CCCLXXIX.—*On Active Nitrogen.  Part IV.  The In-dependence of the Afterglow and the Chemical Properties of Active Nitrogen.*

By Eric John Baxter Willey.

Since the discovery by the present Lord Rayleigh (Strutt, *Proc. Roy. Soc.*, 1911, *A*, **85**, 219) that nitrogen which has been subjected to the action of a condenser discharge at low pressures shows both

an afterglow and chemical activity, there has been much discussion as to whether this active modification of the element is (a) atomic, (b) molecular and metastable, or (c) triatomic.  The evidence for each of these views may shortly be summarised :

(a) (i) The decay process of the glow follows a bimolecular law (Angerer, *Physikal. Z.*, 1921, **22**, 97).

(ii) An analysis of the banded afterglow spectrum (Birge, *Nature*, 1926, **117**, 80), critical potential measurements in connexion with this (Sponer, *Z. Physik*, 1925, **34**, 622), and observations upon the spectra excited by active nitrogen (Mulliken, *Physical Rev.*, 1924, **23**, 259, 767 ; 1925, **26**, 1) lead to the view that the energy associated with this glowing gas is of the order of 200,000—250,000 cals./g.-mol. (10—12 volts).

(b) Saha and Sur (*Phil. Mag.*, 1924, **118**, 421) consider that the spectroscopic evidence indicates a metastable molecule of heat of formation 190,000 cals./g.-mol.

(c) Trautz (*Z. Elektrochem.*, 1919, **25**, 299), from mathematical considerations, favours a triatomic molecule with a heat of formation of 5,000—10,000 cals./g.-mol.

The consensus of opinion regards active nitrogen as possessing a *high* heat of formation and its existence as due to atomic recombination, an excited or metastable and chemically reactive molecule thus being produced.

In Parts I, II, and III of this series (J., 1926, 1804 ; this vol., pp. 669, 2188), evidence has been presented for the view that the energy of active nitrogen is 45,000 cals./g.-mol. (2 volts), and deductions from the spectra excited by active nitrogen have been criticised on the ground that chemiluminescence has not been sufficiently considered as a possible means of production of these luminous phenomena (*Nature*, 1926, **118**, 735).  Efforts recently made (Ruark, Foote, Rudnick, and Chenault, *J. Opt. Soc. Amer.*, 1927, **14**, 17) to answer these objections are unsatisfactory, since the calculations made here are based upon mercurous azoimide, $HgN_3$, and not upon the substituted ammonias, $Hg_3N_2$ and $Hg_3N$, which are the products of the reaction between active nitrogen and mercury vapour.

Thus we are left to reconcile two entirely different views on the energy and nature of active nitrogen, each supported by abundant experimental evidence, and as a tentative explanation it was suggested (Part II) that active nitrogen might emit its energy in a series of 45,000-cal. (2-volt) stages.

Early in 1925 it had been felt that certain seemingly inconsistent observations upon active nitrogen could best be explained by the theory that *two* luminous forms of the element were concerned,

differing both in chemical activity and in nature, but as this view led to the assumption of a possible change in the spectrum of the glow during decay, owing to the transformation rates of the two species not being the same, the hypothesis was for the time being abandoned. Dr. H. W. B. Skinner has recently suggested to the author that the discrepancy in these two sets of experiments can be overcome if we do not regard the chemically active nitrogen as luminous at all, but ascribe all the luminous phenomena (if this be possible upon the basis of available experimental evidence) to the effects of a few atoms produced at the same time as the former substance. This theory has, it is believed, been completely verified, for it has been found that the destruction of the glow by a second weak discharge and also by heat, noticed by Lord Rayleigh, is not accompanied by any decomposition of the chemically active nitrogen ; furthermore, activity can be produced in the gas by the use of a discharge which does not give rise to any glow.

