

(Table I). We attribute this difference to the more precise analytical method used by us. In but one measurement extending over fifty hours did Holmberg⁹ observe a drift; this he attributes to the formation of the thiocarbamine acid.

TABLE III

Na α -bromopropionate			Na β -Bromopropionate		
$a = 0.05215$ m./l. NaSCN			$a = 0.05223$ m./l. NaSCN		
$b = 0.03528$ m./l.			$b = 0.03017$ m./l.		
t	% Conv.	k	t	% Conv.	k
1297	6	0.000899	1342	20	0.00326

Since interference from end-products will be at a minimum during the first few hours of reaction, we may conclude from Table III that the β -ion reacts about 3.4 times more rapidly than the α -bromopropionate ion, a result in good accord with that obtained for the thiosulfate reaction.¹

Summary

Side and consecutive reactions obscure the kinetics of the halogen replacement by thiocyanate ion in the halogenated fatty acids when the elapsed time exceeds 1500 minutes. The greater reactivity of halogen in the beta position in an ion has been confirmed for the thiocyanate ion replacement reaction.

⁹ Ref. 3, p. 155.

NEW YORK CITY

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

TRANSFERENCE NUMBERS OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE, SODIUM CHLORIDE, LITHIUM CHLORIDE AND HYDROCHLORIC ACID AT 25° BY THE MOVING BOUNDARY METHOD¹

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Introduction

In the paper following this one, the conductance and transference data for aqueous solutions of some binary electrolytes will be interpreted from the standpoint of the modern theories of solutions. The transference data obtained for that study were determined by the moving boundary method. The experimental work involved in their measurement is the subject of this paper. An equation which is useful for interpolation and extrapolation to zero concentration is also given.

¹ A portion of the work here reported was completed while the author was a National Research Council Fellow.

Apparatus

The moving boundary cell used in making the measurements is shown in Fig. 1. It is similar to the one described in an earlier paper² in that either rising or falling boundaries may be formed by the shearing mechanism devised by MacInnes and Brighton.³ It has two measuring tubes, A and B, of different cross section, in either of which boundaries may be formed. The lower glass plate C is also provided with a cylindrical recess in which a small disk of metal may be inserted, the recess being placed directly beneath a graduated tube. With this addition boundaries of the type described by Cady and

Longworth⁴ may be made. Since these boundaries are formed automatically under the action of the electric current, thus requiring no shearing mechanism, they will henceforth be termed "autogenic" boundaries. Tube D carries the electrical connection from the metallic disk.

In this new apparatus the electrode chamber E is entirely immersed in the thermostat liquid. This is necessary in order to avoid volume changes due to thermal expansion and contraction which, if allowed to take place, would cause mass displacements of the boundary in the measuring tube.

An important procedure that has not been sufficiently described in previous papers on the moving boundary method as carried out in this Laboratory is the accurate calibration of the graduated tubes. The most recent practice is given below.

The tubes are of Pyrex and are graduated in the manner recommended by MacInnes, Cowperthwaite and Huang.⁵ The calibration was made before the tubes were cemented into the supporting framework of the cell. After the graduation marks were etched on a tube a small glass stopcock with a capillary tip was sealed onto it. The tube and stopcock were then very carefully cleaned. Redistilled mercury was drawn from a weighing bottle into the tube until the mercury meniscus roughly coincided with a graduation on the tube. The exact position of the meniscus with respect to the adjacent graduation was determined to the nearest 0.002 millimeter (by a device which will be described immediately) the bottle with remaining mercury weighed, and the meniscus then roughly adjusted to another graduation and the distance from meniscus to graduation again determined. The device for locating the meniscus with respect to a graduation was constructed as follows. A Brown and Sharpe micrometer head which could be read to 0.002 millimeter was adapted to a sliding support which carried the graduated tube, this in turn being clamped to the stage of a microscope with its optical axis in a horizontal position. The tube was thus held in a vertical position

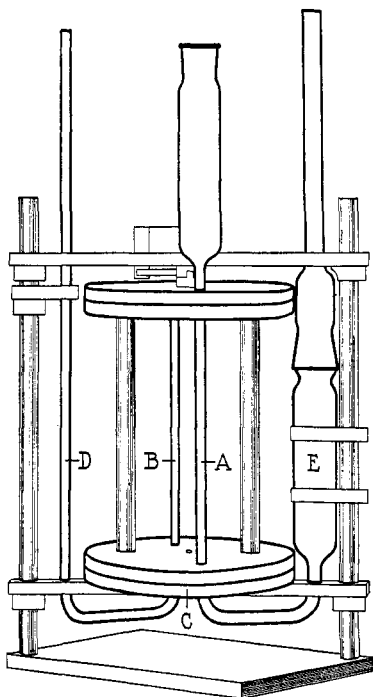


Fig. 1.—The moving boundary cell.

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² Longworth, *THIS JOURNAL*, **52**, 1897 (1930).

³ MacInnes and Brighton, *ibid.*, **47**, 994 (1925).

⁴ Cady and Longworth, *ibid.*, **51**, 1656 (1929).

⁵ MacInnes, Cowperthwaite and Huang, *ibid.*, **49**, 1710 (1927).

and could be moved perpendicularly. A magnification of 40 diameters was employed. With this arrangement it was not necessary to bring the mercury meniscus exactly in line with a graduation, which is an advantage as it is difficult to carry out with tubes of small diameter. In this manner accurate calibrations can be made quite readily. The following figures are the results of five determinations on the volume in milliliters between the first and last graduations of one of the tubes: 1.2114, 1.2112, 1.2108, 1.2110, 1.2108. The mean of these values is 1.2110₄ with a probable error of the mean of 0.00008 ml. The calibration of a tube includes, of course, a determination of the volumes between successive graduations.

Tubes A and B of Fig. 1 have average cross sectional areas of about 0.12 and 0.08 square centimeters, respectively. A third tube, of 0.05 square centimeter area, in a similar cell was also used in some of the measurements.

The constant current regulator and other auxiliary apparatus were the same as described in previous papers.² The regulation was accurate to about 0.01%.

