

THE DETERMINATION OF ION TRANSFERENCE IN SOLUTIONS
OF ELECTROLYTES IN ANHYDROUS ACETIC ACID

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THE DETERMINATION OF ION TRANSFERENCE IN SOLUTIONS
OF ELECTROLYTES IN ANHYDROUS ACETIC ACID

Some determinations of transference numbers have been made previously as a part of the investigation of the anhydrous acetic acid system at the University of Kansas. Longworth (1) made use of the moving boundary method to obtain a few measurements on solutions of sodium and potassium acetates. The transference numbers calculated approach a value of 0.5 with increasing dilution, indicating a type of ion transference similar to that usually found in aqueous solutions. In later work, Holm (2), who was interested primarily in transference in mixed salt solutions, made some determinations of a preliminary nature by the Hittorf method. The results appeared to indicate highly abnormal behavior. The calculated transference numbers decreased with increasing dilution, and were practically zero in the most dilute solutions studied.

There is no reason to expect such abnormality in the dilute solutions, and, furthermore, it has been shown (3) that the moving boundary and Hittorf methods give close agreement in aqueous solutions. In view of these facts it appeared to be of interest to re-determine the transference numbers by the Hittorf

under conditions which promised greater accuracy.

The chief difficulty encountered in the carrying out of such a project lies in the fact that solutions of electrolytes in acetic acid are very much poorer conductors of electricity than similar aqueous solutions. Now, if appreciable transference is to be obtained in a reasonable length of time the current cannot be reduced much below 6 to 8 milliamperes. Consequently, the higher resistance of the solutions causes an appreciable heating effect, which in turn brings about a greater degree of mixing. Further, in order to make possible the passage of an adequate current of electricity, either the distance between electrodes must be comparatively short or the cross section of the cell must be large. These conditions are exactly opposite to those which would be favorable to sharp separation of the several compartments of a cell and to the attaining of high precision in the measurement of transference numbers.

Electrode reactions which are suitable with regard to density changes, and to accurate analysis of the solutions, are also difficult to obtain. It has been necessary to introduce an additional ion at each electrode of the cell, and this usually complicates the analyses and lowers their precision.

In most of the measurements of transference numbers in non-aqueous solutions that have been reported in the literature (9), the lower alcohols have been used as solvents, and since these solvents are much more polar than acetic acid, the experimental difficulties due to the high resistance of the solutions were less. Even so, the determinations have been comparatively few in number, and appeared to be of uncertain accuracy. The most precise results were those which were obtained for lithium chloride (6) from measurements of the electromotive force of concentration cells.

In the work reported here, cation transference numbers have been obtained for solutions of sodium acetate, ammonium acetate and lithium chloride in acetic acid, over as wide a range of concentrations as was practicable. Studies on transference numbers for salts having an anion different from that of the solvent are of particular interest in that a better comparison can be made for the same salt in different solvents. Determinations have been made for lithium chloride in quite a number of solvents. It happens that lithium chloride is readily soluble in acetic acid, and consequently some measurements on this salt were included in this work.

PREPARATION OF MATERIALS

Anhydrous acetic acid, having a melting point of 16.58° to 16.60° C., was prepared as in previous work from high-grade acid obtained from the Niacet Chemical Company.

To prepare ammonium acetate (4), anhydrous acetic acid in an evaporating dish was placed in a desiccator over potassium hydroxide, and dry ammonia vapor was circulated over it. As the mixture solidified it was broken up several times with a stirring rod to obtain a more uniform product. No attempt was made to obtain the pure salt, since exposure to moist air during the preparation may thus be minimized and the presence of excess acetic acid is of no consequence. The melting point of the product was slightly above that reported for the same composition by McAllister (4), indicating the absence of any moisture. Analyses showed that it was largely the acid salt which was obtained after one day of circulating ammonia over the acid.

Sodium acetate was thrice recrystallized from dilute acetic acid, and then dried in the oven for a week at 150° . Analyses on different lots gave $28.017 \pm .002$ and $28.033 \pm .002$ per cent Na (calculated, 28.031 per cent Na).

Lead acetate was prepared from the C. P. hydrate as in previous work (10). Analyses gave 62.70 to 62.83 per cent Pb. (calculated, 62.71 per cent Pb).

Zinc acetate was prepared by adding acetic acid to zinc carbonate. The salt was then recrystallized and dried according to the method given by McAllister (5). The product was not analyzed, but was used to prepare a solution of zinc chloride. Pure hydrogen chloride was prepared and passed through drying tubes containing, successively, calcium chloride and phosphorus pentoxide. It was then passed into a suspension of zinc acetate in acetic acid of such proportions that the resulting zinc chloride solution was of a concentration of one gram per gram of solution.

C. P. lithium chloride (7) was recrystallized four times from water, hydrogen chloride being passed into the hot saturated solution each time to counteract hydrolysis. The salt was spread on a large evaporating dish in an oven, the temperature of which was raised gradually to 150°C . and held there for several hours. The hot salt was crushed with a hot agate pestle, transferred to a desiccator containing phosphorus pentoxide, and dry hydrogen chloride was passed over it for half an hour. Air which had been dried in successive long tubes of potassium hydroxide and phosphorus pentoxide

was then drawn through the desiccator for a week to remove the last traces of moisture. Because of the great tendency of lithium chloride to deliquesce, it could be transferred to weighing bottles only when hot or when in a very dry place. Only one sample was taken from a given weighing bottle, the remainder being discarded. Three analyses of the product gave 83.66, 83.8, and 83.67 per cent Cl (theoretical = 83.63 per cent Cl).

In order to obtain pure lead in a form which would amalgamate readily, reagent lead was melted and allowed to solidify under purified hydrogen gas. The sheet thus obtained could easily be cut, and it dissolved in mercury without delay. In some of the earlier work, lead amalgam was prepared electrolytically according to the procedure of LaMer and Parks (7). However, the other method proved to be entirely satisfactory, and it avoided the difficulty of storing the amalgam. The zinc metal used was C. P. stick zinc. It amalgamated readily when freshly cut.

Tank hydrogen was purified by passing the gas through hot platinized asbestos and then through two long tubes which contained fused calcium chloride.

Mercury was cleaned thoroughly by shaking it with mercurous nitrate and dilute nitric acid solution for a week and then distilling it under vacuum.

APPARATUS AND PROCEDURE

The essential parts of the transference apparatus are shown in Figure 1. The cells used in the final determinations are of a modified H-type. Their dimensions may be estimated from the fact that the two arms of the H were made from 1" by 8" Pyrex test-tubes. The cross arm is of 1" diameter and is about 1.5" in length. The electrodes are at the bottom of the two arms of the cell, electrical contact with the external circuit being made by means of platinum wires sealed in at the base.

The flask A which contains the original test solution is an Erlenmeyer flask of 250 cc. capacity. The overhead system of tubing and stop-cocks is so arranged that the cell and solution can be swept out with purified hydrogen, and the cell can be filled and emptied by means of the gas pressure, without access to the atmosphere.

