CCXII.—*On Active Nitrogen. Part V. The Decay of the Nitrogen After-glow.*

By Eric John Baxter Willey.

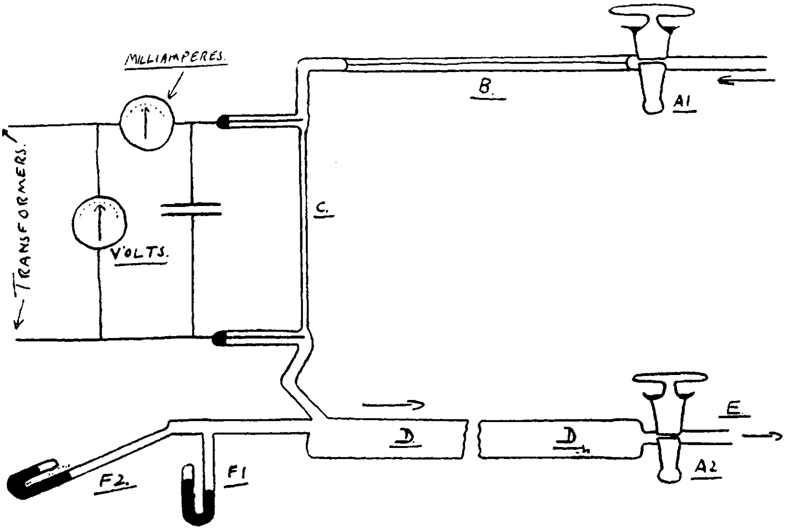
In searching for information which would reconcile the evidence as to the energy and nature of active nitrogen, as presented in the present series of papers, with the results obtained by spectroscopists, it appeared that a study of the decay process of the glow would probably be of considerable value. Lord Rayleigh has shown (*Proc. Roy. Soc.*, 1912, *A*, **86**, 262; **87**, 179) that the glow transformation is multimolecular, whereas the results of Angerer (*Physikal. Z.*, 1921, **22**, 97) and of Bonhoeffer and Kaminsky (*Z. physikal. Chem.*, 1927, **127**, 385) indicate that it is bimolecular with regard to the active nitrogen. The assumption of a simple process of recombination of nitrogen atoms, as postulated by Angerer and to a certain extent by Bonhoeffer and Kaminsky and others in explanation of this result, is open to certain formidable objections, *viz.*, (*a*) the negative temperature coefficient of the glow decay (Rayleigh, *loc. cit.*), and (*b*) the familiar and marked destructive effect of the surrounding gas on the glowing nitrogen, first observed by Rayleigh (*Proc. Roy. Soc.*, 1916, **92**, 438).

In Part I (J., 1926, 1804) it was suggested that there are some points of similarity between the nitrogen glow-decay process and the reaction $2NO + O_2 \longrightarrow 2NO_2$, which has been shown by Bodenstein and Lindner (*Z. physikal. Chem.*, 1922, **100**, 68) to be kinetically of the third order and to possess a true negative temperature coefficient. If this hypothesis be correct, the total pressure of the nitrogen will exert a great influence on the decay process of the glow, and the present communication describes an investigation of the matter.

EXPERIMENTAL.

Nitrogen purified as before (Part I, J., 1926, 1804) was drawn *via* the tap A1, through the capillary choke B, the discharge tube C, the observation tube D, and the tap A2 to exhaust at E (see Fig. 1). Two manometers, one vertical (F1) and the other inclined (F2), were provided, and a cadmium trap for mercury vapour (omitted from the diagram) was interposed between the manometers and the gas line; this last arrangement was deemed advisable since the quantity of mercury vapour gaining access to the discharge even at ordinary temperatures is sufficient to produce a noticeable fouling of the apparatus after continuous running for a week or two. Aluminium electrodes were used as before. The discharge was obtained from the 100-cycle converter and transformers mentioned in the previous paper, and could, if desired, take 300 milliamps. at 10,000 volts on full load ; this was greatly in excess of normal requirements

FIG. 1.

