XLIX.—*On Active Nitrogen. Part VII. Further Studies upon the Decay of the Nitrogen After-glow.*

By Eric John Baxter Willey.

In previous papers (Part V; J., 1928, 1620; see also 1929, 228) it was shown that the ternary reaction $2N + N_2 \longrightarrow 2N_2$ (+ glow) would provide, upon a simple kinetic basis, a quantitative explanation of (i) the long life of the nitrogen after-glow, (ii) the negative temperature coefficient of the decay, and (iii) the amount of the chemically active species present under given conditions. Experimental work showed, however, that the process was to be represented as $2N + 2N_2 \longrightarrow 3N_2$, rather than as the simpler ternary reaction given above. It has, moreover, been concluded that the luminosity and chemical activity are closely related, and not independent, as suggested formerly (Part IV; J., 1927, 2831), and that it is not improbable that the chemically active species, which persists after the glow has been destroyed either by heat or by an electric discharge (Part IV; *loc. cit.*), represents a molecule which has acquired part of the energy of association of atoms recombining in a three-body process.

Shortly after Part V appeared, Kneser showed (*Ann. Physik*, 1929, **87**, 717) that the effects of pressure upon the decay of the after-glow are in agreement with the three-body theory; he also concluded, in agreement with Lord Rayleigh (*Proc. Roy. Soc.*, 1912, *A*, **86**, 262), that the walls may exert a considerable influence upon the reaction, but that the process is usually homogeneous, and that the Kaplan–Cario theory of the nature of active nitrogen is not in disagreement with these findings. Herzberg also has (*Z. Physik*, 1928, **46**, 578) emphasised the probable part played by the walls in the after-glow phenomena. The present author has suggested that the discrepancy between the two investigations might be due to different experimental conditions, and that a surface reaction occurring simultaneously with that in the gas phase masked the true homogeneous decay which it was desired to measure.

An unsatisfactory feature of both investigations was the measurement of the glow intensities by direct visual methods, a personal factor thus being introduced. It appeared advisable, therefore, to study the matter more completely, with special reference to any possible wall reaction which might enter. Bonhoeffer and Kaminsky (*Z. physikal. Chem.*, 1927, **127**, 385) have concluded that the spectrum of the after-glow is independent of the nature of the impurity which, as is well known, must be present to cause nitrogen to develop its glow when sparked, and the view has gained ground that these " photogens " (as they may be termed) " poison " the walls and prevent recombination of atoms thereupon, the case being analogous to that of atomic hydrogen, whose life in " wet " vessels is much longer than in " dry " ones. If this theory be correct, a quantitative relation will exist between the decay mechanism and the purity of the nitrogen employed for any one vessel; it was decided to examine this point experimentally and to measure the glow by means of a photo-cell, the personal factor thus being eliminated.

EXPERIMENTAL.

Apparatus.—This was similar to that employed in the author's earlier investigation, save (i) that additional drying tubes were provided, together with an extra large trap, cooled by liquid air, through which the nitrogen passed after leaving the purification system, and (ii) that inlets were provided both (A) above and (B) below the discharge for admission of other gases as desired. The discharge, some 30 cm. long, burned between water-cooled aluminium electrodes; a condenser of 0·0125 microfarad was shunted across the spark gap, and the r.m.s. current was about 30 milliamps. The observation tube and manometer were built into a sheet-iron box ($5' \times 3' \times 3'$), with black cloth curtains on the front, and all precautions were taken to keep the observation cabinet light-tight, and to prevent light from the spark entering the observation tube, which was 60 cm. long and 2·5 cm. wide.

Nitrogen.—Preliminary experiments showed that after phosphorus has been in use for a fortnight or so to remove oxygen from the nitrogen, it becomes very slow in action, and about 0·03% of the gas escapes absorption, unless contact is very prolonged. Copper at 600° gave a gas which was found, by addition of other gases through inlet A (the photogen feed tap) and observation of their effects upon the glow, to contain *ca.* 0·3% of argon (which did not appear to have any influence) and less than 0·01% of other gases, and to give little or no glow. It was therefore employed as the standard " pure " gas, and the use of phosphorus was discontinued.

