ACTIVE NITROGEN

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I. INTRODUCTION

When nitrogen is subjected to an electrical discharge, a characteristic yellow-orange glow is produced which persists when the discharge is shut off or if the gas is observed in a separate vessel away from the discharge. The first observation of this striking phenomenon was reported by Warburg in 1884 (155). Lewis next studied the afterglow, referring to it as a "β fluorescence" (98, 99). In the Bakerian lecture for 1911, R. J. Strutt (later, the second Lord Rayleigh) discussed a "chemically active modification" of nitrogen which he had obtained by passing nitrogen through an electrical discharge of the type suggested by Lewis (144). This paper can be taken both as the genesis of systematic investigation of the phenomenon known from then on as active nitrogen and for Rayleigh's identification with this phenomenon through his classical studies until his death in 1947.

Active nitrogen has been studied by chemists and physicists for over half a century, but only in the past few years has any considerable progress been made in explaining the processes involved. This sustained activity was in part due to purely academic interest in the system. It is also partly explained by the fact that active nitrogen has properties which attract researchers in many different disciplines. The presence of nitrogen atoms in the afterglow categorizes active nitrogen as a free radical phenomenon, perhaps one of the first free radical systems studied in the gas phase. Active nitrogen also bears a close relationship with the chemistry and physics of the upper atmosphere; the similarity of certain features of the aurora and the airglow with active nitrogen was first noted by Kaplan who indicated that a better understanding of chemospheric phenomena could be obtained through studies of what he termed the Lewis–Rayleigh afterglow (81).

Active nitrogen has been investigated with regard to its spectra, its chemical reactivity, its physical properties, the nature of energy storage and release in the glowing gas, and indeed with any property that might conceivably provide useful information on the nature of the phenomenon. Much knowledge has been gleaned from the mass of experimental reports, but the rate of progress has at times been painfully slow. These studies have been marked as perhaps no other chemical endeavor with a plethora of disagreement, contradictory data, and general scientific frustration. Part of this was due simply to the lack of agreement on a comprehensive definition or specification of the phenomenological nature of active nitrogen, which definition would have avoided much confusion. To be sure, a good part was also due to the magnitude of the technical problems involved whose solution required great strides in free radical measurements, molecular structure, and other challenging fields.

A classical review of active-nitrogen investigations was compiled by Mitra, actually as a preview for presentation of his theory on the nature of the chemical activity of the gas (111). This review is excellent coverage through about 1945 and suffers only from the fact that it is generally unavailable. More recent reviews cover the literature through 1957 (78, 130). It is hoped that this review, which is complete through 1961, will help to illustrate the progress made in the past few years and point out our more nearly complete understanding of active nitrogen today. General statements regarding the salient features as reported in previous reviews are given.

II. GENERAL NATURE OF THE PHENOMENON

The afterglow of postluminescence produced when nitrogen is activated by some suitable means appears yellow-orange and lasts for periods up to hours, slowly diminishing in intensity. Depending on the conditions of the experiment the afterglow intensity can be quite high and generally can be seen for a distance of many feet in a darkened room. The main spectral features of the postluminescence, viewed through a direct-vision spectroscope, are three broad red, green, and yellow bands of the N_2 first positive system. The afterglow is extremely long-lived for a free radical system and decays without significant generation of heat if the walls of the observation vessel are suitably conditioned with anticatalytic materials such as mineral acids. Early explanations on the mode of energy storage and release postulated ground-state N atoms, metastable N and N_2, or molecular nitrogen ions as the labile species. Lack of knowledge prior to 1950 concerning the heat of dissociation of N_2 was a major stumbling block in obtaining an acceptable mechanism. The principal active species in the afterglow is now known to be N atoms, and a mechanism consistent with the observed facts based on N recombination has been formulated.

The afterglow has been obtained with condensed direct current discharge, uncondensed alternating current discharge, high-frequency electrodeless discharge, electron bombardment of particles of 16.3 e.v. or greater energy, and by other methods such as exposure to radioactive sources or generation of low-temperature plasma (105, 143). Shock-tube techniques have been shown to give an excitation different from electron impact wherein the rotational temperature determined from the observed bands equals that of the gas (36, 43). Afterglows have been produced from a few microns to atmospheric pressure (117), in pure nitrogen and with impurities such as O_2. Active nitrogen also has been produced by passing NO or NH_3 through a discharge (5). There is considerable disagreement about the effect of impurities, although generally they appear to increase the concentration of active species (146). Controversy also exists over whether "absolutely pure" N_2 will afterglow, but this appears to be strongly dependent on the actual degree of purity, the nature of the contaminant, and, perhaps most importantly, on the condition of the walls in the observation vessel.

A. SPECTRUM OF THE AFTERGLOW

The spectrum of the Lewis–Rayleigh afterglow probably constitutes the most universally accepted definition of active nitrogen. The spectrum generally consists of selected bands of nitrogen first positive system, the $N_2(B^3\Pi_g–A^3\Sigma_u{}^+)$ interaction. The spectrum of the afterglow must be carefully distinguished from that of the discharge tube, which also shows the N_2 second positive system, the $(C^3\Pi_u–B^3\Pi_g)$ transition. The first positive bands which are most prominent are due to transitions from the twelfth, eleventh, tenth, and sixth vibrational levels of the upper, or B state (Fig. 1). It appears that transitions from $v' = 13$ or higher are never observed. The β and γ bands of NO also usually are present in the afterglow. The intensity of these bands appears to be related to the amount of oxygen impurity in the system. The bands arise from the three-body process

$$N + O + M \rightarrow NO^* + M \tag{1}$$

$$NO^* \rightarrow NO + h\nu \ (\beta \text{ and } \gamma \text{ systems}) \tag{2}$$

B. REACTIVITY OF ACTIVE NITROGEN

The active nature of the species in the afterglow has been amply demonstrated by many investigators, but the work of Rayleigh is perhaps most illustrative on this point (145). Active nitrogen will excite spectra of many substances added to it or will react with them to produce luminous zones in the observation chamber. Materials investigated include most of the metals, the inorganic gases, and many organics.

One of the most important examples of reactivity with another gas is the reaction of active nitrogen with NO. If sufficient NO is added to the Lewis–Rayleigh afterglow, a green–white luminescence replaces the orange-yellow afterglow. This flame shows a continuous spectrum which was linked very early

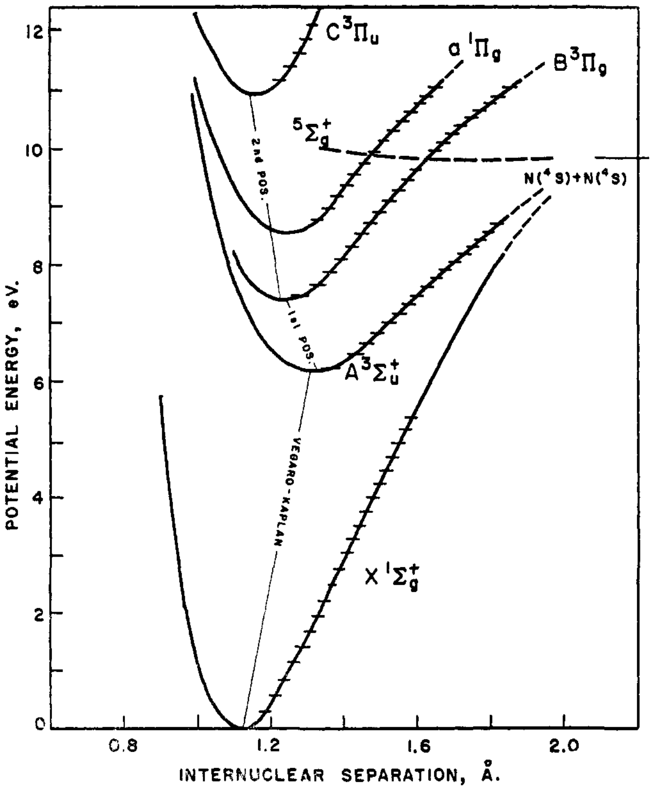

Fig. 1.—Potential curves of the nitrogen molecule.

to the airglow or to the glow produced by the reaction of NO and ozone. This reaction of NO and active nitrogen often was used to estimate the chemical reactivity of the afterglow and was ultimately developed into a quantitative method for obtaining the concentration of N atoms, as is shown in Section III–C–1.

C. DECAY OF THE AFTERGLOW

Observations concerning the decay of light intensity of the afterglow showed two simultaneous processes—a wall reaction and a volume reaction. The wall reaction is difficult to categorize completely since the lifetime of the glow is a strong function of conditioning of the vessel walls. Mineral acids, paraffin, and similar materials have been shown to prolong the lifetime of the glow in varying degrees (132). The rate of decay of the glow is proportional to the square of the concentration of active species in the gas.

The glow is enhanced by cooling and decreased by heating. Rayleigh found the rate of production of the glow to be proportional to $T^{-0.64}$ (133). The gross effect of pressure on active nitrogen is that the intensity varies as the volume cubed. If the partial pressure of the neutral component of the gas, N_2, is increased while the active species concentration remains constant, there is an increase in intensity of the afterglow. Decreasing the concentration of active species while the neutral particles are kept constant results in a decrease in afterglow intensity which is roughly proportional to the square of the pressure decrease.

D. THEORIES OF ACTIVE NITROGEN

Over the years, many theories have been achieved regarding the active particles in active nitrogen, the mechanism of the afterglow energy release, and the long lifetime of active nitrogen. One of the earliest was the suggestion by Rayleigh that the afterglow was due to nitrogen atoms; Sponer enlarged on this to suggest (142, 144)

$$N + N + M \rightarrow N_2^* + M \tag{3}$$

$$N_2^* \rightarrow N_2 + h\nu \ (N_2 \text{ 1st pos.}) \tag{4}$$

Since the mechanism begins with a three-body recombination, this apparently explained the long lifetime. This mechanism will satisfy most of the specifications of the afterglow except the selective enhancement of bands from $v' = 12, 11, 10$, and 6. This theory also requires only ground-state N atoms; no metastable atomic N states have ever been detected in significant concentration.

A theory put forth by Cario and Kaplan (34) postulated

$$N(^2P) + N_2(A^3\Sigma_u^+) \rightarrow N_2(B^3\Pi_g) + N(^4S) \tag{5}$$

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu \tag{6}$$

The energetics of these equations are such that the B state would be formed in the twelfth vibrational level, thus explaining part of the selective enhancement of the first positive system. However, as stated above, no evidence of N(^{2}P) in concentrations suitable for this type of excitation has ever been detected. It was also thought that the lifetime of the $N_2(A^3\Sigma_u^+)$ was too short to permit any member of these states to exist together. More recent work, however, suggests that this is not a valid objection (100, 162).