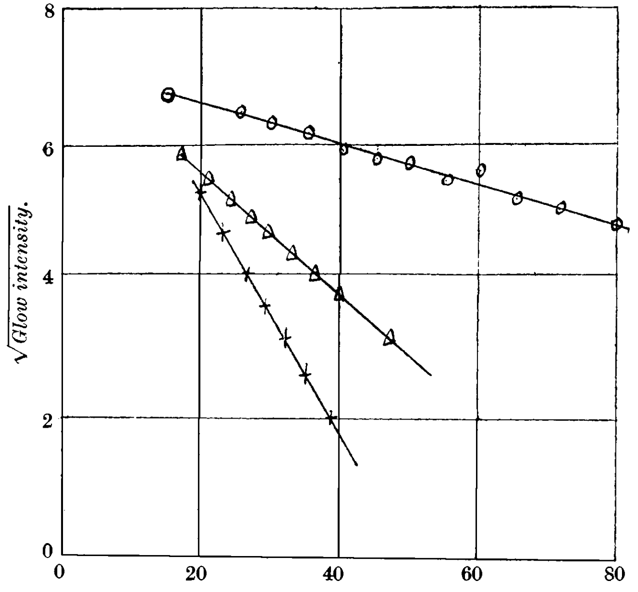


and an r.m.s. current of 20 milliamps. was generally used, four quart-size Leyden jars being provided in parallel with the discharge as shown. A brilliant glow was obtained when the gas was drawn through the apparatus at flow speeds up to 3500 c.c./hr. (at *N.T.P.*) and pressures of 10 mm. and less. Before being fitted, the discharge and observation tubes were cleansed as already described (Part I) and the electrodes submitted to a long preliminary run in another tube to free them thoroughly from gas. D was about 1½ m. long and of 2 cm. internal diameter, and all glass parts were heated as strongly as possible under a pressure of 0·0001 mm. before starting the experiments.

The intensities of the glow were measured by means of an Eastman colorimeter (*Nature*, 1926, **118**, 30; see also Jones, *J. Opt. Soc. Amer.*, 1920, **4**, 420). The observation field of this instrument is divided into upper and lower halves, one giving direct vision of the substance to be examined, and the other being illuminated by a small constant-current glow lamp, the light from which passes through four wedges of gelatin dyed respectively red, green, blue, and " neutral " or grey. These wedges can be introduced to any degree desired, either singly or in combination, according to an arbitrary scale which reads from 0 to 50 for each. Since the colour-quality of the glow does not appreciably alter during decay, the process can conveniently be followed by matching the initial intensity by means of the red, green, and blue wedges and introducing the grey as the luminosity decreases with the passage of the gas along D. The instrument was mounted so as to be movable parallel to the observation tube and at a fixed distance, its position being read by means of a pointer on the base which moved along a scale placed below the tube containing the glowing gas. The intense light from the discharge was screened off by means of black cloth, and a similar black background was provided for the observation tube.

In the experiment, the glowing nitrogen was first drawn through the apparatus for some 20—30 minutes in order that the intensity, often low at first, should rise to its constant value. The comparison and observation fields were then matched, the " neutral " wedge remaining at zero, the colorimeter was moved along D, and the intensities were re-matched at about ten fixed points by means of the " neutral " wedge. Since the reading on this is 50 when fully introduced, the intensity of the glow on the arbitrary scale of the instrument is (50 minus the scale reading of the wedge). This procedure was repeated on the return journey of the colorimeter to its zero position, the points at which the observations were made in this case being half-way between those for the outward journey. Measurements of the decay of the glow along D were thus obtained under a variety of conditions of flow speed and pressure, these being determined respectively by a calibrated Venturi meter in the gas line and by the tilted manometer F2, the vertical gauge serving to check the former. Curves were then plotted showing the relation between the square root of the intensity and the time, the latter expressed in terms of the distance along the scale below the observation tube. Typical results are shown in Fig. 2.

FIG. 2.