The anode consisted of lead or zinc amalgam, and the cathode of mercury. Drain tubes are sealed to the cell so that the solution may be removed in three separate portions without taking the cell from the constant temperature bath. A tube D sealed to the bottom of the cross arm served to drain the solution to

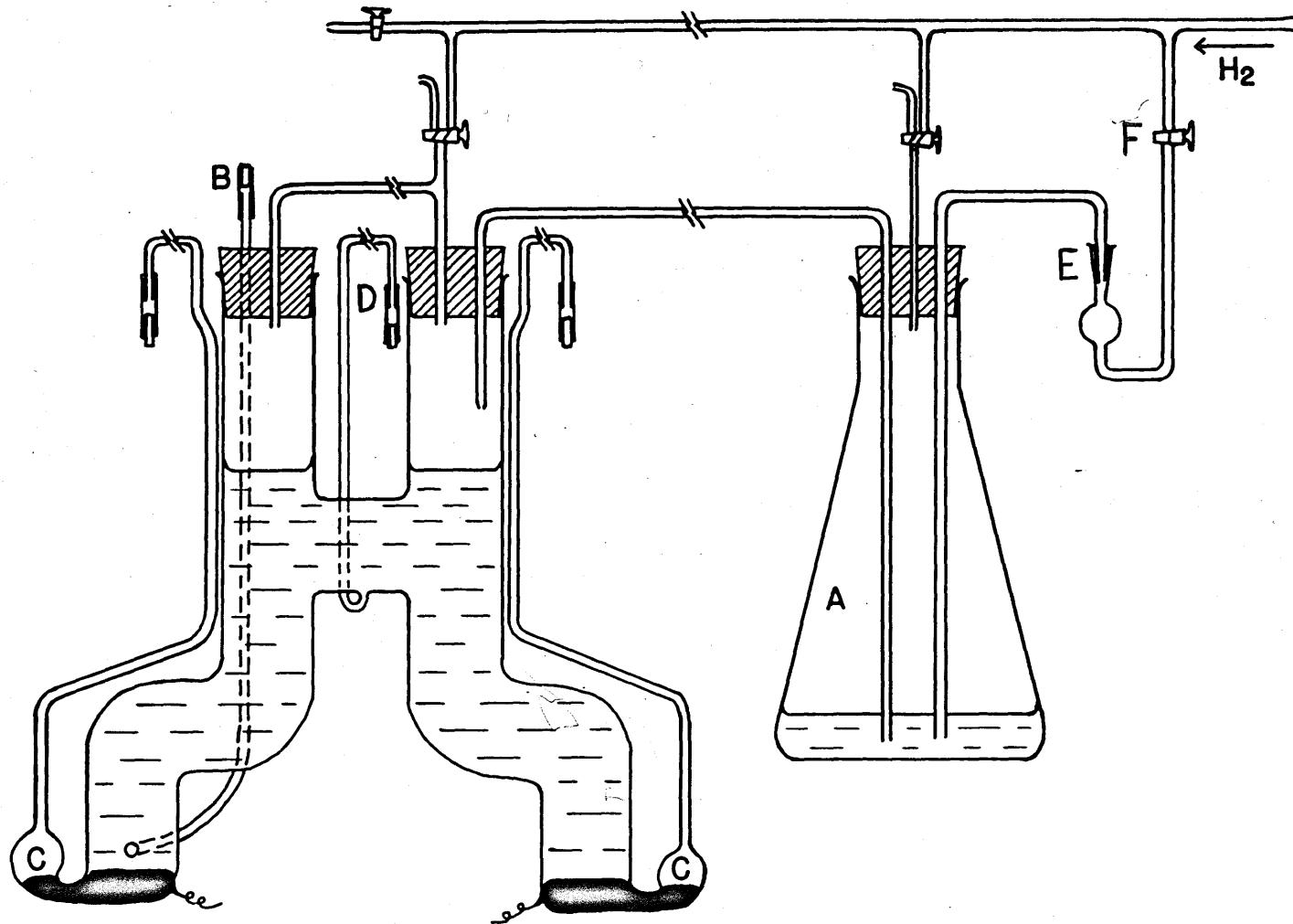


Fig. 1. Diagram of Apparatus for Determination of Transference Numbers.

that level, thus removing a middle portion and separating the anode and cathode compartments. The latter could then be drained through the tubes labeled C. The bulbs at the base of these tubes have a capacity of about two cubic centimeters and serve to trap the mercury of the electrodes. Their size, their position with reference to the base of the cell, and the diameter of the short connecting tube require rather nice adjustment in order to make possible the nearly complete removal of solution without the entrainment of mercury.

The constant temperature bath, in which the cell was immersed during all the experiments, was maintained at 25.0 C. It was filled with a light mineral oil to prevent any current leakage through the bath liquid. The bath and all the apparatus were firmly supported so as to be as free from vibration as possible. An occasional trembling of the surface of the mercury electrodes was apparently due to the shaking of the building itself. The stirring device was attached to a very solid separate support, and its operation caused no detectable vibration. Rapid stirring of the bath liquid proved to be quite essential for the dissipation of heat from the transference cell.

The source of current was a rectifier built to deliver a fairly smooth direct potential of from 200

to 700 volts in seven steps. A finer adjustment of potential was built into the instrument, but it was on the high potential side and did not survive much usage. The coarse adjustment proved to be all that was necessary.

Quantities of electricity were measured with two simple silver coulometers, one placed ahead of the transference cell and the other following it in the electrical circuit. The coulometers consisted of anodes of assay silver and cathodes of platinum foil, 2.5 by 2.5 cm., suspended in a small beaker containing a twenty per cent neutral solution of silver nitrate. The slight sedimentation from the anodes caused no difficulty for the small quantities of electricity to be measured, and the weights of silver deposited in the two coulometers always checked perfectly. A milliammeter was placed in the circuit to indicate the current being passed. The brass weights used throughout the investigation had been carefully standardized against similar ones which had been checked by the Bureau of Standards. The weights of all solutions were reduced to vacuum.

To carry out a typical run with a solution of sodium or ammonium acetate, the apparatus was first cleaned and then dried in a current of dry air. The

cell was placed in the oil bath, where it was held firmly in place by two clamps. About two cubic centimeters of mercury was introduced into each side of the cell and a piece of freshly cut lead which would be about three times that required for the expected amount of anodic oxidation was dropped into the anode side. The overhead system of tubing without flask A, was then put in place. Connection was made between the two arms of the cell at the top in order to keep the solution leveled, particularly during the emptying process. The source of hydrogen gas was attached to the system through a ground glass joint, and the cell with all its side-tubes was swept free from air. The tubes were capped with short pieces of rubber tubing containing glass plugs. The removal of air from the system was necessary in order to prevent quite appreciable oxidation of the lead other than by electrolysis.

The next step was to attach the flask A containing the test solution. Before this was done a small amount of anhydrous acetic acid was introduced into the bulb of the ground glass joint E just ahead of the flask. This served to slow down evaporation of solvent, with subsequent crystallization of the salt, during the sweeping out process. With a stream of hydrogen flowing from the tube connecting the flask A to the

cell, and the stopcock F opened, the flask was slipped up into its place, and the gas bubbling through the solution was allowed to escape through the two-way stopcock above. In this way very little solution ever entered the tubes and therefore little difficulty was experienced from evaporation there. As hydrogen was bubbled through the solution, the latter was heated to about 90° to facilitate the removal of air, and was then cooled in ice water to room temperature. Tests showed that after thirty minutes of this treatment, lead ion could not be detected with hydrogen sulfide in the anode solution, even after it had stood in the cell several hours.

By the suitable adjustment of stopcocks, a few cc. of solution was pumped into the anode compartment of the cell for rinsing the amalgam. This was forced out of the cell through the tube C, and the anode was washed with another portion of solution. The whole anode section and drain tube was then filled, the tube being capped against an outflowing stream of solution in order to exclude air. A few cc. of solution was allowed to overflow onto the mercury cathode for rinsing. After this had been once repeated, the cell was completely filled to a level just above the cross arm. The other two drain tubes were also filled. The flask A was next removed, samples were poured into

weighed, glass-stoppered flasks, and the remaining solution was kept tightly stoppered for rinsing the cell after the run.

