

second and third columns of Table II. The maximum deviation is 0.003 at 50° and the average deviation is only 0.001.

The changes in heat content and heat capacity accompanying the ionization reaction are given by the equations

$$\Delta H = -5.69 \times 10^{-4} T^2(t - \theta) \quad (4)$$

$$\Delta C_p = -5.49 \times 10^{-4} T(T + 2(t - \theta)) \quad (5)$$

which are derived by differentiation of equation (1). Values of these quantities are contained in the last two columns of Table II.

### Summary

1. By means of suitable cells without liquid junction, the second ionization constant of oxalic acid,  $K_2$ , has been determined at 5° intervals from 0 to 50°.

2. The equation  $\log K_2 = 5.771 - 0.000816t - 6 \times 10^{-5} t^2$  expresses the observed values of  $\log K_2$  with an average accuracy of  $\pm 0.001$ .

3. Values of the heat content and heat capacity of the ionization reaction have been tabulated.

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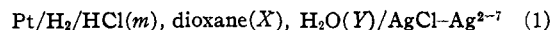
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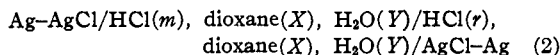
## Properties of Electrolytes in Mixtures of Water and Organic Solvents. IV. Transference Numbers of Hydrochloric Acid in Water and Dioxane-Water Mixtures from 0 to 50°

BY HERBERT S. HARNED AND EDWIN C. DREBY<sup>1</sup>

In conjunction with the extensive study of the thermodynamic properties of hydrochloric acid in water and in media covering a wide range of the dielectric constant by measurements of the electromotive force of cells of the type



it was considered appropriate to investigate the phenomenon of transference for this acid in the same media by means of the cells with transference of the type



Very extensive measurements were made which covered the acid concentration range from 0.005 to 3 *M*, a temperature range from 0 to 50° in solvents consisting of 0, 20, 45 and 70% dioxane-water mixtures. Results of less accuracy were also obtained in 82% dioxane-water mixtures ( $D \sim 10$ ).

The transference number which has been calculated is that defined by the well-known thermodynamic relation

$$T^+ = dE_t/dE \quad (3)$$

(1) This communication contains material from a dissertation presented by Edwin C. Dreby to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939.

(2) Harned and Donelson, *THIS JOURNAL*, **60**, 339 (1938).

(3) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

(4) Harned and Morrison, *ibid.*, **58**, 1908 (1936); *Am. J. Sci.*, **33**, 161 (1937).

(5) Harned and Donelson, *THIS JOURNAL*, **60**, 2128 (1938).

(6) Harned and Walker, *ibid.*, **61**, 48 (1939).

(7) Harned, Donelson and Calmon, *ibid.*, **60**, 2133 (1938).

where the transference number,  $T^+$ , at any particular concentration is the slope at the corresponding point on the plot of  $E_t$ , the electromotive force of the cell with transference, versus  $E$  the electromotive force of the cell without transference.

This is by far the most extensive study of the transference number of an electrolyte as a function of its concentration, the temperature and solvent composition. It is well known that this method is not so accurate as the moving boundary method, but it is reliable, rapid and therefore suitable for an extensive survey of the subject.

### Experimental Procedure

A diagram of the cell used is shown in Fig. 1. It consisted of two half-cells connected by means of a stopcock at

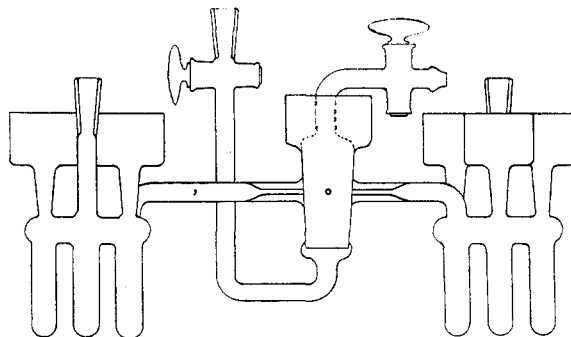


Fig. 1.—Transference cell.

which the liquid junction was formed. Each half-cell contained three legs into which the silver-silver chloride electrodes were inserted. Interchangeable ground glass joints were used between cell and electrode to give air-tight

joints which would not contaminate the dioxane mixtures with grease or rubber. The side arm on each half-cell was used for filling purposes. The junction stopcock consisted of a three-way hollow core with one-inch (2.5-cm.) capillaries leading to the half-cells. The three way stopcock was essential in filling the cells and between measurements the stopcock was set at an intermediate position to prevent diffusion between the two half-cells.

The vacuum technique used in electromotive force work in this Laboratory was not applicable in this case. The procedure was to insert the electrodes and the filling vessels in their respective holes and evacuate the apparatus through the junction stopcock. It was then filled with hydrogen and reëvacuated. This process was carried out three times, finally leaving the whole apparatus under a slight pressure of hydrogen. The solution was then allowed to run in, forcing out the atmosphere of hydrogen. The solutions had previously been saturated with hydrogen and were air free.

