

## ACTIVE NITROGEN

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WHEN nitrogen is subjected to an electrical discharge at low pressures, a brilliant peach-coloured glow is emitted. In 1900 Lewis<sup>1</sup> discovered that when the discharge is switched off a golden-yellow afterglow remained for several seconds. In 1911 Strutt<sup>2</sup> named the glowing gas "active nitrogen" and suggested that many of its properties could be attributed to the presence of atomic nitrogen. Since then several other theories have been put forward, invoking excited atoms and molecules and even ions to explain the afterglow, but during the past ten years the application of modern experimental techniques has shown that the main reactive component in active nitrogen is the nitrogen atom in the ground state. The purpose of this Review is to present the results of recent experiments, and to show how these have led to a more detailed exposition of the atomic theory of active nitrogen.

### Summary of early work

An excellent review of experimental work up to 1945 is given in a short book by Mitra<sup>3</sup> in which there are many references to original papers. The more important results are summarised below.

*Production of active nitrogen.* Nitrogen can be activated by means of a condensed electrode discharge, or by a high-frequency electrodeless discharge, the latter being preferred since the gas does not become contaminated with electrode materials. Active nitrogen has also been produced by bombarding the gas with electrons of energy greater than 16.3 eV,<sup>4</sup> and Stanley<sup>5</sup> has recently used an arc discharge to produce active nitrogen at pressures as high as 20 cm. Hg.

The purity of the gas appears to be important: a trace (0.1%) of an electronegative element such as oxygen enhances the glow. Absolutely pure nitrogen in a baked-out vessel appears not to give the afterglow.<sup>6</sup> This is almost certainly due to the rapid removal of nitrogen atoms from the gaseous phase by recombination at the walls. Higher concentrations of impurities inhibit the production of the afterglow, since atoms are then removed by chemical reaction.

*Kinetics of decay of the afterglow.* The lifetime of the afterglow is very

<sup>1</sup> P. Lewis, *Astrophys. J.*, 1900, **12**, 8.

<sup>2</sup> Strutt, *Proc. Roy. Soc.*, 1911, *A*, **85**, 219; 1911, *A*, **86**, 56; 1913, *A*, **88**, 539; 1915, *A*, **91**, 303.

<sup>3</sup> Mitra, "Active Nitrogen—A New Theory", Association for the Cultivation of Science, Calcutta, India, 1945.

<sup>4</sup> Kenty and Turner, *Phys. Rev.*, 1928, **32**, 799.

<sup>5</sup> Stanley, *Proc. Phys. Soc.*, 1954, **67**, *A*, 821.

<sup>6</sup> B. Lewis, *J. Amer. Chem. Soc.*, 1929, **51**, 564.

dependent upon the condition of the walls of the containing vessel. A coating of metaphosphoric acid prolongs the lifetime of the glow considerably, but a coating of Apiezon oil rapidly destroys it. The lifetime of the afterglow is also very sensitive to pressure, the optimum pressure for the production of an afterglow of long life being between  $10^{-1}$  and  $10^{-2}$  mm. Hg. Rayleigh<sup>7</sup> showed that the rate of decay was proportional to the square of the concentration of the active species and to the concentration of the unexcited nitrogen molecules. He also showed that the process responsible for the afterglow has a negative temperature coefficient, since  $I \propto T^{-0.64}$ , where  $T$  is the absolute temperature.

*Emission spectrum of the afterglow.* Until very recently, it was thought that this consisted only of selected bands of the First Positive System of the  $N_2$  molecule, in the visible region of the spectrum, which are normally observed in the positive column of an electrode discharge through nitrogen. These bands are due to a transition from a more highly-excited state (the  $B$  state) to a lower excited state (the  $A$  state), from which the molecules reach the ground state (the  $X$  state) by losing their excess of energy in collisions with other molecules and with the containing walls. From the intensity distribution of the vibrational bands within the system, it appeared that the process leading to the formation of excited molecules in the  $B$  state never produced them with more than 12 vibrational quanta, and preferentially produced them with 12, 11, 10, 6, 4, 3, and 2 vibrational quanta. However, as will be seen later, it has recently been suggested that the bands which were thought to be due to transitions from the lower vibrational levels of the  $B$  state may be part of a different system involving neither the  $B$  nor the  $A$  state.

Bands due to the NO molecule are usually present in the blue and ultra-violet regions of the spectrum, owing to the presence of small quantities of oxygen or compounds containing oxygen.

*Electrical properties of the afterglow.* If a stream of glowing gas from the discharge tube is passed between two auxiliary electrodes it is found that the gas has a high electrical conductivity. On increase of the applied voltage a saturation current is obtained, the magnitude of which is proportional to the area of the cathode.<sup>8</sup> This suggested that electrons are emitted from the cathode owing to atomic or molecular bombardment, but Rayleigh<sup>9</sup> used a hot cathode and found that the saturation current decreased rather than increased. He suggested that positive ions in the gaseous phase were responsible for the conductivity, but more recent work<sup>10</sup> indicates that the charged particles are electrons, and that their concentration is less than  $10^{-6}$  of the concentration of the active species in active nitrogen. Several workers have shown that passage of the glowing gas through an ion trap does not affect the glow, making it very improbable that charged particles play any part in the production of the glow.

<sup>7</sup> Rayleigh (Strutt), *Proc. Roy. Soc.*, 1935, *A*, **151**, 567; 1940, *A*, **176**, 1.

<sup>8</sup> Constantinides, *Phys. Rev.*, 1927, **30**, 95.

<sup>9</sup> Rayleigh, *Proc. Roy. Soc.*, 1942, *A*, **180**, 140.

<sup>10</sup> Benson, *J. Appl. Phys.*, 1952, **23**, 757.

*Excitation of spectra and chemical reactions.* When other substances are introduced into a stream of active nitrogen, a luminous zone is very often observed at the point of mixing. The spectra excited in these glows are either those of the unchanged substance or those of radicals or molecules formed by chemical reaction. Summaries of the many systems investigated are given by Strutt,<sup>2</sup> Strutt and Fowler,<sup>11</sup> and Willey and Rideal.<sup>12</sup>

Metallic vapours usually give rise to spectra consisting of atomic lines of the metal, accompanied by the formation of the nitride. The reaction with nitric oxide produces mainly nitrogen and oxygen<sup>13</sup> with some nitrogen dioxide as a by-product.

