

CCXXXIX.—*On Active Nitrogen. Part I. Its Nature and Heat of Formation.*

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It was shown by Strutt, now Lord Rayleigh (*Proc. Roy. Soc.*, 1911, **85**, 219; 1911, **86**, 56; 1912, **86**, 262; 1912, **87**, 180; 1913, **88**, 539; 1915, **91**, 303; 1916, **92**, 438; *J.*, 1918, **113**, 200) that the glowing nitrogen, which is formed (compare Morren, *Ann. Chim. Phys.*, 1865, **4**, 293; Lewis, *Astrophys. J.*, 1900, **12**, 8) when a moderately condensed discharge with a spark gap in series is passed through the gas at low pressures, readily effects the decomposition of hydrocarbons, and the formation of nitrides with metals and of nitrogen peroxide with nitric oxide. Oxygen, if admitted to the glowing gas, produced an instantaneous catalytic decay. He also showed that the removal of charged particles surviving the discharge had no effect on the afterglow and concluded that active nitrogen did not consist of any ionic form of nitrogen, a conclusion with which Wien is in agreement.

As the result of further work (Strutt, *loc. cit.*; Baker, Strutt, Tiede, and Domcke, *Ber.*, 1914, **47**, 2283; Baker and Strutt, *ibid.*, pp. 801, 1049; Pirani, *Chem. Zentr.*, 1923, i, 17), it was shown that, although the presence of traces of oxygen or certain other impurities in the nitrogen intensified the afterglow, yet the pure gas was undoubtedly capable of a faint luminescence under the same conditions.

There are two views as to the nature of this active nitrogen: it may consist either of atoms or of metastable molecules in an excited form. The atomic hypothesis has been suggested on the following grounds:

(1) Angerer (*Physikal. Z.*, 1921, **22**, 4, 97) has shown that the glow decay rate follows a bimolecular law, a result confirmed by experiments of the present authors, to be published later.

(2) The anomalous behaviour of the afterglow in being sustained by heating and destroyed by cooling makes it appear that the reacting systems are unique and perhaps atomic (Lord Rayleigh).

(3) From the simple nature of the spectrum of the afterglow and the failure of all investigators to condense out any form of active nitrogen, such as may readily be effected in the case of ozone, Lord Rayleigh concluded that the formation of complex molecules, such as N_3 , was not the cause of the activity and that a recombination of atoms with consequent liberation of energy was involved. Such deductions from the spectrum may be vitiated by the presence of products of high energy content which undergo much more rapid decomposition than the comparatively long-lived afterglow under discussion.

In favour of the alternative hypothesis of metastable molecules being the cause of the activity, Saha and Sur (*Phil. Mag.*, 1924, **118**, 421) postulate that, since when active nitrogen reacts with certain metals no lines requiring more than 8.5 volts for their production are to be observed in the spectra of the accompanying luminous phenomena, this figure represents an upper limit to the energy of active nitrogen. To quote Saha and Sur: "Hydrogen and the inert gases have no other influence on active nitrogen except a mere dilution of the glow. This is in accordance with the fact that the minimum excitation potential of these gases is much higher than the maximum energy which can be transferred by active nitrogen." On the other hand, nitrogen should be activated by excited helium (19.2 volts), a view which is supported to a certain extent by the experiments of Rayleigh (Strutt, *Proc. Roy. Soc.*, 1916, **102**, 454). The validity of this argument is somewhat impaired in view of our knowledge of the effects of chemiluminescence, since the heats of formation of the nitrides of magnesium,

calcium, and barium are respectively of the order of 120,000, 112,000, and 199,000 cal. per g.-mol. If the formation of magnesium nitride occurred through interaction between a metastable molecule of nitrogen with an energy of excitation of 2—3 volts and inactive magnesium, then the total energy liberated in combination, if expelled as monochromatic radiation, would be of the order of 8.5 volts. The passage of warm nitrogen over finely-divided magnesium does in fact produce chemiluminescence, a phenomenon more readily observed in the case of lithium. In addition, excited mercury atoms (4.9 volts) readily excite molecular hydrogen whereas active nitrogen fails to do so.