The preparation of the solutions and electrodes and the method of measurement was identical with that described by Harned and Morrison.<sup>4</sup> The arrangement of having three electrodes in each half-cell permitted the checking of the electrodes against each other, thus facilitating the detection of faulty electrodes.

### Electromotive Forces

In order to obtain reproducible and consistent results, it was found advisable to keep the acid activity ratio in the transference cells less than ten to one. This made it impossible to use the same reference concentration in every cell measured. Instead, a series of cells, interrelated, was measured over the concentration range, and the results were combined in such a manner as to give values of the electromotive force over the entire acid concentration range all referred to one reference concentration<sup>11</sup>

The procedure was to least square the original experimentally determined values of the electromotive force to fit the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \quad (4)$$

These equations were then combined so as to give the electromotive forces in terms of the reference concentration. The resultant constants were then smoothed concentration-wise. Table I gives values of the constants  $E_{25}$ ,  $a$  and  $b$  at the measured concentrations for water, 20, 45 and 70% dioxane-water mixtures.

The average deviations listed in the last column of Table I are the differences in millivolts between the values calculated by equation (4) and the original experimental values, averaged over the temperature range for each cell. The values with the asterisk obviously are associated with poor experimental results and these were not included in

TABLE I  
SMOOTHED CONSTANTS OF EQUATION (4) EXPRESSING  
EXPERIMENTAL ELECTROMOTIVE FORCES. RANGE OF  
VALIDITY IS 0 TO 50°

$m$	$E_{25}$	$a \times 10^4$	$b \times 10^6$	$\Delta_{av.}$
Water, $m_r = 0.100313$				
2.99000	0.16695	2.50	-0.62	0.07
1.69357	.12844	2.15	-.51	.05
0.97192	.09787	1.78	-.41	.04
.55472	.07131	1.38	-.31	.03
.31804	.04711	0.93	-.21	.04
.179939	.02351	.48	-.11	.01
.100313	.00000	.00	.00	.00
.058486	-.02171	-.44	.10	.01
.018028	-.06885	-1.38	.31	.01
.0061880	-.11217	-2.25	.51	.03
.0047006	-.12341	-2.48	.56	.01
.0018611	-.16120	-3.41	.73	.01
			Mean $\Delta_{av.}$	.03
20% Dioxane, $m_r = 0.038278$				
2.78348	0.20077	3.10	-1.69	0.08
1.49548	.15870	2.67	-1.07	.07
0.70003	.11908	2.13	-0.66	.07
.33243	.08634	1.60	-.46	.03
.165267	.05796	1.10	-.29	.09
.080510	.02935	0.59	-.15	.26*
.038278	.00000	.00	.00	.00
.018333	-.02900	-.58	.15	.76*
.0085061	-.05954	-1.19	.29	.02
.0038779	-.09090	-1.82	.44	.28*
.0020142	-.11700	-2.47	.64	.17
			Mean $\Delta_{av.}$	.07
45% Dioxane, $m_r = 0.037604$				
2.99791	0.20336	2.35	-1.32	0.31*
2.44143	.18579	2.36	-1.26	.04
1.50730	.15212	2.29	-1.11	.04
0.68931	.11058	1.86	-0.87	.06
.29646	.07540	1.32	-.62	.03
.16490	.05313	0.95	-.44	.14*
.076748	.02546	.45	-.20	.04
.037604	.00000	.00	.00	.00
.018603	-.02516	-.44	.19	.07
.0084476	-.05442	-.95	.34	.08
.0035521	-.08765	-1.74	.44	.03
			Mean $\Delta_{av.}$	.04
70% Dioxane, $m_r = 0.036576$				
1.30623	0.12916	1.76	-1.62	0.03
0.91788	.11065	1.57	-1.42	.13
.63909	.09225	1.39	-1.23	.15
.35639	.06796	1.10	-0.92	.08
.33140	.06499	1.08	-.91	.69*
.15798	.04211	0.71	-.57	.05
.077959	.02090	.37	-.28	.08
.036576	.00000	.00	.00	.00
.0199096	-.01673	-.28	.17	.10
.0085917	-.03905	-.60	.31	.16
.0038857	-.06200	-.82	.40	.03
			Mean $\Delta_{av.}$	.08

computing the over-all  $\Delta_{av}$ , listed at the bottom of the column. The experimental results were the average of at least four readings. The spread in these readings was, in the majority of cases, less than 0.1 mv. Only in the higher dioxane mixtures was it impossible to keep within this limit, and here the average was taken from a greater number of readings. The values obtained are believed to be correct within  $\pm 0.05$  mv. The  $\Delta_{av}$ , listed in Table I would indicate that the quadratic formula is adequate for expressing the data.

