alcohol. To this alcoholic solution of boric acid, a known amount of barium hydroxide solution is added in excess over that required to form a barium metaborate, BaB_2O_4. Carbon dioxide is then passed into the solution in accordance with the hypothesis that the excess only of barium is acted upon. The aqueous mixture of barium metaborate and barium carbonate is evaporated and the residue is heated to a constant weight over a triple burner. From the following proportion the boric acid present may be calculated. The molecular weight of boric acid — the molecular weight of carbon dioxide : the molecular weight of boric acid = the total weight found — the theoretical weight of barium as carbonate : the weight of boric acid present. It is obvious, inasmuch as the difference between the calculated weight of the barium as carbonate and the actual weight of the residue is multiplied nearly three times to get the boric oxide, that the actual error of the process, whatever it may be, is magnified threefold by the method of computation.

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[*] From Am. Jour. Sci., v, 442.

[†] Am. Chem. Jour., x, 154.

I have made a study of this method applied to pure boric acid, but have been unable to obtain results similar to those of Morse and Burton.

For this investigation boric acid of standard strength was made by dissolving in a given amount of water a known weight of anhydrous boric oxide, prepared by igniting over a blast lamp boric acid several times recrystallized and washed. A solution of barium hydroxide was filtered free from carbonate and then standardized by precipitation as carbonate and also by the Phelps method with iodine.* To a measured amount of the boric acid solution an excess of barium hydroxide was added, carbon dioxide passed, and the whole evaporated and by successive ignitions brought to a constant weight. Below are tabulated some of the results:

Exp.	$Ba(OH)_2$ taken. Calculated as $BaCO_3$.	B_2O_3 taken.	Weight of residue after successive ignitions.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(1)	0.9391	0.2200	1st wt., 0.9860	0.1263	0.0937–
			2d " 0.9786	0.1063	0.1137–
(2)	0.9318	0.1295	1st " 0.9605	0.0744	0.0528–
			2d " 0.9558	0.0646	0.0649–
			3d " 0.9510	0.0517	0.0778–
(3)	0.9253	0.2192	1st " 1.0357	0.2972	0.0780+
			2d " 1.0248	0.2679	0.0487+
			3d " 1.0149	0.2412	0.0220+
			4th " 1.0064	0.2183	0.0009–
			5th " 0.9975	0.1944	0.0248–
			6th " 0.9855	0.1621	0.0671–
(4)	0.7301	0.0810	1st " 0.8017	0.1927	0.1117+
			2d " 0.7777	0.1281	0.0471+
			3d " 0.7642	0.0918	0.0108+
			4th " 0.7582	0.0757	0.0053–
			5th " 0.7517	0.0582	0.0228–
			6th " 0.7482	0.0487	0.0323–
			7th " 0.7447	0.0393	0.0417–
			8th " 0.7427	0.0339	0.0471–
			9th " 0.7422	0.0326	0.0484–
			10th " 0.7407	0.0285	0.0525–

Plainly the results vary with the degree of the ignition. At the outset the residue may or may not weigh more than the theory requires for the known amounts of barium hydrox-

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* Am. Jour. Sci., ii, 70. Volume I, p. 369.

ide and boric acid taken upon the assumption that the residue is barium metaborate and barium carbonate. This is obviously natural if the carbon dioxide acts upon the barium borate as well as upon the excess of barium hydroxide; for, it is to be expected that in the evaporation more or less of the free boric acid will volatilize, and that in the subsequent ignition the boric acid remaining will tend to recombine more or less completely, replacing carbon dioxide. If the boric acid present were to recombine completely with the barium carbonate to form a metaborate, the final result would always be low by just the amount of free boric acid volatilized in the process of evaporation and ignition. The evidence of an experiment, however, in which 0.25 grm. of previously prepared barium metaborate was fused in contact with 0.5 grm. of barium carbonate, resulting in a loss of 0.0871 grm., goes to show that the metaborate and carbonate of barium interact still further to liberate carbon dioxide.

These results were so surprising in the light of the experience of Morse and Burton that the question of the possibility of breaking up by carbon dioxide the barium metaborate already formed was put to the test directly. A known amount of barium hydroxide was taken in solution and to it added an amount of boric acid very little in excess of that theoretically necessary to form the barium metaborate. The solution was evaporated to dryness and the residue ignited. The weight obtained proved to be 0.0008 grm. less than the sum of the barium and boric oxides taken, doubtless because the slight excess of boric acid was somewhat volatile in the evaporation. The mass, presumably barium metaborate, was now dissolved as completely as possible in hot water, carbon dioxide was passed through the solution, the whole was evaporated, and the residue ignited and weighed. The increase in the weight showed that carbon dioxide had been absorbed, while a corresponding amount of boric acid had not volatilized.

Exp.	$Ba(OH)_2$ taken. Calculated as $BaCO_3$.	B_2O_3 taken.	Residue after ignition.	Residue after CO_2 treatment and ignition.
	grm.	grm.	grm.	grm.
(5)	0.8377	0.2990	0.9491	0.9771

After passing in carbon dioxide and igniting the increase in weight was 0.0280 grm., representing the gas absorbed less the boric acid volatilized.

It was plain that barium metaborate is decomposed in solution by carbon dioxide. The possibility remained, however, that the action of carbon dioxide might be so regulated as to leave the metaborate practically unattacked. In experiment (6), therefore, carbon dioxide was passed above the stirred solution until no further precipitate formed upon the surface, the barium present being in excess of that required to form a metaborate.

Exp.	$Ba(OH)_2$ taken. Calculated as $BaCO_3$.	B_2O_3 taken.	Weight of residue after ignition.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(6)	0.7094	0.2070	0.7710	0.1658	0.0412—

The variation of this result from the theory shows that under these conditions the metaborate is not unaffected by carbon dioxide, the loss being due, of course, to the escape of boric acid.

An attempt was now made therefore to gauge the amount of the carbon dioxide introduced by means of an indicator. In experiment (7) phenolphthalein was added to the solution of boric acid containing an excess of barium hydroxide and the current of gas was stopped when the color of the indicator disappeared.

Exp.	$Ba(OH)_2$ taken. Calculated as $BaCO_3$.	B_2O_3 taken.	Weight of residue after ignition.	B_2O_3 found.	Error.
	grm.	grm.	grm.	grm.	grm.
(7)	0.6073	0.1573	1st wt., 0.6820	0.2011	0.0438+
			2d " 0.6788	0.1911	0.0338+
			3d " 0.6720	0.1742	0.0169+
			4th " 0.6700	0.1688	0.0115+
			5th " 0.6655	0.1567	0.0006—
			6th " 0.6630	0.1499	0.0074—
			7th " 0.6609	0.1443	0.0130—

This result is manifestly an improvement over those obtained without the careful restriction of the supply of carbon dioxide.

A similar experiment, differing only in the single point that the carbon dioxide was made to act upon a boiling solution, resulted in like manner.

In the light of these observations it is plain that a sufficiently prolonged action of carbon dioxide should result in the displacement of all the boric acid if that acid can be removed from the field of action as fast as it is liberated. Experiments were made which clearly demonstrate the truth of this hypothesis. A small side-necked flask was charged with a solution of boric acid (0.1143 grm.) and barium hydroxide (0.3227 grm.) in proportion to form the metaborate. The mass was brought nearly to dryness by distillation and methyl alcohol (15 cm^3) added. Through this flask, in which the alcohol was kept boiling by a Bunsen burner, was passed the vapor of methyl alcohol, while carbon dioxide, purified by a neutral solution of silver nitrate, bubbled continually through the entire system. The methyl alcohol vapor coming from the side-neck flask was kept lighted by contact with the flame of a Bunsen burner and the distillation continued for two hours until the flame showed not the slightest tinge of green. The residue in the flask originally containing barium metaborate was brought to dryness and tested for boric acid. Only a trace was found, and this was thought to be due to inclusion by the insoluble barium carbonate. In a similar experiment in which borax was used instead of barium borate, no trace of boric acid was found in the residue of sodium carbonate, either by turmeric or the flame test, while the distillation was continued only one-half the time of the preceding experiment. This result is quite in harmony with the views of P. Georgevic* to the effect that the large absorption of carbon dioxide in solutions of borax indicates that the boric acid is displaced from its union with the base.

Obviously, the division of the base between boric acid and carbonic acid falls under the principle of mass action, and if the boric acid is taken in sufficient excess over the barium hydroxide, the action of the carbonic acid should be inappreci-

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* Jour. prak. Chem. xxxviii, 118.

able. This idea is sustained by an experiment in which about 1 grm. of boric acid was dissolved with 0.15 grm. of barium hydroxide. No precipitate could be obtained by passing carbon dioxide and boiling. In fact, in the French process of borax manufacture just this action of an excess of boric acid upon a boiling solution of sodium carbonate is used. On the other hand to prevent the formation of a carbonate this excess of boric acid must be considerable if the action of carbon dioxide is prolonged. Thus in an experiment in which a current of carbon dioxide was passed into a solution containing 0.1219 grm. of boric anhydride and one-half the amount of barium needed to form a metaborate, the solution (60 cm^3) deposited on boiling 90 per cent of the barium present in the form of the carbonate.

In view of the facts which I have described, it is difficult to see under what conditions Morse and Burton prevented the excessive action of carbon dioxide and obtained in their analytical method the excellent results which they record.

XV

FURTHER SEPARATIONS OF ALUMINUM BY HYDROCHLORIC ACID.

By FRANKE STUART HAVENS.*

In former papers† from this laboratory methods have been described for the separation of aluminum from ferric iron, and from beryllium, based on the insolubility of the hydrous aluminum chloride in a mixture of equal parts of aqueous hydrochloric acid and ether saturated with hydrochloric acid gas, the ferric and beryllium chlorides being exceedingly soluble in this mixture.

It was the purpose of the investigations herein described to discover how far this process could be extended, with certain modifications, to cover the separation of aluminum from such other metals as might occur with it, either in artificially prepared alloys or in naturally-occurring compounds.

The aluminum used in all the following experiments was in the form of a solution of the chloride. This chloride was purified, as previously described,‡ from iron by precipitation with hydrochloric acid, and from the alkalies by precipitation as the hydroxide and continued washing with water until the washings gave no test with silver nitrate. The hydroxide thus obtained was dissolved in hot hydrochloric acid to get it into the form of the chloride. The chloride solution was standardized by precipitating weighed portions with ammonia and weighing as the oxide.

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* From the Am. Jour. Sci., vi, 45.

† Gooch and Havens, Am. Jour. Sci., vol. ii, p. 416. This volume, p. 20; Havens, Am. Jour. Sci., vol., iv, p. 111. This volume, p. 47.

‡ Loc. cit.

Separation of Aluminum from Zinc.

A solution of pure zinc chloride made by dissolving metallic zinc, free from impurities, in hydrochloric acid, is not precipitated when treated with an equal volume of ether and saturated with hydrochloric acid gas.

To prepare a definite zinc salt free from traces of the alkalies which would be precipitated with the aluminum by strong hydrochloric acid, pure metallic zinc was dissolved in hydrochloric acid, the dilute solution precipitated with ammonium carbonate, and the resulting carbonate ignited to a constant weight as zinc oxide. This oxide dissolved in hydrochloric acid gave a pure chloride.

The aluminum in all these experiments was determined in the following manner: — Portions of the prepared solution of aluminum chloride were weighed in a small beaker, weighed portions of zinc oxide added and sufficient aqueous hydrochloric acid to dissolve it. The beaker was then cooled by immersion in an inverted bell-jar supplied with running water by means of inlet and outlet tubes, and a current of gaseous hydrochloric acid (generated by the gradual addition of sulphuric acid to a mixture of hydrochloric acid and salt) passed through the solution in the beaker to complete saturation. Ether was added in volume equal to that of the original solution, and the whole again saturated with hydrochloric acid gas. The crystalline chloride precipitated was caught on asbestos in a filter crucible, washed with a previously prepared solution of equal parts of ether and hydrochloric acid, saturated with hydrochloric acid gas, dried for half an hour at 150°–180° C., covered with a layer of pure mercury oxide, heated gently over a low flame under a ventilating hood, ignited over the blast, and weighed as the oxide. The results show that aluminum can be determined with reasonable accuracy in the presence of a pure zinc salt.

The zinc can be determined, after the evaporation of the strong acid filtrate, by any of the well known methods. It was found, however, that after thorough conversion to the nitrate by repeated evaporation with nitric acid the salt could be ignited directly to the oxide with satisfactory results. This is shown clearly in Table I, (3) to (5). In experiments (3) and (4), zinc oxide was dissolved in nitric acid and the nitrate ignited again to the oxide. In experiment (5), the zinc oxide was first dissolved in hydrochloric acid and the chloride thus obtained was converted to the nitrate by evaporating the solution (5 cm^3) with nitric acid (2 cm^3), treating the residue with nitric acid (2 cm^3) and evaporating to dryness.

TABLE I.

Exp.	Al_2O_3 taken as the chloride.	Al_2O_3 found.	Error.	ZnO taken.	ZnO found.	Error.	Error corrected.	Final. vol.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	cm^3
(1)	0.0562	0.0562	0.0000	0.1110	. .	. .	. .	. .
(2)	0.0580	0.0577	0.0003−	0.1034	. .	. .	. .	. .
(3)	. .	. .	. .	0.1019	0.1016	0.0003−	. .	. .
(4)	. .	. .	. .	0.1010	0.1007	0.0003−	. .	. .
(5)	. .	. .	. .	0.1100	0.1095	0.0005−	. .	. .
(6)	0.0572	0.0572	0.0000	0.1014	0.1027	0.0013+	0.0007−	12
(7)	0.0563	0.0550	0.0013−	0.1026	0.1038	0.0012+	0.0008−	16
(8)	0.0577	0.0576	0.0001−	0.1000	0.1014	0.0014+	0.0006−	16
(9)	0.0559	0.0558	0.0001−	0.1020	0 1035	0.0015+	0.0005−	16
(10)	0.0563	0.0556	0.0007−	0.2024	0.2046	0.0022+	0.0002+	20
(11)	0.1111	0.1107	0.0004−	0.2092	0.2116	0.0024+	0.0004+	20

In Table I, (6) to (11), are given the results of experiments in which both the aluminum and zinc were determined, — the former, as described, by precipitating as the hydrous chloride and weighing as the oxide, and the latter by carefully evaporating the strongly acid filtrate (best with a small current of air playing on the surface of the liquid to avoid spattering due to the too violent evolution of the ether and gaseous acid) and finally converting the chloride through the nitrate into the oxide. It is, of course, absolutely necessary that the treatment with nitric acid shall be thorough, so that no zinc chloride may remain to volatilize when the residue is ignited. On account of the danger to platinum from the aqua regia generated by the action of nitric acid on zinc chloride, the evaporations of the filtrates from the aluminum chloride and the treatment with nitric acid were carried on in porcelain and the residual nitrate was transferred to a small crucible for ignition. In this process the porcelain was evidently attacked somewhat, so that the residual nitrate was slightly contaminated with material from the large porcelain dish. This fact accounts for the high results given in the first column of errors. However, on introducing a correction (0.0020) found by carrying through the process in blank with the quantities of reagents employed in the regular process, the results on zinc, slightly deficient, agree closely with those obtained in (3)–(5), Table I, where the zinc nitrate was converted directly to the oxide without the previous evaporation in porcelain of a large volume of strongly acid liquid. The errors thus corrected stand in another column of the table.

These results show clearly that aluminum and zinc may be separated from one another by the action of hydrochloric acid gas in aqueous ethereal solution with a reasonable degree of accuracy.

Separation of Aluminum from Copper, Mercury, and Bismuth.

The separation of aluminum from copper, mercury, and bismuth does not differ materially from the separation of

TABLE II.

Exp.	Al_2O_3 taken as the chloride.	Al_2O_3 found.	Error.	CuO taken.	CuO found.	Error.	$HgCl_2$ taken.	Bi_2O_3 taken.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.0576	0.0571	0.0005–	0.0500	. .	. .	. .	. .
(2)	0.0561	0.0557	0.0004–	0.0400	. .	. .	. .	. .
(3)	0.0570	0.0574	0.0004+	. .	. .	. .	0.1000	. .
(4)	0.0548	0.0557	0.0009+	. .	. .	. .	0.1000	. .
(5)	0.0565	0.0571	0.0006+	. .	. .	. .	. .	0.1000
(6)	0.0576	0.0577	0.0001+	. .	. .	. .	. .	0.2000
(7)	. .	. .	. .	0.0437	0.0432	0.0005–	. .	. .
(8)	. .	. .	. .	0.0359	0.0359	0.0000	. .	. .
(9)	. .	. .	. .	0.0345	0.0340	0.0005–	. .	. .
(10)	0.0558	0.0545	0.0013–	0.0319	0.0324	0.0005+	. .	. .
(11)	0.0538	0.0536	0 0002–	0.0343	0.0356	0.0013+	. .	. .
(12)	0.0566	0.0562	0.0004–	0.0337	0.0349	0.0012+	. .	. .
(13)	0.0577	0.0575	0.0002–	0.0651	0.0644	0.0007–	. .	. .

aluminum and zinc. Aluminum chloride is precipitated quantitatively in the presence of pure salts of these elements as shown in experiments of Table II.

In determining the copper in the acid filtrate it was found advantageous to weigh as the oxide, but to arrive at that condition through the sulphate rather than through the nitrate (which was the transition salt in the case of zinc), as this process can be carried on safely in platinum.

In Table II, (10)–(13), are given results of experiments in which the aluminum was determined as previously described by precipitation as the hydrous chloride and conversion to the oxide. The acid filtrate was evaporated in platinum and the copper determined by treating the residue with a few drops of strong sulphuric acid, heating gently to drive off the excess of sulphuric acid, and then igniting the sulphate to the oxide at a red heat. That the copper sulphate is converted to the oxide by ignition at a red heat over a Bunsen burner is shown in experiments (7) to (9) of Table II.

XVI

THE IODOMETRIC DETERMINATION OF MOLYBDENUM.

BY F. A. GOOCH AND JOHN T. NORTON JR.*

A PROCESS for the iodometric determination of molybdic acid, which consists in treating a soluble molybdate in a Bunsen distillation-apparatus with potassium iodide and hydrochloric acid, has been advocated by Friedheim and Euler.† According to this process the molybdate, containing from 0.2 grm. to 0.3 grm. of molybdenum trioxide, is treated with from 0.5 grm. to 0.75 grm. of potassium iodide and enough hydrochloric acid, of sp. gr. 1.12, to fill two-thirds of the flask of the apparatus. The liquid is warmed until heavy vapors of iodine fill the flask and then boiled until iodine vapor is no longer visible and the color of the liquid residue is a clear green. The iodine liberated is collected in the distillate and titrated with sodium thiosulphate, every atom of iodine found indicating presumably the reduction of a molecule of molybdic acid to the condition of the pentoxide Mo_2O_5.

It was pointed out in a former article from this laboratory,‡ that greater precaution than was taken by Friedheim and Euler is necessary in order that the reduction may proceed according to theory, and that the iodine collected may serve as a reliable measure of the molybdic acid. It was found that the green color of the liquid comes gradually and that it may develop distinctly before the molybdic acid is fully reduced. It was found, also, that since even a trace of oxygen liberates iodine from the hot mixture of potassium

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* From Am. Jour. Sci., vi, 168.

† Ber. Dtsch. chem. Ges., xxviii, 2066.

‡ Gooch and Fairbanks, Am. Jour. Sci., ii, 156. Volume I, p. 375.

iodide and hydrochloric acid of the strength employed, it is not sufficient to rely upon the volatilization of iodine to expel the air originally in the apparatus, but that it is essential to conduct the distillation in an atmosphere devoid of oxygen. The suggestion was made therefore that the operation should be carried on in a current of carbon dioxide and that the mixture, constituted definitely, should be boiled between stated limits of concentration which were determined by experiment. It was found that when amounts of a soluble molybdate containing less than 0.3 grm. of molybdenum trioxide are treated with potassium iodide, not exceeding the theoretical proportion by more than 0.5 grm., and 40 cm^3 of a mixture of the strongest hydrochloric acid and water in equal parts, the reduction proceeds with a fair degree of regularity and is practically complete when the volume has diminished to 25 cm^3. If the operation is properly conducted in an atmosphere of carbon dioxide, it was shown that the iodine in the distillate may be trusted to indicate the molybdic acid within reasonable limits of accuracy. It appeared, however, that too great an excess of potassium iodide tends to induce excessive reduction, and that the same tendency shows when the liquid is concentrated to too low a limit.

To this criticism Friedheim took exception [*] and contrasted, to their disadvantage, our results by the modified method with those of Friedheim and Euler by the original method. It became necessary, therefore, to point out [†] the fact that of the results published by Friedheim and Euler, upon which reliance was placed to prove the reliability of their method, five out of seven in one series and one out of five in another series had been calculated incorrectly from data given. Another series of six determinations was, however, apparently faultless in this respect. More recently [‡] Euler has explained that the errors were not really arithmetical. Two of them may be presumed, inferentially, to be due to careless copying

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[*] Ber. Dtsch. chem. Ges., xxix, 2981.

[†] Gooch, Am. Jour. Sci., iii, 237.

[‡] Zeit. anorg. Chem., xv, 454.

or proof-reading; and four, we are told by Euler, were introduced into the series by mistake, and actually represent (as Prof. Friedheim kindly informs him) the analysis of a sample of ammonium molybdate of undetermined constitution: that is to say, the figures now given by Euler represent the original percentages of molybdenum trioxide which had been changed by some unconscious process from

80.62 per cent to 81.85 per cent.
80.71 " " 81.69 "
80.63 " " 81.67 "
80.78 " " 81.78 "

Curiously enough, Euler's corrected figures, as given here, are still affected by trifling arithmetical errors of from one to four units in the second decimal place. The agreement of these results among themselves is no proof of the correctness of the process of analysis. The great variation between the average percentage of molybdenum trioxide in ammonium molybdate as found by Euler in a molybdate of known constitution and the percentage of the trioxide as found by Friedheim (if we understand Euler aright) may be due conceivably to either or both of two causes, viz.: the change of material analyzed, and the change of operator or conduct of the operation. We shall show in the following account of our work that the exact control of the conditions of treatment, along the lines laid down formerly, is actually essential to the reduction of molybdic acid according to the theory of the process.

Our experiments were made with ammonium molybdate twice recrystallized from the presumably pure salt. The constitution of the preparation was determined by careful ignition *per se*, and, for greater security, with sodium tungstate free from carbonate. It contained 81.83 per cent of molybdenum trioxide.

The potassium iodide which we used was prepared by acting with re-sublimed iodine upon iron wire, and precipitating by potassium carbonate — the proportions of iodine and iron having been adjusted to secure the formation of the hydrous magnetic oxide of iron. The filtrate from the iron hydroxide gave on evaporation and crystallization potassium iodide which was free from iodate.

The hydrochloric acid was taken of sp. gr. 1.12, because this is the strength used by Friedheim and Euler.

The sodium thiosulphate employed was taken in nearly decinormal solution, and was standardized by running it into an approximately decinormal solution of iodine which had been determined by comparison with decinormal arsenious acid made from carefully re-sublimed arsenious oxide. We chose this method of standardizing — the introduction of the thiosulphate into the iodine — rather than the reverse operation, in order that the conditions of the actual analysis might be followed in the standardization.

The distillation apparatus was constructed with sealed or ground joints of glass wherever contact with iodine was a possibility. It was made by sealing together a separating funnel A, a 100 cm^3 Voit flask B, a Drexel wash-bottle C, and a bulbed trap *g*, as shown in the figure. Upon the side of the distillation-flask B was pasted a graduated scale by means of which the volume of the liquid within the flask might be known at any time. Carbon dioxide, generated in a Kipp apparatus by the action of dilute hydrochloric acid (carrying in solution cuprous chloride to take up free oxygen) upon marble previously boiled in water, was passed through the apparatus before and during the operation, so that it was possible to interrupt the process of boiling at any point of concentration, to remove the receiver by easy manipulation, to replace the receiver, and to continue

Fig. 20.

the distillation without danger of admitting air to the distillation flask.

In experiments to be described — (1) to (5) of the table — the proportions of potassium iodide and molybdic acid, and the strength of the hydrochloric acid recommended by Friedheim and Euler were retained. The essential change of condition is the removal of atmospheric air from the distillation flask before the acid is admitted to contact with the other reagents. Potassium iodide (3 grm.) and water (200 cm^3) were put into the receiver C, and a little of this solution was allowed to flow into the trap *g*. Ammonium molybdate carefully weighed (0.3 grm.) and potassium iodide (0.5 grm. to 0.75 grm.) were introduced into the distillation flask B, the apparatus was connected as shown in the figure, and carbon dioxide was passed freely through the whole apparatus for some minutes. The stop-cock *d*, between the bulb of the funnel A and the flask B, was closed, and hydrochloric acid (40 cm^3, sp. gr. 1.12) was poured into the funnel; the air above the liquid in the funnel was displaced by carbon dioxide through the space between the neck of the funnel and the loosely adjusted stopper carrying the inlet tube; the connection between the funnel and inlet tube was tightened, the stop-cock opened, and the acid, under the pressure of carbon dioxide, was permitted to flow into the flask. In this way the acid, iodide, and molybdate were made to interact with little danger of the presence of oxygen. The flask was heated by the Bunsen burner, and the iodine evolved, passing over quietly in the slow current of carbon dioxide, collected in the receiver. The liquid was boiled until fumes of iodine were no longer visible above the liquid in the flask and connecting tubes backed by a ground of white, and then a full minute more. At this stage, the green color of the liquid having developed fully, the apparatus was permitted to cool, the current of carbon dioxide was increased, the cap of the receiver was loosened at *f*, the contents of the trap were washed back into the receiver, the rest of the apparatus was lifted bodily from the receiver, the liquid adhering to the inlet tube was washed off into the receiver, and the end of the tube was dipped immediately into a solution of potassium iodide. The constant flow of carbon dioxide prevented reflux of air during the transfer, and as soon as the end of the tube had been submerged in the solution of potassium iodide (which was employed not only as a water-seal, but to catch any iodine still carried in the gas), it was possible to reduce the rapidity of the current.

After titrating the iodine in the distillate the receiver was again placed in the train and the process of distillation was resumed under the former conditions and continued until the volume of the liquid, as indicated upon the scale, had diminished to 25 cm^3, when the distillation was interrupted. The apparatus was manipulated as before to prevent access of air, and the iodine evolved in the second treatment determined. A third period of distillation served to show the iodine liberated during the concentration of the liquid from 25 cm^3 to 10 cm^3.

During the first period of distillation the liquid assumed the clear green color, which changed but slightly until the beginning of the third period, when the tint verged upon olive, and at the end of the operation the color of the liquid was an olive brown which grew browner on cooling. The addition of considerable hydrochloric acid to the residual liquid restored the clear green color, while water changed the olive brown to reddish yellow, the tint varying with the dilution. The results of these experiments are recorded in (1) to (5) of the accompanying table. In division A are given the weights of molybdenum trioxide corresponding to the amounts of iodine found in the three stages of distillation; in division B, the molybdenum trioxide corresponding to the iodine evolved from the beginning of the process to the end of each stage.

The mean error of the indications taken during the period of distillation advocated by Friedheim and Euler is 0.0045 grm. —;* that of the period of concentration from 40 cm^3 to

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* Even this figure does not disclose the full error, which is partly counterbalanced, as will appear later, by the effect of oxygen dissolved in the acid used in the process.

A.

Exp.	HCl Sp. gr. 1.12 taken.	KI in retort.	MoO_3 taken as ammonium molybdate.	MoO_3 corresponding to iodine found.		
				First stage 40cm^3 to 32cm^3. Green color.	Second stage 32cm^3 to 25 cm^3.	Third stage 25cm^3 to 10cm^3.
	cm^3	grm.	grm.	grm.	grm.	grm.
(1)	40	0.5	0.2455	0.2399	0.0076	0.0004
(2)	40	0.5	0.2455	0.2402	0.0053	0.0013
(3)	40	0.5	0.2455	0.2414	0.0040	0.0004
(4)	40	0.75	0.2455	0.2404	0.0061	0.0004
(5)	40	0.75	0.2455	0.2431	0.0037	0.0004
(6)	40	1	0.2455	0.2404	0.0085	0.0019
(7)	40	2	0.2455	. .	. .	. .

B.

Exp.	MoO_3 corresponding to iodine found during period of Friedheim and Euler. (1st stage.)	Error.	MoO_3 corresponding to iodine found in concentrating from 40cm^3 to 25cm^3.	Error.	MoO_3 corresponding to iodine found in concentrating from 40cm^3 to 10 cm^3.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.2399	0.0056−	0.2475	0.0020+	0.2479	0.0024+
(2)	0.2402	0.0053−	0.2455	0.0000	0.2468	0.0013+
(3)	0.2414	0.0041−	0.2454	0.0001−	0.2458	0.0003+
(4)	0.2404	0.0051−	0.2465	0.0010+	0.2469	0.0014+
(5)	0.2431	0.0024−	0.2468	0.0013+	0.2472	0.0017+
(6)	0.2404	0.0051−	0.2489	0.0034+	0.2508	0.0053+
(7)	. .	. .	. .	. .	0.2495 0.2529*	0.0040+ 0.0074+

25 cm^3 is 0.0008 grm. + ; and that of the full period of distillation is 0.0014 +. It is plain beyond a peradventure that in the process as conducted by Friedheim and Euler, excepting the protection against atmospheric action the theoretical reduction of the molybdic acid does not take place. The best results are obtained when the distillation is prolonged until the original volume of 40 cm^3 has been diminished to 25 cm^3. Concentration beyond the limit of 25 cm^3 tends to develop a tendency toward over-reduction, especially when the amount of potassium iodide is increased beyond about 0.5 grm. in

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* On repeating distillation with a fresh charge of acid.

excess of that theoretically required. This is shown in experiments (6) and (7), conducted otherwise similarly to those described above, in which the amount of potassium iodide was increased to 1 grm. and 2 grms. The error after distilling from 40 cm^3 to 10 cm^3, the lowest limit of the preceding experiments, was 0.0053 grm. + and 0.0040 grm. +, and the latter error was increased to 0.0074 grm. + on repeating the distillation with a fresh portion (30 cm^3) of the acid. It is interesting to note incidentally that in the experiment in which the largest amount of iodide (2 grms.) was used the solution did not take the green color at any stage of the distillation, probably because the large excess of iodide held the free iodine and so masked the color until the degree of concentration was reached at which the olive-brown color displaces the green.

The possibility of the interaction of atmospheric oxygen and gaseous hydriodic in the analytical process, even to the extent of producing errors of from one to three per cent reckoned as molybdenum trioxide, was recognized by Friedheim and Euter; and it was to obviate this difficulty that the recommendation was made by them to warm very gradually the distillation flask filled two-thirds with the mixture of iodide, molybdate, and acid, and to raise the liquid to actual boiling only when the space above the liquid in the retort and in the connecting tube is filled as completely as possible with iodine vapor, while the liquid in the receiver begins to rise in the tube.

The action of atmospheric oxygen upon the solution of hydriodic acid must, however, be also taken into account. It is a familiar fact that when a considerable excess of strong hydrochloric acid is allowed to act in contact with air upon potassium iodide (free from iodate) dissolved in a little water, the mixture is colored by free iodine. The amount of iodine liberated by atmospheric action is insignificant when the acid is very dilute, but is considerable when the acid is strong, and increases with time and rise in temperature, as shown in the experiments recorded in the accompanying table.

KI taken.	Volume.	Percentage of HCl in aqueous acid.	Time in minutes.	Temperature. Centigrade.	MoO_3 equivalent to iodine found.	Remarks.
grm.	cm³				grm.	
1	66	2	1	28°	None.	
1	66	2	10	28°	0.0001	
1	66	24*	10	23°	0.0017	Diluted to 500 cm³ before titrating with $Na_2S_2O_3$.
1	66	24*	4	From 23° to the boiling point.	0.0067	
1	66	24*	10		0.0121	

Even the precaution to conduct the operation in an atmosphere of carbon dioxide does not eliminate all chance of error of this sort unless the liquid of the mixture — the hydrochloric acid — is free from air. The experiments of the following statement, which were conducted in the apparatus and manner previously described, show this point clearly. Thus,

KI taken.	Vol.	Percentage of HCl in aqueous acid.	Concentration by boiling.	MoO^3 equivalent to iodine found.	Remarks.
grm.	cm³		cm³.	grm.	
1	40	24	40–30	0.0013	Iodine determined in distillate.
			30–20	0.0002	1 grm. of KI added to retort at the beginning of the 2d stage.
1	40	20	40–25	0.0005	The acid taken, sp. gr. 1.1, was freshly boiled and introduced at once upon KI in retort in CO_2.

40 cm³ of unboiled acid, sp. gr. 1.12, introduced enough air into the apparatus to cause an error of 0.0013 grm. reckoned in terms of molybdenum trioxide, while the iodine set free by the action of the residual acid of this experiment upon another gram of potassium iodide introduced without admission of air corresponded to only 0.0002 grm. in terms of molybdenum

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* This corresponds nearly to sp. gr. 1.12.

trioxide. The use of acid of sp. gr. 1.1, freshly boiled in the air, obviously reduces the error due to the unboiled acid, but even in this case the effect of included oxygen was not wholly obviated.

It is obvious that the procedure recommended by Friedheim and Euler can by no possibility eliminate the effect of atmospheric action upon the mixture of acid and iodide. The extent of such action must depend upon such conditions as the size of the apparatus, the time of exposure, the body of air above and dissolved in the liquid, and the rate of displacement of the air. How great the error due to atmospheric action actually was in the process as conducted by Friedheim and Euler we, of course, have no means of knowing. It is to be hoped, however, that it was sufficiently great to counterbalance that other inevitable error (of about five milligrams) which exists by reason of the incompleteness with which molybdic acid is reduced under the conditions which these investigators prescribe; for, the value of Euler's work upon the vanadio-molybdates rests upon the chance that these two very considerable and indisputable tendencies to error may have neutralized one another.

It has been shown clearly that our former criticism of the procedure of Friedheim and Euler is justified in every particular. We have no change to make in the recommendation made therein as to necessary modifications.

If the conditions seem difficult, there is an alternative in the method proposed in the former article,* according to which the molybdate is reduced by the acid and iodide in an Erlenmeyer beaker (trapped loosely by means of a short bulbed tube hung in the neck) and the molybdenum pentoxide, freed from iodine by boiling, is reoxidized by standard iodine in alkaline solution.

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* Am. Jour. Sci., ii, 156. Volume I, p. 375.

XVII

ON THE DETERMINATION OF MANGANESE AS THE PYROPHOSPHATE.

BY F. A. GOOCH AND MARTHA AUSTIN.*

FOR the estimation of manganese in a gravimetric way when accuracy is a consideration, recourse is usually taken to the excellent method of Wolcott Gibbs.† This method consists in the precipitation of a manganous salt by an alkaline phosphate, the conversion of the tribasic phosphate into the ammonium manganese phosphate, and the weighing of the product of ignition as the pyrophosphate.

By Gibbs' original method the orthophosphate of manganese was precipitated by hydrogen disodium phosphate in large excess above the quantity required to cause the precipitation. The flocky white precipitate was dissolved either in sulphuric or hydrochloric acid, and precipitated again at the boiling temperature by ammonia in excess. This semi-gelatinous precipitate on boiling or long standing even in the cold becomes crystalline, the crystals forming beautiful talcose scales which have a pearly luster and a pale rose color. The precipitate was filtered off, washed with hot water, dried and ignited. The results obtained by Gibbs' students for the pyrophosphate accord closely with the theory.

Fresenius ‡ showed subsequently that ammonium manganese phosphate dissolves in cold water, in hot water, and in an aqueous solution of ammonium chloride [1 : 70] to the extent of 1 part in 32,000, 1 part in 20,000, and 1 part in 18,000, respectively. It is clear, however, that the solubility of this

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* From Am. Jour. Sci., vi, 233.

† Am. Jour. Sci., xliv, 216.

‡ Zeitschr. anal. Chem., vi, 415.

precipitate is not indicated necessarily by the proportions given so long as an excess of the precipitant is present during the washing, though Fresenius did find in the filtrate traces of manganese which to his mind were sufficient to account for losses indicated by his test analyses, viz., one to three milligrams of oxide, or from two to six milligrams of phosphate.

Another mode of manipulation has been advocated by Blair* in order that the precipitate may be obtained more easily in crystalline condition. According to this method dilute ammonia is added drop by drop to the hot acid solution until the precipitate begins to form, the boiling and stirring are continued until the small amount of flocky precipitate is converted completely to crystalline condition, and the process of adding ammonia drop by drop is repeated until the manganese is all down in crystalline condition. The dilute ammonia is added in excess and the liquid filtered after cooling in ice water.

In discussing these methods of precipitation, McKenna † points out that both give good and accordant results, and that the process may be carried on in glass as well as in platinum, if the time of crystallization is made short enough.

When a manganous salt is precipitated in the cold by an excess of an alkaline phosphate, it falls, as Heintz ‡ has shown, in the form of the trimanganous phosphate of the formula $Mn_3P_2O_8$. This same phosphate constitutes, as we have found, the greater part of the precipitate which forms when a manganous salt reacts in the cold in the presence of ammonium chloride with microcosmic salt and ammonia in slight excess. Boiling or even subsequent standing may, as is well known, effect a more or less complete conversion of the manganese phosphate to the ammonium manganese phosphate. Thus, in one experiment in which an amount of manganous chloride enough to produce 0.2214 gram of the pyrophosphate was precipitated in the cold by 5 cm^3 of a saturated solution of microcosmic salt, with the subsequent addition of ammonia

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* The Chemical Analysis of Iron, 106. † Jour. Anal. Chem., v, 141.

‡ Ann. Phys., cl, 449.

in excess, in a volume of 200 cm^3 containing also 5 grams of ammonium chloride, the residue after ignition weighed 0.1904 gram. Presuming this residue to consist entirely of the pyrophosphate and the trimanganous orthophosphate, the proportion of the former to the latter calculated from the relation of symbols, and the weights taken and found, is nearly one to six. That is to say, about six-sevenths of the precipitate fell in this experiment in the form of the tribasic orthophosphate. In another experiment made exactly similarly, excepting that the liquid was heated to boiling, the proportion of the manganese pyrophosphate to the trimanganous orthophosphate in the only partially crystallized precipitate proved to be two to one. That is, in this case, two-thirds of the precipitate was in the form of the pyrophosphate. In the former of the experiments a small amount of manganese was found in the filtrate, but not enough to change materially the ratio recorded. The slight solubility appears to be connected with the incomplete conversion of the trimanganous phosphate to the ammonium manganese phosphate, for as will appear later, the manganese found in the filtrate, when the conversion is known to be nearly complete, is inappreciable unless extraordinary amounts of the ammonium salt are present. The success of the analytical process under discussion turns, therefore, upon the change of the trimanganous phosphate $Mn_3P_2O_8$ to the ammonium manganese phosphate NH_4MnPO_4. In the work to be described the attempt was made to learn the conditions under which this conversion may be best and most completely accomplished.

The conversion of a molecule of trimanganous phosphate to the ammonium manganese phosphate might be due, conceivably, either to the action of free ammonia or to the action of a salt of ammonium. The action of ammonia could only take place at the expense of a partial loss of manganese from the phosphate and its appearance as a hydroxide, two-thirds of the manganese going into two molecules of the ammonium manganese phosphate. In the presence of ammonium salts it is possible that the manganese oxide thus replaced might enter into union with the acid radical of the ammonium salt setting free ammonia; but if the ammonium salt present were the phosphate, or if an alkaline phosphate were present with other suitable ammonium salts, it is conceivable that the replaced manganese might appear as a constituent of a third molecule of ammonium manganese phosphate. In any event, it would be the ammonium salt and not the free ammonia which would determine the formation of the third molecule of the ammonium manganese phosphate. Plainly, too, the ammonium salt by itself, if it were a phosphate, or if a soluble phosphate were also present, might accomplish the conversion without the intermediate action of free ammonia. Unless, therefore, free ammonia favors the insolubility of the ammonium manganese phosphate, its presence would be unnecessary and might even be an actual disadvantage if the hydroxide naturally formed by its action upon the manganese phosphate were to fail to reunite fully with a phosphoric acid radical. It is plain, too, that the action of free ammonia might not stop with the replacement of one out of the three of the manganese atoms present in the molecule, but might even proceed under favorable conditions to the formation of phosphate richer in ammonium and to the separation of more manganese from its union with the acid radical. As a matter of fact Munroe * has shown that the prolonged action of hot ammonia upon the precipitate produced by the interaction of a manganous salt and an alkaline phosphate does actually produce a hydroxide which blackens as it takes oxygen from the air. Our attention has been given, therefore, more especially to a study of the conditions of action under which a salt of ammonium — the chloride — may bring about the conversion of the precipitate first thrown down by an alkaline phosphate to the form of the ammonium manganese phosphate. Experiments were made upon solutions of pure manganous chloride prepared and standardized by means of the sulphate method, as described in a former paper, † to show the effect of varying amounts of ammonium chloride on the condition

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* Amer. Chemist, 1877.

† Am. Jour. Sci., v, 209. This volume, p. 77.

of the precipitate and upon the solubility of the precipitate when once formed. The ammonium chloride for this work was prepared pure by boiling the chemically pure salt of commerce with a faint excess of ammonium hydrate and filtering — to free it from traces of iron, silica and alumina. In the first series of experiments dilute ammonia was added slowly to the hot faintly acidulated solution containing the manganous chloride and more than enough, theoretically, of a saturated solution of microcosmic salt to precipitate the manganese present. The liquid was heated and stirred until the flocky mass was changed to a crystalline condition. The addition of ammonia drop by drop, with constant stirring and heating, was continued until the manganese was all precipitated in crystalline form. A slight excess of ammonia was added and the liquid with the precipitate was allowed to stand for a half hour, cooling gradually or chilled in ice water. The precipitate was filtered off on asbestos under pressure, washed carefully in water made faintly ammoniacal, dried and ignited. The filtrates were tested for manganese by treatment with bromine and heating. The results of these experiments are given in the following table.

TABLE I.

$Mn_2P_2O_7$ equivalent to $MnCl_2$.		Error in terms of $Mn_2P_2O_7$.	Error in terms of Manganese.	Saturated solution of $HNH_4NaPO_4 . 4H_2O$.	Total volume.	Manganese in filtrate.
Taken.	Found.					
grm.	grm.	grm.	grm.	cm³	cm³	
0.4033	0.3769	0.0264—	0.0102—	5	60*	None.
0.4033	0.3728	0.0305—	0.0118—	5	60*	None.
0.3770	0.3530	0.0240—	0.0090—	5	60	None.
0.3770	0.3620	0.0150—	0.0058—	5	60	None.
0.4033	0.3751	0.0282—	0.0109—	10	60	None.
0.4033	0.3774	0.0259—	0.0100—	10	60	None.
0.4033	0.3871	0.0162—	0.0062—	5	200	None.
0.3226	0 3066	0.0160—	0.0062—	5	200	None.

In this method of precipitation of the manganese in a pure solution of a manganous salt the results are all wrong. The

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* Chilled in ice-water.

proportion of the trimanganous phosphate to the pyrophosphate in the residue, calculated from the symbols and the weights taken and found, is in the average two to five. That is to say, five-sevenths of the trimanganous phosphate has been converted to the form of the ammonium manganous phosphate.

The precipitate obtained in this manner is white and granular but not silky, and after ignition it shows the same dead white color, and is powdery. Evidently the regulation of the volume in which the precipitation is made is not essential, and the chilling of the liquid is of no importance in changing the manganese to the ammonium manganese salt under the given conditions. It is plain, moreover, that the assumption of a crystalline condition cannot serve as an indication that the composition of the salt is ideal. It is to be noted, however, that the conditions obtaining here are essentially different from those in common practice; for, ordinarily, when manganese is to be determined ammonium salts are abundantly present as the result of previous steps in analysis.

In the experiments of the next series the conditions are varied simply in this respect, that ammonium salts are introduced before the precipitation. The precipitate was less granular and more silky. After ignition the mass was white with a faint rose color. In the experiments of section A of the table the precipitate first thrown down was redissolved, reprecipitated and filtered after cooling; in those of section B, the precipitate was filtered after cooling without re-solution and without reprecipitation; and in those of section C, the first precipitate was filtered at once while the solution was still hot. The length of digestion before filtering and the indications of manganese in the filtrate are recorded in the table.

It was observed in these experiments that when the amount of ammonium chloride is present in considerable quantity a fine crystalline condition is got much more readily than when the amount of that salt is small: with maximum amounts of ammonium chloride the change from the flocky to the crystal-

TABLE II.

$Mn_2P_2O_7$ equivalent to the $MnCl_2$.		Error in terms of $Mn_2P_2O_7$.	Error in terms of Manganese.	Saturated solution of $HNaNH_4PO_4 \cdot 4H_2O$.	NH_4Cl.	Total volume.	Time of standing cold.	Manganese in the filtrate.
Taken.	Found.							
				A.				
grm.	grm.	grm.	grm.	cm^3	grm.	cm^3	hrs.	
0.1542	0.1520	0.0022–	0.0008–	5	5	200	15	None.
0.1542	0.1540	0.0002–	0.0000	5	10	200	15	None.
0.1542	0.1536	0.0006–	0.0002–	5	10	100	5	None.
0.1542	0.1535	0.0007–	0.0002–	5	20	200	2½	None.
0.3770	0.3712	0.0058–	0.0022–	5	20	200	½	None.
0.3770	0.3724	0.0046–	0.0018–	5	20	200	½	None.
0.3084	0.3069	0.0015–	0.0006–	5	40	200	1	None.
0.3084	0.3060	0.0024–	0.0009–	5	40	200	1	None.
0.3084	0.3059	0.0025–	0.0009–	5	40	200	15	Trace.
0.3084	0.3057	0.0027–	0.0010–	5	60	200	15	None.
				B.				
0.1542	0.1521	0.0021–	0.0008–	5	10	100	40	None.
0.1542	0.1512	0.0030–	0.0010–	5	10	200	40	None.
0.1542	0.1532	0.0010–	0.0003–	5	20	200	15	None.
0.1542	0.1531	0.0011–	0.0004–	5	20	100	15	None.
0.3770	0.3720	0.0050–	0.0019–	5	20	200	½	None.
0.3770	0.3745	0.0035–	0.0014–	5	20	200	½	None.
				C.				
0.1542	0.1519	0.0023–	0.0009–	5	15	200	. .	None.
0.1542	0.1530	0.0012–	0.0004–	5	20	200	. .	None.
0.1542	0.1525	0.0017–	0.0007–	5	30	200	. .	None.
0.3084	0.3020	0.0064–	0.0025–	5	10	200	. .	None.
0.3084	0.3053	0.0031–	0.0012–	5	20	200	. .	None.
0.3084	0.3033	0.0051–	0.0020–	5	20	200	. .	None.
0.3084	0.3039	0.0045–	0.0017–	5	60	200	. .	Trace.

line condition is almost immediate; even in the cold the change takes place to a marked extent in a few seconds. No manganese was found in the filtrate by boiling with bromine and ammonia — a test which is capable of indicating 0.0001 grm. of manganous sulphate in 500 cm^3 of water containing 60 grm. of ammonium chloride — until the ammonium chloride amounted to 20 per cent of the mass, or to 40 grm. in 200 cm^3 of the liquid, and even then but once in three trials: even when the proportion was 30 per cent — 60 grm. in 200 cm^3 — the solvent action of the ammonium chloride upon the manganese salt was trifling. The pyrophosphate residues obtained in these experiments, as well as in all those recorded in this paper, were dissolved in nitric acid and tested for contamination by a chloride; in no single case did silver nitrate produce more than an inappreciable opalescence in the solution. It is plain, therefore, that the variations of the results from theory are occasioned by variation in the degree of conversion of the trimanganese phosphate to the ammonium manganese phosphate, and that, while the ammonium chloride shows no appreciable solvent action on the precipitate in the presence of the precipitant, its effect in the process of conversion is plainly evident. For the smaller amounts of the manganese salts (equivalent to 0.1542 grm. of the pyrophosphate) the effect of the ammonium chloride reaches a maximum when that salt amounts to 10 per cent of the solution; for twice that amount of manganese salt, the best results were obtained by doubling the amounts of ammonium chloride. Either line of treatment yields under the most favorable conditions, results which are passably good, but the advantage inclines slightly to the first method in which the first precipitate was dissolved and reprecipitated while the liquid was cooled before filtering.

TABLE III.

$Mn_2P_2O_7$ equivalent to $MnCl_2$.		Error in terms of $MN_2P_2O_7$.	Error in terms of Manganese.	Saturated solution of $HNaNH_4PO_4 . 4H_2O$.	NH_4Cl.	Total volume.	Manganese in the filtrate.
Taken.	Found.						
grm.	grm.	grm.	grm.	cm^3	grm.	cm^3	
0.2214	0.2202	0.0012–	0.0005–	5	20	200	None.
0.2214	0.2202	0.0012–	0.0005–	5	20	200	None.
0.2214	0.2191	0.0023–	0.0009–	5	20	200	None.
0.2214	0.2191	0.0028–	0.0009–	5	20	300	None.
0.2214	0.2191	0.0023–	0.0009–	5	20	300	None.
0.2214	0.2185	0.0029–	0.0011–	10	20	200	None.
0.2214	0.2186	0.0028–	0.0010–	20	20	800	None.
0.2214	0.2192	0.0022–	0.0009–	20	20	800	None.

In Table III are recorded results obtained by precipitating the cold acid solution of the manganese salt and the microcosmic salt with a strong excess of ammonia. The mixture was heated to boiling for from five to ten minutes and filtered hot. In this series of determinations the amount of ammonium chloride present was constant while the volume of the liquid present was varied and the amounts of the microcosmic salt.

These results are possibly a trifle less satisfactory than those obtained for the smaller amounts of manganese by the method of Table II, it may be because the prolonged boiling tends to form a trifling amount of free oxide; but the fact is disclosed that an increase of the microcosmic salt is without influence and that a variation in volume from 200 cm^3 to 300 cm^3 is the occasion of little change in the indications of the process.

In another series of experiments the solution of manganous chloride was added drop by drop to the mixture of microcosmic salt and ammonium chloride made alkaline with ammonia. The precipitate which fell in the cold was crystallized by boiling the mixture a few minutes. The results are given below:

TABLE IV.

$Mn_2P_2O_7$ equivalent to $MnCl_2$.		Error.	Error in terms of manganese.	Saturated solution of $HNaNH_4PO_4$.	NH_4Cl.	Total volume.	Manganese in the filtrate.
Taken.	Found.						
grm.	grm.	grm.	grm.	cm^3	grm.	cm^3	
0.1542	0.1521	0.0021–	0.0008–	5	5	200	None.
0.2214	0.2203	0.0011–	0.0004–	5	10	275	None.
0.2214	0.2192	0.0022–	0.0009–	5	15	275	None.
0.2214	0.2197	0.0017–	0.0007–	5	20	275	None.
0.2214	0.2223	0.0009+	0.0003+	5	20	200	None.
0.1542	0.1528	0.0014–	0.0005–	5	30	275	None.

The experience of this series of experiments demonstrated again that the ease with which the flocky precipitate is converted to the crystalline ammonium manganese phosphate is proportioned to the ammonium chloride present, and the mean error of the results for the phosphate when the ammonium chloride reached 20 grams (0.0007 grm.) is considerably less than the mean error (0.0018 grm.) when the amount of the ammonium salt was less than 20 grms.

Experiments were also made according to the modifications suggested by Munroe,* viz., the boiling of the manganous salt with an excess of microcosmic salt until the precipitate becomes crystalline and just neutralizing with dilute ammonia; but we have been unable to find the conditions of this treatment by which uniform results may be obtained in even moderate agreement with the theory.

We have tried also the effect of substituting ammonium nitrate for ammonium chloride in the conversion process; but, so far as our experience goes, the nitrate is not so effective weight for weight in producing the change of the trimanganous phosphate to the ammonium manganese phosphates, while the solubility of the product in the solution of the ammonium nitrate becomes appreciable more rapidly with the increase of the amount present than is the case when the ammonium salt is the chloride.

In the light of the experiments described it would seem to be reasonable to expect the best results from the phosphate method for determining manganese when the conditions are so arranged that precipitation may take place in the cold solution in the presence of but little free ammonia, and of enough ammonium chloride to bring about the rapid conversion of the precipitate to the crystalline condition. Under such circumstances it should be possible to secure the conversion of the phosphate to the ideal constitution as completely as possible without danger of subsequent decomposition by the prolonged action of the hot free ammonia. In carrying out this idea, the solution of manganese chloride was treated as before with microcosmic salt and a large amount of ammonium chloride, the precipitate first formed was redissolved in hydrochloric acid and precipitation again brought about by the very careful addition of dilute ammonia in slight but distinct excess. The mixture was heated only until the precipitate became silky and crystalline, when it was allowed to stand and cool for a half hour. The precipitate was filtered off upon asbestos in a perforated platinum crucible under pressure, ignited and weighed. Table V comprises the results of experiments made

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* Loc. cit.

in this manner. In those of section A the precipitation was made in platinum vessels; in those of section B the treatment was in glass.

TABLE V.

$Mn_2P_2O_7$ equivalent to MnO_2.		Error in terms of $Mn_2P_2O_7$.	Error in terms of Manganese.	Saturated solution of $HNaNH_4PO_4$.	NH_4Cl.	Total volume.	Manganese in the filtrate.
Taken.	Found.						
A. In Platinum.							
grm.	grm.	grm.	grm.	cm^3	grm.	cm^3	
0.1885	0.1903	0.0018+	0.0007+	5	20	200	None.
0.1885	0.1910	0.0025+	0.0010+	5	20	200	None.
0.1885	0.1913	0.0028+	0.0011+	5	20	200	None.
0.1885	0.1911	0.0026+	0.0010+	5	20	200	None.
0.3770	0.3776	0.0006+	0.0002+	5	20	200	None.
0.3770	0.3773	0.0003+	0.0001+	5	20	200	None.
0.3770	0.3778	0.0008+	0.0003+	5	20	200	None.
0.3770	0.3783	0.0013+	0.0005+	5	20	200	None.
B. In Glass.							
0.1885	0.1904	0.0019+	0.0007+	5	20	200	None.
0.1885	0.1898	0.0013+	0.0005+	5	20	200	None.
0.3770	0.3767	0.0003–	0.0001–	5	20	200	None.
0.3770	0.3784	0.0014+	0.0005+	5	20	200	None.

In this series of experiments the mean indication is, for the first time, in excess of the theory. Previously the error has been one of deficiency, and that in proportion to the amount of manganese handled, no doubt because the amount of unconverted trimanganese phosphate is proportioned to the entire amount of the phosphate. The positive error which is developed in this last series of determinations is probably due to the appearance of the natural error of all precipitation processes — viz., the tendency on the part of the precipitate to include matter in solution. In the previous experiments this effect was doubtless obscured by the incompleteness of the conversion of the trimanganous phosphate to the ammonium manganese phosphate. Indeed it is quite possible that even in the last determinations the conversion is not absolute, and that this is so suggested by the fact that the errors of excess are larger in the case of the smaller amounts of manganese for which the conversion throughout the entire work has appeared to be more complete. From the consideration of the results tabulated and described it would seem to be obvious that not only is the presence of ammonium chloride not objectionable in this analytical process, which depends upon obtaining the ammonium manganese phosphate from the trimanganese phosphate precipitated from a pure solution of manganese, but that its presence in not too small amount, or that of a substitute, is absolutely essential to make this conversion complete. For a given amount of manganese and a given volume of solution it seems essential that the amount of ammonium chloride should reach a certain limit. According to our experience the proportion of ammonium chloride to the pyrophosphate should be at least 50 : 1; or, speaking approximately, more than 200 molecules of ammonium chloride must be present in the liquid (100 cm^3 or 200 cm^3) to every molecule of the ammonium manganese phosphate to be formed. However, the quantity of the ammonium salt may be increased almost to the point of saturation of the liquid without causing more than a trifling solubility of the ammonium manganese phosphate in the presence of an excess of the precipitant. The statement of Fresenius and Munroe that ammonium manganese phosphate is soluble in ammonium chloride does not hold if there is an abundance of the soluble precipitating phosphate present. Further, our experience goes to show that the precipitate may be washed with perfect safety with pure water as well as with slightly ammoniacal water, or with ammoniacal water containing ammonium nitrate, if the filtration is performed rapidly and the precipitate is gathered in small space, as is the case when the phosphate is collected on asbestos in a perforated crucible. The finely granular precipitate which may be obtained by slow action of dilute ammonia added gradually to the hot solution of the manganese salt apparently includes a portion of unconverted phosphate which resists the replacement of the manganese by ammonium. On the other hand, the precipitate of flocky condition thrown down in the cold passes easily to the silky and crystalline condition when heated with the proper amount of ammonium salt and possesses a constitution approaching the ideal under such conditions. The conversion of the flocky manganous phosphate is so rapid that the precipitation may be carried on safely in glass vessels. If the ammonium chloride in the solution were to be included in the precipitate it would volatilize entirely during the ignition, leaving no trace unless, possibly, a portion of its chlorine were to combine with the manganese. Tests for chlorine in the residue of pyrophosphate resulted negatively — no more than a mere trace being found in any case, so that the contaminating effect of the ammonium chloride proves to be insignificant and the responsibility for the increase in weight above the theory must apparently rest with the included microcosmic salt.

In the practical determination of manganese by the phosphate method of Gibbs, therefore, we advocate strongly the presence of large amounts of ammonium chloride. Good results may be obtained by the method of precipitation originally laid down by Gibbs, or by the modification proposed by Blair, if the ammonium salt is present in sufficient quantity. On the whole trustworthy results are obtained most easily and surely, according to our experience, by following the method of the experiments of Table V. The slightly acid solution, containing in a volume of 200 cm^3 (in platinum or glass) an amount of manganese not more than enough to make 0.4 grm. of the pyrophosphate, 20 grm. of ammonium chloride and 5 to 10 cm^3 of a cold saturated solution of microcosmic salt, is precipitated in the cold by the careful addition of dilute ammonia in only slight excess. The mixture is heated until the precipitate becomes silky and crystalline, the whole is allowed to stand and cool a half hour, the precipitate is collected upon asbestos in a perforated platinum crucible, washed (best with slightly ammoniacal water), dried at gentle heat and ignited as usual. By this process determinations of the larger amounts of manganese — 0.4 grm. of the pyrophosphate — approximate rather more closely to the theoretical values than do those of the smaller amounts — 0.15 grm. In either case the average error should not exceed 0.0010 grm. in terms of manganese.

XVIII

ON THE DETECTION OF SULPHIDES, SULPHATES, SULPHITES AND THIOSULPHATES IN THE PRESENCE OF EACH OTHER.

BY PHILIP E. BROWNING AND ERNEST HOWE.*

SOME three years ago R. Greig Smith † published a method for the detection of sulphates, sulphites and thiosulphates in the presence of each other, which promised much toward the solution of this most difficult problem. The method may best be described in the author's own language: To a solution of the salts of the above mentioned acids "barium chloride is added in excess, together with a good quantity of ammonium chloride, which, like many salts of ammonium, potassium and calcium, acts as a flocculent or coagulant, and facilitates the filtration of the barium sulphate. Hydrochloric acid is next added, drop by drop, until it is evident that there is no further solution of barium sulphite and thiosulphate, and that only the sulphate remains undissolved; the solution is then filtered through a moistened double filter paper, which should be free from 'pin holes.' The filtrate will probably be clear, but if not it should be returned to the filter for a second filtration. When too much thiosulphuric acid is present, the clear filtrate will visibly become clouded, or from being whitish will become more opaque; if this occurs the solution should be thrown out, and a fresh portion made more dilute. A solution of iodine is added to half of the filtrate until the color is of a permanent yellow tinge; a white precipitate indicates the presence of a sulphite which has been oxidized by the iodine

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* From Am. Jour. Sci., vi, 317.

† Chem. News, lxxii, 39.

to sulphate. In the absence of a decided precipitate traces of sulphite may easily be detected by comparing the treated and untreated halves of the filtrate — a procedure which very often saves a good deal of time, as it is unnecessary to wait until a clear filtrate is obtained. The two halves are mixed, and if the yellow color disappears more iodine is added, the solution filtered and the filtrate divided into two halves as before. With a slight turbidity filtration may be omitted. Bromine water is added to one of the halves when any thiosulphate in the original solution shows itself as a white precipitate of barium sulphate, readily seen on comparing the two test-tubes. The thiosulphate is by iodine converted to tetrathionate, which is oxidized by bromine water to sulphate." Three objections to this method as described will readily occur to the reader: first, the readiness with which the thiosulphate is decomposed by free hydrochloric acid; second, the comparatively large amount of acid necessary to effect the complete solution of the barium sulphite and thiosulphate when precipitated with the sulphate as compared with the amount required to prevent the precipitation; third, the lack of delicacy necessitated by a comparison of portions of a colored solution in looking for small precipitates. The work to be described was undertaken to overcome these difficulties and to test the accuracy of a modified method. Solutions of potassium sulphite and sodium thiosulphate were made approximately decinormal and standardized in the usual manner against an iodine solution of known value. It was found that by making a solution containing sulphates, sulphites, and thiosulphates very faintly acid, the sulphites and thiosulphates were held completely in solution when the barium sulphate was precipitated. The extreme sensitiveness of a thiosulphate to the decomposing action of free hydrochloric acid suggested the possible substitution of acetic acid to hold the sulphites and thiosulphates in solution. This being a weaker acid, we hoped to avoid the decomposition of the thiosulphate into sulphur and sulphurous acid, or at least to delay the decomposing action. The results of these experiments appear in the following table:

TABLE I.

Exp.	Volume cm^3 of water.	Hydrochloric acid (1:4).	Acetic acid.	$Na_2S_2O_3$ taken.	Result.
		drops.	drops.	grm.	
(1)	10	2	. .	0.01	No sulphur in 20 minutes.
(2)	10	2	. .	0.1	Sulphur in 45 seconds.
(3)	100	3	. .	0.1	Sulphur in 15 minutes.
(4)	10	. .	8	0.01	No sulphur in 20 minutes.
(5)	10	. .	8	0.1	Sulphur in 90 seconds.
(6)	100	. .	10	0.1	No sulphur in 20 minutes.
(7)	100	. .	10	0.25	Sulphur in 15 minutes.
(8)	100	. .	10	0.5	Sulphur in 60 seconds.
(9)	100	. .	10	1.0	Sulphur in 80 seconds.

From these results it would seem that the decomposition of a thiosulphate is more rapid in presence of hydrochloric acid than in presence of a much larger amount of acetic acid.

Our next experiments were directed toward a determination of the effect of adding stannous chloride to bleach the color of the free iodine and bromine used in the oxidation and of acidifying with acetic acid, before treating with barium chloride. That is to say, the process as we used it, consisted in acidifying the solution to be tested with acetic acid, adding barium chloride, filtering to remove precipitated sulphate (always present in the sulphite), adding iodine to the filtrate until the color was permanent, bleaching with stannous chloride, filtering off the sulphate which represents the sulphite originally present, adding bromine in excess to the filtrate and again bleaching with stannous chloride to increase the visibility of the sulphate which now represents the thiosulphate originally present. The details of experiments in which the sulphite was taken alone and oxidized with iodine are given in Table II.

A corresponding series of experiments was made in which hydrochloric acid was substituted for acetic acid and essentially the same results were obtained.

A similar series of experiments was made to test the effect of treating the thiosulphate in an acidified solution, first with

TABLE II.

