In precisely the same way we can show that for a mixture of more than two constituents,

$$N\frac{dp}{p}+N'\frac{dp'}{p'}+N''\frac{dp''}{p''}+----=0.$$

These equations are true when both the temperature and the pressure of the mixture are constant, and when the vapors behave like perfect gases. As a matter of fact the latter condition is never exactly fulfilled, and the equations must therefore be regarded only as approximations to the truth. How these approximate equations may be replaced by exact equations of similar form will be shown in another place.

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THE COMBINATION OF A SOLVENT WITH THE IONS.

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I. INTRODUCTION.

THE possibility of the combination of the ions of an electrolyte with the solvent has been suggested by several investigators. Ciamician[1] suggested that the attraction between the solvent and the positive and negative parts of the salt is actually the cause of dissociation. This idea receives support in the fact that the solvents that ionize salts largely are the ones that combine with them to the greatest extent, forming compounds with water of crystallization, alcohol of crystallization, etc.; but the mere fact that such compounds separate out in the solid state is not positive evidence that they exist in the solution.

In this connection it is interesting to note that few of the salts, whose ions are both univalent, separate with water of crystallization, while those with ions of higher valency almost all do. From this we might suspect that univalent ions are less hydrated than bivalent or trivalent ones, and this view is supported by the comparison of the velocities of the ions of different valencies. If we calculate the absolute velocities with which the ions move when subjected to the same force (not the same potential gradient for all

[1] Z. physik. Chem. 6, 403 (1890).

ions, but the same potential gradient for univalent ions, half of this for divalent ions, etc.), we find that in almost all cases monovalent ions move faster than bivalent, and bivalent faster than trivalent. It is to be expected that ions carrying molecules of solvent along with them will meet with greater resistance, and therefore move slower. But here again the evidence is far from being conclusive.

Recently, several methods have been used to show that electrolytes combine with the solvents, but there has been very little evidence obtained that the ions of the electrolytes so combine. There are difficulties in the use of the boiling-point and freezing-point methods in this case, for the effect of a dissolved substance upon the boiling-point or freezing-point of a solvent depends approximately upon the ratio of the number of particles of the dissolved substance to the number of molecules of the solvent. If the solute combines with the solvent the number of molecules of the solute is not changed, but only their size, and the only effect is that due to the removal of a small amount of the solvent from the field. In the case of the dilute solutions, this effect is very slight, but in very concentrated solutions, it becomes appreciable. Jones and his coworkers have made extensive use of this method and have concluded that a considerable number of substances combine with water in solution, and others with alcohol. The results, however, do not show conclusively whether it is the free ions that are so combined, and it can not be considered entirely certain that the observed variations of the boiling-points and freezing-points from the theoretical values are due to hydration and not to something else.

If instead of finding the boiling-point or freezing-point of the solution of a salt in water, we dissolve the hydrated salt in a second solvent and observe the effect on the boiling-point or freezing-point of this solvent, we can determine whether the water of crystallization still remains attached to the salt. Lobry de Bruyn and Jungius[1], and Bruni and Manuelli[2] have used this method and have found evidence of hydration in some cases.

A quantitative determination of the change in the color of a salt solution with dilution is capable of giving some evidence regarding hydration.[3]

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[1] Kon. Akad. Amsterdam, June 27, 1903, p. 91.

[2] Z. Elektrochem. 10, 601 (1904).

[3] See Lewis: Z. physik. Chem. 52, 224 (1905).

As the difference of potential between a metal and a solution containing its ions must depend upon the degree of hydration of the ions, a study of such differences of potential might add to our knowledge of hydration, but would alone hardly be conclusive proof of the existence of such hydration.

More direct evidence is to be obtained by observing whether the solvent is carried along by the ions during the electrolysis of a solution. If we simply electrolyze a solution of a salt in water, we cannot tell how much of the change in concentration about the poles is due to the migration of the ions and how much to the water carried by the ions. We might use an apparatus like that of Lodge or that of Whetham, and surround one electrode with a solution containing no water, and observe by some qualitative reaction whether water migrated into this solution, but a suitable qualitative test for water might be hard to find.