The existence of charged particles in active nitrogen has always been a matter difficult to resolve since the glowing gas shows conductivity. On the basis of metal-foil experiments by Rayleigh, Mitra suggested that $N_2^+(X^-)$ ions were the active species produced. The mechanism of the afterglow was then proposed to be:

$$N_2^+ + e^- + N_2 \rightarrow N_2(B^3\Pi_g) + N_2(A^3\Sigma_u^+) \tag{7}$$

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu \tag{8}$$

This, as in other proposed mechanisms, involves a three-body step to explain the long lifetime of the glow. However, Rayleigh's work was shown to be somewhat in doubt by Gaydon who suggested that cathode rays from the discharge probably interfered (57). Benson later repeated Rayleigh's experiments with a modified apparatus to remove electrons from the flowing gas and could not reproduce Rayleigh's results (19). The conductive nature of the gas then was assumed to be due to a low (relative to the active species) concentration of electrons and the ion theory was abandoned.

As part of the investigation of the charged particles in active nitrogen, the coefficient of electron recombination has been measured in the afterglowing gas (33). The difference in values obtained in regular and active nitrogen was explained on the basis of long-lived molecular ions originating in the discharge. Some of the earlier observations in active nitrogen have been attributed to the presence of molecular ions (21, 47). Ionization of NO during the recombination of nitrogen atoms (with the NO as the third body) also has been advanced as the electron source (94). The question of whether electrons were responsible for the glow was conclusively answered by injecting small amounts of benzene vapor into active nitrogen. This effectively removed all the electrons; the afterglow was actually enhanced and prolonged.

The presently accepted theory of the afterglow involves the recombination of N atoms along the $N_2(^5\Sigma_g^+)$ potential energy curve. This weakly bound molecule, as seen in Fig. 1, crosses the B state at $v = 12$ as suggested by Gaydon in his work on predissociation of the N_2 first positive system (56). An inverse-predissociation or preassociation occurs at the crossing of the $^5\Sigma_g^+$ and $B^3\Pi$ curves, resulting in $N_2(B^3\Pi)_{v=12}$ being formed. This explains the observed transitions of the N_2 first positive group, except for the anomalous $v' = 6$ enhancement. This theory then accounts for the major features of active nitrogen on the basis of N being the active species. Whether this is the only active species or whether different modes of excitation produce the same active species has not been resolved. Intensity measurements of the nitrogen first positive system using a photoelectric recording monochromator have shown that the observed vibrational intensity distribution cannot be explained by the preassociation model of the afterglow (96). An additional mechanism to explain the strong transitions from $v' = 8, 6$ would not necessarily invalidate the above major theory. But sufficient acceptance of this theory has made N atoms the major active species in active nitrogen, and reactions of active nitrogen are now regarded more or less as reactions involving only N (75, 138).

III. RECENT WORK ON ACTIVE NITROGEN

A. SPECTRA OF THE AFTERGLOW

Since active nitrogen generally has been studied in the pressure range of 0.1 to 0.01 mm., spectra associated with the afterglow arise from processes favored by this pressure range. Until quite recently, it was conceded that the spectrum of the afterglow consisted solely of members of the N_2 first positive system. However, as studies of the phenomenon branched out to include spectroscopy of the glowing gas at more unusual conditions, other spectral features became apparent.

1. Active Nitrogen at High Pressures

The spectrum of nitrogen passed through an ozonizer discharge near one atmosphere pressure has been studied and it has been shown that very pure N_2 was necessary to obtain an afterglow (115, 116, 117). Suitable afterglows were obtained using N_2 generated by thermal decomposition of NaN_3. This study showed that the relative intensity distribution of the first positive system was identical with that obtained at low pressures, which is at variance with previous findings (143). The first positive system as studied under these conditions was actually less intense than three forbidden transitions observed *i.e.*, the N_2 Vegard–Kaplan bands, the $NI(^2P)$ line at 3466 Å., and the $OI(^1S_0–^1D_2)$ auroral green line at 5577 Å.

The observed transitions in the Vegard–Kaplan $(A^3\Sigma_u^+–X^1\Sigma)$ interaction were mostly from $v' = 0, 1$. Since the Vegard–Kaplan system is more intense than the first positive system, the $A^3\Sigma_u^+$ states must be produced by some mechanism other than radiation from the $B^3\Pi$ state. Some $N_2(A^3\Sigma_u^+)$ might be formed by a three-body recombination of N atoms, but these would necessarily be in a high vibrational state and would have to survive many relaxation collisions to $v' = 0, 1$. The origin of the $N(^2P)$ state is suggested *via* a collision of the second kind:

$$N_2(A^3\Sigma_u^+)_{v=0} + N(^4S) \rightarrow N(^2P) + N_2(X^1\Sigma) \qquad (9)$$

The general explanation of the appearance of these forbidden systems is that the higher pressure prevents diffusion of the metastable species to the walls, where they would normally quench.

A somewhat different study of nitrogen in an electric discharge at one atmosphere and 1500°K. has been reported wherein a blue afterglow lasting 10^{-3} sec. was obtained (140). The first, second, and fourth positive, the Vegard–Kaplan, Goldstein–Kaplan, and Hermann–Kaplan systems of N_2 were identified. The Gaydon–Herman singlet system of N_2 and first negative system of N_2^+ were also identified along with NO and CN bands. Excitation of the metastable molecules involved was explained by three-body recombination of $N(^4S)$, $N(^2P)$, and $N(^2D)$ which resulted in either stabilization of metastable N_2 through inverse predissociation, or transfer of excitation energy to the third body. However, this does not appear to be a study of the Lewis–Rayleigh afterglow but of the plasma associated with the discharge through N_2 which is blown out of the discharge tube as a tail flame. It is interesting to note that even in this type of "afterglow" it was found that a certain oxygen impurity level was necessary to produce a visible flame.

2. *Studies in the Ultraviolet*

Four different stages of afterglow produced by varying the O_2 partial pressure in a N_2 stream have been identified on the basis of color and emission spectra (147). The first stage, obtained by using very pure N_2, appeared to be the Lewis–Rayleigh afterglow. However, in addition to first positive bands, the Lyman–Birge–Hopfield $N_2(a^1\Pi_g–X^1\Sigma_g{}^+)$ system was also observed in emission. Mechanism (10) was proposed to account for this latter system

$$N(^4S) + N(^4S) + M \rightarrow N_2(^5\Sigma_g{}^+) + M \qquad (10)$$

$$N_2(^5\Sigma_g{}^+) + N_2 \rightarrow N_2(a^1\Pi_g) + N_2 \qquad (11)$$

$$N_2(a^1\Pi_g) \rightarrow N_2(X^1\Sigma_g{}^+) + h\nu \qquad (12)$$

Whether the $^5\Sigma_g{}^+$ state has a sufficiently long lifetime for this mechanism is unknown; however, the bands observed were very weak compared to the first positive system.

Absorption spectra of this afterglow showed NI($^4S \rightarrow 2p^4P$), ($^4S \rightarrow 3s^4P$), ($2p^3\ ^2D \rightarrow 3s^2P$), and ($2p^3\ ^2p \rightarrow 3s^2P$) transitions. Concentration measurements of the atomic species showed definite peaks for N(^{2}D) and N(^{2}P). The ratio of partial pressures of metastable N atoms, however, was about 0.002 times that of ground-state atoms for both N(^{2}P) and N(^{2}D).

In addition to the Lyman–Birge–Hopfield bands, a new system consisting of six bands in the 1600 to 2050 Å. interval also has been reported (118). These bands were studied at liquid N_2 temperature to eliminate higher rotational lines of the Lyman–Birge–Hopfield system which interfered with spectral analysis. It is suggested that these bands originate from a single upper level, and the transitions observed are to the $v'' = 3, 4, 5, 6, 7$, and 8 levels of the $X^1\Sigma_g{}^+$ ground state. Transitions involving the twenty-sixth vibrational level of the $B^3\Pi_g$ state and the twentieth level of the $A^3\Sigma_u{}^+$ state have been observed by immersing the entire discharge bulb in liquid nitrogen (149).

The N_2 second positive system has been observed in certain types of N_2 afterglows, but never in the conventional long-lived Lewis–Rayleigh afterglow. However, cooling the normal afterglow to liquid nitrogen temperatures produces this system at about equal intensity to the first positive system (148). The intensity distribution, as would be expected, is quite different from that obtained for the second positive system in a nitrogen discharge, in that transitions from $v' = 4$ were abnormally strong. Based on predissociation data for the upper or $C^3\Pi_u$ state, a mechanism consisting of reactions (13) and (14) was proposed

$$N(^4S) + N(^2D) \rightarrow N_2(C^3\Pi_u)_{v=4} \qquad (13)$$

$$N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu \qquad (14)$$

Since it is known that all of the levels of the $C^3\Pi_u$ state involved show predissociation, the enhancement of the $v' = 4$ transitions is explained by the low temperature which would favor the higher vibrational levels and restrain rearrangement by collisional deactivation before transition. The existence of N(^{2}D) was reported previously by Tanaka and co-workers, as described above (147). The low concentrations of these species would seem to pose a serious problem to the mechanism proposed. However, it is postulated that the low temperature prevents the wall from quenching the metastable states and permits of build-up of N(^{2}D) concentration for reaction (13) to occur at a reasonable rate.

An unusual example of spectra obtained from a high-frequency discharge through very pure nitrogen in a Xe atmosphere has been reported (66). The spectrum of the afterglow obtained with an f/8 glass spectrograph was compared with that of the discharge by using a rotating disk and having half the slit admit light from the discharge during the pulse of a 10 μsec. generator while the other half admitted light from the early afterglow emission. The short afterglow emission showed a vibrational structure which merged into a continuum at 4790 Å. and extended to about 4600 Å. This emission did not appear to be dependent on discharge excitation, but had about the same intensity in both the discharge and the afterglow.

