determination must be uncertain, since a wide variation in the assumed degree of dissociation corresponds in most instances to a very small change in the solubility, any decrease in undissociated substance dissolved being almost entirely balanced by an increase in dissociated, and *vice versâ.* This fact explains also why, although the degrees of dissociation of the strong acids used in the above research are not yet accurately determined, being liable to an uncertainty of several per cent. in dilute solutions, the solubility results of other acids with them, as calculated from these values, are subject to a much smaller degree of error.

In conclusion, I have much pleasure in expressing my thanks to Prof. Walker, at whose suggestion and under whose direction the above research was carried out, for his advice and assistance during the whole period of its execution.

BAKERIAN LECTURE.—*A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge.*

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(Received March 16,—Lecture delivered April 6, 1911.)

[PLATE 8.]

§ 1. *Afterglow of Nitrogen.*

It is known that vacuum tubes frequently show a luminosity of the contained gas after discharge is over. In a previous paper* I was able to show that this effect, as it occurs in air, is of the nature of a phosphorescent combustion, and is due to the mutual reaction of nitric oxide and ozone, each formed in the discharge. In a second paper† it was shown that other phosphorescent combustions can be observed in ozone, notably of sulphur, sulphuretted hydrogen, acetylene, and iodine. Some of these give continuous spectra, but the majority band spectra.

In the first paper it was stated that pure nitrogen gives no afterglow whatever, and, with the simple induction coil discharge with which I was then working, this has been frequently verified since. Mr. Percival Lewis has however, described an afterglow obtained in nitrogen when a jar

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* 'Phys. Soc. Proc.,' Dec. 15, 1910, vol. 23, p. 66.

† *Ibid.*, Feb. 15, 1911, vol. 23, p. 147.

discharge with spark-gap is used.* I had no difficulty in obtaining this glow as soon as the jar discharge was used, and have applied to its examination the method used in the former papers. This is due to Sir James Dewar,† and consists in drawing a current of gas through the vacuum tube into an observing vessel, where the glow is developed, and thence into an air pump, which must be a mechanical one of good construction, driven by power. It is thus possible to examine the properties of the glowing nitrogen much more satisfactorily than can be done by intermittent examination after successive discharges.

As Lewis observed, the glow has a characteristic band spectrum not known in any other connection. Its most conspicuous features in the visual region are a green, a yellow, and a red band, of not very unequal intensity. The yellow one is usually the brightest, and imparts a yellow colour to the glow, not very dissimilar to that of the afterglow in air, due to the union of nitric oxide and ozone. The two glows are, however, instantly distinguished by the spectroscope, the air glow giving a continuous spectrum. I have obtained the nitrogen afterglow intense enough to be conspicuous to an observer 30 feet off, when it was 18 inches below a 32-candle electric lamp.

With regard to the conditions for its production, my observations do not altogether agree with those of Lewis. He obtained it with nitrogen from sodium nitrite and ammonium chloride, but was unable to do so from atmospheric nitrogen. He was disposed to regard the presence of a trace of nitric oxide as necessary. I obtained it first from air which had passed over red-hot copper, and afterwards from air which had been freed from oxygen in the wet way by Hempel's copper and ammonia method.‡

It has been shown by Von Mosengeil§ that nitrogen completely freed from oxygen by sodium can give the afterglow. I have confirmed this by bubbling atmospheric nitrogen through melted phosphorus, and thence into the vacuum tube. The glow seemed rather improved than otherwise by this treatment. No luminosity was observed in the phosphorus.

Nitrogen prepared by burning phosphorus in air under a large bell-jar gives the glow, but not well. It is not free enough from oxygen. In short, all the evidence obtained points to the conclusion that the glow is connected with nitrogen, and nothing but nitrogen.

For experiments on the glow, particularly if they are to be prolonged, it is

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* 'Ann. d. Phys.,' 1900, vol. 2, p. 466; 'Phys. Zeit.,' 1904, vol. 5, p. 546.

† 'Roy. Inst. Proc.,' 1888, and 'Engineering,' June 18, 1909.

‡ It is necessary to remove carbon dioxide and ammonia by appropriate absorbents when using this method, or the glow fails. Special drying of the nitrogen, on the other hand, seems to be of no advantage.