Materials.—A good grade of potassium chloride was recrystallized twice from conductivity water, dried and fused. The sodium chloride was precipitated from a saturated solution with pure hydrogen chloride gas, dried and fused *in vacuo*. The best obtainable grade of hydrochloric acid was diluted to constant boiling strength and distilled, the end fractions being rejected. The concentration of this constant boiling acid was interpolated from the data of Foulk and Hollingsworth.⁵ The author is indebted to Dr. Shedlovsky for the purification of lithium chloride and preparation of the solutions of this salt. This procedure is described in connection with the conductance measurements on this salt. Solutions were usually prepared by direct weighing of both solute (or concentrated stock solution) and solvent, the concentration being converted to a volume formal basis by means of the density data taken from the "International Critical Tables." Solutions of sodium chloride above 0.02 *N*, however, were prepared in carefully calibrated flasks. All concentrations are expressed in gram equivalents per liter of solution at 25°.

An excellent grade of sodium and potassium salts of tetra-iodofluorescein, which served as indicators in many of the determinations, was furnished by the Eastman Kodak Co. These salts were further purified in this Laboratory by several recrystallizations. The solutions of the indicator electrolytes, the concentrations of which do not need to be known with great accuracy, were prepared in volumetric flasks. The metallic cadmium employed was of "c. p." grade and on qualitative analysis proved to be free from impurities which would yield on solution ions faster than cadmium.

Experimental Procedure

A large proportion of the data was obtained by the Cady and Longworth method using a cadmium disk anode as mentioned above. Where applicable this is the simplest procedure and gives results of high precision. However, the CdCl₂-HCl and CdCl₂-KCl boundaries become invisible below 0.01 *N* and the CdCl₂-NaCl boundary cannot be detected much below 0.02 *N*. CdCl₂-LiCl boundaries were obtained only at 0.05 *N* and above, and even at 0.05 *N* they were diffuse and difficult to locate accurately except at relatively high current densities. Lithium iodate proved to be the most satisfactory indicator for the lithium chloride solutions. To study solutions of sodium chloride and potassium chloride at concentrations lower than those mentioned, the corresponding salts

⁵ Foulk and Hollingsworth, *THIS JOURNAL*, **45**, 1220 (1923).

of tetra-iodofluorescein served as indicators, though in special cases other indicators were also used. MacInnes and Brighton's³ shearing mechanism was used for forming these boundaries. With the tetra-iodofluorescein as indicator boundaries were sharp and readily visible at concentrations considerably below 0.001 N . However, as will be shown later, the data obtained on the most dilute solutions are of lower precision due to a large and somewhat ambiguous solvent correction, which was, however, kept at a minimum.

The upper limit of concentration of solutions for which accurate transference numbers have been obtained is 0.2 N . At this and to an increasing extent at higher concentrations, the heat developed in the moving boundary cell gives rise to convection currents which tend to distort the boundary and cause mixing. In order to obtain accurate transference numbers at 0.2 N it was found necessary to employ the tube of smallest cross sectional area since the actual amount of heat developed is smaller and the area of tube surface exposed to the thermostat is relatively greater. In addition, at 0.2 N the volume correction for the processes behind the boundary is in many cases quite large. This correction, as will be shown below, is not an exact one, but has relatively little effect on the results, except in extreme cases.

In order to keep the volume correction as definite as possible one electrode is kept closed. In the case of the autogenic boundaries the anode side is necessarily the closed one. Using sheared boundaries the electrode chamber completely immersed in the thermostat is always the closed side of the system.

Among the advantages of the moving boundary method over the Hittorf method are the rapidity with which measurements can be made and the fact that the progress of the determination can be followed from the beginning. In contrast, a Hittorf determination in which, at best, two figures are obtained, requires several days and the success of a determination is in doubt until the final analyses are completed.

To show the number and relative accuracy of the data obtained in a single determination by the moving boundary method, the figures recorded in a quite typical experiment, lasting about ninety minutes, are given in Table I. It will be recalled that by this method the transference number T is obtained from the formula

$$T = \frac{VCF}{1000It}$$

in which V is the volume in milliliters swept through by the boundary in t seconds when a current of I amperes is flowing. C is the concentration and F the faraday in coulombs.

Column 2 of the table gives the time required for the boundary to move through the volume between the etch marks spaced by the distance

in centimeters given in Column 1. Column 3 contains the factor $VCF/1000 I$, which gives, on division by the value of t in the preceding column, a value of T_+ (Column 4) corresponding to the total volume through which the boundary has moved in that time. The values in Column 4 thus constitute a running check on the progress of the experiment.

TABLE I
THE DATA AND COMPUTATIONS FOR A TYPICAL DETERMINATION
 T_+ at 25° for NaCl at $C = 0.02$. Autogenic boundary—Cd anode; Ag-AgCl cathode; current, 0.0016001 ampere.

1 x	2 t	3 $VCF/1000 I$	4 T_+	5 Δx	6 Δt	7 $VCF/1000 I$	8 T_+
0.0	0			0.0-10.0	3453	1344.7	0.3894
0.5	172			0.5-10.0	3281	1277.6	.3894
1.0	344	133.9	0.3892	1.0-10.0	3109	1210.8	.3894
1.5	516			1.5-10.0	2937	1142.9	.3891
2.0	689	268.3	.3894	2.0-10.0	2764	1076.4	.3894
3.0	1036	402.8	.3888	0.0- 9.5	3276	1276.4	.3896
4.0	1380	536.5	.3888	0.5- 9.5	3104	1209.2	.3896
5.0		670.6		1.0- 9.5	2932	1142.5	.3897
6.0	2070	805.5	.3891	1.5- 9.5	2760	1074.6	.3894
7.0	2414	939.4	.3891	0.0- 9.0	3104	1208.6	.3894
8.0	2757	1074.6	.3898	0.5- 9.0	2932	1141.5	.3893
8.5	2933			1.0- 9.0	2760	1074.7	.3894
9.0	3104	1208.6	.3894	0.0- 8.5	2933	1142.0	.3894
9.5	3276			0.5- 8.5	2761	1075.0	.3894
10.0	3453	1344.7	.3894	0.0- 8.0	2757	1074.6	.3898

Mean 0.3894

In Column 5 there are fifteen combinations of readings in which the boundary has traveled eight or more centimeters, and in Column 6 the corresponding times in seconds. Hence, by calculating a value of T_+ (Column 8) for each of these combinations from the data of Columns 6 and 7, errors in individual observations are minimized. The probable error of the mean of this typical experiment is 0.00003, corresponding to an error of 0.3 second. This is, of course, merely an indication of the accuracy of the time observation. Errors may also arise from determinations of the volumes, the current and the concentration. The accuracy of all these measurements is within 0.02%. Uncertainties in the necessary corrections to be described below may also introduce small errors.

