

CXXXVI.—*The Estimation of Hydroxylamine.*

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THE authors, while attempting to estimate hydroxylamine in the presence of inorganic salts, found that all the methods hitherto described for the estimation of hydroxylamine were very unreliable in the presence of many substances which would not be expected to interfere with the reaction. Moreover, most of the methods suffered from other defects, such as being affected by the rate of titration and temperature, even when a pure hydroxylamine salt was used.

The authors have therefore worked out another method for the estimation of hydroxylamine, depending on the reduction of cupric oxide to cuprous oxide, which is free from these defects.

Meyeringh (*Ber.*, 1877, 10, 1940), who first investigated methods for

the quantitative estimation of hydroxylamine, proposed to estimate the base in three different ways.

(1) By titration with iodine in presence of magnesia or sodium phosphate. The reaction which takes place was shown to be $2\text{NH}_3\text{O} + 2\text{I}_2 = \text{N}_2\text{O} + \text{H}_2\text{O} + 4\text{HI}$.

(2) By heating with ferric sulphate and titration of the ferrous salt produced with permanganate or dichromate, the reaction in this case being $2\text{Fe}_2(\text{SO}_4)_3 + 2\text{NH}_3\text{O} \cdot \text{HCl} = 4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{N}_2\text{O} + \text{H}_2\text{O} + 2\text{HCl}$.

(3) By titration with standard Fehling's solution. It was proved that nitrous oxide was produced, and the reaction was represented by the equation, $2\text{NH}_3\text{O} + 4\text{CuO} = \text{N}_2\text{O} + 2\text{Cu}_2\text{O} + 3\text{H}_2\text{O}$.

Haga (Trans., 1887, 51, 794), who examined the method of titration with iodine, found that the best substance for removing the hydriodic acid was sodium hydrogen carbonate, and that dilution had a marked effect, concentrated solutions requiring less iodine, and very dilute solutions taking more iodine, than that indicated by theory. Moreover, the presence of carbon dioxide or of neutral alkali salts, such as sodium chloride, always increased the quantity of iodine required.

Maxwell Adams (*Amer. Chem. J.*, 1902, 28, 198), who found that the titration with iodine in presence of magnesia and sodium hydrogen carbonate was untrustworthy, accordingly used sodium phosphate, and obtained good results when the proportion of hydroxylamine and the phosphate was kept approximately constant.

The authors find that, on using any of the three reagents proposed to remove hydriodic acid, the results obtained are untrustworthy, and are affected by dilution, by the rate at which iodine solution is added, and, very largely, by the presence of impurities.

The following experiments, selected from a large number, serve to show the magnitude of these effects.

Ten c.c. of a solution of hydroxylamine hydrochloride, which theoretically required 28.6 c.c. of *N*/10 iodine solution, were used for the following experiments.

Conditions of experiment.	c.c. of iodine solution required.
Magnesia added	28 c.c.
Sodium phosphate added	28.4—28.6 c.c.
Sodium hydrogen carbonate	30.0 c.c.
Magnesia, 27 c.c. of iodine added rapidly	29.2 „
Magnesia + trace of ammonium chloride	30.6 „
Magnesia + trace of nickel sulphate	30.8 „
Sodium phosphate + trace of nickel sulphate	29.7—30 c.c.

The end-point in most cases was very slowly attained and uncertain. In estimating pure hydroxylamine solutions, sodium phosphate is undoubtedly the best reagent for removing hydriodic acid, as stated by Maxwell Adams (*loc. cit.*).

This investigator found that Meyeringh's second method was untrustworthy, the amount of permanganate or dichromate required depending on the quantity of ferric salt employed.

The authors found that the amount of ferrous salt produced depended on the strength of the solution of hydroxylamine, the time of heating, and the amounts of ferric salt and acid present, even when the reaction was carried out and the mixture cooled in an atmosphere of carbon dioxide. The quantities of permanganate solution used, in a series of experiments made with the same quantity of hydroxylamine solution under varying conditions, varied between 12.0 c.c. and 15.77 c.c., so that no trustworthy results can be obtained even with pure hydroxylamine solutions.

Simon (*Compt. rend.*, 1902, 135, 1339) proposed to estimate hydroxylamine by titration with potassium permanganate in neutral solution and in presence of rather more than one molecule of normal sodium oxalate to each molecule of hydroxylamine. Under these conditions, the reaction is represented by the equation, $4(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{C}_2\text{O}_4 + 2\text{KMnO}_4 = 2\text{MnC}_2\text{O}_4 + 2\text{KHC}_2\text{O}_4 + \text{N}_2\text{O} + 3\text{N}_2 + 15\text{H}_2\text{O}$.

The authors found several difficulties in carrying out this estimation which rendered it unsuitable for their purpose.

