of the spectrum, but if our values of δ_1 and δ_2 are correct some revision of Mecke's correlation with experiments must be made.

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THE TRANSFERENCE NUMBER OF LITHIUM CHLORIDE AS A FUNCTION OF THE CONCENTRATION

BY GRINNELL JONES AND BENJAMIN C. BRADSHAW

Introduction

According to the classical dissociation theory of Arrhenius the mobilities of the ions are expected to be independent of the concentration and hence transference numbers should be constants which do not vary with the concentration. On the other hand, according to the modern interionic attraction theory of Debye and Hückel, the mobilities of the ions vary with the concentration and this variation is not relatively the same for all ions but depends on the size of the ions and especially on the valence. Therefore it may be predicted from this theory that transference numbers will vary with the concentration. It has been shown by Jones and Dole[1] that the transference numbers of the barium ion in barium chloride can be expressed by an equation having the form, $t = *[A/(1 + B\sqrt{c})] - 1$, (1) over the entire range from 0.001 to 1.0 molal. It was also shown that although erroneous values for the transference number of barium chloride were obtained by Lucasse[2] from data on the electromotive force of concentration cells with and without transference, the fault lay, not in the data themselves, but in their interpretation, and that a more rigid mathematical procedure gave results in essential agreement with the analytical method.

It seemed to be desirable to test the general validity of the equation, $t = [A/(1 + B\sqrt{c})] - 1$, for the variation of the transference number with the concentration. The experimental determination of transference numbers is tedious and difficult and the classical theory gave no incentive for studying the variation of transference numbers with the concentration. These considerations are probably responsible for the fact that sets of data on transference numbers for any salt of sufficient precision for our purpose and covering a wide range of concentration and obtained by the same method are extremely rare in the chemical literature. The most important exception to this general rule is the set of values for lithium chloride from 0.001 to 3.0 normal obtained by the electromotive force

[1] Grinnell Jones and Malcolm Dole, THIS JOURNAL, 51, 1073 (1929); Malcom Dole, J. Phys. Chem., 35, 3647 (1931).

[2] W. W. Lucasse, ibid., 47, 743 (1925).

method by MacInnes and Beattie.[3]   These results are shown by the points inside triangles in Fig. 1.   It should be noted that the curve depicting these data shows a steep slope at low concentrations.

The equation, $t = [A/(1 + B\sqrt{c})] - 1$, may be readily transformed into $\frac{1}{t + 1} = \frac{1}{A} + \frac{B\sqrt{c}}{A}$, (2) and hence if the equation is valid for any values of A and B, a straight line should be obtained when $1/(t + 1)$ is plotted against $\sqrt{c}$.
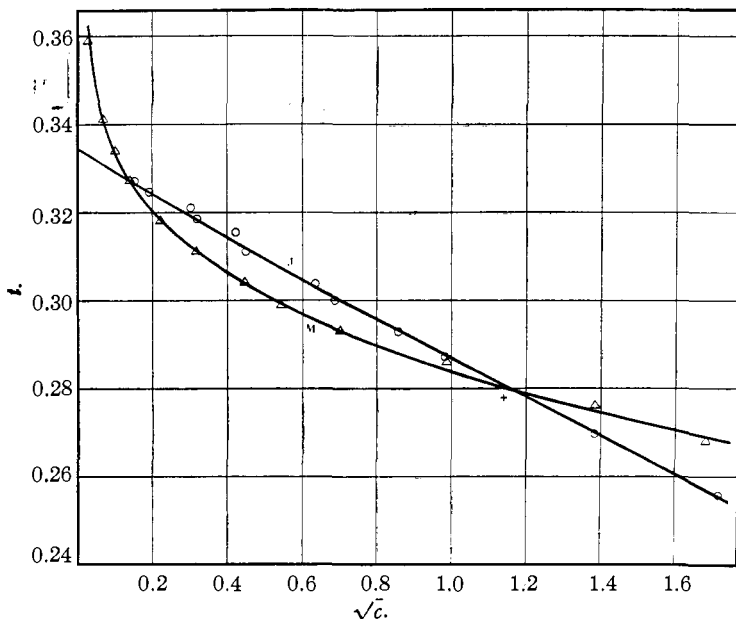

Fig. 1.—Transference number of the lithium ion in lithium chloride, t, plotted against $\sqrt{c}$: △, Curve M, MacInnes and Beattie; ⊙, Curve J, Jones and Bradshaw; +, Washburn.

