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ELECTRICAL PROPERTIES AND NATURE OF ACTIVE NITROGEN

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Abstract

Source of currents between electrodes in active nitrogen.—Glowing active nitrogen from an electrodeless discharge tube was drawn in succession through two sets of coaxial cylindrical electrodes. The current between the electrodes of the second set was found to remain constant when the potential between the electrodes of the first set was varied from 0 to 250 volts. This indicates that the conductivity is not due to ions drawn from the discharge chamber. By varying the ratio of the areas of the second set of electrodes it was established that the saturation currents were proportional to the area of the negative electrode. It is concluded that the current between electrodes in active nitrogen is due to electrons emitted from the surfaces of the electrodes either photoelectrically or by direct action of the active nitrogen on the metal. The form of the current-potential curves indicates that the electrons are emitted with relatively high velocities.

Effect of He, N_2, H_2, O_2 on the duration of the afterglow.—Helium did not affect the afterglow up to pressures ten times that of the nitrogen. The other gases shortened the afterglow in the order named.

Ionization of foreign gases by active nitrogen.—It was found that active nitrogen did not ionize hydrogen or mercury vapor. Indications of ionization of iodine vapor were obtained. This suggests that the molecule of active nitrogen is N_2 in a metastable state with energy between 9.4 and 10.4 volts.

Introduction

IN THE year 1900, E. P. Lewis[1] described an afterglow obtained in nitrogen when a condensed discharge with spark gap was used. It is to R. J. Strutt,[2] however, that we owe perhaps the most systematic study of the physical and chemical properties of what he calls "the active modification of nitrogen" or, simply, "active nitrogen" produced when nitrogen is subjected to a condensed discharge. Nitrogen, whatever the source or method of its production, under the proper conditions emits an afterglow, the intensity and duration of which is governed by factors whose exact determination has been the subject of long discussions and tedious experiments. One question of interest was that of the degree of purity of the nitrogen necessary for the production of the afterglow. At first it was thought that the afterglow could be produced in very pure nitrogen as well as in nitrogen containing a certain amount of impurities. However, Compte,[3] Tiede,[4] Domcke, and Pirani,[5] showed that it is impossible to produce the glow in very pure

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[1] E. P. Lewis, Astrophys. J. **12,** 219 (1900); Ann. d. Physik **2,** 249 (1900); Astrophys. J. **20,** 49 (1904); Phys. Rev. **1,** 469 (1913); Nature **111,** 599 (1923).

[2] R. J. Strutt (now Lord Rayleigh), Proc. Roy. Soc. **A85,** 219 (1911); ibid, **A86,** 56 (1911–12); ibid, **A86,** 262 (1911–12); ibid, **A87,** 179 (1912); ibid, **A88,** 539 (1913).

[3] F. Compte, Phys. Zeits. **14,** 74 (1913).

[4] Tiede, Ber. d. D. Phys. Ges. **46,** 4065 (1913).

[5] Pirani, Chemical Abstracts, 157 (1923).

nitrogen. The remarkable conductivity of active nitrogen is also of interest. Strutt, in a series of papers, describes a number of experiments conducted in connection with the determination of the electrical conductivity of glowing nitrogen. He does not, however, arrive at a definite conclusion concerning the cause of the ionization or nature of the conductivity. It was thought that this question demanded further investigation; furthermore, the determination of the mechanism of ionization in active nitrogen could possibly be of assistance in the better understanding of its physical and chemical properties.

I. Electrical Properties of Active Nitrogen

(A) *Method of activation.* It is possible to activate nitrogen in several ways,[6] but the simplest and best recognized of all are those of the condensed electric discharge with spark gap, and the electrodeless discharge. By the first method the active nitrogen is produced by introducing nitrogen at low pressure into a discharge tube whose electrodes, made of aluminum, platinum or tungsten, are attached to the secondary terminals of a large induction coil or to the terminals of a 2200 volt alternating current transformer. By the second method, nitrogen is introduced at low pressure into a glass bulb around which are wound a few turns of well insulated wire connected in series with a condenser of suitable capacity and then to the secondary terminals of a high tension transformer. The spark gap is connected in parallel with the coil.

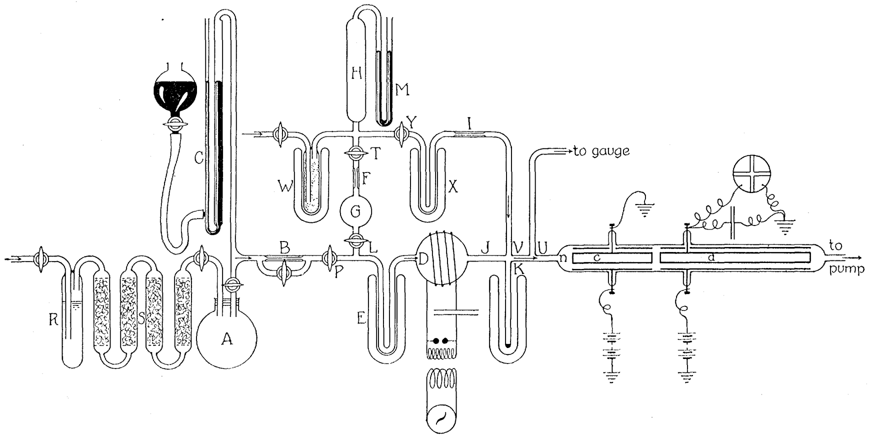

Fig. 1. Diagram of apparatus.

