XXVI.—*The Oxides of Nitrogen.*

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THE researches of chemists on the methods of production and formula of nitrogen trioxide are somewhat difficult to reconcile with each other. It is commonly believed that the indigo-blue or green liquid produced by the action of arsenious anhydride on nitric acid has the formula N_2O_3; and that it is capable of direct union with oxygen, forming nitric peroxide. Early in 1884 an attempt was made in this laboratory to convert this green liquid into a red one by passing a current of oxygen through the green liquid kept in a freezing mixture; but the change of colour was so slow, and the excess of oxygen used was apparently so large, that there was some doubt as to the possibility of direct union. And on referring to the literature of the subject there appeared sufficient grounds for a new investigation. The colour of nitrogen tetroxide is markedly red, and that of the product of the action of arsenious anhydride on nitric acid of so deep a blue, that it appeared probable that a mixture of the trioxide and tetroxide of nitrogen would be of some intermediate tint; yet analyses of the blue liquid always point to its being a mixture of both trioxide and tetroxide. Hasenbach (*J. pr. Chem.* [2], **4**, 1) states that nitric oxide and peroxide unite to form the trioxide when passed through a red-hot tube; and he also states that the trioxide prepared in this way can be reconverted into nitric peroxide by passing a current of oxygen through it when kept in a freezing mixture.

It has been remarked by J. Moser (*Pogg. Ann.* [2], **2**, 139) that the absorption-spectra of gaseous trioxide and tetroxide are identical; this would imply at least partial dissociation according to the equation: $N_2O_3 = NO_2 + NO$.

It is hardly to be expected that a liquid of a deep blue colour would yield a gas having properties optically identical with the gas of a red liquid, and a dispute has arisen on that point (*Berl. Ber.*, **11**, 1229—1641; **12**, 357 and 2188) between Lunge and Witt. Whilst Witt maintains that the product of the action of arsenious oxide or starch on nitric acid consists essentially of peroxide, any nitrous anhydride fumes dissociating completely on passing into gas, Lunge has endeavoured to show that the gas absorbed by sulphuric acid consists wholly of N_2O_3. His argument is that if dissociation were to take place the nitric oxide would escape absorption; Witt, however, replies that sulphuric acid containing nitric acid is capable of absorbing nitric oxide.

We hope that this research may be considered as reconciling these contradictory statements.

The substance which served as a starting-point for our investigations was prepared by the action of nitric acid on arsenious oxide. Sometimes pure strong nitric acid (density 1·5) was used, and in some cases strong sulphuric acid was added to the mixture before applying heat.

The gas was first passed through a **U**-tube containing arsenious oxide to react with any nitric acid that might have been carried over, and it was then dried. The only suitable drying agent was found to be phosphoric pentoxide, as the gas dissolved in sulphuric acid (reacting with it), and it also reacted with calcium chloride forming nitrosyl chloride.

The gas after passing through **U**-tubes containing phosphorus pentoxide was led into a bulb with two necks surrounded with a freezing mixture of ice and hydrochloric acid. To complete the apparatus, another drying tube was added to prevent moisture diffusing back. Joints as far as possible had to be sealed; where this was impossible, corks were used, india-rubber being quite inadmissible. The liquid was then put into small weighed bulbs with long stalks, the bulbs holding about 0·75 c.c. The stalks were afterwards sealed and re-weighed, thus giving the weight of liquid taken.

The first method of analysis which we adopted was as follows:—One of the weighed bulbs of oxide was placed in a well-stoppered bottle holding about 700 c.c., together with 25 c.c. of normal standard caustic soda (in case of very large bulbs 50 c.c. of soda were taken); some water was added to prevent heating, and the bulb was broken by shaking the bottle. The bottle was then well shaken until all the oxide had combined with the soda; and the uncombined soda was titrated with standard sulphuric acid, phenolphthaleïn being used as an indicator.

Method of Calculation.

Let x = number of c.c. of standard soda
and y = " " acid
$\therefore x-y$ = " soda neutralised by the nitrogen oxide.

1 c.c. of standard soda contains 0·04013 gram of NaHO.

$\therefore (x - y)\ 0{\cdot}04013$ = weight of NaHO neutralised by the nitrogen oxide.

