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XL.—On the Action of Nitric Acid upon Copper, Mercury, etc., and on the influence of the presence of Metallic Nitrates.

# By J. J. ACWORTH.

THE action of nitric acid upon metals is known to give rise to the evolution of lower oxides of nitrogen, or nitrogen itself, and finally to the formation of ammonia, as the case may be. The products of the decomposition are usually stated in chemical text-books to be of a well-defined nature, and are expressed by definite equations. Several instances are known, however, from which the contrary must be inferred.

Thus it is a common lecture-room experiment to exhibit the extinction of a lighted taper in nitric oxide, obtained in the ordinary way by the action of nitric acid upon copper, but it has recently been observed that the gas so prepared sometimes causes the flame to burn with greater brilliancy than it does in atmospheric air.

Again, it was reported a few years ago, that Liebig, wishing to exhibit the brilliant flash of light produced by igniting a mixture of nitric oxide gas and vapour of carbon disulphide, before the Court of Bavaria, had a smart explosion, much to his astonishment and discomfort. Liebig, I believe, attributed this mishap to some mistake on the part of his assistant, who, he thought, had handed him a jar containing nitrous instead of nitric oxide. The matter, as far as I know, was never gone into further. It is probable, however, that the explosion may have been due to a mixture of nitrous and nitric oxide; and with a view of throwing some further light upon the reaction which takes place when metals are acted upon by nitric acid, I undertook, at the instance of Dr. Frankland, to re-investigate and to define the conditions under which the different gases are obtained.

As the action of the acid was found to vary with the temperature, the experiments were, for the most part, conducted at the ordinary temperature, or at such a higher temperature as I found compatible with the slow evolution of the gases; whenever it differed from the normal, viz.,  $15^{\circ}$  C., in any of the experiments to be described, it will be mentioned specially.

For the evolution of the gases a simple apparatus was employed, consisting of a small flask, fitted with an india-rubber plug, through which passed a dropping funnel and delivery-tube. At first the gases were passed through a second flask containing a solution of caustic potash, but as I found, on analysis of the gases collected directly, that no absorption took place when potash was introduced into the laboratory-tube containing the gases, the second flask was abandoned.

The gases, after the air had been displaced from the apparatus, were invariably collected over mercury.

In a few experiments only, when the temperature was allowed somewhat to rise or when a stronger acid or a more concentrated solution of a salt had been used, I observed ruddy fumes of nitrogen tri- and tetroxide, which, as they act upon mercury, were not as a rule collected.

The evolution of gas generally went on very slowly. Test-tubes were filled usually at intervals varying from ten to twenty minutes to half an hour or more.

The analysis of the gases—for mixtures of two or more gases had invariably to be dealt with-was conducted in a Frankland's gas apparatus. A portion was introduced into the laboratory-tube, then transferred to the eudiometer and read off, the usual corrections for temperature being made in each instance. The gas was next transferred back to the laboratory-tube, into which a small quantity of a saturated solution of caustic potash, and afterwards oxygen, had been introduced. The nitric oxide present in the mixture was converted into the next higher oxides, which were immediately absorbed by the potash. The excess of oxygen was removed by introducing a few drops of a concentrated solution of pyrogallic acid-potash being already present in the laboratory-tube-and the remaining gas-volume ascertained by transferring back to the endiometer-tube. After this reading the laboratory-tube was disconnected and thoroughly washed to free it from the alkaline pyrogallate, and after drying and refilling with mercury it was replaced in its usual position. In conducting the subsequent analysis, I was guided by the amount and the relative proportions of nitrous oxide and nitrogen present. If, for instance, the mixture was large enough and was thought to consist almost entirely of nitrous oxide, hydrogen was introduced into the laboratorytube and the volume measured in the eudiometer. This mixture was then fired by means of the electric spark and the contraction ascertained, which would, of course, be equal to the amount of nitrous oxide present. Occasionally, when no explosion could be obtained, and when the gas consisted almost entirely of nitrogen, a small volume of oxygen was introduced so as to ensure an explosion with the hydrogen. This. known volume of oxygen, multiplied by three, was subtracted from the total contraction, the residual contraction then equalling the volume of nitrous oxide. The gas now consisted of a mixture of nitrogen and hydrogen.

To ascertain the accuracy of the analysis, the volume of hydrogen consumed in the contraction, and the total nitrogen present as nitrous

This was done by adding excess oxide and nitrogen were determined. of oxygen and again exploding and ascertaining the contraction. These data enabled me then to verify the determinations of nitrous oxide and nitrogen in the gas.

Whenever the least uncertainty was felt as to the value of the results of an analysis, duplicate determinations were invariably made.

For all the experiments I used the ordinary concentrated acid of specific gravity 1.42 containing 60 per cent. of the anhydride,  $N_2O_5$ ; and whenever nitric acid is mentioned in this paper, this strength of acid is to be understood.

