ART. XXXV.—*The Hydrolysis of Salts of Ammonium in the Presence of Iodides and Iodates*; by SETH E. MOODY.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxlix.]

BRUCK* has shown that when salts of ammonium are subjected to heat they are hydrolyzed and that as the acid is increased, either as a direct product of this hydrolysis, or by addition, further dissociation is inhibited. The decrease in dissociation is dependent upon the increase of the acid, and when sufficient acid is present, further hydrolysis is entirely prevented. The amount of hydrolysis is, however, small under the most favorable conditions.

It is interesting to discover how rapidly hydrolysis will proceed if the free acid is constantly removed by the presence of a mixture of potassium iodide and potassium iodate, and with this end in view a solution of ammonium sulphate, containing 5 grms. to a liter, was prepared with which to carry out subsequent experiments. The value of the solution was determined by precipitating barium sulphate, and by calculation its equivalent in iodine according to the equation

$$3H_2SO_4 + 5KI + KIO_3 = 3K_2SO_4 + 3H_2O + 6I$$

was found to be 0·4773 grm. of iodine to 25^{cm^3} of the ammonium sulphate, upon the supposition that all the sulphate of ammonia can be broken up and that the full amount of sulphuric acid may be made available for reaction with the iodide-iodate mixture.

To the solution of ammonium sulphate were added potassium iodide and potassium iodate and the mixture was allowed to stand. At the ordinary temperature of the room little effect was noticed, as shown by the following results:

TABLE I.

$(NH_4)_2SO_4$. cm³.	KI. grm.	KIO_3. cm³.	Time in hours.	Approx. N/10 $Na_2S_2O_3$. cm³.	I. grm.
25	1·0	20	3	0·25	0·0031
25	1·0	20	3	0·25	0·0031
25	1·0	10	19	0·35	0·0044
25	1·0	10	19	0·35	0·0044

In another series of experiments in which the solution of ammonium sulphate was boiled for three hours in an Erlenmeyer beaker before adding the iodide-iodate mixture, results were obtained which vary with the vigor of the boiling, but which show that small amounts of ammonia are volatilized, as

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* Dissertation, Giessen, 1903.

shown by the subsequent slight liberation of iodine upon the addition of the iodide-iodate mixture to react with the sulphuric acid left behind. Yet the amount of hydrolysis which takes place when the ammonium sulphate is boiled with water is greater than when the ammonium sulphate and the iodide-iodate mixture are allowed to stand at the ordinary room temperature.

The following table shows the results of these experiments:

TABLE II.

$(NH_4)_2SO_4$ cm³.	Time in hours.	KI. grm.	KIO_3. cm³.	Approx. N/10 $Na_2S_2O_3$. cm³.	I. grm.
25	3	1·0	10	1·25	0·0156
25	3	1·0	10	1·55	0·0193
25	3	1·0	10	1·30	0·0162
25	3	1·0	10	1·47	0·0183

If the acid produced is eliminated as fast as it is formed, the hydrolysis of the salt should proceed more rapidly. The action of the iodide-iodate mixture, which reacts with the sulphuric acid to form potassium sulphate and iodine, should bring this about; and the iodine may be removed by boiling, in the presence of a current of hydrogen, and collected for estimation. In experiments made under these conditions it was found, curiously enough, to be impossible to collect the iodine in the Drexel flask used as a receiver when charged with potassium iodide only, although it was evident that much iodine came over. It appeared, upon investigation, that ammonium iodide and ammonium iodate were formed by reaction in the receiver between the liberated iodine and the ammonia also volatilized, and to obviate the difficulty sulphuric acid was added to the contents of the receiver into which the distillate was passed. Under these conditions iodine is obtained in amount corresponding to that which should be eliminated when the ammonium sulphate is entirely hydrolyzed.

This is shown in the subjoined table:

TABLE III.

$(NH_4)_2SO_4$. cm³.	KI. grm.	KIO_3. cm³.	Time in hours.	H_2SO_4 (1:1) in the receiver. cm³.	Approx. N/10 $Na_2S_2O_3$. cm³.	I. grm.	Diff. grm.
25	1·0	10	3	40	38·25	0·4769	−0·0004
25	1·0	10	3	40	38·25	0·4769	−0·0004
25	1·0	10	3	40	38·30	0·4775	+0·0002
25	1·0	10	3	40	38·25	0·4769	−0·0004
25	1·0	10	3	40	38·23	0·4766	−0·0007

In another series of experiments, the apparatus was changed, so that the distillate passed from the first Voit flask, V^1, through a second Voit flask, V^2, containing an excess of standard acid to take up the ammonia and then into the receiver containing potassium iodide without acid.

