443

LXI.—On the Production of Hydroxylamine from Nitric Acid.

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DURING the last few months I have resumed an investigation of the conversion of free nitric acid into hydroxylamine, which I began in 1872, but the pursuit of which I had soon after to relinquish. So far as I can learn, this field of research has in the interim not been occupied, and I am therefore in a position, with the aid of recent work, to publish something of interest on this subject as yet unrecorded.

Lossen having discovered hydroxylamine in 1865 by reducing ethyl nitrate with tin and hydrochloric acid, Maumené followed by showing that for ethyl nitrate ammonium nitrate might be substituted (*Compt.* rend., 1870). Having confirmed for my own satisfaction the accuracy of Maumené's observations, I found that sodium nitrate could be equally well employed, and then, proceeding one step further, that nitric acid itself could be used with excellent results. My further work, then and since, forms the subject of this communication.*

Experiments with Tin.

Tin is I believe the only metal which has hitherto been known to produce hydroxylamine, and then only in conjunction with hydrochloric acid. This metal will, however, not only convert nitrates and nitric acid into hydroxylamine when used with hydrochloric acid, but will also form this base by acting alone upon pure dilute nitric acid. In attempting to verify this statement, it will be found very easy to fail. A 3 or 4 per cent. solution of nitric acid, free from other acids (or a false appearance of success will be almost certain), should be left on an abundance of granulated tin for about half an hour, after which

* In Watts's Dictionary, 1st Suppl., 1872, full mention is made that nitric acid yields hydroxylamine when treated with tin and hydrochloric acid, but no authority is given for the statement. Groves, in the account he gives of hydroxylaminæ in the last edition of Miller's Chemistry, 1878, makes no mention of the reduction of nitric acid itself. The same is true of Roscoe and Schorlemmer in their Treatise on Chemistry, 1878; Acworth and Armstrong in their elaborate paper "On the Reduction of Nitric Acid" (Part I), in this Journal for 1877, recognise the possibility of hydroxylamine being a source of the nitrous oxide produced by nitric acid acting on metals, but do not treat of its formation in this way as an ascertained fact.

So little indeed does this fact of the formation of hydroxylamine by the action of metals upon nitric acid appear to be known, that in all the discussions of the difficulties in estimating nitrates and nitrites as ammonia produced in acid solutions

VOL. XLIII.

hydroxylamine may generally be detected in the usual way.* Nitric acid, after standing a sufficient time upon tin, no longer yields hydroxylamine. Ammonia is one of the products in all cases, whether the nitric acid is dilute or the strongest that will act upon tin, and at any stage of the action.

Tin and Sulphuric Acid.-In examining the effect of sulphuric acid upon the reaction between nitric acid and tin, two comparative experiments were carried on together. In each experiment about 45 grams of granulated tin were placed in a flask filled with carbon dioxide gas, † and a solution poured in, measuring 250 c.c., and containing in one case 5 grams of nitric acid (hydrogen nitrate) alone, in the other case the same quantity of nitric acid together with 20 c.c. of sulphuric acid, about $4\frac{1}{2}$ mols., that is, to 1 mol. of nitric acid. The flasks were closed and set aside for two days in very hot weather, there being scarcely any evolution of gas. Much grey and dense stannoso-stannic hydroxide was deposited, about the same quantity in each, and the solutions became yellow. But the solutions differed in composition. That without sulphuric acid contained some stannous salt dissolved and a very little stannic salt, but no hydroxylamine. The sulphuric acid solution contained much hydroxylamine, much stannous salt, and so much stannic salt as to give a copious precipitate with water. These tin solutions proved very unstable, but would no doubt have been much less so in winter, when there would also have been formed much less stannic salt; but these points are here unimportant, except perhaps to those who may repeat the experiments. These parallel experiments demonstrate the great effect of sulphuric acid upon the yield, if not upon the production, of hydroxylamine.

Another experiment was made, in which the sulphuric acid and nitric acid were diluted scarcely more than sufficient to allow of their free action upon the tin; for without some dilution there is hardly any action. In this experiment 5 grams (1 mol.) of nitric acid and 35 grams ($4\frac{1}{2}$ mols.) of sulphuric acid, diluted to about 62 c.c. only of solution, were poured upon 35 grams of tin contained in a flask filled with carbon dioxide, and having its mouth loosely stopped. Action was at once apparent by the heating up of the mixture and the escape of nitrogen oxides, but it never grew violent, and the amount of gases evolved was not very great. Nitric oxide constituted the bulk of

⁻even as late as that contained in a paper in the Chem. News, 46, 63, by Kinnearno reference is made to it.

^{*} Namely, by treating the liquid with hydrogen sulphide and filtering off the tin sulphide, adding copper sulphate in the least possible excess and filtering off the copper sulphide, and lastly, adding potassium hydroxide in excess to precipitate cuprous oxide by means of the hydroxylamine.

⁺ To exclude air.

these gases, but at first red vapours were set free, and afterwards nitrous oxide. Effervescence soon ceased, and then the solution was clear and colourless. At first it had been milky white, but probably only from very fine effervescence. The tendency to heat up soon ceased to show itself, and altogether the action was strikingly moderate, considering that about 11 grams of tin (a little more than 1 atom) went into solution. The liquid poured off and diluted to 1 litre gave a copious cream-yellow precipitate of stannoso-stannic hydroxide, which rapidly bleached by oxidation on exposure to the air. The mother-liquor contained sulphuric acid and ammonia, but neither nitric acid, hydroxylamine, nor tin salt. The effect, therefore, of scarcity of water is to cause higher oxidation of the tin, and this apparently at the expense of the hydroxylamine, which changes to ammonia. Von Dumreicher (this Journal, Abstr., 1882) has pointed out the readiness with which stannous salts and hydroxylamine react: $NH_3O + SnO = NH_3 + SnO_2$.

Tin and hydrochloric acid, as stated in Watts's Dictionary, 1st Suppl., convert nitric acid into hydroxylamine. Hydrochloric acid exerts a still more striking influence upon the production of hydroxylamine by tin than sulphuric acid. While with nitric acid alone only traces of hydroxylamine can be obtained at all, and even these only by watchful precautions, this substance is obtained in abundance in presence of hydrochloric acid under almost any circumstances. Although I have made many experiments upon the production of hydroxylamine in this way, there are only two which need be recorded here. One of these illustrates a reaction which appeared to me, when I first observed it years ago, as little less than marvellous. This is the reaction of concentrated nitrie and hydrochloric acids (aqua regia) with granulated tin. Taking about 8 mols. of hydrochloric acid in fuming solution to 1 mol. of nitric acid sp. gr. 142, and pouring the mixture upon tin, very little gas if any is evolved, nearly all the nitric acid is converted into hydroxylamine, the tin is dissolved as stannous chloride, and the action, though energetic, is quite under control and very soon com-If the acids are mixed some time before use, and in hot pleted. weather, the evolution of chlorous gases renders the storage of the mixture in bottles almost unmanageable. It is better, therefore, to mix the acids just before using them, although tin will at once bleach the orange mixture on coming in contact with it, and but little hydroxylamine will be destroyed. An experiment illustrative of this action I shall now describe. Fuming hydrochloric acid, 58 c.c., and nitric acid, 1.42 sp. gr., 5 c.c., that is, about 9 mols. of hydrochloric acid to 1 of nitric acid, were mixed, and quickly poured upon 35 grams of granulated tin lying in a flask filled with carbon dioxide. The flask, loosely corked, was plunged into a pail of water and agitated.