Interpolated values of the measurements of these cells at 25° in aqueous solutions by Shedlovsky and MacInnes agree to within 0.1 mv. or less with our results.<sup>8</sup>

### Computation of the Transference Number

From equation (3), it is seen that it is necessary to construct a graph of  $E_i$ , the electromotive force of the cell with liquid junction, against  $E$ , the electromotive force of the cell without liquid junction. The range of values of  $E_i$  and  $E$ , however, is so large that graphing them directly would cause the loss of significant figures necessary for the accurate determination of the slope. A method was devised whereby values of  $E$  at equally spaced intervals of  $E_i$  were determined without the loss of significant figures. Furthermore, the results in this form made it possible to determine the slope analytically and hence improve the accuracy.

Deviation functions, defined by the relations

$$X = E + 2k \log m/m_r; \quad X_i = E_i + 2k \log m/m_r.$$

gave values of  $X_i$  and  $X$  corresponding to the values of  $E_i$  and  $E$  where  $k$  is defined by  $2.303 RT/F$ . These values of  $X_i$  and  $X$  covered a very small range, so they could be plotted very accurately and with no loss of significant figures. Values of  $X_i$  were interpolated graphically to the round concentrations for which values of  $X$  existed. These data were used to make a plot of  $X - X_i$  versus  $X$ . It is to be noted that  $X - X_i$  is simply  $E - E_i$ . From this graph, values of  $X - X_i$  were read off for values of  $X_i$  corresponding to values of  $E_i$  spaced at equal intervals of 0.01 v., the latter being obtained from a plot of  $E_i$  against  $X_i$ . Adding together the appropriate values of  $X - X_i$  and  $E_i$  gave the desired results, namely, values of  $E$  for values of  $E_i$  spaced at intervals of 0.01 v. The data were then in a form for

the analytical determination of the slope, which is the transference number.

A derivative function derived by Rutledge<sup>9</sup> was employed for the determination of the transference number. It is of the form

$$\frac{dE}{dE_i}(E) = \frac{1}{12h} (C_{-2}E_{-2} + C_{-1}E_{-1} + C_0E_0 + C_1E_1 + C_2E_2)$$

where  $(dE/dE_i)(E)$  is the slope at a value,  $E$ , of the dependent variable;  $h$  is the magnitude of the chosen interval in the independent variable;  $E_{-2}$ ,  $E_{-1}$ , etc., are consecutive values of the dependent variable; and  $C_{-2}$ ,  $C_{-1}$ , etc., are constants. There are three sets of constants, the choice of any one being dependent on whether the slope is to be determined at  $E_{-1}$ ,  $E_0$  or  $E_1$ . Except at the extremes, the values of the slope were determined by taking the average of the results obtained by placing the Rutledge formula in the three possible positions.

This method, as well as any other method used for the determination of slopes, has decreased accuracy at the extremes of the curve. Beside this difficulty, there is also the added fact that data in the more dilute regions are less accurate because of greater experimental difficulties. Thus, in subsequent handling of the data, less stress is laid on the values of the transference number below 0.03  $M$  than on the values at the higher concentrations.

The values of the transference number obtained by application of the Rutledge formula to the data were smoothed by plotting them against values of  $E_i$  and reading back values of  $T^+$  for values of  $E$  corresponding to round concentrations. Typical of such plots is that shown in Fig. 2 for water at 25°. This is, of course, a concentration-wise smoothing. Subsequently a temperature-wise smoothing was also performed but not until the limiting value of the transference number had been evaluated.

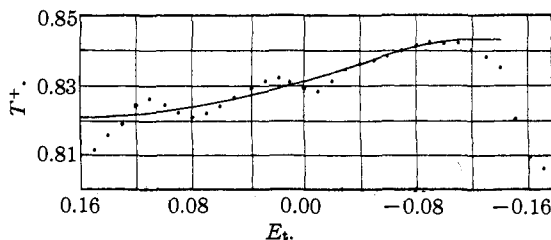


Fig. 2.—Smoothing of transference numbers. Solvent is water.

(9) Rutledge, *J. Math. Phys. M. I. T.*, **8**, 1 (1929); *Phys. Rev.*, **40**, 262 (1932).

(8) Shedlovsky and MacInnes, *THIS JOURNAL*, **58**, 1970 (1936).