Measurement of Glow Intensity.—The photographic method, with ordinary plates, was valueless, since the α-bands were not recorded by reason of their long wave-length, while the number of observations to be made rendered the adoption of panchromatic plates inadvisable.

Attempts were therefore made to measure the luminosity by photoelectric methods, the phosphorus method of purification being temporarily used to obtain a gas which gave a strong glow. The ordinary potassium photo-cell is practically insensitive to yellow light,* and when such a cell was employed, the photo-currents were found to be of the order of 10^{-11} amp., even with strong glows. Such currents can be measured (*a*) by observing by means of a quadrant electrometer the fall in potential across an alcohol–xylene resistance of *ca.* 10^{11} ohms; (*b*) by means of a Paschen or Downing galvanometer directly in circuit; or (*c*) by applying the potential obtained by method (*a*) to a valve amplifier specially constructed to deal with such cases—devices such as that of Wynn-Williams are admissible only with larger currents. When any one of these methods was tried, great difficulties were encountered owing to the discharge which produced the active nitrogen setting up a diversity of electromagnetic disturbances which necessitated the most rigorous shielding; the movement of a photo-cell along a tube through which active nitrogen was being streamed required flexible leads, and the difficulties were thus at once increased.

The method adopted after numerous failures was rendered possible through the kindness of Mr. C. F. Trippe, and the British Thomson Houston Co., Ltd., who placed at the author's disposal two special cæsium cells having an emission some 50 times that of the best cell of any other type which was tried. These were placed in parallel and fitted in series with (*a*) a Tinsley moving-coil galvanometer of sensitivity 5×10^{-10} amp., and practically constant zero, and (*b*) a high-tension accumulator giving 130 volts; practically no " dark " current was obtained, and calibration experiments using an ordinary optical bench method showed that the deflexion of the galvanometer was directly proportional to the brightness of the light incident upon the cells. For the actual experiments,

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* Ordinary cæsium cells have a much greater emission for yellow light, but are very unsatisfactory for quantitative work.

these were fixed in a light wooden frame held in a retort stand provided with a pointer on the base, and fitted to slide between rails parallel to and underneath the horizontal observation tube; the rails carried a scale, and the zero point was chosen some 10 cm. along the tube and 5 cm. downstream from the side limb B (see above).

Procedure.—For measurements of the glow, the cells were first placed at the zero point and screened from the light by means of a black cloth. The galvanometer reading was taken, and the cloth withdrawn to cause the cells to become illuminated; the second reading was then made, the instrument being practically dead-beat and coming to rest in 30 secs. or so. This was then repeated with the cells at the 5, 10, 15, 20, 25, etc., points until the deflexion became less than 0·3 cm., after which further measurements were made at the 22·5, 17·5, 12·5, 7·5, and 2·5 cm. points, some 15—20 observations being made for each run according to the glow intensity. The data were then plotted as the reciprocal of the square root of glow intensity against distance along the observation tube; for a reaction which is bimolecular with respect to the glow-producing system, a linear relation should thus be obtained (see, *e.g.*, Willey, *loc. cit.*).

Results.

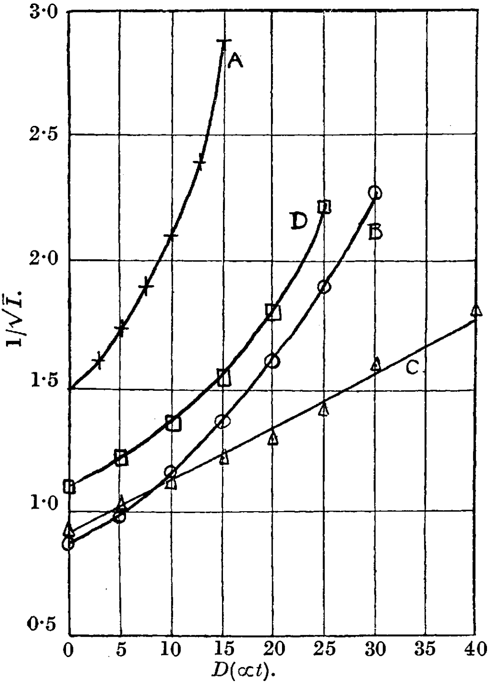
The Production of a Glow in Pure Nitrogen.—It was found that with the hot-copper method of purifying nitrogen and with the trap well cooled by liquid air, the faint glow visible in the nitrogen at first quickly diminished until the gas was quite non-luminous as it passed along the observation tube. Moreover, entirely negative results were obtained in attempts to detect chemical activity in the nitrogen by means of nitric oxide admitted at B, the peroxide being tested for according to the method previously described (Part IV). It appears then that nitrogen which is so pure as to give no glow is not chemically active.