2к2

At first boiling occurred, but the vapours evolved appeared to be only hydrochloric acid and water. This soon ceased, and soon after, the development of heat also. The solution was poured off, and the tin found to have diminished in weight 21 grams, or about $2\frac{1}{4}$ atoms. Of the solution, diluted with the washings of the tin to 500 c.c., 25 c.c. were measured off, further diluted, deprived of tin by hydrogen sulphide, and of the latter by carbon dioxide gas, and then treated with decinormal solution of iodine, with addition of sodium carbonate to keep the solution alkaline. The 25 c.c. required 69 c.c. of iodine solution, and therefore, reckoning 2 atoms of iodine as indicating 1 mol. of hydroxylamine, the quantity of nitric acid converted into this substance was $4\frac{1}{3}$ grams out of 5, and the quantity of hydroxylamine itself $2\frac{1}{4}$ grams. It thus appears that, carried out in this way, the reduction of nitric acid by tin and hydrochloric acid is well suited for preparing hydroxylamine.*

The other experiment I record is one differing from the last in the acids being diluted to 250 c.c., and left on the tin for two days. No gas was given off, and about 21 grams $(2\frac{1}{4} \text{ atoms})$ of tin were dissolved. In this case a little more than half the nitric acid was found as hydroxylamine.

Von Dumreicher has shown (*loc. cit.*) that stannous chloride in acid solution reduces nitric acid to hydroxylamine, and this again to ammonia. He states, however, that the conversion of the hydroxylamine into ammonia proceeds nearly at the same rate as its formation, and that consequently the reaction of nitric acid and stannous chloride is not available for the preparation of hydroxylamine. So that from his observations it follows that the formation I have here described of this base is the result of the primary reaction of the tin and acids, and is independent of the operation of stannous chloride, and that on the other hand the formation of ammonia is largely owing to the action of this salt. It is probable, too, that the smaller yield of hydroxylamine when sulphuric acid is used instead of hydrochloric acid, is to be attributed to a greater deoxidising action by stannous sulphate than by stannous chloride.

* The precipitation of the tin as sulphide, and the evaporation of so much acid are very troublesome operations, and the latter is destructive. Victor Meyer has lately (*Ber.*, 1882, 2) brought to notice again the use of sodium carbonate to precipitate the tin and neutralise the acid, a process described ten years ago in *Watts's Dictionary*, 1st Suppl. (p. 723). Another method which probably works well is that recommended by Bertoni (this Journal, Abstr., 1880) of removing tin and hydrochloric acid by litharge. I may shortly be able to offer to the Society an account of the actual preparation of hydroxylamine from nitric acid by tin.

HYDROXYLAMINE FROM NITRIC ACID.

Experiments with Zinc.

Zinc is very effective in converting nitric acid into hydroxylamine. Ammonia is always produced at the same time. In the presence of another acid hydroxylamine is easily obtained, but traces of it can also be obtained from nitric acid alone. If nitric acid of the dilution recommended for the similar experiment with tin is poured upon granulated zine and very shortly poured off again, hydroxylamine may generally be detected by Lossen's copper test. To guard against deceptive appearance of success, care must be taken, as with tin, to use nitric acid free from either hydrochloric acid or sulphuric acid. Failure in this experiment is not unfrequent, but the trouble of repeating the experiment is much less than in the case of tin, inasmuch as the dissolved zinc, unlike the tin, need not be removed before applying Lossen's test.

Zinc and Sulphuric Acid on Hydrochloric Acid.—The production of hydroxylamine from nitric acid by the action of zinc and sulphuric acid takes place so readily, and the presence of hydroxylamine is in this case so easy to demonstrate, that it furnishes a good experiment for the lecture-room, which may be thus performed :—Pour some dilute sulphuric acid on zinc and then a little nitric acid, when the effervescence will lessen to a marked extent; in half a minute pour off the acid solution and add potassium hydroxide in large excess to dissolve zinc hydroxide, and then a very little copper sulphate solution, when a copious yellow precipitate will be obtained on stirring.

I have made a number of quantitative experiments to determine the extent of the formation and destruction of hydroxylamine by nitric acid, and either sulphuric or hydrochloric acid acting upon zinc. These are not complete as a series, but serve to demonstrate several points. The hydroxylamine was estimated by decinormal iodine solution according to the reaction $2NH_3O + 2I_2 = N_2O + H_2O + 4HI$ (Meveringh). The hydroxylamine solution measured off was mixed with sodium carbonate solution until there remained suspended in it some zinc carbonate, a salt which has no action on iodine. Starch did not work well with the carbonate precipitate, and was therefore not But this caused no inconvenience, as the bleaching of the used. iodine solution was very evident in presence of the white precipitate. The zinc carbonate, however, neutralises the last portions of hydriodic acid but slowly, so that for an hour after the rough finish of the titration, small additions of iodine are required. Practice simplifies matters by teaching what excess of iodine may be added at first, while the end-reaction when reached is sharply enough defined. $\mathbf{B}\mathbf{y}$ keeping sodium carbonate slightly in excess (it becomes of course acid carbonate), the end-reaction can be reached at once; but there is

a risk of adding too much, and with a number of titrations on hand, the other method was deemed safer. The results are best expressed, I think, in terms of the nitric acid converted into hydroxylamine out of 100 parts taken. As nitric acid wholly converted to hydroxylamine would yield 52:38 per cent. of its weight, or roughly stated half its weight, half the percentages of nitric acid will express those of hydroxylamine.

A table of the results of these experiments is here inserted, which needs a little explanation, and the addition of some remarks to make it clear, and to enable me to simplify the statement of my conclusions

Percentage Amounts of Nitric Acid left as Hydroxylamine by the Action of Zinc and another Acid.