○ = 3·5 *mm.* 1150 *c.c./hr.* △ = 5·0 *mm.* 1150 *c.c./hr.*
+ = 7·0 *mm.* 2200 *c.c./hr.*

(*Flow speeds given at atmospheric pressure.*)

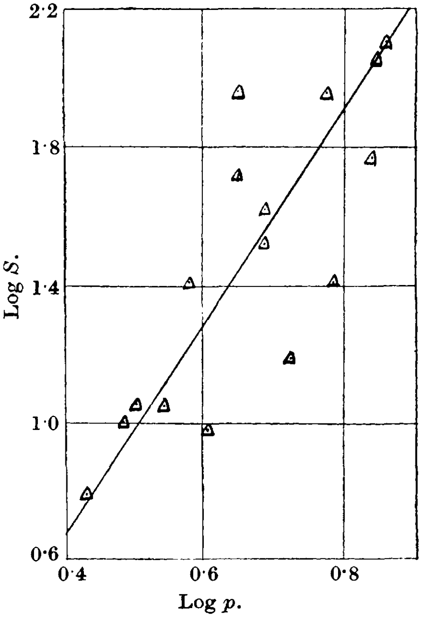
In order to reduce these observations to a common basis for comparison, the following procedure was adopted. Applying Boyle's law, we see that if distances along the observation tube are to be taken as expressing times the slopes of the lines as actually observed must be multiplied by the gas pressure and divided by the flow rate in order that comparable results shall be obtained; it is unnecessary to express them upon an absolute basis. The "corrected" slopes × 100 are in Table I, and it will be noticed that the greater the pressure the greater the gradient, *i.e.*, the rate of decay increases with the gas pressure: moreover, when the logarithms of

TABLE I.

No.	Expt.	Observed slope.	Pressure (mm.).	Flow rate (c.c./hr.).	Corrected slope, S.	log p.	log S.
A.	1	0·051	4·0	2200	9	0·60	0·97
	2	0·178	7·0	,,	57	0·84	1·76
	3	0·062	5·3	,,	15	0·72	1·17
	4	0·086	6·2	,,	24	0·79	1·38
B.	1	0·036	3·5	1150	11	0·54	1·04
	2	0·094	5·0	,,	41	0·69	1·61
	3	0·188	7·3	,,	120	0·86	2·08
	4	0·039	3·2	,,	11	0·50	1·04
	5	0·180	7·0	,,	110	0·84	2·04
	6	0·076	5·0	,,	33	0·69	1·52
C.	1	0·03	2·7	1320	6	0·43	0·78
	2	0·15	4·5	,,	51	0·65	1·71
	3	0·03	3·0	900	10	0·48	1·00
	4	0·06	3·8	,,	26	0·58	1·40
	5	0·17	4·5	,,	87	0·65	1·94
	6	0·136	6·0	,,	90	0·78	1·95

the slope S and the gas pressure p are plotted against each other, we find that the slope of the line thus obtained gives fairly closely $\log S/\log p = 3$, *i.e.*, *the slope varies as the cube of the gas pressure* (Fig. 3).

FIG. 3.



Experiments A3, A4, and C5 are doubtful but have been included for completeness.

Discussion.

Let us follow the consensus of opinion and regard the after-glow as representing the energy of recombination emitted either as a whole or in part as radiation consequent upon binary collisions among atoms. The glow intensity I expressed on an arbitrary scale will then be proportional to the rate at which the atoms are recombining, and if ν be their concentration at any instant, $d\nu/dt = kI$, where k is a constant. If Z be the number of such collisions per second, we have

$$Z = \nu^2[2\sigma^2\sqrt{4\pi BT/m}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ = diameter of nitrogen atom, taken as $1{\cdot}9 \times 10^{-8}$ cm.; m = mass of nitrogen atom, taken as $2{\cdot}3 \times 10^{-23}$ g.; B = Boltzmann's constant $= 1{\cdot}37 \times 10^{-16}$; and $T =$ absolute temperature, taken as 288°. Hence K (the quantity in the square bracket) $= 1{\cdot}05 \times 10^{-10}$, and

$$d\nu/dt = kI = K\nu^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence it follows that if a linear relation exists (such as these experiments show) between $\sqrt{I}$ and t, the decay process is bimolecular with respect to the glow-producing system. This is in complete agreement with the conclusions of other investigators (*vide supra*), and hence we may write $d[\mathrm{N}]/dt = K[\mathrm{N}]^2$. The slope of the $\sqrt{I}$–t curve should not, however, be affected in any way by the total gas pressure, as in these experiments, but be determined solely by the constant K; we are thus led at once to the conclusion that the decay process is not kinetically a binary reaction except with respect to the glow-producing system, assumed atomic. We may examine the hypothesis of a ternary reaction as follows.

