[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLVII. Conductance of Some Quaternary Ammonium and Other Salts in Water at Low Concentration[1]

BY HARRY M. DAGGETT, JR.,[2] EDWARD J. BAIR AND CHARLES A. KRAUS

I. Introduction

For an understanding of free ions in solution we are largely dependent on their conductances. In aqueous solution these may be obtained from precise conductance measurements at low concentrations in conjunction with transference measurements for one or more salts. For the ions of many inorganic salts conductance measurements have been carried out by Shedlovsky[3] and his coworkers and transference measurements by Longsworth.[4]

However, for organic ions, conductance measurements of the same precision are lacking. The present investigation has been, in the main, directed toward determining the conductance of quaternary ammonium ions with a view to learning how the conductance of such ions is dependent upon structural and constitutional factors.

To determine the limiting conductance of salts with precision, it is necessary to carry the measurements to low concentration, approaching 2×10^{-5} N in some instances. Such measurements have been carried out by Shedlovsky for some inorganic salts, but his method is not well adapted to some of the organic salts whose properties are such that certain inherent difficulties are involved in the preparation and manipulation of their solutions. Kuhn[5] has evolved a method of measurement in which the atmosphere with which the solution comes in contact is reliably and simply controlled in a chamber or "box" similar to the well-known "dry box." Kuhn made up his solutions by weighing a known quantity of a more concentrated solution into a known weight of water. This method has the disadvantage that additional errors are introduced in the making up and transfer of the concentrated solution. At the same time, the manipulations in the box with rubber gloves are awkward and time-consuming.

Accordingly, using the box procedure of Kuhn, solutions were made up by dropping weighed samples of salt directly into the conductance cell, the samples being weighed on a microbalance. Techniques were developed whereby the necessary operations could be carried out speedily and with precision.

The ions with which the present investigation is particularly concerned are those of the homologous series of quaternary ammonium ions from tetramethyl to tetra-*n*-amyl, inclusive. Potassium chloride was measured for the purpose of testing the reliability of the method used in these measurements.

II. Experimental

(1) **Outline of Method.**—The method employed follows that of Kuhn in the preparation of water and in the conditioning of the atmosphere in a closed chamber by air that has passed through aspirator pumps. It differs in that solutions were prepared by introducing weighed salt samples directly into the conductance cell. The salt samples were weighed out in quartz cups with platinum covers and were dropped into the cell in the conditioned box. For transferring the quartz cups, a special holder was devised as will be described below.

(2) **Cup Holder.**—The cup holders are illustrated in Fig. 1. The cup is held in the glass tube A and rests on the platinum foot B, which is attached to the rod, C. The foot may be turned through an angle of 90° by means of the knurled head D. The member E fits into and rests on the top of the cell; the sample is released by turning the head D through the necessary angle. The cup, to put it in the holder, is placed on a clean sheet of paper, the glass tube A is placed over it and the foot is slid under the cup by turning the head D. The cups are provided with platinum covers which are pressed out in the center to fit the cups and hold the covers in position. A small stand is provided to hold six cup holders. The stand rotates around a vertical axis. All metal parts are of brass and are rhodium plated. A convenient and assured method of transferring the salt from the balance to the cell is an essential element of any method of conductance measurements in which solutions are made up in the cell.

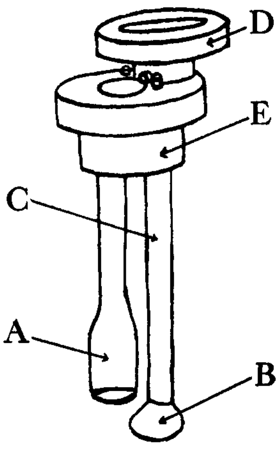

Fig. 1.—Cup holder.

(3) **Conductance Cell.**—The conductance cell was constructed of a one-liter erlenmeyer flask; it is illustrated in Fig. 2. The electrode chamber Q is attached to the flask by two tubes, R and Z. Such construction is necessary if the contents of the electrode chamber are to be thoroughly mixed with the solution in the main body of the cell. The electrodes are platinum discs of 15 mm. diameter and 0.2 mm. thickness. Seals are made according to the method of Hnizda and Kraus.[6] The leads are widely spread and contact is made by means of copper wire and a drop of mercury. The cell is provided with a 35/45 standard taper cap. Up to 850 cc. of water may be used in the cell and the observed resistance of the solution is independent of volume as long as the electrode chamber is filled.

