

The temperature was taken as that of the boiling point of water, 99.3° at the mean barometric pressure, 740.7 m.m., for the days during which the experiment was performed. Number 9 is omitted from the calculations. Using the mean of the other eleven determinations for the calculation, the vapor pressure for this temperature was found to be 0.0070 mm. The vapor pressure calculated from the results of the other method for this temperature is 0.0070 mm., which agrees with this result. If determination 9 be included the vapor pressure calculated is 0.0069, a result not materially different from the other.

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IONIZATION OF WATER AT 0° , 18° AND 25° DERIVED FROM CONDUCTIVITY MEASUREMENTS OF THE HYDROLYSIS OF THE AMMONIUM SALT OF DIKETO-TETRAHYDROTHIAZOLE.

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I. Plan of the Investigation.

The degree of ionization of water at ordinary temperatures has been determined by a number of different methods—namely (1) from the hydrolysis of sodium acetate¹ as derived from the rate at which it saponifies an ester,² and from that of aniline acetate³ as derived from conductivity measurements⁴; (2) from the rate of saponification of methyl acetate by water itself;⁵ (3) from the electromotive force of the alkali-acid hydrogen cell;⁶ and (4) from the conductivity of the purest water thus far obtained.⁷ Although these entirely independent measurements have all given for the ionization of water values of the same order of magnitude and have thereby furnished one of the most striking evidences of the ionic theory, yet for none of the values so obtained can any considerable percentage accuracy be claimed. It has therefore seemed advisable to make a special study of this constant at ordinary temperatures by the same method that has been employed at higher temperatures by Noyes and Kato and by Sosman,⁸ that is, by measuring the increase

¹ Arrhenius, *Z. physik Chem.*, **11**, 822 (1893)

² Shields, *Ibid.*, **12**, 184 (1893).

³ Arrhenius, *Ibid.*, **5**, 19 (1890); Bredig, *Ibid.*, **11**, 829 (1893).

⁴ Walker, *Ibid.*, **4**, 334 (1889).

⁵ Wijs, *Ibid.*, **11**, 492 (1893).

⁶ Ostwald, *Ibid.*, **11**, 521 (1893); Nerust, *Ibid.*, **14**, 155 (1894); Löwenherz, *Ibid.*, **20**, 293 (1896).

⁷ Kohlrausch and Heydweiller, *Ibid.*, **14**, 330 (1894).

⁸ These articles together with the present one are being published by the Carnegie Institution of Washington.

in conductance produced by adding to a partially hydrolyzed salt of a weak acid and a weak base an excess of the acid or of the base, whereby the hydrolysis is reduced.

In calculating from such data the ionization of water a knowledge of the ionization-constants of the acid and the base and of the degree of ionization of the salt is also necessary.

The salt selected for this purpose must be sufficiently hydrolyzed to give rise to a marked change in the unhydrolyzed portion of it when the excess of acid or base is added. On the other hand, both the acid and the base of the salt must be strong enough to permit their ionization-constants to be directly and accurately determined by conductivity measurements. An examination of the available substances previously investigated seemed to show that ammonium hydroxide was the most suitable base, and that diketotetrahydrothiazole was the most suitable acid. This acid has also been called dioxythiazole and mustard-oil acetic acid, and has, according

to the investigation of Hantzsch¹, the structure² $\begin{array}{c} \text{CO}-\text{CH}_2 \\ | \\ \text{NH}-\text{CO} \end{array} \text{S}$. The base has at 25° an ionization-constant of 18.1×10^{-6} and the acid, one of 0.181×10^{-6} , and their salt a hydrolysis of about 4 per cent. as the measurements presented below show. This base is more easily obtained pure than any other base of similar strength; and the acid can be readily prepared in quantity from thiourea and chloroacetic acid. It is, however, so weak, that its salt is about ten times as much hydrolyzed as ammonium acetate (which is 0.4 per cent. hydrolyzed at 25°); and yet it is strong enough to have a conductance which can be fairly accurately determined, though it lies near the limit in this respect.

In detail, therefore, this investigation has consisted in the preparation and purification of the diketotetrahydrothiazole and the determination of its ionization by conductivity measurements at 0°, 18°, and 25° at various concentrations, in corresponding measurements with ammonium hydroxide, and in measurements at these three temperatures of the conductance of the salt at 0.02 and 0.05 normal both in water alone and in the presence of about the equivalent amount and half the equivalent amount of the free acid and of the free base in separate experiments. In order to determine the conductance of the completely ionized acid and salt, measurements were also made with the latter at a concentration of 0.002 normal.

2. Preparation of the Substances and Solutions.

The diketotetrahydrothiazole was prepared as described by Volhard³

¹ Ber., 20, 3129 (1887).

² Even assuming that this substance exists in part in the desmotropic "enol" form, this would make no difference in the values of the ionization of water derived from the study of its equilibria; for the concentrations of the two forms must be under all circumstances proportional to each other.