The long decay time of the emission was interpreted to suggest a slow reaction as the excitation mechanism. Assuming that any polyatomic molecule would be quickly dissociated in the discharge, it was suggested that the emitting species was either XeN or a weakly bound excited nitrogen molecule. The emission was attributed to two-body recombination of metastable or normal nitrogen atoms. If the second body is also a N atom, there is the possibility for direct transition between unstable repulsive potential curves. The reaction scheme would then be limited to

$$N(^4S) + N(^2D) \rightarrow N(^4S) + N(^4S) + h\nu\ (2.383\ \text{e.v.}) \qquad (15)$$

$$N(^4S) + N(^2P) \rightarrow N(^4S) + N(^4S) + h\nu\ (3.575\ \text{e.v.}) \qquad (16)$$

$$N(^4S) + N(^2P) \rightarrow N(^4S) + N(^2D) + h\nu\ (1.192\ \text{e.v.}) \qquad (17)$$

$$N(^2D) + N(^2D) \rightarrow N(^4S) + N(^4S) + h\nu\ (4.766\ \text{e.v.}) \qquad (18)$$

$$N(^2D) + N(^2D) \rightarrow N(^4S) + N(^2D) + h\nu\ (2.383\ \text{e.v.}) \qquad (19)$$

$$N(^2D) + N(^2D) \rightarrow N(^4S) + N(^2P) + h\nu\ (1.91\ \text{e.v.}) \qquad (20)$$

On the basis of observed wave lengths, reactions (15) and (19) are possible. The former is assumed to be more probable since the ratio of N(^{2}D) to N(^{4}S) is generally very small. These observations are of interest because the processes occurring in the afterglow are generally assumed to be three-body; this is the first two-body spectrum proposed for the recombination of N atoms in any afterglow.

3. *Pressure Dependence of the Afterglow Spectrum*

The intensity ratios of the infrared (7000 to 11000 Å.) and vacuum ultraviolet (1050 to 1350 Å.) emissions to the visible (5300 to 6500 Å.) portion of the afterglow spectrum in the 1-mm. pressure region were studied as a function of pressure up to about 8 mm. (167). It was found that all three of these portions of the afterglow decay identically with time. The major emission in the ultraviolet was due to the (6, 1), (5, 0) and (4, 0) bands of the Lyman–Birge–Hopfield bands. From the decay-curve study at various pressures, it was concluded that the excitation process for the system was that suggested by Bayes and Kistiakowsky (16). Collisional deactivation of the upper or a $^1\Pi_g$ state to levels below $v' = 4$ was calculated to require approximately 400 collisions. Since the nitrogen used in this study was generated from sodium azide and is generally considered to be free from impurities, it is suggested that the collision partner in the deactivation must be N_2.

Below 1-mm. pressure, the infrared bands decrease relative to the visible bands as the pressure is decreased, while above 1 mm. the intensity ratio of the two spectral portions is invariant with pressure. The selective quenching of the infrared bands by an impurity whose concentration is in equilibrium with its sources and whose mole fraction would be significant at pressures below 1 mm. was considered as a possible explanation of this anomalous behavior. Measurements of the pressure rise in the system due to impurities showed the rate to be extremely low so that regardless what the nature of the impurity might be (H_2 instead of N_2 for example) this could not be an acceptable mechanism. An alternative explanation involving excitation modes other than those directly involving the $^5\Sigma$ state shows good agreement with observed results if one assumes that a fraction of the first positive system is excited by a process involving a second precursor, $N_2(\alpha)$. Assuming that the probability for inducing the transition from $N_2(\alpha)$ to $N_2(B^3\Pi_g)_{v'<6}$ is unity and the collision rate for ground-state N_2 is the same as for $N_2(\alpha)$ and $N_2(X^1\Sigma_g^+)$, the minimum lifetime of the second precursor would be 10^{-7} sec.

4. The Nitrogen Afterglow and the Auroral Green Line

The OI(^1S–^1D) 5577 Å. line is often observed in active nitrogen (95, 117). It has generally been assumed that in the strong sources an electron impact excitation of the O(^1S) is responsible. A recent study of the late portions of the nitrogen afterglow discloses the first verifiable chemical excitation mechanism to be reported (166). A very fast spectrograph of low resolution was used to generate a time-resolved spectrum over 30 sec. of decay in a static gas system. The 5577 Å. line was enhanced by leaking O_2 into the 12-liter observation bulb which contained N_2 at 1-mm. pressure and which was electrically activated.

Spectrographs showed that the auroral line was emitted from the gas volume and not the walls, since no wave length shift associated with a wall perturbation was observed. The spin-disallowed reaction

$$NO(^2\Pi)_{v \geq 4} + N(^4S) \rightarrow N_2(^1\Sigma) + O(^1S) \qquad (21)$$

is suggested as a possible mechanism if the reactant populations are high enough to produce a significant rate. The reaction

$$N(^4S) + O(^3P) + M \rightarrow NO(B^2\Pi \text{ or } A^2\Sigma) + M \qquad (22)$$

occurs in the afterglow and has been shown to populate NO vibrational levels from $v = 5$–9 almost exclusively (135).

The classic explanation of the auroral green line is given by the Chapman mechanism (35)

$$O + O + O \rightarrow O_2 + O(^1S) \qquad (23)$$

$$N + N + O \rightarrow N_2 + O(^1S) \qquad (24)$$

Comparison of the time dependence of the decay of afterglow emissions indicates that reaction (24) is not an important source of excitation in the afterglow. Reaction (23) is the accepted excitation mechanism occurring in the upper atmosphere.

5. Absorption Spectra of the Afterglow

The question of what species constitute the active nature of the gas exhibiting the afterglow has been one of the most difficult to resolve, partly due to a lack of definite relationship between the activity and the afterglow because of the so-called "dark modification." This was discovered quite early by Rayleigh and others and shows that although the afterglow itself can be destroyed by heating, the gas retains its reactivity (34, 131). The recent mass spectrometric experiments which establish the presence of N in the afterglow do not necessarily rule out the existence of other species which might exhibit chemical activity. The most commonly looked for of such species is vibrationally excited $N_2(X^1\Sigma)$. The lifetime of such species has been measured at high temperature and found to be of the order of 10^6 collisions with regard to vibrational relaxation (102). The A state also has been the subject of unsuccessful absorption studies (119).

The effect of added gases on the intensity of the afterglow was determined by monitoring the product from a microwave discharge with a photomultiplier (84). Addition of helium, argon, nitrogen, and oxygen did not have a noticeable effect on the afterglow. The effect of N_2O, which does not react with N atoms, was to cause a sharp decrease of the afterglow intensity at the point of mixing but to result in a slight increase downstream. The decrease in intensity was accompanied by a temperature rise. Addition of NO removed N *via*

$$NO + N \rightarrow N_2 + O \qquad (25)$$

At the extinction point of the above reaction, all N are converted to O; addition of N_2O at this point caused an even greater heat release, indicating that reaction (25) actually produces *more* heat-releasing species. On the basis of this effect, these authors postulated that there are considerable amounts of vibrationally excited ground-state nitrogen molecules formed, at least in an electrodeless type of discharge.

The continuum of Ar from 1100 to 1500 Å. has been used to obtain absorption spectra of active nitrogen at 60-mm. pressure (40). Nine bands of the Lyman–Birge–Hopfield ($X^1\Sigma_g^+ \rightarrow a^1\Pi_g$) system, all of the $v' = 0$ progression, were obtained. The concentration of vibrationally excited N_2 was estimated at 10%.

A new band system in the region of the N_2 first positive system has been obtained by cooling the afterglow tube with liquid nitrogen (97). The spectra of the new system were obtained with a 1.5-m. spectrograph with a first-order dispersion of 10.8 Å. The bands were of a complex structure with three easily distinguishable heads. Analysis of the system indicated that the lower state was probably the $N_2(B^3\Pi_g)$ because of the close fit of the observed and calculated ΔG values. From theoretical predictions by Mulliken, it was postulated that the upper state is $^3\Delta_u$ (171).

This so-called Y system has been studied under a variety of conditions using both N^{14} and N^{15} molecules (15). The bands originating from the $n + 4$ levels of the two isotopic molecules are least overlapped by the first positive bands, and were used to measure the isotopic shift. These measurements showed that the electronic energy of the upper state and the ω_e values were midway between those predicted by Mulliken for $^2\Sigma_u$ and $^3\Delta_u$, making selection uncertain (171). The behavior of the band system with regard to temperature indicated a mechanism similar to that responsible for the $B^3\Pi_g$, *i.e.*, collision-induced radiationless transition from the $^5\Sigma_g^+$ state.

Further study of this system showed that the Y–$B^3\Pi_g$ bands could be classified into five groups of different kinetic origins (16). The vibrational levels of both the Y and B states which lie just below D_{N_2} were not populated. Some of the emission from low vibrational levels of the B state was associated with the cascade Y–$B^3\Pi_g$–$A^3\Sigma_u^+$ but the rest had a different kinetic origin. The emission from $v' = 7, 6, 5$ of the B state is interpreted as the second step in the $^3\Delta_u$–$B^3\Pi_g$–$A^3\Sigma_u^+$ cascade. The proposed mechanism to account for the bands was given as

$$N(^4S) + N(^4S) \rightarrow N_2(^5\Sigma_g^+) + M \tag{26}$$

$$N(^5\Sigma_g^+) + M \rightarrow N_2(B^3\Pi_g)_{v=12,\,11,\,10} \tag{27}$$

$$\rightarrow N_2(Y^3\Sigma_u^-)_{v=8,\,7,\,6} \tag{28}$$

$$\rightarrow N_2(^3\Delta_u) \tag{29}$$

$$\rightarrow N_2(a^1\Pi_g) \tag{30}$$

The radiative transfer from those metastable nitrogen states to appropriate vibrational levels of the A and B states accounts for the observed groups of bands.

The $Y(^3\Sigma_u^-)$–$X^1\Sigma_g^+$ system has been observed in absorption (163). This study confirmed the Y state as being $^3\Sigma_u^-$ rather than $^3\Delta_u$. The identification of this state with the upper state of the Y system was made by comparison of the predicted structure of the Y–B transition with the observed bands.

B. TYPES OF AFTERGLOW

The usual Lewis–Rayleigh "late" afterglow of nitrogen is not the only type of post-luminescence associated with discharged N_2. A different type of afterglow in rapidly flowing N_2 at 4 to 15 mm. pressure about 5 msec. after the discharge has been observed (18). The pink-colored glow which persisted for about one msec. was both preceded and followed by the usual Lewis–Rayleigh glow. Spectral examination showed the strong features to be $N_2^+(B^2\Sigma_u^+$–$X^2\Sigma_g^+)$ and N_2 first positive bands plus weak second positive bands. The vibrational intensity distributions of these bands in the afterglow were similar to those in the discharge, including strong emission from vibrational levels above the predissociation limit of the $B^3\Pi_g$ state. This was interpreted to show the existence of highly energetic species (other than N atoms) in the discharge.

