

# HITTORF TRANSFERENCE NUMBERS OF SOLUTIONS OF POTASSIUM, SODIUM, AND LITHIUM CHLORIDES IN WATER AND IN ONE-TENTH MOLAR HYDROCHLORIC ACID

L. NICKELS AND A. J. ALLMAND

*King's College, University of London, London, England*

*Received September 15, 1936*

Apart from quite early experiments and the few data obtained by Mackay (12) on mixtures of potassium sulfate and potassium chloride, and by Braley and Hall (3) on solutions containing sodium chloride and potassium chloride, no work on transference in mixtures of simple electrolytes had appeared when we commenced our experiments. With the exception of further papers arising out of the work of Braley and Hall (15, 7, 16, 4), the only experiments published since by the Hittorf method have been those of Van Rysselberghe (17) and of Bennewitz, Wagner, and Küchler (1). Longworth (10) has applied the moving boundary method to mixtures of hydrochloric acid and potassium chloride. In our own work, the concentration of hydrochloric acid was kept constant at 0.1 *M* or nearly so, and that of the alkali metal chloride varied over a considerable range. Parallel experiments with solutions free from hydrochloric acid, and with 0.1 *M* hydrochloric acid alone, were also carried out. The omission of experiments with more concentrated solutions of hydrochloric acid has made it impossible for us to test the MacInnes (11) formula for transference numbers in a mixed electrolyte. According, however, to Van Rysselberghe and Nutting (18), the presence of hydrochloric acid as one of the constituents in any case makes the measurements "less suitable" for the purpose of testing such formulas.

## EXPERIMENTAL

The transport tube (figure 1a) was 2.25 cm. in internal diameter and about 1 meter in total length. Cuts at the points a and b were joined together by wide rubber tubing. The inlet tubes c, d, e, and f were closed by rubber stoppers during an experiment. The ends A and F were also closed by rubber stoppers through which passed the electrodes, the cathode being a silver disc, 2 cm. in diameter, covered with a layer of precipitated silver chloride during an experiment, and the anode a rod of the purest cadmium obtainable. The whole tube was firmly mounted in a wooden stand on the laboratory bench, and all measurements were made at the

prevailing room temperature. Two such transference tubes in series were generally used. The coulometer was placed between them and, under these conditions, agreement between the values given by the two tubes showed the absence of possible current leakage.

When working with 0.1 *M* hydrochloric acid, and to a much greater extent when using mixtures of hydrochloric acid and the alkali metal chlorides, it was found that the acid content of the middle anolyte (DE in the figure) decreased appreciably long before, say, the concentration in the middle catholyte (BC) increased; the change soon extended to the middle layer itself (CD), thus rendering the experiment useless. To counteract this difficulty, the tube Fb was replaced in such cases by F'b' (figure 1b), which was provided with a horizontal side-arm of capacity between E' and G of the same order as E'F'. In this way the volume of the anolyte was approximately doubled. In spite however of this change,

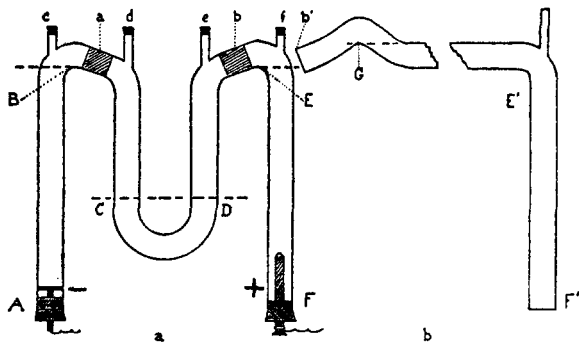


FIG. 1. The transport tube

the existence of the "middle layer effect" resulted in a very considerable curtailment of the series of experiments on hydrochloric acid-lithium chloride mixtures.

The silver coulometer was set up and employed in accordance with the directions of the Bureau of Standards (1916). The platinum crucible was of about 100-cc. capacity. The anode, of assay silver, was surrounded by a porous alundum thimble. In some experiments, where large weights (up to 4 or 5 g.) of silver were deposited, the capacity of the coulometer was increased to about 250 cc. by placing the anode thimble in a separate glass vessel provided with a wide-bore siphon which made connection with the platinum crucible. A number of experiments were carried out with the iodine coulometer of Washburn and Bates (21). In accuracy, reproducibility, and convenience, this instrument left nothing to be desired, provided that the quantities of electricity measured were relatively small, not exceeding 0.005 faraday. But in long-continued experiments, or

when using relatively heavy currents, migration of  $I_3^-$  ions caused trouble, and for this reason and because of the heavy cost of the large quantities of potassium iodide necessary, we reverted to the silver coulometer.