In the experiments to be described below, the second method was used. The Pyrex glass bulb D (see Fig. 1) was 8 cm in diameter. The Thordarson transformer was rated at 24000 volts, 60 cycles, 1 K.W. The coil had four turns and the capacity consisted of nine 12 by 14 in. glass plates of $\frac{1}{4}$ in.

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[6] Nitrogen in the proximity of radioactive substances presents the chemical activity characteristic of active nitrogen.

thickness, the sides of which were coated with 10 by 12 in. tin-foil sheets. The condenser plates were connected in parallel and immersed in transformer oil. The nitrogen used was supplied from a compressed nitrogen gas tank (manufactured by Tilden Air Products). At first it was freed from traces of oxygen by passing through five bottles *R* containing alkaline pyrogallol solution (22% aqueous solution of pyrogallol mixed with five or six times as much potassium hydroxide solution (3:2)) through drying tubes *S* containing phosphorous pentoxide, potassium hydroxide and calcium chloride. Later it was found that the commercially prepared nitrogen was sufficiently free from oxygen and could be used without passing through the pyrogallol solution without any perceptible dimunition of the intensity and duration of the afterglow. The uniform flow of the gas through the bulb was regulated by introducing the gas into a reservoir *A* of considerable size and then through a capillary tube *B* to the bulb *D*. The reservoir *A* was connected to a graduate manometer *C* which kept the pressure within *A* constant. Changes in volume could be measured with a precision of 0.1 cc. The pressure within *A* was kept at 80 cm of mercury. The intensity of the afterglow in the bulb was found to be greatest at a pressure of 0. 7 mm. The color of the afterglow at that pressure was deep yellow. The range of pressures between which the activation was satisfactory was from 1 mm to 0.5 mm. With pressure above 1 mm the nature of the discharge changed and no afterglow or ionization could be observed. Below 0.5 mm pressure the glow was a faint yellow and of shorter duration, due, apparently, to the faster diffusion of the active gas to the walls of the vessel.

(B) *Electrical properties.* In order to determine directly that the ionization is not due to the survival of ions produced during the discharge, the active nitrogen was drawn through two sets of electrodes (see Fig. 1), each one consisting of two coaxial cylinders. The *c* electrodes were used as an ion trap and were 50 cm long, the diameters of the coaxial cylinders being respectively 3.34 cm and 2.25 cm. They were placed 50 cm from the source of activation. The *d* electrodes were 36.5 cm long, the diameters of the coaxial cylinders being 1.9 and 1.27 cm and were placed 50 cm from the end of the ion trap. One of the ion trap electrodes was connected with the ground, the other to a battery whose maximum potential was 135 volts so that the field between the electrodes could be varied from zero to 250 volts per cm. One of the *d* electrodes was connected to a Dolezalek electrometer and the other to a 16 volt battery. It was observed that the ionization current in *d* was not affected more than two percent when the field between the ion trap electrodes was varied from zero to 250 volts per cm. Now any preexisting ionization due to the disruptive discharge or to any other cause could not pass through the strong field between the ion trap electrodes. Therefore one may conclude that the ionization observed in *d* was produced by changes taking place after the passage of active nitrogen through the ion trap. The slight changes observed can be explained in the light of what follows.

Before going further it is necessary to say a few words about the method of measuring the ionization and the determination of the conductivity of active nitrogen. In this determination great difficulty is experienced in view of the fact that the energy of discharge for the production of active nitrogen is so great that despite the precautions taken to screen the electrometer, the electrodes and the connecting leads, the electrometer needle oscillated violently during the discharge. The disturbing effects were due to the existence of the small opening *n* (Fig. 1) through which the gas flowed from the activation chamber to the electrodes. When the passage *n* was closed with a stop cock the electrometer was unaffected by the discharge. A high resistance galvanometer is not so much affected but it is not sensitive enough to measure ionization unless the activation is very strong and the electrodes are very near to the place where activation is produced. Moreover, with a continuous discharge it is difficult to have uniform temperature on the walls of the bulb *D* and, consequently, uniform activation, since the destructive effect of the walls increases with their temperature.

