CXLVI.—*On Active Nitrogen. Part VIII.* (i) *The Influence of Photogens and of Surfaces upon Glow Phenomena in Nitrogen.* (ii) *The Effects of Addition of Other Gases to Luminous Nitrogen.*

By Eric John Baxter Willey.

Section (i).

It was shown in Part VII (this vol., p. 336) that the decay of the nitrogen after-glow is markedly controlled in its kinetic aspects by the purity of the gas employed, for a number of observations were satisfactorily explained upon the hypothesis that the action of the impurities (which, it now appears, must certainly be present to the extent of about 0·1% in order that the yellow luminescence may be exhibited) is to cover the walls of the reaction vessels, thus converting what would otherwise be a " dark " heterogeneous recombination of atoms into a homogeneous process accompanied by the emission of the after-glow. When adequate quantities of these photogens are present or pressure conditions are such that the walls may be supposed covered by nitrogen, the volume decay process is influenced by the over-all gas pressure in a manner which permits of the reaction being expressed as a third-order change, probably $N' + N + N_2 \longrightarrow 2N_2 +$ after-glow, where N' is a metastable atom with an energy of 2·3 volts, in agreement with calculations given in the same paper.

It follows from this theory that it should be possible to enhance the luminosity of a stream of nitrogen by adding the photogen above or below the discharge, always provided, in the first case, that it be not destroyed by the spark. An attempt made by Lewis (*J. Amer. Chem. Soc.*, 1929, **51**, 654), however, in which nitrogen at a fraction of 1 mm. pressure was subjected to the electrodeless discharge and then rapidly treated with a small amount of oxygen, did not show the effect anticipated. This may have been due either to the hypothetical wall reaction being so rapid that all the atoms had recombined before the oxygen reached the surfaces, or else to too much oxygen having been added, the small glow being catalytically destroyed at once; a further possibility is that suggested by Lewis, *viz.*, that ordinary oxygen plays no part in the production of the after-glow. Experiments are now described which prove directly that the photogens act, at any rate in the case studied, after the nitrogen has been through the discharge, and that their effects can be reproduced by changing the walls of the vessel, probably the most weighty evidence yet presented in favour of the hypothesis that photogens are essentially wall-poisons.

EXPERIMENTAL.

The observation tube employed in these experiments was 80 × 3 cm., and arrangements were made for the admission to it of (*a*) nitrogen (purified by hot copper, etc., as described in Part VII, *loc. cit.*), and (*b*) hydrogen similarly treated; both of these gases could be passed through powerful discharges (condensed or not, as desired), which were operated independently from different electrical circuits. The down-stream end of the tube was closed by means of a rubber bung, faced on the inside with a polished aluminium disc, which was cut to fit the glass tube accurately and held in position by a rod passing through the bung and rendered vacuum-tight by picein wax applied to the outside; the exhaust line was taken off some 20 cm. above this end, and the space between the side tube and the bung disc was filled with tightly packed tin-foil to prevent access of the active nitrogen to any rubber surfaces accidentally exposed. After leaving the discharge, the two gases flowed through some 20 cm. of 5 mm.-bore tubing bent in a **W**-shape and blackened to prevent light from the discharges reaching the observation tube, the inlet for the hydrogen being about 10 cm. below that for the nitrogen; traps cooled by liquid air were placed in the exhaust line for the collection of products of any reaction between active nitrogen and active hydrogen, it having been stated that under these conditions ammonia is formed (Lewis, *J. Amer. Chem. Soc.*, 1928, **50**, 27). The glow was measured by means of the cæsium photocells employed in the earlier investigation (Part VII).