A further argument in favour of the second hypothesis is to be found in the approximate energy content of active nitrogen determined by Lord Rayleigh. He found that this was of the order of 1.2 to 1.8 times that of nitric oxide, *i.e.*, from 26,000—39,000 cal. per g.-mol., whilst the evidence of Langmuir (*J. Amer. Chem. Soc.*, 1912, **34**, 860) and of Eucken (*Annalen*, 1924, **440**, 111) shows that the heat of dissociation of nitrogen into atoms is greater than 190,000 and probably of the order of 300,000—400,000 cal. per g.-mol. The destruction of the afterglow by a second weak discharge observed by Lord Rayleigh also suggests the deactivation of metastable molecules by electrons.

It is noteworthy that some experiments of Fowler and Strutt (*Proc. Roy. Soc.*, 1911, **85**, 377), in which no afterglow was observed when the discharge was such as to give only the line spectrum of nitrogen, *i.e.*, when the nitrogen atoms are definitely present, are antagonistic to the first hypothesis, as is also the absence from the afterglow spectrum of nitrogen lines which would indicate the presence of atoms therein. Whilst it is maintained by some (*e.g.*, Duffieux, *Compt. rend.*, 1922, **175**, 159) that free atoms *may* give rise to band spectra, the view that the banded nitrogen afterglow represents the deactivation of excited molecules rather than the recombination of atoms is more plausible. Although Birge now favours the hypothesis of the atomic nature of active nitrogen (*Nature*, 1926, **117**, 80), yet he was formerly of the opinion that the α bands of the afterglow spectra at least are due to metastable nitrogen molecules at an energy level of 11.5 volts (9.3 volts electronic and 2.2 oscillatory) and that the β and probably the γ bands also are due to the presence of small traces of oxygen, perhaps in the form of excited nitric oxide—a view supported by the experiments of Lord Rayleigh (Strutt, *Proc. Roy. Soc.*, 1917, **93**, 254) (see also Mulliken, *Nature*, 1924, **114**, 349).

From these considerations, it is clear that the only definite thermal data on the energy content of active nitrogen are those of

Lord Rayleigh, *i.e.*, 26,000—39,000 cal. The other views lead us to the hypothesis of metastable molecules of the energy content of *ca.* 195,000 cal. or of atoms with a molecular heat of dissociation of *ca.* 300,000 cal. Since the chemical properties of active nitrogen are probably largely determined by the energy content, it seemed desirable to attempt its evaluation. This has been measured by two different methods which lead to the conclusion that active nitrogen consists of metastable molecules excited to a level of *ca.* 2.0 volts (43,800—41,000 cal.), a value comparable with the "oscillatory" energy of 2.2 volts (50,400 cal.) postulated by Birge (*loc. cit.*). This relatively low energy content of active nitrogen is, as we hope to show in a subsequent communication, consonant with the chemical reactivity of the gas, and may provide an explanation for the excitation of nitrogen in low voltage arcs observed by Duffendack and Compton (*Physical Rev.*, 1924, **23**, 583).

EXPERIMENTAL.

