

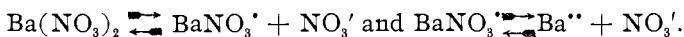
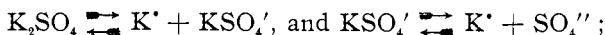
**A MODIFICATION OF THE USUAL METHOD OF DETERMINING TRANSFERENCE NUMBERS, AND AN INVESTIGATION OF THE INFLUENCE OF THE CONCENTRATION ON THEIR VALUES IN THE CASE OF SOME TRI-IONIC SALTS.**

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I. PURPOSE OF THE INVESTIGATION.

AS has been frequently pointed out, the dissociation of tri-ionic salts, such as potassium sulphate and barium nitrate, like that of most dibasic acids, might well be expected to take place in the two stages expressed by the following equations:



Up to the present time, however, no conclusive experimental evidence of the existence of such intermediate complex ions as  $KSO_4'$  and  $BaNO_3'$  has been presented. The freezing-point lowering and electrical conductivity of such salts prove, to be sure, that, even in moderately concentrated solutions, the intermediate ions, if they exist at all, are present only in relatively small amounts. Nevertheless, the question is still unanswered, whether the portion of the salt that is not completely dissociated consists wholly of undissociated molecules ( $K_2SO_4$  and  $Ba(NO_3)_2$ ) or mainly of the partially dissociated ones ( $KSO_4'$  and  $BaNO_3'$ ). The answer to this question cannot be reached by the method used in the case of dibasic acids, since it is only for hydrogen and hydroxyl ions that we possess specific quantitative methods of determination. The property adapted to throw the most light on the matter would seem to be the change of the transference numbers of such salts with the concentration; for, if  $KSO_4'$  or  $BaNO_3'$  ions exist in moderately concentrated solution, and if these ions are dissociated in diluter solutions, as they must be, into  $K'$  and  $SO_4''$  or  $Ba''$  and  $NO_3'$  ions, it is evident that the proportion of potassium or barium transferred in the differently concentrated solutions will be markedly different. This investiga-

tion was, therefore, undertaken in order to determine the effect of dilution on the transference numbers of some tri-ionic salts. Since the results, to be of much value in connection with the theoretical question just referred to, must have a high degree of accuracy, my first efforts were, however, devoted to perfecting the usual method of determining transference numbers, and these have led to a modification of it, which it is one of the main purposes of this article to describe.

## 2. RESULTS OF PREVIOUS INVESTIGATORS.

Before describing my own experiments, the results of previous investigators bearing directly on the subject may be mentioned.

In the first place, it may be recalled that various investigators have proved that the transference numbers of *di*-ionic salts do not vary with the concentration, provided the latter does not exceed a moderate value; for example, 0.5 mol per liter. Thus, this has been shown by Hittorf in the case of potassium chloride, bromide, iodide, chlorate, nitrate, cyanide and acetate, ammonium chloride, sodium chloride, nitrate and acetate, and silver nitrate. This constancy of the transference numbers has been confirmed by other investigators<sup>1</sup> in the case of many of these salts, and has been found by Loeb and Nerust<sup>2</sup> to apply also to silver acetate and silver ethyl sulphate. The only exceptions thus far discovered are in the cases of lithium iodide and chloride which have been found by Kuschel<sup>3</sup> and Bein<sup>4</sup> to behave like the halides of the alkaline earth metals (see below). Aside from these exceptions, which are probably to be explained by assuming the formation of intermediate complex ions, the statement made above in regard to the non-variation of transference values with the dilution holds true.

Hitherto only very few tri-ionic salts have been satisfactorily investigated in this direction. Aside from the earlier experiments of Hittorf, Weiske, Kuschel, and others, which are not sufficiently accurate to throw any light on the present question,<sup>5</sup>

<sup>1</sup> For the original literature on transference determinations see Bein: *Ztschr. phys. Chem.*, **27**, 1. For a summary of all existing values for concentrations up to 0.1 normal, see Kohlrausch: *Wied. Ann.*, **66**, 816.

<sup>2</sup> *Ztschr. phys. Chem.*, **2**, 948.

<sup>3</sup> *Wied. Ann.*, **13**, 289.

<sup>4</sup> *Ztschr. phys. Chem.*, **27**, 50.

<sup>5</sup> Compare Bein: *Ztschr. phys. Chem.*, **28**, 439-452, in regard to the errors of the early determinations; also Kohlrausch: *Wied. Ann.*, **66**, 818, in regard to the disagreement of the results.

and aside from the more recent experiments on the halogen compounds of cadmium and zinc, which exhibit unusually complicated relations, the only determinations available for our purpose are those of Bein<sup>1</sup> on barium, strontium and calcium chlorides and of Hopfgartner<sup>2</sup> on barium chloride. It is desirable that even these determinations should be confirmed, since the results obtained are somewhat remarkable in their character. It was found, namely, that the transference number of the cation increases with increasing dilution, which is just the opposite of the effect which would arise from the presence of BaCl' or CaCl' ions in the more concentrated solution. Barium chloride was, therefore, included among the salts which I have investigated. The significance of the behavior which it exhibits will be further considered below.

### 3. DESCRIPTION OF THE METHOD.

As is well known, the principal difficulty met with in determining the transference numbers of salts for which electrodes of the same metal cannot be used, arises from the fact that free alkali and acid are generated at the cathode and anode respectively, and that the hydroxyl and hydrogen ions thus produced, on account of their high rates of migration, rapidly pass into the middle portions of the solution, thus changing its composition and its transference relations.<sup>3</sup> This change in composition can be greatly retarded on the anode side by the use of a cadmium electrode, since the cadmium ions that pass into solution have a rate of migration very much smaller than that of hydrogen ions. This kind of anode has, in fact, been generally employed.<sup>4</sup> There has been, however, no equally satisfactory method described for preventing the dispersion of the hydroxyl ions produced at the cathode,<sup>5</sup> and Hittorf, Bein, and others in their investigations have simply taken care to stop the electrolysis before the alkali reached the middle portions.