But the values of MacInnes and Beattie do not yield a straight line when plotted in this way (see Fig. 2, points shown inside triangles).   This demonstrates that it is impossible to find values of A and B which will make this equation agree with the results of MacInnes and Beattie; but this is not necessarily conclusive against the general validity of the equation because the method of computing the transference numbers used by MacInnes and Beattie was the prototype followed by Lucasse, which has been shown to give erroneous results in the case of barium chloride.

Washburn[4] has determined the transference number of the lithium ion in lithium chloride of 1.25 normal to be 0.279, using the analytical method.

[3] D. A. MacInnes and J. A. Beattie, THIS JOURNAL, **42**, 1117 (1920).

[4] E. W. Washburn, *ibid.*, **31**, 322 (1909).

This result is shown by a cross in Figs. 1 and 2.   Determinations have also been made by Kuschel, by Bein, by Jahn and by Pearce and Mortimer,[5] but the results when plotted are quite erratic.[6]

As a first step in testing the general validity of the Jones and Dole equation we decided to redetermine the transference numbers of lithium chloride over a wide range of concentration by the analytical method.   Another object of this investigation was to determine whether or not the electromotive force method when interpreted in the manner developed by Jones and Dole would give the same results as the analytical method.
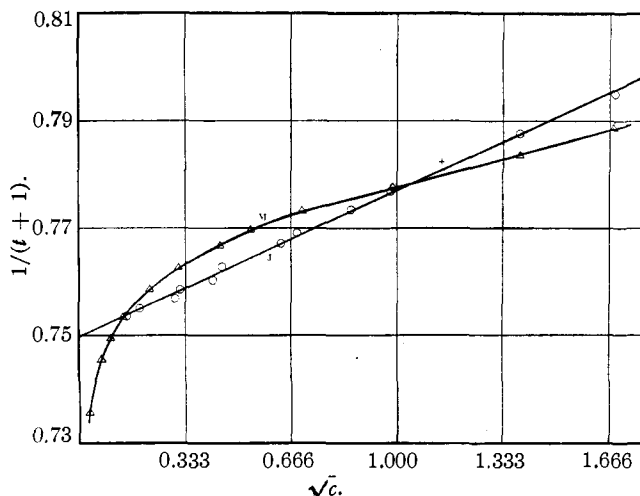

Fig. 2.—Transference number of the lithium ion in lithium chloride, $1/(t + 1)$ plotted against $\sqrt{c}$: △, Curve M, MacInnes and Beattie; ⊙, Straight line J, Jones and Bradshaw; +, Washburn.

At the time that this experimental work was started the moving boundary method had been much improved by MacInnes but its reliability had not been demonstrated completely by direct comparison with the analytical method, although MacInnes and Dole and Longsworth had kindly told us that they were engaged in making such a comparison.   This work has since been completed brilliantly.[7]   After making important improvements in the experimental details of both methods MacInnes and Dole and Longsworth have shown that the moving boundary method and the analytical method give identical results for potassium chloride within the concentration range 0.02 to 0.2 normal.

[5] J. Kuschel, *Wied. Ann. Physik*, **13**, 295 (1881); W. Bein, *Z. physik. Chem.*, **27**, 38 (1898); H. Jahn, *ibid.*, **37**, 691 (1901); J. N. Pearce and F. S. Mortimer, THIS JOURNAL, **40**, 509 (1918).

[6] Ref. 3, p. 1126.

[7] D. A. MacInnes and Malcolm Dole, THIS JOURNAL, **53**, 1357 (1931).

Experimental Part

Lithium nitrate of good quality was dissolved in hot water and freshly distilled ammonium carbonate solution added. The precipitated lithium carbonate was washed repeatedly with hot water until free from nitrate as shown by testing with diphenylamine dissolved in concentrated sulfuric acid. The lithium carbonate was dissolved in redistilled hydrochloric acid and evaporated to dryness, then redissolved in water and evaporated to dryness several times to remove excess of acid. The resulting salt gave a neutral solution and is believed to have contained no impurity in significant amounts except water.

The apparatus and procedure were essentially the same as that described by Washburn[4] with the modifications given by Jones and Dole and hence need not be described in detail. All measurements were carried out at 25 ± 0.02°. Concentrations are expressed in gram molecules per liter.