The short-duration afterglow produced by passing a beam of electrons through low-pressure nitrogen has been shown recently to be the Lewis–Rayleigh type (120, 151). The sharply defined glow that is emitted when the energy of the electrons exceeds 10.5 e.v. is composed of N_2 first positive bands limited to $v' = 12$. However, the emission is not predominantly from $v' = 12, 11, 10$ as expected, but shows all the vibrational levels from 12 on down to be well represented. Hence, a mechanism other than the three-body recombination must be responsible, particularly since the pressure was 3×10^{-3} mm. The proposed explanation is that $a^1\Pi$ states are formed which diffuse out and are thrown into the $B^3\Pi$ level by collisions (this is contrasted with the normal $^5\Sigma$–$B^3\Pi$ transfer). The limitation of $v' = 12$ in the afterglow is explained by the fact that *both* the $a^1\Pi$ and $B^3\Pi$ predissociate at about 2.76 e.v.; the appearance of transitions from levels below $v' = 12$ arises from the fact that the colliding $a^1\Pi$ may be in various vibrational levels.

C. DECAY OF ACTIVE NITROGEN

The decay of the light intensity coupled with the reactive nature of the glowing gas has long been studied with the idea of formulating mechanisms for energy storage and energy release. Since the presence of $N(^4S)$ in the afterglow is now well established, studies of the gas-phase decay are concerned with the three-body gas-phase recombination of ground-state N atoms and surface decay is generally a catalytic process. The latter has been shown to produce some unusual species if the surface recombination does not result in the transfer of all of the dissociation energy to the surface.

1. *Rate of Recombination in the Gas Phase*

Aside from the academic interest in the volume recombination, the postulated presence of N atoms in the upper atmosphere, in shock-heated air, and in other areas of geophysical and geochemical interest made the kinetics of N atoms one of the most important areas of research connected with active nitrogen. For the reaction

$$N + N + M \rightarrow N_2 + M \tag{31}$$

the differential form of the rate equation is

$$-d(N)/dt = 2k(N)^2(M) \tag{32}$$

and the integrated form is

$$\frac{1}{(N)_2}\left[\frac{(N)_1}{(N)_2} - 1\right] = 2k(M)(t_2 - t_1) \tag{33}$$

if the concentration of M, the third body, is constant. From equation (33) it is seen that experimental determination of the rate constant requires, among other variables, a direct measurement of at least one of the atom concentrations $(N)_1$ or $(N)_2$. Prior to 1958, no method existed for such measurements that could give the accuracy required; the usual Harteck–Wrede diffusion gages or hot-wire gages generally were not able to produce consistent results, although the diffusion technique has been used recently with some success (59).

The study of afterglow kinetics has included an evaluation of k_{31} based on estimates of atom concentration and afterglow intensity: the value obtained was $2.1 \times 10^{-32\pm2}$ cm.^{6}/molecule–sec. (20). (All rate constants are given in units of cc./molecule and seconds unless otherwise noted.) Rabinowitch had made a much earlier estimate of k_{31} by assuming the Lewis–Rayleigh afterglow was due to N atom recombination (129). His value, which coincides remarkably with the currently accepted value, was 3×10^{-32}.

The actual method used to obtain values of k_{31} involved titration of the N atom stream with NO. This procedure had been inferred by Kistiakowsky and Volpi (91). The titration is based on the fact that the reaction

$$NO + N \rightarrow N_2 + O \tag{25}$$

is very rapid and that NO thus converts N atoms to O atoms instantaneously. When the N atoms are all consumed by reaction (25), the O atoms react with excess NO *via*

$$NO + O \rightarrow NO_2 + h\nu \text{ (continuum)} \tag{34}$$

The light emitted is the easily distinguished oxygen afterglow which is greenish white. When the amount of NO added to the afterglow was insufficient to convert all the N atoms to O atoms, a blue radiation could be observed *via*

$$N + O + M \rightarrow NO(B^2\Pi, A^2\Sigma) + M \tag{35}$$

$$NO(B \text{ or } A) \rightarrow NO(X^2\Pi) + h\nu \tag{36}$$

Here the light emitted is composed of the NO β and γ bands. Thus, if NO is added to the afterglow through a leak and the forepressure on the leak is increased gradually, the following changes are observed: yellow glow turning blue and then suddenly turning white. At the point where the white appears the NO leaking into the system is equal to the N atom concentration. This simple titration can be performed in a few minutes, giving extremely reproducible results if the leak system is carefully designed and calibrated.

The sharpness of the endpoint depends on the reaction of NO with N being faster than any other N atom consuming reaction. This reaction rate constant has been measured by Clyne and Thrush (37) to be 4.2×10^{-11}, which is considerably faster than reported earlier (91). However, Herron recently has measured the rate of reaction (25) by a mass spectrometric technique and reports $k = 1.6 \times 10^{-11}$ (70, 71). It is now generally accepted that the NO + N reaction is extremely fast, occurring perhaps every two or three gas-kinetic collisions.

The intensity of the Lewis–Rayleigh afterglow, according to the recombination kinetics now accepted, is proportional to the rate of disappearance of N atoms or to $(N)^2$ in view of equation (32). This has been substantiated by mass spectrometry (20). A plot of $(1/I)^{1/2}$ *versus* time would then give a straight line. The ratio of the intercepts at t_1 and t_2 gives the ratio of N atoms at these times. Hence, if one N atom concentration is measured, the other can be ascertained from the intensity plot. This method was used by Harteck, Reeves and Mannella in a flow system wherein N atoms were produced by a condensed direct-current discharge (62). A value of $k_{31} = 1.72 \times 10^{-32}$ was obtained. Herron, Franklin, Bradt, and Dibeler used a similar technique to obtain a $k = 1.5 \times 10^{-30}$ (67). Wentink, Sullivan, and Wray substantiated these values with an experimental $k = 3.3 \times 10^{-32}$ using a platinum hot-wire resistance thermometer whose signal was recorded on an oscillograph (159). These studies show that the rate of recombination is not strongly dependent on the nature of the third body if M is N, N_2, Ar, or He (68). However, shock-tube studies indicate that N is at least 13 times more efficient than N_2 as a third body at 6400° (1).

The NO titration technique has been questioned by some researchers on the ground that other active species may react with the NO. The validity of the titration was checked by electron paramagnetic resonance techniques which seemed to establish that accurate atom concentrations could be measured with NO (73). Zinman, however, has also inferred that the accuracy of this method is not as good as the original developers claim (175).

The intensity of the afterglow over a 10:1 range also has been studied as a function of temperature, pressure, and oxygen content (3, 9). The volume decay has been shown to have a positive temperature coefficient (86). The main process occurring, the three-body atom recombination, now appears to be kinetically well defined.

2. *Surface Recombination of N Atoms*

The catalytic efficiency of various films was studied by using films deposited on thermistors, coupled with the negative temperature coefficient of resistance of the thermistor, to accurately measure the heat released by the recombining atoms (127). The purely convective heat flow was first measured with an uncoated probe and then subtracted from the total heat flow obtained by using a coated sensor. This method requires that the uncoated probe be essentially noncatalytic. The N atoms were produced by the usual electrodeless discharge technique and their concentration measured by NO titration.

The best catalyst in the group was PbO which showed a catalytic efficiency, γ, of 4.5×10^{-2}; γ is defined as that fraction of the atoms striking the surface that recombines. A time effect was noticed on many films. LiCl was initially a poor catalyst but after one hour of N atom exposure showed a γ of 7.2×10^{-3}. Platinum had the reverse characteristic; it showed a γ of 2.2×10^{-2} initially but poisoned very quickly. A 3-hour exposure to N atoms restored the surface to its original activity. The time effect in the case of LiCl probably was due to removal of noncatalytic species by N atom attack, whereas for Pt a build-up of reactant products from impurities in the active nitrogen may have occurred.

A study of surface treatment and flow conditions on catalytic surfaces showed that the recombination coefficient was independent of flow rate and atom concentration (128). Various types of surface treatment including polishing, degreasing with chlorinated hydrocarbon, washing with nitric acid, and rinsing with water, were tried. Values of γ for platinum ranging from 0.016 to 0.032 were thus obtained. For copper values of γ from 0.012 to 0.039 were determined. When the copper films were deposited on a glass substrate, however, the fraction of atoms recombining was reduced greatly. If a second film of copper was deposited over the first, this effect could be overcome.

A combined study of surface and volume decay which utilized the production of HCN in the reaction of active nitrogen with ethylene and with acetylene has been carried out (86). The results of this work are based on the assumptions of complete initial dissociation of nitrogen and complete conversion to HCN of the N atoms. The walls of the reaction vessel were coated with Na_2HPO_4. The surface decay proceeded by a first-order mechanism between 55 and 400° and with a collision efficiency at the surface of 2.75×10^{-4}. The surface reaction was assumed to lead directly to molecules in the ground state. The homogeneous decay was interpreted to have a positive temperature coefficient and was of secondary importance only. This work was also extended to higher temperatures (9). It was found that the surface recombination may be zero or first order, but not second order. For both $AlPO_4$ and $Mg_3(PO_4)_2$ coatings, little temperature dependence was noted. No surface poison was found that was sufficiently stable to permit studies at 1000°.

The pressure dependence of the catalytic efficiency of surfaces has been determined by monitoring the intensity of the first positive system of the afterglow over the various surfaces (168). The results showed essentially no pressure dependence for γ for clean Pyrex, metaphosphoric acid, Teflon, and eicosane. Coefficients for these materials were 1.7×10^{-5}, 1.4×10^{-6}, 2.9×10^{-5}, and $\leqq 10^{-4}$, respectively. Copper oxide and silver surfaces showed a pressure dependence of the form $\gamma = a/(bp + c)$ where b and c are constants for the surface, a is independent of the surface, and p is the molecular nitrogen pressure (169). The observed pressure dependence can be attributed to the formation of a protective molecular nitrogen layer over a saturated atomic layer at the catalytic surface. The catalytic action of the surface may also rise from the formation of nitrogen compounds requiring the presence of N_2 which would also explain the inverse relationship observed. Values of the catalytic efficiency are tabulated in Table I.

