

SOME STUDIES IN THE TRANSFERENCE OF IONS
IN ANHYDROUS ACETIC ACID SOLUTIONS

by

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INTRODUCTION: Amphoterism in non-aqueous solutions.

It is a well known fact that zinc hydroxide dissolves in an aqueous solution of a strong base such as sodium hydroxide. If the solubility is studied over a range of concentrations of sodium hydroxide, it is observed that if a sufficiently high concentration is used, the solubility of zinc hydroxide appears to decrease, with increasing concentration of sodium hydroxide. The solid phase which separates out under these conditions is a compound having a formula, similar to NaHZnO_2 or Na_2ZnO_2 , with a number of molecules of water of hydration. Zinc hydroxide is not the only hydroxide which behaves in this manner. Analogous reactions may be observed when sodium hydroxide solutions are allowed to react with the hydroxides of aluminum, chromium, lead, tin, antimony, and perhaps many others. Reactions of this type are not peculiar to aqueous systems and in the liquid ammonia

The following compounds have been isolated: $\text{NaHZnO}_2 \cdot 3\text{H}_2\text{O}$ [Foerster and Günther, Z. Elektrochem., 6, 301 (1899)], $\text{Na}_2\text{ZnO}_2 \cdot 4\text{H}_2\text{O}$ [Fricke, Z. Anorg. Allgem. Chem., 172, 234 (1928)], and $\text{NaHZnO}_2 \cdot 4\text{H}_2\text{O}$ [Goudriaan, Rec. trav. chim., 39, 505 (1920)].

system we have an even greater number of examples of this phenomenon. In the water system only the bases of the metals which appear in the center of the electrochemical series show this behavior in the presence of strong hydroxides, while the metal amides that form compounds with potassium amide in liquid ammonia are very numerous and are represented not only by the metals that show this same characteristic in aqueous solutions, but also by some which are decidedly electropositive. Thus we have not only such compounds, as potassium ammonozincate, $Zn(NHK)_2 \cdot 2NH_3$, potassium ammonoplumbite, $PbNK \cdot 2NH_3$, and potassium ammonostannate, $Sn(NK)_2 \cdot 4NH_3$, but also salts like potassium ammonolithiate, $LiNK_2 \cdot 2NH_3$, and potassium ammonosodiate, $NaNK_2 \cdot 2NH_3$.

In acetic acid solutions, as well, this phenomenon appears. Zinc acetate₂ shows a behavior with sodium acetate solutions quite parallel to the reaction of zinc hydroxide with solutions of sodium hydroxide. The solubility of zinc acetate in sodium acetate solutions

₁Franklin, J. Am. Chem. Soc., 35, 1455 (1913).

₂Davidson and McAllister, J. Am. Chem. Soc., 52, 519 (1930)

increases with increasing concentration of sodium acetate until the compound, $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$, appears as the solid phase instead of unsolvated zinc acetate. Then the solubility of zinc acetate decreases as the concentration of sodium acetate increases further. Copper acetate likewise dissolves in solutions of the strong bases, potassium, and ammonium acetates,¹ and in the case of the latter, an addition compound of the formula, $Cu(C_2H_3O_2)_2 \cdot 4NH_4C_2H_3O_2 \cdot 4HC_2H_3O_2$, has been isolated.

In all the cases mentioned above, we have examples of the reaction of a strong base upon a weaker one with the formation of addition compounds which are either assumed to exist in solution or which have been actually isolated. In the aqueous system, this type of reaction is said to occur because of the amphoteric nature of the weaker base. In liquid ammonia, the formation of the complex amides is explained in the same manner.² The data for acetic acid solutions are not as complete as in the case of the water and ammonia systems, but if

¹Davidson and Griswold, J. Am. Chem. Soc., 53, 1341 (1931).

²Franklin, loca cita.

amphoterism is defined by the characteristic reactions of which we have been speaking, the term can certainly be applied to designate phenomena of this sort in acetic acid solutions as well as in aqueous and other non-aqueous systems.

In explaining the action of sodium hydroxide solutions upon zinc hydroxide, it is usually assumed that zinc hydroxide is a weakly acidic substance and is therefore capable of dissociating not only as a base but also as an acid. The reaction with sodium hydroxide, on that basis, would consist of the neutralization of the hydrogen ions to form water and also in the formation of the soluble salt of the zinc acid. If this hypothesis is correct, there will exist in such a solution complex anions that are made up in part of zinc and are called zincate or metallate₁ ions, in addition to the sodium and hydroxyl ions which are present.

A study of the nature of the anion present in this system has been made₂ by determining the changes in

₁The name metallate has been suggested as a general term for all salts of amphoteric bases, regardless of the system in which they appear.

Fernelius and Bergstrom, J. Phys. Chem., 35, 741 (1931).

₂Kremann, Z. Anorg. Chem., 33, 87 (1903).

concentration of zinc around the electrodes caused by an electrolysis of the solution in a transference cell. The concentration of zinc was found to increase around the anode, indicating that the anion contained zinc.

This is the only conclusive evidence that we have for the existence of metallate ions in aqueous solutions, although the explanation for the behavior of all amphoteric hydroxides in the presence of sodium hydroxide is based upon the hypothesis that metallate ions are present in the solution.

Likewise, the existence of metallate ions in liquid ammonia solutions was merely taken for granted until very recently, when it has apparently been definitely established by Detrick and Fernelius, who in an unpublished paper¹ have reported that in the electrolyses of liquid ammonia solutions of such salts as potassium ammonocupriate, $\text{CuNK}_2 \cdot 3\text{NH}_3$, potassium ammonoaluminate, $\text{Al}(\text{NH}_2)_2\text{NHK} \cdot 2\text{NH}_3$, and potassium ammonoplumbite, $\text{PbNK} \cdot \text{NH}_3$, they have obtained quantitative deposits of the less positive metal on a platinum anode in the form of some nitrogen compound.

¹Presented at the Indianapolis meeting of the Am. Chem. Soc. 7 April, 1931.

It appears therefore that if the word amphoteric is to be given the most inclusive meaning, it may be used simply to characterize a base which is capable of reacting with a stronger base to form an addition compound. If we impose upon the concept of amphoterism, the added restriction that if a soluble salt is formed, the less negative metal must appear in the anion, then the amphoteric nature of a great number of compounds becomes open to question.

As has been mentioned above, zinc acetate, which is only slightly soluble in pure acetic acid, dissolves readily in an excess of an acetic acid solution of sodium acetate, just as zinc hydroxide dissolves in aqueous sodium hydroxide solutions and as zinc amide dissolves in liquid ammonia solutions of potassium amide. Copper acetate likewise dissolves in the presence of potassium or ammonium acetate. In both of these cases addition compounds are formed. Because of this analogy in chemical behavior the question arises whether or not zinc and copper acetates, which according to the first criterion mentioned above, are to be regarded as amphoteric bases, also have the property of forming metallate ions. If that is the case, there should exist

in such a solution a complex anion which is made up in part of the metal, copper, or zinc, as the case might be. In other words, we might expect that the salt which is present in solution, and which can be obtained as a solid phase, is the salt of an amphoteric base rather than a double acetate.

OBJECT AND GENERAL METHOD OF ATTACK:

It seemed to be of interest, therefore, to attempt to determine the ionic species present in such acetic acid systems and by so doing to extend our knowledge, both with respect to amphoterism in general and to the properties of acetic acid solutions in particular. This constituted the original objective of the present work, although circumstances which could hardly have been foreseen caused the plan to be somewhat modified as the work proceeded.

A determination of ionic species may be undertaken by various methods, but the one which lends itself most readily to the conditions of the case is perhaps a study of the results of electrolysis of the substance under consideration. The results of the electrolysis may manifest themselves in two different ways. In the work of Detrick and Fernelius it was possible to obtain the deposition of solid products at the anode, resulting from the

discharge of the anion. On the other hand, the electrode reaction may not bring about the discharge of the anion in which we are interested, and in that case the usual Hittorf₁ method of determining transport numbers is available.

