entropy in accordance with the requirements of the third law of thermodynamics leads to a considerable heat capacity below 1 °K. This heat capacity has been determined to 0.3 °K. by means of a series of adiabatic demagnetizations from known starting temperatures and magnetic fields. The entropy corresponding to the initial conditions being known, the variation of entropy over the low temperature range is thus determined. $dS/d \ln T = C$ approaches a maximum of 1.60 cal./deg. per one-half mole of $Gd_2(SO_4)_3 \cdot 8H_2O$ at 0.3 °K.

It has been made evident that, when obviously practicable improved experimental conditions become available, the temperature range at present open for various investigations can be greatly extended. The term greatly seems very applicable since temperature range is most significant and should be thought of in logarithmic increments. On this proper basis there is still infinite room for extension.

BERKELEY, CALIFORNIA
CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 26, 1935

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

Transference Numbers of Aqueous Solutions of Some Electrolytes at 25° by the Moving Boundary Method

BY L. G. LONGSWORTH

This paper deals with the results of a systematic research undertaken to provide transference numbers at 25° as functions of the concentration for aqueous solutions of the more common salts. MacInnes and Longsworth[1] have summarized the present knowledge of the moving boundary method for measuring transference numbers. They have also very briefly indicated the utility of these numbers in the various branches of electrochemistry. The most important uses of transference numbers are as follows. The conductances of individual ion constituents as functions of the concentration may be obtained by combining transference numbers with conductance measurements. These results may be used to obtain limiting ion mobilities.[2] Also, accurate values of activity coefficients may be evaluated from transference data and electromotive force measurements on certain cells with liquid junctions.[3] The results of both preceding combinations of transference data with other measurements are of interest in connection with the interionic attraction theory of electrolytes. The variation of transference numbers with the concentration has, however, a direct bearing on that theory, as will be shown after the experimental results have been presented.

Apparatus and Materials

The same moving boundary apparatus was used, in making the measurements which are reported in this paper, as in previous work from this Laboratory and an adequate description has already been published.[1]

The following general precautions were taken in the purification of the salts and the preparation of the solutions. The chemicals were of the best grade obtainable and all recrystallizations of these materials were made with conductivity water and centrifugal draining of the crystals. All solutions were prepared with conductivity water by direct weighing of both solvent and solute, or stock solution, and the weight formal concentrations were then converted to a volume basis. Unless otherwise indicated the density data which are necessary for this conversion were taken from the "I. C. T."[4] Moreover, all molecular weights were taken from the same source.[5] The Richards bottling apparatus[6] was used extensively in the fusion and preparation of salts for direct weighing. Platinum ware was used as containers for salts which were fused or dried at high temperatures and any solutions prepared from such salts were rejected if they were alkaline to phenolphthalein. Individual salts were purified and solutions prepared therefrom as follows.

Potassium bromide was recrystallized twice, fused in air and weighed directly.

Potassium iodide was recrystallized twice and dried in an electric oven at 120°. This product was then finely pulverized in an agate mortar and a concentrated stock solution prepared by drying the powder at 500° for two hours in the Richards bottling apparatus before weighing. This stock solution, although persistently neutral, acquired a slight brownish color on exposure to sunlight. The dilute solutions which were prepared from the stock solution were not discolored, however, and the conductance of a 0.03 *N* solution changed by less than 0.03% on standing six days, during which time it was repeatedly exposed to laboratory air and light.

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[1] MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).

[2] MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

[3] MacInnes and Brown, *ibid.*, in press.

[4] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 51.

[5] *Ibid.*, 1926, Vol. I, p. 106.

[6] Richards and Parker, *Proc. Am. Acad. Arts and Sci.*, **32**, 55 (1896).

Potassium nitrate was recrystallized twice and dried in the oven. It was then fused in the bottling apparatus in a current of dry air, care being taken that the temperature did not greatly exceed the fusion point. The stock solution prepared from the potassium nitrate fused in this manner gave no test for nitrite.