## EXPERIMENTAL.

*First Method.*—Lord Rayleigh has shown (*Proc. Roy. Soc.*, 1916, *A*, **92**, 438) that when a stream of glowing nitrogen is drawn through a second and weak discharge, the glow is completely or very largely destroyed, and it appeared possible that this second discharge might prove fatal to the luminous nitrogen without affecting the chemically active modification which is, *ex hypothesi*, also present. This possibility was tested in the following manner.

Nitrogen, purified as described in Part I, was drawn at 10 mm. pressure and a constant speed (1—3 litres/hr., at *N.T.P.*) through the discharge tubes A and B and the test chamber P to exhaust at D (Fig. 1). The aluminium electrodes E1, E2, E3, and E4 were held in position by rubber sleeves and their relative positions so adjusted that the distance between E2 and E3 was $1\frac{1}{2}$ times the distance between E3 and E4. Projecting into the test chamber P were two identical and carefully calibrated thermometers, T1 and T2, the bulb of the former being coated with a small and closely adherent piece of oxidised copper gauze, while the latter was bare. It was found in calibration experiments that, when active nitrogen was drawn through the apparatus, the glow was extinguished at the surface of the copper oxide, and that the rise in temperature shown by T1 above that indicated by T2 was strictly proportional to the concentration of active nitrogen at the position of the bulb of T1, this concentration being determined by means of nitric oxide, as described in Part I. This heating effect in T1 is obviously due to the catalytic decay of the active nitrogen at the copper oxide surface (compare Part III), as was proved by warming the tubes A and B

by small flames while a stream of inert nitrogen was drawn through the apparatus; the temperatures recorded on T1 and T2 were then identical.

The difference in temperature between T1 and T2 is thus a measure of the concentration of active nitrogen in the gas. A strong discharge, capable of developing the afterglow, was maintained in A from the coil, condensers, and spark gaps connected as shown, and a weak direct induction coil or transformer discharge from another circuit could, if desired, be run in B.

Lord Rayleigh's observation as to the destruction of the afterglow in these circumstances was confirmed, no luminosity being visible in the gases emerging from B when a weak discharge was maintained

FIG. 1.
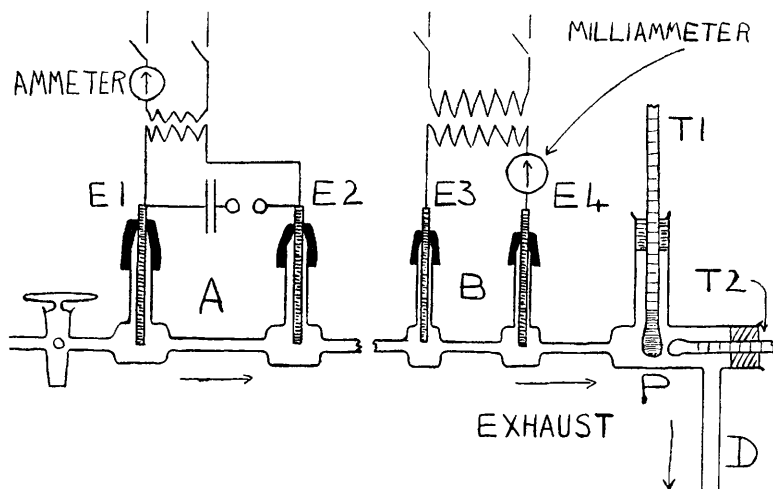


between E3 and E4. (Any tendency for the auxiliary discharge to wander and pass between E2 and E3, E2 being connected to earth, was overcome by the electrode-spacing arrangement already mentioned.)

