[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 125.]

THE FREE ENERGY OF DILUTION AND THE TRANSFERENCE NUMBERS OF LITHIUM CHLORIDE SOLUTIONS.

BY DUNCAN A. MACINNES AND JAMES A. BEATTIE.

Received March 12, 1920.

1. Purpose and Outline of Investigation.

The following investigation, which includes measurements of the electromotive forces of cells containing solutions of lithium chloride follows, in general outline, the research by MacInnes and Parker[1] on solutions of potassium chloride. Both investigations involve measurements on cells with and without liquid junctions, from which it will be recalled that the activities of the ions and the transference numbers of the salt may be computed.

Lithium chloride was chosen for this research since lithium is the lightest of the alkali metals, and its salts probably indicate one extreme of behavior in their physical properties. Further, the transference numbers of lithium chloride change rapidly with the concentration, a phenomenon which, it seemed to us, needed further investigation, since it has an important bearing on the theory of strong electrolytes.

As the properties of lithium chloride and of metallic lithium differ greatly from those of potassium chloride and metallic potassium, quite different procedures from those adopted by MacInnes and Parker were necessary in certain parts of the work. Improvements in manipulation have also been developed during the course of both investigations. For these reasons the procedure finally adopted will be described below in some detail. Pearce and Mortimer[2] have carried out a research on lithium chloride solutions similar to the one to be described. Their results, however, lead to very different conclusions from those arrived at in this investigation. Further reference will be made to their work in a later section.

Our investigation included measurements, at 25°, of cells, without liquid junction of the form

$$\mathrm{Ag, AgCl + LiCl}\ (C_1),\ \mathrm{Li(Hg)}_x\text{-}\mathrm{Li(Hg)}_x,\ \mathrm{LiCl}\ (C_2) + \mathrm{AgCl, Ag} \qquad \text{(A)}$$

and cells with liquid junction

$$\mathrm{Ag, AgCl + LiCl}\ (C_1),\ \mathrm{LiCl}\ (C_2) + \mathrm{AgCl, Ag} \qquad \text{(B)}$$

in which the concentrations, C_1 and C_2, varied between 3.0 and 0.001 molal.

The work has been carried out with the aid of a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington, for which we wish to express our gratitude.

---

[1] THIS JOURNAL, 37, 1445 (1915).

[2] *Ibid.*, 40, 509 (1918).

In the earlier paper[1] it was shown that the electromotive force of a concentration cell without liquid junction, E, can be expressed by the relation:

$$E = \frac{RT}{F} ln \frac{a_1{}^+ a_1{}^-}{a_2{}^+ a_2{}^-} \qquad (1)$$

in which $a^+ a^- a_2{}^+ a_2{}^-$ are the "activities"[2] of the positive and negative ions, respectively, at 2 salt concentrations. It was further shown that if the transference number, n, is a constant within the concentration range involved, the electromotive force of a cell with liquid junction, E_t, can be expressed by the equation:

$$E_t = \frac{nRT}{F} ln \frac{a_1{}^+ a_1{}^+}{a_2{}^+ a_2{}^-} \qquad (2)$$

n, being the transference number of the ion to which the electrodes of the cell are not reversible.

If, however, the transference number changes with the concentration, as is the case with nearly all electrolytes, E_t will be an integral, between limits, of the equation

$$dE_t = \frac{RT}{F} n\ d\ ln\ (a^+a^-). \qquad (3)$$

Since n, a^+ and a^- are functions of the concentration of the electrolyte, Equation 3 is a complete differential. This expression will be referred to again in a later section.

2. The Concentration Cells without Liquid Junctions.

The concentration cells without liquid junctions involve (*a*) silver-silver chloride electrodes, (*b*) lithium amalgam electrodes, (*c*) air-free lithium chloride solutions.