#### Action of Nitric Acid upon Copper.

Experiment I.-In this experiment 60 c.c. of concentrated nitric acid were diluted with 120 c.c. of water and 130 c.c. of this dilute (1 in 3) acid measured into the flask containing 15 grams of copper (in thin strips). This amount of dilute acid added should, according to the usual formula given for the action of nitric acid upon copper, have been rather more than sufficient to dissolve the 15 grams of copper, with evolution of nitric oxide gas. The temperature was about 10°. In two or three minutes gas began to come off. Sample I was collected twenty minutes after the action commenced and submitted to analysis, the results of which I will give in full, so as to illustrate the method adopted :---

|   | Eudio-<br>meter<br>readings.           | Observed<br>pressure in<br>the baro-<br>meter tube.  | Tempera-<br>ture.   | Corrected<br>volume<br>at 0°.  |
|---|--|--|---|--|
| Volume introduced<br>After absorbing nitric oxide {<br>Upon addition of oxygen<br>"hydrogen<br>After explosion<br>Oxygen added<br>After explosion | II<br>II<br>I<br>I<br>I<br>I<br>I<br>I | $705 \cdot 75$ 508 \cdot 4<br>677 \cdot 4<br>710 \cdot 4<br>883 \cdot 2<br>766 \cdot 5<br>912 \cdot 0<br>778 \cdot 7 | $11 \cdot 8^{\circ}$ $11 \cdot 9^{\circ}$ $12 \cdot 0^{\circ}$ $12 \cdot 1^{\circ}$ $12 \cdot 1^{\circ}$ $12 \cdot 1^{\circ}$ $12 \cdot 2^{\circ}$ $12 \cdot 2^{\circ}$ | $198.96 \\ 10.14 \\ 20.37 \\ 51.9 \\ 217.04 \\ 105.51 \\ 244.47 \\ 117.13$ |

The level in the barometer-tube at reading II = 497.8. Reading I = 656.1 mm.

The above analysis will be found on calculation to give :---

Nitric oxide, 94.89 p. c.; nitrous oxide, 4.27 p. c.; nitrogen, .84.

In order to save space, I shall not hereafter give the details of my

numerous analyses, but merely the summary of the results obtained in a tabular form :---

|  | Time of collection.   | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide.  | Percentage<br>of<br>Nitrogen.           |
|--|---|-----------------------------------|---|---|
| Sample I<br>" II<br>" III<br>" IV<br>" V | 20 minutes after the evolu-<br>tion began30 minutes40 minutesditto1 hour1 hour 15 minutes ditto | 94.8996.8392.7884.4483.31         | $\begin{array}{c} 4 \cdot 27 \\ 2 \cdot 11 \\ 6 \cdot 04 \\ 12 \cdot 70 \\ 13 \cdot 44 \end{array}$ | ·84<br>1 ·06<br>1 ·18<br>2 ·86<br>3 ·25 |

In this experiment it is noticeable that after collection of sample II, the percentages of nitrogen and nitrous oxide, and especially of the latter, gradually increased, whilst as a consequence, the percentage of nitric oxide gradually became less; and had the experiment been continued, there is reason to believe that the percentages of nitrous oxide and nitrogen would have kept on augmenting, whilst the percentage of nitric oxide would have continued to diminish.

Experiment II.—In this experiment 26 c.c. of nitric acid and 104 c.c. of water were measured into the flask containing 15 grams of copper. The temperature of the diluted acid (1 in 5) was 17°, that of the room about 10°. The action throughout was very slow indeed, but regular. The evolution of the gas was so sluggish that none was collected, in order to allow for the displacement of the air, till about  $2\frac{1}{2}$  hours after their action had commenced.

|   | Time of collection.   | Percentage<br>of Nitric<br>Oxide.  | Percentage<br>of Nitrous<br>Oxide.  | Percentage<br>of<br>Nitrogen.  | Remarks.   |
|---|---|--|---|--|--|
| Sample 7<br>,, 11<br>,, 111<br>,, IV<br>,, V<br>,, V1<br>,, V11 | 2½ hours after reac-<br>tion had commenced<br>10 min. after sample I<br>25 min. ditto<br>1 hr. 5 min. ditto<br>1 hr. 20 min. ditto<br>1 hr. 25 min. ditto<br>2 hrs. ditto | $\begin{array}{c} 84 \cdot 91 \\ 93 \cdot 22 \\ 95 \cdot 09 \\ 95 \cdot 27 \\ 94 \cdot 28 \\ 95 \cdot 48 \\ 95 \cdot 96 \end{array}$ | $   \begin{array}{r}     4 \cdot 56 \\     3  73 \\     3 \cdot 64 \\     \\     3 \cdot 93 \\     3 \cdot 26   \end{array} $ | $   \begin{array}{r}     10.53 \\     3.05 \\     1.27 \\     - \\     - \\     .59 \\     .78   \end{array} $ | Took ¼ hr. to<br>collect<br>" 10 m. "<br>" 5 m. "<br>" 5 m. "<br>" 5 m. "<br>" 10 m. " |