³ J. pr. Chem., (2), 9, 6 (1874).

by heating together thiourea and chloracetic acid in aqueous solution. The product was purified by a large number of crystallizations from methyl alcohol and from water. No boneblack was used. The crystallization from water was continued until the sample was perfectly white and no further change in conductance was produced, as will be shown in section 4. The last crystallizations were made from conductivity water in platinum vessels, and the crystals were filtered out and dried at 100° in a platinum Gooch crucible in purified air. A portion of the product so dried was finely powdered and kept in a desiccator over sulphuric acid for several weeks; it lost only a few hundredths of one per cent. in weight, showing that it was dry. The melting point of the purified sample was found to be 123.4°

The solutions of the acid were always prepared just before the conductance was measured, by dissolving weighed portions of it in a known weight of conductivity water in a Jena flask. The solutions were prepared and transferred to the conductivity vessel in contact with only purified air. The water used for dissolving the acid, and in general throughout this investigation, had at 18° a specific conductance which always lay between 0.15 and 0.60×10^{-6} reciprocal ohms. The solutions of the acid, even when kept for several hours in the conductivity-vessel, showed a change in conductance of not more than 0.1 per cent.

The ammonium hydroxide solution used was approximately 0.1 normal made by diluting with conductivity water a special sample of strong ammonia water (spec. grav., 0.90) furnished by the Baker & Adamson Chemical Co. and certified to be free from amines, carbonates, and silicates. The solution was titrated by running a slight excess of it directly into a known weight of standard hydrochloric acid, and running back to the end point with hydrochloric acid with the help of methyl orange. The solutions were all measured by weight, not by volume. The hydrochloric acid was itself standardized by precipitating a known weight of it with silver nitrate and weighing the silver chloride. The solution was kept in a two-liter "non sol" bottle (furnished by Whittall, Tatum & Co.). To protect it from evaporation and contamination it was connected through another bottle of ammonium hydroxide solution of the same strength with a long soda-lime tube through which air was admitted when samples were withdrawn. The solution was transferred through delivery tubes into the conductivity vessel or into a Jena flask in which it was diluted or mixed with the acid solution, in contact with only purified air. In order to use comparatively fresh solutions for the measurements, a new stock solution was prepared in the same way in the course of the experiments, so that the solution employed was never more than ten days old. Determinations of the alkaline strength showed that during this period the change in it was less than 0.1 per cent. The con-

ductance of this solution was found to be substantially identical with that of one prepared from liquid ammonia by Mr. R. B. Sosman.

The solutions of the salt, both alone and with an excess of acid or base, were prepared by introducing into a Jena flask, provided with a perforated ground-glass stopper and filled with purified air, a weighed quantity of the solid acid, and then introducing without opening the flask the proper quantity of conductivity water and of the stock ammonium hydroxide solution to produce as nearly as possible any desired round concentrations. These were in general attained within 0.1 or 0.2 per cent., but the exact concentration was always considered.

The content by weight of the various solutions obtained as above described was reduced to volume concentration by means of the density of the solution, which in the case of the acid or salt solutions was calculated from the densities of the solid acid and of the water or ammonium hydroxide solution, under the assumption that no change in the total volume occurs on mixing.¹ The concentration given in the tables below is always that at the temperature of the measurement.

The atomic weights used were those referred to oxygen as 16.00 as given in the report of the International Committee for 1906² All weights were corrected for the buoyancy of the air.

3. Apparatus and Method.

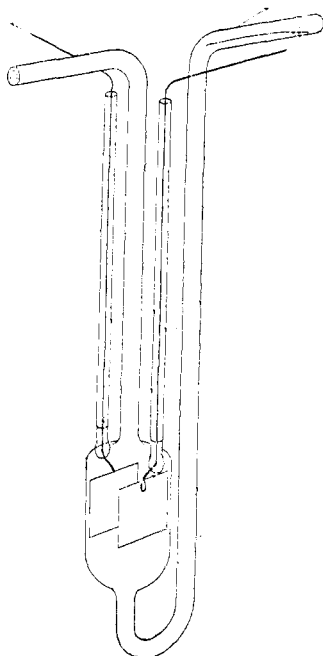
The conductivity measurements were made with a slide-wire bridge by the usual Kohlrausch method. The slide-wire was calibrated and the resistance coils were compared with each other. The conductivity vessel used was one of pipette form devised by Mr. G. A. Abbott in this laboratory. It is shown in the figure. It has the advantages that the solution can be introduced into it and kept in it entirely out of contact with the air, that the electrodes are fully protected against change in position, and that the vessel can be entirely immersed in the thermostat. The capacity of the vessel was about 25 cc.; and the vertical electrodes were about 2 cm. square and 1.3 cm. apart. The electrodes were used unplatinized in the measurements with the acid, so as to reduce contamination; but were platinized in the measurements with better conducting base and salt. The conductance-capacity of the vessel was determined by measuring in it (when unplatinized) a freshly prepared 0.002136 normal or (when platinized) a 0.0500 normal solution of potassium chloride,³ and allowing for the conductance of the water employed.