(a) **Silver-silver Chloride Electrodes.**—The supports for the silver-silver chloride electrodes consisted, as in the work of MacInnes and Parker, of pieces of fine platinum gauze (about $1^1/_2$ cm. sq.) welded to platinum wire which, in turn, made contact with mercury through glass tubes. The gauze was given a thick coating of silver from a solution of potassium silver cyanide, using 3 milliamperes, per electrode, for 24 hours. After thorough washing, a coating of chloride was formed on the silver by electrolyzing in a lithium chloride solution with a current of 5 to 7 milliamperes per electrode for 20 minutes. A variation from the former procedure was the formation of this chloride in lithium chloride solutions of the same concentration as those in which the electrodes were to be used. This avoided possible inclusions in the chloride of small amounts of electrolyte of unknown concentration, and resulted in much more

---

[1] MacInnes and Parker, *loc. cit.*

[2] Lewis, *Proc. Am. Acad.*, 43, 259 (1907). A discussion of the concept of "activity" is also given in a recent paper by Noyes and MacInnes, THIS JOURNAL, 42, 239 (1920).

constant and reproducible electrodes. We feel that our success with these electrodes is, to a large extent, due to this method of preparation. The electrodes for 0.001 and 0.003 *N* solutions were, however, formed in 0.01 *N* lithium chloride, since, at these low concentrations, it was difficult to get enough current through the solutions and the electrolysis produced silver chloride in a non-adherent form.[1] A small rubber stopper on each glass stem, as is shown in Fig. 3, aided greatly in the handling of these electrodes, as they frequently became damaged while being pushed through the holes in the large rubber stoppers used in the earlier work. The electrodes used were usually within 0.03 mv. of the same potential. In the more dilute solutions, however, the differences occasionally reaches 0.05 mv. When two electrodes, formed in different solutions, were put into the same solution they rapidly assumed the same potential within 0.1 or 0.2 mv., indicating that the same modification of silver chloride was present on all the electrodes.

(b) **Lithium Amalgam Electrodes.**—The lithium amalgam electrodes (H in Fig. 2) differ from those used by MacInnes and Parker in having the amalgam flow in a thin stream from fine capillaries instead of overflowing as large drops from a cup-shaped tip. In this investigation, constant potentials were not obtained with the latter design. The lithium amalgam apparently reacts more rapidly with water than potassium amalgam does under the same conditions, as is, possibly, to be expected from the higher potential of the former metal.

In the preparation of lithium amalgam, a number of attempts were made to remove the surface layer of oxide from the lithium by running the molten metal through glass capillary tubing. The glass walls of the tubing were, however, rapidly disintegrated by the metal. The amalgam was, therefore, made in the vessel A as represented in Fig. 1. Pellets of metallic lithium were inserted through tube B, which was then connected to a mercury still. After distilling the desired amount of mercury, the tube was sealed off. Since a coating of oxide covered the lithium, solution did not take place until the mercury was heated. After complete amalgamation the apparatus was inverted as shown and allowed to stand for a week to permit the lithium oxide to separate and rise to the top. The amalgam could then be drawn out through the capillary tube and stopcock C and D. The amalgam was then transferred to another flask, of similar construction, which further separated the oxide. The amalgam electrode vessel was filled by connecting the 2 vessels by means of a T-tube, one arm of which was joined to a vacuum pump.

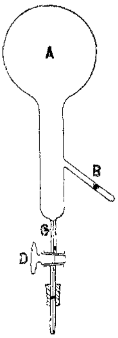

Fig. 1.

---

[1] An interesting explanation of the phenomenon is given by Reedy, *Am. J. Sci.*, 40, 281 (1915).

(c) **Air-free Lithium Chloride Solutions.**—The work on potassium chloride solutions showed definitely that air must be *completely* excluded from the solutions that come in contact with the amalgam electrodes since oxygen reacts instantly with the amalgam, reducing its alkali metal content and increasing the ion concentration of the surrounding electrolyte, both of which have the same result, *i. e.*, to reduce the potential at the electrode. Since solid lithium chloride is very hygroscopic, the solutions could not be made up by adding weighed amounts of the salt to water, in an inert atmosphere, as in the work with potassium chloride. The procedure with lithium chloride adopted was to make up a strong solution of the salt and determine its concentration, by weight, by precipitating the chloride with silver nitrate. A round-bottomed flask (F of Fig. 2) was weighed with its stopper and connecting tubes, a quantity of the strong solution added, and the flask weighed again. The solution was then vigorously boiled for some time under reduced pressure to remove the dissolved air. In the meantime, water was collected hot with a rapid evolution of steam in a resistance glass container, from the still for conductivity water, and boiled in a partial vacuum. The free space in the container was then filled with nitrogen. Using a pressure of this gas the air-free water was run through glass tubing into the round-bottomed flask F, until nearly the right dilution was attained, special provision being made to keep air out of all connections. The flask F, was again weighed, and water added in successive small amounts, out of contact of air, until the required concentration (within 0.3%) was obtained. Our belief that air was completely excluded from the solutions is borne out by the reproducibility of the measurements of the cells without liquid junctions.

