hundred times as muchus eless heat as the total radiation of the firefly for equal luminosity. In other words, the firefly is the most efficient light source known. This is illustrated by the energy distribution curves from several light sources taken from Prof. Langley's work (Fig. 4). The difficulties attendant upon the accurate determination of the curve for the firefly are so great that we ought not to expect very great accuracy in this case. These curves, which in each case refer to the energy after passing through glass, which cuts off energy of long wave lengths, represent the same quantities of radiant energy. While the sun is much more efficient than the gas flame or carbon arc, it still presents far the largest part of its energy in the invisible long wave lengths (above 0.8), while the firefly seems to have its radiant energy confined to a narrow part of the visible spectrum.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 46.]

THE HYDROLYSIS OF AMMONIUM ACETATE AND THE IONIZATION OF WATER AT HIGH TEMPERATURES.

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Contents.

1. Outline of the Investigation.

In a paper from this laboratory published six years ago[1] an apparatus and method were described by which accurate measurements of the electrical conductivity of aqueous solutions could be made at temperatures up to 306°. In a second paper[2] were presented the results of the measurements of the conductivity of aqueous solutions of various salts, bases, and acids, and the ionization relations of these substances were discussed. The purpose of the research to be described in this article was to study another phenomenon—that of the hydrolysis of salts into

[1] THIS JOURNAL, **26**, 134–170 (1904).

[2] *Ibid.*, **30**, 335–352 (1908).

free acid and base—by measuring the change of conductance produced by adding an excess of the weak acid or base. Since the degree of hydrolysis is dependent on the degree of ionization of the water, this important quantity can be computed from it, when the knowledge of the hydrolysis is supplemented by that of the ionization of the acid and base involved. In this research there have been made measurements of the hydrolysis of ammonium acetate and of the ionization of ammonium hydroxide and acetic acid at temperatures of 100, 156, 218, and 306°.

The method employed for determining the hydrolysis is in principle that described first by Walker,[1] and later in more exact form by Bredig.[2] It consists in measuring the change in conductance produced by adding to the salt solution, in which the salt is partially hydrolyzed, a sufficient quantity of the slightly ionized acid or base to reduce the hydrolysis appreciably, and in computing, from the change produced by different quantities of acid or base added, the degree of hydrolysis. In this case it was practicable to reduce the hydrolysis by the addition of an excess both of the acid and of the base, since both are only slightly conducting substances; and in this case there results an increase in conductance corresponding almost exactly to that of the new quantity of ammonium acetate produced out of the free acid and base originally present.

The calculation of the ionization constant of water from the hydrolysis of the salt involves, as stated, a knowledge of the ionization constants of the acid and base. The determination of the former quantity therefore involves measurements of the conductance at various concentrations of solutions of the following substances; ammonium acetate; ammonium acetate with varying proportions of ammonium hydroxide and of acetic acid; ammonium hydroxide; acetic acid; ammonium chloride; sodium acetate; sodium chloride; sodium hydroxide; and hydrochloric acid. Measurements with dilute solutions of the last five substances are needed for the computation of the equivalent conductance at zero concentration of ammonium hydroxide and acetic acid. The results of such measurements with the last three substances have been previously published in THIS JOURNAL. The data for ammonium chloride and sodium acetate will be presented in this article.

2. Apparatus and Method of Procedure.

The conductivity cell used was like that previously described.[3] It consisted of a platinum-lined steel bomb, through the bottom of which passed a platinum electrode insulated from the bomb by being supported upon a quartz cylinder or by being contained in a quartz cup.

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[1] *Z. physik. Chem.*, 4, 333 (1889).

[2] *Ibid.*, 13, 214–321 (1894).

[3] THIS JOURNAL, 26, 135–141 (1904).

The method of making the measurements was also in general similar to that followed in the previous researches in this laboratory. For a full description of the experimental procedure, of the preparation of the substances and analysis of the solutions, of the corrections applied for the conductance of the water and for contamination, and of all other experimental details, and also for a record of the original observations, the reader is referred to the more complete publication of this work which has been issued by the Carnegie Institution of Washington.[1] In this briefer article only the final results and the computations and conclusions based upon them will be presented.

3. Equivalent Conductance of Ammonium Chloride and Sodium Acetate.

Since ammonium chloride and sodium acetate are appreciably hydrolyzed at high temperatures (thus in 0.01 normal solution about 1.6 per cent. at 218° and 3.4–4.1 per cent. at 306°), the conductance of these salts was measured (except at 18 and 25°) in the presence of a greater or less proportion of ammonium hydroxide or of acetic acid;[2] and from the result was subtracted the conductance of the base or acid calculated from the ionization constants (given in Section 6) with the aid of the mass-action relations, $C_{OH} = K_B.C_{NH_4OH}/C_{NH_4}$ and $C_H = K_A C_{HAc}/C_{Ac}$. The measurements with ammonium chloride at 18, 100, and 156° were made by Prof. Yogoro Kato; at 18, 25, 218, 306° by Dr. R. B. Sosman; those with sodium acetate were made at 18, 100, 156 and 218° by Dr. H. C. Cooper;[3] and at 306° by Dr. R. B. Sosman.

Table 1 contains the final values derived from all these measurements by correcting the observed data for all known sources of error, so that they represent only the conductance of the pure unhydrolyzed salts. The concentration given in the second column represents the number of milli-equivalents of salt contained in one liter of solution at the temperatures corresponding to the conductance values given in the following columns. The latter are expressed in reciprocal ohms. In regard to the values at zero concentration see the next section. The temperatures are those on the hydrogen-gas scale (based at 218 and 306° upon the results of Jaquerod and Wassmer[4]).

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[1] Publication No. 63 of the Carnegie Institution of Washington entitled "The Electrical Conductivity of Aqueous Solutions." This monograph may be obtained from the Institution at the rate of $2.50 per copy. The work with which this article is directly concerned will be found in Parts VI and VII of the publication.

[2] The ratio of NH_4OH to NH_4Cl in equivalents was 0.1 at 100 and 156°, about 0.5 at 218° and 1.0 to 4.6 at 306°. The ratio of $HC_2H_3O_2$ to $NaC_2H_3O_2$ was about 0.2–0.6 at 156 and 218° and 1.1 to 4.1 at 306°.

[3] These have been already published in THIS JOURNAL, **30**, 306, but are included here for the sake of completeness.

[4] *J. chim. phys.*, **2**, 52 (1904).

TABLE 1.—THE EQUIVALENT CONDUCTANCE OF AMMONIUM CHLORIDE AND SODIUM ACETATE.