Sodium Acetate.—Carefully purified sodium carbonate was fused in an atmosphere of carbon dioxide and weighed out of contact with moist air by means of the bottling apparatus. This weighed quantity of sodium carbonate was then dissolved in water and treated at 0° with a 0.1% excess of anhydrous acetic acid. Carbon dioxide was then expelled, without loss of salt, by heating, and the total weight of the stock solution of sodium acetate measured. The concentration was computed on the basis of the weight of fused sodium carbonate which had been taken. Four stock solutions were prepared in this manner and 0.1 N dilutions made therefrom had conductances whose average deviation from the mean was 0.04%. The concentration of the stock solution which was used in making most of the dilutions for the transference number measurements was corrected to the mean for all stock solutions, this correction amounting to -0.02%.

The **ammonium chloride** was recrystallized twice and dried in the oven at 110°. A 0.1 N dilution of a stock solution was analyzed by differential electrometric titration[7] with silver nitrate, the latter being standardized against a 0.1 N potassium chloride solution. The average deviation of duplicate determinations was 0.002%.

Solutions of **calcium chloride** were prepared as follows. The slight precipitate which formed when a concentrated solution of calcium nitrate was treated with calcium oxide was removed by filtration and the calcium then precipitated as the carbonate with distilled ammonium carbonate. This precipitate was washed by decantation, dissolved in distilled hydrochloric acid and the calcium chloride recrystallized from this solution. After drying the salt over phosphorus pentoxide in a vacuum it was fused in an atmosphere of dry hydrogen chloride gas in the bottling apparatus and weighed out of contact with moist air.

The **sodium sulfate** was repeatedly recrystallized, fused in air and weighed directly.

A similar degree of care was exercised in the purification of the chemicals which were used as indicators. The concentrations of the indicator solutions need to be known only approximately, however, and consequently only ordinary care was exercised in the preparation of the indicator salts for weighing.

Experimental Procedure and Results

In a description of experimental procedure with the moving boundary method it is necessary to distinguish between two general types of boundaries. *Autogenic* boundaries are formed automatically by the electrochemical solution of an appropriate metal anode. *Sheared* boundaries, so-called because of the shearing mechanism used in their formation, are made by the superposition of the leading and indicator solution. This process involves a special mechanism, first described by MacInnes and Brighton,[8] by means of which one solution is superimposed upon another with a minimum of disturbance to either solution. Sheared boundaries may be either of the falling or rising type but autogenic boundaries are, from the manner of their formation, restricted to the latter type.

In the present research autogenic boundaries with a cadmium metal anode have been used in all possible cases because of the simplicity and reliability of this type of boundary, although the sheared type has been used where necessary and for purposes of obtaining confirmation of the results from the simpler type of boundary. The indicator materials and types of boundaries are recorded in Table I. In the column headed "Concentration range" is given the upper and lower limit of salt concentration for which the designated indicator was employed, although it does not necessarily mean that this is the only concentration interval for which the indicator may be used. The numerals recorded under "Volume correction" refer to the equations listed in Table III and will be explained below.

Although the moving boundary method may be used over a wide range of concentration if the proper indicators are available, results are most readily obtained in the interval 0.01–0.2 N. At concentrations below 0.01 N the boundary is frequently difficult to locate and the precision of the measurements is decreased owing to the magnitude of the solvent correction. On the other hand, at concentrations above 0.2 N the disturbing effect due to heating of the electrolyte by the current and the magnitude and uncertainty of the volume correction introduce errors which are often difficult to overcome. The solvent and volume corrections will be considered in the next section.

Consequently I have attempted to cover the concentration range, 0.01–0.2 N, systematically and have been successful except for 0.01 N sodium acetate. The boundary $Cd(C_2H_3O_2)_2/NaC_2H_3O_2$ is difficult to observe at concentrations below 0.02 N and no other satisfactory indicator for 0.01 N sodium acetate has been found.

The experimental results are recorded in Table II. In this table each section is devoted to the salt indicated and the concentrations are expressed in equivalents per liter of solution at 25°.

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(7) MacInnes and Dole, THIS JOURNAL, **51**, 1119 (1929).