But 1 equivalent of NaHO = 1 equivalent of nitrogen, whether as nitrous or nitric acid.

Hence $\dfrac{(x-y)\ 0{\cdot}04013 \times 14}{40}$ = weight of nitrogen in 3 grams of oxide (the weight taken).

$\therefore$ Percentage of nitrogen in oxide $= \dfrac{(x-y)\ 0{\cdot}04013 \times 14 \times 100}{40 \times 2}$

and subtracting this number from 100 gives the percentage of oxygen.

In the first batch of bulbs, the liquid was of indigo-green colour. Bulb 1 contained 0·7627 gram of liquid, and was broken into 25 c.c. of soda; calculating as above, this gives the result 30·4 per cent. of nitrogen and 69·6 per cent. of oxygen. Bulbs 2 and 3 gave the same result, which is therefore the mean of the batch, and is precisely the percentage in nitrogen peroxide (N_2O_4). Tabulating this and subsequent results gives the following table:—

Batch.	Bulb.	Nitrogen per cent.	Oxygen per cent.	Mean per cent. of N.	Colour.	Method of formation.
I....	1	30·4	69·6	—	indigo-green	From As_2O_3, HNO_3, and H_2SO_4.
	2	30·4	69·6	30·4		
	3	30·4	69·6	—	—	
II....	1	28·1	71·9	28·94	olive-green	Similar to I.
	2	29·79	70·21	—		
III....	1	29·6	70·4	28·65	red	Similar to I.
	2	27·7	72·3	—	—	
IV....	1	31·93	68·07	31·56	indigo-blue	By passing NO over batch III.
	2	31·20	68·80	—		
V....	1	31·2	68·8	—	—	Similar to I.
	2	29·98	70·02	29·82	red	
	3	28·3	71·7	—	—	
VI....	1	30·4	69·6	30·5	indigo-blue	By passing NO over batch V.
	2	29·7	70·3	—		
VII....	1	28·6	71·4	28·5	green	By passing O over batch VI.
	2	28·4	71·6	—	—	

The inferences that may be drawn from these figures are, firstly, that the method of estimation gives the nitrogen too low, probably on account of nitric oxide being formed and not being acted on by the soda. Secondly, that the blue liquid contains a far smaller percentage of nitrogen, if it be N_2O_3, than it should proportionally to the red liquid which is presumably N_2O_4. Thirdly, that passing nitric oxide over the red liquid gives a blue liquid in which the percentage of nitrogen is increased, but only to a limited extent. And, lastly, that passing oxygen in the same way reduces the percentage of nitrogen.

After this plan had been tried, some confirmatory methods were sought, but for some time without success. The first of these was to estimate the nitrous acid in the neutralised solutions of the previous process by means of standard potassium permanganate, but this was found unsatisfactory on account of the inconvenient and tedious time reactions which take place. Then a method involving the use of iodide of potassium and standard sodium thiosulphate was tried in the same manner, but failed for a similar reason.

An entirely different principle was now tried, depending on the fact that when nitrous acid is warmed with hypobromite of soda it gives off its nitrogen; in this case, however, the results were found to be so untrustworthy as to be useless. This last remark also applies to the fourth unsuccessful method, which consisted in combining the oxide with ammonium hydrate; it was thought that ammonium nitrite would be formed and that, on boiling, this would decompose into nitrogen and water. It was found, however, that the results obtained in this reaction were not quantitative. Advantage was then taken of the fact that when nitrogen trioxide or tetroxide is dissolved in sulphuric acid, and the solution is shaken with mercury, all the trioxide or tetroxide is evolved as nitric oxide. This reaction was made use of in the following way:—

A thickish glass tube, about 90 cm. long and 2 cm. in cross section, was graduated into mm., filled with mercury, and inverted in a trough. One of the bulbs was then slipped in and the height of the mercury measured both with a cathetometer and on the tube; this gave the barometric pressure. The bulb was then broken by shaking (a piece of glass rod being inserted to aid this process), and when all the liquid had evaporated the height of the mercury was measured in the same way. (This reading was taken for a purpose to be considered hereafter.) It may be well to mention here that the mercury was not appreciably attacked by the gas.* Then about 10—20 c.c. of strong sulphuric acid was passed up the tube by means of a bent pipette, and the tube was shaken to make the gas dissolve; nitric oxide was immediately evolved, and to complete the action the tube was shaken lengthways to break up the mercury and bring it in thorough contact with the sulphuric acid. The tube was allowed to stand until it had acquired the temperature of the air; this was then observed, and the height of the mercury read as before. The volume occupied by the gas was found by emptying the tube, inverting it, and filling it up to the read height with water from a burette, allowance of course being made for the volume of the piece of glass used to break the bulb.