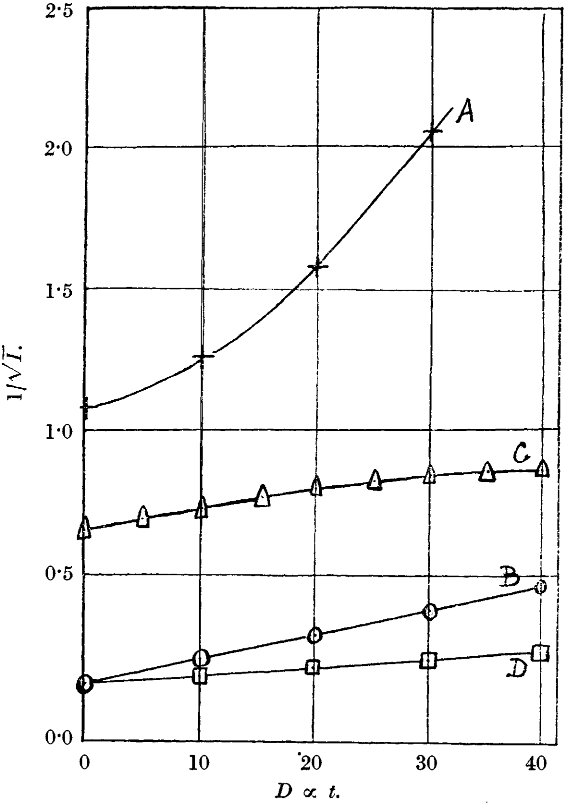
Addition of Photogens below the Discharge.—Nitrogen (prepared as described in Part VII, and containing 0·3% of argon and less than 0·01% of other gases) was allowed to stream through the apparatus for 3 hours at the rate of 2500 c.c./hour, the discharge being maintained as usual and the pressure kept at 4 mm. of mercury. The after-glow rapidly became faint in the observation tube, and when at the end of this period it had practically vanished, a small current of hydrogen (300 c.c./hour) was fed through the second inlet to the tube. No effect upon the glow was observed as long as the hydrogen was inert, but when the hydrogen discharge was switched on, the yellow nitrogen after-glow appeared with great brilliance, only to disappear in a few seconds when the second (hydrogen) discharge was interrupted.

A second experiment was then performed in which 0·06% of a 1 : 1 nitrogen–oxygen mixture was fed to the nitrogen above its discharge. The glow was thus developed sufficiently to permit of its being measured, and the corresponding decay curve was of the same form as Curve A, Fig. 1 of Part VII (*i.e.*, steep and strongly curved); the feed of hydrogen was as before, and the brightening of the glow again appeared when the second discharge was started, the decay curve then showing a closely linear relation between $1/\sqrt{I}$ and time (I = glow intensity, here proportional to photo-electric current) exactly as in the figure mentioned. Since, when the hydrogen was sparked alone, the feed of nitrogen being shut off, ammonia condensed in the traps cooled by liquid air in the exhaust line, the hydrogen was analysed; it was found to contain 0·04% of nitrogen, derived from the water in the Boyle-bubbler aspirator in which the hydrogen had been stored. When the air in the constant-pressure reservoir of this device was replaced by hydrogen, tests for nitrogen in the gas stored under the new conditions were negative, and at the same time the pure hydrogen lost its ability to enhance the nitrogen after-glow when sparked, as in the experiments just described. For later experiments, a trap filled with activated charcoal and cooled by liquid air was added to the hydrogen circuit, and this satisfactorily removed the traces of nitrogen. It appeared, then, that a small amount of nitrogen is an essential ingredient of the hydrogen if, upon sparking, this gas is to enhance the glow in fairly pure nitrogen, a supposition verified by experiment.

The explanation of the phenomenon is clear: the discharge in hydrogen containing a trace of nitrogen produces a small amount of ammonia, and this, when added to the nitrogen below the discharge, produces an effect which is simulated exactly by the admission of other photogens above the discharge. It was therefore anticipated that addition of hydrogen to nitrogen above the discharge would lead to a strong glow, and this was in fact observed, provided that a feed of some 1% was employed in order that the nitrogen–hydrogen–ammonia equilibrium should not yield a merely insignificant proportion of the last substance. It may be mentioned that, with the small feed of pure and sparked hydrogen to the glowless nitrogen, mentioned earlier, no ammonia could be detected save after very long runs. With photogenic nitrogen and larger feeds of hydrogen, the yellow after-glow was markedly reduced when the latter gas was sparked, and at the same time small amounts of ammonia condensed in the traps, in agreement with Lewis's observations (*loc. cit.*). It must, however, be emphasised that the hydrogen must be in large excess, otherwise no ammonia is obtained. This matter is now being investigated quantitatively, and it appears that there are probably several factors operating simultaneously which render the case rather complicated.

