CONTRIBUTION TO THE STUDY OF HYDROXYLAMINE.*—BY G. M. JOHNSTONE MACKAY, B. A., *Dalhousie University, Halifax, Nova Scotia.*

The following investigation, carried out in the laboratories of Dalhousie University, was undertaken at the suggestion of Dr. E. MacKay. The chief object in view was the study of solutions more concentrated than those investigated by W. H. Ross.[1]

Preparation of Hydroxylamine Sulphate.

Considerable difficulty was found in preparing large quantities of hydroxylamine sulphate, and as about 600 grams were required, a portion of the salt used was purchased.

The method adopted was that of Divers and Haga[2] as modified by Maxwell Adams,[3] which method appears to be more satisfactory than the older methods.

On looking over the literature on the subject, several conflicting statements were found. Thus Divers and Haga say that the mixture to be sulphonated should consist of sodium nitrite and sodium carbonate in the proportion of two molecules of the former to one molecule of the latter; Maxwell Adams on the other hand, says one molecule of sodium nitrite to two of sodium carbonate, while Lengfeld[4] gives more than two molecules of sodium nitrite to one of sodium carbonate.

All three proportions were tried, but the two latter were found to give no satisfactory result. Maxwell Adams' directions probably contain a misprint, and should read " one *part* of sodium

*CONTRIBUTIONS FROM THE SCIENCE LABORATORIES OF DALHOUSIE UNIVERSITY —[CHEMISTRY]

1. Trans. N. S. Inst. Sci., XI, I, 96.
2 Jour. Chem. Soc (Lond.) 69, 1665 (1896).
3. Am. Chem. Jour. 28, 198, (1902).
4. Inorganic Chemical Preparations.

nitrite to two *parts* of sodium carbonate," which would give approximately the same proportions as Divers and Haga, which correspond to the equation

$$2NaNO_2 + Na_2CO_3 + 4SO_2 + H_2O = 2HON(SO_3Na)_2 + CO_2.$$
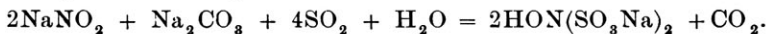
The method of procedure was as follows :—

500 grams of commercial crystallized sodium carbonate and 237 grams of commercial sodium nitrite were dissolved in 800cc. of warm water, and the solution, contained in a glass cylinder about 10 cm. by 30 cm. in size, placed in a freezing mixture of snow and salt. When the temperature fell to —5° C., sulphur dioxide was passed into the solution from a siphon, the delivery tube acting as a stirrer by being attached to a swivel gear fastened near the circumference of a wooden wheel kept in motion by means of a small air engine. When the flow of sulphur dioxide was so regulated that the temperature did not rise above —3°, sulphonation took from 6 to 8 hours. When the solution thus became neutralized, it was poured into a large flask, a few drops of sulphuric acid added, and the whole heated to between 90 and 95 degrees in a large water bath until the hydrolysis of the sodium oxyamidosulphonate was about complete, the process requiring about 50 hours.

The solution was then almost neutralized with sodium carbonate, cooled to O° C, evaporated, cooled again to —8°, and a saturated solution of tertiary sodium phosphate added, when the comparatively insoluble hydroxylamine phosphate would separate out.

Contrary to the experience of Divers and Haga, on adding the few drops of sulphuric acid to the sulphonated solution to start hydrolysis, no marked rise of temperature took place.

The following variations in treatment were tried without marked improvement in the yield :

The addition of more water to the solution before starting hydrolysis ;

The addition of a larger quantity of acid to start hydrolysis ;

The addition of sodium carbonate during hydrolysis to neutralize the large excess of acid formed ;

Increase of length of time of hydrolysis until disappearance of last trace of the oxyamidosulphonate, 5 or 6 days.

In order to be able to pass sulphur dioxide into the solution more rapidly without raising the temperature above —3°, a copper vessel forming an annular ring was designed so that the freezing mixture could be put around the outside of the solution, and also in the central bottomless cylinder. The solution to be sulphonated, in the annular space, had thus a large surface exposed to the action of the freezing mixture. The delivery tube was rotated in the ring as before.

Little or no hydroxylamine was obtained in this way, however ; and a great deal of time was spent in trying to improve other conditions before it was found that the copper had a specific catalytic reducing action on hydroxylamine salts, converting them mainly into ammonium compounds.

Preparation of Free Hydroxylamine.