The source of the chemicals used and the preparation and the analysis of the solutions have been dealt with in the preceding paper, but it is necessary to mention a difficulty met with when using the cadmium anodes. These were naturally of the purest metal available at the time. The first consignment gave no trouble; the very small loose residue observed when they were corroded anodically was of the same color as the metal, and was attributed to irregular solution of the same. Subsequent specimens however, from another source, gave a deposit distinctly lighter in color than the metal and, simultaneously, when working with acid solutions, the discrepancy between the hydrogen ion transference numbers calculated from the changes in concentration of anolyte and catholyte became more pronounced. These effects were traced to the presence of small quantities of basic material in the cadmium, which would of course neutralize some of the acid in the anolyte during an experiment. Further investigation showed this substance, probably zinc oxide, to be present throughout the whole mass of the metal, not merely superficially. Unfortunately, its distribution proved not to be uniform, and this fact made it impossible to work out a correction factor. However, as will be seen from the tables, the errors introduced appear to be small.

The experimental procedure presented no novel feature. The currents and durations of run used in practice varied between 0.02–0.1 ampere and six to twenty-four hours, respectively, the actual values being determined by the concentration relations. At the end of a run, stoppers d and e (figure 1a) were removed. Two identical glass tubes, doubly bent, were lowered to the same depth (C, D) in the limbs of the center U, and the portions BC and DE, middle catholyte and middle anolyte, respectively, simultaneously removed by suction into two tared stoppered flasks. CD, the middle layer, was pipetted out. Cathode and anode tubes were then detached, closed by waxed corks, thoroughly shaken, their contents run out into tared flasks, and the tubes washed out with several small portions of test solution, the washings being run into the same flasks. In the case of AB, the partially reduced silver chloride was broken up by a glass rod, and a more thorough washing was naturally necessary to remove the last traces of solid precipitate. After determining the total weights of the different portions, weighed fractions were titrated for acid and for total chloride, the amount of cadmium in the anode layers being known from the coulometer result, and the amount of alkali metal cation being obtained by difference. If either middle anolyte or middle catholyte had changed in composition, its data were of course included with those of the anolyte or catholyte, respectively. If the middle layer had altered, the experi-

TABLE 1  
*Results for solutions of a single electrolyte*

WEIGHT MOLARITY	TEMPERATURE IN °C.	FARADAYS PASSED	EQUIVALENTS TRANSFERRED		$\eta_c$
			From anode	To cathode	
Hydrogen chloride					
0.0970		0.005508	0.004599 0.004606	0.004584 0.004587	0.8344
0.0970		0.005735	0.004784 0.004798	0.004780 0.004786	
Potassium chloride					
0.0978	18	0.004093	0.002016 (0.001992)	0.002015 0.002006	0.493
0.0987	18	0.004922	0.002442	0.002436	
0.1192	15	0.004215	0.002076 0.002079	(0.002057) 0.002080	
0.3878		0.01689	(0.008079) 0.008248	(0.008415) 0.008252	0.4884
1.167	18	0.03059	0.01473	0.01472	0.4846
2.032	17	0.04239	0.02044	0.02057	0.4835
2.09	20	0.03165	0.01529	0.01534 0.01528	
3.185		0.05346	0.02563	0.02582	
Sodium chloride					
0.0964	19	0.005327	0.002079 0.002074	(0.002002) 0.002082	0.3897
0.0989	16	0.005805	0.002261 0.002259	0.002256 0.002263	
0.1010	17	0.005373	0.002093 0.002097	0.002095 0.002094	
0.1997	23	0.010025	0.003787 0.003784	0.003798 0.003774	0.3777
0.306	17	0.009575	0.003629 0.003563	0.003440 0.003644	0.373
0.417	20	0.010012	0.003729 0.003727	0.003721 0.003712	0.3717
0.993		0.014765	0.005369 0.005357	(0.00532) 0.00537	0.3635
2.34	17	0.02752	0.00986 0.00990	0.00969 0.00967	0.355
2.92		0.02796	0.00987 0.00982	(0.0097) 0.00991	0.353