Table I gives the fundamental experimental data for all successful experiments and the transference numbers computed from these data. It will be noted that the greatest difference between the results at the anode and at the cathode is only 0.0006 and the average difference is less than 0.0002.

In addition to these successful experiments there were about an equal number which failed for one reason or another. In some cases there was evolution of gas at one or both electrodes due to the use of too high a current or to the continuation of the experiment for too long a time so that the effective capacity of the electrodes was exceeded. In some cases when working with the more dilute solutions colloidal silver chloride appeared in the solution around the anode and fell through the solution, causing stirring. Several experiments had to be rejected because the results from the anode and cathode did not agree, which may have been due to some error in the analysis. The most dilute solution for which we succeeded in obtaining a trustworthy result was 0.023 normal. Several attempts were made to obtain results with a 0.01 normal solution but these failed owing to the appearance of colloidal silver chloride at the anode and to the fact that the amount of lithium chloride transferred was so small that sufficient precision could not be obtained in the analysis.

With 2 N and 3 N solutions the amount of lithium chloride which can be transferred is such a small fraction of the amount originally present that its determination with sufficient precision is difficult. Moreover, in these strong solutions silver chloride dissolves with the formation of a complex ion[8] in an appreciable amount and must introduce some error. These strong solutions were always diluted as the first step in the analysis, this causing the precipitation of a small amount of silver chloride, which was filtered out, and then the filtrate was treated with silver nitrate solution and the silver chloride thus formed collected and weighed. By this pro-

[8] G. S. Forbes, This JOURNAL, **33**, 1937 (1911).

Table I

Experimental Data

Concn., moles per liter............	0.023243	0.037011	0.090633	0.101135	0.17840	0.20217	0.40444	0.47301	0.73453	0.96562	1.91578	2.95322
Density...........	.99766	.99801	.99944	.99963	1.00153	1.00213	1.00723	1.00873	1.01498	1.02049	1.04229	1.06464
Amperes..........		.012	.025	.03	0.03	0.05	0.05	0.055	0.1	0.1	0.07	0.2-0.1
Volts.............		70	70	69	55	70	41	35	50	40.5	17	30-13
Hours of electrolysis..		8	6	8	4	7	8	6	7	6	7	7
Ag in coulometers, g.	0.20865	0.30802	0.57585	0.73935	0.51677	1.37588	1.43908	1.27409	2.03070	2.44671	2.00121	4.83599
			0.57588	0.73937	0.51682	1.37587	1.43902	1.27409	2.03081		2.00120	4.83600
Middle portion, mg. LiCl per g. H_2O...	0.98977	1.5762	3.8643	4.3124	7.6176	8.6356	17.337	20.305	31.686	41.838	84.604	133.428
Weight anode portion, g...........	126.775	127.002	123.340	128.615	128.135	124.894	122.740	129.529	124.017	132.90	124.224	121.497
Mg. LiCl per g. H_2O anode.....	0.77707	1.2685	3.3043	3.5941	7.1141	7.2899	15.923	19.126	29.754	39.678	82.7655	128.937
Mg. LiCl transferred from anode......	26.688	39.033	72.19	92.053	64.059	166.85	170.83	149.85	232.68	276.11	210.93	483.32
Corr. for LiCl trans. from anode middle	0.143	0.258	0.46	0.505	0	1.29	0.96	0.44	0.98	0	1.02	6.38
Total LiCl transferred from anode..	26.831	39.291	72.65	92.558	64.059	168.14	171.79	150.29	233.66	276.11	211.95	489.70
Weight cathode portion. g...........	121.456	120.415	121.453	123.074	123.440	123.456	123.950	123.329	122.507	128.542	127.227	128.246
Mg. LiCl per g. H_2O cathode.........	1.20939	1.9031	4.4626	5.0797	8.1409	10.0032	18.739	21.5465	33.652	44.143	86.410	137.743
Mg. LiCl transferred to cathode........	26.642	39.289	72.34	92.429	64.075	167.16	170.58	149.94	233.01	276.16	211.50	486.39
Corr. LiCl trans. to cathode middle....	0.179	0	0.32	0.775	0	0.97	0.92	0.40	0.71	0	0.68	2.68
Total LiCl trans. to cathode mg.......	26.821	39.289	72.66	93.204	64.075	168.13	171.50	150.34	233.72	276.16	212.18	489.07
Transference number anode...........	0.3272	0.3246	0.3210	0.3185	0.3153	0.3109	0.3038	0.30015	0.2928	0.2871	0.2695	0.2577
Transference number cathode.........	.3271	.3246	.3210	.3184	.3155	.3109	.3032	.30025	.2928	.2872	.2698	.2573
Accepted value.....	.3272	.3246	.3210	.3184	.3154	.3109	.3035	.3002	.2928	.2872	.2696	.2575