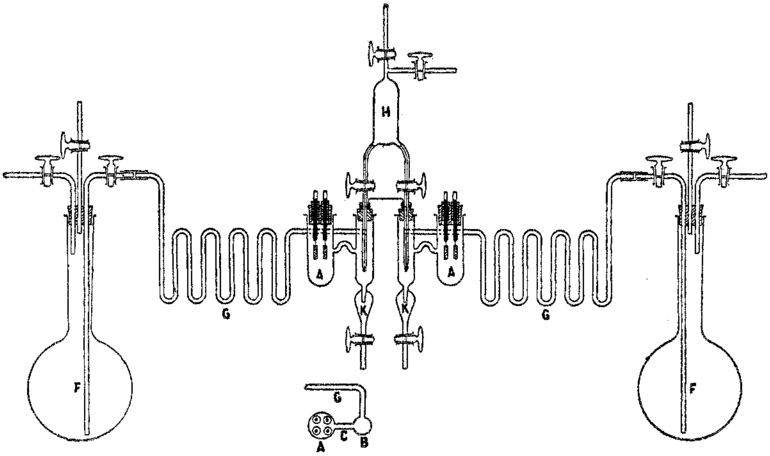

Fig. 2.

The complete cell without liquid junction is shown in Fig. 2, which is nearly self explanatory. The grids of glass tubing G, served to bring the flowing solutions to the exact temperature of the thermostat, and gave a useful flexibility in making connections with the flasks F. The rejected solutions and amalgam flowed through the air spaces K into tubes leading through the bottom of the thermostat. The silver-silver chloride electrodes were placed in the vessels A separated by a bent tube from the flowing solution.

3. **The Concentration Cells with Liquid Junction.**—Our greatest improvement in manipulation, since the work with KCl solutions, was, possibly, made in the concentration cells with liquid junctions. A complete cell is shown in section of Fig. 3. In filling the cell the more concentrated solution was placed in Vessel A, the Ag-AgCl electrodes were placed in the side tubes, and additional solution was run into Tube E until D was completely filled, when the *pinchcock* F was closed. The vessel B was then filled, with the dilute solution, to the end of the tube D′. The D and D′ were then placed, as shown, into the *empty* cup C. The whole apparatus was next immersed in a thermostat and the electrodes were allowed to come to equilibrium, when a solution of a strength intermediate between those in the vessels A and B was cautiously run into cup C. Readings of the electromotive force of the cell were then made. The potentials of liquid junctions formed in the manner described were surprisingly constant, often showing no perceptible change in several hours and seldom decreasing more than 0.1 mv. in 24 hours. The potential is independent of the concentration of the intermediate solution provided it is within the concentration limits of the solutions in A and B; this was shown in an extended investigation on potassium chloride concentration cells by F. F. Footitt and one of the present authors. Reversal of the positions of the solutions in the cell (*i. e.*, the dilute solution in vessel A) leads to low and erratic results.

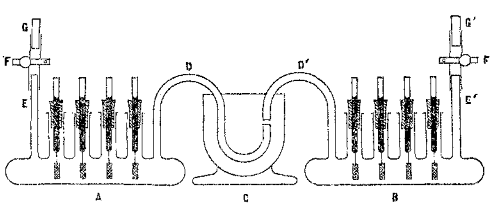

Fig. 3.