TABLE 1—*Concluded*

WEIGHT MOLARITY	TEMPERATURE IN °C.	FARADAYS PASSED	EQUIVALENTS TRANSFERRED		$\eta_c$
			From anode	To cathode	
Lithium chloride					
0.1008	17	0.006478	0.002037 0.002036	0.002049	0.315
0.2529	19	0.01138	0.003419 0.003411	0.003444 0.003447	0.301
0.5182	15	0.01916	0.005556 0.005558	0.005458 0.005482	0.288
1.102	20	0.02694	0.007226 0.007223	0.007223 (0.007255)	0.268
2.257	22	0.04570	0.01170 0.01155	0.01175 0.01162	0.255
4.832	25	0.05264	0.01296	0.01277	0.244

ment was discarded. From the results obtained, the quantities of the different electrolytes transferred can readily be computed, and there seems no need to give a specimen of such a calculation.

## RESULTS

Table 1 contains the results for solutions of a single electrolyte. The amounts of electrolyte transferred are given in every case, as affording the best indication of the degree of accuracy obtained. The cationic transference numbers in the last column are average values, and those experimental figures which have been omitted in calculating them are bracketed.

The value for 0.1 *M* hydrochloric acid is in good agreement with the accepted figure. The results for the alkali metal chlorides are plotted in figure 2 in the form of  $\eta_c$  against the logarithm of the volume normality. Values taken from standard reference works are also shown. Our figures for potassium chloride and sodium chloride tend to fall slightly below the latter. Apart from the uncertainty introduced by the temperature variation, we think they are to be relied on experimentally. There is, however, one point to which attention does not seem to have been drawn hitherto. Apparent or Hittorf transference numbers are affected by differential ionic hydration. The relation between the true and the Hittorf cationic transport numbers for a simple salt as deduced by Washburn (20) is

$$T_H = T_T - N_w^F \cdot N_s / N_w$$

where  $N_w^F$  is the net transfer of water to the catholyte per faraday of electricity passed, and  $N_s/N_w$  the ratio of moles of salt to moles of water in the solution. Strictly speaking  $N_s/N_w$  in this expression should be replaced

by the corresponding ratio for the electrode layer at the conclusion of the experiment, the relation quoted being rigorous only if the quantity of water transferred to the catholyte or anolyte during a run can be neglected in comparison with the water present at the start. The correct expressions for the left-hand side of the equation, depending on whether catholyte or anolyte is analyzed, are respectively

$$T_H(1 + n/N_w^c \cdot N_w^F) \quad \text{and} \quad T_H(1 - n/N_w^a \cdot N_w^F)$$

where  $n$  is the number of faradays passed during the experiment, and  $N_w^c$ ,  $N_w^a$  the moles of water in catholyte and anolyte at the start.

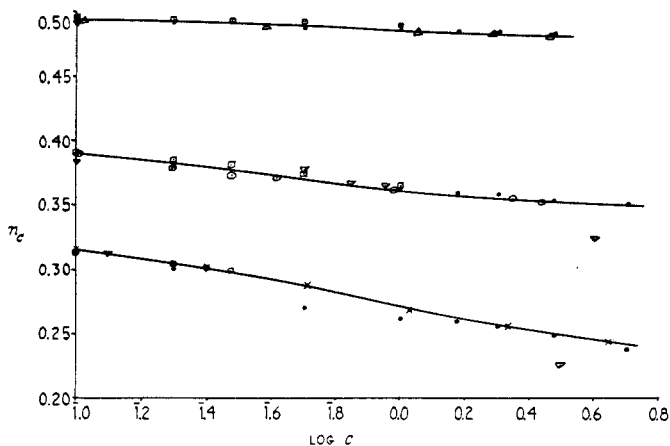


FIG. 2.  $\gamma_c$ , plotted against the logarithm of the volume normality

Authors' data		Other data	
$\Delta$ , potassium chloride		$\square$ potassium chloride, from International Critical Tables	
$\bigcirc$ , sodium chloride		$\nabla$ , sodium chloride, from Landolt-Bornstein	
$\times$ , lithium chloride		$\bullet$ lithium chloride, from Kohlrausch-Holborn	

Analyses of anolyte and catholyte will therefore, in principle, give different values for  $T_H$ , and values which will depend on the duration of the run. The values derived from the analysis of the anolyte should be the greater, but the data in table 1 show no sign of such a trend. In our experiments,  $n$  varied between 0.004 and 0.053.  $N_w^c$  and  $N_w^a$  were about 5, except in the very few experiments in which the middle anolyte had changed in composition, when  $N_w^a$  was 8 to 9. According to the work of Remy (14) and of Velisek (19),  $N_w^F$  decreases as concentration increases, though rather less rapidly than the latter. If we take as a basis the figures quoted by these authors (at 1 N in fair agreement with the earlier data of Washburn), the calculated correction terms are of the following order:

