CLXXIX.—Gaseous Nitrogen Trioxide.

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NITROGEN trioxide has been shown to exist (Ramsay and Cundall, Trans., 1885, 47, 187; Ramsay, Trans., 1890, 57, 590) in the green liquid obtained by the condensation of the gas evolved by the action of nitric acid on arsenic trioxide. It was found that on allowing the liquid to evaporate, almost complete dissociation took place, and the gas consisted almost entirely of nitrogen peroxide and nitric oxide. The discovery by one of us that traces of moisture were necessary for the dissociation of ammonium chloride (Trans., 1894, 65, 616), mercurous chloride, and other substances (Trans., 1900, 77, 645), led us to investigate the question whether, in the dried condition, nitrogen trioxide could be obtained in the gaseous state.

In order to obtain the liquid available for experiment, it was necessary to seal it up in bulbs without contact with atmospheric moisture. In order to do this, a series of ten bulbs was blown on a thin capillary tube the outside diameter of which was about 0.5 mm. The end of this tube was sealed to a tube of about 20 c.c. capacity, and the whole dried by heating while a current of dried air was drawn through. A plug of ignited asbestos was placed in the junction of the capillary and the wide tube, and plugs of redistilled phosphorus pentoxide introduced. The tube was closed and allowed to stand for a week to ensure the drying of the internal surface of the glass. The nitrogen trioxide was prepared by the action of nitric acid (sp. gr. 1.3) on arsenic trioxide. The gas was passed first through a long worm tube cooled by ice in order to condense any nitric acid carried over. It was then dried by a tube of phosphorus pentoxide, and condensed in the tube described above, which was cooled by pounded ice and calcium chloride. When sufficient liquid had been condensed, a current of nitric oxide, dried by phosphorus pentoxide, was bubbled through it for an hour, and the tube sealed. It was left to dry for three weeks. By cooling the bulbs, the liquid distilled over, and by means of a very fine-pointed blow-pipe flame the capillaries between the bulbs were drawn off, and the bulbs containing the liquid were washed in distilled water and dried in a desiccator. The sealing off of these bulbs was an operation of extreme delicacy, and many attempts resulted in failure. Sealing by means of a fine, red-hot platinum wire was tried, but the method left the ends of the capillaries so thin that they burst when the liquid attained the ordinary temperature.

Many methods were tried before a satisfactory analysis of the liquid could be obtained. Potassium permanganate, potassium iodide, ammonia, and carbamide solution were all tried as reagents for estimating the oxygen or nitrogen, and failed to give constant This was also the case with the ordinary nitrometer method results. with mercury and sulphuric acid, the volume of the nitric oxide evolved being always too small. A possible explanation of the latter fact is that nitric oxide is not the only gas produced. In one experiment, the gas was transferred to another nitrometer and showed considerable contraction when treated with alcohol, and the residue was not all absorbed by ferrous sulphate solution, indicating the presence of nitrogen and nitrous oxide. A direct method was then resorted to. A weighed bulb of the liquid was introduced into a thick-walled Jena glass tube with a piece of glass rod for breaking it. In the other end was placed a weighed roll of copper gauze enclosed in a thin-walled Jena tube open at both ends. The wider tube was then drawn out at each end, filled with dried nitrogen and sealed. The bulb was broken and the part of the tube containing the copper was heated in an improvised furnace for By breaking the capillary end of the wider tube twelve hours. in a thick-walled indiarubber tube, the excess of nitrogen was made to displace water from a wash-bottle into a weighed flask, thus giving a rough estimation of the nitrogen in the trioxide. This estimation must always give results which are too low, since the sealing of the tube, however carefully done, must heat and expand some of the original nitrogen. If it had been possible to use large quantities of the liquid, the error would have been minimised, but attempts to do this led to the explosion of the whole. The oxygen was estimated by the gain in weight of the copper. The results were:

	Weight of liquid.	Increase in weight of copper.	Percentage of nitrogen.	Percentage of oxygen.
1.	0.0856	0.0240		63.0
2.	0.1875	0.1189	35.1	63.4
3.	0.1076	0.0667	33.8	62.1
4.	0.0937	0.02980	33.9	63.8
5.	0.1145	. 0.0722	34.7	63.1

The mean percentage of oxygen is 63.08, that calculated for N_2O_3 is 63.17.

In order to show that the deficiency of nitrogen is really caused as stated above, and not by the presence of dissolved phosphorus pentoxide, a large quantity of the liquid was dissolved in cooled nitric acid, but this produced no colour with ammonium molybdate. The liquid also evaporated in air without leaving any residue. Its composition therefore corresponds to the formula N_2O_3 .

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In order to determine the density of the gas evolved by the evaporation of the liquid, weighed bulbs were broken in a Lunge's nitrometer over purified and dried mercury. The breaking of the bulb was effected by the pressure of a long glass rod which passed through an indiarubber stopper at the bottom of the nitrometer. The gas has very little effect on dried mercury. The following results were obtained by this method:

	Weight of	Time of drying			
	liquid used.	pentoxide.	Temperature.	Pressure.	Density.
1.	0.0645	6 days	15°	770 mm.	43.2
2.	0.0274	27 ,	14	747 ,,	43.6
3.	0.0512	13 "	13	768 ,,	48.6

On adding concentrated sulphuric acid to the gas, solution took place so rapidly that the rush of the mercury up the tube could not be followed by the eye, and the impact of the metal against the top of the tube threatened its destruction. This observation makes it clear that the gas does not contain a mixture of nitrogen peroxide and nitric oxide, which is shown by experiment to undergo only a comparatively slow absorption by sulphuric acid.