The ground glass joint at E was originally intended for the removal of samples of the original solution. However, it was found to be difficult to get perfectly uniform samples because of the evaporation which took place in this tube, as discussed previously, even after the tube had been flushed out. Samples were therefore poured directly from the flask.

If the electrolysis were started at this stage, there would, of course, be gassing at the cathode. The most desirable cathode reaction would be obtained by the use of a very slightly soluble salt the metal of which would be reduced by the current, a more dense layer of solution being left immediately above the cathode. An attempt was made to use mercurous acetate, but it was found that the salt would not dissolve with sufficient rapidity to provide for a current of even a few milliamperes. The method finally used was to dissolve pure plumbous acetate in a few cc. of the original solution in a stoppered test-tube. A suitable quantity of this dense solution was then introduced into the bottom of the cathode compartment through the tube B, by means of a pipette. Finally the circuit was completed, and the electrolysis continued for the desired length of

time. At the end of the run the platinum electrodes were rinsed, dried and weighed. The cell was emptied in three portions, middle, anode and cathode, into weighed glass-stoppered flasks. Each electrode was rinsed twice with a few cc. of original solution, the cell being opened briefly and the solution poured directly from flask A. Each solution was thoroughly mixed in the flask in which it was weighed, and samples were then removed for analysis.

Ammonium acetate solutions were analyzed by distillation of the ammonia from alkaline solution into standard acid. Since both anode and cathode solutions contained lead acetate, and even the middle section usually contained a small amount, separate small samples were also taken for the determination of lead as lead sulfate. Some precautions had to be taken with the ammonia distillations in order to obtain the high precision desired. The quantities of ammonia to be determined were almost always large and consequently there was danger of loss of un-neutralized ammonia from the receiving flask. As a result of many distillation tests, it was shown that the rate of distillation had little effect on the results. However, it was found that the attachment to the end of the condenser tube of a small bulb, containing many small holes around its base, effectively insured complete absorption of the ammonia. The other

item to be considered was the presence of acetic acid vapor. For solutions above 0.5 molal it was found to be sufficient to sweep out the Kjeldahl flask with a rapid stream of air immediately before the alkali was added. In more dilute solutions, the results were much less dependable, although in a few runs sulfuric acid was added to the samples and most of the acetic acid boiled off under the hood.

Sodium acetate was determined as sodium sulfate in covered platinum crucibles, the samples being ignited to a bright red heat over the Bunsen burner. Solutions taken from the cell were necessarily analyzed for both lead and sodium on the same sample. After the addition of excess sulfuric acid, the sample was evaporated on the water bath and heated to strong fuming. The residue was then taken up in 30 per cent alcohol. The lead sulfate was filtered off on a weighed Gooch crucible and washed thoroughly with 30 per cent alcohol containing 3 per cent sulfuric acid, first by decantation and then on the filter. The Gooch was dried and heated inside a large iron crucible, over the full flame of the Meker burner. The filtrate was evaporated on the water bath, and sodium sulfate was determined in the usual manner. It was, however, found convenient to drive off most, but not all, of the accumulated sulfuric acid before the transfer of the residue to platinum.

The presence of some acid seemed to be necessary to prevent the creeping of sodium sulfate during the final evaporation.

In the presence of lead, it was never possible to determine the sodium acetate with quite the high degree of precision that could be attained with the sodium acetate alone. After a considerable proportion of the runs had been made, and the procedure had become more uniform, it began to be apparent that the quantities of sodium acetate found by the above method were slightly high, in spite of the fact that preliminary analyses on synthetic mixtures had given correct results. In two of the later runs, the analysis was made in this manner : the mixed sulfates were weighed in a platinum crucible, the solid digested in wash solution, and the lead sulfate filtered off. The results of these runs and of test analyses showed that while the weights of mixed sulfates were quite accurate, the lead acetate came out high, and consequently the sodium acetate obtained by difference was low. An improvement on this method which was, unfortunately, not used, would be to determine the lead acetate on a separate sample of the solution. This could be done with accuracy and should result in a more nearly correct value for the sodium acetate. However, we shall see that some of these small systematic errors cancel out when an average

of anode and cathode transferences is calculated.

Different electrode reactions were required for solutions of lithium chloride. Since zinc forms one of the few chlorides which are readily soluble in acetic acid, it was used for the anode in the form of a dilute amalgam. Holm (2) reported that zinc amalgam was unsatisfactory for this purpose. It is true that zinc dissolves from the more concentrated amalgams, containing one per cent or more of zinc, with rapid evolution of gas. However, when the concentration was kept below 0.7 per cent there was only a very minute amount of gas evolved from the freshly rinsed electrode, and practically none after the current was started. The careful exclusion of air from the electrode probably had some inhibitive effect also.

A fairly satisfactory cathode reaction was obtained by introducing a concentrated zinc chloride solution onto the cathode. This, of course, made analysis of solutions from this compartment useless because of the impossibility of determining just how much chloride ion had been introduced. The mercury cathode usually blackened during a run, and a very slight evolution of gas occurred. This was apparently a result of the fact that the discharged zinc did not go into the amalgam readily, the unprotected zinc thus redissolving to a small extent.

Chlorine was determined by a modified Volhard method. An excess of standard silver nitrate solution was added from a weight burette, with rapid stirring of the solution. The mixture was then heated nearly to boiling and stirred until the precipitate was thoroughly coagulated, and a clear supernatant liquid remained. Back titration was carried out with 0.1 normal sodium thiocyanate solution, ferric alum being used as indicator. The end-points were sharp and surprisingly permanent.

Zinc was determined by titration with 1/36 molar potassium ferrocyanide solution. 1/20 molar uranyl nitrate solution was used as an outside indicator.

The determinations were not highly accurate; but they were probably correct within 10 per cent or less, which happened to be all that was necessary for our purposes. The potentiometric method was not used since no definite end-point could be found in the presence of so high a concentration of acetic acid.

Before the methods of calculation of results are considered, it will be necessary to discuss the changes which take place in the transference cell during electrolysis. Let us consider a solution of ammonium acetate, as an example, although the description also applies to sodium acetate solutions. Ammonium acetate is transferred from the anode compartment, and it is transferred to the cathode compartment. The electrode reactions involve only lead and acetate ions. At the

anode lead is oxidized quantitatively to form a dense layer of plumbous acetate solution, the sharp upper boundary of which is clearly visible. Plumbous ion is reduced to free lead at the cathode, forming a dilute amalgam from which there is no gas evolved. If sufficient lead acetate has been added, the heavy layer of solution over the cathode remains very clearly defined throughout the run. Even if nearly all the lead ion were reduced during an electrolysis, there would still be a solution immediately above the cathode of greater density than that of the unchanged solution, because of the transference of ammonium acetate into the cathode compartment. It may be mentioned that, since we know neither the extent of solvation of ions in these solutions nor the relative solvation of cation and anion, no account has been taken of the transfer of solvent during the electrolysis.

The cation transference number is given by the fraction of a mole of ammonium acetate lost from the anode compartment, and by the fraction of a mole gained in the cathode compartment, per faraday of electricity passed. Particularly since the determination of ammonia is unaffected by the presence of lead, we have in this instance an excellent opportunity for obtaining transference numbers at both electrodes. The quantity of

lead acetate is needed only as a correction to be applied to a large weight of solution, in order that the reference amount of acetic acid may be calculated.