¹The density of the acid at 25° was found to be 1.673 by weighing a large excess of it in a pycnometer under its saturated solution. That there was in fact no appreciable volume-change on mixing was shown by direct measurements of the density of known solutions of the acid and of its salt.

²See this Journal, 28, 1 (1906).

³The actual conductances of these solutions in the vessel after allowing for the conductance of the water were 0.0015095 and 0.03256 reciprocal ohms at 18°, which correspond to conductance-capacities of 0.17861 and 0.17775, respectively, using Kohlrausch and Maltby's equivalent conductance values. The same value was obtained at the end of the measurements as at the start.

The vessel was immersed in well-stirred baths whose temperature was kept constant within 0.01° by thermostats. That, at 0° was maintained by a mix



ture of water and finely crushed ice in large proportion. The thermometers used were compared with the laboratory standard.

The final bridge reading was not recorded until it had become constant, which required 15-30 minutes. It then remained constant, even over night, in almost all cases, but with a few solutions containing the salt with an excess of ammonium hydroxide there was a slight progressive increase in conductance, for which a small correction (never more than 0.25 per cent.) was applied, depending upon the time which had elapsed before the reading and upon the temperature to which the cell had been exposed.

4. The Conductivity and Ionization-Constants of Ammonium Hydroxide and Diketotetrahydrothiazole.

Tables 1 and 2 contain the results of the conductivity measurements with ammonium hydroxide and with diketotetrahydrothiazole. The first column gives the temperature; the second, the date; the third, the concentration in equivalents per liter of solution at the temperature of the measurement; the fourth, the conductance in reciprocal ohms as actually measured in the conductivity vessel, multiplied by 10^6 ; the fifth, the same diminished by the conductance of the water; the sixth,

the equivalent conductance (Λ) calculated by multiplying the values of the preceding column by the conductance-capacity (0.17861 for the acid and 0.17775 for the base) and dividing by the concentration given in the third column and by 10^3 ; and the seventh, the ionization-constant (K) calculated from the expression $K = \frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda)}$ and multiplied by 10^6 .

The values Λ_0 (the equivalent conductance for complete ionization) used in the calculation of the ionization-constant were derived as follows. That for the OH^- ion at 18° was found to be 173.0 by subtracting Kohlrausch's value¹ for the sodium ion (43.55) from Noyes and Kato's value for sodium hydroxide (216.5). That for the NH_4^+ ion at 18° was found to be 65.4 by subtracting Kohlrausch's value for chloride ion (65.44) from Sosman's value for ammonium chloride (130.9). In this way the value for ammonium hydroxide was found to be 238.4 at 18° . Those for ammonium hydroxide at 0° and 25° were obtained from the corresponding equivalent conductances of the NH_4^+ and OH^- ions at 18° by means of the temperature-coefficients for the conductivities of these ions derived by Kohlrausch.² The values so obtained are $\Lambda_{\text{NH}_4} = 39.3$, $\Lambda_{\text{OH}} = 117.7$

TABLE I.—EQUIVALENT CONDUCTANCE AND IONIZATION OF DIKETOTETRAHYDROTHIAZOLE.

Temperature.	Date	Equivalent leilts per liter	Conductance $\times 10^6$		Equivalent conduct- ance	Ionization-constant $\times 10^6$.	
			Observed	Corrected		Separate values.	Mean values.
	1906						
0	May 24..	0.2503	185.9	184.5	0.1316	0.0710	} 0.0709 } 0.0711 } 0.0713
	May 21..	0.1251	131.0	129.7	0.1852	0.0703	
	May 25 .	0.1251	132.3	131.2	0.1873	0.0720	
	May 22..	0.0626	92.9	91.6	0.2613	0.0701	
	June 1..	0.2503	185.7	184.7	0.1318	0.0712	
	June 2..	0.2503	187.1	186.1	0.1328	0.0723	
	May 30..	0.1251	130.6	128.9	0.1840	0.0694	
	June 5..	0.0626	94.0	93.2	0.2659	0.0725	
18	May 24..	0.2500	372.5	370.1	0.2644	0.1436	} 0.1463 } 0.1459 } 0.1455
	May 21..	0.1250	266.1	263.9	0.3770	0.1460	
	May 25..	0.1250	268.0	266.2	0.3803	0.1487	
	May 22..	0.0625	189.5	187.2	0.5349	0.1471	
	June 1..	0.2500	371.5	369.9	0.2643	0.1435	
	June 2..	0.2500	373.3	371.6	0.2654	0.1447	
	May 30..	0.1250	264.8	261.9	0.3740	0.1437	
	June 5..	0.0625	190.8	189.3	0.5410	0.1504	
25	May 24..	0.2496	463.7	460.7	0.3297	0.1780	} 0.1818 } 0.1814 } 0.1811
	May 21..	0.1248	330.5	328.0	0.4693	0.1804	
	May 25..	0.1248	333.1	331.0	0.4737	0.1838	
	May 22..	0.0624	237.5	234.8	0.6719	0.1850	
	June 1..	0.2496	462.6	460.7	0.3297	0.1780	
	June 2..	0.2496	462.6	460.6	0.3296	0.1779	
	May 30..	0.1248	331.5	328.1	0.4701	0.1810	
	June 5..	0.0624	238.3	236.6	0.6772	0.1876	

¹ Sitzsber. preuss. Akad, Wiss., 1901, 1026-1033.