TABLE I

EFFICIENCY OF VARIOUS FILMS FOR THE RECOMBINATION OF NITROGEN ATOMS

Material	Efficiency, γ	Reference
PbO	4.5×10^{-2}	127
LiCl	7.2×10^{-3}	127
Pt	2.2×10^{-2} (initial)	127
Pt	$1.6–3.2 \times 10^{-2}$	128
Cu	$1.2–3.9 \times 10^{-2}$	128
Na_2HPO_4	2.75×10^{-4}	86
Pyrex (clean)	1.7×10^{-5}	168
HPO_3	1.4×10^{-6}	168
Teflon	2.9×10^{-5}	168
Eicosane	10^{-4} (upper limit)	168

A somewhat different study of active nitrogen at a solid surface involved the surface dissociation of AgN_3 (7). The active nitrogen thus produced was shown to have two half-lives (40 and 16 sec.) which were characterized by different emission spectra. The half-life was shown to vary with the surface condition of the reactor and the diluent (8). The activation energies observed in the pyrolysis that produced the active nitrogen were independent of the azide cation.

3. *Surface-Catalyzed Excitation*

An unusual example of surface catalysis in active nitrogen has been reported wherein the decay of N atoms on certain surfaces does not result in the transfer of all or essentially all of the recombination energy to the surface (63, 103, 134). Instead, a small part usually 0.5 e.v. or less of the recombination energy is lost and a metastable electronically excited molecule is formed which diffuses from the surface and radiates its characteristic band spectra.

The first observations of the effect were made when a sample of silver, nickel, or cobalt was placed in a stream of active nitrogen with a small amount of O-atoms present. If the normal, heat-releasing catalysis was not too severe, a bright red luminosity was seen over the metal sample. This luminosity was observed to be pressure dependent in a way suggesting diffusion of active species away from the surface and showed no sign of being a corona or otherwise being connected with charged particles.

Spectrographic analysis of the glow showed the N_2 first positive bands and NO β bands which are also observed in active nitrogen alone. However, the intensity distribution was quite different from that in the normal afterglow; transitions from $v' = 8$ and 6 were strongest in the case of catalyzed luminosity. This was interpreted in the light of diffusion distances and known radiative lifetimes of the species produced, to mean that two parallel processes were occurring on the surface. One process involved the formation of NO *via*

$$\mathrm{N}(^4\mathrm{S}) + \mathrm{O}(^3\mathrm{P}) \xrightarrow{\text{surface}} \mathrm{NO}(\mathrm{B}^2\Pi) \qquad (37)$$

followed by

$$\mathrm{NO}(\mathrm{B}^2\Pi) \rightarrow \mathrm{NO}(\mathrm{X}^2\Pi) + h\nu\ (\beta \text{ bands}) \qquad (38)$$

The second process was interpreted to involve formation of an excited N_2 as the direct primary product. By assuming that this product was $N_2(A^3\Sigma_u^+)$, the strong radiation from $v' = 8$ and 6 of the $B^3\Pi_g$ state could be explained. The $A^3\Sigma_u^+$ and $B^3\Pi_g$ potential energy curves cross at 8.5–9.0 e.v., or $v = 8$–6 (Figure 1). The metastable $N_2(A^3\Sigma_u^+)$ then forms on the metal surface, diffuses out into the gas phase, and, in collision, crosses into the $B^3\Pi_g$ state. The crossing would occur at $v' = 8$–6 and would be followed immediately by radiation transition back to the A state. Estimates of the lifetime of the species responsible for the glow, based on diffusion times and asymmetry of the luminosity, indicate a value of 10^{-3} sec. This represents the time required for the $N_2(A^3\Sigma_u^+)$ to vibrationally deactivate to the crossing point and by collision cross into the $B^3\Pi_g$ state. This time interval is substantially less than the radiative lifetime of the A state.

Certain differences in the nature of the luminosity were noticed between cobalt and nickel, particularly when O atoms were added to the active nitrogen stream from a separate discharge. The luminosity over the nickel showed considerably more NO formation. If the surfaces are specific for some reason, that is, the cobalt forming $N_2(A^3\Sigma_u^+)$ exclusively and nickel forming $NO(B^2\Pi)$ exclusively, these exchange reactions are possibly responsible for some of the observed radiation

$$\mathrm{N_2}(\mathrm{A}^3\Sigma_u^+) + \mathrm{O}(^3\mathrm{P}) \rightarrow \mathrm{NO}(\mathrm{B}^2\Pi) + \mathrm{N}(^4\mathrm{S}) \qquad (39)$$

$$\mathrm{NO}(\mathrm{B}^2\Pi) + \mathrm{N}(^4\mathrm{S}) \rightarrow \mathrm{N_2}(\mathrm{B}^3\Pi_g) + \mathrm{O}(^3\mathrm{P}) \qquad (40)$$

Further evidence of surface-catalyzed excitation in active nitrogen was found. If a cooled copper sample was introduced into active nitrogen, a blue glow showing the N_2 second positive system ($C^3\Pi_u$–$B^3\Pi_g$) appeared. This is somewhat more difficult to explain than the red luminosity, since the C state is 1.4 e.v. above D_{N_2} and has an extremely short lifetime (14, 114). The $N_2(C^3\Pi_u)$ is probably not the primary surface product analogous to $N_2(A^3\Sigma_u^+)$. It is interesting to note that copper generally has been found to extinguish the afterglow (144, 164).

The N_2 A–B crossing may explain the anomalous $v' = 8$–6 intensity observed in the nitrogen afterglow. From Fig. 1, it is seen that two N(^{4}S) atoms can combine along $^5\Sigma$, $^3\Sigma$, and $^1\Sigma$ curves. The accepted mechanism outlined earlier postulates recombination along the $^5\Sigma$ and crossing into the $B^3\Pi_g$ at $v' = 10$, 11 *(62)*. A certain fraction of three-body collisions may also result in $A^3\Sigma_u^+$ formation which preferentially populates the sixth level of the B state by the $A^3\Sigma_u^+$–$B^3\Pi_g$ crossing over as postulated for the red-glow mechanism.

While this effect is certainly not a characteristic of active nitrogen alone, and while examples of surface catalysis have been found in other systems and most likely will be expected in yet further systems, it is interesting to recognize that its discovery grew out of a study of active nitrogen and that the first observations were made in active nitrogen (104).

D. REACTIONS OF ACTIVE NITROGEN

Study of the reactions of active nitrogen can have a twofold purpose, *i.e.*, to obtain kinetic data on N atom reactions and also to ascertain the nature of the species that contribute to the activity of the glowing gas. A further delineation can be made in the area of kinetic data. The geochemical nature of the earth's atmosphere generates considerable interest in reactions that occur in the oxygen-nitrogen system, so that this can be considered a separate phase of the reaction kinetics (65). The reaction of N atoms with organics is oriented more toward determination of active species, methods of excitation, and attack of N atoms on large molecules. Each of these separate areas will be discussed in turn. A summary of rate constants for some of the more important reactions is given in Table II.

TABLE II

RATE CONSTANTS FOR SOME REACTIONS OF ACTIVE NITROGEN

Reaction	Rate constant	References
$N + N + M \rightarrow N_2 + M$	3×10^{-32} cc.^{2}/molecule-sec.	129
	1.7×10^{-32} cc.^{2}/molecule-sec.	66
	1.5×10^{-32} cc.^{2}/molecule sec.	67
	3.3×10^{-32} cc.^{2}/molecule-sec.	159
$N + O + M \rightarrow NO + M$	5.5×10^{-33} cc.^{2}/molecule-sec.	107
	1.5×10^{-33} cc.^{2}/molecule-sec.	10
$NO + N \rightarrow N_2 + O$	4.2×10^{-11} cc./molecule-sec.	37
	1.6×10^{-11} cc./molecule-sec.	70, 71
$N + O_2 \rightarrow NO + O$	$2 \times 10^{12} \exp(-6200/RT)$ cc.-mole-sec.$^{-1}$	92
	$8.3 \pm 1.0 \times 10^{12} \exp(-3100 \pm 400/RT)$ cc.-mole-sec.$^{-1}$	38
$N + O_3 \rightarrow NO_2 + O$	1.7×10^{-14} cc./molecule-sec.	32
$N + HBr \rightarrow NH + Br$	3.8×10^{-14} cc./molecule-sec.	109
$N + C_2H_4 \rightarrow HCN + CH_3$	1.6×10^{-13} cc./molecule-sec.	109

1. *Reaction with Oxygen and Oxides*

From the standpoint of the upper-atmosphere chemist, these reactions of N atoms are the most important.

$$N + N + M \rightarrow N_2 + M \qquad (31)$$

$$N + O + M \rightarrow NO + M \qquad (41)$$

$$N + NO \rightarrow N_2 + O \qquad (25)$$

$$N + O_2 \rightarrow NO + O \qquad (42)$$

$$N + NO_2 \rightarrow N_2O + O \qquad (43)$$

$$N + N_2O \rightarrow N_2 + NO \qquad (44)$$

$$N + O_3 \rightarrow NO + O_2 \qquad (45)$$

The kinetics of reactions (31) and (25) have already been discussed in connection with the volume decay of active nitrogen. The remainder of the reactions represent interaction of N atoms with other atmospheric species.

The rate of reaction (41) has been studied in fast flow system where NO was added to excess active nitrogen (107). The rapid reaction (25) then caused conversion of N atoms to O atoms, resulting in a mixture of the two atomic species. The disappearance of N atoms was then attributed to (1) reaction of O atoms *via* reaction (41), (2) three-body recombination of N atoms *via* reaction (31), and (3) wall recombination. The concentration of N atoms at various points was measured by NO titration and the three processes were separated. A value of $k_{41} = 5.5 \times 10^{-33}$ was obtained at room temperature and 3 to 4-mm. total pressure. This value agrees fairly well with the value of 1.5×10^{-32} reported in a discussion of chemospheric reactions (10).

A mass spectrometric determination of the reaction of molecular O_2 with active nitrogen has been made in a stirred reactor between 390 to 520°K. (92). A value of $2 \times 10^{12} \exp(-6200/RT)$ cc.-mole-sec.$^{-1}$ was obtained. A more recent study has been made in the 412 to 755°K. range using active nitrogen produced in an electrodeless discharge and NO titration for following N atom decay (38). Results showed that N atom removal was first order in both nitrogen atoms and oxygen molecules, and that two N atoms were removed for every oxygen molecule consumed (because of reaction (25)); a value of $k_{42} = 8.3 \pm 1.0 \times 10^{12} (\exp -3100 \pm 400/RT)$ was obtained, which is in good agreement with the previously reported figure.