It was found, however, that provided too strong a discharge was not employed in B, the concentration of active nitrogen as measured on T1 and T2 did not change appreciably, in spite of the complete destruction of the glow by the auxiliary discharge; too strong a discharge in B destroyed both the glow and the chemical activity (Table I). The conditions necessary for the retention of the latter were best realised in practice by means of a discharge from a small transformer run off the 100-volt A.C. mains and provided with a series resistance of 825 ohms in the primary; the secondary current was then about 0·1 milliamp. (R.M.S. value) at 500 volts. The same

TABLE I.

| No. | No. of observations. | T1. | T2. | T1—T2. | Flow speed of gas at 13 mm. press. (c.c./hr.). | Auxiliary transformer discharge. | Effect on afterglow. |
|-----|-----|-----|-----|-----|-----|-----|-----|
| 1 | 9 | 1·6° | 1·2° | 0·4° | — | Coil. | Completely extinguished. |
| 2 | 8 | 1·0 | 1·0 | 0·0 | — | Weak. | ,,       ,, |
| 3 | 15 | 1·0 | 1·0 | 0·0 | — | ,, | ,,       ,, |
| 4 | 11 | 0·9 | 0·9 | 0·0 | — | ,, | ,,       ,, |
| 5 | 17 | 2·7 | 1·3 | 1·4 | 2800 | Medium. | ,,       ,, |
| 6 | 8 | 4·3 | 0·6 | 3·7 | 3000 | Strong. | ,,       ,, |
| 7 | 10 | 2·9 | 0·4 | 2·5 | — | ,, | ,,       ,, |
| 8 | 10 | 0·8 | 0·6 | 0·2 | 1900 | Weak. | ,,       ,, |
| 9 | 12 | 2·0 | 0·8 | 1·2 | 2000 | ,, | ,,       ,, |
| 10 | 12 | 2·1 | 0·7 | 1·4 | ,, | Medium. | ,,       ,, |
| 11 | 12 | 2·1 | 0·6 | 1·5 | ,, | ,, | ,,       ,, |

effect could be produced by the use of a direct coil discharge in B, but on account of the difficulty in regulation, the transformer was more generally used.

Furthermore, whilst in some cases a decrease in the concentration of active nitrogen was noticed, this was by no means comparable with the complete or almost complete destruction of the afterglow, and hence it appears that there is no simple relation between the intensity of the afterglow and the amount of chemically active nitrogen present.

*Second Method.*—In view of the comparatively insensitive nature of this device for detecting and determining the active nitrogen, the experiments were repeated, the estimations being carried out with nitric oxide; the other experimental arrangements remained unaltered. The technique of this method has been considerably improved and a short account of it may be given.

The nitrogen from the discharge tube B entered the reaction chamber at E (Fig. 2), and at N an inlet was provided for the nitric oxide, regulation of this gas being effected by means of the capillary choke at C and the tap S5. (The nitric oxide was prepared by dropping a solution of sodium nitrite into an acidified solution of ferrous sulphate, and was dried by phosphorus pentoxide.) The gases then passed to exhaust *via* the two-way tap S1, the condensing trap R1, and the second two-way tap S2. The system S3, R2, and S4 was identical with and parallel to the circuit just described. One side of S1 and S3 was connected to a supply of pure, dry hydrogen, and S2 and S4 were connected to exhaust and also to a train of absorption bulbs for the determination of the nitrogen peroxide. Hence, by the use of these two condensing systems, continuous estimations of the concentration of active nitrogen can be made without stopping the apparatus; the nitrogen peroxide