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

TABLE I

INDICATOR MATERIALS AND TYPES OF BOUNDARIES

	Cation boundaries				Anion boundaries			
Salt	Indicator	Type	Concn. range	Vol. corrn.	Indicator	Type	Concn. range	Vol. corrn.
KBr	$CdBr_2$	Autogenic	0.01–0.1	I	KIO_3	Sheared	0.1–0.2	V
KI					$KC_2H_3O_2$	Sheared[a]	.02– .2	VI
					$K_2C_{20}H_6O_5I_4$	Sheared	.01– .02	V
KNO_3	$Ba(NO_3)_2$	Sheared	.1 – .2	II	$K_2C_{20}H_6O_5I_4$	Sheared	.01– .04	V
					KIO_3	Sheared	.04– .2	V
$NaC_2H_3O_2$	$Cd(C_2H_3O_2)_2$	Autogenic	.02– .2	I				
NH_4Cl	$CdCl_2$	Autogenic	.01– .2	I	NH_4IO_3	Sheared	.1	VII
$CaCl_2$	$CdCl_2$	Autogenic	.02– .2	III	$Ca(IO_3)_2$	Sheared	.01– .02	VIII
Na_2SO_4	$CdSO_4$	Autogenic	.01– .2	IV				

[a] Falling boundaries; all others in this table are rising boundaries.

In the row beginning with $T_\pm$ obsd. the uncorrected results of individual experiments at each concentration are given. The results of measurements on cation boundaries are included under the group heading T_+ while those on anion boundaries are headed T_-. The mean values of

TABLE II

TRANSFERENCE NUMBERS FOR KBr, KI, KNO_3, NH_4Cl, $NaC_2H_3O_2$, $CaCl_2$ AND Na_2SO_4 AT 25°

KI	T_-										
Concn.	0.010001	0.010996	0.015107	0.020044	0.021096	0.036164	0.049865	0.05040	0.063342	0.10214	0.20287
$T_\pm$ obsd.	0.5117	0.5108	0.5108	0.5114	0.5111	0.5110	0.5114	0.5112	0.5111	0.5104	0.5097
	.5117	.5108	.5109	.5115	.5110	.5112		.5113	.5111	.5110	.5095
			.5109					.5112		.5109	.5095
								.5114		.5107	
										.5109	
$T_\pm$ mean	.5117	.5108	.5109	.5115	.5111	.5111	.5114	.5113	.5111	.5108	.5096
Soln. corrn.	.0006	.0006	.0004	.0003	.0003	.0002	.0001	.0001	.0001		
Vol. corrn.	.0001	.0001	.0001	.0002	.0002	.0003	.0004	.0004	.0006	.0009	.0017
$T_\pm$ corrd.	.5124	.5115	.5114	.5120	.5116	.5116	.5119	.5118	.5118	.5117	.5113

KNO_3	T_+		T_-							
Concn.	0.10031	0.19871	0.010087	0.010155	0.019747	0.041899	0.068105	0.101105	0.10160	0.19871
$T_\pm$ obsd.	0.5099	0.5117	0.4913	0.4905	0.4909	0.4899	0.4900	0.4889	0.4890	0.4864
	.5099	.5117	.4911	.4908	.4907	.4903	.4896	.4893	.4890	.4864
	.5101	.5117	.4911							.4867
	.5100	.5115								
$T_\pm$ mean	.5100	.5117	.4912	.4907	.4908	.4901	.4898	.4891	.4890	.4865
Soln. corrn.			.0005	.0005	.0003	.0001	.0001			
Vol. corrn.	.0001	.0002	.0001	.0001	.0002	.0003	.0005	.0007	.0007	.0013
$T_\pm$ corrd.	.5101	.5119	.4918	.4913	.4913	.4905	.4904	.4898	.4897	.4878

$NaC_2H_3O_2$	T_+								
Concn.	0.019558	0.026343	0.032676	0.047532	0.070932	0.10000	0.13214	0.17194	0.20599
$T_\pm$ obsd.	0.5550	0.5559	0.5559	0.5575	0.5589	0.5603	0.5613	0.5623	0.5630
	.5550	.5554	.5558	.5576	.5588		.5609		.5629
	.5542	.5557		.5576					
	.5546								
	.5544								
$T_\pm$ mean	.5546	.5557	.5559	.5576	.5589	.5603	.5611	.5623	.5630
Soln. corrn.	.0005	.0004	.0003	.0002	.0001	.0001	.0001		
Vol. corrn.	−.0002	−.0002	−.0003	−.0004	−.0006	−.0009	−.0012	−.0016	−.0020
$T_\pm$ corrd.	.5549	.5559	.5559	.5574	.5584	.5595	.5600	.5607	.5610

