CHAPTER III.

Active Nitrogen - Survey of Earlier Experimental Work.

During the last sixty years much time and patience have been devoted to the study of active nitrogen by large number of investigators. Any one attempting to study the literature on this subject is not only struck by the large amount of experimental work done, but at the same time, is greatly confused by the divergent results and conflicting statements of the different authors and not infrequently of the same author on different occasions. A typical illustrative example of this may be cited here. This is on the effect of slight admixture of $O_2$ in the nitrogen employed. While Strutt$^1$ firmly held that oxygen is necessary for the production of nitrogen afterglow, Tiede and Domcke$^2$ held equally firmly that slight admixture is essential for its production. The controversy was only settled when Tiede and Domcke demonstrated their point of view to Strutt by actual experiment. The result of this is best described in the words of Strutt, "In the controversy which has been reviewed it was maintained on the one side, that pure nitrogen would give the full effect, and on the other, that the presence of oxygen was essential. It is now seen that as in so many scientific controversies neither
side was entirely right. Almost any contamination with the exception of argon and helium, increases the yield of active nitrogen as judged by the intensity of the afterglow. Therefore, it is not always easy to make categorical statements on the experimental results which are not well established. These contradictory results and statements are due to the fact that the properties exhibited by the glowing gas are extremely sensitive to the physical conditions under which the gas is excited; viz., the purity of the gas employed, the condition of the walls of the containing vessel, the mode of excitation, etc. In the following pages an attempt will be made to give an account of some of the earlier important experiments constituting the study of active nitrogen and of the results and conclusions therefrom so as to appreciate the various available theories and hypotheses about the mechanism of active nitrogen that are so far prevalent.

(1) Life of the afterglow.

One of the important properties of any afterglow is its duration or life. In the case of nitrogen afterglow, long life is known to be favoured by coating the containing vessel with suitable substances. Among the substances used are paraffin as reported by Lewis and Willey and metaphosphoric or Sulphuric acid by Rayleigh. By coating with
metaphosphoric acid, Rayleigh was able to prolong the life of the glow for more than five and half hours. Formation of adsorbed layers always increases the life of the glow. These adsorbed layers are formed when the nitrogen used contains impurities of electronegative elements, the most important of which is oxygen and also by conditioning the wall by prolonged discharge. Kaplan in course of some of his experiments on the afterglow, has remarked "the long running of the tube undoubtedly conditioned the surface of the tube in such a way as to allow it to adsorb nitrogen atoms."

There are also agents which have definite destructive effects on the afterglow. Apiezon oil is one such substance. Heating the wall of the vessel containing active nitrogen also results in the disappearance of the glow as per finding of Rayleigh. Further, according to Kaplan, hydrogen may inhibit the afterglow by being adsorbed on the walls of the tube, thus preventing the adsorption of nitrogen atoms and the subsequent recombination to form metastable atoms.

(ii) Formation of chemical radicals and excitation of spectra.

When foreign vapours 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 substances or those of radicals or molecules formed by chemical reaction. Summaries of the many spectral systems investigated are given by Strutt and Fowler\textsuperscript{9} and Willey and Rideal\textsuperscript{10}. Metallic vapours usually give rise to spectra consisting of atomic lines of the metal. Hydrocarbons react to form hydrogen cyanide as the main product. Such reactions have been recently studied by Haggart and Winkler\textsuperscript{11} and by Bayes.\textsuperscript{12}

(iii) Energy Measurements.

Experiments on the measurement of energy content of active nitrogen were made by Strutt\textsuperscript{13} from which he came to the conclusion that the content was not abnormally high. Calorimetric experiments of Willey and Rideal\textsuperscript{10} gave the energy content as 2. e.v./mole of the total nitrogen. In general, observations of all the above authors pointed to the conclusion that the energy was not at all high. Rayleigh from exposure of a metal plate to active nitrogen found high temperature developed in it. By this he interpreted that energy of active nitrogen may be as high as 12.9 e.v./mole. Subsequently it was discovered\textsuperscript{14} that much of this heating effect was due to the electrons in the discharge and the energy of active nitrogen part was small.
(iv) **Studies of Decay of the glow.**

Rayleigh's study of the decay of afterglow intensity at a pressure of 0.07 mm. showed that when the inside of the afterglow vessel was moistened with apiezon oil, the decay was exponential, but in the case of metaphosphoric acid it was not exponential. Mitra using Rayleigh's data found that the active nitrogen is destroyed by bimolecular reaction. With the use of refined techniques involving photomultiplier tubes, Kash has made a systematic study of the decay curves in the pressure ranges from 1 mm. to 50 mm. and in the discharge current ranges from 10 ma. to 125 ma. Some important conclusions are drawn from these observations regarding the possible processes operating in the afterglow. Anderson, Kavadas and McKay have studied the decay by a method similar to Kash in many respects, over the pressure range from 0.9 mm. to 7 mm. and the temperature range from 30° to 180°. They have discussed critically their observations in terms of monomolecular and bimolecular reactions for the decay. More recently Anderson and Barry have taken simultaneous records of intensity of the afterglow and of the magnetic resonance absorption in it and found that the afterglow intensity (I) decayed according to an $I^{-2}$ law in a somewhat longer time.