<sup>1</sup> *Ztschr. phys. Chem.*, 27, 50, 51.

<sup>2</sup> *Ibid.*, 25, 137.

<sup>3</sup> See Bein (*Ztschr. phys. Chem.*, 27, 3-18) for a full discussion of this matter.

<sup>4</sup> Compare Bein (*Ztschr. phys. Chem.*, 27, 21) in regard to the source of error arising from the deposition of small quantities of basic salt on the anode.

<sup>5</sup> Both Lenz and Hopfgartner, with this purpose in view, covered the cathode, which consisted of mercury, with concentrated zinc chloride solution, but this prevented an accurate analysis of the solution around the cathode.

This procedure is, however, open to the objection that the absolute amount of substance transferred is necessarily small, and since this small amount is obtained as a difference of two much larger experimentally determined quantities, the percentage errors in the final results are necessarily large. Thus in Bein's experiments on metallic chlorides, which are probably the most accurate with polarizable electrodes thus far published, the amount of chlorine transferred was in almost all cases between 9 and 40 milligrams, and this value was obtained by taking the difference between two quantities usually four to ten times as great. It is true, to be sure, owing to the great accuracy of the volumetric determination of chlorine, that the corresponding transference values exhibit an average deviation from the mean of only 0.6-0.7 per cent.<sup>1</sup> This degree of accuracy could probably not be reached in the case of most other ions, and even it leaves very much to be desired.

It occurred to me now that the difficulty just considered, arising from the dispersion of the hydrogen and hydroxyl ions into the solution, might be entirely obviated by the simple device of gradually adding during the electrolysis to the solutions around the cathode and anode, sufficient amounts of the acid and base, respectively, of which the salt is composed, to keep those solutions neutral (or, preferably in practice, slightly acid and alkaline respectively). If, furthermore, the acid and base added are dissolved in suitable quantities of water, it is evident that not only the formation of new substances around the electrode may be prevented, but also that the changes of concentration of the original salt due to transference may be compensated, so that the whole solution will remain unchanged in composition, and the electrolysis can be continued indefinitely. Thus if the transference number (which is approximately 0.5) of a 0.2 normal potassium sulphate solution were to be determined, one would add gradually at the cathode 0.4 normal sulphuric acid in such (measured) amounts, determined with the help of an indicator or calculated from the electricity passing through, as will keep the solution slightly acid; and would add at the anode an equal amount of 0.4 normal potassium hydroxide. If, however, the transference number of the positive ion were  $\frac{2}{3}$  and the salt 0.2 normal as

<sup>1</sup> This estimate is based on a consideration of Bein's results with the chlorides of the alkali- and alkaline earth metals at ordinary temperatures (p. 49-51 of his article).

before, the acid solution used would have to be 0.3 and the base solution 0.6 normal, and the volume of the former added would have to be twice that of the latter, in order to keep the concentration constant. In practice, however, it is desirable that the added solutions should be somewhat stronger (or weaker) than the theory requires, in order to prevent the solution around the electrodes from rising (or sinking) into the middle portions.

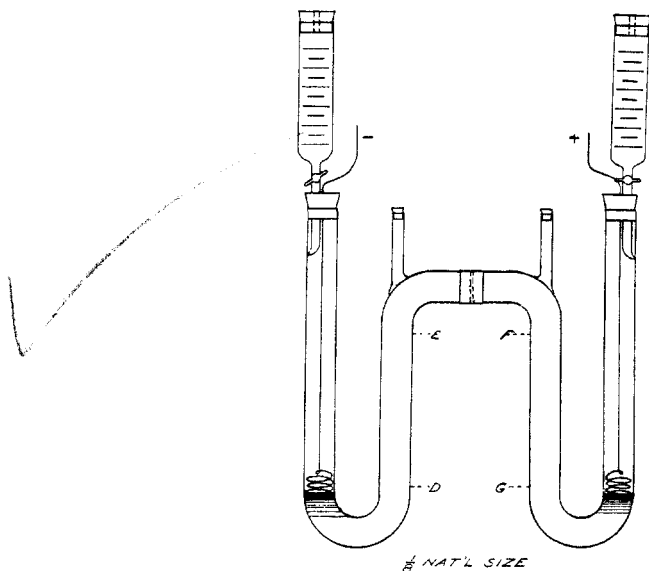
Three salts, potassium sulphate, barium chloride, and barium nitrate, were investigated in the order in which they are here named, each one at two concentrations, 0.1 and 0.02 molar.<sup>1</sup> The samples used were prepared by recrystallizing the commercial chemically pure salts two or three times from water. In the case of the potassium sulphate, the analyses of the solutions, both before and after the electrolysis, were made by evaporating them, after exactly neutralizing, if necessary, with sulphuric acid to dryness on a water-bath in platinum dishes, and igniting the residue, at first very gently and then intensely. Great difficulty was experienced by reason of decrepitation on first heating; but this source of error was entirely removed by tying ash-free filter-paper closely over the top of the dish, heating carefully only the bottom of the dish so as to avoid igniting the paper, and afterwards incinerating the paper. In the case of the two barium salts, the analyses were made by adding a slight excess of sulphuric acid to the solution, evaporating to dryness as before, and igniting the residue to a constant weight at a moderate red heat. During the evaporation the dishes were covered with filter-paper (which was afterwards incinerated), in order to avoid a loss of the precipitate by spattering, occasioned by the escape of small bubbles of air from the solution. This subtle source of error caused, before it was discovered, the loss of several transference determinations. The barium hydroxide solution added at the anode was, in the case of the barium nitrate experiments, analyzed in just the same manner.

