pares well with potassium bromate solutions in stability. With sulfuric and phosphoric acids, barium bromate solutions are affected to the same extent as are potassium bromate solutions.

Neutral solutions of potassium and barium bromate were found to be perfectly stable over long periods of time. Acid solutions of potassium bromate are not correspondingly stable.

Summary

1. 0.025 *N* solutions of pure potassium bromate, 2 *N* with perchloric, nitric or acetic acid, are not decomposed after boiling for 5 minutes; sulfuric and phosphoric acid solutions are much less stable.

2. The presence of free bromine has no effect except with acetic acid, but 10 mg. of chloride exerts a very slight reducing action.

3. Bromide in bromate may be determined by acidifying the solution and distilling the bromine liberated.

4. Barium bromate may be substituted for potassium bromate with equally good results.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM IN MIXED CHLORIDE SOLUTION[1]

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In 1920 Braley and Hall[3] presented some preliminary experiments on the transference numbers of sodium and potassium in mixed chloride solution, which indicated, in equivalent chloride mixtures ranging from 0.2 *N* to 1.6 *N* total concentration, a relatively higher transference number for sodium than called for by calculation from the conductance data of the simple salt solutions. As this agreed so favorably with the work of Smith and his students[4,5] on heterogeneous equilibria between aqueous and metallic solutions, it seemed entirely advisable that a more extensive study should be made with the idea of throwing further light on the composition of salt solutions and their degree of association and dissociation, with special reference to the complete-dissociation theory and the application of the mass law.

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[1] Read at the Pittsburgh meeting of the American Chemical Society, September, 1922.

[2] An abstract of a thesis presented to the Faculty of the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Braley and Hall, THIS JOURNAL, **42**, 1770 (1920).

[4] Smith and Ball, *ibid.*, **39**, 179 (1917).

[5] Smith and Wells, *ibid.*, **42**, 185 (1920).

In spite of the vast amount of work that has been performed on the degree of dissociation of salts in solution it still remains a very debatable question. It is of course known, by our ordinary methods of calculation, that the mass law does not hold in cases of strong electrolytes, and that the deviation increases with increase of concentration. It seems highly probable since these electrolytes more nearly approach the mass law constant with decreasing concentration that some change must be taking place which we should be able to detect by experiment. It is definitely known that ions become hydrated in solution, and it is also known that we have double salts, some of which dissociate readily into the simple salts, such as ammonium ferrous alum, $(NH_4)_2Fe(SO_4)_2.6H_2O$, and others which do not, such as potassium ferricyanide, $K_3Fe(CN)_6$, as well as hydration of a salt, such as hydrated cupric sulfate, $CuSO_4.7H_2O$. All of these give evidence of complex formations of different types, some between very similar molecules, and others between dissimilar ones. Since these things are known and accepted it is also reasonable to suppose that in a solution of like molecules of the same salt or of very similar salts similar association or complex formation would take place.

Assuming that in a mixed solution of sodium and potassium chlorides such complexes exist, we should then by transference measurements be able to show abnormal transference of some of the ions. If we assume the possibilities, $K_x(NaCl_2)_y$ and $Na_m(KCl_2)_n$, sodium would be transferred with the chlorine to the anode in the first case, and if enough of the complex were formed we should obtain a negative transference of the sodium. This would be reversed in the second case.

Working on this basis we will in this investigation attempt to show by transference data that such complexes must be formed, and that the salt entering into the complex ion cannot be completely dissociated as claimed by Ghosh.[6]

Theoretical Part

In any simple salt solution there are two ions that carry the electricity and since we are here using a solution containing 3 individual ions, the total electricity will be carried by these ions. Assuming that no complex formation takes place,

$$N_e = N_{\mathrm{K}} + N_{\mathrm{Na}} + N_{\mathrm{Cl}} \qquad (1)$$

where N_e represents the total equivalents of electricity and N_{K}, N_{Na}, and N_{Cl} represent, respectively, the equivalents carried by each ion constituent.

With this as a basis an equation can be developed for the ratio of the transference numbers of the ions in solution as shown by Braley and Hall which is

$$\frac{T_{\mathrm{Na}}}{T_{\mathrm{K}}} = K\,\frac{C_{\mathrm{NaCl}}\cdot\Lambda_{\mathrm{NaCl}}/\Lambda_{0\ \mathrm{NaCl}}\cdot\Lambda_{0\ \mathrm{Na^+}}}{C_{\mathrm{KCl}}\cdot\Lambda_{\mathrm{KCl}}/\Lambda_{0\ \mathrm{KCl}}\cdot\Lambda_{0\ \mathrm{K^+}}} \qquad (2)$$

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[6] Ghosh, *J. Chem. Soc.*, **113**, 449, 637, 707 (1918).