² Ibid., 1901, 10. These coefficients are:

$$(\Lambda_{\text{NH}_4})_t = (\Lambda_{\text{NH}_4})_{18} [1 + 0.0223 (t - 18) + 0.000079 (t - 18)^2]$$

$$(\Lambda_{\text{OH}})_t = (\Lambda_{\text{OH}})_{18} [1 - 0.0179 (t - 18) + 0.000008 (t - 18)^2]$$

$$(\Lambda_{\text{H}})_t = (\Lambda_{\text{H}})_{18} [1 + 0.0154 (t - 18) - 0.000033 (t - 18)^2]$$

and $\Lambda_{0(\text{NH}_4\text{OH})} = 157.0$ at 0° ; and $\Lambda_{\text{NH}_4} = 75.9$, $\Lambda_{\text{OH}} = 194.7$ and $\Lambda_{0(\text{NH}_4\text{OH})} = 270.6$ at 25° . The Λ_0 values for the acid at each temperature were obtained from those for its ammonium salt by subtracting the equivalent conductance of the NH_4^+ ion derived as just described, and adding that of the H^+ ion. The Λ_0 values for the ammonium salt were derived from direct conductance measurements which will be presented and discussed in section 5. For the equivalent conductance of the H^+ ion at 18° the value, 315, derived from the measurements of Goodwin and Haskell¹ upon very dilute acid solutions was adopted; while at 0° and 25° the values 224.3 and 348.5, respectively, were obtained from this one at 18° by means of Kohlrausch's temperature-coefficients just referred to.

TABLE 2.—EQUIVALENT CONDUCTANCE AND IONIZATION OF AMMONIUM HYDROXIDE

Temperature	Date	Equivalents per liter	Conductance $\times 10^6$.		Equivalent conductance	Ionization-constant $\times 10^8$	
			Observed	Corrected		Separate values	Mean values
1906							
0	July 22..	0.09569	1,015	1,014	1.884	13.95	13.91
	July 24..	0.04540	696	695	2.722	13.88	
18	July 22..	0.09557	1,709	1,708	3.177	17.21	17.15
	July 24..	0.04534	1,171	1,170	4.584	17.09	
25	July 22..	0.09542	1,989	1,988	3.703	18.11	18.06
	July 24..	0.04527	1,363	1,362	5.346	18.02	

The measurements of May 30 to June 5, given in Table 1, were made with a sample of the acid obtained by recrystallizing three times from conductivity water with the usual precautions, the material used in these measurements of May 21-25. The agreement of the results with the two samples shows that the material underwent no change in the three crystallizations. Ostwald² obtained the value 0.24×10^{-6} for the constant at 25° without using special precautions.

Sosman with solutions prepared both from liquid ammonia and from the pure ammonia water, obtained for the constant of ammonium hydroxide at 18° , as the mean of a large number of determinations at concentrations from 0.01 to 0.1, the value 17.15×10^{-6} , which is identical with that given in Table 2. He obtained the value 17.9×10^{-6} as the means of two determinations at 25° . This value agrees closely with the value 18.06×10^{-6} here presented. Earlier investigators³ obtained considerably higher results, partly owing to the incomplete elimination of impurities and to the use of other values for complete ionization.

The results given in the tables show that the constants of the two substances do not vary considerably with the concentration. Sosman, using a much greater range of concentration, also found that the variation of the constant for ammonium hydroxide at 18° was very small.

It will be observed that with rising temperature the ionization of the

¹ Physic. Rev., 19, 386, (1904).

² Z. physik. Chem., 3, 181 (1889).

³ Bredig, Z. physik. Chem., 13, 294, (1894). Davidson, Ber., 31, 1612 (1898). Hantzsch and Sebaldt, Z. physik. Chem., 30, 296 (1899).

acid increases very rapidly and that that of the ammonium hydroxide also increases, but to a much smaller extent.

No reliable estimate of the accuracy of these constants can be made. It seems, however not improbable that the equivalent-conductance values for the acid may be too high by one per cent., owing to the effect of impurities; and also that its equivalent-conductance values for complete ionization may be in error by one per cent. at 18° and 25°, and by even 2-3 per cent. at 0°. Under these assumptions the error in its ionization-constant may be 3.4 per cent. at 18° and 25°, and 5.7 per cent. at 0°. In the case of ammonium hydroxide, although the values of the equivalent conductance at the higher concentrations are probably somewhat more exact than those for the acid, yet there is an even greater uncertainty in the values for complete ionization, so that the ionization-constants are probably of the same order of accuracy.

