cules to total molecules (*e. g.*, at 390° to 50.8:51.8), and therefore the calculated partial pressures of the mercury in the solution. Figuring on this basis, the final divergencies between calculated and observed data (col. 9) now become —12.2, —9.7, —11.1, —13.5, —18.0, etc., up to —36.6 at 400°. The excellent correspondence thus disappears, and the divergencies increase rapidly with ascending temperature.

Conclusions.—1. A series of vapor pressures of calomel from 360 to 400° has been obtained. The boiling point is found to be 382.5°.

2. It has been shown by a quantitative vapor pressure method (static), that calomel vapor, even when saturated, is wholly dissociated, and that molecules of the classes HgCl and Hg_2Cl_2 are not present.

3. Independent measurements, with an apparatus working on the dynamic principle, lead to the same conclusion.

4. It has been shown that the molecular weight of calomel dissolved in mercury at 360–400° corresponds to the monomolecular formula, HgCl.

5. It has been shown that, by the use of the isoteniscope, chemical problems can be investigated, and results can be obtained, possessing the same order of accuracy that is claimed for the most refined methods of quantitative analysis.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 60.]

TRANSFERENCE EXPERIMENTS WITH THALLOUS SULPHATE AND LEAD NITRATE.

BY K. GEORGE FALK.

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1. Introduction.

In a paper published some years ago, A. A. Noyes[1] pointed out that the change of the transference number of tri-ionic salts with the concentration might be expected to throw light on the question as to whether intermediate ions, such as KSO_4^- in the case of potassium sulphate, or NO_3Ba^+ in the case of barium nitrate, existed in appreciable quantities in solutions of such salts. Results for potassium sulphate, barium chloride, and barium nitrate were published. In this paper, the results obtained with two other salts of this type, thallous sulphate and lead nitrate, will be given; and the theoretical significance of the transference results will be considered.

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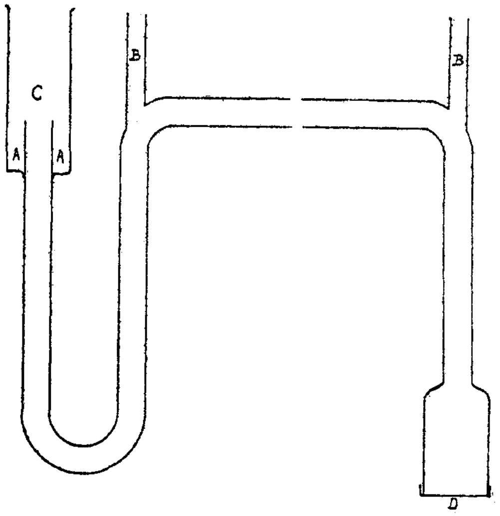
[1] THIS JOURNAL, 23, 37 (1901).

This investigation was undertaken at the suggestion of Prof. A. A. Noyes, and was carried out with the aid of a grant made to him by the Carnegie Institution of Washington.

2. Apparatus.[1]

A cross section of the apparatus, drawn to scale but reduced to 1/5 its natural size, is shown in the accompanying sketch.

The U tube served as the cathode side. The cathode itself rested in the annular space AA in the compartment C. It consisted of an annular strip of sheet platinum fused to a platinum wire, which in turn was fused into a piece of small glass tubing containing mercury, which passed through a rubber stopper closing that side of the apparatus. The diameter of the glass tube throughout the apparatus was 1.5 cm., except at the electrodes, where it was widened to 3.5 cm.



The anode part consisted of the straight tube with the side arm. The widened part at the lower end was closed by fitting over it a gold cup, D. Gold was used instead of platinum because it was easier to work into shape and gave a closer fit. Ceresin was poured in between the upper edge of the cup and the glass, and the joint was covered with two layers of rubber tubing securely wired on. The bottom of the cup was insulated from the bath by a large rubber stopper held up against it by the rubber tubing, which extended sufficiently far down for this purpose. Electric connection with the bottom of the cup was made by a small sheet of platinum pressed against it and fused to a platinum wire which passed through a glass tube in the stopper. The platinum wire was connected below to a copper wire, which was enclosed in black rubber tubing and led up through the bath.

The cathode and anode parts of the apparatus were joined by a double layer of rubber tubing wired in several places and covered with ceresin.

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[1] To Mr. A. C. Melcher, who rendered valuable assistance in the preparation of the apparatus and development of the experimental method, the writer desires to express his indebtedness.

The two parts were brought so near together that there was practically no free space betwen the glass.

The tubes BB, 1 cm. in diameter, served to introduce or remove the solutions.

The current was taken from the 110-volt city circuit with a sufficient number of 32-candle power 220-volt lamps in series to give the strength of current desired, as shown by a milliammeter placed in series with the apparatus.

The current was measured accurately by means of two silver coulometers, each consisting of a platinum dish 7 cm. in diameter as cathode, a silver disk riveted through its center to a silver rod and wrapped in filter paper as anode, and a 15 per cent. silver nitrate solution as electrolyte. The two coulometers were introduced into the circuit at opposite ends of the transference apparatus, thus guarding against error from leakage of electricity.

3. Description of the Experiments with Thallous Sulphate.

In carrying out the experimental determinations of the transference number of thallous sulphate, a current of electricity was passed through the solution of this salt for a certain length of time, using a definit weight of thallium as anode and allowing thallium to be deposited on the platinum plate at the cathode. The thallium at the two electrodes was dissolved after the experiment and added to the respective electrode solutions; and these were then analyzed. The middle portions were also analyzed, in order to determin whether the changes in concentration extended into them. In this way a theoretically perfect method was attained; for only thallous sulphate was present in the solution, even in the neighborhood of the electrodes; and both the electrode portions, as well as all the middle portions, were analyzed.

The detailed description of the experiments may for convenience be divided into four parts: (1) preparation of the solution; (2) preparation of the anode; (3) electrolysis of the solution and removal of the portions; and (4) analysis of the portions.