The method employed in carrying out the transference experi-

<sup>1</sup> I use this term (previously suggested by Ostwald) to designate the concentration of solutions containing 1 mol (one molecular weight in grams) in 1 liter of solution. The general introduction of some such term seems highly desirable, first in order to avoid a very frequently occurring circumlocution; and second, in order to avoid the serious confusion which is beginning to arise through the double use of some writers of the term *normal*; namely, its use in this sense, as well as in its appropriate sense of one equivalent per liter.

ments with barium nitrate, was somewhat different in its details from that used in the case of the other two salts. I will first fully describe the former method, for it has, I believe, some advantages over the latter; and will then briefly mention the respects in which the two methods differ.

At the beginning of each experiment the apparatus, shown in the accompanying sketch, consisting essentially of two large glass



U-tubes, 3.5 cm. in diameter, joined by a piece of soft rubber tubing, was charged with such an amount of barium nitrate solution that the inside arm of the U-tubes and their outside arms up to a point about 2 cm. above the top of the bend were filled with it. Rubber stoppers were inserted in the small upright arms on the middle of the tube, so as to keep the solution in place. To the portions in the bends were added a few drops (a known weight) of phenolphthalein solution, in order to assist in regulating the addition of alkali and acid. The indicator is rapidly decolorized in the immediate neighborhood of the anode, but is nevertheless useful, since it retains its color in the bend beneath. Cork stoppers with one large and one small hole were inserted in the top of each side-arm. Through the small holes passed heavy platinum wires bent at

the bottom into the form of a spiral. These were made to dip only a few millimeters into the solution, and were gradually raised during the electrolysis so as to be always near the top of the liquid. The distance between the electrodes was 80–100 cm. Through the larger holes in the stoppers were inserted the stems of cylindrical drop-funnels, like those shown in the drawing. These were graduated with divisions corresponding to each 5 cc. The stems were bent slightly at their ends and drawn to a point, so as to cause them to remain full of liquid and to deliver against the sides of the U-tubes. These two drop-funnels were filled at the start with approximately 0.5 normal nitric acid<sup>1</sup> and barium hydroxide for the experiments with the more concentrated solution, and with 0.1 normal acid and base for those with the more dilute. These funnels, which were closed above with one-hole rubber stoppers, were weighed to the nearest centigram before and after the electrolysis, the stems being capped with small test-tubes during the weighing. The base solution was protected from the air during the electrolysis by a soda-lime tube inserted in the rubber stopper.

At least twenty minutes before the electrolysis was started the U-tubes were immersed in a large thermostat at 25°, to such a depth that the middle horizontal part of the apparatus was entirely covered. After the temperature differences had become equalized, 2.5 cc. of the nitric acid solution were added at the cathode and 10–15 cc. of the barium hydroxide solution at the anode. This excess of the latter was added at the start, in order to make the anode solution distinctly heavier than the middle portion above, and to introduce into the bend enough free base to neutralize any acid which might escape neutralization in the immediate neighborhood of the electrode. The electrodes were then connected through a switch, one 16-candle power 110 volt lamp, a Weston milliammeter, and a silver voltameter, all in series, with the terminals of the city circuit of 110 volts potential, and the current was turned on. The silver voltameter consisted of a platinum dish (which served as the cathode) which contained a 15 per cent. silver nitrate solution, just beneath the surface of which

<sup>1</sup> The acid solution used in the first experiments was prepared by diluting the concentrated acid with pure distilled hydrogen peroxide solution, in order to entirely prevent reduction of the nitrate to nitrite and ammonia; but this precaution was later dispensed with, as it was found to make no difference in the results.

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. The milliammeter served merely to indicate the strength of the current, and was not used for a quantitative determination of it.

As the electrolysis proceeded, at intervals of ten to twelve minutes, each time as soon as the pink color appeared at the cathode, 2.5 cc. of the nitric acid solution and an equal volume of the barium hydroxide solution were added. The electrolysis was continued for about three hours. At the end of this time the electrodes and drop-funnels were removed, perforated rubber stoppers were inserted in the side arms, their holes were closed by pushing in pieces of glass rod, and the stoppers in the small middle arms were taken out. Through these arms three middle portions (lying between the points *E* and *F*, *D* and *E*, and *F* and *G* in the figure) were slowly removed by means of a pipette connected with a suction-pump, the tip of the pipette being gradually lowered so as to be always just beneath the surface of the liquid; the portions were then transferred to small flasks. The apparatus was next removed from the thermostat and separated at the rubber band; the U-tubes were wiped off outside with a dry cloth, the liquid on the inside adhering to the upper part of the middle arms also being removed; and the tubes were weighed separately on a large balance, after adding to the anode portion a weighed amount of dilute nitric acid, sufficient to make the solution acid, thus avoiding later the absorption of carbon dioxide from the air. The contents of the U-tubes were now transferred as completely as possible to small flasks, the liquid being once poured back to secure thorough mixing. The U-tubes were then washed out, dried, and weighed. The flasks were all weighed, their contents poured out into the platinum dishes, and the nearly empty flasks again weighed. The weights of barium sulphate obtained from the cathode and anode portions were corrected for the small known weights of solution remaining in the U-tubes.

In the case of the potassium sulphate and barium chloride experiments, only the cathode and middle portions were analyzed. The method of conducting the electrolysis was also somewhat different in these cases. The side-arms of the U-tubes were at the beginning filled with solution for two-thirds of their length



(instead of up to a point only a little above the bends), and the concentrations of the acid and base solutions added were made 10 per cent. less (instead of greater) than would be required to maintain a constant concentration, in order to prevent the portions around the electrodes from sinking into the unchanged solution beneath. These solutions were added from burettes with tips turned upward and delivering a little below the bottom of the electrodes, which reached as before just beneath the surface of the liquid. The weight of the sulphuric or hydrochloric acid solution added was calculated from the measured number of cubic centimeters with the help of the known specific gravity of the solution; this volume measurement is unobjectionable in the case of the acid solution added, since no non-volatile matter is introduced, and the greatest accuracy is therefore not required; but direct weighing of the base solution is far preferable in case the anode portion is to be analyzed. Both methods of charging the U-tubes and of regulating the concentration at the electrodes give satisfactory results; in that last described, the middle portion is of greater length, and the electrolysis could perhaps be longer continued, if it were desired to do so. The method used in the case of the barium nitrate is preferable, however, when the base solution to be added, like that of barium hydroxide, is heavy; for, if the other method is used, it is difficult to prevent the added portions from sinking down before they become mixed with the liquid already surrounding the electrode. The electrolyses of the potassium sulphate and barium chloride solutions were continued from four to eight hours.