Another method that has suggested itself depends upon the probability that hydration diminishes considerably with rise of temperature. If we place our two electrodes in two separate vessels, and connect them by a siphon, and maintain the two vessels at widely different temperatures, the ions passing from the hot vessel to the cold vessel will combine with more water, and those passing in the opposite direction will lose water. Hence we will have a change of concentration at the point of change of temperature, *i. e.*, in the siphon. By making the two vessels sufficiently large, we can eliminate to a large extent the disturbing influence of the change in concentration about the electrodes. The difficulty is that the change of the migration velocities with the temperature would also cause a change of concentration in the siphon, and the amount of this effect would have to be determined.

If we electrolyze a solution of a salt in a mixture of two solvents the combination of the ions with either of the solvents will make itself evident by changes in the ratio of the amounts of the two solvents about the poles. The same result is obtained if, instead of using a second solvent, we use an inert non-electrolyte. Garrard and Oppermann,[1] and Oppermann[2] electrolyzed solutions of various acids, using boric acid as the non-electrolyte. Their results apparently indicated that the hydrogen ions carried water

[1] Nach. Königl. Gesell. Wissen. Göttingen, 56, 86 (1900).

[2] Dissertation, Göttingen, 1901.

with them, but Oppermann suggested that the changes in concentration observed might be due to the negative ions carrying boric acid in the opposite direction; and this explanation becomes very probable when we consider that only one part of boric acid to about fifty parts of water was used. It can easily be shown that the addition of one milligram of boric acid to such a mixture would have fifty times the effect upon the percentage composition that the addition of the same amount of water would. If we had a mixture of fifty parts of boric acid to one of water, the migration of water would have the greater effect upon the composition, and we might disregard the migration of the boric acid; but, of course, boric acid is not sufficiently soluble. Oppermann made another series of experiments with silver acetate as the electrolyte and acetic acid as the non-electrolyte, and the results apparently indicated the hydration of the negative ions; but he used only one part of acetic acid to about twenty-two parts of water, and hence it is more probable that the results were due to the acetic acid being carried in the opposite direction.

Lobry de Bruyn[1] carried out similar experiments with silver nitrate dissolved in mixtures of methyl alcohol and water. Solvents containing 25 per cent., 35 per cent. and 64 per cent. of methyl alcohol were used. He determined the alcohol in each case by distilling a known volume of the solution, and weighing a known volume of the distillate. In this way, he obtained substantially the same weights after electrolysis as before. He neglected, however, the change in volume due to the change in the amount of silver nitrate in the solution, for he found this change in volume to be small. His conclusion was that the results gave no indication of hydration. They certainly do not indicate much hydration; but if he had made corrections for the error mentioned, they would have indicated a slight hydration of the silver ions, which is the result obtained in the present work.

The method used in this work was the same as that used by Oppermann and by Lobry de Bruyn. Silver has great advantages over other metals for this work, because it can be deposited readily from a water solution, and its salts are not hydrolyzed. Some experiments were made with copper nitrate in a mixture of ethyl alcohol and water, but the experiments were abandoned.

[1] Rec. trav. chim. 22, 430 (1903); Konink. Akad. Wetensch. Amsterdam. Proc. 6, 97 (1903).

The amount of acid normally present from hydrolysis was increased during electrolysis, and this caused an uncertainty on account of the water taking part in the reaction, and the acid formed was likely to act upon the alcohol. Perhaps some way of overcoming these difficulties is possible, and, if so, the method could be extended to the large class of hydrolyzed salts.

