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TRANSFERENCE EXPERIMENTS WITH MIXTURES OF POTASSIUM CHLORIDE AND SULFATE IN AQUEOUS SOLUTION.

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1. Plan of the Investigation.—The object of this investigation was to study further, by means of transference experiments, the validity of the empirical principle which seems to determin the conductance and ionization of the separate salts in mixtures of them in aqueous solution. This principle, first stated and tested with reference to uniunivalent salts with a common ion by Arrhenius,[1] tested further by the conductivity investigations of MacGregor, McIntosh, Archibald, and McKay,[2] and shown by Noyes[3] on the basis of existing data to apply also to unibivalent salts, even though the mass-action law require a very different effect, may be stated as follows: In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it has when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture.

The previous tests of this principle have, however, only shown that the sum of the conductances of the two salts in the mixture is substantially equal to that calculated by the principle; and they do not exclude the possibility, at any rate in a mixture of a uniuni- and a unibivalent salt, that there may be a compensation resulting from the fact that one salt is more ionized, and the other less ionized, than the principle requires. Transference experiments, however, should enable the conductance of the ions in the mixture to be separately determined. Thus, in a mixture of potassium chloride and sulfate, the transference numbers T_{Cl} and T_{SO_4} for the chloride and sulfate (*i. e.*, the number of equivalents of Cl or SO_4 transferred per faraday of electricity) are evidently given by the expressions:

$$T_{Cl} = \frac{C_{Cl^-}\Lambda_{Cl^-}}{C_{Cl^-}\Lambda_{Cl^-} + C_{SO_4^=}\Lambda_{SO_4^=} + C_{K^+}\Lambda_{K^+}} \text{ and}$$

$$T_{SO_4} = \frac{C_{SO_4^=}\Lambda_{SO_4^=}}{C_{Cl^-}\Lambda_{Cl^-} + C_{SO_4^=}\Lambda_{SO_4^=} + C_{K^+}\Lambda_{K^+}}$$

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[1] *Z. physik. Chem.*, 2, 285 (1888); 31, 218 (1899).

[2] *Trans. Nova Scotia Inst. Science*, 9 and 10 (1895–1899).

[3] *Z. physik. Chem.*, 52, 635 (1905).

where C_{Cl^-}, $C_{SO}=$, and C_{K^+} represent the equivalent concentrations, and Λ_{Cl^-}, $\Lambda_{SO_4^=}$ and Λ_{K^+} the equivalent conductances, in the mixture of the ions represented by the subscripts. We have therefore for the ratio of the transference numbers:

$$\frac{T_{Cl}}{T_{SO_4}} = \frac{C_{Cl^-}\Lambda_{Cl^-}}{C_{SO_4^=}\Lambda_{SO_4^=}} = \frac{C_1\gamma_1\Lambda_{Cl^-}}{C_2\gamma_2\Lambda_{SO_4^=}},$$

where C_1 and γ_1 represent the equivalent concentration and ionization of potassium chloride, and C_2 and γ_2 the corresponding values for potassium sulfate. Determinations of the relative quantities of chloride and sulfate transferred will therefore give the ratio of the specific conductances ($C\Lambda$) of the two ions. Moreover, if their equivalent conductances be assumed known (for example, equal to those known to be true at zero concentration) the results will show the ratio of the ionization of the two salts in the mixture.

With these purposes in view this investigation was carried out. It was undertaken at the suggestion of Prof. A. A. Noyes; and I desire to express my indebtedness to him and also to Prof. W. C. Bray, of this laboratory, for the assistance given me in connection with the experimental work and in the preparation of this article for publication.

2. Description of the Apparatus and of the Transference Experiments.—The apparatus employed in the final experiments was that previously used in this laboratory by Dr. E. W. Washburn and described by him in THIS JOURNAL, **31**, 330 (1909). It is represented in Fig. 1.

The width of the tubes was about 2 cm. and the length between the anode and cathode was about 1 meter. One tube was fitted to the other at D by means of a ground glass joint. Each electrode compartment could be separated from the middle part of the apparatus by means of a large glass stopcock, whose bore was large enough not to make a constriction in the tube.

