TABLE I

THE TRIALKYL TRITHIOPHOSPHITES AND ANTIMONITE AND THEIR ADDITION COMPOUNDS

Formula	B. p., °C.	Press.	M. p., °C.	n^{25}_D	d^0_4	d^{25}_4	M. p.'s add. comps. with			
							CH_3I	$HgBr_2$	HgI_2	$AuCl_3$
$(EtS)_3P$	140–143	18	− 32–31	1.5689	1.1883[a]	1.1585	191	184	187	225
$(PrS)_3P$	164–169	15	− 65–64	1.5350	1.1277	1.0932	191	176	182	208
$(BuS)_3P$	174–180	15	−101–100	1.5305	1.0773	1.0421	198	148	162	182
$(EtS)_3PO$[b]	165–168	15	− 24–23	....	....	1.1890				
$(EtS)_3Sb$	167–170	4	....	....	1.6224	1.5873				

[a] Claisson gives sp. g. at 12° 1.24. [b] Pischtschimuka gives b. p. 174–175 (20 mm.) d^0_0 1.1969.

stirring which was continued for an hour after all was in. The product was heated to 70° at atmospheric pressure and the residue distilled at 18 mm., yield 7.5 g. or 35%. To a solution of 18.6 g. of mercaptan and 24 g. of dimethylaniline in 100 cc. of ether, 13.7 g. of phosphorus trichloride was added under the same conditions. The dimethylaniline hydrochloride was filtered off and extracted with ether. The ether solution was treated as above, yield 13.3 g. or 62%. Using 10% excess of mercaptan brought the yield to 70%. *Anal.* Calcd.: P, 14.48; S, 44.86. Found: P, 14.58; S, 44.31.

The tripropyl ester was prepared similarly, yield 58%. *Anal.* Calcd.: P, 12.11; S, 37.50. Found: P, 12.25; S, 37.43.

Similarly the tributyl ester was obtained in 58% yield. *Anal.* Calcd.: P, 10.40; S, 32.21. Found: P, 10.41; S, 31.86.

To a solution of 10 g. of the triethyl ester in 200 cc. of acetic acid, 50 cc. of 3% hydrogen peroxide was added and the mixture stirred for twelve hours. The acid was neutralized with ammonia and the oil extracted with ether and distilled, b. p. 165–170° at 15–18 mm., yield 34%.

An ether solution of antimony trichloride was added with rapid stirring and efficient cooling to sodium ethyl mercaptide in a flask with reflux. Reaction took place immediately but the mixture was stirred for six hours, after which the salt was filtered off and the solution distilled. The yield of ester was 80%, analysis Sb found 39.48%. calculated 39.60%.

Summary

Triethyl, tripropyl and tributyl trithiophosphites, triethyl trithioantimonite and bismuth triethyl mercaptide have been prepared and their properties determined. The trithiophosphites form many addition products.

BALTIMORE, MARYLAND RECEIVED JULY 11, 1938

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Conductance of Hydrochloric Acid in Dioxane–Water Mixtures from 15 to 45°

BY BENTON BROOKS OWEN AND GEORGE W. WATERS[1]

The effects of viscosity, temperature and dielectric constant upon the conductivity of solutions of electrolytes have long been popular subjects for investigation. In view of the peculiar conductance mechanism of the hydrogen ion, it is surprising that such a small part of this work has dealt with solutions of acids. Goldschmidt[2] and his co-workers have measured the conductance of several acids at 25° in alcohol–water mixtures rich in alcohol, and a number of investigators[3] have studied acids in pure non-aqueous solvents, for the most part at 25°. In the present research, we have measured the conductance of hydrochloric acid in four dioxane–water mixtures, 20, 45, 70 and 82% dioxane by weight, at 15, 25, 35 and 45°. By subjecting this important electrolyte to considerable variation in both dielectric constant and temperature, we not only extend our knowledge of the effects of these variables upon conductance, but also derive some information regarding its thermodynamic properties. This thermodynamic information is of immediate interest, because it supplements the extensive electrochemical investigation of hydrochloric acid in dioxane–water mixtures by Harned[4] and his students.

Materials, Technique and Fundamental Constants

Conductivity water was distilled from alkaline permanganate in an electrically heated Barnstead still. The dioxane was obtained from the Carbide and Carbon Chemi-

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[1] This communication embodies part of the thesis presented by George W. Waters to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1914); **91**, 46 (1916); **91**, 51 (1916); **70**, 633 (1910).

[3] For bibliography consult the review by Hartley, Gatty, MacFarlane and Murray-Rust, *Ann. Repts. Chem. Soc.* (London), **27**, 326 (1931).

[4] Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937); THIS JOURNAL, **58**, 1908 (1936); Harned, *ibid.*, **60**, 336 (1938); Harned and Donelson, *ibid.*, **60**, 339 (1938); **60**, 2128 (1938); Harned and Calmon, *ibid.*, **60**, 2130 (1938); Harned, Donelson and Calmon, *ibid.*, **60**, 2133 (1938).

cals Corporation, and purified in the manner described by Harned and Morrison.[4] It was protected carefully from moisture and stopcock grease. The freezing point of the purified product was always within the range 11.76 to 11.78°, in good agreement with the value 11.78° reported by Kraus and Vingee.[5]

Baker "Analyzed" arsenic-free hydrochloric acid was diluted to the constant-boiling mixture, and twice distilled from an all-glass apparatus. Only the middle fractions were retained. The concentrations of stock solutions prepared from this acid were always checked gravimetrically, using recrystallized silver nitrate. The precision of these analyses was 0.05%. The mixed solvents and stock solutions were freshly prepared, by weight, before each run. Carbon dioxide was removed from both the water and pure dioxane by a stream of purified nitrogen. Conversion of concentrations from a weight basis to moles per liter (hereafter designated by c) was performed with the aid of the density data of Harned and Calmon.[6]

The conductivity cells were the Type B described by Saxton and Langer,[7] and the experimental technique was essentially the same. The cell constants were determined at 18 and 25° from the specific conductivity of a 0.1 demal potassium chloride solution proposed by Jones and Bradshaw,[8] and at 15° from the results of Bremner and Thompson.[9] The variation with temperature was linear, and was used to calculate the cell constants at 35 and 45°.