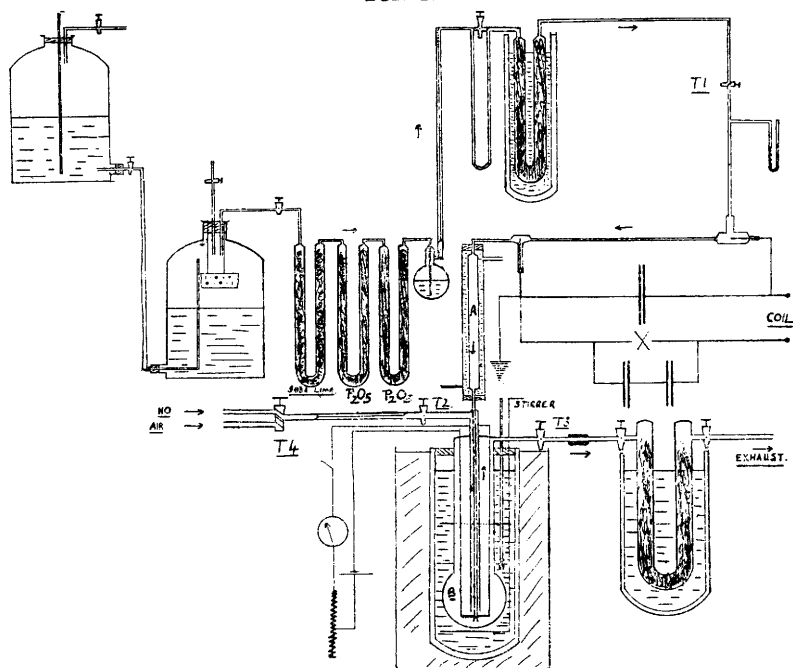
Nitrogen freed from oxygen by standing over-night in contact with yellow phosphorus, as described by Lord Rayleigh, was drawn from a constant-head aspirator, through soda lime and phosphorus pentoxide drying tubes, a paraffin bubbler, a Venturi flow-meter, a liquid-air condensing tube, and a capillary choke, to the discharge tube. Here it was converted into the active form by a powerful discharge obtained from a coil, condensers, and spark gap as indicated in Fig. 1. (The current in the primary circuit was 3.5 amps. at 16 volts; aluminium electrodes were used, and the discharge was 30 cm. in length.) From the discharge, the nitrogen passed through the water-jacketed tube, A, where it was cooled to a constant temperature, and thence down the fine tube which terminated in a jet in the bulb B. Surrounding the active nitrogen inlet was a second tube whereby the nitric oxide could be admitted from a similar drying train and control system and the mixture of gases was then drawn to the exhaust through the outer wide tube (as shown), the vacuum tap T3, and the U-tube packed with glass wool and immersed in liquid air. Sealed into the wide outer tube of the calorimeter were two heavy copper leads carrying at their lower end, in the bulb itself, a platinum heating spiral of known resistance which was connected in series with a switch, a rheostat, an accurate ammeter, and a storage cell.

The outer tube was surrounded by toluene contained in a Dewar flask provided with a stirrer and a thermometer and itself heavily lagged with cotton wool. The apparatus was constructed of Pyrex glass and all joints were sealed together; the discharge tube and calorimeter were also enclosed in a large box lined with black

cloth and fitted as an air thermostat. (The scale of the calorimeter and U-tube is exaggerated in the diagram in order to show the necessary details clearly.)

The decay of active nitrogen is extraordinarily susceptible to catalytic impurities on the glass, but with scrupulously clean Pyrex glass this may be reduced to a minimum. The discharge tube and calorimeter, before being fitted up, were treated over-night with hot chromic acid and, after being washed fifteen times with conductivity water, were sealed together; the electrodes were fixed in

FIG. 1.

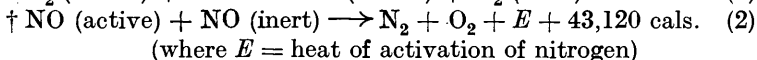
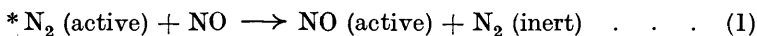


position by means of Faraday wax and, after the apparatus had been thoroughly exhausted several times by means of a Fleuss pump, the discharge was started and the active nitrogen drawn through until it passed to the U-tube and pump without appreciable loss of glow intensity.

The gas was drawn through the apparatus at 10 mm. pressure and a constant rate of 1.0—1.5 litres per hour (at normal pressures), as desired, until the calorimeter temperature was constant. The difference in pressure between the two sides of the capillary choke of the Venturi meter, which by calibration experiments was found to be proportional to the rate of flow of gas within the velocity