Substance.	Concentration.	18°.	25°.	100°.	156°.	218°.	306°.
NH_4Cl	0	130.9	152.0	415	628	841	1176
	2	126.5[1]	146.5	399	601	801	1031
	10	122.5	141.7	382	570	758	925
	12.5	121.5	...	379	567	..	..
	30	118.1	...	...	..	..	828
$NaC_2H_3O_2$	0	78.1	...	285	450	660	924
	2	74.6	...	267.6	421	578	801
	10	71.2	...	253.3	396	542	702
	30	...	...	...	..	..	613
	80	63.4	...	221.0	340	452	..

4. Equivalent Conductance at Zero Concentration of the Various Substances.

The values of the equivalent conductance (Λ_0) at zero concentration for ammonium chloride and sodium acetate were obtained by extrapolation with the aid of the equation $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$. This when written in the form $1/\Lambda = 1/\Lambda_0 + K_1(C\Lambda)^{n-1}$ may be conveniently employed graphically by plotting $1/\Lambda$ against $(C\Lambda)^{n-1}$, the exponent $n - 1$ being taken equal to that value in the neighborhood of 0.5 which is found by trial to give most nearly a straight-line graph.[2] The values of Λ_0 for these two substances, already given in Table 1, are reproduced in Table 2, together with those previously determined for the various other substances which are needed in calculating the values of Λ_0 for ammonium hydroxide and acetic acid by means of the relations:

$$\Lambda_0(NH_4OH) = \Lambda_0(NH_4Cl) + \Lambda_0(NaOH) - \Lambda_0(NaCl)$$
$$\Lambda_0(HC_2H_3O_2) = \Lambda_0(NaC_2H_3O_2) + \Lambda_0(HCl) - \Lambda_0(NaCl).$$

The determinations of Λ_0 for sodium chloride, hydrochloric acid, and sodium hydroxide (up to 156°) have been previously described in THIS JOURNAL.[3] The value for sodium hydroxide at 218 and at 306°, where no measurements or no sufficiently accurate measurements exist, was derived under the assumption that it lies at such a proportional distance between the Λ_0 values for sodium chloride and hydrochloric acid at these temperatures as is indicated by its position between them at the lower temperatures of 18, 100, and 156°.

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[1] This same value (within 0.1) was obtained entirely independently by Prof. Kato and Dr. Sosman, and also by the latter on two separate preparations obtained respectively by recrystallizing the solid salt and by neutralizing ammonium hydroxide and hydrochloric acid.

[2] The exponent for ammonium chloride was assumed to be the same as for potassium chloride at those temperatures where it was not possible to determine it owing to the fact that the measurements did not extend to a higher concentration than 12.5 millinormal.

[3] Vol. 30, p. 339.

TABLE 2.—EQUIVALENT CONDUCTANCE AT ZERO CONCENTRATION.

Substance.	18°.	100°.	156°.	218°.	306°.
NH_4Cl	130.9	415	628	841	1176
$NaC_2H_3O_2$	78.1	285	450	660	924
$NaCl$	109.0	362	555	760	1080
$NaOH$	216.5	594	835	1060	1310
HCl	379	850	1085	1265	1424
NH_4OH	238	647	908	1141	1406
$HC_2H_3O_2$	348	773	980	1165	1268

5. The Equivalent Conductance of Ammonium Hydroxide and Acetic Acid.

In deriving the final values of the equivalent conductance of ammonium hydroxide and acetic acid, all appropriate corrections were applied to the observed data, including that for the conductance of the water and for the small proportion of the ammonia oxidized during the heating. The ammonia used was obtained from two sources—by diluting a specially prepared commercial sample of ammonia water and by distilling liquid ammonia which had stood in contact with sodium. Great care was taken to avoid contamination by the carbon dioxide of the air.

The final values, expressed in the same way as in Table 1, are presented in Table 3. The measurements with acetic acid at 100 and 156° and some of those at 218° were made by Dr. H. C. Cooper; some of those at 218° and all at 306° by R. B. Sosman. Those with ammonium hydroxide at 100 and 156° were made by Yogoro Kato, at 18, 218 and 306° by R. B. Sosman.

TABLE 3.—FINAL VALUES OF THE EQUIVALENT CONDUCTANCE OF AMMONIUM HYDROXIDE AND ACETIC ACID.

Substance.	Concentration.	18°.	100°.	156°.	218°.	306°.
NH_4OH	10.0	9.66	23.25	22.31	15.56	...
	30.0	5.66	13.58	12.99	...	...
	80.0	3.47	...	...	5.39	...
	100.0	3.103	7.47	7.17	4.82	1.329
	300.0	1.752	...	...	...	0.785
	500.0	1.325	...	...	...	...
$HC_2H_3O_2$	10.0	14.50	25.10	22.15	14.70	...
	30.0	8.50	14.70	12.95	8.65	...
	80.0	5.23	9.05	8.00	5.39	...
	100.0	4.68	8.10	...	4.82	1.57
	300.0	2.68	...	...	...	0.84

Values were also obtained for ammonium hydroxide at 100 milli-normal at three temperatures between 18 and 100° and at 125°. These values are as follows:

25°.	50°.	75°.	125°.
3.62	5.35	6.70	7.76

Entirely independent determinations made in this laboratory at different times by Messrs. Yogoro Kato, R. B. Sosman, and C. W. Kanolt have given for 100 millinormal ammonium hydroxide at low temperatures closely concordant values, namely, 3.10, 3.10, and 3.11 at 18°, and 3.62 and 3.61 at 25°. Concordant results were also obtained independently by H. C. Cooper and R. B. Sosman for 100 millinormal acetic acid at 18°, namely 4.67 and 4.685.

6. The Ionization of Ammonium Hydroxide and Acetic Acid.

The values of the ratio 100 Λ/Λ_0 corresponding to the percentage ionization (100γ) are given in Table 4. They were obtained by dividing the Λ values given in Table 3 by the appropriate Λ_0 value given in Table 2.

TABLE 4.—PERCENTAGE IONIZATION OF AMMONIUM HYDROXIDE AND ACETIC ACID.