The anode A consisted of a coil made of about ten meters of fine silver wire. The cathode C consisted of a silver plate which had been chloridized on the surface by electrolysis, and was held in place by a stout silver wire welded to it and passing through a rubber stopper; on the top of the plate were placed several grams of freshly precipitated silver chloride which had been well washed, first with pure water, and finally with the solution under investigation. These electrodes served to prevent the separation of oxygen and hydrogen at the electrodes and to provide for the formation of silver chloride alone at the anode and its reduction to silver at the cathode. Hence the total result of the passage of a current of electricity was an increase at the cathode in the concentrations of K and Cl and a decrease in that of SO_4, and the opposit changes at the anode. The solution at the anode therefore grows lighter and that at the cathode heavier; hence to prevent stirring the anode was placed at the top of the open arm of the U-tube and the cathode at the bottom of the straight tube.

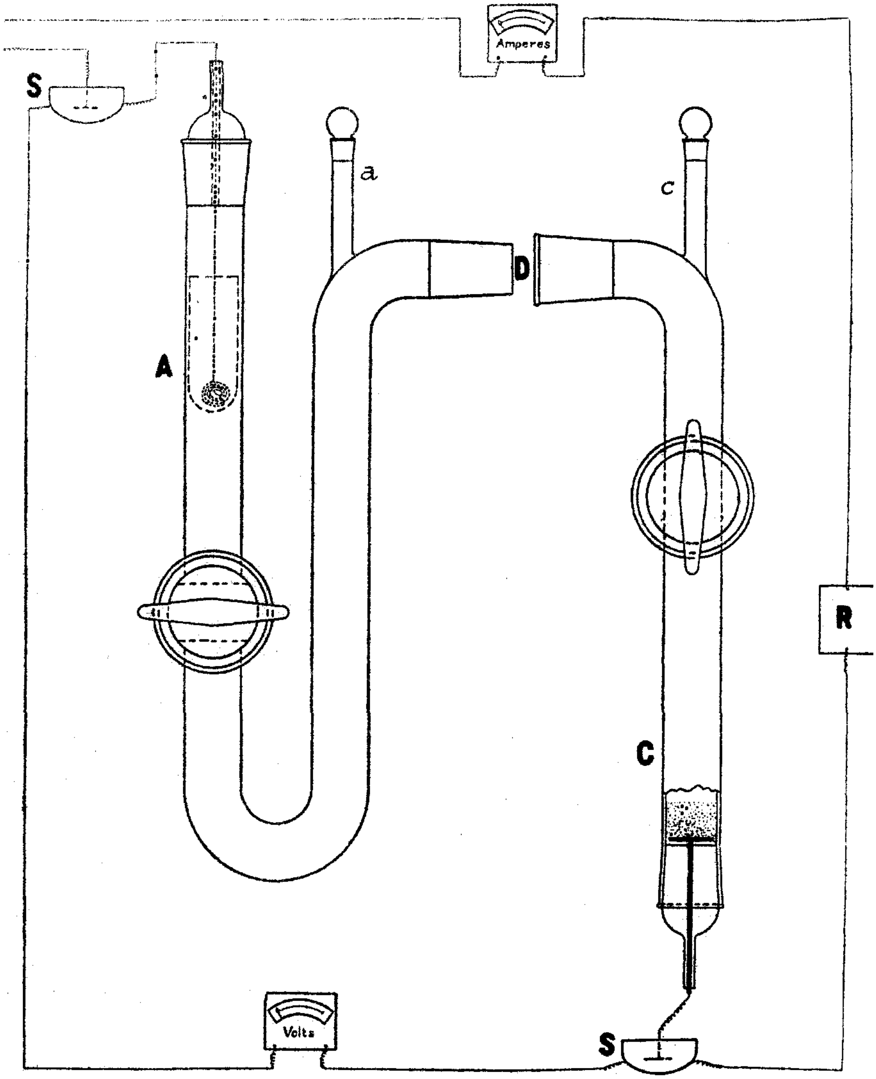

Fig. 1.

