

CONTRIBUTION TO THE STUDY OF HYDROXYLAMINE AND ITS
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On account of the difficulty and expense experienced in preparing the inorganic compounds of hydroxylamine, they have not received much attention until recently. The organic compounds of hydroxylamine, however, being easier of preparation have been prepared in considerable numbers, and rather carefully studied. By the method of Divers and Haga² the cost and difficulty in preparing the inorganic salts of hydroxylamine have been considerably reduced. Notwithstanding this, however, their preparation in a chemically pure condition is still attended with considerable difficulty. This is due to the fact that they are for the most part unstable when heated much above the ordinary temperature, and also that, like sodium salts, hydroxylamine salts do not give a precipitate with any of the ordinary inorganic reagents.


The analogy which hydroxylamine has to both water and ammonia makes it difficult to predict which it would resemble the more in its physico-chemical properties. Accordingly, at the suggestion of Dr. E. Mackay, I have undertaken the preparation of hydroxylamine and its principal inorganic salts, with a view to studying especially their electrical conductivities. The results which I have obtained on following out this suggestion form the subject matter of this paper.

Preparation of Hydroxylamine Sulphate.

The preparation of hydroxylamine sulphate was used as the starting point in the preparation of all the other compounds of

¹ It is intended that henceforth papers embodying researches carried out in the laboratories of Dalhousie College, either by students or by members of the staff shall, when published in these Transactions, appear with the general title, "Contributions from the Science Laboratories of Dalhousie University."

² Journ. Chem. Soc. (London), 69, 1665 (1896).

hydroxylamine. The method followed was that of Divers and Haga. To start with, 900 gms. of sodium nitrite and the corresponding amount of sodium carbonate were taken. The sulphur dioxide was prepared by acting upon copper with sulphuric acid. When this gas is passed into a mixed solution of sodium nitrite and sodium carbonate a marked rise in temperature takes place. To keep the solution cool, which is necessary in order to prevent decomposition, the vessel containing it was surrounded by ice and salt. Further precautions were taken to prevent decomposition of the solution by keeping it well stirred. The delivery tube was made to act as a stirring rod. It consisted of a piece of glass tubing shaped thus, —the longer arm dipping into the liquid, while the shorter was made to pass through a cork and connected with the generating apparatus by a fairly stout piece of rubber tubing. The cork supporting this part of the delivery tube was attached to a small wooden axle, fitted near the circumference of a horizontal wheel which was driven by a small air engine. The wheel revolving carried the tube round with it, causing it to describe a circular motion in the liquid. By means of this arrangement, the liquid could be stirred much more effectively than by having the delivery tube stationary and using another rod to do the stirring. To prevent the end of the delivery tube from freezing up, a piece of copper wire was placed in that part of the tube dipping into the liquid, and then bent up almost parallel to itself and fastened loosely to the side of the vessel containing the solution. The circular motion of the delivery tube caused it to have a motion relative to the wire thus preventing it from becoming frozen up. During a part of the experiment the solution was simply surrounded with ice. As far as I could determine, the same results were obtained at this higher temperature, so long as the liquid was kept well stirred. The sulphur dioxide was passed in until the liquid became slightly acid, and the odour of the gas became perceptible. This operation took about one hour for every 100 gms. of sodium carbonate taken. The solution thus prepared was then heated gently,

after adding a few drops of sulphuric acid. Hydrolysis was found to take place quite rapidly accompanied by a marked rise in temperature. Care had to be taken not to heat the solution too strongly at first, as it had a tendency to froth over. Effervescence was seen to cease in a short time, and the liquid was then heated to 90°. To complete the second stage in the hydrolysis, it was found necessary to keep the solution at this temperature for about 55 hours. When hydrolysis was completed, was determined by adding to a small portion of the liquid, an excess of barium chloride. If on filtering and treating the filtrate with a few crystals of potassium chlorate, no cloudiness took place on boiling, then the oxyamidodisulphonate was known to be wholly converted to sulphate. The liquid was heated in porcelain jars instead of glass vessels on account of their being less liable to break, and also on account of the ease with which the solution could be heated to 90°-95° without bumping.