For the above reasons the discharge was made intermittent, lasting one second every two minutes. The electrometer readings were made at some definite time after the discharge had been interrupted. The points of the conductivity curves (see Fig. 2) were obtained by connecting the electrometer to the electrodes twenty-five seconds after each discharge and measuring the total deflection (i.e. total charge instead of rate of charging). In order to obtain conductivity curves whose saturation point was below the ionization potential of nitrogen, it was necessary to use comparatively long electrodes.

In the experiment described above, it was shown that the conductivity observed in active nitrogen is not due to the survival of ionization produced during the disruptive discharge. If the conductivity observed is due to the presence in the gas of ions, these ions must have been spontaneously produced. Such spontaneous ionization is conceivable with the help of a simple hypothesis concerning the nature of active nitrogen. Assuming that active nitrogen is an ordinary molecule of N_2 whose valence electrons have been transferred to higher energy levels, then spontaneous ionization could be produced after an elastic collision of the second type between two excited molecules. In that case all the energy in one of the molecules is transferred during the collision to the other with possible ionization of the latter. However, as will be seen from the experiments to be described below, the conductivity in active nitrogen is not due to spontaneous ionization but to electrons apparently emitted by the electrodes either by photo-electric action when active nitrogen reverts to the normal state, or by the direct action of impinging atoms as observed by Holst and Oosterhuis,[7] Webb,[8] Messenger.[9]

A second series of experiments was carried out to test this point by a method analogous to those that have been employed to distinguish between radiating and ionization potentials in gases. If the conductivity were due

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[7] Oosterhuis and Holst, Phil. Mag. **46,** 1117 (1923).

[8] H. W. Webb, Phys. Rev. **24,** 113 (1923).

[9] H. A. Messenger, Phys. Rev. **28,** 962 (1926).

to spontaneous ionization, the number of positive and negative ions present would be equal, and the saturation positive or negative currents would be equal irrespectively of the relative size of the coaxial cylinders between which the active nitrogen flowed. If, however, the conductivity were due entirely to electrons from the walls, since the number of the emitted electrons is proportional to the surface exposed, the number of electrons emitted from the outer cylinder will be to that emitted from the inner cylinder exactly in the ratio of their respective exposed surfaces. That is, the negative charges must be proportional to the areas of the negative electrodes or, what amounts to the same thing, the ratio K between the positive and negative saturation currents must be equal to the ratio of the surfaces of their respective electrodes. Besides the above two cases which represent extreme conditions we have a third possibility in which the conductivity is due at the same time to spontaneous ionization and to electron emission.

In the determination of the ratio K of the value of negative and positive saturation currents certain precautions are necessary, which, if omitted, may lead to considerable error in the determination of that value. From the analysis of the spectrum emitted by the afterglow it appears that the first positive band, to which the α-group bands characteristic of the afterglow belong, corresponds to a high excitation potential. It is possible, therefore, that the active nitrogen might ionize any impurity whose ionization potential is below the potential corresponding to the α-group bands. Such impurities might be the hydrocarbon vapors due to stop-cock grease, mercury vapor, etc. All these vapors were condensed by using a liquid air trap E through which the nitrogen gas passed before going to the activation chamber. Moreover, all the connections from that point to the pump were of glass. Incondensable impurities that are in the gas, such as oxygen, helium, or argon, have ionization potentials above the resonance potentials of active nitrogen and consequently no ionization can take place by collision.

In preparing the surfaces of the electrodes particular care was taken to give them similar finishing and not to touch them with the hands or any substances which would affect the electron emission from the surfaces. These surfaces were also polished several times during the experiments. The electrodes used were of brass and the ratios of the surface of the outer cylinder to the inner changeable cylinder were 1.7, 1.5, and 3. The readings were taken by applying alternately positive and negative potentials to the outer cylinder so that, in determining the values of positive and negative ionization currents corresponding to a given field, any change that could take place, such as diminution of photo-electric emission, would affect equally both values. It was essential during definite intervals of time to observe the conductivity corresponding to a field taken as standard in order to be sure that the general conditions determining the conductivity corresponding to other potentials were identical. Factors that could influence most effectively the conductivity were variations in the energy of the disruptive discharge and slight changes in the density of the flowing gas since, under these influences, the amount of activated nitrogen would vary and consequently the observed ionization. The curves of Fig. 2 represent the conductivity obtained using electrodes whose ratio of surfaces were 3:1 and 1.5:1. It will be observed that in the neighborhood of 4 volts the ratio between the negative and positive currents is about 3 to 1 in the one case and 1.5 to 1 in the other, these ratios remaining constant for saturation currents obtained in the neighborhood of 14 volts. For potentials above the ionization potential of nitrogen we have a slow increase of conductivity, the ratios, however, remaining constant. The observed slight discrepancies in the ratios must be attributed to the cumulative ionization of active nitrogen, or to the possible ionization of slight impurities present. Greater ratios between the surfaces of the electrodes have been used and analogous results have been obtained.