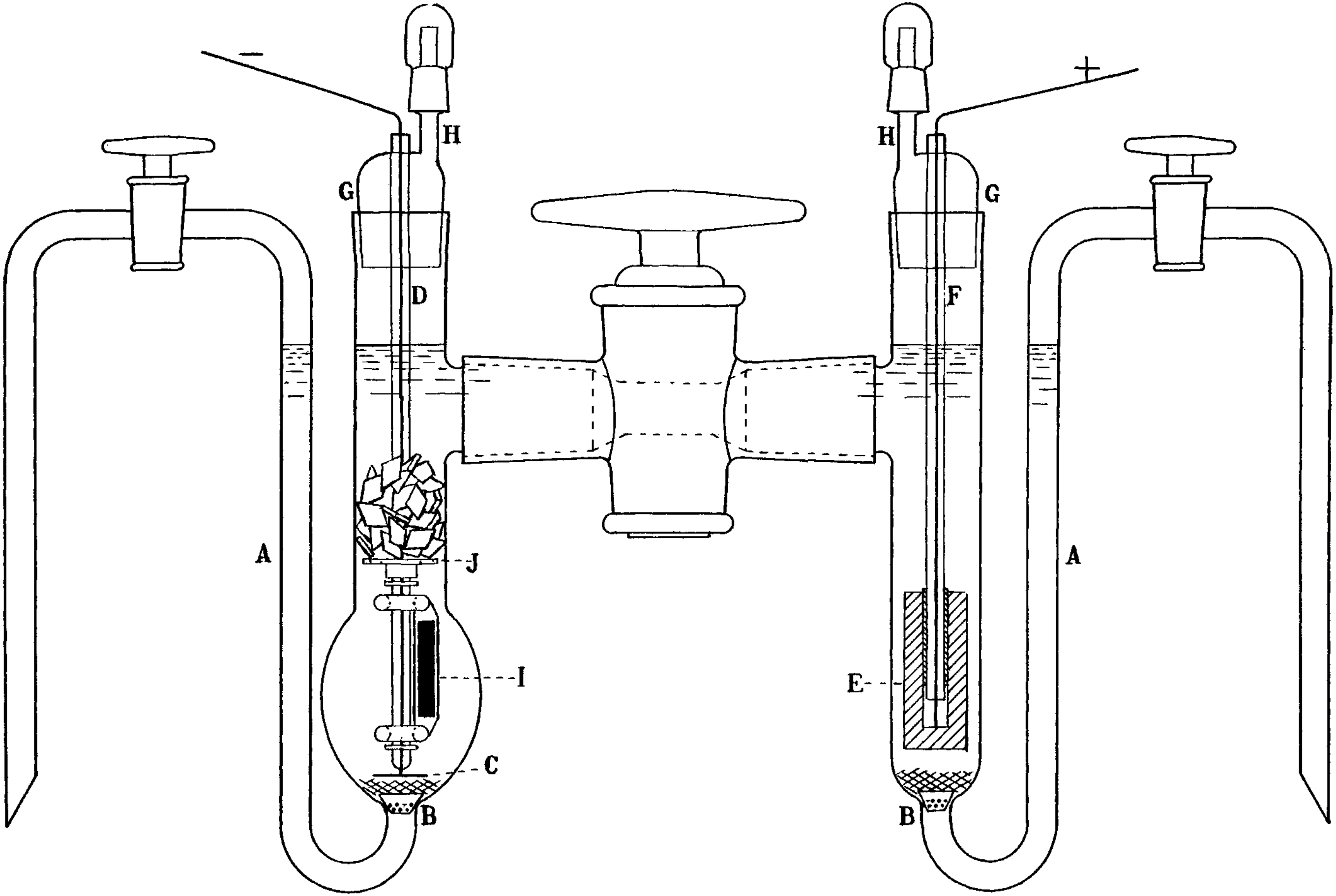
Experiments were made with silver nitrate in a mixture of pyridine and water, with silver nitrate in a mixture of ethyl alcohol and water, and with a mixture of silver nitrate and calcium nitrate in ethyl alcohol and water. The last-named mixture was used with the hope of finding a change of composition too great to be due to silver nitrate alone, in which case it must be due in part to the calcium nitrate. Silver nitrate may crystallize with two and also with three molecules of pyridine of crystallization. That such compounds exist in solution is also indicated by the fact that if a large excess of silver nitrate be added to a dilute aqueous solution of pyridine the solution becomes almost odorless, and no longer gives an alkaline reaction with methyl orange.

II. APPARATUS.

The apparatus used is shown in the figure. It consisted of two vertical tubes of 1.7 cm. internal diameter, connected by a horizontal stop-cock of 1.2 cm. bore. The lower ends of the two vertical tubes bore smaller tubes *A*, *A*, with stop-cocks for the removal of solution. At the junctures of these tubes were perforated platinum cups *B*,*B*, covered with asbestos, to prevent the removal of particles of metallic silver with the solution.

The object of this arrangement was to permit the quantitative removal of the solution from each electrode separately. A known amount of material was put into the apparatus, and the sum of the amounts of each constituent found ought to be the same as the original amount taken. A check was thus obtained upon the results.