The Influence of Surfaces upon the Decay of the After-glow.—(*a*) According to the views expressed earlier, *viz.*, that photogens are wall-poisons and inhibit the non-luminous heterogeneous reassociation of atoms, thus favouring the volume process which gives rise to the after-glow, it follows that a glow should be induced in pure, non-photogenic nitrogen which, at the time of sparking or immediately afterwards, is placed in contact with the right kind of surface.

Fig. 1.



Curve A: "pure" nitrogen, glass surface.
Curve B: photogenic nitrogen, glass surface.
Curve C: "pure" nitrogen, paraffined surface.
Curve D: photogenic nitrogen, paraffined surface.

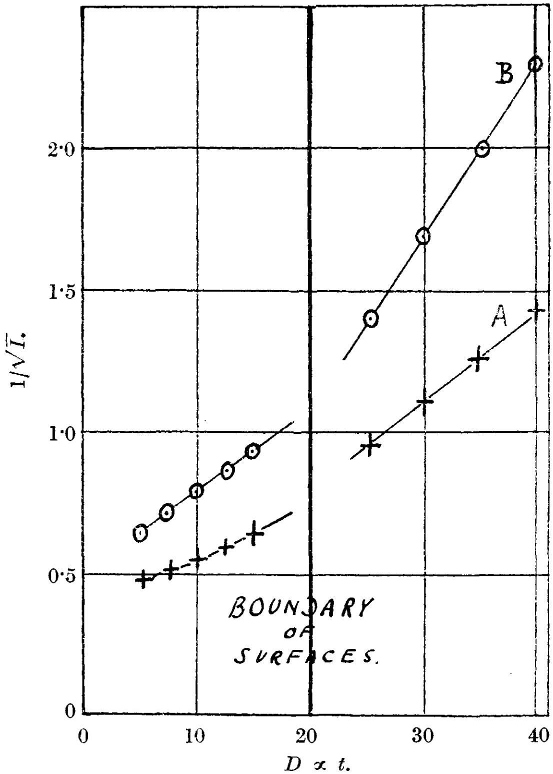
It would also be expected that the glow decay process in pure nitrogen should pass to that observed in the photogenic gas if the reaction could be studied in vessels with adequately poisoned walls.

A simple modification of the apparatus just described enabled this to be done. Tubes were cut from wide-bore glass tubing, of external diameter such that it just fitted into the main observation tube, and coated on the inside with various waxes and transparent varnishes, thus enabling the glow decay to be studied as the stream passed over the different treated surfaces. Many organic substances were tried, but in every case save one the glow became blue and hydrogen cyanide condensed in the traps, so that the chemical action rendered true decay studies out of the question. A high-melting wax of the type employed in electrical work was eventually found which reacted a little at first, but upon prolonged exposure to the active nitrogen stream gave hydrogen cyanide in amounts which could be detected only by the guaiacum–copper sulphate method (Anderson, *Z. anal. Chem.*, 1916, **55**, 459) and corresponded to a concentration of less than 0·0003% of the latter gas in the nitrogen. A series of decay runs was then made and the results are shown in Fig. 1.