§ 'Ann. d. Phys.,' 1906, vol. 20, p. 833.

convenient to make use of commercial cylinders of compressed nitrogen, provided with the usual automatic regulators as used in connection with the limelight. Commercial nitrogen is not free enough from oxygen for immediate use, but it can readily be made so by passage through a tube filled with freshly cut or cast fragments of phosphorus. A glow is seen where the nitrogen enters, indicating that an absorption of residual oxygen is in progress. This only extends a short way down the tube, and the darkness of the remainder is a guarantee that absorption is complete, and that the issuing nitrogen is fit for use. The phosphorus tube should not be unnecessarily exposed to daylight, as this causes deterioration of the absorbent surface.

§ 2. *Effect of Temperature.*

If a long tube, through which a stream of glowing nitrogen passes, is moderately heated, the glow is locally extinguished. As the gas passes on to a cooler part of the tube its luminosity is recovered. If, on the other hand, the gas is led through a tube immersed in liquid air, it glows out with increased brilliancy where it approaches the liquid air. The luminosity is completely and finally extinguished when, or before, the fully cooled portion of the tube is reached. This increased brilliancy is obviously the counterpart of the temporary obscurity observed with heat. Whatever the atomic or molecular change may be, of which the afterglow is a sign, these experiments show that it is accelerated by cooling, and retarded by heating. The kind of change which may be expected to behave in this way is an association, *e.g.* of dissociated nitrogen atoms into molecular nitrogen.

It may be doubted, however, whether the visual glow is a perfect measure of the changes in progress. I find that if a tube carrying the glow is strongly heated the glow is permanently extinguished. It is clear that the view suggested above is incomplete.

§ 3. *Effect of an Electric Field.*

The question will naturally present itself whether the gaseous ions of the discharge, which no doubt remain in the glowing nitrogen, have any direct connection with its peculiarities. If this were the case, we should expect that by passing the glowing gas through an electric field so as to remove the ions, the glow, and its power of exciting metallic spectra, to to be presently described, would be destroyed. Glowing nitrogen was passed down a tube about 40 cm. long and 2 cm. in diameter, provided internally with tin-foil strips along the whole length on the opposite sides. The glow was in no way affected at any part of the tube, if an E.M.F.

of 200 volts was applied to these strips. Nor was its power of exciting the spectrum of some sodium vapour at the further end at all diminished (see below, § 5).

§ 4. *Action of the After-glowing Nitrogen on the Non-metals.*

The glowing nitrogen has remarkable chemical properties.

Drawing it by the pump over a small pellet of phosphorus a violent reaction occurs, red phosphorus is formed,* and the yellow glow is quenched. At the same time the gas is absorbed. This latter experiment can readily be shown by means of a tube illustrated in fig. 1. The tube is in this case closed, and has no current of nitrogen through it. The discharge passes between the electrodes A and B as indicated by the dotted line. The afterglow diffuses into the annex C, where its characteristic colour and spectrum may be seen. On the other hand, phosphorus vapour diffuses out from the pellet of that substance at D, and they meet at a point E, where the reaction occurs, and red phosphorus is deposited as a film along the walls of the tube. The changed appearance of the discharge shows that absorption is in progress. Beginning with enough nitrogen to give a threadlike discharge, in a few minutes the pressure is sufficiently reduced to broaden out the discharge so as to fill the tube. Shortly after that the vacuum becomes quite high, and conduction ceases.

Returning to the experiment where a continuous stream of nitrogen is maintained by the pump, it is found that if the Leyden jar is suppressed, and the ordinary coil discharge employed, a piece of phosphorus in the stream of nitrogen is very little acted on. There is just perceptible action in a few minutes, and a faint greenish flame may be seen round the phosphorus. The same flame may be seen more conspicuously with the jar discharge, but only for a moment; for it is almost immediately obscured in this case by the opaque deposit of red phosphorus on the walls of the tube.

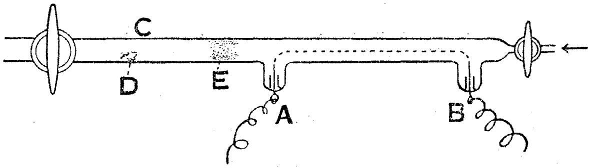

FIG. 1.

No doubt the ordinary coil discharge has the same kind of effect as the jar discharge, but in a degree too slight to make the afterglow visible, and only apparent by prolonged action on phosphorus.

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* Other cases are known where the reaction of phosphorus with another body convert the excess into red phosphorus. Iodine behaves thus.