The ratio T_{Na}/T_K in this equation may be obtained directly from the experimental data. However, to use the right-hand side to calculate this value, for comparison, it is necessary to evaluate the proportionality constant K. By the method shown in the previous paper it is found to be 1.17. (Viscosity corrections have been neglected, as they apply alike to numerator and denominator.)

It has seemed advisable also to determine the actual conductivity of each transference solution in order that a direct comparison of ion mobilities may be made and for this purpose the following equation will be used

$$U_{ion} = \frac{T_{ion}\Lambda}{F} \tag{3}$$

where T_{ion} is the transference number of the ion as determined, "Λ" the equivalent conductance of the solution, "F" the Faraday, and U_{ion} the mobility of the ion.

Materials, Apparatus and Method of Experimentation

Materials. WATER.—For the transference experiments ordinary distilled water was redistilled from alkaline permanganate and subsequently from dil. sulfuric acid in Pyrex or Jena glass distilling vessels. For the conductivity determinations it was distilled from alkaline permanganate in a copper still with the condensing water so regulated that steam continually escaped from the condensing coils. All the water was stored in resistance glass bottles.

SODIUM AND POTASSIUM CHLORIDES.—Commercial sodium chloride was twice precipitated by means of hydrogen chloride with an intermittent and subsequent centrifuging, and finally dried in an electric muffle at 750°. The potassium chloride was prepared from C. P. salt by recrystallizing thrice from hot distilled water with intermittent centrifuging, and subsequent drying at 750° in the muffle.

COULOMETER MATERIALS.—The silver for the anodes was prepared by electrolyzing a pure grade of silver in a solution of silver nitrate using a rod of pure silver as the cathode. The silver crystals were then washed free from nitrates (by the diphenylamine test) dried, then melted on bone ash, attached to a piece of heavy silver wire wrapped in filter paper and used for the coulometer anodes.

Platinum dishes were used for the cathodes; and a 10% solution of pure silver nitrate was used as a medium.

SILVER CHLORIDE FOR CATHODE.—This was prepared as described by Washburn.[7]

TRANSFERENCE ANODE.—This was prepared in the same manner as was the "Type B Anode" described by Washburn.[7]

CHLOROPLATINIC ACID.—This reagent was prepared by the ordinary method of dissolving platinum black in aqua regia. The factor 0.3056 was used in converting the potassium chloroplatinate to potassium chloride.

Apparatus. TRANSFERENCE APPARATUS.—The transference apparatus was that used by Washburn,[7] the current being supplied from a 12-volt Willard storage battery.

CONDUCTIVITY APPARATUS.—The conductivities of the mixed salt solutions were measured on a commercial Kohlrausch slide wire bridge, with an ordinary resistance box with variations of 0.1 to 1000 ohms, and a Washburn Type "B" cell with electrodes 7 cm. apart. The e.m.f. employed was obtained from a constant-speed, high-frequency generator. A 150ohm, 1000cycle telephone receiver was used as a detector.

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[7] Washburn, *Tech. Quart.*, **21**, 187 (1908).

THERMOSTAT.—A large Freas electrically-controlled thermostat was used, adjusted to 25° and remaining constant to within 0.02°, and with water of sufficient depth to allow the transference apparatus to be immersed just below the horizontal part.

WEIGHTS, PIPETS. FLASKS AND BURETS.—The weights used were calibrated against a set of standard weights. and the corrections were applied to all weighings.

All the volumetric apparatus was calibrated by the United States Bureau of Standards.

Method of Experimentation. Transference.—Essentially the same procedure as used by Washburn[7] was employed. To detect any leakage of current through the apparatus and to serve as a check on the electricity passed, one coulometer was placed at the cathode and another at the anode.

Conductivities.—The regular conductivity procedure was employed.

Analysis of Transference Experiments.—Triplicate analysis of the anode and cathode portions and duplicate analysis of the middle portions were analyzed by the chloroplatinate method as described by Smith and Ball.[4] The chloride content of each portion was determined by the Mohr method and served as a check on the other work.

Calculations.—Ordinary methods of calculation were used with the following atomic weights: Na, 23.0; K, 39.1; Cl, 35.46; and Ag, 107.88.

Experimental Part

Transference.—Table I shows the experimental data obtained for the transference numbers of solutions of varying total concentration, and with