The excess of acid in solution was neutralized by adding the required amount of sodium carbonate. This amount was calculated by titrating a small portion of the solution with a portion of the prepared sodium carbonate solution—methyl orange being used as an indicator. The neutral solution was then evaporated down until it weighed about eleven times the weight of the sodium nitrite taken. On setting aside to cool, a large amount of sodium sulphate crystals separated out. Successive crops of crystals were then removed until no further separation of crystals would take place from the mother liquor. The last evaporation was brought about at reduced pressure to prevent decomposition. The crop of crystals containing the largest proportion of hydroxylamine was then taken, dissolved in water, and successive small portions of crystals removed by evaporating off the required amount of water at reduced pressure. This was kept up until the whole of the solution was crystallized. No crop of crystals, however, was found to be entirely free from sodium. The crop of crystals richest in hydroxylamine was then taken and recrystallised a great number of times. Although

I had a large amount of the impure salt to start with, and made many crystallisations, yet I failed to obtain crystals sufficiently free from sodium to be used in determining the electrical conductivity of the salt. The purity of the salt was determined roughly by heating a few crystals on a crucible cover. The amount of sodium sulphate left behind after the hydroxylamine sulphate had been volatilised, gave a rough idea of the amount of sodium present.

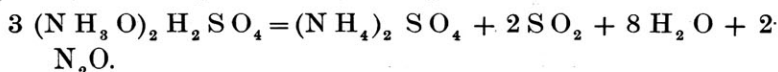
The hydroxylamine sulphate obtained in this way, however, was sufficiently pure for the preparation of the other salts of hydroxylamine, and finally hydroxylamine itself. By treating a dilute standard solution of the latter with the required amount of a dilute standard solution of sulphuric acid, a solution of hydroxylamine sulphate was obtained. This solution was evaporated to dryness on the water bath, first in an open vessel and then at reduced pressure. The salt thus obtained was purified by digesting with alcohol in an upright condenser. As both hydroxylamine and sulphuric acid are readily soluble in alcohol, while hydroxylamine sulphate is not, the latter was thus obtained in perfectly pure condition by decanting off the alcohol, and repeating the process a couple of times.

Properties of Hydroxylamine Sulphate.

Hydroxylamine sulphate was obtained on crystallising from water in the form of irregular transparent crystals, which were found to be slightly hygroscopic. The melting point of the crystals was found to be about 163° . This is somewhat difficult to determine exactly, as they undergo decomposition at the same temperature. According to Lossen they melt at 170° ; while Preibisch reports the melting point as being only 140° .

On heating above the melting point, the salt was found to break up into water, sulphur dioxide, nitrous oxide and ammonium sulphate—the greater part of the latter remaining behind after the other products have passed off.

The nitrous oxide was tested for by exploding with hydrogen in a eudiometer. When a spark from an induction coil was passed through the gas and hydrogen mixed in equal volumes, it was found that, after exploding, the volume of the mixed gases was reduced one-half. Taking a larger amount of hydrogen, the reduction of one volume in the same way took place. Two gms. of hydroxylamine sulphate yielded 180cc. of nitrogen under standard conditions. Hence the reaction which takes place must be represented by the equation :



Preparation of Hydroxylamine Chloride.

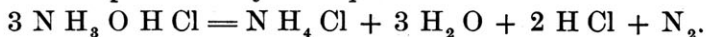
Hydroxylamine chloride was prepared by adding to a solution of hydroxylamine sulphate a slight excess of barium chloride. The solution was set aside over night to allow the precipitated barium sulphate to settle. The clear solution was then decanted off through a filter. On filtering a second time a perfectly clear solution was obtained. This was evaporated to dryness in the same way as the solution of hydroxylamine sulphate mentioned above. The residue left behind from the evaporation of the liquid was found to consist principally of hydroxylamine chloride, together with a little barium chloride and sodium chloride. By digesting these salts with successive small portions of absolute alcohol in an upright condenser, the hydroxylamine chloride was separated out, leaving the sodium chloride and barium chloride behind. On cooling, the hydroxylamine chloride at once began to separate out from its solution in alcohol in the form of white needle-shaped crystals. On recrystallizing from alcohol several times, crystals were obtained which gave no trace of either sodium or barium, and which volatilized completely when heated on a clean porcelain surface.