By equation (2) we have $d\nu/dt = K\nu^2$, and integration of this from an initial concentration of atoms α when $t = 0$ to a value ν at time t, gives

$$Kt = \int_{\nu}^{\alpha} d\nu/\nu^2 \text{ or } K = (\alpha - \nu)/t\alpha\nu \quad . \quad . \quad . \quad (3)$$

This is the usual equation for the velocity coefficient in a bimolecular reaction. Bodenstein and Lindner (*loc. cit.*) have shown that good agreement between calculated and observed values for velocity coefficients in the reaction $2\mathrm{NO} + \mathrm{O}_2 \longrightarrow 2\mathrm{NO}_2$ may be obtained upon the assumption that the probability of an oxygen molecule striking a nitric oxide molecule actually in collision with another bears to the probability of the binary collision the same relation as the molecular diameter does to the mean free path (see Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," p. 111); applying this reasoning to the hypothetical reaction $2\mathrm{N} + \mathrm{N}_2 \longrightarrow 2\mathrm{N}_2$, we have, for nitrogen at 10 mm. pressure, $3{\cdot}8 \times 10^{-8} \div 4{\cdot}5 \times 10^{-4} = 8{\cdot}4 \times 10^{-5}$ as the ratio of ternary to binary collisions, *i.e.*, as the ratio of the rates of the reactions $2\mathrm{N} + \mathrm{N}_2 \longrightarrow 2\mathrm{N}_2$ and $\mathrm{N} + \mathrm{N} \longrightarrow \mathrm{N}_2$. We may then transform equation (3) to one for calculations in ternary collisions by multiplying the velocity coefficient K by this quantity. Taking 3 secs. as the average visible life of the glow in nitrogen at 10 mm. pressure, and assuming that it corresponds to a change of intensity from I to $I/100$, *i.e.*, to a change of concentration of atoms from α to ν, where $\nu = \alpha/10$, we have (from equation 3)

$$K \times 8{\cdot}4 \times 10^{-5} = \frac{1}{3}\left(\alpha - \frac{\alpha}{10}\right)\frac{10}{\alpha^2},$$

and since $K = 1{\cdot}05 \times 10^{-10}$, $\alpha = 3{\cdot}4 \times 10^{14}$ atoms per c.c. Since the concentration of chemically active nitrogen (1—1·5%) is approximately 4×10^{15} molecules per c.c., it follows that the assumption of a ternary process renders it just possible for the glowing and chemically active forms of nitrogen to be identical, or, more probably (see later), present in comparable concentrations, provided (*a*) that an extremely high fraction of the total atomic collisions (*i.e.*, N + N impacts) results in the production of a complex which can within its life, since it is likely to be " excited," undergo collision with another neutral molecule, and (*b*) that we are justified in assuming the same molecular diameter to obtain in the neutral and excited states. We may assume that condition (*a*) is likely to be realised (see Hinshelwood, *op. cit.*, p. 101), but with regard to (*b*), Stuart (*Z. Physik*, 1925, **32**, 262), Tolman, Yost, and Dickinson (*Proc. Nat. Acad. Sci.*, 1927, **13**, 188), and others have shown that the diameter of an excited or " active " molecule may be considerably greater than the normal; were this so in the present case an increase in σ would diminish the values calculated for the concentration of chemically active nitrogen. It is also clear that the assumption of a purely binary decay will lead to a concentration of glowing nitrogen of the order 10^{-5}—10^{-6} of the chemically active nitrogen. It appears then that by this simple calculation we can obtain excellent correlation between the life of the glow and the quantity of chemically active nitrogen present, but if the glow decay were truly ternary, its rate would vary inversely as the mean free path of the nitrogen molecule, *i.e.*, as the total pressure p, and not as p^3.

The author suggests that this difficulty is overcome by the hypothesis that the decay process really consists of an initial ternary collision $2N + N_2 \longrightarrow 2N_2$ followed by two binary impacts, one of the two entities concerned in each of these last two being neutral nitrogen molecules.