By determining the concentration of the solution surrounding one or both electrodes before and after electrolysis, it is possible to ascertain the direction in which the metal, whose amphoteric nature we are studying, is migrating. It was originally planned to employ this method merely to determine the direction of transference of the ion of the less electropositive metal in solutions containing two acetates, but the results of preliminary experiments showed such marked peculiarities of behavior that it seemed desirable first to determine quantitatively the migration ratios in a number of simpler systems, especially since no such determinations for acetic acid solutions have been reported hitherto.₂

₁Hittorf, *Über die Wanderungen der Ionen während der Elektrolyse*, 1853-1859. See also Noyes and Falk, *J. Am. Chem. Soc.*, 33, 1436 (1911).

₂Transference numbers in acetic acid solutions have however been measured by Longworth, Ph.D. Thesis, University of Kansas (1928), by the moving boundary method. He concluded that the transference number of sodium ion in sodium acetate showed no abnormality, that it changed little with concentration, and that it approached a value of 0.5 in dilute solutions. It is significant to note that in the method he used the existence of simple ions was assumed and no actual analytical measure of transference was made.

PRELIMINARY EXPERIMENTS:

In early experiments it was determined that the resistance of the acetate solutions which we hoped to use was so high that an electromotive force even of the one hundred and ten volts of the D.C. line was insufficient to secure appreciable transfer of material in a reasonable length of time. For this reason a transformer and rectifier capable of delivering six hundred volts was obtained, and this enabled us to electrolyze even the more dilute solutions quite satisfactorily.

At the low current densities which were used (less than twelve hundredths of an ampere per square decimeter or about ten milliamperes for the cell), no regular evolution of gas occurred at the anode and in many cases no evolution of gas whatsoever was observed at this electrode. At the cathode, hydrogen was given off in each instance. For this reason it appeared that it would be preferable to study the changes of concentration around the anode, since at that electrode there was no disturbance due to constant stirring of the solution by the gas evolved. Some trial runs were made using a solution composed of sodium acetate, zinc acetate, and acetic acid and electrolyzing between platinum electrodes.

In one of these runs where the concentration of zinc acetate was practically sufficient to saturate the solution, a deposit was obtained at the anode which was shown by analysis to be zinc acetate. At first this was thought to be due to the discharge of an anion corresponding to the zincate ion in the water system, but the observations could not be repeated and later roughly quantitative measurements on similar solutions indicated that zinc migrated toward the cathode. In any case, it is difficult to determine just what reaction occurs at the anode in these solutions, or, for that matter, even in solutions of alkali acetates when electrolyzed under similar conditions. It seems fairly certain that changes of a variable nature occur at the anode. In the electrolysis of sodium acetate₁, for example, carbon dioxide, ethane, oxygen, methyl acetate, and other substances are formed at the anode, the relative quantities of which vary with current density, concentration, and temperature. Because of this uncertainty as to the nature of the anode reaction at a platinum electrode, it seemed preferable to arrange a cell with a known electrode reaction.

¹Hopfgartner, Monatsch., 32, 523 (1911).

If the anode solution is to be taken for analysis, the reaction products at the anode must not stir the solution, and must have no effect on the solution we are electrolyzing, either in changing migration ratios or in making analyses difficult. In view of the fact that a silver-silver chloride electrode had been used in studying the hydration of ions₁ we hoped to find an electrode of this type that would work as satisfactorily in acetic acid solutions. After zinc amalgam had been tried and found to be unsatisfactory, a mercury anode proved to be the solution of the problem. The electrode reaction was found to consist in the quantitative oxidation of mercury to mercurous acetate, which formed in a layer upon the mercury. That this is the case in an electrode of this type was demonstrated by the fact that in one run .911 grams of mercury disappeared at the anode, while on the basis of the current passed as measured by the copper coulometer, .905 grams of mercury should have been transformed to mercurous acetate. Further, the precipitate of mercurous acetate was dissolved in water, hydrochloric acid was added to precipitate the mercurous ion as calomel, and the solution was then filtered. The filtrate failed to show a test for mercuric ion when it

¹Washburn, J. Am. Chem. Soc., 31, 322, (1909)

was treated with hydrogen sulfide. Thus there can be no doubt that the mercurous ion, and that ion only, is formed at a mercury anode in an electrolysis of an acetic acid solution under the conditions used.

The mercurous acetate was found to be sufficiently insoluble in every acetate solution studied to obviate the introduction of appreciable quantities of mercurous ion into the solution; only a faint yellow coloration could be obtained when the solution, which had remained in contact with the mercurous acetate for several days, was treated with hydrogen sulfide.

The mercury-mercurous acetate electrode could be used without gassing up to current densities of eight-tenths of an ampere per square decimeter or a current of forty milliamperes for the cell. Even with this improved type of electrode, because of analytical difficulties, further study of the sodium acetate-zinc acetate system did not promise to be profitable. It was therefore decided to study instead the ammonium acetate-copper acetate system, in which case more accurate methods of analysis were available.

APPARATUS:

In the preliminary experiments a simple cell was used which consisted of two concentric test tubes, the

smaller one being held in place by means of a cork stopper, and communicating with the larger one by means of a large hole blown in the side of the tube. The electrodes were of platinum foil and were supported by glass tubes which passed through holes in the stoppers.

In the quantitative experiments a special cell₁ of the Loeb-Nernst type was used (illustrated in Figure 1). It consisted essentially of two large test tubes, one longer than the other, each fitted with a stopcock at the bottom and communicating with each other a few centimeters from the top by means of a piece of glass tubing of practically the same diameter as the tubes themselves. In the longer leg of the cell was placed about thirty grams of redistilled mercury, which served as an anode, and the connection to this was made by means of a platinum wire sealed through a glass tube. This glass tube also contained mercury and was held in place by a two-holed rubber stopper. The other hole of the stopper carried a glass tube which was connected by a piece of rubber tubing to a drying tube filled with granular calcium chloride. This arrangement allowed equalization of gaseous pressure in the anode chamber, but prevented any possibility of moisture entering the apparatus.

₁The writer is indebted to Mr. Jesse Stareck for the construction of this cell.

The cathode was a piece of platinum foil to which connection was made by means of a long, fine gauge platinum wire that reached from the bottom of the cathode chamber to the top of the cell. To prevent excessive stirring of the cathode and middle portions of the solutions in the cell, a funnel-like deflector was used. The larger end of this deflector was placed over the cathode while the smaller end passed through the one hole stopper at the mouth of the cathode compartment. This deflector carried the hydrogen liberated at the cathode to the mouth of the tube, where it escaped through a drying tube filled with calcium chloride. A small hole in the deflector tube just above the surface of the liquid in the cathode compartment allowed equalization of pressure in this part of the cell, with the atmospheric pressure. The platinum wire leading from the cathode was taken out through the end of the deflector tube, to which was attached a short piece of rubber tubing. The wire was passed between this piece of rubber tubing and the end of the drying tube with which the rubber tubing made connection. In this manner a glass platinum seal was eliminated, and at the same time direct contact of the contents of the cell with the atmosphere was avoided.

The source of current used was a Majestic B battery eliminator which had been rebuilt to deliver approximately twice the normal potential. A type 280 Kenetron tube rectified both phases of the hundred and ten volt alternating current. A choke coil and a pair of condensers of large capacity were supplied for the purpose of evening out the rectified current, but this refinement was, of course, unnecessary in the work for which the rectifier was here used. The maximum voltage obtainable was approximately six hundred volts. The voltage was adjusted to suit special cases by means of a potential divider connected across the A. C. input.

The quantity of electricity which was passed through the cell was measured by means of a copper coulometer made up according to standard specifications.¹

The electrical circuit consisted of the electrolytic cell, the coulometer, a Weston three-range ammeter and then, of course, the output leads of the rectifier, as is shown diagrammatically in Figure 1.

