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.
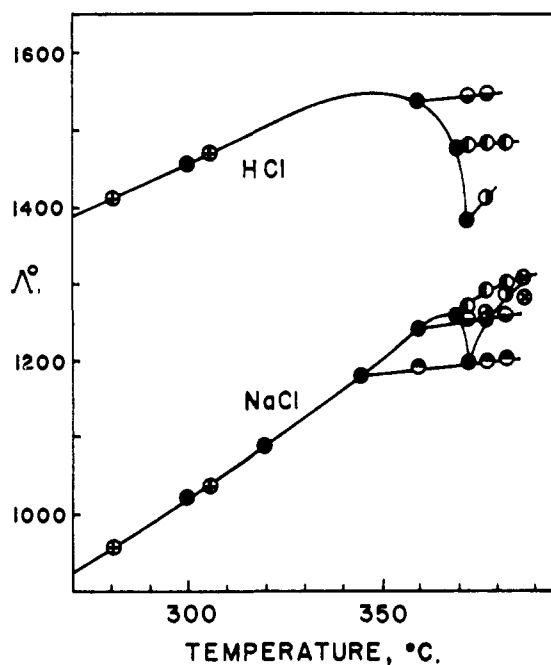
Fig. 1.—Limiting equivalent conductances of NaCl and HCl in water as a function of temperature: ●, orthobaric; ◕, 0.591 g./cc.; ◖, 0.525 g./cc.; ◐, 0.447 g./cc.; ◑, 0.399 g./cc.; ⊕, orthobaric, from data of Noyes, et al. (ref. 3a); ⊗, 0.400 g./cc., Fogo, et al. (ref. 9); ⊖, 0.400 g./cc., recalculated from data of Fogo, et al. (ref. 9).

The "hydrolyzed" electrolyte existing at high temperatures appears to be a stronger electrolyte than hydrochloric acid, with a mobility intermediate between sodium chloride and hydrochloric acid.

Discussion

The equivalent conductance–concentration data were treated by Shedlovsky's method[8] to yield limiting equivalent conductances and dissociation constants, which are listed in Table II. The limiting equivalent conductances are shown, together with results for sodium chloride,[2,3a,9] as a function of temperature in Fig. 1 and as a function of solution density in Fig. 2. Agreement between the present data and previously existing data is well within experimental error.[10]

TABLE II
Limiting Equivalent Conductances and Dissociation Constants for Hydrochloric Acid

Density, g./cc.	Temp., °C.	Λ_0, cm.^{2}ohm^{-1}mole^{-1}	pK^a
0.712	300	1455 ± 5	...
.525	360	1538 ± 10	3.26 ± 0.01
.525	373	1546 ± 10	3.42 ± .01
.525	378	1546 ± 10	3.47 ± .01
.447	370	1475 ± 20	4.11 ± .01
.447	373	1480 ± 20	4.14 ± .01
.447	378	1482 ± 20	4.24 ± .01
.447	383	1485 ± 20	4.32 ± .01
.399	373	1380 ± 20	4.61 ± .01
.399	378	1410 ± 60	4.74 ± .03

" Based on hypothetical one molar standard state.

(8) T. Shedlovsky, J. Franklin Inst., 225, 739 (1938). See preceding paper for values of dielectric constant and viscosity used.

(9) J. K. Fogo, S. W. Benson and C. S. Copeland, J. Chem. Phys., 22, 212 (1954).