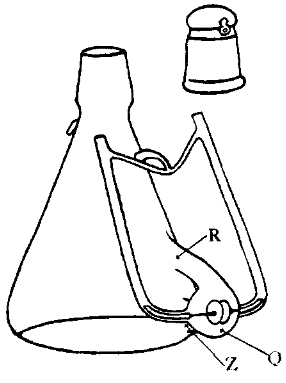

Fig. 2.—Conductance cell.

(4) **Procedure.**—The cups were soaked in fuming nitric acid, thoroughly washed with distilled water and then with a small amount of redistilled ethanol. They were then

---

[1] This paper is based on a portion of a thesis presented by Harry M. Daggett in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1949.

[2] Fellowship of the Calco Division of the American Cyanamid Co., Brown University, 1947–1949.

[3] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932); Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

[4] Longsworth, THIS JOURNAL, **54**, 2741 (1932).

[5] Kuhn and Kraus, *ibid.*, **72**, 3676 (1950).

[6] Hnizda and Kraus, *ibid.*, **71**, 1565 (1949).

wrapped in a sheet of aluminum foil and dried in an oven at 110°. After cooling, the cups were placed in the case of the microbalance. The salts, previously prepared and dried, were first introduced into a special transfer tube. This consisted of a small cylindrical quartz tube the top of which was somewhat constricted. To the bottom of this tube was sealed a short length of another tube that fitted the inside of the cups. A small quartz rod was ground into the upper end of the delivery tube where it joined the tube; this functioned as a valve in holding or releasing the salt. The end of the filling tube was inserted into a cup, the rod was raised and the salt fell into the bottom of the cup without dusting. The operation required only a few seconds. The cup was now capped, reweighed and placed in a holder. Usually, enough cups for a series (5 or 6) were weighed out at one time. The holders were placed in a rack and introduced into the box to be used as needed.

The conductance cell was treated with fuming nitric acid, washed, steamed, dried in an oven at 110° and, finally, in a vacuum desiccator. It was then weighed. Mercury in the lead tubes had previously been dissolved with nitric acid. After weighing, the cell was washed with fuming nitric acid which was added to the cell while hot. Then it was again steamed and introduced into the box while still wet.

Air from the box was drawn into the cell at the bottom and out at the top to remove carbon dioxide. It was then rinsed repeatedly with conductivity water after which the desired volume (about 850 cc.) of water was introduced. Air from the box was now drawn through the water to equilibrate it with the atmosphere of the box; this required about five minutes. Ordinarily, the cell was left uncapped in the box for half an hour or more. After capping the cell, the cap being lubricated with apiezon grease, it was weighed, placed in the thermostat and the conductance of the water was measured. After reaching temperature equilibrium, the conductance was followed up for half an hour or more to make sure that the conductance remained constant. In the event that the conductance increased, the cell was recleaned.

The cell, after removal of the oil from its surface, was returned to the box, the cap was removed, the cup was dropped into the cell from the holder and the cell was recapped. This operation required not more than 10 seconds. The cell was now returned to the thermostat and the conductance of the solution measured. Thereafter, it was returned to the box and another sample of salt was introduced. The above-described procedure was repeated until the desired amount of salt had been added.

It was found that, with certain cells, the conductance diminished on standing; on stirring, the original value was reproduced. It was shown that the correct value is that found upon stirring. By making the electrode chamber large, this effect could be minimized. Similar observations have been recorded by other investigators.[7]

To test the procedure, an empty cup was dropped into water whose conductance had previously been measured. The conductance of the water initially was 0.4548×10^{-6}. After introducing the cup, the conductance was 0.4553×10^{-6}; the conductance had changed 0.1%. For a solution whose specific conductance due to electrolyte is 5×10^{-6} mho, this would mean an error of 0.01%.

(5) **Calibration.**—Cells of low constant are commonly calibrated by intercomparison with a standard cell which has been calibrated directly. An intercomparison cell of pipet form is usually employed for this purpose. We have adopted the procedure of calibrating cells by making up a 1×10^{-3} *N* solution of potassium chloride directly in the cell. The water in the cell is weighed and its conductance determined, the necessary quantity of salt is weighed out on a microbalance and added to the water. Correction is made for the water conductance; this amounts to about 0.3% and is precisely known.

