Summary

A biochemical investigation on the immature herring (used in sardine packing) to determine the cause of the decomposition of feedy fish, which makes them unacceptable for food purposes within a few hours, showed the following points.

1. The pepsin extracted with water from the stomach of the fish is more active at 37° than at lower temperatures and at hydrogen-ion concentrations between P_H 2.5 and P_H 2.85 than at higher or lower values. It is comparatively inactive above P_H 4.0. Less pepsin is extractable from the stomach of feedy fish than from the stomach of non-feedy fish.

2. The trypsin extracted with water from the pyloric ceca is more active at blood heat than at lower temperatures and between P_H 8.5 and 9.5 than at higher or lower values. It acts slowly, however, at P_H 6.85. Decidedly more trypsin is extractable from the ceca of feedy fish than from the ceca of non-feedy fish.

3. In mixtures of ground flesh and digestive organs, enzymic digestion is rapid and is attributable mainly to the presence of the pyloric ceca. The stomach and intestines, as well as muscle autolysis, play only an insignificant part in the breaking down of the proteins.

4. The flesh of feedy fish is invaded by bacteria and by the trypsin of the pyloric ceca, but the visible evidence of decomposition—the softening of the abdominal wall—is due almost solely to the action of the trypsin, which is greater in amount or more active than that in the ceca of non-feedy fish, and which readily escapes from the delicate and highly congested tubules, quickly penetrating to the adjacent tissues of the ventral wall.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE BASIS FOR THE PHYSIOLOGICAL ACTIVITY OF CERTAIN -ONIUM COMPOUNDS. V. THE MOBILITIES OF THE -ONIUM IONS. II[1]

BY ISAAC BENCOWITZ[2] WITH R. R. RENSHAW

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The problem of determining which properties of the -onium compounds are responsible for their physiological effects has been discussed in some detail elsewhere. It was there pointed out that evidence exists for believing that some sort of an electrical effect[3] is involved. It seems de-

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[1] This problem is being carried on in coöperation with Dr. Reid Hunt of the Harvard Medical School. The physiological data are the basis of a series of papers published elsewhere by him.

[2] National Research Fellow in Chemistry.

[3] Renshaw, *Science*, **62**, 384 (1925).

sirable, therefore, to obtain data on the mobilities of several of the -onium ions, including such ions as would give a representative variation in activity. No attempt will be made to discuss relationship of mobilities with muscarine and nicotine effects of these ions until further data are available.

In this, the second paper on the mobilities of -onium ions, data are presented for the mobilities of the tetramethyl-, tetra-ethyl- and tetrapropylammonium ions.

Preparation of Materials

Tetramethylammonium Bromide.—The tetramethylammonium bromide used in this investigation was an Eastman Kodak Company product. It was twice recrystallized from conductivity water, washed with absolute alcohol and dried in a vacuum desiccator over phosphorus pentoxide.

Tetra-ethylammonium Chloride and Tetrapropylammonium Iodide.—These salts were Kahlbaum products. They were purified by recrystallization from alcohol and subsequent washing with ether. The salts were then dried in vacuum desiccators. The tetrapropylammonium iodide was kept in the dark inasmuch as on exposure to light it turned yellow. As an additional precaution, the upper layer was scraped off and discarded; only the white crystals were used in making up the stock solution.

Water.—The water employed in this investigation was prepared by a method developed in this Laboratory.[4] The conductivity of the water used was about 0.1×10^{-6}.

Measuring Apparatus

The bridge assembly, cells and the technique of cleaning and drying the latter have been described in an earlier paper.[5] The large quartz cell was slightly modified in order to avoid any possible error in making up the solutions.