Preparation of the Solution.—Kahlbaum's thallous sulphate was used. Though it apparently contained no impurity, it was crystallized from conductivity water. The solutions were made up approximately 0.1 and 0.03 normal with conductivity water, and the exact strength determined gravimetrically as described below. The average of four or five results was adopted as the content of each solution. The solutions used were tested repeatedly with litmus and found to be neutral; and a 0.02 normal solution was more accurately tested with rosolic acid, showing that the solution was no more acid than the water used in preparing it.[1]

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[1] Reference is made to this fact since Denham (*J. Chem. Soc.*, **93**, 59 (1908)) states that his thallous sulphate solution was acid and was largely hydrolyzed.

Preparation of the Anode.—The anode was prepared by depositing electrolytically an accurately known weight of thallium in the gold cup. The procedure differed slightly for the 0.1 and 0.03 normal solutions. In the former case, about thirty grams of the thallous sulphate solution, the exact amount being immaterial, were poured into the anode compartment; about 1.3 grams (accurately weighed) of dilute sulphuric acid were added; and the solution was electrolyzed, with the gold cup as cathode and a small platinum wire as anode, for about 2 hours with a current of 0.030 to 0.040 amperes. Metallic thallium deposited on the cup, and oxygen was evolved at the platinum wire; but at the same time a very small amount of thallic hydroxide deposited on the latter. The presence of the sulphuric acid prevents the formation of all but a minute quantity of thallic hydroxide, whereas the addition of a considerably larger quantity of sulphuric acid would prevent the deposition of metallic thallium. After a sufficient quantity (about 0.5 gram) of thallium had been deposited, the solution was drawn by suction directly into a weighed flask, the platinum wire and the apparatus containing the deposited thallium were washed three times with successive portions of the original solution, and the washings were transformed to the weighed flask. This was then weighed; and the thallium in the solution was determined, after dividing the liquid into two portions so as to obtain check results. By subtracting this weight of thallium from that originally associated with the quantity of water[1] present in the analyzed solution, the quantity of thallium deposited on the gold cup could be accurately determined (within 0.1 mg.).

For the 0.03 normal solution, some slight modifications were necessary. About 40 to 50 grams of the original solution were used for electrolysis and no sulphuric acid was added, since not enough thallic hydroxide formed to interfere with the experiment. The electrolysis was continued only for an hour, as the solution then became exhausted and hydrogen began to be evolved. Duplicate analyses were not made, as there was not enough thallium present in the solution to permit of it. The thallium deposited amounted to about 0.2 gram.

Electrolysis of the Solution.—After the preparation of the thallium deposit on the anode, the apparatus was charged with the solution so that the cathode compartment, C, was filled to three-fifths of its height, air bubbles in the horizontal portion were dislodged, and the apparatus placed in a thermostat at 25°, only the upper ends (two centimeters)

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[1] This quantity of water was calculated by subtracting from the weight of the analyzed solution that of the thallous sulphate found to be present in it, that of the dilute sulphuric acid added, and that of the SO_3 produced by the electrolysis (according to the reaction $Tl_2SO_4 = Tl + 1/2O_2 + SO_3$). The last quantity was calculated from the weight of thallium deposited, after this had been found approximately by a preliminary computation.

of the tubes BB and of the cathode tube being above the surface of the water. The tubes were closed with rubber stoppers, and electric connection was made with the cathode by the column of mercury contained in the glass tube.[1]

The apparatus was allowed to remain in the thermostat long enough to attain its temperature (25°) before starting the current. The electrolysis was continued for three hours or somewhat longer. The approximate strength of the current (as shown by the milliammeter) for the more concentrated solution was 0.012 amperes in the first experiment and 0.015 in the second; for the dilute solution in all three experiments, 0.007 amperes. During the electrolysis no bubbles of gas were evolved at either electrode; and at the end of it the electrode portions were both neutral to litmus.

At the end of the electrolysis the stoppers in the tubes BB were taken out, and the middle portions were drawn out by suction through glass tubes bent at two right angles directly into weighed flasks. In the experiments with the more concentrated solution three middle portions were taken, one consisting of the liquid contained in the horizontal part of the apparatus, one of the liquid in the vertical arm of the cathode side of the apparatus down to the bend, and one of the liquid in the vertical part of the anode side of the apparatus down to one centimeter above the anode compartment. These solutions were weighed and analyzed. In the experiments with the more dilute solution, two middle portions were taken, one consisting of the liquid in the horizontal part and in the upper half of the vertical arm on the anode side, the other of the liquid in the vertical arm on the cathode side down to the bend.

After the removal of the middle portions, the apparatus was taken from the thermostat, and the two parts were disconnected and closed by stoppers. After being dried on the outside the two parts were weighed separately to the nearest centigram.

The cathode portion was poured into a flask, and the apparatus washed several times with water, the washings being added to the flask. The thallium deposited on the cathode was dissolved in sulphuric acid and this solution united with the other. Duplicate determinations of the thallium present in known fractional parts of this solution were then made. The apparatus was dried and weighed, together with the stoppers and cathode, so as to obtain the total weight of the cathode portion before it was diluted (including the deposited thallium). The weight of water present in the cathode portion was calculated by subtracting from

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[1] Attempts were made to use as cathode mercury containing a very small quantity of zinc, as recommended by Morden (THIS JOURNAL, 31, 1045 (1909)); but it was found that the zinc rapidly replaced the thallium in the aqueous solution.

its total weight that of the thallium[1] and thallous sulphate. From this the amount of thallium in the original solution associated with this quantity of water could be found, whereby the amount of thallium transferred by the current became known.

With the anode portion, the procedure was similar. After weighing the part of the apparatus containing it, the solution was poured into a flask, the thallium remaining on the anode was dissolved in sulphuric acid either directly or by passing a current through the solution with the cup as anode, and this solution, as well as the water used to rinse the apparatus, was added to the flask and duplicate analyses of known fractions of this solution were made. The anode part of the apparatus was dried and weighed, thus giving the weight of the anode solution plus the thallium remaining on the anode. Assuming the thallium to dissolve according to Faraday's law, and knowing the amount of thallium deposited on the anode originally, the weight of water in the anode portion was calculated, and from that the amount of thallium which originally was present in the solution and on the anode and also the amount of it transferred was determined.