The coulometers S, S used consisted of platinum dishes partially filled with a 15 per cent. silver nitrate solution, just beneath the surface of which was placed a horizontal silver plate (to serve as anode) which was wrapped with filter paper, and supported by a silver rod riveted through it. One coulometer was placed on each side of the apparatus. In this way any leakage of current in the apparatus itself could be at once detected.

As it was found that there was likely to be mixing of the electrode portion with the middle portion, especially on the cathode side, a piece of coarse-mesh silk cloth was placed in each stopcock, being held in place by a very thin ring of hard rubber. The ring was placed in that part of the stopcock nearer the electrode, so that, even if there were any selective transmission of the ions or any electrical endosmose (which in view of the coarse mesh was very improbable), the experiment would not be vitiated, inasmuch as the electrode portion was taken so as to extend from the electrode to the side of the stopcock farther from it.

The method of procedure was as follows: After filling the tubes with the solution, the ground joint and the glass stoppers were painted with paraffin, and the electrode ends were covered with wide rubber tubing, through which the leads passed. The whole apparatus, rigidly supported, was then immersed in a large thermostat at 18°, to such a depth that the middle horizontal part of the apparatus was entirely covered. After about twenty minutes when all temperature differences had become equalized, the electrodes were connected in series with a lamp, an ammeter, and the two coulometers, between terminals of 110 volts potential difference. The ammeter was in circuit for convenience only, as the coulometers were depended upon wholly for measurement of the current. After the current had been passed for a suitable time, it was cut off and the stoppers were turned through 90°, thereby completely separating the electrode compartments from the middle portions. The three middle portions were then removed by a pipet through the small vertical arms.

The electrode portions were next removed from the apparatus. For this purpose the whole apparatus was taken out of the thermostat, the stopcocks were opened, and the two tubes separated, the openings being closed by rubber stoppers. The anode lead was cut and the coil of wire allowed to drop down into the solution, after which all the stoppers were well paraffined to prevent leakage, and each tube well shaken so as to insure thorough mixing. In some cases it was necessary to introduce a piece of glass tubing, in order to break the cloth diaphragm. The tubes were then cleaned thoroughly on the outside with alcohol and ether, and weighed (without the rubber stoppers). The solution was then poured and rinsed into a glass-stoppered flask, being filtered to retain the silver chloride and silver particles, which were subsequently weighed. The tubes were then cleaned inside with water, alcohol, and ether, and weighed again together with the electrode. From the difference in the weights the weight of the solution was obtained, allowance being made for the weight of the silver chloride collected on the filter, the silver anode and the glass rod. A known portion of the solution was then evaporated and analyzed as described below.

The middle portions were not analyzed by the same time-consuming procedure, and it seemed unnecessary to do so. A method of titration was employed instead, comparative determinations being made with the original and electrolyzed solution. This consisted in adding a known weight of a standard solution of silver nitrate, using such a quantity that a very small excess of silver was left in the mixture. This mixture was then warmed and filtered through a Gooch filter into a flask, where the filtrate was titrated with a very dilute potassium thiocyanate solution, using ferric alum as an indicator. The final titration in the case of the middle portions was carried to the same shade of color as in the case of the original solution, thus enabling small differences in the chloride content to be detected. Each portion was titrated in duplicate.

When any difference was found to exist between the chloride content in the middle portions and in the original solution, mixing was assumed to have occurred, and the experiment was discontinued. When the chloride content was found to be the same, however, the analyses of the electrode portions were proceeded with, on the assumption that no mixing had occurred.

Three experiments, judging from the constancy of the middle portions and other external evidence, were successfully completed, though in one of these the cathode portion was not analyzed, owing to an accident. Unfortunately the work had to be broken off before more experiments could be made. It is believed, however, that the results obtained are sufficient to afford reliable conclusions.

3. Preparation of the Solution.—The potassium chloride and sulfate used were obtained from Eimer & Amend as being of the highest grade. The samples were crystallized twice from hot water, and were ignited in large platinum dishes. About ten liters of solution were made up at one time by weighing out the proper amount of the salts and adding the necessary weight of water.