Hydrocarbons react to form hydrogen cyanide as the main product, the CN bands being prominent in the spectrum of the glow. Neither hydrogen nor oxygen reacts with active nitrogen.

*Energy measurements.* Strutt<sup>14</sup> observed the temperature rise when active nitrogen was destroyed on a copper oxide probe, and compared it with the temperature rise recorded when the active nitrogen was made to react with nitric oxide before it reached the probe. Since these were similar, he concluded that active nitrogen did not contain an abnormally high amount of energy.

Willey and Rideal,<sup>12</sup> using calorimetric methods, estimated that the energy content was about 2 ev/mole of total nitrogen. Since active nitrogen does not react with hydrogen, hydrogen chloride, or nitrous oxide, all with dissociation energies of over 60 kcal./mole, they concluded that it contained insufficient energy to do so. Spectroscopic excitation up to about 9.6 ev is known, but the above workers suggested that all except 2 ev of this was due to chemiluminescence in nitride formation.

Rayleigh<sup>15</sup> exposed metal foil to streams of active nitrogen, and from the temperature attained by the foil calculated that the energy available in active nitrogen may be as high as 12.9 ev/mole of total nitrogen. It has since been shown, however, that much of this heating effect was due to electron bombardment from the discharge so that these results are invalid.<sup>10</sup>

*Other results.* Wrede,<sup>16</sup> using the gauge which now bears his name, detected concentrations of up to 30–40% of atoms in active nitrogen produced by a strong condensed electrode discharge. The results of a Stern–Gerlach type of experiment on active nitrogen suggested that only  $^2P_{\frac{1}{2}}$  atoms were present,<sup>17</sup> but no absorption in the region of 1400–1800 Å, in which both  $^2P$  and  $^2D$  atoms would absorb, could be found,<sup>18</sup> suggesting that any atoms present were in the ground state. Many experiments since then have confirmed that the vast majority of atoms present in active nitrogen are in the ground state.

<sup>11</sup> Strutt and Fowler, *Proc. Roy. Soc.*, 1911, *A*, **86**, 105.

<sup>12</sup> Willey and Rideal, *J.*, 1927, 669.

<sup>13</sup> Spealman and Rodebush, *J. Amer. Chem. Soc.*, 1935, **57**, 1474.

<sup>14</sup> Strutt, *Proc. Roy. Soc.*, 1912, *A*, **87**, 179.

<sup>15</sup> Rayleigh, *ibid.*, 1940, *A*, **176**, 16.

<sup>16</sup> Wrede, *Z. Physik*, 1929, **54**, 53.

<sup>17</sup> Jackson and Broadway, *Proc. Roy. Soc.*, 1930, *A*, **127**, 678.

<sup>18</sup> Herbert, Herzberg, and Mills, *Canad. J. Res.* 1937, **15**, *A*, 35.

### Theories of active nitrogen

Attempts to formulate a theory of active nitrogen have been hindered by the uncertainty and divergence of opinion on almost every experimental observation. The purity of the nitrogen and the condition of the walls are very important but, not unnaturally, this was not always recognised by some of the earlier workers. The importance of the electrical properties has been difficult to assess, and only Mitra's theory, now abandoned, attempted to explain them.

Energy considerations have been one of the main sources of trouble. Both the energy content of active nitrogen and the dissociation energy of

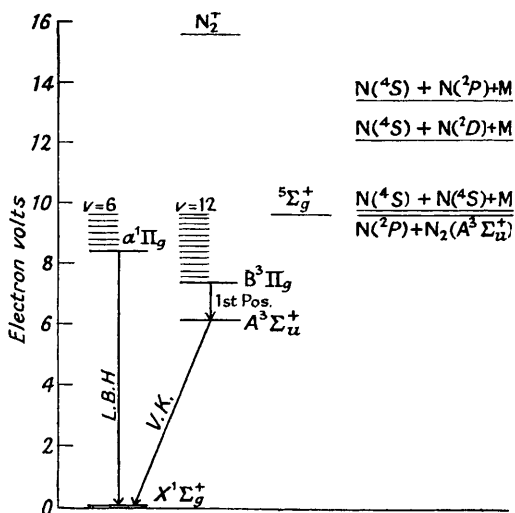


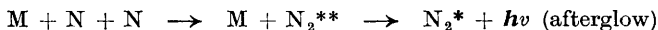
FIG. 1

Energy levels of molecular and atomic nitrogen relative to the energy of the molecule in its ground state.

the  $N_2$  molecule have been extremely uncertain until quite recently. In addition, the number and complexity of the excited levels of the  $N_2$  molecule make a detailed interpretation more difficult.

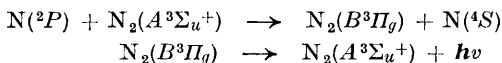
Consequently, it is not difficult to see why there were *three* totally different theories of active nitrogen in 1945. These are outlined below. (In the following pages, the different electronic levels of nitrogen atoms and molecules are referred to by their spectroscopic designations. Although these are important in deciding whether or not a particular transition or reaction may occur, they may be looked upon, for the purposes of this Review, as mere labels for the different electronic levels. The energies of these states relative to the ground states are given in Fig. 1. In discussion of vibrational levels,  $v'$  indicates the vibrational level of the upper electronic state,  $v''$  that of the lower state.)

*The atomic theory.* Rayleigh<sup>2</sup> first suggested that active nitrogen contained nitrogen atoms, and Sponer<sup>19</sup> later suggested a two-step mechanism:



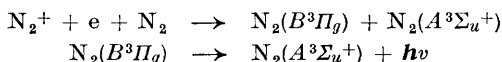
Since three-body collisions are rare in the gaseous phase at low pressures, this could explain the long life of the glow, and it would also explain the kinetics of the decay. Now that the dissociation energy of the  $N_2$  molecule is known to be 9.76 eV,<sup>20</sup> this theory can satisfy all energy observations (except Rayleigh's invalid metal-foil experiments). The work of Wrede<sup>16</sup> and of Herbert, Herzberg, and Mills<sup>17</sup> suggests that active nitrogen contains appreciable quantities of ground-state atoms, thus supporting this theory. However, it does not explain the selective enhancement of certain vibrational bands in the spectrum of the afterglow, nor does it offer any explanation of the electrical properties of active nitrogen.

