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The Electrical Conductance of Aqueous Sodium Chloride in the Range 300 to 383°[1a]

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Values of equivalent conductance are tabulated at 300, 320, 345, 360, 370 and 373° for orthobaric liquid solutions, and at 360, 370, 373, 378 and 383° for solutions at densities of 0.591, 0.525, 0.447 and 0.399 g./cc., at compositions in the range $2-30 \times 10^{-4}$ molal. Limiting equivalent conductances and dissociation constants are obtained by Shedlovsky's method. The orthobaric liquid phase limiting equivalent conductance is depressed in the vicinity of the critical point. Neither hydrolysis nor the existence of triple ions appears to have a significant effect on the conductances reported.

Several investigations have been made of the electrical conductance of aqueous solutions of electrolytes at elevated temperatures,[2-5] but most of these have not approached the critical temperature closely. Noyes and co-workers[2] studied the conductances of many electrolytes—including sodium chloride—up to 306° (T_c (water) is 374°). Fogo, Benson and Copeland[3b] have measured the conductance of sodium chloride in the supercritical region 378–393° at solution densities from 0.2 to 0.4 g./cc. The present paper gives our results on the conductance of aqueous sodium chloride between 300 and 383°.

Experimental

Apparatus.—The conductance cell and the related equipment to permit its use at elevated temperatures and pressures have been described previously.[3b,6,7]

To permit use of the cell with a two-phase system, a platinum disk was attached to the cell wall near the interior electrode, between the interior electrode and the diaphragm. The disk was notched at two points on the perimeter to permit passage of solution and vapor when the cell is oscillated. The disk succeeded in making the cell constant independent of the solution volume when the meniscus is between the disk and the diaphragm. For studying the conductance of water, an auxiliary cylindrical electrode was attached to the inner electrode to decrease the cell constant.

The cell volume was determined from the weight of water required to fill the cell at room temperature. The cell constant was determined by comparison with a Jones-type glass cell, using dilute hydrochloric acid. The glass cell was calibrated with 0.01 N potassium chloride. Both cell constant and cell volume were redetermined whenever the cell was altered in any way. Corrections were made to the cell constant and volume to allow for the expansion of the cell material with temperature. At the highest temperature these corrections amounted to about −0.3% and +1.0%, respectively.

Because of the design of the cell, solutions were introduced with a glass syringe, equipped with a Pyrex needle. In order to have a constant mean density of solution in the cell for a series of salt concentrations the syringe was equipped with a calibrated, adjustable plunger stop, which permitted resetting of the syringe volume to within 0.1%.

For some of the experiments, the cell was sealed while under partial vacuum, both to eliminate most non-condensable gas from the vapor phase and to avoid solution–air contact. The cell was clamped in a specially constructed steel box, from the exterior of which the cell could be sealed after the box had been evacuated nearly to the vapor pressure of water. It was determined that the loss of water vapor from the cell during this operation was negligible.

The pressure gage and the thermocouples used were calibrated only by observing the filling points of solutions of various mean densities in the cell. The temperatures and pressures observed at each filling point have all been within 0.8° and 40 p.s.i. of the values interpolated from steam table data.[8] The discrepancies were normally less than half of these figures, indicating no serious errors in either measurement.

Electrolyte Solutions.—Water was prepared either by careful distillation or by rapid distillation followed by passage through an ion-exchange column packed with Amberlite MB-2 resin. All water had a specific conductance at 25° of less than 10^{-6} ohm^{-1} cm.$^{-1}$. Reagent grade sodium chloride was dried to constant weight, but was not otherwise purified. Sodium chloride solutions in the range $2-30 \times 10^{-4}$ molal were prepared by weight.

To determine the effect of dissolved air on the conductances at high temperature, a few samples of both water and salt solutions were de-aerated. De-ionized water was placed in a 500-cc. flask equipped with electrodes, thermometer well, insealed gas bubbling tube, and connections for partial evacuation and for sampling. Connections were made with Tygon tubing which did not contact the liquid. As nitrogen or helium was bubbled through the sample into a partial vacuum (water vapor pressure), the conductance change was followed. The 25° specific conductance of water reached $6.2-8.3 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$ (theoretical: 5.5×10^{-8} for pure water), indicating that the de-ionized water contained very little non-volatile, ionizable impurity. To prepare de-aerated sodium chloride solutions, salt crystals were added to de-aerated water. The solution was then further de-aerated. Solution concentrations were determined from the 25° conductance using the data obtained from gravimetrically prepared solutions, with appropriate solvent corrections.