The cathode was a platinum disc, *C*, attached to the glass stem *D*. The anode was a cylinder of silver, which is shown in section at *E*. The silver wire by which connection was made with the anode passed through the stem *F*, which extended into a hole bored deep into the anode, and contact was made at the bottom of the hole. The joint between the glass stem and the anode was made tight by a piece of thin rubber tubing. The glass stoppers *G*, *G*, which



−
+
H
H
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J
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C
B
B

bore the electrode stems, also bore the short tubes *H*, *H*, which were closed by ground glass caps.

The stop-cock was connected to the two vertical tubes by ground-glass joints, for it was found that if the apparatus was made in one piece, it was very likely to crack, either during the annealing, or when in use. All ground-glass parts were greased with a mixture of tallow and lard. The amount of this which dissolved in the alcohol was determined in several cases, and was found to be quite negligible.

When certain solutions were used, the silver trees which formed on the cathode grew so rapidly that they would reach the large stop-cock if not prevented. To prevent this without opening the apparatus and thereby allowing evaporation, the device shown at *I* was used. It consisted of a piece of iron within a sealed glass tube so mounted that it could rotate about the electrode stem. When the trees became too high, a large electromagnet was moved about the outside of the apparatus, causing the device within to rotate and break down the trees.

When the more dilute solutions were used, the cathode solution was liable to become very dilute and therefore of high resistance. To prevent this, a weighed amount of dry silver nitrate was placed upon the perforated glass disc *J*, before electrolysis. The use of platinum for such parts is objectionable, for the current is liable to pass through it, causing secondary reactions. Rather large crystals of silver nitrate were used, to avoid great obstruction of the current.

During electrolysis, the apparatus was kept in a tank of water, which was well stirred and kept at a constant temperature. The temperature within the apparatus must have been slightly higher than that of the tank, owing to the heating effect of the current, this effect being different in different parts of the solution.

A mil-ammeter and a silver voltameter were placed in circuit with the apparatus.

In handling the solutions considerable care was necessary to prevent evaporation. The stock solutions were contained in bottles provided with a stop-cock, which was fitted by a ground joint into a tubulure near the bottom of the bottle. To this was attached beyond the stop-cock, by means of another ground joint, a tube bent at right angles, so as to permit this portion of the tube to be cleaned and dried. In filling the apparatus this tube was connected with one of the tubes *H*, *H*. The air was then exhausted from the apparatus through one of the side tubes, *A*, *A*, and the solution allowed to run into the vacuum. The amount of solution used was found from the increase in the weight of the apparatus. A similar method was used in case a sample of the solution was removed from the bottle to a flask for analysis. In this way all loss of vapor was avoided.

As soon as the electrolysis was finished, the large stop-cock was closed. The solution was then removed from one side of the apparatus by introducing the side-tube *A* into a flask, and blowing into the tube *H*. This side of the apparatus was then washed, and was dried by a current of dry air. The weight of the solution removed was found from the decrease in the weight of the apparatus. The process was then repeated with the other part of the solution, the solution retained in the bore of the stop-cock being allowed to run into the second part. In the case of alcohol solutions, the air displaced from the apparatus and the flask by each portion of wash-water was caused to bubble through cold water, and this water was used for the succeeding washing. Loss of alcohol vapor was thus avoided. This precaution was not considered necessary in the case of pyridine solutions, as the vapor pressure of pyridine from these solutions was so slight that they were almost odorless.

The apparatus was so designed as to offer as little resistance as possible when solutions of high resistance were used, and electrolysis was continued for a rather long time, in order to obtain as great changes of composition as possible. Consequently, a certain amount of mixing of the two solutions undoubtedly occurred, but the aim was to obtain certain evidence of the migration of a solvent rather than an exact determination of the amount of migration. The apparatus was not of the best form for the complete separation of the cathode solution from the anode solution, for there was a tendency for the light cathode solution to circulate through the stop-cock to the upper part of the anode tube. This might have been prevented by making the stop-cock inclined, with the cathode side the higher, or by inclining the whole apparatus during electrolysis.

III. CHEMICALS.

The pyridine used was purified by precipitation as the ferrocyanide according to the method of Mohler.[1] It was then dried by

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[1] Ber. 21, 1015 (1888).

potassium hydroxide and distilled. It distilled completely between 115.1° and 115.3° at a barometric pressure of 760 mm. The alcohol was from Kahlbaum, and was redistilled before use. The calcium nitrate was from Kahlbaum. The silver nitrate was Eimer & Amend's C. P.