The volume of the nitric oxide was corrected for temperature, and for the pressure diminished by the length of the column of mercury. The pressure exerted by the column of sulphuric acid was calculated and added.

The percentage of nitrogen in that volume, and hence in the weight of liquid taken, was calculated in the usual way. The following table gives the results of the analyses:—

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* Naumann states that the peroxide slowly attacks mercury. In ascertaining the vapour-density of the peroxide at various temperatures and pressures, he allowed for a slow contraction produced by this action on mercury. It is probable that the care which was taken in drying the product we used was the cause of the mercury remaining unattacked: certainly no contraction was observed, even after some hours' standing, although the surface of the mercury became at once somewhat tarnished.

Batch.	Bulb.	Percentage of N.	Percentage of O.	Mean per cent. of N.	Remarks.
A......	1	29·9	70·1	—	Colour greenish, made from As_2O_3, HNO_3, and H_2SO_4.
	2	30·5	69·5	30·2	
B......	1	29·67	70·33	29·8	Colour olive-green. Made similarly to A.
	2	29·93	7·07	—	
C......	1	29·59	70·41	29·69	Colour red. Made similarly to A.
	2	29·79	70·21	—	
D......	1	31·47	68·53	—	Colour indigo-blue. Made by bubbling NO into batch C. Bulb 1 taken half way, 2 three quarters, and 3 at end of process.
	2	31·73	68·27	—	
	3	32·50	67·50	—	
E......	1	28·82	71·18	29·06	Colour red. Made similarly to A.
	2	29·31	70·69		
F......	1	32·81	67·19	32·44	Colour indigo-blue. Made by mixing the vapour of E with excess of NO, and condensing product at − 20° to − 25° C. Liquid very volatile.
	2	32·50	67·50		
	3	32·70	67·30		
	4	32·80	67·20		
	5	31·75	68·25		
	6	31·60	68·40		
	7	31·97	68·03		
	8	32·97	67·03		
	9	32·88	67·12		

In batch A only a small proportion of sulphuric acid was used, hence the greenish colour, which in batch B we find is turning more olive-green, *i.e.*, is more nearly peroxide, more sulphuric acid having been used.

With batches C and E excess of sulphuric acid was employed, and pure peroxide was produced. With batch D the NO was bubbled through the liquid; and it is noticeable that the end percentage is about the same as the mean percentage in batch F, when a greater excess of NO was used, and the oxides were mixed in the gaseous state. From the reading taken before the sulphuric acid was passed up, the vapour-densities at the particular temperatures and pressures were calculated for batch F, and this leads to an important result.

The volumes being read and corrected, and their weights being known, the vapour-densities were easily calculated. They are given in the subjoined table :—

Bulb.	Volume.	Weight taken.	Temperature.	Pressure.	Derived V.D.
1	125·0 c.c.	0·1590 grm.	19·5° C.	342·8 mm.	33·73
2	125·5 ,,	0·1679 ,,	13·2 ,,	356·7 ,,	33·36
3	143·2 ,,	0·1625 ,,	17·4 ,,	298·5 ,,	34·31
4	153·0 ,,	0·1990 ,,	15·7 ,,	331·8 ,,	35·18
5	142·0 ,,	0·2186 ,,	10·9 ,,	396·0 ,,	34·22
6	144·5 ,,	0·2280 ,,	10·0 ,,	403·5 ,,	34·39
7	147·0 ,,	0·2400 ,,	9·8 ,,	415·3 ,,	34·55
8	164·5 ,,	0·3242 ,,	10·5 ,,	481·5 ,,	36·05
9	179·0 ,,	0·3887 ,,	9·8 ,,	521·5 ,,	36·90

From the analyses (here we are only dealing with batch F) the mean percentage of nitrogen was found to be 32·44 per cent. Let us call this percentage a. Then percentage of oxygen $= 100—a$.