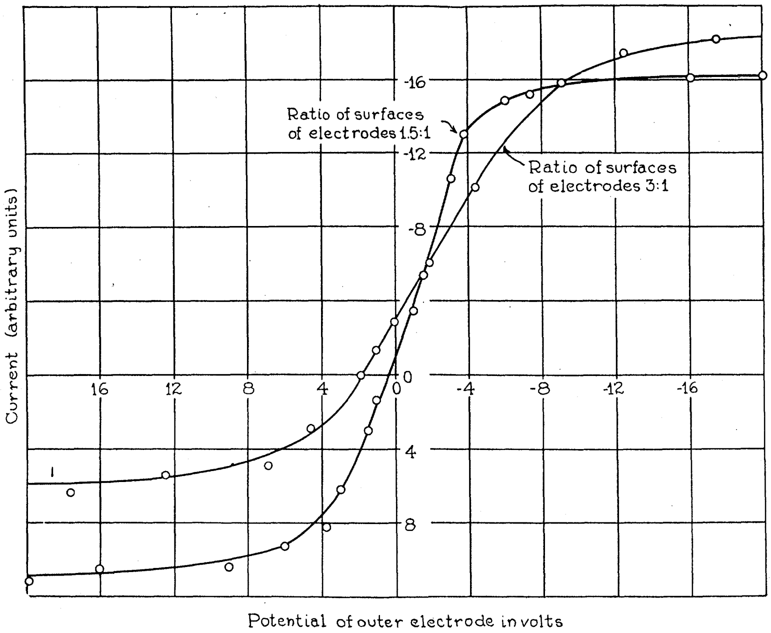

Fig. 2. Saturation curves with electrodes of different areas.

However, in using as an inner electrode a cylinder of small diameter, it was impossible to obtain saturation below the ionization potential of nitrogen. This equality of the ratios of the surfaces of the electrodes and of the saturation currents indicates that the conductivity of active nitrogen is due to electrons emitted from the surfaces of the electrodes. In the curve of Fig. 2, where the ratio of the surfaces is 3:1, a positive potential of 1.8 volts on the outer cylinder was necessary to obtain zero current. This may be interpreted as due to the electrons leaving the surfaces with considerable velocity so that a retarding potential must be applied to the larger surface to prevent a charging of the inner electrode. The slow saturation may also be interpreted as due to the electrons emitted having a high velocity.

In this connection experiments were also carried out in which a hot oxycathode arc in nitrogen served as a source of active nitrogen in place of the disruptive discharge. A steady arc was maintained with approximately 50 volts while the gas was allowed to flow past into the cylindrical electrodes. The characteristic yellowish glow of active nitrogen could be observed in the neighborhood of the arc. Between the electrodes the same type of conductivity curve was observed as with the methods described in the last paragraph. However, when an ion trap was introduced to prevent any possible ions reaching the electrodes, the active nitrogen was so weakened as to make measurements unreliable.

Experiments were carried out with the pressure adjusted to be above that at which active nitrogen is formed. Here the ion trap was adjusted so that the radiation from the arc could pass through and cause photo-electric emission directly from the surfaces of the electrodes. It was found that the same type of ionization curve with saturation at about 14 volts (see Fig. 3) was obtained in this case. This confirmation of the interpretation of the conductivity as due to the emission of electrons from the electrodes with high velocity was repeated with three other gases, oxygen, helium and hydrogen. The gas in each case was allowed to flow past the arc at about the same pressure as the active nitrogen.

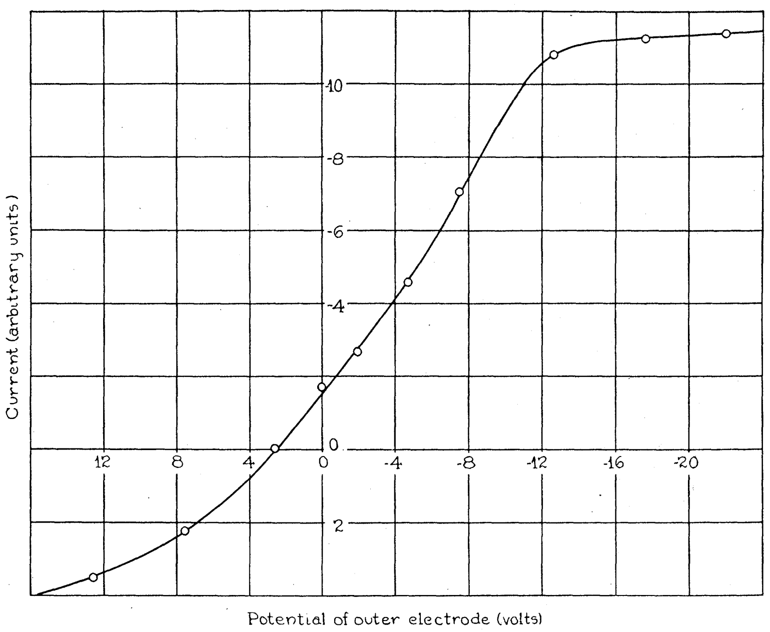

Fig. 3. Saturation curve of photoelectrons from electrodes.

