CXXX.—*The Hydrolysis of Ammonium Salts by Water.*

By ERNEST GEORGE HILL.

VELEY has recently described (Trans., 1905, 87, 26) a method by which he attempted to measure the amount of hydrolytic dissociation of aqueous solutions of ammonium salts. The method consisted in boiling the solutions in Jena flasks under an inverted condenser and estimating the loss of ammonia at the end of a given time. The results were not very satisfactory, but the conclusion was drawn that three cases are presented: (1) that hydrolysis may be inappreciable, (2) that it may be dependent on dilution, (3) that it may be independent of the dilution beyond a limiting value. Veley also showed that the extent to which various acids retain ammonia is more or less analogous to their avidity, but that the absolute order of magnitude is not the same in the two cases.

Veley's most striking results were those obtained from the nitrate

and chlorate, which allowed the escape of comparatively large quantities of ammonia, whereas both nitric and chloric acid, being of the same order as hydrochloric, should hydrolyse to a very slight extent. Thus, taking hydrochloric acid as 100, Veley found the avidity of chloric acid to be 6.9, and he omitted nitric acid from the discussion on the assumption that at the temperature of the experiment the nitric acid decomposed and caused secondary reactions. Formic acid also gave anomalous results.

It was suggested by Dr. Veley that measurements of the electric conductivity of the solutions of ammonium salts before and after treatment as in his experiments would give a more accurate means of determining the amount of hydrolysis. A few preliminary experiments showed that this was not so, and that in the case, for example, of ammonium sulphate there was very little change, before or after boiling.

The amount of ammonia escaping is so small, and the ionisation in the solution is so great, that the variation in the conductivity of a normal or fifth-normal solution was almost inappreciable, and the method was abandoned. It seemed, however, possible that if the escaping ammonia could be led into pure water, the conductivity of the water might be used to measure the amount of ammonia evolved. This method proved much more satisfactory.

Estimation of Very Dilute Ammonia by the Conductivity of its Solution.

From the conductivity or resistance curve, it is possible to estimate the amount of ammonia which corresponds to any particular conductivity. Accordingly, if precautions are taken to avoid contamination of the water, it should be possible, by aspirating a current of purified air through a solution containing free ammonia, and passing the ammoniacal air into conductivity water, to obtain a solution of ammonia in water, the conductivity of which is a measure of the ammonia dissolved. The method would be specially applicable when the ammonia to be measured is very small. After a number of experiments with various forms of aspirators, flasks, and absorption vessels, it was found necessary to purify the aspirated air from all carbon dioxide, to secure a uniform rate of flow, to avoid transfer of the ammonia solution from one vessel to another, to avoid condensation of water vapour on the limb of the flask containing the ammonium salt solution, and to measure accurately the ammonia solution before taking its conductivity, also the air passing through the whole apparatus.

These conditions were obtained as follows:

The air was supplied from an ordinary gas holder and was purified

by passing it through a series of wash bottles containing potassium hydroxide solution, and then through a tube containing glass wool moistened with water. The rate of flow was regulated once for all by placing a constricted capillary tube between the purifiers and the laboratory vessel to be described.

The volume of air passed was measured by collecting it, after it had passed through the absorption vessel over water at 15° , in a graduated 800 c.c. flask with a narrow neck. To avoid condensation of water vapour on any part of the apparatus before the absorption vessel, a special form of vessel was designed for containing the salt solutions, every part of which was kept at the temperature of steam, so that no condensation could take place until the air passing through the apparatus had reached the absorption vessel. And lastly, to avoid transfer of solutions and to obviate the difficulty of measuring the volume of the solution before taking its conductivity, the cell itself was graduated and was designed of such a pattern that it served as the absorption vessel.

The Conductivity Cell and Absorption Vessel.

A tube of about 4 mm. cross section, bent twice at right angles, was constricted at the end *D* and sealed into the cell *E*. The constriction was less than 1 mm., the diameter of the cell being about 10 mm. The cell was about 6 cm. long, and at its upper end a tube of 6 mm. diameter was sealed with a slight constriction at the joint. At a distance of 16 cm. from the cell, a small pipette-like bulb was blown as a safety trap for any water forced up the tube, but this was never needed during the experiments. The electrodes were as large as possible and about 5 mm. apart. They were drawn up against the sides of the cell, so as to be quite rigid, and the connecting wire passed into mercury cups bent upwards and extending well above the cell.