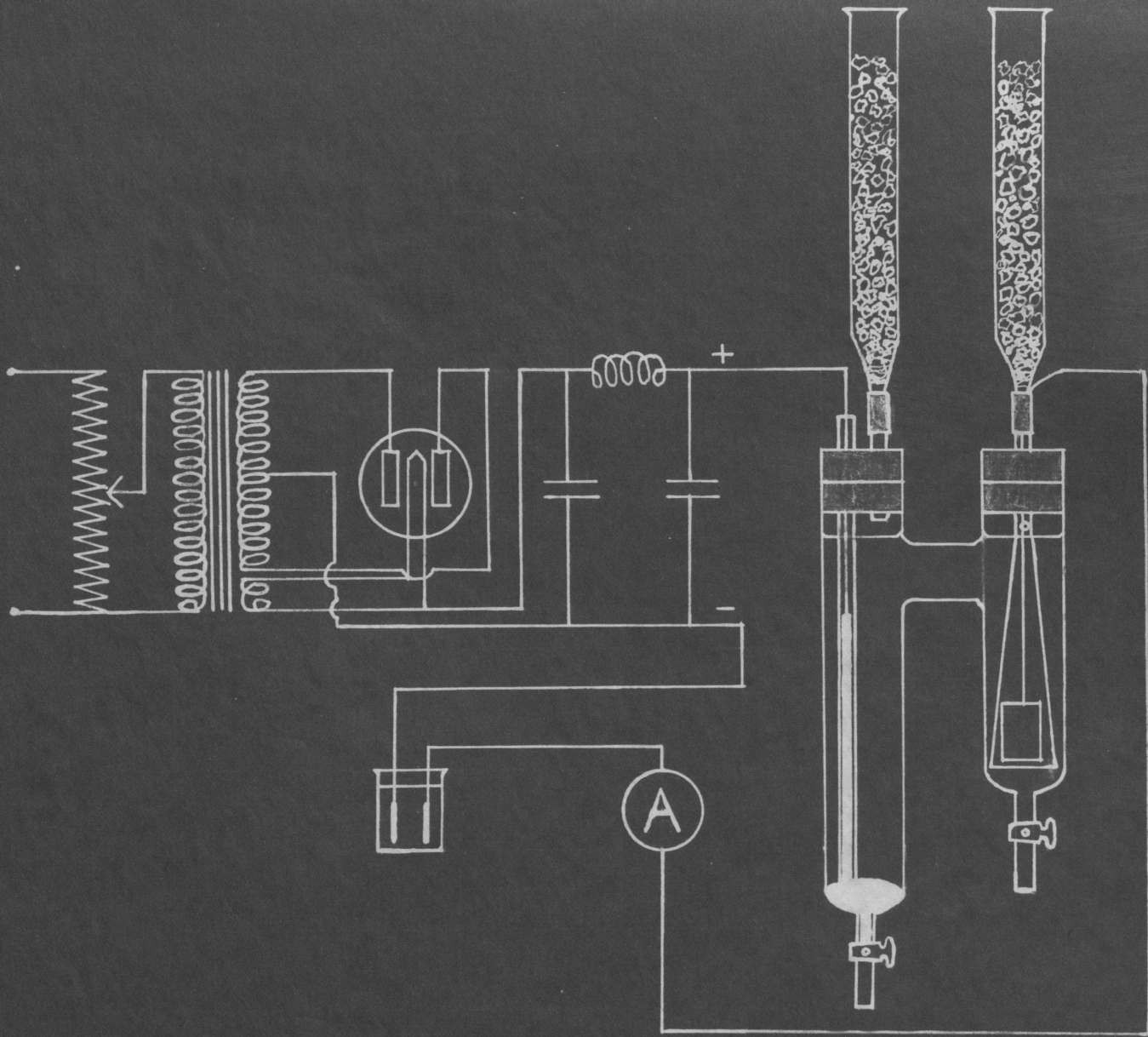
PREPARATION OF MATERIALS:

The anhydrous acetic acid used was prepared according to the method of Kendall and Gross.² A C.P. grade of

¹Cady, Principles of Electrochemistry (1927)

²Kendall and Gross, J. Am. Chem. Soc., 43, 1426 (1921)

FIGURE 1.



glacial acetic acid was redistilled, treated with the required amount of acetic anhydride and refluxed for several days. The resulting acid was distilled again and this product, which was used in these experiments, had a freezing point of 16.5 to 16.6° C.

The sodium acetate employed in these experiments was a C.P. grade which was dehydrated for several days at about 150° and then placed in stoppered bottles in a desiccator. Its purity was verified by making up various solutions of the salt in acetic acid and checking the freezing points with values given in the literature.¹

The zinc acetate was prepared by recrystallizing a C.P. hydrate from dilute acetic acid and heating this to 90° for several days. The resulting product was then moistened with pure acetic acid and heated again at 85° for about six hours, as described by Davidson and McAllister.² Analyses of the resulting product averaged 35.70% for zinc; the zinc content calculated for $Zn(C_2H_3O_2)_2$ is 35.65%.

The ammonium acetate was prepared by the method³ described by the above investigators also. Anhydrous

¹Kendall and Adler, J. Am. Chem. Soc., 43, 1470 (1921)

²Davidson and McAllister, loc. cit.

³Davidson and McAllister, J. Am. Chem. Soc., 52, 507 (1930)

ammonia gas obtained from boiling liquid ammonia was passed over anhydrous acetic acid contained in an evaporating dish over soda lime in a vacuum desiccator. After this preliminary treatment had been carried on for a day, the resulting product was pulverized and again treated with ammonia gas for several days. In following this procedure it was possible to obtain either the neutral salt, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, or the acid salt, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$. It is not known whether variation in temperature or some other factor caused this unusual behavior. Since the ammonium acetate concentration of all solutions used in this experiment was determined by analysis, it was of no importance whether the salt used for preparing these solutions was the acid or neutral salt.

The copper acetate was prepared as described by Davidson and Griswold.¹ The hydrate was recrystallized from dilute acetic acid and then dehydrated at 90° until analysis showed no water to be present. This required about sixty hours. Samples of this product, analyzed by the electrolytic method, averaged 34.96% of copper; the copper content of pure copper acetate is 35.00%.

¹Davidson and Griswold, loc. cit.

METHODS OF ANALYSIS:

The analyses of the sodium acetate solutions were made by adding a slight excess of sulfuric acid to the sample, evaporating slowly to dryness, fuming off the excess sulfuric acid, heating strongly over Fisher burners, and finally weighing as the sulfate.

The method of analysis used for solutions of sodium acetate-zinc acetate consisted of first converting the mixed acetates to sulfates and weighing them as such. Then the zinc was determined by potentiometric titration with potassium ferrocyanide solution. These analyses, for some reason which could not be determined, failed to give results as consistent as was desired; this was one of the reasons for discontinuing the study of these solutions.

The analyses for copper were made by the iodimetric method described by Talbot.¹

The analyses for ammonium acetate were made by adding an excess of base to the solution and distilling the ammonia liberated into known quantities of standard hydrochloric acid. The quantity of ammonia was then determined by back titration of the excess acid.

¹Talbot, Quantitative Chemical Analysis (1921).

Check analyses were made in all cases except in a few of the most dilute sodium acetate solutions. These duplicate analyses agreed to well within the error inherent in the method used for determining transference.

MANIPULATIONS:

The experimental procedure in the use of the apparatus may be given in a description of a typical run.

About thirty grams of redistilled mercury were accurately weighed out and transferred to the longer leg of the electrolytic cell, which was to serve as the anode compartment. The solution to be electrolyzed was then poured into the cell to a level only slightly above that of the connecting tube. The rubber stoppers, which were fitted as described above, were then attached and the electrical circuit completed. The current was adjusted to the correct value and the apparatus was then left undisturbed until a sufficient quantity of electricity had passed. This required from six hours, in some cases, to about twenty-four hours in the case of the more dilute solutions, where the resistance was so high that a current of only two or three milliamperes could flow. The current was adjusted to a low enough value so that heating of the solution was avoided, no constant temperature bath being used, since transference phenomena do not

show appreciable variation for small temperature changes. The experimental temperatures varied with the room temperature and ranged from 20° to 30° C. Enough electricity was passed to deposit on the average .05 to .15 grams of copper on the cathode in the coulometer.

When the run was completed, the circuit was broken and the coulometer cathode immediately washed and dried for weighing. The stopcock in the cathode compartment was then opened and the solutions from the cathode tube and the connecting tube were withdrawn slowly, without disturbing the solution remaining in the cell. The stopcock in the anode compartment was then opened and the total contents including the mercury, mercurous acetate, and solution, were transferred to a weighed, stoppered flask. This flask was weighed again and then set aside for a few hours in order to allow the mercurous acetate to settle to the bottom of the flask. After this had taken place, portions of the solution were decanted into weighing bottles for analysis. Data were thus obtained for calculating the net weight of the anode portion of the solution in the cell.