*Cario and Kaplan's theory.* This theory<sup>21</sup> suggests that active nitrogen is a mixture of metastable atoms and molecules, which produce the afterglow as follows:



This can explain the selective enhancement of certain vibrational bands, since the  $A$  state is about 6.2 eV and the  $^2P$  state 3.56 eV above the respective ground states, and between them they can provide 9.76 eV, which is just enough to produce molecules in the twelfth vibrational level of the  $B$  state. This theory was preferred to the atomic theory when the dissociation energy of  $N_2$  was thought to be 7.37 eV, and was apparently supported by the results of the Stern-Gerlach experiment<sup>17</sup> but not by the vacuum-ultra-violet absorption spectrum.<sup>18</sup> The absence from the afterglow of the Vegard-Kaplan bands, due to the transition  $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ , suggests that there is no appreciable stationary concentration of molecules in the  $A$  state as would be required by this theory.

*Mitra's theory.* In 1945 Mitra<sup>3</sup> suggested that active nitrogen consisted of a mixture of  $N_2^+$  ions and electrons, which would readily explain the electrical conductivity of the gas. The afterglow would be produced by the reactions:



Since this required a three-body collision, it would explain the long life of the afterglow, but it is unsatisfactory from the point of view of energy. The reaction  $N_2^+ + e$  can liberate only 15.58 eV and 15.85 eV are required to produce one nitrogen molecule in the twelfth vibrational level of the  $B$  state, and one in the zeroth vibrational level of the  $A$  state. Mitra suggests that the energy deficiency of 0.27 eV may be derived from kinetic energy,

<sup>19</sup> Sponer, *Z. Physik*, 1925, **34**, 622.

<sup>20</sup> Gaydon, "Dissociation Energies", Chapman and Hall, London, 1st edn., 1947; 2nd edn., 1953.

<sup>21</sup> Cario and Kaplan, *Z. Physik*, 1929, **58**, 769.

but this seems an improbable source of so much energy (6 kcal./mole). The theory can clearly account for energy contents of up to about  $15\frac{1}{2}$  ev/mole and so explain Rayleigh's metal-foil experiments. Chemical reactions were formulated in terms such as  $X + e \rightarrow X^-$ , followed by  $N_2^+ + X^- \rightarrow$  products. However, for reasons which are explained later, Mitra abandoned his theory in 1953.

Since 1945, use of new and more refined experimental methods has made possible the elucidation of many of the problems concerning the nature of active nitrogen. Although a theory which will explain all the experimental facts has not yet been formulated, it will be seen that a modification of the simple atomic recombination theory accounts for most of them.

*Evidence against Mitra's theory.* As early as 1947, Gaydon<sup>20</sup> pointed out that the results of Rayleigh's metal-foil experiments could probably be explained by assuming that the test surfaces were heated by cathode rays from the discharge as well as by active nitrogen. He considered that Mitra's theory was untenable since it does not explain why an electric field does not quench the glow and, as explained above, there was an energy deficiency of 0.27 ev. In 1948 Worley<sup>22</sup> failed to find any absorption in the visible region in the glowing gas, using a path length of 13 metres. If this theory were correct, absorption by ground-state  $N_2^+$  ions should occur in this region.

Strong evidence against this theory was obtained by Benson in 1952.<sup>10</sup> He repeated Rayleigh's metal-foil experiments, but placed an earthed aluminium tube, bent at a right-angle, between the discharge and the metal foil so as to remove electrons coming from the discharge. He was unable to reproduce Rayleigh's results, obtaining an energy content of only 1/400 of that obtained by Rayleigh. He also showed that the intensity of the glow was unaffected by the removal of charged particles, and that a beam of the glowing gas was not affected by a magnetic field. The concentration of electrons in the afterglow was found to be only about  $10^9$ /c.c., compared with a concentration of active particles of about  $10^{15}$ /c.c. As a result of this, it became clear that active nitrogen did not consist of a mixture of  $N_2^+$  and electrons, and the theory was abandoned.

*Evidence against Cario and Kaplan's theory.* This theory requires that the glowing gas should contain appreciable concentrations of excited atoms in the  $^2P$  and  $^2D$  states, and excited molecules in the  $A$  state. Worley<sup>22</sup> failed to find any absorption due to transitions from the  $A$  state of the nitrogen molecule, suggesting a very low concentration of molecules in this state. The lifetime of the  $A$  state with respect to radiation was estimated by Muschlitz and Goodman<sup>23</sup> to be about  $10^{-4}$  sec., but Lichten<sup>24</sup> considers that they were producing molecules in the  $a^1\Pi_g$  state, and that the true lifetime of the  $A$  state molecules is probably as high as  $10^{-1}$  sec. The lifetime is nevertheless very short if these molecules are to account for an

<sup>22</sup> Worley, *Phys. Rev.*, 1948, **73**, 531.

<sup>23</sup> Muschlitz and Goodman, *J. Chem. Phys.*, 1953, **21**, 2213.

<sup>24</sup> Lichten, *ibid.*, 1957, **26**, 306.

afterglow which may last for several hours.<sup>7</sup> The evidence supporting the presence of  $^4S$  atoms rather  $^2P$  or  $^2D$  atoms is summarised in the following section. It became unnecessary to postulate the presence of excited atoms when the higher dissociation energy (9.76 eV) for  $N_2$  was accepted during the present decade.

**Evidence supporting the Presence of Ground-state Atoms in the Afterglow.**—The Wrede gauge showed the presence of appreciable concentrations of atoms in the afterglow,<sup>16</sup> but the gauge does not distinguish between ground-state and excited atoms. Whereas the Stern–Gerlach experiment<sup>17</sup> suggested that atoms in the *ground* state were absent from the afterglow, the vacuum-ultraviolet absorption spectrum<sup>18</sup> suggested that *excited* atoms were absent from the afterglow.

The first positive evidence of the presence of ground-state atoms in the afterglow was obtained by examining the paramagnetic resonance spectrum of active nitrogen.<sup>25</sup> This indicated the presence of  $^4S$  atoms only, but concentrations of excited atoms of up to 1% of the total atom concentration would not be detected by this method.