cedure the dissolved silver chloride did not cause an error in the analysis directly although, of course, the extra filtration increased the danger of accidental errors.   But the conversion of a part of the chloride into a complex ion must have a slight effect on the effective transference number of the chloride ion; and since there is some doubt as to the formula of the complex ion, its mobility is unknown and the amount present was small, no attempt has been made to apply a correction for this source of error. Since the proportion of the complex ion increases with the concentration, together with the fact that the measurements of MacInnes and Beattie do not extend beyond 3 normal, we made no attempt to make any measurements on still more concentrated solutions.

When these results are plotted as transference number, t, against the square root of the concentration, $\sqrt{c}$, a curve is obtained which is nearly but not quite straight, as is shown in Fig. 1, curve J.   When $1/(t + 1)$ is plotted against $\sqrt{c}$, a straight line is obtained as is shown in Fig. 2, curve J.   The equation of the best straight line through these twelve points was found by the method of least squares to be

$$\frac{1}{t + 1} = 0.74979 + 0.02703\sqrt{c} \qquad (3)$$

This may be readily transformed into

$$t = \frac{1.3337}{1 + 0.03605\sqrt{c}} - 1 \qquad (4)$$

Table II contains a comparison between the observed values of the transference number and the values computed for each concentration by this equation.   The average deviation between the observed and computed values is less than 0.0010.   Although these deviations are greater than had been found by Jones and Dole in the case of barium chloride, they are not systematic.   Since we have fitted twelve points to a two parameter

TABLE II

TRANSFERENCE NUMBERS OF LITHIUM ION IN LITHIUM CHLORIDE AT 25°.   COMPARISON OF OBSERVED VALUES AND VALUES COMPUTED BY EQUATION 4

c	$\sqrt{c}$	t obs.	$\dfrac{1}{t + 1}$	t calcd.	t obs. $-t$ calcd.
0.023243	0.15246	0.3272	0.75347	0.3264	+0.0008
.037011	.19238	.3246	.75495	.3245	+ .0001
.090633	.30105	.3210	.75700	.3194	+ .0016
.101135	.31802	.3184	.75849	.3186	− .0002
.17840	.42238	.3154	.76022	.3137	+ .0017
.20217	.44963	.3109	.76283	.3124	− .0015
.40444	.63596	.3035	.76717	.3038	− .0003
.47301	.68776	.3002	.76911	.3014	− .0012
.73453	.85705	.2928	.77351	.2937	− .0009
.96562	.98266	.2872	.77688	.2881	− .0009
1.91578	1.38412	.2696	.78765	.2703	− .0007
2.95322	1.71851	.2575	.79522	.2559	+ .0016

equation and the independent variable is varied over a 127-fold range, it seems probable that the equation is significant and useful for interpolation and for extrapolation to zero concentration. In Table III are given the values for the transference number of the lithium ion in lithium chloride solutions at 25° at round concentrations as computed by this equation, (4). The value for the transference number at infinite dilution extrapolated by this equation is 0.3337.

<div align="center">TABLE III</div>

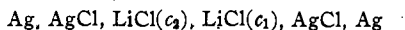<div align="center">TRANSFERENCE NUMBERS OF THE LITHIUM ION IN LITHIUM CHLORIDE SOLUTIONS AT 25° AS COMPUTED FROM EQUATION 4</div>

c	0	0.001	0.002	0.003	0.005	0.01	0.02	0.03
t	0.3337	.3322	.3316	.3311	.3303	.3289	.3269	.3254
c	.05	.1	.2	.3	.5	1.0	2.0	3.0
t	.3230	.3187	.3125	.3079	.3006	0.2873	0.2690	0.2553

Our results for the density of lithium chloride solutions at 25° agree with the equation $d = 0.99707 + 0.02494\,c - 0.000698\,c^2$ (5)

Reinterpretation of the Data of MacInnes and Beattie.—MacInnes and Beattie have measured the electromotive force of concentration cells without transference of the type

<div align="center">Ag, AgCl, LiCl(c_1), LiHg$_x$....LiHg$_x$, LiCl(c_1), AgCl, Ag</div>

and with transference of the type

<div align="center">Ag, AgCl, LiCl(c_2), LiCl(c_1), AgCl, Ag</div>

over a range of concentration from 0.001 to 3.0 molal. The values of the transference numbers computed by these authors from their data are shown in Figs. 1 and 2 by points inside triangles and as will be seen are not in agreement with our results obtained by the analytical method, which are shown by the circles in the same figures.