produced by the action of the active nitrogen upon nitric oxide condenses in R1 (or R2), which is cooled by liquid air. At the end of the experiment the gas stream is diverted to the other condensing system, the contents of R1 are allowed to warm to room temperature, and then blown by means of hydrogen (admitted at S1) through a train of absorption bottles containing a 10% solution of potassium iodide, the current of gas being maintained for some 20 minutes in order to clear the last traces of nitric oxide from the solution ; the iodine is then titrated by means of standard sodium thiosulphate solution and the concentration of active nitrogen
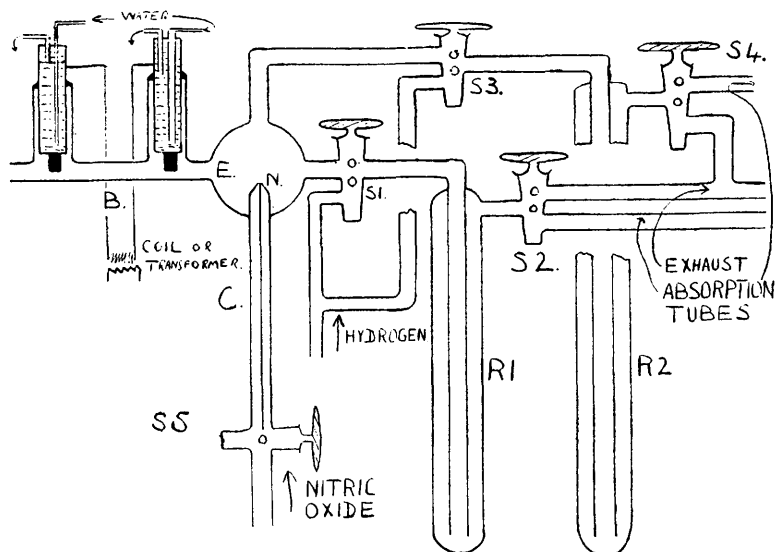
FIG. 2.



TABLE II.

% Active nitrogen.

| Series. | No. of expts. | (1) main discharge. | (2) main+ auxiliary discharge. | Difference (2) — (1). | Auxiliary transformer discharge. |
|---|---|---|---|---|---|
| 1 | 5 | 0·90 | 1·20 | 0·30 | Weak. |
| 2 | 4 | 2·30 | 2·50 | 0·20 | ,, |
| 3 | 4 | 1·70 | 1·70 | 0·00 | ,, |
| 4 | 4 | 1·75 | 2·00 | 0·25 | ,, |
| 5 | 5 | 1·40 | 1·30 | −0·10 | Strong. |
| 6 | 7 | 1·85 | 1·75 | −0·10 | ,, |
| 7 | 5 | 1·15 | 1·30 | 0·15 | Weak. |
| 8 | 8 | 1·30 | 1·30 | 0·00 | ,, |

calculated as already described (Part I). The results of these experiments are given in Table II, and it will be noticed that, whilst in some cases the concentration of active nitrogen has diminished,

yet in other cases it has increased when the second discharge is employed. Since in every case the destruction of the glow is complete in the gases issuing from the auxiliary discharge, it appears that the results already obtained are confirmed, and that it is possible by this method to destroy the glow and yet retain the chemical properties of active nitrogen.

*Third Method.*—It was felt that these observations could be made still more convincing if a stream of non-luminous but chemically active nitrogen could be obtained by a single operation, and in view of the known production of active nitrogen in the arc, where none of the luminous phenomena connected with active nitrogen are to be seen (Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 260), it was decided to study the effect of the uncondensed discharge upon nitrogen.

For this purpose, the apparatus employed was as in Fig. 2, except that the tubes A and B were replaced by another discharge tube with water-cooled Armco electrodes. The discharge was obtained from a rotary converter and transformers and took 10—20 milliamps. at 2000—3000 volts; in these circumstances, the emergent gases showed no perceptible luminosity but contained a considerable quantity of active nitrogen (Table III). No traces appeared here

TABLE III.

| Series ..................... | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| No. of expts. ............ | 6 | 6 | 4 | 6 | 5 | 3 | 5 |
| % Active nitrogen   ... | 0·84 | 0·98 | 1·28 | 0·64 | 0·85 | 1·52 | 1·52 |

of the green flame usually to be seen where nitric oxide enters a stream of glowing nitrogen, and hence we must conclude that most probably this particular development of luminosity is independent of the actual chemical reaction in progress (compare Lord Rayleigh, *Proc. Roy. Soc.*, 1911, *A*, **86**, 56). Furthermore, strong indications of the presence of active nitrogen were obtained by the use of the two-thermometer device already described.

