AN OXIDIZABLE VARIETY OF NITROGEN.

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The photographs which are reproduced in the present Paper are of interest both from the spectroscopic and from the chemical point of view. On the spectroscopic side they represent an application of this method of investigation to gases which were so dilute that a column of gas 64 feet in length was required to produce an adequate absorption. On the chemical side they provide evidence, which appears to be unique, of the existence of an oxidizable modification of nitrogen, an allotropic form of the element which is perhaps the first essential product in its fixation. A brief summary of the conclusions arrived at has been published in the *Transactions* of the Chemical Society,* but the photographic evidence on which those conclusions were based is now reproduced for the first time as a contribution to a subject which has figured frequently in preceding volumes of the *Transactions* of the Faraday Society.

The gases under investigation were obtained by the action of the electric discharge on air. Two forms of discharge were used. First, the "silent" discharge in a large Andreoli ozoniser containing sheets and grids of aluminium, thirteen in number and 30″ × 30″ in area, separated by sheets of micanite. Second, a sparking discharge between a series of iron studs separated to a distance of $\frac{3}{32}$″. Three groups of 6 spark-gaps and two of the Andreoli ozonisers were used at various times.

The chief interest of the work consisted in a comparison of the gases obtained from the ozoniser and spark-gaps separately with the "combined" gas obtained by using both forms of discharge, in accordance with a process devised by Mr. Sydney Leetham, of York, in 1903. At the time when the experiments were made the bleaching gases manufactured by this process were usually obtained by blowing air at the rate of about 70 c.f.m. through one of the ozonisers and then through a box in which 3 spark-gaps were energized in series with the ozoniser by an alternating current of 0·1 ampere at 9,000 volts. Other arrangements were, however, described, and some of these were tested by the spectroscopic method.

The *spectroscopic apparatus* consisted of three parts:

(1) A wooden *trunk* 64 feet in length and 3″ × 3″ in section, the volume being thus about 4 cubic feet. The trunk was provided with glass windows at each end, and inlet and outlet pipes were provided for the gases under examination. The effective length of the trunk could also be reduced to 16 feet by inserting a glass slide and using an additional "blow-off" hole so that the gas was confined to the earlier portion of the trunk.

(2) A *Nernst lamp* with filament vertical served as a source of light. It was placed in the focus of a condensing lens of 3¼″ focal length, fixed

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* *Trans.*, 1912, **101**, 1152–58.

immediately in front of one of the glass windows. At the other end of the trunk the light was picked up again by a condensing lens of 11″ focus, but on account of the great length of the trunk the image formed by the second lens was circular in form, all the light from the upper and lower portions of the filament being lost against the sides of the trunk, so that the effective illumination was derived only from a minute portion in the centre of the filament.

(3) The *spectroscope* was provided with achromatic quartz-calcite lenses of 13″ focus, but when it was desired to photograph the spectrum a camera with a lens of 22″ focus was used. Wratten and Wainwright's "panchromatic plates" were used with six minutes' exposure and two minutes' development in the dark.

The exposures shown in Plate 1 at once revealed the fact that, whilst the ozoniser and spark-gaps separately produced no visible absorption, the flutings characteristic of nitrogen peroxide could be recognized clearly in the spectrum which had been photographed through the "combined" gas. The copper spectrum shown at the bottom of the plate served for calibration, the two yellow and three green lines being clearly seen at one end and two violet lines at the other end of the spectrum.

In order to estimate the amount of nitrogen peroxide in the "combined" gas it was necessary to prepare a series of standard photographs. Some of these are shown in Plate 2, and indicate that the proportion of nitrogen peroxide in the "combined gas" is not far from $\frac{1}{1000}$ by volume. The standard photographs were taken with mixtures of nitric oxide and air, prepared with the help of the apparatus shown in Fig. 1. The nitric oxide was made from mercury and nitric acid; its purity was tested by absorption with ferrous sulphate. It was collected in a cylinder funnel, provided with a T-piece and a capillary funnel through which mercury could be poured: the volume of mercury used in a given time afforded a measure of the volume of nitric oxide transferred to the "mixing jar." In this jar nitric oxide was diluted with known volumes of air run in from a standard meter. The mixture of nitric oxide and air was taken from the bottom of the mixing-jar and passed on to the trunk for observation.