We have, however, found that when these data are interpreted in a more rigorous manner, the computed transference numbers agree with our data much better.

The rigid differential equation for the electromotive force of a concentration cell with transference with electrodes reversible with respect to the anion is

$$dE = -\frac{2RT}{F}\, t\, d \ln a \qquad (6)$$

where t is the transference number of the cation, a is the geometric mean of the activities of the two ions and the other symbols have their usual significance.[9] In order to integrate this equation we need reliable expressions for the t and a as functions of the concentration.

[9] MacInnes and Beattie give this equation without the negative sign but since the cells under consideration are reversible with respect to the negative ion, increasing the concentration or the activity of the ions in the solution causes the electrode to become more negative and hence dE/da should be negative.

At the time that the paper of MacInnes and Beattie was published (1920), the Debye-Hückel theory had not yet been proposed and no reliable expression for t and a as functions of the concentration was known. MacInnes and Beattie were, therefore, compelled to rely on empirical methods of integration and interpretation instead of analytical methods. The unavoidable errors in plotting plus the guesswork in drawing smooth curves through the experimental points may cause errors much greater than the experimental errors. MacInnes and Beattie reached the conclusion that the transference number of the lithium ion in lithium chloride is given by the expression

$$t = 0.3834 - 0.0259 \log A \quad \text{(where } A = a \times 10^4\text{)} \tag{7}$$

This expression may be readily transformed into

$$t = 0.28224 - 0.0259 \log a \tag{8}$$

As c approaches zero, a also approaches zero and $\log a$ approaches $-\infty$; hence equation (8) requires that t approaches $+\infty$. This expression, therefore, gives an abnormally rapid rise in the transference number as the concentration approaches zero, as is shown in Fig. 1, and must therefore be incorrect. Jones and Dole have pointed out that the empirical method may now be advantageously replaced by a more rigid although more laborious algebraic method based on the equation of Hückel[10] for the variation of the activity coefficient with the concentration and the equation of Jones and Dole for the variation of the transference number with the concentration.

Hückel has derived the following equation for the activity coefficient as a function of the concentration

$$\log f = -\frac{0.354\sqrt{2c}}{1 + N\sqrt{c}} + Pc \tag{9}$$

where N and P are constants for any given salt and temperature and solvent, and he has cited evidence tending to show that unlike most of the equations derived from the interionic attraction theory, this equation is valid even up to 3 normal. The first step is therefore to determine the numerical values of N and P for lithium chloride at 25° from the data of MacInnes and Beattie on the electromotive force of concentration cells without transference. MacInnes and Beattie express their concentrations, m, in terms of moles per 1000 grams of water. We have found it more convenient to make the calculations in terms of moles per liter, c, and therefore have first computed the concentration of each of their solutions on this basis. MacInnes and Beattie do not give the densities of their solutions and we have therefore used our equation $d = 0.99707 + 0.02494\,c - 0.000698\,c^2$ for this purpose. It is convenient for the calculation to use the 3.0 molal solutions as a common reference solution. The

10 E. Hückel, *Physik. Z.*, **26**, 93 (1925).

differential equation for the electromotive force of concentration cells without transference for a monovalent metal is

$$dE = -\frac{2RT}{F} d \ln a = -\frac{2RT}{F} 2.3026 d (\log c + \log f) =$$
$$- \frac{2RT}{F} 2.3026 \, d \left(\log c - \frac{0.500632\sqrt{c}}{1 + N\sqrt{c}} + Pc \right) \quad (10)$$

This equation when integrated between the limits c_2 and c_1 gives

$$E_2 - E_1 = -5.6052 \frac{RT}{F} \left[\left(\log c_2 - \frac{0.500632\sqrt{c_2}}{1 + N\sqrt{c_2}} + Pc_2 \right) \right.$$
$$\left. - \left(\log c_1 - \frac{0.500632\sqrt{c_1}}{1 + N\sqrt{c_1}} + Pc_1 \right) \right] \quad (11)$$

For the details of the mathematical procedure by which N and P may be computed from the data by this equation we refer to the paper of Jones and Dole and give only the result that $N = 0.89055$ and $P = 0.15003$. The figures 5.6052 and 0.500632 are theoretical values not selected to fit the data.

$$\log a = \log c + \log f = \log c - \frac{0.500632\sqrt{c}}{1 + 0.89055\sqrt{c}} + 0.15003 \, c \quad (12)^{11}$$

The results of these calculations are shown in Table IV.