This cell, shown in Fig. 1, consisted of a 1-liter Vitreosil flask A. The electrodes had an area of about 5 sq. cm. and were placed approximately 4 mm. apart. The electrodes were sealed into the quartz tube C. The stock solution was introduced into the cell from a weight pipet through the quartz tube D. The lower end of this tube was below the surface of the solution in the cell; the upper end was connected by means of rubber tubing to a wide glass tube E. The latter contained an inner tube F. When suction was applied to tube F, the solution in the cell was lifted up to the very end of the quartz tube D. This washed out any of the stock solution that might cling to the walls of the tube and cause an error in the concentrations. The water in the tube E formed a seal between the solution and the outside air. A blank test showed that no change in the conductivity took place during the time required to introduce the stock solution into Tube D. This arrangement was found to be very satisfactory. The solution was stirred by a slow current of purified air which had been

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[4] Bencowitz and Hotchkiss, *J. Phys. Chem.*, **29**, 705 (1925).

[5] Bencowitz and Renshaw, THIS JOURNAL, **47**, 1904 (1925).

previously saturated and brought to the required temperature. The air was blown into the cell through the quartz tube B. While collecting conductivity water the cell was connected with the still by means of Tube D.

Cell Constants.—Two auxiliary cells previously described by the authors were employed for the purpose of calibrating the quartz cell. The cell constant of Cell I was calibrated with 0.1 *D* (0.1 mole per 1000 cc. of solution) potassium chloride solution made up as directed by Parker and Parker.[6] The cell constant of Cell I determined in May, 1925, and used in this investigation was 2.0807 which checked very closely with the cell constant of 2.0813 and 2.0810 determined on June 7 and October 24, 1924, respectively. It will be seen that there is a general drift in the constant. This was also noticed by Kraus.

Cell II was intercompared with Cell I and the quartz cell was intercompared with Cell II. All precautions recommended by previous investigators[7] and employed by the authors in an earlier paper were closely observed and need not be described here. Suffice it to say that the cell constant of the quartz cell was redetermined after each run.

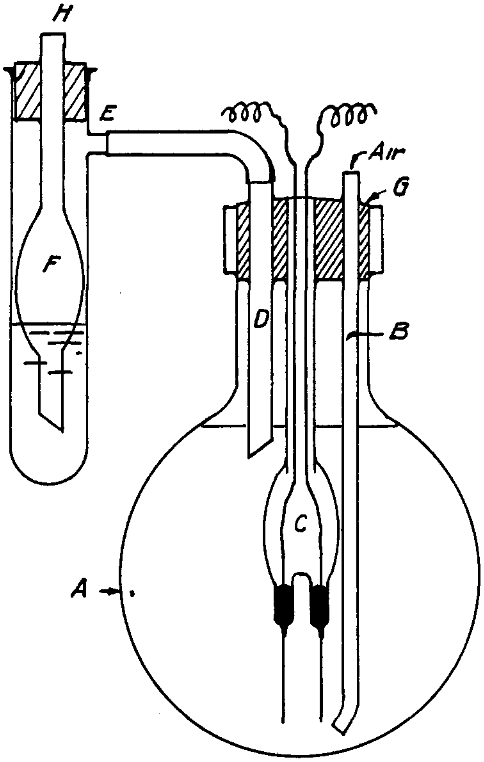

Fig. 1.

TABLE I

CONSTANTS OF QUARTZ CELL USED IN MEASURING THE CONDUCTANCE OF AMMONIUM SALTS

	Tetra-methylammonium bromide	Tetra-ethylammonium chloride	Tetrapropyl-ammonium iodide
Run I	0.029759_8	0.030578_2	0.031985_9
Run II	$.030876_1$	$.033172_9$	$.032117_5$
Run III	$.022715_0$	$.031569_9$	$.032108_0$

Density.—In order to reduce the concentrations to a volume normal basis, it was necessary to determine the density of the salt solution. An

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[6] (a) Parker and Parker, THIS JOURNAL, **46**, 312 (1924). (b) See also Ref. 5.

[7] Kraus and Parker, *ibid.*, **44**, 2429 (1922). Parker, *ibid.*, **45**, 1369 (1923). Morgan and Lammert, *ibid.*, **45**, 1692 (1923). Ref. 5.