De-aerated water and solutions were transferred to the conductance cell under a helium blanket in such a way that solution–air contact was avoided. Quickly, the cell side-arm assembly was screwed on, the cell was mounted in the vacuum box and the box was evacuated to the vapor pressure of water. The cell was then sealed.

Conductance Measurements.—Before each run, the 25° conductance of a solution was determined—either the sample in the high temperature cell, when its volume was sufficient, or a separate sample in a conventional glass cell.

Experiments were performed in the general manner described previously.[3b,6] The cell was first heated to 300°, where measurements were made of the pressure, temperature and liquid phase resistance. These were repeated until the measurements became constant, except for small mutually consistent drifts with time. Between measurements the cell contents were stirred by rocking the oven in 180° oscillations. The cell was then heated to 320° and the measurements were repeated.

The cell was then heated to the filling temperature—345, 360, 370 or 373°. As the filling temperature was approached, the heating rate was reduced to nearly zero, in order to provide

(1) (a) This work has been supported by a contract from the United States Office of Naval Research; (b) Taken in part from the Ph.D. thesis presented by D. Pearson to the Graduate School (1960).

(2) A. A. Noyes, *et al.*, Publication No. 63, Carnegie Institution of Washington, Washington, D. C., 1907. Parts of this report are published in: *J. Am. Chem. Soc.*, **26**, 134 (1904); **30**, 335 (1908); **31**, 987 (1909); **32**, 159 (1910); *Z. physik. Chem.*, **46**, 323 (1903); **70**, 335 (1910).

(3) (a) A. C. Swinnerton, G. E. Owen and J. F. Corwin, *Discussions Faraday Soc.*, **5**, 172 (1949); (b) J. K. Fogo, S. W. Benson and C. S. Copeland, *J. Chem. Phys.*, **22**, 212 (1954).

(4) I. M. Rodnyanskii and I. S. Galinker, *Doklady Akad. Nauk S. S. S. R.*, **105**, 115 (1955).

(5) E. U. Franck, *Z. physik. Chem.* (Frankfurt), **8**, 92, 107, 192 (1956).

(6) J. K. Fogo, C. S. Copeland and S. W. Benson, *Rev. Sci. Instr.*, **22**, 765 (1951).

(7) J. K. Fogo, S. W. Benson and C. S. Copeland, *J. Chem. Phys.*, **22**, 209 (1954).

(8) J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936.

time to stir the cell contents thoroughly. As the liquid phase filled the cell and the size of the vapor phase bubble decreased, the stirring became increasingly inefficient. The oscilloscope which serves as detector for the resistance bridge made the detection of the filling point easy. As the cell is rocked, each passage of the bubble past the electrode causes a sudden momentary rise in resistance. This rise decreases as the bubble becomes smaller. At the filling point, as at higher temperatures, rocking the cell causes no change in resistance. Heating was continued for 10–15° above the filling point, the cell being rocked continuously. Enough measurements were made to determine satisfactorily the variation of resistance with temperature. On cooling, the filling temperature was again approached very slowly, the first variation of resistance with cell position during rocking being easily observed.

Although the resistance did not depend on cell position after the cell filled, continuous rocking of the cell for about 15 minutes was required before the resistance became constant. Thereafter, all measurements were reproducible, as long as the cell was rocked continuously. If rocking was stopped, the resistance and pressure began to drift in directions consistent with the development of a density (and therefore concentration) gradient in the cell. This was most pronounced at the lowest mean densities where both density and temperature are nearest to the critical values. When the rocking was resumed, the resistance varied with cell position in a continuous manner. Continued rocking for a few minutes removed the resistance variation. In some cases the cell had been rocked continuously for 40 minutes while being heated through the last one to two degrees below the filling temperature. Because this behavior was most pronounced at the lowest mean densities (where the density of the vapor phase which condenses into the liquid phase is greatest) it is interpreted as due to concentration gradients existing in the cell at the time of filling. Accordingly, measurements taken at the filling point during cooling are representative of the filling point, and are reproducible.