Composition by theory, N_2O_4. N p. c. = 30·43. O p. c. = 69·57.
N_2O_3. N p. c. = 36·84. O ,, = 63·16.

But the liquid obviously consists of a mixture of N_2O_3 and N_2O_4.

Let $x = N_2O_4$ per cent.; then $100 - x = N_2O_3$ per cent.
Then $30{\cdot}43x + 36{\cdot}84\,(100 - x) = 3244$.
whence $n = 68{\cdot}64$.

Therefore the percentage of N_2O_3 in the mixture = 31·3, and N_2O_4 = 68·7.

It seems highly probable that the nitrogen trioxide dissociates when it changes into gas, $N_2O_3 = NO + NO_2$, or more correctly, $N_2O_3 = NO$ + a varying mixture of NO_2 and N_2O_4, according to temperature and pressure.

Now, as it is doubtful to what extent this dissociation takes place, it was necessary to find what the vapour-density would be if the gas were wholly dissociated into NO and N_2O_4. But N_2O_4 is itself a dissociable gas, giving NO_2 in varying quantities, at different temperatures and pressures. The extent of this dissociation has been investigated by Playfair and Wanklyn, by Troost, and by Naumann, and from their numbers a formula representing the extent of dissociation has been calculated by J. W. Gibbs (*Amer. Jour. Sci.*, **18**, 1879).

This equation is—

$$\text{Log}\,\frac{15{\cdot}89(D - 1{\cdot}589)}{(3{\cdot}178 - D)} = \frac{3118{\cdot}6}{t_c + 273} + \log p\ 12{\cdot}451,$$

t_c denoting the temperature on the centigrade scale. The numbers 3·178 and 1·589 represent the theoretical densities of N_2O_4 and NO_2 respectively, as compared with air. The two other constants were determined by the experiments of Deville and Troost. Another difficulty arises from the presence of NO, owing to the decomposition of the N_2O_3. This nitric oxide occupies volume and reduces pressure as far as the NO_2 and N_2O_4 are concerned. As in air at 760 mm., the oxygen is exposed to a partial pressure (for it occupies one-fifth of the total volume, and is spread out through the whole volume), so the presence of nitric oxide reduces the pressure on the other constituents of the gaseous mixture. Hence it is necessary to calculate the weight and volume of the NO present, on the supposition that all the N_2O_3 has been decomposed into NO and (NO_2 + N_2O_4). This amount was accordingly calculated; analysis and the previous calculation showing the substance to contain 31·3 per cent. of nitrogen trioxide. This nitrogen trioxide, if we may regard it as dissociated, would give the following numbers: 76 parts by weight of nitrogen trioxide would dissociate into 46 parts of (N_2O_4 + NO_2) and 30 parts of nitric oxide. Therefore, by a very simple calculation, we find that the above-mentioned 31·3 per cent. of trioxide would give, by dissociation, 18·967 per cent. of tetroxide. Adding this 18·967 per cent. to the 68·7 per cent. already present, we have a total of 87·67 per cent. of (N_2O_4 and NO_2). Subtracting this number from 100 gives 12·33 per cent. by weight of NO. Now, applying this to the result with bulb 1, we have as the weight of substance taken 0·1590 gram, containing 12·33 per cent. of NO, or 0·019605 gram; this weight occupies at standard temperature and pressure, a volume of 14·59 c.c., which, being corrected to the observed temperature (195° C.) and pressure (342 mm.), gives a volume of 34·74 c.c. But the total volume at the observed temperature and pressure is 125 c.c. Subtracting from that the volume of NO (34·74 c.c.), we arrive at the volume of the (NO_2 + N_2O_4) = 90·26 c.c. Therefore the pressure is diminished (as in the before cited case of oxygen in air) in the proportion of 125 : 90·26. And calculating from this the actual pressure to which the (NO_2 + N_2O_4) is subjected, we find that the observed pressure is reduced from 342·0 mm. to 247·0 mm.