Properties of Hydroxylamine Chloride.

The crystals of hydroxylamine chloride obtained from water much resembled those of the sulphate, but were more inclined to

be tabular. The crystals from alcohol were needle-shaped, and were found to be not hygroscopic. The melting point of the crystals was observed to be 157° . This agrees with that given in Graham-Otto's *Chemie*.¹

Like the sulphate, hydroxylamine chloride decomposes when heated to the melting point. According to Graham-Otto,¹ the products of decomposition are:—Ammonium chloride, hydrochloric acid, water, nitrous oxide, and nitrogen. Nitrous oxide was tested for by passing an electric spark through the gas mixed with hydrogen, as in the case of the gas given off from hydroxylamine sulphate. Although the gases were mixed in different proportions, yet no explosion could be made to take place, showing the absence of nitrous oxide. Further, 2 gms. of the salt yielded 210cc. of nitrogen under standard conditions. Hence the decomposition of hydroxylamine chloride must be represented by the equation:



Preparation of Hydroxylamine Phosphate.

Hydroxylamine phosphate is only slightly soluble in cold water, and hence may be prepared by adding a saturated solution of normal sodium phosphate to one of hydroxylamine chloride. 200 gms. of the normal phosphate were dissolved in 400 cc. of water. To bring the salt into solution, it had to be heated almost to boiling. At the same time 110 gms. of hydroxylamine chloride were dissolved in 240 cc. of water. As the chloride is very soluble, this amount of the salt dissolved on simply warming the solution. It could then be cooled down to the ordinary temperature without immediately crystallising. In the same way the phosphate was cooled down to 30° or 40° by immersing in cold water. On now mixing the two solutions, crystals of hydroxylamine phosphate soon began to crystallise out in a very peculiar manner. Instead of starting at some point and branching out as in the case of most super-saturated solutions, the crystals of hydroxylamine phosphate

¹ Vol. 2, pt. 3, page 518 (5te Aufl.).

seemed to form independently throughout the liquid, and then fall to the bottom like flakes of snow. The formation of hydroxylamine phosphate thus more resembles the crystallisation of a salt from its supersaturated solution, than the formation of a precipitate in a solution where two soluble salts react so as to form an insoluble one.

About 75 gms. of the salt were obtained. On account of its being but slightly soluble in water, it can be purified with less difficulty than the other salts of hydroxylamine. Like the sulphate, however, it was found to decompose when a concentrated solution was heated to boiling. Considerable care had to be taken to prevent this when purifying the salt by recrystallising from water. On recrystallising eight times no trace of sodium was found.

Like many of the other salts of hydroxylamine, the phosphate forms supersaturated solutions of wonderful stability. On account of this property, I had considerable difficulty in first preparing the salt. The two solutions were mixed while hot. No phosphate crystallised out even when the solution was allowed to stand over night, and stirred briskly. On cooling down the solutions before mixing, as already mentioned, the salt was finally obtained.

Properties of Hydroxylamine Phosphate.

Hydroxylamine phosphate is much more soluble in hot than in cold water. It is almost insoluble in alcohol. Its crystals from water are coarsely, or finely, granular according to whether the solution from which they separate is very concentrated or less so. The crystals are not hygroscopic. When heated in a confined space they explode quite violently. Heated in a vacuum, the salt decomposes into hydroxylamine, water and pyrophosphoric acid :



When heated in an open vessel the salt was found to decompose at about 148° into ammonia, water, phosphoric acid, normal ammonium phosphate and nitrous oxide. The relative proportion

of the products formed depend largely on the degree to which the salt is heated, and hence the reaction cannot be represented by a definite equation.

Preparation of Hydroxylamine Nitrate.