Exp.	K_2SO_3 taken.	Volume of water.	$BaSO_4$ precipitated after oxidation with iodine.	Remarks.
	grm.	cm³		
(1)	0.1	10	Very abundant.	Plainly visible before adding $SnCl_2$.
(2)	0.01	10	Abundant.	Plainly visible before adding $SnCl_2$.
(3)	0.001	10	Distinct.	More distinct after adding $SnCl_2$.
(4)	0.0005	10	Fair.	Hardly visible before adding $SnCl_2$.
(5)	0.0001	10	Faint.	Invisible before adding $SnCl_2$.

iodine and then after filtration (if a precipitate had formed) with bromine. In the experiments of division A hydrochloric acid (a few drops) was added before treating with barium chloride, and in those of division B acetic acid was used similarly. Stannous chloride was employed to bleach the excess of iodine and bromine.

TABLE III.

Exp.	$Na_2S_2O_3$ taken.	Volume of water.	$BaSO_4$ precipitated by action of iodine.	$BaSO_4$ precipitated by action of bromine.	Remarks.
			A.		
	grm.	cm³			
(1)	0.1	10	Distinct.	Abundant.	Sulphur separated in 30 seconds.
(2)	0.01	10	Faint.	Abundant.	No sulphur in 90 seconds.
(3)	0.001	10	None.	Distinct.	No sulphur in several minutes.
(4)	0.0005	10	None.	Faint.	No sulphur; $SnCl_2$ necessary.
(5)	0.0001	10	None.	Very faint.	No sulphur; $SnCl_2$ necessary.
			B.		
(1)	0.1	10	Faint.	Abundant.	No sulphur separated in 1 minute.
(2)	0.01	10	None.	Abundant.	No sulphur separated in several minutes.
(3)	0.001	10	None.	Distinct.	No sulphur.
(4)	0.0005	10	None.	Faint.	No sulphur; $SnCl_2$ necessary.
(5)	0.0001	10	None.	Very faint.	No sulphur; $SnCl_2$ necessary.

From these experiments the advantage of the use of acetic acid becomes apparent, as does also the use of stannous chloride in increasing the delicacy of this indication, so that a small fraction of a milligram may easily be detected.

If relatively large amounts of thiosulphate are present with small amounts of sulphite, we have sometimes found it advantageous to manipulate so that even the slow decomposition of the thiosulphate by acetic acid may be avoided by first attempting precipitation with barium chloride in a dilute ammoniacal solution. By this method the barium sulphate and sulphite are separated from the thiosulphate and identified — the sulphate by its insolubility in dilute hydrochloric acid, and the sulphite by the action of iodine upon the acid filtrate from the barium sulphate. After filtering, the thiosulphate may be detected in the filtrate by the use of iodine and bromine as described above. Table IV gives some results by this treatment.

TABLE IV.

Exp.	$Na_2S_2O_3$ taken.	$BaSO_4$ precipitated by iodine.	$BaSO_4$ precipitated by bromine.	Remarks.
	grm.			
(1)	0.1	None.	Abundant.	
(2)	0.01	None.	Good.	
(3)	0.001	None.	Fair.	$SnCl_2$ necessary.
(4)	0.0005	None.	Faint.	$SnCl_2$ necessary.
(5)	0.0001	None.	None.	

As will be seen, the test for the thiosulphate by this method of treatment is not so delicate, probably on account of mechanical holding of the barium thiosulphate by the precipitated sulphate and sulphite.

Having determined the limits of accuracy of the method as applied to the sulphite and thiosulphate taken separately, our next experiments were directed toward an investigation of the working of the method when these two acids are found together in solution. Sulphates, almost invariably present with sulphites, are of course quite easily separated by filtration and treating with the barium salt in acid solution. Sulphides if present in the solution would seriously interfere with the working of this method if not removed, being readily oxidized by the iodine or bromine to sulphite, sulphate, or, should sulphur also separate, to thiosulphate. We found in course of our work that in attempting to neutralize a mixture of freshly prepared alkaline sulphide together with a sulphite we often obtained a precipitate of sulphur. After the removal of the sulphide and sulphate, we were surprised to find on treating with iodine scarcely a trace of sulphite. On treating with bromine however an abundant indication of thiosulphate was obtained. It is well known of course that thiosulphate may be formed by boiling a sulphite with sulphur, but that this reaction should take place so readily and completely seemed to us rather unusual.

For the removal of a sulphide before proceeding with the tests for sulphite and thiosulphate Greig Smith recommends the passing of carbon dioxide through the solution until the escaping gas gives no indication of hydrogen sulphide, but Bloxam * calls attention to the tedious and wholly unsatisfactory character of this method of removal and recommends a mixture of zinc chloride, cadmium chloride, ammonium chloride and ammonia. We have found that the addition of zinc acetate to a faintly alkaline solution accomplishes the same purpose in an entirely satisfactory manner. The sulphide used in our work was freshly made by passing hydrogen sulphide through a dilute solution of sodium hydroxide. When portions of this solution, still alkaline, were treated with zinc acetate in excess, and the zinc hydroxide and sulphide removed by filtration, the filtrate gave no test for either sulphite or thiosulphate by the application of iodine and bromine as described, and the vapor evolved on boiling caused no darkening of lead paper. The following table shows the results of a few experiments in which tests were made for the sulphite and thiosulphate, after removing a considerable amount of the sulphide in the manner described, and of the sulphate by acidifying and adding barium chloride.

The method as we have modified it may be summarized as follows: To about 0.1 grm. of the substance to be analyzed dissolved in 10 cm^3 of water or more, add sodium, potassium or

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* Chem. News, lxxii, 63.

TABLE V.

K_2SO_3 taken.	$Na_2S_2O_3$ taken.	$BaSO_4$ precipitated after oxidation with iodine.	$BaSO_4$ precipitated after oxidation with bromine.
grm.	grm.		
0.1	0.01	Abundant.	Good.
0.1	0.001	Abundant.	Distinct.
0.01	0.1	Good.	Abundant.
0.001	0.1	Faint.	Abundant.
0.001	0.001	Fair.	Fair.

ammonium hydroxide to distinct but faintly alkaline reaction. The solution should be neutral or alkaline rather than even faintly acid, owing to the readiness with which sulphur separates. To the alkaline solution add zinc acetate in distinct excess and filter. The precipitate may be tested for hydrogen sulphide, on acidifying, in the usual manner. To the filtrate add acetic acid, a few drops in excess of the amount necessary to neutralize, and barium chloride, and filter through a double filter. To the filtrate add iodine until the solution takes on a permanent yellow tinge, and then bleach with stannous chloride, best after adding a few drops of hydrochloric acid to prevent the possible precipitation of a basic salt of tin. A precipitate at this point indicates the sulphite. Filter, add bromine water in faint excess to the filtrate, bleaching again with stannous chloride. A precipitate on adding bromine indicates a thiosulphate originally present.

XIX

ON THE SEPARATION OF NICKEL AND COBALT BY HYDROCHLORIC ACID.

BY FRANKE STUART HAVENS.

A QUANTITATIVE separation of nickel and cobalt by a process analogous to that published from this laboratory for the separation of aluminum and iron[†] has been put forward in a recent paper by E. Pinerùa.[‡] The process may be described briefly as follows: The hydrous chlorides of nickel and cobalt (0.3–0.4 grms.) are dissolved in a little water and to the solution are added 10 to 12 cm^3 of aqueous hydrochloric acid and 10 cm^3 of ether, and the whole, contained in a little beaker surrounded with water, and ice, is saturated with gaseous hydrochloric acid. The cobalt, which remains in solution, is decanted off and the yellow insoluble nickel chloride washed with a previously prepared solution of ether saturated with hydrochloric acid gas at a low temperature. The nickel is determined by known methods, preferably as the sulphate. The author claims very precise results for the process, but gives no experimental proof of his work. Previous to the appearance of this paper my experiments upon the solubility of nickel chloride in an ether-hydrochloric acid solution, such as used in our process for the separation of aluminum and iron, which is practically the same in proportions as that used by Pinerùa to effect precipitation, had shown that, while nickel chloride is somewhat insoluble in such a mixture, the degree of insolubility is not sufficient for a quantitative separation. Since the appearance of Pinerùa's work I have

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[*] From Am. Jour. Sci., vi, 396.

[†] Gooch and Havens, Am. Jour. Sci., ii, 416. This volume, p. 20.

[‡] Gaz. chim. ital., xxvii, 56.

been over the ground again and have reached the same conclusions as before, as shown in the following experiments.

When a solution of 0.02 grm. of nickel chloride (free from iron and cobalt) in 7 cm^3 of aqueous hydrochloric acid, was saturated with hydrochloric acid gas at a temperature of –2° C. (obtained by immersing the container in a mixture of ice and salt) no precipitation resulted. When, however, an equal volume of ether was added and the whole was again saturated with hydrochloric acid gas a yellow precipitate formed, while the supernatant liquid still remained of a deep green color. The solution was filtered quickly through asbestos in a filter crucible, and the clear filtrate after evaporation with sulphuric acid was electrolyzed. The metallic deposit of 0.0020 grm. proved to be pure nickel; for when dissolved in nitric acid it gave no test for iron with potassium sulphocyanide or ferrocyanide, and neither the apple-green hydroxide nor the black sulphide, prepared by the usual methods, showed any trace of cobalt in the borax bead. It is obvious, therefore, that nickel chloride is not fully precipitated under these conditions and that the green color of the solution is due to nickel in solution and not to traces of iron, as Pinerùa has supposed.* A second experiment similar to the first showed a solubility of the nickel chloride represented by 0.0018 grm. of metallic nickel. It is evident, then, that the solubility of nickel chloride in this mixture of aqueous hydrochloric acid and ether thoroughly saturated with hydrochloric acid gas is not far from an amount represented by 0.0020 grm. of metallic nickel for every 14 cm^3 of solution.

Still another experiment, in which nickel chloride representing 0.0020 grm. of metallic nickel was treated with 14 cm^3 of the ether-hydrochloric acid solution and the whole saturated for one hour at a low temperature with hydrochloric acid gas without precipitation, showed the same thing.

When the nickel chloride remaining on the asbestos was washed with about 40 cm^3 of a mixture of equal parts ether and aqueous hydrochloric acid saturated with hydrochloric acid gas,

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* Loc. cit.

the washings evaporated with sulphuric acid and treated by the battery gave a deposit of metallic nickel weighing 0.0027 grm.—an amount proportionately less than that found in the filtrate proper.

Although employing a mixture of aqueous hydrochloric acid and ether saturated with gaseous hydrochloric acid for the precipitation, Pinerùa has advised the use of pure ether saturated with gaseous hydrochloric acid for the washing. In my experiments with such a mixture I find that in it the hydrous nickel chloride is practically insoluble and that 30 cm^3 of the washings of the precipitated chloride with such a mixture gave no deposit of nickel by the battery. It seemed possible, therefore, that by reducing the water present to the lowest possible amount necessary to dissolve the chlorides to be treated the precipitation of the nickel might be made more complete. The experiments of the following table were made to put this idea to the test.

Solutions of the pure chlorides of nickel and cobalt, carefully purified and freed from other metals and each other, were, after conversion to the form of the sulphate, standardized by the battery. Weighed portions of these solutions were taken in a small beaker, evaporated to dryness, the dry salts dissolved in as little water as possible (about 1 cm^3), 10 to 15 cm^3 of ether added, and the whole saturated with hydrochloric acid gas, the beaker being meanwhile immersed in running water and cooled to about 15° C. When saturation was complete the precipitated chloride was caught on asbestos in a filter crucible, washed thoroughly with a previously saturated solution of ether, dissolved in water, evaporated with sulphuric acid and determined as metallic nickel by the battery. The cobalt in the filtrate was recovered by evaporation and electrolysis in like manner.

Experiments (1), (2), and (3) of the accompanying table show that by this process the nickel is thrown down quantitatively, and experiments (2) and (3) show that in the presence of a few milligrams of the cobalt salt the separation of a small amount of nickel is sharp. The residue of nickel in these experiments gave no test for cobalt with the borax bead. When, however, the cobalt is present to the amount of a few centigrams as in (4), (5), and (6), the precipitated nickel chloride, which forms a hard mass, includes the cobalt salt so that even a large quantity of washing solution (100 cm^3 was used in experiment 6) cannot remove it.

Exp.	Nickel taken as the hydrous chloride.	Nickel found.	Error.	Cobalt taken as the hydrous chloride.	Cobalt found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.0068	0.0066	0.0002−	. .	. .	. .
(2)	0.0090	0.0090	0.0000	0.0030	. .	. .
(3)	0.0090	0.0091	0.0001+	0.0123	0.0127	0.0004+
(4)	0.0469	0.0490	0.0021+	0.0700	. .	. .
(5)	0.0468	0.0503	0.0035+	0.0700	. .	. .
(6)	0.0472	0.0493	0.0021+	0.0700	. .	. .

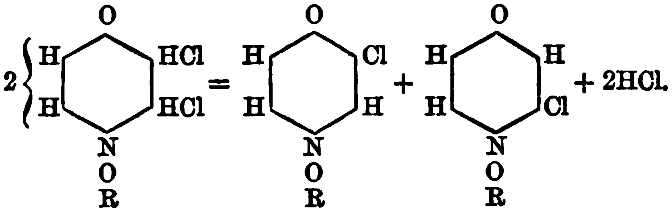
From the experiments described it is obvious that the process as proposed by Pinerùa will not give a complete precipitation of the nickel chloride. Nickel chloride is, however, practically insoluble in pure ether saturated with hydrochloric acid gas and can be separated from small quantities of the soluble cobalt salt in that medium. In the presence of even a few centigrams of the cobalt chloride, however, the process is not practicable on account of the inclusion of the cobalt by the massive nickel chloride. It is possible that by repeated solutions and reprecipitations the nickel salt might be sufficiently freed from the cobalt, but the process must naturally be long and tedious.

XX

THE ETHERS OF TOLUQUINONEOXIME AND THEIR BEARING ON THE SPACE ISOMERISM OF NITROGEN.

BY JOHN L. BRIDGE AND WILLIAM CONGER MORGAN.*

IN an article on the ethers of quinoneoxine (isonitrosophenol) published by one of us,† it was stated, that when boiled with alcohol, the benzoyl ether of quinoneoxime dichloride gave gave two monochlor substitution-products. Naturally it was supposed that the chlorine atom occupied, in the one, an ortho position, and, in the other, a meta position to the radical NOR, the reaction being:



It was also found that these same isomers were formed when monochlorquinone was treated with hydroxylamine hydrochloride, and the sodium salt of the chlorquinoneoxime thus formed, treated with benzoyl chloride.

The preceding explanation regarding the splitting off of hydrochloric acid from the dichloride is not in accord with results of work done by Kehrmann,‡ published in his article on the influence of radicals in the action of hydroxylamine on

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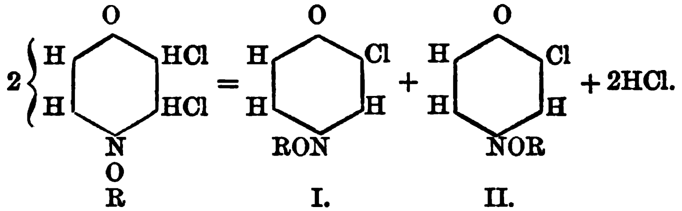
* From Am. Chem. Jour., xx, 761.

† Ann. Chem. (Liebig), cclxvii, 79.

‡ Ber. Dtsch. chem. Ges., xxi, 3315; Jour. prakt. Chem. [2], xl, 258.

quinones, in which he generalizes the results of his observations in the statement that the presence of a radical attached to the ring so much lessens the replaceability of the quinone oxygen atom neighboring to the radical that the principal part if not the whole of the resulting product, is a meta-substituted quinoneoxime. The work of his former article has been repeated by Kehrmann,* who finds the same isomeric benzoyl ethers of monochlorquinoneoxime; but believing that observations of their behavior indicate the substantiation of his rule, he states that both these ethers have the chlorine atom in the meta position to the oximido group, and attributes their difference to space isomerism of nitrogen, writing the reaction thus:



Kehrmann designates the compound represented by symbol I. as "chlorquinonemetaantioxime ether" and II. as "chlorquinonemetasynoxime ether." The question as to whether the chlorine atom occupies the same position in both compounds could be definitely settled if ortho- and metachlorphenols could be changed to the corresponding chlorquinoneoximes or so-called isonitrosophenols. This transformation has, however, unfortunately not yet been accomplished, and repeated efforts to obtain the corresponding bromquinoneoximes have resulted in failure, orthobromphenol not being attacked by nitrous acid or amyl nitrite.

The toluquinoneoximes, obtained by the action of nitrous acid on ortho- and metacresol, we have taken up for study as being the most closely analogous compounds in which the position of the side groups is definitely known, believing that

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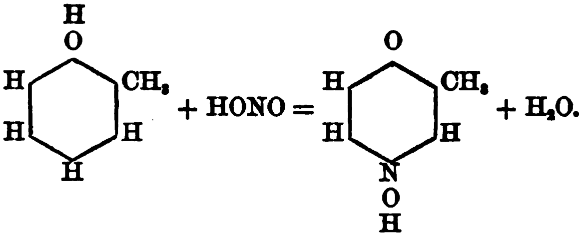
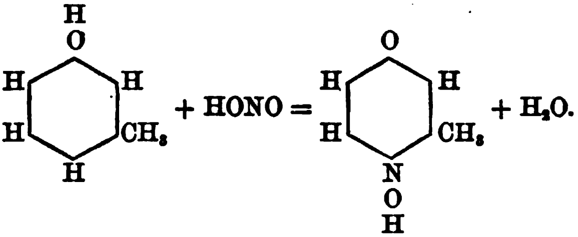
* Ann. Chem. (Liebig), cclxxix, 27.

by an examination of these bodies, light may be thrown upon the nature of the others.

When orthocresol is acted upon by nitrous acid, a toluquinonemetaoxine is formed according to the following reaction:



The metacresol forms similarly a corresponding orthooxime:



The benzoyl ethers of the toluquinoneoximes prove to be exceedingly well fitted to characterize these bodies since they are formed from the oximes in quantitative proportions, are easily crystallized, and readily distinguished from each other.

The benzoyl ether of toluquinoneorthooxime produced from metacresol, crystallizes in light brownish-yellow crystals melting at 177° C. and appearing under the microscope as long rectangular blades, suggesting the orthorhombic system. The benzoyl ether of toluquinonemetaoxime produced from orthocresol is obtained in the form of yellow crystals which begin to soften at about 150° and do not melt entirely until at about 190°. Subjected to fractional crystallization, a portion of the metaoxime is readily obtained consisting of branching needle-like crystals, melting at 193° C. These, as well as lower-melting fractions, can be readily distinguished from the orthooxime by their less regular appearance under the lens, as well as by their crystal habit, tending to produce curved forms.

The marked difference in the form and habit of the crystals of the benzoyl ethers of the ortho- and metatoluquinone oximes makes it possible to study carefully the product of the action of toluquinone on hydroxylamine. Goldschmidt and Schmidt * have shown that the principal product of this reaction is toluquinonemetaoxime. This they demonstrated by oxidizing to a dinitro compound; but as some of the theoretically possible nitro-derivatives of the cresols are not known, this method can scarcely be considered to prove conclusively the absence of toluquinoneorthooxime. We have, therefore, studied further the product of the action of hydroxylamine on toluquinone by the aid of the benzoyl ethers. When the sodium salt of the oxime thus formed was treated in alcoholic solution with benzoyl chloride, and the benzoyl ether obtained was subjected to fractional crystallization, not a trace of the orthooxime ether, crystallizing in blades and melting at 177°, was found. This proves that when toluquinone is treated with hydroxylamine the whole of the resulting product is toluquinonemetaoxime. The inference is plain that Kehrmann's rule concerning the influence of side-chains, attached to the ring in quinones, upon the entering oximido radical is quantitatively true in this case; and similar indications furnished by the corresponding methyl ethers, as will appear later, strengthen this conclusion.

As has been previously shown, the benzoyl ether of the metaoxime does not consist of a single compound, but is a mixture. The body melting at 193° is readily separated in considerable quantities, while the remainder consists of a very intimate mixture of this body with one of much lower melting-point, separated, if it can be separated at all, only with the greatest difficulty. By concentration of the mother-liquor from which the high-melting fractions have been

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* Ber. Dtsch. chem. Ges., xvii, 2063.

obtained, and carefully crystallizing, fractions may be separated melting almost completely at temperatures, varying with the fraction, between 130° and 150°. Repeated crystallizations separated each fraction into portions melting, on the one hand, always considerably higher, and, on the other hand, often somewhat lower, and ordinarily no definite body of low melting-point could be isolated. Twice, however, a nearly complete separation seemed to have been obtained. Thus, from fractions melting between 140° and 150°, a few short, thick prisms melting once at 142° and again at 144° separated, leaving the compound which melts at 193°. Of these crystals there was not enough for a combustion, but an analysis of a fraction melting almost completely at 137° gave figures which show without doubt that this portion had the same percentage composition as the body melting at 193°. If we are to regard the product as it is first obtained as a mixture of two ethers, and consider that 142°–144° is the melting-point of the lower body, we can account for the melting of fractions below 142° on the ground that mixtures may have a lower melting-point than either of the component substances. These results were obtained repeatedly from three separate portions of Kahlbaum's C. P. orthocresol, purchased at different times, as well as from toluquinone melting at 67° C. and wholly volatile when exposed to the air.

When the silver salt of toluquinonemetaoxime acts upon methyl iodide, the product is, likewise, not a single ether but a mixture of ethers, softening at 55° and not melting completely below 70°. From it a body melting at 73°–74° can easily be separated, but no other compound of definite melting-point or different crystal form could be obtained.

The acetyl compound of toluquinonemetaoxime presents phenomena similar to those of the benzoyl ethers, but in rather more marked degree. The product, as first obtained by the action of acetyl chloride on the silver salt of the oxime, or by acetic anhydride on the oxime itself, begins to soften at 90° and melts completely at 110°. Upon the first recrystallization a distinction in crystal form appears, and a second crystallization of the separated portions gave short, thick prisms melting at 112°–113°, and some smaller, spherically grouped crystals, melting at 85°–87°. The extreme difficulty of preparing the acetyl compound prevented further investigation.

In like manner, the benzoyl ether of monobromtoluquinonemetaoxime seems to be a mixture of isomeric bodies. Thus, it was found possible to add two atoms of bromine to the ethers of toluquinoneoxime forming colorless dibromides corresponding to the dibrom addition-products of quinoneoxime, and these dibromides, when boiled with dilute alcohol, split off hydrobromic acid with the formation of colored monobrom substitution-products. The benzoyl ether of monobromtoluquinonemetaoxime thus formed shows a variation in melting-point similar to that of the ethers previously discussed.

The foregoing facts speak in favor of Kehrmann's theory of space isomerism in the oximes so far as the metaoximes are concerned. On the other hand, there is no evidence to show the presence of isomers in the ethers of toluquinoneorthooxime: the methyl, acetyl, and benzoyl ethers all act as simple substances, each product melting completely at a definite temperature. It is difficult to understand why isomerism should be so much more evident in the ethers of toluquinonemetaoxime than in the ethers of the orthooximes, unless, possibly, the closer proximity of the side-chain to the oximido-group prevents the formation of a space isomer. There is, however, a remote possibility that isomeric bodies may exist, so similar in properties that they cannot be detected by the ordinary methods.

EXPERIMENTAL PART.

Preparation of the Oximes and their Salts.

The toluquinone-, ortho-, and metaoximes used in the experiments to be described were made in the following manner: To a solution of 10 grams of cresol and 8 grams of potassium nitrite in 900 cm^3 of water, a solution of 6 grams of concentrated sulphuric acid in 100 cm^3 of water was added in small portions during the course of half an hour, care being taken that both original solutions should be between 5° and 10°, and that this temperature be maintained during the mixing. Nearly all of the oxime separates out on standing in ice-water for one to two hours, and after filtering and washing with 200–300 cm^3 of ice-water, the amount of oxime obtained by extracting the filtered solution with ether is so small that it may be disregarded. The substances were purified by dissolving in a saturated solution of sodium carbonate and filtering into dilute sulphuric acid, cooled with ice. At this stage it is generally ready for use, but if further purification is desired, it may be accomplished by dissolving the oxime in ether and shaking with animal charcoal. Upon filtering and evaporating, the oxime crystallizes in long, slightly colored needles. The yield is large in both cases, that of the orthooxime being nearly theoretical. As given by Beilstein, toluquinone-*m*-oxime melts at 134° C. Toluquinone-*o*-oxime melts at 155° C.; Beilstein gives 145°–150°.

The silver salt of the metaoxime was made in the following manner: 5 grams of toluquinone-*m*-oxime were dissolved in a solution of sodium hydroxide, a little less than the quantity calculated to form the sodium salt, and this solution was filtered into 500 cm^3 of water containing 1⅓ times the calculated amount of silver nitrate. The precipitate comes down in a flocky, gelatinous condition, but goes over into a granular form on heating to 50° in a water-bath. When dissolved in the least possible amount of warm dilute ammonia, and the solution precipitated with hydrochloric acid,

0.1006 gram of the substance, dried over H_2SO_4, gave 0.0590 gram AgCl.

	Calculated for $C_7H_6NO_2Ag$.	Found.
Ag	44.23	44.14

The salt is light reddish-brown when first formed, but turns darker on standing or heating. It decomposes when heated to 100° and, when thoroughly dry, is spontaneously inflammable at a temperature above 60°. It is a rather unstable body and cannot be kept long when at all impure.

The silver salt of toluquinone-*o*-oxime was made in the manner described for the preparation of the silver salt of the meta form. The salt falls in the cold as reddish-brown crystals, tending to darken when exposed to light or heat.

0.2560 gram, dried over H_2SO_4, gave 0.1498 gram AgCl.

	Calculated for $C_7H_6NO_2Ag$.	Found.
Ag	44.23	44.06

Although very similar in all its properties to the silver salt of toluquinone-*m*-oxime, this salt is like all the ethers of the ortho form, much more stable than its corresponding meta isomer.

Toluquinone-m-oxime Methyl Ether.

From o-Cresol. — Of the silver salt of toluquinone-*m*-oxime, 2 or 3 grams were suspended in 10–15 cm^3 of ligroin and twice the calculated quantity of methyl iodide added. After standing for an hour with frequent shaking, the liquid was filtered off and the residue extracted with a little hot ligroin. The united ligroin solutions were allowed to evaporate spontaneously, and the methyl ether came out in large, dark-yellow, hexagonal prisms. A little more may be obtained by allowing the residue to stand for a week with methyl iodide. The yield in any case is small, the best results apparently being obtained by using not more than 2 or 3 grams of the silver salt at one time. After purifying with animal charcoal and recrystallizing from ligroin, the product obtained softens at 55° yet does not melt completely below 70°. Portions melting at 73°–74° C. were separated by fractional crystallization, and, on analysis,

0.1101 gram of this body, dried over H_2SO_4, gave 0.2582 gram CO_2 and 0.0599 gram H_2O.

0.0881 gram of the substance gave 7.1 cm^3 N at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	63.96
H	6.00	6.05
C	9.29	9.59

Although fractions were often obtained melting from 55°–60°, no other compound of very definite melting-point could be separated. The methyl ether is very soluble in all organic reagents; in hot ligroin it is much more soluble than in cold, from which it crystallizes in small bright-yellow prisms.

From Toluquinone.—To a solution of 2 grams of toluquinone in 800 cm³ of water, the calculated amount of methoxylamine hydrochloride was added. Yellow crystals began to precipitate in the course of two hours, and at the end of twelve hours the reaction was completed. The liquid was filtered off and extracted with ether, which, upon evaporation, left behind a yellow crystalline mass. The two portions were united and recrystallized from ligroin. The yield was very good, being 75 per cent of the theory. Even after boiling in ligroin with animal charcoal and recrystallizing several times, the substance acts like a mixture, softening at 58° and melting at 70°. A portion, less soluble than any other, was easily separated, which melted at 73°–74° C. and was identical in all respects with the methyl ether obtained from the silver salt of toluquinone-*m*-oxime made from *o*-cresol.

0.1263 gram, dried over H_2SO_4, gave 0.2962 gram CO_2 and 0.0672 gram H_2O.

0.2952 gram gave 25 cm³ N at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	63.96
H	6.00	5.91
N	9.29	10.00

Toluquinonemetaoxime Acetyl Ether.

This ether can be made in two ways: By adding the calculated amount of acetyl chloride, drop by drop, to 2–3 grams of the silver salt suspended in 15–20 cm^3 of ligroin or absolute ether, kept cool by ice-water, evaporating at once, and extracting the residue with hot ligroin; or by heating 1 molecule of the oxime on the water-bath for an hour with 1.5 molecules of acetic anhydride, adding cold water, filtering off the tarry mass which separates, and extracting it with hot ligroin. The yield by either method is extremely poor, and sometimes after purifying by boiling with animal charcoal, the total product consisted of a few small crystals. By fractional crystallization two portions were separated, the less soluble composed of thick irregular prisms melting at 112°–113°, and a much smaller fraction of minute, spherically grouped crystals, melting at 85°–87°. In analyzing the original product unfractioned:

0.0953 gram, dried over H_2SO_4, gave 0.2090 gram CO_2 and 0.0444 gram H_2O.

0.0848 gram gave 5.8 cm^3 N at 15° C. and 760 mm. pressure.

	Calculated for $C_9H_9NO_3$.	Found.
C	60.30	59.91
H	5.06	5.18
N	7.84	8.01

The acetyl ether is very soluble in alcohol and ether, much less in ligroin, and very little soluble in water.

Toluquinone-m-oxime Benzoyl Ether.

From o-Cresol. — This ether can be made from the silver salt suspended in absolute ether, or, better, from the sodium salt in alcohol solution. Slightly less than the amount of sodium calculated to form a sodium oxime is dissolved in 100 cm^3 of alcohol, 2–5 grams of the oxime added, and into the filtered solution slightly more than the theoretical quantity of benzoyl chloride is dropped slowly, the solution being kept cool. The benzoyl ether begins to separate immediately, and after a few moments the alcohol can be filtered off and rejected, as it contains little of the substance. After boiling in alcohol with animal charcoal, when the solution is submitted to fractional crystallization, three-fourths of the crude product can be readily separated in the form of bright-yellow needles melting at 193°. Upon concentrating the mother-liquor to a small volume and cooling, nearly the theoretical quantity of the benzoyl ether can be recovered. Nothing further was ever obtained save a few flakes of benzoic acid formed by the saponifying action of hydrochloric acid, produced by the slight excess of benzoyl chloride acting on alcohol. When the portion obtained upon concentration was repeatedly fractioned, it could be separated into portions melting approximately at 193°, and others melting almost completely from as low as 135° to 155°. There seemed to be a tendency, however, for these lower fractions to liquefy at 142°–144°, and once, from an alcoholic solution of a fraction melting at 140°–150°, that evaporated at ordinary temperature, short, thick, prismatic crystals separated from the curved needles of the higher melting (193°) fraction. These few prisms melted at 144° without decomposition. An analysis of the body liquefying at 193° C. gave the following figures:

0.2277 gram, dried over H_2SO_4, gave 0.5785 gram CO_2 and 0.0945 gram H_2O.

0.2001 gram gave 10 cm^3 N at 15° C. and 760 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.30
H	4.60	4.61
N	5.82	5.85

An analysis of a fraction melting from 145°–165° gave these percentages:

0.1421 gram, dried over H_2SO_4, gave 0.3635 gram CO_2 and 0.0565 gram H_2O.

0.6726 gram gave 34.1 cm^3 N at 15° C. and 770 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.74
H	4.60	4.43
N	5.82	6.02

The benzoyl ether is not at all soluble in water or ligroin, is slightly soluble in cold alcohol, but dissolves readily in ether, chloroform, and glacial acetic acid. The low-melting body seems to be more soluble in alcohol than its higher-melting isomer, but, as nine-tenths of the total product appeared to be the body melting at 193°, the small proportion of the low-melting compound may account partially for the idea that the latter is more soluble.

From Toluquinone. — The oxime was made according to the method of Goldschmidt and Schmidt,[*] by treating toluquinone in aqueous solution with an excess of hydroxylamine hydrochloride, extracting with ether, and purifying with animal charcoal. From the sodium salt of the oxime thus formed the benzoyl ether was made in the manner previously described. The product is identical with the benzoyl ether made from *o*-cresol. The body melting at 193° C. was readily isolated and analyzed:

0.1002 gram, dried over H_2SO_4, gave 0.2565 gram CO_2 and 0.0452 gram H_2O.

0.3581 gram gave 17.8 cm^3 N at 15° C. and 760 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.81
H	4.60	5.01
N	5.82	5.77

By fractional crystallization, low-melting portions were separated, exactly as in the case of the benzoyl ether made from *o*-cresol, except that some fractions were obtained melting partially as low as 129°. In order to be certain that benzoic acid (m. p., 120° C.) was not unduly lowering these melting-points, these fractions were boiled with water and filtered hot. The filtrate was not acid to litmus and contained only a trace of organic matter. The ethers, when dried, gave the same melting-point as before boiling with water, and, upon recrystallizing from a little alcohol, did not exhibit any

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[*] Ber. Dtsch. chem. Ges., xvii, 2063.

change. Furthermore, the benzoyl ether obtained by the usual method, when only 75 per cent. of the theoretical quantity of benzoyl chloride was used, gave fractions beginning to melt at 129°. Obviously benzoic acid could not be present in these instances.

By slow, spontaneous evaporation of the alcoholic solution of a fraction liquefying at 140°–150°, a few crystals melting at 142°, similar to those obtained in the same manner from the oxime made from *o*-cresol, separated from the body melting at 193°. Since there was not enough of this compound for a combustion, an analysis was made of a fraction melting at 187° C. with the following results:

0.1131 gram, dried over H_2SO_4, gave 0.2901 gram CO_2 and 0.0480 gram H_2O.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.96
H	4.60	4.72

Fractions were frequently obtained melting at about 177° C., and from these attempts were repeatedly made to isolate some of the ortho isomer. None was ever detected under the lens, and fractional crystallization always separated such portions, principally into the body melting at 190°, and a small fraction melting much lower.

Since the benzoyl ether will decompose into a dark-brown liquid with the evolution of brown fumes of nitrogen oxides when heated above 160°, it is only by rapidly heating that 193° can be observed as a melting-point. This applies also to the bromine addition-products of the benzoates of both the ortho- and metaoximes.

Dibromtoluquinone-m-oxime Benzoyl Ether.

The benzoyl ether was dissolved in chloroform and cooled while the theoretical quantity of bromine was added in small portions. After standing for an hour, the chloroform was evaporated spontaneously, and the light-brown residue recrystallized from glacial acetic acid. It can also be purified by dissolving in fuming nitric acid and pouring into water. On analysis:

0.1437 gram, dried over H_2SO_4, gave 0.2176 gram CO_2 and 0.0339 gram H_2O.

0.1215 gram gave 0.1140 gram AgBr.

	Calculated for $C_{14}H_{11}Br_2NO_3$.	Found.
C	41.90	41.30
H	2.76	2.62
Br	39.87	39.93

The dibromide is insoluble in water, somewhat soluble in cold alcohol, and readily dissolves in chloroform and glacial acetic acid, from which it crystallizes in white prisms melting at 165° C. with decomposition.

Monobromtoluquinone-m-oxime Benzoyl Ether.

When the dibromide is boiled with alcohol hydrobromic acid splits off, two hours being required to complete the process, during which little or no saponification takes place. After recrystallizing from alcohol, a mixture of monobrom compounds is obtained, melting from 155°–170°. A portion melting with decomposition at 174° C., was separated and analyzed:

0.1208 gram, dried over H_2SO_4, gave 0.2319 gram CO_2 and 0.0345 gram H_2O.

0.0735 gram gave 0.0425 gram AgBr.

	Calculated for $C_{14}H_{10}BrNO_3$.	Found.
C	52.49	52.36
H	3.15	3.17
Br	24.98	24.63

It is very similar in its properties to toluquinone-*m*-oxime benzoyl ether, crystallizing from alcohol in bright-yellow needles.

Toluquinone-o-oxime Methyl Ether.

The methyl ether of toluquinone-*o*-oxime was made from the silver salt and methyl iodide in the same manner as its meta isomer, the yield being somewhat better. Once recrystallized from ligroin:

0.1247 gram of the ether, dried over H_2SO_4, gave 0.2931 gram CO_2 and 0.0675 gram H_2O.

0.3484 gram gave 27 cm^3 N at 15° C. and 772 mm. pressure.

	Calculated for $C_8H_9NO_2$.	Found.
C	63.53	64.10
H	6.00	6.01
N	9.29	9.22

Its properties are almost identical with the methyl ether of the meta form. It crystallizes from ligroin in long yellow needles, every portion of which, obtained by fractional crystallization, melts at 69° C.

Dibromtoluquinone-o-oxime Methyl Ether.

The methyl ether was dissolved in chloroform, cooled, and the calculated quantity of bromine added. The reaction is completed in twenty minutes, and, on evaporation of the chloroform, the dibromide is left behind as a dirty white mass. Once recrystallized from ligroin, the substance is ready for analysis:

0.1690 gram, dried over H_2SO_4, gave 0.1877 gram CO_2 and 0.0456 gram H_2O.

0.0744 gram gave 0.0909 gram AgBr.

	Calculated for $C_8H_9Br_2NO_2$.	Found.
C	30.87	30.29
H	2.92	3.00
Br	51.41	52.00

It is insoluble in water but quite soluble in most organic reagents. From ligroin it crystallizes in white prisms, melting at 112° C.

Toluquinone-o-oxime Acetyl Ether.

This ether was made by Wurster and Riedel[*] from toluquinone-*o*-oxime and acetic anhydride. It can be prepared also from the silver salt and acetyl chloride, the yield being very poor, only a trifle better than its meta isomer, which it closely resembles in its properties.

0.1194 gram, dried over H_2SO_4, gave 0.2666 gram CO_2 and 0.0545 gram H_2O.

0.2389 gram gave 15 cm^3 N. at 15° C. and 760 mm. pressure.

	Calculated for $C_9H_9NO_3$.	Found.
C	60.30	60.89
H	5.06	5.07
N	7.84	7.35

From ligroin it crystallizes in irregular yellow prisms, melting at 92° C.

Toluquinone-o-oxime Benzoyl Ether.

This ether was made in alcohol solution from the sodium salt in the manner already described for the benzoyl ether of the meta form. The yield is practically theoretical, and, after one recrystallization from alcohol, the product is ready for analysis.

0.1589 gram, dried over H_2SO_4, gave 0.4074 gram CO_2 and 0.0686 gram H_2O.

0.5101 gram gave 26.1 cm^3 N at 15° C. and 7.66 mm. pressure.

	Calculated for $C_{14}H_{11}NO_3$.	Found.
C	69.68	69.92
H	4.60	4.80
N	5.82	6.04

Although submitted to the most careful fractional crystallization, every particle obtained melted sharply at 177° C., with slight decomposition. From alcohol it crystallizes in light, brownish-yellow blades, which have all the properties

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[*] Ber. Dtsch. chem. Ges., xii, 1799.

of the metaoxime benzoyl ether except that it is a little more soluble in organic reagents.

Dibromtoluquinone-o-oxime Benzoyl Ether.

The benzoyl ether was dissolved in chloroform, bromine added to the cooled solution, and the product recrystallized from glacial acetic acid.

0.2111 gram, dried over H_2SO_4, gave 0.3208 gram CO_2 and 0.0564 gram H_2O.

0.1003 gram gave 0.0924 gram AgBr.

	Calculated for $C_{14}H_{11}Br_2NO_3$.	Found.
C	41.90	41.44
H	2.76	2.97
Br	39.87	39.21

It is insoluble in ligroin and water and but little soluble in cold alcohol. Fuming nitric acid dissolves it readily, and from the solution it is precipitated unchanged by water. It crystallizes from glacial acetic acid in short, thick, orthorhombic prisms melting at 159° C. with decomposition.

XXI

THE APPLICATION OF IODINE IN THE ANALYSIS OF ALKALIES AND ACIDS.

By CLAUDE F. WALKER and DAVID H. M. GILLESPIE.*

It is well known that when a free mineral acid is added to a neutral mixture of metallic iodate and iodide, the iodate is reduced and iodine is liberated according to the equation:

$$RIO_3 + 5RI + 3H_2SO_4 = 3I_2 + 3R_2SO_4 + 3H_2O.$$

This reaction is complete and non-reversible under the conditions of analysis, and it may therefore be applied to the estimation of amounts of iodate, iodide or mineral acid present in an unknown solution. A solution of iodate to be analyzed is mixed with an excess of iodide and mineral acid, the resulting free iodine estimated by directly titrating with sodium thiosulphate or arsenious acid, and one-sixth of the amount found taken as equivalent to the iodate originally present.† Similarly, a solution of iodide to be analyzed is mixed with an excess of iodate and mineral acid, the resulting free iodine estimated by directly titrating in alkaline solution with arsenious acid, and five-sixths of its amount taken as equivalent to the iodide originally present.‡ A solution of mineral acid to be analyzed is mixed with an excess of iodate and iodide, the resulting free iodine estimated by directly titrating with sodium thiosulphate, and its entire amount taken as equivalent to the amount of mineral acid originally present.§ Gröger has applied the last mentioned method to

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* From Am. Jour. Sci., vi, 455.

† Rammelsberg, Pogg. Ann., cxxxv, 493; Walker, Am. Jour. Sci., iv, 235. This volume, p. 52.

‡ Gooch and Walker, Am. Jour. Sci., iii, 293. This volume, p. 33.

§ Kjeldahl, Zeitschr. anal. Chem., xxii, 366; Furry, Am. Chem. Jour., vi, 341; Gröger, Zeitschr. angew. Chem., 1894, 52.

the direct analysis of various mineral acids, and has obtained results manifestly better than those afforded by the use of vegetable indicators. Gröger has also indirectly analyzed solutions of alkali hydroxides and carbonates by adding the solution to be analyzed to a measured volume of mineral acid, previously standardized by the above method, and estimating the small excess of free mineral acid that finally remains by the same method. The only difficulty with the Gröger process lies in the fact that under the conditions present the end-point of the final reaction between iodine and sodium thiosulphate is somewhat obscured by a peculiar back-play of color due to a continuous slow liberation of iodine in the system.

When a solution of a metallic hydroxide is acted on by iodine at a temperature high enough to decompose the small amounts of hypoiodites that might otherwise be present, the final action results in the formation of an exactly neutral mixture of iodate and iodide, according to the equation:

$$6ROH + 3I_2 = RIO_3 + 5RI + 3H_2O.$$

Phelps* has shown that in the case of barium hydroxide at least this reaction is regular and complete under the conditions of analysis, and is independent of the excess of iodine which remains in the neutral mixture unacted upon and may be estimated by directly titrating with arsenious acid. Phelps not only applies this principle of action to the standardization of solutions of barium hydroxide by boiling with an excess of iodine in a trapped flask, but also bases thereon a differential method for determining carbon-dioxide, in which the liberated gas is run into a measured amount of barium hydroxide, the final excess of which is estimated by treating with iodine in the presence of the precipitated barium carbonate. The good result obtained by Phelps with barium hydroxide suggested that the attempt be made to analyze alkali hydroxides, and possibly carbonates, by a method, simpler than that devised by Gröger, based on the direct treatment of these compounds

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* Am. Jour. Sci., ii, 70. Volume I, p. 369.

with iodine in hot solution. It also seemed possible to apply the differential method not only to carbon dioxide but to any acid or other compound that will act definitely and completely with the metallic hydroxide employed, provided the soluble or insoluble product formed will not be attacked when heated in the presence of iodine. It was decided to modify the Phelps process, however, in order to obviate the necessity of handling large measured amounts of iodine in a flask trapped to prevent mechanical loss by heating. The flask was therefore dispensed with altogether, and the hydroxide solution to be analyzed was mixed with an approximately measured excess of iodine solution, in an Erlenmeyer beaker, the mouth of which was lightly closed with a little trap to prevent loss by spattering. The excess of iodine was then completely removed by boiling, and the cooled colorless solution remaining, which contained a neutral mixture of iodate and iodide, was acidified with a mineral acid and the liberated iodine titrated with sodium thiosulphate, the amount found being equivalent to the amount of hydroxide taken for analysis.

The present investigation was undertaken to study the limitations and possible applications in analysis of the reactions between iodine on the one hand, and barium hydroxide, potassium hydroxide and sodium carbonate on the other. It was soon found that the reaction in the case of sodium carbonate is entirely dependent on conditions of time, mass, and temperature, and cannot be pushed to completion except under conditions that make its application in analysis impossible. In the case of barium and potassium hydroxides both the original procedure of Phelps and the modification above described were employed. The modified method was found to be the more convenient and speedy of the two. The results obtained in both cases agreed with one another, but were invariably lower by a small nearly constant amount than those obtained by both the gravimetric and the Gröger processes. This error of the Phelps process and its modification is possibly due to the action of atmospheric carbon dioxide on the hydroxide solution during the short time it is exposed. While it will affect the value of the method as a means of accurately determining the absolute amount of hydroxide present in a given volume of solution, it cannot so affect the accuracy of any differential method founded on the original Phelps process or its modification. This is demonstrated by the work of Phelps in the case of carbon dioxide, and by the present investigation in the case of hydrochloric and sulphuric acid. Analyses of these two acids were made by adding the solution to be analyzed to a measured volume of barium or potassium hydroxide, previously standardized by the modified Phelps method. The small excess of hydroxide remaining was then estimated by the same method, the results agreeing with those already obtained by both the gravimetric and the Gröger processes. It seems probable that other acids and compounds for which there is now no rapid iodometric method may be analyzed by a method similar to this, which has given good results with carbonic, hydrochloric, and sulphuric acids.

Decinormal solutions of the alkali hydroxides were prepared, and kept with great care in trapped bottles, from which portions for analysis were measured by means of a self-feeding burette, which was also fitted with a trap. All vessels and water used were made as free as possible from carbon dioxide, and the operations were conducted as rapidly as possible.

In the analyses by the Phelps method a carefully measured excess of decinormal iodine was drawn into a small ether wash-bottle, and the desired amount of alkali was rapidly run into it. The stopper, to which had been sealed a Will and Varrentrapp absorption bulb was placed in the bottle and the bulb was charged with a 5 per cent solution of potassium iodide to catch any escaping vapors of iodine. The apparatus was placed over a low flame and the contents heated to boiling or slightly longer, and then cooled in a stream of water. The contents of the bulb and connecting tubes were then washed into the flask, and the excess of free iodine remaining was titrated with arsenious acid, in the presence of 5 cm^3 of starch emulsion. Blank analyses were made to insure against mechanical loss of iodine during boiling and to prevent any error on account of the presence of carbonate or other impurity in the solutions employed.

Some of the results obtained with barium hydroxide are given in Table I. The variation in different analyses of the same series is not large, and the results are independent of the amount taken for analysis and of the excess of iodine employed.

TABLE I.

ANALYSES OF $\frac{N}{10}$ BARIUM HYDROXIDE SOLUTION.

(By boiling in a trapped flask with an excess of iodine.)

Exp.	$Ba(OH)_2$ taken.	Iodine taken.	Iodine absorbed by $Ba(OH)_2$.	$Ba(OH)_2$ found.	Mean.	Variation.
	cm³	grm.	grm.	grm.	grm.	grm
(1)	10	0.18	0.1054	0.0712	0.0699	0.0013+
(2)	10	0.14	0.1028	0.0692	0.0699	0.0007–
(3)	20	0.28	0.2072	0.1399	0.1398	0.0001+
(4)	20	0.25	0.2074	0.1401	0.1398	0.0003+
(5)	40	0.44	0.4143	0.2798	0.2796	0.0002+
(6)	40	0.44	0.4148	0.2802	0.2796	0.0006+
(7)	40	0.48	0.4160	0.2809	0.2796	0.0013+
(8)	40	0.48	0.4126	0.2786	0.2796	0.0010–
(9)	40	0.51	0.4115	0.2779	0.2796	0.0017–
(10)	40	0.51	0.4136	0.2793	0.2796	0.0003–

The analyses of potassium hydroxide were made in the same way as were those of barium hydroxide, and gave quite similar results. They follow in Table II.

TABLE II.

ANALYSIS OF $\frac{N}{10}$ POTASSIUM HYDROXIDE SOLUTION.

(By boiling in a trapped flask with an excess of iodine.)

Exp.	KOH taken.	Iodine taken.	Iodine absorbed by KOH.	KOH found.	Mean.	Variation.
	cm³	grm.	grm.	grm.	grm.	grm.
(1)	10	0.20	0.1621	0.0716	0.0717	0.0001–
(2)	10	0.23	0.1618	0.0715	0.0717	0.0002–
(3)	15	0.30	0.2404	0.1063	0.1076	0.0013–
(4)	15	0.30	0.2429	0.1074	0.1076	0.0002–
(5)	15	0.34	0.2431	0.1075	0.1076	0.0001–
(6)	25	0.51	0.4089	0.1808	0.1792	0.0016+
(7)	25	0.51	0.4058	0.1794	0.1792	0.0002+

The analyses by the modification of the Phelps method were made by drawing into an Erlenmeyer beaker of convenient size an approximately measured excess of decinormal iodine, and rapidly running the desired amount of alkali into it. The neck of the beaker was then closed by a little trap, made of one of the halves of a double end calcium chloride drying tube, to prevent appreciable loss by spattering. The beaker was then placed over a low flame, and the contents boiled until the last trace of the excess of iodine had volatilized from the solution and the trap. The volume was carefully regulated before and during the boiling, being kept as small as possible, usually amounting to about 100 cm^3 at the start and 35 cm^3 at the close. In the case of barium hydroxide care had to be taken to keep the dilution sufficient to prevent the separation the crystalline barium iodate, which is soluble with difficulty. To steady the ebullition a little spiral of platinum was introduced into the beaker. After the boiling had ceased, the colorless solution, containing a neutral mixture of iodate and iodide, was cooled in running water and treated with 10 cm^3 of dilute (1:3) hydrochloric acid or (1:3) sulphuric acid. The liberated iodine was titrated directly with sodium thiosulphate, in the presence of 5 cm^3 of starch emulsion. In the case of barium hydroxide the iodine was liberated with dilute (1:3) hydrochloric acid to save the inconvenience of working in the presence of precipitated barium sulphate; with potassium hydroxide, however, dilute (1:3) sulphuric acid was employed. In view of a statement by Pickering* that titrations with sodium thiosulphate in the presence of acid involve an error, a series of blank analyses was made which showed conclusively that no such error exists under the conditions which obtain in the process under consideration. Care was also taken, as in a former case, to guard against the possible presence of carbonates or other impurities in the reagents employed.

In Table III are given the results of a series of analyses of barium hydroxide by the modified method just described. They agree fairly well with those of Table I.

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* Jour. Chem. Soc., xxxvii, 134.

TABLE III.

ANALYSES OF $\frac{N}{10}$ BARIUM HYDROXIDE SOLUTION.

(By boiling with excess of iodine in an open beaker to decoloration, and acidifying the residue.)

Exp.	$Ba(OH)_2$ taken.	Iodine taken.	Iodine absorbed by $Ba(OH)_2$.	$Ba(OH)_2$ found.	Mean.	Variation.
	cm^3	grm.	grm.	grm.	grm.	grm.
(1)	10	0.13	0.1023	0.0691	0.0695	0.0004−
(2)	10	0.16	0.1020	0.0689	0.0695	0.0006−
(3)	15	0.18	0.1548	0.1046	0.1043	0.0003+
(4)	15	0.20	0.1546	0.1045	0.1043	0.0002+
(5)	20	0.23	0.2049	0.1384	0.1390	0.0006−
(6)	20	0.25	0.2058	0.1390	0.1390	0.0000
(7)	20	0.32	0.2065	0.1394	0.1390	0.0004+
(8)	25	0.29	0.2567	0.1734	0.1738	0.0004−
(9)	25	0.32	0.2562	0.1730	0.1738	0.0008−
(10)	40	0.47	0.4120	0.2783	0.2780	0.0003+
(11)	40	0.48	0.4119	0.2782	0.2780	0.0002+
(12)	40	0.48	0.4152	0.2804	0.2780	0.0024+
(13)	40	0.49	0.4109	0.2775	0.2780	0.0005−

The analyses of potassium hydroxide by the modified method are given in Table IV, and are found to agree well with those of Table II.

TABLE IV.

ANALYSES OF $\frac{N}{10}$ POTASSIUM HYDROXIDE SOLUTION.

(By boiling with excess of iodine in an open beaker to decoloration, and acidifying the residue.)

Exp.	KOH taken.	Iodine taken.	Iodine absorbed by KOH.	$Ba(OH)_2$ found.	Mean.	Variation.
	cm^3	grm.	grm.	grm.	grm.	grm.
(1)	10	0.20	0.1624	0.0718	0.0721	0.0003−
(2)	10	0.23	0.1618	0.0715	0.0721	0.0006−
(3)	10	0.25	0.1622	0.0717	0.0721	0.0004−
(4)	15	0.30	0.2459	0.1087	0.1082	0.0005+
(5)	15	0.34	0.2473	0.1093	0.1082	0.0011+
(6)	15	0.38	0.2441	0.1079	0.1082	0.0003−
(7)	20	0.41	0.3274	0.1447	0.1442	0.0005+
(8)	20	0.46	0.3259	0.1441	0.1442	0.0001−
(9)	20	0.51	0.3269	0.1445	0.1442	0.0003+
(10)	25	0.51	0.4052	0.1791	0.1803	0.0012−
(11)	25	0.57	0.4082	0.1805	0.1803	0.0002+
(12)	25	0.63	0.4080	0.1804	0.1803	0.0001+

A gravimetric analysis of the barium hydroxide solution in which the barium was weighed as the sulphate, gave as a result 0.1411 grm. $Ba(OH)_2$ for each 20 cm³ taken. An analysis of the same solution by the Gröger process gave for the same volume 0.1420 grm. The result by the Phelps process, however, was 0.1398 grm., and by the modified process 0.1390 grm. That the difference of 2 mg. between the results by the gravimetric and the Gröger processes on one hand, and the Phelps process and its modification on the other, may be due to atmospheric carbon dioxide, has already been pointed out. A gravimetric analysis of the potassium hydroxide solution by evaporating and weighing as KCl gave 0.1111 grm. KOH for each 20 cm³ taken, agreeing with 0.1106 grm. obtained by the Gröger process. The analyses by the Phelps process and its modification for the same solution gave 0.1076 grm. and 0.1082 grm. respectively. These results are strikingly in accord with those obtained with barium hydroxide.

In the application of the modification of the Phelps process to the indirect analysis of hydrochloric and sulphuric acids the procedure was essentially the same as that detailed for the analysis of barium and potassium hydroxides in Tables III and IV. The acid solution to be analyzed was drawn into an Erlenmeyer beaker, a measured excess of standardized alkali

TABLE V.

ANALYSES OF $\frac{N}{10}$ HYDROCHLORIC ACID SOLUTION.

(By adding to excess of $\frac{N}{10}$ $Ba(OH)_2$, boiling with excess of iodine to decoloration and acidifying the residue.)

Exp.	HCl taken.	$Ba(OH)_2$ taken.	$Ba(OH)_2$ neutralized by HCl.	HCl found.	Mean.	Variation.
	cm³	grm.	grm.	grm.	grm.	grm.
(1)	15	0.17	0.1128	0.0480	0.0476	0.0004+
(2)	15	0.17	0.1118	0.0475	0.0476	0.0001−
(3)	15	0.17	0.1112	0.0473	0.0476	0.0003−
(4)	25	0.26	0.1860	0.0791	0.0794	0.0003−
(5)	25	0.26	0.1866	0.0794	0.0794	0.0000
(6)	35	0.34	0.2634	0.1120	0.1111	0.0009+
(7)	35	0.34	0.2603	0.1107	0.1111	0.0004−

added, and the operation completed as described. It was found that barium hydroxide and potassium hydroxide may be applied with equal accuracy to the analysis of both hydrochloric and sulphuric acids. Some of the results obtained are given in Tables V, VI and VII.

TABLE VI.

ANALYSES OF $\frac{N}{10}$ HYDROCHLORIC ACID SOLUTION.

(By adding to excess of $\frac{N}{10}$ KOH, boiling with excess of iodine to decoloration, and acidifying the residue.)

Exp.	HCl taken.	KOH taken.	KOH neutralized by HCl.	HCl found.	Mean.	Variation.
	cm³.	grm.	grm.	grm.	grm.	grm.
(1)	20	0.14	0.0972	0.0683	0.0683	0.0000
(2)	20	0.14	0.0975	0.0684	0.0683	0.0001+
(3)	25	0.14	0.1222	0.0795	0.0791	0.0004+
(4)	25	0.14	0.1207	0.0785	0.0791	0.0006−

TABLE VII.

ANALYSES OF $\frac{N}{10}$ SULPHURIC ACID SOLUTION.

(By adding to excess of $\frac{N}{10}$ $Ba(OH)_2$, boiling with excess of iodine to decoloration, and acidifying the residue.)

Exp.	H_2SO_4 taken.	$BaOH_2$ taken.	$Ba(OH)_2$ neutralized by H_2SO_4.	H_2SO_4 found.	Mean.	Variation.
	cm³	grm.	grm.	grm.	grm.	grm.
(1)	10	0.21	0.0884	0.0506	0.0498	0.0008+
(2)	10	0.21	0.0880	0.0503	0.0498	0.0005+
(3)	15	0.30	0.1328	0.0754	0.0748	0.0006+
(4)	15	0.30	0.1318	0.0751	0.0748	0.0003+
(5)	25	0.43	0.2168	0.1239	0.1246	0.0007−
(6)	30	0.43	0.2600	0.1481	0.1495	0.0014−

An analysis of the hydrochloric acid solution by the Gröger method, which was found to agree in every case with the gravimetric determination, gave for each 25 cm³ 0.0801 grm. of HCl, agreeing with 0.0794 grm. and 0.0791 grm. obtained by the new method. An analysis of the sulphuric acid solution by the Gröger method gave for each 25 cm^3 0.1241 grm. of H_2SO_4 agreeing with 0.1246 grm. obtained by the new method.

This investigation shows that the reaction between iodine and hydroxides of the alkalies and alkaline earths in hot solution is regular and complete under analytical conditions, not being appreciably affected by the mass action of considerable excesses of iodine. The reaction is best applied in analysis by titrating the alkali with an excess of iodine, removing this excess by boiling, and estimating the iodine in the residue. While certain mechanical difficulties may effect the extreme accuracy of the process as a direct means for analyzing alkalies, the action is at all times regular and may be indirectly applied with fair accuracy to the analysis of various acids and possibly to other compounds. The reaction between iodine and alkali carbonates on the contrary is irregular and cannot be made the basis of any analytical process.

XXII

THE ESTIMATION OF BORIC ACID.

BY F. A. GOOCH AND LOUIS CLEVELAND JONES.[*]

THE estimation of boric acid by treating the salts of that acid with sulphuric acid, distilling with methyl alcohol, evaporating the distillate over magnesium oxide, igniting and weighing, was proposed by Rosenbladt.[†] A little later, and without knowledge of Rosenbladt's experience, a somewhat similar process,[‡] which consisted in the treating of the compound of boric acid with acetic acid or nitric acid, distillation with methyl alcohol, evaporation of the distillate over calcium oxide, and ignition of the residue, was described by one of us. In the course of the development of this process, it transpired that the insolubility of magnesium oxide retards the absorption of boric acid by that substance, and that the more soluble calcium oxide retains boric acid more actively and is therefore to be preferred.

Points in the treatment upon which special emphasis was laid in the original description of this process were the choice of a suitable apparatus for the distillation, the employment of a loosely stoppered receiver for the reception of the distillate upon slaked lime, the careful removal of water from the substance in the retort before acidifying and treating with the methyl alcohol, regulated use of acid, and care in the evaporation and ignition.

The attainment of good results in this process depends upon attention to details. Modifications have been suggested by several investigators. Thus, instead of igniting the calcium oxide in a large platinum crucible, transferring it to the

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[*] From Am. Jour. Sci., vii, 34.

[†] Zeitschr. anal. Chem., xxvi, 21.

[‡] Am. Chem. Jour., ix, 23.

receiver to hold the boric acid, and returning the calcium oxide with the distillate to the same crucible for subsequent ignition of the residue, as was originally proposed, Penfield* prefers to ignite the calcium oxide in a small crucible, to collect the distillate in ammoniacal water, to evaporate the latter over the calcium oxide in a large platinum dish, and to transfer this residue back to the small crucible for the final evaporation and ignition. Kraut † suggests a modification of form in the apparatus with no other essential change in conditions. Moissan‡ has suggested changes in the apparatus and avoids a transfer of the calcium oxide — collecting the distillate by itself in a closed receiver, trapped with an ammonia bulb to prevent the escape of the boric acid from the distillate; furthermore, Moissan's process calls for the use of an amount of calcium oxide from fifteen to twenty times greater than that theoretically required. From our experience it seems obvious that the demand for this amount of calcium oxide arises from an excessive use of nitric acid in the retort and the consequent modification of conditions in the distillate. Fortunately this difficulty may be avoided by the use of a little phenolphthalein as an indicator in the retort and care to limit the addition of nitric acid to the amount required to produce distinct acidity. The addition of a drop of the acid and another of the indicator should be repeated once or twice during the distillation to insure the return of the volatilized acid to the salt slightly decomposed in the process. The effect of much nitric acid is bad, not only because it neutralizes the calcium oxide when it passes to the distillate, but because when it is used a tendency is developed on the part of the dried mixture of calcium hydroxide and borate to puff explosively if the ignition is begun as soon as the residue is dry. If the residue is heated gradually and as strongly as possible over a radiator before the flame is actually applied to the crucible, no such action takes place; we are disposed to attribute it to the effect of the nitrate and nitrite, produced by

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* Am. Jour. Sci., xxxiv, 222.

† Zeitschr. anal. Chem., xxxvi, 3.

‡ Comp. rend., cxvi, 1084.

the absorption of nitrous fumes in the lime, upon the alcohol or other organic matter retained by the lime in the evaporation and drying unless the latter process is prolonged at high temperature.

That good results may be obtained with small amounts of calcium oxide, provided care as to the use of nitric acid and the conditions of ignition be taken, is shown by the figures of the original description and by the following experiments, in which phenolphthalein was employed as an indicator and the residue heated strongly over the radiator before actual ignition.

CaO taken.	B_2O_3 taken.	B_2O_3 found.	Error.
grm.	grm.	grm.	grm.
2.8405	0.1788	0.1792	0.0004+
1.7620	0.1790	0.1785	0.0005−
2.1757	0.1824	0.1840	0.0016+
2.5656	0.1788	0.1786	0.0002−

These results are accurate within reasonable limits. On the other hand, without care to ignite gradually we have noted errors of from 0.0030 grm. to 0.0060 grm. in the process otherwise conducted similarly. Doubtless the use of large amounts of calcium oxide as suggested by Moissan may serve the purpose of diffusing the explosive mixture through a mass of inert matter sufficient to prevent violent puffing, but care to heat over the radiator as strongly as possible before opening the flame directly to the crucible answers the same end. The difficulty does not exist when acetic acid is used in place of nitric acid, though even in this case it is safer to use the radiator in the first stages of heating, thus avoiding the danger of mechanical loss by too rapid ignition.

Following are determinations made by this method with the use of acetic acid. The results of these experiments, as well as those of the investigators mentioned, are a sufficient answer to the criticism of Reischle,* that acetic acid and nitric acid do not liberate boric acid in the distillation pro-

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* Zeitschr. anal. Chem., xxvi, 512.