Ostwald pycnometer of about 15cc. capacity was employed for the measurements. No fineness in the technique of the density measurement was observed. The experimental error of these measurements, however, is much less than the error with which the concentrations were determined. Furthermore, the corrections for the change in density of dilute solutions employed in this investigation are almost negligible. The densities finally used were read off a smooth curve drawn straight down to the density of water at 25°. For tetraethylammonium chloride the densities of Schiff and Monsacchi[8] were adopted.

Experimental Procedure and Results.—The experimental procedure was very similar to that described in the first paper of this series. The slight changes made were necessitated by the modification of the quartz cell. When the desired quality of conductivity water was collected in the cell, the latter was placed in the thermostat where it was allowed to stand for several hours until temperature equilibrium was reached. This was determined by several resistance measurements. The resistance of the water having been determined, the first concentration was made by introducing a weighed quantity of the stock solution which had been made up previously. This solution was prepared by weighing out carefully a calculated amount of the salt and introducing it into a weighed quantity of conductivity water. The solution was approximately 0.1 *N* and was stored in a quartz flask.

In all, about 15 g. of the solution was added to the cell in each run. This amount of liquid did not change the height of the solution in the cell sufficiently to change the cell constant appreciably. The resistance at each concentration was measured thrice at 15-minute intervals, each measurement being taken with four known resistances. The average deviation from the average was never more than 0.02%. When the run was completed the cell was removed from the thermostat, the outside was washed and the cell was dried and weighed. The weight of the quartz cell was determined several times during the investigation and found to be constant within 0.01%. This is seen from the following series.

July 14	325.95_6 g.	August 31	326.00_3 g.
Sept. 25	326.01_0 g.	November 30	325.98_7 g.
May 8	326.01_5 g.	August 15	325.98_3 g.

Conductance Data.—The results obtained in this investigation are given in Table II where the values of the equivalent conductance, and the concentration C are shown. The latter is expressed in millimoles per liter. The molecular weights were assumed to be 154.023 for tetramethylammonium bromide, 165.625 for tetra-ethylammonium chloride and 313.212 for tetrapropylammonium iodide. At the head of each sub-table are given

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[8] Schiff and Monsacchi, *Z. physik. Chem.*, **24**, 517 (1897).

the cell constant K, the specific conductance of the water used L_w, and the total weight of the water, W, employed in making up the solution in the cell. These data are shown in Fig. 2 where $1/\Lambda_c$ is plotted against the specific conductance L_s of the solution. In extrapolating to infinite dilution, the *minimum* value for Λ_∞, the conductivity at infinite dilution, is obtained.[9]