	0.1 N	5 N
Potassium chloride.....	0.004	0.002
Sodium chloride.....	0.009	0.002
Lithium chloride.....	0.013	0.007

These relations in turn imply that, whilst in concentrated solutions the experimental values of  $T_H$  will only be affected by perhaps 0.001, in 0.1 N

TABLE 2  
*Data obtained for the mixtures*

NO. OF EXPERI- MENT	WEIGHT MOLARITY		TEMPER- ATURE IN °C.	FARA- DAYS PASSED	EQUIVALENTS OF HCl TRANSFERRED		EQUIVALENTS OF RCl TRANSFERRED	
	HCl	RCl			From anode	To cathode	From anode	To cathode
Potassium chloride								
1	0.0995	0.0984	23	0.01461	0.008971	0.009001	0.00151	0.00153)
2	0.1007	0.1008	18	0.00978	0.00625	0.00621	0.001212	0.001204
3	0.1068	0.2538	18	0.02005	0.00954	0.00954	0.004384	0.00440
4	0.1050	0.4930	18	0.02985	0.01006	0.01003	0.00913	0.009175
5	0.1028	1.024	18	0.03460	0.006598	0.006635	0.01317	0.01312
6	0.1131	2.076	17	0.04159	0.004821	0.004784	0.01653	0.01679
7	0.1112	2.909	18	0.04814	0.003598	0.003576	0.02226	0.02240
8	0.1137	3.420	20	0.04280	0.003195	0.003106	(0.02132)	0.01958
Sodium chloride								
9	0.1013	0.1001	20	0.01123	0.00743	0.007425	0.00097	0.00099
					0.00740	(0.00723)	0.00097	0.00094
10	0.0985	0.1976	19	0.009637	0.005226	0.005200	0.001268	0.001331
					0.005212	0.005228	0.001294	0.001295
11	0.1072	0.4558	21	0.01591	0.006305	0.006157	0.003346	0.003244
					0.006261		0.003326	
12	0.1063	1.035	14	0.02474		0.005736		0.006615
						0.005737		0.006542
13	0.0952	1.978	21	0.02481	0.002942	0.003023	0.007645	0.00760
					0.002913	0.002915	0.007790	0.00773
14	0.1089	2.365	20	0.03951	0.00437		0.01371	
15	0.1049	4.775	21	0.05554	0.002715		0.01832	
Lithium chloride								
16	0.1173	0.08945	20	0.009874	(0.007241)	0.006971	(0.0005205)	0.000566
					(0.007305)	0.006945	(0.0005190)	0.000531
17	0.1006	0.3099	17	0.01181		0.005621		0.001730
						0.005624		0.001767

solutions the anodic and cathodic values for potassium chloride, sodium chloride, and lithium chloride obtained in our experiments should have differed by about 0.004, 0.007, and 0.008, respectively. The obvious

absence of any such effect indicates that the high hydration values quoted for 0.1 *N* solutions in the papers of Remy and Velisek referred to are spurious, and due to electroosmotic effects. The experimental errors in our own work must be responsible for masking at higher concentrations the presence of smaller effects in the predicted direction.

Table 2 contains the data for the mixtures. Those not used in subsequent calculations are bracketed. Where appreciable disagreement exists between the anodic and cathodic figures for amounts transferred, the latter have been preferred, partly because of the possibility of disturbance arising out of the basic material in the anode, but chiefly on account of the "middle layer" effect. This effect was responsible for two experiments only having been carried out with hydrochloric acid-lithium chloride mixtures. In the second of these, the middle layer underwent a very slight change in com-