Curves A and B exhibit the marked difference in form and slope of the $1/\sqrt{I}$–t graphs found in the experiments discussed in Part VII for " pure " and photogenic nitrogen, Curve A being of the form which we have ascribed to the superposition of a strong wall decay upon the volume reaction, and Curve B being that corresponding with the bimolecular and homogeneous process; for both of these runs a clean glass tube was fitted in the main observation tube. The results shown in Curves C and D relate to precisely similar experiments wherein the clean glass tube was replaced by one coated on the inside with a thin uniform layer of the wax mentioned above; the decay in the photogenic nitrogen (Curve D) is even less than in the case of Curve B, but Curve C shows that the expected development of a strong glow in pure nitrogen and the retardation of its decay by the influence of highly poisoned walls are actually realised. It is, moreover, noticeable that up to the 15 cm. point, the curve is almost parallel to Curve B (photogenic nitrogen and a clean glass surface), but that subsequently the slope falls off. That this was not due to inequalities in the wax coating, leading to variations in the amount of light transmitted, was proved by reversing the tube, whereupon the effect was seen just as before; further, the galvanometer deflexions were so large that any error in reading must also be ruled out as an explanation of this curious effect. The author suggests that it is due to the formation of a trace of hydrogen cyanide in the first few cm. of the waxed tube; this gas then acts as photogen and further poisons the paraffin surface, since the effect is not seen in Curve D where larger concentrations of photogen are present. Even if one ignores the possible influence of very small quantities of hydrogen cyanide, it is clear that the paraffined surface is able *per se* to reproduce the effects associated with photogens, thus affording strong confirmatory evidence as to the probable truth of the wall-poison theory.

It followed from the observations described above that it should be possible to vary the decay rate of a stream of glowing nitrogen by drawing it first over clean glass and then over an inactive surface of the type just employed. The waxed tube used earlier was therefore cut in two, one half was carefully cleaned, and further decay runs were made in which glow streams obtained from gases containing 0·03% and *ca.* 0·15% of oxygen as photogen were drawn first over the clean and then over the paraffined glass, the tubes being slipped into the main observation tube to occupy the same position as that taken by the single tube from which they were made. With 0·03% of photogen present, the graph of $1/\sqrt{I}$ against the distance along the tube (proportional to time) was markedly curved for the glass surface (Fig. 2, Curve A), but linear for the paraffin; increase of the quantity of photogen to 0·15% gave a plot which was linear and showed no discontinuity, as in the former case, at the

FIG. 2.



+ = *Glass first, then wax.* ⊙ = *Wax first, then glass.*

junction of the two surfaces. The tubes were then reversed so that the glow came into contact first with the paraffin and then with the glass, and a decay run here revealed that, although with 0·15% photogen the $1/\sqrt{I}$–t plot was linear over the entire length of both tubes as in the corresponding experiment just given, yet with the 0·03% photogen content the break again occurred at the junction of the two surfaces (Fig. 2, Curve B), and that the graph was linear for both the paraffin and the glass but steeper in the latter case. The linearity for the glass may here be due to a trace of hydrogen cyanide being produced when the active nitrogen is in contact with the wax, this gas acting to a certain extent as a photogen and repressing the wall reaction. This shows that with a high photogen concentration the decay rate is, so far as paraffin and glass are concerned, independent of the nature of the surfaces, but with purer nitrogen the decay is very susceptible to wall influence.

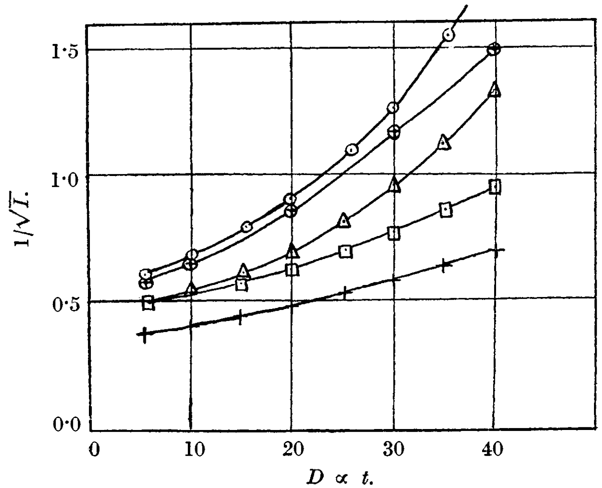
A final and conclusive piece of evidence upon this point was provided by the observation that the amounts of hydrogen cyanide formed in the experiments by interaction of the active nitrogen and the paraffin were much less when the photogenic gas was employed than with the purer material; this clearly suggests that the photogens cover the paraffin with a film protective against the active nitrogen.