#### 4. RESULTS OF THE TRANSFERENCE DETERMINATIONS.

The experimental data and the calculated transference numbers are given in the tables below. All the values given (except, of course, the current, time, and transference numbers) are weights in grams. Those in the columns relating to the salt content are the quantities of the substances actually weighed; namely, of the potassium sulphate and barium sulphate. In the second column, the portion of the solution surrounding the cathode is designated by K, the adjoining middle portion by  $M_I$ , the next one by  $M_{II}$ , that adjoining the anode portion by  $M_{III}$ , and the anode portion itself by A.

The temperature was in all cases  $25^{\circ}$ .

The original solutions submitted to electrolysis, the concentrations of which are only approximately stated in the headings, were found to contain the following amounts of salt in 1,000 grams of solution: in experiments 1 and 2, 17.247 grams, in No. 3, 17.205 grams, and in Nos. 4, 5, and 6, 3.4927 grams  $K_2SO_4$ , in Nos. 7, 8, 9, and 10, 22.906 grams, in Nos. 11, 12, and 13, 4.6448 grams, in Nos. 14, 15, and 16, 21.083 grams, in No. 17, 21.099 grams, in Nos. 18 and 19, 4.6666 grams, and in No. 20, 4.6560 grams barium sulphate. The barium hydroxide solution added in experiments 14, 15, 16, and 17 gave 56.443 grams barium sulphate, and that used in experiments 18, 19, and 20 gave 11.700 grams barium sulphate for 1,000 grams of solution.

The values of the transference numbers, which are given in the last columns of the tables, are those of the positive ions multiplied by 100. The way in which these were calculated may be illustrated with the help of the data obtained in the first experiment with potassium sulphate (see the table below). The cathode portion submitted to analysis weighed 493.12 grams, and was found to contain 8.4394 grams potassium sulphate. To determine what it contained before the electrolysis, we must evidently subtract from the final weight of the portion, the weight of all matter which was introduced in the process of carrying out the electrolysis, and multiply the remainder by the original salt content, which was 0.017247 gram per gram of solution.

The weight of dilute sulphuric acid and phenolphthalein added, which was 60.78 grams in this experiment, must therefore be first subtracted. Secondly, a correction must be made for the fact that the weight of the cathode portion is, by the electrolysis itself, increased by the weight of the potassium ions which have migrated into it, and decreased by the weight of sulphate ions which have migrated out of it<sup>1</sup> by the weight of the hydrogen gas which escaped at the electrode. Since the average value of the transference number is found to be 0.493, the total increase of

<sup>1</sup> It is evidently assumed hereby, as is always done in transference calculations, that the ions are not hydrated. It may not be without value to call attention to the fact that the commonly observed change of the calculated transference numbers with the concentration may be due, wholly or in part, in the case of concentrated solutions, to hydration of the ions, and to the failure to take this into account in the calculation.

weight from these three causes would evidently be:  $(39.1 \times 0.493) - (48.0 \times 0.507) - 1.0 = -6.0$  grams for every 108 grams of silver deposited in the voltameter, or  $-0.14$  gram in this experiment. The increase in the amount of the salt in the cathode portion is therefore  $8.4394 - (493.12 - 60.78 + 0.14) 0.017247 = 0.9803$  gram. Adding to this the change in the adjoining portion ( $+0.0013$  gram) and dividing by the equivalent weight of potassium sulphate (87.18), and by the number of equivalents of silver precipitated in the voltameter, the transference number is found to be 0.4941. (The cases where the adjoining middle portion suffered a change in concentration greater than the analytical error and where consequently this change was combined with that of the cathode or anode portion, are indicated in the table by a brace following the two quantities.) The calculation of the transference number from the change in concentration at the anode was, in the case of the barium nitrate experiments, made in an entirely analogous manner, except that from the weight of barium sulphate obtained from the anode portion after the electrolysis, there was of course subtracted the amount coming from the barium hydroxide solution added. For the sake of greater clearness, the total weight of salt obtained from the anode portion is in the table resolved into the two corresponding components.

## POTASSIUM SULPHATE, 0.1 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid or base solution added.	Original salt content.	Difference in salt content.	Silver in voltameter. Current. Time.	Transference number.
1	K	493.12	8.4394	60.78	7.4591	+0.9803	2.4594 0.118 amp 310 min	49.41
	M <sub>I</sub>	137.47	2.3723		2.3710	+0.0013		
	M <sub>II</sub>	204.82	3.5365		3.5326	+0.0039		
2	K	456.48	7.7762	91.21	6.3033	+1.4729	3.6760 0.134 amp 415 min	49.33
	M <sub>I</sub>	175.15	3.0126		3.0209	-0.0083		
	M <sub>II</sub>	86.96	1.4993		1.4998	-0.0005		
3	K	434.79	7.4142	48.70	6.6446	+0.7696	1.9370 0.063 amp 460 min	49.19
	M <sub>I</sub>	119.85	2.0615		2.0620	-0.0005		
	M <sub>II</sub>	133.38	2.2941		2.2948	-0.0007		