TABLE II  
 TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID IN WATER AND DIOXANE-WATER MIXTURES

<i>m</i>	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
	Water										
0.005		0.842	0.837	0.831	0.826	0.821	0.816	0.811	0.806	0.801	0.796
.01		.844	.840	.834	.829	.824	.819	.814	.809	.804	.799
.02		.845	.841	.835	.830	.825	.821	.816	.811	.806	.801
.05		.846	.842	.836	.832	.827	.822	.818	.813	.808	.803
.1		.848	.844	.838	.834	.830	.825	.821	.816	.811	.806
.2		.850	.846	.840	.837	.832	.828	.823	.819	.814	.810
.5		.851	.847	.843	.839	.835	.830	.827	.823	.818	.814
1.0		.854	.850	.846	.842	.838	.834	.831	.827	.822	.819
1.5		.855	.852	.848	.844	.841	.837	.833	.829	.824	.821
2.0		.857	.853	.849	.845	.842	.839	.835	.830	.825	.822
3.0		.857	.853	.849	.846	.843	.839	.835	.831	.826	.822
		.858	.854	.850	.846	.843	.840	.836	.832	.827	.823
	20%										
0.005	0.856	0.851	0.846	0.841	0.836	0.831	0.825	0.821	0.816	0.810	0.805
.01	.861	.855	.850	.845	.840	.835	.829	.825	.820	.814	.809
.02	.862	.857	.851	.846	.841	.836	.831	.827	.821	.816	.811
.05	.865	.859	.853	.848	.843	.838	.833	.829	.824	.818	.813
.1	.867	.861	.856	.851	.846	.841	.837	.832	.827	.822	.816
.2	.868	.862	.857	.852	.848	.843	.839	.834	.829	.823	.818
.5	.869	.863	.858	.853	.849	.844	.840	.835	.830	.825	.820
1.0	.867	.862	.857	.852	.847	.843	.838	.833	.829	.823	.818
1.5	.864	.860	.854	.849	.844	.840	.836	.831	.826	.821	.816
2.0	.862	.857	.852	.847	.842	.838	.834	.829	.824	.819	.814
3.0	.860	.855	.850	.845	.841	.836	.832	.828	.823	.818	.813
	.856	.852	.847	.842	.838	.833	.829	.825	.820	.816	.811
	45%										
0.005	0.828	0.824	0.820	0.816	0.811	0.806	0.801	0.796	0.791	0.787	0.783
.01	.833	.829	.825	.821	.816	.811	.807	.801	.797	.793	.788
.02	.835	.830	.827	.823	.818	.813	.809	.804	.799	.795	.790
.05	.838	.833	.829	.825	.820	.816	.811	.807	.802	.798	.793
.1	.842	.837	.833	.829	.824	.820	.816	.812	.807	.803	.798
.2	.845	.840	.836	.831	.827	.823	.819	.816	.811	.807	.803
.5	.849	.844	.840	.834	.830	.826	.823	.820	.816	.812	.807
1.0	.851	.846	.842	.836	.833	.829	.826	.822	.819	.815	.811
1.5	.851	.846	.841	.836	.832	.828	.825	.822	.819	.815	.811
2.0	.850	.845	.840	.835	.832	.828	.824	.821	.818	.814	.810
3.0	.849	.844	.839	.835	.831	.827	.824	.820	.817	.813	.809
	.847	.843	.838	.833	.830	.825	.822	.817	.814	.810	.807
	70%										
0.005		0.772	0.768	0.764	0.760	0.755	0.750	0.746	0.742	0.738	0.734
.01		.781	.778	.774	.770	.766	.761	.757	.753	.750	.747
.02		.783	.780	.777	.773	.769	.764	.760	.756	.753	.751
.05		.786	.783	.779	.776	.772	.767	.763	.760	.757	.755
.1		.788	.785	.782	.778	.774	.770	.766	.763	.760	.758
.2		.789	.786	.783	.780	.775	.771	.768	.765	.762	.759
.5		.789	.786	.783	.779	.774	.770	.766	.764	.760	.757
1.0		.788	.785	.782	.777	.772	.768	.764	.762	.758	.754
1.5		.788	.784	.781	.776	.771	.766	.763	.760	.757	.752

The limiting value of the transference number was determined by the method of Longworth.<sup>10</sup> This consisted in plotting the function

$$T_0^{+'} = \frac{T^+ \Lambda' + \beta \sqrt{c}}{\Lambda' + 2\beta \sqrt{c}}$$

(10) Longworth, *THIS JOURNAL*, **54**, 2741 (1932).

where

$$\Lambda' = \Lambda^0 - (\alpha \Lambda^0 + 2\beta) \sqrt{c}$$

against the concentration  $c$  and extrapolating to  $c = 0$  to give the value of the limiting transference number,  $T_0^{+'}$ . In this equation,  $T^+$  is the transference number at concentration  $c$  in moles per