4. Method of Analysis.—The method of analysis employed consisted in evaporating the portions of solution to dryness and heating the residue to about 500° to get the total weight of salt, and then determining the chloride in the residue by precipitating it with silver nitrate and weighing the silver chloride in Gooch crucibles. After much preliminary experimenting, which showed the impracticability of making the evaporation in a platinum dish (owing chiefly to the creeping of the salt), the following process was adopted.

Two round-bottomed 250 cc. flasks of Jena glass were well steamed out in order to get rid of the more soluble portions of the glass. They were then washed with soap and water and finally with distilled water, and were heated in an electric furnace over night to a temperature of about 500°. They were then removed, a little dry air being blown into them to displace any moist air that might have remained, and they were hung inside a bell jar containing calcium chloride by means of platinum wires which were attached to the necks of the flasks. After being in the desiccator for 4 hours they were weighed, one of the flasks serving as a counterpoise. The whole treatment (except the steaming) was then repeated until two consecutive weighings differed by not more than 0.2 mg.l but the flasks seldom had to be weighed more than twice. 70 or 80 grams of solution were then introduced into one of the flasks, which was placed in a bath of lard. The bath was kept slightly above 100° until the solution had evaporated, then the temperature was gradually raised to about 250° in order to dry the residue thoroughly and so prevent spattering, which otherwise occurred when the flasks were placed in the furnace. The flasks were then lifted out of the lard, allowed to drain, and washed first with benzine and then with soap and water as before. They were then heated in the electric furnace to 500°, and treated otherwise like the empty flasks, consecutive weighings being always made until they were practically identical. At first the counterpoise flask was subjected to the same treatment as the other, but afterwards, as this was found to be unnecessary, it was left in the desiccator during the evaporation.

This method was found by trial experiments to give very accurate results, the maximum error in the weights being about 0.4 mg., which corresponded to a percentage error of less than 0.02 per cent. of the weight of residue after evaporation.[1]

In order to determin the chloride present, the residue from the evaporation was dissolved, the solution was filtered and precipitated with silver nitrate, and the resulting precipitate collected in a platinum Gooch crucible, dried, and weighed. All the analytical precautions advised by Richards[2] in his work on the "Revision of the Atomic Weights of Sodium and Chlorine" were observed.

5. The Transference Data and Calculated Transference Numbers.—The following tables contain the experimental data. All weights were reduced to the vacuum standard. The atomic weights employed are O = 16.00, Ag = 107.88, Cl = 35.46, K = 39.10, S = 32.07.

Table I contains analytical data for the original solutions, of which

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[1] The results of one of the trial experiments were as follows: 2.9658 grams of a mixture of potassium chloride and potassium sulfate were dissolved in about 100 cc. of water, and the solution was evaporated in a weighed flask as just described. The difference in the weights of the flask and the counterpoising flask before evaporation, as determined successively, was 10.6307, 10.6303, 10.6303, and after evaporation, 13.5956, 13.5953, 13.5963, the respective differences being 2.9649, 2.9650, 2.9660. The most probable weight is the last; this differs from the weight of salt started with by only 0.2 mg. or less than 0.01 per cent. If the first two weights were taken the error would be about 0.03 per cent.

[2] *Carnegie Institution Publications*, 69, 17 (1907); THIS JOURNAL, 27, 492.

two were used in the three transference experiments that were successfully completed.

TABLE I.—DATA RELATING TO THE COMPOSITION OF THE ORIGINAL SOLUTIONS.

	Solution used in	
	Expts. I and II.	Expt. III.
Weight of solution analyzed	100.20	101.80
Weight AgCl found	2.8222	2.8704
Corresponding weight KCl	1.4680	1.4931
Weight KCl + K_2SO_4 found	3.1836	3.2380
Weight K_2SO_4 (by difference)	1.7156	1.7449
Weight water (by difference)	97.016	98.562
Density 18°/18°	1.0232	1.0231
Equiv. KCl per liter at 18°	0.2008	0.2010
Equiv. K_2SO_4 per liter at 18°	0.2008	0.2010
Specific conductance at 18°	0.03647	0.03658

Table II contains the data of the transference experiments and the values of the transference numbers calculated from them. All the numbers in the table (except those in the last two rows) represent weights in grams corrected for air buoyancy. The temperature during the electrolysis was 18°. In experiment I the analysis of the cathode portion was not completed. The middle portions remained in all these experiments substantially unchanged.[1]

TABLE II.—DATA OF THE TRANSFERENCE EXPERIMENTS AND CALCULATED VALUES OF THE TRANSFERENCE NUMBERS.