## POTASSIUM SULPHATE, 0.02 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid of base solution added.	Original salt content.	Difference in salt content.	Silver in voltameter. Current. Time.	Transference number.
4	K	491.47	1.6964	56.73	1.5185	+0.1779	0.4451	49.68
	M <sub>I</sub>	103.75	0.3631		0.3624	+0.0007	0.028 amp	
	M <sub>II</sub>	102.99	0.3599		0.3597	-0.0002	240 min	
5	K	463.31	1.5869	84.31	1.3238	+0.2631	0.6524	49.59
	M <sub>I</sub>	176.04	0.6131		0.6149	-0.0018	0.040 amp	
	M <sub>II</sub>	94.08	0.3289		0.3286	-0.0003	245 min	
6	K	469.56	1.6246	57.40	1.4397	+0.1849	0.4617	49.58
	M <sub>I</sub>	103.17	0.3604		0.3603	-0.0001	0.018 amp	
	M <sub>II</sub>	107.24	0.3745		0.3746	-0.0001	380 min	

## BARIUM CHLORIDE, 0.1 MOLAR.

7	K	460.04	10.6238	30.33	9.8402	+0.7836	1.7479	41.44
	M <sub>I</sub>	46.30	1.0598		1.0605	-0.0007	0.108 amp	
	M <sub>II</sub>	99.09	2.2686		2.2697	-0.0011	240 min	
8	K	512.08	11.9214	57.06	10.4182	+1.5032	3.3519	41.46
	M <sub>I</sub>	35.77	0.8189		0.8193	-0.0004	0.122 amp	
	M <sub>II</sub>	104.51	2.3911		2.3939	-0.0028	410 min	
9	K	507.37	11.7885	50.98	10.4500	+1.3385	2.9804	41.48
	M <sub>I</sub>	106.63	2.4411		2.4424	-0.0013	0.123 amp	
	M <sub>II</sub>	101.06	2.3116		2.3149	-0.0033	360 min	
10	K	474.93	10.8589	30.31	10.1824	+0.6765	1.5019	41.50
	M <sub>I</sub>	103.15	2.3604		2.3628	-0.0024	0.065 amp	
	M <sub>II</sub>	108.48	2.4821		2.4848	-0.0027	345 min	
10	M <sub>III</sub>	85.59	1.9574		1.9605	-0.0031		

## BARIUM CHLORIDE, 0.02 MOLAR.

11	K	514.75	2.3897	54.95	2.1354	-0.2543	0.5321	44.31
	M <sub>I</sub>	110.70	0.5149		0.5142	+0.0007	0.034 amp	
	M <sub>II</sub>	115.31	0.5362		0.5356	-0.0006	230 min	
	M <sub>III</sub>	89.89	0.4175		0.4175	0.0000		
12	K	499.37	2.3214	50.15	2.0864	+0.2350	0.4928	44.19
	M <sub>I</sub>	110.59	0.5142		0.5137	+0.0005	0.022 amp	
	M <sub>III</sub> <sup>1</sup>	86.12	0.4007		0.4000	+0.0007	275 min	
13	K	493.42	2.2930	49.84	2.0601	+0.2329	0.4885	44.16
	M <sub>I</sub>	106.63	0.4957		0.4953	+0.0004	0.023 amp	
	M <sub>II</sub>	109.52	0.5089		0.5087	+0.0002	260 min	
	M <sub>III</sub>	95.84	0.4451		0.4452	-0.0001		

<sup>1</sup> Portion M<sup>III</sup> was lost in this experiment.

## BARIUM NITRATE, 0.1 MOLAR.

Experiment number.	Portion.	Weight of portion.	Salt content.	Acid of base solution added.	Original salt content.	Difference in salt content.	Silver in voltammeter. Current. Time.	Transference number.
14	K	244.30	5.2507	40.53	4.2970	+0.9537	1.9334 0.175 amp 165 min	45.54
	M <sub>I</sub>	180.57	3.8058		3.8070	-0.0012		
	M <sub>II</sub>	199.75	4.2106		4.2112	-0.0006		
	M <sub>III</sub>	239.02	5.0368		5.0388	-0.0020		
	A	205.23	{ 2.5491 2.2196		39.325	3.5000		
15	K	269.42	5.8130	43.89	4.7562	+1.0568	2.1540 0.178 amp 180 min	45.47
	M <sub>I</sub>	174.74	3.6864		3.6840	+0.0024		
	M <sub>II</sub>	174.33	3.6760		3.6753	+0.0007		
	M <sub>III</sub>	183.50	3.8710		3.8685	+0.0025		
	A	218.25	{ 2.5877 2.5527		45.233	3.6497		
16	K	268.51	5.7520	44.355	4.7270	+1.0250	2.0917 0.173 amp 180 min	45.46
	M <sub>I</sub>	172.63	3.6428		3.6395	+0.0033		
	M <sub>II</sub>	147.53	3.1110		3.1098	+0.0002		
	M <sub>III</sub>	157.03	3.3132		3.3100	+0.0032		
	A	204.41	{ 2.1725 2.9600		52.44	3.2065		
17	K	278.03	5.8841	46.49	4.8846	+0.9995	2.0301 0.168 amp 180 min	45.54
	M <sub>I</sub>	168.20	3.5492		3.5488	+0.0004		
	M <sub>II</sub>	158.30	3.3329		3.3326	+0.0003		
	M <sub>III</sub>	153.30	3.2360		3.2345	+0.0015		
	A	205.69	{ 2.4465 2.3988		42.50	3.4451		
BARIUM NITRATE, 0.02 MOLAR.								
18	K	197.50	1.0234	20.88	0.8242	+0.1992	0.4042 0.033 amp 180 min	45.57
	M <sub>I</sub>	122.58	0.5744		0.5744	±0.0000		
	M <sub>II</sub>	134.06	0.6267		0.6269	-0.0002		
	M <sub>III</sub>	187.20	0.8143		0.8150	-0.0007		
	A	253.88	{ 0.7158 0.6766		57.83	0.9149		
19	K	207.34	1.0631	21.75	0.8660	+0.1971	0.4014 0.033 amp 180 min	45.41
	M <sub>I</sub>	124.05	0.5773		0.5772	+0.0001		
	M <sub>II</sub>	141.65	0.6608		0.6610	-0.0002		
	M <sub>III</sub>	145.38	0.6781		0.6772	+0.0009		
	A	268.13	{ 0.7979 0.6371		54.45	0.9971		
20	K	201.18	1.0346	21.14	0.8382	+0.1964	0.3985 0.035 amp 170 min	45.57
	M <sub>I</sub>	123.27	0.5630		0.5630	+0.0000		
	M <sub>II</sub>	121.00	0.5641		0.5640	+0.0001		
	M <sub>III</sub>	155.48	0.7240		0.7239	+0.0001		
	A	279.26	{ 0.8353 0.6716		57.40	1.0329		