More recently, two mass-spectrometric studies of active nitrogen have been made.<sup>26, 27</sup> In each case, the appearance potential of the peak for mass 14 was found to be about 14.8 v, very close to the ionisation potential<sup>28</sup> of the nitrogen atom in the ground state (14.545 v). Again, small concentrations of excited atoms would not be detected by this method. An appearance potential in the region of 16.1 v was found in the earlier investigation<sup>26</sup> but no satisfactory explanation was given. It has been suggested<sup>29</sup> that this appearance potential is due to the presence of ground-state molecules with about 8 eV of vibrational energy. When 2% of nitrous oxide is added to a stream of the glowing gas, a considerable temperature rise occurs at the point of mixing. Because of the negative temperature coefficient of the process responsible for the afterglow, there is an appreciable decrease in the intensity of the afterglow immediately after the point of mixing, but the intensity actually *increases* farther down the tube. This suggests that the temperature increase is not due to a reaction of nitrogen atoms with the nitrous oxide, especially since no nitric oxide or oxygen are formed, but is caused by the deactivation of vibrationally excited ground-state nitrogen molecules.<sup>29a</sup>

The vacuum-ultraviolet absorption spectrum of active nitrogen has been re-examined recently.<sup>30</sup> There was a very strong absorption line at 1200 Å, indicating the presence of an appreciable concentration of  $^4S$  ground-state atoms. Much weaker lines were found at 1493 and 1743 Å, indicating much lower concentrations of nitrogen atoms in the  $^2D$  and the  $^2P$  state.

<sup>25</sup> Heald and Beringer, *Phys. Rev.*, 1954, **96**, 645.

<sup>26</sup> Jackson and Schiff, *J. Chem. Phys.*, 1955, **23**, 2333.

<sup>27</sup> Berkowitz, Chupka, and Kistiakowsky, *ibid.*, 1956, **25**, 457.

<sup>28</sup> Herzberg, "Atomic Spectra and Atomic Structure", Dover Publications, 2nd edn., 1944.

<sup>29</sup> Evans and Winkler, *Canad. J. Chem.*, 1956, **34**, 1217.

<sup>29a</sup> Kaufman and Kelso, *J. Chem. Phys.*, 1958, **28**, 510.

<sup>30</sup> Tanaka, Chem. Aeronomy Conference, Cambridge, Mass., 1956. Proceedings to be published by Pergamon Press.

From the above evidence, it is clear that the only species present in active nitrogen in appreciable concentrations are atoms and molecules in the ground state.

### Recent work on the afterglow

Until very recently the spectrum of the afterglow was thought to consist entirely of selected bands of the First Positive System of nitrogen, due to the transition  $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ . The enhanced bands appeared to originate mainly in the twelfth, eleventh, and tenth vibrational levels of the  $B$  state, but bands originating in the sixth, fourth, third, and second vibrational levels appeared to be enhanced to a smaller extent. The latter bands lie predominantly in the photographic infrared region, and this, together with

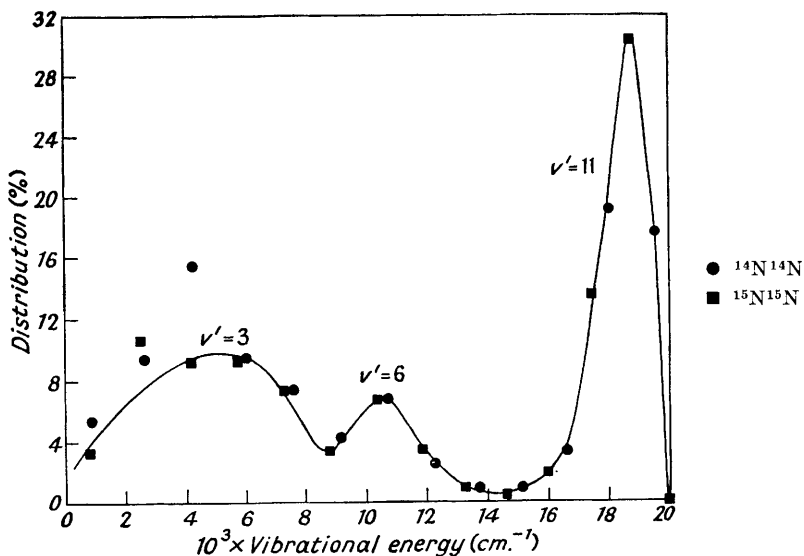


FIG. 2

*Apparent distribution of molecules (at 200°) in the different vibrational levels of the  $B^3\Pi_g$  state as indicated by the intensity distribution in the afterglow on the supposition that all bands in the visible and the photographic infrared region are part of the First Positive System.*

[After Kistiakowsky and Warneck, ref. 31]

their inherent weakness, has made the accurate measurement of their wavelengths difficult.

However, it has recently been suggested that the weaker bands are not in fact members of the First Positive System, but form a new system arising from transitions between unknown states of the nitrogen molecule.<sup>31</sup> By summing intensities of bands originating in the same vibrational level of the  $B$  state, an estimate of population distribution for  $^{14}\text{N}^{14}\text{N}$  and  $^{15}\text{N}^{15}\text{N}$  was obtained at 300°, 200° (Fig. 2), and 100° K, and after dilution with helium.

<sup>31</sup> Kistiakowsky and Warneck, *J. Chem. Phys.*, 1957, **27**, 1417.



The relative band intensities were independent of pressure in the range 2–16 mm. but varied with changes in temperature and addenda. The population curves obtained for each isotope coincided for the  $v' = 12, 11$ , and 10 peak, but there was some disagreement at lower  $v'$  values. The 12–11–10 peak became broader and moved to slightly lower  $v'$  values as the temperature was raised or helium was added. This indicates that vibrational energy is lost during the process leading to the formation of  $B$  state molecules in these levels. The lower peaks behave differently, however, and the evidence that they were not part of the First Positive System has been presented in ref. 31 as follows: (1) The population distributions of the two isotopes disagree at lower  $v'$  levels to an extent which depends upon the conditions. (2) The ratio of intensities of bands originating in the same  $v'$  level (on the above assignment) varies with conditions. (3) The spectrum includes at least three bands which fit poorly into the First Positive System. These are at approximately 6934, 7823, and 8949 Å, the nearest bands of the First Positive System being at 6968, 7896, and 8926 Å approximately. (4) The isotopic shift observed is inconsistent with that expected from the First Positive System assignment, the shift in the supposed (0,0) band being 130 cm.<sup>-1</sup>. Whereas the First Positive System is approximately represented by  $\nu = 9520 + 1733(v' + \frac{1}{2}) - 1460(v'' + \frac{1}{2})$ , the observed bands are better represented by  $\nu = 6050 + 1376(v' + \frac{1}{2}) - 1630(v'' + \frac{1}{2})$ . Hence neither the  $B$  nor the  $A$  state appears to be involved.