CaO taken.	B_2O_3 taken.	B_2O_3 found.	Error.
grm.	grm.	grm.	grm.
0.9977	0.2065	0.2062	0.0003—
1.0220	0.2067	0.2070	0.0008+
1.8717	0.2077	0.2075	0.0002—
1.1810	0.1791	0.1795	0.0004+

cess so that good results may be obtained. Moreover, it has been shown by one of us * that even carbonic acid is strong enough to bring about complete volatility of boric acid with methyl alcohol.

The use of Calcium Oxide as a Retainer.

Quite recently Thaddeeff † has advocated the abandonment of calcium oxide as an agent for holding boric acid in the evaporation of alcoholic and aqueous solutions, on account of the hygroscopic nature of the oxide and the consequent difficulty of securing it in definite conditions for weighing, and proposes, instead of using calcium oxide, to retain and estimate boric acid in solution by converting it into the form of potassium borofluoride.

In the final modification of Thaddeeff's method the proposal is made to liberate the boric acid from its compounds by sulphuric acid, to volatilize it in methyl alcohol with the aid of a current of dry air, to catch the distillate in potassium hydroxide, to treat the mixture of hydroxide and borate with hydrofluoric acid in excess and evaporate on the steam bath, to digest the residue of fluoride and borofluoride at normal temperatures for two hours with 50 cm^3 of a potassium acetate solution (sp. gr. 1.14) and for twelve hours more after adding 100 cm^3 of ethyl alcohol (sp. gr. 0.805), to filter on paper, wash the residue with 62–72 cm^3 of alcohol (sp. gr. 0.805), dry at 100° and weigh as potassium borofluoride, after which the borofluoride is to be dissolved in boiling water and tested with calcium chloride for possible contamination

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* Jones, Am. Jour. Sci., v, 442. This volume, p. 100.

† Zeitschr. anal. Chem., xxxvi, 568.

by the presence of a fluoride. Plainly Thaddeeff's procedure presents at the outset difficulties; for besides the inconvenience of conducting long digestions with reagents of regulated strength, the difficulty of procuring hydrofluoric acid free from silica, which if present (as it usually is in the so-called chemically pure hydrofluoric acid of commerce) would be retained in the borofluoride as potassium fluosilicate, the inaccuracy of the dried paper filter, and the obvious uncertainty of success in an attempt to wash a mixture of acid potassium fluoride and potassium borofluoride in potassium acetate and alcohol so that the one shall be rendered entirely soluble while the other remains sensibly unaffected, —besides these objections, there is the theoretical probability that boric acid mnst be lost by volatilization during the evaporation of the solution of the mixed salts in the presence of free hydrofluoric acid. This last point was put to the proof by submitting to distillation in a platinum retort a mixture of equal quantities of borax and potassium hydroxide with an excess of hydrofluoric acid, collecting the distillate in potassium hydroxide, evaporating it to dryness and testing it for the presence of boric acid. When this residue from the evaporated distillate was treated with sulphuric acid and methyl alcohol, the burning alcohol vapor gave plainly the green flame of boric acid. Another portion showed clearly the presence of boric acid when acidulated with hydrochloric acid tested with turmeric paper. No boric acid could be detected in any of the reagents used. It is plain, therefore, that boric acid does volatilize upon the evaporation of a mixture of potassium fluoride and borofluoride in acid solution. The amount of such loss is disclosed in the record of the following experiment. Portions of a standard solution of boric acid, prepared by dissolving a known weight of anhydrous boric oxide in a liter of water, were mixed with a solution of potassium hydroxide (free from silica and standardized by conversion to the chloride) in the proportions to form the potassium borofluoride, and an excess of hydrofluoric acid was added. The mixture was evaporated and the residue was dried and weighed at 100°, the whole operation being conducted in platinum.

Exp.	HKF_2 equivalent to KOH taken.	B_2O_3 taken.	$KFBF_3$ theoretical weight.	$KFBF_3$ found.	Error in terms of $KFBF_3$.	Error in terms of B_2O_3.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.3531	0.1582	0.5701	0.5580	0.0121–	0.0033–
(2)	0.3192	0.1430	0.5154	0.5100	0.0054–	0.0015–
(3)	0.3192	0.1430	0.5154	0.5030	0.0124–	0.0034–
(4)	0.3192	0.1430	0.5154	0.5088	0.0066–	0.0018–
(5)	0.3192	0.1430	0.5154	0.5114	0.0040–	0.0011–

In experiments (1) to (3) the volume of the solution evaporated was about 50 cm^3. In experiment (4) this volume was reduced about one-half before acidifying with hydrofluoric acid, while in experiment (5) the solution was diluted about one-half before adding the hydrofluoric acid. It is plain, therefore, that in this single step of Thaddeeff's process there is a considerable error of deficiency. On the other hand, the errors for the full process as laid down by Thaddeeff have been in our experience invariably differences of excess — presumably because the loss due to volatilization of boric acid has been overbalanced by the inaccuracy in washing. It is plain that the process can give true indications only by the balancing of considerable errors.

If we take into consideration, therefore, the inevitable inaccuracy and inconvenience of Thaddeeff's proposal, it cannot be regarded as a desirable substitute for the process according to which boric acid is absorbed and retained for weighing with calcium oxide, especially since the difficulties in the way of getting constant weights of that substance are by no means insuperable.

Thus the following table shows the series of weights taken in several experiments in bringing calcium oxide to a constant weight in a 50 cm^3 platinum crucible ignited over a blast lamp, as well as the weight taken after adding a known amount of standard boric acid solution to the slaked oxide, evaporating, and igniting. The results recorded are those of experiments made on days not moist beyond the average and with the greatest care to approach the limit of accuracy with which calcium oxide and the boric acid held thereby can be weighed under ordinarily favorable conditions. The first weight of calcium oxide recorded under each experiment was taken after a strong ignition over the blast lamp for about one-half hour. The succeeding weights were taken after similar ignitions of five minutes. In all cases the crucible was left to stand a definite period in a sulphuric acid desiccator, and, after the approximate value had once been obtained, the weights of the preceding weighing were replaced on the balance before the crucible was taken from the desiccator. The average of the weights bracketed is the weight taken as constant for the calculations.

Exp.	CaO taken.		B_2O_3 taken.	CaO + B_2O_3 taken.	CaO + B_2O_3 found.		Error.
	grm.		grm.	grm.	grm.		grm.
(1)	0.9505 0.9493 0.9493	0.9493	0.2095	1.1588	1.1590 1.1591	1.1591	0.0003+
(2)	1.1319 1.1317 1.1313 1.1315	1.1315	0.2150	1.3465	1.3499 1.3474 1.3475 1.3476	1.3475	0.0010+
(3)	0.8028 0.8025 0.8024	0.8024	0.1184	0.9208	0.9205 0.9206 0.9206	0.9206	0.0002–
(4)	2.6980 2.6975 2.6973 2.6973	2.6973	0.2073	2.9046	2.9048 2.9049 2.9044	2.9048	0.0002+

Obviously calcium oxide may be weighed with accuracy, with or without boric acid; but the fact remains that a less hygroscopic absorbent — one requiring less care in the handling, is to be desired.

The use of Sodium Tungstate as a Retainer.

In searching for a suitable material of less hygroscopicity to replace calcium oxide as a retainer for boric acid, we have found that sodium tungstate, fused with a slight excess of tungstic acid over that contained in the normal tungstate (to insure its freedom from carbonate), answers this purpose excellently. This substance is definite in weight, not hygroscopic, soluble in water, and recoverable in its original weight after evaporation and ignition. To test its value as a retainer for boric acid, portions of it — 4 to 7 grm. — were fused and weighed in a 50 cm^3 crucible, the tungstate was dissolved in water and to it was added a known amount of a standard solution of boric acid. After diluting, mixing, evaporating, and fusing the residue, the increase in weight should represent the boric anhydride held by the tungstate. The results of the accompanying table show how accurately the boric acid is retained under these conditions. In experiments (3) to (7) the tungstate, after its first weighing, was dissolved, transferred to a larger platinum dish and mixed therein with the boric acid. After evaporation to a suitable volume this solution of tungstate and boric acid was transferred to the original crucible for final evaporation and ignition.

Exp.	$Na_2WO_4 + WO_3$ taken.	B_2O_3 taken.	B_2O_3 found.	Error in B_2O_3.
	grm.	grm.	grm.	grm.
(1)	6.5416	0.1784	0.1771	0.0013−
(2)	7.3134	0.1786	0.1773	0.0013−
(3)	5.5003	0.0950	0.0952	0.0002+
(4)	4.1394	0.0944	0.0944	0.0000
(5)	7.5037	0.2148	0.2149	0.0001+
(6)	4.7744	0.2718	0.2702	0.0016−
(7)	6.6470	0.2503	0.2487	0.0016−

It is plain that though the sodium tungstate does not hold the boric acid with absolute accuracy the errors are not unreasonable — 0.0008 grm. in the mean. Upon substituting the tungstate for calcium oxide as a retainer in the distillation process, the results were likewise highly favorable.

We used by preference the apparatus originally proposed, excepting that the Erlenmeyer flask used as a receiver is fitted tightly to the condenser and trapped with water bulbs. The retort is made very easily from a 150 cm^3 pipette and has the special advantage that particles of the residue spattering during distillation are easily washed from the walls of the vessel by a slight rotary motion of the retort. It was found that special care should be taken to give the tungstate ample time for contact with the distillate before exposing the latter to atmospheric evaporation. The distillate was received, therefore, in a dilute solution of sodium tungstate placed in the receiver, cooled by ice and trapped with water, and the mixture was well stirred, allowed to stand one half-hour, evaporated to small volume in a large dish, and transferred to the crucible in which the tungstate had been originally weighed. After thorough drying the residue was ignited to fusion and weighed. When acetic acid was employed in the retort, care was taken in the ignition to expose the fused mass freely to the air (by causing it to flow upon the sides of the crucible) until the color of the cooled tungstate was white, in order that the reducing effect of the acetate might be eliminated. In the experiments recorded in the following table the tungstate was used in the receiver to retain the boric acid distilled as usual with methyl alcohol, from the borates treated with acetic

$Na_2WO_4 + WO_3$ taken.	B_2O_3 taken.	B_2O_3 found.	Error.
WITH NITRIC ACID.			
grm.	grm.	grm.	grm.
8.5516	0.1582	0.1572	0.0010–
4.9639	0.1329	0.1323	0.0006–
8.0083	0.1267	0.1256	0.0011–
WITH ACETIC ACID.			
4.9658	0.1434	0.1418	0.0016–
6.0289	0.1431	0.1433	0.0002+
4.6797	0.1589	0.1587	0.0002–
4.0018	0.1433	0.1422	0.0011–
WITH SULPHURIC ACID.			
6.3439	0.1582	0.1579	0.0003–
8.8227	0.1582	0.1577	0.0005–
10.1516	0.1265	0.1264	0.0001–
6.5788	0.1892	0.1890	0.0002–

acid, nitric acid or sulphuric acid, in amounts regulated by the use of phenolphthalein as an indicator.

Excessive use of acid is disadvantageous, and this is especially true in the case of sulphuric acid; for, if this acid is carried over with the methyl alcohol, as it is at 100° if present in appreciable excess, a part of it, at least, is held permanently by the tungstate to increase the apparent weight of the boric acid to be estimated.

The manipulation of the tungstate presents no difficulties, and the results obtained by its use are reasonably accurate.

XXIII

A VOLUMETRIC METHOD FOR THE ESTIMATION OF BORIC ACID.

By LOUIS CLEVELAND JONES.[*]

When boric acid and mannite are mixed in solution a peculiar compound of strongly acid properties is the result. This compound decomposes carbonates, and its acid taste is comparable to that of citric acid, much stronger than that of boric acid alone. Magnanini[†] has found that the product of such a mixture of boric acid and mannite solutions shows greater electrical conductivity and a lower freezing point than a similar molecular solution of either substance alone. Other polyatomic alcohols (but all to a less degree than mannite) and some organic acids show this peculiar property of combining chemically with boric acid to increase its acid qualities.[‡] Of this reaction between boric acid and the polyatomic alcohols, Thomson,[§] Barthe,[||] and Jörgensen[¶] have taken advantage to develop methods for the volumetric estimation of boric acid. Glycerine is used to form a combination with boric acid, sufficiently acidic to give an acid reaction when used with a sensitive indicator and make possible its titration with an alkaline solution. Hönig and Spitz[**] show that in the method of Jörgensen a very large amount of glycerine must be used to prevent the appearance of the indication of alkalinity with phenolphthalein before all the boric acid is neutralized according to the following equation, $2NaOH+B_2O_3=2NaOBO+H_2O$;

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[*] From Am. Jour. Sci., vii, 147.

[†] Gaz. Chim., xx, 428–440; xxi, 134–145.

[‡] Klein, Jour. Pharm. Chim., 4, vol. xxviii; Lambert, Comp. rend., cviii, 1016–1017.

[§] Jour. Soc. Chem. Ind., xv, 432.

[||] Jour. Pharm. Chim., xxix, 163.

[¶] Zeitschr. angew. Chem., 1897, 5.

[**] Zeitschr. angew. Chem. (1896), 549.

that in the presence of carbonates the solution must be boiled to decompose bicarbonates and the escape of boric acid by volatilization prevented by the use of a return condenser; and that silica must be removed by the process of Berzelius, and the solution then neutralized by the use of methylorange before a titration of the boric acid can be made.

Vadam,[*] for the estimation of boric acid in butter makes use of mannite, which, as he finds, gives sharper indication with litmus than glycerine. According to this process, the solution to be analyzed for boric acid is neutralized by the use of litmus and a solution of sodium hydroxide. Mannite (1–2 grm.) is then added, bringing about an acid reaction with the boric acid present in free condition. The solution is then titrated to alkalinity by sodium hydroxide.

None of the above methods with glycerine have, in my experience, given anything but comparatively crude results. The weak acidic properties of boric acid, the interference (and difficulty of removal) of carbon dioxide with all organic indicators sufficiently delicate to be used with boric acid, and indeed, the procuring of a standard alkali containing no carbonate, together with the supposed detrimental influence of silica and the lack of a convenient method for its removal, have made the process of Gooch,[†] which involves distillation and weighing with calcium oxide, the only means (though requiring long time and exceeding care) in use for the accurate separation and estimation of boric acid. Recently sodium tungstate has been recommended from this laboratory[‡] as a substitute for calcium oxide to retain the distilled boric acid. The entire process, however, is one of the most exacting in analytical chemistry, and for this reason a convenient, rapid and at the same time accurate method for the estimation of boron is especially desirable. The first step toward the development of such a process must be the convenient prepa-

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[*] Jour. Pharm. Chim. (6), viii, 109–111.

[†] Am. Chem. Jour. ix, 23–33; Moissan, Comp. rend., cxvi, 1087; Kraut, Zeitschr. anal. Chem. xxxvi, 165; Montemartini, Gaz. Chim. Ital., xxviii, 1, 344.

[‡] Gooch and Jones, Am. Jour. Sci., vii, 34. This volume, p. 172.

ration and the accurate estimation of the standard solution of alkali to be used for neutralizing the boric acid. This has been found to be easily accomplished by the process recommended by Küsler.[*] This observer, in an extensive investigation of the analytical methods for the volumetric estimation of alkalies and alkali carbonates in solution, finds that both phenolphthalein and methylorange are appreciably sensitive to carbonic acid, but when this interfering agent is removed by precipitation with barium chloride according to the process of Winkler,[†] the remaining free alkali may be estimated with great accuracy by phenolphthalein and decinormal hydrochloric acid.

Obviously, if the difficulties dependent upon the action of carbon dioxide can be obviated, and if the acidity of the boric acid can be increased to such an extent that a sufficiently sensitive indicator will give with accuracy the neutralization point with free alkali, and if the alkali and stronger acid can be combined while boric acid alone remains free, then it should be possible to estimate boric acid volumetrically. Experiment has shown that barium chloride removes carbon dioxide present in carbonates, and that mannite makes a combination with boric acid strongly acidic to phenolphthalein.

To obtain the boric acid alone in free condition many attempts have been made. Gladding,[‡] Thaddeeff [§] and Rosenbladt [||] have isolated the boric acid by distillation with methyl-alcohol and a non-volatile acid. Many indicators theoretically insensible to free boric acid have been used to indicate the neutralization of the stronger acids. Hönig and Spitz,[¶] and Thomson,[**] use methylorange, Morse and Burton,[††] tropaeolin 00, while Vadam [‡‡] makes use of litmus. All these indicators, however, have been found by experiment to be more or less affected by boric acid in solution. On the other hand, I have found in the well known reaction according

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[*] Zeitschr. anorg. Chem., xiii, 124–150.

[†] Massanalyse.

[‡] Jour. Am. Chem. Soc., iv, 568.

[§] Zeitschr. anal. Chem., xxxvi (9), 568.

[||] Zeitschr. anal. Chem., xxvi, 18.

[¶] Zeitschr. anorg. Chem. (18), 549.

[**] Jour. Soc. Chem. Ind., xv, 432.

[††] Am. Chem. Jour., x, 154.

[‡‡] Jour. Pharm. Chim. (6) viii, 109–111.

to which a stronger acid liberates regularly iodine from a mixture of iodide and iodate, the solution of this difficulty. If both the iodide and iodate are in excess of the acid the entire amount of free acid will be neutralized and the corresponding amount of iodine liberated according to the following equation:

$$5KI + KIO3 + 6HCl = 6KCl + 3H_2O + 3I_2.$$

This liberated iodine may be removed by sodium thiosulphate and a solution obtained which is absolutely neutral containing only neutral salts, potassium iodide, iodate, and tetrathionate. The statements made by P. Georgevic* and Furry,† that boric acid present in moderate amount in solution has not the slightest action on a mixture of iodide and iodate, have been experimentally verified. Therefore when this acid is liberated by an excess of a stronger acid, and the iodine set free destroyed by thiosulphate, it remains free in solution to be titrated in any convenient manner possible.

Following along the lines suggested by the above reactions, a volumetric process for the estimation of boric acid has been developed. For a basis of the investigations, a standard solution of boric acid was prepared by dissolving in a liter of water about eight grams of carefully weighed anhydrous boric oxide. This anhydrous boric oxide was prepared from the several times recrystallized hydrous boric acid, by long-continued fusion over a blast lamp. A solution of approximately $\frac{n}{5}$ sodium hydroxide was prepared from the ordinary sodium hydroxide of the laboratory. The free alkali in this solution was estimated by the process of Winkler recommended by Küsler. The acid used to make this estimation was hydrochloric, standardized by silver nitrate.

The full method for the estimation of boric acid as finally elaborated is as follows: The solution is made clearly acid to litmus by hydrochloric acid and 5 cm³ of a solution (10%) of barium chloride added. An amount of iodate and iodide of potassium sufficient to liberate an amount of iodine at

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* Jour. prakt. Chem., xxxviii, 118.

† Am. Chem. Jour., vi, 341.

least equivalent to the excess of hydrochloric acid in the acidified solution is mixed with starch in a separate beaker, and the iodine which is usually thrown out by this mixture, is just bleached by a dilute solution of thiosulphate.

To the now neutral solution of iodide and iodate a single drop of the solution to be analyzed is transferred by a glass rod. If a blue coloration is developed, the solution is acidic with hydrochloric acid, and all the boric acid is in free condition. The amount of iodide and iodate used depends upon the acidity of the solution containing boric acid. Usually 10 cm^3 of a 25 per cent solution of iodide and the same amount of a saturated solution of iodate is sufficient. Any larger excess of hydrochloric acid should be neutralized by sodium hydroxide before the iodide and iodate mixture is added. After the addition of the iodide and iodate solution, containing starch, to the boric acid solution, the liberated iodine should be carefully bleached by thiosulphate. Any excess of thiosulphate in reasonable amount does not seem to be detrimental, but in practice the starch iodide color is clearly bleached, and no more then added. Carbonates prevent a definite indication of the neutral point by thiosulphate and starch iodide, therefore the barium chloride (about 5 cm^3) should be added before this point in the process. The mixture of iodide and iodate is not added to the solution to be analyzed until after it is made acidic, for the reason that when the neutral point is approached by the addition of hydrochloric acid the starch iodide is thrown out locally by the acid, and the small amount of sodium borate remaining undecomposed does not again bleach the coloration produced thus obscuring the neutral point which must be obtained before titrating for boric acid.

The solution after the bleaching of the iodine by thiosulphate is colorless and contains only starch, neutral chloride, potassium tetrathionate, iodide and iodate, and all the boric acid present in uncombined condition. The carbonate lies out of the sphere of action in insoluble form as barium carbonate. A few drops of the indicator, phenolphthalein, are now added, and the alkaline solution run in until a strong red coloration is produced. A pinch of mannite is then added, which bleaches the phenolphthalein coloration, and the alkali solution again run in to a faint indication, which if permanent on the addition of more mannite, may be taken as the reading point. About 1–2 grm. of mannite are necessary for a determination. The boro-mannite compound is sufficiently acidic to liberate iodine abundantly, but it appears to be a time reaction, and at the end of six hours only about 95 per cent of the theoretical amount (considering B_2O_3 as a bivalent acid) has been thrown out. The combination of boric acid and mannite liberates in the presence of iodide and iodate immediately only about one-half the iodine required on the theory that B_2O_3 under these conditions acts as a bivalent acid, or with the neutralizing power of metaboric acid, HOBO. When no mannite is present phenolphthalein gives an alkaline indication when only about one-half the amount of alkali theoretically necessary to form the metaborate, NaOBO, has been added. Obviously, then, the starch iodide coloration will not appear at all on the addition of mannite, if about one-half the free boric acid is first neutralized by the solution of alkali, and the remainder of the alkali immediately added to complete neutralization. The point at which the danger of the appearance of the iodide coloration on the addition of mannite has been passed, is roughly indicated before the mannite has been added by the appearance of the strong alkaline indication of phenolphthalein. This indicator would not need to be added at all, if the boromannite compound quickly and regularly liberated iodine from the iodide and iodate. The fact, however, that this compound of boric acid and mannite — as has been ascertained by experiment — liberates, on standing twelve hours, about 99 per cent of the theoretical amount of iodine, places the strength of this acid above that of citric or tartaric acid as investigated by Furry.* With phenolphthalein, however, the end reaction is sharp and the small amount of carbonate present in the standard solution of alkali is precipitated by the barium

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* Am. Chem. Jour., vi, 341.

chloride already in the solution. The calculation must therefore be based on the amount of free hydroxide in the standard solution of alkali used, according to the following representation:

$$B_2O_3 + 2NaOH = 2NaOBO + H_2O.$$

The best results and the most definite indications are obtained in cold solution of a volume not greater than 50 cm^3. This fact accords with the observations of Magnanini[*] that the relative electrical conductivity of the boro-mannite solution is decreased by dilution and elevation of the temperature. When silicates are present in solution, the silicondioxide is liberated by the excess of hydrochloric acid, and this oxide, whether in hydrous or anhydrous condition, neither affects the indication with iodine nor phenolphthalein, nor does it form with mannite a compound of acidic properties. Ammonium salts interfere with the indication given by phenolphthalein and may be removed by boiling with potassium hydroxide in excess, or an indicator used not affected by them.

To test the action of fluorides in the process, several experiments were made in which hydrofluoric acid (10 cm^3 of $\frac{n}{10}$ solution) was introduced into the solution containing salts of sodium, free hydrochloric and boric acids. Barium chloride was then added and the analysis for boric acid completed in the usual way without the accuracy of the results being in any way interfered with by the presence of hydrofluoric acid.

Table I contains the results of a series of analyses in which the boric acid was first drawn into a excess of sodium hydroxide, then estimated according to the method described.

The standard solutions of boric acid used contained, in A, 7.153 grm., and in B, 7.706 grm. per liter. The solution of free sodium hydroxide was 0.21427 normal.

Practical tests of the method upon specimens of crude calcium borate and colemanite are recorded in Table II and Table III.

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[*] Gaz. chim. ital., xx, 428, and xxi, 134.

TABLE I.

	Exp.	B_2O_3 Sol. taken.	NaOH Sol. required.	B_2O_3 taken.	B_2O_3 found.	Errors on B_2O_3.
		cm_3	cm_3.	grm.	grm.	grm.
A	(1)	21.95	21.02	0.1571	0.1577	0.0006+
	(2)	20.68	19.65	0.1479	0.1474	0.0005–
	(3)	20.73	19.63	0.1483	0.1473	0.0010–
B	(4)	23.05	23.71	0.1776	0.1777	0.0001+
	(5)	23.10	23.80	0.1780	0.1783	0.0003+
	(6)	22.76	23.35	0.1754	0.1750	0.0004–
	(7)	24.08	24.78	0.1855	0.1857	0.0002+
	(8)	22.00	22.50	0.1695	0.1686	0.0009–
	(9)	20.78	21.28	0.1601	0.1595	0.0006–

TABLE II.

ANALYSIS OF CRUDE BORATE OF LIME.

Exp.	Ca borate taken.	B_2O_3 found.	B_2O_3 in %.
	grm.	grm.	
(1)	0.4016	0.2289	56.99
(2)	0.4044	0.2302	56.92
(3)	0.4000	0.2285	57.11

TABLE III.

ANALYSIS OF COLEMANITE.

Exp.	Mineral taken.	B_2O_3 found.	% B_2O_3.	Average.
	grm.	grm.		
(1)	0.4034	0.2064	51.15	50.99%
(2)	0.4070	0.2069	50.80	
(3)	0.6004	0.3054	50.86	
(4)	0.6006	0.3056	50.89	
(5)	0.5059	0.2592	51.24	
(6)	0.5092	0.2592	50.89	

The finely-ground minerals were dissolved in hydrochloric acid and the analyses proceeded with as described above.

An analysis for boric acid by this process can be completed in five minutes and the results are obviously accurate within the limits of ordinary analysis.

The usually interfering substances, fluorine, silica, and carbon dioxide, have no detrimental influence on the results of this process.

XXIV

THE CONSTITUTION OF THE AMMONIUM MAGNESIUM PHOSPHATE OF ANALYSIS.

BY F. A. GOOCH AND MARTHA AUSTIN.*

IN a recent paper from this laboratory † it has been shown that the presence of ammonium chloride or other ammonium salt is necessary in the precipitation of manganese as the ammonium manganese phosphate by microcosmic salt in order that the precipitate may have the ideal constitution represented by the symbol NH_4MnPO_4.

It was also shown that the solvent effect of the ammonium chloride upon the precipitated ammonium manganese phosphate is not marked when an excess of the precipitant is present in solution.

The relations disclosed in this paper suggest that the chemical constitution of the precipitate rather than mechanical contamination and varying solubility — the explanations generally accepted, and, indeed, advocated by one of us in a former paper ‡ — may be responsible for observed variations in the weight of the residue derived by the ignition of the similar salt of magnesium, the ammonium magnesium phosphate, precipitated by an excess of a soluble phosphate from the solution of a magnesium salt, or from the solution of a soluble phosphate by an excess of a magnesium salt.

Precipitation by Excess of the Soluble Phosphate.

The precipitation of the magnesium salt by an excess of the soluble phosphate was first studied. For this work a solution of pure magnesium nitrate was prepared by dissolving the

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* From Am. Jour. Sci., vii, 187.

† Am. Jour. Sci., vi, 233. This volume, p. 121.

‡ Am. Chem. Jour., i, 391.

pure magnesium oxide of commerce in a slight excess of pure hydrochloric acid and boiling with more magnesium oxide. After filtering off the excess of magnesium oxide and any trace of iron or members of the higher groups, the solution was precipitated by ammonium carbonate, the precipitate was washed by repeated boilings and filtrations until silver nitrate gave no precipitate in the solution acidified with nitric acid. This precipitated carbonate was nearly dissolved in nitric acid and the solution was boiled with an excess of the carbonate (for the purpose of removing traces of barium, strontium, and calcium) filtered, and diluted to definite volume. The evaporation of a definite volume of the solution and strong ignition of the residue would be a most natural method of establishing a standard of the solution, were it not for the fact, pointed out by Richards and Rogers,[*] that the oxide of magnesium retains on ignition occluded nitrogen and oxygen enough to increase its weight sensibly. For this reason the nitrate was converted to the sulphate and weighed as such — either by evaporating to dryness in a weighed platinum crucible a definite volume of the solution, igniting as oxide, and changing to the sulphate by heating with sulphuric acid; or, by evaporating the magnesium nitrate directly with an excess of sulphuric acid of half strength. In this treatment the excess of acid was removed by heating the platinum crucible upon a porcelain ring or triangle so placed within a porcelain crucible that the bottom and walls of the inner crucible were distant about one centimeter from the bottom

TABLE I.

$MgSO_4$ obtained by converting ignited MgO into the sulphate.	$MgSO_4$ obtained directly from 50 cm^3 $Mg(NO_3)_2$.	Theoretical amount of MgO in $MgSO_4$.
grm.	grm.	grm.
0.5748	. . .	0.1924
0.5739	. . .	0.1923
. . .	0.5741	0.1922
. . .	0.5750	0.1925

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[*] Amer. Chem. Jour., xvi, 567.

and walls of the outer crucible. The excess of acid is easily removed in this way, and the outer crucible may be heated to redness without danger of breaking up the magnesium sulphate. The results of this work, taking O = 16, Mg = 24.3, N = 14.03, S = 32.06, are given in the accompanying table.

The magnesium oxide obtained by direct ignition of the nitrate weighed on the average about 0.0010 grm. more than the oxide theoretically present in the weighed sulphate from equal portions of the solution.

Before proceeding to study possible chemical effects of ammonium chloride in determining the constitution of the ammonium magnesium phosphate, it is obviously necessary to define the extent to which the ammonium salt may exert a solvent action in presence of the precipitant. Fresenius estimated that ammonium magnesium phosphate is soluble in 15293 parts of cold water, but the method of investigation employed did not entirely preclude the possibility of counting as ammonium magnesium phosphate soluble material included and held in the original precipitate.* According to Kissel † the phosphate, which dissolves in a mixture of ammonia and water in the proportion of 0.0040 grams to the liter and in the proportion of 0.0110 grams to the liter in a similar mixture containing also 18 grm. of ammonium chloride, is practically insoluble in the latter mixture if an excess of magnesia mixture be added; and Heintz‡ showed that the effect of adding an excess of sodium phosphate in the solution is similar.

So far as appears, no quantitative experiments have been recorded in which the behavior of a mixture of ammonium chloride and magnesium salt and an insoluble phosphate in a solution only slightly ammoniacal has been tested, though as a matter of convenience the use of faintly ammoniacal solutions and faintly ammoniacal washwater is to be preferred to the mixture of strong ammonia and water [1 : 3] ordinarily employed. As a preliminary step, therefore, in the work to be

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* Fresenius, 6te Aufl., p. 805.

† Zeitschr. anal. Chem., viii, 173.

‡ Zeitschr. anal. Chem., ix, 16.

described, experiments were made to find how small an amount of magnesium could be detected in solution by precipitating with microcosmic salt, either alone or in presence of ammonium chloride in faintly ammoniacal solutions. The ammonium chloride used for these tests (as well as in the similar quantitative work following) was purified by boiling with a faint excess of ammonia, filtering, digesting twelve hours with microcosmic salt, and filtering again. The results are given in Table II.

TABLE II.

Weight of MgO taken as the nitrate.	$H(NH_4)NaPO_4 \cdot 4H_2O$ taken.	Volume.	NH_4Cl taken.	Opalescent precipitation.
grm.	grm.	cm^3	grm.	
0.0008	1.75	100	. .	Marked.
0.0003	1.75	500	. .	Marked.
0.0008	1.75	100	10	Marked.
0.0003	1.75	500	10	Marked.
0.0003	1.75	500	30	Faint.
0.0001	1.75	100	. .	Marked.
0.0001	1.75	100	10	Marked.
0.0001	1.75	500	10	Faint.
0.0001	1.75	500	60	Faint.

The results of these tests show that even so little as 0.0001 grm. of magnesium oxide may be detected in five hundred cubic centimeters of faintly ammoniacal water containing as much as sixty grams of ammonium chloride.† It is plain that strongly ammoniacal liquids are entirely unnecessary in the precipitation of the ammonium magnesium phosphate under the conditions. In nearly all the experiments to be detailed use was made, therefore, of faintly ammoniacal solutions and wash-water.

In Table III are given the results obtained in a study of the effects of varying proportions of ammonium chloride and the soluble phosphate upon the constitution of the precipitate. All precipitates were gathered upon asbestos in the filtering

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† It was found also, incidentally, that the presence of reasonable amounts of ammonium oxalate (100 cm^3 of the saturated solution) does not interfere with the precipitation of the ammonium magnesium phosphate by microcosmic salt.

crucible, washed in faintly ammoniacal water, and ignited as usual. In every case the precipitation was practically complete; for, upon allowing the filtrates with the wash-water to stand for several days after further addition of microcosmic salt, nothing but insignificant traces of a precipitate — not exceeding 0.0001 grm. — ever appeared. In the experiments of section A precipitations were made in the cold by the action of microcosmic salt in considerable excess upon the solutions of magnesium nitrate containing varying amounts of ammonium chloride. In experiments (1) to (5) the liquid was made faintly ammoniacal after the addition of the precipitant and the precipitate was filtered off immediately after complete subsidence; in experiments (6) to (10) the precipitate first

TABLE III.

Exp.	$Mg_2P_2O_7$ corresponding to $Mg(NO_3)_2$ taken.	$Mg_2P_2O_7$ found.	Error in terms of $Mg_2P_2O_7$.	Error in terms of MgO.	NH_4Cl present.	$HNaNH_4PO_4 \cdot 4H_2O$ used.	Volume.
			A.				
	grm.	grm.	grm.	grm.	grm.	grm.	cm^3.
(1)	0.5311	0.5418	0.0107+	0.0038+	—	2.5	150
(2)	0.5311	0.5462	0.0151+	0.0057+	2	2.5	150
(3)	0.5311	0.5408	0.0097+	0.0035+	2	2.5	150
(4)	0.5311	0.5500	0.0189+	0.0068+	60	2.5	250
(5)	0.5311	0.5520	0.0209+	0.0075+	60	2.5	250
(6)	0.5311	0.5345	0.0034+	0.0012+	*	2.5	150
(7)	0.5311	0.5371	0.0060+	0.0022+	*	2.5	150
(8)	0.5311	0.5384	0.0073+	0.0026+	*	2.5	150
(9)	0.5311	0.5386	0.0075+	0.0027+	*	2.5	150
(10)	0.5311	0.5415	0.0104+	0.0037+	*	2.5	150
			B.				
(11)	0.5311	0.5312	0.0001+	0.0000	*—	2.5	150,100
(12)	0.5311	0.5311	0.0000	0.0000	*—	2.5	150,100
(13)	0.5311	0.5346	0.0035+	0.0013+	2 + 2	2.5	150,100
(14)	0.5311	0.5348	0.0037+	0.0014+	2 + 2	2.5	150,100
(15)	0.5311	0.5383	0.0072+	0.0026+	5 + 5	2.5	150,100
(16)	0.5311	0.5368	0.0057+	0.0021+	5 + 5	2.5	150,100
(17)	0.5311	0.5376	0.0065+	0.0023+	10 + 10	2.5	200,100
(18)	0.5311	0.5395	0.0084+	0.0030+	10 + 10	2.5	200,100
(19)	0.5311	0.5396	0.0085+	0.0031+	60 + 5	2.5	250,100
(20)	0.5311	0.5389	0.0078+	0.0028+	60 + 5	2.5	250,100

* Probably less than 1 grm.

thrown down was redissolved in a very little hydrochloric acid and reprecipitated by dilute ammonia (the operation being repeated several times) with a view to improving the crystalline condition of the precipitate, and this treatment introduced, of course, a small amount of ammonium chloride, probably less than a gram. It will be observed that errors of excess appear in all of these determinations, those being the greatest in the experiments in which the largest amounts of the ammonium salt were present.

In the experiments of section B the manipulation was so changed that the supernatant liquid was poured off (through the filtering crucible which was to be used subsequently to collect the phosphate) after the precipitate had subsided and the insoluble phosphate was dissolved in hydrochloric acid and brought down again, after dilution, by the addition of a faint excess of dilute ammonia. By thus removing the supernatant liquid after the first precipitation, the excess of the precipitant and the amounts of ammonium chloride orginally present were reduced to relatively low limits, so that their effects in the reprecipitation were at a minimum, and by adding varying amounts of ammonium chloride, or none at all, before the reprecipitation, it became possible to demonstrate the individual effect of that reagent apart from that of an excess of the microcosmic salt. It will be noted that in experiments (11) and (12), in which no ammonium salt was added after the decantation from the first precipitate, the results are ideal, and that the errors of excess advance as the amounts of ammonium salt present in the final precipitation increase. The quantity of the ammonium salt present during the first precipitation does not influence the error in the final precipitation unless it is so large that a simple decantation of the supernatant liquid would naturally leave an appreciable amount of it to act when the second precipitation takes place.

It is plain that the errors of excess which appear when either the ammonium chloride or the soluble phosphate is present in considerable amount, must be due either to mechanical inclusion on the part of the highly crystalline precipitate, or to variation in the ammonium magnesium phosphate from the ideal constitution toward a condition represented by a phosphate richer in ammonia and correspondingly deficient in magnesium. If any appreciable amount of the ammonium chloride present were held by the precipitate, it would naturally be represented by magnesium chloride after ignition, but, in no one of these experiments, even in those dealing with sixty grams of ammonium chloride, did the residue, after dissolving in nitric acid, give with silver nitrate evidence of the presence of more than a mere unweighable trace of chloride. A special experiment, moreover, in which an attempt was made to determine the silver chloride precipitated from the solution in nitric acid of an unignited precipitate thrown down by microcosmic salt in presence of sixty grams of ammonium chloride, confirms this conclusion: 'the precipitate was unweighable. If ammonium chloride present in the solution to so great an amount is not included in the precipitate in significant quantity, it would seem to be unnatural that the microcosmic salt should be included mechanically in any very great amount. But unless the microcosmic salt was mechanically included, the increase in weight must be due to the chemical influence of the reagents — that is, to the production of a phosphate rich in ammonium and deficient in magnesium. Berzelius* recognized the existence of such a phosphate of magnesium; but Wach† in following the work of Berzelius, failed to find it. It would be natural to expect its formation, if ever, when the precipitating phosphate is in excess and ammonium salts are present in abundance, with free ammonia. Obviously the natural effects of all these reagents would be toward the production of a salt holding more ammonia and more phosphoric pentoxide for a given amount of magnesium. The results of the table seem to point strongly to such tendencies, and, by inference, toward the existence of such a compound. Thus in experiments (11) and (12), in which the

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* Berzelius, Jahresbericht, 3. Jahrgang (1824), übersetzt von C. G. Gmelin, s. 92.

† Schweigger, 1830, Band 29, s. 265.

greater part of this excess of microcosmic salt was removed by decantation before the second precipitation, while no ammonium chloride was present excepting the small amount made by the solution and reprecipitation of the first precipitate, the error is practically nothing. In experiments (13) and (14), (15) and (16), (17) and (18), all similar to (11) and (12) excepting that ammonium chloride was present, the average errors (+0.0036 grm. in terms of magnesium phosphate, +0.0064 grm., +0.0074, respectively) increase as the ammonium chloride is increased in the final precipitation. In experiments (19) and (20), in which the ammonium chloride amounted to sixty grams in the first precipitation and to five grams in the second in addition to the amount that would naturally remain after decanting the strong solution of the former precipitation, the similarity of this error (+0.0082 in the mean) to that of the experiments in which smaller amounts of the ammonium chloride were used throughout goes to show that only the amount of ammonium salt present in the final precipitation counts. Further, a comparison of corresponding experiments of A and B shows very plainly that the treatment which involves the removal of the large part of the microcosmic salt, the solution of the precipitate, and reprecipitation tends to reduce the higher indications. Thus, for example the error in (2) and (3) is +0.0124 gram in terms of magnesium pyrophosphate, while in (13) and (14), similarly carried out except the decantation of the excess of the precipitant, solution and reprecipitation, the error is +0.0036 grm.

The special influence of free ammonia during precipitation, was investigated in the following experiments. Definite volumes of the magnesium nitrate solution were drawn from a burette into a platinum dish, ammonium chloride — 10 grm. — was added, the magnesium was brought down by dilute ammonia in presence of microcosmic salt, and strong ammonia equal to one-third the volume of the solution was added. The solutions, after standing, were filtered off on asbestos under pressure in a perforated crucible, and the precipitates were washed with ammonia diluted to the proportion of three parts of water to one of ammonia, dried after moistening with a drop of saturated solution of ammonium nitrate, ignited and weighed. The results are given in experiments (1) and (2) of Table IV. In these determinations the mean error reaches +0.0198 grm. in terms of magnesium pyrophosphate; while in experiments (3) and (4), made similarly excepting that the supernatant liquid was decanted from the precipitate first thrown down, the precipitate dissolved in hydrochloric acid, and after dilution reprecipitated by dilute ammonia immediately supplemented by enough strong ammonia to make one-fourth the volume of the entire solution, the error amounts in the mean to +0.0061 in terms of the pyrophosphate.

TABLE IV.

Exp.	$Mg_2P_2O_7$ corresponding to $Mg(NO_3)_2$ taken.	$Mg_2P_2O_7$ found.	Error in terms of $Mg_2P_2O_7$.	Error in terms of MgO.	NH_4Cl present.	$HNaNH_4PO_4.4H_2O$ used.	Volume.
	grm.	grm.	grm.	grm.	grm.	grm.	cm^3
(1)	0.5311	0.5503	0.0192+	0.0069+	10	2.5	200
(2)	0.5311	0.5505	0.0194+	0.0070+	10	2.5	200
(3)	0.5311	0.5398	0.0082+	0.0029+	10, —	2.5	200,100
(4)	0.5311	0.5351	0.0040+	0.0017+	10, —	2.5	200,100

In experiments (1) and (2) the precipitate was influenced by an excess of microcosmic salt, ammonium chloride, and free ammonia in large amount; in experiments (3) and (4), by decanting in the manner previously described, by dissolving the precipitate, and reprecipitating, the effects of an excess of microcosmic salt and ammonium chloride are reduced to a minimum, and, in a comparison of the results with those of experiments (11) and (12) of Table III the tendency of the free ammonia comes to view. The results discussed seem certainly to point to a general tendency on the part of free ammonia, ammonium choride and excess of the phosphate to produce a salt rich in ammonia and deficient in magnesium, which for a definite amount of magnesia precipitated must leave upon ignition a residue weighing more than the normal phosphate.

If it be assumed that a salt of the symbol $(NH_4)_4Mg(PO_4)_2$

—the next natural step to the normal salt, NH_4MgPO_4—is present in the precipitate, the residue which such a salt would leave upon ignition would be the metaphosphate $Mg(PO_3)_2$. From the relations of the symbols for magnesium pyrophosphate and magnesium metaphosphate the weight of the residue obtained, and the weight of the pyrophosphate theoretically derivable from the weight of magnesium salt used, it is possible, of course, to calculate the proportionate amounts of pyrophosphate and metaphosphate present in any ignited residue. Proceeding in this manner, it appears that, in order to account for the variations noted, it is necessary to assume the presence in many cases of very considerable amounts of the metaphosphate. Thus, in the case of those results obtained according to the usually accepted method of precipitating and washing with strongly ammoniacal liquids, viz., in experiments (1) and (2) of Table IV, the proportion of metaphosphate needed to account for the observed error reaches ten per cent.

Precipitation by Excess of the Magnesium Salt.

The relations which obtain in the reverse process of precipitation—the action of an excess of the magnesium salt upon a soluble phosphate—were studied in experiments to be described. A solution of pure hydrogen disodium phosphate was prepared by carefully recrystallizing the pure salt of commerce five times from distilled water in a platinum dish, dissolving the crystals, and diluting to definite volume. The standard of the solution was established by evaporating to dryness in a weighed platinum crucible known volumes of the solution, igniting the residue and weighing the sodium pyrophosphate. Magnesia mixture, the precipitant, was prepared by dissolving fifty-five grams of magnesium chloride in as little water as possible and filtering, mixing with this solution twenty-eight grams of ammonium chloride purified by treating it in strong solution with bromine water and a slight excess of ammonia, filtering, diluting to one liter, and, after standing for some hours, filtering again.

The tests of the following table show that the precipitation of a soluble phosphate by the magnesia mixture is practically complete in faintly ammoniacal solutions even when very dilute and charged with large amounts of ammonium chloride, provided the magnesia mixture is present in sufficiently large excess.

TABLE V.

P_2O_5 in HNa_2PO_4 taken.	Magnesia mixture.	Volume.	NH_4Cl.	Precipitation visible.
grm.	cm³	cm³	grm.	
0.0005	10	100	. .	At once throughout the liquid.
0.0005	50	100	. .	
0.0005	10	100	10	"
0.0005	10	200	60	"
0.0001	50	250	60	"
0.0001	10	100	. .	"
0.0001	10	100	10	"
0.0001	50	200	10	"
0.0001	10	250	60	"
0.0001	50	800	60	After settling out.
0.0001	50	500	60	"

This conclusion was further substantiated by an actual test (by the molybdate method) of the ignited residue, obtained by evaporating a filtrate from ammonium magnesium phosphate (equivalent to 0.8614 grm. of the pyrophosphate) precipitated by a faintly ammoniacal solution of magnesia mixture in presence of 60 grm. of ammonium chloride, which gave a precipitate of ammonium phosphomolybdate yielding 0.0002 grm. of magnesium pyrophosphate. It is evident, therefore, that any considerable deficiencies of weight of the magnesium phosphate obtained by precipitating equal amounts of a soluble phosphate by magnesia mixture in presence of varying amounts of ammonium chloride, cannot be attributed to varying solubility of the magnesium phosphate under changing proportions of the ammonium chloride.

The results recorded in section A of Table VI were obtained by treating definite volumes of the pure solution of hydrogen disodium phosphate with magnesia mixture, in slight excess above the amount required to bring down the phosphate, and making the solution distinctly ammoniacal. After thorough subsidence, the precipitate was filtered off on asbestos under pressure in a perforated platinum crucible, washed in water faintly ammoniacal, dried, ignited and weighed. In experiments (1), (5) and (6), only the ammonium chloride present in the magnesia mixture was used; in the other cases weighed portions were added. In the experiments of section B, the precipitate was dissolved in hydrochloric acid after filtering off the supernatant liquid, brought down again in dilute solution by ammonia in distinct excess, and thereafter treated as in the experiments of section A. The experiments of section C were conducted similarly to (1), (5) and (6) of A excepting that the magnesium mixture was introduced into the am-

TABLE VI.

Exp.	$Mg_2P_2O_7$ corresponding to HNa_2PO_4 taken.	$Mg_2P_2O_7$ found.	Error in terms of $Mg_2P_2O_7$.	Error in terms of P.	Volume.	NH_4Cl in magnesia mixture.	NH_4Cl added.	$MgCl_2 6H_2O$ in magnesia mixture.
				A				
	grm.	grm.	grm.	grm.	cm^3	grm.	grm.	grm.
(1)	0.8615	0.8613	0.0002−	0.00005−	150	1.68	. . .	3.3
(2)	0.8615	0.8615	0.0000	0.00000	200	1.68	20	3.3
(3)	0.8615	0.8602	0.0013−	0.00036−	200	1.68	20	3.3
(4)	0.8615	0.8561	0.0054−	0.00151−	300	1.68	60	3.3
(5)	0.0852	0.0862	0.0010+	0.00028+	100	0.28	. . .	0.55
(6)	0.0852	0.0866	0.0014+	0.00039+	100	0.28	. . .	0.55
(7)	0.0852	0.0847	0.0005−	0.00014−	200	0.28	20	0.55
(8)	0.0852	0.0830	0.0022−	0.00062−	200	0.28	20	0.55
(9)	0.0852	0.0811	0.0041−	0.00115−	300	0.28	60	0.55
				B				
(10)	0.8111	0.8114	0.0003+	0.00008+	150,100	1.68	. . .	3.3
(11)	0.8615	0.8613	0.0002−	0.00006−	150,000	1.68	. . .	3.3
(12)	0.8615	0.8578	0.0037−	0.00103−	200,100	1.68	. ,20	3.3
(13)	0.8615	0.8487	0.0128−	0.00358−	200,100	1.68	. ,60	3.3
(14)	0.0852	0.0855	0.0003+	0.00008+	100,100	0.28	. . .	0.55
(15)	0.0852	0.0656	0.0004+	0.00011+	100,100	0.28	10, .	0.55
(16)	0.0852	0.0853	0.0001+	0.00003+	150,100	0.28	10,10	0.55
(17)	0.0852	0.0819	0.0033−	0.00092−	200,100	0.28	20,20	0.55
				C				
(18)	0.8111	0.8071	0.0040−	0.00112−	120	1.4	. . .	2.75
(19)	0.8111	0.8052	0.0059−	0.00165−	120	1.4	. . .	2.75

moniacal solution of the phosphate drop by drop from a burette. The precipitations in A, B, and C were proved to be practically complete; for by treatment of the filtrates with more magnesia mixture and standing, no more than a trace — 0.0001 grm. at the most — of the phosphate was found. The ignited residues never contained more than a mere trace of chlorine.

While the results are not entirely regular, the tendency of the ammonium salt to produce errors of deficiency in proportion to its amount is plain if we compare among themselves the experiments of A upon similar amounts of phosphate, and then those of B upon similar amounts of phosphate among themselves; and by a comparison of corresponding results in A and B it is clearly shown that the presence of an excess of magnesia mixture tends to counteract more or less completely errors of deficiency due to the action of the ammonium chloride. These facts are quite in harmony with the hypothesis that the ammonium salt tends to produce an ammonium magnesium phosphate richer in ammonia and phosphoric acid and poorer in magnesia than the normal salt NH_4MgPO_4; for, though the production of such a salt in presence of an excess of the soluble phosphate compels the combination of a definite amount of magnesium with more than the normal amounts of phosphoric acid and ammonia (as was the case in the former series of experiments), when the supply of the soluble phosphate is limited the amount of magnesium associated with it must fall below the normal (as is the case in the present series of experiments). Moreover, the behavior of the precipitant is quite in accord with the hypothesis; for, though the influence of an excess of the soluble phosphate would naturally tend (as was observed) in the same direction as that of the ammonium salt and free ammonia, viz., to the production of the phosphate deficient in magnesium, the tendency of an excess of the magnesium salt must obviously be to increase the amount of magnesium in the phosphate, as was observed in the experiments of Table VI. The hypothesis fits the facts, therefore, on both sides; and, if precipitation is practically complete (as was shown to be the case throughout) the argument for the existence of an ammonium magnesium phosphate — poorer than the normal salt in magnesium — possibly the salt $(NH_4)_4Mg(PO_4)_2$ — seems to be strong.

The Practical Determination of Magnesium and Phosphoric Acid.

In determining magnesium by the procedure in ordinary use, the tendency is strong — as is shown in experiments (1) and (2) of Table IV — toward high plus errors, and the error is due to the combined effects of excesses of the precipitant, the ammonium salt, and free ammonia. The experiments (11) and (12) of B, Table III, show conclusively that such tendencies to error may be counteracted effectively by pouring off the supernatant liquid (through the filter to be used subsequently to collect the precipitate) as soon as the precipitate subsides, dissolving the phosphate in the least amount of hydrochloric acid, bringing it down again, after dilution, by a faint excess of ammonia, filtering (best, we think, on asbestos, under pressure), washing with faintly ammoniacal water, and igniting as usual.

Many years ago* a method of precipitating the ammonium magnesium phosphate was advocated by Professor Wolcott Gibbs, which consists, essentially, in boiling the solution of the magnesium salt with microcosmic salt and adding ammonia after cooling, and by which most exact analytical results were obtained. Our experience confirms completely that of Gibbs, and we desire to direct attention again to a procedure the advantage of which has, unfortunately, not been broadly known and accepted. Even in the presence of considerable amounts of ammonium chloride this process yields a phosphate of nearly ideal constitution if only the boiling be prolonged from three to five minutes. The greater part of the ammonium magnesium phosphate — about 90 per cent — forms in this process before free ammonia is added, and the ammonium which enters the phosphate thus formed is derived from the

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* Am. Jour. Sci. [3], v, 114.

microcosmic salt, which must become correspondingly acidic. Under these conditions, the tendency to form an insoluble ammonium magnesium phosphate richer in ammonia and poorer in magnesia than the normal salt, does not develop. In the process of Gibbs, as well as in the modified precipitation process in the cold, the use of the faintly ammoniacal solution and wash-water is sufficient and advantageous.

In the precipitation of a soluble phosphate by magnesia mixture the tendency of the precipitant and that of the ammonium salt are antagonistic, so that the effect of the latter salt is somewhat masked, though manifest. This opposition of effects has been noted by Mahon,* who, though regarding the actual attainment of an exact balance as uncertain, ventures the opinion that accurate results should be attainable by the careful relative adjustment of the proportions of the precipitant and ammonium salt. Mahon claims to get the best results by a very gradual addition of magnesia mixture to the ammoniacal solution of the phosphate containing about sixteen per cent of ammonium chloride, strong ammonia being added subsequently. From our observations, however, recorded in section C of Table VI, it appears that the method of introducing the magnesia mixture gradually into the ammoniacal phosphate (taken in quantity sufficiently large to give unmistakable indications) produces a precipitate deficient in magnesium and so leads to errors of deficiency in the phosphorus indicated. The use of strong ammonia, moreover, we have shown to be both unnecessary and disadvantageous. Our experiments go to show that good results may be expected when the solution of the phosphate containing a moderate excess of the magnesium salt and not more than five to ten per cent of ammonium chloride is precipitated by making it slightly ammoniacal, the precipitate being washed in slightly ammoniacal wash-water. In general, however, and especially when more ammonium chloride than this proportion, or more magnesium salt than twice the amount theoretically necessary, is present, it is safer to decant the supernatant liquid from the precipitate (through the filter to

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* Jour. Am. Chem. Soc., xx, 445.

be used subsequently to hold the phosphate), to dissolve the precipitate in a little hydrochloric acid, and reprecipitate by dilute ammonia, washing with faintly ammoniacal wash-water.

Since our first publication of the work described above, Neubauer* has called attention to the fact that the influence of ammonia and ammonium salts upon the constitution of the ammonium magnesium phosphate obtained in determining phosphoric acid had been previously pointed out by him in a paper † discussing methods for the estimation of that acid. We take pleasure, therefore, in conceding to Neubauer full priority in the observation of the effect which we have endeavored to overcome in the determination of magnesium and of phosphoric acid.

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* Zeitschr. anorg. Chem., xxii, 162.

† Zeitschr. anorg. Chem., ii, 45.

XXV

THE INFLUENCE OF HYDROCHLORIC ACID IN TITRATIONS BY SODIUM THIOSULPHATE WITH SPECIAL REFERENCE TO THE ESTIMATION OF SELENIOUS ACIDS.

BY JOHN T. NORTON JR.*

IN the method of Norris and Fay † for the iodometric determination of selenious acid, advantage is taken of a direct and unique action of sodium thiosulphate upon selenium dioxide in the presence of hydrochloric acid. Most excellent results are claimed for this method; but the explicit statement of the originators of the method, that the amount of hydrochloric acid present does not influence the result, provided the titration is made at the temperature of melting ice, is so extraordinary in view of generally accepted ideas in regard to the interaction of hydrochloric acid and sodium thiosulphate, as to suggest the necessity of careful investigation of this point.

Pickering,‡ in his investigation of the reaction between iodine and sodium thiosulphate, has shown that more iodine is required to oxidize the thiosulphate as the proportion of hydrochloric acid increases. He ascribed this effect to the formation of a sulphate, apparently, by the increased activity of the iodine, but the more rational explanation is that, although some sulphate is ultimately formed, the thiosulphate is first partially decomposed into free sulphur and

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* From Am. Jour., Sci. vii, 287.

† Am. Chem. Jour., vol. xviii, p. 703.

‡ Jour. Chem. Soc., vol. xxxvii, p. 135.

sulphur dioxide. Finkener* and Mohr† also mention the decomposing effect of free acid upon sodium thiosulphate.

The sodium thiosulphate used in the following experiments was taken in nearly decinormal solution and was standardized by running it into an approximately decinormal solution of iodine, the value of which had been determined by comparison with decinormal arsenious acid made from carefully resublimed arsenious oxide. In the experiments of Table I the solutions were stirred continuously and kept at a temperature of from 0° to 5° C., while the thiosulphate ran into the acidified liquid. The volume of the solution, though fixed at the beginning as given in the table was considerably increased during the operation by the melting of the ice. Titrations were conducted as rapidly as possible to avoid the separation of sulphur, which is likely to occur, especially when the acid and thiosulphate are present in large quantities. A perusal of the table shows that the influence of the hydrochloric acid upon the thiosulphate depends chiefly upon the amount of

TABLE I.

Volume of liquid at beginning of titration.	$Na_2S_2O_3$ approximately $\frac{n}{10}$ taken.	Volume of $\frac{N}{10}$ iodine used in titration.				
		HCl = none.		= 1 cm³.	= 5 cm³.	= 10 cm³.
cm³	cm³	cm³		cm³	cm³	cm³
100	30	30.25	mean = 30.22	30.75	30.76	31.20
200	30	30.22		30.21	30.56	31.40
300	30	30.20		30.22	31.03	30.90
400	30	30.21		30.20	30.20	30.55
500	30	30.20		30.20	30.21	30.55
100	25	25.29	mean = 25.27	25.32	25.98	25.70
200	25	25.28		25.84	25.40	25.45
300	25	25.29		25.41	25.38	25.83
400	25	25.27		25.24	25.30	25.63
500	25	25.22		25.23	25.40	25.30
100	20	20.15	mean = 20.15	20.17	20.83	20.28
200	20	20.20		20.18	20.27	20.23
300	20	20.21		20.15	20.20	20.17
400	20	20.20		20.10	20.27	20.07
500	20	20.10		20.10	20.17	20.18

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* Anal. Chem., 6. Aufl., p. 620.

† Titrirmethode, 6. Aufl., p. 279.

the thiosulphate present and afterwards upon the degree of dilution and its own absolute quantity. Thus when 30 cm³ of sodium thiosulphate were employed the effect of 10 cm³ of acid is marked at all dilutions within the range of the experiments; the effect of 5 cm³ of acid is inappreciable only at a dilution of from 400 to 500 cm³, and when 1 cm³ of acid is employed the effect is only perceptible at a volume of 100 cm³. When 25 cm³ of the thiosulphate were used the influence of the acid is less marked; for at a dilution of 500 cm³ the effect of 10 cm³ of acid is not seen, and 20 cm³ of the thiosulphate may be present at any dilution down to 100 cm³ in the presence of as much as 10 cm³ of the acid, and even considerably more, as experiments not included in the table indicated.

The slight discrepancies which appear occasionally in the table were due, no doubt, to unavoidable differences in the time of action.

This influence of time upon the reaction between sodium thiosulphate, iodine, and hydrochloric acid comes out clearly in the following series of experiments, in which the thiosulphate was run into the acidified water, cooled to a temperature of from 0 to 5° C. by means of ice, the solution being allowed to stand 5, 10, and 15 minutes. Sulphur was thrown down in nearly every case.

TABLE II.

Volume of the liquid at beginning of titration.	HCl (sp. gr. 1.12) present.	$Na_2S_2O_3$ approximately. $\frac{N}{10}$ taken.	Volume of $\frac{N}{10}$ iodine used in titration after standing.		
			5 minutes.	10 minutes.	15 minutes.
cm³	cm³	cm³	cm³	cm³	cm³
200	10	30	30.80	31.30	32.32
200	10	25	25.50	26.00	26.30
200	10	20	20.30	20.70	20.68

The results of the table emphasize sufficiently the necessity of proceeding as rapidly as possible with the titration of sodium thiosulphate by iodine in presence of hydrochloric acid, when the thiosulphate is present in considerable amount. As would be expected, the effect of temperature upon the reaction is also marked. In the following experiments the sodium thiosulphate was run into the acidified water, previously heated to the temperature indicated, and then titrated with iodine.

TABLE III.

Volume of liquid at beginning of titration.	HCl (sp. gr. 1.12) taken.	Temperature Centigrade.	$Na_2S_2O_3$ approximately. $\frac{N}{10}$ taken.	Volume of $\frac{N}{10}$ iodine used in titrations at different temperatures.
cm^3	cm^3	C.	cm^3	cm^3
400	10	6°	25	23.52
400	10	22°	25	23.78
400	10	34°	25	24.85
400	10	42°	25	24.5
400	10	54°	25	25
400	10	64°	25	26.1

From these results it is plain that the conditions under which considerable amounts of sodium thiosulphate are titrated in presence of hydrochloric acid must be carefully guarded when accuracy is a consideration. It is also apparent that in all cases the temperature should be reduced as nearly to 0° C. as possible and rapidity of titration by the iodine is an essential. So long as the thiosulphate present does not exceed 20 cm^3 of the $\frac{n}{10}$ solution, rapid titration in cold solution proceeds with fair regularity in presence of hydrochloric acid up to 10 cm^3 of the acid of sp. gr. 1.12. When, however, the amount of thiosulphate is greater than 20cm^3 of the $\frac{n}{10}$ solution, care as to the restriction of the acid and dilution of the solution becomes a necessity. Fortunately, in most analytical processes involving the use of the thiosulphate it is possible to add that reagent from the burette to the solution to be acted upon, so that it is destroyed normally as fast as it is introduced and the danger of interaction with the acid does not occur. In the process of Norris and Fay, however, the method involves the addition of an excess of the thiosulphate to the solution of selenious and hydrochloric acids, and thus the conditions prevail which demand care as to the relation of the acid, the thiosulphate and the degree of dilution. I have experimented, therefore, with this process under varying conditions.

The process of Norris and Fay for the iodometric determination of selenious acid consists briefly in treating the solution of that acid in ice water, in the presence of hydrochloric acid, with an excess of a $\frac{n}{10}$ solution of sodium thiosulphate and titrating back the excess of the thiosulphate with iodine. Four molecules of sodium thiosulphate act, apparently, upon one molecule of selenious acid according to a reaction which the authors propose to study.

The selenium dioxide used was made by dissolving presumably pure selenium in nitric acid and evaporating to dryness. The residue was then treated with water, and a little barium hydroxide was added to remove any sulphate which might be present. The solution was then filtered and the filtrate evaporated to dryness. The residue was mixed with four or five times its volume of dried pulverized pyrolusite, and the whole was put into a porcelain crucible and heated. The sublimate of selenium dioxide was carefully collected on a dry watch-glass and put into a drying bottle as quickly as possible. The pyrolusite prevents any reduction of the selenium dioxide to selenium and the product consisted of beautiful long white needles. This method of preparing the selenium dioxide, which has been used for some time in this laboratory, avoids contamination of the selenium dioxide by nitric acid or water, resulting from the decomposition of the latter, which would be possible in case this reagent were employed in the final sublimation, as is recommended by Norris and Fay. The hydrochloric acid used was of a sp. gr. 1.12, as recommended by the originators of the process. For the experiments of Table IV the dilution at the beginning was fixed at 400 cm^3, and this was increased in every case by the melting of the ice used to cool the liquid. A glance at the preceding part of this paper will show that at this degree of dilution the hydrochloric acid present has the least effect.

TABLE IV.