The cell was graduated on the two limbs to hold exactly 20 c.c. (see diagram, p. 1277).

The Laboratory Vessel.

This vessel, used for containing the solution of a salt of ammonium during the passage of 800 c.c. of air, was made as follows :

One of the tubes of a 50 c.c. pipette was lengthened considerably and the other was replaced by a narrow tube with a constriction at the entrance to the bulb. This tube was bent twice at right angles, and the end of it (*C*) shaped conveniently as in the figure. The wider tube was bent so as to incline at about 115° to the bulb, and on this was placed a small condenser, the end subsequently being bent downwards

parallel to the bulb. The construction is best shown by the figure. The end *A* was drawn out into a strong, narrow point, which could enter the narrow limb of the conductivity cell. The condenser was kept hot by a supply of steam from a boiler, and the bend of the tube was covered by lengthening the condenser with wide bore rubber tubing cut to shape.

Round the narrow limb of the cell a second steam jacket was placed, so that the latter met the rubber prolongation of the condenser described above. Thus the whole of the limb *B B B* was kept at the temperature of steam. It was therefore no longer possible for any condensation to take place in this limb (see diagram).

The bulb of the pipette was immersed in a very deep water-bath, and the latter was covered with the usual rings and a small cap, which fitted over the ends of the condenser and the side tube *C*. In this way the whole of the laboratory vessel was kept at a high and constant temperature. Owing to the shape of the limb *B B* there could be no spurting of the solution into the cell.

The end of the tube *B B* was connected with the cell by a small piece of rubber tube, which was wired on to the outside of the narrow limb of the cell, the latter being widened for 10 mm. at its end to allow the tube *B B* to enter. This joint was so made that the glass of the two tubes just touched and the rubber came into contact with only the outside of the tubes. The point *A* entered into the limb of the cell for about 8 mm. The cell was immersed in cold water during the experiment.

Method of Experiment.

At the beginning of an experiment, conductivity water, prepared as subsequently described, was placed in the cell and its conductivity measured. This was found to be slightly diminished by passing the air, purified as above, through the cell for fifteen minutes. No water was considered suitable which had a greater conductivity than 1.5×10^{-6} units.

A solution of the salt was made in conductivity water in a 200 c.c. flask kept for the purpose. Of this solution, 50 c.c. were withdrawn by a pipette, also kept for this purpose but not specially standardised, placed in a small beaker, and immediately drawn into the laboratory vessel by connecting a rubber tube to *B A* and aspirating the solution through *C*. The rubber tube was then removed and the end of the glass tube *A* rinsed with conductivity water. The laboratory vessel was then placed in the water-bath and joined up with the cell, which contained about 16 c.c. of water at the beginning of an experiment. A bent hood fitted over the top of the cell by means of a rubber collar led by a long delivery tube to the 800 c.c. flask inverted over water,

in which the air passing through the apparatus was collected and measured. The water was always kept at 15° , and towards the end of the experiment the flask was sponged with water at that temperature.

When the connections were made, the boilers and water-bath were heated, and after a few minutes air regulated as previously described was passed until exactly 800 c.c. had been collected in the measuring flask. This took a little less than an hour. The air was then stopped and the cell disconnected. The cell was filled up to the graduation mark with water directly from the conductivity still and placed in the thermostat, which held several gallons of distilled water. It was

W, water-bath; *XX*, graduation mark on the cell; *Y*, copper cap fitting over the water-bath rings, with openings for the limbs of the vessel; *ZZ*, mercury cups.

heated to a little above 18° by a current of steam and allowed to cool slowly. When the temperature reached exactly 18° , the conductivity was measured.

With the apparatus above described, sixteen experiments were made with five different concentrations of ammonium sulphate solution. The results were quite satisfactory, the resistances measured differing by less than three per cent. from the mean for a particular concentration. Thus for normal ammonium sulphate the values were 1019, 1027, 1069, 1087, 1083. These were the most discordant results obtained, and a resistance of about 1000 ohms is the least favourable resistance for estimating ammonia by the conductivity method. The