	Equivalents of hydrochloric to one nitric acid.							
	3.	5.	7.	9.	11.			
2 minutes	16 .0	19 .3	23.2	23 · 2	16.4			
5 "	13 8	17.1	lost	12.6	5.7			
0 ,,	$13 \cdot 1$	14.6	15.1	8.7	3.2			
3 hours	11.2	11.4	10.5	3.7	1.1			

1. HYDROCHLORIC ACID, WITHOUT COOLING.

2. HYDROCHLORIC ACID, WITH COOLING.

	Equivalents of hydrochloric to one nitric acid.						
	3.	5.	7.	9.	(9).	11.	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{r} 12 \cdot 7 \\ 18 \cdot 1 \\ 17 \cdot 3 \\ 16 \cdot 2 \end{array} $	$ \begin{array}{c} 16.0 \\ 20.7 \\ 18.0 \\ 15.6 \end{array} $	$22 \cdot 1$ 26 \cdot 3 22 \cdot 8 18 \cdot 9	$21 \cdot 0$ $23 \cdot 8$ $16 \cdot 8$ $13 \cdot 1$	$\begin{array}{c}(27 \cdot 9)\\(32 \cdot 5)\\(27 \cdot 9)\\(17 \cdot 4)\end{array}$	$24.4 \\ 23.5 \\ 19.1 \\ 9.8$	

3. SULPHURIC ACID, WITH COOLING.

	Equivalents of sulphuric to one nitric acid.						
	3.	5.	7.	9.	(9).	11.	
2 minutes 5 ,, 10 ,, 1 ¹ / ₂ hours	$8 \cdot 4$ 18 · 3 20 · 8 21 · 7	17 ·4 29 ·6 32 ·9 32 ·0	$18.2 \\ 31.2 \\ 39.7 \\ 34.0$	$20.0 \\ 31.9 \\ 35.3 \\ 22.6$	$(13 \cdot 7) \\ (29 \cdot 0) \\ (35 \cdot 1) \\ (21 \cdot 3)$	$25 \cdot 1 39 \cdot 1 47 \cdot 0 25 \cdot 0$	

respecting the course of the reduction of nitric acid to hydroxylamine by zinc in presence of another acid, these conclusions being drawn from the results in this table and others allied to them.

Three series of experiments are tabulated, each of which was completed in one day, excepting the duplicate experiments, the results of which are placed in brackets. The quantity of liquid was in every case a quarter-litre, consisting of water holding five grams of hydrogen nitrate and 3, 5, 7, 9, or 11 equivalents of these five grams, of hydrochloric or sulphuric acid, as shown in the table. It will be seen that the acidity of the liquids varied greatly, being in the experiments recorded in the last column, three times that of the solutions used in the experiments of the first column. In the first series of experiments 70 grams of granulated zinc were taken in each case, but in the other series only 35 grams, in order to make the reduction slower. The experiments were made in hot summer weather; the first series without cooling, the others with cooling by shaking the flasks in wellwater during the reaction. The very large surface of zinc exposed, and the want of cooling in the first series of experiments, led to the more acid liquids becoming boiling hot and continuing so for a few minutes. Effervescence occurred in all cases, but from being very mild and creamy where only three equivalents of the other acid were present, became violent and coarse-bubbled when nine and eleven equivalents of the acid were used. The effervescence ceased soonest where least acid was used; in the first series the time it stopped was about $2\frac{1}{2}$ minutes with 3 equivalents of acid, to 9 minutes with 11 equivalents; in the second series from $6\frac{1}{2}$ minutes with 3 to $9\frac{1}{2}$ with 11 equivalents; and in the third series from $8\frac{1}{3}$ minutes with 3 to 17 minutes with 11 equivalents, counting from the beginning of the In the first series cooling not being practised, the experiments. liquid grew turbid during the course of the experiment, much zinc hydroxide being deposited. This did not happen when only three equivalents of hydrochloric acid had been used until 15 minutes, long after effervescence had ceased. But, approaching regularly through the intermediate cases, the times of appearance of turbidity and of cessation of effervescence became identical in the last one where 11 equivalents of acid had been added, namely, at nine minutes from the commencement. Another noteworthy circumstance was, that though all the solutions were clear at the end of five minutes, portions of them then removed slowly became turbid on standing, and deposited a marked quantity of zinc hydroxide; that in the three-equivalent experiment most slowly; and that in the eleven-equivalent experiment most quickly, and in a very short time. In the second and third series of experiments-that is, those in which artificial cooling was appliedzinc hydroxide was not deposited even after considerable time.

The extent to which the nitric acid was decomposed requires to be noticed, as this was full in some only of the experiments. Where only three equivalents of sulphuric or hydrochloric acid were used, considerable quantities of nitrate remained after the acids had become neutralised by the zinc. With the use of more and more of the second acid, the quantity of nitrate left was found to be very markedly less and less, a trace only with nine equivalents of the second acid, and none at all with eleven in the case of cooling. After conversion to zinc salt, the nitrate is slowly reduced by the excess of zinc to nitrite, so that while after but five minutes' action nitrite is only to be found with doubt, it is abundant after one or two hours.*

Nitrite and hydroxylamine salt are thus found together in solution, although in acid solutions they at once destroy each other (V. Meyer). Where nitrate had almost or entirely disappeared by the action, no nitrite was detected. Ammonia was always found, whether the solutions were examined shortly after they had been in contact with zinc or at any later stage. Most ammonia was present where all the nitric acid had been reduced, and where the hydroxylamine from it had been most destroyed.

In testing for ammonia with potassium hydroxide, the precaution was taken of first destroying hydroxylamine with iodine. There was generally, however, no difficulty in directly detecting the ammonia with platinum chloride. The nitrite was detected by the ferrous sulphate reaction. In a number of cases its quantity was imperfectly estimated by the iodine method in the following way:—After determining the hydroxylamine by iodine, the liquid was acidulated, and this iodine again liberated by reaction between hydrogen iodide and hydrogen nitrite; then as quickly as possible this iodine was titrated with sulphurous acid. The quantities of nitrite being small and of hydrogen iodide large, the atmospheric action upon the latter was too rapid to leave the results very accurate.

Having now described summarily the experiments of which the principal results have been arranged in the table, I proceed to state some deductions from these and other experiments as to the influence of some of the circumstances upon the results.

First, as to the Relative Effect of the Two Acids.—The action of hydrochloric acid upon zinc is much more rapid than that of sulphuric acid. Hence hydrochloric acid becomes more rapidly neutralised, and out of the field of activity, as regards nitric acid and hydroxylamine, while its solution grows hotter, and therefore must make other changes go on more rapidly. Either indirectly from the greater activity of this acid upon zinc, or directly by some action upon nitric acid

* This change is in accordance with the known reducing action of zinc and other metals upon their nitrates in solution.

and hydroxylamine, greater than that of sulphuric acid, the increase in quantity of the hydroxylamine and the decrease which follows, occur more rapidly with hydrochloric acid. It is also difficult, if not impossible, with strong solutions at least, to get a yield of hydroxylamine with this acid as good as that with sulphuric acid.

Secondly, as to the Effect of the Proportion of the other Acid to the Nitric Acid.-The greater this is, the greater is the proportion of the nitric acid which can be found converted to hydroxylamine. The experiments I have tabulated, in which sulphuric acid was used, are in agreement with this proposition, but those in which the acid was hydrochloric show rather a maximum of hydroxylamine from the same weight of nitric acid, when but seven to nine equivalents of hydrochloric acid were present. I have, however, the results of other experiments relating to this point, which are more positive, while those here given were certainly affected by another circumstance leading to the destruction of the hydroxylamine. The evidence afforded of this being the case, by the duplicate experiments with nine equivalents of hydrochloric acid, is alone almost sufficient on this point, for we see from these that there may be a much greater difference between two similar experiments, both with nine equivalents of acid, than between two in which nine and eleven are used. Now, these experiments were all performed, to the best of my ability and knowledge, in the same way in everything. The one circumstance liable to vary, and easily escaping regular control, was the rise in temperature, in consequence of its highly cumulative rate. Hydrochloric acid solutions, so strong as were those used in the nine and eleven equivalent experiments, are thus too active for their purpose, and are so destructive to hydroxylamine in contact with zinc as to mask the effect of varying degree of acidity. It will be seen that, owing to this, the descent in equal times from the maximum quantity of hydroxylamine is much more marked with the use of the larger than with the smaller quantities of acids.