Glow Phenomena.—The after-glow could easily be developed either by reducing the temperature of the copper or by the addition of small amounts of other gases through the photogen feed tap. The results of systematic investigation of the effect of added impurity are now given; I is the intensity of the glow, and t the time, which is proportional to D, the distance along the observation tube.

(a) *Form of the* $1/\sqrt{I}$–t *graph.* (α) With fairly pure nitrogen the line is strongly curved (Fig. 1, A), becoming less so with continued increase of photogen (Fig. 1, B) until it passes through a linear form (Fig. 1, C), and then again becomes curved (Fig. 1, D). This shows that the apparent " order " of the decay reaction is dependent upon the purity of the nitrogen employed. The points for Fig. 1, A give a fairly straight line when plotted as log I against D, indicating a decay reaction of approximately the first order.

(β) During a series of experiments which had as their object the determination of the relation between glow intensity and concentration of chemically active species, the following measurements were taken: (i) Decay curve (Fig. 2, A); (ii) three estimations of the chemically active species; (iii) 20 minutes after this, a further decay curve (Fig. 2, B); and finally (iv) three more analyses. During runs (i) and (iii), the nitric oxide stream was replaced by an equal one of pure nitrogen to keep the pressure constant, and the flow of gases and the spark were maintained throughout. It will be seen that the graphs are linear after the first few cm. but vary widely in slope; in spite of this the same amount of chemically active nitrogen was found in all six cases. Hence it follows that a stream of luminous nitrogen may decay at widely different rates although it contains the same amount of the chemically active form throughout.

FIG. 1.



A = *nitrogen with* 0·03% *photogen supply.*
B = ,, ,, 0·07% ,, ,,
C = ,, ,, 0·10% ,, ,,
D = ,, ,, 1·3% ,, ,,

(γ) In another experiment a decay curve (Fig. 3, A) was plotted for fairly pure nitrogen (*ca.* 0·03% of oxygen being used as photogen), and the photogen concentration then increased to *ca.* 0·07%, after which Fig. 3, B was obtained. The apparatus was allowed to function for 90 minutes, and a further decay curve (3, C) obtained; the observation tube was then flamed gently, the gases and spark being shut off and a vacuum of 0·0001 mm. maintained. After cooling, the gases were readmitted, the spark was run for 90 minutes, and curve 3, D was obtained.

(δ) The clearest explanation of the results described in sections (α), (β), and (γ) is that they are due to wall effects. With nitrogen of a high degree of purity the walls are so clean that recombination of the atoms, assured now, as before, to be the primary glow-producing elements, occurs with great ease; adopting the author's earlier view (Part V) as to the origin of the chemical activity, the failure to obtain this in the absence of photogens is also readily explained, and is discussed later in the light of the Kaplan–Cario theory. The findings given in (α) arise from the progressive poisoning of the walls by the photogen until probably a point of minimum wall activity is reached when the reaction becomes homogeneous and bimolecular (with respect to the glow-producing elements) as in Fig. 1, C, while in 1, D too much photogen is present and is influencing the gas phase reaction either by direct participation in the glow emission process or else possibly by reaction with the chemically active species.

Fig. 2.