(v) **Pressure variation and afterglow intensity.**

The effect of pressure on the intensity of the
afterglow is of consequence for the theory of active nitrogen. Rayleigh\textsuperscript{19} after noticing that compression increased the intensity of active nitrogen, studied the effect carefully by systematic experiments, using mixtures of active and inert nitrogen in various relative concentrations and at different pressures. His experiments gave evidence that within the limits of accuracy, the intensity of afterglow changed as cube of pressure. Some aspect of such experiments were studied earlier with some success by Kneser.\textsuperscript{20}

(vi) \textbf{Constituent particles.}

(a) \textbf{Nitrogen atoms in the ground state:} Wrede\textsuperscript{21} using the gauze, detected appreciable concentration of atoms in the active nitrogen, but the gauze does not distinguish between ground state and excited atoms. The results of Stern-Gerlach experiment by Jackson and Broadway\textsuperscript{22} on active nitrogen, indicated that the ground state atoms were absent, whereas the vacuum-ultraviolet absorption spectrum studied by Herbert, Herzberg and Mills\textsuperscript{23} suggested that the excited atoms were absent from the afterglow. The first positive evidence for the presence of ground state atoms in the afterglow was obtained by Heald and Beringer\textsuperscript{24} by examining the paramagnetic resonance spectrum of active nitrogen. There was indication of the presence of $^4S$ atoms only.

Recently mass spectrometric studies by two sets of independent workers, have been more effective in demonstrating
the presence of N atoms in the afterglow. Jackson and Schiff\(^2\) concluded from such experiments that \(^4S\) atoms were present, whereas Berkowitz, Chupka and Kistiakowsky\(^2\) stated that in addition to \(^4S\) atoms, there were present N atoms in the \(^2P\) and \(^2D\) states in amounts less than 1% atomic concentration. More recently Tanaka, Jursa, Leblanc and Inn\(^2\) from re-examination of the ultraviolet spectrum of active nitrogen showed that there was presence of an appreciable concentration of \(^4S\) ground state atoms and very small concentration of \(^2D\) and \(^2P\) atoms.

(b) **Metastable molecules of N\(_2\) in the \(^3\Sigma^-\) state:** The observation of Vegard-Kaplan bands in the Kaplan's afterglow indicates, according to Kash\(^1\), the presence of the A state molecules. But it is doubtful whether they can be said to be primarily responsible for the afterglow in view of the contentions of Gaydon\(^2\) and experimental observations of Warley\(^2\) and of Berkowitz, Chupka and Kistiakowsky\(^2\). Life of the A state molecules is about \(10^{-4}\) sec. as estimated by Muschlitz and Goodman\(^2\), but Lichten\(^3\) considers that they are producing molecules of the \(^1\Pi\) states and that the true life-time of the A state molecules is probably as high as \(10^{-1}\) sec. Bayes and Kistiakowsky\(^3\) suggested that these A state molecules are formed directly from ground state nitrogen atoms in triple collisions and
are then converted into the lowest levels of \( B^3 \Pi \) state either by emission of low frequency radiation or by collisions.

(c) \( N_2 \) Molecules in the high vibrational levels of the \( X \)-state: Kash\textsuperscript{16} and Anderson\textsuperscript{33} have included these molecules in their picture of the afterglow mechanisms. According to Beale and Broida\textsuperscript{34} these species are of consequence for the mechanism of short duration afterglow. But recent absorption studies by Dressler\textsuperscript{35} confirmed the presence of an appreciable concentration of vibrationally excited \( N_2 \) molecules in \( v' = 1 \) of the ground state.

(d) \( N_2^+ \) Ions and Electrons: These are doubtless, the particles of the discharge producing active nitrogen. The condensed discharges and h.f. discharges as good sources of active nitrogen are rich in \( N_2^+ \) ions and electrons. Therefore the production of nitrogen atoms in the afterglow may be due to the dissociative recombination of \( N_2^+ \) ions and electrons since such process is considered to be of high probability in electrical discharges and in upper atmosphere by Kaplan\textsuperscript{36}, Bates\textsuperscript{37} and Stewart and Emeleus\textsuperscript{38}. This process is regarded in Mitra's\textsuperscript{39} recent theory, to be of importance in the production of \( N \) atoms which then form active nitrogen.
The possibility of ions and electrons taking part in the afterglow mechanism as particles of active nitrogen is very remote in view of the work of Benson and Worley. But recent observations of First Negative \( \text{N}_2^+ \) bands by Kaplan, Barth and Schade in an afterglow favour the appreciable concentration of \( \text{N}_2^+ \) ions and hence the possibility of ions participation as active particles.

In the next chapter it is proposed to give a survey of theoretical work on active nitrogen.
REFERENCES

2. Tiede and Domcke, Berichte, 46, 4065 (1913).