The study of reactions (43) and (44) also was carried out using the stirred reactor principle (92). No detectable reaction occurred when N atom concentration was 1% and N_2O concentration was 5% at 280°. This is attributed to the fact that the reaction

$$N(^4S) + N_2O(^1\Sigma) = N_2(^1\Sigma) + NO(^2\Pi) \qquad (44a)$$

is spin disallowed and therefore probably has a very large steric factor. For reaction (43), the value reported was $10^{-2}k_{25} < k_{43} < 10k_{44}$.

The reaction of ozone and atomic nitrogen has been studied by a combination of atomic flame techniques and absorption spectroscopy (32). A blue-white flame was observed but no NO was detected in the system. A mass spectrometric study has also been made of this system which substantiates these findings (150). The only product detected in this system was nitrous oxide. Since the reaction

$$N + O_3 \rightarrow NO_2 + O \qquad (46)$$

disobeys the spin conservation rule, the primary step was taken to be reaction (45). The NO formed would react quickly with other species present and the appearance of only N_2O in the trap is merely an indication of the relative slowness of its reaction in the system. Its formation probably is due to

$$N + NO_2 \rightarrow N_2O + O \qquad (47)$$

Using presently accepted values for specific rates of subsequent reactions, a value for k_{45} of 1.7×10^{-14} was deduced.

The addition of CO to active nitrogen has been observed to yield violet and orange flames (24). Spectrographic analysis of these flames showed both the red and violet band systems of CN. When $Fe(CO)_5$ was added to the CO, spectra revealed Fe lines with an intensity distribution not unlike that of the Fe arc.

The origin of various afterglows in the nitrogen–oxygen system has been investigated extensively (82, 83, 85). The formation of considerable NO was detected when more than 4% O_2 was present. The subsequent reaction of this NO with N atoms was studied along with the competing reaction of NO and O. Using isotopic substitution, the latter reaction was shown to have light intensity proportional to the product of NO and O concentrations, which was the basis for several kinetic studies in the oxygen system (62). The effect of addition of H_2O, NH_3, CO, CO_2, and Cl_2 on the yield of NO in a discharge has shown that only CO_2 and Cl_2 are effective in activating the formation of nitric oxide (170).

2. Reaction wtih Organics

The systematic study of the reaction of active nitrogen with organics by several authors has shown that in general HCN is the main product found frozen out in the trap. Conditions can be fixed easily so that complete removal of nitrogen atoms by the hydrocarbon occurs. No ammonia or hydrazine is generally found, leading to the hypothesis that hydrogen abstraction does not occur but that attack is directly upon the carbon atom itself. However, it should be borne in mind that many of these studies are tangential to problems of mechanism and nature of the active species, and that analysis of materials collected in a cold trap can lead to serious problems in reconstructing the reactions that actually took place in the gas phase.

Although nitrogen atoms are accepted to be present in active nitrogen, there have always been hypotheses advanced that at least one other active species also was present. For example, the N_3 radical and vibrationally excited ground-state nitrogen molecules have been suggested (44, 52). The $N_2(A^3\Sigma_u^+)$ state, which has a definite role in the recombination of N atoms, was not seriously considered because its lifetime was originally reported to be on the order of 10^{-4} sec. (112). Recent studies indicate that the lifetime of this state is probably greater than 10^{-2} sec., which would then fit in better with the absence of Vegard–Kaplan bands in the afterglow (100, 162) Absorption experiments on active nitrogen have not detected transitions from the $A^3\Sigma_u^+$ state, but these results are somewhat in doubt because of possible interferences of mercury (165). It would appear that molecules in the A state could be present in sufficiently high concentration under certain conditions.

The existence of vibrationally excited ground-state molecules in the effluent from an electrodeless discharge has been demonstrated by monitoring the afterglow intensity as various gases were added (82). When N_2O was added, a strong decrease in afterglow intensity occurred at the mixing point, but a small increase resulted downstream. A temperature rise was detected at the mixing point but a temperature decrease was noted downstream at the point of increased intensity. Mass spectrometric analysis of the gas stream showed that no N_2O reacted. The temperature rise then was attributed to deactivation of vibrational states by the polyatomic diluent; the intensity decrease is a result of the negative temperature coefficient of the Lewis–Rayleigh afterglow. The downstream behavior of the intensity is likewise a function of the temperature. Vacuum ultraviolet absorption spectroscopy of active nitrogen has substantiated these findings (40).

The reaction of N atoms with ethylene or ethylenic derivatives has been suggested as a method of measuring the concentration of active species in the afterglow. The results of this method, which is based on HCN production, are somewhat at variance with the NO titration technique (45, 46, 51, 154). The use of C^{14}-labeled propylene to study the reaction of N atoms with an unsaturated organic molecule showed that HCN was not the most abundant product formed, contrary to previous work (101). Rather, methyl cyanide, which had not been mentioned previously, was the single most important species found. However, the reaction also has been studied mass spectrometrically, using NO titration to measure atom concentrations (69). The mechanism deduced in this study was

$$N + C_2H_4 \rightarrow [NC_2H_4] \qquad (48)$$

$$[NC_2H_4] + N \rightarrow N_2 + C_2H_4 \qquad (49)$$

or

$$[NC_2H_4] \rightarrow \text{products} \qquad (50)$$

The products in reaction (50) were assumed to be HCN and CH_3, which then agrees with the mechanism reported in (45). The value of k_{48} determined was 9.7×10^{-14} and the ratio k_{50}/k_{49} was estimated to be about 10^{-11}. The issue is still somewhat unresolved, since kinetic data can apparently be correlated equally well within the limits of experimental error assuming N atoms as the sole species present or assuming a second reactant exists (176).

The reaction of the methyl silane with active nitrogen has been studied along with the reaction of various cyclic hydrocarbons (39). The products were analyzed using a gas–liquid partition chromatography technique. The results showed that in all cases NH_3 was a significant reaction product, which had never been reported previously. With the exception of the NH_3, the results generally agreed with previous work. The formation of ammonia was attributed to possible reaction of nitrogen atoms and hydrogen atoms rather than to a series of hydrogen-atom abstractions. The latter would be unlikely because the imine radicals formed on the first step would very likely disproportionate to nitrogen and hydrogen. The mechanism described in reactions (48), (49), and (50) can also be adapted to these results, if one assumes that reaction (50) yields an imine radical or NH_3 directly.

An unusual effect was reported in the reaction of active nitrogen with methane (55). An "induction" effect which was actually a strong reaction dependence on CH_4 concentration was noted, which decreased with increasing temperature. This effect was attributed to a concomitant H reaction. There was some induction effect also detected with C_2H_6 as the reactant, but to a lesser extent. The general conclusions drawn were that the reaction was actually carried on by H atom reactions. The reaction of N atom and cyclic 3-, 4-, and 5-carbon-atom compounds also was studied (93). Products detected were the usual HCN and miscellaneous hydrocarbons which prompted a mechanism whose first step yields HCN directly, H, and unsaturated radicals. Similar results also were obtained using unsaturated imines as reactants (76). In the case of the olefins, it was suggested that a cyclic complex similar in structure to cyclic ethylenimine radicals might be formed prior to HCN production.

Other organics studied include methylamine, acetylene and its derivatives, and methyl cyanide (50, 53, 136). The general results of these studies were HCN formation and complete consumption of active nitrogen at relatively low temperatures. A decreasing order of activity with N atoms has been detected for the following: cyclohexene, hexane, cyclohexane, benzene, cyclohexanone, acetic acid, butyl oleate, dibutyl phthalate, oleic acid, and stearic acid (6). It is also claimed in this study that HCN was the main product formed in the *vapor phase.* In the reaction of active nitrogen with azomethane, activation energies of 0.5 ± 0.4 and 1.0 ± 0.3 kcal with corresponding steric factors of 10^{-1} to 10^{-3}, and 10^{-2} to 10^{-4}, were reported for methyl radicals and $(MeN)_2$, respectively (4).

For chlorinated hydrocarbons, a rather long series of simpler singly chlorinated hydrocarbons plus HCN and HCl are typical products (41, 141). The products in this case were generally analyzed by low-temperature fractionation and mass spectrometry. The inferred mechanism was that a relatively long-lived complex is formed in the initial attack of a N on an alkyl chloride, perhaps similar to the imine mechanism mentioned above.

In the study of C_2H_4, C_2H_6, and NH_3 reacting with N atoms at 0.3 to 4 mm. in a coated reaction vessel, the active nitrogen pressure was found to be greater than the apparent atom concentration (87). The discrepancy was found to decrease as the N atom concentration approached zero. This behavior was interpreted as evidence that a second active species was entering into the reactions. There is a discrepancy between the maximum extent of reaction with hydrocarbons and values of N atom concentration obtained by NO titration (113). The similar discrepancy in the reaction of NH_3 has been attributed to the presence of excited N_2 molecules, preferably the $N_2(A^3\Sigma_u^+)$. The study of CN emission from organic flames quenched by NH_3 has led to the same conclusion (17). This postulate is more or less compatible with recent analyses of the $A^3\Sigma_u^+$ state and the $N_2(A^3\Sigma_u^+\text{–}X^1\Sigma_g)$ transition (139). Other studies of the decay of active nitrogen itself had indicated that two processes occurred and that the second process involved energy transfer between $N_2(X^1\Sigma_g)$ states in vibrational excitation (2).

The reactions of active nitrogen and hydrocarbons also have been used extensively to study the spectra of species such as biradicals formed in an electronically excited state. The CN systems are generally the most prominent spectra features observed, although chlorinated compounds have yielded CCl bands (77, 79). A complex group in the region of 3290 Å. never has been assigned but is attributed tentatively to the cyanogen molecule or species formed from it. A very complete analysis of the rotationally perturbed lines of the (0, 0) transition of the $CN(B^2\Sigma^+\text{–}X^2\Sigma^+)$ interaction has been made by studying active nitrogen–hydrocarbon reactions (30, 88, 89). The (10, 3) and (10, 5) bands of the $A^2\Pi\text{–}X^2\Sigma$ system have been examined similarly and the perturbed wave functions have been determined in terms of unperturbed functions. An interesting outcome of the intensity study was the indication that CN was formed in the $A^2\Pi$ state more than 20 times as readily as in the $B^2\Sigma$ state in reaction of organics with the nitrogen afterglow.