We may conclude then from the first part of this investigation that the conductivity between two electrodes in active nitrogen is due to electrons emitted from the surfaces of the electrodes. There is no direct ionization of the gas and the electrons have a relatively high velocity.

II. MOLECULAR NATURE OF ACTIVE NITROGEN

The second part of this investigation is concerned with experiments bearing on the molecular nature of active nitrogen and particularly with the determination of the energy possessed by the molecule in this state. Two methods have been used. In one the rate of extinction of the luminous glow when various gases were added showed the degree to which the added gases could take up the energy of the excited active nitrogen. In the second method the transfer or absence of transfer of energy to various added gases was observed by the production of ionization in some and the absence of ionization in others. Most of the previous experimental observation can be interpreted by assuming that active nitrogen is either atomic or molecular in structure. Saha[10] assumes the active nitrogen to be an excited molecule with energy corresponding to 8.5 volts, while Birge[11] calculates the maximum molecular energy to be 11.5 volts, at which level he considers a metastable state to be possible. Foote, Ruark and Chenault[12] conclude that a metastable state of N_2 exists between 9.5 and 9.6 volts while Strutt and Sponer[13] consider that active nitrogen is atomic. We shall see later that the present observations fit in well with the excited molecule theory, and we shall use that theory in discussing the effects to be expected in these experiments.

(A) *Experiments on the effect of foreign gases on the duration of the afterglow.* The study of the effect on the glow due to the introduction of foreign gases can be made with two different arrangements. In the first arrangement the nitrogen from the reservoir *A* (Fig. 1) flows through the capillary tube *B* to the activation chamber *D*. At the point *L* it meets the stream of gas whose effect on the glow is to be studied. The amount of flow of this gas is regulated by the capillary tube *F* and the manometer *M* connected to the reservoir *H*. With this arrangement, when the activation takes place, we have in *D* a thorough mixture of the two gases. In the second arrangement the stop cock *T* is closed and the vessels are cleaned by letting nitrogen flow for a considerable time. Then *P* is closed, and the pressure in *D* is reduced to 0.07 cm. The next step consists in closing *L* and introducing the gas whose effect on the glow is to be studied into the bulb *G*, the amount of gas being regulated by keeping the pressure in *H* constant and the stop cock *T* open for a definite length of time. Under this arrangement, soon after the activation of the pure nitrogen, a definite quantity of the foreign gas is introduced by opening the stop cock *L*. It is to be noted that with the last method, possible activation of the foreign gas during the discharge is avoided, while on the other hand, a complicated manipulation with its concomitant disadvantages is introduced. The gases used were oxygen, hydrogen and helium. Readings were also taken by introducing nitrogen through *L* at

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[10] Saha and Sur, Phil. Mag. **48,** 421 (1924).

[11] Birge, Nature **114,** 642 (1924).

[12] Foote, Ruark and Chenault, Phys. Rev. **25,** 24 (1925). In a later paper Foote, Ruark, Chenault and Rudnik, J.O.S.A. **14,** 17 (1927) give the value of the energy of active nitrogen as greater than 10 volts and consider the probability that active nitrogen is atomic.

[13] H. Sponer, Zeits. f. Physik, **38,** 622 (1925).

various rates in addition to the nitrogen constantly flowing through *B*. The curve so obtained serves as a control to which the other curves can be referred. Helium and hydrogen were purified by passing slowly through a tube filled with charcoal and immersed in liquid air. The curves of Fig. 4 represent the results obtained by the first method. The abscissas represent rate of inflow of foreign gas taking as a unit the rate of flow of nitrogen through *B*. The ordinates give the corresponding duration of the afterglow, observed by a stop-watch from the instant of cutting off the exciting current to the time when no more luminosity could be observed.

The nitrogen-oxygen mixture afterglow presents, perhaps, the most interesting features since, besides changes in duration, we have changes in the color of the afterglow. With increasing rates of inflow of oxygen the glow changes from deep yellow to greenish-yellow, then to greenish-blue and attains a minimum intensity and duration when the inflow of oxygen is about equal to that of nitrogen, the color of the glow being deep blue. With further increases in the amount of oxygen, the duration and intensity of the glow increases, reaching a maximum when the rate of flow of oxygen is about 1.7 times that of nitrogen. So far as I am aware the existence of this maximum in the afterglow of nitrogen-oxygen mixtures has not been observed before. The color of the afterglow is then a brilliant green. With a still further increase of oxygen the glow becomes a dark green, diminishing gradually in intensity and duration. Strutt[14] studied the afterglow of rarified air and