	Expt. I.	Expt. II.		Expt. III.	
	Anode.	Anode.	Cathode.	Anode.	Cathode.
Ag in coulometer	0.6550	0.6523	0.6523	0.8773	0.8773
Whole portion	73.44	88.81	116.66	87.54	86.79
Portion analyzed	68.47	81.90	108.10	82.57	75.99
Residue (KCl + K_2SO_4)	1.9923	2.4080	3.6257	2.3745	2.6564
AgCl obtained	1.3600	1.7429	3.6078	1.5535	2.8615
KCl in whole portion, final	0.7588	0.9831	2.0253	0.8567	1.7000
KCl in whole portion, original	1.0789	1.3043	1.7061	1.2880	1.2688
KCl in whole portion, difference	—0.3201	—0.3212	+0.3192	—0.4313	+0.4312
KCl equiv. to Ag. in coulometer	0.4527	0.4508	0.4508	0.6064	0.6064
K_2SO_4 in whole portion, final	1.3782	1.6281	1.8875	1.6607	1.3339
K_2SO_4 in whole portion, original	1.2609	1.5243	1.9939	1.5052	1.4828
K_2SO_4 in whole portion, difference	+0.1173	+0.1038	—0.1064	+0.1555	—0.1489
Transference number for Cl	0.2929	0.2875	0.2919	0.2887	0.2888
Transference number for SO_4	0.2217	0.1970	0.2019	0.2194	0.2101

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[1] This is shown by the following values, which represent the percentage difference between the quantities of silver nitrate solution consumed in the titration of the middle portion and of an equal weight of the original solution. M_C denotes the middle portion adjoining the cathode portion, and M_A the middle portion adjoining the anode portion.

	Expt. I.	Expt. II.	Expt. III.
M_C	....	+0.01 per cent.	+0.05 per cent.
M_A	— 0.06 per cent.	+0.10 per cent.	—0.04 per cent.

6. *Accuracy of the Results.*—An inspection of the last two rows of Table II shows that the five values obtained for the transference number of the chloride ion agree fairly satisfactorily. The mean of these five values is 0.2900, the average deviation of the separate value from this mean being 0.0020; or omitting the first value, which is probably less reliable, the mean is 0.2892, and the average deviation of the separate values from this is 0.0014. As an expression of the best value and its probable accuracy, 0.289 ± 0.001 will therefore be adopted. The values for the sulfate ion, which it may be recalled were obtained not directly, but by difference, are so discordant as to be of little significance[1]—a fact for which there is no obvious explanation. Therefore only the values for the chloride ion will be considered in the following discussion.

7. *Relative Conductance and Ionization of the Two Salts in the Mixture Calculated from the Transference Values.*—If we make the assumption that the *relative* mobilities of the potassium and chloride ions are the same in the mixture of the two salts as in a dilute solution of potassium chloride, we may calculate the fraction of the electricity transported by the ionized portion of the potassium chloride simply by dividing the transference number (0.289 ± 0.001) for the chloride ion in the mixture by that (0.504)[2] for the chloride ion in potassium chloride. We thus obtain $T_{KCl} = 0.573$ for the fraction of the electricity carried by the ions of the potassium chloride; and by subtracting this from unity, we obtain $T_{K_2SO_4} = 0.427$ for the fraction of the electricity carried by the ions of the potassium sulfate.[3] By multiplying these transference numbers by the specific conductance (L) of the mixture (0.03652, see Table I), the (partial) specific conductance of the two separate salts in the mixture are found to be $L_{KCl} = 0.02093$ and $L_{K_2SO_4} = 0.01559$. The ratio of these two partial conductances or of the two transference numbers is *1.342*.[4] If we divide this ratio by the ratio of the values of the

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[1] Compare the foot-note on the following page.