reason is that when the resistance is less than 1000 ohms, the nature of the resistance curve is such that only a small difference in resistance is shown by a comparatively large difference in the ammonia present. In these cases, therefore, the ammonia was estimated by titration. For such determinations the laboratory vessel was used in conjunction with a long test-tube containing a measured quantity of standard acid. The tube was fitted with a doubly-bored rubber stopper, which carried a straight tube passing to the bottom, and a short bent tube, which just passed through the stopper. The long tube was connected with the end A of the laboratory vessel, whilst the short end was connected with the delivery tube leading to the collecting flask. The test-tube was rather more than three parts filled with acid. The acid was titrated before and after the passage of 800 c.c. of air, with a very dilute ammonia solution. The latter was standardised for every experiment with standard hydrochloric acid, which also was standardised from time to time with both silver nitrate and sodium carbonate. Experiments were made to ascertain whether a second absorption tube was required, but it was found that one tube of acid, containing 50 c.c. of acid (1 c.c. = 0.000475 gram HCl), absorbed all the ammonia.

With ammonium acetate, the following values were obtained on different days with different solutions.

Grams of ammonia absorbed in the acid :

	N.	N/5.	N/25.
A.	0.0323	0.00861	0.00169
B.	0.0322	0.00816	0.00163

To compare the absorption method with the conductivity method in the least favourable cases of the latter, measurements of N/5 salicylate may be quoted.

Two experiments gave 1042 and 1030 for resistances, the mean of these corresponding to 0.00111 gram of ammonia. By the absorption and titration method, the estimated ammonia was 0.001145 gram.

Reduction of Resistances to Percentage of Ammonia.

In order to reduce the numbers obtained for the resistance of the ammonia solution to percentages of ammonia, it was necessary to plot a curve for the specific resistance of dilute ammonia solution, and read off the values corresponding to the specific resistance of the solution.

There are two sets of figures at 25° for the conductivity of ammonia, and a third set at 18°. The first mentioned are by Ostwald (*Allg. Chem.*, 1893) and Bredig (Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*), and the latter by Kohlrausch (Landolt and Börnstein, *Phys. Chem. Tabellen*). For dilutions such as those dealt with in this

paper, these figures do not agree among themselves, and when the curves are plotted side by side it is seen that Kohlrausch's curve and Bredig's curve run parallel, and that when the latter is corrected by the temperature-coefficient for the dilute ammonia, the two curves differ by about 10 per cent., Kohlrausch's figures for the resistance due to a given percentage of ammonia being about 10 per cent. higher than those of Bredig.

Ostwald's curve almost touches Kohlrausch's at 0.025 per cent. ammonia, but then diverges and cuts Bredig's at the point corresponding to 0.0125 per cent. of ammonia.

The difference between these curves was sufficient to make it necessary for the author to determine a curve of resistance for dilute ammonia, and it was obviously most satisfactory to do this part of the work under conditions as similar as possible to those under which the resistances to be converted were obtained.

The method adopted was to pass air through a solution of ammonia in the laboratory vessel, absorb the issuing ammonia in conductivity water in the cell, and determine the resistance. It was found, as will be shown, that the ratio of the escaping ammonia to the total ammonia in the laboratory vessel was constant, and for the conditions of the experiments was 87.5 per cent.

The ammonia solution was prepared by mixing pure ammonium nitrate and a solution of freshly prepared potassium hydroxide in conductivity water in a Jena distilling flask. The arm of the flask passed into an ordinary Jena flask fitted with a doubly-bored rubber stopper, the second hole of which carried a potash tube. A current of washed hydrogen was then passed through the two flasks for several minutes and the distilling flask gently warmed. The ammonia dissolved in the conductivity water, and the distilling flask was removed. The latter was replaced by a burette fitted with a potash tube, and the ammonia solution was drawn up into the burette. It was then titrated against $N/100$ hydrochloric acid. To perform an experiment, a few c.c. of the titrated ammonia solution were run into a small graduated flask containing conductivity water, and the volume was made up to 100 c.c. Fifty c.c. were then introduced into the laboratory vessel, and the other experimental conditions were precisely similar to those already described. During these experiments care was taken to keep the air of the laboratory as free as possible from carbon dioxide.

Two series of experiments with different ammonia solutions were performed. The agreement was satisfactory.

SERIES I.		SERIES II.	
Ammonia in laboratory vessel.	Resistance in cell.	Ammonia in laboratory vessel.	Resistance in cell.
0·000391	2056	0·000759	1321
0·000860	1216	0·001518	939
0·0001955	2990	0·000455	1880
0·0000977	4200	0·001897	840
0·0003333	2311	One c.c. of the ammonia solution contained 0·0000759 gram of ammonia.	
0·000489	6601		
0·0001075	1077		
One c.c. of the ammonia solution in the burette contained 0·0000782 gram of ammonia.			