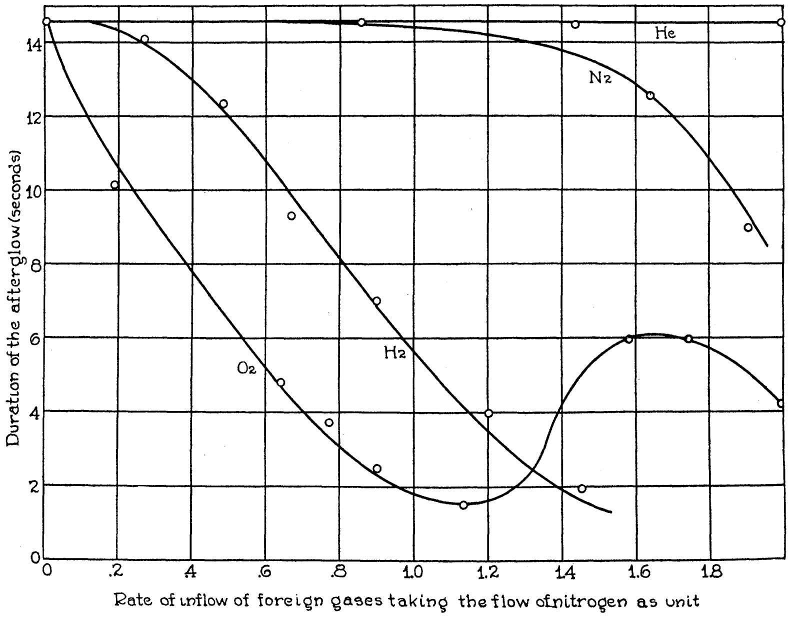

Fig. 4. Effect of foreign gases on the duration of the afterglow

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[14] Strutt, Proc. Roy. Soc. **A85**, 533 (1911).

attributed the greenish-yellow glow to the conbination of ozone and nitrogen oxides formed during the discharge. His observations correspond to the glow observed in the present experiments when the amount of oxygen was about two-tenths that of nitrogen. It seems to me, however, that the afterglow under the above conditions is due mostly to active nitrogen if we judge by its color which, during the first six seconds is yellow and very similar to that of active nitrogen, the greenish yellow becoming prominent only during the last four seconds. The curve for the duration of the afterglow in nitrogen-hydrogen mixtures does not present the anomalies of the oxygen curve. The duration diminishes gradually with increasing amounts of hydrogen and the glow remains a deep yellow. Apparently the energy is not transferred as easily to hydrogen molecules as to those of oxygen. The nitrogen curve serves to show the effect of increase in pressure (increase of molecular collisions) on the duration of the afterglow and serves as a convenient standard of comparison with the other mixtures since the abscissas are proportional to the pressure of the mixtures. The nitrogen-helium curve is of special interest since no decrease in the duration of the afterglow is observed when helium is introduced. When the ratio becomes one part of nitrogen to ten of helium, the only change observed is that in the color of the glow which becomes reddish-yellow. From the study of the nitrogen-helium mixture we derive the important conclusion that not only is no energy transferred in increasing the internal energy of helium molecules, but that even the energy transferred in increasing the translational energy of helium molecules

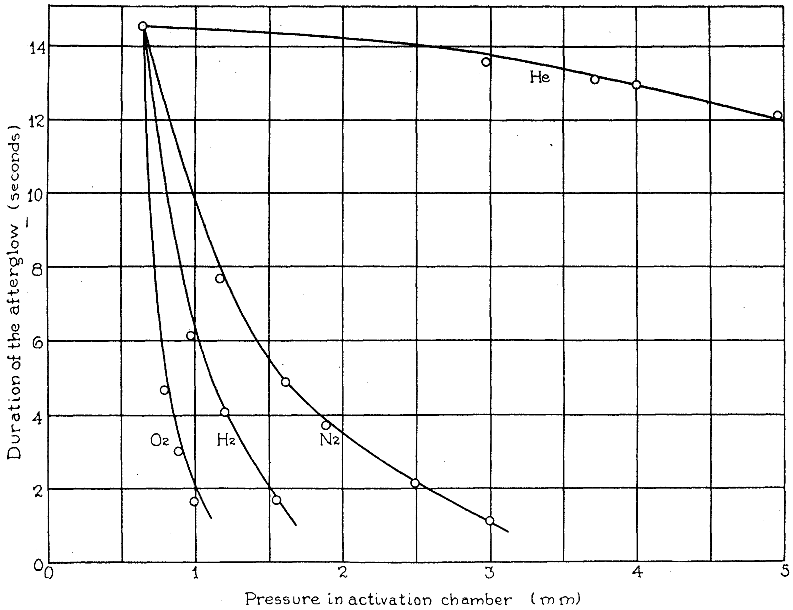

Fig. 5. Effect of foreign gases on the duration of the afterglow.

must be small. The high resonance potential of helium (20.5 volts) would lead us to expect that no energy would go to increasing the internal energy of the helium atom.