Temperatures were read on Beckmann thermometers calibrated by a platinum resistance thermometer which had been checked by the Bureau of Standards. The regulation of the thermostat temperature was better than 0.01° at 25 and 35°. At 15 and 45° the regulation was not so satisfactory, but was always better than 0.02°.

In order to calculate the theoretical coefficients of the Onsager[10] equation

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c} \tag{1}$$

and the Debye–Hückel[11] limiting law

$$\log y = -u\sqrt{c} \tag{2}$$

we made use of the physical constants given in the "International Critical Tables," the dielectric constant data of Åkerlöf and Short[12] and the viscosity data of Geddes.[13] Since some difficulty was encountered in the necessary interpolation[14] of these data, the interpolated values and the calculated constants, u, α and β are collected in Table I.

TABLE I

CONSTANTS PERTAINING TO EQUATIONS (1) AND (2)

Wt. % dioxane	$t°$	D_0	$100\ \eta_0$	u	α	β
20	15	64.01	1.689	0.7245	0.3258	35.73
20	25	60.79	1.292	.7437	.3345	47.17
20	35	57.73	1.017	.7648	.3439	60.42
20	45	54.83	0.8243	.7877	.3542	75.29
45	15	40.70	2.453	1.429	.6425	30.85
45	25	38.48	1.837	1.477	.6642	41.66
45	35	36.37	1.430	1.530	.6878	54.14
45	45	34.39	1.142	1.586	.7131	68.62
70	15	18.72	2.483	4.581	2.060	44.94
70	25	17.69	1.918	4.738	2.131	58.85
70	35	16.72	1.522	4.907	2.207	75.03
70	45	15.80	1.232	5.092	2.290	93.83
82	15	10.01	2.106	11.72	5.268	72.46
82	25	9.53	1.671	11.98	5.389	92.02
82	35	9.06	1.356	12.30	5.532	114.39
82	45	8.62	1.117	12.64	5.683	140.12

Experimental Results and Discussion

The experimental data are so numerous that they can be given only in abbreviated form. Accordingly we have tabulated Λ and $\sqrt{c}$ as the most convenient and generally useful quantities for further calculations. Table II contains these quantities for the four temperatures and four solvent mixtures. Since we are primarily interested in the initial departures from equation (1), and the estimation of the extent of ionic association from this effect, we have recorded only the two runs at the highest dilutions whenever more than two runs were made.[15] Most runs consisted of ten or less measurements, so for convenience in tabulation we have recorded only the ten lowest concentrations, if more than ten were studied. The specific conductivities of the pure solvents, κ_0, are recorded at the ends of the proper columns. No corrections were applied for solvent conductance. It was assumed that the major part of this factor was due to dissolved substances, the dissociation and conductance of which would be effectively repressed by the strong acid. To simplify future reference, individual experimental data can be identified by temperature and the numbers given in the first column of the table. The prime and double-prime refer to runs one and two, respectively.

The results in 20% dioxane are very similar to those in pure water. The dielectric constant is high enough to permit essentially complete dissociation, so the observed conductivities approach the limiting slope (Equation 1) from above. This

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(5) Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

(6) Harned and Calmon, *ibid.*, **60**, 334 (1938).

(7) Saxton and Langer, *ibid.*, **55**, 3638 (1933). The Dike bridge was used throughout with a 1000~ oscillator as source of power.

(8) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(9) Bremner and Thompson, *ibid.*, **59**, 2372 (1937).

(10) Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

(11) Debye and Hückel, *ibid.*, **24**, 185 (1923).

(12) Åkerlöf and Short, THIS JOURNAL, **58**, 1241 (1936).

(13) Geddes, *ibid.*, **55**, 4832 (1933).

(14) Dielectric constants interpolated by Harned and Morrison,[4] and by Walker, Thesis, Yale University, 1937. Viscosities interpolated by Waters, Thesis, Yale University, 1938.

(15) For complete tabulations *cf.* Thesis, ref. 1.

is illustrated by the points plotted as open circles in Fig. 1.

In the case of the 45% dioxane mixtures, however, the limiting slope is approached from below, although the negative departures from the slope are very small (see Fig. 2). This is in accord with Bjerrum's[16] definition of ion association under coulomb forces, which predicts that hydrochloric acid should show the first signs of association at dielectric constants corresponding to our 45% dioxane solutions.