(10) It is difficult to compare the results of Franck[3b] with the present results. There are no data between 320° and 413°, and limiting equivalent conductances and dissociation constants were calculated very indirectly by a method which assumes the validity of Walden's rule for KCl above 300°.
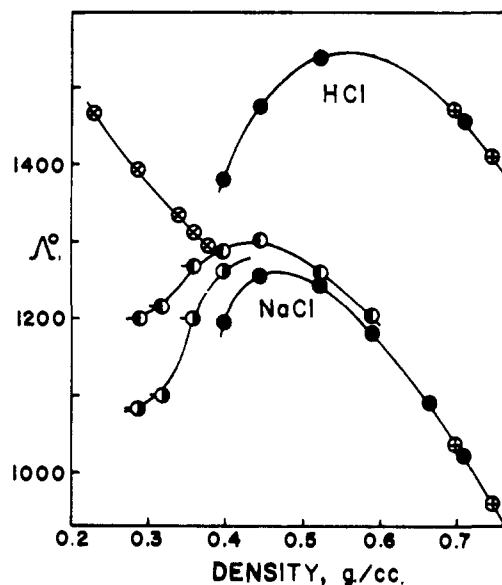
Fig. 2.—Limiting equivalent conductances of NaCl and HCl in water as a function of solution density: ●, orthobaric; ◐, 378°; ◖, 383°; ⊕, orthobaric, from data of Noyes, et al. (ref. 3a); ⊗, 388°, from Fogo, et al. (ref. 9); ◑, 378°, calculated from data of Fogo, et al. (ref. 9); ◖, 383°, calculated from data of Fogo, et al. (ref. 9).

In Fig. 3, pK values are plotted against $298/DT$,[11] where DT is the product of dielectric constant and temperature. Shown also are results of Fogo, et al.,[9] for sodium chloride. The pK's for sodium chloride correspond to reasonable a-values according to either Bjerrum's[12] or Fuoss'[13] theory. The former appears to represent the sodium chloride data slightly better. According to either theory, the pK values for hydrochloric acid correspond to a-values which are approximately the minimum interionic distance for ionized hydrochloric acid. Such a-values suggest that the dissociation constants for hydrochloric acid be split into two constants—one for ionization to ion pairs and one for dissociation into free ions. Then $K_{obs} = K_iK_d/(1 + K_i)$. Since K_{obs} corresponds to a-values showing no systematic variation with DT, K_i must vary with DT if K_d is to correspond to constant a-values larger than 2 Å. Unfortunately, there seems to be no basis which is not arbitrary for dividing K_{obs} between K_i and K_d.[14]

In Fig. 4, the limiting equivalent conductance–viscosity products for sodium chloride and hydrochloric acid are plotted against $298/DT$. The Walden product, $\eta\Lambda^0$, might be expected to be a function of DT, to the extent that $\eta\Lambda^0$ is a measure of the hydrated radii of the ions, which should depend primarily on DT. It is seen from Fig. 4, however, that the Walden product does not depend on DT alone. The difference between $\eta\Lambda^0$ under orthobaric conditions and at 378° may be due partly to errors in the values used for D, but errors in excess of 10% would be required to account for all of the discrepancy. Interestingly,

(11) This variable corresponds to the usual one of $1/D$ at 25°, and was chosen because electrostatic forces depend on the product DT, rather on D alone.

(12) N. Bjerrum, Kgl. Danske Videnskab Selskab., 7, No. 9 (1926), as discussed in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1950, second edition, p. 42.

(13) R. M. Fuoss, J. Am. Chem. Soc., 80, 5059 (1958).

(14) A formally analogous treatment was used by H. Sadek and R. M. Fuoss (ibid., 76, 5904 (1954)) to account for a-values which varied with DT. Since their electrolyte was incapable of covalent bonding, their interpretation of K_i was somewhat different, however.
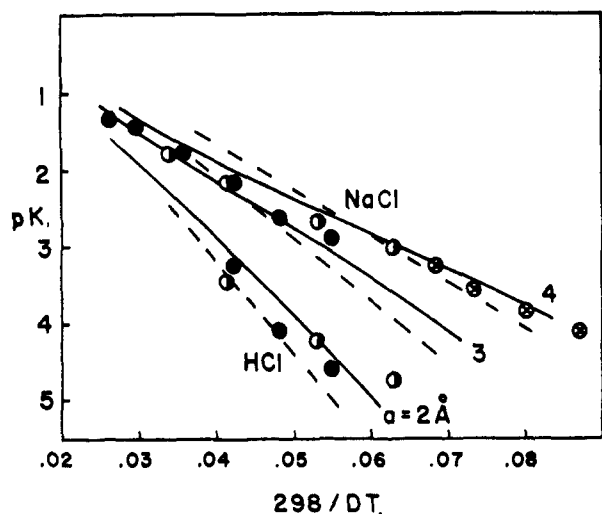
Fig. 3.—Dissociation constants of NaCl and HCl in water: ●, orthobaric; ◑, 378°; ⊗, 388°, from Fogo, *et al.* (ref. 9). Solid line calculated from Bjerrum's theory (ref. 12); dashed line calculated from Fuoss' theory (ref. 13).