5. Conductivity and Hydrolysis of the Ammonium Salt of Diketotetrahydrothiazole.

The data relating to the conductivity of the pure ammonium salt are presented in Table 3, which is arranged like Tables 1 and 2 except that the specific conductance is given in addition to the equivalent conductance.

TABLE 3.—CONDUCTANCE OF THE AMMONIUM SALT OF DIKETOTETRAHYDROTHIAZOLE.

Temperature	Date	Equivalent- conductance per liter	Conductance $\times 10^6$		Specific conduct- ance $\times 10^6$	Equiva- lant con- ductance
			Observed	Corrected		
	1906					
0	July 28..	0.05005	14,424	14,423	2,563.6	51.22
	July 29..	0.04997	14,401	14,400	2,559.4	51.22
	July 12..	0.020047	6,015	6,013	1,068.8	53.32
	July 14..	0.020035	6,016	6,014	1,069.3	53.37
	Aug. 3..	0.002143	686.5	685.2	121.8	56.82
18	July 28..	0.04999	22,895	22,893	4,069	81.40
	July 29..	0.04991	22,828	22,826	4,057	81.30
	July 12..	0.020021	9,566	9,563	1,700.0	84.91
	July 14..	0.020010	9,562	9,559	1,699.1	84.91
	Aug. 3..	0.002141	1,092.2	1,090.0	193.7	90.50
25	July 28..	0.04992	26,408	26,406	4,694	94.03
	July 29..	0.04983	26,355	26,353	4,684	94.00
	July 12..	0.019992	11,044	11,041	1,962.6	98.17
	July 14..	0.019979	11,033	11,030	1,960.0	98.16
	Aug. 3..	0.002137	1,265.6	1,263.0	224.5	105.04

It will be seen that the values of the equivalent conductance at about the same concentration, which were determined with solutions made up separately from the solid acid and the stock ammonium hydroxide solutions, agree in every case within about 0.1 per cent.

For the purpose of facilitating the subsequent calculation of the hydrolysis, the specific conductance L has been expressed as a concentra-

tion-function of the form $C = \alpha L + \beta L^2$ which corresponds to the van't Hoff function $(C\Lambda)^{0.5} = KC(\Lambda_0 - \Lambda)$, which is known to express approximately the variation of the equivalent conductance Λ with the concentration C in the case of neutral salts. As this equation is to be used only for interpolation for a small distance from the values from which it is derived, any possible inaccuracy in the assumed form of the function could not introduce a significant error. Using the conductance values at 0.02 and 0.05 normal as the basis, the corresponding numerical equations are :

$$C = 17.530 L - 43.34 L^2 \text{ at } 0^\circ$$

$$C = 10.832 L + 22.95 L^2 \text{ at } 18^\circ$$

$$C = 9.373 L + 18.45 L^2 \text{ at } 25^\circ$$

Table 4 contains the data for the ammonium salt in the presence of an excess of the free acid or base. The first five columns are self-explanatory.

The sixth column contains the uncorrected specific conductance $\times 10^6$ of the solution in reciprocal ohms obtained by multiplying the observed conductance by the conductance-capacity and by 10^6 .

The seventh column contains the corresponding specific conductance corrected by subtracting that of the water and in some cases the small estimated increase due to progressive contamination during the period of the measurement (see section 3).

The eighth column headed "Salt in solution" contains the same values after correcting them for the specific conduct of acetate ionized ammonium hydroxide, when this was present in excess. (The conductance due to the ionized acid when it was in excess was entirely inappreciable.) This conductance (L_B) was computed by the equations :

$$C_{OH} = \frac{K_B C_{NH_4OH}}{C_{NH_4}} = \frac{K_B C_B}{C}$$

$$L_B = 10^6 C_{OH} (\Lambda_{NH_4} + \Lambda_{OH})$$

in which K_B is the ionization-constant for ammonium hydroxide, C_B the excess of it present, and C is the concentration of the salt and γ its degree of ionization.

The ninth column gives the concentration (C_0) at which the salt in water alone has the same specific conductance as that (given in the eighth column) of the salt in the presence of the acid or base; this concentration C_0 was calculated by the empirical relations between C and L given on the preceding page.

The last column contains the values of the percentage hydrolysis ($100 h_0$) of the salt in water alone at the concentration C_0 . These values have been computed by means of the equation :

$$h_0 = \frac{C_0 - C}{C_0} \cdot \frac{C_B - (C_0 - C)}{C_B - 2(C_0 - C)}$$

in which C represents the concentration of the salt in the mixture and C_B that of the added base (or acid). This equation results from combination of the two equations:

$$\begin{aligned} C_0(1 - h_0) &= C(1 - h), \\ (C_0 h_0)^2 &= Ch(Ch + C_B), \end{aligned}$$

in which h represents the hydrolysis of the salt in the presence of the excess of base (or acid). The first of these, which states that the concentration of the unhydrolyzed portion (which is equal to the sum of the concentrations of the ions and the un-ionized salt) is the same in the two cases, is a consequence of the definition of C_0 . The second of these equations is the expression of the mass-action requirement that the product of the concentrations of the free acid and base be the same when the ion-concentrations are the same.