In any transference experiment the validity of the results is dependent upon the constancy in composition of the middle portion of the solution. However, the changes in concentration are in opposite directions at the two electrodes, and it is therefore possible that the middle portion will maintain a constant average composition even though concentration changes are entering from both ends. The usual method to be followed in such a case for aqueous solutions is to divide the middle compartment into three sections, but for the comparatively short cell which must be used for the solutions in acetic acid, such a division is not feasible.

In order to make any significant use of the analysis of the middle compartment, it then becomes necessary to determine which region of concentration change moves toward the middle compartment with the greater speed. It is very probable that there will be such a difference, and the following method of study can be applied. If we consider successive electrolyses in which the same current is being continued for increasing lengths of time, there will be a certain point along the time axis at which the transference number calculated from

changes at one electrode will begin to fall off. If the change in the middle section is now added to that at the electrode in question, the true transference number will again be obtained. Obviously, if the time of electrolysis be lengthened more and more, there will be mixing from both electrode compartments. The change in concentration of the middle section then reaches a more or less constant amount which is dependent upon the two rates of mixing, and it is no longer useful for the correction of either calculated transference number. The determination of the allowable currents and times of electrolysis by such methods is a tedious one, but such a study will be described in this work.

In all of these experiments the transference numbers are unaffected by the presence of additional salts around the electrodes, provided that none of them ever reach the boundary between electrode compartment and middle compartment. This condition has actually never been perfectly met in this work, but the quantities of lead acetate or zinc chloride found in the middle compartment were in every case so minute that their ions could not conceivably carry a measurable fraction of the current. The point will be considered further when we come to a discussion of the results.

In order to determine the proper conditions of electrolysis, as well as to perfect analytical technique and to develop methods of manipulation, a preliminary series of fifteen experiments was carried out on approximately 0.5 molal ammonium acetate solutions. The transference cell used in this cell was similar to the one which has been described, but it lacked the right-angled bends in the two arms of the cell.

Most of the electrolyses were run until 0.25 to 0.30 gram of silver had been deposited, since that quantity was about the minimum for which good precision could be obtained. It was found that the full 700 volts of the rectifier could never be used successfully. The best conditions found were to set the rectifier at the 280 volt tap and to allow the resulting current of about 9 milliamperes to flow for approximately seven hours. The calculated cation transference numbers obtained under these conditions were close to 0.47. On the other hand, if a current of, say, 18 milliamperes were passed for half the time, the calculated transference numbers were only about 0.35, thus indicating a very marked degree of mixing from both ends of the cell due, no doubt, to convection currents. The change in the middle compartment would obviously have been useless for the correction of such values.

The appearance of the boundary of the heavy layer

of plumbous acetate solution at the anode also changed markedly with variations in current. If, after a distinct boundary had formed at low current, the voltage was suddenly stepped up to nearly full value, the boundary quickly became rough and wavy, and in a short time the heavy liquid began to "mushroom" up into the main body of solution. At lower voltages at which the current was still too large, convection lines could be seen rising from the center of the heavy layer. This was due to local heating at the electrode and in the interior of the comparatively large cell tube, with the resulting convection of the dense solution up into one which was presumably much lighter. The rate of stirring of the constant temperature bath was also discovered to have an easily perceptible effect on the convection. This was discovered accidentally when the direction of rotation of the stirring propeller was reversed during a run. When the direction was such that the propeller drew liquid up instead of forcing it downward, the rate of movement throughout the bath was increased, and convection lines which had previously been clearly visible disappeared completely.

Oddly enough, no such tendency towards mixing was observed at the cathode, even though the deposition of lead was constantly producing a less dense solution at the surface of the mercury cathode. The presence of the lighter solution at the bottom caused visible

but very slow mixing throughout the layer of lead acetate solution. The volume of this layer increased slightly as the slow circulation continued, but its boundary remained clearly visible throughout the run and no convection lines could be detected above the layer.

As for the rate of mixing from the two end sections, it was clearly demonstrated by these experiments that the region of concentration change traveled faster from the anode compartment to the middle than from the cathode. Consequently there was always a slight loss of ammonium acetate from the middle compartment even under the best conditions prescribed above. Since any mixing from the cathode would result in lowered transference numbers, it remained to be determined whether or not further shortening of the electrolyses would raise the values obtained. For the limiting case two runs were made in which electrolysis proceeded for only one-half the usual time, and no appreciable concentration change could possibly reach the middle compartment. The results were necessarily of low precision, but the average of the four transference numbers calculated from the two experiments was 0.49. Now, the precision of the determinations toward the last of the preliminary series had shown gratifying improvement, and the increase of 0.02 of a unit for

the short runs was certainly greater than could be attributed to analytical errors. This indicated the need for more effective prevention of mixing, if results of the highest degree of accuracy compatible with analytical limitations were to be attained.

In the determination of transference numbers in aqueous solutions, improved separation of the regions of concentration change has been obtained (3a) by the provision of sharp right angled turns in the transference tube to break up any convection currents. No very extensive turns could have been made in the cell which we were using, without a substantial increase in the distance between electrodes. However, the improvement which was being sought was small, and it was thought that even a very short bend might be sufficiently effective. The cell of Figure 1, with the double right-angled turns in each arm, was then constructed. The turns produced the desired improvement as shown by subsequent results, and this form of cell was used in all the final determinations recorded in this work.

Once the determination at one concentration was well established, it was a comparatively easy matter to work at other concentrations. In general, the voltage was left constant at 280 volts, and the corresponding current varied from about four to fourteen milliamperes, depending upon the concentration and nature of the electrolyte. Solutions of lithium

chloride of a given concentration were appreciably better conductors than either of the acetate solutions, as might have been expected, particularly in the lower concentration range.

CALCULATION OF RESULTS

There is nothing novel in the method of calculation, but, since additional ions are added to the solution during electrolysis, there is some complication, and the results of a typical experiment with ammonium acetate will be followed through in detail.

$$\text{Molality} = 0.979$$

Gm. NH_4OAc /gm. HOAc in original.	1.	0.07545 ₆
	2.	0.07546 ₂
Amperes current passed		0.012
Gm. silver deposited	1.	0.3874
	2.	0.3873
Gm. of anolyte		56.418
Gm. NH_4OAc in anolyte		3.7951
Gm. $\text{Pb}(\text{OAc})_2$ in anolyte		0.577
Total gm. salt in anolyte		4.372
Gm. HOAc in anolyte		52.046
Gm. NH_4OAc originally associated with 52.046 gm HOAc		3.9274
Gm. NH_4OAc transferred from anolyte		0.1323
Gm. of middle solution		38.243
Gm. NH_4OAc in middle		2.6791
Gm. $\text{Pb}(\text{OAc})_2$ in middle		0.004
Gm. NH_4OAc in original		2.6833
Gm. NH_4OAc transferred from middle		0.0042

Gm. of catholyte	57.994
Gm. NH_4OAc in catholyte	4.1605
Gm. $\text{Pb}(\text{OAc})_2$ in catholyte	0.450
Gm. NH_4OAc in original	4.0282
Gm. NH_4OAc transferred to catholyte	0.1323

From anode transference,

$$t_+(A) = \frac{0.1323}{77.08} \times \frac{107.9}{0.3874} = 0.478.$$

From anode transference + loss in middle,

$$t_+(A+M) = \frac{0.1365}{77.08} \times \frac{107.9}{0.3874} = 0.493.$$

From cathode transference,

$$t_+(C) = \frac{0.1323}{77.08} \times \frac{107.9}{0.3874} = 0.478.$$

total gm. $\text{Pb}(\text{OAc})_2$ in anolyte and middle	0.581
Gm. $\text{Pb}(\text{OAc})_2$ formed at anode calculated from silver deposited	0.583

Calculations for sodium acetate solutions are exactly similar. Those for lithium chloride are based on determination of the chloride, and account is taken of the fact that part of this is present as zinc chloride. The correction is necessary only to make possible the calculation of the quantity of acetic acid in a given solution. The anion transference number is given by the fraction of an equivalent of chlorine transferred to the anolyte during the passage of a faraday of electricity, t_{Li^+} being obtained by subtracting this value from unity.