We have adopted Shedlovsky's value of 146.98×10^{-6} mho[3] for the conductance of a 1×10^{-3} *N* solution of potassium chloride in water at 25°. Shedlovsky's value has been recomputed to bring it into accord with the values of Jones and Bradshaw for solutions at higher concentration.

The bath temperature was controlled at 25 ± 0.002°; it was checked at intervals by means of a platinum resistance thermometer. Lack of temperature control was readily detected by shifting of the resistance which could be read to better than 0.01%. When the room temperature was below 25°, the top of the cell was irradiated with an infrared lamp to prevent condensation of water on exposed parts. This procedure did not affect the temperature of the solution in the cell.

(6) **Electrical Measuring Apparatus.**—Conductances were measured by means of a Jones bridge. There was a slight frequency effect with resistances above 50,000 ohms; this was corrected for by extrapolating to zero frequency. This seemed to be inherent in the bridge since it was not found when measurements were made with the shielded parallel arm bridge which was designed for measuring very high resistances. For high resistances, a 30,000-ohm shunt was used in parallel with the cell. The readings with this shunt were found to check with those of the parallel arm bridge.

(7) **Materials.**—Water was prepared according to the method of Kraus and Dexter,[8] and as obtained from the still had a conductance of $1\text{–}2 \times 10^{-7}$. No attempt was made to obtain especially pure water since its conductance was raised to $3.5\text{–}4.5 \times 10^{-7}$ on equilibrating it with the atmosphere in the box.

Potassium chloride was purified by three different methods: (1) recrystallization from conductivity water three times; (2) precipitation from a saturated aqueous solution by careful addition of reagent grade hydrochloric acid; (3) precipitation from a saturated solution by addition of an equal volume of ethanol. The three preparations gave identical results. Samples were dried *in vacuo* at 110°.

Potassium bromate was recrystallized from water and dried *in vacuo* at 110°. The following quaternary ammonium salts were prepared by conventional methods and purified by repeated recrystallization from suitable solvents: tetramethylammonium picrate, m.p. 324–325° dec.; tetraethylammonium picrate, m.p. 258–259° dec.; tetra-*n*-propylammonium iodide, m.p. 293–295° dec.; tetra-*n*-butylammonium bromide, m.p. 116–117°[9] and tetra-*n*-amylammonium bromide, m.p. 99–100°. These salts were dried *in vacuo* at 40°. Recrystallization was continued until successive products yielded solutions having the same conductance.

III. Results

In computing concentrations, the density of water at 25° has been taken to be 0.99707 g./ml.; the density of the solutions has been assumed to be that of water. In buoyancy corrections, densities of quaternary ammonium salts were assumed to be 1.6; an error of 0.2 in density would lead to an error of less than 0.01%. Densities of other salts were taken from the "International Critical Tables."

In Table I are presented the results of measurements for seven salts. Concentration of the solution in moles of salt per liter of solution is given in the first column, the equivalent conductance in the second column. Here, the specific conductance due to the salt has been assumed to be the difference between the observed conductance of the solution and that of the solvent. The specific conductance of the solvent is given at the head of each series of measurements.

IV. Discussion

(1) **Consistency of Experimental Results.**—The Λ values of Table I were plotted as a function of the square root of concentration and the plots were linearly extrapolated to zero concentration to determine limiting conductances. These values are shown in the second column of Table II. The plots are shown in Fig. 3 where the diameter of the

---

(7) Monk, THIS JOURNAL, **70**, 3281 (1948); Scott and Tartar, *ibid.*, **65**, 692 (1943); Hartley and Donaldson, *Trans. Faraday Soc.*, **33**, 457 (1937).

(8) Kraus and Dexter, THIS JOURNAL, **44**, 2468 (1922).

(9) Crystallizes from ethyl acetate in metastable form, melting at 101–102°.

