LII.—*On the Reaction between Nitric Oxide and Oxygen under varying Conditions.*

By G. LUNGE.

THE controversy touched upon in the preceding paper has caused me to make some experiments on the behaviour of nitric oxide towards oxygen under different circumstances. I did not think it superfluous to go back to this elementary matter, since some of the statements to be found in the text-books are of very old date, and contain important contradictions. Thus Armstrong in the discussion mentioned in the last paper, quotes Gay-Lussac's experiments of 1816, as proving that $NO + O$ always yields nothing but N_2O_4, the formation of N_2O_3 taking place only in the presence of alkalis. On the other hand, several authors (Dulong, Berzelius, &c.) contend that oxygen with nitric oxide in excess forms N_2O_3. It is well known that the reaction between NO and O is very materially influenced, not merely by the presence of alkalis, but also by that of sulphuric acid, and even that of pure water; but there are some gaps in our knowledge of these reactions. The experiments to be described below were not made with the intention of thoroughly exhausting this matter, but merely in order to obtain some more evidence concerning the existence of nitrogen trioxide in the gaseous state, and the theory of the vitriol-chamber process.

The apparatus serving for my experiments was so constructed as to avoid any other but glass joints and taps, wherever caoutchouc might be acted on or might cause a diffusion of gases. The oxygen was collected in a graduated cylinder A holding rather more than half a litre, and was delivered from this by means of water pressure, regulated by a screw-clamp. It passed through two drying-bottles charged with concentrated sulphuric acid, and then by means of a glass three-way tap B, at first in the open air, in order to fill all connecting tubes, &c.; afterwards, by changing the position of the tap, it was passed as required into the vessel C filled with nitric oxide. The latter gas was first absorbed in a solution of ferrous sulphate, expelled from this by heat, and collected in an ordinary gas-holder. From here it travelled through two drying-bottles, and was then introduced at the bottom of a Drechsel's washing-bottle C, holding exactly 497·5 c.c., until not merely this bottle, but a further smaller bottle D, and the tube leading away from it, for some time showed no colour whatever, thus proving that all air had been replaced by dry NO. Between C and D a glass tap E was interposed, which was now closed so that the

NO was entirely confined between glass. Now measured quantities of oxygen were forced from A into C through the three-way tap B. Meanwhile the NO had been expelled from D by a current of carbon dioxide, and a certain quantity of pure strong sulphuric acid had been introduced by a dropping funnel. When the reaction in C was finished, the acid contained in D was brought over into C by opening the tap E and constantly keeping up the current of carbon dioxide, which assisted in forcing over the acid and expelled the unabsorbed gas from C through the three-way tap B, turned for this purpose. The sulphuric acid was then tested for the nitrogen oxides dissolved, the nitrogen being estimated by the nitrometer, the oxygen by my modification of the permanganate method, both mentioned in the preceding paper.

I. *Dry Nitric Oxide and Excess of Oxygen.*—Upon 497·5 c.c. NO, which requires just half the volume of oxygen to pass into N_2O_4, from 400 to 500 c.c. oxygen was allowed to act in three experiments. In one case, the analysis of the sulphuric acid showed that nothing but N_2O_4 had been formed ; in the other two cases I found 3·52 and 1·4 per cent. of the nitrogen as N_2O_3. These quantities—especially the former—exceed the experimental errors possible with my analytical methods, which would support the assumption that even with an excess of oxygen small quantities of N_2O_3 may be formed, but I should not venture to assert this positively on the strength of those few experiments. In any case, dry nitric oxide with an excess of dry oxygen yields almost entirely, perhaps exclusively, N_2O_4.