Exp.	Amount SeO_2 taken.	HCl (sp. gr. 1.12) taken.	Volume at beginning of titration.	Excess $Na_2S_2O_3$ employed.	SeO_2 found.	Error.	
	grm.	cm³	cm³	cm³	grm.	grm.	
(1)	0.0616	10	400	2.28	0.0625	0.0009+	
(2)	0.0628	10	400	7.11	0.0631	0.0006+	
(3)	0.0508	10	400	11.4	0.0511	0.0008+	
(4)	0.0587	10	400	12.8	0.0594	0.0007+	mean.
(5)	0.0807	10	400	15.8	0.0813	0.0006+	0.00005+
(6)	0.0638	10	400	20.85	0.0638	0.0005+	
(7)	0.0682	25	400	1.11	0.0685	0.0003+	
(8)	0.0779	25	400	1.85	0.0788	0.0009+	
(9)	0.0465	25	400	18.98	0.0469	0.0004+	

These results, while not so good as those obtained by Norris and Fay, are satisfactory and show that at this degree of dilution the process is accurate. These results accord closely with those contained in Table I. At a dilution of 400 cm³ or in the presence of only 20 cm³ of sodium thiosulphate in excess the hydrochloric acid present had no perceptible effect. Of course, it must be kept in mind that the hydrochloric acid acts only upon the excess of thiosulphate which is not taken up by the selenium dioxide. The slight constant plus error in these results cannot be accounted for by errors in the standards; they were all carefully determined. Another preparation of selenium dioxide was made, starting with pure selenium carefully precipitated by sulphurous acid, before putting it through the course of treatment previously described, and the results obtained by the action of the sodium thiosulphate recorded in Table V agree closely with those of the preceding table.

TABLE V.

Exp.	Amount SeO_2 taken.	HCl (sp. gr. 1.12.)	H_2O at beginning.	$Na_2S_2O_3$ in excess.	SeO_2 found.	Error.
	grm.	cm³	cm³	cm³	grm.	grm.
(1)	0.0562	10	400	9.52	0.0566	0.0004+
(2)	0.0651	25	400	11.20	0.0655	0.0004+

The next step was to determine the effect of diminishing the dilution and of varying the strength of acid. The following table gives the results of my experiments.

TABLE VI.

Exp.	Amount of SeO_2 taken.	Volume of H_2O at beginning.	HCl (sp. gr. 1.12).	Excess of $Na_2S_2O_3$.	SeO_2 taken.	Error.
	grm.	cm^3	cm^3	cm^3	grm.	grm.
(1)	0.1042	200	5	24.16	0.1041	0.0001–
(2)	0.0611	200	10	18.8	0.0611	0.0000
(3)	0.0850	200	10	21.9	0.0828	0.0022–
(4)	0.0757	200	25	18.07	0.0749	0.0008–
(5)	0.0540	200	25	21.02	0.0522	0.0018–
(6)	0.0674	800	5	10.04	0.0679	0.0005+
(7)	0.2416	400	5	15.9	0.2424	0.0008+

It is apparent that at the dilution of 200 cm^3 we run into difficulties, and the greater the excess of thiosulphate present the greater is the error. When the amount of sodium thiosulphate exceeds 20 cm^3 a reduction in the amount of acid to 5 cm^3 is plainly of advantage, as is shown in a comparison of Exps. (1), (3), and (5), and is not disadvantageous at larger dilutions and with smaller amounts of the thiosulphate, as shown in Exps. (6) and (7). The necessity of placing some limits on the method of Norris and Fay has now, I think, been established. The excess of the thiosulphate must be carefully regulated, as well as the temperature. If one has knowledge of the approximate amount of selenious acid in solution, this is not a matter of great difficulty, and things should be so arranged that no more than 20 cm^3 of the $\frac{N}{10}$ thiosulphate should ever be present in excess of the amount necessary to reduce the selenious acid. If this limit—amounting to 0.0400 cm^3 of SeO_2—is placed upon the thiosulphate, so much as 10 cm^3 of hydrochloric acid (sp. gr. 1.12) may be present without endangering the accuracy of the process, provided the solution is diluted to 400 cm^3 at the outset; if only 5 cm^3 of hydrochloric acid are present, the volume at the beginning may be reduced with safety to 200 cm^3. At all events, 5 cm^3 of the hydrochloric acid are amply sufficient to bring about the reaction between the thiosulphate and the selenium at any dilution within the range of my experiments. With these precautions taken, the process of Norris and Fay is simple, rapid, and accurate; without them, as the experimental results indicate, errors of considerable amount may enter.

According to the method of Muthmann and Shafer,* the determination of selenious acid is effected by the simple addition of potassium iodide to the acidulated solution of selenious acid, and the iodine set free is titrated with sodium thiosulphate. In this procedure the thiosulphate is taken up by the iodine as it is added to the solution, so that the danger of any action between the thiosulphate and the acid is out of the question. It was shown in a former paper from this laboratory † that this simple method is inaccurate on account of the incompleteness of reduction in the cold and in presence of the iodine evolved. In a later article also from this laboratory ‡ it was shown that selenium may be completely precipitated and determined with accuracy gravimetrically provided the amount of potassium iodide employed is enormously in excess of that theoretically required. This suggests naturally the trial of very large excesses of potassium iodide in the procees of Muthmann and Shafer. The details of experiments made in this manner are given in the following table.

TABLE VII.

Exp.	SeO_2 used.	KI.	Vol. of solution.	HCl (sp. gr. 1.12).	SeO_2 found.	Error.
	grm.	grm.	cm^3	cm^3	grm.	grm.
(1)	0.0553	10	150	10	0.0558	0.0005+
(2)	0.0574	5	150	10	0.0567	0.0007–
(3)	0.0683	5	150	10	0.0683	0.0000
(4)	0.0487	5	150	10	0.0484	0.0003–
(5)	0.2617	10	150	10	0.2589	0.0028–

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* Ber. Dtsch. chem. Ges., xxvi, 1008.

† Gooch and Reynolds, Am. Jour. Sci., l, 254. Volume I, p. 310.

‡ Peirce, Am. Jour. Sci., i, 1896, 416. Volume I, p. 365.

It is obvious that for small quantities of selenium dioxide the accuracy of the process is very much increased by the use of large amounts of iodide, though, of course, the difficulty in reading the end reaction due to the presence of precipitated red selenium still remains; but the process is still inaccurate when large amounts of selenium dioxide are employed.

XXVI

THE VOLATILIZATION OF THE IRON CHLORIDES IN ANALYSIS AND THE SEPARATION OF THE OXIDES OF IRON AND ALUMINUM.

BY F. A. GOOCH AND FRANKE STUART HAVENS.[*]

IT is well known that metallic iron is easily acted upon by an excess of chlorine at moderately elevated temperatures with the formation of ferric chloride, and that the product of the action of hydrochloric acid gas upon the metal is ferrous chloride. Out of contact with air, or moisture, both chlorides may be volatilized at appropriate temperatures — the ferric chloride below 200° C.; the ferrous chloride at a bright red heat. If water vapor, or oxygen, or air be present during the heating, both chlorides are partially decomposed with the formation of non-volatile residues, ferric oxide or ferric oxy-chloride.

Analytical processes involving the volatilization of iron at temperatures more or less elevated, in an atmosphere of chlorine or hydrochloric acid, have been the object of considerable attention. Thus, Fresenius,[†] Drown and Shimer,[‡] and Watts,[§] have heated crude iron in chlorine to remove the metal and leave the non-volatile constitutents; and Sainte-Claire Deville[‖] has employed hydrochloric acid to volatilize iron from mixtures of that metal with alumina (obtained by heating the mixed oxides of iron and aluminum in hydrogen according to Rivot),[¶] exposing the mixture, contained in a porcelain boat and placed within a porcelain tube, to the bright red heat of a charcoal furnace — an operation which was bettered by

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[*] From Am. Jour. Sci., vii, 370.

[†] Zeitschr. anal. Chem., iv, 72.

[‡] Jour. Inst. Min. Eng., viii, 513.

[§] Chem. News, xlv, 279.

[‖] Ann. Chim. [3], xxxviii, 23.

[¶] Ann. Chim. [3], xxx, 188.

Cooke's* use of a tube of platinum instead of the porcelain tube and a gas blowpipe in place of the charcoal furnace. Sainte-Claire Deville† showed, further, that ferric oxide may be converted to ferric chloride and volatilized at the heat of the charcoal furnace if the current of hydrochloric acid is sufficiently rapid; but the curious effect was observed that in a sufficiently limited current of the acid no chloride whatever was volatilized, while the amorphous oxide was converted to the highly crystalline oxide of the same composition—a phenomenon which gave rise to a theory of the natural formation of specular iron in volcanic regions.

Quite recently, Moyer ‡ has made record of an unsuccessful attempt (in the course of experimentation upon the volatility of certain chlorides at comparatively low temperatures) to convert ferric oxide completely to ferric chloride by the action of gaseous hydrochloric acid at about 200° C. At this temperature the greater part of the iron sublimed, but a residue remained, which, volatilizing neither on long heating at 200° nor upon considerable elevation of the temperature, proved upon examination to be ferrous chloride. In the experiments to be described we have acted with gaseous hydrochloric acid upon ferric oxide made by igniting the nitrate prepared from pure iron deposited electrolytically by high currents passing between electrodes of platinum in a strong solution of ammonio-ferrous sulphate. The oxide, contained in a porcelain boat, was heated within a roomy glass tube over a small combustion furnace. The hydrochloric acid (generated by dropping sulphuric acid into a mixture of strong hydrochloric acid and salt, and dried by calcium chloride) entered one end of the tube and passed out at the other through a water trap. In early experiments a high-reading thermometer was inserted through the stopper in the exit end of the tube so that its bulb was above and immediately adjacent to the boat carrying the oxide. In this way the actual temperatures of the vapors about the boat were fixed

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* Am. Jour. Sci., xlii, 78.

† Compt. rend., lii, 1264.

‡ Jour. Am. Chem. Soc., xviii, 1029.

with considerable accuracy; later, after a little experience in gauging the effect of the burners, it was found that the temperatures could be regulated very closely without actually depending upon the thermometer. We found, as did Moyer, that ferric oxide, submitted to the action of dry hydrochloric acid gas, volatilizes partially as ferric chloride at low temperatures — 180° to 200° C. — leaving ultimately a crystalline residue which does not change visibly when heated for an hour or two at 200°, or even at 500°, in the pure dry acid. According to our experience, this residue is generally slightly reddish or salmon-colored; but sometimes, especially after a second heating, the boat having been withdrawn from the tube or exposed to the atmosphere (and so to moisture), the residue is white. When it is white it dissolves in water, yields the characteristic reaction for a ferrous salt with potassium ferricyanide, gives no reaction with potassium sulphocyanide, and upon treatment in weighed amount with potassium permanganate destroys the amount of that reagent theoretically required for its oxidation upon the supposition that it is ferrous chloride. The slightly colored residue when treated with water yields a solution showing the reaction of a ferrous salt only, but when treated with hydrochloric acid and then tested shows the presence of a trace of iron in the ferric condition. Doubtless the coloration of the residue is due to an included trace of ferric oxide or oxychloride, which after exposure of the containing crystals to slight atmospheric action, is more easily reached in the second heating by the gaseous acid. The amount of residue is somewhat variable, but approximates under the conditions of our work to from five to ten per cent of the oxide taken: thus, in one typical experiment 0.1 grm. of ferric oxide left a residue which (withdrawn after cooling) weighed 0.0115 grm.

The greater portion of the ferric oxide volatilizes when submitted to the action of the gaseous acid at 200° quickly and abundantly in the form of the greenish vapor of ferric chloride, and if the operation is interrupted at this stage the residue which remains is nearly black, insoluble in water, slightly soluble in cold hydrochloric acid, and readily soluble in hot hydrochloric acid with the formation of ferric chloride. It is probably something analogous to the oxychloride which Rousseau * identifies as the product of the action of water upon ferric chloride at 275° to 300°. This dark residue yields to the action of the hydrochloric acid at 180° to 200° only slowly, but ultimately only the residue which is essentially ferrous chloride remains; thereafter little volatilization occurs within the range of temperature of our experimentation — 200° to 500°.

It is obvious that a reduction of iron in the ferric condition to iron in the ferrous condition takes place under the conditions of our work, and it in difficult to see how this can occur otherwise than by the direct dissociation of ferric chloride under the low partial pressure conditioned by the brisk current of hydrochloric acid gas. The temperature of formation, 180° to 200°, is far below that at which such dissociation is supposed to begin. Thus, Gruenewald and Meyer † found, after cooling, no evidence of the dissociation of ferric chloride which had been heated in the Victor Meyer vapor-density apparatus to 448° in contact or partial mixture with nitrogen; but ten per cent of the residue obtained by heating to 518° was in the ferrous condition. Friedel and Crafts,‡ however, did see crystals of ferrous chloride at 440° on the walls of a Dumas container filled with the vapor of ferric chloride and nitrogen, the former exerting a partial pressure of 0.75; while ferric chloride volatilized into an atmosphere of chlorine without evidence of dissociation. It seems rather surprising, therefore, to find so large a percentage of dissociation as that shown in our experiments at a temperature so low — 180° to 200°. Curiously, too, we find, on repeating the experiment of heating ferric oxide in gaseous hydrochloric acid, that if the temperature of the oxide is 450° to 500° when the brisk current of acid begins to act, the whole mass of oxide is converted and volatilizes without

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* Compt. rend., cxvi, 118.

† Ber. Dtsch. chem. Ges., xxi, 687.

‡ Compt. rend., cvii, 301.

residue. It is hardly to be supposed that the degree of dissociation at 450° to 500° can be less than that at 180° to 200°, and a test of the sublimate, after cooling, shows that it contains a ferrous salt. Plainly, ferrous chloride (formed by dissociation) has volatilized, and inasmuch as the ferrous chloride constituting the residue formed at 180° to 200° does not volatilize in the hydrochloric acid even at 500° it is plain that the volatility of the former is not determined by the presence of the latter. Apparently, the cause of the completeness of volatilization must be sought in its rapidity; and this is not an unreasonable hypothesis, if one considers that an action sufficiently rapid to keep above the boat an atmosphere of ferric chloride and its products of partial dissociation, might naturally provide the very condition which would be effective in counteracting the tendency of the residue to dissociate before it volatilizes. If this hypothesis is correct, it is plain that the introduction of chlorine gas, the active product of dissociation, into the atmosphere of hydrochloric acid ought to bring about the volatilization of the residue of ferrous chloride, formed at 180° to 200°, which refuses to volatilize in the acid alone. As a matter of fact, we find by experiment that if a little manganese dioxide is added to the contents of the generator, so that the hydrochloric acid may carry with it a little chlorine, every trace of ferric oxide is volatilized from the boat at 180° to 200°; and the residue of ferrous chloride found at 180° to 200° when the hydrochloric acid is used alone is likewise volatilized at the same temperature, when the admixture of chlorine is made.

These facts, that ferric oxide is completely volatile in hydrochloric acid gas applied at once at a temperature of 450° to 500° C., and at 180° to 200° if the acid carries a little chlorine, open the way to many analytical separations of iron from substances not volatile under these conditions. In the experiments of the following table we have applied these methods to the separation of intermixed iron and aluminum oxides. The ferric oxide employed was made, as before, by ignition of the nitrate prepared from iron deposited electrolytically by a strong current passing between platinum electrodes in a solution of ammonio-ferrous sulphate.* The aluminum oxide was made by igniting to a constant weight the carefully washed hydroxide precipitated by ammonia from a pure hydrous chloride thrown down from the solution of a commercially pure chloride by hydrochloric acid.† The hydrochloric acid gas was made by dropping sulphuric acid into strong hydrochloric acid mixed with salt, and a little manganese dioxide was added when the mixture with chlorine was desired. The experimental details are given in the table.

Fe_2O_3 taken.	Al_2O_3 taken.	Al_2O_3 found.	Error.	Time.	Temperature.	Atmosphere.
grm.	grm.	grm.	grm.	hrs.	C°.	
0.1000	. . .	. . .	0.0000	½	450–500	HCl
0.2000	. . .	. . .	0.0000	1	450–500	HCl
0.1020	0.1015	0.1015	0.0000	½	450–500	HCl
0.2145	0.1006	0.1008	0.0002+	¾	450–500	HCl
0.1000	. . .	. . .	0.0000	¾	180–200	$HCl + Cl_2$.
0.1000	0.1032	0.1032	0.0000	¾	180–200	$HCl + Cl_2$.
0.1072	0.1018	0.1015	0.0002+	1	180–200	$HCl + Cl_2$.
0.2045	0.1032	0.1033	0.0001+	1½	180–200	$HCl + Cl_2$.
0.1050	0.1028	0.1019	0.0004–	½	450–500	$HCl + Cl_2$.
0.2008	0.1007	0.1006	0.0001–	¾	450–500	$HCl + Cl_2$.
. . .	0.1087	0.1087	0.0000	1	450–500	$HCl + Cl_2$.

The residual alumina tested in several experiments by fusion with sodium carbonate, solution in hydrochloric acid, and addition of potassium sulphocyanide gave no indication of the presence of iron.

The separation of the iron is obviously complete at 450° to 500° when the mixed oxides are submitted at once to the action of hydrochloric acid gas, or at 180° to 200° when

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* The use of an anode of commercially pure iron wire naturally facilitates the operation, but in our experience the deposit thus obtained is likely to carry traces of impurity. In an attempt, too, to prepare pure ferric oxide from the oxalate thrown down out of ferrous sulphate with all precautions, the material obtained still held traces of silica, and possibly alumina, amounting to 0.0004 grm. in 0.1 grm. of the oxide.

† From Am. Jour. Sci., ii, 416. This volume, p. 20.

chlorine is mixed with the hydrochloric acid. Plainly, the extremely high temperatures employed by Deville are unnecessary if the mixed oxides are submitted at once to the action of hydrochloric acid at 450° to 500° without previous gentle heating in the acid atmosphere. We prefer, however, to use the mixture of chlorine and hydrochloric acid, not only because the temperature of the reaction is lower, but because it needs no regulation, while the danger of error arising from the liability of ferric chloride to dissociate, or from deficiency of oxidation in the oxide treated, or from mechanical loss due to rapid volatilization, is avoided.

XXVII

THE TITRATION OF OXALIC ACID BY POTASSIUM PERMANGANATE IN PRESENCE OF HYDROCHLORIC ACID.

BY F. A. GOOCH AND C. A. PETERS.*

LÖWENTHAL and LENSSEN † were the first to show that the titration of a ferrous salt by potassium permanganate in the presence of hydrochloric acid, according to the process of Margueritte ‡ is vitiated by the evolution of chloride outside the main reaction, and to point out that a remedy for the difficulty is to be found in the titration of the ferrous salt in divided portions, other equal volumes of the ferrous solution being added to the liquid in which the first titration is accomplished until the amount of iron indicated by successive titrations becomes constant.

Kessler § showed the restraining influence of certain sulphates, of manganous sulphate in particular, upon the irregular and undesirable interaction of the permanganate and hydrochloric acid, and Zimmermann, ‖ in apparent ignorance of Kessler's forgotten proposal, advocated the introduction of a manganous salt, best the sulphate, into the ferrous salt to be determined, thus accomplishing the purpose of the empirical procedure of Löwenthal and Lenssen.

The tendency toward evolution of chlorine in the oxidation of a ferrous salt by permanganate, as compared with the absence of such tendency in the similar oxidation of oxalic acid, in presence of hydrochloric acid, was explained by

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* From Am. Jour. Sci., vii, 461.

† Zeitschr. anal. Chem., i, 329.

‡ Ann. Chim. Phys. [3], xviii, 244.

§ Ann. Phys., cxciv, 48 (1863); cxcv, 225 (1863).

‖ Ann. Chem., ccxiii, 302.

Zimmermann on the hypothesis that an oxide of iron higher than ferric oxide is formed as an intermediate product, and that this unstable oxide is sufficiently active to break up hydrochloric acid as well as to oxidize more of the ferrous salt. Quite recently, Wagner [*] finds explanation of the sensitiveness of the hydrochloric acid solution of the ferrous salt in the probable formation of chlor-ferrous acid (analogous to chlor-platinic and chlor-auric acids), which suffers oxidation more readily than hydrochloric acid under the action of the permanganate. The protective influence of the manganous salt turns apparently, as Zimmermann suggested, upon the initiation of Guyard's reaction, according to which the permanganate and manganous salt interact to form a higher oxide of manganese of a constitution approaching the dioxide more or less closely — this oxide being capable of oxidizing the ferrous salt, but slow to act upon the hydrochloric acid, or the chlor-ferrous acid of Wagner. According to Volhard,[†] the reaction of Guyard is favored and hastened by heat and concentration of the solution, while it is delayed by acidity and dilution; but even in solutions containing very little manganous salt and a considerable quantity of free acid the faint rose color developed by the careful addition of permanganate ultimately vanishes until every trace of the manganous salt is precipitated. When a considerable amount of the salt is present interaction follows immediately the introduction of the permanganate. Zimmermann advocates the use of 4 grams of manganous sulphate uniformly in titrations of a ferrous salt by permanganate, a procedure to which Wagner gives acquiescence, though pointing out that a ninth of that amount is all that he finds to be necessary. The excess of the manganous salt can do no harm so long as the higher oxide, the product of interaction of the manganous salt and the permanganate, is immediately reduced by even traces of a ferrous salt, and this appears to be the case at least within the limits proposed by Zimmermann and Wagner. Thus we

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[*] **Massanalytische Studien, Habilitationsschrift, Leipzig, 1898.**

[†] **Ann. Chem., cxcviii, 318, 1879.**

find, as shown in results of the accompanying table, that so much as five grams of the sulphate may be present in 135 cm³ of the liquid, containing about 5 cm³ of hydrochloric acid of full strength, without interfering with the regularity of the titration; and the effect is trivial even when the amount of manganous sulphate reaches ten grams. We find also practical regularity of working when manganous chloride is substituted for the sulphate, and in this respect our results accord with those of Zimmermann and differ from those of Wagner.*

Total volume at beginning of titration.	HCl (sp. gr. 1.09).	$FeCl_3$.	$KMnO_4 \frac{N}{10}$.	$MnSO_4 . 5H_2O$.	$MnCl_2 . 4H_2O$.
cm³	cm³	cm³	cm³	grams.	grams.
135	10	25	21.70	1	. .
135	10	25	21.70	3	. .
135	10	25	21.70	5	. .
135	10	25	21.75	7	. .
135	10	25	21.75	10	. .
145	20	25	21.75	10	. .
175	50	25	21.75	10	. .
135	10	25	21.70	. .	1
135	10	25	21.70	. .	2
145	20	25	21.70	. .	2
155	30	25	21.75	. .	3
165	40	25	21.70	. .	4

In all cases, however, in which the larger amounts of manganous salt are present, the end reaction is marked by the advent of a brownish-red precipitate rather than the clear pink of the soluble permanganate, and it is obvious that in case the solutions to be oxidized were not active enough to act with rapidity upon the product of the Guyard reaction, difficulty might follow the failure to adjust the conditions more particularly.

It has been stated by Fleischer† and Zimmermann ‡ that hydrochloric acid interferes in no way with the titration of oxalic acid by potassium permanganate. This statement, however, is not in accord with our experience; for we find that in such titrations there is a small though real waste of

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* Loc. cit., p. 104.

† Volumetric Analysis; trans. by Muir, p. 71.

‡ Loc. cit.

permanganate proportionate to the amount of hydrochloric acid present. This fact is brought out clearly in the comparison of experiments of section A in the following table, in which no hydrochloric acid was present, with experiments B in which hydrochloric acid was present.

Temperature at beginning, about 80° C.

Approximate volume at beginning of titration.	H_2SO_4 1 : 1.	HCl (sp. gr. 1.09.)	Ammonium oxalate $\frac{N}{10}$.	$KMnO_4$.	Variation from mean of A taken as standard.
			A.		
	cm³	cm³	cm³	cm³	cm³
200	5	. .	50	47.50	0.00
200	5	. .	50	47.50	0.00
200	10	. .	50	47.50	0.00
200	10	. .	50	47.50	0.00
200	25	. .	50	47.50	0.00
200	25	. .	50	47.50	0.00
			B.		
150	10	2.5	25	28.80	0.05+
150	10	2.5	25	23.90	0.15+
150	10	5.0	25	23.90	0.15+
150	10	10.0	25	24.00	0.25+
500	5	. .	25	28.80	0.05+
500	10	10.0	25	24.00	0.25+
500	10	10.0	25	24.10	0.85+

From these results it is evident that, though the error introduced by the presence of the hydrochloric acid during the action of the permanganate upon the oxalic acid is small, it is plainly appreciable. The questions arise, therefore, first, as to whether the secondary action of the permanganate upon the hydrochloric acid may be prevented by the presence of a suitable amount of a manganous salt, and, secondly, as to whether in this event the reducing agent — the oxalic acid — is sufficiently active, like the ferrous salt, to prevent the premature establishment of an end color due to the Guyard reaction. The latter question must naturally be settled before the former can be taken up. In the accompanying table are recorded the effects of varying amounts of manganous salt in presence of different amounts of sulphuric acid in the reaction of permanganate upon oxalic acid.

Temperature at beginning, about 80° C.

Volume at beginning.	H_2SO_4 1 : 1.	Ammonium oxalate $\frac{N}{10}$	$MnSO_4 . 5H_2O$.	$KMnO_4$.	Variation from standard.
cm³	cm³	cm³	grm.	cm³	
130	5	25	. .	23.75	0.00
130	5	25	0.0008	23.75	0.00
130	5	25	0.0032	23.75	0.00
130	5	25	0.0160	23.75	0.00
130	5	25	1	23.70	0.05–
130	5	25	2	23.75	0.00
130	5	25	2.5	23.60	0.15–
130	5	25	3.0	23.40	0.25–
130	5	25	4.0	23.60	0.15–
500	5	25	. .	23.80	0.05+
500	5	25	0.0008	23.80	0.05+
500	5	25	0.0032	23.80	0.05+
500	5	25	1	23.70	0.05–
500	5	25	2	23.40	0.35–
500	5	25	3	23.50	0.25–
500	5	25	4	23.30	0.45–
130	10	25	1	23.80	0.05+
130	10	25	2	23.75	0.00
130	10	25	3	23.65	0.10–
130	10	25	4	23.50	0.25–
130	15	25	2	23.75	0.00
130	15	25	4	23.70	0.05–
130	15	25	5	23.50	0.25–
130	30	25	2	23.75	0.00
130	30	25	4	23.70	0.05–
130	30	25	5	23.75	0.00

From the results given it is evident that the persistence of the Güyard reaction is liable to interfere with the end reaction of oxidation of oxalic acid unless an adjustment is made between the quantity of the manganous salt, the amount of acid, and the dilution. In hot solutions of a total volume of 130 cm³ at the beginning, no more than 2 grms. of the manganous sulphate should accompany 5 to 10 cm³ of the 1 : 1 sulphuric acid; when the total volume at the beginning reaches 500 cm³ no more than a single gram of the salt should be present with 5 cm³ of the 1 : 1 sulphuric acid. The amount of manganous salt may, however, be increased considerably if the quantity of acid is increased.

As Kessler has noted, a sufficiency of the manganous salt, acting no doubt as the medium of transfer of oxygen, may bring about interaction between the permanganate and the oxalic acid at atmospheric temperatures without the tedious delay ordinarily encountered in the attempt to consummate that action in cold solutions. It would seem natural that the manganic hydroxide formed in the Guyard reaction at low temperatures should yield more readily to the reducing action of the oxalic acid than the more anhydrous form to be expected in hot solutions, so that at such temperatures the limits as to proportions of manganous salt, acid, and dilution, within which favorable action may take place, should be wider; moreover, the undesirable action of the permanganate upon

Temperature 20°–26° C.

Number of experiment.	Volume at beginning of titration.	H_2SO_4 1 : 1.	HCl (sp. gr. 1.09).	Ammonium oxalate $\frac{N}{10}$.	$KMnO_4$.	$MnSO_4 \cdot 5H_2O$.	$MnCl_2 \cdot 4H_2O$.	Variation from standard.
		cm³	cm³	cm³	cm³	grm.	grm.	cm³
(1)	130	. .	10	25	23.90	0.0040	. .	0.15+
(2)	130	. .	10	25	23.90	0.0120	. .	0.15+
(3)	130	. .	10	25	23.80	0.0250	. .	0.05+
(4)	130	. .	10	25	23.75	0.0400	. .	0.00
(5)	130	. .	10	25	23.76	0.0500	. .	0.01+
(6)	130	. .	10	25	23.70	0.1000	. .	0.05−
(7)	130	. .	10	25	23.75	0.2000	. .	0.00
(8)	130	. .	10	25	24.20	. .	0.0200	0.45+
(9)	130	. .	10	25	23.95	. .	0.0200	0.20+
(10)	130	. .	10	25	23.80	. .	0.0400	0.05+
(11)	130	. .	20	25	23.75	. .	0.0400	0.00
(12)	130	. .	30	25	23.75	. .	0.0400	0.00
(13)	130	. .	10	25	23.75	1.0000	. .	0.00
(14)	130	. .	10	25	23.75	2.0000	. .	0.00
(15)	130	. .	10	25	23.75	3.0000	. .	0.00
(16)	130	1	. .	25	23.72	. .	1.0000	0.03−
(17)	130	1	. .	25	23.74	. .	2.0000	0.01−
(18)	130	1	. .	25	23.72	. .	3.0000	0.03−
(19)	130	2	. .	25	23.70	. .	0.5000	0.05−
(20)	130	3	. .	25	23.75	. .	0.5000	0.00
Temperature about 80°.								
(21)	145	10	10	25	23.90	0.5000	. .	0.15+
(22)	145	10	10	25	23.70	1.0000	. .	0.05−
(23)	500	10	10	25	23.75	1.0000	. .	0.00
(24)	500	. .	10	25	23.70	1.0000	. .	0.05−
(25)	500	. .	10	25	24.10	0.5000	. .	0.35+

hydrochloric acid, when that acid is present, should be less appreciable at lower temperatures. In our experiments, therefore, upon the oxidation of oxalic acid by potassium permanganate in presence of hydrochloric acid, we have studied the effect of varying the proportions of the manganous salt both at atmospheric temperatures and the higher temperatures generally employed.

From these results it appears that the presence of a suitable amount of manganous salt — either the sulphate (4–7), (13–15), (22–24) or the chloride (10–12), (16–20) — is capable, either in cold solution (1–20) or in hot solution (22–24) of preventing the action of the permanganate upon the hydrochloric acid. It appears, also, that, for a given dilution and strength of acid, less manganous salt is needed in the cold solution (4–7) than in the hot solutions (22–24). Thus, in the hot solution, at a dilution at 145 cm^3 to 500 cm^3 1 grm. of manganous sulphate must be present with 5 cm^3 of strong hydrochloric acid, with or without sulphuric acid; while in the cold solution 0.04 grm. of either the sulphate or chloride is enough to secure adequate protective effect. Experience showed, however, that 0.5 grm. or 1.0 grm. of the manganous salt should be present in order to push the reaction with reasonable speed in cold solutions.

Wagner* has made record of the increased evolution of chlorine in oxidations of ferrous chloride by potassium permanganate in presence of various salts, of which barium chloride was the most active. We have made some experiments, therefore, to determine whether such action would appear in the oxidation of oxalic acid in cold solutions containing certain salts, and, if so, whether it would be preventable by the presence of the manganous salt under our conditions of working. From the results given in the accompanying table, it is plain that the evolution of chlorine in cold solutions is less in the presence of these salts than when hydrochloric acid is used without them, and that such evolution may be entirely prevented (within the proportions

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* Loc. cit.

of our work) by the presence of 0.5 grm. to 1 grm. of manganous chloride.

Finally, it appears as the result of an investigation, that the titration of oxalic acid by potassium permanganate in presence of hydrochloric acid is ordinarily attended with some inaccuracy due to liberation of chlorine from the hydrochloric acid; that this tendency may be overcome by the presence of a manganous salt—either the sulphate or chloride; that 1 grm. of the manganous salt is enough to so affect the conditions of equilibrium that titrations in moderate volumes (100 cm^3 to 500 cm^3) and in presence of hydrochloric acid (5 cm^3 to 15 cm^3 of the strong acid) may be conducted with safety and reasonable rapidity, either with or without sulphuric acid, at the ordinary atmospheric temperature.

Volume at Beginning of Titration = 140 cm^3.

Temperature = 20°–24° C.

Ammonium oxalate.	HCl. strongest.	$MnCl_2 . 4H_2O$.	$BaCl_2$.	$SrCl_2$.	$CaCl_2$.	$MgCl_2$.	$KMnO_4$ used.	Error.
cm^3	cm^3	grm.	grm.	grm.	grm.	grm.	cm$_3$	cm^3
25	5	0.5	. .	. .	. .	. .	26.05	0.00
25	5	. .	. .	. .	. .	. .	27.45	1.40+
25	5	. .	2	. .	. .	. .	26.50	0.45+
25	5	. .	. .	2	. .	. .	26.53	0.48+
25	5	. .	. .	. .	2	. .	26.36	0.85+
25	5	. .	. .	. .	. .	2	26.18	0.08+
25	5	0.5	2	. .	. .	. .	26.05	0.00
25	5	0.5	. .	2	. .	. .	26.10	0.05+
25	5	0.5	. .	. .	2	. .	26.10	0.05+
25	5	0.5	. .	. .	. .	2	26.05	0.00
25	10	1.0	2	. .	. .	. .	26.10	+0.05
25	10	1.0	. .	2	. .	. .	26.05	0.00
25	10	1.0	. .	. .	2	. .	26.06	0.01+
25	10	1.0	. .	. .	. .	2	26.11	0.06+

XXVIII

THE ESTIMATION OF IRON IN THE FERRIC STATE BY REDUCTION WITH SODIUM THIOSULPHATE AND TITRATION WITH IODINE.

BY JOHN T. NORTON, JR.[*]

THE action of sodium thiosulphate on ferric iron has long been known and depends upon the following reaction:

$$2FeCl_3 + 2Na_2S_2O_3 = 2FeCl_2 + Na_2S_4O_6 + 2NaCl.$$

As early as 1859 Scherer[†] proposed a method for the estimation of ferric iron depending on the above reaction. Scherer's method of procedure was to act upon a solution of ferric chloride with sodium thiosulphate until the purple color produced by the interaction of these two salts just vanished. Mohr's[‡] experimental tests of this process were not successful. A year or two later Kremer and Landolt,[§] after a careful investigation of Scherer's process, recommended it with the modification that any free hydrochloric acid present should be neutralized by sodium acetate until the solution assumed a red color, just enough hydrochloric acid added to destroy this red color, and sodium thiosulphate run into the solution in slight excess. When the liquid became perfectly colorless and gave no reaction for ferric iron with potassium sulphocyanide, the excess of sodium thiosulphate was titrated back with iodine and starch. The authors also state that the ferric iron should not be present in concentrated solution. Very good results were claimed for this process, but it apparently gained but slight recognition.

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[*] From Am. Jour. Sci., viii, 25.

[†] Gel. Anzeig. k. Bayrisch. Acad., Aug. 31, 1859.

[‡] Ann. Chem. Pharm., cxiii, 260.

[§] Zeitschr. anal. Chem., i, 214.

Oudemanns,[*] who was the next to study the action of ferric iron and sodium thiosulphate, claimed that the addition of a small quantity of cupric salt to the iron solution hastened the reducing action of the sodium thiosulphate. Mohr,[†] however, condemned this method also as unreliable, both because the sodium thiosulphate acted upon the copper as well as the iron and also because the potassium sulphocyanide, added as an indicator of the completeness of the reduction, produced a precipitate of cupric sulphocyanide which interfered with the reaction. In a second paper Oudemanns[‡] reiterated his former statement as to the accuracy of his method but advised the use of a smaller quantity of the cupric salt. An improvement on Oudemanns' process was proposed by Haswell,[§] who mixed the moderately acid solution of ferric chloride in the presence of a cupric salt with a few drops of sodium salicylate and then reduced with sodium thiosulphate previously standardized upon a known quantity of iron by the same process and estimated the excess by potassium dichromate. Bruel[||] modified this process by operating without the copper solution, relying merely on the discharge of the violet color in a boiling solution by sodium thiosulphate standardized on a ferric solution of known strength.

Although considerable work has been done on the reaction between ferric iron and sodium thiosulphate, no process depending upon this reaction has obtained acceptance. In view, therefore, of previous work on the action of hydrochloric acid upon sodium thiosulphate[¶] and with the idea that a careful control of the dilution and quantity of acid present might greatly better the accuracy of the method, it has seemed to me to be desirable to study this process again in detail.

The ferric oxide employed in the experiments was prepared with great care by the ignition of ferrous oxalate obtained by

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[*] Zeitschr. anal. Chem., vi, 129.

[†] Titrirmethode, 5^{te} Aufl., 294.

[‡] Zeitschr. anal. Chem., ix, 362.

[§] Repertorium der analytischen Chem., i, 179.

[||] Compt. rend., xcvii, 954.

[¶] Am. Jour. Sci., vii, 287. This volume, p. 206.

acting with oxalic acid on pure ammonium ferrous sulphate. To ascertain, however, if this oxide contained any impurity, about 0.5 of a grm. was put into a porcelain boat and submitted to the action of a current of hydrochloric acid gas and chlorine at a temperature of about 280° C. (according to a process recently described from this laboratory *) until all the ferric salt is volatilized in the form of ferric chloride. A residue of 0.0010 grm. for every 0.5 of a grm. of the oxide was found, and this correction, small for the amounts generally used, has been applied in the following determinations. The sodium thiosulphate used was taken in nearly $\frac{N}{10}$ solution and was standardized against an approximately decinormal solution of iodine which had been determined by comparison with decinormal arsenious acid made from carefully resublimed arsenious oxide.

In those experiments which deal with amounts of ferric oxide not exceeding 0.2 of a grm., measured portions of a solution of ferric chloride made of known strength by dissolving about 2 grms. of the pure carefully weighed ferric oxide in 20 cm^3 of strong hydrochloric acid and diluting to one liter, were drawn from a burette. In the case of the larger quantities of ferric oxide the salt was weighed out, dissolved in hydrochloric acid and brought to the required dilution. The ferric chloride, either drawn from the burette or prepared directly from the weighed oxide, was diluted with water, a drop of potassium sulphocyanide added to serve as an indicator and an excess of sodium thiosulphate was run in until, after standing for a few minutes, the solution became perfectly colorless, and the excess of sodium thiosulphate was then titrated back with decinormal iodine after the addition of starch.

Several sources of error are, plainly, possible in the process: incompleteness in the reduction of the ferric salt; decomposition of the thiosulphate by the acid, resulting in the subsequent over-run of iodine; the possible tendency of the ferric salt under concentration to oxide the thiosulphate to the condition

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* Gooch and Havens, Am. Jour. Sci., vii, 370. This volume, p. 215.

of the sulphate rather than to that of the tetrathionate; and finally the oxidizing action of the air, which may tend to keep up progressive oxidation of the iron salt and excessive expenditure of thiosulphate. The first three sources of difficulty tend to produce errors of deficiency; the fourth an error of excess.

The first step in the experimental study of the process was to determine the effect of varying dilution upon the estimation of a given quantity of iron reduced by sodium thiosulphate, taken in practically uniform excess above the amount theoretically required, in the presence of 1 cm^3 of hydrochloric acid.

TABLE I.

Exp.	Fe_2O_3 taken.	Fe_2O_3 corrected.	Dilution.	HCl.	$Na_2S_2O_3$ in excess.	Fe_2O_3 found.	Error.
	grm.	grm.	cm^3	cm^3	cm^3	grm.	grm.
(1)	0.1000	0.0998	100	1	18.08	0.0957	0.0041–
(2)	0.1000	0.0998	200	1	20	0.0966	0.0032–
(3)	0.1000	0.0998	300	1	17.56	0.0995	0.0003–
(4)	0.1000	0.0998	400	1	17.16	0.0998	0.0000
(5)	0.1000	0.0998	600	1	17.76	0.0996	0.0002–
(6)	0.1000	0.0998	800	1	17.65	0.0993	0.0005–
(7)	0.1000	0.0998	1000	1	18.02	0.0988	0.0010–
(8)	0.1000	0.0998	1200	1	17.95	0.0977	0.0021–
(9)	0.1000	0.0998	1400	1	17.99	0.0965	0.0033–
(10)	0.1000	0.0998	1600	1	18.01	0.0947	0.0051–
(11)	0.2001	0.1997	400	2	27.05	0.2029	0.0032+
(12)	0.2001	0.1997	800	2	15.95	0.1998	0.0001+
(13)	0.4998	0.4988	1000	2	22.36	0.5104	0.0116+
(14)	0.5051	0.5041	1800	4	15.27	0.5026	0.0015–
(15)	0.4002	0.3994	1500	4	27.29	0.3996	0.0002+
(16)	0.7502	0.7487	1000	1	9.78	0.7572	0.0085+
(17)	0.7029	0.7015	2000	4	12.67	0.7004	0.0011–

This table shows plainly that with quantities of ferric oxide present up to 0.1 grm. the dilution can vary from 400 cm^3 to 1000 cm^3 for each cm^3 of strong hydrochloric acid and still give excellent results. At a dilution greater than 1000 cm^3 the action of the thiosulphate is evidently incomplete, and at a smaller dilution than 400 cm^3 the decomposing action of the acid on the thiosulphate becomes noticeable. When larger quantities of iron oxide are dealt with, it appears that the dilution ought to be increased proportionally with the quantity of ferric oxide present as well as with that of the acid. This is illustrated in experiments 9–15 of the table. On this account it seems necessary, assuming that the quantity of acid present is always kept within the maximum strength mentioned, 1 cm^3 to 400 cm^3, to regulate the dilution from the approximate quantity of the iron so that not less than 400 cm^3 of water shall be used to every 0.1 grm. of iron oxide present. Under properly regulated conditions of dilution as regards acid and the iron salt, the reduction is completed in from five to ten minutes.

Great excesses of acid, however, contrary to the statement of Kremer,* retard the reduction greatly, and, in spite of the tendency of the thiosulphate to decomposition and the production of errors of deficiency under such circumstances, plus errors due to partial oxidation come to light. This fact appears in the following table, which records the results of processes lasting many hours.

TABLE II.

Exp.	Fe_2O_3 taken.	Fe_2O_3 corrected.	Dilution.	HCl.	$Na_2S_2O_3$ in excess.	Fe_2O_3 found.	Error.
	grm.	grm.	cm^3	cm^3	cm^3	grm.	grm.
(18)	0.5012	0.5002	1700	10	25.99	5308	0.0306+
(19)	0.7512	0.7497	1200	15	57.8	7685	0.0188+
(20)	0.7520	0.7505	2000	15	56.4	7983	0.0478+
(21)	0.7520	0.7505	1700	15	27.2	7627	0.0122+

As to the temperature at which the reduction should be made, my experience, contrary to that of Kremer, goes to show that no elevation above atmospheric conditions is necessary; under the conditions of acidity and dilution laid down, the process of reduction is complete within ten minutes after the introduction of the thiosulphate; moreover, former experience † shows clearly the danger of submitting mixtures of sodium thiosulphate and acid to temperatures much above the ordinary. On the other hand, artificial reduction of temperature tends

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* Zeitschr. anal. Chem., i, 214.

† Am. Jour. Sci., vol. vii, 287. This volume, p. 206.

to retard the action to an impossible degree. Thus, in an experiment it took five minutes to reduce 0.0500 of ferric oxide at 21° C. completely at a dilution of 200 cm³ and in the presence of ½ cm³ of hydrochloric acid; under conditions otherwise precisely similar excepting that the temperature was lowered to 0° C., the action lingered forty-five minutes.

Lastly, the question as to the excess of thiosulphate necessary to complete the reduction within a reasonable time must be considered. In nearly all previously recorded experiments the excess of thiosulphate was not less than 15 cm³ of the $\frac{N}{10}$ solution. The following table shows the effect of diminishing this excess.

TABLE III.

Exp.	Fe_2O_3 taken.	Fe_2O_3 corrected.	Dilution.	HCl.	$Na_2S_2O_3$ in excess.	Fe_2O_3 found.	Error.
	grm.	grm.	cm³	cm³	cm³	grm.	grm.
(22)	0.0250	0.0250	400	½	12.2	0.0241	0.0009–
(23)	0.0500	0.0499	400	½	12.2	0.0495	0.0004–
(24)	0.0500	0.0499	400	½	13.66	0.0493	0.0006–
(25)	0.1000	0.0998	400	1	7.31	0.0984	0.0014–
(26)	0.1000	0.0998	400	1	7.63	0.0972	0.0026–
(27)	0.1001	0.0999	400	1	12.88	0.1007	0.0008+
(28)	0.1498	0.1495	600	1½	11.97	0.1475	0.0020–
(29)	0.1996	0.1992	800	2	12.43	0.1980	0.0012–

From the above experiments taken in connection with those of Table I it is clear that there should always be present an excess of at least 15 cm³ of the $\frac{N}{10}$ solution of sodium thiosulphate. If the quantity of hydrochloric acid is kept very low there is no reason why this excess of thiosulphate could not be considerable without producing any disturbing effect. Practically, however, the presence of an excess between the limits of 15 cm³ and 35 cm³ of the $\frac{N}{10}$ solution has been found to give the most satisfactory results.

To recapitulate, then, it has been shown that the dilution must be at least 400 cm³ for each 0.1 of a grm. of iron oxide present, that the quantity of acid should never exceed 1 cm³ of the strong acid to each 400 cm³ of water, that the time of reduction must be short to avoid progressive oxidation, that the temperature of the solution should be kept at the normal temperature of the atmosphere, and finally that the excess of sodium thiosulphate present should never be less than 15 cm³ of the $\frac{N}{10}$ solution. In the case of large dilution the use of freshly boiled water is recommended so as to avoid the reoxidizing effect of the air upon the reduced iron. In the experiments included in the following table, the above precautions were closely adhered to and manifestly satisfactory results were obtained.

TABLE IV.

Exp.	Fe_2O_3 taken.	Fe_2O_3 corrected.	Dilution.	HCl.	Excess $Na_2S_2O_3$	Fe_2O_3 found.	Error.
	grm.	grm.	cm³	cm³	cm³	grm.	grm.
(30)	0.0125	0.0125	200	½	23.5	0.0125	0.0000
(31)	0.0250	0.0250	400	½	21.98	0.0250	0.0000
(32)	0.0250	0.0250	400	½	17	0.0250	0.0000
(33)	0.0250	0.0250	400	½	17	0.0250	0.0000
(34)	0.0500	0.0499	400	½	24	0.0498	0.0001–
(35)	0.0500	0.0499	400	½	19	0.0498	0.0001–
(36)	0.0500	0.0499	400	½	15.1	0.0497	0.0002–
(37)	0.0500	0.0499	400	½	19	0.0498	0.0001–
(38)	0.1001	0.0999	400	1	23.1	0.0993	0.0006–
(39)	0.1001	0.0999	400	1	17.98	0.0997	0.0002–
(40)	0.1001	0.0999	400	1	22.92	0.0997	0.0002–
(41)	0.1001	0.0999	400	1	18	0.0997	0.0002–
(42)	0.1001	0.0999	400	1	16	0.0996	0.0003–
(43)	0.1498	0.1495	600	1½	23.26	0.1493	0.0002–
(44)	0.1498	0.1495	600	1½	16.66	0.1493	0.0002–
(45)	0.1498	0.1495	600	1½	26.87	0.1475	0.0020–
(46)	0.1996	0.1992	800	2	22.38	0.1990	0.0002–
(47)	0.1996	0.1992	800	2	17.29	0.1999	0.0007+
(48)	0.1996	0.1992	800	2	22.20	0.1991	0.0001–
(49)	0.4045	0.4037	1600	4	16.03	0.4042	0.0005+
(50)	0.4045	0.4037	1600	4	16.2	0.4023	0.0014–
(51)	0.4018	0.4010	1600	4	16.34	0.4007	0.0003–
(52)	0.5051	0.5041	1800	4	15.27	0.5026	0.0015–

As seen in the table this process is very accurate, especially in the use of small amounts of ferric oxide. The introduction of cupric sulphate as recommended by Oudemanns, or of sodium salicylate according to Haswell's method, seems to be unnecessary and only complicates the process.

In treating ferric oxide, the following method of procedure is recommended. Dissolve an amount not exceeding 0.2 grm. of the oxide in hydrochloric acid, evaporate to a pasty mass dilute to about 800 cm^3 with freshly boiled water, add a drop of potassium sulphocyanide, and into this solution run 50 cm^3 of approximately $\frac{N}{10}$ sodium thiosulphate; allow the liquid to stand until perfectly colorless and determine the excess of thiosulphate by $\frac{N}{10}$ iodine and starch. For quantities of iron oxide up to 0.2 of a gram this process is quick and most accurate; when care is taken to preserve the relations of acidity and dilution, twice the amount of ferric oxide mentioned above may be handled.

XXIX

THE DETERMINATION OF TELLUROUS ACID IN PRESENCE OF HALOID SALTS.

By F. A. GOOCH and C. A. PETERS.*

THE estimation of tellurous acid by oxidation with excess of potassium permanganate (either in acid or alkaline solution), destruction of the higher oxides of manganese or the manganate by standard oxalic acid in presence of sulphuric acid, and titration of the residual oxalic acid by more permanganate, has been shown by Brauner† to be feasible. The tendency of the permanganate to throw off too much oxygen when the oxidation is made in solutions strongly acidified with sulphuric acid (as must be the case if the tellurous oxide is to be held permanently in solution by sulphuric acid) necessitates the application of a considerable correction.‡ Fortunately, however, as has been shown in a former paper from this laboratory,§ when the tellurous oxide is dissolved originally in an alkaline hydroxide and the solution made acid only to a limited degree with sulphuric acid either before or after oxidation by the permanganate, no correction appears to be necessary. Thus, when an excess of permanganate is added to the alkaline solution, followed by an excess of oxalic acid and sulphuric acid to an amount not exceeding 5 cm^3 of the [1:1] mixture with water, the titration of the residual oxalic acid by more permanganate (after heating to 80° C.) leads to results which give no indication of over-decomposition of the permanganate; so also, when the process is similarly conducted excepting that before addition of the permanganate the original alkaline solution is acidified with sulphuric acid [1:1] to an amount 1 cm^3 in excess

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* From Am. Jour. Sci., viii, 122.

† Jour. Chem. Soc., lix, 238.

‡ Loc. cit., p. 249.

§ Gooch and Danner, Am. Jour. Sci., xliv, 301. Volume I, p. 145.

of that necessary to redissolve the first precipitate, the results are theoretically accurate, and in close agreement with those obtained by the former procedure.

In the presence of free hydrochloric acid the action of the permanganate upon tellurous acid has been shown by Brauner* to be irregular and excessive, and the irregularity cannot be corrected (as in the titration of ferrous salts in presence of hydrochloric acid) by the addition of a manganous salt according to the well-known procedure of Kessler† and Zimmermann.‡ So far as appears, however, there should be nothing to prevent the accurate determination of tellurium in tellurous compounds in the presence of chlorides by the permanganate process providing the first oxidation is made in alkaline solution, and the second oxidation carried out with such precautions as are necessary to a correct determination of oxalic acid by permanganate in presence of hydrochloric acid; for the special danger of over-action on the part of the permanganate cannot exist while the solution is alkaline, and has passed when the tellurite has become a tellurate and before the solution is made acid. As to the proper conditions for the titration of oxalic acid by permanganate we have shown recently§ that the presence of a manganous salt is necessary and sufficient to secure regularity of action when a considerable amount of hydrochloric acid is in the solution; when the amount is small — so much as would be formed in the decomposition of a gram or two of halogen salt of tellurium — the disturbing effect under ordinary conditions of work is probably inappreciable, but even in such a case it is better to work in the presence of a manganous salt for the reason that the titration of the oxalic acid may then be made at the ordinary atmospheric temperature.

In the following table are gathered the results of experiments made with, and without, the addition of the manganous salt.

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* Loc. cit., p. 241.

† Ann. Phys. cxviii, 48; cxix, 225, 226.

‡ Ann. Chem. (Liebig), ccxiii, 302.

§ Am. Jour. Sci., vii, p. 461. This volume, p. 222.

TABLE I.

$O = 16$, $Te = 127.5$.

Volume at beginning, 150 cm^3.

Temperature of titration, 60–80° C.

TeO_2 taken.	NaCl.	H_2SO_4 1 : 1.	$MnCl_2 . 4H_2O$.	TeO_2 found.	Error.
grm.	grm.	cm^3	grm.	grm.	grm.
0.1000	0.4	5	. . .	0.1003	0.0003+
0.1000	0.4	5	. . .	0.1000	0.0000
0.1000	0.4	5	. . .	0.1004	0.0004+
0.1000	1.0	5	. . .	0.1003	0.0003+
0.0650	1.0	5	. . .	0.0658	0.0003+
B. Temperature of titration, 20–26° C.					
0.0700	0.4	5.7	1.0	0.0705	0.0005+
0.0700	0.4	5.7	1.0	0.0698	0.0002–
0.0700	0.4	5.7	0.5	0.0701	0.0001+
0.1000	0.4	5.7	0.5	0.1008	0.0008+

The tellurium dioxide, made by the careful ignition of the crystallized basic nitrate obtained by oxidizing tellurium with nitric acid, was dissolved in a small amount of sodium hydroxide, the halogen salt was added to the amount shown, the permanganate standardized against ammonium oxalate was run in until its characteristic color appeared, standard ammonium oxalate was added in excess of the quantity required to reduce the excess of permanganate, manganate, and higher oxides, and the solution was heated with enough sulphuric acid [1 : 1] to neutralize the alkaline hydroxide and have an excess of about 5 cm^3. In the experiments of Section A the liquid was heated to 60° – 80° C. to dissolve the oxides at the final titration begun at that temperature; in those of Section B, manganous chloride (0.5 to 1 gram) was added, so that the reduction of the higher oxides of manganese and the final titration of the excess of oxalic acid might take place at the ordinary temperature of the room.

Plainly the presence of the chloride does not interfere materially in the determination of the tellurium by this process whether the titration is made at a high or low temperature.

It appears, also, upon putting the matter to the test, that fairly good determinations of tellurous acid may be made similarly in the presence of a bromide, provided the titration is made at the atmospheric temperature in the presence of a sufficiency (0.5 gram to 1 gram) of a manganous salt and of an excess of sulphuric acid limited to about 5 cm^3 or less of the 12.5 per cent mixture. At the higher temperatures bromine is liberated at once from the acid solution by the permanganate. The experimental results are given in Table II.

TABLE II.

O = 16, Te = 127.5.

Volume at beginning, 150 cm^3.

Temperature of titration, 24°–26° C.

TeO_2 taken.	NaCl	KBr.	H_2SO_4 12.5%	$MnCl_2 \cdot 4H_2O$.	TeO_2 found.	Error.
grm.	grm.	grm.	cm^3	grm.	grm.	grm.
0.1000	. . .	0.5	20	1.0	0.1022	0.0022+
0.3000	. . .	1.5	25	1.0	0.3030	0.0030+
0.0650	. . .	0.5	1	1.0	0.0661	0.0011+
0.0650	. . .	0.5	1	1.0	0.0647	0.0003−
0.1000	. . .	0.5	1	1.0	0.1002	0.0002+
0.3000	. . .	0.5	5	0.5	0.3010	0.0010+
0.0650	0.5	0.5	1	1.0	0.0661	0.0011+

It is obvious, therefore, that tellurous acid may be determined with a fair degree of accuracy by the permanganate method in the presence of chlorides and bromides, provided the first oxidation is made in alkaline solution and the final titration of the residual oxalic acid is made at ordinary temperatures in the presence of a manganous salt and restricted amounts of free sulphuric acid.

In the presence of an iodide, however, the case is different. Upon acidifying the mixture of iodide and the higher oxygen compounds of manganese, produced in the action of the permanganate upon the solution, iodine is at once set free, and oxalic acid does not suffice to reconvert it. In the presence of an excess of potassium iodide the higher manganic compounds are completely reduced with rapidity and the iodine liberated is the measure of the excess of permanganate over that required to oxidize the tellurous acid; the difference between the amount of permanganate thus indicated and that originally introduced should determine the amount of the tellurous acid. It is upon this basis that Norris and Fay * have founded their excellent iodometric determination of tellurous acid. This process consists in treating the alkaline solution of tellurous acid with standard permanganate until the meniscus of the liquid shows a deep pink color, then diluting the solution with ice-water, adding potassium iodide and sulphuric acid, and titrating with sodium thiosulphate. The results are excellent.

It is plain that any agent capable of converting the iodine to hydriodic acid without at the same time reducing telluric acid should be capable of measuring the excess of the permanganate, and so the amount of tellurous acid originally present. We find that the standard arsenite made, as usual, by dissolving 4.95 grams of pure resublimed arsenious oxide to the liter of water containing potassium bicarbonate answers the purpose admirably, and possesses the further advantage of fixing at once the entire standard of the process, the strength of the permanganate (approximately $\frac{N}{10}$ being determined by running a definite volume of its solution into water containing potassium iodide (1 gram) with 2 to 3 cm^3 of dilute sulphuric acid and titrating by the standard arsenite the iodine (set free by the action of the excess of permanganate and higher oxides) after neutralization with acid potassium bicarbonate. In this titration of iodine by the arsenite we find it best to dispense with the starch solution usually employed to secure the end reaction. The color of the free iodine itself is sufficiently definite, even at a dilution so much as 300 cm^3, and its disappearance under the action of the arsenite is much sharper than that of the blue starch iodide.

In Table III are recorded results obtained by adding the alkaline solution of tellurous oxide to 100 cm^3 of water containing 0.5 gram or 1 gram of potassium iodide, introducing the standardized potassium permanganate until the green color of the manganate appears (about 30 cm^3 of the $\frac{N}{10}$ solution for

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* Am. Chem. Jour., xx, 278.

every 0.1 gram of TeO_2), adding a few cubic centimeters of dilute sulphuric acid, followed, when the solution has cleared and separated iodine, by an excess of acid potassium carbonate, and titrating to the destruction of color with the standard solution of arsenic. It is essential, in order that oxygen may not go to waste in the breaking down of the oxides, that more than enough iodide should be present when the solution is acidified to complete the reduction of the manganese oxides, or else, that the arsenious acid should be present in suitable amount before the sulphuric acid is put in. This latter procedure may be used in case, for any reason, it is preferred not to introduce more iodide into the solution than may be present originally: when, for example, a direct determination of the iodine present is to follow.

TABLE III.

O = 16, Te = 127.5.

TeO_2 taken.	NaCl.	KBr.	KI.	Total volume at end.	NaOH present during oxidation.	TeO_2 found.	Error.
grm.	grm.	grm.	grm.	cm^3.	grm.	grm.	grm.
0.1000	..	..	0.5	160	0.1	0.1005	0.0005+
0.1000	..	..	0.5	160	0.1	0.1001	0.0001+
0.1000	..	..	0.5	160	0.1	0.1008	0.0008+
0.1000	..	..	1.0	250	0.1	0.1007	0.0007+
0.2000	..	..	1.0	250	0.2	0.1997	0.0003+
0.1000	0.5	0.5	0.5	250	0.1	0.1000	0.0000
0.2100	1.0	1.0	1.0	225	0.2	0.2105	0.0005+
0.1000	..	..	0.5	160	1.0	0.1011	0.0011+
0.2000	..	..	1.0	300	2.0	0.2009	0.0009+

These results are reasonably good. Like those of Table I they would be brought practically in the average to the figure demanded by theory if the value of the Committee of the German Chemical Society, Te = 127, were to be taken instead of Te = 127.5, the value of Clarke and of Richards.

XXX

AN IODOMETRIC METHOD FOR THE ESTIMATION OF BORIC ACID.

By LOUIS CLEVELAND JONES.*

In a recent article,† I have described a process for the alkalimetric estimation of boric acid, depending upon the formation of a strongly acidic compound when boric acid and a polyatomic alcohol are placed together in solution. The method in brief consists in destroying the free mineral acid in a solution containing boric acid, by means of a mixture of potassium iodide and iodate, bleaching the liberated iodine by sodium thiosulphate, adding the indicator phenolphthalein and sufficient standard solution of caustic soda to give a faint alkaline coloration, bleaching by a small amount of mannite and adding caustic soda again to alkalinity, and thus alternating with mannite and alkali until the alkaline coloration produced is permanent. The amount of sodium hydroxide used represents the amount of acidity developed by the influence of the mannite upon the boric acid present, according to the hypothesis that the molecule B_2O_3 acts as two molecules of a univalent acid, HOBO.

On making further study of this reaction, I have found that the acid developed by the combination of boric acid and mannite is, under certain definite conditions, sufficiently strong to liberate, quantitatively, from a mixture of potassium iodide and iodate, the amount of iodine required on the supposition that each molecule of metaboric acid (HOBO) acts in a manner similar to a univalent mineral acid under the same conditions. ($5KI + KIO_3 + 6HOBO = 3I_2 +$

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* From Am. Jour. Sci., viii, 127.

† Am. Jour. Sci., vii, 147. This volume, p. 182.

$6KOBO + 3H_2O$.) Obviously, this reaction depends upon the behavior of the acidic boromannite compound as a strong acid, stronger than acetic, tartaric, or citric acid; for these acids have been found by Furry[*] to be incapable of liberating iodine regularly from a mixture of iodide and iodate. Conditions which tend to increase the acidic activity of this compound are concentrated solutions and moderately low temperatures.[†]

Glycerine acts in general like mannite to produce acidic compounds with boric acid; and in a preliminary way, the relative acidity of the products formed by these two polyatomic alcohols with boric acid may be indicated by the results of two experiments in which the iodine liberated from a mixture of potassium iodide and iodate, proportionately to the time required for the liberation, is taken as a measure of the strengths of the acids developed.

Equal amounts (10 cm^3) of a standard solution of boric acid, prepared from the anhydride,[‡] were drawn into separate Erlenmeyer flasks and a neutral solution of iodide and iodate added to each in an amount sufficient to liberate iodine in quantities corresponding to the acid used. One solution was treated with glycerine enough to constitute one-half the entire volume of the liquid: mannite (about 5 grms.) was added to the other. The thiosulphate required immediately and after definite periods of time, is shown for each solution in the following table.

The solution of boric acid contained 7.706 grm. per liter. The thiosulphate was 0.0999 normal. According to theory, the amount of thiosulphate required for 10 cm^3 of the boric

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[*] Am. Chem. Jour., vi, 341.

[†] Magnanini, Gaz. chim. ital. xx, 428, xxi, 134; and Lambert, Compt. rend., cviii, 1016, 1017.

[‡] The recrystallized hydrous boric acid should be fused in a platinum dish and, after cooling and breaking into small pieces, the desired amount placed in a small weighed platinum crucible and again fused until no more water escapes. After cooling and weighing, the boric oxide may be separated from the crucible, or with it placed in warm water, dissolved and made up to a definite volume.

TABLE I.

B_2O_3 solution (10 cm^3) with mannite. Thiosulphate required.	Time.	B_2O_3 solution (10 cm^3) with glycerine. Thiosulphate required.
cm^3		cm^3
18.60	Immediately.	8.48
21.30	After 15 minutes.	10.50
22.00	After 30 minutes.	11.15
22.05	After 2 hours.	11.60

acid solution is 22.02 cm^3. From these data we may observe that at the end of 30 minutes, in the solution containing mannite, practically the theoretical amount of thiosulphate had been used, while only about 50 per cent of that amount had been required to bleach the iodine liberated by the glycerine compound. Obviously, mannite forms with boric acid a more acidic compound than glycerine does, and, from the indication given in the above experiments, may be relied upon, under certain conditions, to liberate the theoretical amount of iodine. If, from the iodide and iodate used to destroy the excess of mineral acid already present, the boric acid, upon the addition of mannite does liberate iodine regularly — as the previous experiments seem to indicate — this liberated iodine should form a most convenient measure of the boric acid present.

