and D, Fig. 2, show that breaks in the curve obtained at 26° occur at points corresponding to hydrates of 14, 11, 10, 6 and 3 molecules of water. As the presence of the hydrates containing 10 and 11 molecules of water seemed a little doubtful, owing to the slight change in pressure (1 mm.) between them and the next higher hydrate, and in order to obtain more information regarding the location of the curve between the hexa- and octahydrate, this experiment was repeated at 30°. The curve obtained at the higher temperature indicates the presence of hydrates containing 14, 10, 6 and 3 molecules of water. The rounding-off effect due to the presence of higher hydrates in the interior of the particles, as suggested by Beutell and Blaschke,[1] is clearly demonstrated between the deca- and hexahydrates which differ in pressure by 13 mm.

As already mentioned, tartrazin after exposure to air contains about 17% of water. This corresponds to the hexahydrate, which has a vapor pressure approximately that of the aqueous tension of the air.

Summary

Vapor pressure-water content curves have been obtained for methylene blue, crystal violet, erythrosin, magenta and tartrazin, for the purpose of determining whether the water present in these dyes is adsorbed or held as water of crystallization. Crystal violet and tartrazin alone show hydrate formation. Further proof was also obtained that the equivalent of 1 molecule of water in erythrosin is present as part of the molecule and a new theory of the structure of this dye is offered.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. III. THE DETERMINATION OF BROMATE IN THE PRESENCE OF FERRIC IRON

BY G. FREDERICK SMITH

Received April 27, 1923

In the former papers of this series,[1] the stability of boiling solutions of potassium bromate in the presence of mineral acids was demonstrated and the relation of this stability to further applications in the use of bromate for volumetric analysis suggested. The use of bromate in acid solution in the presence of mercuric ion was shown to alter the course of several reactions of analytical importance, increasing the oxidation value of the bromate from 5 to 6 equivalents of oxygen, thus preventing the troublesome formation of free bromine and in other ways increasing the flexibility and value of bromate oxidimetric processes.

Determinations involving the use of bromic acid in excess generally

---

[1] THIS JOURNAL, 45, 1115, 1417 (1923).

involve the determination of this excess in the presence of ferric iron. The most common procedure consists in adding potassium iodide to the acid solution followed by a determination with thiosulfate solution of the iodine liberated. Ferric iron, therefore, interferes through the simultaneous liberation of iodine. Methods employed for preventing this influence of ferric iron in iodimetric estimations of strong oxidizing agents, have been devised. The object of the present paper is not only to demonstrate how these known methods may be improved and adapted to the determination of bromates, but also to introduce entirely new reactions for the determination of bromate in the presence of ferric iron.

These reactions, which proceed in the presence of mercuric ion in accordance with the principles stated in the second paper of this series,[1] employ pure sodium oxalate and standard ferrous sulfate solutions in excess as reducing agents, and the excess is determined by titration with standard permanganate in the usual manner. The reactions follow: (1) $3H_2C_2O_4 + KBrO_3 \longrightarrow 6CO_2 + KBr + 3H_2O$; (2) $6FeSO_4 + KBrO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + KBr + 3H_2O$.

Previous Work

Iodimetric determinations in the presence of ferric iron involve the formation of complex ferric salts which do not give ferric ions in solution and which consequently do not act on potassium iodide. Phosphoric acid thus converts ferric salts to complex salts containing the diphosphatoferric ion, $(Fe(PO_4)_2)^{---}$. Sodium pyrophosphate in excess dissolves ferric phosphate to give a colorless solution according to the same principle. Other reagents likewise form complex salts with ferric iron which do not give reactions of the ferric ion. Phosphoric acid and phosphate complexes only are of importance here.

Moser[2] determined copper iodimetrically in the presence of iron by the addition of an excess of sodium pyrophosphate to a solution of copper sulfate and ferric chloride with the formation of cupric and ferric pyrophosphates, of which the copper precipitate was readily soluble and the ferric precipitate difficultly soluble in the excess employed. The solution was then treated with an excess of potassium iodide, acidified with acetic acid and the iodine liberated after 10–15 minutes by the action of the copper alone, was titrated with sodium thiosulfate. This process is objectionable because of the time required for the liberation of iodine, the difficult solubility of ferric pyrophosphate in the excess of pyrophosphate, and the limitation in the amount of ferric iron that may be present without interference.