The values of the transference numbers obtained (multiplied by 100) are summarized in the following table. At the foot of each column are given the mean of the values just above, and the average deviation of the separate values from this mean. To the final results in the case of the barium nitrate, the probable error, calculated in the usual manner, is appended :

POTASSIUM SULPHATE.		BARIUM CHLORIDE.	
0.1 Molar.	0.02 Molar.	0.1 Molar.	0.02 Molar.
49.41	49.68	41.44	44.31
49.33	49.59	41.46	44.19
49.19	49.58	41.48	44.16
—	—	41.50	—
49.31	49.62	—	—
0.08	0.04	41.47	44.22
		0.02	0.06

BARIUM NITRATE.			
0.1 Molar.		0.02 Molar.	
Cathode values.	Anode values.	Cathode values.	Anode values.
45.54	45.56	45.57	45.70
45.47	45.48	45.41	45.68
45.46	45.56	45.57	45.85
45.54	45.42	—	—
—	—	—	—
45.50	45.50	45.52	45.74
0.04	0.06	0.07	0.07
—	—	—	—
45.50 ± 0.02		45.59 ± 0.10	

### 5. ACCURACY OF THE RESULTS.

The probable degree of accuracy of the results and the consequent reliability and value of the method employed may be next considered. It should be first stated that in the above tables all the determinations are recorded which were carried to completion after certain errors which were found to exist in the analyses were eliminated.

In the cases of potassium sulphate and barium chloride, there are two indications of the degree of accuracy of the results ; first, the change in weight of the middle portions, and second, the variations in the transference values calculated from the different experiments. In regard to the former, it should be stated that in the analyses of portions of the original solutions, variations from the mean salt-content of 0.0010 gram in the more concentrated, and of 0.0005 gram in the more dilute solution, were found

to exist ; so that only when the middle portions change by more than these amounts, do the changes have much significance. It will be seen that the changes in the  $M_I$  portions do not much exceed these amounts except in the cases of Experiments 2, 5, and 10 ; and in the first two of these experiments, the changes in the  $M_{II}$  portions are so small as to cause no hesitation in combining the changes of the  $M_I$  portions with those of the cathode portions. It will also be seen from the summary in the last table that the average deviation of the separate transference values from the mean is in every case less than 0.2 per cent. Taking into account the possibility of an error of 0.1 per cent. in the determination of the original salt content, it can, I think, be safely asserted that it is almost certain that the error in the mean transference values does not exceed 0.25 per cent. ; in other words, the third figure cannot be in error by more than one unit. The probable error is, of course, much less.

In the case of the barium nitrate experiments, a more conclusive confirmation of the degree of accuracy of the results is furnished by a comparison of the cathode and anode values ; for an error in the determination of the original salt content of the solution or any error arising from mechanical loss in the analysis of the portions would affect these values in the opposite direction. In the case of the 0.1 molar solutions, the agreement is complete between the mean cathode and anode values. Taking into account, moreover, the smallness of the variations of the separate values from the mean, and the slight changes (0.2-0.7 mg.) exhibited by the  $M_{II}$  portions, the final result (45.50) can, I believe, be regarded as almost surely accurate to 0.1 per cent. of its value. In the case of the 0.02 molar solution, the values calculated from the changes at the two electrodes differ by a little less than 0.5 per cent. Attributing double weight to the cathode results, since an increase of the salt content is produced by the base solution added at the anode, I adopt 45.59 as the most probable value. This may possibly be in error by 0.3 per cent., but is probably accurate to one-half that amount. Since, at both concentrations, the final values are derived by the combination of the results of two independent methods, which are liable to error in opposite directions, the probable errors given in the table are to be regarded as a measure not merely of the variable errors, but probably of all errors involved.

These considerations show that the degree of accuracy attained with the help of the method described in this article, is much greater than that which it has heretofore been found possible to secure. This arises mainly from the fact that the electrolysis could be continued until a much larger weight of salt was transferred. Thus, in my experiments, the quantities transferred were 180-260 mg. in the 0.02 molar, 700-1500 mg. in the 0.1 molar solution, while, in Bein's determinations at corresponding concentrations, only 20-50 mg. were transferred.

#### 6. COMPARISON WITH EARLIER RESULTS.

Potassium sulphate was investigated by Hittorf<sup>1</sup> at 4°-12° at two concentrations, at about 0.5 and about 0.014 molar. The transference numbers found were 0.500 and 0.498, respectively. The differences from my values (0.4931 and 0.4962) are, therefore, not very large.

Barium chloride has been studied by various investigators with widely divergent results. Thus Hittorf<sup>2</sup> obtained the value 0.385 at 10°-20° for 0.04-0.06 molar solutions, while from Bein's results,<sup>3</sup> one finds by interpolation for 25° and 0.1 and 0.02 molar concentrations, the values 0.424 and 0.445, respectively. The latter differ by 2.2 and by 0.7 per cent., respectively, from those presented in this article (0.4147 and 0.4422). Hopfgartner's<sup>4</sup> determinations (at 15°) for a 0.1 molar solution lead to the value 0.408, which is nearly as much below my result as Bein's is above it.