Analysis of the Solutions.—The method of analysis employed was in all cases the determination of the thallium by precipitating and weighing it as thallous iodide. The original solution and the middle portions when analyzed were perfectly neutral toward litmus; the electrode portions had been made acid with dilute sulphuric acid. To the latter, to provide for any oxidation to the thallic state that might have occurred, a few cubic centimeters of a 5 per cent. potassium sulphite solution were added before the precipitation. The solution of thallous sulphate was heated to boiling and a 5 to 10 per cent. solution of potassium iodide, also heated to boiling, was added with stirring. Sufficient iodide was added so that the solution, after precipitation, contained two per cent. or more of potassium iodide. The solution was then boiled vigorously for about a minute, so as to break up the lumps of thallous iodide and enable it to be filtered and washed more readily. The iodide as first precipitated was orange in color, but very soon became light yellow. The solution was allowed to stand overnight, the precipitate collected on a platinum Gooch crucible, washed with about 100 cc. of a 2 per cent. potassium iodide solution until free from sulphate and then with 80 per cent. alcohol to remove the potassium iodide. The precipitates were heated at 160° for an hour, which, as preliminary experiments proved, was sufficient to ensure a perfectly constant weight.

Duplicate analyses in almost all the cases checked within 0.1 per cent., and the method of analysis may therefore be considered accurate to that

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[1] In making this correction the thallium deposited was assumed to be equivalent to the silver precipitated in the coulometers.

degree. The presence of sulphuric acid up to the amount used had no apparent influence. The amount of thallous iodide weighed was between 0.3 and 1.2 grams.

4. The Transference Data for Thallous Sulphate.

The experimental data are given in Tables I and II. The headings are sufficiently explanatory, or become so when considered in connection with the description given above. The letters in the second column have the following significance: PA, Solution from which the thallium was deposited in preparing the anode. A, Anode solution. M_A, Middle portion adjoining the anode solution. M, Middle portion. M_C, Middle portion adjoining the cathode solution. C, Cathode solution. In the case of the 0.02999 normal solution there were only two middle portions, which are designated M_A and M_C, respectively. The changes

TABLE I.—TRANSFERENCE DATA FOR 0.09972 NORMAL THALLOUS SULPHATE SOLUTION AT 25°.*

(Containing 100.11 milli-equivalents of Tl_2SO_4 per 1000 grams of water.[1])

Expt. No.	Portion.	Wt. of portion (+ Tl).	Wt. of Tl_2SO_4 in portion.	Calc. wt. of water in portion.	Milli-equivalents Tl_2SO_4. After electrolysis.	Before electrolysis.	Change by electrolysis.	Ag in g. and milli-equiv.	Transference number for cation.
1	PA	63.93[2]	1.0651 1.0621	62.75	4.220	6.285	2.065		
	A	64.36	1.9331 1.9311	62.46	7.666	6.252	—0.651	0.1472 g. 1.3645 m.e.	0.477
	M_A	19.87	0.4890	19.38	1.940	1.940	0		
	M	32.78	0.8073	31.97	3.203	3.200	+0.003		
	M_C	29.24	0.7197	28.52	2.855	2.855	0		
	C	87.98	2.3260 2.3273	85.72	9.2315	8.5804	+0.651	0.1472 g. 1.3645 m.e.	0.477
2	PA	59.63[3]	0.8634	58.67	3.426	5.873	2.447		
	A	62.58	1.9391 1.9397	60.67	7.695	6.073	—0.825	0.1856 g. 1.720 m.e.	0.479
	M_A	25.90	0.6377	25.26	2.530	2.5285	+0.0015		
	M	28.36	0.6981	27.66	2.770	2.769	+0.001		
	M_C	30.22	0.7440	29.48	2.952	2.951	+0.001		
	C	84.04	2.2681 2.2706	81.85	9.004	8.193	+0.811	0.1855 g. 1.720 m.e.	0.472

[1] The data upon which this value is based are as follows:

Wt. of solution analyzed..	18.00	20.61	34.02	32.22	30.16
Wt. of TlI obtained......	0.5817	0.6662	1.0992	1.0406	0.9750
Milli-equiv. Tl per 1000 g. water..................	100.11	100.16	100.11	100.05	100.15

[2] Not including 1.29 grams H_2SO_4 added.

[3] Not including 1.39 grams H_2SO_4 added.

in concentration in the portions adjoining the electrode portions were in all cases within the experimental error of the analyses, and they have therefore not been included in the changes in concentration of the electrode portions.

A number of experiments were made which were faulty in one respect or another; for example, because of a leak of the current between the coulometers, or of unsatisfactory preparation of the thallium deposit on the anode. None of these experiments are reproduced here; but all of those are included in which from external evidence alone, without considering the results, the process appeared to be successful.

TABLE II.—TRANSFERENCE DATA FOR 0.02999 NORMAL THALLOUS SULPHATE SOLUTION AT 25°.*

(Containing 30.08 milli-equivalents of Tl_2SO_4 per 1000 grams of water.[1])