Plate 3 reveals the remarkable fact that the proportion of nitrogen peroxide in the "combined" gas is but little affected by passing the air through the ozoniser and spark-gaps in the reverse order. Under these conditions the ozoniser alters its function completely and becomes a very efficient generator of nitrogen peroxide, producing this gas in larger quantities even than the series of 17 spark-gaps used for the last exposure on the plate.

Up to this point the efficiency of the "combined" arrangement appeared to be due to some alteration in the function of the spark-discharge when supplied with ozonised air, and of the silent discharge when supplied with sparked air. Plate 4 shows, however, that the problem is essentially chemical rather than electrical or electrochemical in character. The three exposures at the top of the plate show that almost equal yields of nitrogen peroxide are produced when part of the air is passed through the ozoniser only, and part through the spark-gaps only, the two products being afterwards mixed on the way to the trunk. In this arrangement a greatly increased yield of nitrogen peroxide is seen to result from the *chemical* interaction of two parallel currents of air after both have passed away from the electric discharge.

This result might be interpreted as meaning that the ozone produced by the silent discharge oxidizes to nitrogen peroxide some lower oxide of nitrogen produced by the spark-discharge. But this oxide could only be nitric oxide,

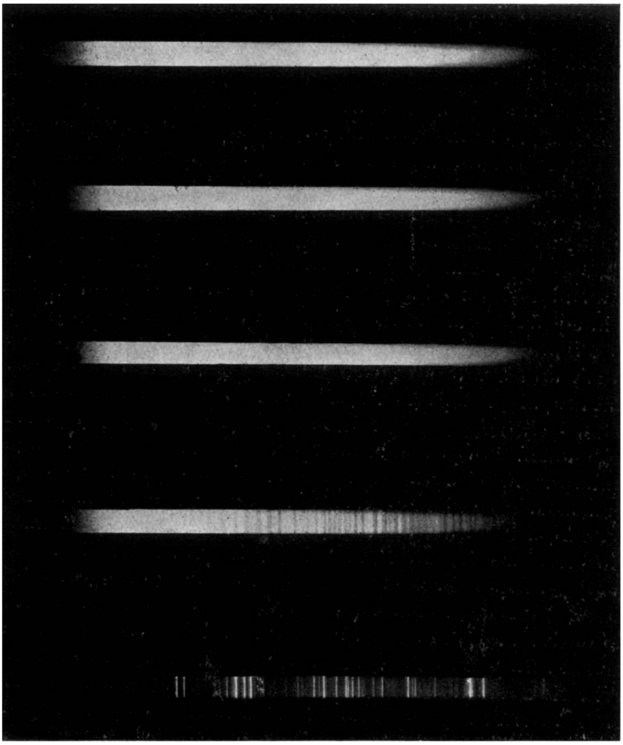

(*a*) Blank
(*b*) Ozoniser only.
(*c*) 3 Spark-gaps only.
(*d*) "Combined" gas.
(*e*) Copper arc.

PLATE I.