During cooling, measurements at 300° were repeated in order to establish the internal consistency of the high temperature measurements.

After cooling, the 25° conductance and weight of the cell were redetermined. Negligible values of weight loss and conductance change were used as criteria of a successful run.

Results

Conductance of Water.—Several experiments were made to determine the conductance of water. No difference was observed between water prepared by distillation and by ion exchange, but de-aerated water had a lower high-temperature conductance. To determine whether carbon dioxide was responsible for this difference, a sample of water saturated with carbon dioxide at room temperature was studied. The results of this experiment indicate that the carbon dioxide in ordinary "conductivity water" contributes a negligible amount to the conductance of that water above 300°.[9] More importantly, the conductances of two de-aerated sodium chloride solutions agreed with the conductances of solutions which were not de-aerated. The slight superiority of de-aerated water is believed to be due primarily to the improved handling techniques which accompanied its use.

The solvent corrections used with sodium chloride solutions are given in Table I. The 20% uncertainty reflects the range of conductances observed with the sample-handling techniques used with sodium chloride solutions. Since the variation of conductance with temperature at constant density was negligibly small, it was taken to be zero.

(9) The composition of this sample was estimated from the 25° conductance to be 0.025 molal. The specific conductance (ohm⁻¹ cm.⁻¹ × 10⁶) ranged from 19 at 280° to 10.0 at 343°. Using an estimated value of 1400 for the sum of the ionic equivalent conductances of the hydrogen and bicarbonate ions at 340° and assuming all of the carbon dioxide to be in the liquid phase, the first dissociation constant of carbonic acid at 340° was estimated to be 2×10^{-9}. From this result, carbon dioxide must contribute less than 0.2×10^{-6} ohm⁻¹ cm.⁻¹ at 340° to the conductance of water with a 25° specific conductance of 1×10^{-6} ohm⁻¹ cm.⁻¹ due to carbon dioxide.

At the highest temperature reached, 4% of the cell volume was occupied by vapor. If the presence of carbon dioxide in the vapor phase significantly affected the observed conductance, the conductance should rise as the cell fills. Since no such rise in conductance has been observed with ordinary water, it is concluded that this effect is not serious.

TABLE I

SOLVENT CONDUCTANCE CORRECTIONS

Temp., °C.	300	320	345	360	370	373
Soln. density, g./cc.	0.712	0.667	0.591	0.525	0.447	0.399
Spec. conduct., ohm⁻¹ cm.⁻¹ × 10⁶, ±20%	6.2	5.4	4.0	2.8	1.9	1.6

Conductance of Sodium Chloride.—The original data consisted of sets of simultaneous values of temperature, pressure and resistance (at 700 and 1000 c.p.s.). Resistances, corrected for lead resistance and polarization, were plotted against pressure for each experiment.[10] Resistances were then interpolated at the pressures corresponding[8] to the temperatures of interest—300, 320, 345, 360, 370, 373, 378 and 383°. Data were not available at 345, 360 and 370° for samples which filled the cell at higher temperatures. For samples filling the cell at 345 and 360°, resistance values above 360 and 373°, respectively, were obtained by extrapolation. Since the plots were linear and had small slopes, it is felt that the extrapolation introduced little error. From the corrected, interpolated resistances and the cell constant, specific conductances were calculated. These were corrected for solvent conductance.

Because the presence of a solute increases the orthobaric liquid density, the filling temperature of a solution is higher than that of water of the same mean density. This effect is neglible for the concentrations used here except at 373°, where an increase of filling temperature of 0.7° was observed with the most concentrated solution used. From the temperature derivative of the conductance at the filling point, it is estimated that this temperature increase produces an increase of less than 0.2% in the filling point conductance. No correction for this was made.