For the preparation of free hydroxylamine the method of Uhlenhuth[1] was followed. When the chloride was used as the basis of preparation, it was necessary to convert it into the phosphate. 500 grams of tertiary sodium phosphate, prepared from the secondary sodium salt by adding the necessary amount of sodium hydroxide and recrystallizing, were dissolved in 1000cc. of water and added to 273 grams of hydroxylamine chloride dissolved in 600cc. of water. About 200 grams of hydroxylamine phosphate separated from the hot filtered solution on cooling. As there was such a large volume of water present, and as the reagents were pure to start with, it was not necessary to recrystallize.

From 20 to 50 grams of the dried salt, the amount of salt varying with the amount of hydroxylamine required, were put

1. Ann. Chem. (Liebig), 311, 117 (1900).

in a distilling flask fitted with a thermometer with its bulb dipping into the salt. An air condenser about 400mm. long and 10mm. in diameter with about 50mm. of smaller glass tubing joined on to the end, which passed through a rubber cork into a wide mouthed bottle of 250cc. capacity, was attached to the flask. Through another hole in the cork there passed a glass tube to which the exhaust apparatus was connected.

As it was necessary to weigh the pure hydroxylamine, a small tared weighing bottle was placed in the receiver immediately under the condenser so that it would collect most of the hydroxylamine.

The apparatus was exhausted by means of a "Geryk" vacuum pump, a U tube filled with pumice stone soaked in sulphuric acid followed by a calcium chloride tower filled with fused sodium hydroxide and finally by a tower lying on its side spread with phosphorus pentoxide, being placed between the receiver and the pump in order to prevent access of hydroxylamine, sulphuric acid or water vapor to the oil valves. A mercury manometer was connected in parallel with the drying tubes.

After the apparatus was exhausted to 6 or 8mm. pressure, heat was gradually applied to the flask, hydroxylamine passing slowly off until a temperature between 115° and 125° was attained, when, under the same pressure, the greater quantity of the hydroxylamine was expelled. Distillation was stopped when the thermometer rose to 140° as it was desirous to obtain as pure a product as possible, although Uhlenhuth allows the temperature to rise to 170° with the pressure as high as 40mm.

The hydroxylamine, of which about 4 grams would be obtained from 20 grams of phosphate, would condense in the weighing tube, and when jarred or cooled would form perfectly clear crystals, thus showing itself to be practically pure. There was generally, however, a slight odor of ammonia noticeable.

Preparation of Solutions.

The best method for the analysis of hydroxylamine, according to the investigations of Maxwell Adams,[1] is the titration by iodine in the presence of tertiary sodium phosphate. He, however, states that it is not very trustworthy.

My experience has been the same. Working with a standard solution, concordant results could be obtained by always using the same amount of phosphate, but where an unknown amount of hydroxylamine was present in the solution, there being no guide as to the amount of phosphate to be added, very unsatisfactory results were obtained. The end point is also very uncertain, the blue color of the starch fading out almost immediately.

Accordingly in making up my standard solutions, I proceeded directly from the weight of the crystalline hydroxylamine itself, which should give more accurate results than standardization by the iodine titration.

As the solutions when once used in the conductivity cell could not be used again on account of decomposition, each concentration required was made up separately. In the case of 2, 5, and 10 normal solutions, 50cc. and 25cc. graduated flasks were used, and as all of this was needed to rinse the cell and to fill it, a comparatively large amount of hydroxylamine was used.

The flasks used in making up the solutions were 500cc., 400cc., 250cc., 150cc., 100cc., 50cc., and 25cc. 50cc. and 25cc. pipettes, a 10cc. pipette graduated to 1/10cc, and a 50cc. burette were used for diluting. All were carefully calibrated at 18° C.

The various concentrations were made up in the usual way, by dissolving a weighed quantity of hydroxylamine in so much water, removing a portion in a pipette, adding required amount of pure water to bring to the required standard, and then filling up to the mark with the solution which had been removed in the pipette.

---

1. Loc. cit.

New solutions were made up each day as there was evidence of slight decomposition on standing.

The water used was purified according to Hulett's[1] method. 5cc. of sulphuric acid and 5cc. of a saturated solution of potassium dichromate per liter of water were added to ordinary distilled water in a large flask with a block tin condenser thrust into the neck and held there by means of a cork made of a mixture of asbestos and plaster of Paris. The water thus obtained was redistilled after addition of a small quantity of barium hydroxide. The water finally received had a mean conductivity of 1.6×10^{-6} expressed in Kohlrausch's new unit.[2] The best water obtained had a conductivity of 1.05×10^{-6} and was used for the more dilute solutions. The conductivities obtained were corrected by substracting the conductivity of the water.