[2] Bein, *Z. physik. Chem.*, **27**, 50 (1898). Jahn and Bogdan, *Ibid.*, **37**, 684 (1901). Cf. Noyes and Sammet, THIS JOURNAL, **24**, 965 (1902).

[3] The fraction of the electricity carried by the sulfate ion may be calculated from this quantity by multiplying it by the transference number for pure potassium sulfate. This fraction becomes 0.220, if the transference number be taken as 0.514 in correspondence with the conductances of the ions at zero concentration. It becomes 0.217, if the transference number 0.507 found for a 0.2 normal solution be employed (Noyes, THIS JOURNAL, 23, 52 (1901)). These values will be seen to agree with two of the five experimental values recorded in the last row of Table II.

[4] The error in this ratio corresponding to the error ±0.001 in the transference value 0.289 is ±0.011. A larger and more uncertain error, however, probably arises from that in the assumed transference number 0.504. If it be assumed that, owing to hydration of the ions in the mixture or to any other cause, this value is in error by ±0.005, the ratio 1.342 would be in error from this cause by ∓0.027.

equivalent conductances of the two salts at zero concentration,[1] we shall evidently obtain the ratio of the ionization of two salts in the mixture. That is:

$$\frac{\gamma_{\mathrm{KCl}}}{\gamma_{\mathrm{K_2SO_4}}} = \frac{L_{\mathrm{KCl}}/\Lambda_{0\,\mathrm{KCl}}}{L_{\mathrm{K_2SO_4}}/\Lambda_{0\,\mathrm{K_2SO_4}}} = \frac{0.573/130.1}{0.427/133.0} = 1.372$$

8. Relative Conductance and Ionization of the Two Salts in the Mixture Calculated from their Conductance in Water.—It remains now to calculate, by means of the principle stated in the first paragraph of this article, from the ionization values for the separate salts the ionization of each of them in the mixture, and to compare the result with that derived from the transference data.

The ionization γ of the separate salts was first calculated by the equation $\gamma' = \Lambda/\Lambda_0$ (the conductance ratio), and also by the unquestionably more exact equation $\gamma'' = \Lambda\eta/\Lambda_0\eta_0$ (where η represents the viscosity of the solution and η_0 that of pure water). For this purpose the data given in the second to fifth columns of the following table were used; and the results given in the last four columns were obtained.

TABLE III.—CONDUCTANCE, VISCOSITY AND IONIZATION VALUES FOR POTASSIUM CHLORIDE AND SULFATE AT 18°.

Equiv. conc (C).	Λ at 18°.		η/η_0 at 18°.		$\gamma' = \Lambda/\Lambda_0$.		$\gamma'' = \Lambda\eta/\Lambda_0\eta_0$.	
	KCl.[2]	K_2SO_4[3]	KCl.[4]	K_2SO_4.[4]	KCl.	K_2SO_4.	KCl.	K_2SO_4.
1.00	98.27	71.6	0.9820	1.1012	0.755	0.538	0.742	0.593
0.50	102.41	78.5	0.9898	(1.052)	0.787	0.590	0.779	0.621
0.40	(103.8)	(80.7)	(0.992)	(1.042)	(0.798)	(0.607)	(0.792)	(0.632)
0.20	107.96	87.8	0.9959	(1.021)	0.830	0.660	0.826	0.674
0.10	112.03	94.9	0.9982	1.0111	0.861	0.714	0.859	0.721
0.00	130.10	133.0	1.0000	1.0000	1.000	1.000	1.000	1.000

The two sets of values of $1/\gamma$ for each salt were then plotted against those of $(C\gamma)^{1/2}$, which is advantageous since a nearly linear graph is thereby obtained. From these plots values of γ corresponding to any given value of $C\gamma$, could be readily derived.