In order to calculate the salt concentration when a vapor phase was present, two assumptions were made. It was first assumed that the phase densities for solutions were the same as those of pure water. This seems reasonable because even in the vicinity of the critical temperature the apparent molal volume does not appear to be greater than −0.5 liter per mole at densities of 0.6 g./cc. or higher.[11] For concentrations of less than 0.003 M, this means that the density of the solution is less than 0.2% greater than that of pure water at temperatures below 345°. It was further assumed that the quantity of salt in the vapor phase was negligible in comparison with that in the liquid phase. The data of Olander and Liander[12] indicate that at 353° the weight fraction of salt in the vapor phase is about 0.2% of that in the liquid phase. This means that the quantity of salt which is in the vapor phase is less than 0.05% of the total, and is therefore negligible.

Using these two assumptions, equations for volume balance, total mass balance and solute mass balance in the system lead to the equation $C^t = C^0 \bar{d}/f$ where C^t is the concentration of salt in the liquid phase at temperature t, C^0 is the concentration of salt in the liquid phase at 0°, $\bar{d}$ is the mean density of the solution in the cell in g./cc., and f is the filling ratio, or fraction of the total volume occupied by the liquid phase. In terms of densities, $f = (\bar{d} - d^v)/(d^e - d^v)$, where d^v and d^e are the densities of the vapor and liquid

(10) Pressure was chosen instead of temperature because during the small temperature drifts which unavoidably accompanied measurements, the cell properties (resistance and pressure) lagged behind the thermocouple temperature slightly. Also, the pressure measurements are more precise than the temperature measurements at high temperatures.

(11) S. W. Benson, C. S. Copeland and D. Pearson, *J. Chem. Phys.*, **21**, 2208 (1953).

(12) A. Olander and H. Liander, *Acta Chem. Scand.*, **4**, 1437 (1950).

phases, respectively. When the cell is full, the equation reduces to $C^t = C^0\bar{d}$. The orthobaric densities were calculated from the data of Keenan and Keyes,[8] and values of $\bar{d}$ and f were corrected for cell expansion.

From the specific conductance and the concentration for each solution at each selected temperature, the equivalent conductance was calculated. Table II lists the equivalent conductances for each satisfactory experiment.

TABLE II

EQUIVALENT CONDUCTANCES OF SODIUM CHLORIDE SOLUTIONS[a]

Mean density, g./cc., 25°	Concn. at 0°, mole/1. ×10⁴	Temperature, °C.							
		300	320	345	360	370	373	378	383
0.4036	3.564	993	1052	..	..	..	*1052*	1084	1098
.4021	8.029	976	1032	1103	..	..	*963*	986	1000
.4035	14.27	..	1013	..	..	..	*882*	900	906
.4033	30.61	927	973	1019	..	..	*757*	769	771
.4527	3.184	1000	1060	..	..	*1154*	1163	1175	1182
.4524	7.169	978	1036	1104	1144	*1087*	1095	1105	1111
.4520	12.74	959	1014	1074	1095	*1017*	1024	1031	1036
.4520	27.35	934	979	1024	..	*915*	919	923	924
.5301	2.716	1001	1061	1142	*1186*	1197	1199	1201	1203
.5302	2.717	991	1051	1150	*1181*	1190	1192	1194	1196
.5291	3.968	995	..	..	*1163*	1173	1175	..	..
.5294	4.276	987	..	..	*1164*	..	..	..	..
.5299	6.112	983	1043	1120	*1149*	1156	1157	1160	1163
.5302	10.87	966	1025	1091	*1106*	1114	1115	1117	1119
.5296	23.32	942	992	1046	*1040*	1045	1046	1047	1048
.5968	2.413	1000	1062	*1146*	1156	1161	1162	1164	1165
.5968	2.415	1000	1067	..	..	..	..	..	..
.5969	5.432	986	1043	*1119*	1127	1131	..	1133	1134
.5969	9.66	972	1029	*1096*	1103	1107	..	1109	1109
.5968	20.73	952	998	*1053*	1061	..	1065	1066	1067

[a] Italic values are at the filling point. They and values at higher temperatures are at constant density, which is approximately 1% less than the 25° mean density.