RESULTS

The numerical data have been summarized and tabulated in Tables I, II, and III. The data have been given in as great detail as is possible, if the tables are not to become excessively voluminous. Where duplicate analyses were possible, both results have been tabulated, the gain or loss of solute in the given compartment having been calculated by use of the average. A few numbers in Table I which are in parenthesis are considered to be doubtful although there was no evidence to warrant their being omitted. Analyses lost by accidents are indicated by dashes in the blank space.

TABLE I

AMMONIUM ACETATE

Molality		0.165	0.192	0.220	0.300	0.381	0.521
Gm./gm. acetic acid	1.	1.278	1.483	1.696	2.316	(2.927)	4.017
x 10 ²	2.	1.273	1.481	1.691	2.314	2.940	4.021
Amperes		.004	.003	.005	.007	.008	.010
Hours of electrolysis		7.5	--	7	7	6	8
Gm. Ag deposited	1.	.1277	.0858	.1440	.1829	.2017	.3177
	2.	.1277	.0857	.1438	.1829	.2018	.3176
Gm. of anolyte		55.20	51.08	55.56	55.40	50.99	56.70
Gm. NH ₄ OAc in anolyte		0.6581	0.7169	0.8811	----	1.3921	2.0750
Gm. Pb(OAc) ₂ in anolyte		.147	.117	.178	----	.265	.483
Gm. NH ₄ OAc Transferred from anolyte		.036	.0278	.0416	----	.058	.1009
Gm. of middle solution		39.11	38.64	39.45	38.77	40.74	38.11
Gm. NH ₄ OAc in middle		0.4679	0.5601	0.6473	----	1.1518	1.4655
Gm. Pb(OAc) ₂ in middle		.048	.014	.037	----	.033	.023
Gm. NH ₄ OAc transferred from middle		.024	.0041	.0089	----	.011	.0063
Gm. of catholyte		58.43	50.06	56.59	56.40	51.72	58.00
Gm. NH ₄ OAc in catholyte		0.7642	0.7507	0.9730	1.3207	1.5116	2.3225
Gm. Pb(OAc) ₂ in catholyte		1.137	0.807	1.039	0.848	1.120	0.636
Gm. NH ₄ OAc transferred to catholyte		.043	.032	.049	.065	.069	.1103
t ₊ (A)	0.39	0.45	0.41		0.40	0.445
t ₊ (A+M)	0.66	0.52	0.49		0.48	0.473
t ₊ (C)	0.47	0.52	0.48	0.50	0.48	0.486

TABLE I (continued)

AMMONIUM ACETATE

Molality		0.671	0.979	1.45	1.61	2.43
Gm./gm. acetic acid	1.	5.175	7.564	11.142	12.376	18.727
	2.	-----	7.546	11.142	12.372	18.733
$\times 10^2$						
Amperes		.011	.012	.012	.012	.013
Hours of electrolysis		6	7	8	8	8.5
Gm. Ag deposited	1.	.2596	.3874	.4168	.4049	.4464
	2.	.2697	.3873	.4167	.4051	.4462
Gm. of anolyte		55.37	56.418	57.443	52.634	57.831
Gm. NH_4OAc in anolyte	1.	2.6199	3.7951	5.5734	5.6060	8.9028
	2.			5.5733	5.6118	8.8986
Gm. $\text{Pb}(\text{OAc})_2$ in anolyte		.387	.577	.621	.606	.669
Gm. NH_4OAc transferred from anolyte		.0926	.1323	.1368	.1350	.1387
Gm. of middle solution		38.96	38.243	38.746	41.565	40.811
Gm. NH_4OAc in middle		1.9135	2.6791	3.8822	(4.5676)	6.4365
Gm. $\text{Pb}(\text{OAc})_2$ in middle		.007	.004	.002	.0015	.001
Gm. NH_4OAc transferred from middle		.0034	.0042	.0022	(.010)	.0016
Gm. of catholyte		56.93	57.994	57.990	53.091	60.603
Gm. NH_4OAc in catholyte	1.	2.8856	4.1605	(5.3818)	5.3358	9.5850
	2.			5.3887	5.3389	9.5830
Gm. $\text{Pb}(\text{OAc})_2$ in catholyte		.080	.450	.504	1.157	.615
Gm. NH_4OAc transferred to catholyte		.6903	.1323	.1396	.1334	.1432
$t_+(A)$		0.499	0.478	0.460	0.466	0.435
$t_+(A+M)$		0.518	0.493	0.467	----	0.440
$t_+(C)$		0.487	0.478	0.469	0.463	0.449

TABLE II

SODIUM ACETATE

Molality		0.344	0.481	0.558	0.583	0.627
Gm./gm. acetic acid	1.	2.820	3.945	4.576	4.785	5.142
x 10 ²	2.	2.821	3.945	4.576	4.782	5.143
Amperes		.004	.006	.007	.010	.010
Hours of electrolysis			6.	7.	7	7
Gm. Ag deposited	1.	.0886	.1574	.2152	.2823	.2986
	2.	.0887	.1575	.2153	.2824	.2987
Gm. of anolyte		50.44	51.51	55.65	55.36	51.65
Gm. NaOAc in anolyte	1.	1.3516	1.8999	2.3579	2.4110	2.4208
	2.		1.8953			
Gm. Pb(OAc) ₂ in anolyte		.130	.229	.317	.410	.428
Gm. NaOAc transferred from anolyte		.029 ₄	.050 ₆	.066 ₅	.103	.089
Gm. of middle solution		39.23	41.26	40.60	39.77	39.65
Gm. NaOAc in middle		1.0780	1.5601	1.7753	1.8082	1.9327
Gm. Pb(OAc) ₂ in middle		.009	.016	.017	.030	.036
Gm. NaOAc transferred from middle		.000 ₆	.005 ₅	.000 ₅	.007	.005
Bm. catholyte		49.33	51.52	57.99	57.43	53.06
Gm. NaOAc in catholyte		1.3660	1.9562	2.5517	2.6740	2.6511
Gm. Pb(OAc) ₂ in catholyte		.776	1.338	1.382	.752	.889
Gm. NaOAc transferred to catholyte		.0348	.0537	.0785	.091	.104
1. t ₊ (A)		0.44	0.42	0.41	0.48	0.39
2. t ₊ (A+M)		0.45	0.47	0.41	0.51	0.41
3. t ₊ (C)		0.52	0.45	0.48	0.42	0.46
Average t ₊ (2 and 3) ...		0.48	0.46	0.45	0.47	0.44

TABLE II (continued)