On studying the conditions requisite for the complete liberation of iodine according to theory, several important points have come to light.

It has not been found possible under any conditions to rely upon the immediate liberation of the full amount of iodine: a certain period of time is required for the completion of the reaction. When the solution is of small volume and saturated with mannite, the reaction goes to the end most quickly — sometimes almost immediately — but there is this limitation, which must be made emphatic, viz.: that if the solution of boric acid is too concentrated — near saturation — the boric acid alone, when the iodate and iodide are added to destroy any other free acid present, throws out some iodine and on bleaching with thiosulphate a starting-point is obtained at which some of the boric acid has already entered into combination. The amount of iodine thus liberated by the boric acid is, however, not large, and if upon the addition of the iodide and iodate, the iodine thrown out by the free hydrochloric acid present is immediately bleached by thiosulphate and the analysis proceeded with from this as the neutral point, even in concentrated solutions the error is almost inappreciable. If, however, considerable time intervenes between the adding of the iodide and iodate and the determination of the neutral point by thiosulphate, as much as several milligrams of boric acid may have liberated its amount of iodine and is, therefore, not capable of being registered by thiosulphate after the addition of mannite. This difficulty was not met with in those experiments in which the iodide and iodate were added at a dilution little greater than that of the standard solution used (7.738 grm. per liter), but in an attempt to estimate the boric acid in colemanite, where the solution was kept as concentrated as possible, hoping in this way to decrease the time required for the complete liberation of iodine, low values were obtained; that is, a false starting point was used.

The dilution found most convenient at the time of adding the iodide and iodate is not less than 25 cm^3 for each decigram of boric acid (B_2O_3) present and should not be much greater than two or three times that amount. This limitation as regards volume is equally applicable, whether after obtaining the neutral point and treating with mannite, the boric acid is to be measured by a standard solution of alkali as before described or as here by the iodine liberated. As has been suggested, a large volume, even though saturated with mannite, prolongs the time of standing necessary and increases the effect of carbon dioxide upon the iodide and iodate present, for carbon dioxide, whether derived from the atmosphere or existing dissolved in the solution, upon standing, slowly liberates iodine. The amount, however, is small, and, in the time required for the completion of the process, has never been found equivalent to more than a single drop of the solution of thiosulphate used. Even if the material to be analyzed contains carbonates, after acidifying in concentrated solution and shaking vigorously, the small amount of uncombined carbon dioxide remaining has almost an inappreciable effect upon the results. The length of time required for the liberation of the theoretical amount of iodine in a solution of the volume suggested above, is 20 to 45 minutes, and at the end of 45 minutes standing in a solution saturated with mannite the reaction may be considered complete. During this period, however, it is well to keep the solution cool — at zero will do no harm — and shake occasionally to insure thorough mixture. The free iodine would tend to escape upon standing unless kept in a closed flask, but it is more convenient, immediately after the addition of mannite, to treat with an excess of the standard solution of thiosulphate — 8 or 10 cm^3 more than the amount required to bleach the iodine liberated, and at the expiration of 40 to 60 minutes titrate back with $\frac{N}{10}$ iodine. The strength of the thiosulphate solution found most convenient is $\frac{N}{5}$, while the use of iodine of one-half this strength ($\frac{N}{10}$) enables the error of reading to be correspondingly diminished. In solutions of the volume recommended the addition of starch to give the indication with iodine is unnecessary and even detrimental, since a single drop of one-twentieth normal iodine in excess is sufficient to give a strong lemon coloration, while in the presence of starch an indefinite dirty red first appears and remains until the blue is brought out by the further addition of iodine.

With these observations in mind, a series of experiments was made in which the standard solution of boric acid was drawn into an Erlenmeyer flask, containing a small amount of free hydrochloric acid and made up to a definite volume. To bring the conditions to those of an actual analysis about 1 grm. of crystalline calcium chloride in solution was also added. Potassium iodate (5–10 cm^3 of a 5 per cent solution) and iodide (3–5 cm^3 of a 40 per cent solution) were added, and the iodine liberated by the hydrochloric acid, barely bleached and again brought to coloration by iodine. Mannite was added to saturate the solution, an excess of standard thiosulphate put in, and the solution set aside for various periods of time, at the end of which the excess of thiosulphate was titrated by iodine and the amount of unrecovered thiosulphate taken as a measure of the boric acid present.

The thiosulphate used was 0.198 normal and the iodine 0.0996 normal. The solution of boric acid contained 7.738 grm. per liter.

TABLE II.

B_2O_3 taken.	Thio. taken.	Iodine taken.	Time of standing.	Volume.	B_2O_3 taken.	B_2O_3 found.	Error.
				A			
cm³	cm³	cm³	hrs.	cm³	grm.	grm.	grm.
28.00	82.00	1.88	0.30	28	0.2165	0.2168	0.0008+
27.03	82.00	4.87	0.27	27	0.2090	0.2081	0.0009−
27.02	81.97	4.04	1.00	27	0.2089	0.2090	0.0001+
				B			
27.06	82.04	8.88	1.00	50–60	0.2093	0.2101	0.0008+
27.02	82.02	4.40	1.00	50–60	0.2089	0.2081	0.0058−
27.04	81.72	8.39	1.00	50–60	0.2091	0.2096	0.0005+
				C			
27.01	81.58	2.88	2.00	50–60	0.2089	0.2100	0.0011+
26.05	31.01	4.01	3.00	50–60	0.2014	0.2025	0.0011+
				D			
27.00	81.00	2.12	0.30	50–60	0.2088	0.2089	0.0001+
27.00	82.00	4.05	0.30	50–60	0.2088	0.2092	0.0004+
26.01	32.02	6.20	0.30	50–60	0.2011	0.2018	0.0007+
27.08	31.01	2.21	0.48	50–60	0.2090	0.2087	0.0008−
27.05	81.89	8.81	0.45	50–60	0.2092	0.2003	0.0001+
26.07	31.02	4.14	0.40	50–60	0.2016	0.2020	0.0004+
27.00	32.04	4.30	0.40	60	0.2088	0.2086	0.0002−

These results are so regular that the method seems worthy of high commendation, and especially since the standard solutions, thiosulphate and iodine, upon which the process depends, are so easily prepared and generally at hand.

The full method of procedure recommended is as follows: The borate is dissolved in as small volume and as little hydrochloric acid as possible, shaking well to remove free carbon dioxide and diluting so that, at the time of adding potassium iodide and iodate, there shall be approximately 25–50 cm^3 of solution for each decigram of boric anhydride present. The greater part of the excess of hydrochloric acid in the solution is destroyed by sodium hydroxide and the use of litmus paper, leaving the solution distinctly acid in reaction. Potassium iodide (3–5 cm^3 of a 40 per cent solution), and iodate (5–10 cm^3 of a 5 per cent solution) are added in excess of that required to liberate iodine in an amount corresponding to the hydrochloric acid and the boric acid present. The iodine liberated by the free hydrochloric acid is bleached by a small amount of a strong solution of thiosulphate, and after agitating to insure thorough mixture, iodine is added to faint coloration. Sufficient mannite is now used to saturate the solution — about 10–15 grm. for a volume of 50 cm^3 — and sodium thiosulphate added in standard solution 8–10 cm^3 in excess of that required to bleach the iodine immediately thrown out by the mannite. The solution is again brought to saturation, if necessary, by mannite and after standing in a cool place for 40–60 minutes, titrated with decinormal iodine to determine the excess of thiosulphate present. In the manner described, specimens of crude calcium borate and crystals of colemanite were analyzed with the results given below.

TABLE III.

CALCIUM BORATE.

Mineral.	Thio. taken.	Iodine taken.	Time standing.	Volume of solutions.	B_2O_3 found.	Per cent.
grm.	cm^3	cm^3	hrs.	cm^3	grm.	
0.4015	35.05	4.75	1.00	40	0.2280	56.92
0.4010	35.34	5.28	2.00	45	0.2283	56.94
COLEMANITE.						
0.4002	32.00	5.50	1.30	50	0.2048	51.04
0.2513	32.01	7.36	1.00	40	0.1279	50.91
0.4007	33.03	7.72	0.50	65	0.2086	50.81

The solution of thiosulphate used was 0.19939 and the iodine 0.0996 normal.

These results show little variation and in the case of colemanite correspond closely to the theory 50.97 per cent. The process is convenient, generally applicable, and accurate within the ordinary limits of analysis.

XXXI

THE DOUBLE AMMONIUM PHOSPHATES OF BERYLLIUM, ZINC, AND CADMIUM IN ANALYSIS.

BY MARTHA AUSTIN.*

IT has been shown † that the composition of the phosphate of manganese thrown down by microcosmic salt from the solution of a pure manganous salt contains more manganese than belongs to the ideal ammonium manganese phosphate NH_4MnPO_4; and, further, that by acting with ammonium chloride in proper proportion the phosphate of manganese thrown down by microcosmic salt may be completely converted to the ideal ammonium manganese phosphate. Ammonium chloride, likewise, in the case of magnesium phosphate ‡ tends to cause the replacement of the metal by ammonia. Indeed, the replacement here is readily carried so far beyond the point corresponding to the normal ammonium magnesium phosphate, NH_4MgPO_4, that the tendency to form a salt richer in ammonia and poorer in magnesium — perhaps something like $Mg(NH_4)_4(PO_4)_2$ — must be recognized.

These facts suggested an investigation into the constitution of certain other ammonium phosphates with reference to their utility in analytical processes. Of the elements of Mendeléeff's second group, beryllium, magnesium, zinc, cadmium, and mercury are capable of yielding double ammonium phosphates, while no such compounds of calcium, strontium and barium have been described. The solubility in ammonia of the double ammonium phosphates of the elements of the former category

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* From Am. Jour. Sci., viii, 206.

† Am. Jour. Sci., vol. vi, 233. This volume, p. 121.

‡ Am. Jour. Sci., vol. vii, 187. This volume, p. 190.

appears to increase as the elements of which they are compounds are removed in the series from the beryllium, and, while the same is true of the simple phosphates of members of the latter category, the extent of such solvent action is slight comparatively. According to the work recorded in the literature, calcium, barium, and strontium form individually a neutral tribasic phosphate or acid phosphates of greater or less degree of acidity according to the conditions of precipitation. In my experience where salts of these elements were precipitated either with ammonium phosphate or microcosmic salt in presence of varying amounts of ammonium chloride, or ammonia, or both, only the recognized phosphates were obtained. The effect of ammonium salts in presence of ammonia seemed to promote the formation of the tribasic salt in the case of calcium and strontium; barium tends to form the barium acid phosphate almost exclusively even in the presence of ammonium salts and free ammonia. No double ammonium phosphate of either calcium, strontium, or barium was produced under any condition. As is well known, mercury does form an ammonium mercury phosphate, but the salt is soluble to so great a degree in ammonia, ammonium chloride, and even in the precipitant itself, that nothing of any value for analytical work seemed likely to come from its study.

The Ammonium Beryllium Phosphate.

The ammonium beryllium phosphate has beeen described by Roessler * as a crystalline salt produced by boiling some time in ammoniacal solution the phosphate precipitated by ammonium phosphate, though the best results of this treatment failed to yield the ideal constitution of this salt, NH_4BePO_4. This same precipitate cannot be obtained, Roessler further states, by using a sodium salt as the precipitant. In order to follow out this work of Roessler, a solution of berryllium chloride for use was prepared as follows: The pure beryllium chloride of commerce was dissolved in as little water as

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* Fresenius, Zeitschr. anal. Chem., xvii, 148.

possible and treated for the precipitation of aluminum by ethereal hydrochloric acid.* After filtering and evaporating from the filtrate the ether and a part of the hydrochloric acid, the beryllium was precipitated with ammonia, filtered to remove any members of the magnesium group, and washed free from ammonium chloride. The larger part of the precipitate was dissolved in hydrochloric acid in slight excess, and boiled with the reserved portion. After filtering, the solution was diluted to definite volume and standardized by precipitating measured portions of the solution with ammonia, filtering on asbestos under pressure in a perforated platinum crucible, igniting the residue and weighing as the oxide. The results recorded in section A of the following table were obtained by precipitating definite volumes of the pure solution of beryllium chloride with ammonium phosphate in a platinum dish, dissolving the precipitate in hydrochloric acid in faint excess, and while hot precipitating slowly with dilute ammonia, boiling (while the solution was kept distinctly ammoniacal) until the flocky precipitate was entirely converted to a fine, powdery, semi-crystalline, rapidly subsiding mass. A quarter to a half-hour is necessary under the most favorable conditions to cause this conversion. After cooling, the precipitate was filtered off on asbestos under pressure in a perforated platinum crucible, washed carefully with distilled water, dried, ignited and weighed. The filtrate was tested for beryllium by boiling with ammonia. None was found in these cases, nor in any of the following work. Faint traces of chloride were found in the residues after ignition after dissolving in nitric acid and testing with silver nitrate.

The results are in every case in excess of the theory for the pyrophosphate derived by ignition of the ammonium beryllium phosphate, possibly because the ammonium chloride present may have a tendency to form a salt too rich in ammonium (as was shown to be the case with the magnesium salt), consequently giving too much phosphoric acid in the ignited residue; or, because of inclusion of the chloride and phosphoric

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* Am. Jour. Sci., iv, 111. This volume, p. 111.

acid. It might reasonably be expected that some phosphoric acid may be held, since a trace of chloride was found. Either or both of these substances may have been held mechanically, or in combination.

It was found that on boiling for some time the solution of beryllium chloride with microcosmic salt — (6) section B of the table — and precipitating in the same manner as when ammonium phosphate was used the same sort of powdery mass remained as was obtained by the ammonium phosphate. The residue being tested for sodium according to the method brought out by Kreider and Breckenridge,* showed sodium present to the amount of 0.0062 grm. reckoned as sodium phosphate. It may be reasonably supposed that the presence of the sodium was due to one of two causes, — inclusion of the soluble phosphate, or a tendency on the part of the beryllium to form an ammonium† sodium beryllium phosphate or a sodium‡ beryllium phosphate, both of which are known to exist. Long boiling of the precipitates is tedious, and, unless great care is taken, may involve small losses of material; hence if the same results could be obtained with less boiling such treatment would be decidedly advantageous. The results in section C of the table were obtained by adding microcosmic salt to the hot solutions of the chloride, boiling five minutes, cooling, filtering off on an ashless filter — because of the flocky condition of the precipitate — treating as usual before igniting the residue in a platinum crucible. The results compare well with those obtained by long boiling of the precipitated beryllium — although all are in excess of the theory. That ammonium chloride here, as in cases above, has a marked effect in changing the constitution of the phosphate precipitated by microcosmic salt is not readily seen. It is obvious that the presence of an excess of the soluble phosphate is essential to precipitate the beryllium as the double ammonium phosphate from the results recorded in section D of the table, where,

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* Am. Jour. Sci., ii, 263. Volume I, p. 401.

† Persoz, Ann. Chem. (Liebig), lxv, 174; Atterberg, Bulletin Soc. Chim., xxiv, 358.

‡ Scheffer, Ann. Chem. (Liebig), cix, 144.

after the precipitate of beryllium phosphate had subsided and the supernatant liquid had been poured off, the precipitate dissolved in hydrochloric acid was brought down again at the boiling temperature with ammonia either alone or in presence of ammonium chloride. The results obtained show that the salt approaches the constitution of the tribasic phosphate, when it is precipitated in presence of a faint excess of phosphoric acid, even though ammonium chloride in large amount be present.

TABLE I.

Exp.	$Be_2P_2O_7$ corresponding to $BeCl_2$.			$Be_3P_2O_8$ corresponding to $BeCl_2$.			$(NH_4)_3PO_4$.	NH_4Cl.
	Taken.	Found.	Error.	Taken.	Found.	Error.		
				A.				
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.3578	0.3613	0.0035+	. . .	. . .	. . .	2	. . .
(2)	0.3578	0.3808	0.0230+	. . .	. . .	. . .	2	. . .
(3)	0.3578	0.3707	0.0129+	. . .	. . .	. . .	2	. . .
(4)	0.3578	0.3640	0.0062+	. . .	. . .	. . .	2	. . .
(5)	0.3578	0.3680	0.0102+	. . .	. . .	. . .	2	30
				B.			$HNaNH_4PO_4 . 4H_2O$.	
(6)	0.3578	0.3697	0.0119+	. . .	. . .	. . .		
				C.				
(7)	0.3578	0.3618	0.0040+	. . .	. . .	. . .	1.2	. . .
(8)	0.3578	0.3680	0.0102+	. . .	. . .	. . .	1.2	. . .
(9)	0.3578	0.3729	0.0151+	. . .	. . .	. . .	1.2	10
(10)	0.3578	0.3631	0.0053+	. . .	. . .	. . .	1.2	60
				D.				
(11)	. . .	. . .	. . .	0.2700	0.2589	0.0111−	0.5	. . .
(12)	. . .	. . .	. . .	0.2700	0.2989	0.0289+	0.5	—10
(13)	. . .	. . .	. . .	0.2700	0.2936	0.0236+	0.5	5–60
(14)	. . .	. . .	. . .	0.2700	0.2507	0.0193−	0.5	—60

From the work described it is clear that the ammonium beryllium phosphate is not obtained in ideal condition by precipitating a solution of the chloride with ammonium phosphate. Roessler's own results were likewise only approximately correct, as he states. It is also plain that hydrogen sodium ammonium phosphate precipitates the ammonium beryllium phosphate in a condition as nearly ideal as does the ammonium phosphate, while the effect of the ammonium chloride in either case is not marked in producing a phosphate containing ammonia. Of most importance in obtaining the ammonium salt is an excess of the soluble phosphate, for when the amount of the precipitant is reduced to a little more than the theoretical amount the condition of the phosphate coincides almost exactly with the theory for the tribasic phosphate, even though a large excess of ammonium chloride be present. When there is an abundance of the precipitant the results are all in excess of the theory, which may be accounted for on the supposition that foreign material is included — the chloride of ammonia and the soluble phosphate — to a greater or less extent by the precipitate. The formation of a phosphate of beryllium containing too much ammonia and phosphoric acid, or, in case of the precipitations by microcosmic salt, sodium by the formation of a sodium ammonium beryllium phosphate and sodium beryllium phosphate (known salts), is not definitely proved.

The Ammonium Zinc Phosphate.

Debray,* Bette † and Heintz ‡ separately found that ammonium zinc phosphate is formed by boiling a solution of zinc sulphate with ammonium phosphate. This salt was investigated later by A. Guyard (Hugo Tamm),§ who found that if to a solution of a zinc salt of an organic or a mineral acid supersaturated with ammonia until all the zinc oxide is dissolved and made faintly acid with hydrochloric acid, sodium phosphate be added, a flocky precipitate resulted, which on being kept near the boiling point for some seconds was converted to crystalline zinc ammonium phosphate, which filtered readily and was washed free from impurities with the greatest facility. He found that all the zinc in solution was thrown down as the ammonium zinc phosphate, which on ignition yielded the zinc pyrophosphate. With care in handling this process to avoid an excess of the precipitant,

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* Compt. rend., lix, 40.

† Ann. Chem. (Liebig), xv, 129.

‡ Ann. Chem. (Liebig), cxliii, 156.

§ Chem. News, xxiv, 148.

and the presence of sodium and potassium salts (on account of the danger of occlusion) the precipitation of the ammonium zinc phosphate, ignition, and weighing as the pyrophosphate made, Guyard believed, an ideal process for the estimation of zinc. Although there was slight solubility of the salt, it made an insignificant loss when the process was handled properly. Acids present, or certain alkalies to any great extent, increased the solubility of the salt so much that the loss became appreciable. Another source of error was to Guyard's mind loss of zinc during the ignition of the zinc ammonium phosphate with the paper on which the precipitate had been collected. Garrigues * found, in estimating zinc in a practical way, that this process advocated by Guyard gives in solutions of zinc free from salts of all metals, even alkaline salts — solutions that from previous steps in analysis, however, must have contained ammonium chloride in large amount — as satisfactory results as Guyard claimed for it. Garrigues' method of procedure was to add acid diammonium phosphate to a warm solution of zinc exactly neutralized with either hydrochloric acid or ammonia, so that the weights of zinc ammonium phosphate and that of the diammonium phosphate added should be as one to five respectively, to heat until the flocky precipitate becomes crystalline and subsides, filtering off on asbestos, drying at 100° C. and weighing preferably, although the residue may be ignited without loss, since the filtration is made on asbestos in a perforated crucible. Langmuir † modifies the method by destroying with dilute acetic acid any free ammonia that may be left in the solution after boiling.

In the work that follows, in which an attempt was made to show what precipitate is formed from a solution of zinc by the action of a soluble phosphate, also what effect ammonium chloride has upon the precipitate, a solution of zinc chloride prepared as detailed below was employed. The pure zinc chloride of commerce was treated with zinc carbonate, filtered and precipitated with ammonium sulphide. This precipitate

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* Jour. Am. Chem. Soc., xix, 936.

† Jour. Am. Chem. Soc., xxi, 115.

was boiled in a slight excess of hydrochloric acid until all the hydrogen sulphide was removed, and then was precipitated with sodium carbonate. After washing carefully until all the chloride was removed, the greater part of the carbonate was dissolved in sulphuric acid in slight excess, boiled with the remaining portion of the carbonate and filtered. This solution diluted to definite volume was standardized as sulphate by evaporating the solution to dryness in a platinum crucible and heating the residue.* The heating is carried on safely by so placing the platinum crucible in a radiator (consisting of a crucible and a triangle) that the bottom of the platinum crucible was held about one centimeter above the bottom of the outside crucible. Constant weights were obtained in successive treatment with a few drops of sulphuric acid and heating over the radiator. The results obtained in this manner were a trifle higher, though in fair agreement (when the nature of the carbonate process is taken into consideration) with determinations of the zinc in the solutions as oxide after precipitating with sodium carbonate with the usual precautions, filtering off on asbestos under pressure in a perforated platinum crucible, washing with distilled water, drying, and igniting. Results are given in Table II showing the amount of zinc sulphate found in five different portions each of forty cubic centimeters of the solution of zinc sulphate, and, for comparison, the results of determinations as zinc oxide by the carbonate processes are included.

TABLE II.

$ZnSO_4$ found in 40 cm^3 of solution.	Mean value of ZnO corresponding to $ZnSO_4$ in 40 cm^3 of solution.	ZnO found in 40 cm^3 of solution by precipitation as the carbonate.
grm.	grm.	grm.
0.5386	0.2712	0.2691
0.5385		0.2685
0.5387		0.2711
0.5387		
0.5390		

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* Rose-Finkener, Analytische Chemie, 6te Auflage, vol. ii, 117.

Definite portions of the solution of zinc sulphate were carefully drawn from a burette into a platinum dish, heated and treated with ammonium phosphate until the solution turned red litmus paper blue. The whole was heated until the flocky precipitate became crystalline and fell to the bottom of the dish. The solution after standing as recorded in section A of the table was filtered off on asbestos under pressure in a perforated platinum crucible, and the precipitate was washed with distilled water, dried, ignited and weighed. The filtrate in each case, as in all following cases, was tested for zinc with sulphuretted hydrogen. The results recorded in section B of the table were obtained in the same manner as those of section A, with microcosmic salt substituted for the ammonium salt as the precipitant. The results are below the theory for the pyrophosphate, but no appreciable amount of zinc appeared in the filtrates. Neither ammonium phosphate nor ammonium sodium phosphate seems to precipitate the ideal ammonium zinc phosphate under these conditions; and the time of standing appears to be without effect.

The results recorded in section C were obtained by precipitating the warm solution of the zinc in presence of large amounts of ammonium chloride by adding microcosmic salt until the solution was alkaline to litmus. From these results it seems that the presence of ammonium chloride is essential for the conversion of the zinc phosphate precipitated by hydrogen sodium ammonium phosphate to the ammonium zinc salt. As a matter of fact the solutions employed by Guyard and those in which estimations are made by practical workers do contain ammonium chloride formed in previous steps of the analysis. The proportion of zinc to phosphate suggested by Garrigues — 1 : 5 — is the amount of soluble phosphate necessary to turn red litmus blue after the zinc is precipitated. In order to find out whether the presence of so large an amount of the soluble phosphate is necessary in presence of ammonium chloride, the solution of zinc sulphate was precipitated in presence of the necessary amount of ammonium chloride by the microcosmic salt in small excess above the equivalent of the zinc salt, and the solution was made just ammoniacal to litmus with a few drops of dilute ammonia both before and after heating to convert the precipitate to crystalline condition. Experiment (15) shows that precipitation is not complete under these conditions. The zinc left in the solution was precipitated at once as sulphide, and estimated as the oxide, after dissolving in hydrochloric acid and precipitating

TABLE III.

Exp.	$Zn_2P_2O_7$ corresponding to $ZnSO_4$. Taken.	Found.	Error.	Error in terms of Zinc.	$Zn_2P_2O_7$ corresponding to Zn left in the filtrate.	$(NH_4)_2PO_4$.	NH_4Cl.	Time of standing.
A.								
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	hrs.
(1)	0.6355	0.6206	0.0149—	0.0060—	Trace.	3.13	. .	1½
(2)	0.6355	0.6254	0.0101—	0.0040—	Trace.	3.13	. .	16
(3)	0.6355	0.6300	0.0055—	0.0022—	Trace.	3.13	. .	16
B.								
						$HNaNH_4PO_4 . 4H_2O$.		
(4)	0.6355	0.6271	0.0084—	0.0034—	Trace.	4.47	0.5	1
(5)	0.6355	0.6256	0.0099—	0.0040—	None.	4.47	0.5	20
C.								
(6)	0.6355	0.6285	0.0070—	0.0028—	None.	4.47	10	½
(7)	0.6355	0.6304	0.0051—	0.0020—	None.	4.47	10	½
(8)	0.6355	0.6295	0.0060—	0.0024—	None.	4.47	10	2½
(9)	0.6355	0.6335	0.0020—	0.0008—	None.	4.47	10	16
(10)	0.6355	0.6381	0.0026+	0.0010+	None.	4.47	20	½
(11)	0.6355	0.6379	0.0024+	0.0009+	None.	4.47	20	2
(12)	0.6355	0.6386	0.0031+	0.0012+	None.	4.47	20	½
(13)	0.6355	0.6393	0.0038+	0.0014+	None.	4.47	20	½
(14)	0.6367	0.6355	0.0012+	0.0005+	None.	4.47	30	16
D.								
(15)	0.6355	0.6172	0.0183—	0.0072—	0.0108	0.894	20	8
(16)	0.6355	I 0.6227 II 0.0040	0.0098—	0.0039—	None.	I 0.894 II 3.576	20	½
E.								
(17)	0.6355	0.6270	0.0085—	0.0034—	None.	4.47	. .	8
(18)	0.6355	0.6125	0.0230—	0.0093—	0.0148	4.47	. .	18
(19)	0.6355	0.6303	0.0052—	0.0021—	0.0020	4.47	10	18

with sodium carbonate. In (16) of the table the first filtrate was treated with an excess of microcosmic salt, and boiled. Another portion of the ammonium zinc phosphate was precipitated, and was filtered off and estimated. No zinc was found by sulphuretted hydrogen in the second filtrate.

From the results it seems obvious also that an excess of the soluble phosphate is necessary to complete the precipitation of the zinc as the ammonium zinc phosphate instead of partly ammonium zinc phosphate and partly tribasic phosphate.

In section E of the table are recorded results where the precipitation was made in presence of an excess of the precipitant either alone or in presence of ammonium chloride, the solution being made faintly acid to litmus with acetic acid, according to the manner in which Langmuir recommends to conduct the precipitation. All the results by the method are low. The condition of the ammonium zinc phosphate most nearly approximating to the ideal is obtained as shown in (9) to (14) by precipitating in presence of ammonium chloride in large amount. Microcosmic salt is added until the solution containing the ammonium salt is alkaline and the whole is heated until the mass subsides in crystalline condition. The amount of ammonium chloride should be twenty grams if the filtration is to be made as soon as the solution cools. One-half the amount will do if the liquid stands a number of hours. Larger amounts tend to give a salt too rich in ammonia. The time of standing seems to be a less important factor than either the excess of microcosmic salt or ammonium chloride.

The Ammonium Cadmium Phosphate.

According to S. Drewsen* the cadmium ammonium phosphate is precipitated by allowing a solution of cadmium sulphate to stand twenty-four hours with ammonium phosphate. It is very soluble both in acids and alkalies. No further preparation of this seems to have been recorded. For the work on this salt to be given below, done with reference to the constitution of the salt precipitated by hydrogen sodium

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* Gmelin-Kraut, 6te Auflage, iii, 74.

ammonium phosphate, the effect of ammonium chloride in the precipitation, and the value of the salt for quantitative work, the solution of cadmium chloride employed was prepared as follows: A solution of cadmium sulphate acidulated with hydrochloric acid was precipitated with sulphuretted hydrogen, filtered and washed, and the precipitated sulphide was dissolved in hydrochloric acid and filtered from possible traces of copper and lead. The solution of the sulphide in hydrochloric acid was boiled until all the sulphuretted hydrogen was expelled, and filtered on asbestos in a perforated crucible of platinum under pressure. The cadmium in the filtrate precipitated with ammonium carbonate in excess was washed free from chloride, dissolved in hydrochloric acid and diluted to definite volume. It was standardized as oxide* after precipitating with sodium carbonate with the necessary precautions.

The standard solution of cadmium chloride was drawn carefully from a burette into a platinum dish, and, while hot, was precipitated by adding hydrogen sodium ammonium phosphate until the solution was alkaline to litmus. After heating until the solution became crystalline, the whole stood three hours in case of (1) of the table and sixteen hours in case of (2) and (3), before filtering. In experiments (4) to (12), inclusive, recorded in the table, precipitation was made in the same manner as in (1) to (3) in presence of varying amounts of ammonium chloride, and the precipitates were filtered after standing as stated below in the table. It is clear from the results that the cadmium separates out completely on long standing only. Moreover, the ideal condition of the ammonium cadmium phosphate is obtained only when an abundance of ammonium chloride is present; but large amounts of ammonium chloride dissolve this salt. In (14), where ammonia was added after precipitation was complete, the salt dissolved somewhat; also in (15), where the solution was left faintly acid with acetic acid, a large part of the salt was dissolved. These weights of cadmium dissolved in the filtrate were obtained by treating the filtrates with sulphuretted

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* Browning, Am. Jour. Sci., xlvi, 280. Volume I, p. 226.

TABLE IV.

Exp.	$Cd_2P_2O_7$ corresponding to $CdCl_2$. Taken.	Found.	Error.	Error in terms of Cadmium.	$Cd_2P_2O_7$ corresponding to Cd found in the filtrate.	$HNaNH_4PO_4.4H_2O$.	NH_4Cl.	Time of standing.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	hrs.
(1)	0.6972	0.6201	0.0771–	0.0434–	0.0059	4.5	. .	3
(2)	0.6972	0.6135	0.0837–	0.0471–	None.	4.5	. .	16
(3)	0.6972	0.6134	0.0838–	0.0471–	None.	4.5	. .	16
(4)	0.6972	0.6792	0.0180–	0.0101–	Trace.	4.5	1	16
(5)	0.6972	0.6831	0.0141–	0.0079–	0.0113	4.5	10	2
(6)	0.6972	0.6976	0.0004+	0.0002+	Trace.	4.5	10	16
(7)	0.6972	0.6969	0.0003–	0.0002–	Trace.	4.5	10	18
(8)	0.6972	0.6962	0.0010–	0.0006–	Trace.	4.5	10	16
(9)	0.6972	0.6891	0.0081–	0.0045–	0.0191	4.5	20	16
(10)	0.6972	0.6972	0.0000	0.0000	Trace.	4.5	20	16
(11)	0.6972	0.6942	0.0030–	0.0016–	Trace.	4.5	20	16
(12)	0.6972	0.6737	0.0235–	0.0132–	0.0304	4.5	30	16
(13)	0.6972	0.5655	0.1317–	0.0741–	0.1378	4.5	30	16
(14)	0.6972	0.6922	0.0050–	0.0023–	0.0088	4.5	10	16
(15)	0.6972	0.3209	0.3763–	0.2117–	0.2449	4.5	. .	16

hydrogen, dissolving the sulphide in nitric acid, and weighing as oxide after precipitating with sodium carbonate.

The ammonium cadmium phosphate is obtained in ideal condition by precipitating with microcosmic salt in presence of 10 grm. ammonium chloride in a total volume of 100 cm^3 to 150 cm^3 — shown in (6), (7), and (8) — filtering after standing some time. On drying and igniting the pyrophosphate is left. Very large amounts of ammonium chloride — 30 grm. — dissolve the salt, and seem to tend to cause the formation of a phosphate too rich in ammonia. Either acid or ammonia in small amount dissolves the salt, as is shown in (14) and (15).

The results of this investigation as to the analytical application of the double ammonium phosphates of beryllium, zinc, and cadmium may be summarized briefly as follows: It is impossible to estimate beryllium with accuracy as the pyrophosphate obtained by igniting the double ammonium phosphate precipitated from beryllium solutions by microcosmic salt or ammonium phosphate in presence of ammonium chloride. In presence of the proper amount of ammonium chloride (10 grm. to 20 grm. in 100 cm^3–200 cm^3 of liquid) zinc ammonium phosphate can be obtained in the ideal condition, which on ignition yields the pyrophosphate. This method may serve, therefore, for the accurate estimation of zinc.

Cadmium may be estimated with accuracy as the pyrophosphate if the precipitate by microcosmic salt in the nearly neutral solution containing ammonium chloride in the proportion of ten grams to one hundred cubic centimeters is allowed to stand several hours before filtering. In this way all cadmium separates out from the solution as a beautiful crystalline mass of cadmium ammonium phosphate of ideal constitution. The conditions, must, however, be preserved with care; there must be no excess of ammonia, no free acid, and no excess of ammonium salt beyond the quantity indicated, while that amount is necessary.

XXXII

SEPARATION OF IRON FROM CHROMIUM, ZIRCONIUM, AND BERYLLIUM, BY THE ACTION OF GASEOUS HYDROCHLORIC ACID ON THE OXIDES.

BY FRANKE STUART HAVENS AND ARTHUR FITCH WAY.*

IT has been shown in a former paper from this laboratory † that iron oxide may be completely volatilized as chloride by a strong current of hydrochloric acid gas acting at a temperature of 450 -500°, and also that the addition of a little free chlorine to the gaseous hydrochloric acid renders this action complete at lower temperatures, 180°-200°, without the danger of error arising from the liability of ferric chloride to dissociation, or from deficiency of oxidation in the oxide treated, or mechanical loss due to too rapid volatilization. It has also been shown that this reaction can be employed for the separation of iron and aluminum, taken as the oxides, and its application to the separation of iron from other metallic oxides has been suggested.

The oxides of chromium, zirconium, and beryllium, like aluminum oxide, are not acted upon by a current of dry hydrochloric acid gas at the temperatures before mentioned, and these oxides also can be entirely freed from iron by this reaction, as the experiments to be described will show. The procedure was the same in each case and analogous to that employed for the separation of iron from aluminum. A mixture of a weighed portion of one of these oxides with a weighed portion of ferric oxide, contained in a porcelain boat and placed within a roomy glass tube supported in a small

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* From Am. Jour. Sci., viii, 217.

† Gooch and Havens, Am. Jour. Sci., vii, 370. This volume, p. 215.

combustion furnace, was submitted to the action of a dry current of hydrochloric acid gas and chlorine generated by dropping sulphuric acid upon a mixture of strong hydrochloric acid, common salt, and a small amount of manganese dioxide. The gas was admitted at one end of the combustion tube and passed out at the other through a water trap, while the required temperature, from 200°–300°, was maintained by regulating the various burners of the furnace. The time of action varies somewhat with the condition of the oxide to be volatilized, and the temperature; generally an hour's heating at 200°, proves sufficient for the complete removal of 0.1 grm. of iron. At higher temperatures the action is more rapid; but the lighter oxide, the beryllium especially, is liable to mechanical loss through the too rapid volatilization of the iron, as experiment (17), where a temperature of 500° was used, will show. It is better, therefore, to use lower temperatures, raising the heat for a few minutes when the action is apparently complete to ensure the removal of the last traces of iron. Tests showed

Exp.	Fe_2O_3 taken.	Cr_2O_3 taken.	Cr_2O_3 found.	Error.
	grm.	grm.	grm.	grm.
(1)	..	0.1003	0.1003	0.0000
(2)	0.1007	0.1006	0.1006	0.0000
(3)	0.1007	0.1000	0.1002	0.0002+
(4)	0.1010	0.1005	0.1003	0.0002−
(5)	0.1019	0.1006	0.1005	0.0001−
(6)	0.2007	0.1003	0.0999	0.0004−
		ZrO_2 taken.	ZrO_2 found.	
(7)	..	0.1516	0.1516	0.0000
(8)	0.1053	0.1010	0.1010	0.0000
(9)	0.1204	0.1519	0.1523	0.0004+
(10)	0.1236	0.1516	0.1517	0.0001+
(11)	0.2150	0.1517	0.1519	0.0002+
		BeO taken.	BeO found.	
(12)	..	0.1309	0.1311	0.0002+
(13)	..	0.1285	0.1285	0.0000
(14)	0.0997	0.0456	0.0457	0.0001+
(15)	0.1045	0.1099	0.1099	0.0000
(16)	0.1215	0.1080	0.1081	0.0001+
(17)	0.1510	0.1305	0.1290	0.0015−
(18)	0.0230	0.1081	0.1083	0.0002+

the residual oxides from which the ferric oxide had been removed in this manner to be entirely free from iron.

The separation of iron from chromium, zirconium, and beryllium by this method is obviously complete within very satisfactory limits of error.

XXXIII

THE IODOMETRIC DETERMINATION OF GOLD.

BY F. A GOOCH AND FREDERICK H. MORLEY.*

IN a recent attempt to measure small amounts of gold in solution by titrating with sodium thiosulphate the iodine set free in the action of an excess of potassium iodide upon auric chloride, Peterson† has been led to conclude that, on the average, one-half more thiosulphate is used up in changing the characteristic starch iodide blue to the faint rose color which precedes entire bleaching than is called for upon the theory that the thiosulphate is simply converted to the tetrathionate in the usual manner. Peterson explains the anomaly upon the hypothesis that, besides acting upon the free iodine, the thiosulphate is used up coincidently by interaction with the aurous salt, formed in the reduction, with formation of a gold sodium thiosulphate on the type of the well-known silver sodium thiosulphate. The reaction of this hypothesis is in the nature of things most improbable, since there is no reason to suppose that the soluble double thiosulphate could resist the action of the free iodine which is present to the end — the appearance of the rose color, and our study of the reaction of sodium thiosulphate upon the mixture of gold chloride and potassium iodide, the account of which follows, discloses no evidence of the consumption of more thiosulphate than is demanded by the usual theory, which postulates the simple formation of the tetrathionate by the interaction of the thiosulphate and free iodine.

It appeared in the course of our preliminary experimenta-

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* From Am. Jour. Sci., viii, 261.

† Zeitschr. anorg. Chem., xix, 63.

tion that, while practically similar results were obtained by adding the thiosulphate until the blue of the starch iodide had changed to rose, the indications were somewhat more concordant when the final rose color was developed by adding iodine to the solution from which the blue had been bleached to colorlessness by a slight excess of the thiosulphate.

It appeared, also, that the reduction of the auric salt, with the consequent liberation of iodine, is conditioned by the volume of the solution, the mass of the iodine present, and the time of action.

The following statement, in which each result is the average of several titrations in close agreement, shows the effect upon the immediate evolution of iodine brought about by adding varying amounts of water to the gold solution before introducing the iodide, and the effect of different amounts of iodide at different dilutions.

	Potassium iodide.					Gold chloride.	Volume before the addition of the thiosulphate.
	0.01 grm.	0.02 grm.	0.05 grm.	0.1 grm.	0.2 grm.	0.00087 grm.	
							cm³
Sodium thiosulphate, nearly $\frac{N}{100}$ cm³.	0.81	0.81	0.81	0.82	0.84	0.00087	15
	0.77	0.78	0.80	0.81	0.81	0.00087	25
	0.74	0.72	0.78	0.79	0.80	0.00087	50
	0.61	0.61	0.68	0.76	0.79	0.00087	100
	0.45	0.49	0.60	0.72	0.75	0.00087	200

It is evident that for the smaller amounts of iodide the liberation of iodine decreases rapidly with the dilution. The larger amounts at the highest concentration show readings a trifle above the normal—perhaps because the well-known effect of concentrated solutions of a soluble iodide upon the delicacy of the starch end-color begins to appear. At volumes lying between the limit of 25 cm³ and 50 cm³ 0.1 grm. of potassium iodide is an appropriate amount to use; at a volume of 15 cm³, 0.01 grm. to 0.05 grm. of the iodide will do the work; and at lower dilutions, as will appear in the tabular statements to follow, even less of the iodide is effective.

In the series of experiments of which the details are given in Table I, use was made of a solution of pure gold chloride containing 0.8710 grm. to the liter — as determined by careful precipitation in the usual manner by ferrous sulphate, and by an alkaline solution of formaldehyde according to the method of Vanino.* A nearly centinormal solution of iodine was prepared by diluting to a liter 100 cm^3 of nearly decinormal iodine in potassium iodide carefully standardized against exactly decinormal arsenious acid. A nearly centinormal solution of sodium thiosulphate (containing 1.7012 grm. of $Na_2S_2O_3$ to the liter) was made by diluting to a liter 100 cm^3 of a nearly decinormal solution of that reagent which had been standardized carefully against the standard iodine prepared as described. The solution of potassium iodide employed contained 10 grm. of that salt in the liter.

In conducting the experiments, a convenient amount of the solution of gold chloride was drawn from a burette, potassium iodide was introduced in the amounts indicated (always several times the theoretical equivalent of the gold, and more than enough to dissolve the aurous iodide precipitated at first), a sufficiency of clear starch indicator was added, the starch blue was bleached by the thiosulphate, and the iodine was added until the liquid assumed a faint rose color. Upon the theory that potassium iodide sets free two atoms of iodine for every molecule of auric chloride (or every atom of gold) present, and that the thiosulphate acts only upon the free iodine to form the tetrathionate in the usual manner, every cubic centimeter of the thiosulphate solution used in the reaction after deducting the amount equivalent to the iodine introduced to get the end-color, should represent

$$\frac{197.3}{2(158.22)} \times 0.0017012 = 0.001061 \text{ grm. of gold.}$$

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* Ber. Dtsch. chem. Ges., xxi, 1763.

TABLE I.

Gold chloride = 0.8710 to 1 liter.
Sodium thiosulphate, nearly $\frac{N}{100}$ = 1.7012 " "
Iodine, nearly $\frac{N}{100}$ = 1.3697 " "
Volume at beginning of titration, approximately 50 cm³.

	$AuCl_3$ taken.	KI taken.	$Na_2S_2O_3$ used.	Gold found.	Theory for gold.	Error.	Per cent.
	cm³	grm.	cm³	grm.	grm.	grm.	
(1)	5	0.05	4.02	0.00426	0.00435	0.00009–	2.1
(2)	5	0.05	4.01	0.00425	0.00435	0.00010–	2.3
(3)	5	0.05	4.06	0.00481	0.00435	0.00004–	0.9
(4)	5	0.05	4.07	0.00432	0.00485	0.00003–	0.7
(5)	5	0.05	4.04	0.00428	0.00435	0.00007–	1.6
(6)	10	0.08	8.17	0.00867	0.00871	0.00004–	0.5
(7)	10	0.08	8.15	0.00864	0.00871	0.00007–	0.8
(8)	10	0.08	8.16	0.00865	0.00871	0.00006–	0.7
(9)	10	0.08	8.15	0.00864	0.00871	0.00007–	0.8
(10)	10	0.08	8.19	0.00869	0.00871	0.00002–	0.2
(11)	10	0.08	8.46	0.00897	0.00871	0.00026+	3.0
(12)	10	0.08	8.24	0.00874	0.00871	0.00003+	0.3

Plainly, these results accord reasonably with the theory that two molecules of the thiosulphate are the equivalent in this reaction of two atoms of iodine and one atom of gold. There is no evidence whatever of the excessive action affirmed by Peterson.

The strength of the standard solutions used in the experiments described was such that an error of 0.01 cm³ in reading the volumes used would correspond to an error of 0.00001 grm. of gold. It is not to be expected that such readings can be trusted ordinarily to a higher degree of accuracy than 0.02 cm³. In case all three solutions should be read to this limit of accuracy with the errors of all lying in the same direction, the summation of error would correspond to 0.00006 grm. of gold.

In the following experiments, therefore, solutions obtained by properly diluting those of the previous series were employed. The use of a more dilute solution of gold obviated the necessity for diluting the mixture of gold chloride and the iodide before titrating with the thiosulphate. It was found,

TABLE II.

A.

Gold chloride = 0.0871 to 1 liter.
Sodium thiosulphate, nearly $\frac{N}{100}$ = 1.7012 " "
Iodine, nearly $\frac{N}{100}$ = 1.3697 " "
Solution of gold chloride not diluted before mixing with potassium iodide.

Exp.	$AuCl_3$ taken.	KI taken.	$Na_2S_2O_3$ used.	Gold taken.	Gold found.	Error.
	cm³	grm.	cm³	grm.	grm.	grm.
(1)	10	0.01	0.83	0.00087	0.00088	0.00001+
(2)	10	0.01	0.83	0.00087	0.00088	0.00001+
(3)	10	0.01	0.80	0.00087	0.00085	0.00002−
(4)	10	0.02	0.84	0.00087	0.00089	0.00002+
(5)	10	0.02	0.88	0.00087	0.00093	0.00006+
(6)	10	0.02	0.82	0.00087	0.00087	0.00000
(7)	10	0.02	0.88	0.00087	0.00093	0.00006+
(8)	10	0.02	0.83	0.00087	0.00088	0.00001+
(9)	10	0.10	0.80	0.00087	0.00085	0.00002−
(10)	10	0.10	0.82	0.00087	0.00087	0.00000
(11)	10	0.01	0.83	0.00087	0.00088	0.00001+
(12)	9	0.01	0.73	0.00078	0.00077	0.00001−
(13)	8	0.01	0.65	0.00070	0.00069	0.00001−
(14)	7	0.01	0.58	0.00061	0.00061	0.00000
(15)	6	0.008	0.51	0.00052	0.00054	0.00002+
(16)	5	0.008	0.41	0.00043	0.00044	0.00001+
(17)	4	0.005	0.35	0.00035	0.00037	0.00002+
(18)	3	0.005	0.24	0.00026	0.00026	0.00000
(19)	2	0.003	0.21	0.00017	0.00022	0.00005+
(20)	1	0.003	0.10	0.00009	0.00011	0.00002+

B.

Gold chloride = 0.0871 to 1 liter.
Sodium thiosulphate, nearly $\frac{N}{1000}$ = 0.17012 " "
Iodine, nearly $\frac{N}{1000}$ = 0.13697 " "

Exp.	$AuCl_3$ taken.	KI taken.	$Na_2S_2O_3$ used.	Gold taken.	Gold found.	Error.
(21)	10	0.01	8.39	0.000871	0.000890	0.000019+
(22)	9	0.01	7.45	0.000784	0.000790	0.000006+
(23)	8	0.01	6.30	0.000697	0.000668	0.000029−
(24)	7	0.008	5.50	0.000610	0.000583	0.000027−
(25)	6	0.008	5.12	0.000523	0.000543	0.000020+
(26)	5	0.005	4.28	0.000435	0.000449	0.000014+
(27)	4	0.005	3.38	0.000348	0.000358	0.000010+
(28)	3	0.003	2.55	0.000261	0.000270	0.000009+
(29)	2	0.003	1.71	0.000174	0.000181	0.000007+
(30)	1	0.003	0.90	0.000087	0.000095	0.000008+

however, that when the $\frac{N}{1000}$ solution of iodine is employed a correction of 0.1 cm³ for volumes not exceeding 30 cm³ becomes necessary — the amount required to bring out the rose color in blank tests containing no gold. After the introduction of 0.1 cm^3 of $\frac{N}{1000}$ iodine into a mixture of potassium iodide and starch indicator of volume not exceeding 30 cm^3, a single drop of the gold solution — equivalent to 0.000002 grm. of gold — gave a distinct rose color: before such adjustment of the solution five drops — equivalent to 0.000010 of gold — were needed to develop the same color.

These results run on the whole as regularly as could be expected, and the use of the dilute standard solutions is obviously of advantage.

In the practical application of any such process for the determination of gold, the elementary form of that metal is the natural starting-point. To get the metal into solution with chlorine water or mixed hydrochloric and nitric acids is an easy matter, but the removal of the excess of the oxidizer by evaporation without reducing some auric chloride to the aurous form is difficult. We have found, however, that the free chlorine may be removed from a solution of auric chloride, without reducing the auric salt, by treatment of the solution with ammonia in excess, boiling gently, acidifying with hydrochloric acid and heating if necessary to redissolve the precipitate by ammonia, again treating with ammonia and heating, and once more acidifying. On the second addition of ammonia no precipitation usually takes place with the amounts of gold which we have thus handled, perhaps because enough ammonium chloride has been found to hold it up.

The following table contains determinations made with such a solution of pure gold leaf — tested gravimetrically as to purity.

Obviously, this method, which rests upon the hypothesis that sodium thiosulphate acts in the normal manner only upon the iodine set free by the interaction of gold chloride and potassium iodide, offers trustworthy means for the determination of small amounts of gold.

TABLE III.

Gold chloride made by dissolving 0.0104 grm. of pure gold in the manner described and diluting to 200 cm^3.

Sodium thiosulphate, nearly $\frac{N}{1000}$ = 0.17012 to 1 liter.

Iodine, nearly $\frac{N}{1000}$ = 0.18697 " "

Potassium iodide = 10 grm. " "

Portions were treated with the potassium iodide without previous dilution.

Exp.	$AuCl_3$ taken.	KI taken.	$Na_2S_2O_3$ used.	Gold taken.	Gold found.	Error.
	cm^3	grm.	cm^3	grm.	grm.	grm.
(1)	1	0.005	0.55	0.000052	0.000058	0.000006+
(2)	1	0.005	0.55	0.000052	0.000058	0.000006+
(3)	2	0.005	1.06	0.000104	0.000112	0.000008+
(4)	2	0.005	1.08	0.000104	0.000114	0.000010+
(5)	5	0.01	2.45	0.000260	0.000260	0.000000
(6)	5	0.01	2.50	0.000260	0.000265	0.000005+
(7)	5	0.01	2.45	0.000260	0.000260	0.000000
(8)	5	0.01	2.50	0.000260	0.000265	0.000005+
(9)	5	0.01	2.50	0.000260	0.000265	0.000005+
(10)	10	0.02	4.86	0.000520	0.000515	0.000005−
(11)	10	0.02	4.85	0.000520	0.000517	0.000003−
(12)	10	0.02	4.90	0.000520	0.000520	0.000000
(13)	10	0.02	4.80	0.000520	0.000512	0.000008−
(14)	10	0.02	4.84	0.000520	0.000516	0.000004−

XXXIV

THE ACTION OF ACETYLENE ON THE OXIDES OF COPPER.

By F. A. GOOCH and DeFOREST BALDWIN.*

In a recent paper by Erdmann and Köthner † an account is given of the formation of a peculiar, light-brown, highly voluminous substance by the action of acetylene below 250° C. upon cuprous oxide, or even (though more slowly) upon copper. The product obtained by passing acetylene during eighteen hours over 1 grm. of cuprous oxide (prepared from copper sulphate, grape sugar, and sodium hydroxide) amounted to 7 grm. and filled a space of nearly 300 cm^3. At higher temperatures a black carbonaceous mass is the result, and at red heat (400°–500° C.) carbon is deposited in graphitic condition. The light-brown fluffy material yielded cuprous chloride to hydrochloric acid, a distillate from its mixture with zinc dust possessing the characteristics of naphthene or, at higher temperature and under rapid heating, aromatic compounds among which naphthalene and a kresol were indicated. Erdmann and Köthner classify this body as a very complex but non-explosive copper acetylene (acetylenkupfer,), and from their analyses deduce the formula $C_{44}H_{64}Cu_{3}$. Apart from the unusual constitution of this symbol, its most striking peculiarity is that it implies a loss of carbon, rather than hydrogen, from the acetylene in the reaction with cuprous oxide — a condition of affairs which would be most remarkable in the light of Campbell's experience,‡ according to which acetylene passed over palladinized copper oxide

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* From Am. Jour. Sci., viii, 354. † Zeitschr. anorg. Chem., xviii, 49.

‡ Amer. Chem. Jour., xvii, 690.

yielded water at 225°-230° and carbon dioxide only when the temperature rose to 315°-320° with the formation of a black deposit. Upon scrutinizing the figures of Erdmann and Köthner with care, however, it appears that the formula given by these investigators rests upon some oversight in calculation: the ratio of carbon atoms to hydrogen atoms proves to be actually, according to the data given, 6.45 : 5.70; which means, of course, that the new product is deficient, as would be expected, in hydrogen (not in carbon) as compared with acetylene.

As to the content of the new substance in copper, the analytical data are unfortunately ambiguous; for we note the weights found of *copper oxide* converted into percentages of *copper* without preliminary reduction. If the fault is typographical and in the analytical data, the calculated percentages of copper being correct, the average percentage of copper amounts to 15.43: if, on the other hand, the analytical data are right, the error being in their reduction, the percentage of copper amounts to 12.92. In the one case the summation of the analysis leaves a deficiency of about 1.5 per cent, and in the other of about 4 per cent, which in either case may really represent oxygen in the substance. This condition of matters leaves the "acetylen-kupfer" of Erdmann and Köthner in uncertain standing.

More than thirty years ago it was noticed by Berthelot * that acetylene is polymerized by heat or decomposed partially into carbon and hydrogen, and that such action takes place more readily and at lower temperatures in presence of metallic iron with production of carbon, hydrogen and compounds different from those formed by heat alone.

Moissan and Moureu † have observed the incandescence of acetylene passed over finely divided iron, cobalt, nickel, or platinum at the ordinary temperature, with production of carbon, hydrogen, and pyrogenic compounds, and have found the occasion of such behavior in the porosity of the metals employed.

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* Ann. Chim. [4], ix, 448.

† Compt. rend., cxxii, 1240.

It would seem natural, however, that the presence of oxygen, free or combined, may also play a considerable part in such phenomena, just as appears to be the case in the peculiar action recorded by Gruner ‡ of carbon monoxide upon iron reduced by hydrogen, which, as Moissan has shown,§ is produced pure only with the greatest precaution and generally carries a large proportion of ferrous oxide. The fact that the "acetylen-kupfer" of Erdmann and Köthner is produced more easily by the action of cuprous oxide upon acetylene than by the action of metallic copper upon acetylene, suggests that it may be the oxidizing power of the cuprous oxide which gives to this reagent its peculiar activity. The question arises, therefore, as to whether the copper is in reality an essential constituent of the compound of Erdmann and Köthner.

In our experiments upon the action of acetylene upon the oxides of copper (and other elements) we have conducted the gas (made in the ordinary way by the action of water on calcium carbide, and kept over water) over the oxide contained in a porcelain boat placed within a glass tube, 2 cm. in diameter and 50 cm. long, which was heated over a small combustion furnace. The glass tube was fitted at each end with a rubber stopper, one carrying a smaller tube for the introduction of the acetylene and a high-temperature thermometer so held that its bulb rested horizontally immediately over the boat containing the oxide, while the other was fitted with a water-trap. In the preliminary experiments no attempt was made to purify the acetylene employed other than to keep it over water, or, since water is a product of its action upon oxides, to dry it: in later experiments to secure products for careful analysis it was dried and purified with care.

We found that 225° C. is the temperature most favorable for the formation of the voluminous product obtained by acting with acetylene upon cuprous oxide as described by Erdmann and Köthner. At this temperature the tube is choked rapidly with the fluffy product and water forms, but, as Campbell found in his experiments upon palladinized copper oxide, no

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‡ Ann. Chim. [4], xxvi, 5.

§ Ann. Chim. [5], xxi, 199.

appreciable amount of carbon dioxide is produced. The content of the product in copper varies in the sample and in different experiments, our results lying between 1.54 per cent and 24.21 per cent of the substance taken for ignition.

It appeared, also, that the action of acetylene upon cupric oxide is precisely similar to that upon cuprous oxide excepting the evident reduction of the former oxide early in the action. The amount of copper in the product of such action varied in our experiments from 6.53 per cent to 21.30 per cent. In one case the experiment of re-submitting to the action of acetylene a product containing 9.34 per cent of copper was made with the result that a new growth of the substance formed which on analysis yielded 3.87 per cent of copper.

A roll of copper gauze carefully reduced in hydrogen and then oxidized at one end in the outer flame of a Bunsen burner gave, when acted upon by acetylene at 225°-250° C., the characteristic deposit upon the oxidized end only, the unoxidized end being merely discolored.

These results go to show that, while metallic copper may at comparatively high temperatures induce the polymerization of acetylene, it is an oxidizing action which starts at moderately low temperatures the formation of the peculiar derivatives under consideration. Thus we find that ferric oxide heated in acetylene at temperatures varying from 150° to 360°, according to circumstances, darkens, glows, and gathers with evolution of heat a dark carbonaceous deposit. In the products of such action we have found the content of iron varying from 2.80 per cent to 5.86 per cent.

Silver oxide, too, acts upon acetylene: thus, in one experiment, action was evident at the ordinary atmospheric temperature, and a violent explosion, which completely shattered the boat and scattered metallic silver upon the sides of the glass tube, followed before the temperature reached 100°.

In the locally violent explosion of the last experiment we have evidence of the formation in the early stage of an acetylide which is decomposed later when the temperature of dissociation is reached. In the experiments with the oxides of copper and iron the temperature at which the acetylene begins to act is evidently above the point at which sensitive acetylides would naturally dissociate, and we have in the observed phenomena no evidence of the formation of such compounds of copper and iron under the conditions of experimentation.

In experiments (1) to (3) of the following table are given the results of the analysis of several products obtained by conducting acetylene (purified by passing through a solution of mercuric chloride in hydrochloric acid and dried over caustic potash) over pure cuprous oxide. The temperature was kept in these experiments at 225°, and in the course of a half-hour the tube was choked completely by material compacted by the pressure to (1) a spongy mass of light-brown color on the exterior next the walls of the tube, (2) darker within and (3) nearly black in the bottom of the boat, where the cuprous oxide lay originally.

Exp.	Weight of substance taken.	Found.			Calculated.			
		CO_2	H_2O	CuO	C	H	Cu	O by difference.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1170	0.3978	0.0678	0.0022	0.1085	0.0075	0.0018	0.0008–
(2)	0.2247	0.7489	0.0979	. . .	0.2042	0.0109	. . .	. . .
(3)	0.1096	0.3678	0.0488	0.0045	0.1003	0.0054	0.0036	0.0003
(4)	0.1360	0.4116	0.0579	0.0182	0.1128	0.0064	0.0146	0.0027
(5)	0.1188	0.3098	0.0461	0.0317	0.0845	0.0051	0.0253	0.0089

	(1)	(2)	(3)	(4)	(5)
Per cent of carbon	92.74	90.88	91.51	82.57	71.13
Per cent of hydrogen	6.41	4.85	4.93	4.71	4.29
Per cent of copper	1.54	. . .	3.29	10.74	21.30
Per cent of oxygen	. . .	. . .	0.27	1.98	3.20
	100.69		100.00	100.00	100.00

In experiments (4) and (5) the substances analyzed represent the products of the action of acetylene (not specially purified) on cupric oxide.

The oxygen present in these products is obviously proportional to the amount of copper and is never more than enough to be completely accounted for upon the supposition that some of the original oxide taken stills holds its oxygen. So far as the analyses show, the product of lightest color (1) contains very little copper and no oxygen; the darkest product (3) obtained from the cuprous oxide contains oxygen corresponding to a mixture of two parts of copper with three parts of cuprous oxide; the oxygen in the products of (4) and (5) obtained by acting upon cupric oxide is approximately enough to correspond to a mixture of cuprous and cupric oxides in equal proportions. This fact, taken in connection with the great range of variation in proportion and the minimum to which the copper falls in the product, which would be least likely to include contaminating metal or oxide, suggests very strongly the probability that the oxygen present is in union with copper and that the copper is held mechanically as metal or oxide and is not the essential constituent of an organic compound. Leaving out of consideration, therefore, the copper and copper oxides, and calculating the composition of the products assumed to consist essentially of carbon and hydrogen, we derive the following statement:

	(1)	(2)	(3)	(4)	(5)
Per cent of carbon	93.54	94.93	94.88	94.60	94.31
Per cent of hydrogen	6.46	5.07	5.12	5.40	5.69
	100.00	100.00	100.00	100.00	100.00

These figures correspond to symbols varying from $C_{12}H_{10}$ to nearly $C_{16}H_{10}$, with an average approximating $C_{14}H_{10}$, the symbol of anthracene or paranthracene. The analytical data of Erdmann and Köthner point in the average to a product corresponding more nearly to the first of these symbols than to either of the others. The product is doubtless variable with the temperature and the activity of oxidation. Thus, in one experiment in which acetylene was passed over ferric oxide the action began at 365° with incandescence, as described by Moissan and Moureu,* and the analysis of the

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* Loc. cit.

product (carbon = 91.53, hydrogen = 1.36, Fe = 5.85, O = 1.26) indicates a proportion of carbon to hydrogen about four times as great as that of the average product of action at 225° on the oxides of copper.

Finally, we find no evidence that the product of the action of acetylene on the oxides of copper under the conditions of our experimentation is other than a mixture of a hydrocarbon or hydrocarbons with metallic copper or an oxide of copper, and, probably, in the darker preparations, some free carbon.

XXXV

NOTES ON THE SPACE ISOMERISM OF THE TOLUQUINONEOXIME ETHERS.

BY WM. CONGER MORGAN.*

IN an article on the "Ethers of Toluquinoneoxime and their Bearing on the Space Isomerism of Nitrogen," † published from this laboratory, it was stated that the methyl, acetyl, and benzoyl ethers of toluquinonemetaoxime, whether formed by the action of hydroxylamine on the quinone or by nitrous acid on the corresponding cresol, showed evidence of existing in isomeric forms. Of these bodies the benzoyl ether received the most careful investigation, and by fractional crystallization, from the crude reaction-product, two portions were obtained, one readily separating from an alcoholic solution in the form of yellow crystals melting at 193°, while a second body, melting approximately at 144°, was never obtained in a state of purity. The fact that from this lower-melting fraction, on recrystallization, a portion of the higher-melting body was always obtained, suggested the possibility that the solvent might have a tendency to cause a transition from one isomer to the other. Since, however, after repeated crystallizations from boiling alcohol a low-melting fraction was obtained, and therefore such rearrangement was evidently incomplete, the action of alcohol under pressure on the different fractions was investigated. From a portion of the ether melting at 139°, heated for three hours in a closed tube to 120°, the product melting at 193° crystallized in a characteristic form and no crystals were obtained melting

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* From Am. Chem. Jour., xxii, 402.

† Bridge and Morgan, Am. Chem. Jour., xx, 761. This volume, p. 145.

lower than 180°. On treating the higher-melting isomer in the same way, no action was observed until the temperature was raised above 150°, when complete decomposition ensued.