RESULTS:

In the course of this research, transference studies were made on acetic acid solutions of sodium acetate and

ammonium acetate over as wide a range of concentrations as was practicable.¹

A study was also made of the transference of copper and ammonium ions in solutions containing both copper and ammonium acetate. These studies were made over a wide range of ammonium acetate concentrations while the concentration of copper acetate was held fairly constant. In this manner the mole ratio, mole per cent. ammonium acetate : mole per cent. copper acetate, was made to vary greatly. In every case a deposit of copper appeared on the cathode during electrolysis, while no trace of copper acetate could be detected in the anode deposit.

From the data obtained, it is not only possible to determine the direction of transfer for a given substance in solution when subjected to the influence of an electric current, but also it is possible to calculate the apparent transport numbers for the cations which were assumed to be present in the solution. In the copper acetate-ammonium acetate systems the calculations were based on the supposition that copper was present as a cation.

¹Studies in more dilute solutions were not possible because of the extremely low conductance of the solutions. On the other hand if the concentration of the solutions is too high, the relative change in concentration during electrolysis becomes so small that the precision of the results is affected. However, solutions of sodium acetate were studied practically up to the saturation point, and values for ammonium acetate were determined through the same concentration range.

As has been stated, in beginning this work it was not the intention to study more than the direction of transference, and for that reason the highest degree of accuracy was not striven for; no temperature control was used, nor was the middle portion analyzed to determine if any concentration changes had extended into this region. The anode portion of the solution, which was usually about thirty grams, represented about forty per cent. of the total capacity of the cell. By virtue of the design of the cell, also, it is believed that the anode solution taken for analysis included the total changes in concentration caused by transference. These concentration changes were in no case great enough to cause marked changes in density and therefore no diffusion effects from that cause were present. A run was made on a copper sulfate solution in water to check the operation of the cell. The results agreed well enough with accepted values of the transference numbers for such a solution to warrant the conclusion that there was no constant error inherent in the apparatus or the method used.

In view of these facts it is believed that the precision obtained is as follows: The transport number

of the cation in the sodium acetate at any concentration can be expressed to a precision of ± 0.03 . This precision is representative of the determinations in the other systems as well, except in the case of the copper acetate-ammonium acetate solution having the highest concentration of ammonium acetate. In this instance the transport number of the ammonium ion is reliable only to within ± 0.06 .

It should be mentioned further that no attempt was made to correct the apparent transport numbers for possible solvation of the ions, as this would have involved a tremendous increase in experimental difficulties without commensurate increase in the significance of the results.

Method of Calculation:

In order to demonstrate how the transference numbers were calculated, it seems desirable to include a complete data and calculations for one trial. For this purpose let us consider the data for one of the runs on an ammonium acetate solution.

Wt. of Hg in anode tube	23.75 gm.
Wt. of Cu deposited in coulometer	.0752
Total wt. of anode contents	58.19

From these data the following values were obtained:

Faradays of electricity passed.....	.00236
Wt. of $C_2H_3O_2^-$ fixed at anode.....	.14 gm.
Net wt. of anode solution ($HC_2H_3O_2 + NH_4C_2H_3O_2$)	
58.19 - (23.75 + .14).....	34.30

The analyses were as follows:

Per cent. $NH_4C_2H_3O_2$ in original solution	8.78
Per cent. $NH_4C_2H_3O_2$ in anode solution	
after electrolysis	8.68

from which the following values could readily be calculated:

Wt. of $NH_4C_2H_3O_2$ in anode portion after	
electrolysis	2.975 gm.
Wt. of $HC_2H_3O_2$ in anode portion after	
electrolysis	31.33
Wt. of $NH_4C_2H_3O_2$ associated with 31.33 gm.	
$HC_2H_3O_2$ in original solution	3.010
Wt. of $NH_4C_2H_3O_2$ transferred from anode	
compartment	.035
Gram equivalents of $NH_4C_2H_3O_2$ transferred	.00045

Now if we assume that the solute is dissociated simply into NH_4^+ and $C_2H_3O_2^-$ ions and that the transport number of the cation is $1-x$, while that of the anion is x ,

then for each faraday of electricity passed through the cell, the following changes occur in the anode compartment:

1 gram equivalent of acetate ion is lost by the solution in the formation of solid mercurous acetate,

$1-x$ gram equivalent of cation is exported,

x gram equivalent of anion is imported.

Thus the net loss for the anode solution is $1-x$ gram equivalent of the salt. This number, $1-x$, is also the transport number of the cation.

Further, if we assume that dissociation follows the simple course mentioned above, it is possible to determine the transport number of the cation; but since this assumption is not necessarily true, the number so obtained is better designated as the apparent transport number. In the example given, .00045 gram equivalent of ammonium acetate was transferred by .00236 faraday of electricity; the apparent transport number for ammonium ion is therefore 0.19.

The results which have been obtained are given in the following tables:

TABLE 1.
SODIUM ACETATE

Concentration of original solution	Trial	Concentration of anode solution after electrolysis (Wt.%)	Copper deposited in coulometer	Transference of sodium acetate from anode compartment	Apparent transport number of cation
.99 mole % or 1.341 wt. %	I	1.355	.0205 gm.	-.004 gm.	-.08
	II	1.351	.0580	-.003	-.02
	III	1.342	.0170	0	0
	IV	1.342	.0176	0	0
					-.03 avege.
2.76 mole % or 3.74 wt. %	I	3.69	.0592	.017	.11
5.06 mole % or 6.80 wt. %	I	6.62	.1279	.066	.20
	II	6.68	.0716	.048	.26
					.23 avege.
7.02 mole % or 9.35 wt. %	I	9.25	.0755	.040	.21

TABLE 2.
AMMONIUM ACETATE

Concentration of original solution	Trial	Concentration of anode solution after electrolysis (Wt.%)	Copper deposited in coulometer	Transference of ammonium acetate from anode compartment	Apparent transport number of cation
.835 mole % or 1.07 wt. %	I	1.06	.0789 gm.	.002 gm.	.01
	II	1.04	.1058	.010	.04 .03 avge.
1.84 mole % or 2.35 wt. %	I	2.28	.1533	.025	.07
	II	2.33	.1076	.008	.03 .05 avge.
3.23 mole % or 4.10 wt. %	I	4.00	.0701	.032	.19
	II	4.02	.0844	.027	.13 .16 avge.
6.97 mole % or 8.78 wt. %	I	8.68	.0752	.035	.19
	II	8.62	.1175	.061	.21 .20 avge.

TABLE 3.