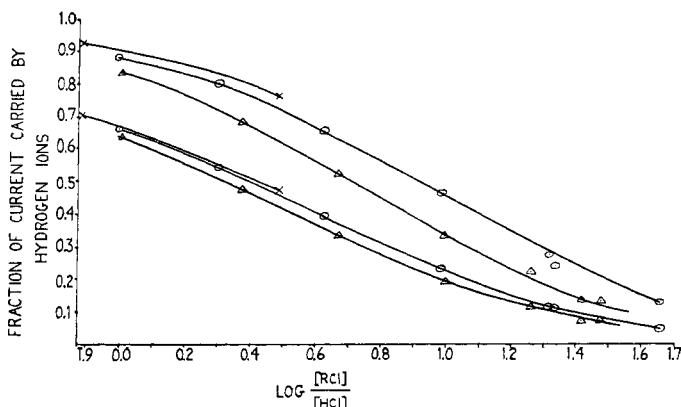


Fig. 3. Fraction of the current carried by the hydrogen ions plotted against the logarithm of the ratio  $[RCl]/[HCl]$ .  $\Delta$ , potassium chloride;  $\circ$ , sodium chloride;  $\times$ , lithium chloride.

position during the run, and it was realized that experiments with higher concentrations of lithium chloride were impracticable with the transference tubes in use. The first experiment with hydrochloric acid-potassium chloride mixtures, carried out at a somewhat higher temperature than the others, has not been utilized. When worked up, it gives results in no way concordant with the remainder, and presumably some unsuspected error was present. In experiments 14 and 15, the values quoted for the quantities transferred are means of the anode and cathode figures; these differed appreciably from one another.

From the total quantity of electricity passed and the amounts of HCl and RCl transferred, the shares of the  $H^+$ ,  $R^+$ , and  $Cl^-$  ions in carrying the current can be directly calculated, any transference of water being neglected, as in the discussion which follows. Figure 3 contains, plotted



against the logarithm of the ratio  $[RCl]/[HCl]$ , the fraction of the *total* current and of the *cationic* current carried by the hydrogen ions (lower and upper set of graphs respectively). At high concentration ratios the experimental points are seen to deviate appreciably from the curves. This is of course due to the considerable effect caused by slight errors of analysis when using concentrated RCl solutions with relatively small concentration changes.

## DISCUSSION

The existence of the errors just mentioned, apart from temperature and concentration differences, makes impossible any correlation with the conductivity results reported in the preceding paper, and the following discussion is based solely on the transference data recorded above.

Each experiment gives us the number of faradays ( $F$ ), and hence the fraction of the total current ( $T$ ), carried by each species of ion. Expressing the molarities ( $M_i$ ) of the same ions as fractions ( $x$ ) of the total ionic molarity ( $\Sigma M_i$ ), division of the  $T$  values by the corresponding  $x$  values gives us figures proportional to the relative mobilities of the ions ( $\lambda$ ) in that particular solution. The ratios  $\lambda_H/\lambda_H + \lambda_{Cl}$  and  $\lambda_R/\lambda_R + \lambda_{Cl}$  in their turn give  $n_H$  and  $n_R$ , the cationic transport numbers of HCl and RCl in the mixture, which can be compared with the values given by the single electrolytes at the same total molarity. The following tabulated example will make this clear. The data are those of experiment 11 (table 2).

	H <sup>+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	
$M_i$ .....	0.1072	0.4558	0.5630	$\Sigma M_i = 1.1260$
$x$ .....	0.0952	0.4049	0.5000	
$F$ .....	0.00624	0.00331	0.00636	$\Sigma F = 0.01591$
$T$ .....	0.3922	0.2080	0.3997	
$\lambda$ .....	4.119	0.5139	0.7994	

For the two cations, we have that  $l_H:l_{Na} = 8.013:1$ ; and, as  $\lambda_H + \lambda_{Cl}$  and  $\lambda_{Na} + \lambda_{Cl}$  are, respectively, 4.918 and 1.313,  $n_H$  becomes 0.8373 and  $n_{Na}$  0.3913.

Table 3 contains the values of  $l_H/l_R$ ,  $n_H$ , and  $n_R$  for the experiments (omitting the first) recorded in table 2. The bracketed figures in the second column are based on the mobilities at 18°C. of H<sup>+</sup> ions and R<sup>+</sup> ions in 0.1 *N* solutions of HCl and RCl, respectively, *viz.*, H<sup>+</sup>, 294; K<sup>+</sup>, 55.1; Na<sup>+</sup>, 36.4; Li<sup>+</sup>, 27.5 (8). Column 5 contains the cationic transference numbers for the neutral alkali metal halide solutions at concentrations equal to the total concentrations of the acid solutions.