Section (ii).

The theory that the after-glow results from a ternary reaction, $2N + N_2 \longrightarrow 2N_2$ + after-glow, was advanced about the same time by Frl. Sponer (*Z. Physik*, 1925, **34**, 622) and by Willey and Rideal (Part I, J., 1926, 1804). The first author based her opinion upon spectroscopic observations, considered in conjunction with the old idea of Clausius, revived by Herzfeld (*Z. Physik*, 1922, **8**, 132), Born and Franck (*Ann. Physik*, 1925, **76**, 225), and others, as to the necessity for the presence of an acceptor for the energy of association of atoms in order that a stable molecule might be formed. On the other hand, Willey and Rideal were influenced by the long life of the glow-emission reaction, comparable in speed with the slow ternary process $2NO + O_2 \longrightarrow 2NO_2$, and by the negative temperature coefficient of the glow decay, another feature of the termolecular change just quoted. In both cases the rôle of the third entity was considered specific, and the possibility was not envisaged of the molecule of nitrogen being replaced by one of another element without affecting the glow, although it was admitted that in some examples (but not the majority) of the excitation of metallic spectra by active nitrogen, a metal atom might act as the entity concerned (Part IV, J., 1927, 2831).

According to this theory, therefore, the initial intensity of the after-glow should be increased at the expense of its duration if nitrogen is added; the luminosity per unit volume of nitrogen should be unaffected, however, if the diluent gas is of another kind and is such as not to react chemically with the active nitrogen or, by reason of its excitation potentials, is not likely to be able to accept energy from the molecule emitting the after-glow radiation, and thus interfere with the normal glow decay process (compare Part II, J., 1927, 669). As mentioned in Part VII (*loc. cit.*, p. 343), there is divergence of experimental evidence upon this point, Kneser having obtained a positive result which Bonhoeffer and Kaminsky had been unable to observe earlier. Kneser has extended the original hypothesis in view of his finding that the addition of argon produces the same effect as nitrogen, and according to his work the third substance need not necessarily be nitrogen; the present author has also described experiments (Part VII) which show that the walls of the apparatus may under appropriate conditions act in the same way. An experimental study of the addition of other gases to the glow has therefore been made, and the conclusion is reached that the ternary reaction with nitrogen as the specific third entity is most probably responsible for the glow emission.

FIG. 3.



+ = N_2O,CO_2. ⊡ = N_2. △ = CO.

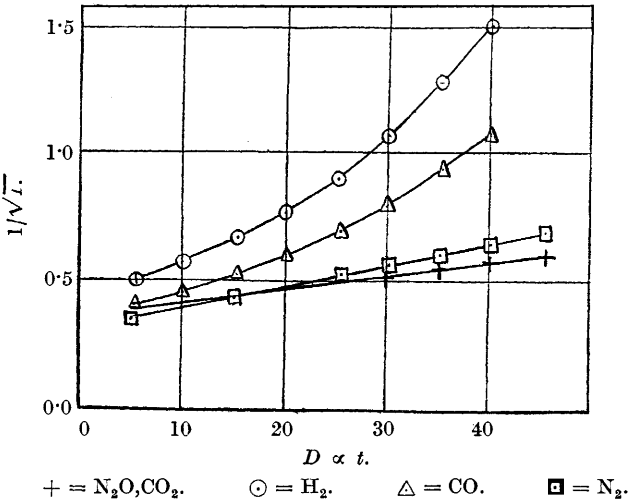
⊕ = N_2 *alone, no feed of other gases.* ⊙ = H_2.

EXPERIMENTAL.

The gases were admitted from a calibrated gas burette and capillary backed by a fine adjustment tap, and entered the glow stream at the inlet B (see Part VII, p. 337), *i.e.*, below the discharge, and the quantity added was, in all cases, 15% of the flow of nitrogen, *i.e.*, 300 c.c. of diluent to 1950 c.c. of nitrogen per hour; the glow decay was, as usual, measured with the cæsium photocells. The results are illustrated in Figs. 3 and 4.