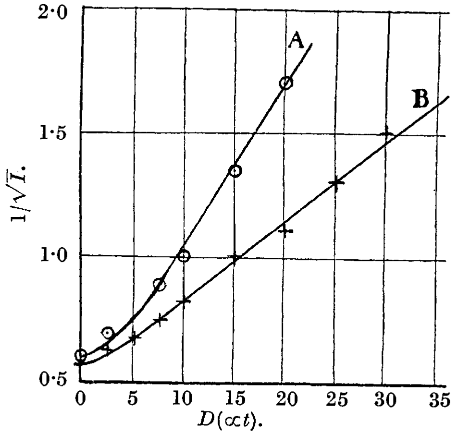
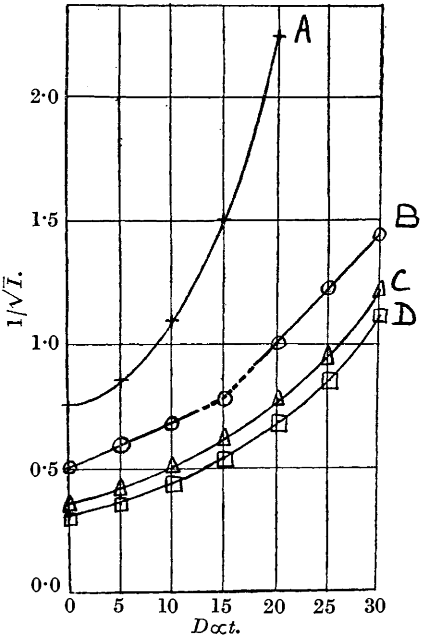


Fig. 3.

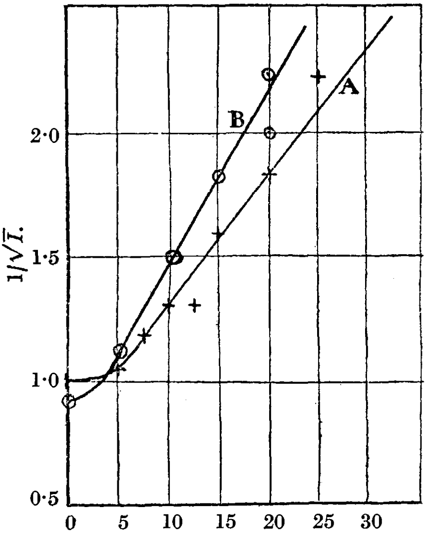


In Fig. 2, B we have shown the influence of an adsorbed nitric oxide film upon the decay rate of the glow: it is much reduced, as would be expected. Furthermore, while the linear nature of the graph shows that the reaction is binary with respect to the primary glow-producing system, the slope of the curve is not determined solely by total gas pressure, as it should be for a reaction

$2N + N_2 \longrightarrow 2N_2$, when the condition of the walls necessitates their being taken into account. A more important phenomenon is the constancy of the chemical activity, suggesting that if, as the Kaplan–Cario theory indicates, the active species is a participant in the glow emission reaction, it has as a complement a substance which is very susceptible to wall influence (see later).

The results given in Fig. 3 are in striking agreement with the wall-effect hypothesis. Fig. 3, A has as its fellow Fig. 1, A, while at the time when 3, B was obtained sufficient photogen had entered the observation tube to poison the walls only so far along the direction of flow as the point of inflexion, and the practical coincidence of 3, C and 3, D shows that they represent the final state of the walls for nitrogen of this particular degree of purity. No marked effect of the photogens upon the electrical conditions has yet been observed, and the findings in Fig. 3 cannot be attributed to progressive changes in the bulk composition of the gas, since the very small volume between the photogen inlet and the observation tube, taken in conjunction with the high flow-speed of the gas at the pressure employed (4·6 mm.), rules it out of consideration.

FIG. 4.



1900 C.c. of nitrogen per hour at N.T.P.
A = *Decay curve for* 4·6 *mm.*
B = ,, ,, ,, 6·8 ,,

(ε) The evidence presented in sections (α), (β), (γ), and (δ), that the condition of the walls determines very largely the mechanism of the decay of the nitrogen after-glow, may be tested in the following manner. The activity of the surface may be expected, *ex hypothesi*, to be proportional to the area exposed; the more the gas adsorbed upon it, the less will it influence the decay, provided that reaction does not occur between the adsorbed film and the glow-emitting system. The simplest way of decreasing the wall effect without introducing any such complication is clearly *to employ nitrogen as a photogen, i.e.*, by raising the over-all pressure to increase the adsorption of molecular nitrogen; if the departure from linearity in the

$1/\sqrt{I}$–t graph is due to wall effects, the curves should be straightened in progressive runs from low to high pressures. This effect may readily be observed and is shown in Fig. 4.