IV. SILVER NITRATE IN WATER AND ALCOHOL.

In these experiments, silver nitrate, alcohol, and nitric acid were determined directly, and the quantity of water found by difference, the whole of each cathode or anode solution being used for the analysis. A trace of nitric acid was always formed during electrolysis. First, the nitric acid was determined by titration with ammonia solution, with luteol as indicator. The titration was carried on in the flask into which the solution was received from the apparatus, care being taken to avoid loss of alcohol vapor. The alcohol was then distilled off.

A slight modification of the usual procedure in alcohol analysis was adopted. In order to obtain the last trace of alcohol, it is necessary to distil off the greater part of the solution. If the original solution is dilute, this makes the distillate so dilute that the determination of the alcohol content from the density is not as accurate as it might be. In this work a distilling head was used and the distillation conducted slowly until about a third of the solution had distilled off. The density of the distillate was determined. During this distillation the air displaced from the apparatus was caused to bubble through cold water to remove the alcohol vapor. The remainder of the solution was then distilled almost to dryness and the trace of alcohol in this distillate and in the water used to absorb the alcohol vapor from the first, determined by oxidation to acetic acid by the method of Dupré.[1] In the density determinations, a pycnometer of the Ostwald type, capable of giving results with a probable error of less than ±0.00002, was used. The density tables used were those given by Morley,[2] based upon the work of Mendeléeff.

After distillation the silver was determined by precipitation as the chloride.

In several instances tests were made for nitrites and for ammonium salts, since these substances may be formed in the electrolysis of a nitrate solution. Only inconsiderable traces were found.

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[1] J. Chem. Soc. **20**, 495 (1867).

[2] This Journal, **26**, 1185 (1904).

All weighings were corrected for the buoyancy of the air whenever the correction was of the least consequence.

Since the theoretically best conditions for the detection of the combination of the water with the ions are found in a solution containing much less water than alcohol, a solvent was tried which contained 95.36 per cent. of alcohol, and was nearly saturated with silver nitrate. When placed in the apparatus, it was found to have a resistance of about 7,000 ohms, which increased to 20,000 ohms. The increase appeared to be due to the formation of the so-called silver peroxide on the anode. As very little current could be driven through this resistance, the experiment was abandoned. Results were readily obtained, however, with solutions containing less alcohol.

Two analyses were made of the first solution used, with the following results:

	A. Per cent.	B. Per cent.	Average. Per cent.
Alcohol	40.29	40.29	40.29
Silver nitrate	23.73	23.73	23.73
Water	35.98	35.98	35.98

From these results it was found that the solvent contained 52.75 per cent. of alcohol.

Experiment 1.

Temperature: 15°. Amperes: 0.100–0.120. Volts: 73–83. Duration of electrolysis: 8 hours. Silver deposited: 2.9516 grams. Dry silver nitrate used: 4.788 grams. Solution used: 71.795 grams.

In the following table the first two columns give the amounts of the substances found in the cathode and the anode solutions, respectively; the third gives the sums of these; and the fourth gives the amounts present in the original solution, including, in the case of silver nitrate, the amount of the soild material added.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.004	0.002	0.006	0.000
Alcohol	17.413	11.480	28.893	28.926
Silver nitrate	12.801	8.986	21.787	21.825
Water	15.602	10.295	25.897	25.832
Total	45.820	30.763	76.583	76.583
Alcohol in solvent	52.74%	52.76%		52.83%

The following are the results of the analyses of the next solution used:

	A. Per cent.	B. Per cent.	Average. Per cent.
Alcohol	56.50	56.43	56.47
Silver nitrate	14.74	14.74	14.74
Water	28.76	28.83	28.79

The amount of alcohol in the solvent was 66.24 per cent.

Experiment 2.

Temperature: 25°. Amperes: 0.100–0.185. Volts: 110. Duration of electrolysis: 10½ hours. Silver deposited: 6.027 grams. Dry silver nitrate used: 6.439 grams. Solution used: 71.139 grams.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.004	0.002	0.006	0.000
Alcohol	23.603	16.558	40.161	40.172
Silver nitrate	8.311	8.522	16.833	16.925
Water	12.348	8.149	20.497	20.481
Total	44.266	33.231	77.497	77.578
Alcohol in solvent	65.65%	67.02%		66.24%

Experiment 3.