From these values a curve of resistances of the ammonia in the cell was plotted and used for converting the other resistances into percentages of ammonia. The proportion of free ammonia passing from the laboratory vessel into the cell was stated above to be 87·5 per cent. This was shown as follows.

A solution of ammonia free from carbon dioxide, prepared in the manner previously described, was titrated against standard acid. Of this solution, a measured quantity was run from the burette into a graduated flask and the volume made up to 200 c.c. Fifty c.c. were now drawn into the laboratory vessel and 800 c.c. of air aspirated through it in the usual manner. The issuing air passed through standard acid which was titrated before and after the experiment.

The following experiments were performed :

The original ammonia solution contained 0·001643 gram per c.c.

The standard acid used for absorption was titrated against the original ammonia solution before and after the experiment. Thus the difference between the two values gave the amount of ammonia absorbed by the acid.

Ammonia introduced into the vessel in c.c.	Ammonia passing into the acid in c.c.	Mean.
15·0	13·25 } 13·15 } 13·15 }	13·18
10·0	8·70 } 8·70 }	8·70
5·0	4·35 } 4·40 }	4·375
2·50	2·20 } 2·15 }	2·183
1·25	2·20 } 1·10 }	1·10

The ratio of the ammonia in the vessel to the escaping ammonia absorbed by the acid is consequently :

$$1 : 0·879, 1 : 0·870, 1 : 0·875, 1 : 0·873, 1 : 0·880.$$

The ratio may thus be considered constant, and it may be assumed that 87.5 per cent. of the ammonia passes from the laboratory vessel into the cell under the conditions of the experiments.

Effect of Dissolved Salts on the Escape of Ammonia.

In the hydrolysis of ammonium salts with water, the amount of free ammonia in the salt solution is small compared with that of the total salt dissolved. It was necessary to ascertain what influence the dissolved salt had on the rate of escape of ammonia under the conditions of these experiments. Raoult (*Ann. Chim. Phys.*, 1874, [v], 1, 262), who used strong solutions, states that ammonium chloride decreases the solubility proportionally to the amount present, but that ammonium nitrate has no effect. The latter statement was confirmed by Gaus (*Zeit. anorg. Chem.*, 1900, 25, 236).

Perman (*Trans.*, 1902, 81, 482) gives details of two series of experiments, from which he concludes that ammonium chloride may form a complex molecule with ammonia and that the effect of this is to decrease the vapour pressure of the ammonia. He, however, was working with very strong solutions of ammonia (12—15 per cent. NH_3), and his conclusions were derived from a comparison with an ammonia solution containing the same percentage of ammonia and water. If the comparison is made with a solution containing the same mass of ammonia in unit volume, it is seen that the effect of the ammonium chloride is to increase the vapour pressure, or to decrease the solubility to the ammonia. Perman's figures also seem to show that the alteration in vapour pressure increases with the amount of salt in solution.

It was necessary, therefore, to determine what happened with such concentration of salt as the author was using.

To ascertain the effect of ammonium salts on the rate of escape of ammonia from its solutions under the conditions of the author's work, the following experiments were made.

A dilute solution of pure ammonia was prepared, 50 c.c. of this introduced into the laboratory vessel, which, as in all cases, was heated in the water-bath and 800 c.c. of air passed through it, the issuing air and ammonia passing through a tube of standardised acid. The conditions of this experiment were in all respects similar to those previously described. The acid was subsequently titrated with dilute ammonia. In another experiment, a gram-molecular solution of ammonium nitrate was made up in some of the ammonia solution and 50 c.c. of this used in the laboratory vessel, and in a third case ammonium chloride was used.

Two series of experiments with different ammonia solutions, which, accidentally, were of the same strength, gave:

SERIES A.

Fifty c.c. of each solution used.	
Ammonium chloride (10.7 grams in 200 c.c. of ammonia solution).....	44.75 c.c.
Ammonium nitrate (18.0 grams)	44.70 „
Ammonia solution alone	44.70 „
The amount of ammonia required before passing air was	52.70 „

SERIES B.