The ratio of the total intensities in the two parts of the population-distribution curve does not vary with pressure, and varies only slightly with temperature. It has been suggested that this indicates that the molecules in each of the upper states involved in these transitions are formed from nitrogen atoms *via* a common intermediate (see next section).

In addition to the above bands, bands of the Lyman-Birge-Hopfield System due to the transition  $a^1\Pi_g \rightarrow X^1\Sigma_g^+$  have recently been observed weakly in the vacuum ultraviolet region.<sup>28</sup> No bands due to transitions from levels higher than  $v' = 6$  are observed.

A combined mass-spectrometric and photometric study of the afterglow<sup>27</sup> showed that the intensity of the afterglow was proportional to the square of the concentration of nitrogen atoms in the ground state. This was shown to be true for bands originating in the  $v' = 11$  level of the  $B$  state and also for bands which were thought to originate in the  $v' = 6$  level, but which, it is now suggested, belong to a different system. The ratio of intensity to the square of the atomic concentration did not alter when oxygen was added to the system, indicating that oxygen plays no part in the production of the afterglow. The ratio increased when helium or argon was added to the nitrogen, indicating that these gases were more efficient than nitrogen as third bodies for the recombination of nitrogen atoms.

### Explanation of the afterglow

The main features of the afterglow can be summarised as follows: (a) The process giving rise to the afterglow is of the second order with respect to nitrogen atoms, and of first order with respect to nitrogen mole-

cules. (b) The process has a negative temperature coefficient. (c) The spectrum of the afterglow consists of two, or three, band systems.

The first two observations are readily explained by assuming that the overall process is of the type  $N + N + M \rightarrow \text{products}$ . From the observed spectrum, it appears that the products are  $N_2$  molecules in the  $a^1\Pi_g$ ,  $B^3\Pi_g$ , and  $Y$  states, where the  $Y$  state is the upper state involved in the proposed new band system. The original atomic theory assumed that the above process occurred in one step, giving  $N_2$  molecules in the  $B$  state, but this theory is incapable of explaining the formation of  $N_2$  molecules in three different electronic states.

The possible products arising from the collision of two  $^4S$  nitrogen

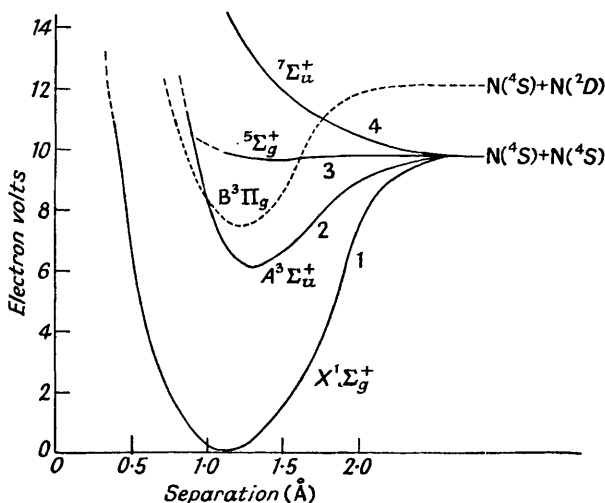


FIG. 3

*Potential-energy curves for some states of the nitrogen molecule which are important in the consideration of the afterglow.*

atoms must now be considered in some detail. The  $^4S$  atom has the electronic configuration  $1s^2 2s^2 2p_x 2p_y 2p_z$ , the three unpaired  $p$  electrons having parallel spins. Two such atoms may approach each other along four different potential-energy paths, corresponding to the pairing of 6, 4, 2, and 0 electrons. The respective paths are labelled 1, 2, 3, and 4 in Fig. 3. The spectroscopic designations of the states of the  $N_2$  molecules formed in following these four paths are respectively  $^1\Sigma_g^+$ ,  $^3\Sigma_u^+$ ,  $^5\Sigma_g^+$ , and  $^7\Sigma_u^+$ , and the relative probabilities of these paths' being followed are in the ratio 1:3:5:7. Whichever path the two atoms follow, they will fly apart again at the end of the first molecular vibration unless a collision with a third body prevents this. The probability of the molecule's losing its excess of energy by radiation is vanishingly small. If the atoms follow paths 1 or 2, a collision with a third body would remove the excess of energy from the newly-formed  $N_2$  molecules, thereby stabilising them in the  $X$  and  $A$  states.

On the other hand, if the atoms follow path 4, they will fly apart again even in the presence of a third body, since no bond is formed between the atoms.

The fourth possibility is that the atoms would follow path 3 and form a very weakly-bound  $N_2$  molecule in the  $^5\Sigma_g^+$  state. Now it will be seen from Fig. 3 that the potential-energy curve of this state crosses that of the  $B$  state. The suggestion that these curves cross was first made by Gaydon<sup>32</sup> to explain the predissociation observed in the First Positive System of nitrogen due to the transition  $B \rightarrow A$ . Bands due to transitions from the  $v' = 13$  to the  $v' = 16$  level have only one head instead of the usual four, and have no fine structure, but for  $v' = 12$  or below, or 17 or above, the bands have the normal structure. This observation is explained by assuming that the molecules in the levels  $v' = 13$ –16 of the  $B$  state can undergo a collision-induced radiationless transition to the  $^5\Sigma_g^+$  state, which would then dissociate into  $^4S$  atoms. For a full account of this phenomenon, see ref. 20.