The novelty of these observations lies in the fact that the phosphorus vapour employed has no access to the region of discharge. It has long been known that phosphorus vapour in the region of discharge would combine with nitrogen, and the fact has been made use of since 1893 in the exhaustion of incandescent lamps.* Discharge takes place through the rarefied air between the ends of the filament. The E.M.F. of, say, 100 volts between these is amply sufficient to produce it with a white-hot cathode.

Sir Oliver Lodge, too, has used phosphorus in exhausting his vacuum valves.† No one, however, seems to have suspected that nitrogen could continue to react with phosphorus after it had left the discharge, and even after it had been deprived of ions by passing through an electric field. Nor has the reaction been connected with the afterglow.

I have made use of the reaction with phosphorus to determine what percentage of active nitrogen is present in the gas shortly after leaving the discharge tube. The principle of the method is to determine the gain in weight of the phosphorus after a measured volume of nitrogen has been passed over it.

Fig. 2 shows the apparatus. Active nitrogen enters from a vacuum tube attached by a short indiarubber connector to the stopcock A. It passes over fragments of phosphorus at B, where it is absorbed with deposition of red phosphorus, and the glow disappears. The gas then passes through a U-tube C, cooled in liquid air. This is to prevent any phosphorus vapour being carried off. Finally, the gas leaves through a stopcock D. The entire arrangement can be detached and hung on the balance by the wire loop E. The phosphorus is originally introduced through F, which is then sealed. The weighings were always carried out with the tube vacuous, and every precaution was taken against the entrance of moisture, which might lead to erroneous results.

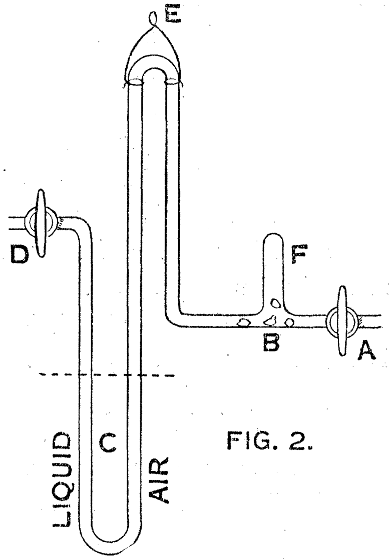

FIG. 2.

In a typical experiment 2540 c.c. of nitrogen were passed, and the gain in weight was 15·5 mgrms. Thus the nitrogen absorbed was 12·2 c.c.,

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[*] See, for instance, J. Rodet, 'Lampes à Incandescence,' p. 107, Paris, Gauthier-Villars, 1907.

[†] Patent No. 25047, 1905.

1/210 part of the whole. It appears that the percentage of nitrogen converted into the active form is comparable with the percentage of oxygen converted in an ozoniser.

The glowing nitrogen also exhibits remarkable phenomena when led over iodine. Its normal yellow glow is replaced by a magnificent light blue flame, at the place where it mingles with the iodine vapour. The appearance is represented in the coloured plate. A slight rise of temperature is observed where the blue glow originates. The iodine is quite volatile enough without the application of heat. I have not succeeded in demonstrating the absorption of nitrogen in this case, nor have I been able to see any signs of a compound deposited further on in the tube. It may be masked by the excess of iodine.

The flame gives a magnificent spectrum of broad bands. Details will follow in a later paper. Brief notes will now be given on the behaviour of a few other non-metallic elements.

Sulphur, when warmed in the current of glowing nitrogen, extinguished it; and, with somewhat stronger heating, a blue flame or glow was apparent, though not comparable in volume or intensity with that of iodine. A transparent green deposit is formed on the glass.

Selenium had no effect.

Arsenic, heated in the glow, gave a not very conspicuous green flame, with a spectrum which seemed continuous, or, at all events, lacking in conspicuous features, and extended over the whole visual region.

Antimony and *carbon* gave no effect.