The high percentage of nitrogen found in samples I and II is in all probability due to the nitrogen of the air which had not been expelled entirely from the flask. This would also account, if we compare these samples with those which follow, for the comparatively high percentage of nitrous oxide, due to the conversion of some of the nitric oxide, by the oxygen of the air in the flask, into higher oxides, and their partial absorption by the liquid. Otherwise, omitting the analyses of samples I and II, the relative percentages of nitric oxide, nitrous oxide, and nitrogen vary within very narrow limits throughout the whole experiment.

It is to be noted also, that the amount of nitric acid used was not sufficient to dissolve much more than half the amount of copper present.

Experiment III.—This experiment is somewhat similar to experiment I, as regards the relative proportions of acid, copper, and water employed. The principal difference consists in the employment of a Sprengel pump to produce a vacuum in the evolution flask previous to the introduction of the acid, in order to ascertain the influence which air, if present, had upon the composition of the gases first evolved, principally upon the percentage of nitrogen.

120 c.c. of water were measured out into a flask containing 20 grams of copper, and the apparatus was then suitably connected with a Sprengel pump. As soon as a vacuum had been obtained, 50 c.c. of nitric acid were run in through the stoppered funnel.

|  | Time of collection.   | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide.                  | Percentage<br>of<br>Nitrogen.   |
|--|---|-----------------------------------|---|---|
| Sample I<br>"II<br>"II<br>"IV<br>"V<br>"V<br>"VI | As soon as evolution began<br>10 min. after ","<br>30 min. after ","<br>1 hr. 15 min. after ","<br>2 hrs. after ","<br>Last portions of gas | 84.4497.0064.2759.5360.8746.52    | $14.33 \\ 1.91 \\ 29.30 \\ 32.73 \\ 31.75 \\ 43.27$ | $     \begin{array}{r}       1 \cdot 23 \\       1 \cdot 09 \\       4 \cdot 43 \\       7 \cdot 74 \\       7 \cdot 38 \\       10 \cdot 21 \\     \end{array} $ |

The conditions under which this experiment and experiment I were conducted are slightly different, for whilst in the latter case the experiment was performed when the atmospheric temperature was about 10°, in the former it was about 19°. And again, in experiment I, the diluted acid was about the temperature of the room; in experiment III the addition of concentrated acid to the water in the flask caused still greater differences of temperature.

For the rise in the percentage of nitric oxide in sample II, I am quite unable to account at present. Otherwise, in this, as in experiment I, the same facts will be observed, namely, that after collecting sample II the percentage of nitric oxide goes on steadily diminishing, whilst the percentages of nitrous oxide and nitrogen, and especially the former, continue gradually to increase towards the end of the experiment.

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On thinking over the altered circumstances capable of producing this relative difference in the percentage of gases evolved, it occurred to me that it was most likely due to the cupric nitrate which had become dissolved in the acid solution. This led then to the next experiment.

# Action of Nitric Acid upon Copper in the presence of Cupric Nitrate.

Experiment IV.—In this experiment the relative proportions of acid, copper, and water were the same as in experiment I.

43 c.c. of nitric acid were diluted with 86 c.c. of water, and in this diluted acid 40 grams of cupric nitrate were dissolved. This was made to act upon 15 grams of copper as before. Temperature of the room about  $13^{\circ}$ .

|          | Time of collection.               | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen. |
|----------|-----------------------------------|-----------------------------------|------------------------------------|-------------------------------|
| Sample I | In the early part of the          | 67 • 65                           | 27 .60                             | 4.75                          |
| " II     | Towards the close of the reaction | 40 • 21                           | 51 · 10                            | 8 .69                         |

In another experiment, performed with the same quantities of materials, I observed similar results, viz., a large increase in the percentages of nitrous oxide and nitrogen evolved. I concluded, therefore, that this result could be due to nothing else than to the 40 grams of cupric nitrate dissolved, in the first instance, and secondly, to the nitrate produced by the action of the acid upon the copper.