NH_4Cl	T_+								T_-
Concn.	0.010003	0.010065	0.020077	0.020097	0.050030	0.10013	0.10096	0.19996	0.10030
$T_\pm$ obsd.	0.4904	0.4902	0.4903	0.4899	0.4898	0.4895	0.4894	0.4888	0.5095
	.4900	.4900	.4903	.4898	.4898	.4895	.4893	.4888	.5091
				.4898	.4897			.4888	
$T_\pm$ mean	.4902	.4901	.4903	.4898	.4898	.4895	.4894	.4888	.5093
Soln. corrn.	.0005	.0005	.0003	.0003	.0001				
Vol. corrn.	.0001	.0001	.0002	.0002	.0006	.0012	.0012	.0023	−.0002
$T_\pm$ corrd.	.4908	.4907	.4908	.4903	.4905	.4907	.4906	.4911	.5091

TABLE II (*Concluded*)

CaCl$_2$	T_+							T_-			
Concn.	0.019041	0.019961	0.020516	0.030013	0.050021	0.10026	0.19563	0.008941	0.009841	0.014821	0.019041
$T_\pm$ obsd.	0.4223	0.4216	0.4213	0.4191	0.4134	0.4062	0.3960	0.5719	0.5726	0.5753	0.5771
		.4216	.4213	.4191	.4137	.4060	.3960	.5720	.5729	.5750	.5773
		.4218			.4141	.4061	.3962	.5722		.5752	
					.4139	.4061	.3960				
					.4140						
$T_\pm$ mean	.4223	.4217	.4213	.4191	.4138	.4061	.3960	.5720	.5728	.5752	.5772
Soln. corrn.	.0003	.0003	.0003	.0002	.0001			.0008	.0008	.0005	.0004
Vol. corrn.				−.0001	−.0001	−.0002	−.0005				
$T_\pm$ corrd.	.4226	.4220	.4216	.4192	.4138	.4059	.3955	.5728	.5736	.5757	.5776

Na$_2$SO$_4$						KBr					
	T_+					T_+				T_-	
Concn.	0.009931	0.019808	0.050347	0.100125	0.19824	0.009986	0.019994	0.050065	0.10153	0.099705	0.20217
$T_\pm$ obsd.	0.3834	0.3830	0.3826	0.3823	0.3816	0.4826	0.4828	0.4827	0.4827	0.5159	0.5147
	.3845	.3833	.3825	.3822	.3823	.4825	.4828	.4828	.4829		.5146
	.3843	.3834			.3820	.4823	.4829	.4828	.4830		.5150
	.3845	.3830			.3820						
	.3842	.3832			.3820						
	.3846										
$T_\pm$ mean	.3842	.3832	.3826	.3823	.3820	.4825	.4828	.4828	.4829	.5159	.5148
Soln. corrn.	.0005	.0003	.0001			.0006	.0003	.0001			
Vol. corrn.	.0001	.0001	.0002	.0005	.0008	.0001	.0001	.0002	.0004	.0006	.0011
$T_\pm$ corrd.	.3848	.3836	.3829	.3828	.3828	.4832	.4832	.4831	.4833	.5165	.5159

the results at a particular concentration are given in the row indicated by $T_\pm$ mean. As has already been mentioned, these results are subject to two minor corrections, the solvent correction and the volume correction. The values of these corrections are given in the rows indicated and the corrected transference numbers are recorded in the last row of each section.

The Solvent and Volume Corrections

The solvent correction[9] is equal to $T_\pm$ ($K_{\text{solvent}}/K_{\text{solution}}$), in which K is a specific conductance.

A value for K_{solvent} of 1.5×10^{-6} has been used in the computation of this correction. This value was obtained by direct measurement after subjecting conductivity water to the same conditions as those under which transference number determinations are made.