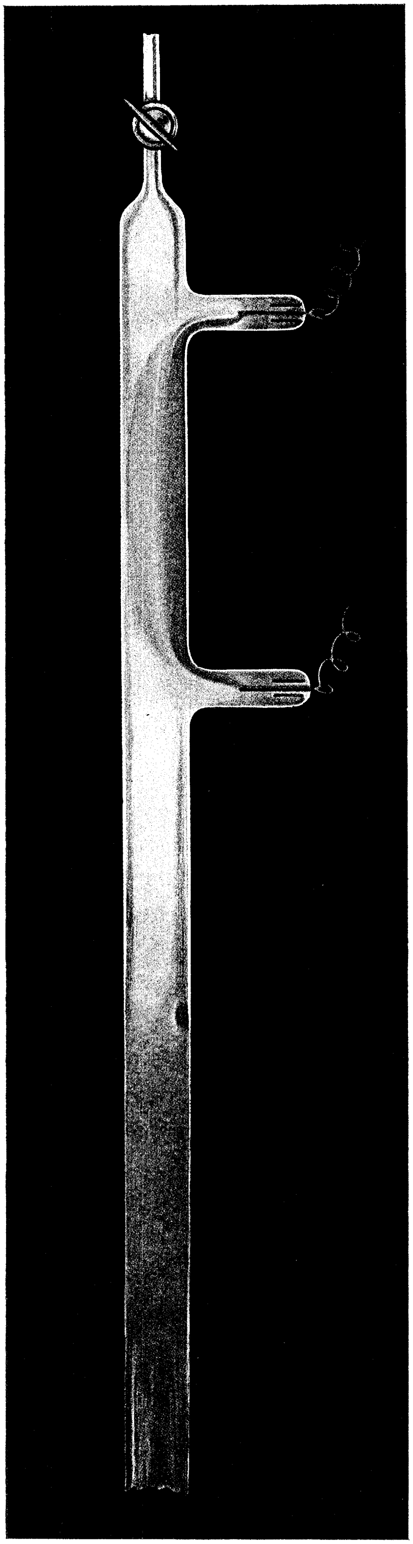
When *hydrogen* is admitted to mix with the glowing nitrogen, after the latter has been through the vacuum tube, no effect is produced, beyond a mere dilution of the glow.

Oxygen, on the other hand, destroys the glow without any other luminosity being developed in the process.

§ 5. *Action on the Metals—Production of Metallic Line Spectra.*

When the glowing nitrogen is led over a fragment of sodium, which is heated a little above its melting point, the sodium spectrum is developed with great brilliancy. Indeed, the power of developing the D line is a more sensitive test for the presence of the active nitrogen than any other.

When the sodium is more strongly heated, say, to 250° C., a curious effect is observed. The denser vapour in the immediate neighbourhood of the metal becomes visually green, showing the green line E very strongly, while the D line is scarcely visible. On either side of the central green light is an outer luminous region in which the D line predominates.



I have been able to observe the absorption of the glowing nitrogen by sodium, by the same method as was employed with phosphorus. The sodium vapour was not allowed to penetrate into the discharge, and its spectrum was not observed there.*

There seems to be no reason for doubting that the sodium spectrum seen in these experiments is simply the flame spectrum of sodium burning spontaneously in the active nitrogen, to form the nitride. It opens up a new field of experiment to be able to produce metallic spectra in a vessel at so low an average temperature, and in the absence of an electric field. The line spectra of many other metals have been obtained similarly. The following have been observed:—Cadmium, magnesium, mercury, potassium, zinc, lead. Thallium was tried in the form of chloride, and gave a magnificent green light, in striking contrast to the yellow afterglow which it replaces.

The sodium spectrum, too, can be obtained when the glow passes through a soda glass tube, heated to near the softening point, but in this case the D line alone appears.

In the case of metallic mercury, absorption of nitrogen was proved, as with sodium and phosphorus, though, working in a closed vessel without a current of gas, it was not found feasible in practice to prevent mercury vapour finding its way into the discharge. There is no doubt that this is the action described by Threlfall.† He observed the absorption of nitrogen when a jar discharge was passed through it at a low pressure in presence of mercury, though there is no reference to the afterglow in his paper. He observed, too, the formation of a compound which decomposed with a slight explosion when moderately heated.

Although in the absorption experiments mercury could not be prevented from getting into the discharge, it was easy to avoid this when the air pump was used, and a continuous current of nitrogen drawn through. Working thus, I have observed that Threlfall's explosive nitride is formed when the mercury spectrum is developed by the afterglow. This seems conclusive evidence that the production of these spectra is a direct result of the chemical union of the metal with the active nitrogen.