TABLE I

CONDUCTANCE OF SOME SALTS IN WATER AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
A. Potassium chloride			
$\kappa_0 = 3.737 \times 10^{-7}$		$\kappa_0 = 3.687 \times 10^{-7}$	
1.1556	148.97	3.3448	148.27
2.6924	148.44	5.0999	147.84
5.2463	147.83	7.3643	147.37
8.9078	147.15	8.9915	147.13
10.092	146.98		
B. Potassium bromate			
$\kappa_0 = 4.511 \times 10^{-7}$		$\kappa_0 = 4.352 \times 10^{-7}$	
0.46348	128.76	1.1521	128.35
1.3136	128.24	5.2033	127.19
2.6864	127.76	9.4095	126.45
4.8984	127.21		
8.4901	126.56		
C. Tetramethylammonium picrate			
$\kappa_0 = 4.506 \times 10^{-7}$		$\kappa_0 = 4.518 \times 10^{-7}$	
0.56115	74.78	0.20761	75.08
1.0169	74.61	.57912	74.73
1.4343	74.51	1.1390	74.49
2.2207	74.24	1.9748	74.21
3.0068	74.06	2.5341	74.09
		3.3334	73.89
D. Tetraethylammonium picrate			
$\kappa_0 = 3.938 \times 10^{-7}$		$\kappa_0 = 4.117 \times 10^{-7}$	
0.31684	62.58	0.16724	62.73
.68370	62.40	.53563	62.47
1.0172	62.28	1.3466	62.19
1.9897	61.97	2.3345	61.91
		4.0677	61.60
E. Tetra-*n*-propylammonium iodide			
$\kappa_0 = 4.620 \times 10^{-7}$		$\kappa_0 = 4.310 \times 10^{-7}$	
0.41669	99.72	0.24238	99.84
.93501	99.40	.61408	99.62
1.5598	99.16	1.4542	99.30
2.3704	99.00	3.1622	98.78
3.8959	98.61	5.4411	98.28
F. Tetra-*n*-butylammonium bromide			
$\kappa_0 = 4.717 \times 10^{-7}$		$\kappa_0 = 3.896 \times 10^{-7}$	
0.27279	97.05	0.35238	97.11
.83588	96.81	.71589	96.85
1.5813	96.56	2.1565	96.43
3.0893	96.17		
5.0748	95.73		
G. Tetra-*n*-amylammonium bromide			
$\kappa_0 = 4.393 \times 10^{-7}$		$\kappa_0 = 4.259 \times 10^{-7}$	
1.2414	94.72	0.16811	95.26
2.6029	94.29	0.52873	94.94
4.4106	93.87	1.2836	94.70
		2.6089	94.27

TABLE II

LIMITING CONDUCTANCE OF SALTS IN WATER AT 25°

Salt	Λ_0 (extrap.)	Λ_0 (calcd.)	Diff. Λ_0
KCl	150.02	149.98 ± 0.01	−0.04
$KBrO_3$	129.28	129.24 ± .04	− .04
Me_4NPi	75.35	75.31 ± .01	− .04
Et_4NPi	63.01	63.05 ± .02	+ .04
Pr_4NI	*100.26*	*100.25* ± *.03*	− *.01*
Bu_4NBr	97.57	97.61 ± .02	+ .04
Am_4NBr	95.62	95.61 ± .01	− .01

circles corresponds to 0.1% of the conductance value.

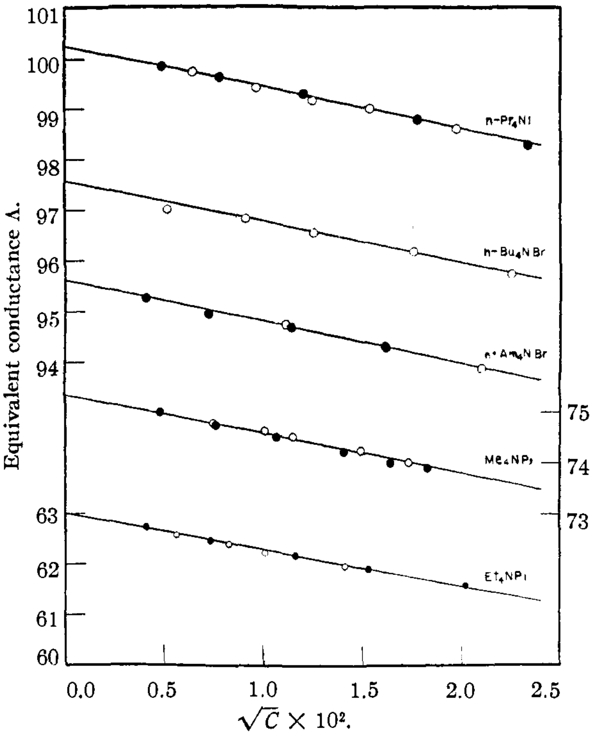

Fig. 3.—The equivalent conductance of some tetra-*n*-alkylammonium salts in water at low concentrations; scale for Me_4NPi on right.