Temperature: 25°. Amperes: 0.10–0.15. Volts: 110. Duration of electrolysis: 9 hours. Silver deposited: 4.394 grams. Dry silver nitrate used: 5.461 grams. Solution used: 69.773 grams.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.015	0.005	0.020	0.000
Alcohol	23.511	15.940	39.451	39.401
Silver nitrate	8.180	7.438	15.618	15.746
Water	12.179	7.909	20.088	20.087
Total	43.885	31.292	75.177	75.234
Alcohol in solvent	65.87%	66.84%		66.24%

It will be seen that in Experiment 1, in which 52.83 per cent. alcohol was used, the composition of the solvent after electrolysis was found to be the same as before, within the experimental error, while in the next two experiments, in which 66.24 percent alcohol was used, there was an appreciable change. This change is in the direction that it would be if the silver ion combined with the water. It is also possible that it was due to the combination of the nitrate ion with the alcohol, but the former explanation is the more probable, for if it were the alcohol that migrated, the change in concentration would be greater in the 52.83 per cent. alcohol than in the 66.24 per cent.

In order to calculate the average number of molecules of water carried by the silver ions, it is necessary to know the relative velocities of the ions in the solvent used. No determinations have been made of the velocities of the ions of silver nitrate in alcohol of the strength used, but if we use the value 0.60 found by Jones and Bassett[1] for the relative velocity of the anion in absolute alcohol, the results will be sufficiently accurate. Using this value, the following results were obtained:

	Total water carried. Gram.	Molecules of water carried by one silver ion.
Expt. 2. Cathode solution	0.318	0.79
" 2. Anode "	0.290	0.72
" 3. Cathode "	0.196	0.67
" 3. Anode "	0.215	0.73

The numbers are calculated from both the cathode analyses and the anode analyses, independently. We may conclude that the silver ion combines with at least one molecule of water.

It will be seen from the table that there was always a little less silver nitrate found on analysis than was put into the apparatus. This is to be expected, on account of the secondary reaction at the anode in which nitric acid and the so-called silver peroxide are formed. Some water undoubtedly takes part in this reaction, but the amount cannot be great enough to have a considerable effect upon the results; for the greatest loss of silver nitrate, that of 0.128 gram in Experiment 3, is equivalent to only 0.007 gram of water.

V. CALCIUM NITRATE AND SILVER NITRATE IN WATER AND ALCOHOL.

On account of the ready solubility of calcium nitrate in alcohol, it is probable that a solution of good conducting power could have been obtained with very strong alcohol as the solvent, but such experiments would be of little use without results with silver nitrate alone in alcohol of the same strength. Consequently, the work was confined to alcohol of about the same strength as that used with silver nitrate alone.

The calcium was determined, after the removal of the silver, by precipitation as oxalate and ignition to sulphate with sulphuric acid. The whole of the solution was used for the analysis, as before. The other substances were determined as before.

The analyses of the original solution gave the following results:

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[1] Am. Ch. J. 32, 438 (1904).

	A. Per cent.	B. Per cent.	Average. Per cent.
Alcohol	49.25	49.31	49.28
Silver nitrate	10.14	10.14	10.14
Calcium nitrate	15.41	15.38	15.39
Water	25.20	25.17	25.19

The amount of alcohol in the solvent was 66.19 per cent.

Experiment 4.

Temperature: 25°. Amperes: 0.140–0.185. Volts: 110. Duration of electrolysis: 7 hours. Silver deposited: 4.632 grams. Dry silver nitrate used: 8.087 grams. Solution used: 78.030 grams.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.008	0.011	0.019	0.000
Alcohol	23.248	15.239	38.487	38.453
Silver nitrate	7.173	8.755	15.928	15.999
Calcium nitrate	7.344	4.688	12.032	12.009
Water	11.972	7.652	19.624	19.656
Total	49.745	36.345	86.090	86.117
Alcohol in solvent	66.01%		66.57%	66.19%

Experiment 5.

Temperature: 25°. Amperes: 0.13–0.18. Volts: 110. Duration of electrolysis: 7½ hours. Silver deposited: 4.781 grams. Dry silver nitrate used: 5.895 grams. Solution used: 74.628 grams.