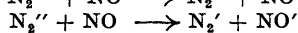
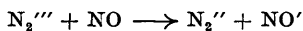
range examined, could be maintained constant during the experiment. The current was then switched on and active nitrogen allowed to flow through the apparatus for some little time, since it was found that the discharge took 15 minutes or so in which to settle down to a steady condition. No rise in temperature in the calorimeter was observed when active nitrogen alone was flowing. The nitric oxide was then admitted and the temperature read at regular intervals until it was constant, which generally took about 45 minutes, after which the experiment was continued for an equal period of time to permit of a good yield of nitrogen peroxide being obtained. The stopcocks on the U-tube were then closed, as were T1, T2, and T3, and the discharge was stopped. The U-tube was disconnected at the pressure tubing junction, allowed to warm up, and the nitrogen peroxide blown by means of carbon dioxide from a Kipp generator through a train of absorption bottles containing 10% potassium iodide solution, the iodine thus produced being subsequently titrated with *N*/50-sodium thiosulphate. The pump was then re-started, and nitrogen and nitric oxide were drawn through the apparatus until the temperature of the toluene was again constant, after which the heater current was switched on and adjusted until the temperature rise observed in the experiment in which the nitrogen had been activated was reproduced and maintained. The current supplied and the resistance of the filament being known, the heat equivalent per second of the nitric oxide-active nitrogen reaction is at once obtained.

Calculation.—The reaction most probably proceeds as follows :



The last reaction, however, does not take place in the calorimeter, since we have calculated from the figures of Bodenstein (*Z. Elektro-*

* There is no definite proof that the reaction proceeds in such a simple manner. It might, for example, be suggested that active nitrogen consists of excited molecules with three steps in the reversion to the normal form; we would then obtain a series of bimolecular reactions



The heat of reaction determined in the above manner would thus be the mean of the energy contents of these three levels. For lack of evidence to the contrary we have adopted the simplest hypothesis.

† Since the reaction proceeds with great speed at low pressures, this molecular process is more probable than the slow reaction involved in the alternative mechanism $2NO' \longrightarrow N_2 + O_2 + 2E + 43,120$.

chem., 1918, **24**, 183) that at the partial pressure of oxygen in the experiment the oxidation of the nitric oxide would take over 1000 seconds whereas the gases are in the calorimeter for 0.7 second only; rather must the oxidation take place at the liquid-air temperature in the U-tube. The reaction $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ is known to have a small negative temperature coefficient.

That this view was correct, *viz.*, that oxygen and not nitrogen peroxide was the primary product of the reaction, was confirmed by the passage of the gases through two absorption tubes in series, the first containing glass wool saturated with potassium iodide and the second being maintained at liquid-air temperature. The ratio of the quantities of nitrogen peroxide caught in the two tubes in a series of experiments was never more than 1 : 20. If nitrogen peroxide had been present in the original gas, it would have been almost completely retained in the first tube.

From (2) we obtain

$$22,400 \text{ c.c. NO}_2 \equiv 21,560 + E/2 \text{ cal.}$$

Now, since the heat liberated by the formation of x c.c. of nitrogen peroxide per second (determined experimentally) is equivalent to y cal. of heat evolved per second (determined in calibration experiment),

$$22,400 \text{ c.c. NO}_2 \equiv 22,400y/x \text{ cal./sec.}$$

or

$$2(22,400y/x - 21,560) = E.$$

The results of two experiments are given.

TABLE I.

Duration of expt.	Temp. rise.	C.c. of NO ₂ formed.	C.c. of NO ₂ per sec.	Cal./sec. (from calibration).	<i>E</i> .
105 mins.	0.205°	25.7	0.00408	0.00775	42,300
90 „	0.170	17.5	0.00325	0.00540	45,300

Other determinations gave similar results with a mean value of 43,800 cal. per g.-mol.

Second Method.

The active nitrogen was drawn through the apparatus just as in the first method, but by turning the two-way tap, T₄, through 180° an exactly equivalent stream of air was admitted instead of nitric oxide. The temperature rise was measured and reproduced as before.