The action of phosphoric acid in preventing the liberation of iodine from potassium iodide by ferric iron was used by Barnebey[3] in the iodimetric determination of iodate. The similar determination of permanganate iodimetrically was carried out by Barnebey and Hawes.[4] In general the methods involving these processes limit the amount of iron permissible without measurable interference.

---

[2] Moser, *Z. anal. Chem.*, **43**, 597 (1904).

[3] Barnebey, This Journal, **37**, 1502 (1915).

[4] Barnebey and Hawes, *ibid.*, **39**, 607 (1917).

Factors Influencing the Determination of Bromate Iodimetrically

The best procedure for the iodimetric determination of bromates should be one which works advantageously in the presence of the largest amount of iron. At the same time conditions must be chosen which require a minimum length of time in the reaction between the bromate to be determined and the iodide added. The method finally devised combined the principles of the phosphoric acid process of Barnebey and the pyrophosphate method of Moser.

With increasing amount of iron in phosphoric acid solution the ferric iron color of the solution increases regardless of increasing concentration of phosphoric acid. That this color is due to the presence of ferric ions formed by the dissociation of the diphosphato-ferric ion may be shown by the liberation of iodine from potassium iodide added to such solutions. To prevent this dissociation from giving ferric ions the phosphate ion must be added in large excess. This was done by adding easily soluble sodium pyrophosphate.

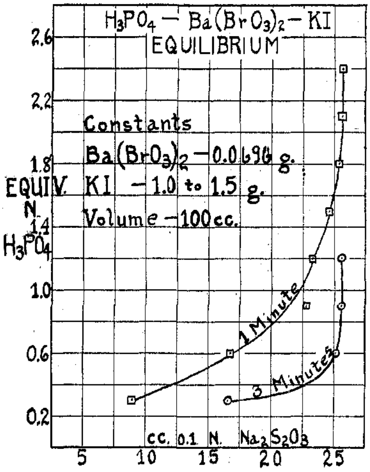

Fig. 1

The addition of sodium pyrophosphate to a phosphoric acid solution greatly decreases the hydrogen-ion concentration. Under these conditions even strong oxidizing agents such as chromic acid fail to liberate iodine rapidly upon the addition of potassium iodide. The very high oxidizing power of bromic acid, however, overcomes this disadvantage. The time rate of oxidation of potassium iodide to free iodine by potassium dichromate with various concentrations of phosphoric acid has been determined by Barnebey.[5] To show the comparative oxidizing power of bromic acid for potassium iodide a curve was constructed showing the equilibrium between barium bromate, potassium iodide and phosphoric acid in the presence of increasing concentrations of phosphoric acid; in the experiments, 1 minute and 3 minutes were allowed as reaction periods. The results are shown in Fig. 1.

The values were obtained as follows. The measured volume of barium bromate solution was diluted with water, the proper amount of phosphoric acid to give the acid normality shown (calculated on the basis of 3 available hydrogen atoms) was added and the whole diluted to 90 cc.; 1 to 1.5 g. of potassium iodide dissolved in 10 cc. of water was added and the mixture stirred vigorously during the allotted time for reaction, whereupon the

---

[5] Barnebey, This Journal, 39, 604 (1917).

liberated iodine was titrated with approximately 0.1 *N* sodium thiosulfate solution. When the reduction of the bromate by potassium iodide was incomplete at the time the thiosulfate was added, part of the thiosulfate was oxidized slightly. The extent of this reaction was negligibly small in all cases.

By comparison with the data of Barnebey for the corresponding dichromate reaction it will be seen that for 2 *N* phosphoric acid the reduction of barium bromate is complete in 1 minute as compared with 3 minutes required by the dichromate reaction. Allowing 3 minutes as reaction period, complete reduction of bromate takes place in a little less than *N* phosphoric acid as compared with 2 *N* acid required by the dichromate reduction. The strength of bromic acid under these conditions compared with that of chromic acid as an oxidizing agent for iodides is, therefore, roughly 3 to 1. It is thus assured that, without increase of the time in the reactions involved, the hydrogen-ion concentration of phosphoric acid may be decreased by the addition of considerable sodium pyrophosphate.