Consequences of this hypothesis are as follows :

(*a*) The decay process is binary with respect to the atoms but effectively ternary, since the last two binary reactions will be much more rapid than the relatively slow ternary reaction which determines the effective speed of the glow transformation and accounts for the comparable values calculated and observed for the concentration of chemically active nitrogen. The total reaction will, however, be of the fifth order since we have

$$d[N]/dt = \text{constant} \times [N]^2 \quad . \quad . \quad . \quad . \quad (4)$$

and as the slope of the $\sqrt{I}$–t curve, *i.e.*, the value of the constant, varies as p^3, we have finally

$$d[N]/dt = K_2[N]^2[N_2]^3 \quad . \quad . \quad . \quad . \quad (5)$$

(*b*) The negative temperature coefficient of the glow decay is accounted for, since this is probably a characteristic feature of ternary reactions (see Hinshelwood, *op. cit.*, p. 111).

(*c*) The decay process is to be regarded as a series of (possibly) complicated reactions, and if we accept the possibility of externally induced changes in the mechanism, the independence of glow and chemical activity (J., 1927, 2831)—see also Kenty and Turner (*Physical Rev.*, 1927, **29**, 914)—is rendered probable under appropriate conditions. The author now prefers this hypothesis to that advanced in the earlier communication (Part IV), *viz.*, that the glowing and chemically active forms of nitrogen, while generally co-existent, are nevertheless not interdependent.

(*d*) The volume change attendant upon the production of the atoms need not be more than quite a small fraction of the volume of chemically active nitrogen, since it follows naturally that the latter may represent metastable or isomeric nitrogen molecules produced during the decay and each possessing a part of the energy of the parent body. This would explain Crew and Hulbert's observation (*Physical Rev.*, 1927, **30**, 134) that no appreciable increase in pressure due to dissociation occurs when a discharge is passed in nitrogen under such conditions as to develop the glow. The decay process might thus tentatively be envisaged

$$2N + N_2 \longrightarrow N_2^A + N_2^B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$N_2^A + N_2 \longrightarrow N_2^C + N_2^D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$N_2^B + N_2 \longrightarrow N_2^E + N_2^F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where N_2^A, etc., represent the various molecules which have acquired fractions of the original energy of recombination. This may not represent the *whole* of the decay process since it simply describes what can be *seen*—the possibility of other " dark " reactions after this must be kept in mind, particularly as after the emission of the α- or visible radiation the molecule is still 8·0 volts above the normal electron level (Johnson, *Nature*, 1927, **119**, 9). In this way we see that comparable values should be obtained for the active nitrogen concentrations as measured chemically and as calculated from the life of the glow, a ternary decay being assumed.

(*e*) If we accept the very probable view that one at least of these decay stages results in the formation of an excited molecule with a life of 10^{-6}—10^{-8} sec., it follows that the order of the decay process and both the luminous and the chemical phenomena connected with active nitrogen are likely to depend upon the total nitrogen pressure; this is evident, for if an excited molecule be not hit within this time it will most probably radiate its energy instead of transmitting it either as a whole or in part to another molecule.

A study of the decay of the glow in the presence of varying quantities of other gases which do not react chemically with active nitrogen would also be of interest.

It is noticeable that Angerer (*loc. cit.*), working at pressures less than 1·0 mm., did not obtain the same slope for his $\sqrt{I}$–t curves in all his experiments, and, moreover, that the slope generally altered in the course of a single run; this is suggestive either of a change in the decay mechanism towards the end of the reaction or the influence of a heterogeneous reaction taking place at the same time (see Rayleigh, *Proc. Roy. Soc.*, 1912, *A*, **86**, 262).