The one condition necessary for the formation of a reproducible liquid junction between 2 differently concentrated solutions of the same electrolyte is the maintenance of the concentration gradient at all points between the stronger and dilute solutions at values which are either negative or zero; that is, the concentration must either be constant or steadily decrease. If this condition is fulfilled, the potential is independent of the distance through which the mixing of the 2 solutions takes place. In addition it is, of course, necessary that the solutions around the electrodes remain constant in composition, a condition which is difficult to attain unless mixing of the solutions due to volume changes of gas in the vessels, differences of specific gravity of the solutions, etc., is carefully guarded against. Reproducible junctions involving 2 different electrolytes cannot, however, be made in the manner just described.

All the measurements were made in a thermostat kept at $25° \pm 0.02°$. The potentials were determined with a Leeds and Northrup potentiometer which was carefully calibrated during the investigation. The standard cell was compared, several times during the investigation, with 2 cells which had been recently calibrated by the Bureau of Standards. The thermometer used was compared with a thermometer calibrated by the same bureau.

4. Materials and Methods of Purification.

Lithium Chloride.—Pure lithium carbonate was treated with pure hydrochloric acid and the resulting chloride was crystallized 5 times from conductivity water. An attempt was made to crystallize the salt from pyridine, but it was found difficult to remove the last traces of the solvent without charring and making the salt alkaline.

Lithium.—The pure metallic lithium used in making the amalgams was very kindly supplied by Dr. A. W. Hull, of the General Electric Co.

Mercury.—The mercury was covered with dil. nitric acid and agitated by a current of air for a week. It was then passed in a thin stream through a tube, about 2 meters long, filled with dil. nitric acid, after which it was distilled several times under reduced pressure.

Water.—Conductivity water was prepared in the special still in this laboratory.

5. The Results of the Electromotive Force Measurements.

The potentials of the cells without liquid junction, of the form: Ag + AgCl, LiCl (c_1), Li(Hg)$_x$, LiCl (c_2), Ag + AgCl, are given in Table I. Each figure for the electromotive force of a cell refers to a complete assembling of the cell, involving *freshly prepared solutions*, and, in each duplicate determination, a different concentration of amalgam.

The potentials of the cells with liquid junction are given in Table II. For each determination recorded the electrodes were reformed, *i. e.*, plated with silver and coated with silver chloride. As shown in Fig. 2, there were 4 electrodes in each solution. The potential given is the average of readings of every possible combination of one electrode in each half cell, or 16 readings in all. The third column of the table gives the average deviation of these readings. Since these results demonstrated the reproducibility of the electrodes, only one electrode in each solution was used in the cells without liquid junction.

TABLE I.

Electromotive Forces of Cells without Liquid Junction.

Conc. LiCl Solns. Mols per 1000 g. water.		Conc. of Lithium Amalgam (Approx.). %.	E. m. f. Millivolts.
C_1.	C_2.		
3.0	0.3	0.001	141.71
		0.005	141.69
1.0	0.1	0.015	116.52
		0.005	116.48
0.3	0.1	0.001	53.73
		0.005	53.67
0.3	0.03	0.005	111.18
		0.002	111.16
0.1	0.01	0.01	110.57
		0.002	110.55
		0.005	110.53
0.03	0.003	0.005	112.80
		0.015	112.70
0.01	0.001	0.001	114.0
		0.001	113.8

TABLE II.

Electromotive Forces of Cells with Liquid Junctions.

Conc. LiCl Solns. Mols per 1000 g. Water.		E. m. f. of cells. Millivolts.	Average deviation.
C_1.	C_2.		
3.0	0.3	39.574	±0.007
		39.577	0.012
1.0	0.1	35.435	0.025
		35.421	0.019
0.3	0.1	16.401	0.021
		16.420	0.016
		16.420[a]	
0.3	0.03	35.210	0.020
		35.211	0.014
0.1	0.01	35.885	0.015
		35.893	0.021
0.03	0.003	37.595	0.019
		37.615	0.021
0.01	0.001	39.074	0.012
		39.039	0.021

[a] Determined with a "flowing" junction by Mr. Y. L. Yeh of this laboratory.