In order to ascertain, if possible, a direct method of transition from one form into the other, the action of alkalies, among other reagents, was tried. No change other than a hydrolytic cleavage was observed, and this was readily completed on warming. By saponifying a fraction melting completely at 142° and treating the isolated oxime in the usual way with benzoyl chloride, the benzoyl ether was again obtained, liquefying at 193°, and, although there was a trifling irregularity in the melting-point of some of the crystals, no low-melting fraction was isolated. On similar treatment of a portion melting at 193° the original ether was obtained, but none of the low-melting isomer.

From these facts it is obvious that the isomer existing in a much smaller proportion in the crude reaction-products, present as the principal constituent in the low-melting fractions, must be regarded as the labile form, tending to go over into the stable form under the influence of boiling alcohol or during the process of a chemical reaction. This action of alcohol increases the difficulty of isolating the labile form and naturally suggests the idea of using other solvents; but imperfect as was the separation of the two isomers, better results were obtained from an alcoholic solution than by any other means.

The phenomena described in the article to which reference was previously made, have been reproduced completely in the ethers made by the action of acid chlorides on the sodium salt of the oxime (to be described later) produced by the action of pure amyl nitrite on the sodium salt of the cresol. In the resulting metathesis, as in the product of the reaction of hydroxylamine on the quinones, there is not the possibility of the formation of a nitro-body as there is in the action of free nitrous acid on the cresols. Consequently the interfering action of an admixture of such a body with the oxime ethers cannot influence the results as obtained, yet the presence of a low-melting body existing in a larger proportion in this product than in the substances formed by the agency of free nitrous acid according to the type fraction, was indisputably evidenced. The identity of the observed phenomena under varying conditions and methods of formation, thus removing the probability of an admixture of an impurity and at the same time of a structural difference, seems to establish the hypothesis of a space isomerism in the case of the ethers of toluquinonemetaoxime.

Inasmuch as the monohalogen derivatives of the quinoneoxime ethers are beautifully crystalline bodies, it was thought advisable to prepare the monochlor- and monobrombenzoyl ethers of toluquinoneorthooxime in the hope of obtaining from these well-characterized products additional evidence as to the existence of isomeric phenomena in the orthooxime ethers. Although there was the possibility of both "space" and "place" isomerism neither body offered any indication of the presence of isomers of any kind, but each appeared to be an entirely homogeneous and simple substance, liquefying sharply at a definite melting-point.

EXPERIMENTAL PART.

The Sodium Salt of Toluquinone-m-oxime.

The sodium salt was prepared according to the general method suggested by Walker.[*] To a molecule of sodium alcoholate freshly prepared by dissolving metallic sodium in as little alcohol as possible, a molecule of the orthocresol was added and the solution treated with slightly more than the theoretical quantity of amyl nitrite, the whole being thoroughly mixed together. On standing in a vacuum over sulphuric acid, the sodium salt separates in fine purple crystals, which, on washing carefully with ether to remove amyl alcohol and excess of nitrite, is ready for use. It may be recrystallized from dilute alcohol if further purification is desired. This

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[*] Walker, Ber. Dtsch. chem. Ges., xvii, 399.

salt is extremely soluble in water, much less in alcohol, and insoluble in most other organic liquids. On standing in the air it tends to decompose, turning almost black. On analysis:

0.1231 gram, dried over H_2SO_4, gave 0.0541 gram Na_2SO_4.

	Calculated for $C_7H_6O_3NNa$.	Found.
Na	14.48	14.26

Monobromtoluquinone-o-oxime Benzoyl Ether.

This ether was obtained from the dibromide previously described* by boiling with dilute 75 per cent alcohol, during which process hydrobromic acid is split off. Being much less soluble in alcohol than the dibromide, the monobrom-body separates from the solution as soon as formed and may be obtained as a yellow crystalline powder by filtration of the cooled liquid. On analysis,

0.1450 gram, dried over H_2SO_4, gave 0.2774 gram CO_2, and 0.0415 gram H_2O.

0.1102 gram gave 0.0643 gram AgBr.

	Calculated for $C_{14}H_{10}BrNO_3$.	Found.
C	52.49	52.17
H	3.15	3.18
Br	24.98	24.83

On crystallizing from alcohol the ether was readily obtained in two, apparently unlike, modifications, one being long prismatic crystals, the other appearing as broad, thick, monoclinic plates. It was at first believed that this distinction in crystal form was due to the presence of isomeric bodies, but no difference in melting-point could be found since each portion liquefied sharply at 184°. Under the lens, moreover, the plates are seen to be striated parallel to one edge and have all the appearance of consisting of a number of the simple crystals united to each other, since both forms are plainly of

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* Bridge and Morgan, Am. Chem. Jour., xx, 776.

the same system. Slow cooling was found to be productive of the massed crystals.

Toluquinone-o-oxime Benzoyl Ether Dichloride.

The benzoyl ether was dissolved in a small amount of chloroform and dry chlorine gas passed into the solution. The action is very rapid and after fifteen minutes the liquid may be allowed to evaporate and the white product, crystallized once from glacial acetic acid, melts sharply to a colorless liquid at 149° without decomposition. Fractional crystallization does not change the melting-point, except as the action of the solvent causes a slight formation of the monochlor-body. On analysis,

0.1241 gram, dried over H_2SO_4, gave 0.2431 gram CO_2, and 0.0424 gram H_2O.

0.2105 gram gave 0.1930 gram AgCl.

	Calculated for $C_{14}H_{11}Cl_2NO_2$.	Found.
C	53.84	53.42
H	3.55	3.80
Cl	22.72	22.67

The dichloride, like the dibromide, is slightly soluble in alcohol, readily soluble in chloroform, glacial acetic acid, and fuming nitric acid. Water precipitates the ether entirely unchanged from the two last-mentioned solvents. In crystal form it resembles very closely the dibromide, separating from a boiling acetic acid solution in short, thick, colorless, almost microscopic prisms, suggesting the orthorhombic system. In point of stability this ether, as well as the monochlor-body, far surpasses the corresponding bromine compounds.

Monochlortoluquinone-o-oxime Benzoyl Ether.

Analogous to the dibromide, by the action of dilute alcohol on the dichloride, hydrochloric acid is split off and a yellow monochlor-substitution-product is formed, one hour being sufficient to complete the reaction. This ether closely resembles the monobrom-derivative in properties and in crystal form. The product as obtained from an alcoholic solution will decompose and melt at a temperature varying ordinarily from 185°–193°, depending on the rapidity with which the heat is applied. "Dipped" for fifteen seconds, the crystals melt without decomposition at 200°. Although carefully fractioned from alcohol, ligroin, and benzol, the substance appeared to be entirely homogeneous, and no variation in the melting-point was observed. On analysis,

0.1209 gram, dried over H_2SO_4, gave 0.2688 gram CO_2, and 0.0424 gram H_2O.

0.1035 gram gave 0.0533 gram AgCl.

	Calculated for $C_{14}H_{10}ClNO_3$.	Found.
C	60.97	60.63
H	3.66	3.90
Cl	12.87	12.75

XXXVI

ON THE VOLUMETRIC ESTIMATION OF CERIUM.

BY PHILIP E. BROWNING.*

SOME forty years ago Bunsen† showed that the oxide obtained by the ignition of cerium oxalate might be estimated volumetrically by bringing it in contact with potassium iodide and strong hydrochloric acid and determining the iodine set free. This method may be briefly described by a translation of part of the original article: "The substance to be determined is weighed out in a glass flask of from ten to fifteen cubic centimeters capacity, a few crystals of potassium iodide are added, and the neck of the flask is drawn out by the aid of a blowpipe to a narrow opening. The flask is filled almost to the narrowing of the neck with hydrochloric acid which is free from chlorine or iron chloride, and a little sodium carbonate is added in order to displace the last trace of air by carbon dioxide. The flask is then closed by sealing off the neck in the blowpipe and warmed in a water bath until the cerium compound is completely dissolved, and the quantity of iodine set free is determined by iodometric analysis."

The anhydrous dioxide prepared by the ignition of the oxalate or hydroxide is very slowly acted on by acids, especially when pure.‡ For this reason the method which Bunsen described has remained the only one adapted to the satisfactory volumetric estimation of the ignited dioxide.

Two portions of the dioxide were prepared by treating the crude cerium chloride in concentrated solution with gaseous

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* From Am. Jour. Sci., viii, 451.

† Ann. Chem. Phar., cv, 49.

‡ Rose, Handbuch der analytischen Chemie, Band i, 219.

hydrochloric acid * to saturation to remove the iron. The cerium chloride was then dissolved in water, potassium hydroxide added in excess and chlorine gas passed until the precipitate became distinctly orange in color and the solution gave a strong odor of chlorine.† This operation was repeated until a portion of the precipitate dissolved in acid showed no didymium absorption bands when examined before the spectroscope. The whole precipitate of the dioxide was then dissolved in hydrochloric acid and the oxalate precipitated by ammonium oxalate in large excess. The precipitated oxalate was then washed thoroughly with hot water until the washings gave no test for hydrochloric or oxalic acids and ignited to the dioxide. Another portion of the dioxide was later prepared by precipitating a solution of pure cerium chloride by means of ammonium oxalate, washing and igniting as described. The dioxide in all three cases was of a light chamois color, and uniform results were obtained from the three portions.

A modification of the method of Bunsen — (with G. A. HANFORD and F. J. HALL).

Weighed portions of the pure cerium dioxide were placed in small glass stoppered bottles of about 100 cm^3 capacity, together with a gram of potassium iodide free from iodate and a few drops of water to dissolve the iodide. A current of carbon dioxide was passed into the bottle for about five minutes to expel the air, 10 cm^3 of pure strong hydrochloric acid were added, the stopper inserted and the bottle heated gently upon a steam radiator for about one hour until the dioxide dissolved completely and the iodine was set free. After cooling the bottle, to prevent loss of iodine upon removing the stopper, the contents were carefully washed into about 400 cm^3 of water and titrated with standard sodium thiosulphate to determine the amount of iodine liberated according to the well known reaction

$$2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 2KCl + 4H_2O + I_2.$$

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* Dennis and Magee, Zeitschr. anorg. Chem., iii, 260.

† Mosander, Phil. Mag., xxviii, 241; Dennis, Zeitschr. anorg. Chem., vii, 252.

A few blank determinations were carried through in the bottles without the presence of the cerium dioxide to determine the amount of iodine set free under these conditions. The amount obtained was uniformly equal to 0.04 cm³ of the $\frac{N}{10}$ iodine solution which was taken as the correction and applied to all the determinations. The results follow in Table I.

TABLE I.

Exp.	CeO_2 taken.	CeO_2 found.	Error.
	grm.	grm.	grm.
(1)	0.1000	0.0994	0.0006−
(2)	0.1032	0.1034	0.0002+
(3)	0.1016	0.1017	0.0001+
(4)	0.1054	0.1041	0.0013−
(5)	0.2010	0.2021	0.0011+
(6)	0.1104	0.1109	0.0005+
(7)	0.1914	0.1907	0.0007−
(8)	0.1604	0.1603	0.0001−
(9)	0.2146	0.2145	0.0001−
(10)	0.1108	0.1099	0.0009−
(11)	0.1346	0.1347	0.0001+
(12)	0.1540	0.1534	0.0006−
(13)	0.1976	0.1968	0.0008−
(14)	0.1230	0.1240	0.0010+
(15)	0.1199	0.1202	0.0003+
(16)	0.1524	0.1528	0.0004+
(17)	0.1212	0.1211	0.0001−
(18)	0.1528	0.1543	0.0015+

In order to obtain a further check upon the accuracy of the method, portions of the cerium dioxide were weighed out and placed in a distillation apparatus previously employed for similar purposes and described in former articles from this laboratory, viz.: a Voit flask, serving as a retort, sealed to the inlet tube of a Drexel wash-bottle, used as a receiver, the outlet tube of which was trapped by sealing on Will and Varrentrapp absorption bulbs. In the retort the cerium dioxide together with 15 cm³ of water, 1 grm. of potassium iodide and 10 cm³ of pure strong hydrochloric acid were placed. In the receiver were 100 cm³ of water and 2 to 3 grm. of potassium iodide, and in the bulbs a dilute solution of potassium iodide. Before adding the hydrochloric acid a current of carbon dioxide was passed through the apparatus for some minutes. After adding the acid, the liquid was boiled in the current of carbon dioxide * to a volume of 15 cm^3, when the free iodine had almost completely left the retort and passed into the receiver, and the apparatus was allowed to cool.

The iodine in the receiver was titrated directly with sodium thiosulphate, and that in the retort after dilution of the residue to about 400 cm^3, the later amount seldom exceeding the equivalent of a few drops of $\frac{N}{10}$ iodine solution.

The results follow in Table II.

Here also blank determinations were made but no correction was found to be necessary.

An attempt early in the work to titrate by an alkaline arsenite the iodine liberated, after neutralizing the hydrochloric acid, brought out some curious results which seem worthy of mention.

TABLE II.

Exp.	CeO_2 taken.	CeO_2 found.	Error.
	grm.	grm.	grm.
(1)	0.1028	0.1013	0.0015–
(2)	0.2060	0.2055	0.0005–
(3)	0.2014	0.2012	0.0002–
(4)	0.1716	0.1711	0.0005–
(5)	0.0974	0.0972	0.0002–
(6)	0.1600	0.1587	0.0013–
(7)	0.1268	0.1254	0.0014–
(8)	0.1276	0.1268	0.0008–
(9)	0.1620	0.1612	0.0008–
(10)	0.1016	0.1011	0.0005–
(11)	0.1548	0.1543	0.0005–
(12)	0.1352	0.1342	0.0010–

In these experiments the contents of the bottles after the cerium had dissolved were carefully washed into a Drexel wash bottle upon the inlet tube of which was fused a thistle tube with a stop-cock and to the outlet tube a Will and Varrentrapp absorption trap. In the trap a solution of potassium iodide was placed and through the thistle tube a saturated

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* The carbon dioxide gas was furnished by a Kipp generator from marble and hydrochloric acid of one-half strength, both of which had been boiled previously to remove all air.

solution of potassium bicarbonate was added to complete neutralization of the acid. Any iodine carried mechanically by the carbon dioxide should be held by the potassium iodide solution in the trap. After neutralization the free iodine was titrated by standard arsenious oxide solution. The results appear in Table III.

TABLE III.

Exp.	CeO_2 taken.	CeO_2 found.	Error.	
	grm.	grm.	grm.	
(1)	0.1000	0.0987	0.0013–	I.
(2)	0.1005	0.0981	0.0024–	
(3)	0.1030	0.1009	0.0021–	
(4)	0.1500	0.1475	0.0025–	
(5)	0.1030	0.1005	0.0025–	II.
(6)	0.1010	0.0988	0.0022–	
(7)	0.1510	0.1508	0.0002–	
(8)	0.1530	0.1485	0.0045–	
(9)	0.2045	0.2011	0.0034–	
(10)	0.2000	0.1958	0.0042–	
(11)	0.1334	0.1302	0.0032–	III.
(12)	0.1354	0.1330	0.0024–	
(13)	0.1312	0.1294	0.0018–	
(14)	0.1308	0.1277	0.0031–	
(15)	0.1060	0.1042	0.0018–	
(16)	0.1602	0.1567	0.0035–	
(17)	0.1504	0.1488	0.0016–	

As will be seen by the table, an average error of about 2 per cent runs through the entire set. The natural conclusion would be that the cerium dioxide contained some impurity; but, as the first, second, and third samples, very carefully prepared, gave the same results, it seemed necessary to look elsewhere for an explanation. Two possible causes suggested themselves: first, mechanical loss during the process of neutralization, and second, the possible formation, under the conditions, of iodine chloride, which if formed would in the process of neutralization probably take the form of potassium chloride, iodide, and iodate, and thus some of the originally free iodine would be withdrawn from the amount titrated. To test these theories, portions of the $\frac{N}{10}$ iodine solution roughly equivalent to the amounts of iodine set free by 0.1 and 0.2 grms. of CeO_2, were drawn off into bottles previously filled with carbon dioxide, treated with the usual amount of strong hydrochloric acid (10 cm^3), and after standing from thirty to forty-five minutes, neutralized and titrated as already described. The results were most interesting and seemed to show a loss of iodine closely equivalent to that shown by the results of Table III, and proportional to the amount of iodine originally present. A few determinations were carried through in the same way except that the neutralization was omitted and dilution and titration with thiosulphate substituted. These showed a loss of iodine well within the limits of such a process. The results follow in Table IV.

TABLE IV.

WITH ARSENIOUS OXIDE.

Exp.	Iodine $\frac{N}{10}$ taken.	Iodine $\frac{N}{10}$ found.	Error.	Equivalent error on CeO_2.
	cm^3	cm^3	cm^3	grm.
(1)	5.22	5.07	0.15–	0.0026–
(2)	5.09	4.97	0.12–	0.0021–
(3)	5.10	4.97	0.13–	0.0022–
(4)	5.66	5.47	0.19–	0.0033–
(5)	5.10	4.97	0.13–	0.0022–
(6)	10.22	9.97	0.25–	0.0043–
(7)	10.21	9.97	0.24–	0.0041–
WITH SODIUM THIOSULPHATE.				
(1)	5	5.01	0.01+	0.0002+
(2)	5	4.99	0.01–	0.0002–
(3)	10	10.02	0.02+	0.0003+
(4)	10.08	10.12	0.04+	0.0007+

The action of arsenious oxide upon Cerium Dioxide — (with WM. D. CUTTER).

The fact that cerium dioxide is reduced by hydriodic acid suggested the possibility of the application of arsenious acid in acid solution to the same end according to the reaction

$$4CeO_2 + As_2O_3 = 2Ce_2O_3 + As_2O_5.$$

The extreme difficulty with which the ignited cerium dioxide when pure dissolves in acids has already been mentioned, and for this reason it was found practically impossible to obtain any results by this method. Weighed portions of the dioxide were placed in Erlenmeyer beakers with an excess of a solution of arsenious oxide $\frac{N}{1}$, 10 cm^3 of (1:1) sulphuric acid were added, and the boiling continued until the fuming point of the acid was reached; but even at this point only a partial solution of the dioxide had taken place.

The dark brown powder obtained by igniting the carefully washed oxalates, precipitated in acid solution by treating a solution of crude cerium chloride with ammonium oxalate or oxalate acid is very fairly soluble in acids. Mengel* has recently shown that this product contains a dioxide of praseodidymium which acts as does cerium dioxide toward reducing agents. This fact makes the results recorded in the treatment of this ignited mixture of oxides of no value analytically, but of interest in the comparative study of the two reducing agents, arsenious oxide and hydriodic acid. Two portions of this mixture of oxides gave the following results, which agree fairly well with those of Mengel.

Exp.	Amount of substance taken.	$CeO_2 + (PrO_2?)$ found.	Calculated on 0.1000 grm.
	grm.	grm.	grm.
(1)	0.1087	0.0580	0.0511
(2)	0.1034	0.0538	0.0520

The average of these results was taken as a standard —0.0515 grm. CeO_2, etc., to every 0.1000 grm. of material. Three carefully weighed portions of this same material were placed in Erlenmeyer beakers with 10 cm^3 of $\frac{N}{10}$ arsenious oxide solution and 10 cm^3 of dilute (1:4) sulphuric acid and boiled until complete solution had taken place. The liquid was then cooled, neutralized with potassium bicarbonate and titrated with standardized iodine to determine the amount of arsenious oxide remaining, and from it the amount used in the reduction of the dioxide according to the reaction given above. The results obtained follow.

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* Zeitschr. anorg. Chem., xix, 67.

Exp.	Amount taken.	Amount CeO_2 found.	CeO_2 calculated for 0.1000 grm.
	grm.	grm.	grm.
(1)	0.1005	0.0493	0.0491
(2)	0.1015	0.0494	0.0487
(3)	0.1005	0.0486	0.0484

As will be seen, the results obtained by this method fall about 0.0030 grm. below the standard as obtained by the distillation method, which seems to show that the arsenious oxide does not effect the complete reduction of the cerium dioxide from CeO_2 to Ce_2O_3.

In order to study this point a little more fully and upon the pure dioxide, definite portions of a standard solution of pure cerium chloride were precipitated by ammonia in the presence of hydrogen dioxide and boiled to reduce the CeO_3 formed to the conditions of CeO_2. The precipitated hydrated dioxide was filtered off and carefully washed until the washings gave no indication of hydrogen dioxide. The moist precipitate was then washed into a beaker, one gram of potassium iodide added and 10 cm^3 of strong HCl. The precipitate dissolved quite readily in the cold and the iodine liberated was determined by standard sodium thiosulphate. The results appear in Table V.

TABLE V.

Exp.	CeO_2 taken.	CeO_2 found.	Error.
	grm.	grm.	grm.
(1)	0.1142	0.1140	0.0002–
(2)	0.1142	0.1147	0.0005+
(3)	0.1142	0.1152	0.0010+
(4)	0.1142	0.1159	0.0017+
(5)	0.1142	0.1152	0.0010+
(6)	0.1142	0.1156	0.0014+

Another series of these precipitates prepared in the same way was boiled with a definite amount of arsenious acid in acid solution, as previously described in the case of the ignited dioxide. The results which are recorded in Table VI show, as in the case of the ignited dioxide, an insufficient reduction of the cerium by the arsenious acid.

TABLE VI.

Exp.	CeO_2 taken.	CeO_2 found.	Error.
	grm.	grm.	grm.
(1)	0.0881	0.0370	0.0011–
(2)	0.0881	0.0361	0.0020–
(3)	0.1142	0.1077	0.0064–
(4)	0.1060	0.1002	0.0058–

The Estimation of Cerium Oxalate by Potassium Permanganate — (with Leo A. Lynch).

Stolba[*] has stated that cerium oxalate may be estimated volumetrically after the same manner as calcium oxalate by treating the washed precipitate, suspended in warm water, to which a moderate amount of sulphuric acid has been added, by potassium permanganate. As the titration proceeds the precipitate disappears and the end reaction is sharp. He also finds that the permanganate does not oxidize the cerium from the lower to the higher condition. So far as we have been able to discover, no experimental evidence has been presented to prove the correctness of Stolba's statement, and the work to be described was undertaken to furnish such evidence.

The solutions used were prepared and standardized as follows: The cerium solutions were made by dissolving 10 grams of pure cerium chloride in one liter of water, and standardized by precipitating measured and weighed portions, in a faintly acid solution, with ammonium oxalate, filtering, washing, igniting, and weighing as the dioxide (CeO_2). A solution of potassium permanganate was prepared and standardized by titration against weighed amounts of ammonium oxalate. A solution of ammonium oxalate was made and its value determined by titrating measured amounts against

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[*] Sitzungsber. d. kgl. böhm. Gesellsch. d. Wissenschaften v. 4. Juli, 1879; Zeitschr. anal. Chem., xix, 194.

potassium permanganate. Definite portions of the cerium solution were drawn from a burette and after diluting with water from 100 to 200 cm^3 a definite amount of ammonium oxalate was added, care being taken to have an excess over the amount necessary, and the whole warmed to insure a more crystalline precipitation.* The precipitate was then filtered off on paper and carefully washed, the filtrate and washings being collected in a liter Erlenmeyer flask and set aside for future use. The precipitate was treated with about 10 cm^3 of hot (1 : 4) sulphuric acid, which dissolved it completely, if not at first, by running it through the filter a few times, and the solution and washings were collected in another liter flask. The total volume of liquid was made up to about 500 cm^3, warmed to about 70° C. to 80° C. and titrated with potassium permanganate to the appearance of the faint blush of color showing the complete oxidation of the oxalic acid. The filtrate from the cerium oxalate containing the excess of oxalic acid was diluted to 500 cm^3, acidified with 10 cm^3 of dilute (1 : 4) sulphuric acid, one gram of manganous sulphate added to prevent the interfering action of the free hydrochloric acid upon the estimation of the oxalic acid,† and titrated with potassium permanganate after the same manner as the dissolved precipitate. A definite quantity of ammonium oxalate having been originally taken, it became possible, by subtracting from it the amount obtained, to derive the measure of the oxalate used in the precipitation of the cerium oxalate. By this procedure, it will be observed a check was made upon the results obtained by the titration of the precipitate. In experiments (1) to (6) the cerium oxalate was thrown down in neutral solution, in experiments (7) to (10) in acid solutions. The treatment of the filtrate in experiment (1) was made without the presence of the manganous sulphate. The results recorded in Table VII seem to uphold the statement of Stolba.

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* As shown by the table, the precipitation was sometimes in neutral, sometimes in faintly acid solution.

† Gooch and Peters, Am. Jour. Sci., vii, 461. This volume, p. 222.

TABLE VII.

Exp.	Amount taken. Calculated as $CeCl_3$.	Amount found. Calculated as $CeCl_3$. Treatment of precipitate.	Error. Calculated as $CeCl_3$.	Amount found. Calculated as $CeCl_3$. Treatment of filtrate.	Error. Calculated as $CeCl_3$.
	grm.	grm.	grm.	grm.	grm.
(1)	[0.1091	0.1087	0.0004−	0.1023	0.0068−]
(2)	0.1091	0.1103	0.0012+	. .	. .
(3)	0.1091	0.1087	0.0004−	0.1087	0.0004−
(4)	0.1364	0.1373	0.0009+	0.1391	0.0027+
(5)	0.1364	0.1367	0.0003+	0.1367	0.0003+
(6)	0.2182	0.2202	0.0020+	0.2206	0.0024+
(7)	0.1091	. .	. .	0.1087	0.0004−
(8)	0.1519	0.1535	0.0016+	0.1535	0.0016+
(9)	0.1364	0.1367	0.0003+	0.1367	0.0003+
(10)	0.2182	0.2183	0.0001+	0.2183	0.0000

XXXVII

ON THE ESTIMATION OF THALLIUM AS THE CHROMATE.

By PHILIP E. BROWNING AND GEORGE P. HUTCHINS.*

Crookes has shown† that the chromate precipitated by the addition of potassium dichromate to an alkaline solution of a thallous salt has the constitution of a neutral salt and is very insoluble in water—100 parts of water at 100° C. dissolving about 0.2 parts and at 60° C. about 0.03 parts. He has also made use of this reaction ‡ to effect a rough separation of thallium from cadmium.

The object of this paper is to describe some work directed toward a study of the application of this reaction to the gravimetric estimation of thallium and the best conditions under which to effect the precipitation. For the work a solution of thallous nitrate was made by dissolving 10 grms. in water and making up to a liter. The standard was determined by taking measured and weighed portions from a burette, precipitating with a slight excess of potassium iodide, agitating to bring about a good separation of the thallous iodide, and allowing to stand until the supernatant liquid was clear. The iodide was then filtered off upon an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed, washed with a mixture of alcohol and water, dried over a low flame and weighed to a constant weight. The filtrate, which together with the washings seldom amounted to more than 50 cm^3, was evaporated to dryness on a water bath, a few drops of water

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* From Am. Jour. Sci., viii, 460.

† Chem. News, viii, 255.

‡ Chem. News, vii, 145.

added and thus the small amount of thallous iodide which had been dissolved recovered. This small insoluble residue, which seldom amounted to one milligram in weight, was filtered off, washed and weighed as previously described. Baubigny * has shown this method to give very satisfactory results, and the uniformity of our determinations certainly confirms his statements.

For convenience in the calculations of results to be described later, a solution of potassium dichromate of definite strength was made. Portions of the thallium solution were drawn from a burette into test tubes of about 100 cm^3 capacity and weighed as a check on the burette reading. The solution was heated to about 70° C. to 80° C. and a few drops of ammonia or potassium carbonate solution added to distinct alkalinity. A definite amount of the potassium dichromate in solution was delivered from a burette, care being taken to have an excess, and the contents agitated to bring about a good separation of the precipitated chromate. After the precipitate had completely settled out and the solution had become cold the chromate was filtered upon asbestos, as described above, dried over a low flame and weighed to a constant weight. The filtrates from several determinations were evaporated to a small volume and in one or two cases a residue amounting to a few tenths of a milligram was obtained, but no appreciable quantity of dissolved chromate was thus recovered. It was found that when the precipitation was made in the cold the chromate did not flock well, but remained partly in a finely divided condition which would run through the felt and require repeated filtration. The addition of ammonium nitrate before precipitation prevented this largely, even in the cold, but the best results were obtained by warming the solution before precipitation and using potassium carbonate rather than ammonium hydroxide. The results follow in Table I.

An attempt was made to estimate the thallium volumetrically by determining the amount of chromate in the filtrate

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* Chem. News, lxiv, 239.

TABLE I.

Exp.	$TlNO_3$ taken. Calculated as Tl_2O.	Tl_2CrO_4 found. Calculated as Tl_2O.	Error. Calculated as Tl_2O.
	grm.	grm.	grm.
(1)	0.0796	0.0791	0.0005–
(2)	0.0792	0.0788	0.0004–
(3)	0.0792	0.0786	0.0006–
(4)	0.1188	0.1177	0.0011–
(5)	0.1192	0.1186	0.0006–
(6)	0.1185	0.1178	0.0007–
(7)	0.1190	0.1185	0.0005–
(8)	0.1189	0.1188	0.0006–
(9)	0.1196	0.2000	0.0004+
(10)	0.1196	0.2005	0.0009+
(11)	0.1178	0.1173	0.0000
(12)	0.1171	0.1163	0.0008–

from the thallous chromate, and by difference (the potassium dichromate originally added being known) the amount combined with the thallium in the precipitate. The method used to determine the standard of the dichromate solutions and also the chromate remaining in the filtrate was described by one of us in a previous paper from this laboratory.* According to this procedure the filtrate from the thallous chromate containing the excess of alkali chromate was acidified with sulphuric acid, a definite amount of a solution of arsenious oxide, previously standardized, was added and the whole was allowed to stand a few moments until the change from the yellow to the bluish green showed the complete reduction of the chromic acid. Potassium bicarbonate was added to distinct alkaline reaction and the arsenious oxide remaining was determined by titration with standard iodine solution. The amount of the arsenious oxide oxidized is of course the measure of the chromate in the solution. The amount of chromate in the original solution used being known, by subtracting the amount thus determined in the filtrate the chromate in combination with the thallium may be readily found, and from it the thallium estimated. Filtrates from certain precipitates, of which the determinations are given in

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* Am. Jour. Sci., i, 35, 1896. Volume I, p. 344.

Table I, were treated in this way, and the results, indicated by corresponding numbers, follow in Table II.

TABLE II.

Exp.	$TlNO_3$ taken. Calculated as Tl_2O.	Tl_2CrO_4 found. Calculated as Tl_2O.	Error. Calculated as Tl_2O.
	grm.	grm.	grm.
(5)	0.1192	0.1198	0.0006+
(8)	0.1189	0.1205	0.0016+
(9)	0.1196	0.1180	0.0016–
(10)	0.1196	0.1192	0.0004–
(11)	0.1178	0.1182	0.0009+
(12)	0.1171	0.1190	0.0019+

The method cannot be very accurate on account of the high molecular weight of thallium oxide as compared with that of the chromic acid determined, but the results check fairly well with the gravimetric method.

XXXVIII

THE ETHERS OF ISONITROSOGUAIACOL IN THEIR RELATION TO THE SPACE ISOMERISM OF NITROGEN.

BY JOHN L. BRIDGE AND WM. CONGER MORGAN.[*]

WHEN the presence of isomerism in the quinoneoximes was first noted by one of us,[†] and the phenomenon exhibited by the two isomeric ethers then described was shown by Kehrmann [‡] to be due to no structural differences, but to necessitate the assumption of a spatial arrangement about the nitrogen atom, according to the theory of Hantzsch and Werner, the plan was adopted of studying the various substituted quinoneoximes, by means of their acyl and alkyl ethers, with reference to this phenomenon. Accordingly we have investigated the toluquinoneoximes,[§] both ortho and meta, producing them by the action of nitrous acid on the cresol as well as by hydroxylamine on toluquinone, and found that, whereas there is abundant evidence for the existence of stereoisomeric bodies in the metaoxime ethers, in the derivatives of the orthooxime, all such indication is wanting. The significance of this observation is furthermore increased by the fact that all oximes, in which isomerism has been reported, may be considered as derivatives of metasubstituted quinones, and it seemed not improbable, therefore, that these observations might be formulated into a general rule regarding the appearance of isomerism in the quinoneoximes.

In the course of his investigation of the properties and reactions of isonitrosoguaiacol, among other derivatives, Pfob [‖]

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[*] From Am. Chem. Jour., xxii, 485. [†] Ann. Chem. (Liebig), cclxxvii, 79.

[‡] Ann. Chem. (Liebig), cclxxix, 27.

[§] Am. Chem. Jour., xx, 761; xxii, 402. This volume, pp. 145, 283.

[‖] Monatsh. Chem., xviii, 467.

made the methyl and acetyl ethers, but did not announce the observation of any cases of isomerism. Isonitrosoguaiacol may be considered as the metamethoxyquinoneoxime, hence this metasubstituted quinoneoxime presented conditions differing widely from the other members of the same series above mentioned. Moreover, because of its close relationship to toluquinonemetaoxime, from which it differs only by the interposition of an oxygen atom between the ring and the methyl group, it seemed possible that isomeric modifications of the ethers might exist, which had been overlooked by the former investigator. When, furthermore, Rupe * made no mention of such appearance in his research on isonitrosoguaiacol, it seemed advisable to undertake anew the investigation of this body with the special purpose of discovering such isomerism, if possible, and to couple with it an investigation of the orthomethoxyquinoneoxime or isonitroso derivative of the monomethyl ether of resorcin, in order by this means to be able to parallel in these closely analogous bodies the experiments with the ortho- and metacresols.

With this idea, the work of Pfob and Rupe was carefully repeated, so far as it pertained to the question in hand, but, aside from minor differences, our results served only to corroborate the testimony of these investigators. New derivatives, to be described later, were prepared in the hope that these bodies might show some variations leading to the discovery of isomeric modifications, but each appeared to be entirely homogeneous and no evidence for isomerism could be found. These results are of course only negative and do not disprove the existence of space isomers in the same bodies, yet the same methods, which gave very positive evidence of their presence in other quinoneoxime ethers, were used to detect them in this instance.

Aside from the difficulty of obtaining the pure monomethyl ether of resorcin in any considerable quantity, because of poor synthetical processes and inefficient methods of separation, inasmuch as preliminary experiments pointed to a multiplicity

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* Ber. Dtsch. chem. Ges., xxx, 2444.

of products in the reaction with nitrous acid such as Kietaibl * found with the monoethyl ether, it was thought inadvisable in the light of the results obtained with the meta body, to continue the work on the ethers of orthomethoxyquinoneoxime. Work along the general line will be continued, and the results of experimentation with mononitrosoresorcin will soon appear.

EXPERIMENTAL PART.

Isonitrosoguaiacol and Salts.

The isonitrosoguaiacol used in the investigation was prepared both by the method of Pfob, working with nascent nitrous acid in alcoholic solution, and also by the general method for the formation of the sodium salts of isonitroso bodies suggested by Walker.† To a concentrated alcoholic solution of sodium alcoholate, guaiacol is added in sufficient quantity to form the sodium salt by the resulting metathesis, then, to this solution of sodium guaiacol, slightly more than the theoretical quantity of amyl nitrite is added and, after thorough mixing, the liquid is allowed to stand over sulphuric acid for twenty-four hours, when the bright olive-green crystalline sodium salt of isonitrosoguaiacol separates. After washing thoroughly with ether, pulverizing and rewashing, the salt may be used directly for the preparation of derivatives, or, if further purification is desirable, it may be dissolved in water, acidified with hydrochloric acid, and the filtered and dried product dissolved in ether and shaken with animal charcoal, when, upon evaporation, the pure isonitrosoguaiacol crystallizes. Of the above methods of preparation the latter is much to be preferred, although Rupe mentions it unfavorably because of poor yields and impure products. He advocates the use of ethyl nitrite in a closed tube; but on trial we were unable to obtain the quantitative yields which he reports and the seventy per cent yield which the amyl nitrite gives, makes this method quite equal, in efficiency as well as purity of reaction-product, to the other more tedious process.

The silver salt, formed from the sodium salt by treating the aqueous solution with a slight excess of silver nitrate, comes

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* Monatsh. Chem., xix, 536.

† Ber. Dtsch. chem. Ges., xvii, 399.

down as a brown gelatinous precipitate, which becomes crystalline on gently warming, or may be obtained in crystalline form at once by heating the separate solutions to 50° C. before mixing. It is a very unstable salt, the dry product decomposing with a very gentle heating.

Isonitrosoguaiacol Benzoyl Ether.

The sodium salt formed as above was dissolved in as little water as possible and four or five times its volume of alcohol added. This solution was thoroughly shaken with a slight excess of benzoyl chloride, added drop by drop. The reaction is immediate and the ether soon begins to come out of the solution in almost pure condition. Recrystallized from alcohol, it separates in straw-colored, branching crystals, which melt sharply at 188° C. when "dipped" for ten seconds. Heated gradually from normal temperatures, it begins to decompose at 175° C. and liquefies at 185°–188° C., the temperature depending on the rapidity with which heat is applied.

Fractional crystallization from alcohol or other solvents did not essentially change the melting-point, nor were any different phenomena observed when the isonitrosoguaiacol was made by the acid reaction. This ether dissolved readily in chloroform and glacial acetic acid, much less in benzene and ligroin, and is practically insoluble in ether and carbon disulphide. On analysis:

0.1100 gram of the substance, dried over H_2SO_4, gave 0.2632 gram CO_2, and 0.0428 gram H_2O.

0.1205 gram of the substance gave 5.45 cm³ N at 15° C. and 772 mm. pressure.

	Calculated for $C_{14}H_{11}O_4N$.	Found.
C	65.34	65.26
H	4.31	4.32
N	5.46	5.38

Isonitrosoguaiacol Benzoyl Ether Dibromide.

Three grams of the benzoyl ether were dissolved in 25 cm³ of chloroform and 2 grams of bromine were added, the mixture being kept cool by running water. The solution was allowed to stand for from one to two hours and then to evaporate spontaneously. The dibromide is left behind as a light-brown substance. Attempts to crystallize from glacial acetic acid proved unsatisfactory since the boiling solvent caused a decomposition of the ether; nor did a solution in fuming nitric acid, precipitated by water, give a pure white product. The best results were obtained by washing with warm dilute alcohol when the product becomes yellowish-white, and melts at 153°–154° C., browning considerably above 140° C. An analysis of the substance purified in this manner shows a low percentage of bromine.

0.1052 gram of the substance, dried over H_2SO_4, gave 0.1547 gram CO_2, and 0.0284 gram H_2O.

0.0509 gram of the substance gave 0.0449 gram AgBr.

	Calculated for $C_{14}H_{11}O_4NBr_2$.	Found.
C	40.29	40.10
H	2.66	3.00
Br	38.34	37.52

Monobromisonitrosoguaiacol Benzoyl Ether.

By boiling the white dibromide with 60 per cent alcohol for three-quarters of an hour, the halogen acid and a bright-yellow monobromine compound are formed. This ether crystallizes from boiling alcohol in the characteristic prismatic form of such bodies and melts with decomposition at 178° C. Repeated recrystallizations did not change this melting-point, and no indication was noted suggesting the possibility of a mixture. On analysis:

0.1317 gram of the substance, dried over H_2SO_4, gave 0.2410 gram CO_2, and 0.0368 gram H_2O.

0.2101 gram of the substance gave 0.1172 gram AgBr.

	Calculated for $C_{14}H_{10}O_4NBr$.	Found.
C	49.99	49.91
H	3.00	3.11
Br	23.79	23.75

XXXIX

THE CONSTITUTION OF THE AMMONIUM MAGNESIUM ARSENIATE OF ANALYSIS.

By MARTHA AUSTIN.*

THE striking analogy between the phosphates and the arseniates led Levol† to undertake the separation of an ammonium arseniate corresponding to the ammonium magnesium phosphate, the composition of which Berzelius had given. Levol states that ammonium magnesium arseniate of the composition $NH_4MgAsO_4 . 10H_2O$ is obtained by adding a solution of a double ammonium magnesium salt to arsenic acid, and that it is a salt possessing about the same degree of solubility in water, in ammoniacal water, and in ammoniacal water containing magnesium salt, as the corresponding phosphate. Further, he found that by heating this salt to red heat after carefully drying, magnesium pyroarseniate was given, from which arsenic can be estimated readily.

Wach‡ and H. Rose § obtained the ammonium magnesium arseniate containing six molecules of water of crystallization by precipitating arsenic acid with magnesia mixture and then adding an excess of ammonia, and by drying at 100° C. were able to estimate the arsenic present as the ammonium-magnesium arseniate containing one-half molecule of water. This method seemed to offer an advantage over the method of estimation as the pyroarseniate, for results obtained below the theoretical amount of arsenic present gave rise to the suspicion that during ignition arsenic was reduced by the ammonia driven off. Rose attempted in another way to avoid this loss by igniting in a current of oxygen; and later Reichelt‖ ignited the residue

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* From Am. Jour. Sci., ix, 55.

† Ann. Chim. III, xvii, 501 (1846).

‡ Schweigger, Jour. f. Ch. u. Phys., lix, 297.

§ Ann. Phys., clii, 20 (1849).

‖ Zeitschr. anal. Chem., xx, 89.

after carefully saturating it with ammonium nitrate and nitric acid, and drying at 100° C. Rammelsberg[*] believed that it was safer to ignite after drying at 120° C. because drying at 100°–110° C. caused a loss of ammonia before ignition. Kaiser[†] dried the residue in a current of air.

A second source of error discussed by H. Rose,[‡] Fresenius, and others is due to the solubility of the ammonium magnesium arseniate in water, in ammoniacal water, and ammoniacal water containing magnesium salts. Wood[§] attempted to avoid this by precipitating the ammonio-magnesium arseniate with an alcoholic magnesia mixture, and by washing the precipitate with an alcoholic solution, by weighing the residue ignited in a crucible held in a second protecting crucible, after treating with nitric acid and ammonium nitrate, he obtained concordant results. Brauner[‖] followed this method with success.

As has been shown by Neubauer,[¶] ammonium chloride tends to form a phosphate of magnesium too rich in ammonia, and in papers[**] from this laboratory the tendency of ammonia and ammonium chloride to influence the proportion of the metal in the ammonium phosphate of manganese, of magnesium and of other metals in the second group of Mendeléeff has been pointed out. The marked similarity as to behavior between the phosphates and the arseniates led to the investigation of the constitution of the ammonium magnesium arseniate under the usual conditions imposed in analysis, and, further, to the effect of ammonium chloride on the salt of ideal constitution.

In the table which follows are recorded a set of qualitative tests, in which the hot filtrates were tested by hydrogen sulphide in presence of hydrochloric acid. These tests were made to show under what conditions of volume, given amounts of arsenic acid can be entirely removed by magnesia mixture

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[*] Ber. Dtsch. chem. Ges., vii, 544.

[†] Zeitschr. anal. Chem., xiv, 250.

[‡] Zeitschr. anal. Chem., iii, 206.

[§] Am. Jour. Sci. III, vi, 368.

[‖] Zeitschr. anal. Chem., xvi, 57.

[¶] Zeitschr. anorg. Chem., ii, 45; iv, 251; x, 60. Zeitschr. angew. Chem., 1896, 435. Jour. Am. Chem. Soc., xiv, 289.

[**] Am. Jour. Sci., vi, 233; vii, 187; viii, 206. This volume, pp. 121, 190, 252.

from ammoniacal solutions alone, or from ammoniacal solutions containing ammonium chloride. The ammonium chloride for this work was carefully purified by heating it to boiling temperature in concentrated solution — 1 grm. to 3 cm³ — with ammonia in slight excess. The magnesia mixture was prepared by dissolving one hundred and ten grams of the crystallized magnesium chloride in a small volume of water, filtering and adding to it fifty-eight grams of ammonium chloride in solution, purified by adding bromine water and bleaching with ammonia, filtering, and then diluting to a volume of two liters, adding enough ammonia — 10 cm³ — to make this solution smell distinctly of ammonia.

The results (1) to (3) recorded in the table were obtained by precipitating the arsenic present in solution by means of the magnesia mixture prepared as described and rendering the

TABLE I.

Exp.	Volume.	Arsenic present in terms of As_2O_5.	Magnesia mixture.	NH_4OH.	NH_4Cl.	Indications of arsenic in the filtrate by H_2S.
	cm³	grm.	cm³	cm³	grm.	
(1)	100	0.05	20	Slight excess.	. .	None.
(2)	200	0.05	20	Slight excess.	. .	None.
(3)	300	0.05	I 20 II 20 III 20	Slight excess.	. .	I Present. II Present. III None.
(4)	200	0.5	50	Slight excess.	. .	None.
(5)	300	0.5	50	Slight excess.	. .	Present.
(6)	300	0.5	50	2	. .	Present.
(7)	200	0.5	50	4	. .	Present.
(8)	200	0.5	30	2	. .	Present.
(9)	200	0.5	I 30 II 10	4	. .	I Present. II None.
(10)	100	0.5	I 30 II 10	2	. .	I Present. II None.
(11)	130	0.5	50	Excess.	10	Present.
(12)	200	0.5	50	Excess.	10	Present.
(13)	150	0.5	75	Excess.	10	None.
(14)	250	0.5	75	Excess.	10	Present.
(15)	300	0.5	75	2	10	Trace.
(16)	400	0.5	75	2	10	Present.
(17)	285	0.5	100	Excess.	10	None.
(18)	215	0.5	100	Excess.	20	None.
(19)	335	0.5	100	Excess.	60	Present.
(20)	360	0.5	125	Excess.	60	Present.
(21)	360	0.5	150	Excess.	60	None.

solution distinctly ammoniacal. After standing until the precipitate subsided, the solution was filtered and tested for arsenic by hydrogen sulphide. Within certain limits of volume all the arsenic is removed from solution by the magnesia mixture. In case of (3) two additional amounts of the precipitant had to be made in order to remove the arsenic, the solution being ammoniacal. Results (4) to (10) of the table were obtained in the same manner as (1) to (3), the amount of arsenic acid present being increased ten times. In (9) and (10), where the smaller amounts of magnesia mixture were used, additional portions had to be added before all the arsenic was removed from solution. When the larger amounts of ammonia were used the results did not seem to be influenced, (7) and (9). The results recorded in (11) to (21) were obtained by precipitating the arsenic in solution in presence of ammonium chloride by the magnesia mixture. It is evident that the presence of ammonium chloride causes some arsenic to be dissolved and further that this solvent effect is overcome by the magnesia mixture added in larger amounts, even when the ammonium chloride present amounts to sixty grams in weight, as in (21).

In order to find how much arsenic is dissolved from the ammonium magnesium arseniate once precipitated so that no arsenic is left in solution, experiments were made in which the arsenic in the filtrate was weighed after precipitating by hydrogen sulphide in hot acid solution, filtering off on asbestos under pressure, washing successively with water, alcohol, carbon disulphide, alcohol, and water, and drying at 100° C.

TABLE II.

H_2O containing 1 cm^3. NH_4OH in 200 cm^3.	NH_4OH (sp. gr. 0.96).	As_2O_5 digested.	As_2O_5 found as As_2S_3.
grm.	cm^3	grm.	grm.
. . .	100	0.5	0.0019
. . .	100	0.5	0.0026
100	. . .	0.5	0.0008
100	. . .	0.5	0.0005
10	. . .	0.5	0.0002
10	. . .	0.5	0.0004

It is evident from these qualitative tests that, so far as concerns the amount of arsenic dissolved from the ammonium magnesium arseniate, it is safe to use a faintly ammoniacal wash water in small amounts — less than 100 cm^3 — to remove traces of reagents from the residue after it is gathered upon the asbestos felt. Usually 25–50 cm^3 of wash water were used in rinsing off the precipitate in the experiments about to be given below.

The solution of arsenic employed in this work was prepared by dissolving ten grams of pure arsenious oxide, carefully resublimed, in a platinum dish in an excess of pure nitric acid and evaporating on the waterbath to dryness, dissolving the arsenic acid produced in water and diluting to a volume of one liter in a standard flask.

Definite portions of this solution were drawn from a burette into a platinum dish and precipitated with magnesia mixture, prepared as described, in the proportion shown necessary by the qualitative tests for the complete removal of the arsenic from solution, and the solution was made distinctly ammoniacal. The precipitate, dissolved in hydrochloric acid in slight excess, was brought down again by ammonia in distinct excess. After standing until the precipitate had completely subsided, the precipitate was gathered on an asbestos felt in a perforated platinum crucible, making use of the filtrate to remove the last portions of the precipitate to the felt, before washing any reagents from it on the felt with faintly ammoniacal water. After carefully drying, the residue was ignited. The results shown in section A of Table III fall so far below the theory for magnesium pyroarseniate that it seems evident that the arseniate shows a tendency here to form a salt richer in ammonia than the ideal $MgNH_4AsO_4$, and yielding on ignition some meta-arseniate instead of the normal pyroarseniate. In section B the magnesium ammonium arseniate was precipitated by adding to the solution of arsenic acid magnesia mixture containing no free ammonia in the proportion necessary (50 cm^3) to remove the arsenic from solution, and then making the solution distinctly ammoniacal. After the precipitate had subsided, it was filtered off on asbestos under pressure in a perforated platinum crucible washed on the felt with ammoniacal water, dried and ignited. These results are also below the theory for the pyroarseniate. Evidently the conditions here are even better for the formation of the salt too rich in ammonia than they were in the first case. No arsenic was found by hydrogen sulphide in any case either in the filtrate or in the wash water after acidifying and heating.

TABLE III.

A.			
$Mg_2As_2O_7$ corresponding to As_2O_5.			As_2O_5 found by H_2S in the filtrate.
Taken.	Found.	Error.	
grm. 0.7848 0.7848	grm. 0.7800 0.7794	grm. 0.0043– 0.0049–	None. None.
B.			
0.7848 0.7843	0.7772 0.7769	0.0071– 0.0074–	None. None.

In section A of Table IV the results recorded were obtained by precipitating definite portions of arsenic acid drawn from a burette into a platinum dish with the distinctly ammoniacal magnesia mixture in proper proportion, and afterward adding a little more ammonia, filtering off on asbestos under pressure in a perforated platinum crucible as soon as the precipitate subsided, washing off on the felt with ammoniacal water any of the reagents left on the precipitate in transferring it to the felt by using the filtrate, drying, and igniting. No arsenic was found in any case in the filtrate or in the wash water by hydrogen sulphide. The conditions of precipitation here prove to be such, as the results show, that the salt of ideal constitution is formed. Comparing these results with those of Table III, it seems that the conditions under which the salt of ideal composition is formed are such that at the moment and in the locality of precipitation the amount of magnesium chloride in a certain volume of solution must be large in proportion to the amount of ammonia present as the chloride and the hydroxide; otherwise the ammonium of the ammonium arseniate, naturally formed first, does not suffer sufficient displacement by magnesium to produce the normal ammonium magnesium arseniate. At all events, the treatment applied in the experiments of A resulted practically in the complete precipitation and in the production of a precipitate of nearly ideal constitution.

TABLE IV.

Exp.	$Mg_2As_2O_7$ corresponding to As_2O_5.			Magnesia mixture.	NH_4Cl.
	Taken.	Found.	Error.		
A.					
	grm.	grm.	grm.	cm^3	grm.
(1)	0.7843	0.7830	0.0013–	50	. .
(2)	0.7843	0.7849	0.0006+	50	. .
(3)	0.7843	0.7841	0.0002–	50	. .
(4)	0.7843	0.7843	0.0000	50	. .
B.					
(5)	0.7843	0.7763	0.0080–	75	10
(6)	0.7843	0.7762	0.0081–	75	10
(7)	0.7843	0.7832	0.0011–	100	10
(8)	0.7843	0.7838	0.0005–	100	10
(9)	0.7843	0.7784	0.0059–	100	20
(10)	0.7843	0.7810	0.0033–	100	20
(11)	0.7843	0.7849	0.0006+	150	60
(12)	0.7843	0.7846	0.0003+	150	60

In section B of the same table the results recorded show the effect of increased amounts of ammonium chloride on the constitution of the ammonium magnesium arseniate. Enough magnesia mixture was used in each case to remove the arsenic completely from solution. The precipitates were gathered on asbestos in a perforated platinum crucible and treated like those described in section A of the table. It is evident as shown by (5) and (6) of the table that ammonium chloride causes a replacement of some of the metal by ammonia in the ammonium magnesium arseniate (to form, possibly, a salt of the constitution $Mg(NH_4)_4AsO_4$) though the solvent effect of the ammonium chloride is overcome by the addition of a sufficient amount of magnesia mixture. No arsenic appeared in the filtrates, and, further, experiments (7) and (8) show that increasing the amount of magnesia mixture present will cause the formation of the salt of ideal constitution even in presence of considerable amounts of ammonium chloride. Indeed this is possible where as large an amount as sixty grams of the salt is present, as results (11) and (12) show. Obviously, ammonium chloride in any amount above what is required for the magnesia mixture tends to dissolve the precipitate, but this solvent effect may be neutralized by increasing the amounts of magnesia mixture even though the precipitate formed is richer in ammonia than the ideal salt.

In no one of the many precipitates tested by silver nitrate for included chlorides was more than an inappreciable trace found.

Evidently, when ammoniacal magnesia mixture, amounting to about thirty cubic centimeters in excess of the theoretical amount necessary to precipitate all the arsenic as the ammonium magnesium arseniate, is added to the faintly acid solution of arsenic acid (carrying no ammonium salts) in a volume not exceeding two hundred cubic centimeters, the precipitate appears to fall in ideal condition. If the precipitated salt is transferred to the filtering crucible by the aid of portions of the filtrate used as the washing liquid and finally washed on the asbestos with about twenty-five cubic centimeters of faintly ammoniacal water — an amount which is quite sufficient after the transfer has been made — no arsenic gets into solution. The weight of the carefully dried and ignited pyroarseniate indicates with accuracy the amount of arsenic present.

XL

ON THE ESTIMATION OF THALLIUM AS THE ACID AND NEUTRAL SULPHATES.

BY PHILIP E. BROWNING.*

CROOKES † has shown that the salt obtained by heating thallous chloride with sulphuric acid until the excess of the latter is expelled and then raising the heat to redness has the constitution of a neutral sulphate.

He also found that continued heating did not result in any essential loss of weight, and suggested the possibility of applying this method of treatment to the estimation of thallium.

Castanjen ‡ in a recent paper discusses thoroughly the compounds of thallium and confirms essentially the statements of Crookes in regard to the neutral sulphate, adding, however, the observation that on strong ignition in the air this salt tends to lose sulphuric acid. He also mentions in the same paper the acid sulphate, and states that on heating it first melts and on continued heating gives off sulphuric acid, leaving the neutral sulphate.

The work to be described in this paper was undertaken to determine under what conditions the formation of these salts may be applied to the estimation of thallium. For the work a solution was made by dissolving a given amount of the nitrate in water and making up to a liter. The value of the solution was determined by precipitating measured and weighed amounts of this solution both as the iodide and chromate, as described in a previous paper.§ Closely agreeing results by

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* From Am. Jour. Sci., ix, 137.

† Chem. News, viii, 243.

‡ Jour. prakt. Chem., cii, 131.

§ Am. Jour. Sci., viii, 460. This volume, p. 300.

both methods were taken as the standard. Measured amounts of this solution were drawn from a burette into weighed platinum crucibles, and the weight taken as a check on the burette reading. To the solution in the crucible a few drops of sulphuric acid were added and the water removed by evaporation over a steam bath. The crucible was then removed to a radiator, consisting of a conical iron cup, and heated at a temperature ranging from 220° C. to 240° C., until fuming ceased and the weight after half-hour periods of heating remained constant. The crucibles were placed in the radiator upon a pipe stem triangle so that they were about 5 cm. from the bottom, which was heated at low redness. A thermometer, hung so that the bulb occupied the same position as the crucible, gave the reading mentioned above.

As will be seen, the results obtained by this treatment agree closely with the calculated amounts of acid sulphate which should be formed. In several experiments this salt was dissolved in water and the sulphuric acid present in combination precipitated by barium nitrate. The results obtained agreed closely with the formula of the acid sulphate of thallium. Having obtained by the method described the acid sulphate, the crucibles were removed and heated carefully over a free flame to low redness, when, after a considerable evolution of sulphuric acid fumes, the weight again became constant, and the results showed a condition closely approximating to that of the neutral sulphate. In several of these experiments the

Exp.	$TlHSO_4$ calculated.	$TlHSO_4$ found.	Error.	Tl_2SO_4 calculated.	Tl_2SO_4 found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1605	0.1596	0.0009—	0.1344	0.1346	0.0002+
(2)	0.1611	0.1608	0.0003—	0.1349	0.1346	0.0008—
(3)	0.1608	0.1608	0.0000	0.1347	0.1352	0.0005+
(4)	0.1612	0.1600	0.0012—	0.1350	0.1346	0.0004—
(5)	0.1602	0.1596	0.0006—	0.1341	0.1346	0.0005+
(6)	0.1608	0.1596	0.0012—	. . .	. . .	. . .
(7)	0.1617	0.1604	0.0013—	. . .	. . .	. . .
(8)	0.1608	0.1592	0.0016—	0.1347	0.1358	0.0011+
(9)	0.1609	0.1590	0.0019—	0.1348	0.1346	0.0002—

sulphuric acid present in combination was determined, and showed amounts closely agreeing with the constitution of the neutral sulphate.

These results would seem to show that thallium may be estimated either as the acid sulphate or as the neutral sulphate by careful attention to the proper conditions of temperature.

XLI

THE SEPARATION AND DETERMINATION OF MERCURY AS MERCUROUS OXALATE.

By C. A. PETERS.[*]

It is stated in the literature[†] that oxalic acid, neutral and acid oxalates of the alkalies, precipitate mercurous salts, and that oxalic acid and the double oxalates of potassium produce no precipitate with mercuric chloride solution. Starting with these facts, the attempt was made to estimate mercurous salts: volumetrically, by precipitating with ammonium oxalate and determining the oxalic acid by potassium permanganate; and gravimetrically by direct weighing of the precipitate.

The Volumetric Estimation.

The mercurous nitrate solution used was standardized by the battery, and contained about 12 grm. of metallic mercury to the liter. To obviate the tendency of the mercury salt to break down and form basic salts[‡] upon the addition of a large amount of water if no nitric acid is added, the solution was prepared in the following manner. About 20 grm. of mercurous nitrate were ground in a mortar, transferred to a flask, and 200–300 cm^3 water added. After shaking well, the solution was filtered and the filtrate diluted to one liter. Five cubic centimeters of this solution when precipitated with a sodium chloride solution gave a filtrate from which only a very slight darkening in color could be obtained, even upon

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[*] From Am. Jour. Sci., ix, 401.

[†] Rose-Finkener, Handbuch der analytischen Chemie, i, 319.

[‡] Graham-Otto, Handbuch, iii, 1102.

several hours' standing, when treated with hydrogen sulphide, thus showing the absence of a mercuric salt.

A solution made in the above manner had not changed its standard after a period of eight weeks. The potassium permanganate solution (approximately $\frac{N}{10}$) was standardized against lead oxalate.

It was first attempted to estimate the mercurous salts as follows. The mercurous oxalate was precipitated cold by means of ammonium oxalate, stirred well, and allowed to settle, the completion of the precipitation being determined by addition of more ammonium oxalate. The precipitate was collected on asbestos, washed once or twice with cold water, and (still in the crucible) treated in a beaker with 5 cm^3 of strong hydrochloric acid. To the solution diluted to 100–200 cm^3 1 grm. of a manganous salt was added, and the oxalic acid was titrated with permanganate at the ordinary temperature of the room. The end color was not stable and was hard to determine. Three experiments, using 0.1217 of mercury in form of mercurous nitrate, gave plus errors of 0.0011 grm., 0.0017 grm. and 0.0028 grm. respectively, or 1.5 per cent. The precipitate when dissolved in sulphuric acid

Exp.	Hg taken as $Hg_2(NO_3)_2$	Hg found.	Excess of ammonium oxalate approximately $\frac{N}{10}$.	HCl (sp. gr. 1.16).	$MnCl_2 . 4H_2O$.	H_2SO_4 1 : 1	Error as Hg.
			A.				
	grm.	grm.	cm^3	cm^3	grm.	cm^3	grm.
(1)	0.1825	0.1823	0.90	5	0.5	. .	0.0002–
(2)	0.1217	0.1218	0.98	5	0.5	. .	0.0001+
(3)	0.1217	0.1206	0.99	5	0.5	. .	0.0011–
(4)	0.1217	0.1210	4.05	5	0.5	. .	0.0007–
(5)	0.3042	0.3034	4.97	5	0.5	. .	0.0008–
			B.				
(6)	0.1217	0.1220	0.98	. .	. . .	5	0.0003+
(7)	0.1217	0.1211	0.97	. .	. . .	5	0.0006–
(8)	0.1825	0.1827	0.89	. .	. . .	5	0.0002+
(9)	0.3042	0.3040	0.82	. .	. . .	5	0.0002–
(10)	0.1217	0.1202	4.10	. .	. . .	5	0.0015–

and titrated gave no better results. To obviate this difficulty the ammonium oxalate solution was matched on the permanganate and the oxalic acid in the filtrate determined. The results obtained by this method, given in the preceding table, are quite accurate.

In the experiments recorded in section A of the table the filtrate was titrated in the presence of hydrochloric acid and a manganous salt, at a temperature of 20°–40°.* In the experiments under section B sulphuric acid was added and the solution heated in the usual manner. An excess of ammonium oxalate, as shown in experiments (4), (5) and (10), interferes in no way.

The separation of the mercurous salt from small quantities of mercuric salts, by the means of dilute nitric acid (sp. gr. 1.15), was next attempted. It is stated † that mercurous oxalate is insoluble in cold dilute nitric acid, while mercuric oxalate is more or less soluble in the same reagent. Before attempting any separation, however, there are three factors with reference to the action of the nitric acid which need to be determined — first, the maximum amount of nitric acid that may be present in the titration of an oxalate without interference; second, the maximum amount of nitric acid that may be present in a precipitation of mercurous oxalate without having any perceptible solvent action upon the same; and, third, the amount of mercuric oxalate which will be held in solution by given amounts of nitric acid.

To determine the amount of nitric acid that may be present in the titration of an oxalate, 10 cm^3 of $\frac{N}{10}$ ammonium oxalate were titrated with permanganate at a dilution of 100 cm^3 with sulphuric acid at 80° C. The event proved that 10 cm^3 of nitric acid (sp. gr. 1.15) may be present without appearance of interfering action. The maximum amount of nitric acid which may be present without action upon the mercurous salt was determined as shown in the following experiments.

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* Gooch and Peters, Am. Jour. Sci., vii, 461, 1899. This volume, p. 222.

† Souchay and Lenssen, Ann. Chem. (Liebig), cii, 43.

Hg taken as $Hg_2(NO_3)_2$.	Excess of ammonium oxalate approximately $\frac{N}{10}$.	HNO_3 (sp. gr. 1.15).	Volume at precipitation.	Hg found.	Error.
grm.	cm³	cm³	cm³	grm.	grm.
0.1122	1.64	10	100	0.1087	0.0035–
0.1122	2.62	6	100	0.1098	0.0024–
0.1122	1.59	6	100	0.1096	0.0026–
0.1122	1.53	5	100	0.1109	0.0013–
0·1122	1.40	5	100	0.1134	0.0012+
0.1122	1.50	5	100	0.1115	0.0007–
0.1122	1.70	4	100	0.1116	0.0006–
0.1122	1.59	8	200	0.1096	0.0026–
0.1122	6.62	8	200	0.1111	0.0011–
0.1122	7.72	8	200	0.1108	0.0014–
0.1122	2.59	5	200	0.1107	0.0015–
0.1010	2.07	5	200	0.1003	0.0007–

Working under the conditions stated in the above table, it is plain that 5 cm³ of nitric acid (sp. gr. 1.15) may be used before its solvent action is sufficient to interfere with the accuracy of the process.