The other experiments to which I have referred in this connection were so carried out for me, that on equal weights of granulated zinc were poured equal volumes of acid mixtures having equal degrees of total acidity. The solutions were poured off the zinc when the fulness of the effervescence was over, and then titrated for hydroxylamine. The series was carried as far as 35 equivalents of hydrochloric acid, and still more of sulphuric, to one of nitric acid; and the proportion of nitric acid found converted to hydroxylamine became greater and greater with the increase in the proportion of the second acid, until so much as 80 per cent. of the nitric acid was thus obtained. The acid liquors were in these experiments very weak, and also, as already mentioned, of the same acidity; rise in temperature, therefore, and its variations, did not appreciably affect the results. But this series of experiments is open, I fear, to the objection that where such large quantities of the second acid were used, the nitric acid was too little to render the estimation of the hydroxylamine quite reliable.

Thirdly, as to the Effect of the Proportion of Water Present .-Strong sulphuric acid mixed with a little nitric acid has no sensible action upon zinc. Slightly diluted acid is active in proportion to the water present, but as heat is generated, cooling is required to keep the action steady. When the concentration is such that 1 gram of sulphuric acid is contained, along with nitric acid, in not more than $2\frac{3}{5}$ c.c. of solution, the zinc is freely attacked without escape of hydrogen, but if the dilution is greater, hydrogen escapes. At first a very moderate effervescence goes on, the escaping gas being principally nitrous oxide, if the nitric acid is present in a proportion of not more than 1 mol. to 34 of sulphuric acid (1 gram to 5.44 grams). Bv working in this way upon 5 grams of nitric acid with sulphuric acid in the proportion of $3\frac{1}{2}$ mols. to 1, keeping the mixture cool while actively agitating for about 40 minutes, nearly the calculated number of grams $(15\frac{1}{2})$ of zinc dissolved and yielded much hydroxylamine. The time in which a given weight of zinc dissolved, necessarily varied with the amount of surface exposed and other circumstances, but the weight dissolved corresponded approximately (in my very few experiments) to the nitric acid decomposed, and to the hydroxylamine obtained. The quantity of nitric acid thus obtained as hydroxylamine was about 0.36 of the whole. In another experiment, where the sulphuric acid was somewhat more concentrated, and in the proportion of $4\frac{1}{2}$ mols. to 1 of nitric acid, water was gradually added in small quantity until effervescence of hydrogen became evident, and the amount of hydroxylamine found was almost the same. But in another experiment again, where also $4\frac{1}{2}$ mols. of sulphuric acid were used, and where the dilution was from the first the same as that existing only in the latter part of the preceding experiment, the hydroxylamine was only half as much, although 151 grams of zinc had here also dissolved. Hydrogen and nitrous oxide escaped all through the reaction in this case.

When the quantity of water in the case of the use of hydrochloric acid is so small that *aqua regia* is abundantly formed, the action of the two acids upon zinc is very violent, and the temperature cannot be kept down. A little hydroxylamine remains at the end of the reaction, but that probably is what has formed in the last period of it. With greater dilution, abundance of hydroxylamine is obtained by the use of either sulphuric or hydrochloric acid, and I conclude from the results of much, but irregular experimentation, that, beyond the least quantity sufficient for chemical action to proceed freely, additional

water acts only indirectly-moderating the rise in temperature and lowering the rate of progress of the reactions, and so rendering it easier to control them, and at the time of the best yield of hydroxylamine to separate the solution from the undissolved zinc. But further testing of this conclusion is needed to confirm it.

Fourth, as to the Effect of Rise of Temperature.—Rise in temperature quickens, as was to be expected, both the formation and destruction of hydroxylamine by zinc. This is very apparent on comparing the first and second series of experiments. Its destruction seems to be accelerated in this way, much more than its formation, but this is a matter also requiring further experiments. Rise in temperature causes the formation of basic solutions, which deposit zinc hydroxide, as may be learned from my description of the tabulated results of experiments. A close connection almost certainly exists between this effect and the destruction of the hydroxylamine, as will be explained when considering the nature of the process of conversion of the hydroxylamine into ammonia.

Experiments with other Metals.

Magnesium.—From its relations to zinc, magnesium ought to form hydroxylamine from nitric acid, and on trial it has been found to do so. But the hydroxylamine is formed and decomposed again very rapidly, and is therefore very apt to escape detection. To obtain it, dilute hydrochloric acid appears to be necessary, sulphuric acid having always proved useless.

Cadmium, in the granulated state, produces small quantities of hydroxylamine from nitric acid in presence of either hydrochloric or sulphuric acid.

Lead.—It remains doubtful whether this metal can give hydroxylamine with nitric acid. Out of very many trials, in only one was a small quantity of hydroxylamine detected. Hydrochloric acid was used in all the trials, and ammonia was always formed. Lead dissolving in nitric acid alone also gives ammonia.

Aluminium.—A mixture of sulphuric and nitric acids is known to be without sensible action upon aluminium. A mixture of dilute hydrochloric and nitric acids may remain for some time on aluminium without hydroxylamine becoming present, but when the effervescence has nearly ceased, and if the whole has been immersed in cold water to keep off the violent accession of action which is apt otherwise to set in, decided though small quantities of hydroxylamine are usually to be found.

Iron always fails to yield hydroxylamine, though it produces much ammonia.*

* In the last Dublin Pharmacopæia there was a formula for the preparation of

Sodium, in form of amalgam, and not in such quantity as to neutralise the acid, has failed to give any hydroxylamine, but gives abundance of ammonia. By its action upon sodium nitrate or nitrite, it produces hyponitrite and hydroxylamine also.

Copper, mercury, silver, and bismuth all fail to produce either hydroxylamine or ammonia from nitric acid.

Other Experiments.

Stannous chloride reduces nitric acid to hydroxylamine and ammonia, as pointed out by von Dumreicher (loc. cit.). Stannous chloride solution dissolves nitric oxide, and it is probably the decomposition by hydrochloric acid of the compound thus formed, and not the union of *nascent* hydrogen with nitric oxide, as commonly represented, that gives hydroxylamine, when tin, hydrochloric acid, and nitric oxide are digested together. Copper nitrate, in the presence of copper and nitric acid-the equivalent that is of cuprous nitrateexercises the reducing action from which nitrous oxide results when copper is treated with nitric acid. (Acworth and Armstrong.) Attempts to convert nitric oxide to hydroxylamine by dissolving it in ferrous sulphate and pouring the solution, mixed with sulphuric acid upon zinc, failed, as might have been anticipated, by the greater activity of ferrous salts than stannous salts in reducing hydroxyl-Ferrous hydroxide reduces nitrates to ammonia, nitrous amine. oxide, nitrogen, and, according to Zorm (Ber., 1882, 1), hyponitrite.