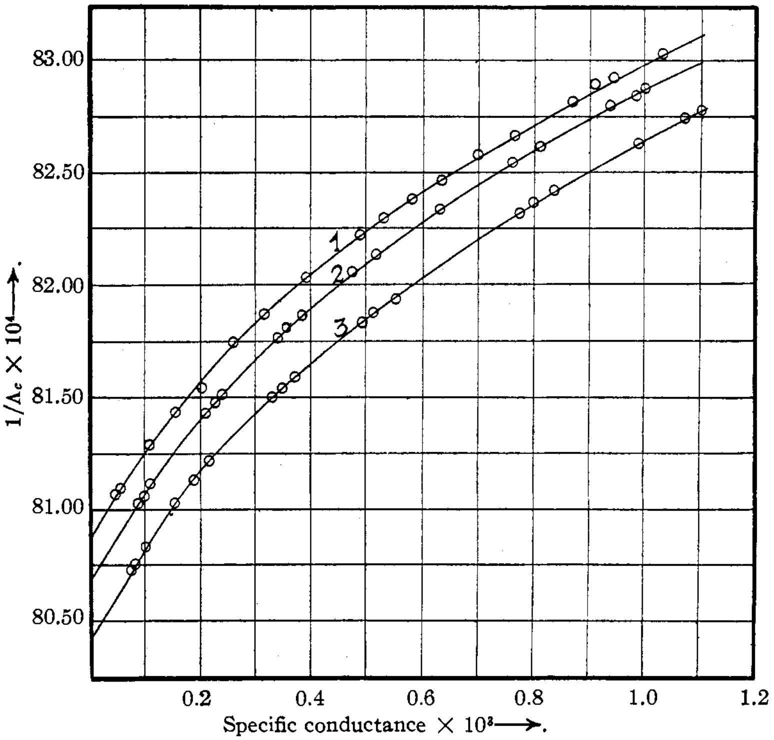

Fig. 2.—1, tetrapropylammonium iodide; add 19.45 to $1/\Lambda_c$. 2, tetraethylammonium chloride; add 10.75 to $1/\Lambda_c$. 3, tetramethylammonium bromide; scale without correction.

Conductance data at round concentrations have been calculated for the three salts. It is possible that these may be published in the International Critical Tables.

Kohlrausch's Rule.—Kohlrausch[10] as early as 1900 had shown that the most accurate conductivity data up to a dilution of 0.001 N were very closely expressed by the simple relation $\Lambda_\infty - \Lambda_c = K\sqrt{C}$. This empirical equation, however, had no theoretical foundation. As a matter of fact, the accepted Arrhenius theory of ionization led to quite a differ-

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[9] Kraus and Parker, This Journal, **44**, 2442 (1922). Parker, *ibid.*, **45**, 2032 (1923).

[10] Kohlrausch, "Gesammelte Abhandlungen," vol. **2**, p. 1137.

ent relationship. The simplicity of the relation and the fact that it reproduced the change of the conductivity with increasing dilution with such exactness led Kohlrausch to insist that it expressed a general law. Washburn,[11] on the other hand, referring to this relationship, contends that "the theoretical basis for the Mass-Action law is so sound that any method which denies the validity of this law as a limiting condition for *all* electrolytes must.... be henceforth rejected on this ground alone, if for no other reason." Nevertheless, Kohlrausch's rule has assumed a theoretical significance since the development of the inter-ionic theory of solution based on the assumption of complete ionization.

The equation of Debye and Hückel[12] for a given solute, solvent and temperature contains the square root of the concentration as the only variable. It has been quite definitely established experimentally that the logarithm of the activity coefficient is proportional to the square root of the concentration.[13]

Recently Walden[14] and others applied Kohlrausch's rule to conductivity data. Davies[15] showed that the rule of the square root expresses exactly Weiland's very accurate conductivity data[16] on potassium chloride and Parker's data[17] on hydrochloric acid.

To test this rule on the experimental data obtained in this paper on the alkyl ammonium salts and data in the preceding paper on the alkyl sulfonium salts, the square roots of the concentrations were plotted against the equivalent conductances. It will be seen in Fig. 3, that all these salts give straight lines. If we accept the theoretical significance of the square-root rule ascribed to it by the inter-ionic attraction theory of Debye and Hückel, then these curves indicate that the alkyl-onium salts are completely ionized and are similar to strong electrolytes like potassium chloride and hydrochloric acid.

Whatever the theoretical significance of Kohlrausch's law may be, it is obvious that it expresses exactly the change in conductance with dilution of dilute solutions of strong electrolytes. It leads to the conclusion that in order to obtain the limiting value for Λ_∞ of strong electrolytes, it is not necessary to work with solutions at concentrations below 0.0001 *N*. This is important, inasmuch as the experimental difficulties involved in working with solutions of concentrations below 0.0001 *N* are enormous.

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[11] Washburn, THIS JOURNAL, **40**, 122 (1918).

[12] Debye and Hückel, *Physik. Z.*, **24**, 201, 305 (1923).

[13] For a discussion of the inter-ionic attraction theory and its application, see Noyes, THIS JOURNAL, **46**, 1080, 1098 (1924). Reference to the literature, will be found in this paper.