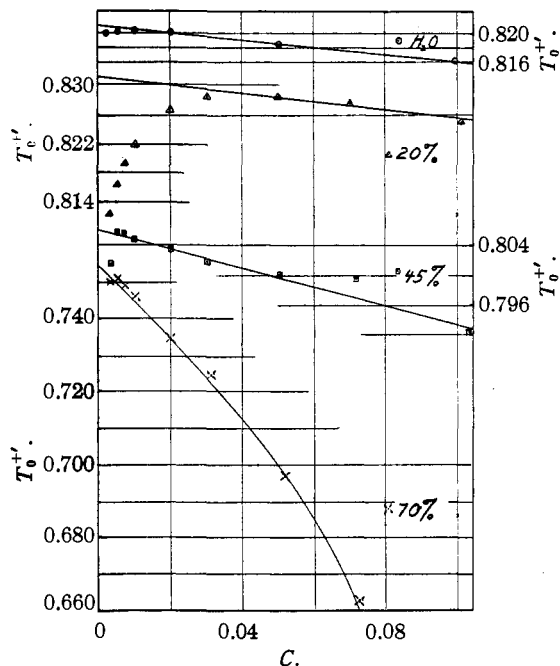


Fig. 3.—Extrapolations for limiting transference numbers.

liter,  $\Lambda^0$  is the equivalent conductance at infinite dilution and  $\alpha$  and  $\beta$  are the constants of the Onsager conductance theory. This function worked very well for water, 20% and 45% dioxane-water mixtures, giving practically straight lines. It began to fail in the 70% mixture, but the curvature was not great enough to seriously affect the extrapolation. Figure 3 shows the nature of these extrapolations in water, 20, 45 and 70% dioxane-water mixtures at 25°. We note that at concentrations below 0.03 M, particularly with the 20% dioxane mixtures, the points do not fall on the line used for the extrapolation. We attribute this behavior to the previously mentioned difficulty of obtaining slopes of a curve at the extreme end of the curve, and to a somewhat greater uncertainty in the measurements in the 20% dioxane mixtures.

With the values of the transference number at infinite dilution and the computed values of the transference number smoothed over the concentration range, plots were now made of the transference number versus the square root of the concentration and the values for the whole temperature range were plotted on the same sheet

of paper. In drawing any one curve the points on either side corresponding to the next higher and lower temperature interval, respectively, were considered. This resulted in a temperature-wise smoothing. In every case but one, the deviations of the drawn curve from the plotted points were well within the expected limit of error. Values of the transference number at round concentrations and at 5° intervals for water, 20, 45 and 70% dioxane-water mixtures are listed in Table II.

Discussion of Errors

From a consideration of the Rutledge derivative function, it can be shown that an error of 0.00001 in  $E$  produces an error of 0.001 in  $T^+$ . The mean deviations in Table I give, in all probability, a close approximation to the expected error in  $E$  from which the error in  $T^+$  can be determined. Also, the average of the deviations of the plotted points from the smooth curve in Fig. 2 will give the order of magnitude of the expected error in the transference number. The results obtained by the first method lead to expected errors of 3, 7, 4 and 8 and the second method of 2, 5, 4 and 8 units in the third place of the transference number for water, 20, 45 and 70% dioxane-water mixtures, respectively. The consistency

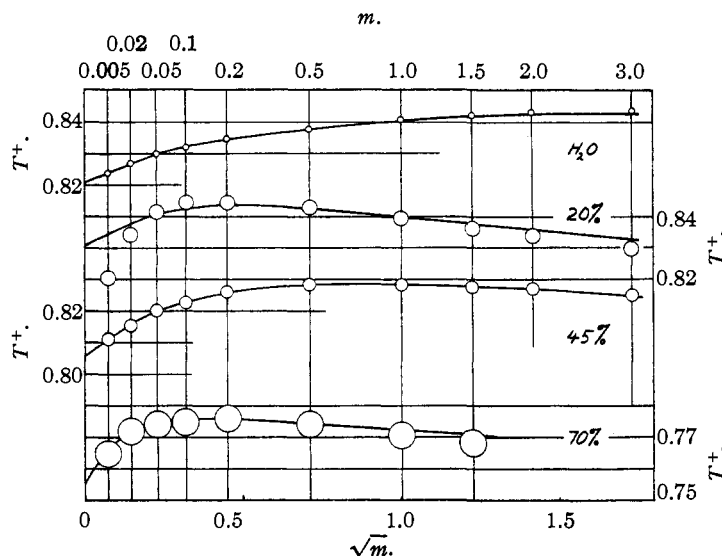


Fig. 4.—Smoothed transference numbers and degree of error.

in the plotted points from which Table II was formed would lead one to believe the error is well within these limits.