AMMONIUM ACETATE - COPPER ACETATE

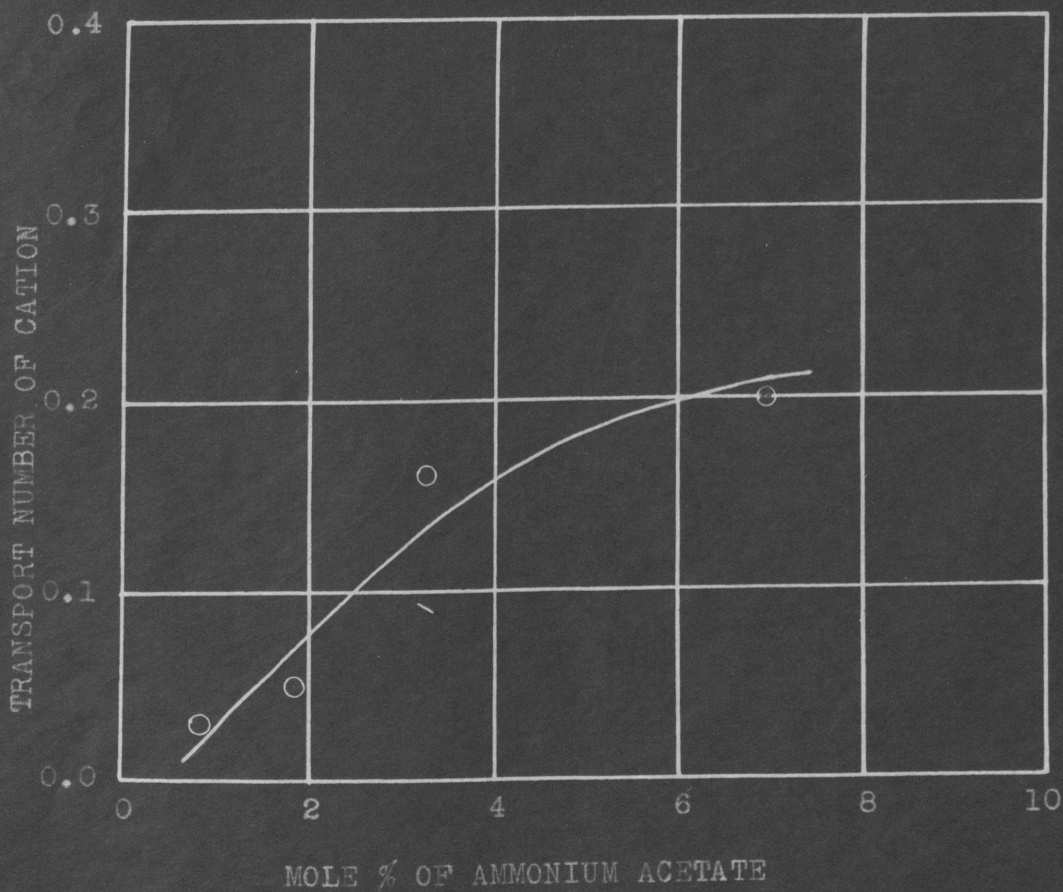
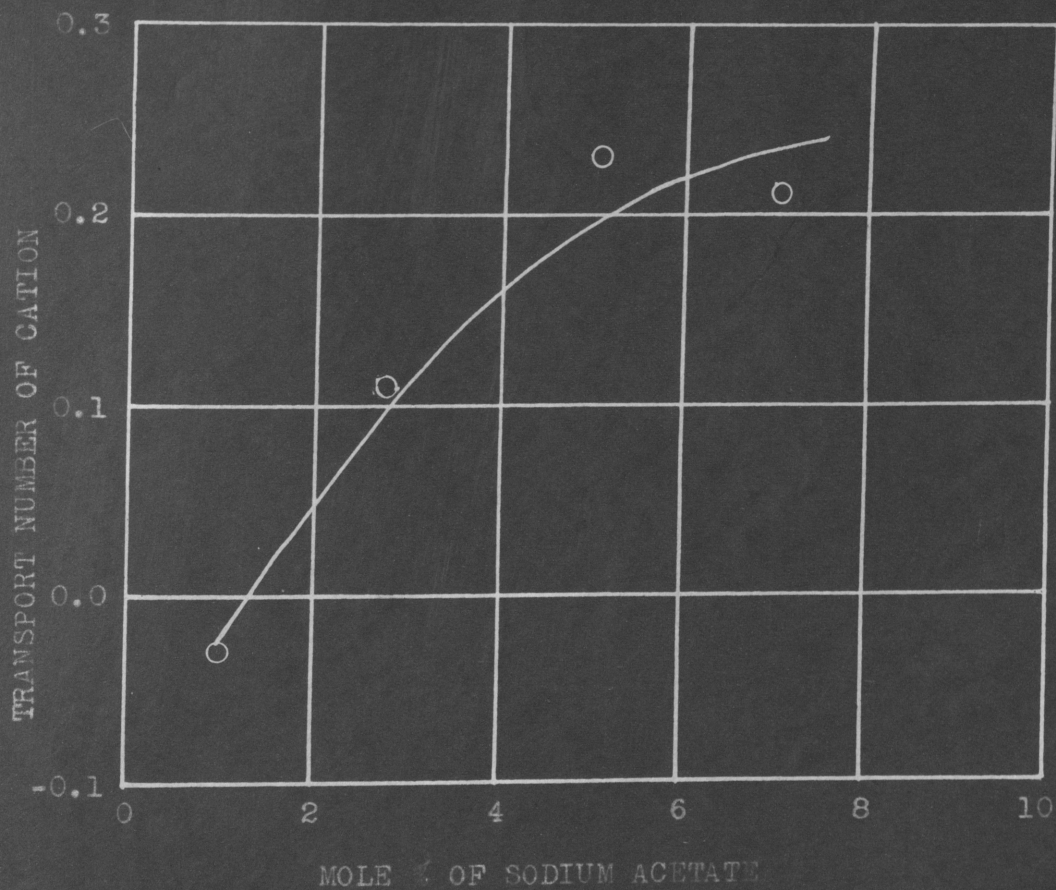
Concentration of original solution (Mole %)		Mole ratio $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$: $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$	Trial	Copper deposited in coulometer	Transference from anode compartment		Apparent transport number of cation	
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$				$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	Cu^{++}	NH_4^+
.214	.808	3.78	I	.1342 gm.	.089 gm.	.015 gm.	.23	.04
			II	.1119	.083	.011	.26	.04
			III	.1379	.088		.22	
							.23	.04 avge.
.300	2.68	8.95	I	.1438	.099	.015	.24	.04
			II	.2339	.116	.028	.17	.05
			III	.1345	.077	.020	.20	.06
							.20	.05 avge.
.440	8.50	19.3	I	.1818	.073	.06	.14	.14
			II	.2112	.072	—	.12	—
			III	.0693	—	.02	—	.12
							.13	.13 avge.
.292	10.83	37.0	I	.0976	.024	.088	.08	.37
			II	.0956	.022	.100	.08	.43
							.08	.40 avge.
.346	22.3	64.3	I	.1203	.006	—	.02	—
			II	.1194	.013	—	.04	—
							.03	.03 avge.

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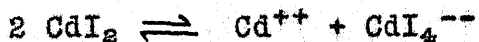
DISCUSSION OF RESULTS: Sodium acetate and ammonium acetate solutions

In the case of both of these salts, as the solutions become more concentrated the transport number of the cation increases and tends to approach a "normal" value, if we compare it with values for transport numbers which are obtained in aqueous systems. The data for sodium and ammonium acetates are shown graphically in Figure 2. This tendency of the transport number to increase from a very small value in dilute solutions to a normal value in concentrated solutions is quite unlike the behavior of solutions of most salts in water, where the transport does not vary greatly with concentration. Further, the fact that in the most dilute solution of sodium acetate, the apparent transport number of the cation assumes a slightly negative value is particularly anomalous. In aqueous solutions marked abnormalities are ordinarily attributed to the formation of complex ions. In cadmium iodide solutions, for instance, the transport number of the cadmium ion decreases with increasing concentration until it reaches a negative value in the most concentrated solutions, and this abnormal behavior has been explained satisfactorily by assuming

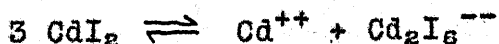
FIGURE 2.



that the more concentrated solutions contain the complex anion, CdI_4^{--} , as if the dissociation occurred as follows:



If the migration ratio of this complex anion is greater than that of the cation, electrolysis will result in an increase in the concentration of cadmium around the anode and a decrease around the cathode. The same change in concentration may be explained without assuming a larger transport for the anion, if we suppose the formation of an anion of even greater degree of complexity. It would be possible, for instance, to have the following type of dissociation:



In this case, if the migration ratios of the two ions are equal and if they are the only ions present, the apparent transport number of the cadmium ion, based on a study of concentration changes, would have a negative value. In the first case, using the same assumption for the dissociation of the double molecule, the transport number of the cation would appear to be zero.

It is not unreasonable to suppose that some similar phenomenon may occur in acetic acid solutions, although

the change of the transport number of the cation with concentration in these cases is in the opposite direction to that observed for the aqueous cadmium iodide solutions; that is, it becomes increasingly "abnormal" with decreasing concentration.

Correlation of transference data with
other properties of the solutions

A comparison of the observed freezing point curves with the curve which would be obtained if both the solute and solvent were assumed ideal, gives us at least some insight in the state of affairs existing in the solutions. In the case of the alkali acetates, there are two factors which might be expected to cause the observed values to fall below those of the ideal curve. The solute is evidently ionized, since the solution conducts electricity. If ionization were complete and if the ions behaved as perfect solutes,¹ the freezing point would be depressed almost twice the normal amount, the effective mole fraction of the solute having been practically doubled.

¹A rigorous treatment of these freezing point curves, from the point of view of thermodynamics, would be extremely complex and would not fall within the scope of this thesis. It is well known that solutions containing ions, especially when the dielectric constant of the solvent is low, deviate very greatly from ideal behavior, but the qualitative conclusions which are here drawn would hardly be invalidated by this fact.