It will be seen from the last column of Table 4 that the values of a , d . (the average deviation of the separate hydrolysis values from the mean) are about 0.10 at 0° and 18° , and 0.15 at 25° for the more dilute salt solution. The deviations for the more concentrated salt solution are much less than these. It is to be remembered in this connection that these hydrolysis values are derived from experiments in some of which an excess of acid, and in others of which an excess of base was present, and in which varying quantities of these were added, and that most constant errors would either have been eliminated in the difference between the measurements with the mixture and the pure salt, or would have shown themselves by producing opposite effects when the acid and base were in excess.

Before calculating the hydrolysis-constant, it is necessary to determine the ionization of the salt at the concentrations in question, and therefore to determine the equivalent conductance Λ_0 for complete ionization. To do this the equivalent conductance of the unhydrolyzed part of the salt has been calculated at the three concentrations at which measurements were made by dividing the specific conductance as given in Table 3 by the concentration of the unhydrolyzed part $C_0(1-h_0)$; and evidently it is to this concentration that the so-obtained values of the equivalent conductance refer. The values for h_0 used at 0.02 and 0.05 normal were the means given in Table 4. The value of h_0 used for the more dilute solution was calculated from these by the mass-action formula given below. From these three values of Λ the values of the three constants n , K , and Λ_0 in the empirical equation, $(\Lambda C)^n = K(\Lambda_0 - \Lambda)C$, were computed. The ionization of the salt was then obtained by dividing the Λ -values by this value of Λ_0 .

TABLE 4.—CONDUCTANCE OF THE SALT WITH AN EXCESS OF ACID OR BASE AND ITS HYDROLYSIS.

Tem- pera- ture	Date	Milli- equivalents per liter			Specific conductance $\times 10^6$.			Concentra- tion (C ₀) of salt in water alone	Percent- age hy- drolysis 100 h_0
		Salt	Acid	Base	Observed	Corrected	Salt in solution		
	1906								
0	July 10	20.025	10.95	1,099.8	1,096.8	1,095.5	20.555	2.71
	July 11	20.025	19.78	1,100.6	1,098.4	1,096.0	20.562	2.68
	July 15	20.068	19.96	1,100.5	1,100.3	1,100.3	20.644	2.87
	July 16	20.068	10.13	1,099.8	1,099.5	1,099.5	20.629	2.88
								Mean..	2.78
								a. d....	0.09
	July 26	50.06	24.60	2,622.9	2,621.7	2,620.4	51.22	2.37
	July 27	50.06	45.29	2,632.7	2,631.7	2,629.2	51.39	*2.66
	July 30	50.10	49.14	2,622.9	2,622.6	2,622.6	51.27	2.34
	July 31	50.10	24.45	2,623.3	2,623.0	2,623.0	51.27	2.40
								Mean..	2.37
								a. d....	0.02
18	July 10	20.000	10.93	1,765.4	1,761.2	1,758.8	20.742	3.82
	July 11	20.000	19.75	1,767.6	1,764.6	1,760.1	20.751	3.76
	July 15	20.044	19.94	1,767.4	1,767.0	1,767.0	20.836	3.95
	July 16	20.044	10.12	1,766.4	1,765.9	1,765.9	20.821	4.04
								Mean..	3.89
								a. d....	0.10
	July 26	50.00	24.57	4,200.0	4,194.1	4,191.6	51.63	3.38
	July 27	50.00	45.23	4,215.3	4,210.3	4,205.5	51.80	*3.61
	July 30	50.04	49.08	4,201.3	4,200.9	4,200.9	51.74	3.41
	July 31	50.04	24.43	4,195.9	4,195.5	4,195.5	51.68	3.39
								Mean..	3.39
								a. d....	0.01
25	July 10	19.968	10.91	2,042.2	2,039.6	2,036.6	20.784	4.25
	July 11	19.968	19.73	2,047.6	2,045.4	2,040.0	20.818	4.24
	July 15	20.013	19.91	2,050.9	2,050.4	2,050.4	20.921	4.52
	July 16	20.013	10.10	2,047.4	2,046.8	2,046.8	20.884	4.58
								Mean..	4.40
								a. d....	0.15
	July 26	49.92	24.53	4,873.9	4,861.7	4,858.7	51.80	3.94
	July 27	49.92	45.17	4,894.7	4,885.1	4,879.4	52.02	*4.22
	July 30	49.96	49.01	4,866.4	4,865.9	4,865.9	51.88	3.85
	July 31	49.96	24.39	4,859.9	4,859.4	4,859.4	51.81	3.86
								Mean..	3.88
								a. d....	0.04

*Omitted in the computation of the mean.