(b) *The triple-collision hypothesis.* Assuming the glow emission to result from a reaction $2N + N_2 \longrightarrow 2N_2$, it follows that for a constant concentration of N the initial intensity will be increased and the life of the glow diminished by addition of N_2. Kneser (*loc. cit.*) confirmed this deduction, but Bonhoeffer and Kaminsky (*loc. cit.*) dissented from it. The probability of the after-glow resulting from a three-body reaction has already been discussed (Part V, J., 1928, 1620; 1929, 228) and the balance of evidence considered to be in its favour; it will now be shown (i) that a further method of calculation produces a result in excellent agreement with experiment, and (ii) that measurements made in the light of the findings discussed earlier in this paper prove that the decay in the gas phase is a ternary reaction.

(i) It is required to calculate the mean life of the atoms, assuming that they can combine only through the medium of a triple collision involving two atoms and one molecule. Let λ_1 be the mean free path of the atoms among themselves, and λ_2 that of the molecules; further, let $\bar{u}$ be the r.m.s. velocity of the molecules, then $\bar{u}\sqrt{2}$ is that of the atoms. Now consider a particular atom a_1; it will collide $\bar{u}\sqrt{2}/\lambda_1$ times per sec. with a similar atom. If a molecule B converts one such atomic impact (between a_1 and a_2) into a triple collision at a point L, it must have travelled from a point distant between $(\lambda_2 - \frac{1}{2}\bar{u}\tau)$ and $(\lambda_2 + \frac{1}{2}\bar{u}\tau)$ from L, τ being the "duration" of the a_1–a_2 collision. Hence, at a time $t = \lambda_2/\bar{u}$ before the impact, the necessary B molecule must lie in a spherical shell of centre L, of mean radius λ_2, and of thickness $\bar{u}\tau$ (assumed small compared with λ_2). The probable number of B molecules in this shell is

$$\nu_B \, . \, 4\pi\lambda_2^2\bar{u}\tau . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ν_B is the concentration of B molecules per c.c. In order, however, that the a_1–a_2–B impact shall occur, B must be definitely alined with regard to the colliding atoms, and the collision can follow only if B starts on its journey towards them in a solid angle $\pi\sigma^2/\lambda_2^2$, where σ is the radius of the a_1–a_2 complex. The probability that it will travel in this direction is

$$(\pi\sigma^2/\lambda_2^2)(1/4\pi) = \sigma^2/4\lambda_2^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the probable number of B molecules present and moving in the right direction is given by the product of (1) and (2), *i.e.*,

$$[B] = \nu_B \, . \, \pi\bar{u}\tau\sigma^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The number of such collisions per sec. which the atom a_1 could make (if it were not demobilised by the collision *) is then given by the product of (3) and the number of atomic collisions, *i.e.*,

$$Z = \pi\nu_B\bar{u}\tau\sigma^2 \times \bar{u}\sqrt{2}/\lambda_1 = \pi\sqrt{2}\bar{u}^2\tau\sigma^2\nu_B/\lambda_1 \quad . \quad . \quad . \quad (4)$$

For nitrogen at 10 mm. pressure and containing 1% of the active form, we have $\lambda_1 = 8{\cdot}8 \times 10^{-1}$ cm., $\nu_B = 3{\cdot}6 \times 10^{17}$, $\bar{u} = 5{\cdot}0 \times 10^4$ cm./sec., and $\sigma = 1{\cdot}9 \times 10^{-8}$ cm.; hence, taking τ as 10^{-14} sec., we have $Z = 1{\cdot}64 \times 10^{-2}$, whence the mean free life of an atom, and thus the duration of the after-glow, will be $1/1{\cdot}64 \times 10^{-2} = 61$ secs. This is rather longer than that actually observed (7—10 secs.), but in view of the uncertainty as to the numerical values of both τ and σ (since the a_1–a_2 complex will probably be an excited molecule, and hence of abnormal diameter), the agreement between calculation and experiment is very good.