The curves of Fig. 5, obtained by the second method give the same general results. The ordinates represent duration of glow and the abscissas the pressure in the bulb after the introduction of the foreign gas. The nitrogen was always activated when at a pressure of 0.07 cm, so that the conditions of the discharge remained identical. The other gases were introduced immediately after the nitrogen had been excited.

(B) *Ionization in foreign gases produced by active nitrogen.* One more avenue to the study of active nitrogen is opened by the knowledge that its conductivity is due to electrons emitted from the electrodes. In a previously described experiment it was shown that the ratio between the negative and positive saturation currents was three to one, that is, exactly the ratio of the exposed surfaces of the electrodes. Now if by the introduction of a certain vapor this ratio becomes smaller, it will indicate that the vapor is ionized by collision. Furthermore, the knowledge of the ionization potential of the introduced vapors will help to place the excitation potential of active nitrogen.

The vapors used were hydrogen (ionization potential 15.9), mercury (ionization potential 10.4), and iodine (ionization potential 9.4[15]). Hydrogen was introduced in a continuous stream and in various amounts at a point V between the activation chamber and the electrodes. No change was observed either in the conductivity or in the ratio between the two saturation currents. This is an indication that ionization by collision does not take place. Mercury vapor was introduced by placing mercury in a tube K where it could be cooled by liquid air or heated by a Bunsen flame. No change was observed either in the conductivity or in the ratio, even when the mercury was heated to the point of active evaporation. Iodine, like mercury, was placed in a tube K where its evaporation could be controlled by suitable changes of temperature. When a small iodine crystal was placed in K and the tube immersed in liquid air no effect was produced either in the color of the glow or in the ratio. When the tube K was directly above the liquid air flask and so kept quite cool, the glow in the activation chamber remained a deep yellow, while in the tube J the color changed to a bright, light blue due to the excitation of iodine vapor. The conductivity decreased and the ratio changed to about 2.5:1. Finally, when the temperature in K was that of the room, the evaporation was greater and the light blue fluorescence due to iodine turned to dark blue, while the conductivity became very small and the ratio decreased to 2:1, indicating a considerable amount of ionization by collision.

(C) *Theoretical inferences.* The experiments above point towards the hypothesis that active nitrogen is an excited molecule of nitrogen having a metastable state between 9.4[16] and 10.4[17] volts if we can judge by the ioniza-

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[15] Smyth and Compton, Phys. Rev. **10,** 501 (1920).

[16] This is the nearest to that determined by Foote, Ruark and Chenault which is between 9.5 and 9.6 volts.

[17] Ionization potential of mercury is 10.4 volts.

tion by collision effects. The metastable hypothesis presents certain obvious difficulties in view of the long duration of the glow. It is, however, theoretically conceivable that an atom might remain for an arbitrary length of time in an excited state provided only that the pressure and temperature are kept sufficiently low. Low pressure and low temperature mean few and less violent collisions. Another external influence that we should expect to be much more destructive to the metastable state than the simple collision between two molecules, is the collision between a metastable molecule and a freely moving electron because of the unneutralized electromagnetic field associated with the electron. The absence of free electrons in active nitrogen as demonstrated in the present investigation adds significance to this view.

The hypothesis that active nitrogen is a metastable state of nitrogen reverting to nitrogen after a collision and that, as was supposed above, collisions with electrons are especially effective in reverting active nitrogen to the normal state, finds additional support in certain exceedingly interesting results obtained by Strutt.[18] He succeeded in making his nitrogen so pure that the afterglow became very dim. Strong restoration of the afterglow was obtained by introducing such impurities as methane, oxygen, chlorine, hydrogen[19] and other electro-negative gases, while the introduction of argon, helium or of nitrogen itself does not restore the glow. We may interpret these observations as follows. During the disruptive discharge the gas is ionized, and in the case of pure nitrogen gas, the electrons move freely and with great translational velocities so that we might expect the number of successful collisions to be great and the reversion of metastable nitrogen to normal nitrogen to be rapid. In the case of the presence of electro-negative impurities such as oxygen, Franck[20] showed that the electrons served as nuclei for the formation of slowly moving ions, in that way decreasing the number of effective collisions.

Strutt gave to the above results an almost diametrically opposite explanation which in brief is as follows. He assumes that active nitrogen consists of monatomic nitrogen which is produced only by the impact of a negative ion in the discharge, while free electrons are not effective in administering the right kind of blow. Experiments by Hogness and Lunn[21] on the ionization of nitrogen by electron impacts have shown that atoms are formed along with charged molecules except with very low pressures where the charged molecules make no collisions. Thus we would expect nitrogen atoms to be present even when the gas was very pure.

H. Sponer has also assumed that active nitrogen is monatomic nitrogen, the afterglow appearing when two atoms of nitrogen collide simultaneously with a neutral nitrogen molecule. In the collision they could excite the nitrogen molecule by transferring to it their dissociation energy, at the same

[18] Strutt, Proc. Roy. Soc. **A91,** 303 (1914–15).