TABLE IV

COMPARISON OF THE ELECTROMOTIVE FORCE OF LiCl CONCENTRATION CELLS WITHOUT TRANSFERENCE AS OBSERVED BY MACINNES AND BEATTIE WITH THE RESULTS COMPUTED BY EQUATION 10

m	c	$\sqrt{c}$	$E_m - E_{3.0}$, volts obs.	$E_m - E_{3.0}$, volts calcd.	E obs. − calcd., volts
3.0	2.8625	1.68121	0	0	0
1.0	0.97931	0.98960	+0.07890	+0.07853	+0.00037
0.3	.29754	.54548	+ .14170	+ .14243	− .00073
.1	.099533	.31549	+ .19540	+ .19505	+ .00035
.03	.029896	.17290	+ .25287	+ .25237	+ .00050
.01	.009969	.099845	+ .30595	+ .30571	+ .00024
.003	.0029911	.054691	+ .36562	+ .36535	+ .00027
.001	.00099705	.031576	+ .41985	+ .42056	− .00071
				$\Sigma \Delta E$ +	.00029

[11] Attention is called to an error in equation 12 of Jones and Dole, THIS JOURNAL, **51**, 1085 (1929). In this equation the square root sign in the numerator should be deleted in two places so that the equation should read

$$\Delta E = -\frac{3 \times 2.3026 \, RT}{2F} \left[\left(\frac{1.734 \, c_2}{1 + N\sqrt{c_2}} - \frac{1.734 \, c_1}{1 + N\sqrt{c_1}} \right) \Delta N + (c_2 - c_1) \Delta P \right]$$

This error is typographical only, as the correct form was used in the calculations whose results are recorded in the earlier paper. The above equation is applicable to a divalent–monovalent salt (BaCl$_2$). For a monovalent salt (LiCl) the factor 3/2 should be replaced by the factor 2 and the factor 1.734 by the factor 0.500632 so that the equation becomes

$$E = -\frac{2 \times 2.3026 \, RT}{F} \left[\left(\frac{0.500632 \, c_2}{(1 + N\sqrt{c_2})^2} - \frac{0.500632 \, c_1}{(1 + N\sqrt{c_1})^2} \right) \Delta N + (c_2 - c_1) \Delta P \right]$$

The deviations are not systematic and in view of the fact that the independent variable (c) is varied over a range of 3000-fold, the agreement between the observed and computed results is good.

Having now found that

$$\ln a = \ln c + \ln f = 2.3026 \,(\log c + \log f) = 2.3026 \left(\log c - \frac{0.500632\sqrt{c}}{1 + N\sqrt{c}} + Pc \right) =$$

$$2.3026 \left(\log c - \frac{0.500632\sqrt{c}}{1 + 0.89055\sqrt{c}} + 0.15003\,c \right) \quad (13)$$

from the data of MacInnes and Beattie on concentration cells without transference and

$$t = \frac{A}{1 + B\sqrt{c}} - 1 = \frac{1.3337}{1 + 0.03605\sqrt{c}} - 1$$

from our own data on transference numbers by the analytical method we may substitute these values in the fundamental differential equation

$$dE = -2\frac{RT}{F}\,t\,d\ln a \quad (6)$$

and integrate the resulting equation between the limits c_2 and c_1. x is substituted for $\sqrt{c}$ as a matter of convenience in integration. The result

$$E_2 - E_1 = 0.118308 \left[-\frac{2APx}{B} + Px^2 - (2A - 2)\log x + \right.$$

$$\left(\frac{2A}{2.3026} + \frac{0.500632AB}{(N-B)^2} + \frac{2AP}{B^2} \right) 2.3026 \log(1 + Bx) -$$

$$\left(\frac{0.500632A}{N-B} - \frac{0.500632}{N} \right) \frac{1}{1 + Nx} - \frac{0.500632AB \times 2.3026 \log(1 + Nx)}{(N-B)^2} \Big]_{x_1}^{x_2} \quad (14)$$

Then substituting the above indicated values for the constants this reduces to

$$E_2 - E_1 = \left[-1.313344x + 0.0177498x^2 - 0.078961 \log x \right.$$

$$+ 84.210421 \log(1 + 0.03605x) - \frac{0.0259366}{1 + 0.89055x}$$

$$\left. - 0.0089803 \log(1 + 0.89055x) \right]_{x_1}^{x_2} \quad (15)$$

$E_2 - E_1$ was then computed for each solution referred to the 3.0 molal solution as a standard of reference and the results are shown in Table V.