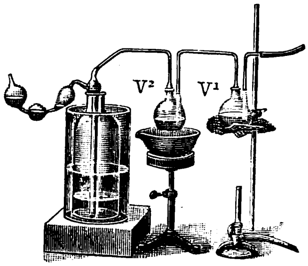
Table IV gives results of experiments thus modified.

TABLE IV.

					Iodine equivalent of ammonia absorbed in Voit flask.			Iodine estimated in Drexel flask.		
Ammonium sulphate. cm³.	KI. grm.	KIO_3. cm³.	Approx. N/10. H_2SO_4. cm³.	Time in hours.	Approx. N/10 $Na_2S_2O_3$. cm³.	I. grm.	Diff. grm.	Approx. N/10 $Na_2S_2O_3$. cm³.	I. grm.	Diff. grm.
25	1·0	20	50	3	38·15	0·4757	−0·0016	38·23	0·4767	−0·0006
25	1·0	20	50	3	38·20	0·4763	−0·0010	38·25	0·4769	−0·0004
25	1·0	20	50	3½	38·15	0·4757	−0·0016	38·20	0·4763	−0·0010
25	1·0	20	50	3	38·20	0·4763	−0·0010	38·27	0·4771	−0·0002
25	1·0	20	50	3½	38·17	0·4759	−0·0014	38·20	0·4763	−0·0010
25	1·0	20	50	3½	38·15	0·4757	−0·0016	38·20	0·4763	−0·0010
25	1·0	20	50	3	38·20	0·4763	−0·0010	38·25	0·4769	−0·0004

These experiments show that the sulphuric acid neutralized in the Voit flask is a measure of the ammonia while the iodine in the Drexel flask corresponds to the sulphuric acid of the ammonium sulphate.

Similar results were obtained with ammonium chloride. The exact value of a solution of 5 grms. of this salt made up to 500cm³ was obtained by precipitating and weighing the silver chloride produced by silver nitrate, 25cm³ of the solution containing of the salt the equivalent of 0·5922 grm. of iodine.



Portions of this solution were measured from a burette into a flask, to which was added, in each experiment, the iodide-iodate mixture and in the presence of a current of hydrogen boiled until no further color, due to iodine, remained. The distillate was passed through a trap of standard sulphuric acid, to absorb the ammonia, into the Drexel flask charged with an aqueous solution of potassium iodide to dissolve the iodine, which became known upon titration with standard sodium thiosulphate. The difference in amount of iodine which equivalent volumes of the sulphuric acid used in the trap liberated from the iodide-iodate mixture before and after the passage of the distillate indicates the amount of ammonia volatilized in the boiling.

A table showing results of such experiments follows:

TABLE V.

					Iodine equivalent of ammonia absorbed in Voit flask.			Iodine estimated in Drexel flask.		
Ammonium chloride. cm³.	KI. grm.	KIO_3. cm³.	Approx. N/10. H_2SO_4. cm³.	Time in hours.	Approx. N/10 $Na_2S_2O_3$. cm³.	I. grm.	Diff. grm.	Approx. N/10 $Na_2S_2O_3$. cm³.	I. grm.	Diff. grm.
25	1·0	20	50	2¾	47·47	0·5918	−0·0004	47·45	0·5916	−0·0006
25	1·0	20	50	2¾	47·40	0·5909	−0·0013	47·44	0·5915	−0·0007
25	1·0	20	50	2½	47·50	0·5922	±0·0000	47·48	0·5920	−0·0002
25	1·0	20	50	2½	47·45	0·5916	−0·0006	47·47	0·5918	−0·0004
25	1·0	20	50	2½	47·47	0·5918	−0·0004	47·48	0·5920	−0·0002

It is to be noticed that the time necessary for the hydrolysis of ammonium chloride is less than that for the sulphate.

On account of the time required, this procedure cannot be considered as having claims to be called an analytical method for determining ammonia, or the acid-ion of either of these ammonium salts, except under circumstances most extraordinary. It is here presented because the hydrolysis of ammonium salts must not be ignored in work wherein such salts are heated in solution with the iodide-iodate mixture.