Substance.	Concentration.	18°.	100°.	156°.	218°.	306°.
NH_4OH............	10	4.05	3.59	2.46	1.36	..
	30	2.38	2.10	1.43	...	..
	80	1.454	..	...	0.47	..
	100	1.302	1.15	0.79	0.42	0.095
	300	0.735	..	...	...	0.0558
	500	0.556	..	...	...	..
$HC_2H_3O_2$..........	10	4.17	3.24	2.26	1.26	..
	30	2.45	1.90	1.32	0.743	..
	80	1.504	1.17	0.815	0.463	..
	100	1.346	1.05	...	0.414	0.124
	300	0.771	..	...	...	0.0663

The values for 100 millinormal ammonium hydroxide at the intermediate temperatures are as follows:

25°.	50°.	75°.	125°.
1.338	1.34	1.27	1.02

The values of the ionization constants were calculated from these data by the expression $K = (C\gamma)^2/C(1-\gamma)$, C being here expressed in equivalents per liter. They are brought together in Table 5. Best values valid for dilute solutions have also been derived, regard being paid to the greater experimental errors in the more dilute solutions and to the deviation from the mass-action law in the more concentrated ones. These are given in italics at the foot of each series.

It is evident from these results that the ionization constant for ammonium hydroxide increases considerably in passing from 0 to 18°, then remains nearly constant up to 50°, and finally decreases with increasing rapidity as higher temperatures are reached, attaining at 306° a value which is only about one two-hundredth of that at 18°. It is also evident that at all temperatures the values for acetic acid are not very different from those for ammonium hydroxide.

TABLE 5.—IONIZATION CONSTANTS × 10^6 OF AMMONIUM HYDROXIDE AND ACETIC ACID.

Substance.	Equivalents per liter.	18°.	100°.	156°.	218°.	306°.
NH_4OH........	0.010	17.1	13.4	6.20	1.89	....
	0.030	17.4	13.5	6.24	...	....
	0.100	17.2	13.5	6.28	1.80	0.090
	0.300	16.3	...	...	...	0.094
	0.500	15.6	...	...	...	....
	Best value	*17.2*	*13.5*	*6.28*	*1.80*	*0.093*
$HC_2H_3O_2$........	0.010	18.2	10.85	5.23	1.61	....
	0.030	18.5	11.04	5.30	1.67	....
	0.080	...	...	5.36	1.69	....
	0.100	18.3	11.14	...	1.72	0.153
	0.300	18.0	...	...	...	0.132
	Best value	*18.3*	*11.14*	*5.36*	*1.72*	*0.139*
		0°	25°	50°	75°	125°
NH_4OH........	0.10	13.9[1]	18.0	18.1	16.4	10.4

7. Conductance of Ammonium Acetate Solutions at 18, 100 and 156°.

Experiments by YOGORO KATO.

The hydrolysis experiments were made by measuring the specific conductance of ammonium acetate solutions containing in one case the salt alone and in other cases the salt together with varying quantities of ammonium hydroxide and acetic acid. In the experiments at the temperatures up to 156°, the observed values of the specific conductance were corrected to round temperatures with the help of temperature coefficients derived from the measurements themselves and then further corrected to uniform concentrations by assuming direct proportionality between the concentration and specific conductance through the small concentration interval involved. The so-reduced values are presented in Table 6. In the columns headed "Initial" are given the equivalent conductances obtained from the measurement at the temperature in question before going to the higher temperatures, while in the columns headed "Final" are given the equivalent conductances obtained after returning to the temperature in question from the higher ones. A comparison of these initial and final values in the separate experiments shows the contamination or destruction of the substance that resulted from the heating.

The final data needed for the computation of the hydrolysis, and the calculated values derived from them are presented in Table 7. The column headed L_M contains the most probable values of the specific conductance derivable from the separate values of Table 6, taking into account the contamination and applying a correction for it. In the next column under L_{HA} or L_{BOH} is given the conductance of the acetic

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[1] This value at 0° is that determined in this laboratory by Kanolt. See *Carnegie Publication*, 63, 290 (1907) or THIS JOURNAL, 29, 1408 (1907).

TABLE 6.—SPECIFIC CONDUCTANCE OF AMMONIUM ACETATE SOLUTIONS AT 18, 100 AND 156°.

			Specific conductance × 10^6.				
	Concentration at 4°.		18°.		100°.		
Expt. No.	$CH_3CO_2NH_4$.	CH_3CO_2H.	Initial.	Final.	Initial.	Final.	156°.
1	26.00	.....	2,281	2,276	6,830	...	8,598
2	26.00	.....	2,282	2,279	6,821	6,816	8,632
Mean	26.00	.....	2,281	2,277	6,825	6,816	8,615
3	10.400	.....	946.6	941.9	2,851	2,841	3,583
4	10.400	.....	946.9	943.4	2,852	2,839	3,581
Mean	10.400	.....	946.7	942.6	2,851	2,840	3,582
5	26.00	26.47	2,291	2,280	7,157	...	9,885
6	26.00	26.47	2,292	2,286	7,158	7,114	9,925
Mean	26.00	26.47	2,291	2,283	7,157	7,114	9,905
7	26.00	52.00	2,295	2,285	7,166	7,125	10,108
8	26.00	52.00	2,293	2,287	7,164	7,128	10,109
Mean	26.00	52.00	2,294	2,286	7,165	7,126	10,108
9	10.400	21.12	964.0	.....	3,016	...	....
10	10.400	21.13	963.2	958.8	3,015	2,991	4,243
Mean	10.400	21.13	963.6	958.8	3,015	2,991	4,243
11	10.400	52.76	983.2	977.8	3,040	3,011	....
12	10.400	52.76	983.9	974.4	....	...	4,318
Mean	10.400	52.76	983.5	976.1	3,040	3,011	4,318
13	10.400	10.569	957.1	954.3	3,000	2,983	4,166
14	10.400	10.577	957.7	955.0	3,002	...	4,170
Mean	10.400	10.573	957.4	954.6	3,001	2,983	4,168
		NH_4OH.					
15	26.00	51.21	2,298	2,303	7,153	...	10,212
16	26.00	51.21	2,298	2,300	7,168	7,164	10,211
Mean	26.00	51.21	2,298	2,301	7,160	7,164	10,211
17	26.00	25.70	2,290	2,291	7,149	...	10,040
18	26.00	25.70	2,291	2,293	7,145	7,145	9,988
Mean	26.00	25.70	2,290	2,292	7,147	7,145	10,014
19	10.400	10.263	954.7	958.5	2,995	2,991	4,186
20	10.400	10.263	954.7	958.4	2,998	2,992	4,185
Mean	10.400	10.263	954.7	958.4	2,996	2,991	4,185
21	10.400	20.52	960.3	965.5	3,010	...	4,292
22	10.400	20.52	961.4	964.8	3,010	3,013	4,286
Mean	10.400	20.52	960.8	965.1	3,010	3,013	4,289
23	10.400	51.29	979.2	984.2	3,043	...	4,403
24	10.400	51.29	980.9	984.4	3,048	3,050	4,398
25	10.400	50.12	976.1	977.6	....	...	4,388
26	10.400	53.54	981.6	987.7	3,053	...	4,408
27	10.400	*43.93	*966.8	*975.3	*3,036	...	*4,391
Mean	10.400	51.56	979.4	983.5	3,048	3,050	4,399