	Cathode. Grams.	Anode. Grams.	Total found. Grams.	Taken. Grams.
Nitric acid	0.003	0.000	0.003	0.000
Alcohol	22.467(?)	14.339	36.806	36.777
Silver nitrate	4.512	8.919	13.431	13.462
Calcium nitrate	7.507	3.964	11.471	11.485
Water	11.509	7.214	18.723	18.799
Total	45.998	34.436	80.434	80.523
Alcohol in solvent	66.13%	66.53%		66.19%

In these experiments there was an appreciable change in the composition of the solvent, but it was so small that it may have been due to the silver nitrate alone, and not to the calcium nitrate. Hence we have no evidence of the hydration of the calcium ion. However, this does not prove that it is not hydrated, for if the calcium ions carried alcohol with them, this might mask the effect of the water carried.

VI. SILVER NITRATE IN PYRIDINE AND WATER.

The stock solution used was made from weighed amounts of material, and was of the following composition:

	Per cent.
Silver nitrate	15.401
Pyridine	3.050
Water	81.549

The amount of pyridine in the solvent was 3.606 per cent.

The solutions to be analyzed were diluted to 250 cc. and 25 cc. taken for each analysis. Two analyses of each solution were made. An excess of hydrochloric acid was added immediately to each sample, to precipitate the silver and convert the pyridine to the hydrochloride, which is less volatile. The silver chloride was filtered out and weighed, and the pyridine determined by the method of François.[1] Pyridine chloraurate, $C_5H_5N,HCl,AuCl_3$, was precipitated by auric chloride, the solution, containing the precipitate, was evaporated to dryness on a water-bath, and the excess of auric chloride washed out with ether. François ignited the precipitate to metallic gold, but in the present work the ether was allowed to evaporate at room temperature, and the precipitate was weighed directly. This method is believed to be preferable, as there appears to be a slight loss when the material is ignited.

Experiment 6.

Temperature: 25°. Amperes: 0.188–0.204. Volts: 30–34. Duration of electrolysis: 6 hours. Silver deposited: 4.663 grams. Dry silver nitrate used: 5.429 grams. Solution used: 72.973 grams.

	Cathode. Grams.	Average cathode. Grams.	Anode. Grams.	Average anode. Grams.	Total found. Grams.	Taken. Grams.
Pyridine	1.477 1.478	1.477	0.696 0.696	0.696	2.173	2.226
Silver	7.263 7.264	7.263	9.321 9.313	9.317	16.580	16.667
Water	....	36.629	....	22.981	59.610	59.509
Total	....	45.369	....	32.994	78.363	78.402
Pyridine in solvent	....	3.876%	....	2.940%	....	3.606%

Experiment 7.

Temperature: 25°. Amperes: 0.155–0.183. Volts: 37–44.

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[1] J. Pharm. Chim. 18, 337 (1903).

Duration of electrolysis: 5½ hours. Silver deposited: 3.450 grams. Dry silver nitrate used: none. Solution used: 80.792 grams.

	Cathode. Grams.	Average cathode. Grams.	Anode. Grams.	Average anode. Grams.	Total found. Grams.	Taken. Grams.
Pyridine	1.785 1.787	1.786	0.654 0.656	0.655	2.441	2.464
Silver nitrate	5.307 5.308	5.307	7.114 7.116	7.115	12.422	12.443
Water	....	41.607	....	24.324	65.931	65.885
Total	....	48.700	....	32.094	80.794	80.792
Pyridine in solvent	....	4.116%	....	2.622%		3.606

In both these experiments with pyridine, the determinations of pyridine in the same solution have agreed well with each other, but the total amount of pyridine found has been low. This was probably due to evaporation, either of pyridine or of pyridine hydrochloride.

Both experiments give good evidence of the combination of the pyridine with the silver ion. The following table gives the amounts of pyridine carried. The value 0.50 was used for the relative velocity of the cathion of silver nitrate.

	Total pyridine carried. Gram.	Molecules of pyridine carried by one silver ion.
Expt. 6. Cathode solution	0.107	0.063
" 6. Anode "	0.164	0.096
" 7. Cathode "	0.230	0.182
" 7. Anode "	0.255	0.202

In both experiments, needle crystals of $AgNO_3 + 2C_5H_5N$ appeared on the cathode side of the apparatus toward the end of the electrolysis. In the first experiment, they also extended into the top of the anode tube, owing to the circulation of the light cathode solution. In the second experiment, this was largely prevented by inclining the apparatus with the cathode side higher. This accounts for the difference in the results from the two experiments. The amount of the crystals formed was also greater in the second.