A preliminary estimate was next made of the concentration C_K of the (common) potassium ion in the mixture of potassium chloride and sulfate

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[1] These have been calculated from $\Lambda_K = 64.6$ and $\Lambda_{Cl} = 65.5$ as given by Kohlrausch (*Z. Electrochem.*, 13, 333 (1907)), and $\Lambda_{SO_4} = 68.4$, a value derived in this laboratory through a consideration of all available data for the sulfates of univalent metals. It is to be noted that this calculation involves the assumption that the *ratio* of the conductances of the ions of the two salts is the same in the mixture in question as it is at zero concentration.

[2] Data of Kohlrausch and Maltby, *Landolt-Börnstein-Meyerhoffen Tabellen*, p. 744. Those at 0.40 normal were obtained by graphical interpolation.

[3] Data of Kohlrausch and Grüneisen, *Ibid.*, p. 745.

[4] Data of Grüneisen, *Wissensch. Abh. phys. techn. Reichsanstalt*, 4, 239–66 (1905). Those for K_2SO_4 at 0.5, 0.2, and 0.05 normal and for both salts at 0.04 normal were interpolated.

in question; thus the values of the ionizations of the two salts was provisionally assumed to be 80 and 60 per cent. respectively, which gives approximately $C_K = 0.28$, since the concentration C of each salt was 0.2009. From the plots more nearly correct ionization values (γ_1 and γ_2) for the two salts corresponding to this ion concentration were then obtained; and from these values a new value of C_K was calculated (by the equation $C_K = C(\gamma_1 + \gamma_2)$). From this new value of C_K corresponding values of γ_1 and γ_2 were again derived, the process being repeated till the assumed value of C_K corresponded completely with those of γ_1 and γ_2 derived from it.

The partial specific conductances of the salts were calculated[1] from these ionization values by multiplying each of them by the concentration (0.2009) and by the appropriate Λ_0 value (130.1 for KCl and 133.0 for K_2SO_4). The products so obtained were, in the case of these values derived by assuming that $\gamma = \Lambda\eta / \Lambda_0\eta_0$, divided by the viscosity of the mixture (1.017);[2] but this was not done in the case of those derived by assuming $\gamma = \Lambda / \Lambda_0$.

The values of the conductance and ionization so obtained and the ratios of them are given in Table IV, together with those derived from the transference numbers as described in the preceding section.

TABLE IV.—VALUES OF THE SPECIFIC CONDUCTANCE AND IONIZATION OF POTASSIUM CHLORIDE AND SULFATE IN THE MIXTURE.

	Calculated by the principle of ionization in mixtures		
	assuming $\gamma = \Lambda/\Lambda_0$.	assuming $\gamma = \Lambda\eta/\Lambda_0\eta_0$.	Derived from the transference and conductance data.
L_{KCl}	0.02102	0.02052	0.02093
$L_{K_2SO_4}$	0.01587	0.01644	0.01559
Sum	0.03689	0.03696	0.03652
Ratio	1.325	1.248	1.342
γ_{KCl}	0.804	0.797	...
$\gamma_{K_2SO_4}$	0.595	0.625	...
Ratio	1.351	1.275	1.372

A comparison of the last two columns in this table shows that the actual partial conductance (as derived from the transference and conductance data) of the potassium chloride is 2.0 per cent. larger, and that of the potassium sulfate is 5.2 per cent. smaller, than that calculated under the assumption that $\gamma = \Lambda\eta / \Lambda_0\eta_0$ from the principle of ionization in mixtures. Assuming the correctness of the transference data and

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[1] It should be mentioned that, though ionization values have been employed in these calculations, the results are only slightly influenced by a considerable variation in the Λ_0 values employed. The principle of ionization in mixtures in question is substantially a principle of partial conductances in mixtures.

[2] This value was obtained by taking the mean of the viscosities of the two 0.40 normal solutions.

of the assumption that the relative mobilities of the K^+ and Cl^- ions are substantially the same in the mixture as in dilute potassium chloride solutions, this result shows that the principle is subject to serious inaccuracy, especially with respect to the effect upon the unibivalent salt, in the case of this mixture, which involves salts of two different types and a moderately high concentration (0.4 normal). This conclusion is justified even if errors are assumed as large as those mentioned above as possible (—0.001 in the value 0.289 and +0.005 in the value 0.504); for the value of the conductance ratio is then reduced only to 1.304, which is still 4.5 per cent. larger than the calculated value 1.248.