Discussion

Conductance data for simple electrolytes is conveniently summarized by the limiting equivalent conductance, dissociation constant and the distance of closest approach of the ions (the a-parameter). Since the present data are not precise enough to supply information about the distance of closest approach, the data were analyzed by Shedlovsky's method.[13]

Existing data[7,14] on the dielectric constant of water were extrapolated into the vicinity of the critical temperature so as to join smoothly. The viscosity data of Sigwart[15] were used; the variation of viscosity with temperature at constant density was assumed to be zero. The values of dielectric constant and viscosity used are given in Table III.

Shedlovsky's treatment of the data resulted in the values of Λ^0 and pK listed in Table IV.[16] Most of the indicated uncertainties in the values arose in the extrapolation.

Hydrolysis of sodium chloride has been neglected. The degree of hydrolysis of a salt depends on the salt concentration and the dissociation constants of water and the conjugate acid and base. Conductance measurements on hydrochloric acid and sodium hydroxide[17] indicate that the dissociation constant of

(13) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938). The error introduced at low pK values because of the inapplicability of Shedlovsky's method (see Fuoss and Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1496 (1949)) is within experimental error. Although an exact correction cannot be made from the present data, the error in the pK value at 300° is estimated to be not greater than 0.1. Ion activities were calculated from Debye–Hückel limiting law, using values of D from Table III.

(14) G. C. Akerlof and H. I. Oshry, *J. Am. Chem. Soc.*, **72**, 2844 (1950).

(15) K. Sigwart, *Forsch. Gebiete Ingenierw.*, **7**, 125 (1936), as quoted in N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publ. Corp., New York, N. Y., 1940, p. 185.

(16) The conductance-concentration data of Table II were adjusted to the (high temperature) densities listed in Table III. All corrections were less than 0.3%.

(17) See following paper, D. Pearson, C. S. Copeland and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 1047 (1963).

TABLE III

DIELECTRIC CONSTANT AND VISCOSITY OF WATER

Density, g./cc.	Temp., °C.	Dielectric constant	Viscosity poise × 10⁴
0.712	300	19.6	9.5
.667	320	16.8	8.65
.591	345	13.4	7.34
.591	383	13.4	7.34
.525	360	11.2	6.3
.525	373	11.1	6.3
.525	378	11.0	6.3
.525	383	11.0	6.3
.447	370	9.6	5.2
.447	373	9.1	5.2
.447	378	8.6	5.2
.447	383	8.5	5.2
.399	373	8.4	4.5
.399	378	7.25	4.5
.399	383	7.2	4.5

TABLE IV

LIMITING EQUIVALENT CONDUCTANCE AND DISSOCIATION CONSTANTS OF AQUEOUS SODIUM CHLORIDE

Density, g./cc.	Temp., °C.	Λ_0, cm.² mole⁻¹ ohm.⁻¹	pK^a
0.712	300	1023 ± 2	1.33 ± 0.14
.667	320	1089 ± 1	1.46 ± .04
.591	345	1180 ± 3	1.79 ± .04
.591	360	1192 ± 6	1.82 ± .08
.591	373	1195 ± 6	1.80 ± .08
.591	378	1198 ± 8	1.82 ± .12
.591	383	1202 ± 5	1.89 ± .07
.525	360	1242 ± 3	2.16 ± .02
.525	373	1254 ± 6	2.18 ± .04
.525	378	1255 ± 6	2.17 ± .04
.525	383	1259 ± 6	2.18 ± .04
.447	370	1256 ± 9	2.64 ± .02
.447	373	1272 ± 6	2.66 ± .02
.447	378	1290 ± 8	2.69 ± .02
.447	383	1300 ± 9	2.71 ± .02
.399	373	1195 ± 10	2.92 ± .03
.399	378	1260 ± 8	3.02 ± .02
.399	383	1285 ± 15	3.06 ± .03

[a] pK values are based on hypothetical one molar standard state.

hydrochloric acid in this region is not less than about 10^{-5}, and that sodium hydroxide is a stronger electrolyte than hydrochloric acid. It is unlikely that K_w is greater than 10^{-12} at orthobaric liquid densities. Using this value for K_w and 10^{-5} for K_{HCl}, it is estimated that the conductance of a 10^{-4} M sodium chloride solution would be increased 1% by hydrolysis. More concentrated solutions would be less affected. Thus, errors in observed conductances due to hydrolysis are approximately within experimental error.