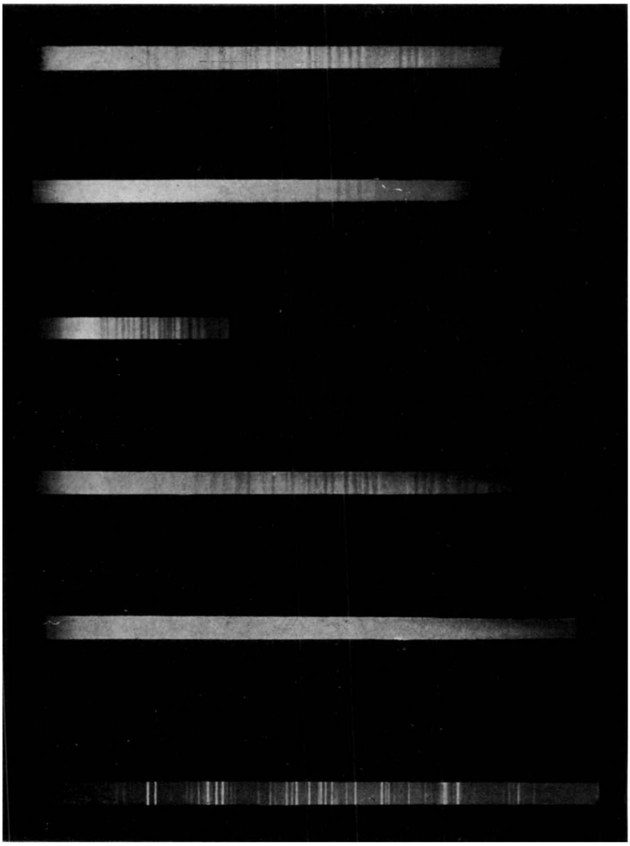
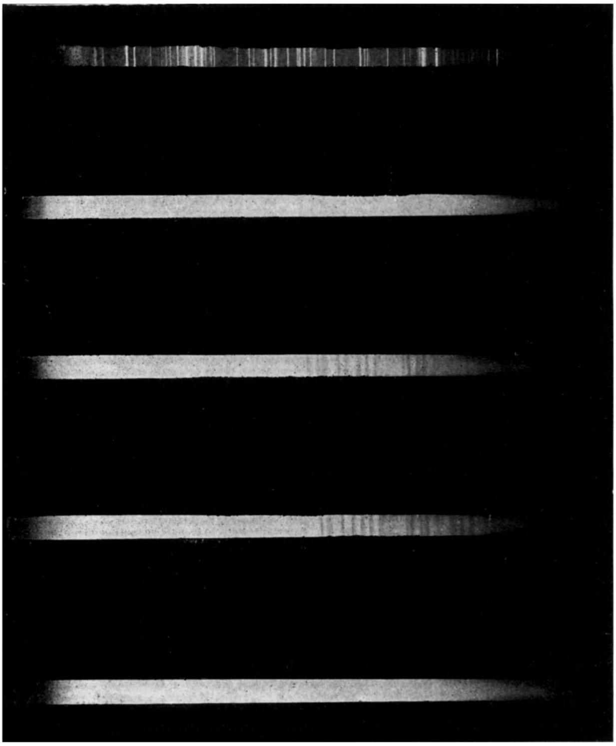

(*a*) "Combined" gas. 64 feet.
(*b*) "Combined" gas. 15 feet.
(*c*) NO_2 $\frac{1}{130}$.
(*d*) NO_2 $\frac{1}{3600}$.
(*e*) NO_2 $\frac{1}{8000}$.
(*f*) Copper arc.

PLATE 2.



(*a*) Copper arc.

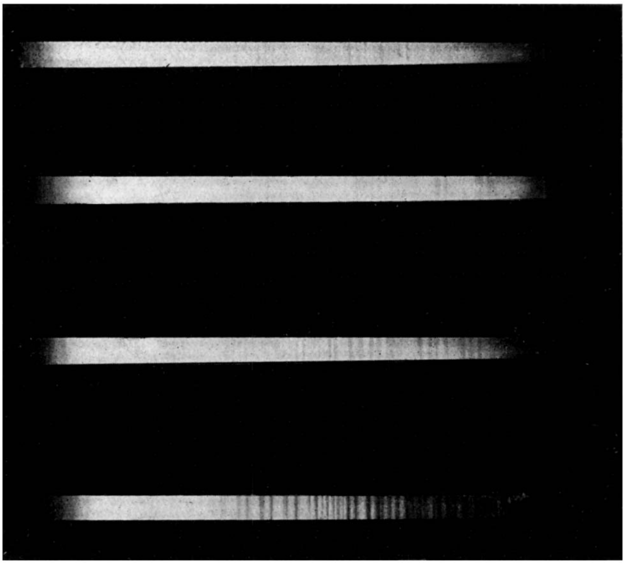
(*b*) Blank.

(*c*) "Combined" gas (reversed arrangement) (3 spark-gaps ⟶ ozoniser).

(*d*) "Combined" gas (ordinary arrangement) (ozoniser ⟶ 3 spark-gaps).

(*e*) 17 Spark-gaps.

PLATE 3.



(*a*) "Combined" gas (½ c.f.m.) parallel arrangement (3 spark-gaps and ozoniser).

(*b*) "Combined" gas (½ c.f.m.) reversed arrangement (3 spark-gaps ⟶ ozoniser).

(*c*) "Combined" gas (½ c.f.m.) ordinary arrangement (ozoniser ⟶ 3 spark-gaps).