Ammonium chloride as above	44.70 c.c.
Ammonium nitrate „ „	44.75 „
Ammonia solution alone	44.70 „

It may thus be concluded that the dissolved salts do not exert any influence on the escape of ammonia when the amount of the latter is small compared with that of the dissolved salt.

There seems no doubt, therefore, that the ammonia evolved under the conditions of the author's experiments is a measure of the relative hydrolysis of the salts used.

The Conductivity Water.

The water used in these experiments, both for preparing the solutions of the salts and for the absorption of the ammonia, was made by distilling tap-water (which had been well boiled for ten minutes) through a dilute solution of permanganate acidified with dilute sulphuric acid and then through a solution of permanganate made alkaline with potassium hydroxide. The two permanganate solutions were contained in Jena flasks of 1000 c.c. capacity and were kept about one-third full.

The issuing steam passed through a trap and was finally condensed in a specially kept Jena flask. With this apparatus it was easy to get a sufficient supply of water with a conductivity not greater than 1.5×10^{-6} at 18°.

The cells were standardised by comparison with solutions of potassium and sodium chloride at 18.0°, and the following values were obtained.

Solution.	Cell 1.	Cell 2.
(1) <i>N</i> /50 Sodium chloride	0·09041	0·06609
(2) <i>N</i> /50 Sodium chloride	—	0·06609
(3) <i>N</i> /500 Sodium chloride	0·09025	0·06549
(4) <i>N</i> /500 Sodium chloride	0·09029	—
(5) <i>N</i> /500 Sodium chloride	0·09020	—
(6) <i>N</i> /100 Potassium chloride	0·09031	0·06597
Mean	0·09024	0·06591

Hence the ratio of the cells to one another was 0·09024 to 0·06591, or 1·369 to 1·000. The first three values were determined before the commencement of the work, but the values in experiments (4), (5), and (6) were obtained during the research, (6) being taken on the completion of the experimental portion. The value of the cells had, consequently, not changed during the work.

The Salts.

The salts used were the chloride, chlorate, nitrate, sulphate, oxalate, salicylate, succinate, citrate, benzoate, acetate, and formate. Of these the organic salts were kindly supplied by Dr. Veley, whilst the others were recrystallised from good specimens in the laboratory. An exception must be made in the case of the chlorate, which was prepared from barium chlorate in the usual manner. It gave no trace of chloride after two crystallisations. The organic salts were all recrystallised with the exception of the citrate, and had all been supplied originally by Kahlbaum.

The ammonium acetate was dried over solid potassium hydroxide in an atmosphere containing ammonia gas, after the crystals had been dried as far as possible on blotting-paper.

In addition to the above, fine crystalline specimens of the ammonium salts of monochloroacetic and trichloroacetic acids were prepared. Unfortunately both decomposed under the conditions of the experiment, the former yielding a considerable amount of hydrochloric acid and the latter chloroform.

The Solutions.

The solutions were made by weighing out exact quantities of the salts in a weighed beaker and making up to 200 c.c. with conductivity water. The strengths used were normal, fifth-normal, and twenty-fifth normal. The solutions were always used immediately after being prepared, and the following table gives the measurements obtained.

Salt,	Normal.		0.2 normal.		0.4 normal.	
	Cell 1.	Cell 2.	Cell 1.	Cell 2.	Cell 1.	Cell 2.
Chloride	3550	(2595)	—	3470	—	5549
	—	2420	—	3577	7314	(5345)
Nitrate	3423	(2495)	5198	(3796)	7611	(5559)
	—	2638	—	3602	—	5443
Chlorate.....	—	2495	—	3569	7156	(5227)
Salicylate	—	—	—	1030	3172	(2317)
	—	—	1427	(1042)	—	2223
Succinate	—	—	—	830	2399	(1752)
	—	—	—	—	—	1639
Formate.....	—	—	—	—	—	1345
Sulphate	—	1048	2298	(1678)	—	2681
	—	—	—	1662	—	2780

The numbers in brackets are the values for cell 1 divided by 1.369, and hence would be the resistances of the solution in cell 2.

As previously stated, the conductivity method was not accurate when the resistance in the cell was less than 1000 ohms, but in such cases the titration method already described could easily be applied. As an example of two experiments, we have :

Ammonium acetate, $N/1$ solution, 50 c.c. acid used for absorption.

Ammonia solution used for titration, 1 c.c. = 0.00087 gram ammonium hydroxide.