The Effect of Sodium Pyrophosphate in Phosphoric Acid Solution Upon the Formation of an Undissociated Diphosphato-Ferric Ion Complex

As has been shown in previous papers of this series, solutions of nitric and perchloric acid are best adapted to the determinations involving bromate oxidations. Solutions containing ferric perchlorate of increasing iron content were treated with phosphoric acid in different concentrations and diluted to 100 cc. Proportionate amounts of crystalline sodium pyrophosphate were then dissolved in these solutions, followed by the addition of 1–1.5 g. of crystalline potassium iodide. The potassium iodide was dissolved by vigorous stirring to prevent high local concentrations of dissolved material and the reaction medium was allowed to stand in covered beakers for 30 minutes. At the end of this time starch indicator was added and the iodine which had been liberated was titrated with 0.1 *N* sodium thiosulfate. A blank determination, under the same conditions without iron, was made to show the effect of atmospheric oxygen in liberating iodine from the iodide added. Under conditions which were least favorable to the rapid reduction of bromate by potassium iodide, the time required for the completion of the reaction between 25.00 cc. of 0.1 *N* potassium bromate and excess of potassium iodide was also determined. The results of the experiments are shown in Table I.

As will be seen, iron to the extent of 600 mg. may be effectively eliminated as an interference in iodimetric determinations of bromates. Substantially the same results were obtained using crystalline ferric nitrate instead of ferric perchlorate. When ferric sulfate solutions are employed, much more iron may be present without interference, as shown by Barnebey.[4] The first and second experiments in Table I show that under similar conditions without the addition of sodium pyrophosphate a prohibitive error is introduced with but half the amount of ferric iron possible with addition of pyrophosphate. In all the above experiments, the solutions remained clear throughout the whole of the time interval employed.

TABLE I

THE ACTION OF FERRIC IRON UPON POTASSIUM IODIDE IN PHOSPHORIC ACID SOLUTION AS INFLUENCED BY SODIUM PYROPHOSPHATE

Iron was added as ferric perchlorate (containing 11% of Fe) free from ferrous iron. Time of reaction, 30 minutes. Volume of solution, 100 cc. The sodium pyrophosphate did not liberate or absorb iodine under the conditions studied. 1.0 g. of potassium iodide was added in the first five experiments and 1.5 g. in the last six.

Amount of Fe G.	Conc. H_3PO_4 M	$Na_4P_2O_7$ 10 H_2O added G.	0.1 N $Na_2S_2O_3$[a] required Cc.	Blank without Fe. Cc. of thiosulfate	Time required for $KBrO_3$ + KI reaction Same conditions Min.
0.2	2.0	None	0.25	..	...
.3	2.0	None	.51	..	...
.2	1.0	3.0	.04	..	...
.3	1.5	3.0	.11	0.01	...
.3	1.5	4.0	.08	none	<3
.4	2.0	4.0	.56	..	...
.4	2.0	6.0	.20	0.01	<3
.5	2.0	5.0	.50	..	...
.5	2.0	6.0	.34	..	...
.5	2.0	8.0	.25	0.01	...
.6	2.0	10.0	.20	0.00	<3

[a] 1/10 of these values is the extent of their effect in practice.

The iodine liberated from potassium iodide by 25.00 cc. of 0.1 N potassium bromate in 0.3 N hydrochloric acid solution required 26.21 cc. of the sodium thiosulfate used in Table I. With 0.66 M phosphoric acid 26.21 cc. also was required. With 2 M phosphoric acid 26.15 cc. was required. With 2 M phosphoric acid to which 10 g. of sodium pyrophosphate decahydrate per 100 cc. had been added, 25.99 cc. of the sodium thiosulfate solution was required. Therefore, the sodium thiosulfate in strong phosphoric acid solution with and without the addition of sodium pyrophosphate should be standardized, using potassium bromate under the same conditions.

The procedure for preparing a nitric or perchloric acid solution containing ferric iron for determination of its bromate content consists, therefore, in adding sodium bicarbonate to neutralize the acid and give a small precipitate, followed by phosphoric acid or phosphoric acid and sodium pyrophosphate, depending upon the amount of iron present, and finally 1–1.5 g. of potassium iodide with stirring. After 2 to 3 minutes the liberated iodine is titrated with standard thiosulfate using starch as indicator. The thiosulfate should be standardized under the same conditions.

The Determination of Bromates with an Excess of Pure Sodium Oxalate Followed by Permanganate Determination of this Excess

Since many oxidation processes involving bromates are best conducted at 100°, iodimetric determination of any excess of bromate can be made only after the solutions have been cooled to room temperature. It would, therefore, be an advantage to develop a method for bromate determination applicable to hot solutions, and Reaction 1 was accordingly studied.