A ternary reaction being assumed to give rise to the glow, the intensity, I, will at any instant be proportional to the rate at which the atoms are combining, *i.e.*, to the number of triple collisions per c.c. per sec.; hence

$$k_1I = -\partial\nu_a/\partial t = k_2\nu_a{}^2\nu_B$$

Integration gives $1/\nu_a = (t + C)k_2\nu_B$, C being a constant, but since $I = k_2\nu_a{}^2\nu_B/k_1$, we have

$$1/\sqrt{I} = \sqrt{k_1k_2}(t + C)\sqrt{\nu_B}$$

and hence the slope of the line giving the relation between $1/\sqrt{I}$ and t should vary as $\sqrt{\nu_B}$, *i.e.*, as the square root of the total gas pressure, P.

(ii) Previous attempts (Part V, *loc. cit.*) to examine this point experimentally led to scattered results which showed that the slope varied as P and not as $\sqrt{P}$, but the dependence of the decay rate upon the purity of the gas, and hence upon wall conditions, according to the results described earlier in the present communication, gave the clue to the source of the disagreement between theory and observation, and clearly indicated that the desired correlation should be carried out either (*a*) by using a gas rich in photogens or (*b*) in a purer gas but at higher over-all pressures.

Glowing nitrogen containing 0·03% of oxygen was streamed through the observation tube and its decay rate was measured as usual. In order to avoid the introduction of any corrections for changed flow-speed a constant flow of 1600 c.c./hr. at atmospheric pressure was maintained, and the pressure in the apparatus was

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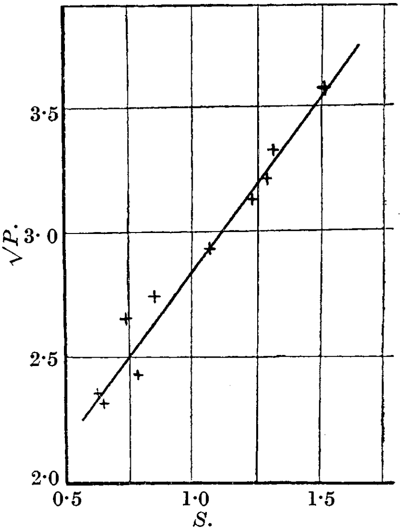
* This does not vitiate the argument, since we are concerned with a statistical discussion of the probable life of the atom.

varied by a choking tap in the exhaust line. Fig. 5 shows that the slope (S) is a linear function of $\sqrt{P}$ between 5·4 and 12·8 mm., and that the decay of the glow may therefore be expressed as a third-order process, in agreement with theory.

(c) *The action of oxygen upon the after-glow.* It has been found that when about 5% or more of oxygen is fed to the glow stream and the yellow luminosity is destroyed, the photo-cells behave as if strongly illuminated, although the gases have apparently become dark at the point of observation just below the oxygen inlet. This can only mean that the glow emission is proceeding in the non-visible portions of the spectrum, and as the cells have been found to be practically insensitive beyond the orange region but slightly more so in the green and blue, it follows that a very large radiation in the blue region and beyond must be proceeding in these circumstances. The author is indebted to Mr. G. C. Eltenton for the information that he too has observed this phenomenon (see also Rayleigh, J., 1918, **113**, 200).

Fig. 5.



(d) *Constancy of decay order with time.* Since, except under conditions which can be attributed to wall influence (*e.g.*, Fig. 3), no change in form of the decay curves is found with time, it follows that the mechanism of the process does not alter, at any rate at these pressures, and that between about 5900 and 4000 Å.U. (the sensitivity limits of the photo-cells) the emission takes place regularly among the various bands concerned. This is probably not in disagreement with König and Klinkmann (*Z. physikal. Chem.*, 1928, **137**, 335), since the range of curve-lengths over which they worked is much greater than here: the present measurements apply practically only to the α-bands.