the 378° data join smoothly with the 388° data of Fogo, *et al.*[9]

The possibility of triple ions existing in sufficient concentration to influence significantly the results obtained was eliminated by the same considerations used for sodium chloride.[2]

From the variations with temperature, pressure and density of the dissociation constants of hydrochloric acid and sodium chloride,[2] thermodynamic functions of dissociation were calculated.[15] Some representative values of volumes and entropies are given in Table III. Noteworthy are the large negative values for ΔV_P^0 and ΔS_P^0.

The most striking feature of the results for both electrolytes is the depression of the mobility in the vicinity of the critical point (374°, 0.32 g./cc.). It is evident that this depression is a function of both temperature and density—at high densities, the temperature has little effect and at the higher temperatures, the effect of the critical density decreases. This behavior is similar to that of the molal volume of sodium chloride,[16] where large (liters/mole) negative

(15) Since the data are not natural functions of pressure, use was made of the functions $(\partial P/\partial T)_T$ and $(\partial P/\partial V)_V$, which were computed from data in J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936.

(16) S. W. Benson, C. S. Copeland and D. Pearson, *J. Chem. Phys.*, **21**, 2208 (1953).
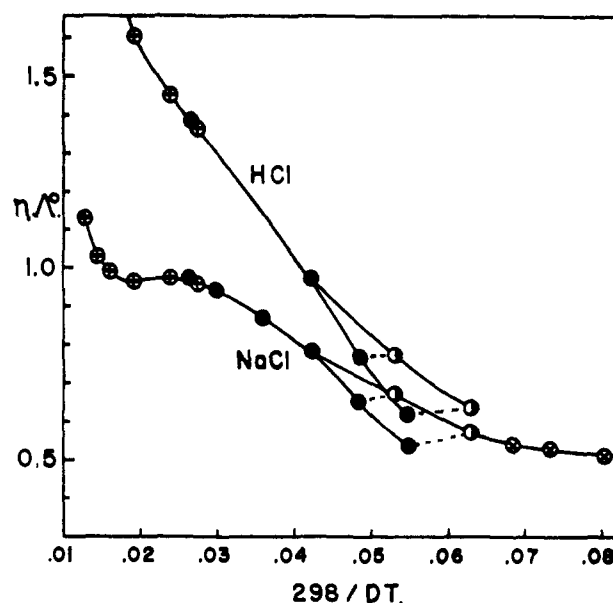
Fig. 4.—Walden products for NaCl and HCl in water: ●, orthobaric; ◑, 378°; ⊕, orthobaric, from data of Noyes, *et al.* (ref. 3a); ⊗, 388°, from Fogo, *et al.* (ref. 9).

values of the apparent molal volume are diminished as either temperature or density is removed from the critical value. The volume and entropy effects of ionic dissociation at constant pressure indicate a considerable contraction associated with the production of

TABLE III

THERMODYNAMIC DISSOCIATION FUNCTIONS[a]

Solute	Density, g./cc.	Temp., °C.	$-\Delta V_P^0$, l.	$-\Delta S_P^0$, e.u.	$-\Delta S_V^0$, e.u.
NaCl	0.525	360	1.55	220	11.4
NaCl	.399	373	11.0	990	53
HCl	.525	360	2.8	430	46
HCl	.399	373	18.6	1690	96
H_2O^b	.997	25	0.02	19	16

[a] Based on one *molal* standard state.   [b] From data in Harned and Owen, ref. 12, pp. 496, 514.

NOTE: ΔV_P^0 and ΔS_P^0 refer to the volume and entropy change, respectively, which accompany the dissociation of an ideal, hypothetical 1 molar solution of electrolyte; ΔS_V^0 is the entropy change at constant volume.

free ions, with an attendant increase in structural ordering. In this region of high solvent compressibility, the attraction of ions for water molecules appears to exceed greatly the attraction of ion pairs.