3. Reaction with Inorganics

The reaction of active nitrogen with phosphine has been found to yield H_2 and the α form of polymeric PN (108). The reaction scheme proposed was

$$H_3P + N \rightarrow NH + PH_2 \tag{51}$$

$$PH_2 + N \rightarrow PN + H_2 \tag{52}$$

Polymerization of the PN then occurs. It is interesting to compare the attack of N on PH_3 with that on other polyatomic reactants, CH_4 for example.

The reaction of N with HBr has been found to give an orange reaction flame which was initially attributed to a resonance transfer of electronic energy in the active nitrogen to bromine (42). Considerable catalysis of the N atom recombination by HBr was found to occur. A later study of the reaction

$$N + HBr \rightarrow NH + Br \tag{53}$$

gave a $k_{53} = 3.8 \times 10^{-14}$ at 40° (109). The source of the orange flame was identified as NBr. However, the flame zone was not well defined and conventional diffusion flame techniques were used to measure rate constants. The N atom concentrations were measured by ethylene titration. For the reaction

$$N + C_2H_4 \rightarrow HCN + CH_3 \tag{54}$$

a $k_{54} = 1.6 \times 10^{-13}$ was obtained at 40°.

The catalytic recombination of N was also detected in the reaction with HCl (161). The decomposition of HCl in this catalysis was studied under the influence of H_2 and Cl_2 addition. Results indicate that the reaction between H atom and Cl_2 is the most important secondary reaction. In the case of hydrazine, it was deduced that NH_3 was formed in secondary reactions only and a scheme was proposed of the type

$$N + N_2H_4 \rightarrow N_2 + H_2 + NH_2 \qquad (55)$$

$$NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3 \qquad (56)$$

$$N_2H_3 + N_2H_3 \rightarrow N_2 + 2NH_3 \qquad (57)$$

$$NH_2 + N_2H_3 \rightarrow N_2 + H_2 + NH_3 \qquad (58)$$

$$NH_2 + NH_2 \rightarrow N_2 + 2H_2 \qquad (59)$$

$$NH_2 + NH_2 + M \rightarrow N_2H_4 + M \qquad (60)$$

The measurement of N atom concentration by ethylene titration agreed very well with the rate of hydrazine disappearance, indicating that excited molecular nitrogen species were not important in the reaction (54).

The role of cyanogen and the CN radical, which often appear in hydrocarbon-active nitrogen systems, has been assessed by studying these reactants directly (61). Cyanogen is destroyed and polymer formation occurs at 80 to 400°. Above 400°, with suitably high $(CN)_2$ flow, the destruction of cyanogen is constant, apparently corresponding to the complete removal of nitrogen atoms. If H_2 or CH_4 was added to the reaction mixture, HCN or CH_3CN was formed and attributed to the definite presence of CN radicals. However, the results also tend to show that CN formation *is not* the initial step in hydrocarbon–active nitrogen reactions, particularly since the formation of nitrides is not noted experimentally. Polymer formation is also quite severe in the case of H_2S or CS_2 addition to active nitrogen (160). The appearance of a blue flame in the case of H_2S was unexplained, but for CS_2 was attributed to the CN radical. Study of the CS_2 reaction was complicated by the fact that only a limited polymer deposition (less than 50 to 100 sec.) could be tolerated before an explosion occurred in the trap, which led to the postulate that the CS radical was being deposited.

A spectrographic study of the reaction of active nitrogen and atomic hydrogen revealed the $NH(A^3\Pi–X^2\Sigma^-)$ system and, unexpectedly, the N_2 second positive system (60, 121). The appearance of the nitrogen second positive system is unusual because of the high excitation of the upper or $C^3\Pi_u$ state. The mechanism proposed for these observations involves an analog of the usual N atom recombination, *viz.*

$$N(^4S) + H(^2S) \rightarrow NH(^5\Sigma^-) \qquad (61)$$

It is assumed that the quintet state is unstable, and on collision crosses into the $A^3\Pi$ configuration. The $N_2(C^3\Pi_u)$ and $NH(A^3\Pi)$ in the vibrational levels appropriate for the observed spectra is explained by

$$NH(A^3\Pi)_{v = hi} + N_2(B^2\Pi_g)_{v = 12} \rightarrow (N_3H) \qquad (62a)$$

$$(N_3H) \rightarrow NH(A^3\Pi)_{v = 0,\, 1} + N_2(C^3\Pi_u) \qquad (62b)$$

An alternate mechanism which does not involve the formation of an unstable intermediate has been advanced (106). The above mechanism requires a stable zone on the $NH(^5\Sigma^-)$ curve in the vicinity of the $NH(A^3\Pi)$ crossing point, which apparently is not the case. Also, reactions (62a) and (62b) require about 1.5 e.v. to be energetically possible because of the necessary high vibrational excitement of the A state; this energy does not appear to be possible *via* thermal excitation of the atoms.

The alternate mechanism assumes the N and H react to form ground-state NH. The excitation is then provided by

$$N_2(B^3\Pi)_{v = 12} + NH(X^3\Sigma^-) \rightarrow NH(A^3\Pi)_{v = 0} + N_2(A^3\Sigma_u{}^+)_{v = 0} \qquad (63)$$

The excitation of the $N_2(C^3\Pi_u)$ state is accomplished *via*

$$N_2(A^3\Sigma_u{}^+)_{v = 6-9} + NH(A^3\Pi)_{v = 0,\, 1} \rightarrow NH(X^3\Sigma^-) + N_2(C^3\Pi) \qquad (64)$$

Both of these reactions are energetically neutral. The appearance of the N_2 second positive system might be regarded with some pessimism, since it usually shows up quite strongly in the discharge tube but never in the reaction zone. If the actual case was that stray light from the discharge was responsible for the second positive spectrum, then reaction (64) would not be necessary.

4. *Reaction with Solids and Liquids*

While most of the interest in N atom reaction has centered about gases, reaction with solids and liquids is not without precedent. Rayleigh included materials such as mercury, glycerol, indigo, and many metals in the extensive list of reactants that he studied. In general, these materials do not lend themselves to investigation in the manner that reactants producing vivid and definitive flames in active nitrogen do, and they have for the most part been ignored until quite recently.

The reaction of nitrogen atoms at the surface of polyethylene, polypropylene, and polyisobutylene was studied by exposing films of these materials to a stream of active nitrogen and condensing the products (156, 157). Condensable products were analyzed by gas chromatography, infrared, and mass spectrometry. Nitrogen atom concentrations were measured by NO titration. Results showed that the products were mainly HCN or $(CH)_2$, as is the case with the monomer reactant, except that considerably more cyanogen was formed than with corresponding hydrocarbons. One difference noted was that when methyl groups were present on the polymer chain, NH_3 was formed. The mechanism formulated for these reactions postulates a reaction complex such as a nitrogen-containing chain as the primary process. The splitting off of HCN and H then occurs, followed by further abstraction of hydrogen in the interior of the chain by the H atoms and subsequent cross linking in the polymer. The formation of ammonia is attributed to simultaneous removal of several hydrogens from a carbon by the nitrogen atom, possibly by the formation of the amine radical, NH_2. The reaction of liquid silane heptamer has been found to yield substantially the same products as hydrocarbons (158). The silane is only about one-tenth as reactive as the hydrocarbons, but $[(CH_3)_2SiO]_7$ yields mainly HCN and NH_3 when exposed to N atoms.

The interaction of carbon with dissociated nitrogen was studied by passing the active gas over carbon rods at 800°, collecting the condensable products in a trap, and analyzing them with infrared techniques (173, 174). No cyanogen was ever detected, which indicated that the direct recombination of C and N is probably very inefficient. When 30 p.p.m. of H_2 was added to the gas before it was activated, considerable HCN was obtained; about 20% of the H_2 was recovered as HCN and 50% as NH_3. The proposed mechanism involves chemisorption of an N on the carbon substrate and perturbation of the adjacent C–C bonds. An H atom then reacts with the chemisorbed CN forming HCN with a collisional efficiency estimated to be at least 10^{-3}. However, a similar study showed that paracyanogen was a principal product in the reaction of active nitrogen and carbon rods (58). Secondary products included HCN and $(CN)_2$ but no NH_3 when the reaction was carried out at room temperature.

E. ACTIVE NITROGEN AT CRYOGENIC TEMPERATURES

Recent interest in radical systems stabilized at extremely low temperatures stems largely from the high specific impulse theoretically possible for rocket propulsion schemes based on the release of the recombination energy of these radicals. Prior to 1950, however, interest in this field was entirely academic and activity was rather sporadic. The first study of radiation from solid nitrogen was made by Vegard in 1924 (152, 153); little was done in this area for the next quarter century.

The initiation of the Free Radical Program of the National Bureau of Standards in 1956 marked the first concerted effort to study the fundamental properties of cryogenic radical systems. The success of this program is illustrated by the significant advances made in this general area, particularly by Broida and his colleagues. As outgrowths of the National Bureau of Standards studies, contributions were made to the routine handling of liquid hydrogen and liquid helium to Dewar development, spectroscopic instrumentation, low-temperature X-ray and electron-diffraction techniques, and electron-spin-resonance (e.s.r.) methods of analysis. The selection of active nitrogen as a popular working medium is logical in view of the tremendous amount of information available on the subject. Further impetus was obtained by the demonstration that active nitrogen condensed at 4.2°K. glowed with a brilliant green light indicating that the deposition did not destroy all the labile species (22). As a result of this and related work, the bulk of the radical stabilization was oriented toward active nitrogen.

The early work has been adequately reviewed elsewhere (12, 13, 25, 172). The results of depositing nitrogen atoms from an electrodeless discharge in a liquid nitrogen–liquid helium Dewar can be summarized: (1) While the discharge is maintained, the solid condensed emits a green light which tends to become yellow at high flow rates. (2) The green afterglow persists for several minutes after the discharge is turned off. (3) Sudden heating to 25–35°K. causes a blue flame to "burn" through the condensed material. (4) Spectra of the green glow shows α and β lines, A bands, and NO, NO_2, NH, and N_2 bands. (5) If very pure nitrogen is used, the Vegard–Kaplan bands are observed.