*Fourth Method.*—The methods of extinguishing the luminosity of the active nitrogen have hitherto been electrical in nature, and it is obviously of importance that other means should be attempted in order that a satisfactory mechanism may be formulated for the glow-destruction process. Lord Rayleigh has shown (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219) that, when a stream of glowing nitrogen is drawn through a tube which is heated, the luminosity ceases at the hot portions and reappears in the colder parts if the temperature is not too high ; if the tube be heated too strongly, however, the glow is not restored at all, and it was thought advisable to study this phenomenon in the light of the present observations.

The apparatus employed is as in Fig. 2, except that the auxiliary discharge tube was replaced by a **U**-tube of some 10″ over-all length and ¼″ internal diameter; determination of the active nitrogen was made with nitric oxide as before. The **U**-tube was immersed in an electrically heated bath of heavy paraffin; for temperatures above 250° the paraffin was replaced by a mixture of sodium and potassium nitrates.

When a stream of glowing nitrogen was drawn through the apparatus at a rate of 2000 c.c./hr. and 10 mm. pressure, the luminosity was considerably enhanced as the temperature of the bath was raised from 20° to 80°; from this point to about 225° no appreciable change in intensity was noticed, but at 235° the luminosity began to decrease in the gas entering the detection chamber, at 250° the effect was pronounced, and at 300—320° the gas lost all glow. Contrary to the observations of Lord Rayleigh, the glow did not as a rule reappear beyond the hot zone when once it had been destroyed, although a 2-litre chamber was provided in the exhaust line in order that this point might be examined; in some cases, however, his observations were confirmed, and it appears that the nature of the hot surface is a very important factor in this connexion.

TABLE IV.

| Series. | No. of expts. | Temp. of bath. | Glow. | | % Active nitrogen. |
|---|---|---|---|---|---|
| 1 | 2 | 15° | Strong. | | 0·64 |
| | 2 | 80 | Slightly enhanced. | | 0·73 |
| | 1 | 139 | ,, | ,, | 0·64 |
| | 1 | 257 | ,, | ,, | 0·66 |
| | 1 | 252 | ,, | ,, | 0·69 |
| 2 | 3 | 15 | Strong. | | 0·71 |
| | 3 | 330 | Practically extinguished. | | 0·71 |

Determinations of the active nitrogen in these experiments showed (Table IV) that, in spite of the alterations in the degree of luminosity, the concentration of the active gas remained sensibly unchanged throughout.

### Discussion.

The experiments just described provide, it is thought, not only a fairly complete solution to the difficulty in reconciling spectroscopic and other optical work upon active nitrogen with the observations made upon the same subject in this laboratory, but also an explanation of certain phenomena alluded to by Lord Rayleigh and others.

Just before these experiments were completed, Bonhoeffer and Kaminsky (*Z. Elektrochem.*, 1926, **32**, 536) showed that the concentration of active nitrogen (measured chemically) and the intensity of the glow are not simply related to one another, at least four

terms being necessary in any expression connecting these two quantities. Details of their experimental procedure are not available, but the present work is in complete agreement with theirs. It may also be noticed that Koenig and Elöd (*Ber.*, 1914, **47**, 516) suspected that the presence of a glow was not a necessary criterion of chemical activity in nitrogen, but here again no experimental evidence was adduced. Furthermore, Lord Rayleigh has stated that " there does not appear to be any close or necessary connexion between the luminous phenomena associated with active nitrogen and the chemical ones " (J., 1918, **113**, 200; see also *Proc. Roy. Soc.*, 1913, *A*, **88**, 539). It appears that we must decide between two theories for an explanation of these phenomena :

(i) Active nitrogen may be regarded as a homogeneous substance which emits its energy in two or more stages, one of these being invariable and giving rise to the chemical activity, and the other or others being capable of modification so that the residual energy may be lost either as ultra-violet radiation or by an increase in the kinetic energy of the molecule. Saha and Sur (*loc. cit.*) regard the visible or $\alpha$-radiation of the afterglow as *secondary* (the primary band in nitrogen lying in the vicinity of $\lambda = 1400$ Å.U.); it is possible therefore that some influence might lead to suppression of these $\alpha$-bands and a corresponding development of other parts of the spectrum without affecting the chemical activity.