The evaluation of Λ_0 in the 20 and 45% mixtures is performed readily by the familiar Shedlovsky[17] extrapolation in which the function

$$\Lambda' = (\Lambda + \beta\sqrt{c})/(1 - \alpha\sqrt{c}) \qquad (3)$$

from equation (1), is plotted against c. Values

TABLE II

EXPERIMENTAL DATA

20% Dioxane

	15°		25°		35°		45°	
No.	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ
$1'$	0.01175	249.28	0.03661	297.68	0.02407	349.65	0.01061	405.28
$2'$	.01638	248.94	.05198	295.56	.03731	347.48	.01553	403.63
$3'$	.03264	247.04	.06577	293.55	.05280	344.86	.02918	401.02
$4'$	.04760	245.45	.08017	291.96	.06902	342.36	.06620	393.30
$5'$	.06544	243.54	.12353	287.01	.08588	339.71	.08490	389.46
$6'$	.08682	241.48	.13512	285.63	.10467	337.03	.09912	387.08
$7'$	.10710	239.63	.14518	285.02	.12217	334.75	.11687	384.48
$8'$	.13062	237.68	.15854	283.68	.14141	332.46	.13701	381.56
$9'$	.15451	235.84	.17329	282.19	.16717	329.50	.15917	378.13
$10'$	.17866	234.11	....	....	....	....	....	....
$1''$	.01142	249.38	.02108	299.81	.02986	349.36	.02543	400.60
$2''$	01573	249.00	.03558	297.73	.03949	347.92	.03777	397.95
$3''$	.02920	247.50	.05650	294.83	.05543	345.16	.05590	394.35
$4''$	.04738	245.69	.06961	293.04	.07534	342.07	.07222	391.34
$5''$	.06771	243.59	.12253	286.97	.08869	339.98	.08763	388.52
$6''$	.08977	241.47	.15637	283.56	....	....	.10478	385.37
$7''$	.10811	239.80	.18618	280.96	....	....	.12187	382.85
$8''$	.13052	238.00	.21592	278.53	....	....	.14250	379.58
$9''$	.15447	236.23	.26133	275.14	....	....	....	....
$10''$	.17844	234.52	.32311	270.94	....	....	....	....
	$\kappa_0' = 1.29 \times 10^{-6}$		$\kappa_0' = 0.470 \times 10^{-6}$		$\kappa_0' = 0.384 \times 10^{-6}$		$\kappa_0' = 0.779 \times 10^{-6}$	
	$\kappa_0'' = 1.73 \times 10^{-6}$		$\kappa_0'' = 0.504 \times 10^{-6}$		$\kappa_0'' = 0.470 \times 10^{-6}$		$\kappa_0'' = 0.599 \times 10^{-6}$	

45% Dioxane

	15°		25°		35°		45°	
No.	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ	$\sqrt{c}$	Λ
$1'$	0.01400	144.99	0.01289	178.05	0.02345	211.79	0.01144	249.62
$2'$	.02749	142.74	.02295	176.40	.03964	208.59	.02406	247.41
$3'$	.04172	140.86	.03190	174.92	.05505	205.36	.03323	245.14
$4'$	.05568	139.23	.04259	173.17	.07365	201.83	.05625	239.25
$5'$	.07298	137.20	.06506	169.65	.09051	198.87	.07146	235.53
$6'$	.09701	134.68	.07728	167.88	.10734	196.16	.08410	232.82
$7'$	.11982	132.72	.09685	165.26	.12552	193.63	.10050	229.52
$8'$	.14143	130.94	.12540	161.84	.14669	190.91	.11804	226.23
$9'$	.16344	129.39	.14632	159.79	.17403	187.84	.13752	222.94
$10'$	....	....	.16230	158.29	....	....	....	....
$1''$	.02318	143.19	.02580	175.86	.01355	213.53	.00816	250.93
$2''$	.03235	142.17	.04046	173.57	.02650	211.23	.01495	250.08
$3''$	.04535	140.53	.05255	171.66	.04510	207.27	.02364	248.02
$4''$	.05985	138.77	.06455	169.80	.06348	203.59	.03268	245.23
$5''$	.07333	137.23	.08604	166.85	.08231	200.14	.04849	241.60
$6''$	.08918	135.58	.11620	163.15	.09827	197.49	.06532	237.35
$7''$	.10494	134.04	.14240	160.35	.11501	194.59	.08089	233.89
$8''$	.12195	132.56	.18350	156.75	.13605	192.02	.09835	230.35
$9''$	....	....	.20297	154.78	.15583	189.88	.13399	224.61
$10''$	....	....	.23196	153.27	....	....	.15547	221.52
	$\kappa_0' = 0.603 \times 10^{-6}$		$\kappa_0' = 0.228 \times 10^{-6}$		$\kappa_0' = 0.179 \times 10^{-6}$		$\kappa_0' = 0.195 \times 10^{-6}$	
	$\kappa_0'' = 0.200 \times 10^{-6}$		$\kappa_0'' = 0.256 \times 10^{-6}$		$\kappa_0'' = 0.192 \times 10^{-6}$		$\kappa_0'' = 0.226 \times 10^{-6}$	

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[16] Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[17] Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

TABLE II (*Concluded*)

70% Dioxane

No.	15° $\sqrt{c}$	15° Λ	25° $\sqrt{c}$	25° Λ	35° $\sqrt{c}$	35° Λ	45° $\sqrt{c}$	45° Λ
1′	0.00819	72.54	0.01160	89.14	0.00835	108.88	0.00936	126.93
2′	.01250	71.67	.02037	85.20	.01498	105.22	.02079	119.05
3′	.02602	67.20	.02888	81.45	.02401	99.97	.03046	112.51
4′	.03717	63.81	.03977	77.11	.03475	94.24	.04020	106.54
5′	.05320	59.71	.05079	73.43	.05080	87.16	.05707	98.19
6′	.06935	56.46	.06282	70.05	.06211	83.12	.07401	91.75
7′	.08484	53.94	.08461	65.25	.07881	78.35	.09200	86.51
8′	.10288	51.61	.10421	62.05	.09131	75.44	.11009	82.54
9′	.12057	49.80	.12238	59.74	.10725	72.45	.12985	79.06
10′	.14058	48.17	.13990	57.94	....	....	.15090	76.27
1″	.01075	71.52	.02420	83.26	.02330	100.52	.01721	121.24
2″	.02144	68.42	.03919	77.20	.03213	95.33	.02435	116.14
3″	.03197	65.13	.05823	71.20	.04471	89.45	.03178	111.11
4″	.04609	61.26	.08119	65.88	.05720	84.66	.04050	105.88
5″	.05949	58.19	.10869	61.41	.06918	80.86	.05486	98.64
6″	.07369	55.54	.13644	58.26	.08470	76.79	.06782	93.39
7″	.09058	53.00	.16818	55.72	.09718	74.17	.08423	88.13
8″	.10444	51.30	....	....	.11758	70.68	.10007	84.11
9″	.12383	49.39	....	....	....	....	.11537	81.04
10″	....	....	....	....	....	....	....	....
	$\kappa_0' = 0.226 \times 10^{-6}$		$\kappa_0' = 0.450 \times 10^{-6}$		$\kappa_0' = 0.085 \times 10^{-6}$		$\kappa_0' = 0.150 \times 10^{-6}$	
	$\kappa_0'' = 0.119 \times 10^{-6}$		$\kappa_0'' = 0.107 \times 10^{-6}$		$\kappa_0'' = 0.094 \times 10^{-6}$		$\kappa_0'' = 0.060 \times 10^{-6}$	