In this predissociation, the sequence of events can be represented by  $B(v' = 13, 14, 15, 16) \rightarrow ^5\Sigma_g^+$  molecules  $\rightarrow$  two  $^4S$  atoms. It is clear that the reverse of these processes enables  $^4S$  atoms to produce molecules in the  $B$  state, and in the nitrogen afterglow it is postulated that two  $^4S$  atoms collide on the  $^5\Sigma_g^+$  potential-energy curve, after which a collision with a third body induces a preassociation into the twelfth vibrational level of the  $B$  state. A similar phenomenon is thought to explain the spectrum of the  $AlH$  molecule.<sup>20</sup> Emission from the  $B$  state constitutes part of the afterglow, and satisfactorily accounts for the cut-off of the  $v'$  levels above 12, and for the enhanced intensity of the bands originating in the  $v' = 12$  level. The effect of temperature and pressure on the intensity distribution of the afterglow spectrum<sup>5, 31</sup> indicates that the preassociation may occur with loss of vibrational energy, thus accounting for the enhancement of the  $v' = 11$  and 10 bands in the spectrum of the afterglow at room temperatures. Stanley,<sup>33</sup> by measuring the intensity distribution at pressures between 3 cm. and 20 cm., has been able to calculate that the relative probabilities of loss by molecules in the eleventh vibrational level of the  $B$ -state of one quantum of vibrational energy by collision and energy by radiation are in the ratio  $10^{-2} : 1$  per cm. of mercury pressure. At pressures of about 20 cm. fairly strong bands are observed owing to transitions from most vibrational levels below the twelfth.

The observation of the Lyman-Birge-Hopfield bands in the afterglow<sup>30</sup> can be explained similarly. A strongly forbidden predissociation occurs in the  $v' = 6$  level of the  $a^1\Pi_g$  state, and Gaydon<sup>20</sup> has suggested that this is due to the process  $a^1\Pi_g \rightarrow ^5\Sigma_g^+ \rightarrow$  two  $^4S$  atoms, *i.e.*, a process entirely analogous to that postulated above. Clearly, the reverse of this process can give rise to the Lyman-Birge-Hopfield bands in emission, and can account for the fact that no bands were observed originating in  $v'$  levels above the sixth.

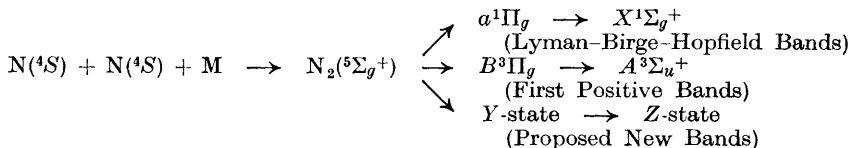
The analogy being carried a stage further, it seems very probable that

<sup>32</sup> Gaydon, *Nature*, 1944, **153**, 407.

<sup>33</sup> Stanley, *Proc. Roy. Soc.*, 1957, *A*, **241**, 180.

the new system could arise in a similar way. The ratio of the total intensities of these bands to those of the First Positive System in the afterglow is approximately constant under all conditions,<sup>31</sup> suggesting that both  $B$ -state and  $Y$ -state molecules are formed from the  ${}^5\Sigma_g^+$ -state molecules by radiationless, collision-induced transitions, these processes being in competition with each other and with the process forming  $a^1\Pi_g$  molecules.

The theory of the afterglow spectrum can be summarised schematically:



The essential correctness of this theory is supported by two further pieces of work. First, the existence of the  ${}^5\Sigma_g^+$  state has been shown by work on active nitrogen at very low temperatures (see next section). The binding energy of the state is 0.13 ev.

Secondly, the non-appearance of bands from the  $v' = 13$  level of the  $B$ -state when  ${}^{15}\text{N}^{15}\text{N}$  was used<sup>34</sup> can readily be explained by the theory. This level lies 0.024 ev below the dissociation energy of nitrogen, and so if the  $B$ -state molecules were formed in a single stage some of them would be formed in the  $v' = 13$  level. On the other hand, this level lies 0.1 ev above the zeroth vibrational level of the  ${}^5\Sigma_g^+$  state, and this amount of energy would have to be derived from kinetic energy if molecules in the thirteenth vibrational level of the  $B$  state of the  ${}^{15}\text{N}^{15}\text{N}$  molecule were to be formed by a collision-induced radiationless transition from the  ${}^5\Sigma_g^+$  state.

There is overwhelming evidence in favour of the preassociation theory. Further work is desirable on the photographic infrared spectrum of the afterglow to clarify the position with regard to the proposed new system, and in particular to obtain more precise information about the states involved. However, it seems unlikely that extensive modifications of the preassociation theory will be necessary.

### Active nitrogen at very low temperatures

During the last few years it has been possible to freeze out solids believed to contain atoms from gases which have been passed through a discharge tube.<sup>35</sup> The gases were passed through a discharge tube at pressures of about 1 mm., and were activated by a 2450 Mc./s generator. They were then led into a specially-constructed Dewar vessel containing liquid helium at  $4.2^\circ \text{K}$ . When nitrogen was subjected to this treatment, most spectacular results were obtained.

While the discharge is maintained, the solid which condenses in the Dewar vessel emits a bright green glow, which becomes yellow-green at higher flow rates. Brilliant blue flashes are observed on the surface of the

<sup>34</sup> Kistiakowsky and Warneck, *J. Chem. Phys.*, in the press.

<sup>35</sup> (a) Broida, *Ann. New York Acad. Sci.*, 1957, **67**, 530; (b) Herzfeld and Broida, *Phys. Rev.*, 1956, **101**, 606; (c) Herzfeld, *ibid.*, 1957, **107**, 1239.

vessel, which are thought to be due to local warming. If the flow of nitrogen is stopped and the discharge turned off, a green afterglow persists for some minutes. When this has died away, a blue "flame" is produced by warming the solid to about  $35^{\circ}\text{K}$ , and after this glow has disappeared a much weaker green glow can be obtained by cooling the solid to  $4.2^{\circ}\text{K}$  again. Coloured photographs of these glows are reproduced in ref. 35*a*.

The spectra of these glows have been studied in detail in the region 2200—9000 Å, the main features being: (a) Five blue-green lines in the region 5214—5240 Å, known as the  $\alpha$ -lines; (b) three diffuse yellow-green lines at 5549, 5616, and 5657 Å, known as  $\beta$ -lines; (c) ten bands stretching from 3572 to 6390 Å, known as *A*-bands; (d) thirty bands of the Vegard-Kaplan system of nitrogen in the region 2320—4450 Å.<sup>36</sup>

*The  $\alpha$ -lines.* These are very sharp and are thought to be due to the transition  $^2D \rightarrow ^4S$  of the nitrogen atom. In the gaseous state this transition is strongly forbidden, but a close doublet due to it has been observed in the auroral spectrum at 5199 Å.<sup>37</sup> The displacement of the  $\alpha$ -lines towards the red end of the spectrum, the appearance of 5 lines rather than 2, and the much higher intensity of the lines in the solid have been discussed in terms of crystal-field effects on the nitrogen atom.