Reduction of Nitrous Acid to Hydroxylamine.—Hydroxylamine is produced by reducing nitrites with sodium or potassium. It is difficult to obtain satisfactory evidence as to whether nitrous acid yields hydroxylamine or not, but there can be little hesitation in believing that it does. Sodium nitrite solution was prepared from some pure silver nitrite, and tried both with tin and hydrochloric acid and

solution of ferric nitrate, in which the quantity of nitric acid ordered was insufficient for the terms of the chemical equation: $2Fe + 8HNO_3 = Fe_2(NO_3)_6 + 2NO + 4H_2O$. When this pharmaceutic formula was transferred to the first edition of the *British Pharmacopæia* (1864), it received some severe criticism, as being a process that could not yield a normal nitrate, and that gave, as was accordingly to be expected, a basic unstable solution. In the new edition of the *Pharmacopæia* (1867) the formula was so altered as to raise the proportion of nitric acid to the quantity required by the above theory. Now, as a matter of fact, the old formula gave a beautifully bright-coloured solution, and quite stable, which is saying much for nitrate of iron solution, while the present one gives an acid preparation, the explanation being that though the gas given off is indeed nearly pure nitric oxide, much of the nitric acid becomes ammonium nitrate during the dissolution of the iron, and this is a product more deoxidised than nitric oxide. Less nitric acid therefore is required than is indicated by the above equation.

HYDROXYLAMINE FROM NITRIC ACID.

with zinc and hydrochloric acid. Sometimes success was attained with zinc, the successful way being to drench some granulated zinc with weak sodium nitrite solution, and then pour on dilute hydrochloric acid. It will be seen that such experiments are open to the objection that the nitrous acid, on being set free in any quantity, will decompose into nitric acid, nitric oxide, and water, and that then the nitric acid, or even the nitric oxide, may furnish the hydroxylamine. In the successful experiments no nitrous smell or colour was however observed. According to von Dumreicher, sodium nitrite gives pure nitrous oxide with acid stannous chloride.

On the Nature of the Reduction of Nitric Acid.

In their relation to nitric acid metals must be divided into two classes, exclusive of the inactive metals, one formed of those which produce ammonia from it, and the other of those which do not. To the former belong tin, lead, zinc, cadmium, magnesium, iron, aluminium, potassium, sodium, and others; while the latter includes copper, mercury, silver, bismuth, and others. Metals of the latter class leave all the hydrogen of the nitric acid combined with oxygen as water.

With this fact before us, there seems to be but one way of interpreting the action of the silver-class of metals upon nitric acid, and that is to recognise that these metals combine with the nitrogen of the acid, and do not decompose its hydroxyl. This combination with nitrogen rather than oxygen is already known to take place in other cases, even in presence of water, as when ammonia and the oxides of these metals are brought in contact. In accordance with current notions of molecular interchange, this action of these metals on nitric acid is represented by the following equations:—

$$2Ag + HONO_2 = HOAg + AgNO_2,$$

 $HOAg + HONO_2 = AgONO_2 + H_2O,$
and $AgNO_2 + HONO_2 = AgONO_2 + HNO_2,$

of which only the first needs consideration here. The interest of this equation lies in its representing the nitrogen as undergoing no change in quantivalence, and the metal as combining directly with the nitrogen, and thus making out silver nitrite and nitrites to be *nitronates*. The conversion of other nitrites to the silver salt by double decomposition is greatly in favour of viewing them as having all the nitronate constitution. The nitronate structure seems also to furnish a definite reason for the loss of oxygen by potassium nitrate when heated, in the metallic radical parting from oxygen to unite directly with the nitrogen, thus:—

$$2\mathrm{KONO}_2 = 2\mathrm{KNO}_2 + \mathrm{O}_2.*$$

On the other hand it is hardly to be doubted that the nitrous ethers are true nitrites, the nitro-paraffins being nitronates.

As regards the formation of a basic substance, silver hydroxide, as represented in the equation, it will be seen that this is in agreement with the known action of metals of the other class upon metallic nitrates, for example—

> $2Na + NaONO_2 = NaONa + NaNO_2$ Zn + Zn(ONO_2)₂ = ZnO₂Zn + Zn(NO₂)₂ and 2Pb + 2NaONO₂ = (NaO)₂Pb + Pb(NO₂)₂.

Having treated of the action of the silver class of metals upon nitric acid as including the union of the metal directly with the nitrogen, in accordance with what appears to be the requirement of the facts, I may now notice the difficulties in accepting the view that the metal unites directly only with oxygen. Recognising that the metal does not replace hydrogen, the symbolic expressions become—

$$2Ag + HONO_2 = HONO + Ag_2O$$

and $Ag_2O + 2HONO_2 = 2AgONO_2 + H_2O$.

* Is there not in the nitronic constitution of nitrous acid a likely explanation of the advantage of *red nitric acid* in dissolving metals of the silver class, that one atom of the metal displacing the hydrogen of the nitronic acid, another can at the same moment more readily displace the hydroxyl of the nitric acid when assisted by the hydrogen from the nitronic acid?—

$$2Ag + HNO_2 + HONO_2 = 2AgNO_2 + H_2O.$$

Have we not also in this constitution an easy conception of the nature of the formation of nitrogen tetroxide from nitrie acid and nitronie acid-

$$HNO_2 + HONO_2 = H_2O + (NO_2)_2,$$

and of the reverse action of nitrogen tetroxide on potassium hydroxide to form nitrite and nitrate?

Note by Dr. Armstrong.—The action of red nitric acid is sufficiently explained by the presence in it of nitrous acid, or it may be of a compound of nitrous and nitric acids. Russell's experiments leave practically no doubt that nitric acid is without action on silver. In like manner, platinum is not attacked by nitric acid, but will dissolve if alloyed with silver; no doubt, because nitrous acid is produced by the dissolution of the silver. Why nitrous acid is a solvent of silver and platinum, while nitric acid is not, we do not exactly know, although probably in the case of the latter metal, the formation of a *platonitrite* plays an important part.

