The Nature of Reactions Occurring in the Production of the Afterglow of Active Nitrogen and the Effect of Temperature on the Phenomena

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THE nature of the processes occurring in N_2 activated by high frequency discharge has not been clearly understood owing to the many diverse and apparently contradictory phenomena occurring. Recent work by Lord Rayleigh has thrown important light on the phenomena but has not led to a clear interpretation in terms of reactions. Recent study by the writer of a phenomenon observed long ago by J. J. Thomson,[1] which indicated that one component of active N_2 was frozen out at liquid-air temperature, has led to a picture of the mechanism which accounts for the puzzling observations.

The application of an electrodeless discharge to one of two connected glass bulbs filled with N_2 at a pressure of about 0.5 mm of Hg gives rise to an easily visible yellow green afterglow in the second bulb. At the same time the pressure of the system was nearly doubled with only a slight increase in the temperature of the glass walls. The application of liquid air on the second bulb to less than one percent of the area of the whole system reduces the pressure to the value it had before the discharge was started. The intensity of the afterglow in the immediate vicinity of the cooled surface greatly increases, and then, within thirty seconds, disappears from the entire chamber. After the liquid air has evaporated, the increase in pressure is accompanied by a reappearance of the afterglow, first at the cooled surface then spreading to fill the bulb. A similar set of phenomena was observed when solid CO_2 and acetone were used as the cooling agent. This is what Thomson termed the freezing out of an active component. It is obvious that the pressure differences set up gas currents of considerable magnitude carrying activated nitrogen to the cooled surface.

The pressure changes are too large to be accounted for by the small average temperature changes of the system, but can be attributed to the nearly complete dissociation of N_2 in the discharge. Rayleigh[2] was able to obtain about 10 ev per molecule from active N_2 in interaction with gold. This energy corresponds to that of completely dissociated N_2 with half the atoms in the metastable ^2D and the rest in the normal ^4S state.
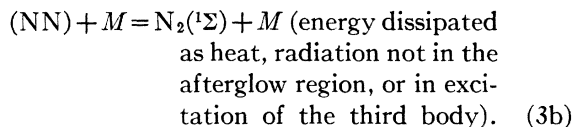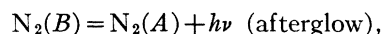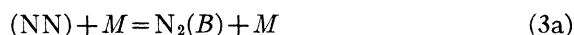
The afterglow is known to originate in the high vibrational levels on the $B^3\Pi$ state of N_2 and to result in the formation of metastable $A^3\Sigma$ molecules of nitrogen. Nitrogen in the B state must then be one of the products of the recombination of atomic nitrogen.

The first step in the recombination is the formation of a collision complex.

$$N + N = (NN) \tag{1}$$
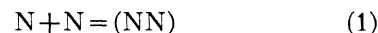
If one of the atoms is in the ^2D state and the other in the ^4S, the complex will have 9.84 ev energy above the ground state of N_2, approximately the energy of the levels which give rise to the afterglow.

The collision complex will be destroyed by one of the following mechanisms

$$(NN) = N + N, \tag{2}$$

$$(NN) + M = N_2(B) + M \tag{3a}$$

$$N_2(B) = N_2(A) + h\nu \text{ (afterglow)},$$

$$(NN) + M = N_2(^1\Sigma) + M \text{ (energy dissipated} \\ \text{as heat, radiation not in the} \\ \text{afterglow region, or in exci-} \\ \text{tation of the third body).} \tag{3b}$$

In general the energy radiated as afterglow is known to be small compared with the energy present in the activated N_2, so that most impacts result in (3b) but the few impacts resulting in (3a) cause the afterglow.

The rapid pressure drop observed after the application of liquid air indicates that the over-all rate of destruction of the nitrogen atoms (reac-

[1] J. J. Thomson and G. P. Thomson, *Conduction of Electricity through Gases,* volume 2 (Cambridge University Press, 1933), p. 444.

[2] Lord Rayleigh, Proc. Roy. Soc. **A176**, 1 (1940).

tion (1)+reaction (3)) increases with *decrease* in temperature. Reactions (1) and (3) are bimolecular and their rates would normally *decrease* with a decrease in temperature. Assuming no change in the rate of reaction (2), we would expect the over-all rate of destruction of nitrogen atoms to decrease with a decrease in temperature. However, if a decrease in temperature greatly increases the lifetime of the collision complex, that is if the rate of (2) is reduced much more than is the rate of (1) there will be a material increase in the concentration of (NN). Thus despite a small decrease in the *rate constant* of reaction (3), a lowering of the temperature will result in a large increase in the total rate of (3) and the destruction of nitrogen atoms with and without radiation to form N_2 and a corresponding decrease in pressure. In what manner the stability of the complex (NN) could be increased as regards spontaneous dissociation as a result of the decrease in energy of the N atoms cannot be specified. It is, however, not unnatural to find that where the heat of formation of a molecule is near the average energy of the components, a small reduction in energy of the components will result in a great increase in the molecule formation. In this system the change in concentration of (NN) is more than sufficient to reverse the expected effect of temperature on the rate of reaction causing a negative temperature coefficient for the over-all reaction.

The changes in the intensity of the afterglow allow us to follow the progress of the reaction. The transitory increase in intensity immediately on cooling is the result of the increased concentration of (NN) and the increased rate of (3a). However, the increased rate of (3) leads to a more rapid destruction of atoms and eventually to a decrease in the concentration of (NN) and the extinction of the afterglow. The reduction in pressure causes a continuous streaming of activated gas to the cooled surface preventing an increase in concentration of atoms until the liquid air evaporates. The afterglow reappears only after the concentration of atoms and of complexes is increased, and appears first at the cooled portion of the chamber where the rate of (3a) is the greatest.

Warming the gas should decrease the intensity of the afterglow without diminishing the concentration of atoms, and therefore the energy available for transfer to a metal surface by reaction (3b) or for excitation of Hg atoms by a collision of the second kind. A dark modification of active nitrogen with these properties has been observed.[3,4]

This picture is in excellent agreement with the high degree of dissociation and activation energy of Rayleigh, the negative temperature coefficient observed by Rayleigh, the data on energy transferred to Hg and other metal atoms by collisions of the second kind, and the available kinetic data.[5,6,7]

The writer wishes to thank Professor Loeb, who suggested this problem and whose helpful guidance was invaluable.

[3] J. Okubo and H. Hamada, Phil. Mag. 15, 103 (1932).
[4] E. J. B. Willey, J. Chem. Soc., 2837 (1927).
[5] E. J. B. Willey, J. Chem. Soc., 1620 (1928).
[6] E. J. B. Willey, J. Chem. Soc., 336 (1930).
[7] H. O. Kneser, Ann. d. Physik 87, 717 (1928).