The volume correction[10] is equal to $-C\ \Delta V/1000$ in which the term ΔV depends upon the nature of the boundary and the electrode processes in the closed side of the moving boundary cell. In this work the electrode chamber which was immersed in the thermostat was always closed. Cadmium or silver anodes and silver-silver chloride cathodes were used exclusively. The expressions for ΔV which correspond to the various boundaries are indicated by the Roman numerals in Table I and are given in Table III. In this table V and $\overline{V}$ denote a molal and a partial molal volume in ml., respectively, while the subscripts indicate the salt, the symbols R and X referring, respectively, to the cation and anion constituents of the salt whose transference number is being determined.

TABLE III

EQUATIONS FOR THE VOLUME CORRECTION

I $\Delta V_+ = {}^1/_2\overline{V}_{\text{CdX}_2} - {}^1/_2V_{\text{Cd}} - T_+\overline{V}_{\text{RX}}$
II $\Delta V_+ = \overline{V}_{\text{AgNO}_3} - V_{\text{Ag}} - T_+\overline{V}_{\text{KNO}_3}$
III $\Delta V_+ = {}^1/_2\overline{V}_{\text{CdCl}_2} - {}^1/_2V_{\text{Cd}} - {}^1/_2T_+\overline{V}_{\text{CaCl}_2}$
IV $\Delta V_+ = {}^1/_2\overline{V}_{\text{CdSO}_4} - {}^1/_2V_{\text{Cd}} - {}^1/_2T_+\overline{V}_{\text{Na}_2\text{SO}_4}$
V $\Delta V_- = \overline{V}_{\text{KCl}} - V_{\text{AgCl}} + V_{\text{Ag}} - T_-\overline{V}_{\text{KX}}$
VI $\Delta V_- = V_{\text{AgI}} - V_{\text{Ag}} - T_+\overline{V}_{\text{KI}}$
VII $\Delta V_- = V_{\text{Ag}} - V_{\text{AgCl}} + T_+\overline{V}_{\text{NH}_4\text{Cl}}$
VIII Volume correction negligible

The partial molal volumes for each salt, with the exception of those for cadmium sulfate, may be adequately expressed by the relation

$$\overline{V} = \overline{V}^0 + a\sqrt{\text{molality}}$$

the density data in "I. C. T."[4] being used for these computations unless otherwise indicated. The constants $\overline{V}^0$ and a are given in Table IV. This table also includes the values for the molal volumes of the solids which are required in making the volume corrections. From the data of Table IV and the expressions of Table III the necessary volume corrections to the observed transference numbers have been computed and are recorded in Table II.

Discussion of the Results

The corrected cation transference numbers of Table II have been plotted against the square

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[9] Longsworth, THIS JOURNAL, 54, 2741 (1932).

[10] Lewis, *ibid.*, 32, 862 (1910).

TABLE IV

DATA EMPLOYED IN MAKING THE VOLUME CORRECTION

Constants of the equation $\bar{V} = \bar{V}^0 + a\sqrt{\text{molality}}$

Salt	$\bar{V}^0$	a
KCl	26.65	3.21
KBr	33.88	2.64
KI	45.34	2.28
KNO_3	37.98	3.48
$AgNO_3$	28.78	2.46[a]
$NaC_2H_3O_2$	39.72	3.42
NH_4Cl	36.26	1.86
$CdCl_2$	23.24	8.82
$CdBr_2$	33.3	18.9
$Cd(C_2H_3O_2)_2$	71.35	24.25[a]
$CaCl_2$	18.54	8.40[a]
Na_2SO_4	11.39	18.27

For $CdSO_4$ $\bar{V} = 0.80 + 19.23\ (\text{molality})^{1/3}$

Values of the molal volumes

Ag	AgCl	AgI	Cd
10.3	25.8	41.4	13.0

[a] From density data obtained by the author.

root of the concentration in Figs. 1 and 2, the experimental points being represented by circles.