(ii) The whole of the observations and measurements which have been made with regard to active nitrogen can, in the author's opinion, be much more readily explained if 'it is assumed that the luminous and chemically active forms are quite distinct, although usually coexistent. The multiplicity of ionised and excited bodies produced by the discharge in any gas renders this quite likely, and examples are known of the formation under these conditions of more than one active form of an element, *e.g.*, the active oxygen, distinct from ozone, of Koenig and Elöd (*loc. cit.*), and the mono-, di-, and tri-atomic forms of hydrogen, all chemically active, whose existence has been claimed severally by Bonhoeffer (*Z. physikal. Chem.*, 1924, **113**, 199; 1925, **116**, 114, 391; 1926, **119**, 474; *Z. Elektrochem.*, 1925, **31**, 521), Phipps and Taylor (*Physical Rev.*, 1927, **29**, 309), and Wendt and Landauer (*J. Amer. Chem. Soc.*, 1922, **44**, 510).*

* It may be suggested that differences in the reactions of active hydrogen reported by certain of these investigators, *e.g.*, the formation of ammonia with nitrogen, noticed by Wendt and Landauer (*loc. cit.*) and denied by Bonhoeffer (*loc. cit.*; see also Paneth, Klener, and Peters, *Z. Elektrochem.*, 1927, **33**, 102), may be due to differences in their experimental conditions leading to the formation of different substances : the chemical activity of H, $H_2$, and $H_3$ is not likely to be the same.

If this view is adopted, it is apparent that the difficulties discussed earlier are overcome, since the observations of an active nitrogen made by spectroscopists and by workers in this laboratory have really been upon different modifications of the same element.    The author now suggests that active nitrogen consists of a mixture of (i) metastable molecules with a heat of formation of *ca.* 45,000 cals./g.-mol. (2 volts), which are exclusively responsible for the chemical activity, and (ii) a much smaller proportion (probably of the order of $10^{-7}$) of atoms which upon recombination produce high-level excited molecules, the energy set free, equivalent to 200,000— 250,000 cals./g.-mol. (10—12 volts) being liberated as radiation; all the luminous phenomena and excitation of spectra, with the possible exception of certain cases of chemiluminescence arising from reactions of the 2-volt metastable molecules, are to be ascribed to this second constituent.

The decay of the afterglow follows a process which is bimolecular only with respect to the atoms, but is in reality a ternary reaction, for it has been shown (Herzfeld, *Z. Physik*, 1922, **8**, 132; Polyani, *ibid.*, 1920, **1**, 337; Born and Franck, *Ann. Physik*, 1925, **76**, 255) that, when two atoms recombine to form a diatomic molecule, the presence of a third body is nearly always necessary in order that considerations of the conservation of energy and momentum shall be satisfied.    Such a view would presuppose a relation between the total pressure of the gas and the rate of decay of the afterglow; this has actually been observed by Lord Rayleigh (*Proc. Roy. Soc.*, 1916, *A*, **92**, 438) and studied by the present author, and it is hoped to publish details in a later communication.

The action of traces of impurities in developing the afterglow would appear to be adequately accounted for by Lord Rayleigh's original explanation (*Proc. Roy. Soc.*, 1912, *A*, **86**, 262; **87**, 179). Its behaviour towards heat and cold will be discussed in a later communication.