All experimental values lie on straight lines within the limit of experimental error. The mean value of the average deviation of all points for five quaternary salts is 0.028% with a maximum average deviation of 0.037%, for one salt. The slope of the Λ–$\sqrt{C}$ plots for these salts differs slightly from the theoretical of Onsager. The ratio of the observed to the theoretical slope varies between 1.032 and 0.979; the mean value of the ratios for the five salts is 1.003. It seems, therefore, that these salts conform to Onsager's equation within the limit of experimental error.

(2) **Method of Evaluating Λ_0.**—Since the salts as here measured conform to the Onsager equation at concentrations below 1×10^{-3} *N*, it would seem that Λ_0 might be evaluated by substituting values of Λ and C in Onsager's equation and solving for Λ_0. Several conductance values between 1×10^{-4} and 1×10^{-3} *N* should provide more reliable Λ_0 values by this method than by extrapolation of Λ values for more dilute solutions.

The conductance of potassium chloride was determined with considerable care for two independent series of 5 and 4 points, respectively. The experimental values of Table IA yield a linear plot in terms of $\sqrt{C}$ and extrapolate to a Λ_0 value of 150.02. The equation of the line is

$$\Lambda_0 = 150.02 - 96.0\sqrt{C} \qquad (1)$$

and the average deviation of the experimental values from this equation is 0.008%.

According to Shedlovsky, the equivalent conductance of a 1×10^{-3} *N* solution of potassium chloride (corrected to Jones and Bradshaw's standard value) is 146.98. Substituting this value in Onsager's equation and solving, we obtain $\Lambda_0 = 149.98$. The conductance equation then becomes

$$\Lambda = 149.98 - 94.5\sqrt{C} \qquad (2)$$

In Table III, experimental Λ values are compared with values computed according to equation (2). Experimental values are given in the first line, computed values in the second and differences, ΔΛ, in the third line. In computing the constants of the conductance equation, the dielectric constant has been taken to be 79.54[10] and the viscosity 8.949×10^{-3} poise.[11] The maximum difference between observed and calculated values is 0.04 Λ unit and the average difference is 0.011 Λ unit. The experimental values approximate the Onsager equation within the limit of experimental error. Since conductances can be measured more accurately at higher than at lower concentrations, we shall adopt the value 149.98 as the limiting equivalent conductance of potassium chloride in water at 25°.

Table III

Comparison of Observed and Calculated Values of Λ for KCl in Water at 25°

Series 1

$C \times 10^4$	1.1556	2.6924	5.2463	8.9078	10.092
Λ obsd.	148.97	148.44	147.83	147.15	146.98
Λ calcd.	148.97	148.43	147.81	147.16	146.98
ΔΛ	0.00	+0.01	+0.02	−0.01	0.00

Series 2

$C \times 10^4$	3.3448	5.0999	7.3643	8.9915
Λ obsd.	148.27	147.84	147.37	147.13
Λ calcd.	148.25	147.84	147.41	147.14
ΔΛ	+0.02	0.00	−0.04	−0.01

Shedlovsky[3,12] has found that the conductance of potassium chloride is reproduced quite accurately up to fairly high concentrations by an equation which may be written

$$\Lambda = \Lambda_0 - \alpha\sqrt{C} + (\alpha^2/\Lambda_0^2)C\Lambda \qquad (3)$$

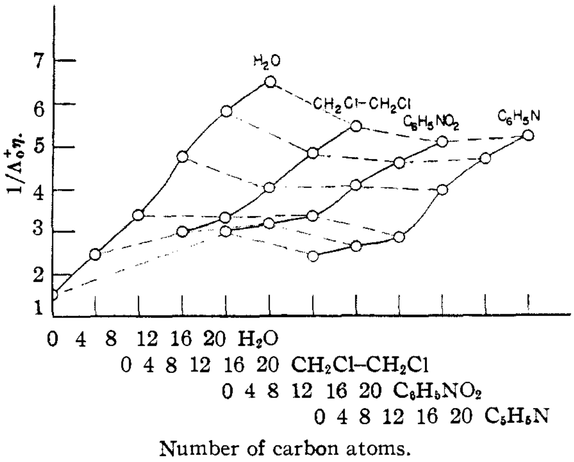

Fig. 4.—Ion resistances in different solvents.