Hydroxylamine nitrate was prepared from the sulphate by adding the required amount of barium nitrate. The solution was set aside over night to allow the precipitated barium sulphate to settle. The supernatant liquid was then decanted off through a filter. On filtering a second time a perfectly clear solution was obtained. This was evaporated to a small volume on the water at a pressure of about half an atmosphere. The concentrated solution thus obtained was then tested for barium and sulphate. By adding carefully barium nitrate, or hydroxylamine sulphate, as the case required, a solution was finally obtained which gave no indication of the presence of either barium, or sulphate. This solution, on filtering, was then distilled in a small flask at a pressure of about 20 mm. At this pressure both water and hydroxylamine nitrate were found to distil over at a temperature below 50°. The distillation was continued until only a few cc. of the solution remained behind in the flask. A few cc. of the last portion of the solution distilled over was separately collected and dried over phosphorus pentoxide. The remainder of the distillate was standardised by titration with iodine, and used in determining the conductivity of the compound,—redistilled water being used to make up the solution.

On account of its explosive nature, a pure solution of the salt was only obtained after repeated trials. I first endeavoured to distill off the water by heating on the water bath at 100° and pressure of half an atmosphere, with a view to purifying the salt by crystallising from absolute alcohol. At this temperature, however, the salt exploded, leaving about 3cc. of water behind in the flask. The solution was again prepared in the same way, and, after being evaporated to a small bulk as before, was heated on a water bath at a temperature of 80°. To hasten evapora-

tion the vapour was drawn off by suction. At this temperature, with normal pressure, the nitrate exploded as before, leaving about 5cc. of water in the flask. On preparing the salt a third time, the final distillation was carried on at a pressure of 20mm., with the result that the nitrate was found to distil over with the water, as already mentioned, leaving b̄arium nitrate or hydroxylamine sulphate, which might be present as impurities, behind in the flask.

Properties of Hydroxylamine Nitrate.

Hydroxylamine nitrate is a thick colorless liquid at the ordinary temperature. It may be solidified by placing in a freezing mixture of ice and salt. It decomposes slowly when heated to 80°. Heated more strongly it decomposes very rapidly, giving off red fumes. The products of decomposition were found to be nitric acid, water, ammonium nitrate, nitrous and nitric oxides. The nitric acid was tested for by passing through a solution of ferrous sulphate. The volumes of the gases given off depend largely on the degree to which the salt is heated.

Preparation of Hydroxylamine.

Hydroxylamine was prepared according to the method of Uhlenhuth¹ by distilling hydroxylamine phosphate in a vacuum. 20 gms. of the salt carefully purified and dried was distilled at a time. The distillation was made in a 100 cc. distilling flask which was connected with an air condenser. This consisted simply of the tube of a Liebig condenser. A second distilling flask served as a receiver. This was connected directly with the glass tube—no adapter being used. The side tube of the receiver was connected by thick-walled tubing with a manometer, which was in turn connected with the air-pump. The manometer consisted of an upright glass tube one meter long, having its lower end resting in a trough of mercury. A graduated scale was placed alongside the tube. In this way any change of pressure, which might take place in the distilling

¹ Ann. Chem. (Liebig), 311, 117.

flask, could be more readily noticed than by the manometer in the air-pump. With the apparatus thus set up, the pressure could be reduced to 15 mm.

A thermometer was placed in the distilling flask so that the bulb dipped in the salt to near the bottom of the flask. Heat was applied to the flask with a free flame. At a pressure of 15-25 mm., the principal part of the hydroxylamine distilled over between 135° and 137°. This part of the distillation occupied about 20 minutes. The hydroxylamine distilled over as a colorless liquid at the rate of about 2 drops a second. A characteristic of the liquid was the small size of the drops formed. The temperature was then gradually raised to 160°. Towards the end of the operation, the temperature could be kept up to this point with considerably less heat than was applied to the flask at first. The distillation was stopped at the end of half an hour. From 20 grms. of the phosphate 5.6 grms. of hydroxylamine were obtained.

The product left in the distilling flask consisted of a thick, viscous, glass-like mass. This was found to consist of orthophosphoric acid, pyrophosphoric acid and a small amount of hydroxylamine which failed to distil over.

The greater part of the hydroxylamine obtained was dissolved in about 50cc. of water and redistilled. At a pressure of 15-25 mm. both water and hydroxylamine were found to distil over at a temperature of 33-35°. In this way a chemically pure solution of hydroxylamine was obtained, which was used to determine its conductivity. The solution was standardised by titration with iodine.