Expt. No.	Portion.	Wt. of portion (+Tl)	Wt. of Tl_2SO_4 in portion.	Calc. wt. of water in portion.	Milli-equivalents Tl_2SO_4. After electrolysis.	Before electrolysis.	Change by electrolysis.	Ag in g. and milli-equiv.	Transference number for cation.
3	PA	83.20	0.3711	82.79	1.4723	2.4904	1.0181		
	A	69.55	0.6792 0.6797	68.88	2.6960	2.0719	—0.3940	0.0891 g. 0.8259 m.e.	0.477
	M_A	47.02	0.3541	46.67	1.4049	1.4038	+0.0011		
	M_C	36.24	0.2724	35.97	1.0804	1.0820	—0.0016		
	C	86.10	0.7466 0.7460	85.39	2.9612	2.5685	+0.3927	0.0891 g. 0.8259 m.e.	0.476
4	PA	86.66	0.3639	86.25	1.4439	2.5944	1.1505		
	A	68.42	0.7012 0.7014	67.73	2.7825	2.0373	—0.4053	0.0909 g. 0.8426 m.e.	0.481
	M_A	43.66	0.3288	43.33	1.3045	1.3034	+0.0011		
	M_C	43.36	0.3264	43.03	1.2952	1.2943	+0.00009		
	C	79.31	0.6976 0.6988	78.65	2.7702	2.3658	+0.4044	0.0909 g. 0.8426 m.e.	0.480
5	PA	98.33	0.4766	97.81	1.8908	2.9421	1.0513		
	A	68.61	0.6804 0.6814	67.94	2.7016	2.0437	—0.3934	0.0875 g. 0.8111 m.e.	0.485
	M_A	36.23	0.2730	35.96	1.0833	1.0817	+0.0016		
	M_C	43.24	0.3254	42.91	1.2909	1.2907	+0.0002		
	C	92.03	0.7890 0.7904	91.28	3.1333	2.7457	+0.3876	0.0875 g. 0.8111 m.e.	0.478

[1] The data upon which this value is based are as follows:

Wt. of solution analyzed......	50.26	50.30	46.07	54.16
Wt. of TlI obtained..........	0.4972	0.4969	0.4547	0.5348
Milli-equiv. Tl. per 1000 g. water....................	30.12	30.08	30.05	30.07

Mr. F. L. Hunt working in this laboratory found $d_4^{25} = 1.0204$ for a solution containing 0.1 equivalent of thallous sulphate in 1 liter solution.

The values of the transference numbers are summarized in Table III. Since there seems to be no error in the method that would tend to make the results at either electrode either too high or too low, and since there was less manipulation involved in the treatment of the cathode than of the anode portion, it seems best to derive the final values of the transference number by taking the mean of the cathode and anode results with double weight assigned to the former. Taking into consideration the variation of the cathode and anode results and the fact that almost all errors are likely to affect them in opposite directions, it seems very improbable that the final values are in error by more than 0.5 per cent.

TABLE III.—SUMMARY OF THE CATION TRANSFERENCE NUMBERS FOR THALLOUS SULPHATE AT 25°.

	0.09972 normal.			0.02999 normal.	
	Cathode.	Anode.		Cathode.	Anode.
	0.477	0.477		0.476	0.477
	0.472	0.479		0.480	0.481
				0.478	0.485
Mean,	0.4745	0.4780	Mean,	0.4780	0.4810
	Final value,	0.4757		Final value,	0.4790

Only one value of the transference number of thallous sulphate is recorded in the literature, that of Bein,[1] who obtained the value 0.472 for the transference number of the cation at 23° at the concentration 0.052 normal.

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[1] *Z. physik. Chem.*, 27, 46 (1898).

* See heading of Tables I and II. The Analytical Data from which the values in Tables I and II were derived are as follows:

Expt. No.		P.A.		A.		M_A.	M.	M_C.	C.	
1	Fraction analyzed.	$\frac{43.66}{79.39}$	$\frac{35.73}{79.39}$	$\frac{53.76}{218.35}$	$\frac{38.17}{218.35}$	Whole	Whole	Whole	$\frac{50.92}{252.62}$	$\frac{53.39}{252.62}$
	Grams TlI..	0.7690	0.6276	0.6250	0.4433	0.6421	1.0599	0.9449	0.6156	0.6458
2	Fraction analyzed.	Whole		$\frac{49.49}{182.32}$	$\frac{59.28}{182.32}$	Whole	Whole	Whole	$\frac{63.17}{260.83}$	$\frac{58.31}{260.83}$
	Grams TlI..	1.1336		0.6911	0.8280	0.8373	0.9166	0.9769	0.7212	0.6665
3	Fraction analyzed.	Whole		$\frac{79.60}{164.86}$	$\frac{84.27}{164.86}$	Whole		Whole	$\frac{75.82}{232.78}$	$\frac{75.62}{232.78}$
	Grams TlI..	0.4872		0.4306	0.4562	0.4649		0.3576	0.3193	0.3182
4	Fraction analyzed.	Whole		$\frac{74.26}{158.87}$	$\frac{83.58}{158.87}$	Whole		Whole	$\frac{73.07}{210.34}$	$\frac{72.24}{210.34}$
	Grams TlI..	0.4778		0.4303	0.4845	0.4317		0.4286	0.3182	0.3151
5	Fraction analyzed.	Whole		$\frac{71.04}{152.44}$	$\frac{80.49}{152.44}$	Whole		Whole	$\frac{86.85}{215.03}$	$\frac{88.43}{215.03}$
	Grams TlI..	0.6257		0.4163	0.4724	0.3585		0.4272	0.4194	0.4268

5. Description of the Experiments with Lead Nitrate.

The apparatus which was used in the transference experiments with thallous sulphate was also used in those with lead nitrate. Except for a few modifications which will be described, the experimental method was essentially the same.

Preparation of the Solution.—Kahlbaum's lead nitrate, recrystallized from conductivity water to which 1 per cent. nitric acid had been added, was used. Solutions approximately 0.1 and 0.03 normal were prepared with conductivity water, and the exact contents determined gravimetrically. These solutions showed a neutral reaction.

Preparation of the Anode.—Finely granulated "test lead," such as is used in assaying, was employed in preparing the anode. It was found by analysis to contain 99.83 per cent. lead, with small amounts of oxide and moisture. A known weight was placed in the gold cup of the apparatus before adding the solution.