Before absorption, 50 c.c. acid = 114.00 c.c. ammonia, after absorption = (a) 77.30, (b) 76.50, mean = 76.90; hence ammonia absorbed = $37.1 \times 0.00087 = 0.0323$ grams.

By using the above method as a supplement to the conductivity method, the following table was obtained. In it the resistances are converted into ammonia, which is given as the actual amount passing over from the laboratory vessel.

In all cases except that of the chlorate, the values are the mean of at least two concordant results. In the case of the chlorate, the values are for single experiments.

Salt.	$N/1$.	$N/5$.	$N/25$.
Chloride	0.000255	0.000118	0.0000523
Nitrate	0.000243	0.000111	0.0000520
Chlorate	0.000256	0.000119	0.0000559
Sulphate	0.001015	0.000443	0.000213
Salicylate	0.00552	0.00113	0.000301 *
Benzoate	0.01998	0.00378	0.000798
Acetate	0.03230	0.00838	0.00166
Formate	0.01121	0.00225	0.000640 *
Succinate	0.00990	0.00200	0.000420
Oxalate	0.0088	0.00185	—
Citrate.....	0.01217	0.00574	0.00272
Monochloroacetate...	0.0024	—	—

* Values high; obtained by conductivity method; probably slight decomposition and evolution of carbon dioxide, hence lowering the resistance in the cell.

In the case of dibasic acids, half molecular weights were dissolved in a litre of normal solution.

In the preceding table we have several sets of cases. There are monobasic, dibasic, and tribasic acids, and the two former contain both weak and strong acids.

Monobasic Acids.

These form only one simple salt, and consequently only one type of hydrolysis is possible. According as the acid is strong or weak, the equation for the hydrolysis constant will be

$$\frac{C_{\text{AH}} \times C_{\text{BOH}}}{C_{\text{salt}}} = K, \text{ or } \frac{C_{\text{AH}} \times C_{\text{BOH}}}{C_{\text{salt}}^2} = K.$$

Dibasic Acids.

In the case of the salts of dibasic acids, hydrolysis may take place in two ways :

- (1) $\text{A}''\text{B}'_2 + \text{H}_2\text{O} = \text{A}''\text{BH} + \text{BOH}.$
- (2) $\text{A}''\text{B}'_2 + 2\text{H}_2\text{O} = \text{A}''\text{H}_2 + 2\text{BOH}.$

Where the amount of hydrolysis is small, as in the above experiments, it may be assumed that the first of these equations holds, and the equation for the hydrolysis constant becomes $K = \frac{C_{\text{ABH}} \times C_{\text{BOH}}}{C_{\text{salt}}}$ or $K = \frac{C_{\text{ABH}} \times C_{\text{BOH}}}{C_{\text{salt}}^2}$, according as the acid is strong or weak.

These equations may be written $K = \frac{C_{\text{BOH}}}{C_{\text{salt}}}$ or $K = \frac{C_{\text{BOH}}}{C_{\text{salt}}^2}$ respectively.

If in the above equations we take the ammonia liberated under the conditions of the experiment as C_{BOH} , we have a means for calculating the hydrolysis constant of the solutions used.

In the following table, the equation $K = \frac{C_{\text{BOH}}}{C_{\text{salt}}}$ has been used for the first four acids, whilst for the rest, $K = \frac{C_{\text{BOH}}}{C_{\text{salt}}^2}$.

Salt.	$K \times 10^5.$			$\sqrt{K} \times 10^4.$		
	<i>N.</i>	<i>N/5.</i>	<i>N/25.</i>	<i>N.</i>	<i>N/5.</i>	<i>N/25.</i>
Chloride	0.00650	0.00690	0.00684	2.55	2.62	2.61
Nitrate	0.00591	0.00605	0.00657	2.43	2.46	2.57
Chlorate	0.00655	0.00708	0.00731	2.56	2.66	2.70
Sulphate	0.103	0.100	0.114	10.15	10.00	10.69
Oxalate	7.74	8.51	—	88.0	92.5	—
Succinate	9.80	10.0	11.0	99.0	100.0	105.0
Formate	12.4	12.6	—	112.1	112.5	—
Benzoate	39.9	34.9	39.8	199.8	189.0	199.5
Acetate	104.0	175.0	172.0	323.0	419.0	415.0
Monochloroacetate	0.576	—	—	24.0	—	—
Salicylate	3.03	3.19	—	55.2	56.5	—

In the foregoing table, the values for K are as constant as can be expected from the experimental method. It may be noted that the nitrate and chlorate behave quite normally, and that the formate gives also a satisfactory result.