With reference to the formation of N_2O_4 during the dissolution of metals, &c., in nitric acid, I some time ago satisfied myself by experiment that it is produced by the reaction here formulated by Dr. Divers, and there is, I believe, no doubt that whatever the nature of the reducing agent—be it hydrogen or metal, or arsenious acid, for example—the primary product of the reduction of nitric acid is nitrous acid. But these require the hypothesis, in opposition to facts, that silver is a very feeble basylous radical with a considerable affinity for oxygen, and this must therefore cause their rejection. Next, disregarding the evidence that the metal cannot substitute itself for the hydrogen of hydroxyl, the equations necessary to express the reaction will be found to be—

$$2Ag + 2HONO_2 = 2AgONO_2 + H_2$$
(1)

and
$$H_2 + HONO_2 = HOH + HNO_2$$
 (2)

or, instead of (2),
$$H_2 + AgONO_2 = AgONO + H_2O$$
 (3)
and $AgONO + HONO_2 = AgONO_2 + HONO$ (4)

in which hydrogen is assumed to be for a time at liberty. Hypotheses are further, therefore, here required to account for the non-appearance of any of the hydrogen, and for the non-production of ammonia. Then comes a difficulty in understanding why, as represented in (2), the hydrogen liberated, which must be chemically feebler than the silver which has displaced it, can separate and combine with the hydroxyl and nitroxyl of nitric acid, while the stronger silver fails to do so, as is contended upon this hypothesis. If instead of (2) the equations (3) and (4) are to be accepted, the deoxidation of silver nitrate must, against facts, be admitted to be easier than that of hydrogen nitrate, and the separation of oxygen and hydrogen to be easier than that of oxygen and silver. The deoxidation of silver nitrate by metallic silver would not be so difficult to admit as possible, but then the hydrogen of (1) would remain unaccounted for, and further we know (Divers, this Journal, 1871), on the contrary, that heated silver nitrite may become metallic silver and silver nitrate. Thus, from no point of view is the union of the metal with the oxygen probable, and therefore its union with the nitrogen of nitric acid becomes the more certain.

The reduction of the nitric acid by the silver class of metals seems not to pass beyond the formation of nitrites. The production of nitric oxide is accounted for by the well-known reaction between nitrous acid and water. The nitrous oxide produced when copper is dissolved in nitric acid alone is due, as already mentioned, to a reducing action of cuprous nitrate (copper and cupric nitrate) upon nitrous acid, as the investigations of Acworth and Armstrong have proved. Perhaps, too, the little nitrogen got in the same reaction is due to a similar reduction of the nitric oxide.

The metals of the tin-zine class, characterised by forming ammonia with nitric acid, and hydrogen with hydrochloric acid, have certainly the power to displace the hydrogen of hydroxyl of such an acid as sulphuric acid, and thus may directly form nitrates by displacing the hydrogen of nitric acid. They differ from the silver class in possess-

ing this power, and consequently, in not forming nitrites from nitric acid directly. On the other hand they have the power, which metals of the silver class seem not to have, of forming nitrites from their own nitrates. When no other acid is present, there will be during the action both nitric acid and nitrate of the metal in the solution, and each undergoing its proper changes, one into hydrogen and metallic nitrate, the other into metallic oxide and nitrite. If a strong acid, such as hydrochloric or sulphuric acid, is present, this, by decomposing the nitrate, will prevent for the most part the secondary reaction by which nitrite is formed. But even in the absence of another acid only traces of nitrite are to be found in the acid solution instead of its abundance when silver or mercury is used, a result owing no doubt to a secondary reaction between hydroxylamine and nitrous acid, by which it is converted into nitrous oxide and water.

Respecting the separation of hydrogen from nitric acid by zinc and allied metals, it is known that with most metals this acid fails to give any free hydrogen. Acworth and Armstrong (loc. cit.) got it indeed by acting upon nickel, but convinced themselves that it was occluded hydrogen, and not derived from the nitric acid. In their case, no doubt they were right, judging from the evidence they adduce, although Gladstone and Tribe have since shown (this Journal, 1879), that occluded hydrogen may be completely oxidised by nitric acid. On the other hand the latter chemists have obtained a little hydrogen by throwing magnesium into nitric acid; but before admitting that this one metal may liberate hydrogen and others not, the possibility of this hydrogen coming from a reaction between water and magnesium, heated as these are by the nitric acid reaction, and coming just as hydrogen does from a mixture of sulphuric acid and nitric acid acting upon the zinc metals, should not be lost sight of until further experiments have been made. Although there is thus good reason to doubt whether nitric acid ever yields hydrogen actually free, the evidence afforded by the production of hydroxylamine and ammonia is nearly conclusive that the zinc metals do detach the hydrogen of nitric acid from its oxygen. The production of hydroxylamine could indeed, like the production of nitrites by the silver metals, take place without liberation of any hydrogen, by the metal uniting with both oxygen and nitrogen, and the resulting compound reacting with water to form hydroxylamine, thus :---

$Zn(NO_2)_2 + 4Zn = Zn_2N_2O_2Zn + 2ZnO$ and $Zn_2N_2(O_2Zn) + 6H_2O = 2H_2N(OH) + 3Zn(OH)_2$.

Such an action indeed may really take place when the metal is potassium or sodium, since these metals do form hydroxylamine and ammonia from their nitrates. But zinc, tin, and other members of the class, though they form these products abundantly from nitric acid, either do not form them from their own nitrates at all or only to a slight extent, a fact inconsistent with the supposition of their direct action. It must therefore be admitted as probable that hydroxylamine is produced by the direct action of hydrogen, and not by the action of the metal.

In obtaining hydroxylamine from nitric acid the presence of a second acid has so very great an effect, that before proceeding further with the examination into the nature of the reduction with nitric acid, the nature of the reduction of the second acid had better be considered. One of its actions is to set the nitric acid free again as fast as it becomes metallic nitrate. Acting in this way it keeps the nitric acid under the influence of the metal until it is all destroyed, and at the same time prevents the formation of products of the reaction between the metal and its nitrate to a large extent, if not entirely. In thus decomposing the metallic nitrate, it also furnishes the additional hydrogen necessary for the production of hydroxylamine, that of the original nitric acid being only sufficient to convert one part out of seven into hydroxylamine—

$7 \text{HNO}_3 + 3 \text{Zn} = \text{H}_3 \text{NO} + 2 \text{H}_2 \text{O} + 3 \text{Zn} (\text{NO}_3)_2$

and the change of the metal nitrate to hydrogen nitrate by the second acid, again allowing one-seventh of this to become hydroxylamine also, and so on to the end. It is generally assumed that the reducing effect of an acid and metal is due to their supplying hydrogen in the nascent state; but the account just given of what it would seem must happen in the case of nitric acid, is sufficient to show this assumption to be unnecessary. Deville indeed employed this very action of a mixture of sulphuric, or hydrochloric, and nitric acids upon zinc to disprove the hypothesis of the nascent state.* He gave an extensive table of the quantities of oxides of nitrogen, ammonia, and hydrogen yielded by different proportions of the acids acting upon zinc, and deduced from them that each acid pursued its action upon the zinc unaffected, except indirectly, by the presence of the other. Whatever hydrogen was liberated from the sulphuric acid escaped; and if no hydrogen escaped, or very little, this was due to the excess of nitric acid forming an envelope of zinc nitrate solution round the zinc, which neutralised the approaching sulphuric acid, and thus protected the zinc from its action. The formation of ammonia did not suggest to him any necessity for a supply of outside hydrogen to the nitric acid, because the ammonia was accompanied by that of oxides of

VOL. XLIII.