Consideration was given to the possibility of the existence of triple ions in the lower density solutions.[18] In order to estimate the effect of triple ions on the conductances of the solutions studied here, calculations were made of the conductances of hypothetical solutions whose properties were similar to the real solutions studied. Various values for the triple ion dissociation constant were used. The data thus generated were treated by Shedlovsky's method.[13] It was found that the Shedlovsky plots were concave upward and that the maximum fractional deviation of the $\Lambda S(z)$ values from the best straight line through the points was approximately equal to the fraction of the total conductance which was due to triple ions. Since no such systematic curvature as this was found for the real

(18) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933); **57**, 1 (1935).

solution data, it is concluded that the contributions of triple ions to the measured conductances are negligible.

Further discussion of the results on sodium chloride solutions is given in the following paper.[17]

The Electrical Conductance of Aqueous Hydrochloric Acid in the Range 300 to 383°[1a]

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Values of equivalent conductance are tabulated at 300, 360, 370 and 373° for orthobaric liquid solutions and at 360, 370, 373, 378 and 383° for solutions at densities of 0.525, 0.447 and 0.399 g./cc., for compositions in the range 0.5–25 × 10⁻⁴ molal. Limiting equivalent conductances and dissociation constants are obtained by Shedlovsky's method. The results are qualitatively similar to those of sodium chloride, but hydrochloric acid is a significantly weaker electrolyte. Ion association theories indicate an a-value of about 2 Å. Like NaCl, HCl solutions have very large negative volumes and entropies in the vicinity of the critical temperature.

In continuation of the study begun with sodium chloride,[2] the electrical conductance of aqueous hydrochloric acid from 300 to 383° is here reported. Previous studies of aqueous hydrochloric acid at elevated temperatures are those of Noyes and co-workers,[3a] whose maximum temperature was 306°, and Franck,[3b] whose data over an extensive range of temperatures and densities do not include the vicinity of the critical point.

Experimental

The experimental apparatus and the preparation of water have been described previously.[2]

Electrolyte Solutions.—Reagent grade hydrochloric acid was diluted with de-ionized water to make a stock solution of approximately 0.03 molar, which was stored in a Pyrex bottle. Hydrochloric acid solutions were prepared from this stock solution by dilution with de-ionized water. Concentrations (in the range 0.5–25 × 10⁻⁴ molal) were calculated from the 25° conductance using the data of Owen and Sweeton.[4] Except for the first few samples studied, hydrochloric acid solutions were de-aerated before use in order to eliminate dissolved oxygen. Portions of stock solution were added to de-ionized water which had been previously de-aerated to ensure by conductance measurement that there was no impurity in excess of 1/2000 of the concentration of the acid solution to be prepared.[5] In addition to the previously described precautions,[2] air contact with the cell interior was avoided by opening the cell in an inert atmosphere and keeping it in an inert atmosphere between experiments.

Conductance Measurements.—Experiments were conducted in the same manner as were the previously described experiments with sodium chloride,[2] except that measurements at 320 and 345° were omitted. At temperatures below the filling temperature, when a vapor phase is present, there is no single way to determine the distribution of a volatile solute like hydrochloric acid between the two phases, and thus calculate the liquid phase concentration. However, measurements were made at 300° as a check on the internal consistency of the constant density data, and with the hope of determining the 300° limiting conductance.