Experimental Results and Computations

The results of individual determinations on solutions of the four electrolytes each at a series of concentrations are given in Tables II to V. In general, more than one potential gradient was employed at each concentration, but over a considerable range of voltage no variation in the observed transference number resulted. As will be shown in the following sections these data are subject to corrections, (a) for volume changes

behind the boundary, and (b) for the conductance of the solvent. The magnitudes of these corrections are also given in the tables. Where results are given in the tables for both anion and cation boundaries at the

TABLE II

DATA CONCERNING DETERMINATION OF TRANSFERENCE NUMBERS OF POTASSIUM CHLORIDE AT 25°

Concn. T_- or T_+	0.001 T_-	0.002 T_-	0.005 T_-	0.01 T_-	0.02 T_-	0.01 T_+	0.02 T_+	0.05 T_+	0.1 T_+	0.2 T_+
Separate deter- mina- tions	0.5052	0.5074	0.5089	0.5091	0.5095	0.4894	0.4894	0.4894		0.4876
	.5052	.5074	.5083	.5092	.5094	.4893	.4892	.4893		.4876
						.4894	.4890	.4895		.4877
						.4890	.4895	.4896		.4877
Mean	.5052	.5074	.5086	.5092	.5095	.4893	.4893	.4895		.4877
Vol. corr.	+ .0001	+ .0002	+ .0004		+ .0015
$K_{H_2O} \times 10^{-6}$	1.3	1.3	1.3	1.3	1.3	2.0	2.0	2.0	
Sol. corr.	0.0045	0.0023	0.0009	0.0005	0.0003	0.0007	0.0004	0.0001	
T corr.	.5097	.5097	.5095	.5097	.5098	.4901	.4899	.4900	0.4898 ^a	.4892
T_+ final	.4903	.4903	.4905	.4902	.49014900	.4898	.4892

^a This value is based on work as reported in a previous paper.¹

TABLE III

DATA CONCERNING DETERMINATION OF TRANSFERENCE NUMBERS OF SODIUM CHLORIDE AT 25°

Concn. T_- or T_+	0.01 T_-	0.02 T_+	0.05 T_+	0.1 T_+	0.2 T_+
Separate de- terminations	0.6073	0.3894	0.3872	0.3851	0.3812
	.6073	.3896	.3874	.3850	.3812
	.6078	.3894	.3875	.3851	.3813
	.6072	.3895	.3877	.3850	.3813
3900	.3875	.3851	...
Mean	.6074	.3896	.3875	.3851	.3813
Vol. corr.	+ .0001	.0000	+ .0001	+ .0001	+ .0001
$K_{H_2O} \times 10^{-6}$	1.3	2.2	2.2	2.2	...
Sol. corr.	0.0006	0.0004	0.0002	0.0001	...
T corr.	.6081	.3900	.3878	.3853	.3814
T_+ final	.3919	.3900	.3878	.3853	.3814

TABLE IV

DATA CONCERNING DETERMINATION OF TRANSFERENCE NUMBERS OF LITHIUM CHLORIDE AT 25°

Concn. T_- or T_+	0.0098356 T_-	0.011104 T_-	0.018515 T_-	0.032550 T_-	0.049942 T_-	0.064021 T_-	0.10000 T_-	0.064021 T_+	0.10000 T_+
Separate deter- mina- tions	0.6699	0.6703	0.6732	0.6764	0.6784	0.6797	0.6829	0.3200	0.3166
	.6695	.6701	.6726	.6759	.6783				.3169
	.6700		.6729	.6757					.3172
			.6731	.6760					.3170
Mean	.6698	.6702	.6729	.6760	.6783	.6797	.6829	.3200	.3169
Vol. corr.	.0001	.0001	.0002	.0003	.0005	.0006	.0010	.0000	-.0001
$K_{H_2O} \times 10^{-6}$	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sol. corr.	0.0010	0.0010	0.0005	0.0003	0.0002	0.0002	0.0001	0.0001
T corr.	.6709	.6713	.6736	.6766	.6790	.6805	.6840	.3201	0.3168
T_+ final	.3291	.3287	.3264	.3234	.3210	.3198	.3167

TABLE V
DATA CONCERNING DETERMINATION OF TRANSFERENCE NUMBERS OF HYDROCHLORIC
ACID AT 25°

Concn.	0.01 T_+	0.02 T_+	0.05 T_+	0.1 T_+
Separate de-terminations	0.8247	0.8260	0.8287	0.8303
	.8249	.8260	.8285	.8302
	.8247	.8258	.8289	.8308
		.8261	.8285	.8301
Mean	.8248	.8260	.8287	.8305
Vol. corr.	+ .0001	+ .0002	+ .0005	+ .0009
$K_{H_2O} \times 10^{-6}$	1.3	1.3
Sol. corr.	0.0003	0.0002
T_+ final	.8252	.8264	.8292	.8314

same concentration, a mean value of T_+ has been taken, and is recorded under the heading T_+ final.

(a) **The Volume Correction.**—G. N. Lewis⁷ has shown that the observed transference number must be corrected for a displacement of the boundary due to volume changes behind the boundary. This correction is most readily applied by means of the equation

$$T = T_{\text{obs.}} + \frac{C \Delta V}{1000}$$

where ΔV is this volume change in milliliters per faraday equivalent and C is the concentration. For the cation boundaries the volume change, ΔV_+ , is

$$\Delta V_+ = \frac{1}{2} \bar{V}_{\text{CdCl}_2} - T_+ \bar{V}_{\text{XCl}} - \frac{1}{2} V_{\text{Cd}}$$

in which the \bar{V} 's are partial molal volumes and V is an atomic volume. The subscripts indicate the salt involved and X may stand for H, K, Na or Li. For the anion boundaries a silver-silver chloride cathode was employed and the volume change, ΔV_- , is

$$\Delta V_- = V_{\text{Ag}} + T_+ \bar{V}_{\text{XCl}} - V_{\text{AgCl}}$$

In a recent paper E. R. Smith⁸ has found experimentally the value of ΔV_- in this reaction, using a potassium chloride solution, and has obtained adequate agreement with the computation as given. This important paper also includes a detailed treatment of the theory of the volume changes affecting the boundary velocity.