82% Dioxane

No.	15° $\sqrt{c}$	15° Λ	25° $\sqrt{c}$	25° Λ	35° $\sqrt{c}$	35° Λ	45° $\sqrt{c}$	45° Λ
1′	0.00819	38.53	0.01212	40.89	0.00563	58.01	0.00751	65.88
2′	.01069	36.38	.01994	33.29	.00956	51.23	.01352	52.25
3′	.02077	28.31	.02842	28.04	.01322	45.63	.02323	39.55
4′	.03293	22.71	.03886	23.83	.01919	38.78	.03342	32.16
5′	.04769	18.86	.05099	20.69	.03239	29.53	.04462	27.25
6′	.06270	16.48	.06343	18.50	.04509	24.65	.06259	22.60
7′	.07662	15.04	.09039	15.75	.06077	21.05	.07695	20.28
8′	.09304	13.87	.10966	14.63	.06916	19.72	.09640	18.36
9′	.10975	13.06	.13067	13.84	.08118	18.28	.11325	17.23
10′	.12698	12.49	.14723	13.42	.11014	16.14	.13223	16.43
1″	.00576	41.73	.01696	36.11	.00903	53.50	.00614	69.15
2″	.00948	37.35	.02840	28.23	.01665	42.00	.00952	60.09
3″	.01880	29.56	.04252	22.86	.02523	34.01	.02038	42.09
4″	.02991	23.80	.05729	19.59	.03989	26.44	.02838	35.03
5″	.04145	20.22	.07372	17.32	.05288	22.67	.04026	28.65
6″	.05635	17.35	.09013	15.85	.06619	20.19	.05307	24.51
7″	.06504	16.18	.11229	14.65	.07745	18.67	.06546	21.87
8″	.07908	14.83	.13450	13.80	.09394	17.17	.07958	19.83
9″	.09370	13.83	.17203	13.10	.12746	15.34	.09254	18.51
10″	.10790	13.13	.20256	12.86	....	....	.10847	17.35
	$\kappa_0' = 0.171 \times 10^{-6}$		$\kappa' = 0.534 \times 10^{-6}$		$\kappa_0' = 0.085 \times 10^{-6}$		$\kappa_0' = 0.102 \times 10^{-6}$	
	$\kappa_0'' = 0.192 \times 10^{-6}$		$\kappa_0'' = 0.064 \times 10^{-6}$		$\kappa_0'' = 0.055 \times 10^{-6}$		$\kappa_0'' = 0.072 \times 10^{-6}$	

of this function are plotted as filled circles in Figs. 1 and 2. Straight lines were used to extrapolate the 20% dioxane data by the method of least squares. A linear extrapolation obviously was unsatisfactory in 45% dioxane, so a stiff spline was used to obtain Λ_0 graphically in this solvent.

The data for the 70 and 82% dioxane solutions are plotted in Figs. 3 and 4. Ionic association is clearly indicated in 70% dioxane by the pronounced negative departures from the Onsager slopes, but the electrolyte is still strong enough to exhibit an inflection in the conductance curve, and approach the limiting law within the experimental concentration range. In the 82% mixtures, the conductance falls off very steeply at the lowest concentrations, and the inflection has been shifted to inaccessible dilutions. At higher concentrations, $c \simeq 0.05$, the curves pass through

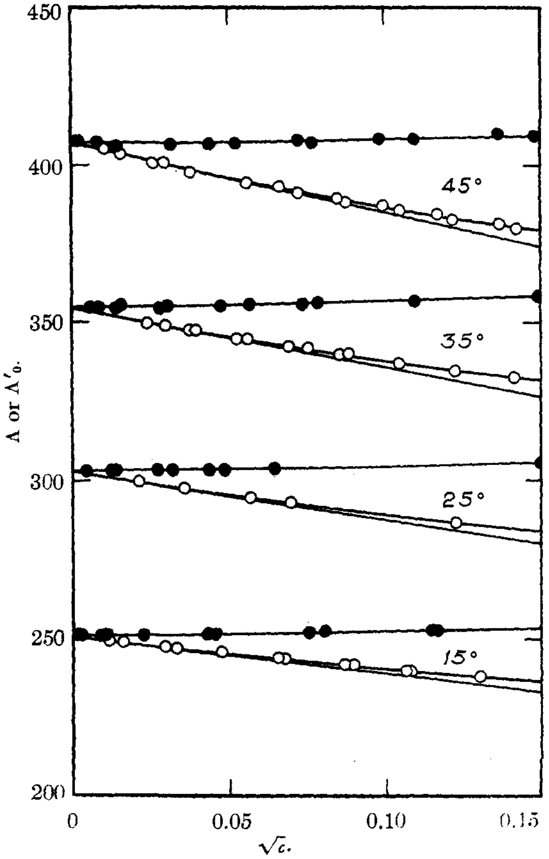

Fig. 1.—Conductance and extrapolation for hydrochloric acid in 20% dioxane.

flat minima not shown on Fig. 4. These minima are attributed to complex ion formation,[18] and have been given approximate quantitative expression by Fuoss and Kraus[19] in terms of triple ion formation. Unfortunately the concentrations at which the minima appear in our data are far beyond the range for which the formulas of Fuoss and Kraus were derived.