* Values with an asterisk were not included in deriving the mean.

acid or ammonium hydroxide present. This was obtained by first calculating C_{OH} or C_H from the mass-action equations

$$\frac{C_B C_{OH}}{C_{BOH}} = K_B \text{ or } \frac{C_A C_H}{C_{HA}} = K_A,$$

by substituting for C_B or C_A the ratio $L_{BA}/\Lambda_{0\,BA}$ of the specific conductance of the ammonium acetate (BA) to its equivalent conductance when completely ionized, and then multiplying the value of C_{OH} or C_H

TABLE 7.—SPECIFIC CONDUCTANCE OF THE CONSTITUENTS IN AMMONIUM ACETATE SOLUTIONS.

	Concentration at t°.		Specific conductance × 10^6.				
Temperature. t°.	Salt. C_{BA}.	Acid (A) or Base (B). C_{HA} or C_{BOH}.	Mixture. L_M.	Acid or base in mixture. L_{HA} or L_{BOH}.	Salt in mixture. L_{BA}.	Salt alone in water. L_S.	Increase. L_{BA}—L_S.
18°	25.96	26.43 A	2,291	7	2,284	2,281	3
	25.96	25.66 B	2,290	4	2,286	2,281	5
	25.96	52.76 A	2,294	15	2,279	2,281	—2
	25.96	51.14 B	2,298	9	2,289	2,281	8
				Mean	2,285	2,281	4
	10.387	10.559 A	957	7	950	947	3
	10.387	10.249 B	955	4	951	947	4
	10.387	21.09 A	964	14	950	947	3
	10.387	20.50 B	961	9	952	947	5
	10.387	52.69 A	983	35	948	947	1
	10.387	51.49 B	976	22	954	947	7
				Mean	951	947	4
100°	24.92	25.37 A	7,157	10	7,147	6,825	322
	24.92	24.63 B	7,144	9	7,135	6,825	310
	24.92	50.64 A	7,165	20	7,145	6,825	320
	24.92	49.09 B	7,156	19	7,137	6,825	312
				Mean	7,141	6,825	316
	9.970	10.136 A	3,001	9	2,992	2,851	141
	9.970	9.838 B	2,990	9	2,981	2,851	130
	9.970	20.25 A	3,015	19	2,996	2,851	145
	9.970	19.675 B	3,003	19	2,984	2,851	133
	9.970	50.58 A	3,040	48	2,992	2,851	141
	9.970	49.43 B	3,041	47	2,994	2,851	143
				Mean	2,990	2,851	139
156°	23.68	24.11 A	9,964	5	9,959	8,625	1,334
	23.68	23.40 B	10,004	5	9,999	8,625	1,374
	23.68	48.12 A	10,163	13	10,150	8,625	1,525
	23.68	46.64 B	10,196	14	10,182	8,625	1,557
	9.473	9.631 A	4,193	6	4,187	3,596	591
	9.473	9.348 B	4,169	6	4,163	3,596	567
	9.473	19.243 A	4,278	13	4,265	3,596	669
	9.473	18.694 B	4,270	13	4,257	3,596	661
	9.473	48.06 A	4,360	31	4,329	3,596	733
	9.473	46.97 B	4,381	32	4,349	3,596	753

by $\Lambda_{0\,BOH}$ or $\Lambda_{0\,HA}$. The difference of the values of L_M and L_{HA} or L_{BOH} given in these two columns gives the specific conductance L_{BA} of the salt in the mixture. This is given in the sixth column, and in the seventh column is given the calculated conductance of the salt (L_S) when present in water alone at the same concentration as it has in the mixture. The last column headed $L_{BA} - L_S$ gives the increase of conductance caused by the reduction of the hydrolysis produced by the addition of the base or acid.

8. Hydrolysis of Ammonium Acetate and Ionization of Water at 100 and 156°.

From Table 7 it will be seen that the excess of base or acid causes an increase in the conductance of about 5 per cent. at 100° and 15–21 per cent. at 156°. It will also be seen that at 100° the addition of a quantity of acid or base equivalent to the salt produced as great an increase as a larger quantity, showing that the hydrolysis had been reduced substantially to zero. The effect of the acid was, as it should be, nearly equal to that of the base, the small differences observed being doubtless due to experimental error. The percentage increase was also nearly the same at the two concentrations of the salt (4.6 and 4.9 per cent.) respectively, showing that the hydrolysis does not increase much with the dilution, which is what the mass-action law requires for a salt whose acid and base are both weak. At 156° the second equivalent of acid or base produces a large further increase in conductance, showing that the salt is still somewhat hydrolyzed. Here again the acid and base have not far from the same effect, as they should have on account of the smallness of their ionization constants.

The quantitative calculation of the ionization at 100° is comparatively simple. Since the hydrolysis is reduced to zero by the added acid or base, the increase in specific conductance produced by it when divided by the equivalent conductance Λ_0 (338) of the completely ionized salt gives at once the number of equivalents per cubic centimeter of free acid and base which have been converted into ions. In addition a quantity of the un-ionized salt, corresponding to the increased concentration of its ions, is produced out of the acid and base. To compute this, we have made use of the equation $\frac{(C\gamma)^n}{C(1-\gamma-h)} = K$ (where γ is the fraction ionized and h the fraction hydrolyzed), in which we have determined the constants n and K from the conductances (L_{BA}) of the unhydrolyzed salt (7141 and 2990×10^{-6} at the two concentrations (24.92 and 9.97 milli-equivalents per liter) investigated and from the Λ_0 value for the salt. We have then calculated from the values of L/Λ_0 (which are equal to $C\gamma$) the concentration of un-ionized salt, $C(1-\gamma-h)$, both in the solution containing the salt alone and in that to which acid or base had been added.

The excess of the second value over the first value gives the un-ionized salt, $\Delta C(1 - \gamma - h)$, that has been produced out of free acid and base: this added to the quantity $(\Delta C\gamma)$ of ions similarly produced gives the quantity of salt in the hydrolyzed state when it is alone present in water; and this divided by the concentration (C) gives the fraction hydrolyzed (h_0). The results of the computations are given in Table 8.

TABLE 8.—HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION CONSTANT OF WATER AT 100°.