Likewise solvation is known to occur (since solid solvates have been isolated), so that some solvent molecules are, in effect, deprived of their ability to act as solvent, and in this manner the mole fraction of the solute is increased and the freezing point should be depressed more than the normal amount. Although both of these factors are involved in the cases under consideration, it should be noted that in dilute solutions, the effect of dissociation is by far the most important.

Figure 3 gives the ideal freezing point curve for acetic acid as well as the curves plotted from observations of freezing points of sodium acetate and ammonium acetate solutions. In calculating the values for the ideal curve, the following equation₁ was used:

$$\ln x = \frac{Q}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

Known values₂ of Q and T_0 were substituted in the equation and the temperature T calculated for various values of x .

₁ x represents the mole fraction of the solvent, Q is the molar heat of fusion of the solvent, R is the gas content, 1.99 cal., T_0 is the absolute freezing point of the solvent, and T , that of the solution.

₂ $Q = 2780$ cal.
 $T_0 = 16.5^\circ + 273^\circ$

Physikalisch-Chemische Tabellen,
Landolt Börnstein.

The data from which the ideal curve was plotted are as follows:

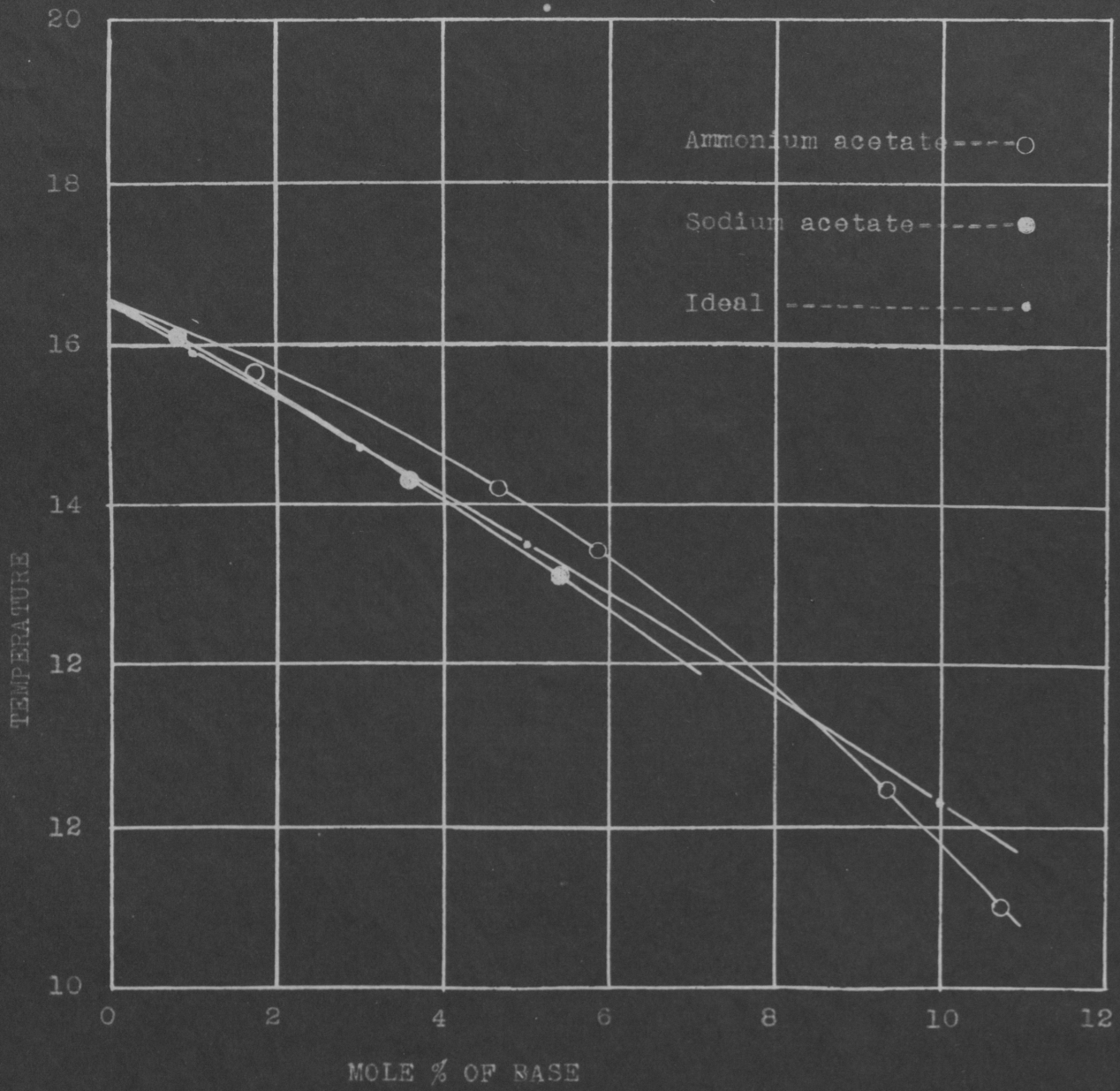
Mole % base	0	1	3	5	10
Temperature, °C.	16.5	15.9	14.7	13.5	10.3

The above values were obtained on the basis of single molecules of acetic acid. There is evidence₁, however, that acetic acid is associated, even in the vapor state, at these temperatures, and for that reason the calculations were also made on the assumption that acetic acid is dimolecular. The values thus obtained are identical with those given above, up to a concentration of five mole per cent., when the calculation based on double molecules gives a temperature only six-hundredths of a degree higher than the value given in the table. This difference is negligible, as far as our discussion here is concerned.

From a consideration of Figure 3, it is at once apparent that we are dealing with a state of affairs far different from that existing in water solutions and that anything like complete dissociation, even in dilute solutions, is quite improbable. The curve for sodium acetate is only very slightly below the ideal curve,

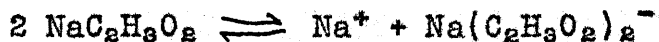
₁Turner, Molecular Association, p.53, Longmans, Green & Co. London (1915)

FIGURE 3.



throughout the concentration range plotted, while that of ammonium acetate rises above the ideal curve for an interval. As has been shown above, both of these substances might be expected to give freezing point curves lying decidedly below the ideal position. How can the fact that the curves approach the ideal curve so closely be explained, in view of the facts of solvation, and especially of dissociation?

If we consider the fact that association of solute molecules in solution would lower the mole fraction of the solute, we can explain the abnormally small lowering of the freezing point of acetic acid shown by both of these solutes. If we consider also that transference studies of both ammonium and sodium acetate solutions in acetic acid give abnormally small values for the transport number of the cation, we can clarify the matter by formulating the hypothesis that the associated solute molecule can dissociate in some such manner as cadmium iodide dissociates in water solution. Thus for sodium acetate we might suppose the following dissociation to take place:



The passage of an electric current through a solution containing the above ions, providing the two types of ions migrated at nearly the same rate, which does not seem unlikely on the basis of the work of Longworth,¹ would result in practically no transference of sodium acetate from the anode portion. A transport number calculated on the basis of supposed transference of the simple ions would have an abnormal value comparable to those which have been experimentally obtained in this work. It seems therefore that on the basis of what little evidence is available, an assumption of associated molecules of sodium and ammonium acetates in acetic acid, which undergo dissociation in some such manner as indicated, affords the only consistent explanation of the experimental facts regarding these substances.² It is difficult, however, to see why the abnormality should be greater in dilute than in concentrated solutions, when all our experience with aqueous systems would lead us to expect the opposite.

¹Longworth, loc. cit.

²Webb, J. Am. Chem. Soc., 48, 2263 (1926), after consideration of the freezing points of dilute solutions of sodium acetate in acetic acid from the viewpoint of the Debye-Hückel theory, came to the conclusion that the hypothesis of complete dissociation into simple ions was probably untenable in this case.