The evaluation of Λ_0 for incompletely dissociated electrolytes presents serious difficulties. It is apparent from Figs. 3 and 4 that departures from the Onsager slope are too great to permit satisfactory extrapolation along the limiting slopes. The Shedlovsky extrapolation becomes so strongly curved under these conditions that it is no longer practicable. Accordingly we have employed the method of Fuoss and Kraus,[20] recently simplified and improved by Fuoss.[21] The application of this method depends upon the equation

$$\mathrm{F}(z)/\Lambda = 1/\Lambda_0 + (cy^2\Lambda/\mathrm{F}(z))/(K\Lambda_0^2) \qquad (4)$$

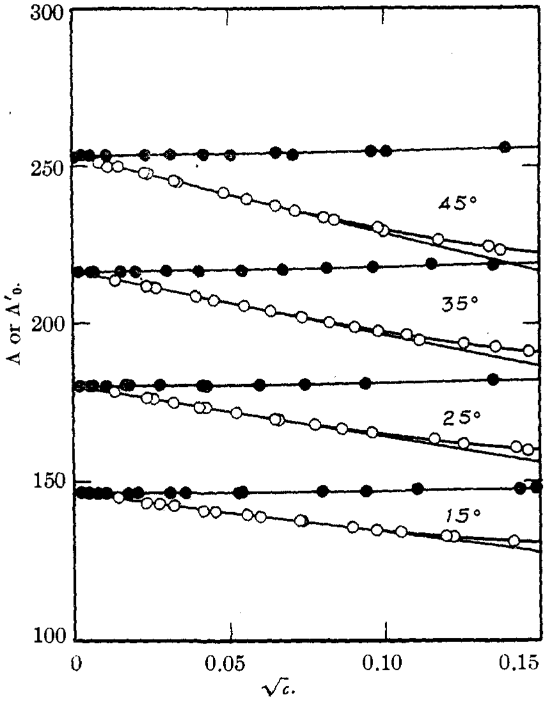

Fig. 2.—Conductance and extrapolation for hydrochloric acid in 45% dioxane.

which is obtained by combining the mass action expression

$$K = c\Theta^2y^2/(1 - \Theta) \qquad (5)$$

with

$$\Lambda = \Theta(\Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c\Theta}) \qquad (6)$$

and

$$\log y = -2u\sqrt{c\Theta} \qquad (7)$$

The last two equations are, of course, equations (1) and (2) modified to account for association of the electrolyte by introduction of its degree of dissociation, Θ. The continued fraction, F(z), permits explicit combination of these equations, and is defined and expressed in tabular form by Fuoss.[21] The extrapolation involves plotting $\mathrm{F}(z)/\Lambda$ against $cy^2\Lambda/\mathrm{F}(z)$, and is illustrated in Figs. 5 and 6. These plots should be linear at sufficiently high dilutions for equations (6) and (7) to hold, and the slopes and intercepts are $1/(K\Lambda_0^2)$ and $1/\Lambda_0$, respectively. Although some deviation from linearity is apparent in several individual plots, it is not consistent, and was therefore disregarded in evaluating the line constants. Two points on the 25° isotherm in Fig. 6 are from a third run which could not be included in Table II. The data are as follows: 82% dioxane, $\kappa_0''' = 0.085 \times 10^{-6}$, $\sqrt{c} = 0.01022$, $\Lambda = 42.97$ and $\sqrt{c} = 0.01450$, $\Lambda = 38.56$. Only the data at the highest dilutions were used in the

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(18) Sachanov, *Z. physik. Chem.*, **83**, 129 (1913).

(19) Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933).

(20) Fuoss and Kraus, *ibid.*, **55**, 476 (1933).

(21) Fuoss, *ibid.*, **57**, 488 (1935).

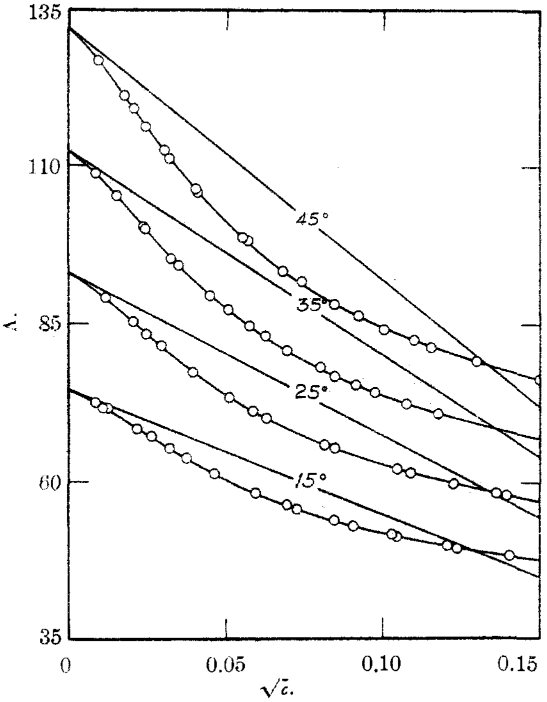

Fig. 3.—Conductance of hydrochloric acid in 70% dioxane.