The partial molal volumes, which were computed from data in the "International Critical Tables" according to the directions of Lewis and Randall⁹ are expressed by the following formulas.

⁷ Lewis, THIS JOURNAL, 32, 862 (1910).

⁸ Smith, *Bur. Standards J. Research*, 8, 457 (1932).

⁹ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, p. 36.

$$\begin{aligned}\bar{V}_{\text{LiCl}} &= 17.06 + 2.13 \sqrt{m} \\ \bar{V}_{\text{KCl}} &= 26.65 + 3.21 \sqrt{m} \\ \bar{V}_{\text{NaCl}} &= 22.85 - 5.32 (0.8105)^m (1 - 0.2101 m) \\ \bar{V}_{\text{HCl}} &= 18.07 + 1.27 \sqrt{m} \\ \bar{V}_{\text{CdCl}_2} &= 23.24 + 8.82 \sqrt{m}\end{aligned}$$

These empirical expressions are based on the linear variation of the apparent molecular volume, ϕ , with the square root of the molality, m , except that in the case of sodium chloride the function given for that salt represents the data somewhat better than the simple square root relation, and is derived from the equation

$$\phi = 22.85 - 5.32 (0.8105)^m$$

The three constants of this equation were determined graphically by a method given by Running.¹⁰ It is interesting to note that this function, unlike the square root relation, may be used to compute the partial molal volume of the solute in the hypothetical solution in which no water is present ($m = \infty$),¹¹ as well as in the infinitely dilute solution ($m = 0$).

The functions given here were developed before the author had noted the appearance of the recent papers by Masson and others,¹² who show the wide validity of the linear variation of ϕ with the square root of the volume formal concentration. Otherwise their formulas could have been directly adapted to the computation of the necessary volume corrections.

In using these equations¹³ in computing the corrections recorded in

¹⁰ Running, "Empirical Formulas," John Wiley and Sons, Inc., New York, 1917, p. 28.

¹¹ A. F. Scott, *J. Phys. Chem.*, **35**, 1410 (1931).

¹² Masson, *Phil. Mag.*, **8**, 218 (1929); Redlich, *Naturwissenschaften*, **19**, 251 (1931); Geffcken, *ibid.*, **19**, 321 (1931); *Z. physik. Chem.*, [A] **155**, 1 (1931); Redlich and Rosenfeld, *ibid.*, [A] **155**, 65 (1931).

¹³ Since the partial molal volumes are functions of the concentration and as the concentration distribution in the neighborhood of the electrode is far from uniform, it is evident that the correction as computed above is an approximation. However, the entire correction is small at moderate concentrations so that the error involved in this case cannot be large. In the case of the autogenic boundaries the diffusion layer is well defined and the concentration distribution resulting from pure diffusion and ionic migration is not destroyed by gravity currents as may be the case with the electrode arrangement used with sheared boundaries. Hence in the case of the autogenic boundaries it is theoretically possible to obtain a better estimate of this correction in the following manner. A passage of one faraday of electricity will cause the boundary to move from $X = 0$ (the face of the electrode, of say metallic cadmium) to a point in the tube X_1 . The region from $X = 0$ to $X = X_1$ will contain one equivalent of cadmium chloride whose concentration distribution may be computed from formulas developed by Sand [*Phil. Mag.*, **6**, 1, 45 (1901)] and by Miller and Rosebrugh [*J. Phys. Chem.*, **14**, 816 (1912)]. Thus, since C_{CdCl_2} is known as a function of X , and \bar{V}_{CdCl_2} as a function of C_{CdCl_2} , \bar{V}_{CdCl_2} may be expressed as a function of the distance. The definite integral

$$\frac{1}{X_1} \int_0^{X_1} \bar{V}_{\text{CdCl}_2} dX$$

will then give the average value of the partial molal volume of the cadmium chloride and

Tables II to V the approximation was made that over the range studied, the concentration could be replaced by the molality, m . For the atomic and molecular volumes the following values were used

$$V_{Ag} = 10.3 \qquad V_{Cd} = 13.0 \qquad V_{AgCl} = 25.8$$

(b) **The Solvent Correction.**—Although the necessity for the correction for the conductance of the solvent has been generally recognized in the case of conductivity measurements, apparently no previous investigator has considered the application of such a correction to transference data. Other workers have either considered the data of insufficient accuracy to warrant the application of the correction or have thought that it would be negligible even at the lowest concentrations which they studied. However, with the precision attained by the moving boundary method, such a correction is imperative. Moreover, a solvent correction should be applied to the results of transference measurements made by all of the available methods. Fortunately it has but little effect on the final results except in the most dilute solutions. In that region, however, it may be the factor determining the accuracy of the data.

The necessity for a solvent correction was impressed on the author as a result of the following observations. If anion and cation boundaries are observed independently for the same solution, the value of $(1 - T_-)$ obtained from an anion boundary, T_- being the anion transference number, should exactly equal the cation transference number, T_+ . At concentrations above 0.02 N such was found to be accurately the case. As the concentration was decreased, however, the two independently observed values were found to diverge. This is illustrated in Fig. 2, where the observed transference data on the lower concentrations of potassium chloride have been plotted, for convenience, against the cube root of the concentration. Curve A gives values of $(1 - T_-)$ in which T_- is here the observed anion transference number which has been corrected for the volume changes behind the boundary, but not for solvent conductance. Curve B gives corresponding values of the directly determined cation transference number, T_+ , to as low a concentration as the boundaries were visible. Curves A and B should coincide and would do so except that at these low concentrations the conducting impurities in the solvent are carrying an appreciable fraction of the total current. Curve C in the figure is a plot of the values of $(1 - T_-)$ and T_+ after being corrected for the solvent conductance according to considerations discussed below.