It may be remarked that, though the hot metals (*e.g.*, zinc) are rapidly skinned over with nitride, cold metals remain bright in the nitrogen glow. This was tried particularly with sodium, and with mercury—the latter in the form of a bright film on a copper plate. The clean cold metals have no unfavourable influence on the luminosity of the glow itself.

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* This distinguishes the present action from the well-known absorbing power of the alkali metals when used as cathode in a discharge.

† 'Phil. Mag.,' Jan., 1893, p. 1.

§ 6. *Action on Compound Bodies.*

Some gases and vapours mixed with the glow merely dilute it. Water and carbon dioxide are examples.

In one case an obvious chemical attack has been observed. This was with naphthalene, which turns brown, a brown deposit forming also in the walls of the tube where the nitrogen is passed over it. The nitrogen glow was destroyed, but no luminous phenomena accompanied the action. Heat was not applied.

Ammonia was another case where the original glow was destroyed without attendant luminous effects. It seems likely that a chemical action occurs here, but proof has not been obtained.

It is certain, however, that in some cases destruction of the glow by contact with another substance may occur without chemical action. Manganese dioxide and copper oxide are at once fatal to it. The analogy to the known destruction of ozone by these substances cannot fail to attract attention.

A small roll of superficially oxidised copper gauze was placed in a glass tube and carefully weighed. It was then inserted between the vacuum tube and the pump by means of indiarubber connectors, and a stream of the glowing nitrogen passed over it for about half an hour. The glow abruptly stopped at the surface of the copper oxide. The tube was detached and reweighed. No change of weight amounting to 1/10 mgrm. could be detected, though the quantity of active nitrogen passed, judged by the phosphorus experiments described above, must have amounted to several milligrammes. I conclude that the glow is destroyed in these cases by a catalytic action.

Another class of compound substances become luminous with characteristic band spectra when vaporised in the glow. Stannous and stannic chloride both give the same brilliant and voluminous blue glow. Most of the light comes from one broad symmetrical band in the blue and violet regions. There are, in addition, a number of lines in the ultra-violet, chiefly due to tin. Mercuric iodide gives a violet glow with a strong unsymmetrical violet band distinct from any in the iodine afterglow spectrum mentioned in § 4. Distinctive glows have also been obtained from other mercury salts. Mercurous chloride gives a green one.

Cuprous chloride gives a blue-green glow, with a spectrum agreeing with that shown by the same compound in the Bunsen flame, but with additional features not present in the latter.

Cyanogen gas fed into the glow gives the lilac flame of cyanogen with its well-known spectrum.

The band spectrum of iodine in the afterglow (see § 4) should probably be regarded as of similar origin with these compound spectra. They are I think, essentially flame spectra, as are also the line spectra of metals produced in the afterglow; but the afterglow must be regarded as a much more searching kind of flame than the ordinary high-temperature flames.

In much of the literature of flame spectra it is implied that temperature is a measure of the spectrum-developing quality of a flame, and no doubt the fact that the oxy-acetylene and oxy-hydrogen flames are, each in its own degree, capable of developing more lines than the Bunsen flame, is favourable to this view. Yet the balance of evidence is greatly against the idea that heat alone is capable of exciting line and band spectra at all; and if we reject this idea it is evidently unreasonable to assume that temperature alone governs the number of lines or bands emitted.

Regarding, then, the afterglow as a flame capable of developing spectra, we have the means of examining the spectra of a number of compounds which will not endure the temperature of an ordinary flame without decomposition. Moreover, the spectrum is better developed. Cuprous chloride, which gives a characteristic spectrum in the Bunsen flame, gives the same spectrum, with additional details, in the afterglow. Compounds like mercuric iodide, instantly decomposed in the Bunsen flame, give in the glow a spectrum not before recognised. It may be possible to obtain valuable generalisations from the examination of a long series of such spectra.

Nitric oxide, allowed to mix with the active nitrogen, shows a very strange behaviour. A greenish flame, possessing a continuous spectrum, is produced, and heat is developed at the point of confluence. To test whether any gas condensable at $-180°$ was produced, the gases from the flame were led through a U-tube cooled in liquid air, and a dark blue substance was condensed out. This melted to an indigo-blue liquid, and finally revealed itself as nitrogen peroxide by evaporating off into an orange gas, soluble in caustic alkali.

It is very surprising that a reaction between nitrogen and nitric oxide should lead to the formation of a substance, not *less*, but *more* oxidised than the latter.