*The  $\beta$ -lines.* These are diffuse and appear only when the discharge is on and disappear with no detectable time-lag when the discharge is switched off. Since the transit time from the discharge tube to the trap was only  $10^{-3}$  sec., the lifetime of the upper state involved in this transition is of that order. As traces of oxygen up to about 1% are added to the very pure nitrogen, these lines are enhanced relative to the  $\alpha$ -lines,<sup>38</sup> and they are thought to be due to the  $^1S_0 \rightarrow ^1D_2$  transition of the oxygen atom. A line due to this transition is observed in the auroral spectrum at 5577 Å.

*The *A*-Bands.* It was at first thought that these bands were emitted in the blue flashes observed on warming the solid to  $35^{\circ}\text{K}$ ,<sup>35</sup> but it now seems more probable that they are emitted in the blue flashes observed when the active nitrogen is deposited in the trap.<sup>36</sup> The bands are attributed to the transition  $^5\Sigma_g^+ \rightarrow A^3\Sigma_u^+$  and are the only bands known which involve the  $^5\Sigma_g^+$  state. They appear with very little rotational structure since free molecular rotation is very difficult in the solid at low temperatures. In *this* experiment, the molecules in the  $^5\Sigma_g^+$  state are formed either in the discharge or from  $^4S$  atoms in the trap.

An analysis of the bands has provided considerable information about the  $^5\Sigma_g^+$  state, which has been of the utmost value in putting the pre-association theory of active nitrogen on a firmer basis. If we assume that  $D_0(\text{N}_2) = 9.76$  eV, then  $D_0(\text{N}_2, ^5\Sigma_g^+) = 0.13$  eV, *i.e.*, this is a weakly-bound state. The vibrational frequency is only  $12.1\text{ cm}^{-1}$  and the internuclear distance about 1.5 Å, compared with 1.21 and 1.29 Å for the *B* and the *A* state respectively. Transitions have been observed from the  $v' = 0, 1$ , and 2 levels, with the intensity maximum at  $v'' = 4$ .

<sup>36</sup> Peyron and Broida, *J. Physique*, 1957, **18**, 593.

<sup>37</sup> Benard, *Ann. Geophys.*, 1947, **3**, 63.

<sup>38</sup> Peyron and Broida, *J. Physique*, in the press.

*The Vegard-Kaplan bands.* These bands are observed if very pure nitrogen is used, and are enhanced in the presence of argon.<sup>36</sup> If as little as 0.01% of oxygen is present the bands are not observed. They become very intense on warming the solid, suggesting that the *A*-state molecules may be formed from <sup>4</sup>S atoms in the solid.

Further evidence of the presence of nitrogen atoms in the solid comes from the large and rapid increase in temperature which is observed when the solid is allowed to warm. If it is assumed that the heat released is due to the recombination of nitrogen atoms, atom concentrations of up to 3% have been recorded.<sup>39</sup>

### Chemical reactions of active nitrogen

Since 1949, Winkler and his co-workers have systematically studied the reactions of active nitrogen with a variety of hydrocarbons and their derivatives.<sup>40</sup> Atoms are produced in a high-voltage condensed electrode discharge, and concentrations of about 30% are indicated by Wrede-gauge measurements. All products of the reaction are frozen out and analysed. The experiments are carried out at pressures of the order of 1 mm. Hg, and different relative flow rates are used in different experiments. The reaction zone is marked by a lilac flame in the case of hydrocarbons, but by an orange flame in the case of halogen compounds.

The main product in these reactions is hydrogen cyanide, and the yield of this rises linearly with increase in hydrocarbon flow rate, finally reaching a maximum whose value depends on the number of nitrogen atoms reaching the reaction zone in unit time. The maximum corresponds to the complete removal of atoms by the hydrocarbon. A troublesome feature of these reactions is the formation of appreciable amounts of polymer in the traps and on the walls of the reaction vessel. In the case of ethylene the elimination of moisture prevented the formation of polymer, and when both the nitrogen atoms and ethylene were just completely consumed the products of the reaction were: hydrogen cyanide, 75; ethane, 10; methane, 9; acetylene, 3; and cyanogen (CN)<sub>2</sub>, 2%. Higher olefins give hydrogen cyanide as the main product, with lower olefins as the principal side-products. Saturated hydrocarbons are much less reactive than olefins, hydrogen cyanide being the only product with methane and ethane at room temperature. Any olefins formed in these reactions are more rapidly attacked by the nitrogen atoms and so are not found as products.

Alkyl chlorides resemble olefins in their reactivity, the main products being hydrogen cyanide and hydrogen chloride, and smaller quantities of olefins and a polymer containing carbon, hydrogen, nitrogen, and chlorine. No chlorine, cyanogen chloride, or methane was obtained from any alkyl chloride.

It is noteworthy that no detectable quantities of ammonia or hydrazine are formed. Because of this it is postulated that the nitrogen atom, alone

<sup>39</sup> Minkoff and Scherber, *J. Chem. Phys.*, in the press.

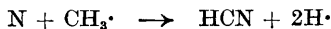
<sup>40</sup> Evans, Freeman and Winkler, *Canad. J. Chem.*, 1956, **34**, 1271; Dunford, Evans, and Winkler, *ibid.*, p. 1074.

of the electronegative atoms, does not attack hydrocarbons by hydrogen-atom abstraction but rather by a direct approach to the carbon atom.

The only reaction with ethylene which is favoured energetically is



This reaction, however, involves a change of spin from 3 unpaired electrons in the nitrogen atom to 1 unpaired electron in the methyl radical, and the transfer of a hydrogen atom from one carbon atom to the other. It is therefore suggested that the first step in this reaction is the formation of a  $\text{C}_2\text{H}_4\text{N}$  complex of long life, which can then rearrange to form hydrogen cyanide and a methyl radical. The methyl radicals are removed by the reaction



This reaction is preferred to that giving  $\text{H}_2$  on grounds of spin conservation.