		SODIUM ACETATE				
Molality		0.673	0.678	0.709	0.797	0.887
Gm./gm. acetic acid	1.	5.520	5.565	5.819	6.541	7.276
	2.	5.518	5.565	5.819	6.542	7.277
	$\times 10^2$					
Amperes		.008	.008	.011	.009	.010
Hours of electrolysis		6	7	7	6.5	7.5
Gm. Ag deposited	1.	.2190	.2407	.3317	.2599	.3066
	2.	.2190	.2407	-----	.2600	.3067
Gm. of anolyte		51.30	56.46	57.02	51.69	56.26
Gm. NaOAc in anolyte	1.	2.5925	2.8851	3.007	3.0765	3.7020
	2.	2.5954	2.8904		3.0737	3.6994
Gm. Pb(OAc) ₂ in anolyte		.328	.358	.487	.387	.459
Gm. NaOAc transferred from anolyte		.076 ₁	.073 ₈	.108	.079 ₇	.096 ₁
Gm. of middle solution		39.74	40.27	40.92	40.11	41.05
Gm. NaOAc in middle		2.0751	2.1226	2.242	2.4617	2.7830
Gm. Pb(OAc) ₂ in middle		.014	.014	.025	.011	.010
Gm. NaOAc transferred from middle		.002 ₈	.000 ₄	.007	.000 ₃	.001 ₂
Gm. of catholyte		53.51	58.65	58.73	53.08	58.28
Gm. NaOAc in catholyte	1.	2.8044	3.1049	3.286	3.2955	3.9594
	2.	2.8025	3.1043		3.2952	
Gm. Pb(OAc) ₂ in catholyte		1.175	1.298	.695	.794	1.158
Gm. NaOAc transferred to catholyte		.0699	.0859	.100	.091 ₁	.0910
1. $t_+(A)$		0.46	0.40	0.43	0.40 ₄	0.39
2. $t_+(A+M)$		0.47	0.40	0.45	0.40 ₈	0.39
3. $t_+(C)$		0.42	0.47	0.40	0.46 ₁	0.39
Average $t_+(2 \text{ and } 3)$...		0.45	0.44	0.43	0.48	0.39

TABLE III

LITHIUM CHLORIDE

Molality		0.158	0.324	0.365	0.498	0.663	0.926	0.979
Gm./gm. acetic acid	1.	0.6715	1.3707	1.5485	2.1113	2.8086	3.9253	4.148
$\times 10^2$	2.	0.6717	1.3700	1.5484	2.1110	2.8103	3.9235	-----
Amperes		.005	.008	.009	.015	.011	.012	.011
Hours of electrolysis		4	5	5	5	6	5	4.5
Gm. Ag deposited	1.	.0749	.1639	.1780	.3523	.2753	.2379	.2145
	2.	.0748	.1640	.1780	.3524	.2753	.2379	.2146
Gm. of anolyte		51.96	51.64	51.22	47.65	54.88	52.64	51.98
Gm. chlorine in	1.	0.3672	0.7419	0.8277	1.0793	1.5704	2.0482	2.1247
anolyte as LiCl	2.		0.7414	0.8290		1.5703	2.0482	2.1238
Gm. ZnCl ₂ in anolyte		.049	.090	.109	.212	.173	.104	.105
Gm. Cl transferred to anolyte, as LiCl		.0208	.0446	.0484	.0979	.0743	.0646	.0581
Gm. of middle solution		38.89	40.11	41.59	40.36	39.25	44.22	41.09
Gm. Cl (as LiCl) in middle		0.2604	0.5428	0.6339	0.8357	1.0703	1.6678	1.6312
Gm. ZnCl ₂ in middle		.011	.012	.0077	.026	.0095	.010	.0058
Gm. LiCl in orig. of middle		0.2594	0.5422	0.6344	0.8340	1.0726	1.6697	1.6365
t_{Cl^-}	0.70 ₆	0.69 ₂	0.69 ₂	0.70 ₆	0.68 ₈	0.69 ₁	0.68 ₆
t_{Li^+}	0.29	0.31	0.31	0.29	0.31	0.31	0.31

DISCUSSION OF RESULTS

Since most of the preliminary work was on ammonium acetate solutions, these will be considered first. The cation transference numbers calculated from concentration changes in the anode compartment are slightly lower than the corresponding cathode values for reasons which have already been discussed in some detail. Although the anode values in successive determinations at the same concentration varied in a somewhat erratic manner, the cathode values were found to be reproducible under rather varied conditions of electrolysis.

Changes in concentration in the middle compartment were small but uniformly negative. When these losses were added to those occurring in the anolyte, the corrected figures agreed fairly well with the cathode values. It must be admitted, however, that such agreement is useful only as a check on analytical accuracy. In addition to the trial and error method used in the preliminary series, further evidence that a satisfactory separation of the cell compartments has been obtained is given by the quantitative determination of lead acetate in all three compartments of the cell. Let us assume that any mixing into the middle compartment comes from the anolyte and that none comes from the

catholyte. Lead acetate is of course formed at the anode, away from which ammonium acetate is being transferred. Then, if any solution of changed concentration reaches the middle, some lead acetate will almost certainly have been carried along, and the sum of that lead acetate found in the middle and anode compartments should equal the quantity formed at the anode. For the most concentrated solutions, where practically perfect separation was obtained, the determination of lead in the anolyte established the fact that the anode reaction was actually the quantitative formation of plumbous acetate. Hence we can at once find the quantity of plumbous acetate formed during an electrolysis from the weight of silver deposited.

Now, if the method of introduction of lead acetate into the cathode compartment is recalled, it is apparent that a small amount of lead acetate might reach the middle compartment without being accompanied by any of the solution having an increased concentration of ammonium acetate. On the other hand it is quite impossible for the latter to reach the middle without being accompanied by an appreciable quantity of lead acetate.

In all but one of the final determinations the quantity of lead acetate found by analysis in the anode and middle compartments agreed closely with the calculated amount. The one exception was obviously

due to a careless analysis, since the amount found in the anolyte alone was more than that actually formed at the anode. This indicates that no appreciable mixing from the cathode has taken place, and therefore the separation of the two regions of concentration change is more surely established.

In view of all these considerations, the cathode transference numbers have been accepted as the correct values, and these have been plotted in Figure 2. The divergence of individual points from the smooth curve gives an indication of the lower limit of concentration to which transference numbers, as measured with the apparatus and methods used in this work, can be considered reliable. At concentrations below 0.5 molal the effective capacity of the electrode compartments was exceeded before a sufficient quantity of electricity could be passed. The greater difficulties of analysis for the dilute solutions have already been discussed. At higher concentrations greater accuracy in analysis was possible, and the resulting values fall close to a smooth curve.

The points on this portion of the curve are probably not in error by more than 0.005 unit. The curve is well established down to concentrations of about 0.5 molal, and below that the points are scattered at