An expression by which the observed transference number can be corrected for the solvent conductance may be derived as follows. The this is the value which should be used in computing the volume correction. The computation of the volume correction in this manner, however, is very laborious. The volume corrections actually used are based on a value of C_{CdCl_2} the same as C_{XCl} , that is, an approximate mean, in all probability sufficiently accurate for the purpose.

current I flowing in a linear conductor is equal to the total flux of electricity through a given cross section per unit time. For a solution of a uni-univalent electrolyte at concentration C , V_+ will represent the actual work-

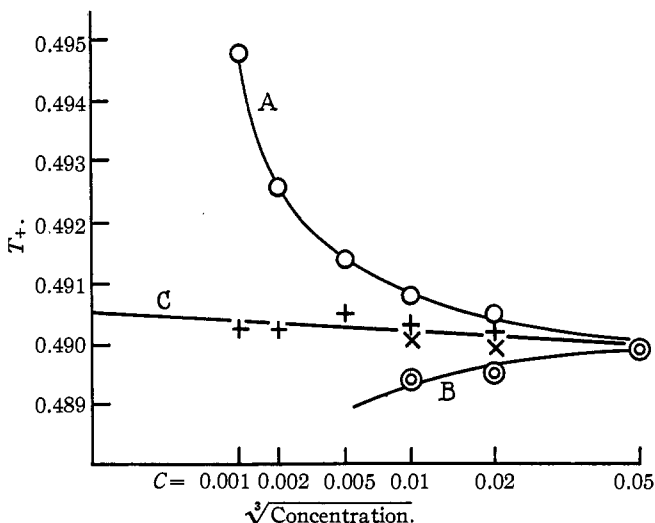


Fig. 2.—Effect of solvent correction on observed transference numbers for potassium chloride solutions: O, $1-T_-$ (observed); +, $1-T_-$ (corrected); \odot , T_+ (observed); X, T_+ (corrected).

ing velocity of the entire cation constituent and V_- that of the anion constituent. The total current flowing in a tube of uniform cross section A is

$$I = \frac{CFA}{1000} (V_+ + V_-) + \frac{FA}{1000} \sum C_i V_i$$

The last term provides for the current carried by impurities in the solvent, whose unknown concentrations and velocities are C_i and V_i , respectively. On multiplying this equation through by $V_+/(V_+ + V_-)$ and rearranging

$$\frac{V_+}{V_+ + V_-} = T_+ = \frac{CFA V_+}{1000 I} + \frac{FA}{1000 I} \cdot T_+ \sum C_i V_i$$

is obtained. Since the mobility, U_i , of an ion constituent is the ratio of the velocity, V_i , to the field strength, E , this equation may be written

$$T_+ = \frac{CFA V_+}{1000 I} + \frac{FEA}{1000 I} T_+ \sum C_i U_i$$

However, the ratio I/EA is the specific conductance of the solution, K_{solution} , and $(F/1000) \sum C_i U_i$ is the specific conductance of the solvent, K_{solvent} , which may be measured independently. If the assumption be made that introduction of the solute into the solution does not alter the concentration and mobilities of the impurities in the solvent, this equation becomes

$$T_+ = T_+ (\text{obs.}) + T_+ \frac{K_{\text{solvent}}}{K_{\text{solution}}}$$

for the cation transference number and there is a corresponding expression for the anion transference number.

A determination of the solvent correction in the manner outlined above leads to a value for that correction which is necessarily too small, since the potential gradient in the indicator region is greater than that in the region ahead of the boundary, with the result that this region will be progressively contaminated with impurities forced across the boundary. It was thought that with the data on potassium chloride which were available a better estimate of this correction could be obtained by assigning to the solvent a conductance which, when the corresponding correction was applied to the data, would bring the two curves of Fig. 2 very nearly into coincidence. The solvent conductance as determined in this manner was but slightly higher than the value experimentally measured, and the data, when thus corrected, give Curve C of Fig. 2.

In order to reduce the solvent correction to as low a value as possible the following procedure was devised. The solutions of sodium chloride and potassium chloride below 0.02 normal, on which anion boundaries were observed, were swept out with carbon dioxide-free nitrogen¹⁴ before introduction into the moving boundary cell. This procedure materially improved the quality of the solvent but by no means eliminated the correction since after introduction into the cell a small portion of the solution must necessarily come in contact with the air of the laboratory. Moreover, the solvent contains minute amounts of ionic impurities other than carbonic acid and may also acquire additional impurities from contact with the lubricant used in the assemblage of the cell.¹⁵ The solvent conductance was therefore determined by direct current measurement in the moving boundary cell after the water had been subjected to the same treatment as the solutions being observed. The values for all solvent conductances are recorded in Tables II to V.

Disturbing and Restoring Effects at the Boundary.—A characteristic of the moving boundary method which largely determines the upper limit of concentration at which accurate measurements can be made is the presence of heat and diffusion effects at the boundary. There is, however, a mechanism operating to oppose such disturbances. This is a restoring effect due to the change of the potential gradient at the boundary. This effect has been studied and described by MacInnes and Cowperthwaite.¹⁶ A large difference in the densities of the two solutions meeting at the boundary appears to reinforce this restoring effect. Ob-

¹⁴ Shedlovsky, *THIS JOURNAL*, **54**, 1411 (1932).

¹⁵ A lubricant which was found to be quite satisfactory was prepared by melting together five parts of vaseline and one part of beeswax. Both ingredients were extracted several times with hot conductivity water before they were mixed.

¹⁶ MacInnes and Cowperthwaite, *Proc. Natl. Acad. Sci.*, **15**, 18 (1929).

viously, to obtain correct transference numbers the restoring effect must be stronger than all the disturbing influences. The indications that this latter condition is fulfilled are (a) the boundaries appear flat and sharp, (b) at constant current they move with constant velocity, (c) the observed transference numbers are, within wide limits, independent of the current density, and (d) independent observations on cation and anion boundaries for the same solution give consistent results. With the exception of condition (d) for hydrochloric acid solutions, as will be explained below, the experiments reported in this paper fulfilled all of these requirements.