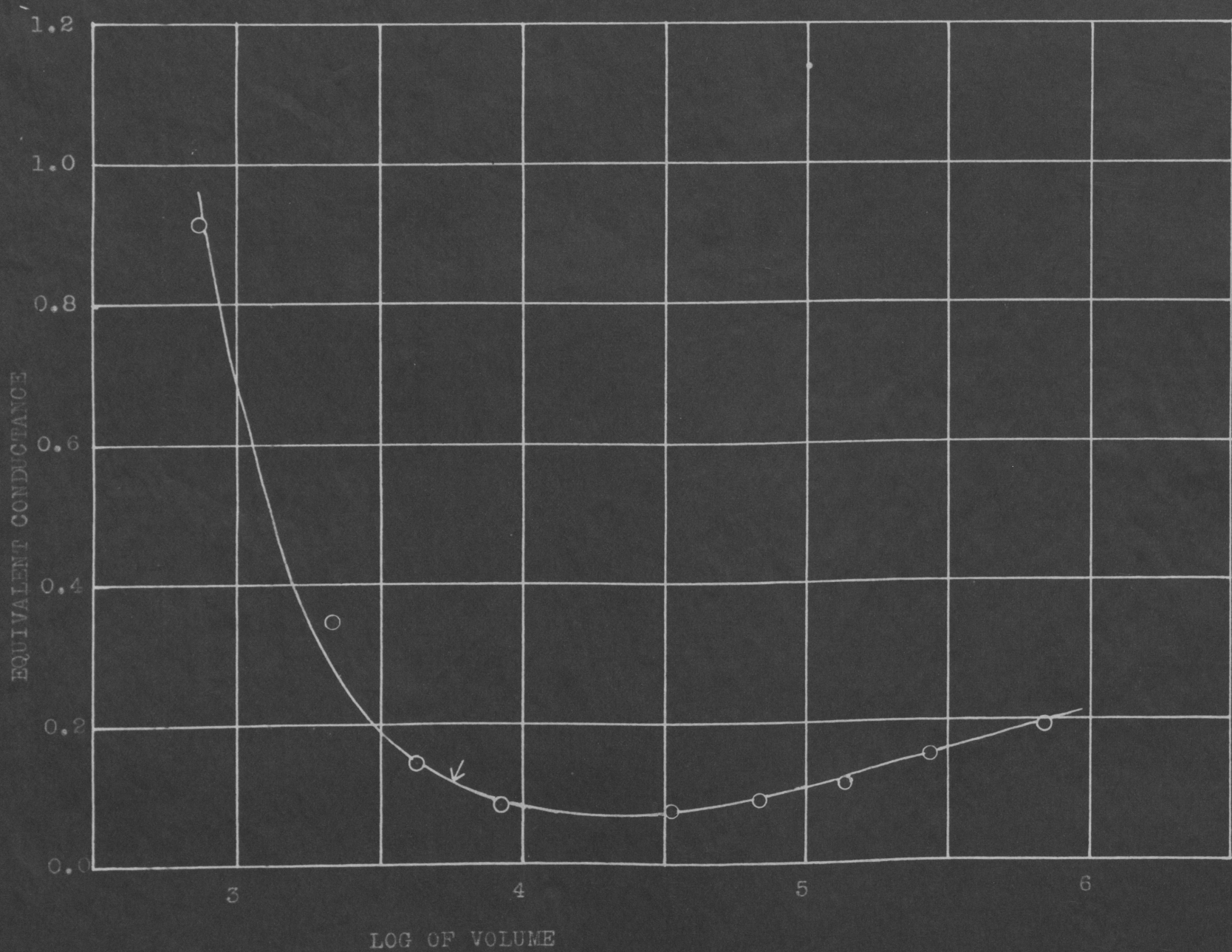
Conductance data₁ for sodium acetate solutions in acetic acid are available over a wide range of concentration. These data are plotted in Figure 4, the equivalent conductance in mhos as the ordinate, and the logarithm of the volume in cubic centimeters which contains one gram equivalent, as the abscissa. In going from a concentrated solution the equivalent conductance approaches a minimum rather sharply and then rises slowly as the dilution is continued. This fact is not significant in itself because this type of curve is quite characteristic of non-aqueous solutions. However, it is of interest to note that the zero transference of sodium ion in sodium acetate solutions first appears at about the same concentration as that at which the equivalent conductance approaches a minimum. This point is indicated by means of an arrow in the graph.

It is impossible to explain this relationship with our scant knowledge of such solutions, but the point is brought up as further evidence of the peculiar behavior of solutions of acetates, at least in this concentration range. Longworth₂ emphasized the anomaly of the fact

₁Hopfgartner, Physikalischemische Tabellen, Landolt-Börnstein.

₂Longworth, loc. cit.

FIGURE 4.



that the transport numbers in such systems, which he had determined, were apparently normal, in spite of the very irregular course of the conductivity curve. The present work tends to show that the transport numbers, too, have abnormal values.

It is evident that any attempt to calculate the degree of dissociation of these solutes from conductivity data by the classical method of Arrhenius would be quite futile, since such calculation is based on the assumption that the mobilities of the ions are independent of concentration. The marked variation of the transference numbers with concentration seems to indicate that not only the apparent mobilities, but even the composition of the ions, may change greatly with concentration. On the other hand, it appears that the newer theories of interionic attraction, based upon the hypothesis of complete ionization, would be equally inadequate to deal with the cases here described, where some sort of ionic association is evidently present.

The effect of ammonium acetate upon
the transference of the copper ion.

Copper displays amphoteric properties in both aqueous and non-aqueous systems, as has previously been

pointed out in this paper. In the acetic acid system, copper acetate dissolves readily in the presence of a strong base such as ammonium acetate or potassium acetate. In the case of ammonium acetate solutions, a solid salt appears, which has the formula, $\text{NH}_4)_4\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_6 \cdot 4\text{HC}_2\text{H}_3\text{O}_2$, if we write it as the salt of an amphoteric base. The solution of copper acetate occurs without the appearance of the copper ammonia ion, which we observe when copper hydroxide dissolves in ammonium hydroxide. This point of similarity suggested a study in the acetic acid system to determine, if possible, the nature of the substances that are formed in solution. It was expected that the copper would appear as a component of the anion and therefore, in the migration experiment, that the concentration of copper would increase around the anode. This seemed particularly likely at high ratios of ammonium acetate to copper acetate, in view of the common occurrence of such "abnormal" transference in aqueous solutions under similar conditions.¹

¹McBain and Van Rysselberge, J. Am. Chem. Soc., 50, 3009 (1928) and 52, 2336 (1930). By the use of a large excess of anion such as sulfate, furnished by potassium sulfate, a metal-like magnesium may be caused to migrate toward the anode during electrolysis of aqueous solutions.

The results, given in Table 3, show that in no case was there a transfer of copper towards the anode, and it was only in the presence of a very large excess of ammonium acetate that the transfer of copper towards the cathode was decreased to such an extent that one might suppose that copper appeared in a complex anion. This decrease in the transfer of copper may well have been due to the difference of concentration of the copper acetate and the ammonium acetate. Assuming equal dissociation, the current should distribute itself between the copper and ammonium ions, in some relation to the relative concentration of each base present. In order to determine whether or not a simple relationship occurred between the transport numbers of ammonium ion and copper ion and the mole ratio, mole per cent. ammonium acetate: mole per cent. copper acetate, these quantities were plotted on opposite coordinates in Figure 5. It is evident that no simple relationship exists.

One interesting point that may be observed in Figure 5 is the unequal distribution of the current between the copper and ammonium ions. It might be expected that the ammonium acetate would be far more

highly dissociated than copper acetate. However, at the mole ratio of twenty, for instance, the apparent transport numbers of the copper ion and the ammonium ion are the same. In other words the copper ion appears to carry the same quantity of electricity through the solution as twenty times its quantity of ammonium ion.

The values for the apparent transport numbers of both copper and ammonium ions are plotted against mole per cent. of ammonium acetate in Figure 6. The change of transport number of copper ion is almost a straight line function of the ammonium acetate concentration. This supports the statement made previously, accounting for the decreasing transference of copper on the basis that it is a phenomenon depending mainly upon change in concentration and not upon any change in ionic species.

These experiments, therefore, give no evidence of the presence in these solutions of an anion containing copper. In view, however, of the highly anomalous nature of the conductance phenomena in this solvent even in solutions of single salts, it can hardly be concluded that the existence of such ions is definitely disproved by these data.

FIGURE 5.