II. *Dry Nitric Oxide with an insufficient Quantity of Oxygen.*—To 497·5 c.c. NO only 180 c.c. oxygen was admitted ; 124 c.c. O would be required to form N_2O_3, 249 c.c. O to form N_2O_4. When the acid began to flow over from D into C, chamber crystals immediately appeared, but of course afterwards dissolved in the excess of acid. On driving out the unabsorbed gas by carbon dioxide no red vapours were noticed in the air. The analysis showed 94 per cent. of the nitrogen to be present as N_2O_3, 6 per cent. as N_2O_4. Those who hold that N_2O_3 does not exist as gas, might say that the reaction in C only produced N_2O_4, NO remaining in excess, and that in contact with sulphuric acid at first the N_2O_4, as usual, dissolved with formation of nitrosyl sulphate and nitric acid, the latter being then reduced by the NO present to nitrosyl sulphate. But when considering this experiment without any bias, it seems much more simple and nearer the truth to assume that in this case, that is in the presence of an insufficient quantity of oxygen, from the first N_2O_3 was formed (in the state of gas !), along with a little N_2O_4 and some free oxygen, but leaving no NO uncombined. The reasons for this are : 1st, that the chamber crystals *instantly* appeared when the acid came in contact with the

gas ; 2nd, both the want of colour of the issuing gas and the analysis of the acid lead to the conclusion that no NO was present, for this does not at all react instantly and completely with nitric acid dissolved in sulphuric acid. This I had found myself in former experiments, and it has been confirmed by others, *i.e.*, by Groves (*Proc. Chem. Sec.*, 1885, p. 24), who remarks that it was difficult to reduce the solution of HNO_3 in H_2SO_4 by NO ; 3rd, if primarily no N_2O_3 had been formed, the 180 c.c. O would have combined with 360 c.c. NO to form N_2O_4, leaving 137·5 c.c. NO in the free state, so that 72·3 per cent. of the nitrogen would have been present as N_2O_4, 27·7 per cent. as NO. Now, even if these 27·7 per cent. NO had instantly and completely acted in the way mentioned in No. 2, they could not have converted more than an equal percentage of nitrogen present as N_2O_4 into nitrosyl sulphate, thus leaving over 44·6 per cent. nitrogen as N_2O_4. But analysis showed 94 per cent. nitrogen as N_2O_3 and only 6 per cent. as N_2O_4. There seems to be no way out of the conclusion, that in the reaction of the gases a considerable quantity of N_2O_3 was formed, along with a little N_2O_4, leaving some oxygen in excess which, as we have seen in the preceding paper, does not act upon N_2O_3. This proves that *oxygen with an excess of nitric oxide forms mostly nitrogen trioxide, and furnishes a further proof that nitrogen trioxide exists in the state of gas.*

III. *Nitric Oxide and Excess of Oxygen in the presence of Moisture.*— The vessel C, before filling it with oxygen, was rinsed with water, so that a very few drops remained therein ; 497·5 c.c. NO and 375 c.c. oxygen were employed. When these were mixed, a strong vacuum was formed in C, the acid rushing into it with vehemence when the tap E was opened, and absorbing the gas. Analysis showed 98 per cent. of the nitrogen to have passed over into nitric acid, and 2 per cent. into N_2O_4. Hence that minimal quantity of water had sufficed for giving a totally different character to the action; NO now passed almost entirely, and with more water no doubt would have passed altogether into HNO_3. Whether an intermediary formation of HNO_2 took place or not, the experiment did not show ; certainly no green colour of the drops could be observed.

IV. *Nitric Oxide and Excess of Oxygen in the presence of Dilute Sulphuric Acid.*—The acid was taken at sp. gr. 1·405, because acids of something like that concentration, according to my former researches, can contain only traces of nitrosyl sulphate, whence it might be inferred that they would not act in favour of the formation of that compound ; it remained to be seen whether for all that the presence of sulphuric acid would induce the formation of N_2O_3. The vessel C was charged with 10 c.c. sulphuric acid of sp. gr. 1·405, and with the remaining 487·5 c.c. NO there was mixed 365 c.c. oxygen, which had

to bubble through the acid. The atmosphere of the vessel as usual assumed a reddish-brown colour, the acid gradually a slight green colour. After standing a quarter of an hour 50 c.c. of strong sulphuric acid was introduced, which at once absorbed the reddish gas—carbon dioxide being passed through as before. The analysis of the acid showed that 89·8 per cent. of the nitrogen was present as nitric acid, and 10·2 per cent. as nitrosyl sulphate. Hence we must conclude that the dilute sulphuric acid acted on the whole like water, that is, it induced the oxidation of NO up to HNO_3. Still it is seen that, even at that dilution, sulphuric acid to a certain extent favours the formation of N_2O_3, probably so far as nitrous acid forms a stable solution in the acid, which seems to produce the green colour. Owing to the complication of the conditions I would not draw any definite conclusions from this experiment.