Now, the theoretical density of (NO_2 + N_2O_4) at 19·5° and 247·0 may be calculated by means of J. W. Gibbs's formula, where if we set—

Δ (a constant given in his table) $= \frac{D}{D_1}$. Then

$$L = \log \frac{1000D_1(D - D_1)}{(2D_1 - D)^2} = \log \frac{1000(\Delta - 1)}{(2 - \Delta)^2},$$

we have for peroxide of nitrogen (NO_2 + N_2O_4).

$$L \text{ (the V.D compared with air)} = \frac{3118·6}{t_c + 273} + \log p - 9·451.$$

On taking the corresponding value of Δ in Gibbs's table, we find that the vapour-density compared with air of the substance in this case is 2·5583, or compared with hydrogen 36·93.

Having now the density of our two components, it is easy to calculate the density of the mixture of 87·67 parts of ($NO_2 + N_2O_4$) of density 36·93 with 12·33 parts of NO of density 15·0.

$$D = \frac{(87{\cdot}67 \times 36{\cdot}93) + (12{\cdot}33 \times 15)}{100};$$

Whence D = 34·225; whereas the found density was 33·73, a sufficiently close approximation. Applying this calculation to all the vapour-densities we get the following table:—

Bulb.	1.	2.	3.	4.	5.
$t°$ (observed)	19·5°	13·2°	17·4°	15·7°	10·9°
p "	342·0	356·7	298·5	331·8	396·0
Weight in grams	0·1590	0·1679	0·1625	0·1990	0·2186
Vol. in c.c. = A	125·0	125·5	143·2	153·0	142·0
Corr. vol. of NO = B	34·74	34·44	39·96	44·24	40·03
A − B	90·26	91·09	103·24	108·76	101·96
Corr. press.	247·0	258·9	215·2	235·8	284·37
L	3·604	3·859	3·732	3·872	3·968
D_1 (Theor. V.D. of $NO_2 + N_2O_4$).	36·93	38·76	37·89	38·92	39·68
D_2 (Theor. V.D. of subs.)	**34·22**	**35·83**	**34·07**	**35·95**	**36·63**
Found V.D. of substance	**33·73**	**33·36**	**34·31**	**35·18**	**34·22**

Bulb.	6.	7.	8.	9.
$t°$ (observed)	10·0°	9·8°	10·5°	9·8°
p "	403·5	415·3	481·5	521·5
Weight in grams	0·2280	0·2400	0·3242	0·3887
Vol. in c.c. = A	144·5	147·0	164·5	179·0
Corr. vol. of NO = B	40·85	41·75	48·76	58·86
A − B	103·65	105·25	115·74	120·14
Corr. press.	289·43	297·35	338·78	350·01
L	4·030	4·050	4·079	4·121
D_1 (Theor. V.D. of $NO_2 + N_2O_4$).	39·86	39·95	40·117	40·37
D_2 (Theor. V.D. of subs.)	**36·80**	**36·88**	**37·02**	**37·24**
Found V.D. of substance	**34·39**	**34·55**	**36·06**	**36·9**

Thus it is plain that the N_2O_3 prepared by us does not exist in the state of gas; but, if cooled, it condenses to a liquid more or less mixed with ($N_2O_4 + NO_2$), in which the highest percentage of N_2O_3 found is only about 30 at − 25° C., but probably would increase at lower temperatures.

To recapitulate, the facts worthy of note are—

Firstly, that arsenious oxide when heated with nitric acid gives a liquid containing N_2O_3 according to the equation—

$$2HNO_3 + As_2O_3 + nH_2O = N_2O_3 + As_2O_5,(n + 1)H_2O;$$

but that when the water given off in this reaction is absorbed by sulphuric acid no N_2O_3 is formed, but a red liquid consisting of $(N_2O_4 + NO_2)$, thus:—

$$4HNO_3 + As_2O_3 + nH_2SO_4 = 2N_2O_4 + As_2O_5 + nH_2SO_4,2H_2O.$$

We may also suppose this to be the normal reaction, and assume that the peroxide is subsequently decomposed by water, thus:—

$$2N_2O_4 + H_2O = 2HNO_3 + N_2O_3.$$

If ordinary nitric acid be used, there is complete dissociation of the resulting N_2O_3 immediately on its passage into the gaseous state; and on cooling with a freezing mixture a portion of the peroxide condenses as such, while a portion combines with the nitric oxide present to form trioxide.