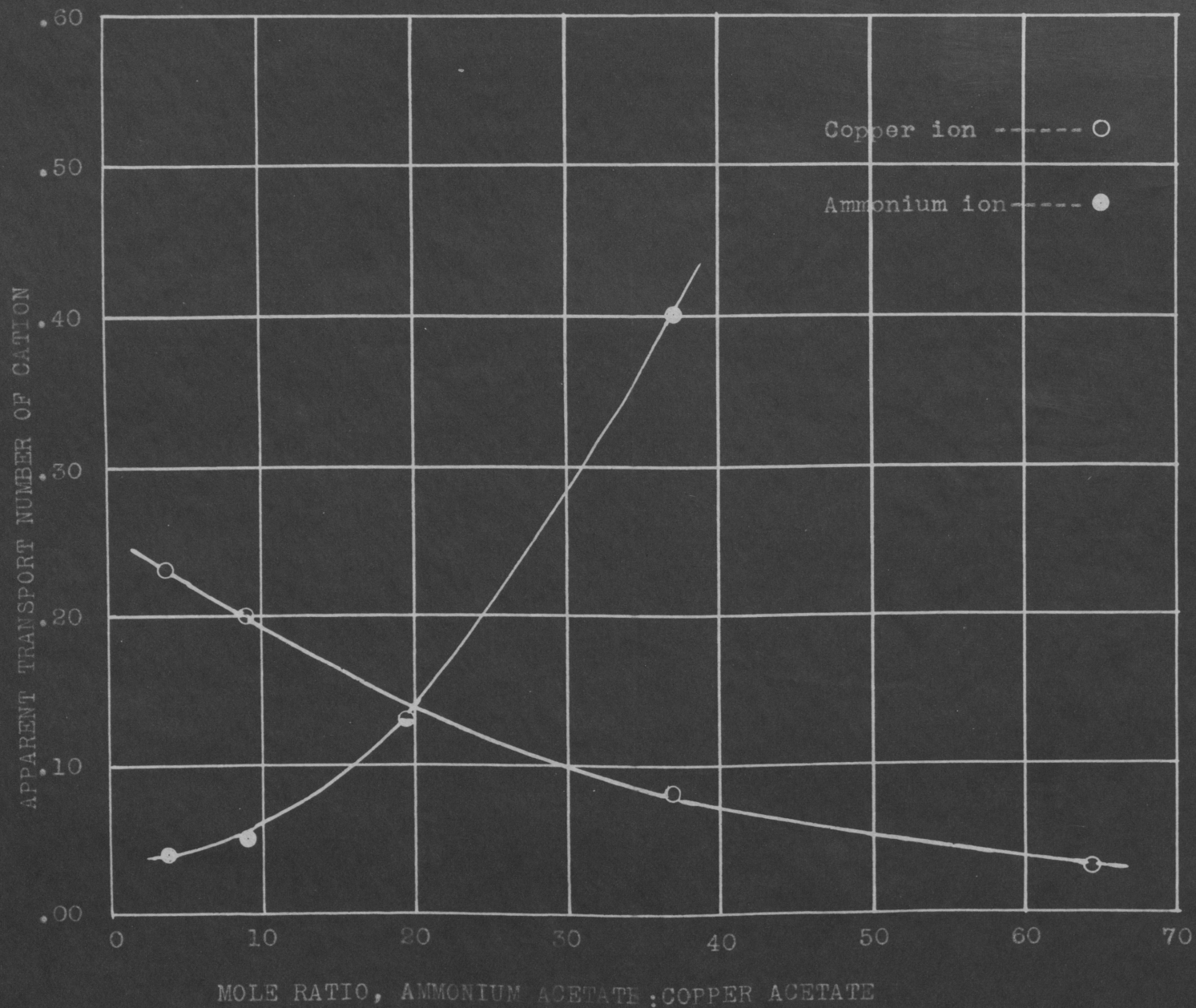
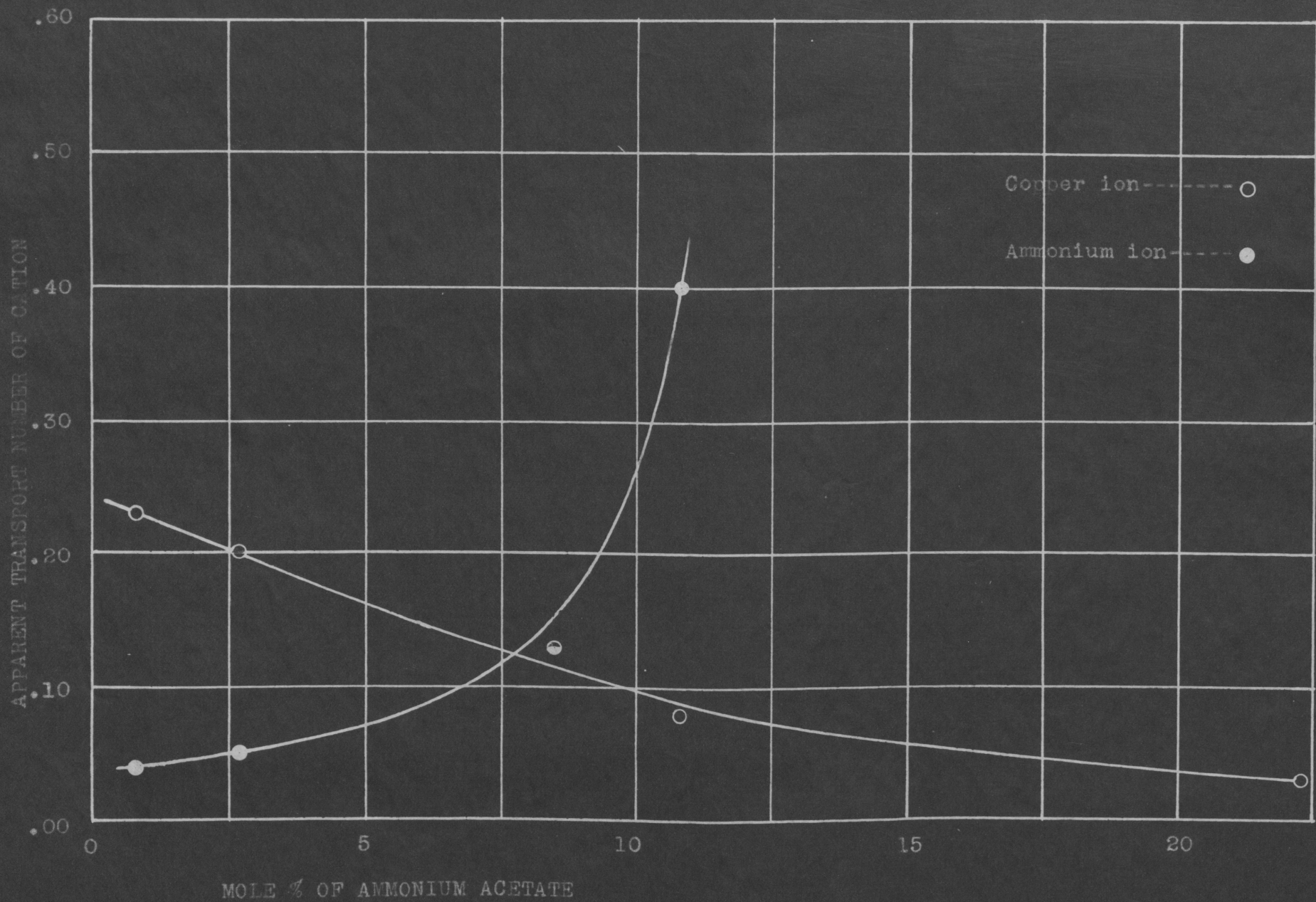


FIGURE 6.



SUMMARY:

1. A method has been worked out for determining transport numbers in acetic acid solution by the Hittorf method.
2. The transport numbers of the cations in solutions of ammonium acetate and sodium acetate have been determined over as wide a range of concentrations as possible. The transport numbers of these cations were found to decrease with decreasing concentration and to have abnormally small values in dilute solutions.
3. The effect on the transport number of copper, of varying greatly the mole ratio of the two salts, in mixed solutions of ammonium and copper acetates, has been studied.
4. The abnormal behavior of the freezing point curve of strong bases in acetic acid, the irregularity of the conductance-concentration curve, and the unusual values obtained for transport numbers, have been pointed out and discussed. The suggestion has been made that these abnormalities may be partially explained on the basis of molecular and ionic association.
5. No evidence for the existence of copper in a complex anion in the presence of a strong base in acetic acid has been obtained. However, the existence of such an ion has not been definitely disproved.