TABLE V

LITHIUM CHLORIDE CONCENTRATION CELLS WITH TRANSFERENCE AT 25°. COMPARISON OF MACINNES AND BEATTIE'S OBSERVED VALUES WITH VALUES COMPUTED BY EQUATIONS

m	c_2	$\sqrt{c_2}$	$E_2 - E_1$ volts $c_1 = 3.0$	$A = 1.3337$ $B = 0.03605$ $E_2 - E_1$ computed, volts	ΔE obs. − comp., volts	$A = 1.3394$ $B = 0.04565$ $E_2 - E_1$ computed, volts	ΔE obs. − comp. volts
3.0	2.8265	1.68121	0	0	0	0	0
1.0	0.97931	0.98960	+0.020561	+0.021401	−0.00084	+0.020637	−0.0000076
0.3	.29754	.54548	+ .039575	+ .040490	− .0009155	+ .039483	+ .0000092
.1	.099533	.31549	+ .055989	+ .056973	− .000984	+ .056015	− .0000026
.03	.029896	.17290	+ .074786	+ .075469	− .000683	+ .074650	+ .0001366
.01	.009969	.099845	+ .091878	+ .092915	− .001037	+ .092320	− .0004442
.003	.0029911	.054691	+ .112391	+ .112630	− .000239	+ .112288	+ .000103
.001	.00099705	.031576	+ .130934	+ .130919	+ .000015	+ .130885	+ .000049
				$\Sigma\Delta E = -0.004633$		$\Sigma\Delta E = - .000164$	

The significance of these data is best made clear by a consideration of Fig. 3, in which $E_2 - E_1$ is plotted against log c_2. This method of plotting was chosen because it gives a curve which is more nearly straight than any other method we have found but careful inspection shows that the curve is not straight but has a point of inflection near the middle with opposite curvature at the two ends.   In Fig. 3 the observed values of MacInnes and
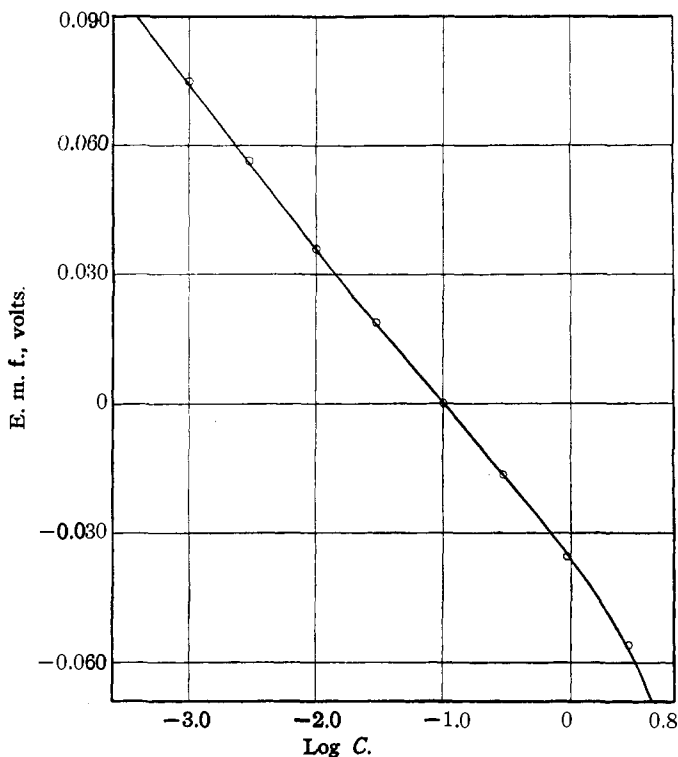

Fig. 3.—Electromotive force of lithium chloride concentration cells with transference, plotted against log C_2.   Points inside circles represent experimental data of MacInnes and Beattie.   The curve is the plot of equation (15).