Whilst the effects of the small inaccuracies in analysis referred to above are magnified by the method of calculation used, there are nevertheless

certain general conclusions to which the results point. The values of  $n_H$  in column 3 are less affected by experimental error than are the other ratios. We found (table 1)  $n_H$  to be 0.8344 for 0.1 *N* hydrochloric acid. It is known to rise with increase of concentration up to, at all events, 1 *N* (thus Kraus (9) gives 0.835 for 0.1 *N* at 18°C., rising to 0.840 at 0.5 *N* and to 0.844 at 1 *N*), whilst according to Buchböck (6), it falls to 0.824 at 2.5 *N*. At the lowest concentrations of added RCl, our figures show no difference exceeding the probable experimental error, either amongst themselves or from the values for pure hydrochloric acid solutions. At concen-

TABLE 3  
*Values of  $l_H/l_R$ ,  $n_H$ , and  $n_R$  for experiments recorded in table 2*

NO. OF EXPERIMENT	$l_H/l_R$	$n_H$	$n_R$	$n_R$ (NEUTRAL SOLUTIONS)	
2	5.15	0.842	0.508	0.491	KCl
3	5.16	0.841	0.505	0.489	
4	5.16	0.843	0.510	0.486	
5	5.02	0.830	0.494	0.484	
6	5.29	0.823	0.466	0.482	
7	4.21	0.814	0.5105	0.481	
8	4.84 (5.334)	0.830	0.502	0.481	
9	7.56	0.8385	0.407	0.382	NaCl
10	8.06	0.834	0.384	0.377	
11	8.01	0.837	0.391	0.369	
12	8.49	0.832	0.369	0.360	
13	7.96	0.820	0.363	0.355	
14	6.92	0.822	0.401	0.354	
15	6.76 (8.076)	0.786	0.352	0.35	
16	10.16	0.8385	0.349	0.304	LiCl
17	9.88 (10.69)	0.838	0.343	0.292	

trations of added potassium chloride or sodium chloride greater than 1 *M*,  $n_H$  clearly diminishes, in general agreement with the result of Buchböck just quoted. On the other hand, whilst the  $n_R$  values, which bear the full brunt of any analytical error, are clearly far from being accurate, in every case except in experiment 6, which is obviously erroneous, they are greater than the  $n_R$  values for the corresponding solutions of the pure salts. In particular,  $n_K$  in HCl + KCl solutions tends to be above, not less than, 0.5. The values for  $l_H/l_R$  conform to the other results; in the most dilute mixtures, they are very near or rather less than the bracketed figures in the same column, and they definitely decrease at higher concentrations of RCl.

Qualitatively, these effects are of the same nature as those predicted by Bennewitz, Wagner, and K  chler (1; see also 13), in their extension to mixtures of electrolytes of Onsager's theory of conductance in highly dilute solutions. As the retarding interionic forces will be greater, the smaller the average mobility of the ions comprising the ionic atmosphere, the mobility of  $H^+$  ions in a solution of  $HCl + RCl$  will be less than in a solution of hydrochloric acid. The reaction accompanying the retardation of the  $H^+$  ions will result in an acceleration of the  $R^+$  ions, whilst the motion of the  $Cl^-$  ions will be very slightly decreased. The measurements of the same authors (Hittorf transference numbers in  $HCl + KCl$ ) are in qualitative agreement with the extended theory, as also are those of Longworth (10) (transference measurements by moving boundary method in  $HCl + KCl$ ), of Bray and Hunt (5) (conductance measurements in  $HCl + NaCl$ ), and of Miss Taylor (16) (Hittorf transference numbers in  $HCl + NaCl$ ). In all these cases, the share of current carried by the alkali metal ion compared with that carried by the  $H^+$  ion is relatively high, but, in general, the observed effects are less than those predicted. This is ascribed to the fact that the total concentration of electrolyte in the experimental work (0.1 to 0.2  $N$ ) was too high for the strict application of the theory.

If, however, the views of Bernal and Fowler (2) are correct, the theory will need considerable quantitative modification. According to these authors, the velocity of actual bodily transport of the hydrogen or  $H_3O^+$  ion in aqueous solutions will be of the same order as that of other ions, and four-fifths of its observed velocity will be due to Grotthuss conduction, acting by a mechanism of proton jumps from one water molecule to another. They give good reason for assuming that, whilst the chloride ion is actually 4-co  rdinated with water molecules, no transport of water takes place when it moves, but merely an exchange of co  rdinated water. The potassium, sodium, and lithium ions, on the other hand, will carry with them on migration increasing proportions of their co  rdinated water,—in 1  $M$  solution about one, two, and five molecules, respectively, per ion, judging from the results of Washburn (20), Remy (14), and Velisek (19) already referred to.<sup>1</sup> Applied to solutions of hydrochloric acid, these conceptions agree well with the results of Buchb  ck (6), who found, in 1  $N$  solution,  $N_w^F$  to be 0.24. This gives an average hydration value of 0.27 for the hydrogen ion if the chloride ion transports no water with it, and this in turn corresponds to 27 per cent of the cationic current being due to actual movement of  $H_3O^+$  ions, and 73 per cent to Grotthuss conduction. The theory also accounts for the fact that, whereas the Hittorf cationic transference numbers for solutions of the alkali metal chlorides decrease