[14] Walden, *Z. physik. Chem.*, **108**, 341 (1922).

[15] Davies, *J. Phys. Chem.*, **29**, 473, 979 (1925).

[16] Weiland, THIS JOURNAL, **40**, 131 (1918).

[17] Parker, *ibid.*, **45**, 2017 (1923).

The limiting values for Λ_∞ obtained from $\Lambda_c - \sqrt{C}$ curves are considerably higher than those obtained from the $1/\Lambda_c - L_s$ curve. This is shown in Table I, in the second column of which are given the limiting values, Λ'_∞ obtained from a $1/\Lambda_c - L_s$ curve and in the third column are given the values Λ''_∞ obtained from a $\Lambda_c - \sqrt{C}$ curve.

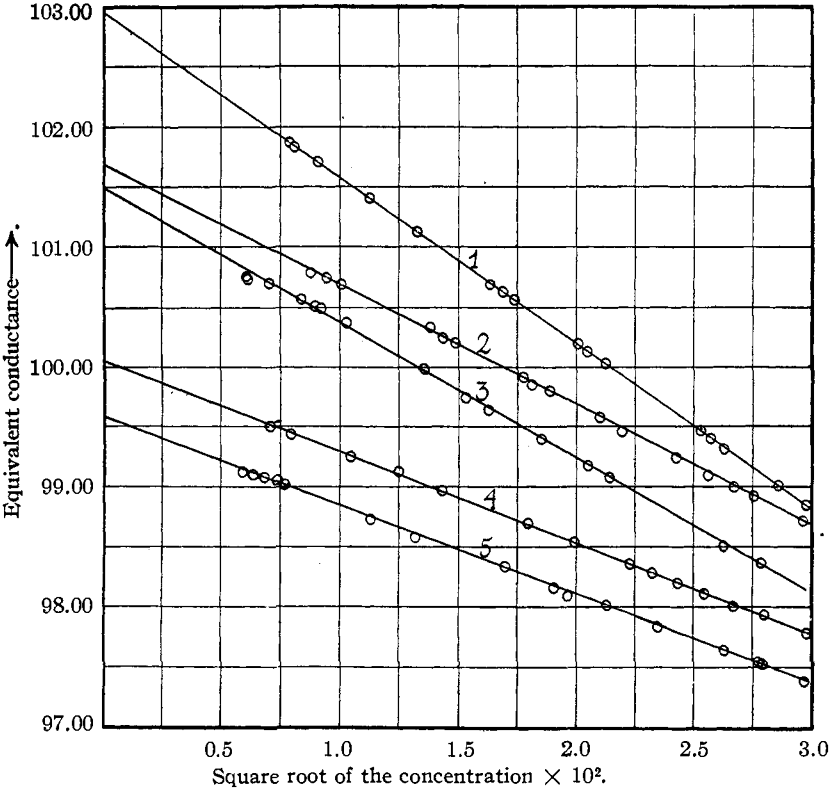

Fig. 3.—1, tetramethylammonium bromide; add 22 to Λ_c. 2, tetra-ethylammonium chloride; add 5 to Λ_c. 3, trimethylsulfonium iodide; add 26.5 to Λ_c. 4, tetrapropylammonium iodide; Λ_c without correction. 5, triethylsulfonium bromide; add 14.2 to Λ_c.

It is difficult to determine which of the two values is the true Λ_∞. It is important to point out, however, that errors inherent in the most accurate

TABLE I

THE MAXIMUM AND MINIMUM VALUES OF ALKYL-ONIUM SALTS

	Λ'_∞	Λ''_∞
Tetramethylammonium bromide	124.34	124.98
Tetra-ethylammonium chloride	109.19	109.73
Tetrapropylammonium iodide	99.69	100.10
Tetramethylsulfonium iodide	127.49	127.76
Tetra-ethylsulfonium bromide	113.49	113.50

experimental work at very high dilution tend to lower this value. Furthermore, the $1/\Lambda_c - L_s$ curves are very much more sensitive to errors in concentration than the $\Lambda_c - \sqrt{C}$ method of extrapolation. These two considerations in addition to the theoretical significance of the square-root rule lead to the conclusion that the maximum value of Λ_∞ obtained by the $\Lambda_c - \sqrt{C}$ curve is probably the more nearly correct value.