Electrolysis of the Solution.—The procedure was the same as with thallous sulphate, except that the lead which remained undissolved at the anode after the electrolysis was dissolved in nitric acid and added to the anode solution after the apparatus had been dried and weighed. It is therefore not included in the weights of anode solutions given in the tables. The electrode solutions remained clear during the passage of the current; but after their removal from the apparatus they became cloudy in a few minutes on account of lead hydroxide formed from the finely divided lead and the oxygen of the air. This shows that nitric acid was not formed at either electrode. The weight of lead which dissolved at the anode and separated at the cathode was assumed to be equivalent to the weight of silver separated in the coulometers. The weight of lead used as anode given in the tables is the calculated weight of pure lead (*i. e.*, the weight of the test lead multiplied by 0.9983).

Analysis of the Solutions.—The lead was precipitated and weighed as lead chromate in all cases. In the case of the neutral solutions, 1 cc. of a 10 per cent. sodium acetate solution and 10 cc. of a 5-fold normal acetic acid solution were added, and the hot solution was precipitated with a one or two per cent. potassium dichromate solution, about 50 per cent. in excess of that required for precipitation being employed. The solutions containing the precipitates were allowed to stand at least 12 hours; the lead chromate was then collected on a platinum Gooch crucible, washed with 200 to 300 cc. water, and dried at 160–170°. To the solutions which contained free nitric acid, either an excess of sodium acetate was added (experiments 1–3), or sodium carbonate solution was added until the acid was neutralized (experiments 4–7), and then acetic acid and dichromate were added as before. Duplicate analyses were found to agree much more satisfactorily when the precipitates were amorphous in character and settled slowly, than when they were crystallin and the solutions cleared rapidly, which last was the case when insufficient sodium acetate was added. Duplicate analyses checked within 0.1 per cent. except in case of some of the dilute solutions (experiments 4–7).

6. The Transference Data for Lead Nitrate.

The data and calculated results are given in Tables IV and V. The changes in the middle portions have not been included in the calculated changes of the electrode portions in any case:

TABLE IV.—TRANSFERENCE DATA FOR 0.1002 NORMAL LEAD NITRATE SOLUTION AT 25°.*

(Containing 100.50 milli-equivalents $Pb(NO_3)_2$ per 1000 grams of water.[1])

Expt. No.	Portion.	Wt. of portion (+ Pb).	Wt. of $Pb(NO_3)_2$ in portion.	Calc. wt. of water in portion.	Grams and milli-equiv. Pb at anode.[2]	Milli-equiv. $Pb(NO_3)_2$.			Ag in grams and milli-equiv.	Transference number for cation.
						Before electrolysis.	After electrolysis.	Change.		
1	A	61.05	1.5829 1.5814	59.94	0.4380 g. 4.230 m.e.	6.024	9.556	—0.698	0.1566 g. 1.452 m.e.	0.481
	M_A	23.02	0.3765	22.64		2.275	2.274	—0.001		
	M	33.36	0.5465	32.81		3.298	3.301	+0.003		
	M_C	31.49	0.5155	30.97		3.112	3.114	+0.002		
	C	71.07	1.2803 1.2824	69.88		7.023	7.740	+0.717	0.1567 g. 1.452 m.e.	0.494
2	A	61.00	1.5283 1.5290	59.88	0.4087 g. 3.947 m.e.	6.018	9.233	—0.732	0.1602 g. 1.485 m.e.	0.493
	M_A	22.85	0.3745	22.48		2.259	2.262	+0.003		
	M	34.66	0.5678	34.09		3.426	3.429	+0.003		
	M_C	28.14	0.4606	27.68		2.782	3.782	0		
	C	74.49	1.3384 1.3391	73.24		7.361	8.086	+0.725	0.1601 g. 1.484 m.e.	0.488
3	A	62.50	1.4573 1.4591	61.35	0.3514 g. 3.394 m.e.	6.166	8.808	—0.752	0.1658 g. 1.537 m.e.	0.489
	M_A	26.15	0.4274	25.72		2.585	2.581	—0.004		
	M	28.90	0.4739	28.43		2.857	2.862	+0.005		
	M_C	30.86	0.5053	30.35		3.050	3.052	+0.002		
	C	80.64	1.4414 1.4416	79.29		7.969	8.707	+0.738	0.1658 g. 1.537 m.e.	0.480

[1] The data upon which this value is based are as follows:

Wt. of solution analyzed..........	27.97	35.95	24.74	24.09
Wt. of $PbCrO_4$ obtained...........	0.4467	0.5745	0.3948	0.3847
Milli-equiv. Pb per 1000 g. of water	100.51	100.57	100.44	100.48

[2] Test lead analyses:

Wt. of test lead analyzed....	0.8538	0.8936	0.1444	0.3794	0.6358
Wt. of $PbCrO_4$ obtained......	1.3300	1.3912	0.2244	0.5916	0.9915
Per cent. Pb................	99.85	99.79	99.61	99.92	99.96

TABLE V.—TRANSFERENCE DATA FOR 0.02995 NORMAL LEAD NITRATE SOLUTION AT 25°.*

(Containing 30.04 milli-equivalents of $Pb(NO_3)_2$ per 1000 grams of water.[1])