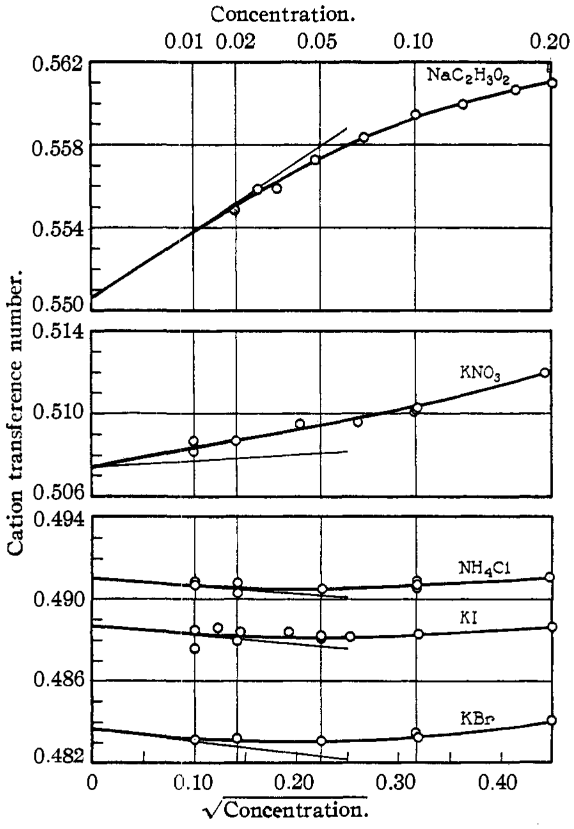

Fig. 1.

The results from anion boundaries have been plotted as $(1-T_-)$ and, for solutions in which both cation and anion boundaries were observed, a mean value of T_+ and $(1-T_-)$ has been plotted. Smooth curves have been drawn through the points for each salt and from these curves values at round concentrations have been interpolated and are recorded in Table VI, which also includes the transference data previously reported from this Laboratory. The average deviation of the experimental points from the smooth curves drawn through them is 0.01%. A few transference data are listed in the "I. C. T."[11] which may be compared with values reported in this paper.

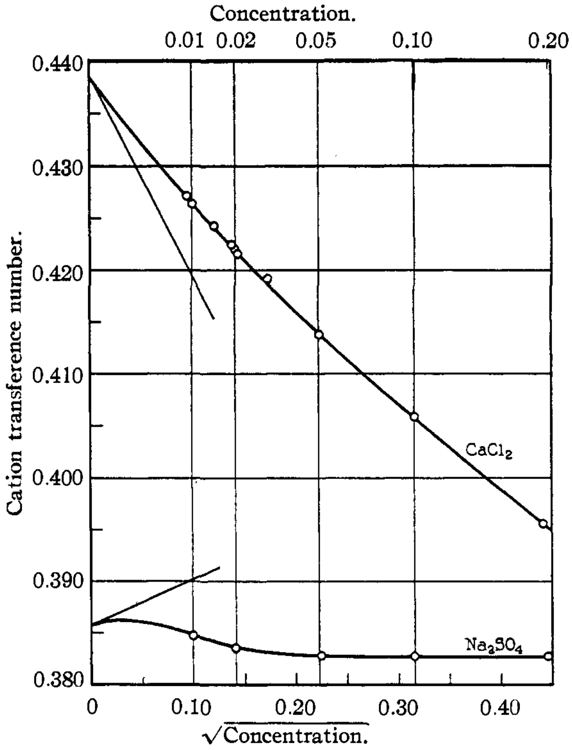

Fig. 2.

The agreement is generally satisfactory when one considers the limit of error for the older values. No extended comparison is possible, however, since previous investigators have not studied the transference numbers of these salts systematically as a function of the concentration at 25°. However, it seems worth while to mention at this point that recent precise measurements by the Hittorf method on potassium chloride[12] and lithium chloride[13] have checked the moving boundary method on these salts within the limits of accuracy of the two methods.

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[11] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 309.

[12] MacInnes and Dole, THIS JOURNAL, **53**, 1357 (1931).

[13] Jones and Bradshaw, *ibid.*, **54**, 138 (1932).