On distilling some hydroxylamine phosphate which was not chemically pure, the hydroxylamine which distilled over was of a reddish color. During the distillation, the temperature was raised to 180°, and the pressure allowed to fall to 50 mm. without explosion. Allowed to stand over night, the reddish color of the distillate was found to have entirely disappeared. The

color was, therefore, obviously due to oxides of nitrogen resulting from decomposition of the phosphate other than that which leads to the formation of hydroxylamine.

Properties of Hydroxylamine.

Hydroxylamine resembles ammonia in many of its chemical reactions. With a neutral solution of ferric chloride, it gives a precipitate of ferric hydroxide, part of the salt being reduced at the same time to the ferrous state.

Hydroxylamine also gives with salts of manganese and zinc a precipitate of the hydroxides of these metals, soluble in hydroxylamine chloride.

With salts of aluminium and chromium, it gives a precipitate of aluminium hydroxide and chromium hydroxide, insoluble in excess.

Hydroxylamine differs from ammonia in acting as a strong reducing agent. Added in excess to an acid solution of a ferric salt, the whole of the iron is reduced to the ferrous condition.

With salts of copper, it gives a precipitate of cuprous oxide on warming.

Added to a solution of mercuric chloride it first precipitates mercurous chloride, and then, on adding an excess, the latter is reduced to metallic mercury.

Added to silver nitrate, it gives a black precipitate of metallic silver.

Its behaviour towards such oxidizing reagents as potassium permanganate and potassium bichromate has been studied by Knorre and Arndt.¹

Although hydroxylamine reacts with litmus, it was found to have no effect on either phenol-phthalein or methyl orange.

When kept in a warm room hydroxylamine slowly breaks up into ammonia, water and nitrogen.



¹ Ber. d. Chem. Ges. 33, 30 (1900).

Any decomposition is readily detected by the odour of ammonia given off, or by adding to a small portion in solution a few drops of a neutral solution of phenol-phthalein. A solution of hydroxylamine in water appears to be stable at ordinary temperatures. A portion of a solution kept for several weeks in a warm room gave no trace of a coloration when treated with a few drops of a perfectly neutral solution of phenol-phthalein.

Titration of Hydroxylamine by Iodine.

The only fairly trustworthy method for the volumetric estimation of hydroxylamine is that devised by Haga¹ and modified by Adams². This volumetric estimation is performed by adding an $\frac{N}{10}$ solution of iodine in potassium iodide to hydroxylamine solution in presence of di-sodium phosphate, as long as the former is bleached—using starch as indicator. Although this method gives better results than any of the others which have been suggested, yet it was found to be far from satisfactory. The end point is very hard to determine, as the blue color given with the starch fades out immediately. It was further noticed that the results obtained were influenced considerably by the amount of sodium phosphate in solution.

In the following experiments the solutions used were:— solution of hydroxylamine sulphate containing 8.2104 gms. per liter ($\frac{N}{10}$); of iodine, containing 12.685 gms. per litre ($\frac{N}{10}$); and of di-sodium phosphate, containing 59.7172 gms. per litre ($\frac{N}{2}$). The solution of iodine was standardised by copper.

According to the equation:

$$(N H_3 O H)_2 S O_4 + 2 I_2 = 4 H I + H_2 S O_4 + N_2 O + H_2 O,$$

5cc. of $\frac{N}{10}$ hydroxylamine sulphate solution = 10cc. of $\frac{N}{10}$ iodine solution. When making the titration it was found that 5cc. of $\frac{N}{10}$ hydroxylamine sulphate would bleach 10cc. of $\frac{N}{10}$ iodine solu-

¹ Journ. Chem. Soc. (London), 51,794 (1887).