Experiment V.—80 grams of cupric nitrate were dissolved in 104 c.c. of water, to which 26 c.c. of nitric acid had been added. When the nitrate had entirely dissolved, it was transferred to a flask containing 15 grams of copper. The reaction went on very slowly at first (the temperature of the room being about  $12^{\circ}$ ), so that the flask and its contents had to be gently heated to about  $45^{\circ}$ , before a quiet reaction was set up.

|                             | Time of collection.   | Percentage<br>of Nitric<br>Oxide.  | Percentage<br>of Nitrous<br>Oxide.                     | Percentage<br>of<br>Nitrogen. |
|-----------------------------|---|--|--|-------------------------------|
| Sample I<br>,, II<br>,, III | 1 hour after reaction began<br>$1\frac{1}{2}$ hour ", ",<br>2 hours ", ", | $\begin{array}{r} 47 \cdot 26 \\ 43 \cdot 45 \\ 41 \cdot 86 \end{array}$ | $\begin{array}{c} 44.72 \\ 48.17 \\ 49.83 \end{array}$ | 8 ·02<br>8 ·38<br>8 ·31       |

The gases were now evolved very slowly, and a tube placed to receive what gas might come off over night, was next morning found nearly filled, the apparatus being still perfectly air-tight. The analysis of this gas (sample IV) gave :---

$$N_2O_2 = 36.61$$
 p.c.  $N_2O = 54.15$  p.c.  $N = 9.24$  p.c.

5 c c. of nitric acid, diluted with 5 c.c. of water, were then introduced. This caused no apparent action. Another similar quantity of dilute acid was next added, when a feeble action became perceptible. Heated to about  $40^{\circ}$  a further quantity of gas was given off (sample V) which on examination gave :---

$$N_2O_2 = 20.54$$
 p.c.  $N_2O = 68.86$  p.c.  $N = 10.6$ 

A more vigorous reaction having been set up, sample VI of gas was soon after collected, and gave on analysis :---

$$N_2O_2 = 11.93$$
 p.c.  $N_2O = 75.62$  p.c.  $N = 12.45$  p.c.

Some of the gas evolved was then collected in a test-tube to try its action on a glowing taper. The taper was immediately re-lighted, thus showing, independently of analysis, the very large percentage of nitrous oxide present.

Soon afterwards sample VII was collected, which on analysis gave :---

$$N_2O_2 = 11.68$$
 p.c.  $N_2O = 76.01$  p.c.  $N = 12.31$  p.c.

The gases were now coming off very slowly. Two more samples were collected at different times. Sample VIII gave :---

$$N_2O_2 = 15.39$$
 p.c.  $N_2O = 73.45$  p.c.  $N = 11.16$  p.c.

After the addition of 6 c.c. of nitric acid, and application of gentle heat, sample IX was collected, which on analysis gave :---

$$N_2O_2 = 6.59$$
 p.c.  $N_2O = 79.94$  p.c.  $N = 13.47$  p.c.

These results being produced with 80 grams of cupric nitrate, I thought it desirable to see if the high percentage of nitrous oxide might not be still further increased by the employment of a nearly saturated solution of cupric nitrate.

Experiment VI.—120 c.c. of a nearly saturated solution of cupric nitrate, and 15 c.c. of nitric acid were measured out into the flask containing 15 grams of copper.

The reaction began and went on quietly.

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|--------------------------|------|---------|----------|-----|
|--------------------------|------|---------|----------|-----|

|          | Time of collection.  | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen.                             |
|----------|--|-----------------------------------|------------------------------------|---|
| Sample I | <ol> <li>hour after the reaction<br/>began<br/>2½ hours ,, ,,</li> </ol> | 32.13<br>25.09                    | 46 ·52<br>61 ·66                   | $\begin{array}{c} 21 \cdot 35 \\ 13 \cdot 25 \end{array}$ |

As the reaction went on very slowly, 10 c.c. of nitric acid were added, when it proceeded more quickly, but still very quietly.

|                    | Time of collection.                               | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen. |
|--------------------|---|-----------------------------------|------------------------------------|-------------------------------|
| Sample III<br>" IV | $1\frac{1}{2}$ hour after sample II 2 hours , , , | $12.06 \\ 13.26$                  | $76.48 \\ 76.36$                   | $11.46 \\ 10.38$              |

10 c.c. more of nitric acid were next added, and sample V collected soon afterwards. Sample VI was collected when the reaction had almost ceased.

|                  | Time of collection. | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen. |
|------------------|---------------------|-----------------------------------|------------------------------------|-------------------------------|
| Sample V<br>" VI | Given               | 9 ·40<br>7 ·73                    | $80.44 \\ 82.64$                   | 10.16 9.63                    |

The apparatus had to be left over night. Next day it was still found perfectly air-tight, and 10 c.c. more of nitric acid were added. The evolved gases were collected soon after. The analysis of sample VII gave :---

 $N_2O_2 = 4.50$  p.c.  $N_2O = 85.33$  p.c. N = 10.17 p.c.

The apparatus was then opened, and 15 grams of fresh copper introduced. Sample VIII was collected about two hours after, and gave on analysis:---

 $N_2O_2 = 13.89$  p.c.  $N_2O = 76.08$  p.c. N = 10.03

10 c.c. of nitric acid were next added, and sample IX collected soon after, which on analysis gave :---

 $N_2O_2 = 5.83$  p.c.  $N_2O = 81.31$  p.c. N = 12.86 p.c.