An exactly 0.1 *N* solution of sodium oxalate and approximately 0.1 *N* solutions of potassium and barium bromate were prepared; 25.00cc. portions of the latter solutions were treated with 0.1 *N* mercuric perchlorate solution in amount slightly more than that equivalent to the bromide ion resulting from the subsequent reduction of the bromate, and 50.00 cc. of the 0.1 *N* sodium oxalate solution was added[6] followed by 5 cc. of 95% sulfuric acid, and the volume was adjusted to 100 cc. The solution was boiled for 3 minutes in a covered beaker and, without cooling, the excess of sodium oxalate was titrated with potassium permanganate solution that had been standardized against pure sodium oxalate.

The standardization of three bromate solutions in this way was accomplished with the results listed in Table II.

TABLE II

STANDARDIZATION OF POTASSIUM AND BARIUM BROMATE SOLUTIONS WITH SODIUM OXALATE IN SULFURIC ACID SOLUTION FOLLOWED BY DETERMINATION OF THE EXCESS OF OXALATE WITH POTASSIUM PERMANGANATE

Fixed quantities: 25.00 cc. of approximately 0.1 *N* $KBrO_3$ or $Ba(BrO_3)_2$; 50.00 cc. of 0.1000 *N* $Na_2C_2O_4$; 5 cc. of 95% H_2SO_4. 7–10 cc. of 0.1 *N* $Hg(ClO_4)_2$ in 0.1 *N* $HClO_4$ solution. Volume of solution, 100 cc. Time of boiling, 3 minutes.

Sample	0.10040 *N* $KMnO_4$ required Cc.	Bromate determined *N*	Bromate using pure As_2O_3 *N*	Difference
1 $KBrO_3$	24.97	0.09971	0.09965	+0.00006
$Ba(BrO_3)_2$	25.125	.09909	.09903	+ .00006
2 $KBrO_3$	24.08	.09972	.09973	− .00001

These results are in each case the means of at least three closely agreeing determinations. The potassium bromate from a measured portion of Sample 2, after reduction with hydrazine, was precipitated with excess of silver nitrate and the weight of the silver bromide gave the closely agreeing value, 0.09967 *N*. The purity of the arsenious oxide used was thus proved.

The end-point in the titrations of Table II in which permanganate was used is the equal in permanency to the ordinary sodium oxalate-permanganate titration in spite of the presence of considerable mercuric bromide, but the last 3 or 4 drops of permanganate added are only slowly reduced. The point at which the pink color produced is permanent for 3/4 to 1 minute[7] is the true end-point of the reaction.

The explanation of the influence of mercury in the determinations given

---

[6] Sodium oxalate solutions should be made up as used to avoid decomposition which occurs upon standing.

[7] It was found that the pink color from 1 drop of 0.1 *N* permanganate in excess often persisted after 12 hours or even longer.

in the second article of this series was further tested by substituting 0.1 *N* silver sulfate solution for mercuric perchlorate, and using a considerable excess. The concentration of the solution of Sample 2 potassium bromate was thus found to be 0.09974 *N*. The silver bromide precipitated during the reaction was without effect on the end-point. The addition of mercuric perchlorate solution to these reactions may be readily obviated through the use of mercuric bromate as standard solution. The use of mercuric bromate for this purpose will be considered in subsequent papers of this series.

Sodium oxalate serves as one of the very best standards of quantitative analysis.[8] The standardization of bromate solutions with sodium oxalate as the only reference reagent, according to the determinations included in Table II, thus shows that bromate is probably the equal of permanganate in accuracy as a standard in volumetric analysis.

The standardization of bromate solutions by comparison with pure arsenious oxide or pure metallic antimony, following the procedure of Györy[9] and more recently the modified Györy electrometric method of Zintl and Wattenberg[10] further increases the value of bromate for volumetric processes. The high purity of metallic antimony available for this purpose has been described by Henz.[11] That it dissolves in hot concd. sulfuric acid to give only trivalent antimony was shown by Osterheld and Honegger.[12] Work now being carried out in another laboratory,[13] involving the use of potassium bromate and including a critical study of its physical properties as related to stability will further increase the value of bromate as a standard.

By the use of bromate solutions standardized against sodium oxalate and potassium permanganate to liberate iodine from potassium iodide in acid solution, sodium oxalate can in general be used in place of arsenious oxide as a primary standard for iodimetric processes with no sacrifice in accuracy or convenience. Another method in which sodium oxalate is used as primary standard was devised by Rosenthaler.[14]

Factors governing the determination of bromate in the presence of ferric iron by the oxalate-permanganate method given above are shown in Table III.