The catalytic destruction of the glow by surfaces, and by copper and other metals in particular, may readily be explained by the well-known analogous case of the surface recombination of hydrogen atoms.    The extinction of the luminosity when a metal surface begins to be active in promoting the decay of the *chemically* active nitrogen is also accounted for when we remember that the surface is, *ex hypothesi*, composed of the metal, and not of the nitride, when the point of activity is reached; there is no apparent reason why a nitride surface should catalyse the recombination of nitrogen atoms, but the parent metal itself may, from the analogy already mentioned, be very effective in this connexion.    It follows that the action of the discharge in extinguishing the luminosity is not intrinsically

electrical, but that the bombardment of the glass of the discharge tube by the ions and electrons present simply leads to the production of a " clean " surface, upon which the recombination of atoms can take place with ease; heat also leads to the production of this very active surface. The production of a few ions during the decay of the afterglow in phenomena studied by Constantinides (*Physical Rev.*, 1927, **30**, 95) is probably due to a side reaction among the atoms undergoing recombination on the surface.

It is clear that the relationship between concentration of active nitrogen, $C$, and glow intensity, $I$, as well as the magnitude and sign of $dI/dC$ at any instant, will vary with the nature and area of the surfaces present. It appears probable that the mechanism whereby the chemically active nitrogen is destroyed in the discharge is analogous to that of the electrical production of ozone, and that the same complicated mixture of electrical and surface factors is involved : much more experimental evidence is needed upon this point.

It remains to discuss the probable nature of the chemically active modification of nitrogen. If this were triatomic, it would be expected that such a large molecule should condense easily (see Lord Rayleigh, *Proc. Roy. Soc.*, 1911, *A*, **86**, 56), and the author is indebted to Sir J. J. Thomson for the information that evidence is not lacking that such a separation can be effected under appropriate conditions.

The present author suggests, however, that the most cogent evidence as to the nature of active nitrogen is provided by the compounds it produces in its chemical reactions. With the metals, compounds are produced which, as a rule, give quantitative yields of ammonia when hydrolysed, *e.g.*, magnesium nitride; pentane gives hydrogen cyanide, amylenes, and ammonia (Koenig and Elöd, *loc. cit.*); and in general *when active nitrogen reacts with other substances it gives rise to derivatives of ammonia and not to substituted azoimides, hydrazines, etc.* These substances are invariably of the type produced in the few reactions of *inert* nitrogen, and hence the presumption is that active and ordinary nitrogen cannot be very different in structure. It is clear that if active nitrogen were atomic in character we should have to postulate dissociation of the molecule as an invariable prelude to the reactions of *inert* nitrogen, which does not appear likely. May it not be that the active modification is simply an isomeride of nitrogen, such as an acetylenic molecule ? By analogy with its family congeners of the Periodic Table, nitrogen might be expected to exhibit allotropy, but much more experimental evidence is necessary before any conclusions can be reached upon this point.

*Summary.*

Four series of experiments are described in which it is shown that nitrogen can be chemically active and yet show no visible luminosity whatever. These are believed to indicate that " active " nitrogen consists of a mixture of a non-luminous, chemically active substance together with a very small proportion of atoms, the latter being responsible, upon a termolecular recombination, for the afterglow and the greater part of the excitation of spectra observed when various substances are admitted to the glowing gas. The heats of formation of the two varieties, the former of which is regarded as being most probably a metastable diatomic or an acetylenic molecule, are respectively about 45,000 and 200,000—250,000 cals./g.-mol.

This explanation is thought to reconcile the chemical and spectroscopic views, and also accounts for the whole of the phenomena connected with active nitrogen.

*Addendum.*—Since the above was written, Crew and Hulbert (*Physical Rev.*, 1927, **30**, 124) have described some experiments on the dissociation of gases in the discharge at low pressures (5 mm. and less). The extent of dissociation is about 100% for wet hydrogen, rather less for the dry gas, 60% for oxygen, but close to zero for nitrogen, carbon monoxide, and carbon dioxide under the same conditions; the results with uncondensed and with condensed discharges, the latter producing the afterglow in nitrogen, are almost identical. This would appear to show once again that the chemically active nitrogen (which is produced to the extent of at least 5% under these conditions) cannot be atomic in character, and the work confirms the author's view upon this subject.