The apparatus was now heated to about 60°, and sample X collected about ten minutes afterwards. The analysis gave :---

$$N_2O_2 = 20.40$$
 p.c.  $N_2O = 66.33$  p.c.  $N = 13.27$  p.c.

Sample XI was collected when the reaction had all but ceased, and gave on analysis :---

$$N_2O_2 = 22.99$$
 p.c.  $N_2O = 64.88$  p.c.  $N = 12.13$  p.c.

I had hoped that in this experiment I should have been able to eliminate the nitric oxide altogether. My efforts, however, in that direction have been unsuccessful. But I believe that by careful management as regards the strength of the acid and the temperature of the liquid (both of which must be found out by experiment), the nitric oxide might be eliminated, for there is no doubt that both temperature and strength of acid influence the relative percentages of the gases evolved, as experiment VII will show.

Experiment VII.—The percentage of nitrogen in the preceding experiment having been found rather high, it was thought desirable to demonstrate that the atmospheric nitrogen had nothing to do with it, and the experiment was repeated in a vacuum by employing, however, more than double the amount of acid, which, together with a rise in temperature, will be seen from the analytical tables to considerably influence the reaction.

120 c.c. of a nearly saturated solution of cupric nitrate were measured out into a flask containing 15 grams of copper. The flask was then connected with the Sprengel pump. As soon as a vacuum had been obtained, 35 c.c. of nitric acid were run in. This addition of acid heated the liquid to about 30°, and soon caused a vigorous reaction.

|   | Time of collection.  | Percentage<br>of Nitric<br>Oxide.                    | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen.  |
|---|--|--|------------------------------------|--|
| Sample I<br>" II<br>" IV<br>" V<br>" VI | Soon after evolution began<br>40 min. ", ",<br>1 hour ", ", ",<br>$1\frac{1}{2}$ hour ", ",<br>$2\frac{1}{2}$ hours ", ",<br>Towards the close | $80.31 \\ 55.99 \\ 50.82 \\ 49.25 \\ 49.01 \\ 43.22$ | 14.4437.7242.5044.2444.5751.11     | $5 \cdot 25  6 \cdot 29  6 \cdot 68  6 \cdot 51  6 \cdot 42  5 \cdot 67$ |

In the early part of this experiment, ruddy fumes of nitrogen triand tetroxide were evolved.

# Action of Nitric Acid upon Copper in presence of Potassic Nitrate.

Experiment VIII.—As in the preceding experiments the presence of cupric nitrate had exerted so marked an influence, I thought it of some interest to try other nitrates, beginning with potassic nitrate.

105 c.c. of a saturated solution of potassic nitrate, and 25 c.c. of nitric acid were measured out into the flask containing 15 grams of copper. At first there was all but no reaction. The flask and contents were then heated to between  $40^{\circ}$ —50°, when the reaction set up, the temperature of the room being 13°.

|                              | Time of collection.  | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen.   |
|------------------------------|--|-----------------------------------|------------------------------------|---|
| Sample I                     | 1 hour after the reaction began  | 94 •75                            | _                                  |   |
| " II<br>" III<br>" IV<br>" V | $1\frac{1}{2}$ hour       ,,       ,,         2 hours       ,,       ,, $2\frac{1}{2}$ hours       ,,       ,,         Towards the close | 94.6994.6393.8088.28              | 3 ·60<br>3 ·96<br>4 ·62<br>9 ·94   | $     \begin{array}{r}       1 \cdot 71 \\       1 \cdot 41 \\       1 \cdot 58 \\       1 \cdot 78     \end{array} $ |

During the whole of this experiment the evolution continued to be very slow; and the relative gas percentages remained very nearly the same throughout. The last sample of gas showed only a slight increase of nitrons oxide. This is due, in all probability, to the cupric nitrate formed and dissolved in the liquid, and the results are very similar to those obtained in experiment II. The inference, therefore, to be drawn from them is, "that the potassic nitrate in solution had little or no influence upon the evolution of the gases."

# Action of Nitric Acid upon Metallic Copper in presence of Ammonic Nitrate.

Experiment IX.—100 c.c. of a saturated solution of ammonic nitrate, 10 c.c. of water, and 25 c.c. of nitric acid were measured out into the flask containing 15 grams of copper. The reaction soon began without the application of heat.

|                                  | Time of collection.  | Percentage<br>of Nitric<br>Oxide.   | Percentage<br>of Nitrous<br>Oxide.  | Percentage<br>of<br>Nitrogen.       |
|----------------------------------|--|---|---|-------------------------------------|
| Sample I<br>"II"<br>"III"<br>"IV | 1 hour after reaction began<br>14 hour ", ",<br>2 hours ", ",<br>3 hours ", ", | $     \begin{array}{r}       19 & 71 \\       10 & 05 \\       7 & 01 \\       5 & 89     \end{array} $ | $\begin{array}{c} 21 & 22 \\ 17 & 69 \\ 19 \cdot 27 \\ 20 & 69 \end{array}$ | 59 ·07<br>72 26<br>73 ·72<br>73 ·42 |