(*d*) 17 Spark-gaps (½ c.f.m.).

All the above gases were passed through the trunk at a slow rate (½ c.f.m. instead of 70 c.f.m.) to give time for the gases to mature.

PLATE 4.

as nitrous oxide is too unstable to be produced by sparking. The explanation would therefore amount to a suggestion that an insufficient time had been allowed for nitric oxide to be oxidized to nitrogen peroxide by atmospheric oxygen before the gas escaped from the trunk, unless the oxidation were accelerated by ozonising the air. That such an effect may exist is shown by the fact that, whilst the proportion of nitrogen peroxide present in the gas obtained from a series of 17 spark-gaps amounted to about $\frac{1}{1000}$ when the gas was passed rapidly through the trunk (Plate 3*e*), it was increased to about $\frac{1}{3000}$ (Plate 4*d*) when the velocity was reduced to $\frac{1}{2}$ c.f.m., by blowing off most of the gas, in order to allow ample time for the gas in the trunk to mature. But this explanation is not sufficient to account for the whole of the observations, since even under the very favourable conditions of the low-velocity experiments 17 spark-gaps were required to produce a yield of nitrogen peroxide only one-third greater than that obtained from 3 spark-gaps with the help of ozone.

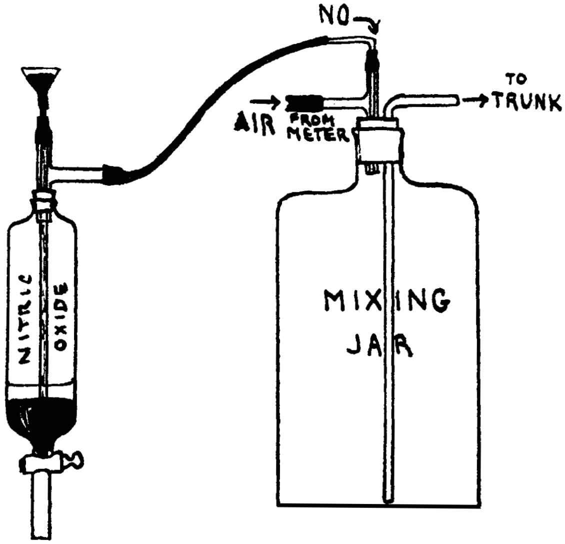


FIG. 1.—Apparatus for preparing Standard Mixtures of Nitric Oxide and Air.

The efficiency of the ozoniser must evidently be attributed to its ability to oxidize to nitrogen peroxide some substance which cannot be so oxidized by air. This oxidizable substance can scarcely be other than a variety of nitrogen itself, produced by the spark-discharge in much the same way that ozone is produced by the silent discharge. The most efficient way of oxidizing it is to produce it in an atmosphere already charged with ozone (Plate 4*c*). A rather less efficient method is to pass the air in which it is produced directly into an ozoniser (Plate 4*b*). Less efficient still is the arrangement whereby the oxidizable nitrogen is mixed with ozonised air in a mixing chamber a few feet away from the discharge apparatus (Plate 4*a*). The slight, but clearly marked gradation in the first three exposures of Plate 4 affords unmistakable evidence of the instability of the oxidizable variety of nitrogen, which appears to revert in the course of a few seconds to a form in which it can no longer be oxidized either by oxygen or by ozone.

The observations now described are probably of importance in connection with the technical fixation of nitrogen. It is not unreasonable to suggest that, since the whole of the oxides of nitrogen must be produced by the union of disrupted molecules of nitrogen with disrupted molecules of oxygen, the most important feature of the process may be to generate the oxidizable variety of nitrogen and then to provide a supply of atomic or of ozonised oxygen to oxidize it before it reverts to the ordinary inactive form.

As a point of contrast it should be noticed that Strutt's chemically active nitrogen is not oxidizable by ozone under the conditions of his experiments.

The author is indebted to Mr. Henry Simon, of Manchester, for permission to publish an account of these experiments.

Full technical particulars of the electrical apparatus may be found in a paper read before the British Association at York entitled "The Electrical Discharge in Air," by W. Cramp and S. Leetham. An account of the effect of ozone on the fixation of nitrogen appears in a paper on "The Electrical Discharge," *Proc. I.E.E.*, 1908, p. 297.