In general, the technique of studying these species has been heavily dependent on optical spectroscopy, although e.s.r. methods are becoming popular. Radicals can be studied by formation *in situ* when a suitable solid is bombarded with high-energy beams, or by formation in electrical discharges and deposition on liquid-helium cold fingers. The latter method has generally been used for N atoms; the active nitrogen is formed in a 2450-mc. electrodeless discharge and the atom stream passed through the special cryogenic Dewar where the atoms are frozen out. The Dewar construction is such that optical windows are incorporated, regardless of whether the material of construction is glass or metal. The optical spectra of the solid can then be taken and the time–temperature curve of the warming up period can be obtained by strategically located thermocouples. The latter information then provides data on the energy content of the film.

1. Spectra of Frozen Radical Systems

The spectra of luminescences induced in solid nitrogen have been vigorously investigated, perhaps partially because of the large number of spectra emitted. No less than four groups of atomic transitions and eight banded features have been reported (122). Some of these were recognized by early workers such as Vegard, but considerable progress has been made only in the past decade in identifying these spectral features and elucidating the processes that occur in the solid. Most of these transitions can now be explained and are attributed to the presence of free N and O atoms in the solid.

The α and β groups are the strongest atomic features in the visible region. The α group has four subgroups based on wave length intensity regions and is attributed to ^2D–^4S transition of the nitrogen atom. The β group has three subgroups and is attributed to ^1S–^1D transitions of the oxygen atom. The ^2P–^2D and ^2P–^4S transitions of atomic nitrogen comprise the δ and μ groups, respectively, but these are not as strong as the α and β

groups; the δ group is placed well toward the infrared while the μ group is at the violet end of the spectrum.

The strongest band system observed is generally the Vegard–Kaplan or ($A^3\Sigma_u^+$–$X^1\Sigma$) interaction of the nitrogen molecule; indeed, the original observations by Vegard and subsequent work by Kaplan at low temperatures which were responsible for the discovery of this system could probably not have been done in the gas phase (80). The A and M bands are also reasonably intense and are attributed to the $O_2(A^3\Sigma$–$X^1\Sigma)$ and $NO(^4\Pi$–$X^2\Pi)$ transitions, respectively. The A bands originally were thought to be due to a $^5\Sigma_g^+$–$A^3\Sigma_u^+$ interaction in nitrogen which would arise from recombination of the N atoms. The use of isotopic substitution has shown no shift with N^{15}, while O^{18} produced conclusive evidence that the emitter is an oxygen molecule (125).

The B bands are observed in the warm-up glow and were found to be sensitive to oxygen impurity (27). Use of isotopes showed a wave length shift to the ultraviolet when O^{18} was used. These bands have tentatively been assigned to the NO_2 molecule. Other less intense bands that have been identified are the NO ($B^2\Pi$–$X^2\Pi$) and ($A^2\Sigma^+$–$X^2\Pi$), NH ($A^3\Pi$–$X^3\Sigma^-$) and N^2 ($B^3\Pi$–$A^3\Sigma$) systems (29). These are designated the D, E, F, and G bands by the National Bureau of Standards system of assignments.

The various methods used to prepare the cryogenic films are equally effective. The results of the bombardment technique and the discharge method have been compared (74). Although the experimental natures of the two techniques were very different, it was found that the main features of the spectra were the same in each case. Four different light sources were also used to irradiate nitrogen and nitrogen–argon films (31). Light of 2,000 to 10,000 Å. produced a phosphorescence which was interpreted as a restimulation of the familiar afterglow. The absorption spectra of the solids condensed from an electric discharge has also been examined (11). Spectra between 0.22 and 3.5 microns show two weak bands at 3400 Å.

The spectra emitted by solid nitrogen, both irradiated and collected from discharges, show strong dependence on the mechanics of deposition (64, 137). Flow-rate dependence has shown spectral changes which are related to the structure of the solid. The rate of deposition, the deposition temperature, small amounts of impurities, and large amounts of inert materials all influence the spectra in a manner not presently understood.

2. Mechanisms of Low-Temperature Afterglows

The majority of the spectral features observed from these films have been explained on the basis of nitrogen molecules and nitrogen and oxygen atoms being trapped in the solid and then reacting. A theoretical explanation of the α lines has been made which assumes that the $NI(^2D$–$^4S)$ transition is perturbed by neighboring N_2 molecules (72). This scheme proposes that the N atoms occupy a definite spatial arrangement relative to the N_2 molecules thus accounting for the sharp nature of the observed lines. The nitrogen atom is assumed to be loosely bound to the molecule with a 2.5 Å. bond length and a 50° angle to the N–N bond. This treatment explains many of the earlier observations but fails to predict the change in fine splitting observed with N^{15} (123).

The α and β features as originally detected were single lines. Overexposure revealed weaker features labeled α' and β' about 2300 cm.$^{-1}$ lower. Continued over exposure showed the α'' and β'' lines 2200 wave numbers higher than the central lines. The explanation given for the satellite lines was that an electronic transition of the appropriate atom was accompanied by a vibrational transition of a neighboring nitrogen molecule in the solid phase (28). Later investigations of the δ feature showed similar satellites at lower and higher frequencies (123). Experiments with N_2^{15} showed no shift of the center line, but the satellites were slightly closer to the central line and the displacement was approximately that predicted by the vibrational isotope shift. Hence, the double transition theory appears to explain most of the observed features.

Since the major active species in active nitrogen is the nitrogen atom, it is logical that the glows from condensed films be attributed to reactivity of this atom. The concentration of atoms in a typical solid film would be an important variable in any mechanism designed to explain the spectra. The concentration has been estimated at 0.2% on the basis of temperature rise in the collection chamber, but estimates as high as 4 to 6% have been arrived at by measuring total heat release upon warm-up and attributing the whole to atom recombination (23, 110). The low-temperature calorimetry involved in the latter estimate is subject to some doubt.

It has been suggested that radicals are not stable at temperatures above 0.1 to 0.5°K. of the condensed-phase melting point (13). The radiation from the solid phase would appear to correlate directly with free atoms, as suggested. Both ground and excited nitrogen atoms have been reported trapped and studied. A mechanism whereby recombination of the ground states was governed by a single activation energy was postulated. The excited states, however, were assumed to be bound in two types of traps: one an ordered array and the other a disordered region of the matrix. The existence of a second active species besides nitrogen atoms was indicated by an evaporation study of frozen films (28). In this work, products were frozen out on a plate at 20°K. and distilled to a second plate 40 cm. away which was at 1.2°K. During evaporation, the

^2D–^4S transition of nitrogen was observed, and a faint blue glow was seen on the second surface indicating that two active species may have been transported. Numerous other studies have shown that the atom concentration in the frozen film cannot be higher than several per cent, and is more likely to be less than 0.1 per cent (26, 27, 48, 124).

The use of thermal and magnetic measurements correlated with gross light effects tend to suggest atom concentrations of several hundreths of a per cent as a logical figure. The studies also showed that with atom concentrations in excess of several per cent in the gas phase, virtually total recombination occurs upon condensation (49). When the gas stream contains less than 0.5% atoms, it appears that 40 to 100% can be stabilized in the solid for short time intervals. NaN_3 irradiated with X-rays at liquid-nitrogen temperatures shows an e.s.r. spectrum of three lines of equal separation of 6.2 oe. This was attributed to N^{14} trapped in the crystal lattice (90).

The banded features of the spectra observed in the warm-up of solid films are attributed to recombination of the atoms as soon as the temperature is high enough to permit diffusion (13). These processes are more or less analogous to the gas-phase recombinations, and results in the formation of N_2 in the $X^1\Sigma$, $A^3\Sigma$, and $^5\Sigma$ states. Reaction with any NO present could also occur giving O atoms, possibly in an excited state. An enhancement of the β lines is explained by reaction of O atoms with N_2^*; *viz.*

$$O + N_2^* \rightarrow O^* + N_2^{**} \tag{65}$$

$$O^* \rightarrow O + h\nu \ (\beta \text{ lines}) \tag{66}$$

The appearance of the α lines is attributed to a nitrogen analog of the above reaction.

$$N + N_2^* \rightarrow N^* + N_2^{**} \tag{67}$$

$$N^* \rightarrow N + h\nu \ (\alpha \text{ lines}) \tag{68}$$

In each case, it is also possible to postulate that the N_2^{**} actually associates with the excited atom during the radiation transition. The strength of the β lines relative to the small amount of O present indicates that the oxygen atom is particularly effective in quenching the N_2 excitation. This would explain why the Vegard–Kaplan bands are observed only when extremely pure N_2 is used; even a minute amount of O might quench the N_2 $(A^3\Sigma_u^+)$ before radiation can occur.

The appearance of the various bands during warm-up is strongly dependent on the temperatures and the heat evolution. The B bands are strong as the film goes through a thermal peak, diminish as the temperature falls, and are again strong on further warming. An argument in favor of an NO_2 assignment for these bands is that during warm-up, oxygen atoms are continuously regenerated as long as N atoms are available *via* reaction (25). When the N atoms have all been recombined, the O atoms could then react with NO *via*

$$NO + O \rightarrow NO_2 \tag{69}$$

The stabilization of the NO_2 could result in banded features, rather than the continuum observed in the analogous gas-phase reaction.

Some of the observed features have yet to be explained fully. There is some question about the double transition theory of the α and β lines because of problems in accurately measuring the magnitude of the isotope shift. There is no doubt that much of this confusion is due to difficulty in obtaining clear, sharp spectra of such weak features of the satellite lines. The effect of a magnetic field on the lines seemed a promising tool, but no definite conclusions have been reached (126).

IV. CONCLUSIONS

1. The question of reactive species appears well resolved since the $N(^4S)$ mechanism explains the afterglow and reactivity of the gas. Both $N(^2P)$ and $N(^2D)$ have been identified in the afterglow but in a ratio to $N(^4S)$ that makes it impossible to attribute significant reactivity to the metastable atoms. Many ground-state N_2 molecules in a vibrationally excited form may exist in the afterglow when a radiofrequency source is used.
2. The anomalous $v' = 8, 6$ intensity of the N_2 first positive system can be explained by the formation of small amounts of $N_2(A^3\Sigma_u^+)$ in the gas-phase recombination. These molecules cross into the $B^3\Pi_g$ state at $v = 8, 6$ and then radiate to the low vibrational levels of the $A^3\Sigma_u^+$ state. This explanation removes the last serious objection to the preassociation mechanism for the afterglow.
3. The three-body recombination of $N(^4S)$ atoms has been shown to have a rate constant of about 2×10^{-32} at room temperature.
4. Labile species can be trapped from active nitrogen at cryogenic temperatures and will result in the emission of line and band spectra. The maximum concentration appears to be 0.1% or less.

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