The small number of molecules of pyridine carried by the ions does not appear so strange when we consider that the original solution contained only 0.4256 molecule of pyridine to one of silver nitrate. Besides, the number of pyridine molecules available to the ions carrying the current must have diminished as the electrolysis progressed. Hence it is evident that a large proportion of the pyridine in the solution was in combination with the silver ions.

It might be suspected that the migration of the pyridine was due to the electrolysis of pyridine nitrate formed by a secondary reaction at the anode. To produce in this way as great changes as those observed, it would be necessary that nearly or quite all of the pyridine should be in the form of salt. That this was not the case is shown by the fact that the amount of silver nitrate remaining unaccounted for by analysis was not greater in these experiments than in the previous ones, from which it is evident that the extent of the secondary reaction was not greater. As further evidence, an attempt was made to determine the actual amounts of free pyridine in the solutions. The chloraurate method previously used gave both the free pyridine and the pyridine present as salt, in case any salt existed. In order to determine the free pyridine, samples of the solutions were titrated with hydrochloric acid with methyl orange as the indicator. As the silver nitrate would interfere in the titration, the silver was first precipitated as chloride and filtered out. The method is inaccurate, because the end point is not sharp, and a little pyridine is lost by evaporation when the silver chloride is filtered out. The results agreed, however, with those of the chloraurate method, as nearly as the results obtained by the titration of a sample of the original solution agreed with the amount of pyridine known to be contained in it. Hence there could not have been enough pyridine salt present to materially affect the results.

VII. SUMMARY.

(1) When a solution of silver nitrate in a mixture of ethyl alcohol and water was electrolyzed, changes in the composition of the solvent about the poles indicated that water was carried by the silver ion. The results did not indicate the presence of more than one molecule with each silver ion.

(2) It is pointed out that the same conclusion can be drawn from the work of Lobry de Bruyn with silver nitrate dissolved in mixtures of methyl alcohol and water.

(3) When silver nitrate and calcium nitrate were both dissolved in a mixture of ethyl alcohol and water, the changes in the composition of the solvent upon electrolysis were so small that they

may have been due to the hydration of the silver alone, and hence there is no evidence of the hydration of the calcium ions. However, it is not proved that they are not hydrated.

(4) By the electrolysis of a solution of silver nitrate in a mixture of pyridine and water, it was found that a large proportion of the pyridine present was combined with the silver ions.

THE BASIC PROPERTIES OF OXYGEN: ADDITIVE COMPOUNDS OF THE HALOGEN ACIDS AND ORGANIC SUBSTANCES CONTAINING OXYGEN.

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THE basic properties of oxygen, as exhibited in some organic compounds at low temperatures, have been discussed in a number of articles, and the quadrivalency of oxygen has been suggested to explain the constitutions of the compounds formed. The six principal classes of organic bodies—the alcohols, ethers, ketones, aldehydes, acids and esters—unite with the halogens, and the substances formed have been investigated. Only the first three classes are known with certainty to give compounds with the halogen acids, so that an examination of typical bodies of the last three classes, described in the following pages, may not be without interest.

The halogen acids were prepared in the ordinary way; the aldehyde was made from paraldehyde, the acetic acid purified by several crystallizations, and the ethyl acetate distilled from phosphorus pentoxide.

The compounds were formed with the evolution of large amounts of heat, were crystalline, and had sharp melting-points. They dissolved easily and formed supersaturated solutions in the acid from which they were formed.

Compounds with Hydrochloric Acid.—Aldehyde at —80° C. was quickly changed to paraldehyde by the addition of a few drops of the liquefied acid. The paraldehyde dissolved in an excess of the halogen·acid, and a compound melting at —18° separated out on standing. The analyses gave 54.1, 52.4, 53.3 per cent. acid, while $(CH_3CHO)_2(HCl)_3$ contains 55.3 per cent.

Acetic acid gave a product which melted at —53°, and was found to contain 45.7 and 44.5 per cent. of the halogen acid.