plots, as it has been pointed out[22] that the concentration

$$c \simeq 12 \times 10^{-15}(DT)^3 \tag{8}$$

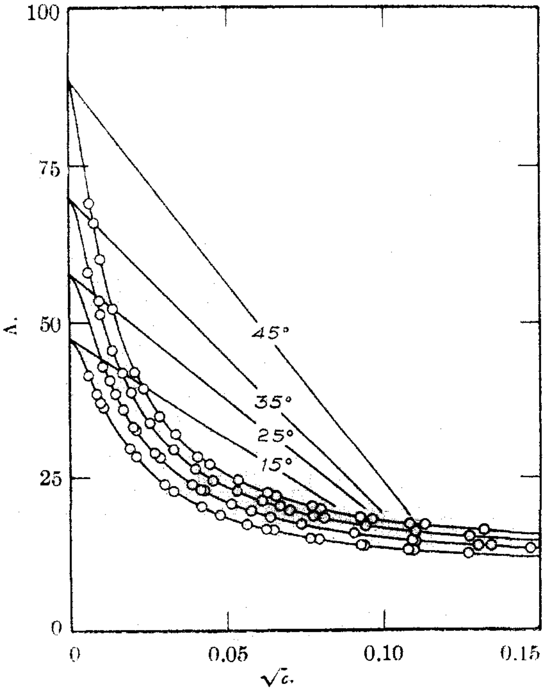

Fig. 4.—Conductance of hydrochloric acid in 82% dioxane.

constitutes a theoretical upper limit to the validity of equation (6).

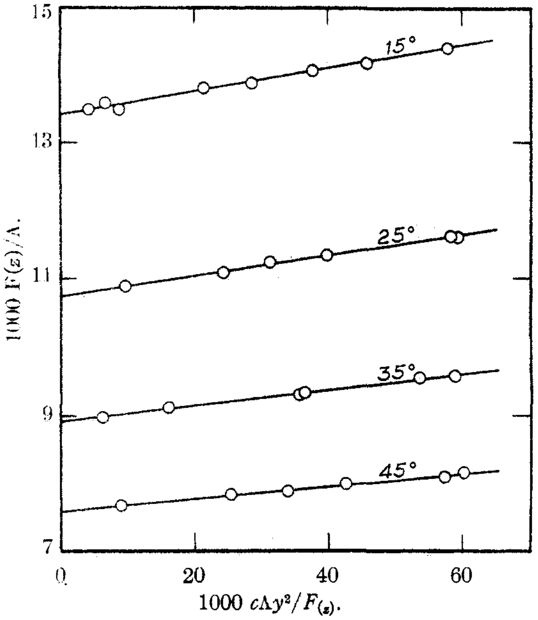

Fig. 5.—Evaluation of Λ_0 and K in 70% dioxane.

The final values of Λ_0 obtained from all of the extrapolations (Figs. 3 to 6) are recorded in Table III. Comparison with Table I brings out several interesting points. At a given temperature Λ_0 decreases very rapidly with increase in dioxane content, being almost halved in passing from one

TABLE III

LIMITING CONDUCTANCE

$t°$	Dioxane percentages 20	45	70	82
15	250.7	146.7	74.5	47.2
25	302.7	180.2	93.1	57.5
35	354.2	216.5	112.4	69.6
45	406.0	253.6	131.9	88.3

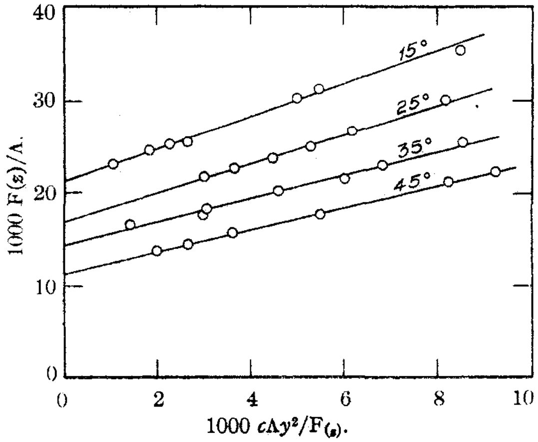

Fig. 6.—Evaluation of Λ_0 and K in 82% dioxane.

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[22] Fuoss, THIS JOURNAL, 57, 2604 (1935).

mixture to the next. On the other hand, the viscosity passed through a maximum between 45 and 70% dioxane, and hardly experiences a 50% change throughout the whole range of solvents. Figure 7 illustrates this phenomenon by the series of isothermal curves. In the same figure the data fall on a series of straight lines representing mixtures of constant composition in which the variation in viscosity is due to change in temperature only. The slopes, *s*, of these straight lines are all less than unity, but increase regularly with the dioxane content. The slopes and intercepts of these lines lead to the evaluation of the parameters, *s* and *r*, for the equation[23]

$$\Lambda_0 \eta_0^s = r \qquad (9)$$

Values of the parameters are given in Table IV.

TABLE IV

PARAMETERS OF EQUATIONS (9) AND (10)

% Dioxane	*s*	*r*	*A*	*B*
20	0.650	17.87	173.0	5.19
45	.725	9.95	92.2	3.57
70	.825	3.55	44.7	1.95
82	.90	1.45	30	1.13

Although the difference between *s* and unity represents a departure from Stokes' law, equation (9) shows that viscosity and conductance are rather simply related in a given solvent at various temperatures.[24]

In terms of the supposition that a large part of the hydrogen ion conductance is due to a succession of proton exchanges,[25] Fig. 7 shows that the presence of dioxane molecules in the solvent decreases the conductance more effectively by lowering the probability of the rapid symmetrical reaction

$$H_3O^+ + H_2O = H_2O + H_3O^+$$

than by increasing the viscosity of the medium.