[19] J. J. Thomson, Proc. Roy. Soc. **A89,** 10 (1910) established the existence of negatively charged atoms of carbon, oxygen, chlorine and hydrogen.

[20] Franck, Verh. d. D. Phys. Ges. **12,** 613 (1910).

[21] Hogness and Lunn, Phys. Rev. **26,** 786 (1925).

time recombining to form a neutral molecule. With this hypothesis one could explain satisfactorily the long duration of the afterglow since collisions such as are described above are rare in comparison with bimolecular collisions. However this hypothesis requires the energy of dissociation of nitrogen to be between 11.4 volts (260,000 cal.) and 13.0 volts (296,000 cal.) or, more specifically as it appears from a later paper,[22] the dissociation potential to be placed at 11.4 volts. This value is very different from Eucken's[23] revised value (16.5) volts and also from A. Grimm's[24] value, obtained from positive ray analysis, which is 15.9 volts. The present investigation also shows that the energy set free in the reversion of active nitrogen to the normal form is not able to ionize mercury (10.4 volts). Moreover, with Sponer's hypothesis it is difficult to explain the lack of afterglow when the nitrogen is free of impurities without making the additional hypothesis that these impurities serve as a protection against the catalytic action of the walls of the vessel.

Wood showed that hydrogen can be dissociated under the influence of an electric discharge and that if this gas in its atomic form is drawn over metals or any other substances having catalytic properties, they can be brought into incandescence by the heat liberated during the process of recombination into molecular form. In the present experiments it had been found that the active nitrogen was much weakened after passing through a metal ion trap and an attempt was made to see if this destruction was accompanied by a heating of the metal. A coil of nichrome wire was placed in the path of the active nitrogen and connected to a Wheatstone bridge. Any change in temperature of the wire greater than 0.1°C could be easily determined from the change in the resistance of the wire. No change in resistance was observed. This suggests that the phenomena in nitrogen are not similar to those in atomic hydrogen, as would be expected if active nitrogen is atomic. On the excited molecule theory the energy can go into the kinetic energy of the ejected electron.

The view that active nitrogen is of a more complex atomic grouping cannot be advanced with any great advantage. Strutt's attempt at condensation of active nitrogen by liquid air was repeated with negative results. A bulb containing nitrogen was immersed in liquid air and the appearance and duration of the afterglow was observed when the duration of the electrodeless discharge was varied from one second to fifteen minutes. The appearance and duration of the afterglow remained the same irrespectively of the changes in the duration of discharge which indicates that no change of pressure took place within the bulb due to condensation of active nitrogen. Since ozone is condensed at liquid air temperature we might expect a complex molecule such as N_3 to be condensed also. This result by analogy, is unfavorable to the idea that active nitrogen is of the form N_3.

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[22] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

[23] A. Eucken, Ann. d. Chemie, **440**, 111 (1924) originally gave the dissociation potential of N_2 obtained from the specific heat calculation as about 19 volts (430,000 calories).

[24] A. Grimm, Zeits. f. Electrochemie **31**, 474 (1925).

The observed increase in the intensity of the glow when active nitrogen is locally cooled can be interpreted as due to an increase in the number of collisions with the active molecule. By locally cooling a closed vessel we obtain a greater density in the part cooled and it can be shown that the number of collisions varies as $T^{-3/2}$ where T is the absolute temperature. For instance, if one part of the vessel is kept at a temperature of 20°C and another at that of liquid air, then the number of collisions in the two parts will be in the ratio of 1:5.5. An experiment was performed in which active nitrogen was produced by an electrodeless discharge inside a closed bulb with a wide, short tube which could be immersed in liquid air.[25] When the bulb was at room temperature the afterglow lasted about 28 seconds. When the lower end of the tube was immersed in liquid air the glow was concentrated in the lower part and lasted about 4 seconds, which gives a 7:1 rate of decay instead of 5.5:1 as predicted by theory.[26] It must be added, however, that it was difficult to make accurate observations on the duration of the afterglow when the tube was immersed in liquid air because of the vapors that condensed on the surface of the bulb. The observations are thus seen to be in good agreement with the hypothesis that the phenomena associated with active nitrogen are due to a metastable form of the molecule.

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[25] This experiment has been suggested by a similar experiment conducted by Strutt in which, however, he observed the intensity instead of the duration of the glow.

[26] In the light of the above considerations we should expect a decrease in the duration of the afterglow with accompanying increase in intensity when the density of the gas in the bulb is kept constant while its temperature is increased in view of the fact that the number of collisions is proportional to the square root of the absolute temperature. The observed decrease in intensity when the gas is heated at constant density, which is in disagreement with the above considerations, may be due to the liberation of water vapor and other gases from the heated bulb which have a great influence in decreasing the intensity of active nitrogen and in that way altering greatly the pure temperature effects.