A comparison of the transference numbers at 25° for the various solvents with the limit of error

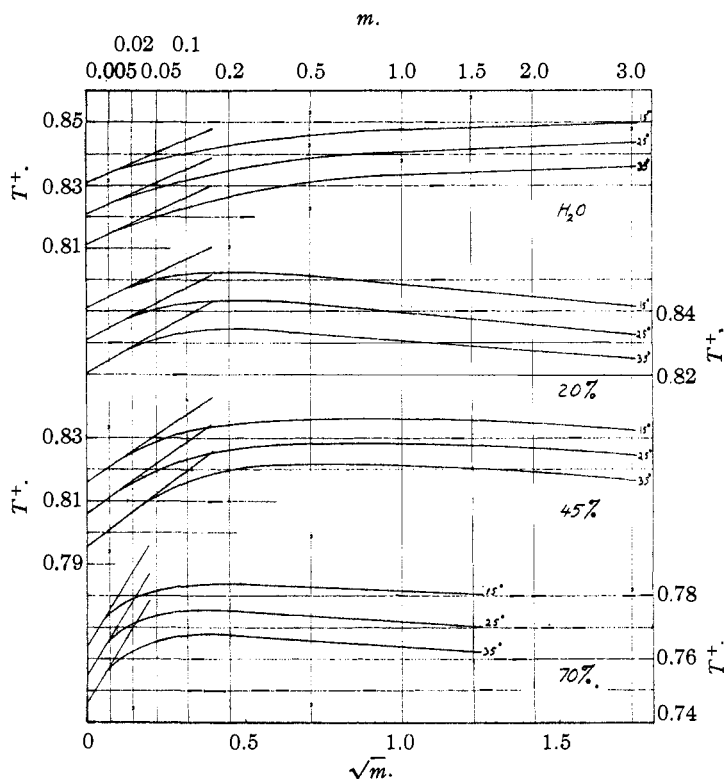


Fig. 5.—Transference numbers and theoretical limiting slopes.

as determined by the second method listed above is shown in Fig. 4. The diameters of the circles represent the size of the error. The circles are drawn about the points determined by the smooth-

TABLE III  
LIMITING SLOPES

	H <sub>2</sub> O	20%	45%	70%
15°	0.04278	0.04906	0.06773	0.1629
25°	.04509	.05195	.07186	.1642
35°	.04714	.05507	.07492	.1664

TABLE IV  
TRANSFERENCE NUMBERS OF HCl IN WATER AS LISTED IN "INTERNATIONAL CRITICAL TABLES"  
*c* = Concentrations in moles per liter

<i>c</i>	0.005	0.010	0.020	0.050	0.100	0.500	1.00
10°: Hitt.	0.840	0.840	0.841				
	(.840) <sup>b</sup>	(.841)	(.842)				
18°: Hitt.	.832	.833	.833	0.834	0.835	0.840	0.844
M. b.			.835		.835		
E. m. f.	.832	.832	.832	.832	.832		
	(.831)	(.832)	(.834)	(.836)	(.838)	(.843)	(.845)
30°: Hitt.		.822	.822	.822	.822		
M. b.				.828	.832		
		(.821)	(.822)	(.825)	(.828)		
50°: Hitt.		.801					
		(.801)					
25°: M. b.	.8239	.8251	.8266	.8292	.8314		
	(.824)	(.825)	(.827)	(.830)	(.830)		

<sup>a</sup> Longworth, THIS JOURNAL, 54, 2741 (1932). <sup>b</sup> Results of present investigation are in parentheses.

ing process of Fig. 2. The lines are drawn through the points listed in Table II.

**Limiting Slopes for the Transference Numbers.**—The Onsager conductance theory leads to an expression for the limiting slope

$$\frac{dT_0^+}{\sqrt{m}} = \frac{(2T_0^+ - 1)\beta}{\Lambda^0} \sqrt{d_0}$$

where  $T_0^+$  is the limiting value of the transference number,  $\Lambda^0$  is the limiting equivalent conductance,  $\beta$  is the constant from the Onsager conductance theory and  $d_0$  is the density of the pure solvent. This is the slope for  $T^+$  versus the  $\sqrt{m}$ . Table III gives the values of the slope in water, 20, 45 and 70% dioxane-water mixtures.

Figure 5 shows plots of the transference numbers at 15, 25 and 35° with the limiting slopes drawn in for water, 20, 45 and 70% dioxane-water mixtures. It is to be noted that, even where the slope is steep as is the case for the higher dioxane mixtures, there

is a tendency for the curve to fall rapidly into the limiting slope from 0.02 *M* on down.

**Comparison with Other Methods.**—Extensive work has not been carried out previously on the determination of the transference numbers of hydrochloric acid over wide concentration and temperature ranges by any one method. Table IV gives values for the transference number of hydrochloric acid in water determined by the three principal methods: electromotive force, Hittorf,

and moving boundary, as listed in the "International Critical Tables." The values found in this investigation are listed within parentheses for comparison. On the whole, the agreement is satisfactory.

The most accurate method for the determination of transference numbers is the moving boundary method, particularly in its refined form as developed at the Rockefeller Institute. Longworth<sup>10</sup> has determined the transference number of hydrochloric acid in water with great precision at 25°. The values determined in this investigation are compared with his in the last two rows of Table IV. The excellent agreement obtained is good confirmation that the method used in computing the transference number from the electromotive forces is a sound one.