² American Chem. Journ., 28,198 (1902).

tion only after adding 12cc. of $\frac{N}{2} \text{Na}_2 \text{HPO}_4$. A larger volume of sodium phosphate added gave results too high thus:—

Vol. of $(\text{NH}_3 \text{OH})_2 \text{SO}_4$ taken.	Vol. of $\frac{N}{2} \text{Na}_2 \text{HPO}_4$ added.	Vol. of iodine required.
5cc.	12cc.	10.04cc.
5 "	24 "	10.96 "
5 "	36 "	11.42 "
5 "	48 "	11.63 "
5 "	60 "	11.78 "

When titrating, iodine was added until it gave with the solution a blue color lasting for a moment. The same amount of starch solution was taken for each titration—being measured from a burette. It was found that by adding unequal amounts of starch irregular results were obtained. This was due to the fact that by using a large amount of starch the blue coloration was found to fade out less quickly than with a less amount, making it almost impossible to identify the true end point in both cases.

Haga,¹ in his experiments on the volumetric estimation of hydroxylamine by iodine, used sodium acid carbonate for producing a non-acid solution. He showed that to get best results by this method, solutions (1) should not be excessively dilute; (2) should contain very little alkali salt; (3) should not have more carbonate added during titration than is necessary to take up the hydriodic acid formed.

To find the effect of varying the dilution of the hydroxylamine salt when in presence of sodium phosphate, I made a series of determinations varying the volume of the solution titrated from 25 cc. to 250 cc. As far as I was able to determine, this range of dilution did not produce any effect on the titration.

A series of titrations was also made with sodium sulphate present in solution. Although amounts of this salt were added

¹ Journ. Chem. Soc. (London), 51, 794 (1887).

varying from 5 cc. to 25 cc. of a fifth-normal solution, yet no effect was produced on the titration, showing that the presence of sodium salts does not effect the estimation of hydroxylamine in a non-acid solution of di-sodium phosphate.

Electrical Conductivity.

The method used in determining the electrical conductivities of solutions of hydroxylamine and its salts, was that of Kohlrausch with alternating current and telephone.

The Wheatstone bridge consisted of four resistance coils which were certified by Queen & Co. of Philadelphia to be correct to one-fiftieth of one per cent., and a platinoid bridge wire wound on a marble drum. The small induction coil used had a very rapid vibrator, and was kept in an adjoining room that its noise might not interfere with the sound minimum in the telephone. The cell in which the solutions were placed for the determination of the resistance was of the form suggested by Arrhenius. Before using, the electrodes were polished to a bright surface and then coated with platinum black. This was done by passing a current from three Edison-Lalande cells backwards and forwards between the electrodes through a solution of platinic chloride. This solution was prepared by dissolving 1 part of platinic chloride and 0.008 part of lead acetate in 30 parts of water. The current was reversed every ten minutes, and continued until the electrodes were covered with a good coating of the platinum black. To dissolve out any platinic chloride which might be adhering to them, they were suspended in boiling water for a couple of hours.

The water used in making up solutions was purified by boiling ordinary distilled water with a few grammes of barium hydroxide. The water was condensed in a block tin worm. The first portion of about 200 cc. that came off was always thrown away. The water thus purified had at 18° a mean conductivity of about 1.1×10^6 , expressed in terms of mercury. Water

purified according to the method of Jones and Lindsay¹ by distilling twice, first from sulphuric acid and potassium bichromate, and then from barium hydroxide did not appear to have any greater resistance than that distilled from barium hydroxide alone.

A constant temperature was maintained by placing the cell containing the solution whose resistance was to be determined in a large vessel of tap water kept stirred by a mechanical stirrer, driven by a small hydraulic motor. The thermometer was graduated to a fiftieth, and had its errors determined at the Physikalisch-Technische Reichsanstalt, Berlin.

When starting to determine the conductivities of the hydroxylamine salts, it was noticed that with each salt the conductivity increased continually. In the case of the stronger solutions the increase in conductivity took place slowly, but rapidly when the solutions were very dilute. A one-tenth normal solution of hydroxylamine chloride was found to have the same conductivity as one made up a month before. The conductivity was also found to remain the same, although the solution was left in an open vessel for some time, showing that the change in conductivity was not due to decomposition of the salt in solution. On placing the electrodes in the solution without being joined in the circuit, the conductivity was found to have changed considerably in a few minutes. It thus became evident that the change in conductivity was due to the decomposition of the salt through the oxidizing power of the platinum black. Bright electrodes produced but little effect.