TABLE I

VARIATION OF TRANSFERENCE NUMBERS AND RATIOS WITH INCREASE IN TOTAL CONCENTRATION OF THE MIXED CHLORIDES

Ratio: 3 KCl to 1 NaCl Temp. 25°

Total N	Pole	Wt. of Ag in Coulom. G.	NaCl transf. G.	KCl transf. G.	T_{Na}	T_K	T_{Na}/T_K	Av. T_{Na}/T_K
0.1	A	0.8037	0.0320	0.2070	0.0735	0.373	0.200	
	C	0.8037	.0417	.1940	.0960	.350	.270	0.235
0.2	A	1.6456	.0363	.4738	.0405	.415	.097	
	C	1.6461	.0079	.4888	.0089	.431	.021	.059
0.2	A	1.6475	.0012	.5190	.0013	.454	.003	
	C	1.6469	.0079	.4864	.0089	.426	.021	.012
0.4	A	2.1198	.0956	.5550	.083	.380	.218	
	C	2.1198	.0740	.4840	.065	.332	.197	.208
0.8	A	2.4685	.0896	.6500	.067	.380	.176	
	C	2.4698	.0787	.5494	.059	.320	.184	.180
1.6	A	2.4670	.1253	.5362	.0937	.314	.299	
	C	2.4681	.1485	.5413	.111	.332	.332	.315
Ratio: 2 KCl to 1 NaCl							Temp. 25°	
0.1	A	0.9202	0.0643	0.2167	0.129	0.340	0.380	
	C	0.9213	.0626	.2013	.126	.316	.398	0.389
0.2	A	1.6601	.0054	.5033	.0615	.347	.140	
	C	1.6613	.0502	.4150	.0558	.361	.154	.147

0.2	A	1.5513	.0619	.4304	.073	.401	.183	
	C	1.5516	.0434	.4098	.0516	.380	.136	.1595
0.4	A	2.1359	.1256	.5278	.1088	.357	.304	
	C	2.1373	.1290	.4407	.1115	.298	.374	.339
0.8	A	2.5360	.1547	.5800	.112	.331	.340	
	C	2.5373	.1450	.5340	.105	.305	.345	.343
1.6	A	2.5201	.1995	.6373	.146	.366	.400	
	C	2.5029	.1477	.5627	.109	.323	.340	.370

Ratio: 1 KCl to 1 NaCl Temp. 25°

0.1	A	0.8089	0.0771	0.1386	0.176	0.240	0.735	
	C	0.8089	.0713	.1210	.162	.213	.762	0.749
0.2	A	2.1436	.2037	.3743	.175	.252	.694	
	C	2.1436	.1806	.3627	.155	.245	.634	.664
0.2	A	1.8161	.1591	.3269	.158	.254	.623	
	C	1.8160	.1503	.3171	.149	.247	.608	.616
0.4	A	3.4233	.2555	.6568	.130	.277	.500	
	C	3.4222	.2658	.5681	.144	.240	.520	.510
0.8	A	2.2823	.1973	.4633	.160	.294	.544	
	C	2.2808	.1453	.3444	.118	.219	.537	.540
1.6	A	2.6884	.2276	.5140	.156	.276	.565	
	C	2.6883	.1616	.4015	.113	.215	.520	.543

Ratio: 1 KCl to 2 NaCl Temp. 25°

0.1	A	0.8964	0.1259	0.1100	0.259	0.176	1.46	
	C	0.8967	.1170	.1023	.241	.165	1.46	1.46
0.2	A	1.7822	.2706	.1991	.279	.162	1.63	
	C	1.7831	.1878	.1991	.195	.162	1.18	1.40
0.2	A	1.6671	.1794	.2359	.199	.208	0.97	
	C	1.6668	.2193	.1978	.243	.171	1.42	1.20
0.4	A	2.0823	.2470	.2284	.219	.153	(1.43)	
	C	2.0836	.2094	.2513	.185	.174	1.07	1.07
0.8	A	2.2605	.2804	.3074	.229	.196	1.17	
	C	2.2609	.2150	.2313	.175	.148	1.18	1.18
1.6	A	2.4584	.3028	.2985	.228	.175	1.29	
	C	2.4590	.3182	.3127	.238	.184	1.30	1.30

Ratio: 1 KCl to 3 NaCl Temp. 25°

0.1	A	0.8731	0.1298	0.0763	0.275	0.127	2.15	
	C	0.8738	.1252	.0765	.266	.128	2.08	2.12
0.2	A	1.6331	.2352	.1661	.266	.147	1.81	
	C	1.6333	.2336	.1502	.262	.133	1.98	1.90
0.2	A	1.6218	.2393	.1610	.273	.135	2.02	
	C	1.6218	.2299	.1623	.263	.145	1.81	1.91
0.4	A	2.0854	.2512	.2145	.222	.148	1.49	
	C	2.0854	.2725	.2055	.241	.143	1.69	1.59
0.8	A	2.2679	.2677	.1881	.218	.120	1.81	
	C	2.2686	.1501	.1098	.122	.070	1.75	1.81
1.6	A	2.4049	.3810	.1977	.293	.119	2.46	
	C	2.4030	.3402	.1878	.262	.113	2.32	2.39

a change of ratio of the salts in the mixture from 3 KCl : 1 NaCl to a ratio of 1 KCl : 3 NaCl. The first column in the table indicates the total concentration in terms of normality; the second, headed "Pole" indicates the anode or cathode portion; the third, fourth and fifth, the weight of silver in the coulometers, and of sodium and potassium transferred; the sixth and seventh the transference numbers of the sodium and potassium, respectively; the eighth gives the ratio of the transference numbers as calculated from Cols. 7 and 8; and the ninth gives the average of the anode and cathode transference ratio for each concentration.