Measurement of Conductivity.

Conductivity was determined by Kohlrausch's method with alternating current and telephone. A bridge of Kohlrausch pattern, with four resistances, of 1000, 100, 10 and 1 true ohms was used, and wire of resistance 1.4 ohms wound on a marble drum. Both wire and coils were certified by the maker, Queen & Co., of Philadelphia, to be accurate to within .01% and .02% respectively at 17.5°, and to have a temperature co-efficient of .000267 per ohm per degree centigrade.

The bridge wire was calibrated according to Stroubal and Barus[3] with ten german silver wires of approximately equal length, soldered to stout pieces of copper wire.

The induction coil was of the form recommended by Ostwald, and was kept in an adjoining room so that the noise of the interrupter would not affect the ear.

As pointed out by W. H. Ross[4], solutions of hydroxylamine and its salts are decomposed by platinum electrodes. It was

1. Ztschr physik. Chem., 21, 297 (1896) and J. Phys. Chem. I., 91 (1896).
2. Kohlrausch u. Holborn ; Leitvermögen der Elektrolyte, 1898.
3. Wied. Ann., 10, 326, (1880).
4. Loc. cit.

found that when a solution of hydroxylamine of fair concentration was put in the ordinary cell of the Arrhenius type with electrodes covered with platinum black, that a vigorous reaction set in with evolution of bubbles of gas and a greal deal of ammonia fumes, due probably to the reducing action of the occluded hydrogen. Even with bright electrodes considerable decomposition occurred, the resistance of a solution in contact with the platinum decreasing from 500 to 200 ohms in 18 hours.

It was thought that it might be possible to use some other metal electroplated on the platinum which would not decompose the solution so much. Accordingly, the following experiment was tried with pieces of the more easily electroplated metals about 18 sq. cm. in area.

Each piece was placed in a beaker and covered with 20cc. of an approximately N/10 solution of hydroxylamine, and allowed to stand at a temperature of 25° for 44 hours. Each beaker was then washed into a 100cc. flask, and duplicates of 25cc. each run out from a burette and titrated with iodine solution in presence of sodium phosphate. Averaging the two results and correcting for end point, it was found that 25cc. of each solution required the following amounts of iodine :

Original solution.............11.1cc. N/10 I solution.
Solution with tin plate 11.1
    "   "   platinum 10.5
    "   "   silver 10.5
    "   "   nickel plate 9.9
    "   "   mercury ....about 8.0
    "   "   copper 0.0

It was thus shown that tin decomposed the solution little or none at all, and that copper decomposed it completely, the other metals arranging themselves in the above order. On these grounds an ordinary cell of the Arrhenius type was tin plated from a solution of tin chloride, ammonium oxalate and oxalic acid at a temperature of 65° according to Classen[1], a greyish white coating being obtained.

---

1. Quantitative Chemical Analysis by Electrolysis.

This cell showed itself to be greatly superior to that constructed of bare platinum, but still slightly decomposed the solution. Thus in a couple of hours an approximately N/5 solution in the platinum and tin cells decreased in resistance as follows :—

	With platinum.	With tin.
Initial resistance	3555 ohms.	3717 ohms.
Final "	2636 "	3201 "
Difference	919 "	516 "

For solutions 1/10 Normal and more dilute, a second cell with pure tin electrodes of larger size and closer together, was fitted up by fusing pieces of stout tin wire to two tin plates about 25 sq. cm. in area, and arranged in the same manner as the Arrhenius cell. The wire was protected by glass tubes passing through holes in the wooden cork and held in place by sealing wax, and as the wire could not be fused into the glass it was left bare for about 25mm. above the electrodes. Of course with this arrangement it was necessary to always introduce the same amount of liquid into the cell so that the same area of the surface of the wires would always come into play. Twenty-five cc. measured from a pipette was the amount used. This cell did not give such a good minimum point with the telephone as the electroplated one.

Before making an observation the cell was first carefully cleaned with pure water, the electrodes suspended at some distance over an electric lamp to dry, the cell rinsed with the solution, the requisite amount put in, and the whole placed in a large thermostat of the form recommended by Ostwald[1], with a stirrer rotated by a small air engine. A thermometer graduated to the 1/50 of a degree and calibrated by the Physikalisch-Technische Reichsanstalt, Berlin, was placed in the bath. By the addition of cold water, or the application of a very small flame under the bath, the temperature of the whole could readily be kept constant to within 1/50 degree of 18°, at which temper-

1. Ztschr. phys. Chem., 2, 565 (1888).

ature the measurements were made. When the electrodes were dry they were connected in the circuit and suspended immediately over the solution in the cell for about ten minutes, when they were dropped carefully into the liquid and a reading made as quickly as possible, the time taken being about half a minute.