Hydroxylamine in solution was found to be oxidized by platinum black much more rapidly than its salts. 75 cc. of a one-fifth normal solution placed in a cell with the electrodes dipping in the solution were found to be completely decomposed in eighteen hours. Bright electrodes were also found to produce a considerable effect. This made an accurate determination of

¹ American Chem. Journ., 23, 329 (1902).

its conductivity very difficult, and, as a result, the conductivities given below for hydroxylamine itself may be only approximate.

The following table shows the change in conductivity produced in one-tenth and one-hundredth normal solutions of hydroxylamine chloride by coated electrodes. The molecular conductivities (μ) are expressed in terms of mercury at 18° multiplied by 10⁸ :—

N/10 N H ₃ O H Cl.				N/100 N H ₃ O H Cl.			
With current passing.		No current passing.		With current passing.		No current passing.	
Time.	μ .	Time.	μ .	Time.	μ .	Time.	μ .
0 min.	867	0 min.	867	0 min.	991	0 min.	991
5 "	871			5 "	1033		
10 "	875			10 "	1074		
15 "	881	15 "	873	15 "	1106	15 "	1083
20 "	885			20 "	1131		
25 "	888			25 "	1149		
30 "	890	30 "	877	30 "	1168	30 "	1134
35 "	893			35 "	1186		
40 "	896			40 "	1200		
45 "	898	45 "	881	45 "	1213	45 "	1181

It thus appears that decomposition takes place somewhat more rapidly when the current is kept passing continuously through the solution, than when it is turned off after each reading.

On account of this change in composition, the conductivities of the solutions below had to be determined in a slightly different method from that ordinarily followed. A solution once used could not be used again to make up another solution of less concentration. This used a larger amount of each salt than I had expected, and, as a result, none of the solutions made up were saturated excepting the phosphate. One-tenth normal solutions and those of greater concentration were made up by weighing out the salt directly. One-hundredth normal solu-

tions were prepared by adding to a half-liter flask 50 cc. of the one-tenth normal solution, and then filling up to the mark with water. Those of one-twentieth and one-fiftieth normal were obtained by adding to the cell directly about 25 cc. of the one-tenth normal solution and water in the proper proportions. Solutions of greater dilution were made up in a corresponding way.

Before determining the resistance of a solution, the cell was first rinsed out twice with a solution of the same strength. It was then placed in the bath for ten minutes, in order to be brought to the same temperature, with the electrodes joined in the circuit and suspended just above the surface of the solution in the cell. The current was then turned on, the electrodes dropped into the solution, and the reading taken as quickly as possible. In this way determinations could be made accurately with coated electrodes up to one-hundredth normal. The plates were then heated very gently until they had assumed a grayish appearance. With the platinum black thus reduced the conductivities of solutions were determined up to one-thousandth normal. For solutions of greater dilution a third cell was fitted up having the electrodes nearer together. They were heated to bright redness, and then rubbed gently with a smooth cloth until almost bright.

All solutions were made up at 18°, and the conductivities determined at the same temperature within one-fiftieth of a degree. The conductivity of the water used in making up each solution was determined, and subtracted from the observed conductivity of the solution.

The constants of the cells were determined by means of standard potassium chloride solutions, the specific electrical conductivities in reciprocal ohms of $\frac{N}{10}$, $\frac{N}{20}$ and $\frac{N}{50}$ solutions, as given by Arrhenius,¹ being as follows:

k, at 18°, for	$\frac{1}{10}$	normal KCl	=	0.011203.
“ “	$\frac{1}{20}$	“ “	=	0.0057875.
“ “	$\frac{1}{50}$	“ “	=	0.0023992.

¹ Electro-Chemistry, p. 135.

In the following tables, the several columns are as follows:—

- (1). Grammes of salt taken per liter (g).
- (2). Volume of solution per gramme molecule of salt (v).
- (3). Specific equivalent conductivity at 18°, in terms of mercury, multiplied by 10⁸ (μ_v).