20 c.c. of nitric acid were then added; a vigorous action was again set up, and a considerable elevation of temperature produced. After allowing the reaction to go on for fifteen minutes, I collected sample V.

|   | Time of collection.   | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen. |
|---|---|-----------------------------------|------------------------------------|-------------------------------|
| Sample V                                | 15 minutes after addition<br>of acid<br>1 hour after sample V | 8 · 38                            | 12 ·10                             | 79 •52<br>68 ·91              |
| ,, ,, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, | i nour aner sample v  | 0 29                              | 50 80                              | 08 51                         |

The presence of ammonic nitrate seems here to be chiefly instrumental in the development of a very high percentage of nitrogen. The percentage of nitrous oxide is, throughout, no doubt much higher than it would have been without the presence of the ammonic nitrate. But how to account for this high percentage of nitrogen, and almost total elimination of nitric oxide, is, I think, not very easy, unless we suppose that the NH<sub>3</sub> of the ammonic nitrate is acted on by the nascent nitric oxide, according to the following equation :—

$$4NH_3 + 3N_2O_2 = 6H_2O + 5N_2$$

or, as I found in a subsequent experiment, that the action of zinc upon ammonic nitrate gives rise to the formation of much nitrite, it may be explained also by the chemical heat splitting up the nitrite into water and nitrogen, thus :---

$$\mathrm{NO}_{2}\mathrm{NH}_{4} = \mathrm{N}_{2} + 2\mathrm{H}_{2}\mathrm{O}.$$

Another experiment performed without the addition of water gave similar results.

*Experiment X.*—In this experiment I ran 100 c.c. of a saturated solution of ammonic nitrate, 30 c.c. of a saturated solution of cupric nitrate, and 20 c.c. of nitric acid into the flask containing 15 grams of copper.

The temperature of the room was about  $13^{\circ}$  C. As very little gas came off, after the lapse of an hour 10 c.c. more of nitric acid were added, which produced, however, but little effect. After leaving the action to go on for rather more than an hour, to allow for the displacement of the air, a gentle heat was applied till the temperature of the flask and its contents rose to about  $60^{\circ}$ . Sample I was collected about fifteen minutes after, when the gases were coming off rather freely.

| UPON  | COPPER. | MERCURY,        | ETC. |
|-------|---------|-----------------|------|
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|                            | Time of collection.  | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide.                                       | Percentage<br>of<br>Nitrogen. |
|----------------------------|--|-----------------------------------|--|-------------------------------|
| Sample I<br>, II<br>,, III | 15 minutes after heating<br>20 ,, after sample II<br>Reaction had all but ceased | $0.69 \\ 0.49 \\ 1.53$            | $\begin{array}{r} 23 \cdot 22 \\ 31 \cdot 20 \\ 31 \cdot 60 \end{array}$ | $76.09 \\ 68.31 \\ 66.87$     |

The apparatus was allowed to remain all night, and next morning it was still found to be perfectly air-tight. 10 c.c. of nitric acid were added, which, however, produced scarcely any action. Heat was then applied, and sample IV soon after collected, which on analysis gave :----

 $N_2O_2 = 1.14$  p.c.  $N_2O = 29.38$  p.c. N = 69.48 p.c.

After the evolution had continued for about an hour, sample V was collected. It was noticed that, whenever the lamp was taken away, the action went on sluggishly. The temperature to which the flask was raised was about  $50^{\circ}$ .

The analysis of sample V gave the following results :---

 $N_2O_2 = 0.74$  p.c.  $N_2O = 34.84$  p.c. N = 64.42 p.c.

In this experiment the average amount of nitric oxide is less than 1 per cent. This I think might have been anticipated on referring to the composition of sample VI of experiment IX; a large quantity of copper had, in fact, become dissolved, whereby the evolution of nitrous oxide was increased. I, therefore, tried to get in this experiment as nearly as possible the same conditions under which the gases of sample VI in the preceding experiment had been collected, with what result will readily be seen by glancing at the analytical numbers.

#### Action of Nitric Acid upon Zinc in the presence of Ammonic Nitrate.

Experiment XI.—150 c.c. of a saturated solution of ammonic nitrate were run into a flask containing 45 grams of pure zinc (in large sticks). 5 c.c. of nitric acid were then added. The reaction began immediately, and went on regularly, but slowly. A quantity of zinc hydrate formed on the zinc, which did not, however, seem to hinder the reaction.

|          | Time of collection.           | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen. |
|----------|-------------------------------|-----------------------------------|------------------------------------|-------------------------------|
| Sample I | 2 hours after evolution began | 9.61 $5.44$                       | 7 · 17                             | 83 ·22                        |
| ,, II    | 4–5 hours ditto               |                                   | 5 · 38                             | 89 ·18                        |

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5 c.c. more of nitric acid were then added, when the reaction again went on briskly, and the hydrate for the most part dissolved. The tubes were examined from time to time; they all gave indication of the presence of nitric oxide down to 2 per cent.