After the lapse of about 6 minutes another reading was taken, the change in conductivity being as follows :—

Strength of Solution.	Molecular Conductivity.	Conductivity after 6 minutes.
N/5	·098	·11
N/10	·28	·32
N/20	·40	·43
N/50	·52	·55
N/100	·76	·86
N/200	1·3	1·80
N/500	1·4	1·85

It thus appears that greater relative decomposition takes place in dilute solution. This may be due, however, to the fact that in concentrated solutions minute bubbles of gas adhere to the electrodes keeping the resistance higher until dislodged by shaking.

The conductivity of the pure hydroxylamine, owing to the small amount of material available, had to be determined in a very small cell of about 6cc. capacity. It was made by hammering out into thin plate the ends of two tin wires, and passing them through a piece of paraffin, which served as a stopper to the cell. The wires were filed to thin diameter where the top of the solution would come into contact with them, and a diamond scratch was run around the outside of the cell so that the same amount of solution could always be added. The cell itself was merely a weighing tube, and the hydroxylamine was collected in it directly from the condenser.

For the measurement of the conductivity of water, a cell of the Arrhenius type was used with electrodes platinised according to the formula of Lummer & Kurlbaum.[1]

1. Wied. Ann., 60, 315, (1897)

The cells were standardized by means of N/50 and N/100, solutions of pure recrystallized potassium chloride made with pure water.

The following results were obtained, the specific equivalent conductivities being expressed in reciprocal ohms multiplied by the number of cubic centimeters containing one gram equivalent of hydroxylamine.

The results obtained by W. H. Ross, with bright platinum electrodes, are given in the last column.

The other columns are :

(1) Grams of salt taken per liter.

(2) Volume of solution in liters per gram molecule of hydroxylamine.

(3) Specific equivalent conductivity expressed in Kohlrausch's new unit.

(1) g	(2) v	(3) μ_v	(4) μ_v (Ross).
332·5760........	0.0994	·031	...
165·3200........	0·2	·018	...
66·1280........	0·5	·027	...
33·0640........	1·0	·051	...
16·5320........	2·0	·093	...
6·6128........	5·0	·098	·4
3·3064........	10·0	·28	·5
1·6532........	20·0	·40	·7
·6612........	50·0	·52	·9
·3306........	100·0	·76	1·2
·1653........	200·0	1·3	1·5
·0661........	500·0	1·4	1·9

In consideration of the relatively small decomposition of hydroxylamine solutions in presence of tin as compared with platinum, column 3 may be taken to give more accurate results than any hitherto obtained.

In determining the conductivity of the pure hydroxylamine, the small cell, containing about 5 grams of the substance, was warmed in water at a temperature of slightly above 33°, the melting point of hydroxylamine, until the crystals had liquefied.

The tin electrodes, joined in the circuit, were then inserted and a reading taken as quickly as possible. So slight was the decomposition that the liquid solidified again in a few minutes. The specific conductivity expressed in reciprocal ohms was approximately 83×10^{-6}.

It thus appears that hydroxylamine has a conductivity between that of liquid ammonia at 30° C., 150×10^{-6}, and that of hydrazine hydrate, 34×10^{-6}. On the addition of water, at the concentration of ten gram molecules to the liter, there is a specific conductivity of 310×10^{-6}, which decreases continuously on dilution. In the molecular conductivities there is a minimum point between the concentrations 2 normal and 10 normal. This may indicate that at high concentrations hydrates are formed which are dissociated on further dilution. Unfortunately, owing to lack of time, I was unable to further investigate this anomaly.

Freezing Points of Solutions of Hydroxylamine.

The method used for the determination of the depression of the freezing point was that described by Loomis.[1]

The thermometer used was of the ordinary Beckmann type and had been calibrated by the Physikalisch-Technische Reichsanstalt, Berlin. It was graduated to 1/100 degree and could be read directly to 1/1000 degree by means of a reading microscope with a micrometer eyepiece.

The freezing tube consisted of two parts, an inner tube with re-entrant bottom, 28cm. × 2.8cm., and an outer tube providing an air jacket of about 1.5mm. thickness. The inner tube was supported in the outer by means of rubber bands. The thermometer was held in position in the inner tube by an ebonite cover and a rubber cork a few centimeters below, through both of which were glass tubes to allow the stirring rod of thin glass

---

1. Phys. Review, 1, 199, (1893); and 9, 257, (1899).

rod bent in a ring at the bottom, to pass through. A platinum stirring rod could not be used owing to its decomposing power on the solution.