Other determinations of the density of the gas were made in a special form of V. Meyer's apparatus, which has been described by one of us (Trans., 1900, 77, 647). The weighed bulb of liquid was placed at the bottom of the cylindrical bulb of the apparatus and the movable glass spoon was used to support a piece of heavy glass rod. On turning the spoon, the rod dropped on to the bulb, so liberating the liquid. In order that the rod should hit the bulb, it was found necessary to seal a perforated glass tube inside the apparatus to act as a guide. The apparatus was dried by heating while a current of nitrogen was passed through. The sealed tube which formed the stopper of the apparatus contained phosphorus pentoxide, and the exit tube, which was connected with a gas measuring apparatus by the phosphorus pentoxide was continued through varying periods as shown in the table on page 1865.

The density of undissociated N_2O_3 is 38, and hence the gas obtained in these experiments must contain a higher polymeride, probably N_4O_6 , corresponding to the analogous oxides of phosphorus and arsenic. It will be noticed that there is a large variation in the densities obtained in the different experiments, and it should be mentioned that the bulbs used came from not less than eight different preparations, the liquid in which was condensed at different temperatures, and which was allowed different lengths of time to dry in contact with the phosphorus pentoxide. We hope that it

	Weight	Time of drying of the vapour density apparat	g us	Pressure	
No.	of liquid.	in days.	Temperature.	in mm.	Density.
1.	0.0649	23	22°	768	38.1
2.	0.0293	4	21	744	38.4
3.	0.0241	14	22	762	41.5
4.	0.0487	6	20	735	42.0
5.	0.0160	6	16	756	42.1
6.	0.0305	20	18	757	42.8
7.	0.0452	6	22	745	42.8
8.	0.0382	14	20	744	49.0
9.	0.1034	8	18	756	49.3
10.	0.0599	28	21	742	57.0
11.	0.1475	22	17	802	59.2
12.	0.0493	7	18	739	59.8
13.	0.0134	33	60	613	62.2

may be possible by drying the liquid at a lower temperature to obtain the higher polymeride in a pure condition.

In order to compare the behaviour of the dried and undried liquid, the same apparatus was used for determining the density of the liquid which had been contaminated by a trace of moisture. This was effected by opening the capillary of the bulb, immersed in a freezing mixture, for a few seconds and then sealing it up. The first difference noted during the density determination was that the boiling liquid rapidly lost its green colour, leaving a yellow liquid which then disappeared, whilst with the dried liquid there was no change in colour as it boiled away. The density given by this moist liquid was 28.2, the temperature being 22°. If it is calculated what density would be given by N₂O₃ breaking up into N₂O₄, NO₂, and NO at 22°, a density of 27.8 is found, so that in presence of a mere trace of moisture practically complete dissociation of the liquid takes place.

Some determinations of the molecular weight by the lowering of the freezing point of purified and dried benzene were made, to see if at the temperature of 4° and in solution the higher polymeride would be in a more concentrated state. This was not found to be the case. Two bulbs from the same preparation were used in the first case, and one from another preparation in the second.

- I. (a) 0.1364 of liquid in 10.2 of benzene gave depression 0.8° . M.W. = 83.
 - (b) 0.0455 of liquid in 10.3 of benzene gave depression 0.26°.
 M.W.=83.2.
- II. 0.0627 of liquid in 10.8 of benzene gave depression 0.29°. M.W. = 95.

In these experiments, the benzene was dried over distilled phosphorus pentoxide, and care was taken that the thermometer and the

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tube in which the experiment was done were as far as possible dried to a similar extent. The dried benzene was quite unaffected by the dried trioxide. After a very short exposure to moist air, the solution lost its green colour, at the same time giving off nitric oxide with effervescence, leaving a yellow solution of nitrogen peroxide.

We hope in a future communication to describe the physical and chemical properties of nitrogen trioxide. Its specific gravity in the state of liquid is about 1.11. The liquid has a green colour at the ordinary temperature, but, when cooled to -2° or below, the colour changes to a deep indigo-blue. The liquid shows no signs of freezing in a mixture of solid carbon dioxide and ether at -81° , but in liquid air it forms very deep blue crystals. It is very little, if at all, soluble in water. When a bulb is broken under ice-water, the liquid sinks to the bottom of the vessel, giving off nitric oxide and nitrogen peroxide, the latter dissolving in the water. The gas is very soluble indeed in concentrated sulphuric acid.

Addendum.

In order to ascertain if similar polymerisation takes place with nitric oxide and carbon monoxide, these gases were introduced into tubes containing phosphorus pentoxide, which were connected with manometers. The tubes were then cooled with liquid air, so that the liquefied gases were in contact with the drying agent. The drying at the low temperature was continued for four days. On regaining the ordinary temperature, the gases showed no change in volume, so that in these circumstances no polymerisation takes place.

The work has been done in the new research laboratory at Christ Church.

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