A critic may naturally object that the formation of nitrogen peroxide may have been due to oxygen which accidentally gained admission to the nitric oxide, quite independently of the active nitrogen. I wish to emphasise a test experiment, which disproves this hypothesis.

The influence of the active nitrogen may be removed by simply turning off the electric discharge. The apparatus being in adjustment, with a suitably regulated flow of the gases, the U-tube was kept cool with liquid air for

10 minutes, after which the liquid air was removed, and the tube allowed to warm up somewhat, for the removal of hoar frost from the outside. No trace of the indigo liquid could be seen. Now the discharge was started, and the tube kept in liquid air for only two minutes. At the end of this time the indigo liquid was extremely conspicuous. The tube could be warmed up to allow the stream of gases to wash out the product, and the experiment could be repeated, on and off, as often as desired. The supply of gas, adjustment of taps, etc., were left absolutely untouched throughout.

It would seem that the reaction which occurs may be of this kind :—

$$2NO+N = NO_2+N_2.$$

However, I lay no stress on this. I wish only to insist on the definite facts above stated.

Brilliant glows are obtained from some carbon compounds containing the halogens, for instance, a lilac glow from ethyl iodide. This, examined spectroscopically, shows a magnificent cyanogen spectrum. The fact is evidence that the active nitrogen attacks the carbon compound, combining with the carbon; iodine is set free, and may be collected as a conspicuous sublimate by cooling the resulting vapours in liquid air. What becomes of the hydrogen has not yet been determined.

Chloroform and carbon tetrachloride also give a fine cyanogen spectrum. In this case the glow is visually orange, owing to greater relative intensity in the red portion of the cyanogen spectrum. Chlorine is set free, and can be collected in liquid air.

Again, the lilac cyanogen glow is obtained when acetylene is fed in. The experiment mentioned above, where cyanogen itself is shown to give this glow under the same conditions, suggests very strongly that in all these cases the active nitrogen attacks the carbon compound, forming cyanogen, which is merely stimulated, without further change, by the peculiar conditions existing in the glow.

The formation of cyanogen was proved more directly as follows :—The gases from the acetylene experiment were condensed by liquid air, and afterwards collected through a Toepler pump. They were agitated with caustic potash solution to absorb any cyanogen present from the excess of acetylene. The presence of a cyanide in this solution was readily proved by abundant formation of Prussian blue, and by the ferric sulphocyanate reaction. It should be mentioned that, in addition to the condensed gases, some black tarry substance was present in the tube.

Finally, the cyanogen spectrum has been observed when the active nitrogen is allowed to react with methane, pentane, ethylene, lcohol, ether, and benzol. It is not, however, so conspicuous in these cases, and probably does not indicate the main course of the reaction.

§ 7. *Summary and Conclusion.*

The leading facts established are:—

(1) That pure nitrogen, from whatever source, subjected to the jar discharge, undergoes some modification which causes it to glow for a short time after it has left the discharge.

(2) The glow which is emitted while the gas returns to its normal condition is not affected by the removal of ions. It is weakened by heating, intensified by cooling. This seems to favour the view that it is due to the recombination of dissociated atoms.

(3) The modified nitrogen acts on ordinary phosphorus, combining with it, and at the same time forming much red phosphorus.

(4) It combines with sodium and also with mercury at a gentle heat, forming in the latter case an explosive compound, and in each case developing the line spectrum of the metal concerned. It also develops the line spectra of other metals, probably combining with them too.

(5) It develops the band spectra of compounds when they are vaporised in it, giving, in many cases, spectra of substances too unstable to be examined at the temperature of the Bunsen flame.

(6) It attacks nitric oxide, with formation, strangely enough, of nitrogen peroxide, a more oxidised substance.

(7) It attacks acetylene and the halogen derivatives of organic radicles, setting free the halogen, where one is present, and combining with the carbon to form cyanogen. This is proved by the brilliant cyanogen spectrum produced, and by direct chemical tests.

It may perhaps be felt that more detailed study of the compounds produced by the active nitrogen should have been made. The importance of this is not underrated, but the difficulties of working with such small quantities of material are considerable, and have led to a postponement of this branch of the work. It may be pointed out how little has been done in studying the compounds produced by ozone.

The spectroscopic data in this paper are merely general and preliminary. An accurate investigation of the various spectra by photographic methods, in collaboration with Prof. A. Fowler, F.R.S., is in progress.