Beattie are shown as points within the circles whereas the curve is the plot of the equation (15) and hence represents the value of the electromotive force of lithium chloride concentration cells with transference predicted from independent data, namely, our values of the transference numbers obtained by the analytical method and MacInnes and Beattie's determinations of the activities of the ions in lithium chloride by measurements of the electromotive force of concentration cells without transference. As will be seen from Fig. 3 the experimental values of the electromotive force of concentration cells with transference fit the computed curve closely

and follow the complicated curvature throughout the range.   This shows
that there is no real discrepancy between our results for the transference
number of lithium chloride obtained by the analytical method and the
data of MacInnes and Beattie.   The apparent discrepancy depicted in
Figs. 1 and 2 is therefore due to faulty computation of transference num-
bers by MacInnes and Beattie from their data.   This case is in every
respect analogous to the case of barium chloride discussed in an earlier
paper by Jones and Dole and therefore furnishes additional evidence
as to the general validity of the equation

$$t = \frac{A}{1 + B \sqrt{c}} - 1$$

But although the deviations between the observed and the computed
values are so small as to be scarcely visible on a 50-cm. plot, the computa-
tions recorded in Table V show that there are deviations which are ap-
parently systematic and somewhat larger than the probable experimental
errors.   We may, therefore, reverse the calculations and compute trans-
ference numbers from the data of MacInnes and Beattie using the as-
sumption that the equation expressing the variation of the transference
number with the concentration will have the form of the Jones and Dole
equation and determine the values for the constants in this equation from
the electromotive force data alone.   The mathematical procedure for
doing this has been explained in detail in the paper of Jones and Dole and
will not be repeated here.   The computations required are extremely
laborious.   However the fundamental differential equation for the electro-
motive force of concentration cells with transference is integrated and
applied without introducing any mathematical assumptions or premises
other than the Hückel activity function and the Jones and Dole transference
function.   The result of these calculations is $A = 1.3394$ and $B = 0.04565$.

The values for the electromotive force of concentration cells with trans-
ference were computed with these values of A and B and the results are
shown in the last two columns of Table V.   As will be seen, the deviations
between the observed and computed values are small.   The sum of all the
deviations is -0.00016 volt and the average deviation disregarding the
sign is 0.00013 volt.

We may conclude, therefore, that the data of MacInnes and Beattie
may be interpreted as showing the transference number of lithium chloride
to be $t = [1.3394/(1 + 0.04565 \sqrt{c})] - 1$.

This equation leads to a value for the transference number at infinite
dilution of 0.3394 instead of 0.3337 obtained by extrapolation from the
analytical data.   As the concentration is increased, the difference between
the results of the two methods decreases up to 0.2 normal, where the
results differ by only 0.001, and then the sign of the difference is reversed
at higher concentrations and becomes -0.0064 at 1 normal and -0.014 at 3

normal. These differences are believed to be due to experimental errors in one or both sets of experimental data. We conclude that the data of MacInnes and Beattie when interpreted with the aid of Hückel's equation for the activity coefficient support the Jones and Dole equation for the variation of transference numbers with the concentration.

Summary

1. The transference numbers of the lithium ion in lithium chloride solutions have been measured by the analytical method at 25° at many different concentrations between 0.023 and 2.95 normal and found to vary from 0.3272 to 0.2575 over this range.

2. The results can be expressed by the equation

$$t = [1.3337/(1 + 0.03605 \sqrt{c})] - 1$$

3. The limiting value of the transference number of the lithium ion in lithium chloride at 25° is 0.3337.

4. It is computed from the data of MacInnes and Beattie on the electromotive force of concentration cells without transference that the mean activity coefficient of the ions in lithium chloride at 25° varies with the concentration in accordance with the equation

$$\log_{10} f = [-0.500632 \sqrt{c}/(1 + 0.89055 \sqrt{c})] + 0.15003 c$$

This function has the form derived by Hückel.

5. The data of MacInnes and Beattie on the electromotive force of lithium chloride concentration cells with transference when interpreted by the method of Jones and Dole lead to the conclusion that the transference number is $t = [1.3394/(1 + 0.04565 \sqrt{c})] - 1$.

6. The equation for the transference number of the cation as a function of the concentration $t = [A/(1 + B\sqrt{c})] - 1$, which Jones and Dole have shown to be valid for barium chloride is proved in this paper to be valid for lithium chloride also.

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