For a given solvent, the effect of increasing the temperature is not only closely associated with the concomitant decrease in viscosity, but can also be expressed by the relationship

$$\Lambda_0 = A + Bt \qquad (10)$$

The parameters *A* and *B* are given in Table IV. With the exception of the value in 82% dioxane at 45°, Λ_0 generally can be reproduced to within about 0.5 conductance unit by equations (9) and (10). Considering the form of equation (9) and the complexity of the accepted hydrogen ion conductance mechanism, it is rather surprising that the temperature dependence of Λ_0 should be as simple as equation (10) for even as much as 30°.

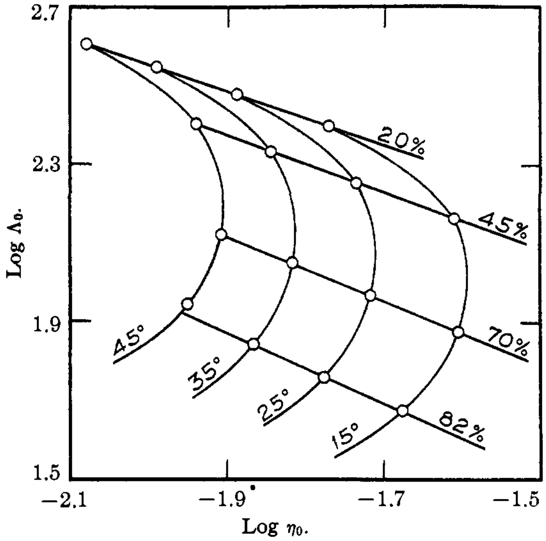

Fig. 7.—Influence of viscosity upon limiting conductance.

The effect of dielectric constant upon conductance is less direct than those of viscosity and temperature, and is given expression mainly through its control of the force of attraction between ions of unlike charges. For this reason we would not expect to find any very close connection between dielectric constant and the conductance at infinite dilution, and must focus our attention upon its influence on ionic association at finite concentrations. The most convenient quantitative measure of ionic association is supplied by the value of the thermodynamic dissociation constant of the electrolyte. The dissociation constant of hydrochloric acid in the various solvents has been calculated from the slopes of the plots in Figs. 5 and 6, and recorded in Table V. No values are given for the 20 and 45% dioxane mixtures because there is at present no satisfactory method of

TABLE V

DISSOCIATION CONSTANTS

	70% Dioxane		82% Dioxane	
t°	$K \times 10^3$	$a \times 10^8$	$K \times 10^4$	$a \times 10^8$
15	10.7	9.1	2.55	6.6
25	7.7	7.9	2.02	6.3
35	6.7	7.7	1.64	6.2
45	5.7	7.4	1.07	5.8

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(23) This relationship was used by Green [*J. Chem. Soc.*, **93**, 2049 (1908)] to describe the effect of η_0 on Λ_0 of salts at a given temperature, and by Johnston [THIS JOURNAL, **31**, 1010 (1909)] to relate η_0 and Λ_0 in a given medium at various temperatures.

(24) Walden and Ulich, *Z. physik. Chem.*, **107**, 219 (1923); Ulich, *Fortschrit. Chem.*, **18**, No. 10 (1926).

(25) Hückel, *Z. Elektrochem.*, **34**, 546 (1928); Bernal and Fowler. *J. Chem. Phys.*, **1**, 515 (1933); Baker and LaMer, *ibid.*, **3**, 406 (1935); Wannier, *Ann. Physik.* **24**, 545. 569 (1935); Longsworth and MacInnes, THIS JOURNAL, **59**, 1666 (1937).

evaluating, or even giving physical definition to, dissociation constants under the experimental conditions encountered in these solutions. Rough estimates from extrapolations similar to those in Figs. 5 and 6, and calculations based upon the Bjerrum[16] equation, indicate that K is of the order of unity in 45% dioxane solutions, and of a higher but undefined order in 20% dioxane solutions. Even in 70% dioxane the dissociation is quite extensive, corresponding closely to that of the first hydrogen of phosphoric acid in water.[26] In 82% dioxane the strength of hydrochloric acid is comparable to that of formic acid in aqueous solutions.[27]

The maximum uncertainty in K which might be assigned to individual notions of curve fitting was found by trial to be about 10%. This figure may therefore be taken as an estimate of the *relative* accuracy of the tabulated values for either mixture as a function of temperature. The absolute accuracy of any values, or the relative accuracy as a function of composition of solvent, depends upon many factors, both experimental and theoretical. With decreasing K, the ambiguity inherent in the physical definition of ionized, or associated, hydrochloric acid decreases rapidly; unfortunately, the experimental accuracy of the measurements and the concentration range in which equations (6) and (7) may be used with confidence, also decrease under this condition. Furthermore this range is not definitely known for the particular system under investigation.

Shedlovsky[28] has suggested recently a modification of equation (6) which would be expected to increase its concentration range, and hence its usefulness, but its application to the present data does not lead to a significant change in the extrapolated values, or improve the linearity of the plots. Equation (7) might be improved by the introduction of the extended terms of Gronwall, La Mer and Sandved,[29] or the use of activity coefficients recently derived from electromotive force measurements by Harned and his students. Although both of these alternatives lead to values of K of the same order ($\pm 20\%$) as those in Table V, we do not regard such agreement, or disagreement, to be particularly significant. Neither method decreases the uncertainties in curve-fitting, and both introduce characteristic errors of their own. The extended terms should represent a correction in the right direction, but their convergence is not satisfactory under our experimental conditions. The e. m. f. activity coefficients involve the extended terms in their own extrapolation, and therefore do not offer an independent solution of the problem, but rather increase the extrapolative uncertainty if used in conjunction with our data. It therefore does not seem worth while to attempt further refinements in calculation at present. More accurate values of K would then be contingent upon measurements at concentrations far beyond the useful range of our present equipment.