The principal feature of this short experiment is the high percentage of nitrogen. It is perhaps rather strange why the percentage of nitrous oxide should be so low. Probably an experiment performed with saturated solutions of ammonic and zincic nitrates would give different results.

I also find that zinc is acted upon by ammonic nitrate, without any acid being present, with evolution of 90-99 p. c. of nitrous oxide, the remainder consisting of nitrogen. The action, however, is exceedingly slow.

### Action of Nitric Acid upon Iron in presence of Ammonic Nitrate.

Experiment XII.-120 c.c. of a saturated solution of ammonic nitrate and 5 c.c. of nitric acid were measured out into the flask containing 4 grams of steel foil. A reaction readily took place.

|                             | Time of collection.  | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen.  |
|-----------------------------|--|-----------------------------------|------------------------------------|--|
| Sample I<br>,, II<br>,, III | 1½ hour after reaction began<br>2–3 hours ditto<br>3–4 hours ditto | $4.93 \\ 7.74 \\ 7.31$            | $13.60 \\ 13.16 \\ 17.55$          | $\begin{array}{c} 81 \cdot 47 \\ 79 \cdot 10 \\ 75 \cdot 14 \end{array}$ |

There is nothing particularly noticeable in this experiment beyond what has already been stated in experiment XI. The results are, as might have been expected, similar to those of the previous experiment. A reddish-brown basic nitrate was left in the flask.

# Action of Nitric Acid upon Mercury in presence of Ammonic Nitrate.

Experiment XIII.—In this experiment I measured out 30 c.c. of a saturated solution of ammonic nitrate and 5 c.c. of nitric acid into the flask containing 6 grams of mercury. The action began and continued very slowly. It was allowed to go on for the remainder of the day, and in the evening a test-tube was placed to receive the evolved gases (sample I). Next morning I found the tube full of gas, and the reaction still going on quietly. Sample II was collected during the second day.

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|          | Percentage                 | Percentage  | Percentage       |
|----------|----------------------------|---|------------------|
|          | of Nitric                  | of Nitrous  | of               |
|          | Oxide.                     | Oxide.  | Nitrogen.        |
| Sample I | $5 \cdot 20 \\ 4 \cdot 05$ | $\begin{array}{c}2\cdot 42\\0\cdot 12\end{array}$ | 92 ·38<br>95 ·83 |

The experiment was then left for a couple of days, when it was found that all the mercury had been dissolved, with the exception of a minute globule. Six grams more of mercury were then added. This caused some slight fresh reaction to be set up. Crystals formed on the mercury, and at length entirely covered the metal. To remove these crystals, I added 4 c.c. of nitric acid and 5 c.c. of water, and heated to between  $30^{\circ}$  and  $35^{\circ}$ , when they dissolved, and the gases came off much more rapidly.

Sample III was then collected, and sample IV a few hours afterwards.

| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ |                     | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of<br>Nitrogen. |
|---|---------------------|-----------------------------------|------------------------------------|-------------------------------|
| ,, 17   | Sample III<br>,, IV | $2.87 \\ 1.85$                    | .09                                | 97 ·13<br>98 ·06              |

In this experiment, more than in any other, the tendency to form nitrogen in the presence of ammonic nitrate was exhibited. Towards the close of the reaction the nitrous oxide had been totally eliminated, and the nitric oxide reduced to less than 2 per cent. I believe that nitrogen only would have been obtained had the necessary conditions, viz., proportions of acid, metal, and nitrate, been accurately known.

# Action of Nitric Acid upon Silver.

Experiment XIV.—In this experiment 15 c.c. of water, 5 c.c. of nitric acid, and 5 grams of silver were employed. The silver was pure, and granulated. The gases came off very slowly. The temperature of the room was about  $19^{\circ}$ .

| Time of collection.   | Percentage                | Percentage              | Percentage                |
|---|---------------------------|-------------------------|---------------------------|
|   | of Nitric                 | of Nitrous              | of                        |
|   | Oxide.                    | Oxide.                  | Nitrogen.                 |
| Sample I $1\frac{1}{3}$ hour after reaction began<br>", II $2\frac{1}{2}$ hours ", ", "<br>", III Towards the end of the re-<br>action. | $85.54 \\ 91.06 \\ 85.94$ | 1 •54<br>lost.<br>none. | 12 ·92<br>lost.<br>14 ·06 |

The only points worthy of notice in this experiment are: 1st, the high percentage of nitrogen; and 2nd, the total absence of nitrogen trioxide, and (in sample III) of nitrous oxide. No ruddy fumes were observed in the evolution flask.