Measurements on Solutions of Hydrochloric Acid.—Due to the high mobility of the hydrogen ion the heat effects were more difficult to eliminate in the measurements on hydrochloric acid than in corresponding determinations with solutions of the other electrolytes. In addition any uncertainty as to the values for these salts was eliminated by check measurements on cation and anion boundaries. Such checks were difficult to obtain with hydrochloric acid solutions, since at the high current densities necessary to bring out sharp HIO_3/HCl boundaries, for example, the heat effects are apparently large enough to produce appreciable mixing. It was therefore considered desirable to make confirmatory determinations of the cation transference numbers using indicators other than cadmium chloride. A comparison of the results with the different indicators is made in Table VI. Results, using cadmium chloride as indicator, with three sizes of tube, are also included.

TABLE VI
A COMPARISON OF RESULTS ON HYDROCHLORIC ACID

Concn.	Tube area	Indicator	Cation trans. no., T_+	Concn.	Tube area	Indicator	Cation trans. no., T_+
0.1	0.12	CdCl_2^a	0.8305	0.02	0.08	CdCl_2^a	0.8264
.1	.08	CdCl_2^a	.8311	.02	.08	0.0133 <i>N</i> CsCl	.8258
.1	.05	CdCl_2^a	.8314	.02	.08	.0133 <i>N</i> TlCl	.8262
.1	.08	0.066 <i>N</i> CsCl	.8309	0.01	0.08	CdCl_2^a	0.8252
0.05	0.08	CdCl_2^a	.8292	.01	.08	0.0066 <i>N</i> TlCl	.8248
.05	.05	CdCl_2^a	.8291				

^a Autogenic boundaries.

From the data in this table it is seen that there is a slight increase in the apparent transference number at 0.1 *N* as the tube size is diminished from 0.12 to 0.08 and but little change on further decrease of tube size. Furthermore, the data of Table VI indicate such a slight dependence on the nature of the indicator ion as to be within the limits of error in the determinations. The data obtained in the smallest tube, with cadmium chloride as indicator, though possibly not quite as accurate as the corresponding data for potassium, sodium and lithium chlorides, are probably correct within 0.05%.¹⁷

¹⁷ The value of T_+ for 0.1 *N* HCl reported in this paper is 0.1% higher than the

Discussion of Results

A comparison between some of the data for potassium chloride given in Table II and that recently obtained by MacInnes and Dole,¹⁸ using the Hittorf method, has already been made by those authors, and showed excellent agreement of the results obtained by the two methods. The earlier work on potassium chloride by Smith and MacInnes¹⁹ and MacInnes and Brighton³ gave results slightly higher at 0.1 *N* than those given in this paper, but agreeing within the limit of error at 0.2 *N*. These researches were, however, carried out before the constant current apparatus was used. After that device was installed, Dr. Cowperthwaite obtained anion and cation results (not published) at 0.1 *N* with falling boundaries agreeing perfectly with those reported here.

In the case of lithium chloride, the recent careful measurements of Jones and Bradshaw²⁰ using the Hittorf method are given in Table VII together with values obtained by the moving boundary method on the same salt.

TABLE VII
VALUES OF T_+ FOR LiCl AT 25° AS DETERMINED BY THE HITTORF AND MOVING BOUNDARY METHOD

Concn.	0.01	0.02	0.05	0.1
T_+ , L.	.329	.326	.321	.317
T_+ , J. and B.	.329	.327	.323	.319

This table shows that there is substantial agreement between the new Hittorf results and the results obtained by the moving boundary method. These new experiments, in addition to those on potassium chloride, furnish ample evidence that the two methods measure the same property of a solution of an electrolyte.²¹

value reported in connection with some work on mixtures of HCl and KCl.¹ This revision affects the magnitude of certain ion conductances reported in the earlier paper but would not alter any of the conclusions.

¹⁸ MacInnes and Dole, *THIS JOURNAL*, **53**, 1357 (1931).

¹⁹ Smith and MacInnes, *ibid.*, **47**, 1009 (1925).

²⁰ Jones and Bradshaw, *ibid.*, **54**, 138 (1932).

²¹ Transference numbers for lithium chloride have also been obtained by the e. m. f. method by MacInnes and Beattie [*THIS JOURNAL*, **42**, 1117 (1920)] and their data have been recomputed by Jones and Bradshaw. The results for several concentrations may be compared as follows:

Concn.	0.01	0.02	0.05	0.1
T_+ , MacInnes and Beattie	.334	.327	.318	.311
T_+ , Jones and Bradshaw	.333	.331	.326	.320

A difficulty with the e. m. f. method is that, since the transference numbers change with the concentration, the experimental data must be fitted to empirical or semi-empirical equations. The difference between the transference numbers obtained from the same data using different equations is shown in the figures just given and indicates that the computed transference numbers are very sensitive to the form of the equation chosen. As can be seen the values in Table VII are roughly the mean of the results by the two

Transference Numbers as a Function of the Concentration.—For purposes of interpolation and for extrapolation to zero concentration it is desirable to express the measured transference numbers as a function of the concentration. Dole²² has recently shown how the Onsager²³ equations for ion conductances may be combined to give an expression for the transference number as a function of the concentration. This expression must be valid in the limiting region of zero concentration if the ion conductance equations are valid and the recent precise conductance measurements of Shedlovsky²⁴ indicate the accuracy of these limiting laws. Hence a plot of any function which may be derived for transference data must go into the axis of zero concentration with the slope required by the Onsager equations.

For the ions of uni-univalent electrolytes at 25° in water

$$\lambda = \lambda^0 - (\alpha\lambda^0 + \beta) \sqrt{C}$$

In this expression λ is the equivalent conductance of the ion at concentration C , λ^0 the equivalent conductance at zero concentration, and α and β are numerically equal to 0.2274 and 29.90, respectively. The cation transference number, on the basis of this expression, is

$$T_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+^0 - (\alpha\lambda_+^0 + \beta) \sqrt{C}}{\lambda_+^0 + \lambda_-^0 - [\alpha(\lambda_+^0 + \lambda_-^0) + 2\beta] \sqrt{C}} \quad (1)$$

Since $T_+^0 = \lambda_+^0 / (\lambda_+^0 + \lambda_-^0)$ and setting, for abbreviation

$$\begin{aligned} \Lambda' &= \lambda_+^0 + \lambda_-^0 - [\alpha(\lambda_+^0 + \lambda_-^0) + 2\beta] \sqrt{C} \\ &= \Lambda_0 - (\alpha\Lambda_0 + 2\beta) \sqrt{C} \end{aligned}$$

Equation (1) may be rearranged to give

$$T_+ = T_+^0 - \frac{(1 - 2T_+^0)}{\Lambda'} \beta \sqrt{C} \quad (2)$$

This limiting expression for the transference number states that a plot of T_+ against \sqrt{C} should go into the axis of zero concentration with the slope

$$\left(\frac{dT_+}{d\sqrt{C}} \right)_{C=0} = \frac{2T_+^0 - 1}{\Lambda_0} \beta$$

The limiting slope is thus seen to be proportional to the deviation of T_+^0 from 0.5 and inversely proportional to the limiting conductance, Λ_0 , of the electrolyte.