Secondly, the passage of NO through this red liquid seems merely to produce N_2O_3 to a certain extent, depending on the temperature; and this amount is not increased by great excess of NO.

Thirdly, the passage of oxygen into the blue liquid converts it into $(N_2O_4 + NO_2)$, but this reaction is a very slow one. It is indeed doubtful if the reaction takes place with liquid trioxide.

Fourthly, the presence or absence of moisture does not appear to influence the combination. To settle this point, on January 10th, 1885, a large bulb of oxygen very carefully dried was sealed up with phosphoric pentoxide, inside a larger bulb of very carefully dried nitric oxide, also in contact with a large amount of phosphoric pentoxide. On January 15th, the inside bulb in the first apparatus was broken, and a red colour appeared. On February 9th another was broken, and the red colour again appeared, showing that combination had taken place. On February 16th a third was broken with the same effect.

Lastly, nitrogen trioxide does not exist in the state of gas, and probably not as a pure liquid, except perhaps at very low temperatures. It is probable that dissociation occurs even in the liquid state. It is well known that the liquid peroxide, when cooled, becomes colourless, and when heated, of a brown-red colour. A very thick piece of barometer tubing filled with a dark-blue specimen, presumably rich in trioxide, was heated in boiling water; and its colour changed to the indefinite mixed shade of red and green. No evolution of gas from the liquid was observable, and, on cooling, the whole of the liquid changed to a blue colour, and not the surface merely; the latter might have been expected if the liquid had given off nitric oxide, which would naturally fill the upper half of the tube, and react gradually with the peroxide, attacking the top layers first. It is, however, conceivable that the deepening in intensity of colour which the peroxide undergoes on heating may have produced the change from blue to the mixed tint.

[ADDENDUM, February 28th.—In the discussion on this paper, Dr. Armstrong stated that, in his opinion, nitrous acid is *the* product of the action of arsenious oxide on nitric acid, and that the reactions of more or less concentrated acid can be explained on this assumption by the following equations :—$3HNO_2 = 2NO + HNO_3 + H_2O$: but in presence of nitric acid, $HNO_2 + HNO_3 = N_2O_4 + H_2O$. Against this view, the authors have nothing to urge; but it appears to them that it is quite as legitimate to state that nitric peroxide is *the* product, and that it undergoes reactions as follows :—

1. If water is absent, (*i.e.*, removed from the sphere of action by a dehydrating agent) the peroxide distils over as such.
2. If water is present, $2N_2O_4 + H_2O = N_2O_3 + 2HNO_3$; and the mixture of gases resulting from the volatilisation of the N_2O_3 pass away.
3. With less water, these products are mixed with the original peroxide.

As regards the formation of nitrosyl sulphate, the authors have recently prepared it in large quantity by what they consider, after many trials, to be by far the simplest method, viz., to add to cooled oil of vitriol in which some crystals of pyrosulphuric acid have been dissolved, liquid nitric peroxide, until the liquid, at first viscous, becomes mobile. At this stage, an abundant crop of crystals separates out, and the supernatant liquid consists largely of nitric acid. They would not, however, be understood to imply that by passing nitric oxide into a mixture of nitric and sulphuric acids, nitrosyl sulphate is not produced.

In conclusion, the authors wish to state definitely that the nitric oxide passed over the tetroxide, converting it into the blue liquid which they believe to be largely trioxide, cannot have contained enough water to cause the reaction $2N_2O_4 + H_2O = N_2O_3 + 2HNO_3$ to take place; for the nitric oxide was dried by slow passage first through strong sulphuric acid, then through three long U tubes filled with phosphoric anhydride, and, finally, was mixed with gaseous peroxide dried in a similar manner; the mixture obtained in this way condensed, forming the blue liquid. This experiment was undertaken with the express object of ascertaining whether water was the determining cause of the combination.

It may be that absolute freedom from water is not attainable even with these precautions; but the minute trace of water, if present, would, in these experiments, play a part analogous to that which Mr. Harold Dixon has recently shown it to perform in determining the combination of carbon monoxide with oxygen.]