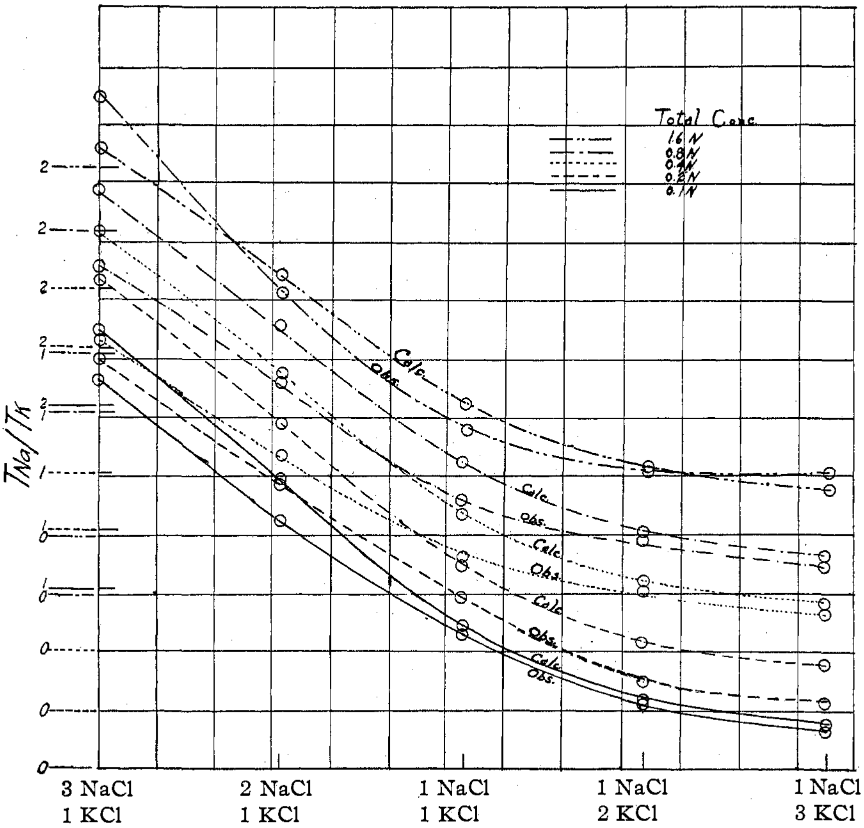

Fig. 1.—Variation between the curves obtained by plotting the observed and calculated values for the transference number ratio (T_{Na}/T_K) against the salt concentration ratio. To facilitate placing all the curves in one figure the zero point on the vertical axis has been shifted one division for each given total concentration.

Table II shows the calculated transference ratios for the sodium and potassium and the comparison with the observed values taken from the tenth column of Table I. As it was not possible to obtain data for the conductance of the salts, at all the concentrations at 25°, these values were obtained by interpolation of conductance data of Kohlrausch[8] after it had been corrected to this temperature.

TABLE II

THE CALCULATED RATIOS OF THE TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM IN THE MIXED CHLORIDE SOLUTIONS AS COMPARED WITH THE OBSERVED VALUES AT 25°

Total Conc.	3 NaCl 1 KCl		2 NaCl KCl		1 NaCl 1 KCl		1 NaCl 2 KCl		1 NaCl 3 KCl	
N	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
0	2.397	..	1.598	..	0.799	..	0.3995	...	0.266	...
0.1	2.352	2.12	1.568	1.46	.784	0.749	.392	0.389	.261	0.235
0.2	2.310	1.90	1.540	1.30	.770	.640	.385	.150	.256	.035
0.4	2.270	1.59	1.510	1.07	.756	.510	.378	.339	.252	.208
0.8	2.220	1.81	1.480	1.18	.740	.540	.370	.343	.247	.180
1.6	2.100	2.39	1.400	1.30	.702	.543	.351	.370	.234	.315

The graphical representations of these data are shown in Figs. 1 and 2. In Fig. 1, the salt concentration ratios, at the indicated total concentrations, are plotted against the ratios of the transference numbers of the sodium and potassium. These plots also show the deviation of the calculated and observed values as obtained from the tables.