6. Discussion of Results.

(a) Activities and Activity Coefficients.—Equation 1 can be put in the form

$$E = \frac{2RT}{F} ln \frac{a_1}{a_2}$$

in which a_1 and a_2 are the (geometrical) mean values of the activities of the two ions at the concentrations C_1 and C_2. From this equation the activity ratios for any pair of concentration ratios can be obtained. To obtain the activities at the various concentrations at which measurements were made, the activity was assumed to be equal to the concentration multiplied by the conductivity ratio Λ/Λ_0 at the lowest concentration (0.001 N). A plot of the potentials of the cell without liquid junction showed, however, that the value assigned in Table I to the cell containing 0.01 and 0.001 N solutions is about 0.5 millivolt too low, a result which would occur from a trace of oxygen in solution, or a very slight reaction of the amalgam with water. To either of these the potentials at the amalgam electrode in the 0.001 N solution would be very sensitive. From the plot just mentioned a potential of 114.43 mv. was interpolated for the 0.01–0.001 N cell. By the obvious methods of computation the activity values in Col. 2 of Table III were obtained. The activity coefficients in Col. 3 are, of course, the activities divided by the corresponding concentrations. The table also includes in Col. 4 the "degrees of dissociation," Λ/Λ_0 computed from the conductance data of Kohlrausch and Maltby.[1] As pointed out in a recent paper,[2] no relation between activity coefficients and "degrees of dissociation" has so far been discovered, the former, in the cases of lithium chloride, hydrochloric acid and potassium hydroxide solutions, being at low concentrations smaller, and at high concentrations larger, than the latter. Multiplication of the "degrees of dissociation" by the viscosity ratio (*i. e.*, the viscosity of the solution divided by the viscosity of water) increases the difference between the activity coefficient and the "degree of dissociation" up to about 0.5 N. Above this point the viscosity correction is in a direction that decreases the discrepancy between the 2 series of numbers, but is entirely inadequate.

TABLE III.

Concentrations of LiCl.	Activity.	Activity coefficient.	Conductance ratio = "degree of dissociation."
0.001	0.000976	(0.976)	(0.976)
0.003	0.00283	0.945	0.962
0.01	0.00905	0.905	0.932
0.03	0.0254	0.848	0.899
0.1	0.0779	0.779	0.834
0.3	0.221	0.738	0.759
1.0	0.752	0.752	0.641
3.0	3.491	1.164	0.458

[1] "Leitvermögen der Electrolyte."

[2] Noyes and MacInnes, THIS JOURNAL, **42**, 239 (1920).

(b) **The Transference Numbers.**—If the potential of a cell with liquid junction is divided by that of a cell without liquid junction, both cells containing the same pair of solutions, of concentrations C_1 and C_2, the transference number (of the ion to which the electrodes of the cell with liquid junction is not reversible) is obtained, provided that the number is a constant within the given concentration limits. This is evident from Equations 1 and 2. If, however, the transference number is a variable, the division indicated above gives a figure whose value lies between the transference numbers at C_1 and C_2. A method by which the transference numbers may be obtained, at any concentration within the concentration limits studied, is outlined below.

According to Equation 3 the electromotive force of a cell with liquid junction is an integral of

$$\mathrm{d}E_t = 2N\frac{RT}{F}\,\mathrm{d}\,ln\,a \qquad (3a)$$

in which a is the geometrical mean of the activities of the ions. The corresponding equation for the cell without liquid junction is:

$$\mathrm{d}E = 2\frac{RT}{F}\,\mathrm{d}\,ln\,a$$

Now, if the electromotive forces of cells of the latter type are plotted as ordinates and the logarithms of the corresponding mean activities as abscissas, a straight line, with a slope equal to $2RT/F$ is necessarily obtained (line A in Fig. 4). The corresponding line for the cells with liquid junction is the curve B. In plotting this curve, the electromotive force for a cell containing lithium chloride at concentrations 0.01 and 0.1 is added to the potential for concentrations 0.001 and 0.01 N, etc. The ordinates for 0.03 and 0.003 N are obtained by subtracting the appropriate potentials from Table II from the ordinate for 0.3 N. It is interesting to note that the result is a smooth curve, even on a large scale plot. The slope of this curve, as can be