C.	$100\gamma_0$ or $100\,L_S/C\Lambda_0$.	$\Delta(C\gamma)$ or $(L_{BA}-L_S)/\Lambda_0$.	$\Delta(C(1-\gamma-h))$.	Ch_0.	$100h_0$.	$K_W \times 10^{14}$.
24.92	82.2	0.94	0.21	1.15	4.61	48.5
9.97	85.9	0.411	0.064	0.475	4.76	47.4

It will be seen from Table 8 that the hydrolysis h_0 is only a little greater at 10 than at 25 millinormal. From each of these values the ionization-constant of water $(K_w = C_H \times C_{OH})$ has been calculated, and the results are given in the last column, the concentration being here expressed in equivalents per liter. The calculation was made by means of the mass-action expression $K_w = K_A K_B h^2/\gamma^2$ in which K_A and K_B are the ionization-constants of the acid and base respectively, and h and γ are the hydrolysis and ionization of the salt when present in water alone. This expression is obtained by multiplying together the two ionization equations $K_A = C_H C_A/C_{HA}$ and $K_B = C_B C_{OH}/C_{BOH}$, substituting K_w for $C_H C_{OH}$, γC_S for C_A and C_B, and $C_S h_0$ for C_{HA} and C_{BOH}, and transposing. It will be noted that the two independent values of K_w agree almost completely.

In order to calculate the hydrolysis at 156° from the conductance data it is necessary, since the hydrolysis is not reduced to zero even by the largest quantity of acid or base added, to unite with the empirical relation between the concentrations of ions and un-ionized molecules, the mass-action relation between the concentration of the ions and the products of the hydrolysis. These two expressions, if γ represents the fraction of the salt existing as ions and h the fraction hydrolyzed into free acid and base and C_S and C_{BOH} are the concentrations of the salt and of the added base (or acid) respectively, are

$$\frac{(\gamma C_S)^n}{C_S(1 - \gamma - h)} = \text{const.} \qquad (1)$$

and

$$\frac{(\gamma C_S)^2}{(C_{BOH} + C_S h)C_S h} = \frac{\gamma^2}{(C_{BOH}/C_S + h)h} = \frac{K_A K_B}{K_W} = \text{const.} \qquad (2)$$

Or, representing by γ_0 and h_0 the ionization and hydrolysis of the salt when in water alone, and by γ_1 and h_1 these same quantities when the concentration of the salt is the same, but base (or acid) is present in excess at a concentration C_{BOH} and writing r for C_{BOH}/C_S we have:

$$\left(\frac{\gamma_1}{\gamma_0}\right)^n = \frac{1-\gamma_1-h_1}{1-\gamma_0-h_0} \quad (3) \quad \text{and} \quad \left(\frac{\gamma_1}{\gamma_0}\right)^2 = \frac{h_1(r+h_1)}{h_0^2} \quad (4)$$

two simultaneous equations which can be solved for h_0 and h since the other quantities may be derived from the measurements. Thus the ratio γ_1/γ_0 is equal to L_{BA}/L_S (see Table 7), and the separate values of γ_1 and γ_0 are given by the quotients $L_{BA}/C_S\Lambda_0$ and $L_S/C_S\Lambda_0$, Λ_0 being equal to 523. For the exponent n we assumed provisionally the value 1.5, which is that for sodium acetate at this temperature; but after the hydrolysis had been computed for the two different salt concentrations it was obtained by direct application of equation (1) to the mean of the two sets of results, and was thus found to be 1.45; and with this new value of n the calculations were repeated, although this variation in n produced a decrease in h_0 of only 0.7 per cent. of its value both at 23.68 and at 9.473 millinormal. Equations (3) and (4) can be completely solved algebraically for h_1 or h_0, but it is far simpler to use only the incomplete solution obtained by taking the logarithm of equation (3) and eliminating h_0 from it by means of equation (4), whereby results the expression:

$$\log \frac{1-\gamma_1-h_1}{[(1-\gamma_0)\gamma_1/\gamma_0]-\sqrt{h(r+h)}} = (n-1)\log\frac{\gamma_1}{\gamma_0}.$$

This equation can be readily solved for h_1 by trial, and h_0 can then be calculated by (4).

TABLE 9.—HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION CONSTANT OF WATER AT 156°.

C_S.	r.	$100\gamma_0$.	100γ.	$100h$.	$100h_0$.	$K_W \times 10^{14}$.
23.68	1.018 A	70.73	81.66	3.95	17.6	221 A
23.68	0.988 B	70.73	81.99	4.34	18.2	236 B
23.68	2.032 A	70.73	83.23	2.13	17.8	225 A
23.68	1.969 B	70.73	83.49	2.46	18.3	238 B
Mean	......	70.73	...	..	17.97	223 A 237 B
9.473	1.017 A	73.71	85.82	4.40	18.5	224 A
9.473	0.987 B	73.71	85.33	4.16	17.8	208 B
9.473	2.031 A	73.71	87.42	2.30	18.3	219 A
9.473	1.973 B	73.71	87.26	2.33	18.2	217 B
9.473	5.073 A	73.71	88.73	1.00	18.6	226 A
9.473	4.958 B	73.71	89.14	1.06	19.0	236 B
Mean	......	73.71	...	..	18.60	223 A 221 B

The results of the calculations are given in Table 9. The headings will be understood by reference to the preceding paragraph. In computing the ionization constant of water, which was done as before by the expression $K_W = K_A K_B\, h_0^2/\gamma_0^2$, the concentration was expressed in equivalents per liter and the values of K_A and K_B used were 5.67×10^{-6} and $6.28 \times$

10^{-6}, respectively. The letter A after the value of the ratio $r(=C_S/C_B)$ signifies that acetic acid, the letter B, that ammonium hydroxide, was present in excess.

An examination of the values of K_w given in the last column of Table 9 shows that those derived from the experiments where acetic acid was added agree closely with one another not only in case of the successive additions of the acid but also at the two different concentrations of the salt, while those from the experiments where ammonium hydroxide was added are far less concordant whether considered with respect to the successive additions (in the second series) or to the different salt concentrations. This fact, taken in conjunction with the experience that the base solutions are far more liable to contamination, justifies the adoption of the value 223×10^{-14} derived from the experiments with the acid as the best final value for the ionization constant of water at 156°. It is worthy of note, however, that the mean value 229×10^{-14} derived from the experiments with the base is less than 3 per cent. higher than this.

9. Conductance of Ammonium Acetate Solutions at 18, 218 and 306°.

Experiments by R. B. SOSMAN.