<sup>1</sup> As mentioned, Bernal and Fowler assume all these univalent ions to be 4-co  rdinated, and reject a co  rdination number of six for the lithium ion, suggested by a consideration of energy of hydration.

with increasing concentration, the reverse is true for solutions of hydrochloric acid up to, at all events, 1 *N*. In the latter case, increasing concentration will retard the mobility of the chloride ion, owing to interionic effects, but up to a point will have relatively little influence on the frequency of proton jumps. On the other hand, the decrease in the transference number reported by Buchböck in 2.5 *N* solutions can reasonably be ascribed to a steric effect, due to the presence of increasing quantities of the large 4-coördinated chloride ions, which decreases the frequency of proton jumps.

If now, in accordance with these ideas, the conductivity of the  $\text{H}_3\text{O}^+$  ion in dilute solution is chiefly due to Grotthuss migration of protons, clearly the predictions of the extended Onsager theory must be modified in the sense that smaller effects are to be expected, which is in accordance with what was found by previous workers. On the other hand, our data suggest that the effects in more concentrated solutions of RCl may be considerable, and, in particular, that the relative mobilities of the  $\text{R}^+$  ions are apparently increased when hydrochloric acid is present, even in solutions where the ratio  $[\text{HCl}]:[\text{RCl}]$  is low. Whilst it is not difficult to imagine that proton migration may become less easy as the structure of the solution becomes "tighter" in the sense of Bernal and Fowler, owing to the increasing numbers of water-coördinating cations, it is less easy to see why the mobilities of the latter should simultaneously increase, as appears to be the case, and it is hardly profitable at the moment to discuss the point. It may, however, be mentioned that we have considered the possibility of the presence of added hydrochloric acid so modifying the conditions in a solution of an alkali metal chloride as to decrease the average size of the hydration shell permanently attached to the cations, thus increasing the relative mobility of the latter. In such a case, one would expect the apparent volume of the salt to be greater dissolved in a solution of hydrochloric acid than in pure water. The density measurements in the preceding paper are sufficiently accurate to test this possibility at 25°C. We have calculated from these data the apparent volumes occupied by 0.25, 1, and 3 moles of potassium chloride, sodium chloride, and lithium chloride dissolved respectively in (a) 1000 g.  $\text{H}_2\text{O} + 0.1 \text{ M HCl}$  and (b) 1000 g.  $\text{H}_2\text{O} + 0.1 \text{ M RCl}$ . The results are as follows:

MOLES OF RCl ADDED	APPARENT VOLUMES IN CC.					
	KCl		NaCl		LiCl	
	In HCl	In KCl	In HCl	In NaCl	In HCl	In LiCl
0.25	7.12	7.19	4.45	4.54	4.55	4.35
1.0	29.34	28.83	18.63	18.50	18.49	18.48
3.0	91.83	91.89	60.25	61.01	57.19	57.76

There is no evidence whatever of any effect of the kind looked for, and this has been confirmed by plots of the whole series of apparent molar volume against molarity; within the experimental error, the points fall on the same curve, whether the RCl be dissolved in water or in 0.1 *M* hydrochloric acid.