Expt. No.	Portion.	Wt. of portion (+ Pb.)	Wt. of $Pb(NO_3)_2$ in portion.	Calc. wt. of water in portion.	Grams and milli-equiv. Pb at anode.	Milli-equiv. $Pb(NO_3)_2$. Before electrolysis.	Milli-equiv. $Pb(NO_3)_2$. After electrolysis.	Milli-equiv. $Pb(NO_3)_2$. Change.	Ag. in grams and milli-equiv.	Transference number for cation.
4	A	63.20	0.6205 0.6224	62.84	0.2321 g. 2.2424 m.e.	1.8877	3.7535	—0.3766	0.0831 g. 0.7703 m.e.	0.489
	M_A	52.02	0.2577	51.76		1.5549	1.5568	+0.0019		
	M_C	33.88	0.1676	33.71		1.0127	1.0121	—0.0006		
	C	68.52	0.3999 0.4008	68.17		2.0478	2.4180	+0.3702	0.0830 g. 0.7694 m.e.	0.481
5	A	66.66	0.8558 0.8556	66.27	0.3693 g. 3.5671 m.e.	1.9908	5.1684	—0.3885	0.0837 g. 0.7759 m.e.	0.502
	M_A	48.07	0.2385	47.83		1.4368	1.4404	+0.0036		
	M_C	36.30	0.1791	36.12		1.0850	1.0820	—0.0030		
	C	67.85	0.3986 0.3993	67.50		2.0277	2.4096	+0.3818	0.0837 g. 0.7759 m.e.	0.492
6	A	66.39	0.6326 0.6327	65.98	0.2343 g. 2.2637 m.e.	1.9820	3.8214	—0.4243	0.0959 g. 0.8890 m.e.	0.478
	M_A	50.35	0.2498	50.10		1.5050	1.5085	+0.0035		
	M_C	34.16	0.1686	33.99		1.0210	1.0183	—0.0027		
	C	68.58	0.4110 0.4112	68.22		2.0493	2.4829	+0.4336	0.0958 g. 0.8880 m.e.	0.489
7	A	64.79	0.6507 0.6485	64.40	0.2498 g. 2.4131 m.e.	1.9346	3.9236	—0.4251	0.0944 g. 0.8750 m.e.	0.486
	M_A	48.58	0.2408	48.34		1.4521	1.4547	+0.0026		
	M_C	36.54	0.1805	36.36		1.0923	1.0900	—0.0023		
	C	65.31	0.3931 0.3924	64.96		1.9547	2.3724	+0.4210	0.0944 g. 0.8750 m.e.	0.481

[1] The data upon which this value is based are as follows:

Wt. of solution analyzed	48.45	71.36	64.28	48.06
Wt. of $PbCrO_4$ obtained	0.2341	0.3447	0.3101	0.2321
Milli-equiv. Pb per 1000 g. of water	30.057	30.048	30.011	30.044

* See heading of Tables IV and V. The Analytical Data from which the values in Tables IV and V were derived are as follows:

Expt. No.		A.		M_A.	M.	M_C.	C.	
1	Part analyzed	$\frac{47.35}{232.17}$	$\frac{68.68}{232.17}$	All	All	All	$\frac{61.69}{250.07}$	$\frac{56.65}{250.07}$
	Grams $PbCrO_4$	0.3150	0.4565	0.3674	0.5333	0.5030	0.3082	0.2835
2	Part analyzed	$\frac{51.91}{208.67}$	$\frac{52.11}{208.67}$	All	All	All	$\frac{48.88}{210.75}$	$\frac{48.47}{210.75}$
	Grams $PbCrO_4$	0.3710	0.3726	0.3654	0.5540	0.4494	0.3029	0.3005
3	Part analyzed	$\frac{56.27}{206.18}$	$\frac{59.26}{206.18}$	All	All	All	$\frac{54.52}{204.53}$	$\frac{56.14}{204.53}$
	Grams $PbCrO_4$	0.3881	0.4092	0.4170	0.4624	0.4931	0.3749	0.3861

(*Continued on bottom of p. 1567.*)

TABLE VI.—SUMMARY OF THE CATION TRANSFERENCE NUMBERS FOR LEAD NITRATE AT 25°.

	0.1002 normal.			0.02994 normal.	
	Cathode.	Anode.		Cathode.	Anode.
	0.494	0.481		0.481	0.489
	0.488	0.493		0.492	0.502
	0.480	0.489		0.489	0.478
				0.481	0.486
Mean,	0.4873	0.4877	Mean,	0.4858	0.4889
	Final value,	0.4875		Final value,	0.4874

The results are summarized in Table VI. In deriving the final values equal weight has been given to the results obtained from the anode and cathode solutions. It is hardly possible that the error in these final values exceeds ±0.003 or 0.6 per cent.

7. Discussion of the Results.

An examination of the final values given in Tables III and VI shows that for either salt between the concentrations 0.03 and 0.10 normal there is no variation (greater than the probable experimental error) in the transference number of the cation. Within this range of concentration the values **0.477** (±0.003) for thallous sulphate, and **0.487** (±0.003) for lead nitrate may therefore be adopted.

It is of interest to compare these values with those at zero concentration which may be calculated from the equivalent conductances of the separate ions. For the ions in question Kohlrausch[1] has derived the following values:

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[1] *Landolt-Börnstein-Meyerhoffer Tabellen*, p. 763 (1905); also *Z. Elektrochem.*, **13**, 342 (1907). The values at 25° have been calculated with the aid of Kohlrausch's temperature coefficients. A partially independent determination of Λ_{Tl} and Λ_{SO_4} from new data upon the conductance of potassium sulphate and thallous sulphate at 18° and 25° recently obtained in this laboratory has led to the following values at 25°: $\Lambda_{\text{Tl}} = 76.0$ and $\Lambda_{\text{SO}_4} = 80.0$. These are seen to be closely concordant with those of Kohlrausch.

(Continued from p. 1566.)

Expt. No.		A.		M_A.	M.	M_C.	C.	
4	Part analyzed.......	$\frac{70.05}{197.82}$	$\frac{65.05}{197.82}$	All		All	$\frac{62.30}{225.07}$	$\frac{75.68}{225.07}$
	Grams $PbCrO_4$.......	0.2144	0.1997	0.2515		0.1635	0.1080	0.1315
5	Part analyzed.......	$\frac{83.10}{184.65}$	$\frac{75.00}{184.65}$	All		All	$\frac{89.26}{190.42}$	$\frac{82.35}{190.42}$
	Grams $PbCrO_4$.......	0.3758	0.3391	0.2327		0.1748	0.1823	0.1685
6	Part analyzed.......	$\frac{75.62}{149.91}$	$\frac{73.55}{149.91}$	All		All	$\frac{66.86}{171.55}$	$\frac{84.00}{171.55}$
	Grams $PbCrO_4$.......	0.3114	0.3029	0.2437		0.1645	0.1563	0.1964
7	Part analyzed.......	$\frac{69.94}{170.40}$	$\frac{92.28}{170.40}$	All		All	$\frac{81.97}{155.81}$	$\frac{72.63}{155.81}$
	Grams $PbCrO_4$.......	0.2606	0.3427	0.2350		0.1761	0.2018	0.1785

At 18°: $\Lambda_{Tl} = 66.0$; $\Lambda_{SO_4} = 68.4$; $\Lambda_{Pb} = 61.0$; $\Lambda_{NO_3} = 61.7$.
At 25°: $\Lambda_{Tl} = 75.9$; $\Lambda_{SO_4} = 79.3$; $\Lambda_{Pb} = 71.4$; $\Lambda_{NO_3} = 70.6$.