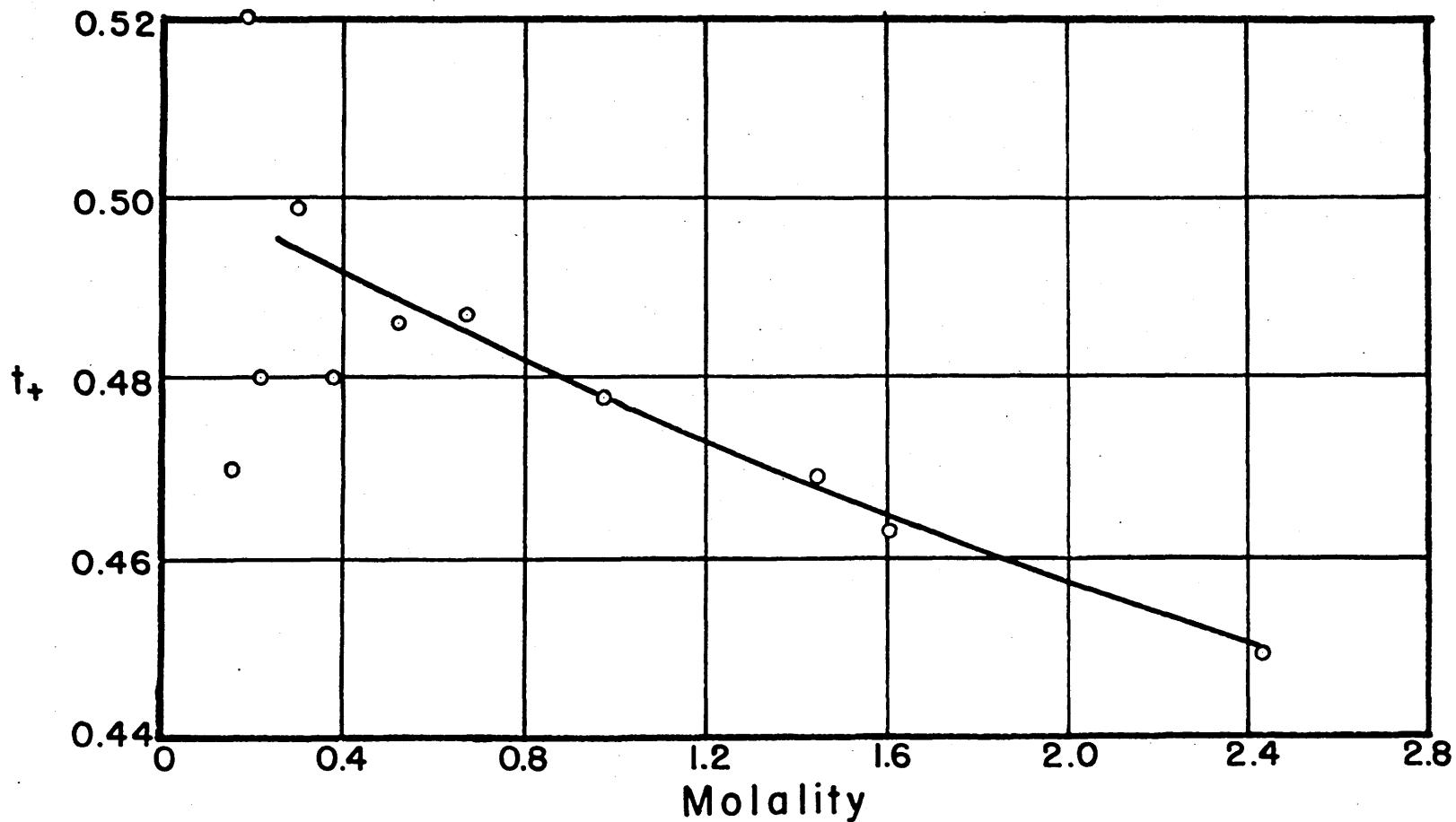


Fig. II. Cation transference numbers for NH_4OAc .

random from the extended curve with a variation of about 0.02 unit.

The range of concentration of the sodium acetate solutions of Table II was more limited than that of the ammonium acetate solutions. This salt is considerably less soluble, and the conductance of its dilute solutions is lower. In most of the experiments the change in the middle compartment was within the experimental error. Nevertheless, the presence of a quantity of lead acetate in the anode and middle compartments, slightly in excess of that formed electrolytically, indicated a slight degree of mixing at both ends of the middle section. Hence, the runs were kept so short that there was usually only 0.01 to 0.02 gram of lead acetate in the middle compartment.

Because of the difficulty of determining sodium accurately in the presence of lead, we are led to conclude that the errors of analysis are probably larger than any due to imperfect separation of the cell compartments. The transference numbers calculated from anode and cathode changes would therefore appear to be of equal reliability. An average of the two values from each experiment has been calculated, and it is these averages which are plotted in Figure 3. Points taken from the curve are probably correct to

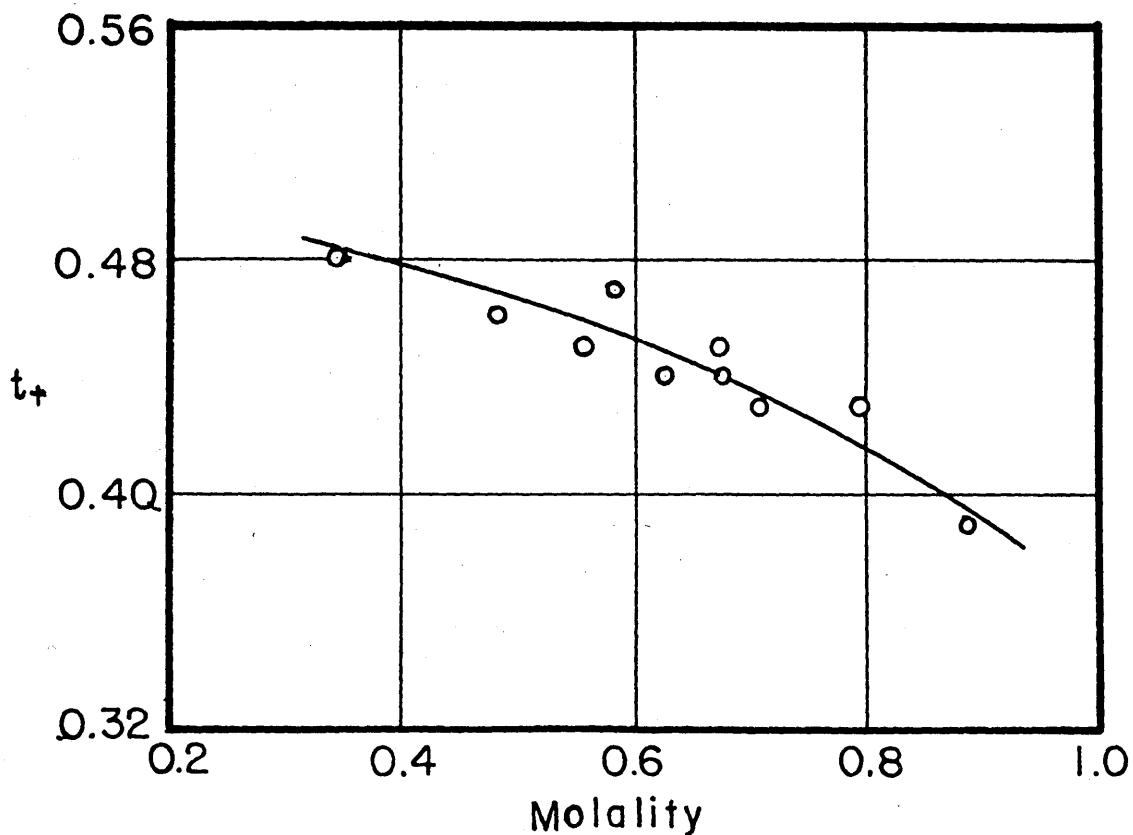


Fig. III. Cation transference numbers for NaOAc.

within 0.02 unit. No large variation of transference number with concentration was found, but the values slowly approach 0.5 with increasing dilution, as is usually the case in aqueous solutions.

It is of interest to compare these results with those obtained by Longworth from moving boundary experiments. His determinations were all at concentrations less than 0.5 molal, the calculated transference numbers varying between 0.41 and 0.43. The two methods are therefore in agreement as to order of magnitude, and experimental errors undoubtedly explain the small discrepancies. In favor of the numbers calculated in the present work is the fact that any errors due to mixing would lower the transference numbers, whereas ours are some 0.03 to 0.04 higher than those of Longworth at similar concentrations. Furthermore, with the autogenic type of moving boundary used in that work, it was not found possible to obtain concordant results for different anode metals. Those obtained with a lead anode were tentatively accepted as the correct ones. Our further experience with diffusion of lead acetate from the lead anode would indicate that even those might easily have been too low.

The numerical results for lithium chloride, summarized in Table III, indicate the degree of precision which was rather readily attained, with out any modification of the apparatus used for the previous experiments.