It was found difficult to make solutions of free hydroxylamine and acid solutions of its salts exactly neutral, since the use of an indicator had to be avoided owing to its action in causing the solution to become brown, and thus making it impossible to see the end-point in the subsequent permanganate titration. The amount of permanganate required varied somewhat with the rate of addition and also with the amount of oxalate present. The former effect is not surprising, since the reaction is far from simple, and potassium hydrogen oxalate is one of the final products.

The authors now turned their attention to the reduction of copper oxide by hydroxylamine, as proposed by Meyeringh, but, apparently, never used subsequently, and found that a simple and trustworthy method of estimation could be based on this reaction. The method of titration was found to be inconvenient on account of the uncertainty of the end-point, and, moreover, did not give very consistent results.

It was found that on pouring a solution of pure hydroxylamine hydrochloride into a quantity of boiling Fehling's solution or the copper potassium carbonate solution of Soldaini (*Gazzetta*, 1876, 6,

322) and Ost (*Ber.*, 1890, 23, 1035),* raising the mixture to the boiling point, collecting the precipitated cuprous oxide on asbestos felt in a Gooch tube-crucible of Jena glass, reducing in hydrogen, and weighing the copper thus produced, very constant results were obtained, which, however, did not agree with the theoretical values calculated from the equation $4\text{CuO} + 2\text{NH}_2\cdot\text{OH} = 2\text{Cu}_2\text{O} + \text{N}_2\text{O} + 3\text{H}_2\text{O}$.

The following are two estimations made by this method, which show the agreement among the results obtained :

- (i) 1.6087 grams of $\text{NH}_2\cdot\text{OH}, \text{HCl}$ in 200 c.c. : 10 c.c. gave 0.1416 gram of Cu or 122.4 grams per gram-molecule of $\text{NH}_2\cdot\text{OH}$.
- (ii) 1.4812 grams of $\text{NH}_2\cdot\text{OH}, \text{HCl}$ in 250 c.c. : 10 c.c. gave 0.1046 gram of Cu or 122.7 grams per gram-molecule of $\text{NH}_2\cdot\text{OH}$.

The hydroxylamine hydrochloride used throughout these experiments was prepared by crystallising the best commercial specimen obtainable, from hot 98 per cent. alcohol containing a drop of platinic chloride, filtering, and drying *in vacuo* over calcium oxide; it was found to contain $\text{Cl} = 50.7$ per cent. (theory, 51.0).

The same kind of deviation was observed when the cuprous oxide was estimated by the method proposed by Wood and Berry (*Proc. Camb. Phil. Soc.*, 1902, 12, 2, 97) and by Sonntag (*Chem. Centr.*, 1903, i, 998) for the estimation of sugars. The cuprous oxide, after being collected on asbestos felt in a Gooch's crucible, was washed with boiling water and transferred to a wide-mouthed stoppered bottle, already filled with carbon dioxide. A solution of ferric salt, containing 35 grams of ferric alum and 5 c.c. of strong sulphuric acid in 500 c.c. of water, was added in sufficient quantity to dissolve the cuprous oxide; a portion of the same solution served to completely remove all traces of cuprous oxide from the crucible. On shaking the bottle, the cuprous oxide rapidly dissolved, and the ferrous salt produced was estimated by titration with potassium permanganate: 4KMnO_4 corresponds to $10\text{NH}_2\cdot\text{OH}$.

The following experiments correspond with those mentioned above :

Ten c.c. of the first hydroxylamine solution required 21.9 c.c. of permanganate (1 c.c. = 0.00321 gram of KMnO_4) or 60.7 grams of KMnO_4 per gram-molecule of $\text{NH}_2\cdot\text{OH}$.

Ten c.c. of the second solution required 16.1 c.c. of the same solution of permanganate or 60.63 grams of KMnO_4 per gram-molecule

* This solution is best made by dissolving 23.5 grams of copper sulphate, 250 grams of potassium carbonate, and 100 grams of potassium hydrogen carbonate in water, warming until complete solution takes place, and making up the volume to one litre.

of $\text{NH}_2\cdot\text{OH}$, the value calculated from the copper obtained being 60.71.

The theoretical values of copper and potassium permanganate are 127.2 and 63.2 respectively.

There is, therefore, a deviation of about 5 per cent. from the theoretical value in each case.

Various modifications of the experiment were made in order to find out the cause of this discrepancy. It was found that the relative proportions of the hydroxylamine and copper solution, duration of boiling, and amount of ferric solution used had no effect. Dilution had a slight but decided effect, the amount of permanganate used rose gradually to about 62.0 grams as the solutions were diluted from 1 to 0.05 per cent. of hydroxylamine hydrochloride.