Results

The first few hydrochloric acid solutions studied were air-saturated, and suffered a decrease of 20–55% in

their 25° conductances as a result of heating.[6] Subsequent solutions were de-aerated in the manner described earlier and their 25° conductance changes were mostly less than 1%. The high temperature data on hydrochloric acid solutions were treated in the same manner as were the data on sodium chloride solutions,[2] except that no solvent correction was applied to the specific conductances. Equivalent conductances are listed in Table I.[7]

TABLE I

EQUIVALENT CONDUCTANCES OF HYDROCHLORIC ACID SOLUTIONS[a]

Mean density at 25°, g./cc.	Concn. at 0°, mole/l. × 10⁴	Temperature, °C.					
		300[b]	360	370	373	378	383
0.4027	1.020	1410	..	..	745	695	650
.4027	2.243	1422	..	..	570	522	478
.4040	9.173	1371	..	..	332	299	269
.4026	23.69	1258	..	..	222	198	179
.4513	1.055	1427	..	1042	1023	982	942
.4513	2.202	1416	..	864	841	792	749
.4513	6.450	1373	..	610	591	547	511
.4514	7.762	1375	..	582	563	521	486
.4514	18.54	1304	..	416	404	372	346
.5296	0.513	1464	1469	..	1458	1449	..
.5294	1.984	1424	1306	..	1260	1238	..
.5297	2.447	1420	1264	..	1214	1191	..
.5291	3.872	1417	1192	..	1123	1093	..
.5296	9.330	1379	997	..	915	883	..
.5297	19.07	1348	830	..	740	709	..
.5294	23.47	1311	757	..	673	642	..

[a] Italic values are at the filling point. They and values at higher temperatures are at constant density, which is approximately 1% less than the 25° mean density. [b] See footnote 7.

Limited observations were made on sodium hydroxide solutions. On heating to 300° or higher, solutions prepared from distilled sodium metal and water invariably decomposed to form an electrolyte of lower 25° conductance. Attack occurred on both the platinum cell body and the synthetic sapphire insulator. At 360°, the conductance slowly rose, probably because of partial hydrolysis to sodium hydroxide.

(1) (a) This work has been supported by a contract from the United States Office of Naval Research; (b) Taken in part from the Ph.D. thesis presented by D. Pearson to the Graduate School (1960).

(2) See preceding paper: D. Pearson, C. S. Copeland and S. W. Benson, J. Am. Chem. Soc., 85, 1044 (1963).

(3) (a) A. A. Noyes, et al., Publication No. 63, Carnegie Institution of Washington, Washington, D. C., 1907; (b) E. U. Franck. Z. physik. Chem. (Frankfurt), 8, 192 (1956).

(4) B. B. Owen and F. G. Sweeton, J. Am. Chem. Soc., 63, 2811 (1941).

(5) In the course of the work, it was noticed that the minimum conductance obtainable during de-aeration was dependent on the recent history of the flask. After reaching a minimum of 6.2–10 × 10⁻⁸ ohm⁻¹ cm.⁻¹, the conductance rose steadily with time. Without gas flow, the conductance rose much more rapidly, but decreased to (approximately) the former value upon either resumption of gas bubbling or mechanical agitation of the flask. A lower minimum conductance was attainable with each replacement of the water in the flask with a fresh portion. This behavior is interpreted as due to desorption of hydrochloric acid from the (bright) platinum electrodes, during which the local concentration of acid between the electrodes may increase rapidly in the absence of agitation. This phenomenon has been observed by others; see, for example, J. C. Nichol and R. M. Fuoss, J. Am. Chem. Soc., 77, 198 (1955).

Adsorption of acid was observed in the platinum conductance cell, also. It is assumed that by 300° desorption has occurred.

(6) Noyes, et al., ref. 3a, solved this difficulty by briefly boiling their hydrochloric acid solutions in the autoclave at 60° under reduced pressure before heating.

(7) Because the 300° liquid phase concentrations were calculated on the arbitrary (and false) assumption that all of the acid was in the liquid phase, the equivalent conductances correspond to those of an electrolyte with the same mobility as hydrochloric acid but with an apparent dissociation constant which is a function of the true liquid phase dissociation constant, the liquid–vapor distribution ratio and the cell filling ratio. The limiting equivalent conductance is that of hydrochloric acid. From the conductance–concentration data at the three mean densities used, it was hoped to determine the liquid–vapor distribution ratio and the true liquid phase dissociation constant. However, the data do not permit a distinction between finite and infinite values of the dissociation constant. It appears that $a_{HCl}(v)/a_{\pm}^2(l) = 65 \pm 20$ l. mole⁻¹.