2 г

^{*} I can at present speak of the contents of his papers (*Compt. rend.*, **70**, pp. 20 and 550) only from memory, as I have not seen them since the year in which they appeared, and have only preserved a reference to them in my note-book.

nitrogen, and therefore the hydrogen of the nitric acid might of itself be sufficient. His papers are imperfect, I consider, in their purpose of disproving the hypothesis of *nascency*, from the apparently insufficient explanation of the non-appearance of hydrogen when the nitric acid was in excess; for until enough zinc had dissolved to neutralise the sulphuric acid present, hydrogen ought, on his explanation, to have been found among the gases. However that may be, there is, as I have explained, no need to resort to the hypothesis of nascent hydrogen to account for the transfer of the hydrogen of the second acid to the nitric acid in its transformation into hydroxylamine and ammonia.

In connection with this point I may refer to the experiment, recorded in the previous part of this paper, with zinc and sulphuric acid in very little water. In this experiment no hydrogen escaped, and yet much hydroxylamine and ammonia were formed from the nitric acid, from which it would seem that nascent hydrogen from sulphuric acid has nothing to do with the formation of hydroxylamine, since sulphuric acid of such a degree of concentration must be nearly inactive upon zinc. The experiments, the results of which I have tabulated, also serve, like Deville's, to show the improbability of nascent hydrogen from the sulphuric or hydrochloric acid being concerned in the formation of the hydroxylamine. For if this were the case, at least seven equivalents of one of these acids to one of nitric should have all its hydrogen taken up by the nitric acid,

3Zn + 7HCl + HNO₃ = H₃NOHCl + 3ZnCl₂ + 2H₂O,

and this is far from being so, hydrogen escaping. No escape of the hydrogen should be possible, considering the thorough commixture of the two acids as they come in contact with the zinc.

Another way in which the second acid acts is in preserving the hydroxylamine from destruction immediately upon its production. Thus, in keeping the solution free from metallic nitrate, it cuts off the source of nitrous acid, as already pointed out, and to that extent protects the hydroxylamine, so that while with the second acid present we get hydroxylamine, without it we get nitrous oxide, this oxide and water always resulting from the contact of nitrous acid and hydroxylamine. It may also be pretty safely accepted that hydroxyammonium chloride or sulphate is less sensitive to the action of both nitric acid and metal, than is the nitrate or the free base; for with the use of nitric acid alone and much diluted, most of the acid which suffers reduction becomes ammonia, very little becoming nitrous oxide, and ammonia is the product of the reduction of hydroxylamine by metals. This fact, too, the formation of much ammonia, serves to show that it is not want of hydrogen from another source that prevents the finding of hydroxylamine when nitric acid alone acts on metals.

The use of the second acid, the hydrochloric or sulphuric acid added, appears then to be, not to take part in the reduction of the nitric acid, but to secure the reduction of all of it to hydroxylamine by supplying it with hydrogen in the way of double decomposition, and thus keeping it subject to the requisite reducing influence; and further to preserve it more or less from destructive influences when formed.

Nascent hydrogen from the second acid playing no part in reducing nitric acid, the action of the acid upon the metal is not wanted, and is further undesirable because it wastes acid and metal, and loads the solution with metallic salt. It is because of useless consumption of the second acid in dissolving zinc, that the calculated quantity of it—seven equivalents—is insufficient to secure the reduction of one of nitric acid, the excess required representing that part acting directly on the zinc with liberation of hydrogen. The greater effectiveness of sulphuric acid, recorded in the account of the experiments with zinc, is partly attributable to the fact that this acid acts more slowly than hydrochloric upon zinc, and remains therefore longer unsaturated at the service of the nitric acid. It is in part due, no doubt, to the fact of the slower action of this acid causing a less rise in temperature and consequent less destruction of hydroxylamine.

The superiority of one metal over another for the production of hydroxylamine is to be traced to this among other things, that it is less attacked by acids than the other metal. Thus tin has the advantage of being sufficiently basylous and very readily acted upon by nitric acid, without being very briskly acted upon by solution of hydrochloric or sulphuric acid. The destructive action upon hydroxylamine, however, of stannous chloride goes far to neutralise this advantage. A perfect metal for making hydroxylamine would be one readily acting upon dilute nitric acid and displacing its hydrogen, inactive upon sulphuric or hydrochloric acid, and inactive itself and giving a salt inactive upon hydroxylamine.

To resume now the long-deferred discussion of the nature of the change of nitric acid to hydroxylamine:—the conclusions already reached are, that the zinc-tin metals displace the hydrogen of nitric acid; that they do not themselves deoxidise it; and that the displaced hydrogen of one portion of nitric acid acts as the deoxidising and hydrogenising agent upon another portion of it. It may be admitted that this change takes place in successive stages, but it is doubtful whether there is any evidence of such a division of the reduction, while there are difficulties in reconciling their occurrence with the

2 г 2

attainment of the final result. Nitrous acid and hyponitrous acid, if present in the solution at all during the reduction, are so only in traces. The products of their reaction with hydroxylamine-nitrous oxide in the case of nitrous acid, and nitrogen (?) in the case of hyponitrous acid-appear also to be present only in traces when a sufficiency of the second acid is taken, and Kinnear (loc. cit.) finds all the nitric acid then as ammonia in the solution. The presence of a little nitrous oxide need not even be due to nitrous acid, but to a slight reaction between the metal and its nitrate, before the second acid can decompose it, generating nitrite, which then would act upon hydroxylamine. It seems more probable that, as a portion of nitric acid comes in contact with the metal, it is converted into hydroxylamine before giving place to a fresh portion of nitric acid, than that in contact with the metal there are portions of nitric acid in various stages of reduction. The change into hydroxylamine may indeed be a compound one, with its operations partly consecutive, partly simultaneous, but all occurring so close together as to be completed before the intermediate products can move out of the influence of the metal, and meet pre-formed hydroxylamine upon which to act. Or to view the change from another light, the action of the metal appears to be such that the nitric acid which has its hydrogen displaced does not suffer this change, independently of the other portion of the acid which takes up this hydrogen, but in connection with it. Admitting, however, that the change does take place in a succession of steps, it has still to be remembered that these are not necessarily, or even probably, the formation of nitrite and hyponitrite. In most chemical changes there are probably complex transition-bodies formed which then break up into the ultimate products; and in the present case it seems likely that nitrous acid, for example, if itself formed at all, passes next to a transition-body capable of decomposing to hyponitrous acid, but readily passing on directly to hydroxylamine, thus:

 $HNO_2 + 2H = HN(OH)_2 = HNO + OH_2,$

or otherwise :

 $HN(OH)_2 + 2H = H_2NOH + OH_2,$

a repetition of which action would give ammonia.

In considering the action of hydrogen upon nitric acid in stages, the combination of hydrogen with hydroxyl, and removal of its oxygen therefore from the nitrogen, must be regarded as preceding the attack upon either of the other oxygens, to hydroxylise which would be the first step in its removal. Thus, assuming the formation of nitrous acid, the reaction would be

 $HONO_2 + 2H = HOH + HNO_2.*$

* To guard against a possible misconception, I may here add that in admitting

This seems to prove that the hydroxyl of hydroxylamine is not that of the nitric acid from which it was formed; and the conversion of ethyl nitrate to hydroxylamine leads to the same conclusion, the ethoxyl becoming replaced by hydrogen:

$$C_2H_5ONO + 2H = C_2H_5OH + HNO_2$$
, &c.