Equation (2) is not valid in the concentration range where the measurements have been made. However, the striking success of the Shedlovsky methods of calculation. MacInnes and Beattie did not use graphical methods in their computation as Jones and Bradshaw imply. Both methods of calculation are analytical, the difference being in the form of function used.

²² Dole, *J. Phys. Chem.*, **35**, 3647 (1931).

²³ Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

²⁴ Shedlovsky, *THIS JOURNAL*, **54**, 1405, 1411 (1932).

method of treating conductance data suggested the possibility of a similar treatment of transference data. Solution of Equation (2) for T_+^0 gives

$$T_+^0 = \frac{T_+ \Lambda' + \beta \sqrt{C}}{\Lambda' + 2\beta \sqrt{C}}$$

Values of T_+^0 were computed from each pair of observed values for T_+ and C . These computed values of T_+^0 —plotted as $T_+^{0'}$ —were found to vary

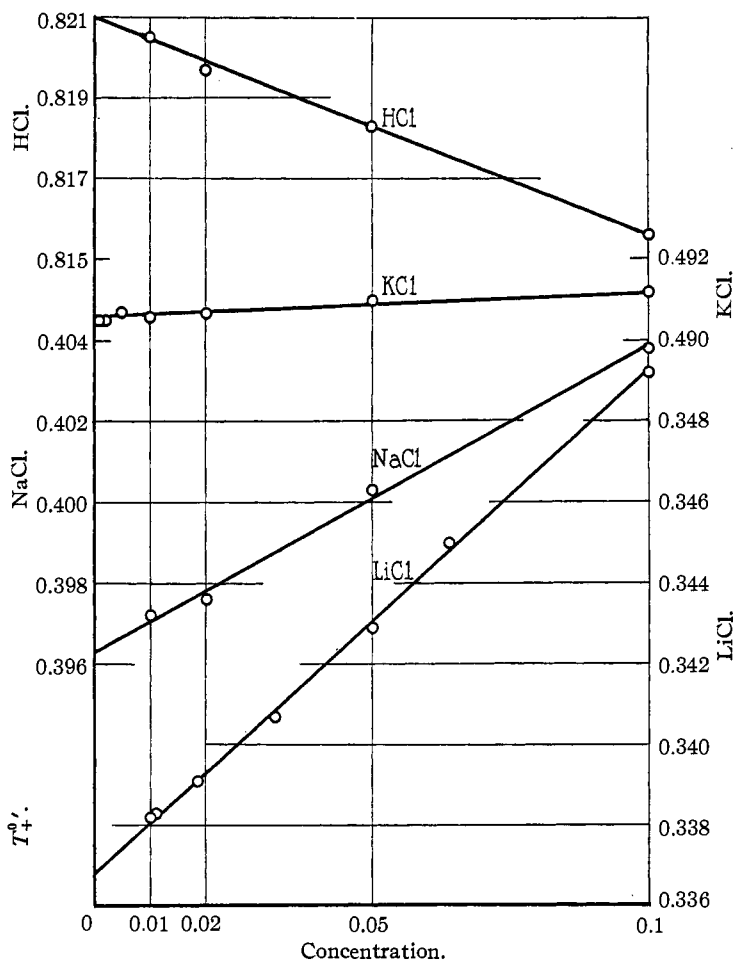


Fig. 3.—Test of Equation (4) and the evaluation of the constants T_+^0 and A .

linearly with the concentration as shown in Fig. 3 up to a concentration of 0.1 normal. Thus $T_+^{0'}$ is a linear function of the concentration

$$T_+^{0'} = T_+^0 + AC = \frac{T_+ \Lambda' + \beta \sqrt{C}}{\Lambda' + 2\beta \sqrt{C}} \tag{3}$$

Solution of (3) for T_+ gives

$$T_+ = T_+^0 - \frac{1 - 2T_+^0}{\Lambda'} \beta \sqrt{C} + AC \left(1 + \frac{2\beta \sqrt{C}}{\Lambda'} \right) \quad (4)$$

an expression for T_+ which has the theoretical limiting slope. A simple interpolation formula which appears to be valid to much higher concentrations than Equation (4) has been proposed and tested by Jones and Dole.²⁵ Their formula, however, does not in general extrapolate to infinite dilution with the correct limiting slope.

The constants of Equation (4) as obtained from a plot similar to Fig. 3 are given in Table VIII together with the values of Λ_0 given by Shedlovsky.

TABLE VIII
CONSTANTS OF EQUATION (4)

	T_+^0	A	Λ_0
LiCl	0.3368	0.125	115.00
NaCl	.3963	.076	126.42
KCl	.4906	.006	149.82
HCl	.8210	-.054	426.04

Values of T_+ computed by means of (4) and the data of Table VIII are compared with the observed values in Table IX. The deviations between observed and computed values are neither systematic nor large and Equation (4) can therefore safely be used for interpolation to 0.1 normal and for extrapolation to lower concentrations. Values computed by means of Equation (4) for round concentrations except the values for 0.2 N are summarized in Table X. In cases where the last figure appears in smaller type, that figure may be in error ± 3 units, except for the data on potassium chloride below 0.005 N , where the error may be slightly greater.