It will be seen from Table III that solutions containing only free sulfuric acid serve for oxalate reduction of bromate in hot solution in the presence of mercuric perchlorate. Phosphoric acid, if added to decolorize

[8] Sörensen, *Z. anal. Chem.*, **42**, 352, 512 (1903); **45**, 272 (1906).

[9] Györy, *Z. anal. Chem.*, **32**, 415 (1893).

[10] Zintl and Wattenberg, *Ber.*, **56**, 472 (1923).

[11] Henz, *Z. anorg. Chem.*, **37**, 1 (1903).

[12] Osterheld and Honegger, *Helv. chim. acta*, **2**, 398 (1919).

[13] Private communication.

[14] Rosenthaler, *Z. anal. Chem.*, **61**, 219 (1922).

the iron present, should be added just before titration or, better, at the end of the titration with permanganate. The preparation of the nitric or perchloric acid solution of a bromate containing ferric iron for determination of its bromate content is, therefore, the same as that for iodimetric determination, addition of sulfuric acid following neutralization, in place of phosphoric acid and sodium pyrophosphate. The effect of more than 3 minutes' boiling was not tested when using phosphoric or perchloric acid instead of sulfuric acid.

TABLE III

THE DETERMINATION OF POTASSIUM BROMATE WITH AN EXCESS OF SODIUM OXALATE IN SULFURIC, PHOSPHORIC AND PERCHLORIC ACID SOLUTIONS IN THE PRESENCE OF MERCURIC PERCHLORATE

Fixed quantites: 25.00 cc. of 0.09973 *N* $KBrO_3$; 50.00 cc. of 0.1000 *N* $Na_2C_2O_4$; 10 cc. of 0.1 *N* $Hg(ClO_4)_2$ in 0.1 *N* $HClO_4$. Reaction volume, 100 cc. Time of boiling, 3 minutes. Theoretical $KMnO_4$ for excess of $Na_2C_2O_4$, 26.18 cc.

Acid used Cc.		Other material present G.	Salt	Amount $KMnO_4$ used Cc.	Difference from calc. Cc. $KMnO_4$
3	95% H_2SO_4 +	...	....	26.35	+0.17
3	85% H_3PO_4				
10	60% $HClO_4$	0.1	Ferric iron	26.33	+0.13
5	95% H_2SO_4	5	$NaClO_4.H_2O$	26.21	+0.03
		5	KNO_3	26.20	+0.02
		0.1	Ferric iron[a]	26.20	+0.02
				26.20	+0.02
				26.21	+0.03

[a] 3 cc. of 85% H_3PO_4 added just before titration with permanganate.

The Determination of Bromate in the Presence of Mercuric Salt Using Ferrous Sulfate Followed by Titration of the Excess with Permanganate Solution

A second substitute for the iodimetric determination of bromates, using standard ferrous sulfate and potassium permanganate solutions, following the second reaction given above, would prove highly desirable if accurate because, as in the oxalate and iodimetric methods already described, the standard solutions used are the common stock reagents of any analytical laboratory. The determinations of bromates by this reaction would be most convenient if they could be made applicable in the presence of nitric, perchloric and phosphoric acid solutions, since bromate oxidation processes are best carried out in the presence of the two former acids, and phosphoric acid could be used to decolorize the ferric iron, giving a sharper permanganate end-point.

Standard solutions of potassium permanganate and ferrous sulfate were prepared in the usual manner by comparison with each other and with pure sodium oxalate. Potassium bromate was standardized with pure arsenic trioxide. Measured amounts of potassium bromate solution were treated with an excess of the equivalent amount of mercuric perchlorate solution and a considerable excess of standard ferrous sulfate solution was added. In the presence of 0.5 *N* nitric, perchloric and sulfuric acids complete reduction of the bromate was obtained in 2 to 3 minutes at room temperature. Molar phosphoric acid gave the same time of reduction. The results are listed in Table IV.