(e) *Photogens and chemical activity in nitrogen.* It has been found that the addition of photo-gas to " pure " nitrogen causes a large increase in the concentration of the chemically active species, this being determined by the reaction with nitric oxide as described in Part IV. Attempts to establish the relationship between glow intensity and concentration of active nitrogen have not yet led to results which can be treated quantitatively, but it appears, in agreement with Bonhoeffer and Kaminsky (*Z. Elektrochem.*, 1926, **32**, 536) and König and Klinkmann (*loc. cit.*), that there is no simple expression which connects them; the former generally tends to rise more rapidly, as is shown in a typical experiment in which the brightness of the glow changed from 0·3 to 3·45, as measured at the point where the analysis was made by the galvanometer deflexion, whilst the concentration increased from 0·44 to 1·40%. The intensity of the green flame produced during the reaction between glowing active nitrogen and nitric oxide appears to bear much the same relation towards the concentration of active species as does the nitrogen glow alone under the same conditions, the supply of nitric oxide being replaced by an equal one of nitrogen to hold the pressure constant. The experiments do, however, show that the same amount of chemically active nitrogen may be present in glows which decay at widely different rates, a point to be discussed later.

(f) *The nature of photogens.* In agreement with Rayleigh (*Proc. Roy. Soc.*, 1915, *A*, **91**, 303) and with Bonhoeffer and Kaminsky (*Z. Elektrochem.*, 1926, **32**, 536), it has been found that the optimum supplies of these gaseous impurities correspond to about 0·1% concentration in the nitrogen, and that water vapour is to be placed very high in the order of effectiveness (compare Herzberg, *loc. cit.*; Lewis, *J. Amer. Chem. Soc.*, 1929, **51**, 654, 665). It has not been found possible to trace any effects of the photogens which can be ascribed to their specific natures, and hence it appears that their action is general in character.

Discussion.

These experiments appear definitely to clarify the state of our knowledge of active nitrogen. The existence of wall effect now demonstrated is in complete harmony with the results of Lewis and of Herzberg (published during the course of the present research). Among the phenomena to be anticipated from these researches are the reversal of the pressure and temperature effects normally found for the after-glow, and actually observed by Lewis, and also the divergences in the order of the decay process as observed by Kneser and the present author, the cause of this clearly being slight differences in composition of the nitrogen employed and in the surface of the vessels.

More important, however, is the strong evidence for the triple-collision hypothesis and consequent deductions as to the origin of the chemical activity and the close connexion apparently existing between this and the luminosity. It has already been shown, both in this and in earlier papers, that the ternary-reaction theory leads to the assumption that the glow-producing and chemically active species are present in comparable concentrations, and Kaplan and Cario (*Nature,* 1929, **121**, 906) and Compton and Boyce (*Physical Rev.*, 1929, **33**, 145) have recently shown that active nitrogen contains two species of metastable atoms (2·3 and 3·6 volts) and a metastable molecule (8·2 volts), evidence thus being forthcoming for a substance whose energy agrees well with the value 2·0—2·2 volts (equivalent to 46,000—50,000 cals./g.-mol.) advanced in earlier papers of this series (Parts I, II, and III; J., 1926, 1804; 1927, 669, 2188) for the energy of active nitrogen as it appears in its chemical reactions. Upon these spectroscopic findings, Kaplan and Cario base a theory of the origin of the after-glow. Its emission may result from one or more of three reactions, *viz.*: (i) recombination of one neutral and one 2·3-volt atom; (ii) recombination of two neutral atoms, followed by excitation of the metastable molecule thus produced by collision with a 2·3-volt atom; (iii) collisional excitation of an 8·2 volt metastable molecule by a 3·6-volt atom: since the latest work (*e.g.*, Gaviola, *Nature*, 1928, **122**, 313) shows that the heat of dissociation of $N_2 \longrightarrow 2N$ is *ca.* 9·5 volts, the 11—11·5 volts necessary for emission of the α-bands by the molecule are provided.