In the determination of the freezing point of the solution, these tubes were surrounded to their neck in a glass vessel 35cm. high and 11cm. in diameter, called the protection bath. This stood in a large earthenware jar containing snow and water. The bath was kept at $0 \cdot 3$ degrees below the freezing point of the solution under investigation. The vessel was provided with a stirrer made of stout copper wire, and was covered with a thick wooden cover.

Two more glass vessels of about the same size as the protection bath were also used. One contained a mixture of snow and salt at a temperature of about—10°, and was used to super-cool the solution whose freezing point was to be determined. The other contained water at a temperature of $+5°$ and was used to melt the ice formed in the tube.

The hammer of an electric bell supported over the protection bath and driven by an Edison-Lalande battery was used to tap the top of the thermometer before the reading.

In determining the freezing point, the inner tube was filled up to a mark on the glass with about 50cc. of the solution at about 0°, and placed in the freezing bath where it was kept with continuous stirring until ice formed, when it was removed to the melting bath and stirred until nearly all the ice had disappeared. It was then again removed to the freezing bath and stirred until the mercury after falling commenced to rise when it it was quickly transferred to the protection bath, the hammer set in motion, and after two minutes of continuous stirring and tapping, during which time the mercury assumed its highest position, a reading of the thermometer was taken. The whole operation was then repeated 6 times and the mean of the different readings taken.

By judiciously controlling the degree of overwarming, the overcooling could be kept within 1/10 of a degree. As the overcooling seldom exceeded this, it was not considered necessary to make any correction for change in concentration, as the degree of accuracy otherwise attained would not justify it.

The solutions used were made up according to volume at 18° C., and the molecular depresssion calculated according to Arrhenius. The water used was the same as that used for the conductivity measurements, and the freezing point was determined each day in order to eliminate errors due to variation in the barometer.

The following results were obtained :—

Grams of NH_2OH used per liter of solution.	Number of liters per gram molecule.	Depression of freezing point	Molecular depression.
33·0640	1	1·7746	1·77
16·5320	2	·8900	1·78
6·6128	5	·3607	1·80
3·3064	10	·1808	1·81
1·6532	20	·0950	1·90
·6612	50	·0391	1·96
·3306	100	·0204	2·04
·0661	500	·0045	2·25

These results are in general agreement with the conductivity measurements, at corresponding dilution, in showing the slight dissociation of hydroxylamine solutions.

For the sake of comparison, it may be of interest to give the values of the molecular d pression by ammonia in aqueous solution as found by Jones[1], and also the specific equivalent conductivities for ammonia, and potassium hydroxide, taken from Whetham's[2] tables.

1. Zeitschr. phys. Chem., 12, 623, (1893).
2. Theory of Solution, 1902.

Molecular depression of ammonium hydroxide in solution :—

Grams per 1000cc.	Normal.	Lowering.	Molecular lowering.
.081	.002310	.0053	2.2943
.16078	.004586	.0099	2.1587
.23937	.006827	.0142	2.0800
.31678	.009035	.0185	2.0476
.40500	.01155	.0229	1.9827
.90450	.02580	.0510	1.9767
1.35405	.03862	.0759	1.9653
1.75865	.05016	.0984	1.9617

Specific equivalent conductivity of solutions of ammonia, potassium hydroxide and hydroxylamine, expressed in Kohlrausch's units :

NUMBER OF GRAM EQUIVALENTS PER 1000cc.	10	5	3	2	1	0.5
Specific equiv. cond of NH_2OH	.03	.02	....	.03	.05	.09
" " NH_3	.05	.25	.35	....	.89	1.27
" " KOH	45.0	105 2	139.7	......	182.6	195.7

0.2	0.1	.05	.03	.02	.01	.006	.005	.002
0.1	0.3	0.4	....	0.5	0.8	......	1.3	1.4
....	3.3	4 6	5.3	....	9.8	12 3	....	20.2
....	211.1	217.4	220.9	..... .	225.8	227.6	.....	227.5

The results obtained in the present paper may be summarized as follows :

(1). By the use of tin electrodes, the conductivity of solutions of hydroxylamine has been more accurately determined than hitherto.

(2). The molecular conductivities show a minimum point between the concentrations 2 and 10 normal.

(3). The specific conductivity of pure hydroxylamine has been determined.