Mobilities of the Alkyl Ammonium Ions

Accepting the minimum values for the conductivity of infinite dilutions, obtained from the $1/\Lambda_c - L_s$ curves of Fig. 2, for the time being, we get the following results: tetramethylammonium bromide, 124.34; tetraethylammonium chloride, 109.19; tetrapropylammonium iodide, 99.69. Assuming the mobilities of the chloride, bromide and iodide ion at 25° to be 75.10, 77.44 and 76.12, respectively,[18] we obtain for the limiting values of the tetramethylammonium ion, 46.90 for that of the tetra-ethylammonium ion 34.09, and for that of the tetrapropylammonium ion, 23.57.

TABLE II[a]

CONDUCTANCE OF TETRAMETHYLAMMONIUM BROMIDE

RUN I

$K = 0.0297598$ $L_w = 0.11 \times 10^{-6}$ $W = 1025.37$ g.

Concn. $\times 10^3$	Λ_c	Concn. $\times 10^3$	Λ_c
0.062411	123.873	0.404018	122.198
.127691	123.401	.691700	121.331
.268956	122.695	.888060	120.850

RUN II

$K = 0.0308761$ $L_w = 0.12 \times 10^{-6}$ $W = 1005.10$ g.

Concn. $\times 10^3$	Λ_c	Concn. $\times 10^3$	Λ_c
0.065611	123.831	0.453690	122.039
.176888	123.125	.640086	121.478
.302764	122.563	.817980	121.021

RUN III

$K = 0.0227150$ $L_w = 0.15 \times 10^{-6}$ $W = 1021.56$ g.

Concn. $\times 10^3$	Λ_c	Concn. $\times 10^3$	Λ_c
0.002810	123.713	0.420166	122.130
.154064	123.257	.660876	121.402
.285613	122.631	.915818	120.795

Concentration of stock solution = 0.0924498 mole per 1000 g. of solution (weights in air).

CONDUCTANCE OF TETRA-ETHYLAMMONIUM CHLORIDE

RUN I

$K = 0.0305782$ $L_w = 0.17 \times 10^{-6}$ $W = 1023.52$ g.

Concn. $\times 10^3$	Λ_c	Concn. $\times 10^3$	Λ_c
0.102712	108.685	0.591929	107.245
.206856	108.242	.713995	107.006
.330585	107.862	.878990	106.725

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[18] These mobilities have been accepted by Washburn for the "International Critical Tables."

TABLE II (*Concluded*)

RUN II

$K = 0.0331729$ $L_w = 0.14 \times 10^{-6}$ $W = 1009.79$ g.

Concn. $\times 10^3$	Λ_c	Concn. $\times 10^3$	Λ_c
0.08099_1	108.78_0	0.44170_6	107.57_6
$.22253_4$	108.20_1	$.76176_6$	106.93_0
$.35673_8$	107.80_0	$.92240_2$	106.66_9

RUN III

$K = 0.0315693$ $L_w = 0.11 \times 10^{-6}$ $W = 1015.67$ g.

0.09021_2	108.74_5	0.48315_6	107.47_5
$.19468_3$	108.33_7	$.65840_0$	107.10_2
$.31509_3$	107.91_6	$.93815_6$	106.63_0

Concentration of stock solution = 0.11518_2 mole per 1000 g. of solution (weights in air).

CONDUCTANCE OF TETRAPROPYLAMMONIUM IODIDE

RUN I

$K = 0.0319859$ $L_w = 0.11 \times 10^{-6}$ $W = 952.11$ g.