If we substitute the values $\Lambda = 146.98$, and $C = 1 \times 10^{-3}$ in this equation and solve, we obtain $\Lambda_0 = 149.93$. In the concentration range, 0 to 1×10^{-3} N, the differences between the Onsager and the Shedlovsky equations are at maximum about 0.05 Λ unit. Our measured values for potassium chloride conform much more closely to the Onsager than to the Shedlovsky equation. However, the differences are so small that further precise measurements are needed before this question can be finally resolved. In the meantime, we shall employ the Onsager equation and compute values of Λ_0 from measurements between 1×10^{-4} and 1×10^{-3} N. In the third column of Table II are shown Λ_0 values computed on this basis. The difference between computed and extrapolated values are given in the last column of this table. The maximum difference is 0.04 Λ unit and positive and negative differences are well distributed.

(3) **Ion conductances** have been computed from the Λ_0 values of Table II. Using 149.98 for the limiting conductance of potassium chloride and 0.4906[4] for the transference number of this salt, we obtain the ion conductances of Table IV. Values for the conductance of the bromide and the picrate ion are due to McDowell[13] and values for the iodide and the nitrate ions are derived from data of Shedlovsky.

Table IV

Ion Conductance Based on Λ_0 $K^+ = 73.58$

Ion	Λ_0^-	Ion	Λ_0^+
Cl^-	76.40	K^+	73.58
Br^-	78.48	Me_4N^+	44.92
I^-	76.80	Et_4N^+	32.66
NO_3^-	71.38	Pr_4N^+	23.45
BrO_3^-	55.66	Bu_4N^+	19.13
Pi^-	30.39	Am_4N^+	17.13

It is of interest to note that the conductance of the picrate ion is relatively high in comparison with that of the quaternary ammonium ions. Thus, the picrate ion, with 16 atoms other than hydrogen, is almost as good a conductor as is the tetraethylammonium ion, with 9 atoms, and a much better conductor than the tetrapropylammonium ion, with 13 atoms other than hydrogen.

It has been of interest to learn how the conductance of the symmetrical ammonium ions varies as a function of the number of carbon atoms in the substituent groups. However, as Thompson[14] has suggested, it is better to compare equivalent ion resistances rather than conductances. Since we shall want to compare resistance values in water with similar values in other solvents of different viscosity, we shall employ the reciprocals of the conductance–viscosity product, $1/\Lambda_0\eta$, rather than the reciprocal of the ion conductances.

In Fig. 4 are shown resistance plots for the symmetrical quaternary ammonium ions from tetramethyl to tetra-*n*-amylammonium, inclusive, in water, ethylene chloride, nitrobenzene and pyridine. Values are also shown for the ammonium ion, except for ethylene chloride. The curve for water is only slightly flexed and it is

---

[10] Wyman, *Phys. Rev.*, **35**, 623 (1930).

[11] Dorsey, "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y. 1939, p. 10.

[12] Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

[13] M. J. McDowell, Thesis, Brown University, 1950.

[14] Walter C. Thompson, Thesis, Brown University, May, 1941.

much steeper than are the curves for the other solvents. In solvents other than water, the ammonium and the tetramethylammonium ions have a relatively high resistance and the resistance change in going from the ammonium to the tetraethylammonium ion is relatively small. In water the resistances of the smaller ions is low and the increase in resistance on the addition of four carbon atoms is much the same all the way from the ammonium to the tetra-*n*-amylammonium ion. Compared to other solvents, in water, small ions have much too low a resistance, large ions have too high a resistance. The exceptionally low resistance of small ions in water has not been accounted for up to now.

It may be pointed out that Walden's rule is only an approximation. In water, the resistance of the tetraethylammonium ion is approximately the same as that of this ion in ethylene chloride and nitrobenzene. In pyridine, however, the resistance is much less than in water. The tetrabutylammonium ion has much the same resistance in pyridine, nitrobenzene and ethylene chloride, but it has a much higher resistance in water.