It was then found that practically theoretical results could be obtained if the hydroxylamine solution was added slowly to the copper solution, the latter being well stirred and kept boiling during the addition. About 25 c.c. of the hydroxylamine solution were added from a pipette directly into about 50 c.c. of a well-stirred boiling copper solution. The precipitated oxide was treated in the manner already described, any cuprous oxide deposited on the stirrer being easily dissolved off subsequently by the ferric solution.

The rapid mixture of the hydroxylamine with the copper solution evidently determines the completion of the reaction, and it may be suggested, on the basis of the following experiment, that when hydroxylamine comes into contact with excess of copper oxide the former is oxidised to nitrous oxide according to Meyer's equation, $4\text{CuO} + 2\text{NH}_3\text{O} = 2\text{Cu}_2\text{O} + \text{N}_2\text{O} + 3\text{H}_2\text{O}$, but that when there is an excess of hydroxylamine, nitrogen is produced, thus: $2\text{CuO} + 2\text{NH}_2\cdot\text{OH} = \text{Cu}_2\text{O} + \text{N}_2 + 3\text{H}_2\text{O}$.

This view is supported by the following experiment on the gas evolved from Fehling's solution (the copper potassium carbonate solution is inconvenient on account of the carbon dioxide evolved).

Twenty-five c.c. of a solution containing 0.0948 gram of hydroxylamine hydrochloride gave 16.0 c.c. of gas at 20° and 759 mm. (solution added without stirring). Volume corrected to 0° and 760 mm. = 14.6 c.c. Theory requires 15.2 c.c.

This gas contained nitrous oxide, but on explosion with hydrogen and electrolytic gas, 6.4 c.c. of the gas only gave a contraction of 5.6 c.c., so that it must have contained some nitrogen.

The mixture produced by adding the solution from a dropping funnel to a closed flask was not sufficiently intimate to give pure nitrous oxide.

The following experiments serve to show that, in all cases under

the above-mentioned conditions, the amount of copper obtained and the amount of permanganate used, agree, almost within the limits of experimental error, with the values required by theory.

Strength of $\text{NH}_2\cdot\text{OH}, \text{HCl}$ solution.	Number of c.c. used.	Weight of Cu obtained.	Grams of Cu per gram-molecule of $\text{NH}_2\cdot\text{OH}, \text{HCl}$.
0.7736 grams in 250 c.c.	25 c.c.	0.1414	127.0
0.8508 grams in 250 c.c.	"	0.1404	126.1
	"	0.1548	126.6

Strength of $\text{NH}_2\cdot\text{OH}, \text{HCl}$ solution.	Number of c.c. used.	Number of c.c. of KMnO_4 solution used.	Strength of KMnO_4 solution in grams per c.c.	Number of grams of KMnO_4 per gram-molecule of $\text{NH}_2\cdot\text{OH}, \text{HCl}$.
1.2057 grams in 250 c.c.	20 c.c.	27.1	0.00321	62.8
" " "	"	27.0	"	62.5
—	$\left\{ \begin{array}{l} 20 \text{ c.c.} \\ + 10 \text{ c.c.} \\ \text{H}_2\text{O} \end{array} \right\}$	27.2	"	63.0
0.7736 grams in 250 c.c.	25 c.c.	23.3	0.00300	62.8
—	"	23.25	"	62.7
—	"	23.45	"	63.2
0.9484 grams in 250 c.c.	"	28.8	0.00290	63.1
—	"	28.7	"	62.9

It is therefore clear that when a solution of a hydroxylamine salt containing not more than 0.5 per cent. of hydroxylamine is introduced into an excess of the boiling alkaline copper solution with stirring, the hydroxylamine is completely oxidised to nitrous oxide, and each molecule produces two molecules of cuprous oxide.

Some of the above determinations were made with Fehling's solution and some with copper potassium carbonate, the results being the same in both cases. The latter solution is much preferable on account of the small change which it undergoes on keeping, and because the cuprous oxide from Fehling's solution must be washed much more thoroughly, otherwise the tartrates interfere with the end-point in the permanganate titration, whereas the substances in the solution when copper potassium carbonate is used do not interfere with the final estimation.

The marked difference in the state of aggregation of the cuprous

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oxide precipitated from these two solutions by sugars does not arise when hydroxylamine is used.

The reaction is particularly free from the disturbing effects of impurities, which constitute its chief claim to superiority over other methods. Potassium and sodium salts have no effect. Solutions containing ammonium salts must be boiled sufficiently to expel all the ammonia, in order that no cuprous oxide may be held in solution by the ammonia.

Cobalt, nickel, and zinc salts have no effect when present to the extent of about 0.4 per cent., and although large quantities apparently have no direct influence on the reaction, yet owing to the formation of a precipitate, which greatly delays the filtration, some of the cuprous oxide is probably oxidised, and low results are accordingly obtained. Excess of carbon dioxide or small quantities of alcohol and acetic acid have no effect. Ketoximes have no effect, except on very prolonged boiling, when a very slight reduction is effected.

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