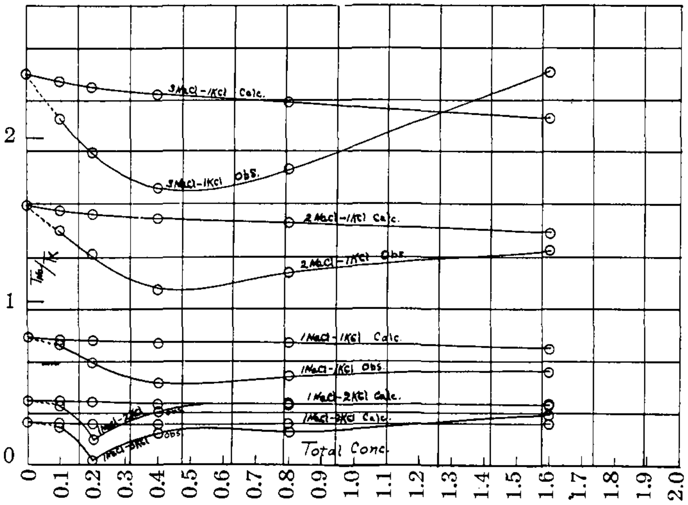

Fig. 2.—The curves obtained by plotting the observed and calculated values for the transference number ratio against total salt concentration.

Fig. 2 is the graphical representation of the deviation of the observed and calculated transference ratio with increase of total concentration, the concentration ratio being indicated on each curve.

Conductivity.—Table III gives the equivalent conductance values

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[8] Landolt-Börnstein-Meyerhoffer, "Tabellen," *Physikalisch-Chemische Tabellen*, 3rd ed., Julius Springer, 1905.

TABLE III

OBSERVED EQUIVALENT CONDUCTANCE OF THE MIXED CHLORIDE SOLUTIONS AT 25°

Total Conc. N	Ratio KCl	NaCl	Equiv. cond.[a]	Total conc. N	Ratio KCl	NaCl	Equid. cond.[a]
0.1	3	1	124.210	0.8	3	1	104.998
	2	1	121.750		2	1	103.288
	1	1	118.760		1	1	98.316
	1	2	114.530		1	2	94.369
	1	3	113.570		1	3	92.921
0.2	3	1	116.320	1.6	3	1	97.550
	2	1	113.990		2	1	95.550
	1	1	110.820		1	1	91.031
	1	2	106.890		1	2	86.518
	1	3	105.090		1	3	84.222
0.4	3	1	110.635				
	2	1	108.690				
	1	1	104.615				
	1	2	101.305				
	1	3	99.615				

[a] Equivalent conductance is equal to the specific conductance ($\times 10^2$) divided by total concentration given in Col. 1.

for the same solutions as used for the transference numbers, and is self explanatory. These same values are plotted in Fig. 3 and 4, Fig. 3 showing concentration against equivalent conductance and Fig. 4 showing total concentration against equivalent conductance.

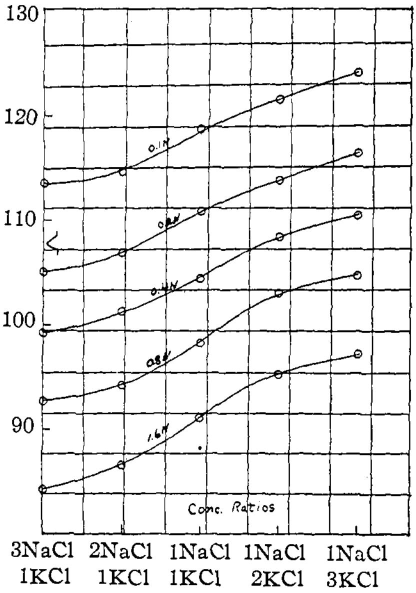

Fig. 3.—The change of equivalent conductance with change of salt concentration ratio and with various total salt concentrations.

Ion Mobilities.—Table IV shows the values of the mobilities of ions times the Faraday as calculated from the transference and equivalent conductance data given in Tables I to III, by use of Equation 3. For purposes of comparison the mobilities at any given total salt concentration are grouped together.

In Figs. 5, 6 and 7 the mobilities of the sodium, potassium and chlorine, respectively, have been plotted against concentration ratios. Fig. 8 shows the relationship of the computed concentration of the sodium and potassium ions, in the solution of total salt concentration indicated on the curve, and the mobilities of these ions in the same solution.