The value for the normal solution of the acetate is abnormal. This does not seem to be due to experimental error, since two sets of experiments with different solutions gave concordant results. In this respect, attention may be directed to Veley's figures for the acetate. He found that the normal solution gave a little more than half the percentage of ammonia which was given by 0.2 normal and more dilute solutions, and since the acetate is the salt of the weakest acid used, the figures for this salt should be the most accurate. It therefore appears that in concentrated solution the acetate is proportionately less dissociated.

If we take the inverse of the above figures, we ought to find $1/K$ proportional to the dissociation constants of the acids the salts of which are used, and $\sqrt{1/K}$ proportional to the avidities of the acids obtained by dynamical methods. Since, however, the dissociation constants of the strong acids cannot be used for comparison, we must use the molecular conductivities of their solutions and compare these with $\sqrt{1/K}$. In the following table are given the values for $\sqrt{1/K}$ (hydrochloric acid = 1), also the ratios of the molecular conductivities, and the values for the avidities of the acids obtained from the velocity of decomposition of methyl acetate and the inversion of cane sugar.

Salt.	$\sqrt{1/K}$.	Molecular conductivity.	Inversion of cane sugar.	Decomposition of methyl acetate.
Chloride.....	1.000	1.000	1.000	1.000
Nitrate	1.065	0.991	1.000	0.915
Chlorate.....	0.985	1.000	1.035	0.944
Salicylate	0.046	0.032	—	—
Formate	0.023	0.017	0.015	0.013
Benzoate	0.013	0.008	—	—
Acetate	0.006	0.004	0.004	0.0034
Monochloroacetate ...	0.106	0.049	0.048	0.013
Sulphate	0.262	0.625	0.536	0.541
Oxalate	0.029	0.197	0.185	0.174
Succinate	0.026	0.006	0.005	0.005

NOTE.—In the above table, the conductivities for salicylic and benzoic acids which will not form normal solutions have been calculated from their ratios to acetic acid at lower dilutions.

In discussing the above results, we may first take the monobasic acids. Here we find a very good agreement both in order and magnitude with the figures obtained by any of the other methods. The strong acids are almost equal and the ratio of the four weak acids is the same as that of the conductivities. The agreement here is particularly striking, the ratios being :

	Salicylic.	Formic.	Benzoic.	Acetic.
$\sqrt{1/K} \propto$	0.032	0.016	0.0087	0.004
Conductivities	0.032	0.017	0.003	0.004

Or we may compare $1/K$ with the dissociation constants of these acids, in which case, again making the values for salicylic acid the same, we obtain :

	Salicylic.	Formic.	Benzoic.	Acetic.
$1/K \propto$	102	26.0	8.2	1.8
Diss. const. $\times 10^8$	102	21.4	6.0	1.8

Here again the numbers are distinctly of the same order of magnitude. It will be noted in the table, that when hydrochloric acid is taken as the standard for comparison, the weak monobasic acids give slightly higher figures than are given by the conductivities, &c. In this connection it may be suggested that the discrepancy is due to the different temperature-coefficients of strong and weak acids, the conductivities being at 25° and the author's experiments at nearly 100° . It would not appear likely that it is due to experimental error, either in the curve for the resistance of ammonia solutions or in the other observations, since the values obtained for K in the different dilutions are so closely constant.

Dealing next with dibasic acids, we have to remember that, in the hydrolysis of a salt of a dibasic acid, the ammonia neutralising the weaker acid hydrogen is removed first. Thus the method described could not be used to measure the strength of the first hydrogen (or ionisation). That it depends on both the ionisation constants is shown below. With dibasic acids we have :

$$K_1 C_{AH_2} = C_{AH'} \times C_{H'} \text{ and } K_2 C_{AH'} = C_{A''} \times C_{H'},$$

where K_1 and K_2 are the first and second ionisation constants.