In Fig. 3 are shown the curves obtained with equal feeds of carefully purified hydrogen, carbon monoxide, nitrous oxide, carbon dioxide, and nitrogen, and in Fig. 4 are given corresponding results obtained by using the nitrogen containing *ca.* 0·07% of oxygen as photogen. It will be seen that with feeds of nitrous oxide and carbon dioxide, the decay curves are practically coincident and linear for both photogenic and "pure" nitrogen, but with carbon monoxide and hydrogen the curves are much flatter when 0·07% oxygen is present in the nitrogen than when only 0·03% is there. Moreover, with the first two gases the glow is brightened during the whole of its passage down the observation tube. The results agree in a striking manner with both the three-body collision theory and the view advanced as to photogens being wall-poisons.

FIG. 4.



Let us first consider the results with the "pure" nitrogen, temporarily ignoring the results obtained with the inert nitrogen as diluent. It has already been shown that the introduction of a photogen *below* the discharge enhances the glow, and as photogens are almost certainly gases which are strongly adsorbed by glass, we should expect, making the usual assumption that at these pressures the adsorption of a gas varies inversely as its boiling point, that easily condensable gases (*e.g.*, nitrous oxide, carbon dioxide) would reduce wall activity and thus intensify the glow more than those difficult to liquefy (*e.g.*, carbon monoxide, nitrogen); this is actually observed (Fig. 3), the decay curves with feeds of the two last-named gases being of the type associated with " pure " nitrogen (compare Curves A and B, Fig. 1, Part VII), while with the other pair the plot is typically that of a glow stream produced in highly photogenic nitrogen, and, most of all, the retardation of the rate of decay is in exactly the inverse order of the boiling points of the gases concerned (hydrogen, b. p. $-253°$; nitrogen, $-196°$; carbon monoxide, $-191°$; nitrous oxide, $-90°$; carbon dioxide, $-78°$).

With photogenic nitrogen (0·07% oxygen) the walls are fairly well covered, and hence the decay with feeds of carbon monoxide and nitrogen approximates to that observed in the less pure nitrogen alone, while with feeds of carbon dioxide and nitrous oxide the adsorption is complete. It would thus be expected that with a glow stream of high photogen concentration the decay curves obtained with feeds of all these four gases should be linear and coincident, and this has actually been found for nitrogen containing 0·12% of oxygen.

The case where the gas added is nitrogen is more complicated, for two factors have to be considered, *viz.*, (i) the adsorption or photogen effect, and (ii) the direct participation by the added nitrogen in the homogeneous glow-emission process, in accordance with the specific three-body collision theory. These two factors are considered separately. (i) It has already been shown (Part VII) that the wall effect is probably much reduced at higher over-all pressures of nitrogen, and we should therefore expect that the addition of nitrogen would reduce the rate of decay of the glow in the moderately pure gas, and, by diminishing the surface reactions, automatically lead to a straightening of the $1/\sqrt{I}$–t graph, which should (in this consideration alone) lie between the curves for hydrogen and carbon monoxide; in photogenic nitrogen, however, nitrogen should have no more effect than any of the other gases when added to the glow stream. (ii) It being assumed that the glow emission results either from a triple impact $N + N' + N_2 \longrightarrow 2N_2 +$ after-glow, or a reaction $N + N' \longrightarrow N_2'$, followed rapidly by $N_2' + N_2 \longrightarrow 2N_2 +$ after-glow, N′ being a metastable 2·3-volt atom and N_2' an excited or metastable molecule (11 volts), it follows that the initial intensity of the glow should be increased and its duration diminished by addition of nitrogen. We might thus expect that with the combined operation of both these factors, the decay should correspond with that observed in nitrogen at a fairly high over-all pressure, *i.e.*, would give a linear $1/\sqrt{I}$–t plot of fairly steep slope, whereas Fig. 3 shows that the graph is slightly curved and nearly parallel to that for the experiments wherein the gases added were nitrous oxide and carbon dioxide; apparently, then, in this case the greater part of the influence of the added nitrogen goes to suppress the wall reaction.