Table 5 contains the so-derived values of the equivalent conductance and percentage ionization of the salt. The values of the exponent n were found to be 1.35 at 0°, 1.39 at 18°, and 1.35 at 25°, thus, of about the same magnitude as for ordinary salts. The ionization will also be seen to be about the same as that of other salts of the same ionic type.

TABLE 5.—EQUIVALENT CONDUCTANCE AND IONIZATION OF THE UNHYDROLYZED AMMONIUM SALT.

Temperature	Equivalents per liter	Equivalent conductance	Percentage Ionization
0	0.04875	52.55	84.5
	0.01950	54.81	88.1
	0.002080	58.5	94.1
	0.00	62.2
18	0.04816	84.38	85.0
	0.01926	88.22	88.8
	0.002055	94.3	94.9
	0.00	99.3	...
25	0.04782	98.03	83.1
	0.01913	102.54	87.0
	0.002035	110.1	93.4
	0.00	117.9

From the values of the hydrolysis and ionization given in Tables 4 and 5, the hydrolysis-constant K_H (equal to $\sqrt{\frac{K_W}{K_A K_B}}$) can be readily calculated by the mass-action relation $\frac{h_0}{(1-h_0)\gamma} = K_H$, in which h_0 represents the hydrolysis of the salt in water alone at any concentration C_0 , γ is the fraction of the unhydrolyzed salt $C_0(1-h_0)$ which exists as ions, and K_W , K_A and K_B are the ionization-constants for water, the acid, and the base respectively. This equation is readily derived by combining the three simple mass-action equations, $C_H C_{OH} = K_W$, $C_H C_A = K_A C_{HA}$, and $C_B C_{OH} = K_B C_{BOH}$, substituting for C_B and C_A the expression $C_0(1-h_0)\gamma$ and for C_{HA} and C_{BOH} the expression $C_0 h_0$, and taking the square root. The values of the hydrolysis constant K_H thus calculated are given in Table 6. The values at the two concentrations will be seen to differ by from 12 to 9 per cent. As those at the higher concentration are influenced to a less extent by impurities and contamination, a double weight has been assigned to them in deriving the final mean values. It is not improbable that these values are still too high but it is unlikely that the error exceeds 5 per cent.

TABLE 6.
THE HYDROLYSIS-CONSTANT FOR
THE AMMONIUM SALT.

Temperature	Equivalents per liter	Hydrolysis-constant	
		Separate values	Mean values
0	0.05	0.0287	
	0.02	0.0324	0.0299
18	0.05	0.0413	
	0.02	0.0456	0.0427
25	0.05	0.0486	
	0.02	0.0529	0.0500

6. The Ionization of Water.

The ionization-constants of water ($K_w = C_H C_{OH}$) can be calculated from the hydrolysis-constants given in Table 6, and the ionization-constants of the acid and base given in section 4. Table 7 contains the values of this constant for water, and also those of its square-root, which last represent the concentration of the hydrogen and hydroxide ion in pure water (in equivalents per liter).

TABLE 7.—THE IONIZATION-CONSTANT OF WATER AND THE HYDROGEN OR HYDROXIDE-ION CONCENTRATION.

Temperature	Ionization-constant $K_w \times 10^4$	Ion Concentration ($\sqrt{K_w = C_H = C_{OH}} \times 10^7$)
0	0.089	0.30
18	0.46	0.68
25	0.82	0.91

To compare these results with those previously obtained the various values for the hydrogen-ion or hydroxide-ion concentration in pure water, have been brought together in Table 8.

TABLE 8.—THE HYDROGEN-ION CONCENTRATION ($\times 10^7$) IN PURE WATER. RESULTS OF VARIOUS INVESTIGATORS.¹

Investigator	Method of Determination	0°	18°	25°
Arrhenius.....	Hydrolysis of sodium acetate by ester-saponification	1.1
Wijs.....	Catalysis of ester by pure water	1.2
Nernst.....	Electromotive force of gas cell.....	0.8
Löwenherz.....	Electromotive force of gas cell.....	1.19
Kohlrausch & Heydweiller..	Conductance of pure water	0.36	0.80	1.06
Kanolt.....	Hydrolysis.....	0.30	0.68	0.91

It will be seen that the new values are uniformly lower than those of Kohlrausch and Heydweiller, but only by from 16 to 20 per cent. This approximate agreement is of interest not only in indicating the absence of any considerable error in the values of Kohlrausch and Heydweiller, in spite of the somewhat uncertain correction that had to be applied for the impurities in the water; but also in proving that the ionization of water is nearly, if not quite, the same when pure, as it is when an ionized salt is present in it at a concentration of 0.02 to 0.05 normal.