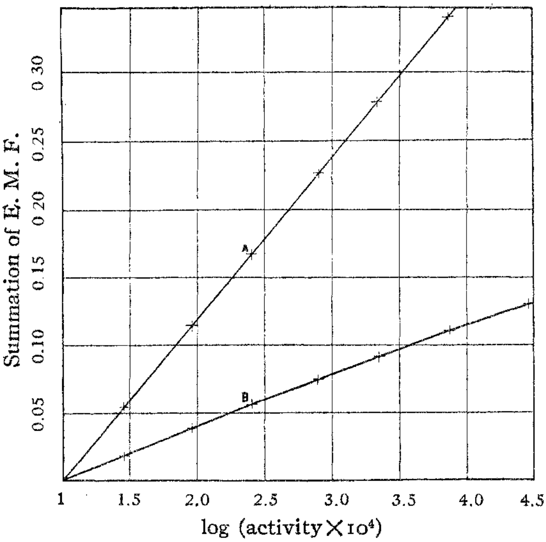

Fig. 4.

seen from Equation 3, is nRT/F, and the transference number at any activity, and thus at any concentration, is the ratio of the slopes of the lines A and B at the corresponding points. To obtain the slope of line B the following empirical equation,

$$E_t = -43.865 + 45.363\,(\log A) - 1.4902\,(\log A)^2, \qquad (5)$$

in which E is the summed up electromotive force and A the activity ($\times\ 10^4$), was computed by means of the method of least squares. This expression was then differentiated with respect to log A and its constants divided through by the (constant) slope of line A [0.011830], with the following result:

$$n = 0.3834 - 0.02529 \log A \qquad (6)$$

In Fig. 5 transference numbers computed from Equation 6 are plotted as ordinates and logarithms of the corresponding concentrations as abscissas. Jahn and Goldhaber's[1] values at 18°, Washburn's[2] determination at 25°, and two measurements by Bein[3] at 22.5° and 25°, are also included. The trend of the previous determinations with the concentrations is definitely that of the figures obtained from our measurements. Since our curve passes through Jahn's values, and Bein's and Washburn's values are on opposite sides of the curve, it seems probable that there is little or no change of the transference numbers between 18° and 25°. The fact that this treatment of the results yields transference numbers *at definite concentrations* removes one objection to the method which is, in our opinion, the most accurate method of obtaining these important constants in the cases where its application is possi-

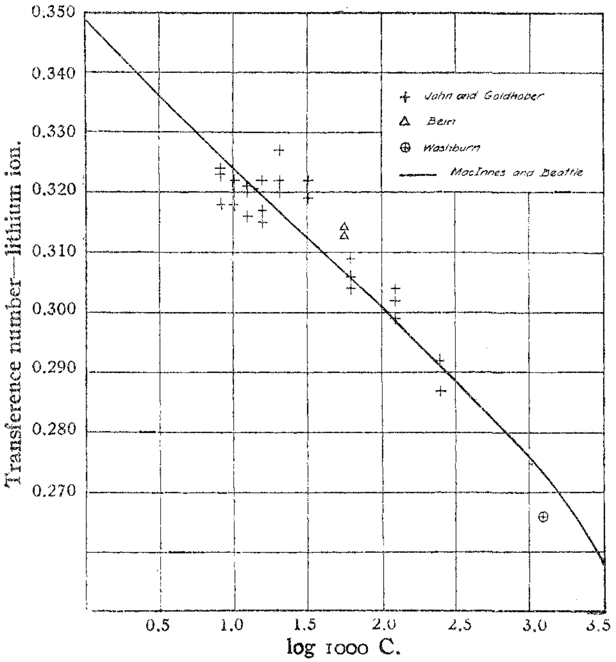

Fig. 5.

---

[1] *Z. physik. Chem.*, **37**, 673 (1901).

[2] *Technology Quarterly*, **21**, 288 (1908); the solution contained 0.1 mol raffinose.

[3] *Z. physik. Chem.*, **27**, 1 (1898).

ble. Transference numbers at round concentrations are given in Table IV and compared with the "best values" as given in Noyes and Falk's compilation[1] of all of the more recently determined data.

TABLE IV.

Transference Numbers of Lithium Ion in Lithium Chloride.