Table IV

The Determination of Potassium Bromate Using Ferrous Sulfate and Potassium Permanganate in Presence of Mercuric Perchlorate

Fixed quantities: 25.00 cc. of 0.09803 *N* $KBrO_3$; 25–30 cc. of 0.1 *N* $Hg(ClO_4)_2$ in 0.1 *N* $HClO_4$; 50.00 cc. of 0.09412 *N* $FeSO_4$ in 0.1 *N* H_2SO_4. Dilution to 150 cc. 2–3 minutes allowed for reduction of $KBrO_3$. 24.24 cc. of 0.09404 *N* $KMnO_4$ required for theoretical excess of $FeSO_4$.

Acid	Equiv. norm. of acid	0.09303 *N* $KMnO_4$ required Cc.	Difference from calc. Cc. of $KMnO_4$	Acid	Equiv. norm. of acid	0.09303 *N* $KMnO_4$ required Cc.	Difference from calc. Cc. of $KMnO_4$
$HClO_4$	0.5	24.22	−0.02	HNO_3	0.25	24.06	−0.18
	0.5	24.24	±0.00		0.5	24.05	−0.19
	0.5	24.22	−0.02	H_3PO_4	1.0	24.24	±0.00
	1.0	24.24	±0.00		1.0	24.21	−0.03
	1.0	24.27	+0.03		1.0	24.21	−0.03
H_2SO_4	0.25	24.07	−0.17				
	0.5	24.07	−0.18				
	0.5	24.03	−0.21				
	1.0	24.02	−0.22				

Phosphoric acid sufficient to decolorize the iron present was added at the end-point in all these experiments if not already present.

From Table IV it is seen that the experimental and theoretical results obtained agree excellently in the case of phosphoric and perchloric acid solutions but are uniformly in error for nitric and sulfuric acid solutions. The end-point is best and most permanent in phosphoric acid solution but is very satisfactory as well in perchloric acid solution. As with a permanganate-oxalate end-point in the presence of mercuric salt, the last few drops of permanganate added are but slowly reduced and the pink tinge should persist for $^3/_4$ to 1 minute while the solution is stirred. The explanation of the error with nitric and sulfuric acid solutions is not apparent and is unusual in its constancy. The study of the electrometric end-point as applied to the reaction will be considered later in connection with work on volumetric processes involving bromate solutions, but the slowness of the reaction at the end-point would probably interfere with this method.

The preparation of bromate solutions in nitric acid containing ferric iron for determination of their bromate content according to the procedure of Table IV is the same as that for the iodimetric determination and the oxalate procedure already given.

The results here reported were obtained with mutually calibrated flasks, burets and pipets and are believed to be accurate to ±0.02 cc.

Summary

The determination of bromates in the presence of ferric iron was studied, three methods proposed and their applicability demonstrated experimentally.

1. Iodimetric Method. Phosphoric acid solutions containing sodium pyrophosphate in which the dissociation of the resulting iron complex to give ferric ions is less than in the presence of either reagent alone, were analyzed for their content of bromate by the addition of potassium iodide in excess and titration of the liberated iodine with sodium thiosulfate. The time rate of reduction of bromate by potassium iodide with various concentrations of phosphoric acid was determined. The necessary variation in the concentration of phosphoric acid and sodium pyrophosphate with increasing amounts of ferric iron was determined.

2. Oxalate-Permanganate Method. The bromate was reduced by excess sodium oxalate in boiling sulfuric acid solution in the presence of mercuric perchlorate and the excess oxalate determined by titration with potassium permanganate. It was shown that this reaction furnishes the basis of an improved method for iodimetric standardization using sodium oxalate as primary standard.

3. Ferrous Sulfate-Permanganate Method. This involved the same procedures as in the Oxalate-Permanganate Method except that ferrous sulfate was substituted for sodium oxalate and titration was effected cold instead of in a hot solution.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF McGILL UNIVERSITY]

OXONIUM COMPOUNDS IN THE VAPOR STATE. METHYL ETHER—HYDROGEN CHLORIDE

BY O. MAASS AND D. M. MORRISON

Received May 2, 1923

Organic compounds containing oxygen have been shown to form complexes with the halogen hydrides; these are known as oxonium compounds. For reasons which are discussed below, further work dealing with their stability is of interest. In the investigation which is the subject of this paper, methyl ether and hydrogen chloride were mixed in the gaseous state with the object of determining whether or not association of these molecules occurred.

A thorough investigation of oxonium compounds has been made by D. McIntosh[1] and some of his co-workers. In one of his papers[2] on the sub-

---

[1] McIntosh, THIS JOURNAL, **27,** 26, 1013 (1905); **33,** 71 (1911).

[2] *Ibid.*, **34,** 1273 (1912).