Now

$$C_{NH_4^+} + C_{NH_4OH} = C_{A''} + C_{AH'} + C_{AH_2} \quad . \quad . \quad . \quad (1).$$

and (positive = negative charges)

$$C_{NH_4^+} + C_{H^+} = 2C_{A''} + C_{AH'} + C_{OH'},$$

where $C_{H'}$ and $C_{OH'}$ are very small and may be neglected, so that

$$C_{NH_4^+} = 2C_{A''} + C_{AH'} \quad . \quad . \quad . \quad . \quad . \quad (2).$$

From (1) and (2) we get

$$C_{NH_4OH} + C_{A''} = C_{AH_2} \quad . \quad . \quad . \quad . \quad . \quad (3).$$

But

$$\begin{aligned} C_{NH_4^+} &= 2C_{A''} + C_{AH'} = 2C_{A''} + \frac{C_{A''} \times C_{H'}}{K_2} \\ &= C_{A''} \left(2 + \frac{C_{H'}}{K_2} \right) \quad . \quad . \quad . \quad . \quad . \quad (4). \end{aligned}$$

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Similarly from (1),

$$\begin{aligned}
 C_{\text{NH}_4^+} + C_{\text{NH}_4\text{OH}} &= C_{\text{A}''} + C_{\text{AH}'} + \frac{C_{\text{AH}'} \times C_{\text{H}^+}}{K_1}, \\
 &= C_{\text{A}''} + C_{\text{AH}'} \left\{ 1 + \frac{C_{\text{H}^+}}{K_1} \right\}, \\
 &= C_{\text{A}''} + \frac{C_{\text{A}''} \times C_{\text{H}^+}}{K_2} \left\{ 1 + \frac{C_{\text{H}^+}}{K_1} \right\}, \\
 &= C_{\text{A}''} \left\{ 1 + \frac{C_{\text{H}^+}}{K_2} + \frac{C_{\text{H}^+}^2}{K_1 K_2} \right\} \quad \dots \quad (5);
 \end{aligned}$$

from (4) and (5),

$$C_{\text{NH}_4\text{OH}} = C_{\text{A}''} \left\{ \frac{C_{\text{H}^+}^2}{K_1 K_2} - 1 \right\},$$

and hence

$$\begin{aligned}
 \frac{C_{\text{NH}_4\text{OH}}}{C_{\text{NH}_4^+} + C_{\text{NH}_4\text{OH}}} &= \frac{C_{\text{A}''} \left\{ \frac{C_{\text{H}^+}^2}{K_1 K_2} - 1 \right\}}{C_{\text{A}''} \left\{ 1 + \frac{C_{\text{H}^+}}{K_2} + \frac{C_{\text{H}^+}^2}{K_1 K_2} \right\}}, \\
 &= \frac{C_{\text{H}^+}^2 - K_1 K_2}{K_1 K_2 + K_1 C_{\text{H}^+} + C_{\text{H}^+}^2}.
 \end{aligned}$$

That is, the relative amount of hydrolysis is proportional to a term involving both the first and second ionisation constants.

The Percentage Hydrolysis in Solutions of Ammonium Salts at 100°.

This may be to some degree determined from the above data; thus, in normal ammonium chloride we have 17 grams of ammonia (combined) per litre, and in the laboratory vessel (50 c.c.) we have 0.85 gram. But the free ammonia is 0.000255×1.143 (the inverse of the partition coefficient for ammonia, 0.875).

Thus the percentage hydrolysis is $\frac{100 \times 0.000291}{0.85} = 0.0341$ per cent.

Similarly, for *N*/5 acetic acid we get

$$\frac{0.0323 \times 1.141 \times 100}{0.85} = 4.34 \text{ per cent.}$$

These values are doubtless too high, since, as ammonia is evolved from the solution, hydrolytic action, to a less degree, continues.

They cannot be compared with values obtained by other methods, as the author is not aware of any determined at so high a temperature.

Conclusions.

1. The hydrolysis of ammonia salts with water is in accordance with the laws of mass action for salts of strong and weak acids.
2. This hydrolytic dissociation is inversely proportional to the "strength" of the acid, that is, to the square of the conductivities of solutions of the acid, or their ionisation constants, in the case of univalent acids only.
3. In the case of bivalent acids, the relation between hydrolytic dissociation of salts and the two ionisation constants of the acids is complicated, and the hydrolysis cannot be used as a direct measure of either of the ionisation constants or the "strength" of either of the acid hydrogen atoms in the acid.
4. Certain maximum values are determined for the degree of hydrolysis at 100°.

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