Calculation.—If $\Delta\theta_1$ be the temperature rise in the reaction when active nitrogen forms its equivalent of nitrogen peroxide, and $\Delta\theta_2$ be that observed when the active nitrogen undergoes the catalytic

decay in the presence of oxygen, then the heat of formation of active nitrogen is given by the equation

$$\Delta\theta_1/\Delta\theta_2 = (E + 2Q_{\text{NO}})/E = (E + 43,120)/E.$$

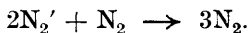
In three experiments the values obtained for $\Delta\theta_1$ were 0.33, 0.37, 0.35°, and for $\Delta\theta_2$, 0.17, 0.17, 0.17°. Hence $E =$ (a) 46,000, (b) 36,700, (c) 40,800, whence we obtain a mean value for $E = 41,200$ cal./g.-mol.

Conclusions.

By these two methods the energy content of active nitrogen is found to be 43,800 and 41,200, or a mean of 42,500 cal. per g.-mol. (*ca.* 2.0 volts). This value is obtained on the hypothesis that active nitrogen can activate only one molecule of nitric oxide during its reversion to the normal form. The possibility that active nitrogen might possess several intermediary levels between the active and normal states must not be overlooked. If this were the case, the energy content of active nitrogen would be $42,500 \times n$, where n is the number of nitric oxide molecules activated by active nitrogen during the process of reversion.

That the spectrum of active nitrogen reveals the presence of some bands with heads at higher energy levels than 2.0 volts presents a difficulty in view of the low calorimetric energy content. Since, however, the decay of active nitrogen is a bimolecular process the radiations corresponding to the higher energy levels observed may be emitted as a result of bi- and multi-molecular collisions among the excited molecules. We therefore conclude that active nitrogen consists of metastable molecules excited to about 2 volts.

To effect this excitation, it appears that the molecule has to be excited to a high level (*ca.* 11.5 volts), but the electronic energy rapidly disappears after departure of the gas from the discharge zone—the lives of excited molecules according to Wien's experimental determinations are usually of the order 10^{-6} — 10^{-7} second—leaving metastable nitrogen molecules which might be regarded as the acetylenic form postulated on simple valency considerations. In support of this view the following considerations may be advanced. (i) The decay of active nitrogen appears to be comparable with the oxidation of nitric oxide ($2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$) and the reaction has a similar temperature coefficient. The similarity between the two reactions suggests the mechanism



The decay of active nitrogen would thus be a termolecular process, but bimolecular with respect to the active nitrogen. Whether the third reacting molecule consists of nitrogen or some impurity cannot

be stated at present. (ii) The view that the energy content of active nitrogen is more than 40,000, but less than 90,000 cal. per g.-mol. receives some support from a consideration of the minimum *chemical* critical energy increments or energies of activation of substances which extinguish the fluorescence of active nitrogen, but do not combine with it to form markedly exothermic compounds which might give rise to the phenomenon of chemiluminescence. The following substances have been examined by Lord Rayleigh and others, including ourselves.

Substance.	E per g.-mol.	Effect on fluorescence.
NH ₃	22,000	+
O ₂	30,000	+
I ₂	35,000	+
NO	47,500 (mean value)	+
H ₂	90,000	-

The critical increment for oxygen of 30,000 cal. was calculated from the data of Chapman and Jones (J., 1910, 97, 2463) on the decomposition of ozone, and of iodine and hydrogen from their heats of dissociation. The value of 47,500 for the energy of excitation of nitric oxide is the mean of the values, 24,290 at 962° K and 70,870 at 1525° K, obtained from the experiments of Jellinek (*Z. anorg. Chem.*, 1906, 49, 2229), in which, however, a heterogeneous as well as a homogeneous reaction was undoubtedly taking place.

It is hoped to investigate in more detail some of these reactions which are sensitised by active nitrogen.

Summary.

The heat of formation of active nitrogen has been determined by two different methods giving a mean value of 42,500 calories per g.-mol. It is concluded that "active" nitrogen is nitrogen in a metastable molecular form.

A comparison of the reactions of active nitrogen with those of nitric oxide and observations of the effect of various gases in extinguishing the fluorescence of active nitrogen are made.

We have to thank Lord Rayleigh and Prof. T. M. Lowry for their kind interest in the work and the Department of Scientific and Industrial Research for a grant which enabled one of us (E. J. B. W.) to pursue these investigations.

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