A test of the accuracy of some of the results presented in Table II may be made. From the definition of the transference number it is evident that for a binary electrolyte the sum of the cation and anion transference numbers must be unity. Thus if cation and anion boundaries are independently observed with the same solution, the sum of the transference numbers computed therefrom should be 1.0000. The data of Table II that could be used in making this test are given in Table V. In columns 5 and 6 are given independent values of T_+ and T_-, and in the last column the sum of these numbers. As may be seen, the deviation of this sum from unity is only a few hundredths of a per cent. Tests of this type, together with the excellent reproducibility of individual determinations, indicate that the values compiled in Table VI are subject to errors of not over 3 or 4 units in the fourth decimal. Where this figure is given in dropped numbers the errors may be somewhat larger, owing to uncertainties in the necessary corrections.

TABLE V

TRANSFERENCE NUMBERS FROM CATION AND ANION BOUNDARIES. AN EXPERIMENTAL TEST OF THE RELATION $T_+ + T_- = 1$

1 Salt	2 Concn.	3 Cation indicator	4 Anion indicator	5 T_+	6 T_-	7 $T_+ + T_-$
KNO_3	0.1	$Ba(NO_3)_2$	KIO_3	0.5101	0.4898	0.9999
	.2	$Ba(NO_3)_2$	KIO_3	.5119	.4878	.9997
NH_4Cl	.1	$CdCl_2$	NH_4IO_3	.4907	.5091	.9998
KBr	.1	$CdBr_2$	KIO_3	.4833	.5165	.9998
$CaCl_2$	.02	$CdCl_2$	$Ca(IO_3)_2$	.4226	.5776	1.0002

The transference numbers at zero concentration, to which the curves of Figs. 1 and 2 are extrapolated, were obtained as follows. Values for the limiting conductances of potassium nitrate,[14] sodium acetate[15] and calcium chloride[16] have already been published and these may be combined with the appropriate limiting ion conductance[2] to give the corresponding transference number at zero concentration. Thus, for example, Λ_0 for calcium chloride is 135.84 and the limiting conductance of the chloride ion is 76.32, so that

$$T^0_+ = \left(1 - \frac{76.32}{135.84}\right) = 0.4382$$

From unpublished conductance measurements on the solutions of potassium bromide, potassium iodide and ammonium chloride that were used in the transference number determinations, values of Λ_0 for these salts have been obtained by extrapolation with the function suggested by Shedlovsky.[17] These values are Λ_0 (KBr) = 151.9, Λ_0 (KI) = 150.4 and Λ_0 (NH_4Cl) = 149.9. Since the lowest concentration for which data were available in making this extrapolation was 0.01 *N*, these values are less precise than those mentioned above. The author is indebted to Dr. Shedlovsky of these Laboratories for a preliminary value of 129.8 for the limiting conductance of sodium sulfate. On the basis of the foregoing Λ_0-values the limiting transference numbers are as follows: KBr, 0.4837; KI, 0.4887; KNO_3, 0.5072; NH_4Cl, 0.4909; $NaC_2H_3O_2$, 0.5507; $CaCl_2$, 0.4382; and $NaSO_4$, 0.3859.

The limiting slope required by the interionic attraction theory[18] is given by the expression

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

in which β has the value 21.14 for solutions in water at 25°. The magnitudes of the ion valences are indicated by Z_+ and Z_- while Λ_0 and T^0_+ are the limiting conductance and limiting transference number, respectively. It is evident from this equation that, for salts of symmetrical valence type, the limiting slope is positive if $T_+ > 0.5$ and negative if $T_+ < 0.5$. For salts of unsymmetrical valence type, however, the sign of this slope is not subject to the foregoing restriction.

The limiting slope has been drawn for each salt in Figs. 1 and 2 as a straight light line. From the consistent behavior of KBr, KI, NH_4Cl and $NaC_2H_3O_2$ in Fig. 1 and HCl, KCl, NaCl and LiCl of a previous paper[9] it may be inferred (a) that the curve representing the transference number of a typical, strong uni-univalent electrolyte merges into the limiting slope at low concentrations and (b) if the limiting slope is negative it is approached from *above*, whereas it is approached from *below* if the limiting slope is positive. The very slight minima at about 0.05 *N* in the curves for NH_4Cl, KBr and KI do not contradict the foregoing generalization and are due, possibly, to a viscosity effect since solutions of these salts have relative viscosities less than unity in this concentration range.