I.			II.		
Hydroxylamine Sulphate [equivalent gramme molecule, (N H ₃ O H) ₂ S O ₄].			Hydroxylamine Chloride [equivalent gramme molecule, N H ₃ O H Cl].		
g	v	μ_v	g	v.	μ_v
.0082104	10000	1203	.006952	10000	1124
.016421	5000	1189	.013904	5000	1116
.041052	2000	1159	.03476	2000	1099
.082104	1000	1130	.06952	1000	1076
.16421	500	1093	.13904	500	1046
.41052	200	1030	.3476	200	1015
.8210	100	977	.6952	100	989
1.6421	50	920	1.3904	50	958
4.1052	20	805	3.476	20	909
8.2104	10	716	6.952	10	866
16.4208	5	638	13.904	5	805
			34.760	2	733

III.			IV.		
Hydroxylamine Phosphate [equivalent gramme molecule, (N H ₃ O H) ₃ P O ₄].			Hydroxylamine Nitrate [equivalent gramme molecule, N H ₃ O H N O ₃].		
g	v	μ_v	g	v	μ_v
.0065743	10000	271	.009611	10000	1355
.013148	5000	270	.01922	5000	1340
.032871	2000	268	.048055	2000	1318
.065743	1000	266	.09611	1000	1298
.13148	500	264	.1922	500	1271
.32871	200	260	.48055	200	1247
.65743	100	255	.9611	100	1223
1.3148	50	247	1.922	50	1191
3.2871	20	236	4.8055	20	1126
6.5743	10	220	9.611	10	1067
13.1486	5	198			

V.

Hydroxylamine [equivalent gramme molecule, $N H_3 O$].		
g	v	μ_v
.03306	1000	22
.06612	500	19
.1653	200	15
.3306	100	12
.6612	50	9
1.653	20	7
3.306	10	5
6.612	5	4

From the above results, it may be seen that the nitrate has a greater conductivity than the chloride, which in turn has a greater conductivity than the sulphate. This is different from what might be expected from a comparison of the corresponding salts of the alkalies. In the case of these salts, the chlorides, without exception, have a greater conductivity than the nitrates. The sulphates, however, as in the case of the hydroxylamine salt, have the lowest conductivity. When making a comparison with the salts of copper, cadmium, etc., it is seen that the nitrates, as in the case of the hydroxylamine salt, have the greatest conductivities. It seems probable, therefore, that hydroxylamine nitrate, differing from the other salts of hydroxylamine in being a liquid at ordinary temperatures, also differs from the chlorides and sulphates in its greater dissociation.

In the following table the conductivities¹ of a few salts of sodium, potassium and ammonium are given for the sake of comparison with those of hydroxylamine:—

¹ Whetham, *Theory of Solutions*, p. 407 (1902).

VI.

v	K Cl	Na Cl	NH ₄ Cl	NH ₃ OHCl	K ₂ S O ₄	Na ₂ S O ₄	(NH ₄) ₂ S O ₄
5	958	757	948	805	736	559	702
10	1047	865	1035	866	897	734
100	1147	962	1142	989	1098	906
1000	1193	1008	1190	1076	1207	998

v	(NH ₃ OH) ₂ S O ₄	KNO ₃	NaNO ₃	NH ₄ NO ₃	NH ₃ OHNO ₃	NH ₄ OH	NH ₄ O
5	638	839	694	865	12	4
10	716	983	817	1067	31	5
100	977	1122	907	1223	92	12
1000	1130	1180	952	1298	260	22

Compared in this way, it is seen that the conductivity of the chloride and sulphate of hydroxylamine is lower than the corresponding salts of potassium and ammonium, being almost the same as sodium. It may also be noted that while the chloride and sulphate of ammonium have a lower conductivity than the corresponding salts of potassium, yet, like hydroxylamine, in the case of the nitrate it has a higher conductivity than either sodium or potassium.

No data for comparison of the conductivity of phosphates were obtainable.

From the results obtained on the conductivity of hydroxylamine in solution, it is evident that although it has a very high resistance, greater than that of ammonia, indicating weaker basicity, yet it can not be classed, like water, as a non-electrolyte.