TABLE IV

MOBILITIES OF THE IONS IN THE MIXED CHLORIDE SOLUTIONS, AT 25°

Ratio KCl	NaCl	T_{Na}	T_{K}		$U_{\text{Na}}F$	$U_{\text{K}}F$	$U_{\text{Cl}}F$
			Total conc. 0.1 N				
3	1	0.084	0.361	124.210	10.43	44.84	68.94
2	1	.127	.328	121.750	14.46	39.93	67.36
1	1	.169	.226	118.760	20.07	26.83	71.85
1	2	.250	.170	114.530	28.06	19.47	67.00
1	3	.270	.127	113.570	30.66	14.48	68.43
			Total conc. 0.2 N				
3	1	.005	.430	116.320	0.58	51.18	64.56
2	1	.052	.395	113.990	5.93	45.03	63.03
1	1	.157	.250	110.820	17.40	27.70	65.73
1	2	.240	.165	106.890	25.68	17.64	63.57
1	3	.265	.138	105.090	27.85	14.50	62.71
			Total conc. 0.4 N				
3	1	.073	.355	110.635	8.08	39.27	57.64
2	1	.110	.330	108.690	11.96	35.88	60.85
1	1	.140	.257	104.615	14.65	26.89	63.07
1	2	.204	.163	101.305	20.67	16.51	64.12
1	3	.233	.144	99.615	23.21	13.34	63.06
			Total conc. 0.8 N				
3	1	.060	.350	104.998	6.30	36.75	60.95
2	1	.110	.318	103.228	11.35	39.83	59.04
1	1	.150	.257	98.316	14.75	25.27	58.30
1	2	.202	.170	94.369	20.07	15.94	58.36
1	3	.215	.095	92.921	19.98	8.83	64.11
			Total conc. 1.6 N				
3	1	.110	.322	97.500	10.73	31.41	55.41
2	1	.130	.305	95.550	12.68	29.14	53.73
1	1	.135	.245	91.031	12.30	22.30	56.43
1	2	.230	.180	86.518	19.89	15.57	51.06
1	3	.278	.115	84.222	23.40	9.68	51.05

Discussion

From a study of the tables and curves here presented the first fact that presents itself is that the solutions with which we are dealing are very complex. It would also seem from the data given that we could not draw definite conclusions, which is true, but there are certain facts presented that are of extreme importance. From the results given a rather high percentage error is shown which, however, cannot be avoided, owing to the nature of the indirect method of determination and calculation necessary in such an experiment. The results, however, are not the less significant, as the actual variations are far greater than experimental error. This is perhaps better shown by Fig. 1 where the circles indicating points on the determined curves will in each case contain the maximum and minimum determined value for that point.

In Table I and Fig. 1, it will be noted that the transference ratio does not vary in direct proportion to the variation in the concentration ratio.

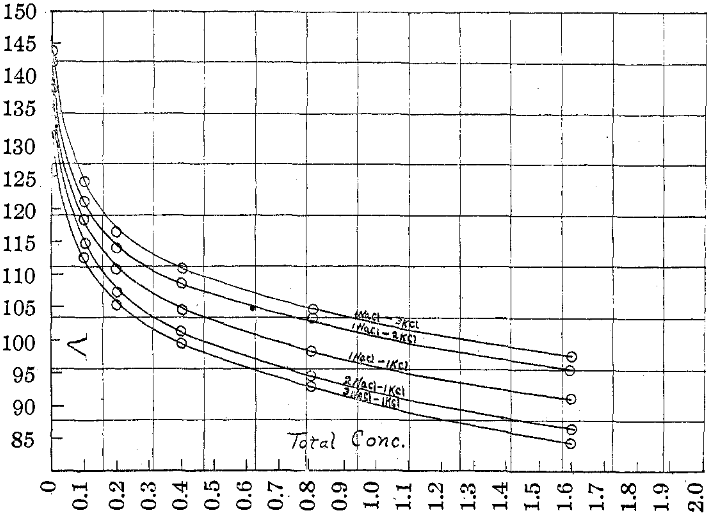

Fig. 4.—The change of conductance with increase in total salt concentration at various salt concentration ratios.

In all concentrations with the exception of 1.6 *N* (Fig. 1) the deviation decreases with increase of the proportion of potassium chloride in the mixture. Also in Table II and Fig. 2 attention is called to the fact that

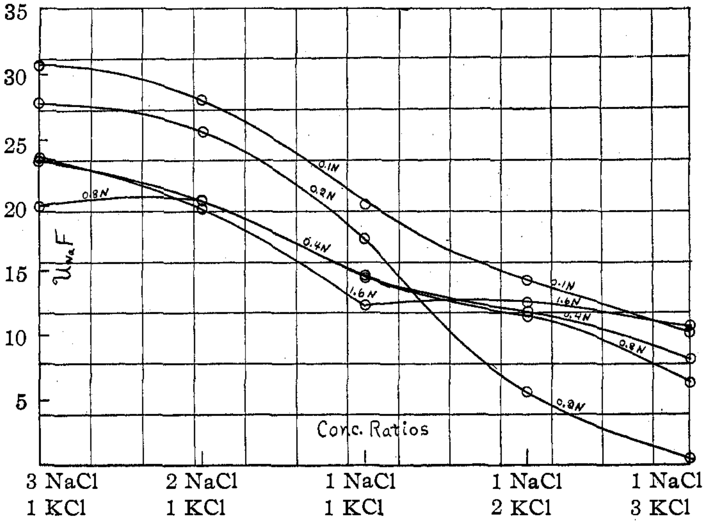

Fig. 5.—The change of mobility of the sodium in the solution with change of salt concentration ratio and at various total concentrations.

at each concentration ratio the transference ratio decreases with increase in total salt concentration to a point between 0.2 N and 0.4 N total concentration and then either remains constant or increases. In other words, increase of potassium ratio in the solution tends to cause the solution to act more nearly as calculated from conductivity data on the pure solutions; however, the increase of total concentration above 0.2 N to 0.4 N seems to have the same effect.