V. Summary

1. A new technique is described for measuring the conductance of aqueous salt solutions to low concentrations.

2. The conductance of five symmetrical quaternary ammonium salts, from tetramethyl to tetra-*n*-amylammonium, has been measured.

3. The conductance of potassium chloride has been remeasured as has also that of potassium bromate.

4. All salts conform to Onsager's equation within the limit of experimental error.

5. It is suggested that, in evaluating Λ_0, measured values of Λ and C between 1×10^{-4} and 1×10^{-3} N be substituted in Onsager's equation and the equation solved for Λ_0.

6. Ion conductances have been computed from the Λ_0 values obtained from the measured conductances.

7. Equivalent ion resistances in water are compared with those of the same ions in several nonaqueous solvents.

The resistance of small ions in water is much smaller than it is in other solvents; the resistance of large ions is greater. The resistance change per added carbon atom is much greater in water than it is in other solvents.

PROVIDENCE, R. I. RECEIVED AUGUST 9, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL, INORGANIC, AND CATALYTIC CHEMISTRY OF THE INSTITUTE "NICOLAOS CANELLOPOULOS," PIRAEUS (GREECE)]

Kinetics of the Kjeldahl Reaction

BY GEORGE-MARIA SCHWAB[1] AND ELLY SCHWAB-AGALLIDIS[1a]

Introduction

The oxidation of organic compounds by concentrated sulfuric acid with the transformation of organic nitrogen to ammonium sulfate in the Kjeldahl analysis is well known. The kinetics of this reaction were first studied by Bredig and Brown,[2] who found the oxidation of aniline and naphthalene to be of the first order. They investigated the dependence of the reaction velocity on the concentration of copper and mercury present as catalysts, and determined the temperature coefficient of the reaction. Numerous papers are available on the Kjeldahl reaction, which have been ably reviewed by Lindner.[3] Kinetic studies, however, are largely lacking, and it is the intention of this paper to re-examine the catalysis and kinetics of this reaction on modern grounds.

The oxidation of aniline by sulfuric acid may be written

$$(C_6H_5NH_3)_2SO_4 + 28H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 28SO_2 + 12CO_2 + 32H_2O \quad (1)$$

although it is improbable that so complicated a reaction will proceed in one step. As is seen from the equation, large quantities of gas are evolved, approaching 5.4 l. of dry gas per gram of aniline. Bredig and Brown followed the reaction by observing the volume of the dried reaction gases at successive time intervals. In the present paper the actual reaction velocity was observed by measurement of the rate of gas evolution with a suitable flowmeter. This method is extremely simple and allows the making of a large number of observations in a short period of time.

Experimental

The apparatus used is represented by Fig. 1. The reaction vessel consisted of a test-tube B, suspended in a flask A containing anhydrous sulfuric acid which acted as a temperature control bath. The reaction tube was closed with a rubber stopper bearing a thermometer and delivery tube. The reaction gases were dried in the sulfuric acid bubbler C, and freed from acid droplets by means of glass wool in the tube D. Rate of gas evolution was measured by the flowmeter E. This was of a dead space free design, having the retarding capillary at (a) protected by glass wool at (b). The measuring liquid was sulfuric acid. The wide capillary at (c) had the purpose of damping the unavoidable fluctuations of flow. Calibration gave 2.2 cc./min. of air per cm. of H_2SO_4 or 2.95 cc./min. of reaction gas per cm. of H_2SO_4. The apparatus was heated by a hand regulated bunsen burner or electric hot-plate, and the temperature kept constant to ±1°.

For each determination the bath A was heated to the desired reaction temperature and tube B with the cold

---

(1a) Physikalisch-Chemisches Institut der Universität München, Germany.

[1] In the development of the experimental method and part of the measurements we were most effectively supported by Mr. C. Parisis, and we wish to express our gratitude and acknowledgment here, as equally to Mr. W. C. Oelke (Iowa) for rewriting and editing the manuscript.

[2] G. Bredig and J. W. Brown, *Z. physik. Chem.*, **46**, 502 (1903).

[3] J. Lindner, in G.-M. Schwab's "Handbook of Catalysis," Vol. VII, Catalysis in Organic Chemistry," R. Criegee, Springer, Vienna, 1943, II, 605.