In conclusion, brief reference may be made to the "middle layer effect", which, it may be remembered, was the cause of the curtailment of the projected series of runs with hydrochloric acid-lithium chloride mixtures. Experimentally, this manifested itself by a decrease in concentration of acid in the "middle anode" layer at an early stage in the transference experiment. It was noticed with 0.1 *M* hydrochloric acid, was accentuated when potassium chloride or sodium chloride was present in addition, and became very pronounced with hydrochloric acid-lithium chloride mixtures. Primarily, of course, the effect is due to the fact that the anode layer is losing hydrogen ions by transference and these are being replaced by cadmium and chloride ions. After a time, the fraction of the ionic transference between the anode and middle anode layers which is due to hydrogen ions is bound therefore to fall below the corresponding fraction at the boundary between the middle anode and the middle layers, and the phenomenon is not noticed in the time necessary for an experiment with acid-free RCl solutions because the mobilities of the  $R^+$  ions are so much less than that of the hydrogen ion. Calculation readily shows that the effect will be heightened by the addition of an alkali metal chloride to the hydrochloric acid solution, and to a degree corresponding qualitatively to what was found, but also, on the classical theory of conduction, to the *same degree* in every case. If, however, the extended Onsager theory be applied, then, again qualitatively, it can be shown that the magnitude of the effect should increase in the order  $KCl < NaCl < LiCl$ , as was found. The very considerable difference between the behavior of hydrochloric acid-lithium chloride and hydrochloric acid-sodium chloride solutions can not be explained, but it may be pointed out that it appears analogous to the large increase in  $n_{Li}$  in acid, as compared with neutral solutions of lithium chloride, exhibited in table 3.

#### SUMMARY

1. The transference numbers of solutions of potassium, sodium, and lithium chlorides, both in water and in one-tenth molar hydrochloric acid, have been investigated at room temperature by the Hittorf method over considerable ranges of concentration. Both anode and cathode layers were analyzed, and the majority of the experiments were done in duplicate.

2. The agreement with neutral solutions between the values obtained by analysis of the anode and cathode layers suggests that the high hydration values which have been ascribed to the alkali metal cations in dilute

solution, as the result of transference measurements with and without a reference substance, are spurious.

3. In the acid solutions, the hydrogen ion and the alkali metal cations appear to carry, respectively, less and more of the current than would be expected from their mobilities in solutions of the corresponding single electrolyte. Connected with this is the existence of a so-called "middle layer effect," which causes certain experimental difficulties.

4. These last phenomena are discussed in the light of (i) the extended Onsager theory due to Bennewitz, Wagner, and K  chler and (ii) the views of Bernal and Fowler on the nature of the conductance of the hydrogen ion.

The junior author wishes to acknowledge with gratitude the grant given him by the Department of Scientific and Industrial Research while he was a student in training.

#### REFERENCES

- (1) BENNEWITZ, WAGNER, AND K  CHLER: *Physik. Z.* **30**, 623 (1929).
- (2) BERNAL AND FOWLER: *J. Chem. Physics* **1**, 515 (1933).
- (3) BRALEY AND HALL: *J. Am. Chem. Soc.* **42**, 1770 (1920).
- (4) BRALEY AND RIPPKE: *J. Am. Chem. Soc.* **49**, 1493 (1927).
- (5) BRAY AND HUNT: *J. Am. Chem. Soc.* **33**, 781 (1911).
- (6) BUCHB  CK: *Z. physik. Chem.* **55**, 563 (1906).
- (7) DEWEY: *J. Am. Chem. Soc.* **47**, 1927 (1925).
- (8) KOHLRAUSCH-HOLBORN, p. 214 (1916).
- (9) KRAUS: *Properties of Electrically Conducting Systems*, p. 25. (1922).
- (10) LONGWORTH: *J. Am. Chem. Soc.* **52**, 1897 (1930).
- (11) MACINNES: *J. Am. Chem. Soc.* **47**, 1922 (1925).
- (12) MACKAY: *J. Am. Chem. Soc.* **33**, 308 (1911).
- (13) ONSAGER AND FUOSS: *J. Phys. Chem.* **36**, 2689 (1932).
- (14) REMY: *Z. physik. Chem.* **118**, 161 (1925).
- (15) SCHNEIDER AND BRALEY: *J. Am. Chem. Soc.* **45**, 1121 (1923).
- (16) TAYLOR: *J. Am. Chem. Soc.* **48**, 599 (1926).
- (17) VAN RYSSELBERGHE: *J. Am. Chem. Soc.* **55**, 996 (1933).  
VAN RYSSELBERGHE AND MCBAIN: *J. Am. Chem. Soc.* **50**, 3009 (1928); **52**, 2336 (1930).
- (18) VAN RYSSELBERGHE AND NUTTING: *J. Am. Chem. Soc.* **56**, 1435 (1934).
- (19) VELISEK: *Chem. Listy* **20**, 242 (1926).
- (20) WASHBURN: *J. Am. Chem. Soc.* **31**, 322 (1909).
- (21) WASHBURN AND BATES: *J. Am. Chem. Soc.* **34**, 1341 (1912).