**Transference Numbers in 82% Dioxane.**

The difficulties in obtaining the electromotive forces of the cells with liquid junction for the 82% dioxane-water mixture were not easy to overcome. There was a much greater tendency for diffusion of the electrolyte at the junction and the low conductivity of the solutions made it difficult to make measurements of the electromotive force. A cell was used similar to that in Fig. 1 but without the capillary tubing. It was necessary to have reservoirs of the solutions in the side arms to flush out the junction tubes whenever the junction stopcock had been opened for any length of time. Furthermore, the electrodes took considerable time to come to equilibrium and they did not remain constant over long periods of time.

The electromotive forces of the cells with transference are listed in Table V. The large deviations, particularly in the lower concentrations, indicate that the transference numbers cannot be

determined with great precision for the dilute acid solutions. Figure 6 shows the final smoothed values of the transference number at 15, 25 and 35°, represented by the heavy curved lines.

The Longworth method was not very satisfactory in determining the limiting value of the transference number but the accuracy of the data did not warrant the search for another method. With full knowledge that these values are probably incorrect but that they do give the order of magnitude, the theoretical limiting slopes were calculated. These are shown in Fig. 6 by the heavy straight lines drawn into the origin.

The dashed lines in Fig. 6 show what is believed to be nearer the correct values for the transference number in the dilute region, since they approach

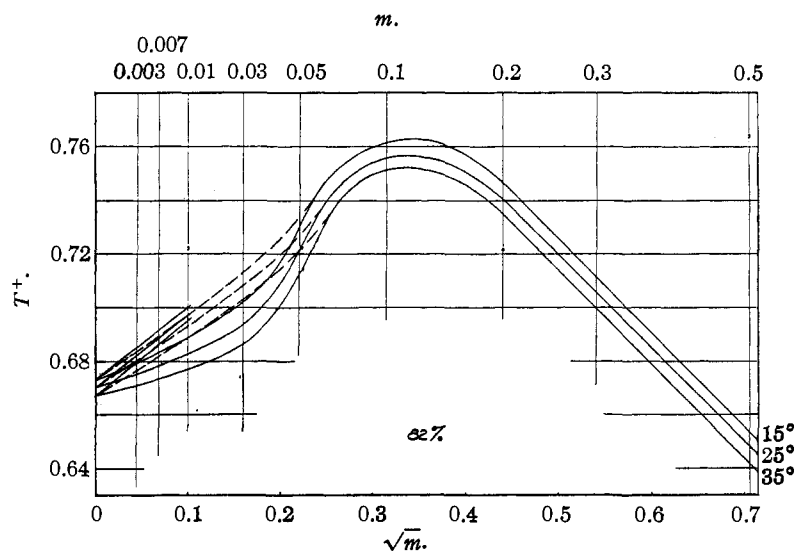


Fig. 6.—Transference numbers in 82% dioxane.

the theoretical limiting slopes in a logical manner. It is not unreasonable to assume this when it is considered that, in this region of concentration, the error must be of the order of 10 or 15 units in the third place of the transference number. Despite the possible justification for these assumptions, the transference numbers for the 82% dioxane-water mixtures are listed in Table VI from 0.05 to 0.5 M only, the region in which reliable

TABLE V

SMOOTHED EXPERIMENTAL RESULTS OF THE CELLS WITH TRANSFERENCE IN 82% DIOXANE-WATER

<i>m</i>	<i>m'</i>	<i>E</i> <sub>25</sub>	<i>a</i> × 10 <sup>4</sup>	<i>b</i> × 10 <sup>6</sup>	$\Delta_{max}$	$\Delta_{mean}$
0.041369	0.0048874	0.04355	0.428	-0.29	0.15	0.08
.041369	.0097702	.02920	.293	-.24	.50	.31
.041369	.025017	.01035	.108	-.11	.70	.32
.041369	.19080	.03820	.306	-.48	.09	.05
.46526	.041369	.06830	.418	-.50	.21	.18
.46526	.073747	.05505	.298	-.28	.25	.09
.46526	.10492	.04625	.228	-.17	.20	.10

TABLE VI

TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID IN 82% DIOXANE-WATER MIXTURES

<i>m</i>	5°	10°	15°	20°	25°	30°	35°	40°	45°
0.0	0.677	0.675	0.673	0.672	0.670	0.668	0.667	0.665	0.663
.05	.742	.735	.730	.726	.722	.717	.712	.708	.702
.1	.767	.764	.762	.759	.756	.754	.752	.750	.747
.2	.755	.751	.747	.744	.740	.738	.735	.732	.729
.3	.718	.715	.711	.708	.705	.702	.699	.696	.693
.5	.660	.657	.654	.651	.648	.645	.642	.639	.637

values for the electromotive force were obtainable. The extrapolated values of the transference number used in the calculation of the limiting slope are listed in the first row of the table.