The final values for the specific conductance of ammonium acetate solutions at 218 and 306° will next be presented. The observed data were first reduced to round temperatures by means of directly determined coefficients, and were then corrected for the conductance of the impurities

TABLE 10. — SPECIFIC CONDUCTANCE AT ROUND TEMPERATURES OF SOLUTIONS CONTAINING ONLY AMMONIUM ACETATE.

Milli-equivalents per liter.			Specific conductance × 10^6.		
18°.	218°.	306°.	18°.	218°.	306°.
14.57	....	....	1311.5	....	....
14.44	....	....	1302	....	....
14.01	11.81	....	1266	3770	....
14.18	12.01	....	1281.5	3830	....
14.30	*11.91*	....	*1290*	*3800*	....
7.10	5.93	....	656.0	1918.5	....
7.11	6.025	....	657.0	1944.5	....
7.045	5.96	....	651.0	1921.5	....
7.085	*5.97*	....	*654.7*	*1928*	....
43.10	....	....	3691	....	....
43.10	....	29.38	3694	....	2412
43.10	....	29.32	....	....	2394
43.10	....	*29.35*	*3693*	....	*2403*
14.335	....	9.97	1294.5	....	812
14.335	....	10.015	1294.5	....	818
14.335	....	*9.995*	*1294.5*	....	*815*

in the water, for that of the water itself, and for that of the added base or acid. The last two corrections, which never exceeded 0.25 per cent., were computed with aid of the ionization constants of the three substances.

Table 10 contains the so-corrected data for the pure salt, and Table 11 those for the salt with an excess of base or acid. In the latter table are given for 218° and 306° in two additional columns (1) the specific conductance (L_0) which the pure salt has at the same concentration as that (C) of the salt in the mixture, and (2) the ratio of the specific conductance (L) of the salt in the mixture to this conductance L_0. The specific conductance L_0 is calculated from that given in Table 10 for nearly the same concentration under the assumption of proportionality between conductance and concentration through the small interval involved.

TABLE 11.—SPECIFIC CONDUCTANCE AT ROUND TEMPERATURES OF AMMONIUM ACETATE SOLUTIONS CONTAINING AMMONIUM HYDROXIDE OR ACETIC ACID.

	Milli-equivalents per liter.		Specific conductance $\times 10^6$.		
Temperature. t.	Salt in mixture. $C \times 10^3$.	Acid (A) or base (B). C_A or $C_B \times 10^3$.	Salt in mixture. $L \times 10^6$.	Salt in water alone. $L_0 \times 10^6$.	Ratio. L/L_0.
218°	11.94	11.88 A	5057	3809	1.328
	12.015	12.075 B	5010	3833	1.307
	11.90	23.61 A	5651	3797	1.488
	11.92	23.41 B	5482	3803	1.442
	11.825	47.38 A	6173	3773	1.636
	11.875	46.75 B	6093	3789	1.608
	6.08	5.985 A	2606	1963	1.328
	6.00	6.25 B	2563	1944	1.318
	6.04	6.25 B	2562		
	6.10	12.055 A	2944	1969	1.495
	6.025	11.78 B	2875	1944	1.476
	6.015	11.78 B	2863		
	5.975	24.12 A	3207	1930	1.662
	6.015	23.62 A	3150	1942	1.622
306°	28.76	31.91 A	3430	2355	1.457
	27.53	88.6 A	4482	2254	1.988
	28.34	68.4 B	4210	2320	1.815
	9.96	10.025 A	1146	813	1.412
	9.965	10.01 A	1150		
	10.01	8.19 B	1092	816	1.338
	9.855	30.06 A	1589	803	1.979
	9.735	25.22 B	1480	794	1.864

10. Hydrolysis of Ammonium Acetate and Ionization of Water at 218 and 306°.

From the data given in Table 11 the hydrolysis of the salt at 218 and 306° was calculated by two different methods.

The first method was that employed by Noyes and Kato and described in Section 8 of this article.

In the second method the ion concentration is, as before, calculated by dividing the specific conductance of the solution (multiplied by 10^3) by the equivalent conductance of the completely ionized salt; and then the concentration of the un-ionized salt is estimated under the assumption that it has the same value as in a solution of an ordinary unhydrolyzed salt of the same ionic type at the same ionic concentration. Then merely by subtracting the un-ionized fraction (u) and the ionized fraction (γ) from unity, the hydrolyzed fraction (h) is obtained; that is, $h = 1 - \gamma - u$. In this calculation the mean value of the ionization of potassium and sodium chlorides was used as a basis. This calculation can give accurate hydrolysis values only when the hydrolyzed fraction is large and the un-ionized fraction very small; but under such conditions, which are in fact realized in the foregoing experiments fairly well at 218° and in much higher degree at 306°, it is the most direct method and a fairly reliable one.

Table 12 contains the results of the calculations. In the fifth and sixth columns are given the values of the percentage hydrolysis ($100\,h$) calculated by the first and second methods, respectively. In the seventh column is given a mean derived from these. Since the results by the second method are more accurate the greater the hydrolysis, in deriving this mean a weight has been assigned to them equal to the percentage hydrolysis, the results by the first method being always given a weight of 100. It is desirable to combine the results by the two methods in some such way as this, since any error in the conductance ratio L/L_0 influences them in opposite directions. In the last three columns of the table are given the values of the percentage hydrolysis ($100\,h_0$) of the salt in pure water at the same concentration C. The values in the first of these columns are derived by the first method simultaneously with those of $100\,h$. Those in the second of these colums are calculated from the mean value of $100\,h$ given in the seventh column by the equation $h_0{}^2 = \dfrac{h(h + C_B/C)}{(L/L_0)^2}$ Those in the last column are obtained directly by the second method from the conductance in pure water.

A comparison of the values of the percentage hydrolysis ($100\,h$) of the salt in the mixture calculated by the two methods shows at 218° a considerable divergence, especially in the experiments where an excess of base was added. This was doubtless due largely to the destruction of some of the base during the heating. At 306° where this was determined and allowed for, and where the calculation by the second method is more accurate, the agreement is far more satisfactory (except in the first experiment which appears to be affected by some accidental error). From an examination of the values of the percentage hydrolysis ($100\,h_0$) of the salt in pure water it is seen that the experiments in which different

TABLE 12.—HYDROLYSIS AND IONIZATION OF AMMONIUM ACETATE AT 218 AND 306°.