To determine the amount of mercuric salt that would be held up by 5 cm³ of nitric acid (sp. gr. 1.15), the following experiments were made.

Hg taken as $Hg_2(NO_3)_2$.	HNO_3 (sp. gr. 1.15).	Ammonium oxalate $\frac{N}{10}$ in excess.	Volume.	Time before precipitation.
gms.	cm³	cm³	cm³	
0.0385	4	0.75	100	5 hours.
0.0095	4	1.00	100	No ppt., 20 hours.
0.0143	5	6.5	100	No ppt., 20 hours.
0.0238	5	1.5	100	Slight ppt. 20 hours.
0.0238	5	5.5	100	25 minutes.

Five cm³ of dilute nitric acid (sp. gr. 1.15) will prevent the precipitation of small amounts of mercuric salt, 10–20 mgrm. calculated as mercury, depending upon the amount of ammonium oxalate present in excess. This amount of nitric acid has no apparent solvent action on a precipitate of mercurous oxalate under conditions already stated and does not interfere with the titration of an oxalate by permanganate as already shown.

Carrying out the process of separation of mercurous salts from mercuric salts, the precipitation was made as described for the estimation of mercurous salts alone, excepting that nitric acid and the mercuric salt were added. The experiments in A, B, and C, of the accompanying table show the amounts of mercuric salt from which the mercurous oxalate may be separated with 2 cm³ of nitric acid. In experiments in section A the results are quite accurate, but an excess of ammonium oxalate tends to increase the results a little as seen in experiments under B. An increase in the amount of mercuric salt present causes also, as shown in section C, the results to be a trifle high.

In experiments D, using 4 cm³ of nitric acid even in the

	Hg taken as $Hg_2(NO_3)_2$.	$Hg(NO_3)_2$ present calculated as Hg.	Ammonium oxalate. approximately $\frac{N}{10}$ in excess.	HNO_3 (sp. gr. 1.15).	Volume at precipitation.	Hg found.	Error.
	grm.	grm.	cm³	cm³	grm.	grm.	grm.
A	0.1217	0.0067	0.86	2	100	0.1232	0.0015+
	0.1217	0.0067	0.92	2	100	0.1220	0.0003+
	0.1217	0.0067	0.97	2	100	0.1218	0.0001+
	0.1217	0.0067	0.90	2	100	0.1224	0.0007+
	0.1217	0.0067	0.91	2	100	0.1213	0.0004—
B	0.1221	0.0067	8.92	2	100	0.1237	0.0016+
	0.1217	0.0067	3.93	2	100	0.1235	0.0018+
	0.1242	0.0067	8.75	2	100	0.1263	0.0021+
C	0.1217	0.0134	0.87	2	100	0.1230	0.0013+
	0.1217	0.0184	0.86	2	100	0.1232	0.0015+
D	0.1217	0.0184	8.93	4	100	0.1218	0.0001+
	0.1217	0.0134	3.90	4	100	0.1211	0.0006—
E	0.2244	0.0067	1.88	4	115	0.2244	0.0000
	0.2244	0.0067	1.91	4	130	0.2240	0.0004—
EE	0.2244	0.0141	2.98	4	100	0.2230	0.0014—
	0.2244	0.0141	2.94	4	100	0.2241	0.0003—
F	0.2244	0.0067	8.88	4	100	0.2289	0.0045+
	0.2244	0.0067	8.90	4	100	0.2285	0.0041+
G	0.2424	0.0067	1.75	4	200	0.2432	0.0008+
	0.2424	0.0067	2.00	4	200	0.2414	0.0010—
	0.2424	0.0067	2.96	4	200	0.2421	0.0003—
H	0.2241	0.0184	1.74	4	200	0.2271	0.0026+
	0.2245	0.0184	1.81	4	200	0.2256	0.0011+
I	0.1122	0.0144	6.62	5	200	0.1121	0.0001—
K	0.1122	0.0240	6.54	5	200	0.1136	0.0014+
	0.1122	0.0240	6.57	5	200	0.1130	0.0008+

presence of an excess of ammonium oxalate, the results are accurate. In experiments E the amount of mercurous salt was doubled and the results are accurate. In EE the amount of mercuric salt was also doubled and the results are still fairly accurate; but when a large excess of ammonium oxalate is present as in experiments F, even with the smaller amount of mercuric salt, the results are high. At a dilution of 200 cm^3 the results are normal as seen in experiments G; but the introduction of more mercuric salt, as in experiments H, causes a plus error.

Using 5 cm^3 of nitric acid, the larger amount of mercuric salt together with a large excess of ammonium oxalate, as recorded in experiments K, the error is raised a trifle; but with a smaller amount of mercurous salt, as in experiment I, the result is normal.

In precipitating mercurous salts by ammonium oxalate ($\frac{N}{10}$) it is an easy matter to keep the excess of the precipitant within the limits of 1 or two cm^3, because the mercurous oxalate, when properly stirred, settled very rapidly.

The Gravimetric Estimation.

All the conditions described above in the volumetric estimation of mercurous oxalate, for the separation of mercurous from mercuric salts, may be applied to the gravimetric estimation of mercurous oxalate. The precipitate is collected on a weighed asbestos filter, washed two or three times with cold water and dried over sulphuric acid to a constant weight. Amounts of mercurous oxalate equivalent to 0.1217 and 0.2244 grm. of metallic mercury dried to a constant weight over sulphuric acid in about 15 hours; a larger amount equivalent to 0.3 grm. of metallic mercury, required about 2 days to dry to a constant weight. Souchay and Lenssen* state that mercurous oxalate breaks up at 100°; consequently this temperature cannot be used for drying. For example, a precipitate containing 0.1122 grm. mercury as the oxalate which when

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* Ann. Chem. (Liebig), ciii, 308.

brought to a constant weight at the ordinary temperature over sulphuric acid weighed 0.1371 grm., when heated weighed as follows:

After 7 hours at 110°, weight = 0.1338 grm.
" 2 " " " 0.1328 "
" 7 " " " 0.1302 "

The result shows a loss of 0.0069 grm. for 16 hours, heating, and agrees with the statement of Souchay and Lenssen.

The following experiments give the results of the gravimetric work, in which the drying was effected, by exposure for 15 hours or less, at ordinary temperatures over sulphuric acid. The larger amounts of nitric acid present in the separations cause the precipitate to be more granular and aid in the filtering process.

	Hg taken as $Hg_2(NO_3)_2$	Hg present as $Hg(NO_3)_2$	Excess of ammonium oxalate present approximately $\frac{N}{10}$.	HNO_3 (sp. gr. 1.15).	Volume at precipitation.	Hg found.	Error.
	grm.	grm.	cm³	cm³	cm³	grm.	grm.
K	0.1217	. . .	2–4	. .	100	0.1217	0.0000
	0.1217	. . .	2–4	. .	100	0.1217	0.0000
	0.1122	. . .	2–4	. .	100	0.1124	0.0002+
L	0.1122	0.0067	0.98	2	100	0.1130	0.0008–
	0.1122	0.0067	0.98	2	100	0.1112	0.0010–
M	0.1122	0.0067	4.40	2	100	0.1124	0.0002+
N	0.1122	0.0185	0.72	4	100	0.1125	0.0003+
O	0.2244	0.0071	1.68	4	100	0 2253	0.0009+
	0.2244	0.0071	2.46	4	100	0.2241	0.0003–
P	0.2244	0.0048	0.54	4	200	0.2248	0.0004+
	0.2244	0.0048	2.44	4	200	0.2245	0.0001+

In section K are experiments showing the accuracy of the process where a mercurous salt is precipitated in the absence of a mercuric salt. A small amount of mercuric salt was introduced in experiments L, and an excess of ammonium oxalate in experiment M, a still larger amount of mercuric salt was present in experiment N, and a larger amount of mercurous salt in experiments under O. In experiments in section P a dilution of 200 cm³ was employed both with and without an excess of ammonium oxalate. All the results are within reasonable limits of error.

The work may be summed up briefly as follows: Mercurous nitrate may be estimated volumetrically by precipitating as the oxalate and determining the excess of the precipitant with permanganate.

The precipitated mercurous oxalate may also be estimated gravimetrically by drying it over sulphuric acid and weighing directly.

In solutions containing 2–5 per cent dilute nitric acid, sp. gr. 1.15, mercurous salts may be separated quantitatively as the oxalate from small quantities of mercuric salts.

If about 0.12 grm. of mercury is present as the nitrate in 100 cm^3 of water, about 12 per cent of that amount of mercury as the mercuric salt may be present without interfering with the accuracy of the estimation, and even 20 per cent may be present before an appreciable rise in the result is apparent. If the amount of mercurous salt present is doubled, the amount of mercuric salt which may be present is cut down about one-half.

XLII

THE TITRATION OF MERCURY BY SODIUM THIOSULPHATE.

BY JOHN T. NORTON, JR.*

ACCORDING to J. J. Scherer † mercurous nitrate, mercuric nitrate and mercuric chloride may be estimated by direct titration with sodium thiosulphate, Hg_2S, $2HgS \cdot Hg(NO_3)_2$, and $2HgS \cdot HgCl_2$ being the precipitates obtained in each case. I have been unable to obtain access to Scherer's original publication, but Sutton ‡ gives the following very general directions for this process:

"(*a*) *Mercurous salts.* — The solution containing the metal as a protosalt only is diluted, gently heated and the thiosulphate delivered in from the burette at intervals, meanwhile well shaking until the last drop produces no brown color. The sulphide settles freely and allows the end of the reaction to be easily seen. One cm³ of the $\frac{1}{20}$ normal solution of thiosulphate = 0.02 grm. Hg or 0.0208 grm. Hg_2O.

"(*b*) *Mercuric nitrate.* — The solution is considerably diluted, put into a stoppered flask, nitric acid added and the thiosulphate cautiously added from the burette, vigorously shaken meanwhile, until the last drop produces no further precipitate. Scherer recommends that when the greater part of the metal is precipitated the mixture should be diluted to a definite volume, the precipitate allowed to settle and a measured quantity of the clear liquid taken for titration; the analysis may then be checked by a second titration of the clear liquid if needful. One cm³ of $\frac{1}{20}$ normal thiosulphate = 0.015 grm. Hg or 0.0162 grm. HgO.

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* From Am. Jour. Sci., x, 48.

† Scherer's Lehrbuch der Chemie, i, 513.

‡ Volumetric Analysis, p. 220.

"(*c*) *Mercuric chloride.* — With mercuric chloride the end of the process is not so easily seen. The very dilute solution is acidified with hydrochloric acid, heated nearly to boiling, and the thiosulphate cautiously added so long as a white precipitate is seen to form; any great excess of the precipitant produces a dirty-looking color. Filtration is necessary to distinguish the exact ending of the reaction. One cm^3 of $\frac{1}{10}$ normal thiosulphate = 0.015 grm. Hg or 0.0162 grm. HgO."

Fresenius * gives practically the same directions, but omits all mention of that portion of the process dealing with mercurous nitrate.

In view, therefore, of the scant information available on the subject and of the apparent difficulty of working the process accurately according to the directions given, an attempt was made to ascertain whether the careful regulation of temperature, dilution, and amount of acid present might not produce beneficial results.

That portion of the process dealing with mercuric chloride was first taken up. The mercuric chloride used was pulverized, dried at 100° and its purity proved by several determinations as mercuric sulphide. The sodium thiosulphate was made up of approximately $\frac{1}{10}$ normal strength and standardized on decinormal iodine, which in turn was titrated against decinormal arsenious acid made from pure resublimed arsenious oxide.

For the action of sodium thiosulphate upon the mercuric chloride Scherer gives the equation,

$$3HgCl_2 + 2Na_2S_2O_3 + 3H_2O = 2HgS . HgCl_2 + 2Na_2SO_4 + 4HCl.$$

According to my experience, the action results in the formation of a dense white precipitate which refuses to settle either by shaking or standing, thus making it impossible to fix the end reaction by reading the first drop of thiosulphate which produces no further white precipitate in the solution containing the mercuric chloride. Recourse must be had therefore to filtering. By far the quickest and neatest method is to use the asbestos

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* Quantitative Analysis.

filter deposited on a large perforated platinum cone.* This cone is set in a glass funnel by means of a rubber connector and the funnel is passed through the stopper of a large side-necked Erlenmeyer connected with an exhaust pump. A little asbestos fiber shaken in the liquid to be filtered was found to be very beneficial in preventing the precipitate from running through the filter. In all the following experiments the thiosulphate was run into the solution containing the mercuric chloride in excess, the whole shaken up with asbestos fiber, filtered and the excess of thiosulphate determined by $\frac{1}{10}$ normal iodine. This procedure seems to be far preferable to attempting to catch the end of the reaction by running in the thiosulphate until the last drop produces no precipitate. In the experiments shown in Table I no attention was paid to the temperature of the solution, and the thiosulphate was run in until the liquid turned brown. In every case the solution was allowed to stand until there was no further visible change of color.

TABLE I.

Exp.	$HgCl_2$ taken, calc'd as Hg.	$Na_2S_2O_3$ in excess.	Volume at beginning.	$HgCl_2$ found, calc'd as Hg.	Error.
	grm.	cm^3	cm^3	grm.	grm.
(1)	0.0446	46.28	200	0.0348	0.0108–
(2)	0.0354	46.28	400	0.0326	0.0028–
(3)	0.0356	44.97	400	0.0225	0.0131–
(4)	0.0345	44.5	100	0.0308	0.0037–
(5)	0.0354	44.43	50	0.0326	0.0028–
(6)	0.0382	22.59	50	0.0354	0.0028–
(7)	0.0375	8.58	50	0.0385	0.0010+
(8)	0.0371	1.84	50	0.0304	0.0067–
(9)	0.0731	2.28	50	0.0774	0.0043+
(10)	0.1486	9.34	50	0.1489	0.0003+

A glance at the table shows that the results are most irregular. In Table II is seen the result of regulating the temperature and the length of standing after the addition of the sodium thiosulphate.

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* Amer. Chem. Jour., i, 321.

TABLE II.

Exp.	$HgCl_2$ taken as Hg.	Volume at beginning.	Temperature.	Standing.	$Na_2S_2O_3$ in excess.	$HgCl_2$ as Hg found.	Error.
	grm.	cm³	C.	minutes.	cm³	grm.	grm.
(1)	0.0738	50	36°	40	16.68	0.0494	0.0244—
(2)	0.0741	50	70°	15	15.42	0.0738	0.0003—
(3)	0.0741	75	70°	12	16.07	0.0733	0.0008—
(4)	0.0744	50	70°	10	14.6	0.0755	0.0011+
(5)	0.0764	50	72°	7	6.77	0.0771	0.0007+
(6)	0.0762	50	75°	10	8.54	0.0799	0.0037+
(7)	0.0756	50	73°	15	9.99	0.0815	0.0059+
(8)	0.0774	50	68°	15	10.84	0.0767	0.0007—
(9)	0.0745	75	69°	7	6.62	0.0805	0.0060+
(10)	0.0736	50	68°	5	15.82	0.0714	0.0022—

These results, although better than those of Table I, are still very uncertain. On the supposition that the change from white to black, which takes place in the solution after the addition of an excess of sodium thiosulphate more or less quickly according to the temperature, was due to an increased amount of HgS in the compound $2HgS . HgCl_2$, the next step was to ascertain whether this could be avoided by stopping the addition of the thiosulphate at the first indication of a change of color in the white precipitate, diluting the solution with a large amount of cold water and immediately throwing it on the filter. Table III shows the result of the experiments.

TABLE III.

Exp.	$HgCl_2$ taken as Hg.	Volume at beginning.	Temperature.	$Na_2S_2O_3$ in excess.	$HgCl_2$ found as Hg.	Error.
	grm.	cm³	C.	cm³	grm.	grm.
(1)	0.0749	50	70°	4.15	0.0751	0.0002+
(2)	0.0749	50	75°	0.72	0.0728	0.0021—
(3)	0.0756	50	72°	1.46	0.0759	0.0003+
(4)	0.0753	50	70°	2.57	0.0750	0.0003—
(5)	0.0390	50	70°	8.43	0.0395	0.0005+
(6)	0.0388	50	72°	8.19	0.0390	0.0002+
(7)	0.0380	50	76°	2.03	0.0398	0.0018+
(8)	0.1494	50	78°	4.99	0.1498	0.0004+
(9)	0.1489	150	78°	4.38	0.1512	0.0023+
(10)	0.1480	50	70°	0.52	0.1438	0.0042—
(11)	0.1498	50	78°	1.47	0.1540	0.0042+
(12)	0.1484	50	71°	2.09	0.1517	0.0033+
(13)	0.1480	75	72°	1.59	0.1509	0.0029+

In the case of quantities of mercuric chloride up to 0.1 grm. the results shown in Table III are very satisfactory, but when larger amounts of mercuric chloride are used the errors again become prominent. In Table IV, the effect of lowering the temperature to 60° C. and of increasing the dilution to 100 cm^3 is shown.

TABLE IV.

Exp.	$HgCl_2$ taken as Hg.	Volume at beginning.	Temperature.	$Na_2S_2O_3$ in excess.	$HgCl_2$ found as Hg.	Error.
	grm.	cm^3	C.	cm^3	grm.	grm.
(1)	0.0759	100	60°	3.06	0.0766	0.0007+
(2)	0.0384	100	60°	2.81	0.0387	0.0003+
(3)	0.1492	100	60°	1.1	0.1500	0.0008+
(4)	0.1503	100	60°	1.63	0.1506	0.0003+
(5)	0.1479	100	60°	2.41	0.1480	0.0001+
(6)	0.1489	100	60°	2.12	0.1503	0.0014+
(7)	0.2244	100	60°	2.63	0.2259	0.0015+
(8)	0.1490	100	60°	2.33	0.1484	0.0006−
(9)	0.0758	100	60°	2	0.0762	0.0004+
(10)	0.0383	100	60°	2.53	0.0379	0.0004−

From this table it is plain that Scherer's process for the estimation of mercury in the form of mercuric chloride is capable of yielding accurate results if carried out under certain fixed conditions. These conditions, which must be closely adhered to, are as follows: The solution containing the mercury in the form of mercuric chloride is placed in a liter flask, diluted to 100 cm^3 and heated to a temperature of 60° C. The sodium thiosulphate in $\frac{1}{10}$ normal solution is run in from a burette until the white precipitate formed begins to take on a brownish tinge. The solution is then diluted with cold water, some asbestos fiber added to coagulate the precipitate and the whole is quickly thrown on the filter. After careful washing of the precipitate, the filtrate is diluted to a definite volume, 3 grm. of potassium iodide added and the excess thiosulphate titrated with iodine and starch solution. The duration of the process need not exceed 15 minutes. It is worthy of note that there is no necessity of using any hydrochloric acid in addition to that formed in the reaction. This certainly eliminates one probable source of error — the interaction of hydrochloric acid and sodium thiosulphate.

In dealing with the estimation of mercury in the form of mercurous nitrate the same procedure was employed as in the case of mercuric chloride. A solution of mercurous nitrate was prepared by dissolving as much as possible of 20 grm. of the salt in about 200 cm^3 of water, filtering off the clear liquid and diluting to a definite volume. The standard of the solution was determined by precipitation as metallic mercury by means of the electric current. Contrary to the statement made in Sutton, the brown precipitate of Hg_2S, formed as shown in the equation,

$$Hg_2(NO_3)_2 + Na_2S_2O_3 = Hg_2S + Na_2SO_4 + N_2O_5,$$

does not settle and leave a clear supernatant liquid, but the solution remains cloudy and it is impossible to see any end reaction. Although the conditions of dilution, temperature and amount of acid present were carefully considered, no arrangement or adjustment of these conditions was found

TABLE V.

Exp.	$Hg_2(NO_3)_2$ taken as Hg.	HNO_3 1 : 3.	Volume at beginning.	Temperature.	$Na_2S_2O_3$ in excess.	$Hg_2(NO_3)_2$ found as Hg.	Error.
	grm.	cm^3	cm^3	C.	cm^3	grm.	grm.
(1)	0.0148	None.	50	50°	4.28	0.0129	0.0019–
(2)	0.0148	None.	75	60°	4.45	0.0117	0.0031–
(3)	0.2976	None.	300	60°	12.67	0.2760	0.0216–
(4)	0.1488	None.	100	40°	2.19	0.1386	0.0102–
(5)	0.1488	None.	100	50°	6.92	0.1378	0.0110–
(6)	0.1488	None.	200	50°	0.78	0.1388	0.0100–
(7)	0.0744	None.	100	65°	0.73	0.0636	0.0108–
(8)	0.0744	1	100	55°	0.49	0.0733	0.0011–
(9)	0.0744	2	100	40°	1.16	0.0660	0.0084–
(10)	0.0744	1	100	55°	1.85	0.0685	0.0059–
(11)	0.0744	1	100	55°	0.82	0.0686	0.0058–
(12)	0.0744	½	200	55°	1.71	0.0685	0.0059–
(13)	0.0744	4	100	40°	1.77	0.0649	0.0095–
(14)	0.0744	5½	100	40°	1.34	0.0645	0.0099–
(15)	0.0744	1	100	45°	1.71	0.0654	0.0090–
(16)	0.0744	10	100	45°	1.55	0.0669	0.0075–
(17)	0.1488	1	100	40°	0.73	0.1391	0.0097–

under which satisfactory results could be obtained. Table V gives the result of experiments.

The errors in experiments (1), (3) to (6), (10) to (12), and (17) are, proportionally to the amount of material handled, practically the same and this fact caused me to make a careful revision of all standards; but no mistake could be found. The reaction upon which the process depends requires the formation of Hg_2S, but this mercurous sulphide breaks down immediately into mercuric sulphide and mercury. The latter is probably acted upon by the free nitric acid present to form mercuric nitrate, which in turn is transformed into the compound $2HgS \cdot Hg(NO_3)_2$ by the action of the thiosulphate. At any rate, with an error so large, whatever its source may be, the process is plainly impracticable.

The third step in Scherer's process deals with the action of sodium thiosulphate on mercuric nitrate. In the following experiments a solution of mercuric nitrate was prepared either by dissolving as far as possible 20 grm. of mercuric nitrate in about 200 cm^3 of cold water, filtering off the supernatant liquid and diluting to a definite volume (1)–(8), or by dissolving the salt in strong nitric acid and diluting (9)–(19). The standard of the solution was obtained by precipitation as metallic mercury by means of the electric current. The yellow precipitate, formed according to Scherer's reaction,

$$3Hg(NO_3)_2 + 2Na_2S_2O_3 = 2HgS \cdot Hg(NO_3)_2 + 2Na_2SO_4 + 2N_2O_5,$$

on adding the sodium thiosulphate settles much better than in the case of either mercuric chloride or mercurous nitrate; but, as the supernatant liquid takes on a permanent yellow color towards the end of the reaction, it is impossible to see when the thiosulphate produces no further precipitation. On this account, therefore, the same procedure was adopted as in the case of the mercuric chloride and mercurous nitrate, i. e., filtration and titration of the excess of sodium thiosulphate with iodine and starch solution. The result of the experiments is shown in the following table.

TABLE VI.

Exp.	$Hg(NO_3)_2$ taken as Hg.	Volume at beginning.	HNO_3 1 : 3	Temperature.	$NA_2S_2O_3$ in excess.	$Hg(NO_3)_2$ found as Hg.	Error.
	grm.	cm³	cm³	C.	cm³	grm.	grm.
(1)	0.1167	200	None.	60°	0.46	0.1384	0.0217+
(2)	0.1167	100	1	60°	3.68	0.1348	0.0181+
(3)	0.1167	100	2	60°	0.23	0.1375	0.0208+
(4)	0.1167	100	None.	60°	0.17	0.1360	0.0193+
(5)	0.1167	300	None.	21°	0.12	0.1232	0.0065+
(6)	0.1167	300	None.	21°	0.15	0.1375	0.0208+
(7)	0.1167	200	None.	21°	11.8	0.1461	0.0294+
(8)	0.1167	200	20	21°	15.97	0.1403	0.0236+
(9)	0.1278	200	None.	21°	5.23	0.1647	0.0369+
(10)	0.1278	200	None.	21°	1.35	0.1653	0.0375+
(11)	0.1278	100	None.	21°	1.48	0.1662	0.0384+
(12)	0.0752	200	None.	21°	2.09	0.0996	0.0244+
(13)	0.0255	100	None.	21°	2.01	0.0280	0.0025+
(14)	0.0255	200	5	21°	3.44	0.0264	0.0009+
(15)	0.0255	200	10	21°	0.85	0.0334	0.0079+
(16)	0.0255	300	None.	21°	1.96	0.0264	0.0009+
(17)	0.0255	200	None.	21°	1.9	0.0287	0.0032+
(18)	0.0255	200	None.	21°	1.76	0.0290	0.0035+
(19)	0.0639	200	None.	60°	1.53	0.0831	0.0192+

These results seem to show the impossibility of obtaining accurate results according to Scherer's method for the determination of mercuric nitrate by direct titration with sodium thiosulphate. The constant plus error cannot be accounted for on the hypothesis that the nitric acid present decomposes the sodium thiosulphate, for in that case the error would lie in the other direction. It is more probable that the constitution of the compound 2HgS . $Hg(NO_3)_2$ is not definite enough to make it the basis for an analytical process.

XLIII

THE IODOMETRIC ESTIMATION OF ARSENIC ACID.

By F. A. GOOCH AND JULIA C. MORRIS.*

THE interaction of a soluble arseniate and a soluble iodide in a suitably acidulated solution results, as is well known, in the reduction of the arsenic acid (more or less completely according to conditions of temperature and proportions of reagents and solvents) with the corresponding liberation of two atoms of iodine for every molecule of arsenic acid (H_3O_3AsO) reduced. Inasmuch, however, as the reaction of this process is reversible, it is necessary, in order that the reduction may be complete, to nullify the oxidizing action of the iodine liberated. Theoretically this end may be accomplished in either of two ways, by volatilizing the free iodine bodily or by destroying the oxidizing power of the iodine by converting it to hydriodic acid. The former method was followed in a processs devised for the estimation of arsenic acid and elaborated in this laboratory.† This method, as originally put forward, consisted in adding to the solution of the arseniate potassium iodide in excess of the amount theoretically indicated, with 10 cm^3 of sulphuric acid of half strength, and so arranging the dilution that the total volume of the liquid should be about 100 cm^3, boiling until the volume decreased to 40 cm^3, bleaching by the cautious addition of sulphurous acid the trace of free iodine still held by the hydriodic acids, diluting, cooling, neutralizing with acid potassium carbonate, and titrating with iodine, after adding the starch indicator. This process, depending upon the removal by volatilization of all but the

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* From Am. Jour. Sci., x, 151.

† Gooch and Browning, Am. Jour. Sci., xl, 66. Volume I, p. 30.

last traces of liberated iodine and the conversion of this minute residue by sulphurous acid, involves no secondary reactions of a sort likely to influence the main effect. It is exact and fairly rapid.

The method of Williamson,* brought forward more recently, depends upon the conversion of the liberated iodine to hydriodic acid. The interaction at ordinary temperatures of a suitably strong acid, hydrochloric or sulphuric acid, upon the mixture of the arseniate and iodide sets free iodine, and the liberated iodine is converted to hydriodic acid by the action of sodium thiosulphate, the end point being the disappearance of the iodine color.

According to Williamson's directions, 25 cm^3 portions of the solution of the arseniate are treated with potassium iodide and mixed with an equal volume of hydrochloric acid of sp. gr. 1.16. The precaution is recommended that the strength of the solution of the arseniate shall not exceed the decinormal value, in order that the dilution consequent upon titration by the thiosulphate may not be too great — the reducing action brought about by the action of the strong acid upon the arseniate and iodide being reversible upon the dilution of liquid with water. This procedure thus limits the process to the determination of about 0.18 grm. of arsenic acid in 25 cm^3 of the solution to be treated with an equal volume of hydrochloric acid of sp. gr. 1.16. Obviously, however, the process should, so far as the reduction is concerned, be applicable to larger amounts of arsenic provided the strength of the acid is kept up proportionately. It is essential that the liquid at the end of the titration should contain approximately ten per cent of its mass of absolute hydrochloric acid or about one-third of its volume of the aqueous acid of sp. gr. 1.16.

The arsenic acid is measured either by the amount of standard thiosulphate required to bleach the iodine or by the amount of iodine required to reoxidize the reduced arsenious acid, after neutralizing with acid potassium carbonate. If the former alternative is followed, the end-reaction must be the

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* Jour. Soc. Dyers and Colorists, 1896, 86–89.

disappearance of the yellow color of the iodine, since in solutions so strongly acid it is impossible to place dependence upon the starch indicator; in using the latter alternative, the starch indicator is, of course, permissible and preferable.

In the direct titration of the iodine by thiosulphate two sources of error present themselves as possibilities; first, the excessive liberation of iodine by the action of air upon the strongly acidulated iodide; and second, the liability of the thiosulphate,* if present even in momentary or local excess during the process of titration, to break down under the action of strong acid, thus changing its capacity to convert iodine to hydriodic acid. The latter contingency should be remote in proportion to the caution used in adding the thiosulphate and in keeping the liquid well stirred; the former must of necessity vary with the acidity of the solution containing the iodide, the time of exposure to atmospheric action, and the degree of contact with the air incidental to stirring. We have thought it desirable, therefore, to see how far each of these possibilities is likely to interfere in the practical conduct of an ordinary analysis.

HCl (sp. gr. 1.16) taken.	KI taken.	Total volume.	$Na_2S_2O_3$ added at once. In terms of H_3O_3AsO.	$Na_2S_2O_3$ added after 5 minutes. In terms of H_3O_3AsO.	$Na_2S_2O_3$ added after stirring 5 minutes. In terms of H_3O_3AsO.
cm^3	grm.	cm^3	grm.	grm.	grm.
25	2	50	0.0013	. . .	. . .
25	2	75	0.0004	. . .	. . .
25	2	50	. . .	0.0035	. . .
25	2	75	. . .	0.0019	. . .
25	2	50	. . .	. . .	0.0042
25	2	75	. . .	. . .	0.0021
50	2	100	0.0017	. . .	. . .
50	2	150	0.0004	. . .	. . .
50	2	100	. . .	0.0035	. . .
50	2	150	. . .	0.0019	. . .
50	2	100	. . .	. . .	0.0035
50	2	150	. . .	. . .	0.0014

The effects likely to result simply from the strong acidification of the solution containing potassium iodide and their variation for conditions of dilution representing the beginning

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* Norton, Am. Jour. Sci., vii, 287. This volume, p. 206.

and the end of a titration on the lines laid down are shown in the preceding table. The solution of potassium iodide was diluted as indicated before the addition of the acid and the iodine set free was titrated by thiosulphate. The proportionate strength of acid and the time before titration are, obviously, the essential factors. The absolute amount of acid present and the stirring seem to make little difference.

As to the action of the hydrochloric acid on small amounts of the thiosulphate, we have the evidence of the experiments detailed in the following statements in which 1, 2, and 5 cm³ of nearly $\frac{N}{10}$ thiosulphate are exposed to the action of 25 cm³ hydrochloric acid, sp. gr. 1.16, without dilution or diluted with an equal volume of water, were titrated with nearly $\frac{N}{10}$ iodine. The condition of acidity when the volume of 50 cm³ contains 25 cm³ of hydrochloric acid, sp. gr. 1.16, is that of the beginning of titration of Williamson's process. In order that the effect of error due to such action upon the determination of arsenic acid may appear immediately, the thiosulphate and iodine used are expressed in terms of that acid.

HCl (sp. gr. 1.16).	Volume before titration.	$Na_2S_2O_3$ nearly $\frac{N}{10}$ in terms of H_3O_3AsO.		Iodine to color without dilution, in terms of H_3O_3AsO.	Error of titration without dilution, in terms of H_3O_3AsO.	Iodine to color after diluting to 75 cm³, in terms of H_3O_3AsO.	Error of titration after dilution, in terms of H_3O_3AsO.
cm³	cm³	cm³	grm.	grm.	grm.	grm.	grm.
25	26	1	0.0071	0.0062	0.0009–	0.0071	0.0000
25	50	1	0.0071	0.0071	0.0000	0.0071	0.0000
25*	50	1	0.0071	0.0079	0.0008+	0.0079	0.0008+
25	50	2	0.0141	0.0146	0.0005+	0.0146	0.0005+
25*	50	2	0.0141	0.0157	0.0016+	0.0157	0.0016+
25	30	5	0.0353	0.0336	0.0017–	0.0374	0.0021+
25	50	5	0.0353	0.0359	0.0006+	0.0359	0.0006+
25*	50	5	0.0353	0.0411	0.0058+	0.0411	0.0058+

These two sources of error, the one due to a liberation of iodine and the other due to decomposition of the thiosulphate, would naturally tend to overcome one another, but the completeness of such neutralization would naturally be largely a

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* In these experiments the acid stood in contact with the thiosulphate 5 minutes before titration.

matter of chance in the varying conditions of actual analysis. The experiments of the following table, however, in which $\frac{N}{10}$ thiosulphate, to the amount of 1, 2, and 5 cm³, was added to the liquid, 50 cm³ and 75 cm³, containing 25 cm³ acid, and titrated with iodine at once, and after five minutes, were made to test the matter for the conditions of dilution at the beginning and at the end of a titration.

HCl (sp. gr. 1.16).	KI.	Volume.	$Na_2S_2O_3$ nearly $\frac{N}{10}$ in terms of H_3O_3AsO.		Iodine in terms of H_3O_3AsO, at once.	Iodine in terms of H_3O_3AsO, after 5 min.	Error in terms of H_3O_3AsO.
cm³	grm.	cm³	cm³	grm.	grm.	grm.	grm.
25	2	50	1	0.0071	0.0057	. . .	0.0014–
25	2	75	1	0.0071	0.0071	. . .	0.0000
25	2	50	2	0.0141	0.0131	. . .	0.0010–
25	2	75	2	0.0141	0.0143	. . .	0.0002+
25	2	50	5	0.0353	0.0332	. . .	0.0021–
25	2	75	5	0.0353	0.0357	. . .	0.0004+
25	2	50	1	0.0071	. . .	0.0028	0.0043–
25	2	75	1	0.0071	. . .	0.0067	0.0004–
25	2	50	2	0.0141	. . .	0.0116	0.0025–
25	2	75	2	0.0141	. . .	0.0139	0.0002–
25	2	50	5	0.0353	. . .	0.0312	0.0041–
25	2	75	5	0.0353	. . .	0.0361	0.0008+

It is clear that under the conditions covered by the experiments of the two preceding tables the decomposition of the thiosulphate is likely to occur in greater or less degree, and that when the acid of sp. gr. 1.16 is not much diluted, the products of decomposition are not oxidized by the iodine completely. The latter observation is quite in harmony with the fact that sulphur dioxide bleaches iodine in strong hydrochloric acid only slowly and incompletely. In such cases dilution favors further action of the iodine, but results obtained by titration with iodine in the acid solution diluted with an equal amount of water are unmodified by further dilution.

In the following tables are recorded actual determinations of arsenic according to Williamson's process. To each 25 cm³ of the arseniate were added 1, 2, or 3 grms. of potassium iodide and 25 cm³ hydrochloric acid, sp. gr. 1.16. The iodine was bleached by nearly decinormal thiosulphate without addition of the starch indicator, which loses all delicacy in the presence of strong acid. The time occupied by each titration was about five minutes. The standards of the arseniate were determined by the vaporization process,* the purity of reagents employed in that process having been proved by trying the process in the estimation of a solution of arsenic acid made by oxidizing pure decinormal arsenious acid by iodine.

HCl.	KI.	Volume at beginning of titration.	Volume at end of titration.	H_3KAsO_4 in terms of H_3O_3AsO.	H_3O_3AsO found.	Error.
cm³.	grm.	cm³.	cm³.	grm.	grm.	grm.
25	2	50	51	0.0062	0.0085	0.0023+
25	2	50	52	0.0125	0.0156	0.0031+
25	2	50	55	0.0312	0.0350	0.0038+
25	2	50	55	0.0624	0.0666	0.0042+
25	2	50	73	0.1559	0.1588	0.0029+
25	2	50	73	0.1559	0.1587	0.0028+
25	2	50	73	0.1559	0.1591	0.0032+
25	2	50	73	0.1559	0.1595	0.0036+
25	3	50	73	0.1559	0.1595	0.0036+
25	1	50	73	0.1559	0.1581	0.0022+
25	2	50	73	0.1559	0.1581	0.0022+
25	2	50	73	0.1559	0.1588	0.0029+

The range of error in these results is from + 0.0022 grm. to + 0.0042 grm. with a mean of + 0.0031 grm. — not very different from what might be expected from the effect of the interaction of the strong hydrochloric acid and the iodide alone. The counter-effect due to the decomposition of the thiosulphate is not large, yet it is probably real, as will appear in the sequel. In the following series of determinations, made with new solutions and new standards throughout, the arsenic acid was determined, first, by titrating the iodine set free by 25 cm³ of hydrochloric acid, sp. gr. 1.16 and 3 grms. potassium iodide, the solution having a total volume of 50 cm³ at beginning and of 75 cm³ at the end of titration and, secondly, the arsenious acid produced in the first reaction was titrated, after being neutralized with acid potassium carbonate by iodine in the presence of the starch indicator.

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* Gooch and Browning, loc. cit.

H_2KAsO_4 taken, in terms of H_3O_3AsO.	H_3O_3AsO found by the thiosulphate.	Error.	H_3O_3AsO found by titration of H_3O_3As with iodine.	Error.
grm.	grm.	grm.	grm.	grm.
0.1767	0.1798	0.0031+	0.1776	0.0009+
0.1767	0.1798	0.0031+	0.1777	0.0010+
0.1767	0.1795	0.0028+	0.1785	0.0018+
0.1767	0.1793	0.0026+	0.1785	0.0018+
0.1767	0.1794	0.0027+	0.1780	0.0013+
0.1767	0.1798	0.0031+	0.1785	0.0018+

The average error of the first operation is 0.0029 grm., not far from that of the previous series; the error of the second operation, the titration of the arsenious acid, amounts on the average to 0.0014 grm. In the second operation the error due to over-use of the thiosulphate by iodine set free outside the main reaction is obviously eliminated. The tetrathionate present after neutralization with acid potassium carbonate is unaffected by iodine, as we have found by titrating 25 cm^3 $\frac{N}{10}$ iodine mixed with 25 cm^3 hydrochloric acid, sp. gr. 1.16, by the thiosulphate, neutralizing with acid potassium carbonate,* adding starch and getting the starch blue with a single drop of $\frac{N}{10}$ iodine. The average error of this process, therefore, 0.0014, is probably due to the products of decomposition of the thiosulphate in the first operation.

From the foregoing experiments it is clear that an arbitrary correction of about 0.0030 grm. must be deducted from the indications of Williamson's process of direct titration by thiosulphate, made with the greatest care under the conditions mentioned; and that a correction varying from one-half that amount (0.0015 grm.) to nothing (according to the amount of arsenious acid present) when the determination is made by iodine after neutralization with acid potassium carbonate.

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* It is worthy of note, that, as we have found by experience, it is not possible to substitute an alkaline hydroxide for the carbonate in the early stages of the process of neutralization, on account of the decomposing effect of the former reagent upon the tetrathionate. This effect is in proportion to the heating of the solution, but is never wholly absent even when ice is intermixed with the liquid and the greatest care taken to prevent a rise of temperature.

After making these arbitrary corrections in the results of the preceding table, the individual variations fall within reasonable limits.

On the other hand, the vaporization process, in which the arseniate is reduced by boiling with sulphuric acid and potassium iodide in the manner described,* gives indications reasonably regular and accurate without the application of an arbitrary correction. This process, moreover, may be shortened by restricting the volume at which heating begins so that the boiling need not be extended beyond five or six minutes. According to this slight modification, the solution of the arseniate is heated in an Erlenmeyer flask with potassium iodide to an amount about 0.5 grm. in excess of the amount theoretically required and 10 cm^3 of sulphuric acid of half strength in a total volume of between 50 cm^3 and 75 cm^3. The liquid is boiled till the iodine vapors are no longer visible in the flask above the liquid, the iodine color in the still hot liquid is bleached by the cautious addition of sulphurous acid, the whole is diluted with cold water, and cooled quickly. The solution is nearly neutralized with potassium hydroxide and the neutralization is completed with acid potassium carbonate. The reduced acid is titrated with iodine after adding the starch indicator. By this procedure the results of the following table were obtained.

Volume.	H_3O_3AsO taken.	H_3O_3AsO found.	Error.
cm^3.	grm.	grm.	grm.
35	0.1559	0.1559	0.0000
35	0.1559	0.1560	0.0001+
40	0.1559	0.1559	0.0000
65	0.1559	0.1559	0.0000
50	0.2495	0.2499	0.0004+
50	0.2557	0.2449	0.0008−
60	0.3119	0.3117	0.0002−
60	0.3119	0.3120	0.0001+
75	0.3119	0.3124	0.0005+
75	0.3119	0.3132	0.0013+
75	0.3119	0.3121	0.0002+
75	0.3119	0.3115	0.0004−
75	0.3119	0.3124	0.0005+

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* Loc. cit.

XLIV

ON THE QUALITATIVE SEPARATION OF NICKEL FROM COBALT BY THE ACTION OF AMMONIUM HYDROXIDE ON THE FERRICYANIDES.

BY PHILIP E. BROWNING AND JOHN B. HARTWELL.*

SOME years ago F. W. Clarke† suggested a method for the separation of nickel from cobalt depending upon the solvent action of ammonium hydroxide upon the precipitated ferricyanides. The method may best be described by quoting from the original article: "To the slightly acid solution containing the two metals, I first add an excess of ammonium chloride. This causes the cobalt precipitate, which otherwise would run through the filter, to fall in a denser state, and also of a much darker color, often nearly black. I then add the potassium ferricyanide until the precipitation is complete, and afterwards agitate strongly with a considerable excess of ammonia. Upon filtering, all the cobalt remains upon the filter, being recognized by the characteristic color of the precipitate, and the nickel is readily detected in the filtrate, by means of ammonium sulphide. If, upon filtering, the portion at first running through is turbid, it may be disregarded, or returned to the filter, that which filters through subsequently being almost invariably clear."

In making a study of this method we found two serious objections; first, the practical impossibility of obtaining a good filtration from the cobalt ferricyanide, even in the presence of the ammonium chloride, and, second, the large amount of sulphur thrown down when ammonium sulphide was

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* From Am. Jour. Sci., x, 316.

† Am. Jour. Sci., xlviii, 67.

added to the filtrate containing the nickel with the excess of ferricyanide.

Our first attempt was to secure, if possible, a complete separation of the precipitated cobalt ferricyanide and the dissolved nickel by filtration. This we were able to accomplish by the addition of a small amount of a solution of an aluminum salt to the original solution which held back the cobalt, and, as experiment showed, allowed the complete solvent action of the ammonium hydroxide upon the nickel salt. Amounts of nickel as small as 0.0001 grm. were detected, when mixed with the aluminum salt, by precipitating as ferricyanide, extracting with ammonium hydroxide, and testing in the manner to be described.

On turning our attention to a possible improvement in the method for the detection of the nickel, a reaction first discussed by Allen* was applied. When the ammoniacal solution of the nickel ferricyanide was treated with strong sodium or potassium hydroxide solution, in the presence of an excess of potassium ferricyanide, a black flocky precipitate formed which gave no test for ferro- or ferricyanide, and gave every indication of being nickelic hydroxide. This reaction we found to afford us a most delicate test for nickel.

The method as modified by us may be described as follows: Dissolve not more than 0.1 grm. of the salts of the two elements in about 5 cm^3 of water, add a few drops of a saturated solution of alum, destroy any free mineral acid by neutralizing with ammonium hydroxide, and make faintly acid with acetic acid. To this solution add about 0.5 grm. of potassium ferricyanide and agitate to effect the solution of the ferricyanide and the complete precipitation of the nickel and cobalt salts. Then add about 5 cm^3 of strong ammonium hydroxide and filter. To the filtrate, which should have no reddish color, add a piece of sodium or potassium hydroxide about the size of a pea and boil. The appearance of a black precipitate, showing first as a dark coloration in case of very small amounts, indicates nickel.

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* Chem. News, xxxiii, 290.

The tables following give a record of the experimental results. With the precautions indicated, this method may be applied very satisfactorily.

I.

Exp.	$CoSO_4 7H_2O$.	$NiSO_4$. $7H_2O$.	$KAl(SO_4)_2$ saturated solution.	$K_4FeC_6N_6$	NH_4OH concentrated.	NaOH solid.	Result.
	grm.	grm.	cm^3	grm.	cm^3		
(1)	. . .	0.0100	2	0.5	5	About size of a pea.	Heavy ppt.
(2)	. . .	0.0050	2	0.5	5	"	Heavy ppt.
(3)	. . .	0.0010	2	0.5	5	"	Heavy ppt.
(4)	. . .	0.0003	2	0.5	5	"	Distinct.
(5)	. . .	0.0001	2	0.5	5	"	Plain.
				II.			
(1)	0.10	. . .	2	0.5	5	About size of a pea.	None.
(2)	0.10	0.0100	2	0.5	5	"	Heavy.
(3)	0.10	0.0050	2	0.5	5	"	Distinct.
(4)	0.10	0.0030	2	0.5	5	"	Very faint.
(5)	0.05	. . .	2	0.5	5	"	None.
(6)	0.05	0.0100	2	0.5	5	"	Heavy.
(7)	0.05	0.0050	2	0.5	5	"	Distinct.
(8)	0.05	0.0030	2	0.5	5	"	Plain.
(9)	0.05	0.0010*	2	0.5	5	"	Faint.

* Equivalent to 0.0002 of the metal.

XLV

THE VOLUMETRIC ESTIMATION OF COPPER AS THE OXALATE, WITH SEPARATION FROM CADMIUM, ARSENIC, TIN, IRON, AND ZINC.

By CHARLES A. PETERS.*

IT is a well known fact that copper oxalate is insoluble in water and scarcely attacked by moderate amounts of dilute nitric acid.† Upon this fact Bornemann ‡ has recently based a method for the separation of copper from cadmium by precipitating copper as the oxalate in the presence of nitric acid, filtering hot, and estimating the copper after ignition, by any of the well known gravimetric methods. Six to ten grams of copper, as the oxide, were used for a single determination, and the errors were large. Bornemann does not recommend this process as an accurate analytical method. Classen § describes a method for the separation of metals as oxalates by adding to the solution of the salt of the metals a dilute solution of the potassium oxalate (1 : 6) and concentrated acetic acid to 80 per cent of the total volume. Regarding copper salts in particular, Classen states that precipitation takes place only in dilute solution and then not completely.

It has been the experience of the writer, that the precipitation of copper oxalate from solutions containing at least 0.0128 grm. of the oxide and saturated with the oxalic acid is practically complete. The filtrate in such cases gives no blue color with ammonia, looking down on a column of liquid

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* From Am. Jour. Sci., x, 359.

† Storer, Dictionary of Chemical Solubilities, p. 468.

‡ Chem. Ztg., xxiii, 565.

§ Ber. Dtsch. chem. Ges., x, *b*, 1316.

in a test-tube, and only a faint brown color is developed when the filtrate is neutralized, made acid with acetic acid, and tested with potassium ferrocyanide. It is the object of this paper to show that moderate amounts of copper may be determined quantitatively as the oxalate by precipitation with oxalic acid and titration of the precipitate by potassium permanganate, and also to show that moderate amounts of copper may be separated from other metals in the presence of nitric acid, by the addition of considerable amounts of oxalic acid.

Before attempting the quantitative separation of copper from solution by the addition of oxalic acid a few qualitative experiments upon the precipitation of varying amounts of copper sulphate by varying amounts of oxalic acid were tried at different dilutions. In all the experiments the mixtures stood 16–20 hours, and were filtered from 2 to 4 times through four filters folded together, and the filtrates were tested both with ammonia and with potassium ferrocyanide. In cases where the filtrate gave no blue color with ammonia

TABLE I.

Dilution 50 cm³.

Exp.	CuO taken as $CuSO_4$.	Oxalic acid added in solution.		Oxalic acid added in crystalline form.	
		Filtrate treated with NH_4OH.	Filtrate treated with $K_4FeC_6N_6$.	Filtrated with NH_4OH.	Filtrate treated with $K_4FeC_6N_6$.
	grm.				
2.0 grm. oxalic acid present.	0.018	Blue color.	Abundant ppt.	Blue color.	Abundant ppt.
	0.031	Trace "	Abundant ppt.	Trace "	Evident ppt.
	0.051	. . . .	Evident ppt.	. . . .	Evident ppt.
	0.064	. . . .	Trace ppt.	. . . .	Trace ppt.
1.0 grm. oxalic acid present.	0.018	Blue color.	Abundant ppt.	Blue color.	Abundant ppt.
	0.031	Blue color.	Abundant ppt.	Trace "	Evident ppt.
	0.051	Trace "	Abundant ppt.	. . . .	Evident ppt.
	0.064	. . . .	Evident ppt.	. . . .	Evident ppt.
	0.094	. . . .	Trace ppt.	. . . .	Trace ppt.
0.5 grm. oxalic acid present.	0.018	Blue color.	Abundant ppt.	Blue color.	Abundant ppt.
	0.031	Blue color.	Abundant ppt.	Trace "	Abundant ppt.
	0.051	Trace "	Abundant ppt.	. . . .	Evident ppt.
	0.064	. . . .	Evident ppt.	. . . .	Trace ppt.
	0.094	. . . .	Trace ppt.	. . . .	Trade ppt.

and only a slight precipitate with ferrocyanide the precipitation was considered practically complete and the conditions were regarded suitable for the trial of the method quantitatively. In the following table is recorded the work upon the precipitation of copper sulphate by 0.5 grm., 1.0 grm., and 2.0 grm. of oxalic acid in 50 cm^3 of solution.

It will be seen readily by comparison of the right and left hand sides of the table above that somewhat smaller amounts of copper may be precipitated completely by the addition of crystallized oxalic acid than by the same amount of oxalic acid already in solution. Thus, when dissolved oxalic acid is added to the solution of 50 cm^3, amounts of copper sulphate less than 0.040–0.050 grm. are not precipitated completely, while under conditions otherwise the same excepting that the oxalic acid is added in crystalline form, the precipitation of amounts as small as 0.030 grm. is practically complete. The amount of oxalic acid in solution necessary for the complete

TABLE II.

CuO taken as $CuSO_4$.	Oxalic acid added in solution.	Volume at precipitation.	Filtrate treated with NH_4OH.	Filtrate treated with $K_4FeC_6N_6$.
A.				
grm.	grm.	cm^3		
0.031	0.5	50	Blue color.	Abundant ppt.
0.031	1.0	50	Blue color.	Abundant ppt.
0.031	2.0	50	Trace blue color.	Abundant ppt.
0.031	3.0	50	Slight trace blue color.	Abundant ppt.
0.031	3.5	50	. . . .	Evident ppt.
0.0128	5.0	50	No blue.	Trace ppt.
0.0064	5.0	50	Blue color.	Abundant ppt.
B.				
0.0064	0.5	20	Faint blue.	Abundant ppt.
0.0064	0.5	15	Faint blue.	Abundant ppt.
0.0064	0.5	10	Faint blue.	Faint ppt.
0.0064	0.5	5	. . . .	Trace ppt.
0.0003	0.5	5*	. . . .	. . . .
0.0003	0.1	1†	. . . .	. . . .

* Precipitate redissolved. † Precipitate remained.

precipitation (after 16 to 20 hours) of this minimum amount of copper, 0.031 grm. of copper oxide taken as the sulphate, appears, as shown in Table II, A, which precedes, to be about 3.5 grm. in 50.0 cm^3. If the amount of oxalic acid is increased to 5 grm., making the solution saturated for that substance, using the same volume of liquid, the minimum amount completely precipitable is reduced to 0.0128 grm. but not to one-half that amount.

It appears from the experiments of Table II, B, that the volume of liquid in which precipitation takes place influences the complete precipitation of the copper oxalate. Thus the precipitation of 0.0064 grm. of copper oxide taken as the sulphate by 0.5 grm. of oxalic acid is complete in 5 cm^3 of liquid. The precipitate which falls from 0.0003 grm. of the oxide taken as the sulphate dissolves in 5 cm^3 of liquid, but remains visible in 1 cm^3.

As a result of the preliminary experiments, it may be said that the presence of a certain minimum amount of copper, varying with the conditions, is essential to complete precipitation. Thus, at a dilution of 50 cm^3 a saturated solution of oxalic acid will precipitate with practical completeness copper taken as the sulphate in amounts exceeding the equivalent of 0.0128 grm. of copper oxide; 2.0 grm. of oxalic acid will precipitate almost completely for the same volume of solution the equivalent of 0.03 grm. of copper oxide; and 1.0 grm. or 0.5 grm. of oxalic acid will precipitate the equivalent of 0.064 grm. of the oxide.

In the quantitative separation of copper as the oxalate the method of treatment was in general as follows. Copper sulphate in 50 cm^3 of water was thrown down by the addition of dry oxalic acid to the hot solution, and, after standing over night, the precipitate was filtered on asbestos and washed two or three times with small amounts of cold water. The precipitate, still in the crucible, was returned to the beaker in which precipitation took place, 5 or 10 cm^3 of dilute sulphuric acid (1 : 1) were then added together with a convenient amount of water, and, after heating the liquid to boiling, the oxalic acid was titrated with permanganate, the oxalate of copper dissolving readily as fast as the excess of oxalic acid is removed by the permanganate. The precipitate may also be dissolved in 10 cm³ of strong hydrochloric acid,* and, after adding 0.5 grm. manganous chloride, titrated at 30°–50°. Experiments (4) and (5) were conducted after this manner. In Table III, A, which follows, are recorded results of the quantitative tests of the method.

TABLE III.

Exp.	CuO taken as $CuSO_4$.	Oxalic acid.	Volume at precipitation.	CuO found.	Error.
			A.		
	grm.	grm.	cm³	grm.	grm.
(1)	0.0372	0.15	100	0.0286	0.0086–
(2)	0.1860	0.50	125	0.1831	0.0029–
(3)	0.0398	0.50	50	0.0376	0.0022–
(4)	0.1860	1.0	150	0.1834	0.0026–
(5)	0.1860	0.5	50	0.1864	0.0004+
(6)	0.1860	0.5	50	0.1866	0.0006+
(7)	0.1860	0.5	50	0.1866	0.0006+
(8)	0.1860	1.0	50	0.1866	0.0006+
(9)	0.0398	1.0	50	0.0391	0.0007–

In experiments (1)–(4), deficiencies are found in the amounts of oxalate precipitated at different degrees of dilution and by different amounts of the precipitant which are in agreement with the results obtained in the preliminary work; the results of experiments (5)–(9), in which 0.5 grm. and 1.0 grm. of oxalic acid act in a total volume of 50 cm³, show the precipitation to be essentially complete under these conditions.

To study the insolubility of the copper oxalate in nitric acid the experiments in Section B of the table were made.

In experiments (10)–(13) amounts of oxalic acid varying from 0.5 grm. to 3.0 grm. appear to precipitate the copper completely in the presence of 5 cm³ of strong nitric acid. In experiment (14) the amount of oxalic acid used was not suffi-

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* Gooch and Peters, Am. Jour. Sci., vii, 461. This volume, p. 222.

cient to throw down all the copper in the presence of 10 cm³ of nitric acid, but the copper does come down completely in the presence of the large amount of the nitric acid upon the addition of more oxalic acid, as seen in experiments (15) and (16). In experiments (17) and (18) with a larger volume of water and a larger absolute amount, though approximately the same percentage, of nitric acid present as in experiments (10)–(13), there is a slight loss of copper; but in experiments (21) and (22) when the amount of nitric acid is reduced to 5 cm³ in the larger total volume the results are normal. Experiments (19) and (20) show the increased loss when still larger amounts of nitric are present. These facts would make it seem best to limit the absolute amount of nitric in solution to about 5 cm³.

TABLE III (*continued*).

Exp.	CuO taken as $CuSO_4$.	Oxalic acid.	HNO_3 (sp. gr. 1.40).	Volume at precipitation.	CuO found.	Error.
			B.			
	grm.	grm.	cm³	cm³	grm.	grm.
(10)	0.1860	0.5	5.0	55	0.1859	0.0001–
(11)	0.1860	0.5	5.0	55	0.1860	0.0000
(12)	0.1990	2.0	5.0	55	0.1989	0.0001–
(13)	0.1990	3.0	5.0	55	0.1990	0.0000
(14)	0.1990	2.0	10.0	60	0.1971	0.0019–
(15)	0.1990	3.0	10.0	60	0.1987	0.0003–
(16)	0.1990	3.0	10.0	60	0.1985	0.0005–
(17)	0.1990	5.0	12.0	130	0.1977	0.0013–
(18)	0.1990	5.0	12.0	130	0.1975	0.0015–
(19)	0.1990	5.0	25.0	130	0.1837	0.0153–
(20)	0.1990	5.0	25.0	130	0.1831	0.0159–
(21)	0.1990	5.0	5.0	130	0.1983	0.0007–
(22)	0.1990	5.0	5.0	130	0.1988	0.0002–
			C.			
(23)	0.1990	2.5	5.0*	65	0.1961	0.0029–
(24)	0.1990	2.0	5.0	65	0.1971	0.0019–

One observation may well be noted here: namely, that while one-half gram oxalic acid is all that is needed for the complete

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* About 9 grm. of ammonium nitrate present in addition to the 5 cm³ of nitric acid.

precipitation of the copper in the presence of 5 cm^3 strong nitric acid, still the oxalic acid may be added up to the point of saturation of the solution. More than this causes difficulty owing to the fact that a large amount of water is necessary to wash the precipitated oxalate. About 2.0 grm. of oxalic acid to 50 cm^3 of water is a convenient proportion.

In experiments (23) and (24), 5 cm^3 of nitric acid were neutralized with ammonium hydroxide before adding the 5 cm^3 strong nitric acid in excess. The results show the solubility of copper oxalate in ammonium nitrate and exclude the possibility of such a procedure in this work.

TABLE III (*continued*).

Exp.	CuO taken as $CuSO_4$.	Oxalic acid.	HNO_3 (sp. gr. 1.40).	Volume at precipitation.	CuO found.	Error.	Details of filtration.
				D.			
	grm.	grm.	cm^3	cm^3	grm.	grm.	
(23)	0.1990	2.0	. .	50	0.1984	0.0006–	Filtered hot immediately.
(24)	0.2030	2.0	. .	50	0.2025	0.0005–	Filtered hot immediately.
(25)	0.1990	1.0	. .	50	0.1990	0.0000	Filtered after cooling; stood 15 minutes.
(26)	0.1990	1.0	. .	50	0.1987	0.0003–	Filtered after cooling; stood 15 minutes.
				E.			
(27)	0.1990	2.0	5.0	55	0.1943	0.0047–	Filtered after cooling; stood 15 minutes.
(28)	0.1990	2.0	5.0	55	0.1969	0.0021–	Stood 2¼ hours.
(29)	0.1990	2.0	5.0	55	0.1973	0.0017–	Stood 6 hours.
(30)	0.1990	2.0	5.0	55	0.1989	0.0001–	Stood 16 hours.

Some experiments were made to show the time necessary for the complete precipitation, both in the presence and absence of nitric acid. Above is the record of such work.

The results in section D would seem to show that a solution containing copper may be precipitated hot as the oxalate and filtered either hot or after cooling with a very slight loss.

Tests of the filtrates made with potassium ferrocyanide confirmed these results. When nitric acid is present, however, the mixture must stand after the addition of the precipitant. In section E the gradual decrease of the minus error is noticed, as the time of standing is extended, the precipitation being practically complete upon standing over night.

Separation from Cadmium.

Bornemann * has used nitric acid for a rough separation of copper from cadmium. This method was tried for a quantitative separation in the presence of 6–10 per cent strong nitric acid. The results are found in section F of the table to follow. Experiments (33)–(35) stood six hours before filtering. Experiments (36) and (37) stood over night. Copper is separated from more than twice its weight of cadmium, and the results are accurate.

TABLE III (*continued*).

Exp.	CuO taken as $CuSO_4$.	Element from which copper was separated.	Oxalic acid.	HNO_3 (sp. gr. 1.40).	Volume at precipitation.	CuO found.	Error.
		CdO taken as $CdSO_4$.	F.				
	grm.	grm.	grm.	cm^3	cm^3	grm.	grm.
(33)	0.1990	0.10	2.0	5.0	60	0.1983	0.0007—
(34)	0.1990	0.20	2.0	5.0	65	0.1987	0.0003—
(35)	0.1990	0.30	2.0	5.0	70	0.1987	0.0003—
(36)	0.1990	0.40	2.0	5.0	75	0.1994	0.0004+
(37)	0.1990	0.50	2.0	5.0	80	0.1996	0.0006+
		As_2O_3 taken as Na_3AsO_3.	G.				
(38)	0.1990	0.10	2.0	. .	55	0.1991	0.0001+
(39)	0.1990	0.20	2.0	. .	60	0.1987	0.0003—
(40)	0.1990	0.50	2.0	. .	75	0.1986	0.0004—
(41)	0.1990	0.10	2.0	5.0	60	0.1994	0.0004+
(42)	0.1990	0.20	2.0	5.0	75	0.1992	0.0002+
(43)	0.1990	0.60	2.0	5.0	85	0.1995	0.0005+
		As_2O_5 taken as H_2KAsO_4.	H.				
(44)	0.1990	0.10	2.0	. .	60	0.1985	0.0005—
(45)	0.1990	0.20	2.0	. .	70	0.1990	0.0000
(46)	0.1990	0.10	2.0	5.0	65	0.1990	0.0000
(47)	0.1990	0.20	2.0	5.0	75	0.1992	0.0002+
(48)	0.1990	0.30	2.0	5.0	85	0.1985	0.0005—
(49)	0.2030	0.80	3.0	5.0	85	0.2026	0.0004—

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* Loc. cit.

TABLE III (*continued*).

Exp.	Cu taken as $CuSO_4$.	Element from which copper was separated.	Oxalic acid.	HNO_3 (sp. gr. 1.40).	Volume at precipitation.	Cu found.	Error.
		Sn taken as $SnCl_2 + HCl$.	I.				
grm.	grm.	grm.	grm.	cm³	cm³	grm.	grm.
(50)	0.1590	0.0468	2.0	5.0	55	0.1581	0.0009−
(51)	0.1590	0.0936	2.0	5.0	60	0.1603	0.0013+
(51 *a*)	0.1590	0.0936	2.0	5.0	60	0.1591	0.0001+
(52)	0.1590	0.0936	2.0	5.0	60	0.1594	0.0004+
(53)	0.1590	0.1873	2.0	5.0	65	0.1603	0.0013+
(54)	0.1590	0.2809	2.0	5.0	70	0.1914	0.0324+
(55)	0.1590	0.2809	3.0	5.0	75	0.1988	0.0398+
		Sn taken as $SnCl_4$.	K.				
(56)	0.1590	0.10	2.0	5.0	55	0.1581	0.0009−
(57)	0.1590	0.10	2.0	. .	55	0.1565	0.0025−
(58)	0.1590	0.20	2.0	5.0	55	0.1577	0.0013−
(59)	0.1590	0.50	2.0	5.0	60	0.1562	0.0028−
	CuO taken as $CuSO_4$.	Fe_2O_3 taken as $Fe(NO_3)_3$.	L.			CuO found.	
(60)	0.1990	0.186	2.0	5.0	60	0.1987	0.0003−
(61)	0.1990	0.272	2.0	5.0	60	0.1983	0.0007−
(62)	0.1990	0.364	2.0	5.0	60	0.1988	0.0002−
(63)	0.1990	0.544	2.0	5.0	65	0.1971	0.0019−
(64)	0.1990	0.272	2.0	. .	60	0.1995	0.0005+
(65)	0.1990	0.544	2.0	2.0	60	0.1998	0.0008+
(66)	0.1990	0.218	2.0	2.0	65	0.1999	0.0009+
		ZnO taken as $ZnSO_4$.	M.				
(67)	0.1990	0.028	2.0	5.0	60	0.2007	0.0017+
(68)	0.1990	0.057	2.0	5.0	65	0.2008	0.0018+
(69)	0.1990	0.057	2.0	5.0	65	0.2008	0.0018+
(70)	0.1990	0.085	2.0	5.0	70	0.2035	0.0045+

Separation from Arsenic, in Both Conditions of Oxidation.