### Summary

1. Electromotive forces of the cells Ag-AgCl/HCl (*m*), dioxane (*X*), H<sub>2</sub>O(*Y*)/HCl(*r*), dioxane (*X*), H<sub>2</sub>O(*Y*)/AgCl-Ag have been obtained for 0, 20, 45, 70 and 82% dioxane solutions at 5° intervals from 0 to 50° and from 0.005 to 3.0 *M* acid concentration.

2. The cation transference number has been calculated over these ranges of temperature and

concentration from these results and previous measurements of the cells without liquid junction.

3. The limiting transference number has been determined by extrapolation for all the solutions over the entire temperature range.

4. Agreement with the limiting law of the Onsager conductance theory was observed in the water, 20, 45 and 70% dioxane-water mixtures.

5. Results obtained with the mixtures containing 82% dioxane were less accurate. They have a value, however, since no transference number data in media of as low a dielectric constant ( $D_{25} = 9.57$ ) are available.

NEW HAVEN, CONN.

RECEIVED AUGUST 31, 1939

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

## Phosphoryl Bromofluorides

BY HAROLD SIMMONS BOOTH AND CHARLES GEORGE SEEGMILLER<sup>1</sup>

It has been found in this Laboratory that phosphoryl trichloride can be fluorinated stepwise to yield phosphoryl chlorofluorides<sup>2a</sup> by means of antimony trifluoride with antimony pentachloride as catalyst, and that phosphorus tribromide likewise can be fluorinated stepwise by means of antimony trifluoride but with bromine as the catalyst.<sup>2b</sup>

While the phosphoryl chlorofluorides were quite stable, the compounds PBrF<sub>2</sub> and PBr<sub>2</sub>F decomposed on standing to PF<sub>3</sub> and PBr<sub>3</sub>. Hence it was of interest to learn whether phosphoryl bromide could be similarly fluorinated stepwise and whether the fluorobromides so produced were stable.

### Experimental

Phosphoryl tribromide<sup>3</sup> was prepared by the reaction between phosphorus pentabromide and phosphorus pentoxide: P<sub>2</sub>O<sub>5</sub> + 3PBr<sub>5</sub> = 5POBr<sub>3</sub>. The phosphoryl tribromide was fluorinated at a pressure of 25 to 50 mm. by the slow addition of sublimed antimony trifluoride<sup>4</sup> in the generator as described by Booth and Bozarth.<sup>5</sup> During the early stages, the reaction was vigorous at 60°,

but in its later stages it became quite slow, so that it was found advantageous to raise the temperature gradually to 100°. It was unnecessary to add a catalyst, perhaps due to traces of bromine left in the phosphoryl tribromide.

The product consisted of about 60% phosphoryl trifluoride, 10% phosphoryl monobromodifluoride, and 30% phosphoryl dibromomonofluoride. The products were separated and purified and their physical constants established, as described by Booth and Bozarth.<sup>6</sup> It was found in the case of the POBr<sub>2</sub> and POBr<sub>2</sub>F that an ice-salt mixture made a satisfactory refrigerant for the acetone which was circulated by an automatically actuated centrifugal pump through the fractionating column head.

**Analysis.**—The phosphoryl trifluoride was established by approximate boiling points obtained from a thermocouple in the fractionating column head, by molecular weight determinations by a gas density balance,<sup>6</sup> and by chemical analysis for phosphorus.

Samples of the phosphoryl bromofluorides were condensed in glass bulbs connected to the apparatus by conical joints as previously described<sup>6</sup> and absorbed in an excess of potassium hydroxide. They reacted energetically with the solution on warming and were completely dissolved. The solution was then heated on a steam-bath for fifty hours to ensure completion of the reaction. Bromine was determined gravimetrically as silver bromide, and phosphorus

TABLE I

ANALYSES

	Phosphorus		Bromine	
	Calcd.	Exptl.	Calcd.	Exptl.
POF <sub>2</sub> Br	18.81	18.81	48.45	48.51
		18.67		48.45
POBr <sub>2</sub>	13.73	13.47	70.76	70.54
		13.70		70.85

(1) From a portion of a thesis submitted by Charles George Seegmiller in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Chemistry to the Graduate School of Western Reserve University, May, 1939.

(2) (a) Booth and Dutton, *THIS JOURNAL*, **61**, 2937 (1939); (b) Booth and Frary, *ibid.*, **61**, 2934 (1939).

(3) See "Inorganic Syntheses," Vol. II, for details of this preparation.

(4) Kindly furnished by the Harshaw Chemical Company, Cleveland, Ohio.

(5) Booth and Bozarth, *THIS JOURNAL*, **61**, 2927 (1939).

(6) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).