TABLE IX
COMPARISON OF CALCULATED AND OBSERVED VALUES FOR T_+

Concn.	T_+ calcd.	T_+ obs.	$\Delta \times 10^4$	Concn.	T_+ calcd.	T_+ obs.	$\Delta \times 10^4$
LiCl				KCl			
0.0098356	0.3290	0.3291	+1	0.001	0.4905	0.4903	-2
.011104	.3286	.3287	+1	.002	.4904	.4903	-1
.018515	.3264	.3264	0	.005	.4904	.4905	+1
.032550	.3236	.3234	-2	.01	.4903	.4902	-1
.049942	.3211	.3210	-1	.02	.4901	.4901	0
.064021	.3196	.3198	+2	.05	.4899	.4900	+1
.10000	.3168	.3167	-1	.1	.4898	.4898	0
NaCl				HCl			
0.01	0.3918	0.3919	+1	0.01	0.8251	0.8252	+1
.02	.3902	.3900	-2	.02	.8266	.8264	-2
.05	.3876	.3878	+2	.05	.8292	.8292	0
.1	.3854	.3853	-1	.1	.8314	.8314	0

²⁵ Jones and Dole, THIS JOURNAL, 51, 1073 (1929).

The results are presented graphically in Fig. 4. In this figure the circles represent the experimental points and the smooth curves are the values computed from Equation (4) and the constants of Table VIII.

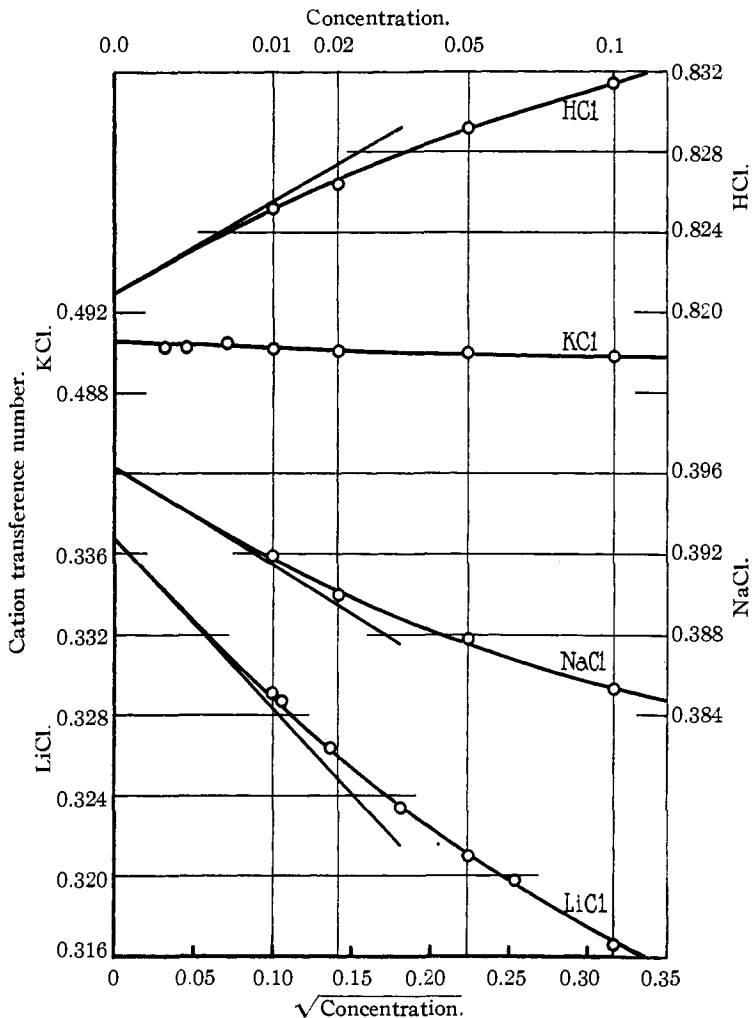


Fig. 4.—Graphical presentation of data showing approach to theoretical limiting slope. Circles represent experimental points; smooth curve represents values computed by Equation (4).

The curves through the experimental points are evidently approaching the limiting slopes which are represented in the figure by the straight full lines. In the case of potassium chloride the limiting slope and the curve given by Equation (4) are nearly coincident up to a concentration of several hundredths normal.

In conclusion the author would like to express his sincere appreciation to Dr. D. A. MacInnes for many suggestions during the course of this work and for valuable criticism during the preparation of this paper.

Summary

Measurements of the transference numbers at 25° of aqueous solutions of potassium chloride, sodium chloride, lithium chloride and hydrochloric acid by the moving boundary method have been made. The results are given in Table X.

TABLE X
TRANSFERENCE NUMBERS AT 25° OF POTASSIUM CHLORIDE, SODIUM CHLORIDE, LITHIUM CHLORIDE AND HYDROCHLORIC ACID

Concn.	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
KCl	.490 ₅	.490 ₄	.490 ₄	.4903	.4901	.4899	.4898	.489 ₂
NaCl3918	.3902	.3876	.3854	.381 ₄
HCl825 ₁	.826 ₆	.829 ₂	.831 ₄	...
LiCl3289	.3261	.3211	.3168	...

A correction for the conductance of the solvent, neglected by previous workers, has been found to be important when dilute solutions are measured.

An equation connecting the transference numbers with the concentration, which is useful for interpolation, and which gives a correct extrapolation to infinite dilution, is given.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR
MEDICAL RESEARCH]

THE LIMITING EQUIVALENT CONDUCTANCES OF SEVERAL UNIVALENT IONS IN WATER AT 25°

BY DUNCAN A. MACINNES, THEODORE SHEDLOVSKY AND LEWIS G. LONGSWORTH

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Data on the conductances of aqueous solutions of a number of binary electrolytes at concentrations ranging from 3×10^{-5} to 0.1 *N* are given in recent papers from this Laboratory,¹ and an article preceding this one describes the accurate determination of the transference numbers of four chlorides in the range 0.01 to 0.1 *N*.² With these data at hand we have been able to arrive at some definite conclusions concerning the equivalent conductances of ion constituents, and the values of the limiting ion mobilities.

Table I contains the assembled data on the equivalent conductances, Λ , of four chlorides and the corresponding transference numbers of the

¹ Shedlovsky, *THIS JOURNAL*, **54**, 1411 (1932); MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

² Longworth, *ibid.*, **54**, 2741 (1932).