			Salt in mixture.				Salt in pure mixture.			
				Percentage hydrolysis (100h).				Percentage hydrolysis (100 h_0).		
Temperature. t.	Concentration of salt. $C \times 10^3$.	Concentration ratio. C_A/C or C_B/C.	Ionization 100γ.	By first method.	By second method.	Weighted mean.	Ionization 100γ_0.	By first method.	From value of h.	By second method
218°	11.91	0	...	..	..	..	43.1	..	..	53.3
	11.94	0.995 A	57.2	35.5	37.4	36.0	43.1	52.1	52.6	..
	11.90	1.984 A	64.1	26.2	29.5	27.0	43.1	51.6	52.4	..
	11.825	4.007 A	70.5	16.5	22.3	17.6	43.1	50.7	51.7	..
	Mean,	....	...	..	..	..	...	51.5	52.2	..
	12.015	1.005 B	56.3	29.6	38.4	32.0	43.1	47.5	49.8	..
	11.92	1.964 B	62.1	21.5	31.8	24.0	43.1	47.4	50.5	..
	11.875	3.937 B	69.2	15.5	23.7	17.1	43.1	49.5	52.1	..
	Mean,	....	...	..	..	..	...	48.1	50.8	..
	5.97	0	...	..	..	..	43.6	..	..	53.7
	6.08	0.984 A	57.8	36.0	38.0	36.5	43.6	52.4	52.9	..
	6.10	1.976 A	65.1	27.1	30.0	27.8	43.6	52.2	52.9	..
	5.975	4.037 A	72.4	17.6	22.0	18.4	43.6	51.8	53.0	..
	Mean,	....	...	..	..	..	...	52.1	52.9	..
	6.02	1.038 B	57.5	30.6	38.4	32.7	43.6	48.6	50.7	..
	6.02	1.957 B	64.3	25.2	30.9	26.5	43.6	50.6	52.0	..
	6.015	3.927 B	70.7	16.1	23.8	17.6	43.6	50.0	52.4	..
	Mean,	....	...	..	..	..	...	49.7	51.7	..
306°	29.35	0	...	..	..	..	8.03	..	..	90.9
	28.76	1.110 A	11.69	93.4	86.3	90.1	8.03	94.8	92.4	..
	27.53	3.218 A	15.96	81.2	81.0	81.1	8.03	91.0	90.9	..
	Mean,	....	...	..	..	..	...	92.9	91.6	..
	28.34	2.414 B	14.56	85.0	82.8	84.0	8.03	91.8	91.1	..
	10.00	0	...	..	..	..	7.99	..	..	91.2
	9.965	1.006 A	11.29	90.2	87.5	88.9	7.99	92.9	91.9	..
	9.855	3.050 A	15.81	86.0	82.3	84.3	7.99	92.7	91.6	..
	Mean,	....	...	..	..	..	...	92.8	91.7	..
	10.01	0.818 B	10.70	86.7	88.2	87.4	7.99	90.3	90.9	..
	9.735	2.591 B	14.91	85.8	83.4	84.7	7.99	92.3	91.5	..
	Mean,	....	...	..	..	..	...	91.3	91.2	..

quantities of acid were added gave very concordant results, whether calculated directly by the first method or from the weighted mean value of the percentage hydrolysis (100 h) for the salt in the mixture. The mean value calculated from the latter is, however, to be considered the most accurate. It will be seen that this agrees well in all cases with the value given in the last column, which was calculated directly by the second method from the conductance of the salt in pure water. To get the best final value from each group of experiments we have combined these two by assigning to the former a weight of 100 and to the latter a weight equal to the percentage hydrolysis. Table 13 contains the final hydrolysis values so obtained, the ionization values for the salt, the ionization-constant of water calculated from them by the equation $K_W = K_A K_B h_0^2/\gamma_0^2$, and the square root of this constant, which represents the concentration C_H of the hydrogen (or hydroxide) ion in pure water.

TABLE 13.—SUMMARY OF VALUES FOR THE IONIZATION AND HYDROLYSIS OF AMMONIUM ACETATE AND FOR THE IONIZATION OF WATER AT 218 AND 306°.

	Ammonium acetate.				
Temperature. $t°$.	Equivalents per liter. C.	Percentage ionization. $100\gamma_0$.	Percentage hydrolysis. $100h_0$.	Ionization-constant of water $\times 10^{14}$. $K_W \times 10^{14}$.	Equivalents of hydrogen-ion per 10^7 liters. $C_H \times 10^7$.
218°	0.012	43.1	52.6	461	21.5
	0.006	43.6	53.2	461	21.5
				Mean, 461	21.5
306°	0.030	8.03	91.3	167	12.9
	0.010	7.99	91.5	170	13.0
				Mean, 168	13.0

11. Summary of the Results on the Hydrolysis of Ammonium Acetate and the Ionization of Water, Ammonium Hydroxide, and Acetic Acid.

The final values of the percentage hydrolysis of ammonium acetate in 0.01 normal solution, of the ionization constants of ammonium hydroxide, acetic acid, and of water ($K_W = C_H C_{OH}$), and of the equivalents (C_H) of hydrogen ion or hydroxide ion present in one liter of pure water, obtained as described in this article, are summarized in Table 14. We have also included in the table values of the ionization constant of water at 0, 18, and 25° derived by Dr. C. W. Kanolt[1] from experiments made by him in this laboratory upon the conductance of ammonium hydroxide and of diketo-tetrahydrothiazole and upon the hydrolysis of the salt of this base and acid, in order to enable the results at the higher temperatures to be compared and combined with these at lower temperatures. The value given in the table for the hydrolysis of ammonium acetate at 18° is not based on direct measurements, but has been computed from the ionization constants of water, ammonium hydroxide, and acetic acid at that temperature.

[1] THIS JOURNAL, 29, 1414 (1907).

Table 14.—Hydrolysis of Ammonium Acetate and Ionization of Water, Ammonium Hydroxide and Acetic Acid.

Temperature. $t°$.	Hydrolysis of ammonium acetate. $100h$.	Ionization constant of water. $K_W \times 10^{14}$.	Hydrogen-ion concentration in pure water. $C_H \times 10^7$.	Ionization constant of ammonium hydroxide. $K_B \times 10^6$.	Ionization constant of acetic acid. $K_A \times 10^6$.
0	.....	0.089	0.30	13.9	....
18	(0.35)	0.46	0.68	17.2	18.3
25	.....	0.82	0.91	18.0	....
100	4.8	48	6.9	13.5	11.14
156	18.6	223	14.9	6.28	5.36
218	52.7	461	21.5	1.80	1.72
306	91.5	168	13.0	0.093	0.139

It will be seen that the hydrogen-ion concentration in pure water increases with extraordinary rapidity between 0 and 100°; namely, by about 3-fold between 0° and 25° and 7½-fold between 25 and 100°. Between the latter temperature and 218° the ionization increases more slowly, afterwards passes through a maximum (which appears to lie between 250 and 275°), and finally decreases. When it is considered that the ionization of weak acids and bases, as shown by the data for ammonium hydroxide, acetic acid, and phosphoric acid, decreases rapidly with rising temperature, and that this acts in the same direction in increasing the hydrolysis of salts as does an increase in the ionization of water, it will be evident that the tendency of salts to hydrolyze is enormously greater at high temperatures, as is well illustrated by the values given for ammonium acetate.