0.05112_0	99.482_3	0.49952_2	98.352_3
$.11025_0$	99.265_9	$.64771_4$	98.113_2
$.26569_4$	99.821_5	$.89100_0$	97.779_6

RUN II

$K = 0.0321175$ $L_w = 0.095 \times 10^{-6}$ $W = 1008.66$ g.

0.060061_4	99.460	0.59292_9	98.199_5
$.15750_0$	99.121_5	$.71555_0$	98.009_8
$.39800_0$	98.539_5	$.93390_0$	97.702_3

Run III

$K = 0.0321080$ $L_w = 0.107 \times 10^{-6}$ $W = 1010.37$ g.

0.20695_6	98.973_0	0.78418_8	97.919_5
$.32312_1$	98.698_0	$.96739_8$	97.678_1
$.54247_1$	98.282_0	1.0601_2	97.581_2

Concentration of stock solution = 0.095708_4 mole per 1000 g. of solution (weights in air).

[a] W indicates the total weight of water in a vacuum. The concentrations are expressed in millimoles per liter in a vacuum, and the conductance in reciprocal ohms. The International Atomic Weights of 1924 were used.

The constant of the reference cell was determined with a 0.1 D (0.1 mole per 1000 cc. of solution) KCl solution as described by Parker and Parker (Ref. 6a). Its specific conductance at 25° was assumed to be 0.012852_4.

The authors wish to express their thanks to the Directors of the Warren Fund, American Academy of Arts and Sciences, for a grant which has covered part of the expenses of this investigation.

Summary

1. Conductivity measurements with tetramethylammonium bromide, tetra-ethylammonium chloride and tetrapropylammonium iodide between concentrations of 0.06 and 1.0 millimole per liter have been carried out.

A quartz cell and water having a conductivity of the order of 0.1×10^{-6} were used. The solutions were made up by weight with an error of less than 0.05%.

2. Values at round concentrations have been interpolated from the results upon the three salts. These data may be published in the "International Critical Tables."

3. Extrapolation of the results, on the assumption that the mass-action law is approached as a limiting form at infinite dilution, gives a value of Λ_∞ for tetramethylammonium bromide, 124.34, for tetra-ethylammonium chloride, 109.19 and for tetrapropylammonium iodide, 99.69.

4. Assuming that the value of Λ_∞ at 25° of the chloride ion is 75.10, of the bromide ion 77.44 and of the iodide ion 76.12, the values 46.90, 34.09 and 23.57 for the Λ_∞ of the tetramethyl-, tetra-ethyl- and tetrapropylammonium ions, respectively, are obtained.

5. The $\Lambda_c - \sqrt{C}$ curves of the three alkyl ammonium as well as the two alkyl sulfonium salts of the previous paper are straight lines. This corroborates Kohlrausch's rule which assumes a theoretical significance in the theory of complete ionization of Debye and Hückel.

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[Contribution from the College of Agriculture of the University of Wyoming]

THE NATURAL OCCURRENCE OF ACONITIC ACID AND ITS ISOMERS

By O. A. Beath

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Review of Literature

Aconitic acid has been reported as being obtained from various plant sources. From the data it is obvious that a compound varying in its melting point from 167° to 191° cannot be in every instance the normal acid, but presumably consists of the normal admixed with its isomeric forms.

Wicke[1] reports the isolation of an acid from *Delphinium consolida* having the same composition as normal aconitic acid. The melting point is not given. His evidence is based upon the composition of the silver salt and the ultimate analysis of the free acid. Parsons[2] detected aconitic acid in sorghum juice by means of characteristic salts. Behr[3] appears to have obtained large quantities of the acid from muscovado sugar and molasses, the composition of which he verified by combustion and formation of the characteristic salts. He proved that lime acting upon the invert

[1] Wicke, *Ann.*, **90**, 98 (1854).

[2] Parsons, *Am. Chem. J.*, **4**, 39 (1882).

[3] Behr, *Ber.*, **10**, 351 (1877).