Experiment XV.-In order to test the action of nitric acid upon silver in presence of ammonic nitrate, I measured out 15 c.c of a saturated solution of ammonic nitrate and 5 c.c. of nitric acid into a flask containing 5 grams of silver. The reaction was set up much sooner, and the gases were evolved at a much greater rate than in the last experiment.

|          | Time of collection.                  | Percentage               | Percentage | Percentage |
|----------|--------------------------------------|--------------------------|------------|------------|
|          |                                      | of Nitric                | of Nitrous | of         |
|          |                                      | Oxide.                   | Oxide.     | Nitrogen.  |
| Sample I | 2 hours after reaction began $\dots$ | $15.96 \\ 12.97 \\ 4.07$ | 1 ·40      | 82 •64     |
| ,, II    | $3\frac{1}{2}$ hours "," "."         |                          | 1 ·04      | 85 •99     |
| ,, III   | Towards the end of the reaction      |                          | 1 ·28      | 94 •65     |

In this experiment, as was to be expected, the ammonic nitrate gives rise to a high percentage of nitrogen. With silver the tendency to form nitrous oxide is not very marked, as throughout the experiment the percentage of this gas remained nearly stationary.

At the suggestion of Dr. Frankland, I also began to study the action of nitric acid upon metals in the presence of nitrates of organic bases. I obtained some rather curious results as far as I have gone; but as I intend to continue my investigation in this direction, I will only briefly state one result already obtained.

# Action of Nitric Acid upon Mercury in presence of Nitrate of Ethylamine.

Experiment XVI.—In this experiment 9 c.c. of nitric acid, 27 c.c. of water, and 20 c.c. of a solution of nitrate of ethylamine were measured out into a flask containing 7 grams of mercury. As, however, no reaction occurred, 10 c.c. more of nitric acid were added. The gas then came off, and appeared to be little soluble in the liquid. About an hour afterwards, however, scarcely a bubble escaped to the surface, as absorption took place before the gas had time to rise to the surface. After the lapse of a few hours, gas was again evolved, and was collected and analysed. It was found to contain-

$$CO_2 = 29.73$$
 p.c.  $N_2O_2 = 11.86$  p.c.  $N = 56.58$  p.c.  $N_2O = 1.83$  p.c.

To confirm this unlooked-for occurrence of a high percentage of carbonic anhydride,

*Experiment XVII* was undertaken. In this experiment I employed 20 c.c. of water, 20 c.c. of nitric acid, 30 c.c. of the nitrate of ethylamine solution, and 8 grams of mercury. The experiment went on very similarly to the previous experiment. Sample I was collected a few hours after the beginning of the reaction. Sample II towards the end.

|                  | Percentage<br>of Carbonic<br>Anhydride. | Percentage<br>of Nitric<br>Oxide. | Percentage<br>of Nitrous<br>Oxide. | Percentage<br>of Nitrogen. |
|------------------|---|-----------------------------------|------------------------------------|----------------------------|
| Sample I<br>" II | 39•35<br>39·90                          | $11.59 \\ 11.57$                  | 2.68<br>1.05                       | $46.38 \\ 47.48$           |

The carbonic anhydride of the latter experiments must of necessity be due to the carbon of the ethylamine. In other respects the ethylamine acts, as was to be expected, in a manner similar to that observed in the case of ammonic nitrate.

#### Summary.

(1.) The action of cold and dilute nitric acid upon copper gives rise chiefly to the evolution of nitric oxide 90—95 p.c. Rise of temperature or increased strength of acid produces a more vigorous reaction. As the solution becomes saturated with cupric nitrate, the volume of nitrous oxide increases.

(2.) Nitric acid acting upon copper, in presence of a strong or nearly saturated solution of cupric nitrate, gives rise to the formation of all but pure nitrous oxide—as much as 85 per cent.

(3.) The presence of potassic nitrate has little or no influence upon the evolution of the nitric oxide from copper and nitric acid.

(4.) The presence of ammonic nitrate gives rise to the evolution chiefly of nitrogen and nitrous oxide, together with varying amounts of nitric oxide.

(5.) The action of nitric acid upon zinc, in presence of ammonic nitrate, gives rise chiefly to the formation of nitrogen gas.

(6.) Iron gives similar results.

(7.) Mercury, nitric acid, and ammonic nitrate, give nearly pure nitrogen. The action is, however, very sluggish.

(8.) Nitric acid upon silver: chiefly nitric oxide and nitrogen. Nitrous oxide is all but absent.

(9.) Silver and ammonic nitrate gives rise to the formation of nitric oxide, but chiefly of nitrogen (82-64 per cent).

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#### MUIR ON NITROSYL BROMIDE

These experiments were made in the Gas Laboratory of the Royal College of Chemistry, South Kensington. I have to thank Dr. Frankland and Mr. Valentin for the interest shown and the assistance they have rendered me.

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