The values of the apparent mean ionic diameter, a, given in Table V, were calculated from the corresponding values of K by the equation of Bjerrum[16] and Fuoss and Kraus.[30] This equation expressed the dissociation constant of an electrolyte in terms of the product DT and the single characteristic parameter, a. For electrolytes yielding large ions, such as tetraisoamylammonium nitrate,[30] the value of a shows little, or no, dependence upon the composition of the solvent. On the other hand, the value of a for acids would be expected to vary with the solvent because of the solvation of the proton. In Table V, however, the variation with solvent is of the opposite sign to that which might be predicted from consideration of the relative sizes of the water and dioxane molecules. For reasons indicated in the last two paragraphs, we are inclined to discount the physical significance of this "observed" variation in the numerical value of a in passing from 70 to 82% dioxane, and attribute it mainly to systematic uncertainties in the absolute values of K in the two solvents. On this basis, the values of a in 70% dioxane would be less reliable than those in 82%. The relative accuracy of K in a given solvent makes it possible that the observed variation of a with temperature is real. It will be noticed that the "observed" values of a decrease regularly (value in 70% at 15° excepted) with increase in temperature, and that the temperature coefficients are the same for both series.

The variation of K with temperature permits evaluation of the heat of ionization and entropy of ionization of hydrochloric acid at unit activity of both ions and associated ion-pairs. At 25°, $\Delta H^0 = -3{,}700$ cal. in 70% dioxane, and $-4{,}900$ cal. in 82% dioxane. The corresponding values of ΔS° are -22 and -33 cal., respectively.

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(26) Nims, THIS JOURNAL, **56**, 1110 (1934).

(27) Harned and Embree, *ibid.*, **56**, 1042 (1934).

(28) Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(29) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

(30) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

Summary

The equivalent conductance of hydrochloric acid has been measured in 20, 45, 70 and 82% dioxane solutions at 15, 25, 35 and 45°. The experimental data closely follow the Onsager limiting slope in 20 and 45% dioxane solutions at high dilutions. Ionic association is too pronounced in 70 and 82% dioxane for convergence with the limiting slope within the accessible concentration range.

In a given solvent mixture, it was shown that the temperature dependence of the limiting conductance is linear, and the variation with viscosity can be expressed by $\Lambda_0\eta_0^s = r(s < 1)$.

The effect of the dielectric constant upon conductance and ionic association was illustrated by graphs, and by evaluation of the dissociation constant of hydrochloric acid in 70 and 82% dioxane solutions. At 25° the estimated values of the dissociation constant are 7.7×10^{-3} and $2.0 \times \times 10^{-4}$ in 70 and 82% dioxane solutions, respectively. Rough values of the heat and entropy of ionization were also reported.

NEW HAVEN, CONN. RECEIVED JULY 13, 1938

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Heat Contents of the Salts of the Alkali Metals in Extremely Dilute Aqueous Solutions

BY T. F. YOUNG AND PAUL SELIGMANN

One of the most significant and interesting tests of the limiting law of Debye and Hückel[1] is the comparison of heats of dilution with the predictions of the theoretical equation. In their review of existing calorimetric data Lange and Robinson[2] concluded that the theory was in fairly satisfactory agreement with experiment. In various other papers, however, they and their respective co-workers have made estimates of the limit, as the concentration approaches zero, of the derivative of the apparent molal heat content with respect to the square root of the concentration ($S = \mathrm{d}\phi H/\mathrm{d}\sqrt{c}$), which differ considerably from the values computed from the modern precise dielectric constant measurements of Wyman.[3] These limiting derivatives for salts of the alkali metals vary from 36% of the theoretical value for potassium nitrate at 12.5° to 89% of the theoretical for lithium sulfate at 25°. They appear to show some significant trends: for example, the limiting derivatives of the five alkali metal sulfates decrease in the order of increasing molecular weights of the salts, whereas the theory demands that the limiting slope be the same for all salts of a given valence type.

In some recent papers of Lange and Robinson and their co-workers,[4] doubt has been expressed of the validity of extrapolations based upon the assumption that S is constant throughout a concentration range such as that between $m = 0$ and 0.01. Young and Groenier[5] have applied to the sodium chloride measurements a method of calculation which avoids the assumption of the constancy of the derivative, S. Their method possesses the further advantage that it deals directly with the measured heats of dilution; the older method[6] of Lange and Robinson was applied to a series of relative values of $-\phi H$ calculated by an addition process which obscured the actual measurements. As applied by Young and Groenier, the method also included a "chord-area" plot of the derivative, S, the property of immediate interest. This representation of the actual dilution data and the derivative on the same graph aids in the selection of a satisfactory type of equation to be used to represent the data, and in an understanding of the significance of the deviations between the derived equation and the experimental values.

In this paper are presented the results of an investigation of the limiting slopes of all salts of the alkali metals for which there are sufficient data for the determination of equations by the method of least squares.[7]

Procedure.—In each dilution experiment, q, the heat absorbed during an isothermal dilution

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[1] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[2] Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

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

[4] *Cf.* Gulbransen and Robinson, THIS JOURNAL, **56**, 2637 (1934).

[5] Young and Groenier, *ibid.*, **58**, 187 (1936).

[6] For details, see Lange and Robinson, *ibid.*, **52**, 4218 (1930).

[7] We are indebted to Mr. J. C. Hesler, Mr. Fred Karush and Mr. R. P. McCormick who duplicated our calculations.