In Fig. 4 a different state of affairs is revealed, the surfaces being to a large extent "poisoned"; the action of the added nitrogen is then apparent in the gas phase, for the $1/\sqrt{I}$–t plot, although linear, is rather steeper than that for the runs where the diluent gases were carbon dioxide and nitrous oxide, *i.e.*, the initial glow intensity and its rate of decay are increased and the duration of the luminosity is diminished by the addition of nitrogen, as demanded by the ternary reaction theory.

A second set of experiments, in which the feeds of gas added were increased to 30%, gave the same types of decay curve, with the exception that, as would be expected, the positive result of the triple-collision theory test by addition of nitrogen, as in the experiments illustrated in Fig. 4, was more marked than when only 15% of diluent was employed.

Discussion.

The experiments upon the influence of a waxed surface upon glow phenomena described in the first part of this paper afford fairly conclusive proof of the theory that photogens are wall-poisons as suggested in Part VII, and further comment is unnecessary.

The observations upon the addition of other gases to the after-glow may be considered in conjunction with the work of Constantinides (*Physical Rev.*, 1927, **30**, 95) and of Bonhoeffer and Kaminsky (*loc. cit.*). The former, in the course of some investigations upon ionisation in active nitrogen, studied the diminution in the life of the after-glow brought about by addition of helium, nitrogen, hydrogen, and oxygen, and found their destructiveness to increase in the order given; helium was remarkable in that it had practically no action. As no mention is made in his paper of any precautions to keep absolutely constant the composition of the nitrogen in which the glow was produced, it is doubtful whether his results can be compared with those of the author given in Part VII and in the present communication, but it is noticeable that the rate of decay increased from nitrogen to hydrogen, as in the experiments here described when the gas was not rich in photogens. Oxygen appears to participate in the glow-emission reaction because of the many levels it possesses at which it can absorb energy, and hence it should not be considered in purely kinetic studies; in the case of helium, however, it appears either that, as Constantinides points out, its lowest excitation level (20 volts) is so high that it cannot acquire energy from the active nitrogen and hence has no effect whatever upon the glow, or that, in this particular experiment, highly photogenic nitrogen was being used and no influence upon the rate of decay was noticed, since the helium could influence neither the state of the walls nor the volume reaction, in accordance with the specific three-body collision theory.

Bonhoeffer and Kaminsky added inert nitrogen to a stream of the glowing gas, and, observing no enhancement of the glow and a diminution of its life, concluded that the decay of the after-glow is not a third-order reaction. This may have been due partly to the design of the apparatus they employed, which would lead to very gradual mixing of the added gas with the glow stream (see footnote, p. 243 of Kneser's article, " Der aktive Stickstoffe," *Ergebnisse der exakten Naturwissenschaften*, 1929, **8**, 229; an admirable summary of work to date) or to their experimental conditions having been comparable with those of the author in the studies described under Fig. 3, *i.e.*, clean glass surfaces and fairly non-photogenic nitrogen; addition of inert nitrogen here produces only a small increase in initial glow intensity, and the duration of the after-glow is somewhat prolonged rather than shortened, both of which might easily escape detection by ordinary visual methods.

Summary.

It is shown (i) that the introduction of a photogen *after* nitrogen has been sparked induces the after-glow in pure nitrogen, (ii) that a strong glow appears if the same gas be placed in contact with a paraffined surface, and (iii) that the amount of chemical reaction between the wax and the active nitrogen is much less in photogenic than in non-photogenic nitrogen. These observations are considered to furnish proof of the correctness of the theory that photogens are wall-poisons and convert the non-luminous heterogeneous re-association of atoms into a homogeneous reaction accompanied by emission of light. Studies are also described upon the addition of other gases to the after-glow, and the results are shown to be in accordance with the three-body collision theory of the emission of the after-glow, provided that the condition of the walls is such that they do not interfere.

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THE SIR WILLIAM RAMSAY LABORATORIES OF
INORGANIC AND PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, March* 13*th*, 1930.]