This may be the explanation of the divergencies observed in the spectra developed by active nitrogen, and also of the recent claim of B. Lewis (*J. Amer. Chem. Soc.*, 1928, **50**, 27) that, when active nitrogen is mixed with active hydrogen at low pressures (0·4—0·02 mm.), ammonia is formed. He suggests that this is due to the reactions: (1) $N + H \longrightarrow NH$; (2) $NH + H_2 \longrightarrow NH_3$, but, as the present author has pointed out (*Nature*, 1928, **121**, 355), this theory is at variance with observations of Rayleigh (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219) and of Willey and Rideal (J., 1927, 671) that ammonia *extinguishes* the glow of nitrogen and chemical action appears to be traceable; he fails to record such changes in the glow phenomena as would be anticipated. If, however, we are prepared to admit another mechanism of glow decay at low pressures and a form of chemically active nitrogen different from that obtained at higher pressures, an alternative explanation is easy. Since the number of collisions which a high-level excited molecule could suffer with neutral molecules during its life will diminish with the gas pressure, it follows that under the right conditions a chemically active molecule might be produced which, by virtue of its abnormal energy content as compared with the Rayleigh active nitrogen, would be capable of participating in reactions denied to the latter. The mechanism of Lewis's ammonia synthesis might then be regarded as (1) $N_2{}^1 + 2H_2 \longrightarrow N_2H_4{}^1$; (2) $N_2H_4{}^1 + H_2{}^1 \longrightarrow N_2H_6{}^1 \longrightarrow 2NH_3$. In this way his failure to obtain hydrazine is accounted for; the quasi-molecule first produced falls apart unless within its life it undergoes collision with an excited hydrogen *molecule* (see Phipps and Taylor, *Physical Rev.*, 1927, **29**, 309), and the reaction may take place without the direct participation of the nitrogen atoms and any changes of glow phenomena in consequence. It does not, moreover, appear valid to assume that such a reaction would occur only at low pressures. That nitrogen may momentarily exist in a more chemically active state than in the Rayleigh form is shown by the experiments of Jolibois and Lefebvre (*Compt. rend.*, 1927, **185**, 853), who found that the reaction $2CO + O_2 \longrightarrow 2CO_2$ in the discharge can be greatly furthered by the addition of nitrogen to the mixture

Presumably the nitrogen is activated and undergoes second-type collisions with either the carbon monoxide or the oxygen or both, leading to the production of active forms of these substances. Moreover, Lowry (J., 1912, **101**, 1152; *Trans. Faraday Soc.*, 1913, 9, 189) has presented evidence that a form of nitrogen oxidisable by ozone can be obtained by the spark discharge in air at atmospheric pressure, and although his observations may be due to the production of an unstable nitrogen oxide which reacts only with ozone and not with oxygen, the statement of Wendt and Grubb (*Chem. Met. Eng.*, 1920, **22**, 771), that the corona discharge in nitrogen at atmospheric pressure also gives rise to a *stable* variety of nitrogen which can react with oxygen and with hydrogen to give nitric oxide and ammonia respectively, leads still further to the view that nitrogen may exist in several chemically active forms. It may also be noticed that Usher and Venkateswaran (J., 1919, **115**, 613) have found that the nitrogen liberated during the electrolysis of sodium azide attacks mercury, a reaction suggestive of the formation of N_3 or N_6.

Summary.

Experiments upon the decay of the nitrogen afterglow show that the reaction is kinetically of the fifth order between 2 and 8 mm. pressure. Calculations applying kinetic theory to observations on the life of the glow show that, if the reaction be bimolecular in reality, the concentration of the glow-producing system, assumed to be atomic, is only 10^{-5}—10^{-6} of the chemically active nitrogen present in the same circumstances, a discrepancy overcome by assuming the process to represent an initial slow ternary reaction, $2N + N_2 \longrightarrow 2N_2$, followed by two rapid binary reactions. This theory accounts for the negative temperature coefficient of the glow-decay, and is considered (*a*) to furnish evidence that the glow and chemical activity in nitrogen represent separate and very variable stages in the complex deactivation process of a high-level molecule first formed from atoms, and (*b*) to explain the existence of other varieties of chemically active nitrogen reported from time to time and also divergencies in the spectroscopic and chemical characteristics of the Rayleigh form.

This work was carried out in the Laboratory of Physical Chemistry, Cambridge, in the summer and autumn of 1927, and the author's warmest thanks are due to Prof. T. M. Lowry, F.R.S., and Dr. E. K. Rideal and to all his colleagues for their constant advice and co-operation.

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[*Received, March 9th,* 1928.]