The great increase in hydrolysis is also exemplified by the hydrolysis values for sodium acetate and ammonium chloride in 0.01 normal solution that can be calculated from the preceding data: these salts, which at 18° are 0.02 per cent. hydrolyzed, are found to be 1.6 per cent. at 218° and 3.4 to 4.1 per cent. hydrolyzed at 306°.

The fact also deserves mention that the values of the concentration of the hydrogen ion in water at 0, 18, and 25° as derived from Kanolt's hydrolysis experiments are 16 to 20 per cent. lower than those obtained by Kohlrausch and Heydweiller[1] from the conductance of their purest water, and by Lunden[2] from his hydrolysis experiments.

From these ionization constants (K_w) approximate values of the internal-energy increase ΔE attending the reaction $H_2O = H^+ + OH^-$ (the so-called heat of ionization) can be computed by the familiar equation[3] derived from the Second Law of Energetics: $d \log K_w/dT =$

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[1] *Ann. Phys.*, [3] 53, 209 (1894); [4] 28, 511 (1909).

[2] Publications of Nobel Inst., 1, No. 8, p. 16 (1907).

[3] This equation ceases to be even approximately exact at high temperatures where the vapor pressure of water becomes very large. The exact expression, which may be derived through the consideration of an appropriate cyclical process, is as follows:

$\Delta E/RT^2$. This is best done by integrating it under the assumption that ΔE is a linear function of the temperature as expressed by the equation $\Delta E = \Delta E_0 + \alpha RT$. The integral then has the form

$$\log \frac{K_2}{K_1} - \alpha \log \frac{T_2}{T_1} = \frac{\Delta E_0}{R} \frac{T_2 - T_1}{T_1 T_2}$$

From the values of the ionization constant K at 0°, 25°, and 100°, the values of the constants ΔE_0 and α have been found to be 28460 and —24.923, respectively. Therefore, the general equation for the energy increase attending the ionization becomes

$$\Delta E = 28460 - 49.5\,T,$$

and that for the ionization constant becomes

$$\log_{10}(10^{16}K) = 84.450 - \frac{6222}{T} - 24.923 \log_{10} T.$$

The values of the energy increase in calories and of the ionization constant of water as calculated by these expressions are given in Table 15.

TABLE 15.—INTERNAL-ENERGY INCREASE ATTENDING THE IONIZATION OF WATER AND ITS IONIZATION CONSTANT CALCULATED BY AN EMPIRICAL EQUATION.

Temperature.	Energy increase. ΔE.	Ionization constant. $K \times 10^{14}$.
0	14950	0.088
18	14055	0.46
25	13710	0.81
50	12470	4.5
75	11230	16.9
100	9995	48
128	8610	114
156	7225	217
218	(4155)	(512)

These values of the ionization constant at 0, 25, and 100° necessarily agree with the directly determined ones given in Table 14. It is of interest to note, however, that this is also true of the calculated value at 156°, which shows that up to this temperature the assumed equations hold

$$\Delta E = RT^2 \frac{d \log Kw}{dT} + \Delta V . T^2 \left[\frac{d(p/T)}{dT} - \frac{d(P/T)}{dT} \right]$$

where ΔE is the energy increase and ΔV is the volume increase that attends the ionization of one mol. of water under the pressure $p - P$, which is substantially identical with the vapor pressure p, since the osmotic pressure P is in this case negligible in comparison. Approximate values of ΔV up to 140° have been computed by Tammann (*Z. physik. Chem.*, 16, 144 (1894)) which show it to be equal to about —26 cm. at 140°; and since it is shown to be increasing at a rate roughly proportional to the compressibility of water, it probably has a value in the neighborhood of —40 cm. at 218°. Assuming this to be the case, the last term in the above equation can, with the help of the existing vapor-pressure data, be shown to have a value of about —170 calories at 218°, while the value of ΔE as computed by the linear equation is 4155 at 218°. Thus at temperatures above 200° this last term begins to form a substantial part of the whole.

true, and that therefore the values interpolated for the intermediate temperatures between 0 and 156° are doubtless substantially correct. Even at 218° the difference between the observed and calculated values (461 and 512), though doubtless real, is not very large; it lies in such a direction as to indicate that the energy change ΔE is decreasing at a more rapid rate at temperatures above 156° than at the temperatures below it. This is also shown by the fact that the ionization constant at 306° is much less than at 218°, while according to the linear equation the value of ΔE should become zero, and therefore that of the ionization constant K should become a maximum, very near the former temperature, namely, at 302°. The real maximum value of the constant seems to lie between 250 and 275°. Above this temperature ΔE assumes a negative value; and therefore the neutralization of completely ionized acids and bases would be attended by an absorption of heat.

It may also be mentioned that at the lower temperatures the calculated values agree well with the heat of neutralization directly measured by Wörmann,[1] who found for hydrochloric and nitric acids when neutralized with potassium and sodium hydroxides as mean values 14,710 calories at 0° and 13,410 calories at 25°.

It seems worth while to call attention to a possible theoretical explanation of the fact that water, unlike all other substances thus far investigated, continues to increase in ionization up to so high a temperature as 250 or 275°. This phenomenon may well arise from the facts that water at low temperatures is a highly associated liquid containing only a small proportion of H_2O molecules, and that this proportion increases rapidly with rising temperature. Therefore, even through the fraction of H_2O molecules dissociated into H^+ and OH^- ions may decrease steadily, yet the actual concentration of these ions continues to increase until a large proportion of the complex water molecules have been depolymerized.

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THE REACTION BETWEEN AMMONIUM CHLORIDE AND POTASSIUM DICHROMATE WHEN HEATED.

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Doubtless every one who has given a course of lectures in general chemistry has used the potassium dichromate and ammonium chloride method for the preparation of nitrogen, inasmuch as this is one of the methods mentioned in nearly all of the old as well as in some of the new texts of

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[1] *Ann. Physik.*, [4] 18, 793 (1905).