From these values one obtains for the cation transference number, at 25°, 0.489 for thallous sulphate and 0.503 for lead nitrate. These values are 2.5 and 3.2 per cent., respectively, higher than those directly measured at the higher concentrations. It is not certain whether these differences are real or are due to errors in the values at zero concentration, which are based on extrapolations in the cases of two different types of salts. The fact that there is little, if any, change between 0.10 and 0.03 normal makes it somewhat improbable that there is any considerable change below 0.03 normal.

Assuming that the change is real, it might be due in the case of thallous sulphate to the presence of the intermediate ion $TlSO_4^-$ in the more concentrated solutions. In the case of lead nitrate, on the other hand, the presence of the intermediate ion NO_3Pb^+ would probably cause a change in a direction opposite to that of the observed one.

The effect of the intermediate ion depends, however, on the value of its equivalent conductance, as will be seen from the following values of the transference number for thallium (T_{Tl}) which have been calculated for the two limiting cases, where the only ions present are (1) Tl^+ and $SO_4^=$, and (2) Tl^+ and $TlSO_4^-$, by the expressions (1) $T_{Tl} = \Lambda_{Tl}/(\Lambda_{Tl} + \Lambda_{SO_4})$, and (2) $T_{Tl} = (\Lambda_{Tl} - \Lambda_{TlSO_4})/(\Lambda_{Tl} + \Lambda_{TlSO_4})$, for various relative values of Λ_{Tl}, Λ_{SO_4}, and Λ_{TlSO_4}.

	Case (1).	Case (2).
For $\Lambda_{Tl} = \Lambda_{SO_4} = \Lambda_{TlSO_4}$:	$T_{Tl} = 0.50$;	$T_{Tl} = 0.0$.
For $\Lambda_{Tl} = \Lambda_{SO_4} = 2\Lambda_{TlSO_4}$:	$T_{Tl} = 0.50$;	$T_{Tl} = 0.33$.
For $\Lambda_{Tl} = \Lambda_{SO_4} = 3\Lambda_{TlSO_4}$:	$T_{Tl} = 0.50$;	$T_{Tl} = 0.50$.
For $\Lambda_{Tl} = \Lambda_{SO_4} = 4\Lambda_{TlSO_4}$:	$T_{Tl} = 0.50$;	$T_{Tl} = 0.60$.

Identical values would obviously be obtained for the transference number of the nitrate-ion ($T_{NO_3} = 1 - T_{Pb}$) in lead nitrate for the corresponding assumptions that $\Lambda_{Pb} = \Lambda_{NO_3} = 1$ to $4\ \Lambda_{NO_3Pb}$.

These values show that for the case that $\Lambda_{Tl} = \Lambda_{SO_4} = 3\Lambda_{TlSO_4}$ or $\Lambda_{NO_3} = \Lambda_{Pb} = 3\Lambda_{NO_3Pb}$ the presence of the intermediate ion would have no influence on the transference number; and, if it be admitted that the value of Λ_{TlSO_4} or Λ_{NO_3Pb} can be as small as this, no positive conclusion can be drawn from the results. Unfortunately, no direct information is at hand as to the values of these ion-conductances, and they can be estimated only on the basis of kinetic considerations or of analogies with other ions of corresponding molecular complexity. Comparing the $TlSO_4^-$ ion with the $SO_4^=$ ion, or the NO_3Pb^+ ion with the Pb^{++} ion, it is evident that, since the electric charge on the former ion is only half as great, the driving force would be only half as great, and that therefore, assuming the ion is of the same size, its velocity and equivalent conductance would also be half as great. If, however, the intermediate ion is formed by direct union of the Tl^+ and $SO_4^=$ or the Pb^{++} and NO_3^- ions, it might be expected that the ion would be larger than either of its constituents, so that its equivalent conductance would be less than one-half, and might well be approximately one-third, as great as that of the simpler bivalent ion.[1] It is, on the other hand, not improbable that the union of the simple bivalent and univalent ions to form the univalent intermediate ion is attended with a dehydration, since the relatively small conductance of the simpler bivalent ions indicates that they are, as a rule, more highly hydrated than the univalent ones. If this is the case, the conductance of the intermediate ion might have any value less than that of the constituent univalent ion. Of ions of composition and complexity analogous to $TlSO_4^-$ the hydrosulphate ion (HSO_4^-) and ethyl sulphate ion ($C_2H_5SO_4^-$) seem to deserve especial consideration. For the former, at 25°, Noyes and Stewart[2] have recently concluded that the value lies between 35 and 40, and for the latter Loeb and Nernst[3] found the value 39, while that for $SO_4^=$ is 79.3. Judging from these analogies, the value for $TlSO_4^-$ might also be about one-half that for $SO_4^=$

These statements make clear how the matter stands. The fact that the transference numbers of both thallous sulphate and lead nitrate show little if any change with the concentration up to 0.1 normal does not prove that the intermediate ions of these salts are not present in considerable quantity at the latter concentration, for it is possible that the