Frl. Sponer (*Z. Physik*, 1925, **34**, 622) has concluded that the emission of the α-bands (the visible after-glow) follows the recombination of atoms in triple collision with a molecule, the energy of association being transferred to the third body, which is thus excited and re-emits the energy as radiation; as, at the time of her publication, the heat of dissociation of $N_2 \longrightarrow 2N$ was regarded as 11·4 volts, no collisional excitation was deemed necessary. It seems not unreasonable that the glow emission may be represented by a combination of the Kaplan–Cario and Sponer theories, and that the process is

$$N + N' + N_2 \longrightarrow 2N_2 + \text{After-glow},$$

where N′ is the 2·3-volt metastable atom, assumed to be the chemically active form.* The right-hand side of this reaction must be regarded as a mere outline, but the left carries with it certain implications which may be considered.

1. It accounts for the third-order decay of the after-glow, and hence for the negative temperature coefficient of this reaction.
2. It is in conformity with the calculations made by the present author as to the comparable concentration of glow-producing and of chemically active species.

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* The findings discussed in sections (α) and (β) (p. 340) suggest also that the walls may under appropriate conditions act as the third body in the reaction.

3. If the analogy with active hydrogen is valid, the existence of strong wall effects may be attributed to adsorption and heterogeneous recombination of nitrogen atoms. Moreover, if we are prepared to admit preferential adsorption of N rather than of N′ unless the surfaces are exceedingly "clean," it follows that the glow intensity and decay rates of an active nitrogen stream may be almost infinitely variable without corresponding changes in chemical activity, in agreement with the findings discussed in Part IV of this series and in sections (α) and (β) (p. 340). Since a metastable atom or molecule can undergo many collisions without suffering deactivation—of which a good proportion must be upon the walls—whereas the case of atomic hydrogen shows that for normal atoms the surface influence is very great indeed, this assumption does not appear unjustifiable.

4. It links up glow effects and chemical activity and provides for an entity of the energy content which earlier work has postulated, *viz.*, the metastable atom of about 2·3 volts energy (53,000 cals./g.-mol.) (see p. 347).

There are, however, other possibilities to be considered. The principal objection to this view is that it accounts for only about one-sixth of the total energy available, and does not provide any clue as to why the other excited and metastable species present are apparently chemically inert. On the other hand, it is significant that in the majority of gaseous reactions the energy exchanges involved are much less than the 200,000 cals./g.-mol. with which we are here concerned, and it is possible that too abundant a supply of energy may be unfavourable to chemical changes in general.

Moreover, the Kaplan–Cario theory does not provide for a three-body recombination process, as found definitely in these experiments and less definitely by Kneser. The existence of the strong wall effects noted in this work suggests that it is just possible, although improbable, that the adsorption of the nitrogen varies as the pressure, leaving less free surface for the wall action and, by thus favouring the homogeneous decay, leading to an erroneous inference as to the effect of pressure upon the glow transformation process.

Summary.

1. The decay of the nitrogen after-glow has been restudied with an improved technique, and found to be most probably partly homogeneous and partly heterogeneous, according to experimental conditions.

2. Unless the walls of the vessels concerned are "poisoned" by foreign gases, the recombination process is non-luminous and occurs as a surface reaction; as the concentration of the impurity rises,

the wall reaction diminishes and the homogeneous decay increases, but above a limit of *ca.* 0·1% the impurity reacts chemically with the active nitrogen and interferes with the normal decay.

3. The order of the decay process is determined by the state of the walls, which in turn depends upon the purity of the nitrogen employed; when the surface reaction is minimised, the effects of pressure and addition of other gases are in agreement with the three-body recombination theory.

4. The after-glow probably originates in a reaction

$$N + N' \longrightarrow N_2'; \; N_2' + N_2 \longrightarrow 2N_2(+ \text{afterglow}),$$

N′ being a 2·3-volt metastable atom which is the chemically active species whose energy has been measured earlier.

5. No changes are to be seen in the order of the decay as it proceeds; neither do the spectral characteristics of the glow between *ca.* 5900 and 4000 Å.U. appear to alter.

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