It may be observed in Fig. 1, however, that the data for potassium nitrate do not approach the limiting slope except at extreme dilutions. More-

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

(15) MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

(16) Shedlovsky and Brown, *ibid.*, **56**, 1066 (1934).

(17) Shedlovsky, *ibid.*, **54**, 1405 (1932).

(18) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

over, this approach is from above, thus being in the opposite direction to that which might be expected for a typical strong electrolyte. This behavior on the part of potassium nitrate is consistent with other abnormal properties of this salt and with the anomalous characteristics of the nitrates in general.[19]

Turning our attention now to the uni-bivalent salts of Fig. 2 it is at once apparent that neither salt entirely satisfies the simple criteria which were suggested in a preceding paragraph as characteristic of a strong uni-univalent electrolyte. Neither curve can be drawn so as to merge into the limiting slope except at extreme dilutions, although calcium chloride appears to be normal in the manner in which the limiting slope is approached. The deviations exhibited by sodium sulfate are, however, very pronounced. For this salt it is necessary for the transference number–concentration curve to have a maximum at about 0.001 *N* in order to approach the limiting value with the theoretical slope. If the limiting slope is ignored and the extrapolation is made by means of a curve without a maximum it is difficult to include the value at 0.01 *N*. The curve, drawn so as to approach the limiting value correctly, includes this point, and it therefore seems probable that the maximum in this curve would be experimentally realized if data in sufficiently dilute solutions were obtained. Conductance data also indicate that sodium sulfate is more abnormal, that is, "weaker," in its electrochemical properties than, for example, the alkaline earth halides.

It is a pleasure to acknowledge my indebtedness to Dr. Theodore Shedlovsky for valuable criticism during the preparation of this paper and to Dr. D. A. MacInnes for advice and encouragement throughout the entire course of the work.

TABLE VI

CATION TRANSFERENCE NUMBERS AT 25° FOR AQUEOUS SOLUTIONS OF ELECTROLYTES BY THE MOVING BOUNDARY METHOD

Salt	Ref.	Concentration (equivalents per liter) 0.01	0.02	0.05	0.1	0.2
HCl	9	0.8251	0.8266	0.8292	0.8314	0.833$_7$
KCl	9	.4902	.4901	.4899	.4898	.489$_4$
NaCl	9	.3918	.3902	.3876	.3854	.382$_1$
LiCl	9	.3289	.3261	.3211	.3168	.311$_2$
NH_4Cl	[a]	.4907	.4906	.4905	.4907	.491$_1$
KBr	[a]	.4833	.4832	.4831	.4833	.484$_1$
KI	[a]	.4884	.4883	.4882	.4883	.488$_7$
KNO_3	[a]	.5084	.5087	.5093	.5103	.512$_0$
$AgNO_3$	[b]	.4648	.4652	.4664	.4682	....
$NaC_2H_3O_2$	[a]	.5537	.5550	.5573	.5594	.561$_0$
$CaCl_2$	[a]	.4264	.4220	.4140	.4060	.395$_3$
Na_2SO_4	[a]	.3848	.3836	.3829	.3828	.382$_8$

[a] This paper. [b] MacInnes and Cowperthwaite, see Ref. 1.

Summary

Measurements of the transference numbers at 25° of aqueous solutions of KBr, KI, KNO_3, NH_4Cl, $NaC_2H_3O_2$, $CaCl_2$ and Na_2SO_4 by the moving boundary method have been made. The results, interpolated to round concentrations, are given in Table VI. This table also includes values for salts which have been previously reported from this Laboratory and thus constitutes a summary of all of the recent determinations by the moving boundary method.

NEW YORK, N. Y.

RECEIVED APRIL 11, 1935

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[19] Bjerrum, *K. Danske Vidensk. Selsk.*, VII, **9**, p. 2 (1926). See also Scatchard, Prentiss and Jones, THIS JOURNAL, **54**, 2690 (1932).