Barium nitrate has been investigated only by Hittorf,<sup>5</sup> who found 0.380 in 0.07, and 0.398 in 0.03 molar solution. These values differ very widely from my own (0.455).

These results make evident the great need of a repetition of much of the earlier work on tri-ionic salts.

#### 7. CHANGE OF THE TRANSFERENCE NUMBERS WITH THE CONCENTRATION.

The effect of concentration, the study of which formed the main object of this investigation, may be now considered.

<sup>1</sup> Ostwald's *Klassiker*, No. 21, 58; or *Pogg. Ann.*, 98, 29-30.

<sup>2</sup> Ostwald's *Klassiker*, No. 23, 41; or *Pogg. Ann.*, 106, 380-381.

<sup>3</sup> *Ztschr. phys. Chem.*, 27, 51.

<sup>4</sup> *Ztschr. phys. Chem.*, 25, 138.

<sup>5</sup> Ostwald's *Klassiker*, No. 23, 41; or *Pogg. Ann.*, 106, 378-379.



The transference number of potassium sulphate varies only from 0.4931 to 0.4962, or about 0.6 per cent., between the concentrations of 0.1 and 0.02 mol per liter. A little consideration will show that this change can be explained by assuming that 1.2 per cent. more of the dissociated part of the salt is dissociated into  $K^+$  and  $KSO_4^-$  ions in the concentrated than in the dilute solution, it being further assumed, as a sufficiently close approximation, that the equivalent conductivities of all the ions involved are equal. But, since, according to Kohlrausch's measurements, the molecular conductivity between these two concentrations changes from 175 to 208 reciprocal ohms (and the dissociation from 64.5 to 77 per cent.) thus by 19 per cent., it is clear that by far the most important chemical change produced by the dilution is the dissociation of  $K_2SO_4$  molecules and not  $KSO_4^-$  ions. Since the change in the transference number is so small, it may, however, be due solely to the hydration of ions.<sup>1</sup> Therefore, only the following negative conclusion is justifiable: *The concentration of  $KSO_4^-$  ions in a 0.1 molar potassium sulphate solution does not exceed a very few per cent. of the total concentration.* If these ions exist at all, they have a very much greater dissociation tendency than the neutral potassium sulphate molecules.

In the case of barium nitrate, the change (0.2 per cent.) caused by the fivefold dilution, is still smaller, and does not exceed the probable experimental error. Therefore, *barium nitrate solutions, up to a concentration of 0.1 mol. per liter, contain in appreciable quantity only  $Ba^{++}$  and  $NO_3^-$  ions and no complex ions formed by the combination of these.*

The difference in the transference numbers (0.4147 and 0.4422) of barium chloride at the two concentrations is very much greater than the differences just considered, amounting as it does to 6.6 per cent. The change is, moreover, in the opposite direction from that required by the assumption of the existence of  $BaCl^+$  ions in the more concentrated solution. In order to explain this behavior and the analogous one of strontium and calcium chlorides, Bein assumed a partial hydrolysis of the salt, basing this view on the disagreement of a single determination of the amount of calcium transferred with determinations of the chlorine trans-

<sup>1</sup> Thus the actual change of 0.6 per cent. would be entirely accounted for, if with the equivalent weight of the  $K^+$  ions migrate two molecules of water more than migrate with the equivalent weight of  $SO_4^{--}$  ions.

ferred. This explanation cannot, however, be correct, since the alkaline earth hydroxides are known to be very strong bases; it is, moreover, entirely disproved in the case of barium chloride, by the substantial agreement (see § 6) of Bein's values, which are based on determinations of the chlorine transferred, with my results which were obtained by determining the transferred barium. On the contrary, the behavior of these chlorides of the alkaline earth metals is entirely similar to that of the halogen compounds of cadmium, though the anomaly is less pronounced; and as far as I am able to see, it admits only of a corresponding explanation. In order to account for the fact that the sum of the transference numbers for the metal and chlorine is equal to unity, and for the change with the dilution, it is, namely, necessary to assume that *there are present in considerable quantity in the 0.1 molar solution of the alkaline earth chlorides, complex negative ions formed by the union of one or more chlorine ions with one or more of the chloride molecules* (such ions for examples as  $\text{BaCl}_3'$  or  $\text{BaCl}_4''$ ) and that these ions dissociate with increasing dilution.

#### 8. RATES OF MIGRATION OF THE BIVALENT IONS.

As Kohlrausch has pointed out, owing to the lack of exact transference values for tri-ionic salts, the Law of the Independent Migration of the ions has not been satisfactorily confirmed in the case of bivalent ions, nor have their rates of migration, calculated with the help of that law, been as accurately determined as have those of univalent ions for the reason just mentioned, and also for the reason that the limiting value of the molecular conductivity of tri-ionic salts cannot be established with as great certainty, since a larger extrapolation is necessary.

With the help of the new transference numbers for potassium sulphate and barium nitrate, the equivalent conductivities of the  $\text{SO}_4''$  and  $\text{Ba}''$  ions can be calculated if it be assumed that the values obtained for 0.02 molar solution at  $25^\circ$  would also hold true for extreme dilution and at  $18^\circ$ . That these assumptions will not give rise to an error greater than 1 per cent. is highly probable in view of the small changes between the concentrations of 0.1 and 0.02 mol per liter, and in view of the general principle that temperature has, as a rule, only a small effect on transference numbers. The calculation can be made in two ways, either by

combining with my transference numbers the conductivities at extreme dilution of the  $K^+$  and  $NO_3^-$  ions, which have been derived by Kohlrausch through a consideration of the transference numbers and the molecular conductivities of the di-ionic salts; or by combining with them the limiting values of the equivalent conductivities of potassium sulphate and barium nitrate. The results so obtained for the  $SO_4^{2-}$  and  $Ba^{2+}$  ions can be then further compared with Kohlrausch's values which were derived by a combination of the two kinds of data last mentioned, without reference to the transference number of any tri-ionic salt.<sup>1</sup>

The three pairs of calculated values of the equivalent conductivities of the two ions are given below in the order in which they have just been referred to. The data used in the calculation are the transference numbers recorded above (0.4962 for  $K_2SO_4$  and 0.4559 for  $Ba(NO_3)_2$ ) and the following values of the equivalent conductivity expressed in reciprocal ohms at extreme dilution<sup>2</sup>: for  $K^+$ , 64.8; for  $NO_3^-$ , 61.3; for  $K_2SO_4$ , 135.5; and for  $Ba(NO_3)_2$ , 119.3.