V. *Nitric Oxide and Oxygen in Excess, in the presence of Concentrated Sulphuric Acid.*—An experiment in this direction was performed against my will the first time I operated, when the glass tap E had not yet been provided, as during the passage of oxygen into the vessel C holding the NO, the sulphuric acid from D passed back into C. Thus the combination between O and NO took place at first in the absence, subsequently in the presence of strong sulphuric acid. The result was that 39·4 per cent. of the nitrogen was found as N_2O_3, and 60·6 per cent. as N_2O_4.

A further experiment was then made in this way. The vessel C was first charged with 50 c.c. strong sulphuric acid and then filled with oxygen, several litres of this gas being passed through the acid and away through E and D. There would now be 447·5 c.c. O in the vessel C. The nitric oxide was this time put into A, and 370 c.c. of this was very gradually forced over into C, so that at first only one or at most two bubbles per second passed through the acid, which was shaken up from time to time. Thus each bubble of NO met with an enormous excess of oxygen, but mostly in immediate contact with concentrated sulphuric acid. The colour of the gas was very faintly yellow ; later on, when, in consequence of the partial vacuum in C, the NO passed over more rapidly, the colour deepened to some extent. On the sides of the cylinder, wetted with acid on shaking about, a strong formation of chamber-crystals took place. After all the NO had been introduced, the whole was allowed to stand a quarter of an hour, the yellow colour gradually disappearing. The final analysis showed 68·7 per cent. of nitrogen to have passed into N_2O_3, 31·3 per cent. into N_2O_4. Since, of course, as shown by the yellow colour, part of the NO did not combine with oxygen in immediate contact with the acid, but higher up in the cylinder, we arrive at the following conclusion. Where nitric oxide meets with

oxygen, even with an enormous excess of this, but in immediate contact with concentrated sulphuric acid, N_2O_3 is formed, which at once combines with sulphuric acid to form nitrosyl sulphate ; but further on, that is, in the space above the acid, the ordinary reaction $2NO + O_2 = N_2O_4$ takes place. This completely agrees with previous observations. On the one hand, it has been observed, first by C. Winkler, and confirmed by myself in several series of experiments, part of which have been published, that, when strong sulphuric acid, oxygen, and nitric oxide meet at the same time, *e.g.*, if nitric oxide and oxygen are made to bubble up through the acid side by side, the acid is found to contain nothing but N_2O_3, *i.e.*, nitrosyl sulphate. On the other hand, I had formerly found that, when the two gases are passed through the acid so quickly that they are not entirely absorbed and can only combine completely in the upper part of the vessel, and when the product here formed is absorbed in a second bottle charged with sulphuric acid, analysis of the latter shows it to be composed of N_2O_4. Hence there is nothing like a " catalytic " action of sulphuric acid for determining the combination of 2N with 3O, without any share in this being taken by H_2SO_4; the sulphuric acid only acts if it can itself enter into the combination.

The conclusions to be drawn from the above-described experiments can be formulated thus :—

1. In the dry state, nitric oxide with an excess of oxygen combines to form N_2O_4 exclusively, or nearly so.

2. Dry nitric oxide and oxygen with an excess of the former, yield a great deal of N_2O_3 along with N_2O_4, both in the state of gas.