The theory of the nitronic constitution of nitrous acid also receives support here.

Hydrogen being the agent which reduces nitric acid to hydroxylamine, the greater activity of one metal over another in bringing about its production would furnish a difficulty, and such a difficulty Armstrong endeavours to meet by suggesting that the hydrogen is in the nascent state, with different degrees of activity determined by the metal which has liberated it. But as regards hydroxylamine, I am not at all sure that this difficulty does present itself. The quantity of hydroxylamine found in the solution is the difference between what has been formed and what has been destroyed. Besides its formation by the hydrogen of the reaction between nitric acid and metal, there may be its formation by the salt in solution, as in the case of tin (v. Dumreicher), but above all there may be its destruction by the salt in solution and also by the metal itself, as I shall endeavour to establish in the next paragraph. The varying results with different metals have apparently therefore sufficient explanation without attributing to the hydrogen different degrees of power.

While hydroxylamine appears to be formed by hydrogen which passes through the state of nitric acid, ammonia appears to be formed by the deoxidising action of the metal upon hydroxylamine; or, putting it in another way and going less beyond the facts, hydroxylamine results from one reaction, in which the metal attacks 7 mols. of nitric acid at a time, coming off with six nitrate radicals and leaving behind the hydroxylamine and water. Ammonia is formed in another reaction in which the metal attacks hydroxylamine and unites with it to form a compound afterwards decomposed by water or acid, as the circumstances may allow. That this is what takes place in the production of ammonia from hydroxylamine by reduction is to be seen in the fact that the change takes place not only in an acid solution, but also in a neutral or basic one in contact with the metal, and that, in the case of zine at least, such a metallic compound actually occurs in the alkaline solution, and slowly decomposes into

the reduction of nitric acid to nitrous acid by hydrogen as perhaps occurring when the metal belongs to the zinc-tin class, I am not contradicting what I have said regarding the metals of the silver class. Of these I endeavour to prove, not that the hydrogen they might displace would not reduce nitric acid, but that they cannot displace hydrogen.

ammonia and metallic hydroxide. First, its formation may be thus represented—

$Zn + H_2NOH = ZnH_2NOH$,

and then the decomposition of the zinc ammonium hydroxide by water, thus:

$\operatorname{ZnH}_2\operatorname{NOH} + \operatorname{H}_2\operatorname{O} = \operatorname{Zn}(\operatorname{OH})_2 + \operatorname{H}_3\operatorname{N}.$

As a matter of fact, while nitric acid passes direct as it were to hydroxylamine, there is a marked pause at the stage of hydroxylamine in its passage to ammonia, for otherwise that substance would not be found in such quantity. Now such a pause suggests a change in the method of attack, just such a one as that above indicated, and is fully accounted for in this way.

A peculiarity in the formation of hydroxylamine by aluminium demands notice. It is that hydroxylamine appears to form only or principally when the hydrochloric acid has been acting for some time, and has become nearly saturated. The experiments of Gladstone and Tribe, showing that this metal decomposes water in presence of aluminium chloride, render it very probable that in the formation of hydroxylamine this salt plays an important part, not, however, by causing the aluminium to act upon water, but to act much more freely upon nitric acid than it can otherwise do. This subject requires more examination. For the remarkable fact that magnesium forms hydroxylamine in presence of hydrochloric acid, but not in presence of sulphuric acid, I have no explanation to offer, except that perhaps its chloride, too, is in some way active.

As already described, the metal lead readily produces ammonia, but apparently not hydroxylamine. This fact can hardly be attributed to any high degree of activity in the metal as a reducing agent. It is probably to be accounted for in some way by its well-known special activity upon its own nitrate,* by its action upon water, or by its slow action upon acids, in consequence of the very slight solubility of its salts. The production of ammonia by iron, and not of hydroxylamine, is explained by the deoxidising action of ferrous salts. This is exerted even at common temperatures. A similar effect is exerted by stannous chloride in hot solution, and to a less extent in cold.

The experimental part of this paper is very incomplete, and the theoretical part of necessity, therefore, insufficiently supported by facts. Investigation of the subject is, however, now being continued in this laboratory, and will, I hope, not be interrupted until further results have been obtained. For great assistance with the experiments I am much indebted to Messrs. T. Fujii and T. Shimidzu, graduates of the Imperial Japanese College of Engineering.

^{*} By this property lead shows relationship to the silver class of metals.

Summary.

Free nitric acid yields hydroxylamine when treated with tin, zinc, cadmium, magnesium, and aluminium. In presence of either hydrochloric or sulphuric acid the quantity obtained may be considerable, that is, at least, when the metal is either tin or zinc. Without a second acid only traces of hydroxylamine can be detected.

There is no reason to believe that the action of the hydrochloric or sulphuric acid upon the metal is instrumental in forming hydroxylamine. The second acid serves to decompose nitrate as fast as it is produced. In this way, (1) it holds the hydroxylamine in a state more stable than the nitrate; (2), it preserves the hydroxylamine from the destructive action of nitrous acid, by preventing that formation of this substance which would otherwise result from the reaction between a metal yielding hyroxylamine and its own nitrate; and (3), it determines the reduction of all the nitric acid to hydroxylamine by supplying the hydrogen for reproducing it, and so keeping it free to the last.

Metals act upon nitric acid in one of two ways, and are accordingly divisible into two classes. The one includes the metals silver, mercury, copper, and bismuth. The metals of this class form nitrite, water, and nitrate, and exert no further action, forming neither ammonia nor hydroxylamine. They do not convert their nitrate to nitrite. Their mode of action is to decompose the nitric acid into hydroxyl and nitroxyl, combining with these radicals to form hydroxide and nitrite, which, by secondary reactions, become water, nitrous acid, and metal nitrate. These metals therefore separate nitrogen from oxygen (hydroxyl) in decomposing nitric acid; they do not in this decomposition separate hydrogen from oxygen, just as they do not do so in any other case.

The other class of metals includes tin, zinc, cadmium, magnesium, aluminium, lead, iron, and the alkali-metals. These form ammonia and generally also hydroxylamine, but do not yield nitrite or nitrous acid with free nitric acid. On the other hand, they readily form nitrite by acting on their own nitrate. They exercise two actions, one upon the nitric acid itself, and one upon the hydroxylamine they have produced. They act first upon 7 mols. of the acid, separating, in the form of hydroxylamine, the hydrogen of six of them by forming nitrate, and leaving the seventh converted to water and the said hydroxylamine. This action occurs without evident break into successive stages. The second action of these metals is that in which they combine with hydroxylamine to form metal-ammonium hydroxide, which decomposes with water into metal hydroxide and ammonia.

DYSON ON SOME COMPOUNDS OF

Nitrites have a constitution indicated by the name "nitronates," that is, they have their metal directly united to their nitrogen. They have the same radical $-NO_2$ — as nitrates have, these being its metaloxyl compounds.

466