Conc.	E. m. f. method.	"Best value" Hittorf method.
0.001	0.359	...
0.005	0.341	...
0.01	0.334	0.332
0.02	0.327	0.328
0.05	0.318	0.320
0.10	0.311	0.313
0.20	0.304	0.304
0.30	0.299	0.299
0.50	0.293	...
1.0	0.286	...
2.0	0.276	...
3.0	0.268	...

7. Discussion of Previous Work.

As has been stated, Pearce and Mortimer[2] have carried out an investigation covering much the same field as the research described in this paper, including measurement with cells containing several other solvents than water. Their results and conclusions, however, differ widely from ours. For instance, the value they record for the 1.0 — 0.1 N concentration cell without liquid junction is 2 mv. lower than that given in Table I. This difference increases progressively with dilution until it reaches about *12 mv.* for the 0.05 — 0.005 N cell. Though the authors state that "greatest care was taken to secure the least possible contact with air," it is evident that oxygen was not sufficiently excluded from their solutions. As would be expected, the effect of this dissolved oxygen on the potential increases with decreasing concentration. The work on potassium chloride cells[3] showed that constant, though erroneous, potentials can be obtained from oxygen bearing solutions. Their values also indicate a decrease of activity coefficients with increasing dilution (below 0.1 N). This is shown by no other electrolyte, and freezing-point measurements give evidence, independent of that outlined in this article, that it is not the case for lithium chloride solutions. The potentials of their cells with liquid junction, being uninfluenced by the presence of oxygen, show somewhat closer concordance with the figures given in Table II.

The transference numbers computed from Pearce and Mortimer's

---

[1] THIS JOURNAL, **33**, 1436 (1911).

[2] *Ibid.*, **40**, 509 (1918).

[3] MacInnes and Parker, *loc. cit.*

data agree roughly with the early data of Kuschel,[1] as quoted in a compilation by Kohlrausch and Holborn.[2] Their results, however, vary widely from the later and far more accurate transference measurements by Jahn, Bein and Washburn.[3]

Recently, Allmand and Polack[4] have published the results of measurements on cells of the type: Hg, HgCl + NaCl, $Na(Hg)_x$. Their work can only be regarded as preliminary, especially for the more dilute solutions, since no attempt was made to keep oxygen out of their solutions.

8. Summary.

The electromotive forces of cells without liquid junction

$$\text{Ag AgCl} + \text{LiCl}\ (c_1),\ \text{Li}\ (\text{Hg})_x,\ \text{LiCl}\ (c_2) + \text{AgCl, Ag},$$

in which the concentrations C_1 and C_2 varied between 3.0 and 0.001 N have been measured at 25°, and the activities of the ions of the salt have been computed. With the aid of measurements on cells with liquid junction

$$\text{Ag AgCl} + \text{LiCl}\ (c_1),\ \text{LiCl}\ (c_2) + \text{AgCl, Ag},$$

the transference numbers of the ions have been obtained. Since these numbers, for lithium chloride, change rapidly with the concentration, a method has been devised by which the numbers can be computed from the electromotive force measurements and expressed as a function of the ion activity. The value of the transference number at any given concentration, within the range studied, can thus be obtained.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 126.]

THE ACTIVITY COEFFICIENT OF NORMAL POTASSIUM CHLORIDE SOLUTION AND THE POTENTIAL OF THE NORMAL CALOMEL ELECTRODE.

BY JAMES A. BEATTIE.

Received March 12, 1920.

Since the normal hydrogen electrode and the normal calomel electrode are both used as standards in electromotive force calculations, it is desirable to know accurately the potential difference between them. The electromotive force of the system

$$\text{Hg, Hg}_2\text{Cl}_2 + \text{KCl}\ (c) \,||\, \text{H}^+\ (1\ N),\ \text{H}_2\ (1\ \text{atm.}) \qquad (1)$$

is given by the equation

---

[1] *Wied. Ann.*, 13, 289 (1881). Kuschel used diaphragms of gold beaters skin so his results were probably seriously influenced by electroendosmosis.

[2] "Leitvermögen der Electrolyte." The determinations were not made by Kohlrausch and Holborn, as stated by Phelps and Mortimer.

[3] *Loc. cit.*, see p. 1126.

[4] *J. Chem. Soc.*, 115, 1020 (1919).