For the separation of arsenic, arsenious oxide dissolved in sodium carbonate, and di-hydrogen sodium arseniate were the forms of arsenic used. The results are accurate and are given in sections G and H of the table. In experiments (38)–(40) and (44)–(45) no nitric acid was added. While the presence of the nitric acid is not necessary for the separation of the copper from the arsenic, still the filtration in the absence of the nitric acid is so slow as to be objectionable. The presence of the nitric acid causes the precipitate to come down in a coarser condition, and in such condition it filters easily and is capable of being washed quickly.

Separation from Tin, in Both Conditions of Oxidation.

For the separation of copper from tin a preparation of stannous chloride (20 cm^3 giving 0.3746 grm. metallic tin by the battery) containing sufficient hydrochloric acid to prevent deposition of oxy-salts was used. The solution of stannic chloride contained 1.0 grm. metallic tin to every 10 cm^3, and was used without hydrochloric acid. The results of the work are found in sections I and K of the table. The experiments go to show that while copper may be separated from small amounts of tin as stannous chloride yet there is a limit to the amount of tin which may be present. One-tenth of a gram of metallic tin is the largest amount that can be present, with 0.15 gm. copper oxide taken as the sulphate, without significant error. Practically the same statement can be made of the separation of copper from tin taken as stannic chloride. Experiment (57) shows a greater loss of copper when the nitric acid is omitted.

Separation of Copper from Iron.

A solution of ferric nitrate was used for the work on the separation of copper from iron. Low results were obtained when a solutien of ferrous or ferric sulphate was used as the source of iron. The results of the experiments are recorded in section L of the table, and show that 0.20 grm. copper oxide as the sulphate may be separated from 0.2–0.3 grm. iron oxide taken as the nitrate. In experiment (64) a good result was obtained when no nitric acid was present, save that added in combination with the iron. A comparison of experiments (63) and (65) shows that it is best to avoid the use of large amounts of nitric acid when the larger amounts of ferric nitrate are present.

For a practical application of the above separation of copper from iron a convenient amount of finely ground chalcopyrite (0.5 grm.) was roasted 2–3 hours in a porcelain crucible until all sulphur was driven off, washed into a beaker, strong nitric acid, about 5 cm^3, was added and, with the beaker covered, allowed to evaporate slowly on a hot plate, nearly to dryness. A little dilute nitric acid was added, the solution was filtered, the residue was washed with water containing dilute nitric acid, the filtrate, about 50 cm^3 in volume, was precipitated with 2.0 grm. oxalic acid, and the precipitate was estimated after standing 12–16 hours, as previously described. The washing with water acidified with nitric acid is important, because the finely ground ferric oxide remaining undissolved passes through the filter when washed with water alone, but gives no trouble if the water be acidic. The results of two estimations are here given.

Chalcopyrite.	Copper found by battery.	Copper found by oxalate method.	Difference.
grm.	%	%	%
0.5000	31.00	30.92	0.08–
1.0000	31.00	31.25	0.25+

Separation of Copper from Zinc.

The separation of copper from zinc was not altogether successful owing to the tendency of the zinc oxalate to come down with the copper oxalate. Some experiments are given in section M of the table.

The separations of copper from bismuth and antimony were unsuccessful.

The work may be briefly summarized as follows: Copper exceeding in amount the equivalent of 0.0128 grm. of the oxide to 50 cm^3 of solution as the sulphate may be separated completely, even in the presence of a moderate amount of strong nitric acid, by the addition of sufficient amount of oxalic acid.

Copper may be separated from cadmium, arsenic, iron, and small amounts of tin, when precipitated by oxalic acid in a volume of 50 cm^3 containing 5 cm^3 strong nitric acid. Inasmuch as the completeness of precipitation of the copper depends upon the presence of a certain minimum amount of the copper salt this method is not applicable when the amount of copper falls below 0.0128 grm. of the oxide to 50 cm^3 of solution.

XLVI

THE SULPHOCYANIDES OF COPPER AND SILVER IN GRAVIMETRIC ANALYSIS.

BY R. G. VAN NAME.*

Cuprous Sulphocyanide.

As early as 1854 attention was drawn by Rivot† to the possibility of estimating copper gravimetrically by weighing as cuprous sulphocyanide, and to the advantages which the process afforded in separating copper from other metals. Rivot's procedure consisted in dissolving the substance to be analyzed in hydrochloric acid, reducing copper with hypophosphorous or sulphurous acid, and precipitating with potassium sulphocyanide. The precipitate dried at a moderate temperature was weighed as cuprous sulphocyanide and then as a control converted by ignition with sulphur into cuprous sulphide and weighed in that condition.

In his well known work upon quantitative analysis Fresenius in one place‡ denies the practicability of the direct weighing of copper as cuprous sulphocyanide on account of the tendency of the latter to hold water even when heated to the temperature of incipient decomposition. As authority for this statement he cites Claus,§ who found 3 per cent of water in the precipitate after drying at 115°, and Meitzendorff, who gave the percentage of water under the same conditions as 1.54.

On a later page of the same volume,‖ however, Fresenius, after a trial of the process which gave 99.66 per cent of the

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* From Am. Jour. Sci., x, 451.

† Compt. rend., xxxviii, 868.

‡ Quant. Anal., 6. Aufl., i, 187.

§ L. Gmelin, Handbuch, iv, 472.

‖ Quant. Anal., 6. Aufl., i, 335.

theory for copper, concludes that the method is practicable although apt to give low results, particularly in the presence of free acid.

The process was again recommended in 1878 by Busse,* who had employed it for the estimation of copper, both alone and in the presence of iron, nickel, zinc, and arsenic, obtaining results very near the theory and plainly comparable with the figures obtained by afterwards igniting the cuprous sulphocyanide with sulphur in hydrogen.

In spite of the evident advantages for certain purposes of Rivot's method over other modes of determining copper, it has never come into general use. The chief reason for this has apparently been the difficulty and inaccuracy attendant upon the weighing of the precipitate upon dried paper filters, a process which can hardly be depended upon unless managed with extreme care.

In the experiments to be described this difficulty was avoided by performing the filtering and weighing upon asbestos in a perforated platinum crucible. The method of conducting a determination was as follows: A suitable quantity of a standard copper sulphate solution was run from a burette, diluted to a convenient volume, a few cubic centimeters of a saturated solution of ammonium bisulphite added, and the copper precipitated by an excess of ammonium sulphocyanide. The precipitate was allowed to settle, collected upon asbestos in a weighed crucible, washed with cold water, and dried at 110° until no further loss of weight took place.

In Table I are given the results of a number of determinations made in this way. The copper sulphate solution was made up exactly decinormal and the standard confirmed electrolytically. As the ammonium sulphocyanide solution was slightly above decinormal, 13 cm^3 represent a small excess (about one cubic centimeter) above the amount theoretically required to precipitate 25 cm^3 of the copper sulphate solution. The ammonium bisulphite, which had been recently prepared by saturating aqueous ammonia with sulphur dioxide, was

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* Zeitschr. anal. Chem., xvii, 53.

always used in sufficient quantity to give the liquid a strong and permanent odor of the latter.

TABLE I.

25 cm³ of $\frac{N}{10}$ $CuSO_4$ solution, equivalent to 0.0795 grm. Cu, taken for each experiment.

Exp.	H_2SO_4. concentrated.	HNH_4SO_3 sat. sol.	NH_4SCN approx. $\frac{N}{10}$.	Final volume.	Time of standing.	Cu found.	Error.
	cm³	cm³	cm³	cm³	hrs.	grm.	grm.
(1)	None.	5	18	68	¼	0.0795	0.0000
(2)	None.	3	18	66	48	0.0793	0.0002–
(3)	None.	3	25	78	½	0.0796	0.0001+
(4)	None.	3	25	78	12	0.0796	0.0001+
(5)	1.5	10	13	85	12	0.0792	0.0003–
(6)	1.5	8	13	105	48	0.0785	0.0010–
(7)	1.5	8	25	85	4	0.0783	0.0012–
(8)	1.5	5	25	85	21	0.0795	0.0000
(9)	5	5	25	85	3	0.0797	0.0002+
(10)	15	10	25	115	21	0.0793	0.0002–
	HCl concentrated.						
(11)	10	5	25	100	20	0.0795	0.0000
(12)	25	10	25	100	28	0.0784	0.0011–

When there is no free acid present the time of standing before filtration and the amount of the excess of ammonium sulphocyanide are practically without effect, as experiments (1) to (4) of the table show.

Experiments (5) to (10) were carried out in the presence of various amounts of free sulphuric acid up to 12 per cent of the total volume of liquid. The acid, at least within this limit, does not exert a sufficient solvent effect upon the cuprous sulphocyanide to interfere materially with the accuracy of the process, but it retards the precipitation, making it necessary to increase the time of standing before filtering in proportion to the amount of acid present. In several of these determinations the precipitation was visibly incomplete even after several hours' standing. This effect of the acid, however, hardly shows in the results of the table because the standing was always prolonged until the copper appeared to be all down before filtering.

The low result of Experiment (7) was probably due chiefly to incomplete precipitation, although (9) shows that even with a much larger amount of acid precipitation may be complete within three hours. In general, however, it is safer to allow ample time (twelve hours or more) for the precipitation when there is much free acid present.

Comparison of Experiments (5) and (6), for which only a bare excess of ammonium sulphocyanide was used, with (7) to (12) shows an apparent advantage in the larger excess in the presence of acid. Hydrochloric acid, judging from the results of (11) and (12), has no greater disturbing influence than sulphuric acid, although in (12), where the concentrated acid constituted one-fourth of the entire volume, there was apparently a slight solvent action. The filtrate from this determination when concentrated to about 25 cm³ and treated with potassium ferrocyanide gave a strong test for copper, as did also the filtrate from (6). Several of the other filtrates were tested in the same way, but none showed more than an insignificant trace of copper. The filtrate of (7), however, was not tested.

Table II contains the results of a series of experiments conducted as before, except that larger amounts of copper were employed. The copper sulphate solution was approximately $\frac{N}{8}$ and standardized by the battery. The solution of ammonium sulphocyanide was the same previously used and a considerable excess was employed in every determination. More

TABLE II.

Exp.	Cu taken.	H_2SO_4 concentrated.	NH_4SCN approx. $\frac{N}{10}$.	Final volume.	$Cu_2S_2(CN)_2$ found, calculated as Cu.	Error.	Cu in filtrate.
	grm.	cm³	cm³	cm³	grm.	grm.	
(1)	0.3175	None.	60	500	0.3176	0.0001+	None.
(2)	0.3175	None.	60	500	0.3177	0.0002+	None.
(3)	0.3175	None.	60	500	0.3176	0.0001+	None.
(4)	0.3175	10	100	500	0.3175	0.0000	None.
		HCl conc.					
(5)	0.3175	20	100	500	0.3165	0.0010−	Distinct.

than twice the amount theoretically required was used in every case where free acid was present, and at least twenty hours were allowed for the precipitation, which was made in cold, and as the table shows, rather dilute solutions. If the solution is too concentrated the copper is apt to be thrown down in a finely divided condition, making it hard to filter.

The time required to dry the cuprous sulphocyanide at 110° is in general from two to three hours. Heating much longer than this is not to be recommended, as a gradual increase in weight begins to take place, as is shown by the following example, which gives a series of weights of the same precipitate at different stages.

	$Cu_2S_2(CN)_2$. grm.	Calculated as Cu. grm.
After 2 hours at 110° . . .	0.6060	0.3167
" 4 " " . . .	0.6059	0.3167
" 19 " " . . .	0.6067	0.3171
" 23 " " . . .	0.6069	0.3172

This tendency to increase in weight is, however, usually less marked than in the above example, and in any case need not interfere materially with the accuracy of the process unless the drying is prolonged far beyond the necessary length of time.

The method is easily handled and, as the results of Tables I and II show, is capable of considerable accuracy. From the nature of the process it is evident that it is much less likely to be interfered with by the presence of other metals than the other gravimetric methods for copper, and may therefore be directly applied with good results in many cases where the use of the electrolytic or the oxide method would involve a previous separation.

Silver Sulphocyanide.

The sulphocyanide of silver, unlike that of copper, is soluble in an excess of ammonium or alkali sulphocyanides and this fact prevents the use of the latter to precipitate silver for gravimetric estimation. The reverse process, however, the precipitation of a soluble sulphocyanide by an excess of silver nitrate, as will be shown by the experiments to be described, furnishes a convenient means of standardizing sulphocyanide solutions and in general for estimating sulphocyanic acid.

When freshly precipitated the sulphocyanide of silver resembles the chloride in appearance, but when allowed to stand a few hours becomes finely granular and is very easily filtered and washed. It may be safely dried to a constant weight upon an asbestos filter at 110°–120°, but at a somewhat higher temperature is decomposed, leaving a residue of silver sulphide.

The determinations which are tabulated below were made as follows. Portions of 25 cm^3 of an approximately decinormal solution of ammonium sulphocyanide were measured from a burette, diluted with 100 cm^3 of water and silver nitrate added in excess. The precipitate was collected upon asbestos in a platinum crucible, washed with cold water and dried to a constant weight at 115° the drying requiring usually between two and three hours.

The filtering is facilitated by allowing a few hours for the precipitate to settle; but this is by no means essential, as it is easy with a little care to obtain a clear filtrate even when the filtering is performed at once.

The solution of ammonium sulphocyanide was prepared from a pure salt, especially tested and found free from choride. This point is of importance, as chlorine is a common impurity and its presence in any considerable quantity will vitiate the results.

In order that the effect of varying the excess of silver might be investigated, an approximately decinormal solution of silver nitrate was titrated against the ammonium sulphocyanide and the ratio between the two solutions determined. This silver nitrate solution was used for the first five determinations of Table III. For the rest the quantity of silver nitrate was not measured but regulated by the eye alone, thus making the conditions the same as would be the case in practical use of the method.

These results are as uniform as could be expected, considering the variations which would be produced by even very small

TABLE III.

Final volume of liquid 150 cm³.

25 cm³ of NH_4SCN sol. equivalent to 25.15 cm³ of $AgNO_3$ sol.

Exp.	NH_4SCN.	$AgNO_3$.	Excess of $AgNO_3$.	AgSCN found.
	cm³	cm³	cm³	grm.
(1)	25	25.3	0.15	0.4372
(2)	25	25.3	0.15	0.4376
(3)	25	25.4	0.25	0.4373
(4)	25	25.4	0.25	0.4375
(5)	25	30.4	5.25	0.4382
(6)	25	Rough excess.		0.4366
(7)	25	Rough excess.		0.4381
(8)	25	Rough excess.		0.4373
(9)	25	Rough excess.		0.4372
(10)	25	Rough excess.		0.4369

errors in measuring out 25 cm³ of decinormal sulphocyanide solution. It is moreover clearly shown that there is no difference in the results whether a bare excess or a moderately large excess of the silver nitrate is used.

The mean of the values in the last column is 0.4374, which is equivalent to 0.2006 grm. of ammonium sulphocyanide for every 25 cm³ of the solution.

The standard of the sulphocyanide solution was also determined volumetrically by Volhard's process. The mean of four titrations carried out with great care against a standard silver nitrate solution gave as the standard 0.2003 grm. of ammonium sulphocyanide for 25 cm³ of solution. This difference between the standards as determined by the two methods (one part in 670) is much less than the variations which frequently appear between successive determinations by Volhard's method, under like conditions as to strength of solutions and amounts used. It is about equal to the error that would be produced in a single volumetric determination by a mistake of one drop in measuring one of the solutions, or of one-half drop in the same direction on each.

It is therefore evident that the standard of a sulphocyanide solution obtained in the above way may be applied directly to

XLVII

ON THE ESTIMATION OF CÆSIUM AND RUBIDIUM AS THE ACID SULPHATES, AND OF POTASSIUM AND SODIUM AS THE PYROSULPHATES.

BY PHILIP E. BROWNING.

BUNSEN[*] is authority for the statement that the acid sulphate of rubidium does not lose sulphuric acid at a heat approaching redness. It is stated in the literature[†] that the acid sulphates of cæsium and rubidium when subjected to a low red heat pass into the form of the pyrosulphates.

R. Weber[‡] found that by treating the dry sulphates of potassium, cæsium, rubidium, and thallium with sulphuric anhydride in a closed tube and heating on a water bath two layers separated. In the lower layer he obtained crystalline bodies which proved to have the constitution $R_2O \cdot 8SO_3$. On strong heating he obtained from these substances, bodies of the form $R_2O \cdot 2SO_3$ and finally $R_2O \cdot SO_3$. He also notes that in the case of the cæsium salt the removal of the excess of the sulphuric anhydride was attended with greater difficulty.

Baum[§] states that the pyrosulphates of the alkalies may be obtained by heating the acid sulphates under atmospneric pressure at low redness, or under diminished pressure at a temperature between 260° C. and 320° C.

In a recent paper[||] from this laboratory I have shown that thallium may be estimated as the acid sulphate by evaporating a thallous salt in solution with an excess of sulphuric acid and bringing the residue to a constant weight at a temperature of about 250° C.

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[*] Ann. Chem. (Liebig), cxix, 110.

[†] Graham-Otto, Lehrbuch d. Chem., iii, 269, 278.

[‡] Ber. Dtsch. Chem. Ges., xvii, 2497. [§] Ber. Dtsch. Chem. Ges. xx, 752.

[||] Am. Jour. Sci., ix (1900), 137. This volume, p. 317.

The similarity which thallium bears in some of its combinations to the alkaline metals suggested the study of the sulphates of these elements under the same general conditions of procedure.

My first experiments were made with a pure cæsium salt as follows: A weighed amount of the nitrate was placed in a previously weighed platinum crucible and treated with an excess of sulphuric acid. The crucible was then placed upon a steam bath until the water and nitric acid were largely expelled and then removed to a radiator, consisting of a porcelain crucible fitted with a pipe-stem triangle so arranged that the bottom of the platinum crucible would be about midway between the top and bottom of the porcelain crucible. This improvised radiator was set in an iron ring and a thermometer so placed that the mercury bulb would be on a level with the bottom and close to the side of the platinum crucible. An ordinary Bunsen burner served as the source of heat and the temperature was kept so far as possible between 250° C. and 270° C. After the fuming attending the removal of the large excess of sulphuric acid ceased, the crucible and contents were removed to a desiccator, and, after being allowed to cool, weighed. This process of heating was continued for half-hour periods until the weights were constant. The results shown in Table I were obtained by this method of treatment. In experiments (1), (4), and (9)

TABLE I.

Exp.	$CsNO_3$ taken.	$CsHSO_4$ calculated.	First constant weight.	Second constant weight.	Error $CsHSO_4$.	Cs_2SO_4 calculated.	Cs_2SO_4 found.	Error Cs_2SO_4.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1706	0.2013	0.2054	0.2020	0.0007+	. .	. .	. .
(2)	0.1706	0.2018	0.2010	. .	0.0003–	. .	. .	. .
(3)	0.1032	0.1217	0.1201	. .	0.0016–	. .	. .	. .
(4)	0.1032	0.1217	0.1252	0.1222	0.0005+	0.0961	0.0948	0.0013–
(5)	0.1218	0.1437	0.1458	. .	0.0021+	0.1130	0.1118	0.0012–
(6)	0.1214	0.1435	0.1430	. .	0.0005–	. .	. .	. .
(7)	0.1214	0.1435	0.1422	. .	0.0013–	. .	. .	. .
(8)	0.1150	0.1356	0.1330	. .	0.0026–	. .	. .	. .
(9)	0.1056	0.1245	0.1272	0.1248	0.0003+	. .	. .	. .
(10)	0.1056	0.1245	0.1252	. .	0.0007+	. .	. .	. .

it will be noticed that the weights were constant somewhat above the condition of the acid sulphate, a fact which would go to show a tendency on the part of the cæsium salt to hold an excess of sulphuric acid over the amount necessary to form the ordinary acid sulphate. The results show that by regulating the heat at a temperature between 250° C. and 270° C. cæsium may be brought, with a fair degree of certainty to the condition of the acid sulphate. As a check upon the results, the acid sulphate was, in a few cases, treated with a little ammonium hydroxide, the excess of this was removed upon a steam bath and the neutral sulphate obtained by ignition at a red heat to a constant weight. These determinations agreed fairly well with the theory. The same procedure was followed with rubidium, a pure rubidium chloride having been chosen as the starting-point. The results are given in Table II. No tendency was observed on the part of this element to hold sulphuric acid in excess of the amount necessary for the formation of the acid sulphate. When the same method was applied to sodium and potassium salts, pure chlorides being used as the starting-point, a somewhat different result was obtained, in that the weight of the final product appeared to indicate the formation of the pyrosulphate. The results given in Tables III and IV, in which the sodium and potassium salts are calculated as pyrosulphates, are sufficiently satisfactory for purposes of quantitative estimation. As in the case of the cæsium and rubidium salts, a number of determinations as the neutral

TABLE II.

Exp.	$RbCl$ taken.	$RbHSO_4$ calculated.	$RbHSO_4$ found.	Error.	Rb_2SO_4 calculated.	Rb_2SO_4 found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1252	0.1889	0.1878	0.0011−	. .	. .	. .
(2)	0.1212	0.1829	0.1840	0.0011+	0.1460	0.1460	0.0000
(3)	0.1280	0.1856	0.1850	0.0006−	. .	. .	. .
(4)	0.1280	0.1856	0.1858	0.0002+	0.1357	0.1850	0.0007−
(5)	0.1610	0.2430	0.2416	0.0014−	0.1777	0.1772	0.0005−
(6)	0.1360	0.2052	0.2082	0.0020−	0.1501	0.1490	0.0011−

TABLE III.

Exp.	KCl taken.	$K_2S_2O_7$ calculated.	$K_2S_2O_7$ found.	Error.	K_2SO_4 calculated.	K_2SO_4 found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.2172	0.3704	0.3698	0.0006–	. .	. .	. .
(2)	0.1706	0.2909	0.2886	0.0023–	0.1993	0.1972	0.0021–
(3)	0.1192	0.2032	0.2022	0.0010–	0.1393	0.1381	0.0012–
(4)	0.1074	0.1830	0.1823	0.0007–	. .	. .	. .
(5)	0.1096	0.1868	0.1860	0.0008–	. .	. .	. .

TABLE IV.

Exp.	NaCl taken.	$Na_2S_2O_7$ calculated.	$Na_2S_2O_7$ found.	Error.	Na_2SO_4 calculated.	Na_2SO_4 found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	0.1042	0.1978	0.1972	0.0006–	0.1266	0.1254	0.0012–
(2)	0.1028	0.1952	0.1952	0.0000	. .	. .	. .
(3)	0.1093	0.2075	0.2065	0.0010–	0.1328	0.1320	0.0008–
(4)	0.1402	0.2662	0.2651	0.0011–	0.1708	0.1696	0.0007–

sulphate were made by ignition of the sodium and potassium pyrosulphates, with results which are recorded. In Table V, two determinations are recorded, in one of which the cæsium and rubidium salts were treated together and in the other the sodium and potassium salts.

TABLE V.

Exp.	$RbCl + CaNO_3$ taken.	$RbHSO_4 + CaHSO_4$ calculated.	$RbHSO_4 + CaHSO_4$ found.	Error.	$Rb_2SO_4 + Ca_2SO_4$ calculated.	$Rb_2SO_4 + Ca_2SO_4$ found.	Error.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.
(1)	RbCl 0.1428 $CsNO_3$ 0.1264	0.3646	0.3666	0.0020+	0.2749	0.2752	0.0003+
	$NaCl + KCl$ taken.	$Na_2S_2O_7 + K_2S_2O_7$ calculated.	$Na_2S_2O_7 + K_2S_2O_7$ found.	Error.	$Na_2SO_4 + K_2SO_4$ calculated.	$Na_2SO_4 + K_2SO_4$ found.	Error.
(2)	NaCl 0.1238 KCl 0.1340	0.4627	0.4630	0.0003+	0.3062	0.3040	0.0022–

An application of this general method to a lithium salt gave no evidence of the existence of a stable acid sulphate or pyrosulphate.

The results may be summed up as follows: — Cæsium and rubidium salts of volatile acids when treated with sulphuric acid in excess and brought to a constant weight at a temperature between 250° C. and 270° C. form acid salts of the type $RHSO_4$ and the neutral salts of the type R_2SO_4 on ignition.

Some tendency of the cæsium salt to hold more sulphuric acid than corresponds to the formation of the acid sulphate $RHSO_4$ was apparent at temperatures between 258° C. and 270° C., but upon raising the temperature above 300° C. the loss was excessive and showed a tendency on the part of the acid sulphate to pass, at this temperature, toward the condition of the pyrosulphate.

Sodium and potassium salts, when heated under the conditions described, give pyrosulphates of the type $R_2S_2O_7$ which on ignition go into the neutral sulphate of the form R_2SO_4. Lithium gives neither salts of the type $RHSO_4$ nor $R_2S_2O_7$ under the conditions of these experiments.

XLVIII

THE ESTIMATION OF CALCIUM, STRONTIUM, AND BARIUM AS THE OXALATES.

By CHARLES A. PETERS.

A FORMER article from this laboratory * describes the conditions under which oxalic acid may be titrated by potassium permanganate in the presence of hydrochloric acid, and states that the extra consumption of permanganate which ordinarily takes place when oxalic acid is titrated by permanganate in the presence of hydrochloric acid, may be prevented by the addition of a manganous salt. This fact led to the idea of effecting the solution of the alkaline earth oxalates in hydrochloric acid and titrating the free oxalic acid with permanganate in the presence of a manganous salt, and so to the study of the conditions under which precipitates of strontium and barium oxalates could be obtained sufficiently insoluble for quantitative purposes, the conditions under which calcium oxalate is insoluble being already well known.

The permanganate solution for this work was standardized against freshly recrystallized ammonium oxalate, and on oxalic acid, the standards agreeing.

Calcium Oxalate.

It is well known that calcium may be estimated by treating the precipitated oxalate with sulphuric acid and titrating by permanganate the oxalic acid set free.† In the work described in the present article, the precipitate of calcium oxalate has been dissolved in hydrochloric acid and the oxalic

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* Gooch and Peters, Am. Jour. Sci., vii, 461. This volume, p. 222.

† Mohr, Titrirmethode, 6. Aufl., S. 227.

acid titrated by permanganate in the presence of a manganous salt. The process was as follows: The boiling hot solution of calcium chloride was precipitated with ammonium oxalate, allowed to stand 12 hours, and the supernatant liquid decanted on asbestos. The precipitate was washed two or three times by decantation with 50–100 cm^3 of cold water and brought on the felt. The crucible containing the precipitate was returned to the beaker, 100–200 cm^3 of water were added, together with 5–10 cm^3 of strong hydrochloric acid and 0.5–1.0 grm. of manganous chloride, and the oxalic acid titrated at a temperature of 35°–45°. The results, given in Table I, are obviously excellent.

TABLE I.

CaO taken as $CaCl_2$.	Ammonium oxalate.	Volume at precipitation.	CaO found.	Error.
grm.	grm.	cm^3	grm.	grm.
0.0656	0.3	100	0.0657	0.0001+
0.0656	0.3	100	0.0656	0.0000
0.0656	0.3	150	0.0658	0.0002+
0.0656	0.3	100	0.0655	0.0001−
0.0985	0.5	175	0.0981	0.0004−
0.1313	0.6	150	0.1315	0.0002+
0.1313	0.6	200	0.1315	0.0002+

Extended washing with hot water, however, is to be avoided after the precipitant, ammonium oxalate, has been removed. In one experiment, for example, in which the precipitate, on the felt, was washed fourteen times with portions of about 50 cm^3 each of hot water, each portion bleached from 2–6 drops of approximately $\frac{N}{10}$ permanganate, making a total loss of 0.0034 grm. of calcium oxide.

Strontium Oxalate.

Souchay and Lenssen[*] state that strontium oxalate is soluble in 12,000 parts of water. This fact would seem sufficient to warrant the study of the quantitative separation of strontium as the oxalate. In the work which follows strontium

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[*] Ann. Chem. (Liebig), cii, 35.

oxalate has been precipitated both in alcoholic solution and in water solution, and for convenience these two conditions of precipitation will be discussed separately.

All the strontium salts, of established purity, were standardized by precipitation with sulphuric acid in a solution containing at least one-half its volume of alcohol, and with some solutions confirmatory standards were also obtained by evaporation with sulphuric acid.

Precipitation in Alcoholic Solution. To determine the completeness of the precipitation in alcoholic solution strontium nitrate was precipitated by ammonium oxalate in a solution containing one-third of its volume of alcohol, the mixture was allowed to stand over night, the liquid was filtered off on asbestos, and the precipitate was treated in the capped filtering crucible with sulphuric acid, ignited, and weighed as the sulphate. The results are given in Table II. It is plain from the results in this table that the precipitation of even small amounts of the strontium salt from a solution containing one-third of its volume of alcohol is practically complete.

TABLE II.

SrO taken as $Sr(NO_3)_2$.	Ammonium oxalate.	Volume at precipitation.	Volume of alcohol.	SrO found as $SrSO_4$.	Difference.
grm.	grm.	cm^3		grm.	grm.
0.2434	0.8	180	⅓	0.2440	0.0006+
0.2434	0.8	180	⅓	0.2437	0.0003+
0.0022	0.2	100	⅓	0.0022	0.0000
0.0013	0.2	100	⅓	0.0014	0.0001+
0.0004	0.04	100	⅓	0.0004	0.0000

To determine the minimum amount of alcohol necessary for the complete precipitation of the strontium oxalate, experiments were made using varying proportions of 85 per cent alcohol with different amounts of ammonium oxalate, and the filtrates from such experiments were tested for strontium by the addition of more alcohol. The results given in Table III show that when a moderate excess of ammonium oxalate is present, a volume of 85 per cent alcohol, amounting to one-fifth of

TABLE III.

SrO present as $Sr(NO_3)_2$.	Ammonium oxalate.	Volume of liquid.	Proportion of 85 per cent alcohol.	SrO found in filtrates, weighed as $SrSO_4$.
grm.	grm.	cm^3		grm.
0.1	0.4	100	$\frac{1}{5}$	0.0000
0.1	0.4	100	$\frac{1}{10}$	0.0000
0.1	0.4	100	$\frac{1}{20}$	0.0004
0.1	0.2	100	$\frac{1}{5}$	0.0000
0.1	0.2	100	$\frac{1}{10}$	0.0009
0.1	0.2	100	$\frac{1}{20}$	0.0020
0.1	0.1	100	$\frac{1}{3}$	0.0002

the whole, is sufficient to complete the precipitation of the strontium as the oxalate.

The conditions under which strontium oxalate is insoluble having been determined, the process for the volumetric estimation of strontium was carried out as follows: The hot solution of a strontium salt was precipitated with ammonium oxalate, 85 per cent alcohol, amounting to from one-fifth to one-third the total volume, was added, the mixture was allowed to stand over night, and the clear liquid was decanted on an asbestos filter. The precipitate was washed with a mixture of equal parts of 85 per cent alcohol and water, transferred to the filter, dried in the filtering crucible over a flame to free it from alcohol, returned to the beaker previously dried, treated with sulphuric acid, or with 5–10 cm^3 of hydrochloric acid (in the latter case 0.5–1.0 grm. of a manganous salt being added) and the liberated oxalic acid was titrated by permanganate. The results obtained by this method are accurate and are given in Table IV.

In the last experiment in which a comparatively large amount of strontium salt was present and the dilution low, there is a slight tendency towards a minus error, due probably to the occlusion of some oxalic acid by the strontium sulphate formed. This phenomenon would favor titration at greater dilution when sulphuric acid is used to liberate the oxalic acid from large amounts of strontium oxalate.

Precipitation in Water Solution. In order to determine the

TABLE IV.

VOLUME DURING TITRATION 150–250 CM³.

SrO taken as $Sr(NO_3)_2$.	Ammonium oxalate.	Volume at precipitation.	Proportion of 85 per cent alcohol.	Acid present during titration.	SrO found.	Error.
grm.	grm.	cm³			grm.	grm.
0.0974	0.4	100	$\frac{1}{3}$	HCl	0.0973	0.0001–
0.0974	0.4	100	$\frac{1}{3}$	HCl	0.0983	0.0009+
0.0974	0.4	100	$\frac{1}{3}$	HCl	0.0975	0.0001+
0.0974	0.8	100	$\frac{1}{3}$	HCl	0.0981	0.0007+
0.1948	0.4	200	$\frac{1}{3}$	HCl	0.1943	0.0005–
0.1948	0.8	200	$\frac{1}{3}$	HCl	0.1942	0.0006–
0.0974	0.4	100	$\frac{1}{3}$	H_2SO_4	0.0970	0.0004–
0.0974	0.4	100	$\frac{1}{3}$	H_2SO_4	0.0977	0.0003+
0.0974	0.4	100	$\frac{1}{3}$	H_2SO_4	0.0976	0.0002+
0.1948	0.6	150	$\frac{1}{3}$	H_2SO_4	0.1938	0.0010–

degree of precipitation of strontium salts in water solution, strontium oxide, taken as the nitrate, was precipitated by ammonium oxalate, the mixture was allowed to stand over night, filtered on asbestos, the precipitate was washed with water containing one-half its volume of 85 per cent alcohol, treated in the capped crucible with a few drops of sulphuric acid, ignited, and weighed as the sulphate. The result gave 0.0973 grm. of strontium oxide instead of 0.0974 grm. taken. The precipitation, therefore, of strontium oxalate, in water solution with a sufficient excess of ammonium oxalate present, is practically complete.

To determine the amount of ammonium oxalate necessary for the precipitation of strontium salts in water solution, experiments were made in which strontium oxalate was precipitated in the presence of varying amounts of ammonium oxalate, allowed to stand over night, the clear liquid was decanted on asbestos, and the precipitate was washed twice with 10–20 cm³ of cold water. The results obtained by the estimation of the oxalic acid by permanganate show that an amount of ammonium oxalate several times larger than that required for the theoretical formation of strontium oxalate is necessary for the separation of the strontium oxalate. The experiments are recorded in Table V.

TABLE V.

SrO, taken as $Sr(NO_3)_2$.	Ammonium oxalate.	Volume at precipitation.	Acid present during titration.	SrO found.	Error.
grm.	grm.	cm³		grm.	grm.
0.0487	0.064	100	H_2SO_4	0.0441	0.0046—
0.0487	0.0768	100	H_2SO_4	0.0465	0.0022—
0.0487	0.16	100	H_2SO_4	0.0488	0.0001+
0.0974	0.128	100	H_2SO_4	0.0939	0.0025—
0.0974	0.16	100	H_2SO_4	0.0959	0.0015—
0.0974	0.32	100	H_2SO_4	0.0975	0.0001+

The solvent action of a large amount of water on a precipitate of strontium oxalate was tested by washing a precipitate equivalent to 0.0974 grm. of the oxide with 150 cm³ of cold water. The precipitate, when weighed as the sulphate, showed a loss of 0.0033 grm., as the oxide, which amount was subsequently recovered from the filtrate by the addition of ammonium oxalate and alcohol. Plainly excessive washing with water is to be avoided. In the estimation, therefore, of strontium precipitated as the oxalate in water solution, the amount of water used in washing was limited. It was found that 40–50 cm³ of water judiciously applied was sufficient to wash out the ammonium salt without producing appreciable solvent effect upon the strontium oxalate. The process of treatment was similar to that used in the precipitations from alcoholic solution, excepting that no alcohol was added to the solution, that the washing was effected with a limited amount of water, and that, there being no alcohol present to effect the titration, the precipitate was not dried before treatment with permanganate. The results are given in Table VI.

In the results recorded in section A of Table VI, the strontium oxalate was treated with sulphuric acid and titrated at 80°, the volume being 200–300 cm³; while in the experiments given in section B, the precipitate was treated with hydrochloric acid and titrated at 35°–45°, at a volume of 100–200 cm³, after the addition of 0.5–1.0 grm. of manganous chloride. The results show that 0.1 grm. of strontium salt, calculated as the oxide, may be estimated as the oxalate with a fair degree of accuracy when precipitated in 100–250 cm^3 of water by a

TABLE VI.

SrO, taken as $Sr(NO_3)_2$.	Ammonium oxalate.	Volume at precipitation.	Acid present during titration.	SrO found.	Error.
			A.		
grm.	grm.	cm$_3$		grm.	grm.
0.0974	0.5	100	H_2SO_4	0.0966	0.0008–
0.0974	0.5	100	H_2SO_4	0.0985	0.0011+
0.0974	0.5	100	H_2SO_4	0.0977	0.0003+
0.0974	0.5	100	H_2SO_4	0.0963	0.0011–
0.0974	0.8	100	H_2SO_4	0.0981	0.0007+
0.0974	0.8	100	H_2SO_4	0.0966	0.0008–
0.0974	1.0	100	H_2SO_4	0.0965	0.0009–
0.0974	2.0	100	H_2SO_4	0.0963	0.0011–
0.0974	2.0	100	H_2SO_4	0.0970	0.0004–
SrO, taken as $SrCl_2$.			**B.**		
0.0778	0.5	100	H_2SO_4	0.0792	0.0014+
0.0778	0.5	100	H_2SO_4	0.0767	0.0011–
0.0778	0.5	100	H_2SO_4	0.0776	0.0002–
0.0778	0.5	100	H_2SO_4	0.0776	0.0002–
SrO, taken as $Sr(NO_3)_2$.					
0.0974	0.8	250	H_2SO_4	0.0973	0.0001–
0.0974	2.0	250	H_2SO_4	0.0975	0.0001+
0.0974	0.8	100	HCl	0.0971	0.0003–
0.0974	0.8	100	HCl	0.0980	0.0006+
0.0974	0.8	100	HCl	0.0975	0.0001+
0.0974	0.8	100	HCl	0.0980	0.0006+
0.0974	0.8	100	HCl	0.0973	0.0001–
0.0974	0.8	100	HCl	0.0978	0.0004+
			C.		
0.2425	0.384	125	H_2SO_4	0.2376	0.0049–
0.2436	0.384	125	H_2SO_4	0.2402	0.0034–
0.2436	0.64	125	H_2SO_4	0.2411	0.0025–
0.2436	0.8	125	H_2SO_4	0.2367	0.0069–
0.2436	2.0	125	H_2SO_4	0.2376	0.0060–
0.2436	2.0	125	H_2SO_4	0.2402	0.0034–
			D.		
0.2436	0.8	250	H_2SO_4	0.2443	0.0007+
0.2436	0.8	250	H_2SO_4	0.2446	0.0010+
0.2436	2.0	250	H_2SO_4	0.2440	0.0004+
0.2436	2.0	250	H_2SO_4	0.2431	0.0005–

TABLE VI (*continued*).

SrO, taken as $Sr(NO_3)_2$.	Ammonium oxalate.	Volume at precipitation.	Acid present during titration.	SrO found.	Error.
			E.		
grm.	grm.	cm^3		grm.	grm.
0.2436	0.8	500	H_2SO_4	0.2396	0.0040–
0.2436	2.0	500	H_2SO_4	0.2403	0.0033–
0.2436	2.0	500	H_2SO_4	0.2418	0.0023–
0.2436	4.0	500	H_2SO_4	0.2410	0.0026–
0.2436	8.0	500	H_2SO_4	0.2407	0.0029–
0.4872	2.0	500	H_2SO_4	0.4837	0.0035–
0.4872	4.0	500	H_2SO_4	0.4855	0.0017–
0.5430	5.0	500	H_2SO_4	0.5422	0.0008–
0.4579	10.0	500	H_2SO_4	0.4554	0.0025–
0.7807	4.0	500	HCl	0.7262	0.0045–

sufficient excess of ammonium oxalate. In the experiments recorded in section C, in which the amount of strontium salt in 125 cm^3 of water is increased, a negative error is introduced, which is not diminished by the presence of a large amount of ammonium oxalate, but when the dilution is increased to 250 cm^3, as is the case in experiments given in section D, so that the conditions correspond more nearly to those recorded in sections A and B, the errors fall to a minimum. In the experiments recorded in section E, in which the dilution is increased to 500 cm^3, an error is introduced which is not prevented by the presence of a large excess of ammonium oxalate and which is independent of the amounts of strontium salt used.

Eight of the water filtrates and wash waters obtained in the experiments recorded in Table VI were tested for traces of strontium by the addition of alcohol, and in all cases a small amount of strontium was found, amounting, in the average, to 0.0010 grm. in 100 cm^3 of water.

Barium Oxalate.

Barium oxalate according to Souchay and Lenssen* is soluble in 2590 parts of cold water, and according to Berg-

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* Ann. Chem. (Liebig), xc, 102.

man * is scarcely at all soluble in alcohol. The attempt was made to estimate barium by precipitation with ammonium oxalate in a mixture containing alcohol. It was found that in filtrates from oxalate precipitations in which 0.1–0.2 grm. of barium oxide, taken as the nitrate, had been precipitated in volumes of 100 cm³, containing 30 cm³ of absolute alcohol, and allowed to stand over night, treatment with sulphuric acid gave barium sulphate amounting in the average to no more than 0.0001 grm. of barium oxide. The insolubility of barium oxalate under these conditions, therefore, is practically complete.

The process for the estimation of barium was as follows: Ammonium oxalate was added to a solution of a barium salt,

TABLE VII.

BaO taken as $Ba(NO_3)_2$.	Ammonium oxalate.	Volume at precipitation.	Acid present during titration.	BaO found.	Error.
			A.		
grm.	grm.	cm³		grm.	grm.
0.1165	0.2	100	HCl	0.1177	0.0012+
0.1165	0.2	100	HCl	0.1170	0.0005+
0.1165	0.2	100	HCl	0.1164	0.0001−
0.1165	0.2	100	HCl	0.1151	0.0014−
0.1165	0.2	100	HCl	0.1165	0.0000
0.1165	0.2	100	HCl	0.1176	0.0011+
0.1165	0.2	100	HCl	0.1164	0.0001−
0.2330	0.4	100	HCl	0.2319	0.0011−
0.2330	0.4	100	HCl	0.2335	0.0005+
0.2330	0.4	100	HCl	0.2342	0.0012+
BaO taken as $BaCl_2$.					
0.0942	0.4	100	HCl	0.0952	0.0010+
0.0942	0.4	100	HCl	0.0939	0.0003−
0.0942	0.4	100	HCl	0.0941	0.0001−
0.1884	0.4	100	HCl	0.1893	0.0009+
0.1884	0.4	100	HCl	0.1892	0.0008+
			B.		
0.0942	0.2	200	H_2SO_4	0.0858	0.0084−
0.1884	0.4	200	H_2SO_4	0.1732	0.0152−
0.0942	0.2	500	H_2SO_4	0.0857	0.0085−

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* Bergman's Essays, i, 320.

containing 80 per cent of its volume of absolute alcohol, the mixture was allowed to stand over night, filtered on asbestos, the precipitate was washed by decantation with 100–200 cm³ of water containing 80 per cent of absolute alcohol, and dried over a flame to insure the removal of the alcohol. The crucible containing the precipitate was returned to the beaker also previously dried over a flame, 100–200 cm³ of water, 5–10 cm³ of strong hydrochloric acid, and 0.5–1.0 grm. of manganous chloride were added, and the solution was titrated at 35°–45° with permanganate. The results of the experiments, given in Table VII, A, show that barium, either as the nitrate or chloride, may be estimated in the manner described with a fair degree of accuracy.

In the experiments given in section B of Table VII, the precipitate of barium oxalate was treated with sulphuric acid after the addition of the stated amount of water. The results show a large loss of oxalic acid probably due to the occlusion of some of the oxalic acid by the barium sulphate. This fact must prevent the use of sulphuric acid in an analytical process which depends upon the liberation of oxalic acid from barium oxalate.

Gravimetric Estimation of the Oxalates of Strontium and Barium.

It is well known that calcium may be weighed as the carbonate after a careful ignition of the oxalate, and it would seem probable that strontium might also be weighed as the carbonate. Precipitates of strontium oxalate, on asbestos, were ignited in a capped crucible from 2–8 minutes in the flame of a Bunsen burner and weighed as the carbonate, and in a single case the carbonate thus produced was converted by treatment with sulphuric acid to the sulphate and weighed as such. The results are given in Table VIII, and while they all show a very slight loss, which amounts in experiment (3) to one milligram, when one-fourth of a gram of strontium oxide taken as the nitrate was used, still the results are fairly accurate.

TABLE VIII.

Exp.	SrO taken as $Sr(NO_3)_2$.	SrO calculated from $SrCO_3$ found.	SrO calculated from $SrSO_4$ found.
	grm.	grm.	grm.
(1)	0.1120	0.1118	. . . .
(2)	0.1120	0.1116	. . . .
(3)	0.2435	0.2425	0.2437

Precipitates of barium oxalate were also ignited from 5–10 minutes and weighed as the carbonate. The results are given in Table IX, and are fairly accurate.

TABLE IX.

Exp.	BaO taken as $Ba(NO_3)_2$.	BaO calculated from $BaCO_3$ found.	Difference.
	grm.	grm.	grm.
(1)	0.2912	0.2909	0.0003–
(2)	0.2912	0.2901	0.0011–
(3)	0.2912	0.2901	0.0011–

The results of this work may be summarized as follows: In the estimation of calcium by titration of the oxalate with permanganate, accurate results may be obtained when hydrochloric acid (with a manganous salt) is used as the solvent. Strontium salts may be precipitated by ammonium oxalate with practical completeness in a solution containing one-fifth of its volume of 85 per cent alcohol, and with approximate completeness from water solutions at a dilution not exceeding 250 cm^3. Furthermore strontium oxalate may be titrated by permanganate with accuracy when either sulphuric acid or hydrochloric acid (with a manganous salt) is used to liberate the oxalic acid. Barium may be precipitated with practical completeness by ammonium oxalate in a solution containing 80 per cent of alcohol, and the barium oxalate thus obtained may be dissolved in hydrochloric acid and titrated by permanganate after the addition of a manganous salt. Strontium and barium oxalates may be converted to carbonates by ignition, and weighed as such.

XLIX

THE ACTION OF SODIUM THIOSULPHATE ON SOLUTIONS OF METALLIC SALTS AT HIGH TEMPERATURES AND PRESSURES.

BY JOHN T. NORTON, JR.

THE use of sodium thiosulphate as a substitute for hydrogen sulphide in effecting precipitations and its application in the case of arsenic, antimony, copper, and platinum was suggested by Himly [*] before the middle of the present century. Thirteen years later Vohl [†] and Slater, independently [‡] drew attention to this use of sodium thiosulphate and extended the investigation to salts of tin, mercury, silver, gold, lead, bismuth, and cadmium. Slater in addition studied the action of sodium thiosulphate upon chromic acid, molybdates, ferrous and ferric ferrocyanides, ferric sulphocyanides and potassium permanganate. Following out these lines, the precipitation of copper, together with arsenic antimony, by treating with sodium thiosulphate the hot solution containing sulphuric acid, and the separation of these elements from tin, zinc, iron, nickel, cobalt, and manganese has been advocated by Westmoreland; [§] and quite recently Faktor [‖] has studied the action of sodium thiosulphate upon neutral salts of several of the elements mentioned, as well as the modifying influence of ammonium chloride and other salts upon the course of the reaction.

Subsequently to the work of Himly, Vohl, and Slater, Chancel [**] developed his well known method for the precipi-

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[*] Ann. Chem. (Liebig), xliii, 150.

[†] Ann. Chem. (Liebig), xcvi, 237.

[‡] Chemical Gazette, 1855, p. 369.

[§] Jour. Soc. Chem. Ind., v, 51.

[‖] Chem. Centralblatt, 1900, ii, 20, 67, 239, 594.

[**] Comp. rend., xlvi, 987.

tation of aluminum as the hydroxide and its separation from salts of iron by boiling with sodium thiosulphate the nearly neutral solution, containing the salt of aluminum and iron, at suitable dilution; and upon an extension of the principle of Chancel's separation of aluminum from iron Stromeyer * founded his well known processes for the separation of titanium and zirconium from iron. The latter process appears to be fairly trustworthy; but of Chancel's method, although it has met with wide acceptance, it was shown by Wolcott Gibbs, very soon after its announcement,† that it fails to bring about complete separation of alumina within a reasonable period of boiling, and this result has been confirmed by Zimmerman,‡ who has shown that the boiling must be continued fifteen hours in order to complete the precipitation of the alumina.

It was shown by Dr. Gibbs that when the treatment of salts of aluminum by thiosulphate was carried on in sealed tubes under pressure at 120° C., the precipitation of alumina was complete, and further that the precipitation of sulphides of nickel, cobalt, and iron, though partial under ordinary atmospheric pressure, was made complete by heating in sealed tubes to 120°-140° C.

In repeating the experiments of Dr. Gibbs qualitatively and extending them, I have made use of the well known Pfungst tube to secure the necessary pressure. In each experiment a test-tube containing the mixture of an excess of sodium thiosulphate with the salt whose action was studied was placed within the Pfungst tube containing some water, the cover of the latter was set in place and firmly bolted upon a washer of lead, and the whole was submitted to temperatures varying from 140° to 200° C. for an hour by immersing in a bath of paraffine. After cooling, the test-tube was taken out, the precipitate was filtered off, and the filtrate tested by appropriate reagents to determine the completeness of precipitation. The following table records the details of these experiments.

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* Ann. Chem. (Liebig), cxiii, 127.

† Zeit. anal. Chem., iii, 889.

‡ Inaug. Diss. Berlin, 1887.

TABLE I.

ACTION OF $Na_2S_2O_3$ ON SALTS UNDER PRESSURE.

Salts used.	Precipitates.	Degree of precipitation.
SULPHIDES.		
$NiSO_4$.	$NiS + S$.	Complete.
$CoSO_4$.	$CoS + S$.	Complete.
$FeCl_3$.	$FeS + S$.	Complete.
$ZnSO_4$.	$ZnS + S$.	Complete.
$PbO_2(C_2H_3O)_2$.	$PbS + S$.	Complete.
$Hg(NO_3)_2$.	$HgS + S$.	Complete.
$AgNO_3$.	$Ag_2S + S$.	Complete.
$CuSO_4$.	$CuS, Cu_2S, + S$.	Complete.
$CdSO_4$.	$CdS + S$.	Complete.
$KSbC_4H_4O_7$.	$Sb_2S_3 + S$.	Complete.
$Bi(NO_3)_3$.	$Bi_2S_3 + S$.	Complete.
HYDROXIDES.		
$(NH_4)Al(SO_4)_2 . 12H_2O$.	$AlO_3H_3 + S$.	Complete.
$K_2Cr_2O_7$.	$CrO_3H_3 + S$.	Complete.
K_2ZrF_6.	$ZrO_4H_4 + S$.	Complete.
K_2TiF_6.	$TiO_4H_4 + S$.	Complete.
$Th(NO_3)_4$.	$ThO_4H_4 + S$.	Complete.
ELEMENTS.		
SeO_2.	$Se + S$.	Complete.
TeO_2.	$Te + S$.	Complete.
SULPHIDES.		
$MnSO_4$.	$MnS + S$.	Partial.
$AuCl_3$.	$Au_2S + S$.	Partial.
$(NH_4)_2MoO_4$.	$MoS_3(?) + S$ — Red liquid.	Partial.
HYDROXIDES.		
$BeCl_2$.	$BeO_2H_2 + S$.	Partial.
UNDETERMINED.		
$(NH_4)_2U_2O_7$.	Black.	Partial.
K_2PtCl_6.	Gray, reddish brown liquid.	Partial.
$CeCl_3$.	White, yellow liquid.	Partial.
$CaCl_2$.	White, yellow liquid.	Partial.
$SrCl_2$.	White, yellow liquid.	Partial.
$BaCl_2$.	White, yellow liquid.	Partial.
$MgSO_4$.	——.	None.
NH_4VO_3.	——, Brown liquid.	None.
H_2KAsO_4.	——.	None.

A perusal of this table brings to light several interesting facts. It appears that salts of nickel, cobalt, iron, zinc, lead, mercury, silver, copper, cadmium, antimony and bismuth are completely precipitated as sulphides by sodium thiosulphate under the prevailing conditions of temperature and pressure. In the case of manganese precipitation is only partial, and arsenic does not seem to be precipitated from an arsenate without the addition of acid. Tin, curiously enough, is not thrown down as the sulphide from a stannous salt, but gives a dirty white precipitate of uncertain composition. Salts of aluminum, chromium, titanium, zirconium and thorium are completely precipitated as the hydroxides; but in the case of beryllium, which one might expect to act similarly, the precipitation as the hydroxide is incomplete. Salts of selenium and tellurium are reduced, and the elements are precipitated. The precipitates obtained with barium, strontium, and calcium were white in a bright yellow liquid, but no study was made of the constitution of either precipitate or liquid. In the case of magnesium there was no precipitate. Salts of molybdenum, vanadium and uranium gave dark colored liquids. Thallium yielded a white spongy mass which on compression was reduced to a very small bulk without disintegrating. Salts of gold and platinum gave slight dark precipitates, presumably sulphides, surrounded by dark colored liquids.

The apparatus used in these experiments and described above is easily handled and answers sufficiently well for qualitative purposes. But, obviously, the introduction into precipitates of foreign matter caused by the action of water on the glass of the test-tube and porcelain lining of the Pfungst tube, precludes the possibility of an exact quantitative study of the reactions involved. For the subsequent experiments, therefore, conducted upon the same general lines, a digester with an interior cylindrical cavity of about 12 cm. in depth by 5 cm. in diameter, and provided with a pressure gauge was employed. As a container for the solutions to be tested, use was made of a platinum cylinder, 4 cm. in diameter and 10 cm. deep, provided with a loose cover.

With this apparatus the following quantitative experiments which deal with those elements which are precipitated as hydroxides — namely, aluminum, beryllium, chromium, zirconium, and titanium — were made.

In each case a weighed quantity of the salt taken for the experiment was dissolved in 50 cm³ of water in the platinum vessel and to this a known amount of sodium thiosulphate was added. The vessel was placed in the digester, and the latter was heated by a Bunsen burner in the customary way until the required pressure was shown on the gauge. The apparatus was then cooled and the platinum vessel removed from the digester. The precipitate was filtered off on ashless paper, ignited, and weighed.

Experiments with a Salt of Aluminum.

In a series of experiments made according to the method of Chancel, the results of which are shown in Table II, the solution in water of a weighed portion of pure ammonium alum was treated with an excess of sodium thiosulphate and boiled vigorously for periods varying from ten minutes to half an hour.

TABLE II.

Exp.	Amount of Alum taken as Al_2O_3.	Amount of $Na_2S_2O_3$.	Al_2O_3 found.	Error.
	grm.	grm.	grm.	grm.
(1)	0.0587	Large excess.	0.0471	0.0066—
(2)	0.0537	Large excess.	0.0397	0.0140—
(3)	0.1083	Large excess.	0.0931	0.0152—
(4)	0.1137	5 grm.	0.0979	0.0158—
(5)	0.1139	2 grm.	0.1002	0.0137—

The results substantiate the observations of Gibbs[*] and of Zimmerman[†] and show clearly that the boiling of solutions of the aluminum salt and sodium thiosulphate for a reasonable time does not effect the complete precipitation of aluminum as the hydroxide.

Table III shows the result of submitting solutions of

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[*] Loc. cit.

[†] Loc. cit.

ammonium alum treated with varying quantities of sodium thiosulphate to a pressure of 20 atmospheres in the digester. It usually required about 40 minutes to raise the pressure to the limit set; but this limit once reached, the digester was allowed to cool slowly. The duration of an experiment was about two hours.

TABLE III.

Alum taken as Al_2O_3.	Amount of $Na_2S_2O_3$ used.	Al_2O_3 found.	Error.
grm.	grm.	grm.	grm.
0.0565	5	0.0633	0.0068+
0.1132	10	0.1154	0.0022+
0.1153	5	0.1186	0.0033+
0.1128	3	0.1129	0.0001+
0.1126	3	0.1142	0.0016+
0.1128	2	0.1120	0.0008–
0.1136	2	0.1121	0.0015–
0.1128	2.5	0.1136	0.0008+
0.1124	2.5	0.1127	0.0003+
0.1134	2.25	0.1133	0.0001–

This table shows that sodium thiosulphate precipitates aluminum completely as the hydroxide when pressure is employed. The high results seen in some of the experiments appear to be due to the difficulty of removing by ignition the large amounts of sulphur found in the action, as well as to the salts mechanically included in the precipitate. The amounts of sulphur and contaminating salts present depend upon the amount of thiosulphate taken; therefore this should be as small as possible, 2–3 grm. being sufficient to precipitate all the alumina in a gram of alum. When the amount of thiosulphate is reasonably restricted the weights of alumina obtained accord fairly well with the theory.

Experiments with a Salt of Chromium.

Up to the time of the completion of this work nothing appears to have been done upon the precipitation of chromium as the hydroxide by means of sodium thiosulphate. Slater * and Rose † make mention of the action of sodium thiosulphate

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* Loc. cit.

† Traité de Chimie Analytique, vol. i, p. 479.

upon chromic acid, bichromates, and neutral chromates, but give no quantitative data. Recently, however, F. Faktor * has studied the action of sodium thiosulphate on chromium compounds. This investigator has found that if aqueous solutions of potassium bichromate and sodium thiosulphate are boiled together a brown precipitate of hydrated Cr_2O_3, CrO_2 separates out and the liquid turns yellow owing to the formation of normal chromate. A solution of potassium chromate is unaffected by boiling with thiosulphate but in presence of ammonium or of magnesium chloride the chromium is separated rapidly and completely in the same form as with the bichromate, and after continued boiling with an excess of thiosulphate all the chromium present is precipitated. Faktor also found that a solution of chromic chloride is completely decomposed by continued boiling with thiosulphate, chromic hydroxide and sulphur being precipitated.

In the experiments shown in Table IV a weighed quantity of pure potassium bichromate was dissolved in water, a known amount of sodium thiosulphate added, and the whole submitted to a pressure of 20 atmospheres in the digester. After cooling, the precipitate was filtered off on an ashless paper, ignited and weighed as Cr_2O_3.

TABLE IV.

Exp.	$K_2Cr_2O_7$ taken as Cr_2O_3.	Amount of $Na_2S_2O_3$.	Cr_2O_3 found.	Error.
	grm.	grm.	grm.	grm.
(1)	0.1830	3	0.1841	0.0011+
(2)	0.1330	2.5	0.1326	0.0004–
(3)	0.1322	2.5	0.1318	0.0004–
(4)	0.1803	2	0.1303	0.0000
(5)	0.1301	2	0.1310	0.0009+
(6)	0.1820	2	0.1322	0.0002+

The results of these experiments are very satisfactory, and show that under pressure sodium thiosulphate precipitates chromium rapidly and completely as the hydroxide. It is advisable to use as small a quantity of thiosulphate as possible

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‡ Zeitschr. anal. Chem., 1900, xxxix, 345.

in order to prevent the presence of much free sulphur in the precipitate.

Experiments with a Salt of Beryllium.

In experiments dealing with beryllium the salt used was the chloride, a certain amount of which was dissolved in water diluted to a liter and the amount of beryllium present determined by precipitating with ammonia and weighing as the oxide. Measured quantities of this solution were drawn from a burette as required. When a solution of a salt of beryllium and sodium thiosulphate are merely boiled together nearly all the beryllium remains in solution. It was expected that the use of pressure would throw out all the beryllium, but, curiously enough, when solutions of beryllium chloride and sodium thiosulphate were submitted in the digester to pressures ranging from 10 to 80 atmospheres only a partial precipitation of the hydroxide took place.

Experiments with Salts of Zirconium.

To prepare a standard solution of the salt of zirconium it was found to be most convenient to heat the double fluoride of potassium and zirconium with sulphuric acid, evaporate to dryness in platinum, dissolve the zirconium sulphate remaining in water and enough sulphuric acid to prevent the precipitation of the basic salt, and dilute to standard volume. Measured portions of the solution were taken from a burette as required for the experiments. The presence, however, of so large an amount of sulphuric acid as was necessary to keep the zirconium salt in solution tends to decompose sodium thiosulphate so rapidly that it was found necessary to nearly neutralize the solution with ammonium carbonate before adding the sodium thiosulphate. The solution of zirconium sulphate was standardized by precipitating with ammonia and weighing as the oxide.

In experiment (1) of Table V, the solutions of zirconium sulphate and sodium thiosulphate were boiled together for a few minutes and then the precipitate filtered off, ignited, and weighed as the oxide. In experiments (2)–(5) inclusive similar solutions were submitted to a pressure of 20 atmospheres in the digester.

TABLE V.

Exp.	ZrO_2 taken.	$Na_2S_2O_3$ taken.	ZrO_2 found.	Error.
	grm.	grm.	grm.	grm.
(1)	0.0658	3	0.0651	0.0007–
(2)	0.0658	3	0.0676	0.0016+
(3)	0.0666	2	0.0670	0.0004+
(4)	0.0641	2	0.0648	0.0007+
(5)	0.0641	2	0.0645	0.0004+

These results clearly show that sodium thiosulphate precipitates zirconium completely as the hydroxide either with or without the aid of pressure.

Experiments with a Salt of Titanium.

The solution of the salt of titanium was obtained by treating the double fluoride of potassium and titanium with sulphuric acid, evaporating to dryness, and dissolving the residue in sulphuric acid and water. The solution was standardized by precipitating the titanium hydroxide with ammonia and then adding an excess of acetic acid as recommended by Gooch.* This method of procedure avoids the tendency to excessive weight observed when the titanium hydroxide is precipitated by ammonia in presence of salts of the alkalies.

In the following table is shown the effect of treating a solution of titanium sulphate with sodium thiosulphate.

TABLE VI.

Exp.	TiO_2 taken.	Na_2S_2O taken.	TiO_2 found.	Error.
	grm.	grm.	grm.	grm.
(1)	0.0240	2	0.0237	0.0003–
(2)	0.0240	2	0.0240	0.0000
(3)	0.0240	2	0.0240	0.0000

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* Am. Chem. Jour., vii, 285.

Experiment (1) was conducted by merely boiling a solution of the reagents named above, filtering off the precipitate and weighing as the oxide. In experiments (2) and (3) the solution of titanium sulphate and sodium thiosulphate was submitted to a pressure of 20 atmospheres in the digester.

These results show that titanium is completely precipitated by sodium thiosulphate either with or without the aid of pressure.

To recapitulate: — I have shown that sodium thiosulphate will completely precipitate aluminum, chromium, zirconium and titanium as the hydroxides with the aid of high temperature and pressure. Beryllium is only partially precipitated under similar conditions. Mere boiling for a reasonable time will not precipitate aluminum and chromium, but it is sufficient in the case of zirconium and titanium.

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Feb. 14