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[1] Prof. G. N. Lewis has suggested the following hypothesis, which requires in the special case here considered that the conductance of the intermediate ion be one-third that of the constituent ions, and which requires in general that the conductance of the intermediate ion has such a value that the transference number would not be influenced by its presence: "By the dissociation of a strong electrolyte the typical physical properties (optical, thermal, volume, etc.) suffer no appreciable change. This is also true of the further dissociation of such intermediate ions as KSO_4^-, $BaNO_3^+$, if they exist. It would not, however, be true of such ions as $HC_2O_4^-$ or HSO_4^-, the dissociation of which is attended by a noticeable heat change. The intermediate ions of the former class are probably loose aggregates in which the constituent parts are not in such intimate proximity as to effect their individual properties. It may be assumed, therefore, that their constituents will show the same resistance to motion through the solution as they show when free. Considering now a salt A_2B yielding the ions A^+, B^{--}, and AB^-, whose specific resistances are represented by R_A, B_B, R_{AB}, this assumption requires that $R_{AB} = R_A + R_B$, and that the corresponding mobilities be $\Lambda_A = \frac{1}{R_A}$, $\Lambda_B = \frac{2}{R_B}$, and $\Lambda_{AB} = \frac{1}{R_A + R_B} = \frac{1}{\frac{2}{\Lambda_B} + \frac{1}{\Lambda_A}} = \frac{\Lambda_A\Lambda_B}{2\Lambda_A + \Lambda_B}$

This can be shown to be the general condition that the transference number is independent of the amount of intermediate ion. In the special case in which $\Lambda_A = \Lambda_B$, it is obvious that $\Lambda_{AB} = {}^1/_3\Lambda_A$."

[2] THIS JOURNAL, **32,** 1142 (1910).

[3] *Z. physik. Chem.*, **2,** 962 (1888).

conductance of these ions has such a value as to make the transference numbers independent of the character of the ionization. Unless some general hypothesis, like that suggested by Lewis, can be substantiated, it is somewhat improbable that the conductance should have this unique value, which is less than that for other univalent ions of similar complexity, in the case of any one salt; and it becomes more improbable that this should be true in the case of a number of different salts. Yet this investigation and the previous one[1] made in this laboratory have shown that four different tri-ionic salts, potassium sulphate, thallous sulphate, barium nitrate, and lead nitrate, all show the same substantial constancy of the transference numbers up to a moderate concentration.[2] Some degree of probability therefore attaches to the hypothesis that such tri-ionic salts do not as a rule give rise to intermediate ions, at any rate in quantity exceeding a few per cent. at 0.1-0.2 normal; but that they dissociate directly into three ions. At any rate the statement can be made with positiveness that the transference relations of these tri-ionic salts afford no indication of the presence of intermediate ions; but whether this is due to the non-existence of such ions or to the fact that they have a conductance of such magnitude as not to influence the transference cannot be definitely stated.

8. Summary.

In this paper have been described transference experiments with 0.03 and 0.1 normal solutions of thallous sulphate and lead nitrate at 25°. The cation transference numbers found for the thallous salt are **0.479** at 0.03, and **0.476** at 0.1 normal; and for the lead salt **0.487** at both concentrations. The changes in content at both electrodes and in the middle portions have been determind, thus fixing the limit of error in the results, which can hardly exceed ±0.003, or about 0.5 per cent. The transference number at zero concentration as calculated from Kohlrausch's extrapolated values of the equivalent conductances of the separate ions is 0.489 for thallous sulphate and 0.503 for lead nitrate; thus 2.5 to 3.2 per cent. higher than the values found by direct measurement at 0.03-0.10 normal. Whether this change of the transference number with the concentration is real, is uncertain. Even if real, it is small, and lies in the case of thallous sulphate in the direction probably required by the presence of the intermediate ion; in the case of lead nitrate, in the

[1] A. A. Noyes, *Ibid.*, 36, 79 (1901).

[2] Almost all the other tri-ionic salts that have been accurately investigated are halides, the transference numbers of which as a rule change considerably with the concentration in a direction opposite to that which the presence of the intermediate ion would require, an effect which is not improbably due to the presence of complex anions. The existing data will be more fully considered with reference to the question here under discussion in a critical review of the results of transference experiments now under preparation.

opposit direction. The theoretical bearing of the results is discussed in the last two paragraphs of the preceding section. Taking also into consideration other accurate transference values for tri-ionic salts previously determined, it has been there shown that transference experiments make necessary one of two alternative conclusions: either the intermediate ion is not formed in any considerable proportion by the dissociation of tri-ionic salts up to moderate concentrations (0.1 to 0.2 normal), or else, if it is formed, its equivalent conductance has a definit value of such magnitude that the transference number is independent of its concentration.

BOSTON, September, 1910.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE CHARACTER OF SILVER DEPOSITS FROM VARIOUS ELECTROLYTES.

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In some work previously undertaken by one of us it became of interest to know the conditions which would give silver deposits of various properties or characteristics. The discussion of this general subject by Bancroft[2] is of great assistance in indicating the variations of conditions which favor satisfactory deposition. The influence of each particular electrolyte on these conditions and the minor details of the deposit characteristics is a matter for experimentation. In this connection Snowdon[3] has gone thoroughly into the deposition of silver from nitric acid and potassium cyanide, using the rotating cathode. Other electrolytes have been used from time to time, especially in electroanalysis.

It was thought therefore that a repetition of some of the earlier work done on the electrolytic determination of silver would not only be helpful in the direction desired but would also be of interest from an analytical view point. The results included here give the outcome of some of these experiments, together with a summary of a series of trials made with new electrolytes.

The same dish cathodes were used that were employed in the work on copper.[4] The anode also was the same except that the diameter of the spiral was 5 cm. in the present case. The current was supplied by storage cells and was measured by Weston, Model 57, switchboard instruments. The ammeter had a range of one ampere and the scale was divided into hundredths. The voltmeter had a range of six volts and the scale was

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[1] The major portion of this work is taken from Mr. Hughes' thesis for the M.A. degree, Ohio State University.

[2] *J. Physic. Chem.*, 9, 277.

[3] *Ibid.*, 9, 399.

[4] THIS JOURNAL, **30**, 381.