If the complex reacts with a further nitrogen atom, the most likely reaction is the formation of  $\text{N}_2$ , the ethylene acting as a third body for atomic recombination. The energy acquired by the ethylene molecule will cause it to be very reactive, and it is possible that it dissociates into acetylene and hydrogen.

Similar reaction schemes are postulated for the reactions of paraffins and alkyl chlorides, the formation of the complex being accompanied by the expulsion of hydrogen and hydrogen chloride respectively. The differences in energy content and ease of formation of the complexes may account for slight differences in products.

The main features of the spectra of these flames are bands due to CN, CH,  $\text{C}_2$ , and NH radicals, and also due to CCl radicals in the case of alkyl chlorides.

The reaction of nitric oxide with active nitrogen has been investigated twice recently. When  $^{15}\text{NO}$  is added to active nitrogen, only  $^{14}\text{NO}$  bands are observed,<sup>41</sup> indicating that the excited NO molecules are formed by chemical reaction and not by the excitation of the original NO molecules.

The effect of nitric oxide on the colour of the afterglow is explained as follows. The addition of a little of it merely weakens the afterglow by rapidly removing nitrogen atoms:  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ . Excited NO molecules may then be formed by the relatively slow combination of a nitrogen atom and an oxygen atom in the presence of a third body, and the emission from these molecules accounts for the range of colours yellow—pink—blue. The addition of more nitric oxide removes all the nitrogen atoms by the above reaction so that none is left to form excited NO molecules, and the glow is extinguished. Excess of nitric oxide produces the yellow-green  $\text{NO} + \text{O}$  continuum of the air afterglow, since fairly high concentrations of oxygen atoms and nitric oxide are present together. The presence of appreciable concentrations of oxygen atoms in the colourless and air afterglows has been confirmed by the observation of oxygen atomic lines in absorption in the vacuum-ultraviolet region.<sup>30</sup>

<sup>41</sup> Kaufman and Kelso, *J. Chem. Phys.*, 1957, **27**, 1209.

The reaction of nitric oxide with nitrogen atoms has been studied quantitatively by sampling the effluent gases from a reaction vessel with a mass spectrometer.<sup>42</sup> A plot of the concentration of inflowing nitric oxide against concentrations recorded by the mass spectrometer is shown in Fig. 4. The

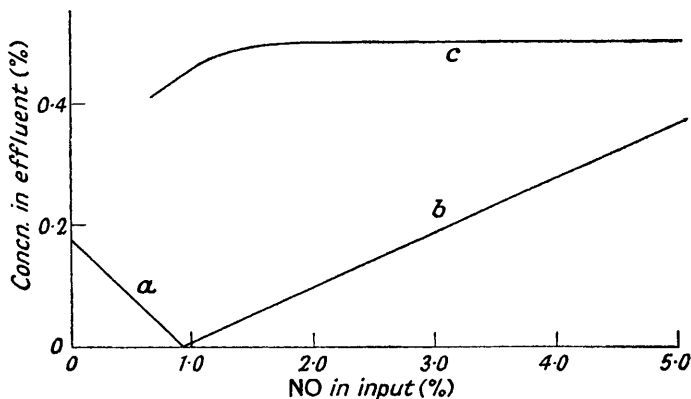


FIG. 4

Variation of percentages of (a) atomic nitrogen (uncorrected), (b) nitric oxide ( $\times 10^{-1}$ ), and (c) oxygen, as measured by a mass spectrometer, when nitric oxide is added to active nitrogen.

[After Kistiakowsky and Volpi, ref. 42]

rapidity of the reaction is indicated by the sharp break in the concentration curve *a-b* (cf. conductometric titration), and this enables one to use nitric oxide as a titrating agent for nitrogen atoms. The concentration of nitrogen atoms recorded by the mass spectrometer is estimated to be only about  $\frac{1}{6}$ th of the true value, owing to removal of the atoms at the walls. This probably also explains the non-stoichiometric relationship between nitrogen atoms and nitric oxide. A similar titration-like plot was obtained with nitrogen dioxide, but the variation of concentrations of oxygen and nitrous oxide with inflowing nitrogen dioxide concentration indicates that the reaction is very complex.

### Conclusion

The achievements of the last ten years' work can be summarised as follows: (a) Charged particles play no part in the production of the afterglow. (b) The only species present in active nitrogen in appreciable concentrations are atoms and molecules in the ground state; the former are responsible for the chemical reactivity. (c) The preassociation theory succeeds in explaining experimental observations and is able to account for the different band systems in the afterglow.

It is reasonable to enquire why nitrogen, but neither hydrogen nor oxygen, has an afterglow which may last for several hours. Since the nitrogen atom has *three* unpaired electrons it can give rise to a variety of

<sup>42</sup> Kistiakowsky and Volpi, *J. Chem. Phys.*, 1957, **27**, 1141.



nitrogen molecules by combining with another atom in the ground or the excited states. By coincidence, the shallow  ${}^5\Sigma_g^+$  curve crosses other curves, allowing preassociation to occur. Since the hydrogen atom has only one electron, two such atoms meet either on the  $X^1\Sigma_g^+$  curve, forming a ground-state molecule in the presence of a third body, or they meet on the purely repulsive  ${}^3\Sigma_u^+$  curve. No state corresponding to the weakly-bound  ${}^5\Sigma_g^+$  state of nitrogen can be formed.

In the case of oxygen, the  ${}^3P$  atoms can give rise to several low-lying states, the highest bound state of which is the  $A^3\Sigma_u^+$  state, which has a dissociation energy of about 0.48 eV. This is somewhat analogous to the  ${}^5\Sigma_g^+$  state of nitrogen but, as far as is known, no other potential-energy curves cross that of the  $A^3\Sigma_u^+$  state, so that no process similar to preassociation can occur. The  $A$  state of the oxygen molecule is much more stable with respect to dissociation than is the  ${}^5\Sigma_g^+$  state of nitrogen, so that molecules in this state survive long enough to emit the Herzberg bands ( $A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ ) in the comparatively short-lived oxygen afterglow.<sup>43</sup>

<sup>43</sup> Broida and Gaydon, *Proc. Roy. Soc.*, 1954, *A*, **222**, 181.