	I.	II.	III.
$SO_4^{2-}$	65.8	68.3	69.7
$Ba^{2+}$	51.4	54.4	57.3

The differences between the three pairs of values are by no means inconsiderable. In the case of the  $Ba^{2+}$  ion, indeed, the first and third methods of calculation give results differing by over 10 per cent. Aside from serious errors in the experimental data, these differences may be due to one or more of the three following causes: first, error in the conductivity values calculated for the univalent ions; second, error in the extrapolated values for the equivalent conductivity at extreme dilution of the tri-ionic salts; and third, inaccuracy in the assumption that the transference numbers for potassium sulphate and barium nitrate at extreme dilution do not differ much from those found in 0.02 and 0.1 molar solution. It seems very improbable that any one of these three errors can be large enough to account for the divergences; a combination of them, however, may possibly do so. In the absence of definite information in regard to the matter, it seems best to adopt provisionally the values given in column II

<sup>1</sup> Wied. *Ann.*, 66, 805.

<sup>2</sup> These values are those given by Kohlrausch, Wied. *Ann.*, 66, 795 and 819, 812 and 804.

( $\text{SO}_4'' = 68.3$ ;  $\text{Ba}'' = 54.4$ ) which are the ones most directly derived from experimental data, and which are not far from the means of the other two pairs of values. These numbers give for the equivalent conductivities of potassium sulphate and barium nitrate, 133.1 and 115.7, respectively, while Kohlrausch's extrapolated values are 135.5 and 119.3. In this connection it should be pointed out that in Kohlrausch's method of treatment of tri-ionic salts, the assumption involved that the conductivity of bivalent ions decreases with increasing concentration more rapidly than that of the univalent ions simultaneously present, is entirely inconsistent with the transference results on potassium sulphate and barium nitrate presented in this article. This is shown by the following transference numbers which are calculated for these two salts from his values for the separate ions at the various normal concentrations which are stated below in the head line :

	0.1	0.05	0.02	0.01	0.001
$\text{K}_2\text{SO}_4$	0.571	0.557	0.534	0.522	0.499
$\text{Ba}(\text{NO}_3)_2$	0.397	0.414	0.434	0.446	0.468

It is certain from my results that any such change of the transference numbers with the concentration is out of the question in the case of these two salts. It ought to be added that Kohlrausch regarded his assumption only as a provisional one, having an empirical justification. That the results obtained with its help were at all satisfactory is probably due, first to the fact that the compounds considered were mostly those of the halogens, and secondly, to the large errors in some of the transference numbers.

It is impossible to utilize the transference numbers of barium chloride, as was done with those of the nitrate, for the calculation of the conductivity of the barium ion, since the transference number of the former salt does change greatly with the dilution. It is of interest, however, to make the converse calculation so as to compare the transference number calculated for extreme dilution with that found at the concentrations investigated. Assuming as above,  $\text{Ba}'' = 54.4$ , and according to Kohlrausch,  $\text{Cl}' = 66.4$ , the transference number for complete dissociation is found to be 0.450. (Even assuming Kohlrausch's much higher value (57.3) for the  $\text{Ba}''$  ion, the transference number becomes only 0.464.) The value found for a 0.02 molar solution was 0.442, so that the change produced by further dilution is relatively small.

At this concentration, therefore, the complex negative ions present in considerable quantity in more concentrated barium chloride solutions are, for the most part, dissociated.

In closing, I desire to state that the accuracy of the experimental results presented in this article are to be attributed in large measure to the analytical skill and perseverance of my assistants, Mr. A. A. Blanchard and Mr. G. V. Sammet.

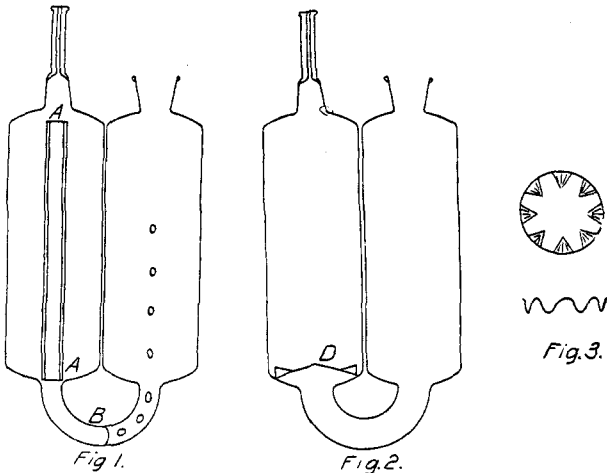
### IMPROVEMENT IN ORSAT APPARATUS.

BY A. BEMENT.

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HAVING experienced considerable trouble in using the Orsat gas apparatus, I have devised a modification with the object of removing what I have found to be a serious and troublesome fault.

Fig. 1 will illustrate the particular difficulty in question. It is that of the usual form of pipette used especially for the caustic and pyrogallate reagents, having a number of small glass tubes



inclosed in the front leg. For purpose of illustration only one of these tubes is shown by AA. As this chamber in practice is full of these tubes, it necessarily follows that one of them must