3. In the presence of water, nitric oxide, with an excess of oxygen, is altogether converted into HNO_3.

4. If nitric oxide and oxygen meet in the presence of concentrated sulphuric acid, there is neither N_2O_4 nor HNO_3 formed, even with the greatest excess of oxygen, but the reaction is—

$$2SO_4H_2 + 2NO + O = 2SO_2(OH)(ONO) + H_2O.$$

Regarding the theory of the vitriol-chamber process, the above-established facts, taken in connection with those elicited by myself and Naef from the examination of a working set of chambers (*Chemische Industrie*, 1884, p. 5), where it was proved that under normal conditions the back chambers contain no N_2O_4, but N_2O_3, lead to the following conclusions. Since the chamber always contains an enormous excess of oxygen, any NO (which according to the general assumption as held hitherto is being constantly liberated) must principally pass into N_2O_4; for the particles of sulphuric acid, floating about in the shape of a mist, cannot act on the molecules of gas coming in contact with one another at some distance from the acid

particles.   But it has been established that little or no N_2O_4 is formed
so long as there is any appreciable formation of H_2SO_4, *i.e.*, so long
as appreciable quantities of SO_2 are present in the chamber.   Hence
no free NO can be given off at all, but the process must take place in
the following phases, both of them very well-known reactions :—

(1.) $2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2(OH)(ONO)$,
(2.) $2SO_2(OH)(ONO) + H_2O = 2SO_2(OH)_2 + N_2O_3$.
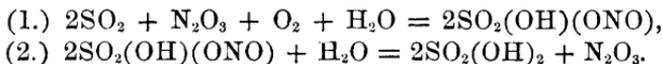
That is, sulphur dioxide combines directly with nitrogen trioxide,
oxygen, and a little water to form nitrosyl sulphate, which floats in
the chamber as a mist; on meeting an excess of water, equally
floating about as a mist, the nitrosyl sulphate splits up into sulphuric
acid, which sinks to the bottom, and nitrogen trioxide, which begins
to act anew.   *Hence it is not, as hitherto generally assumed, the nitric
oxide*, NO, *but the nitrogen trioxide*, N_2O_3, *which acts as carrier of the
oxygen in the vitriol-chamber process*.   This process is to some extent
modified in the first part of the set of chambers by the excess of SO_2,
in the last part sometimes by the complete absence of SO_2, and in
some places by an excess of water.   On this, as well as on several
other points of importance, I shall enter in a special communication
to be published later on.

[ADDENDUM.—After the above two papers had been read, Dr. Arm-
strong made some observations to which I beg to reply here, as I was
not present at the meeting.   Dr. Armstrong says that my results are
vitiated by the fact that NO reduces NO_3H to the nitrous state.   This
is a mistake; in the only case where that reaction comes into play
(Experiment No. II), I have shown that, even if the reducing action
of NO is assumed to have taken place to the fullest possible extent,
a large excess of N_2O_3 remains unaccounted for by any other theory
than that it existed in the gaseous state.   With my experiments of
1879 that action of NO has no connection whatever.   Dr. Armstrong
says it is probable that in those experiments the gases never became
thoroughly mixed.   This is also a mistake; the gases (that is, the
vapour of N_2O_3 and a large excess of atmospheric air) were introduced
in concentric layers at the top of a **U**-tube, kept at different tempera-
tures, from $4—150°$ (where the changes of temperature must have pro-
duced constant currents), were passed along the tube and through
some very narrow tubing into sulphuric acid, where all the absorbable
part was taken up.   It is hardly conceivable that in this way any NO
could have escaped coming into contact with oxygen present up to
$10\frac{1}{2}$ times the theoretical quantity, and practically impossible that this
should have taken place to the extent observed, namely, up to 75 per
cent. of the total nitrogen compounds present.   Lastly, Dr. Armstrong

says that Naef's and my own observations on the composition of the chamber gases are a complete riddle to him. Those observations, extending over several months, are *facts*, and must be dealt with as such; they cease to be a riddle the moment one drops the idea that N_2O_3 cannot exist as a gas. That N_2O_3 once formed is not oxidised by any excess of O has been proved by myself for the gaseous state, and by Ramsay and Cundall for the liquid state. If there are really no other objections to my views than those advanced by Dr. Armstrong, then it must be considered as definitely proved that N_2O_3 exists as a gas.]