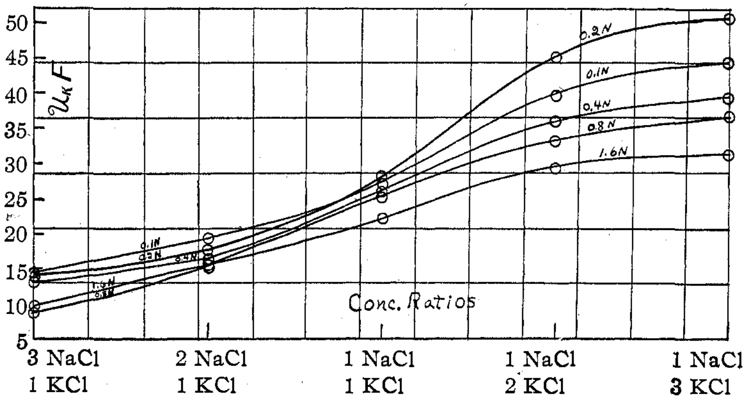

Fig. 6.—The change of mobility of the potassium in the solution with change of salt concentration ratio and at various total concentrations.

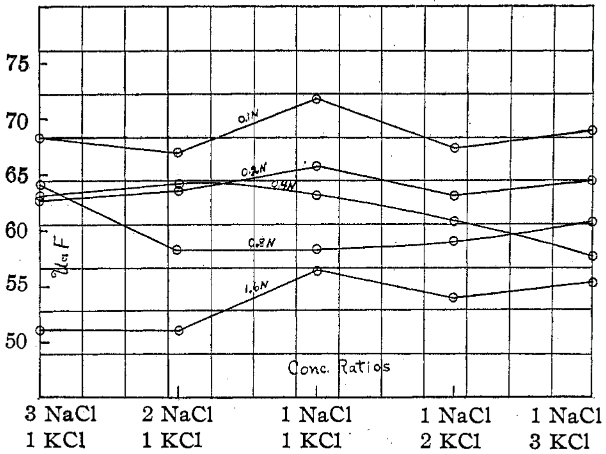

Fig. 7.—The change of the mobility of the chlorine in the solution with change of salt concentration ratio at various total concentrations.

This corresponds to the data obtained by Smith and his students,[4,5] whereby they found that the sodium ion increased more rapidly than the potassium ion in solutions above 0.2 N.

From these facts we may say, then, that the sodium by some means gains a "transference advantage" over the potassium. If we consider a set of equations such as the following,

$$KCl \rightleftharpoons K^+ + Cl^- \qquad NaCl \rightleftharpoons Na^+ + Cl^-$$
$$KCl + Cl^- \rightleftharpoons (KCl_2)^- \qquad NaCl + Cl^- \rightleftharpoons (NaCl_2)^-$$

we then have the simplest possibilities of complex formation. This complex formation, however, may increase to a greater extent and give rise to ions such as $(Na_xCl_y)^{p-}$ or $(K_mCl_n)^{q-}$ and all the intermediates as well as similarly formed, positively charged complexes. Dissociation of such complexes may vary either with change of total concentration or with varying ratios of the salts. We should then have a series of both negatively and positively charged particles proceeding in each direction, on passage of a current, which would give rise to apparently anomalous results as compared with conductivity data. Such possibilities will nevertheless explain the transference results.

We must, however, consider a second possibility of complex formation, that is known to exist, namely, hydration. Washburn[9] has found that the sodium ion is more highly hydrated in solution than the potassium ion, that is, it forms complexes with water more readily. This would of course cause the sodium ion to lose in "transference advantage," for it would necessarily become more voluminous and move more slowly through the solution. This, then, might account for the decrease in the transference ratio to the point of break in the curves at 0.2 to 0.4 N but probably not for the reversal above this point. Thus far then we might conclude that hydration is the interfering factor.

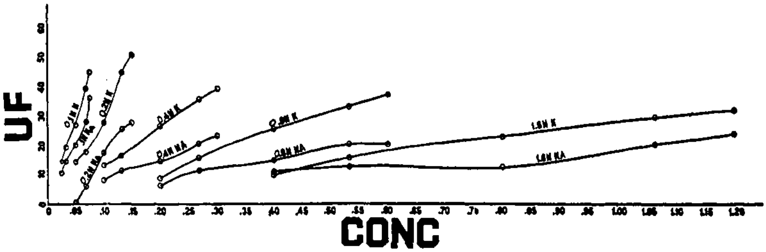

Fig. 8.—The change of mobility of the indicated ion constituent with increase of concentration. Each curve indicates the given ion constituent and its concentration in solution of total concentration shown.