Changes in the chlorine content of the middle compartment were exceedingly small when all the chlorine was calculated as lithium chloride. However, when correction was made for the fact that a small amount of the chlorine was present as zinc chloride, a loss of lithium chloride of from five to nine milligrams was always found. In fact, in most of the trials a very small loss of chloride ion was found even if no correction was made for the zinc chloride. Now, a moment's consideration of conditions in both electrode compartments shows that if there is any mixing into the middle, an increase in chlorine content would result. The table shows that a few milligrams of zinc chloride was always found in the middle, proving that some slight mixing had occurred. Hence some other explanation must be sought for the observed change of concentration.

The first possible explanation for this discrepancy in chlorine content which was considered, was that the presence of zinc might affect the chlorine analysis. However, test analyses were carried out in which zinc acetate, free from chloride, was added in different amounts to part of the samples. The results showed no variations due to the zinc. Another possibility is related to the fact that the activity of hydrogen chloride (8) from its solutions in acetic acid is very high. If, when lithium chloride is dissolved in acetic

acid, solvolysis takes place even to a small extent, the very slightly soluble hydrogen chloride which would form might be lost. In the transference cell, the only part of the solution which has an exposed surface where such loss could occur is that which is largely drained as the middle section. Nevertheless, test solutions which were weighed and then left open to the air for several hours showed no loss in chlorine content. A third possible explanation is that lithium chloride may diffuse into the electrode compartments faster than zinc chloride diffuses out. Such diffusion is at least possible, since the concentration of lithium chloride around both electrodes is actually lower during the electrolysis than in the middle (lithium ion migrates away from the anode, and there is no lithium in the zinc chloride solution added at the cathode). However, the suggestion is hardly amenable to experimental confirmation. Hence, the author has as yet been unable to account for the peculiar observation.

In view of the nearly constant composition of the middle portion, and of the lack of any means to account for the variations, the calculated transference numbers may be accepted as being close to the correct values. Within the experimental error, no variation of cation

transference number was found in the range of concentrations studied. It is interesting to note that the cation transference number for aqueous lithium chloride solutions (3a) varies between 0.29 and 0.32 over the same range of concentrations used in the present work, whereas the average value obtained here is 0.30. The variation with concentration in aqueous solutions of only 0.03 unit is no more than our probable error. In solvents other than water, most of the existing values for lithium chloride are of low precision, varying from 0.3 to 0.6 for the range we have been considering. The most precise values found in the literature were those of Pearce and Mortimer (6), obtained from electromotive force measurements of concentration cells. Several of the alcohols were used as solvents, and the transference numbers of lithium ion for concentrations close to those used in this work were around 0.35. Apparently, then, there is very little variation in the transference number for lithium chloride dissolved in solvents of widely differing dielectric constant. The small values of t_{Li^+} in water and other solvents are usually considered as being due to the high degree of solvation of the small ion. If such is the case, the results obtained here would indicate that lithium ion is highly solvated in acetic acid also.

The equivalent conductance of solutions of electrolytes in acetic acid (11) has been found to decrease with increasing concentration, going through a minimum at as low concentrations as 0.05 normal; the conductance then increases at higher concentrations. It is at once apparent that, in spite of this quite anomalous variation of equivalent conductance with concentration, no indication of any significant departure from a simple conductance mechanism is to be found in the transference numbers. Indeed, the magnitude of the transference numbers in acetic acid, as well as their variation with concentration do not differ to any marked degree from the values in aqueous solutions. If it is assumed, in order to explain the phenomena of conductance variation, that complex ions such as $\text{Na}(\text{OAc})_2^-$ and Na_2OAc^- are formed (2, 12), then they must be formed in approximately equal amounts. Mention should also be made of the fact that no unusually high transference number for the acetate ion in acetic acid has been found, in contrast to that found for the hydroxyl ion in aqueous solutions of hydroxides.

Practically no transference measurements have ever been made on solutions in solvents having nearly as low a dielectric constant as acetic acid, so that the work has made a definite contribution in this field. Furthermore, it is believed that the results for ammon-

ium acetate are the most accurate determinations which have as yet been obtained in any non-aqueous solvent.

SUMMARY

Apparatus and experimental methods have been devised for the improved determination of "Hittorf" transference numbers in solutions of electrolytes in anhydrous acetic acid.

Cation transference numbers for solutions of ammonium acetate in anhydrous acetic acid have been determined over a range of molalities from 0.16 to 2.5. The corresponding values of t_+ varied from 0.49₅ to 0.449.

Cation transference numbers for sodium acetate have been obtained over a range of molalities from 0.5 to 0.9, values of t_+ varying between 0.48 and 0.39.

Cation transference numbers for solutions of lithium chloride have been determined at molalities from 0.16 to 0.98. Within the experimental error, there was no variation of transference number with concentration, the average value being $0.30 \pm .02$.

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ABSTRACT

THE DETERMINATION OF ION TRANSFERENCE IN SOLUTIONS
OF ELECTROLYTES IN ANHYDROUS ACETIC ACID

Improved apparatus and methods of manipulation have been devised for the determination of "Hittorf" transference numbers in anhydrous acetic acid solutions. The cell which was used in the final determinations was a modified H-cell prepared from 1" by 8" Pyrex test tubes. The electrodes were at the bottom of each arm of the H. Drain tubes were attached to the cell in such a manner as to make it possible to empty the cell in three portions, anode, middle and cathode, without removing the cell from the constant temperature bath.

By means of a system of tubing and stopcocks, the cell and a flask which contained the test solution were connected together and to a source of purified hydrogen in such a way that the whole system could be swept free from air, and the cell could be filled and emptied without being opened.

Cation transference numbers have been determined for solutions of ammonium acetate, sodium acetate, and lithium chloride over as wide a range of concentrations as was practicable.

For the acetate solutions, the layer of electrolyte immediately above each electrode was maintained at a density higher than that of the remaining solution by the use of lead amalgam as anode and a layer of lead acetate on the mercury cathode. For lithium chloride solutions, zinc amalgam formed the anode, and a solution of zinc chloride in acetic acid was introduced onto the mercury cathode.

An extensive series of preliminary experiments was carried out with approximately 0.5 molal ammonium acetate in order to develop the experimental methods and to determine the limits of current and time of electrolysis which could be used successfully.

Concentration changes in both anode and cathode compartments were determined for the acetate solutions. In the case of ammonium acetate, transference numbers calculated from the cathode changes were found to be more reliable. The cation transference numbers decreased with increasing concentration, varying from 0.49₅ at 0.16 molal to 0.449 at 2.5 molal. At concentrations greater than 0.5 molal, these values were probably not in error by more than 0.005 unit. The values obtained from anode and cathode transference were found to be of equal reliability for sodium acetate. The average cation transference numbers decreased from 0.48 at 0.3 molal to 0.39 at 0.9 molal, were

accurate within ± 0.02 unit.

Transference numbers for lithium chloride were based on the determination of chlorine, and consequently only the anolyte analyses could be used. Within the experimental error, no variation of cation transference number with concentration was found. The calculated values, determined at seven concentrations between 0.16 and 0.98 molal, varied at random between 0.29 and 0.31.

In all the experiments, the changes in composition of the middle compartments were quite small, and they indicated good separation of the regions of concentration change.

The transference numbers thus determined are quite similar in their magnitude and in their variation with concentration to those found in aqueous solutions, in spite of the fact that, over this range of concentrations, the equivalent conductances of electrolytes in acetic acid vary in a highly abnormal manner. The transference numbers do not change greatly with concentration, but approach 0.5 in the more dilute solutions.