As the most probable values of the hydrogen-ion concentration in pure water it would seem best to adopt for the present the lower ones derived above; for, although it is not impossible that these are in error by as much as 10 per cent., yet it is reasonably certain that the error lies in such a direction as to produce too high rather than too low results. This will be evident when it is considered that the effect of impurities in the

¹ For references to their articles see section 1.

water or the solutes would be to give rise not only to too high values for the ionization-constants of the acid and base, but also by combining with the excess of either of them added in the hydrolysis experiments, to give too great an increase in the conductance and therefore too great a value for the hydrolysis.

It will be seen from Table 7 that the hydrogen-ion concentration increases with great rapidity with the temperature, being three times as great at 25° as at 0°. It is of interest to calculate from this increase the heat of ionization of water, and to compare its value with that obtained for the heat of neutralization of strong acids and bases. The calculation has been made for the two temperature intervals by the equation log,

$$\log_e \frac{K_2}{K_1} = \frac{Q}{R} \frac{T_2 - T_1}{T_1 T_2},$$

where K_1 and K_2 represent the ionization-constants of water at T_1 and T_2 , R is the gas-constant (1.986 cal. per degree), and Q is the heat of ionization of one mol. of water. The value of Q is thus found to be 14,500 calories at 9°, and 14,200 calories at 21.5°. The mean value of the heats of neutralization of potassium and sodium hydroxides by hydrochloric and nitric acids as recently determined by Wörmann¹ is 14,240 calories at 9°

¹ Drude's Ann. Physik., 18, 793 (1905).

and 13,590 calories at 21.5°. The agreement is a surprisingly close one, and shows that the ionization-values at the three temperatures, if affected by errors, must be affected by the same percentage amount.

7. Summary.

In this article have been presented the results of measurements of the conductivity at 0°, 18°, and 25° of ammonium hydroxide, diketotetrahydrothiazole, and of the salt of this base and acid, both alone and in the presence of an excess of the base or acid. From these measurements have been calculated the ionization-constants of the base and acid, the hydrolysis and hydrolysis-constant of the salt, the ionization-constant of water and the concentration of the hydrogen or hydroxide ion in it. The final results may be summarized as follows:

TABLE 9.
IONIZATION-CONSTANTS OF AMMONIUM HYDROXIDE OF DIKETOTETRAHYDROTHIAZOLE, AND OF WATER.

Temperature	Ammonium hydroxide	Ionization-Constants Diketotetrahydrothiazole	Water	Concentration of hydrogen ion in pure water
0	13.91×10^{-6}	0.0711×10^{-6}	0.089×10^{-14}	0.30×10^{-7}
18	17.15×10^{-6}	0.146×10^{-6}	0.46×10^{-14}	0.68×10^{-7}
25	18.06×10^{-6}	0.181×10^{-6}	0.82×10^{-14}	0.91×10^{-7}

The values for the hydrogen-ion concentration given in the last column are 16 to 20 per cent. lower than those derived by Kohlrausch and Heydweiller from the conductivity of the purest water. From their variation

with the temperature the heat of ionization of water has been calculated, and found to be in close agreement with the directly measured heat of neutralization of strong acids and bases.

I wish in closing to acknowledge my great indebtedness to Dr. A. A. Noyes, at whose suggestion this work was undertaken, for aid therein.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF THE ORGANIC ACIDS IN LIQUID HYDROGEN CHLORIDE AND BROMIDE.

BY E. H. ARCHIBALD.
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Introduction.

It has been shown in a previous paper,¹ that the majority of the organic hydroxy bodies dissolve in liquid hydrogen bromide to give solutions which conduct the electric current. It was found however, that, as first pointed out by Steele, McIntosh and Archibald,² the behavior of these solutions toward the electric current was very different from that of aqueous solutions of the ordinary electrolytes. As distinguished from these solutions, the molecular conductivity, except in the case of the more dilute solutions, decreased rapidly as the dilution increased. It was found, too, that in a number of cases the specific conductivity decreased with rise of temperature, giving negative temperature coefficients. It was thought that the organic acids would be an interesting class of substances to study as regards their power of forming conducting solutions when dissolved in this medium, and the nature of the variation of the molecular conductivity with dilution, particularly for the more dilute solutions. At the same time it was thought advisable to extend this study to include solutions of these substances in liquid hydrogen chloride, as it has been shown by Steele, McIntosh and Archibald,³ that in many cases solutions of organic substances in this solvent exceed those formed with the liquid hydrogen bromide in their power of conduction.

It has been pointed out by Walker, McIntosh and Archibald,⁴ that several of the organic acids form conducting solutions with liquid hydrogen chloride; but in the case of the hydrogen bromide solutions, the specific conductivity seemed to be so small as to be almost unmeasurable. It will be shown below, that with the form of electrolytic cell here used, the conductivity of a large number of these acids, when dissolved in the liquid hydrogen bromide, can be followed over a considerable range of dilution.

The Materials Used.—The preparation of the liquid hydrogen bromide

¹ This Journal, 29, 665 (1907).

² Phil. Trans., A. 205, 99 (1905).

³ Loc. cit. p. 132.

⁴ J. Chem. Soc., 85, 1098 (1904).