In Fig. 2 the curve representing the observed values for the ratio 1NaCl: 3KCl becomes almost zero. In other words the transference number of the sodium ion is almost zero as shown in Table I. Zero transference of any ion in solution would indicate that that ion was standing still, which is, of course, absurd as long as we assume that it carries an electric charge. What then must we assume to take place to produce such results? The sodium ion must be moving in both directions at nearly the same rate.

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[9] Ref. 7, p. 288.

In order that this condition may exist we must assume that it is contained in the negatively charged particle as well as the positively charged one, for then and only then can it move in both directions. This condition can be fulfilled by complex formation between the salts and their ions but not by hydration.

By studying Table III and Figs. 3 and 4 it is noted that the conductivities for these same solutions are regular at all concentrations. This is important for it indicates, on the assumption that complex formation is the cause of the irregularities of the transference-ratio curves, that the complex ions formed are of such nature that their average mobility does not affect the resistance of the solution.

In Fig. 4 it is shown that the mobility of the sodium ion approaches zero in a solution of 3KCl to 1NaCl and a total concentration of 0.2 *N*. This, of course, corresponds to the zero transference previously considered. Let us further consider this fact in the light of the theory of Ghosh,[6] that is, of total dissociation. One of two conditions would give rise to the apparent immobility of the sodium ion; first, that it is in an electrically neutral molecule, which of course would mean that it was not at all dissociated; second, that it is in a negative complex to an extent that it moves in both directions at the same speed. Either of these conditions absolutely excludes complete dissociation, for in either case the sodium must be attached to something that has neutralized or overcome its charge.

Figs. 6, 7 and 8, showing curves for the change of mobilities with change in concentration, throw a little more light on the disturbing factors in the solution. It is seen that the mobility changes for the potassium and chlorine are more or less regular, while those for the sodium are decidedly irregular. This would indicate that the sodium was the ion causing the disturbance.

Fig. 8 is interesting in itself in that it shows that when computed concentrations of the ions in the mixtures for any given concentration are plotted against their mobilities the curves are very regular.

Summary

1. The transference numbers of sodium and potassium and the transference ratios have been determined in mixtures of the chlorides of these two alkali metals in solutions from 0.1 *N* to 1.6 *N*. The ratio of the salts has been varied from 3KCl:1NaCl to 1KCl:3NaCl.
2. The equivalent conductances have also been determined for these same mixed solutions.
3. The mobilities of the ions have been calculated from the transference numbers and the equivalent conductances for the different solutions.
4. The results show that the solutions are extremely complex and that they are not in accord with the hypothesis of complete dissociation.

5. The mobility of the sodium ion at a total concentration of 0.2 *N* and a ratio of 3KCl:1NaCl has been shown to be practically zero.
6. The deviations between the calculated values and the experimental values of the transference ratios are not due to hydration of ions alone but must be due also to complex formations in solution.
7. The results agree with the work of Smith and Ball[4] and Smith and Wells[5] in which they found that the sodium ion fraction increases with increase in total concentration above 0.2 *N*. Below this concentration the sodium decreases with respect to the potassium.

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THE DECOMPOSITION OF POTASSIUM PERCHLORATE AND ITS CATALYSIS BY FERRIC OXIDE

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Introduction

Previous investigations of the decomposition of potassium perchlorate have been made but only incidentally to the study of the decomposition of potassium chlorate. The meagerness of the available data regarding perchlorate decomposition is the occasion for the present study.

Scobai[2] has found that the loss in weight of potassium perchlorate heated to 395° was negligible. Likewise, McLeod[3] noted that even in the presence of manganese dioxide as catalyst potassium perchlorate did not decompose at the boiling point of mercury, but Frankland and Dingwald[4] reported a loss of 3% by weight on heating it for 56 hours in sulfur vapor.

The presence of chlorate in residues of moderately heated perchlorate was observed by Millon,[5] Teed,[6] and Frankland and Dingwald.[4] The latter claimed to have effected its separation by fractional crystallization. Scobai also occasionally found traces of chlorate. It is noteworthy that none of these investigators has found chlorate in perchlorate residues when manganese dioxide or other catalysts were used.

In the present study, the speed of the decomposition of potassium perchlorate by heat has been investigated both without and with a catalyst, *ferric oxide*, which is preferable to the more commonly employed manganese dioxide because it is stable and can be obtained in a state of standard purity as ferric oxide.

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[1] Abstract of one section of a thesis submitted to the Graduate Faculty of the University of Cincinnati by Carl E. Otto, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Scobai, *Z. physik. Chem.*, **44**, 319 (1903).

[3] McLeod, *J. Chem. Soc.*, **57**, 272 (1890).

[4] Frankland and Dingwald, *ibid.*, **51**, 274 (1887).

[5] Millon, *Ann. chim. phys.*, [3] **7**, 298 (1843).

[6] Teed, *J. Chem. Soc.*, **51**, 283 (1887); *Abst. Proc. Chem. Soc.*, **1**, 141 (1885).