It is to be noted that, though the ratio of the actual partial conductances of the two salts is 7.5 per cent. larger than that required by the principle, yet the observed conductance of the mixture differs from the sum of the calculated partial conductances by only about 1 per cent., a result which is in accord with the previous tests of the principle which have been based upon conductance measurements alone.[1]

An examination of the partial conductance values in the second column of Table IV, which were calculated under the assumption that $\gamma = \Lambda/\Lambda_0$, without taking the influence of viscosity into account, shows that these agree fairly well (within 0.4 per cent. and 1.7 per cent.) with the partial conductances derived from the transference and conductance data. It seems, however, probable that this agreement is an accidental one, resulting from a compensation of the effect of the viscosity correction by that of a deviation from the principle of ionization in mixtures; for it seems almost certain that the ionization will be more accurately obtained when the change in viscosity of the medium is taken into account.

9. Summary.—In this article transference experiments made at 18° with a solution 0.2009 normal with respect both to potassium chloride and to potassium sulfate have been described. The quantity of chlorine transferred per faraday of electricity was found to be 0.289 ± 0.001 equivalent, this value being the mean of five results obtained by determining the changes in content at both the cathode and anode in three independent experiments.

Under the assumption that the transference number of the chlorine

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[1] It may be mentioned that the principle that the ionization of each salt in the mixture is equal to that which it has when present alone at a concentration equivalent to the sum of the concentrations of the two salts leads to results which differ but little from those calculated by the principle considered above (according to whch it is the common ion concentration, rather than the total salt concentration, which determins the ionization). Thus the partial conductances calculated by the former principle under the assumption that $\gamma = \Lambda\eta/\Lambda_0\eta_0$ from the values Λ and η at 0.40 normal given in Table III are: $L_{KCl} = 0.02034$, and $L_{K_2SO_4} = 0.01663$. These will be seen to differ from those given in the third column of Table IV by only about 1 per cent.

in the potassium chloride in this mixture is the same (0.504) as it is in dilute potassium chloride solutions, the proportion of the current carried by its ions was found to be 0.573, and the proportion carried by the ions of the potassium sulfate to be 0.427. By multiplying these values by the measured specific conductance of the mixture, the partial specific conductances of the two salts in the mixture were obtained.

The partial specific conductance of the potassium chloride so obtained was found to be 2.0 per cent. larger, and that of the potassium sulfate 5.2 per cent. smaller, than the values calculated by the principle, previously tested only by conductance measurements, that each salt in the mixture has an ionization equal to that which it has when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture, the ionization being taken equal to the ratio $\Lambda\eta/\Lambda_0\eta_0$, in which Λ and Λ_0 represent the equivalent conductances, and η and η_0 the viscosities, of solutions of the separate salts at the ion concentration in question and at zero concentration.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF IRON.

[THIRD PAPER.]

THE ANALYSIS OF FERROUS BROMIDE.

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1. Introduction.

The atomic weight of iron has already been subjected to two investigations in this laboratory. In one[1] ferric oxide was analyzed by reduction, in the other[2] the per cent. of bromine in ferrous bromide was determined. The first investigation yielded as a result 55.883 (O = 16.000), a value somewhat lower than the one in general use at the time, 56.0. The result of the second investigation, 55.871 (Ag = 107.93) confirmed so closely the value resulting from the oxide analysis, that, since the methods of the two investigations differ so radically, the matter was allowed to rest at this point until very recently. During the last few years much evidence has been brought forward to show that the older value for the atomic weight of silver, 107.93, is several hundredths of a unit too high and that the probable value lies at least as low as 107.88. With this lower value for silver and a correspondingly lower value for bromine the atomic weight of iron calculated from the bromide

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[1] Richards and Baxter, *Proc. Am. Acad.*, **35**, 253 (1900).

[2] Baxter, *Ibid.*, **39**, 245 (1903).