XXXII.—*On Active Nitrogen. Part V* (Amended). *The Decay of the Nitrogen After-glow.*

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THE author regrets that an unfortunate error in the calculations upon his measurements of the decay of the nitrogen after-glow (J., 1928, 1620) has led to incorrect conclusions as to the process in question. It was previously stated that the reaction is of the fifth order, whereas it is now shown to be probably of the third, in agreement with the calculations made upon the life of the glow, a ternary decay process $2N + N_2 \longrightarrow 2N_2$ being assumed.

The experimental work is in no way affected.

Plotting the reciprocal of the square root of glow intensity against distance along the tube D (*loc. cit.*, p. 1621), *i.e.*, against time, so far as any one experiment is concerned, we obtain a linear relation as shown in Fig. 1 of the present paper. (The corresponding figure and legends in the earlier paper, Fig. 2, were incorrectly given, since the abscissæ represent $1/\sqrt{I}$ plotted with increasing values, and the ordinates represent D plotted with decreasing values, so the figure should be rotated through an angle of 90° in an anticlockwise direction; moreover, the descriptions of the first and last of the three curves should be interchanged.) The results must then be brought to a common basis for comparison, since the scale of time taken as proportional to distance along D will clearly alter for each change of pressure and gas flow rate as measured on the Venturi meter.

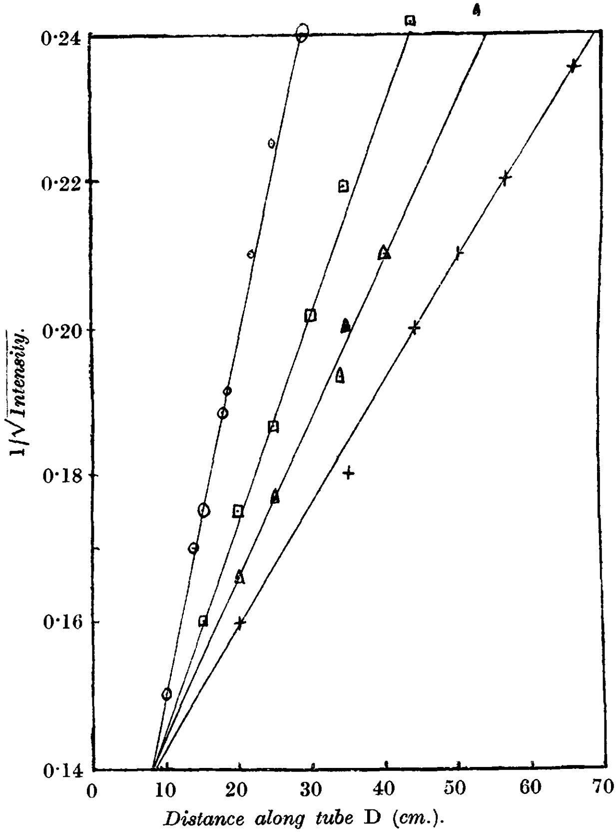
This must be done as follows: The " observed slope " gives $\frac{\Delta(1/\sqrt{I})}{\Delta\text{ (distance along tube)}}$, whilst the " corrected slope " is desired to give $\Delta(1/\sqrt{I})/\Delta t$, whence $\frac{\text{(corrected slope)}}{\text{(observed slope)}} = \frac{\Delta\text{ (distance along tube)}}{\Delta t}$ which varies as $\frac{\text{(flow rate at } N.T.P.)}{\text{(gas pressure)}}$.

Hence the " corrected slope " $= \frac{\text{" observed slope "} \times \text{flow rate}}{\text{gas pressure}}$.

In the previous paper the error was made of multiplying the observed slopes by $\frac{\text{gas pressure}}{\text{flow rate}}$ instead of applying this correction to distances measured along the observation tube D; in this way the *inverse* of the true factor was employed.

The author has accordingly replotted his experimental data, using the correct factor for reducing them to a common basis, and the plot of corrected slopes against gas pressure is given in Fig. 2. It appears now that the slopes of the $1/\sqrt{I},t$ plot vary as the total gas pressure p.

Fig. 1.



Flow rate of 2200 *c.c./hr. at* N.T.P. *in all cases.*

+ = 4·0 *mm. pressure.*
△ = 5·3 „ „
⊡ = 6·2 *mm. pressure.*
⊙ = 7·0 „ „

All curves pass through the same point on the axis of distance for $1/\sqrt{I}=0{\cdot}14$.

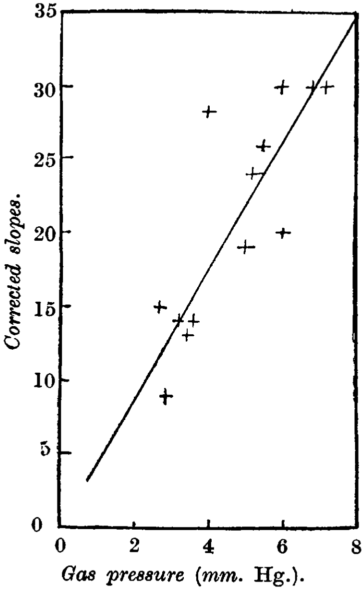
The interpretation of this is not clear. Assuming that the emission of the glow occurs through a ternary collision $2N+N_2 \rightarrow 2N_2$, we may show that the slope of the $1\sqrt{I},t$ plot should vary as $\sqrt{p}$ as follows: Let the concentration of atoms per c.c. at any instant be ν and that of the molecules N: A, B, and C are constants.

Then $-\frac{d\nu}{dt} = A\nu^2 N$, whence $\nu = \frac{1}{AN} \cdot \frac{1}{t+B}$, and I will thus be given by $I = C\nu^2 N$. Hence

$$\frac{1}{\sqrt{I}} = \frac{1}{\sqrt{CN}} \cdot \frac{1}{\nu} = \frac{A}{\sqrt{C}} \cdot \sqrt{N} \,.\, (t + B);$$

and therefore the slope of the $1/\sqrt{I}, t$ plot will vary as the square root of the gas pressure.

Fig. 2.



It follows then that, although these results show the calculations on p. 1625 of the earlier paper to be approximately supported, the measurements indicate that the reaction proceeds in a manner other than would be the case were it truly of the third order; for a ternary decay we should have $d\nu/dt = K_1[\mathrm{N}]^2[\mathrm{N}_2]$, whereas these experiments give

$$d\nu/dt = K_2[\mathrm{N}]^2[\mathrm{N}_2]^2,$$

since the value of K_1 varies as $[\mathrm{N}_2]$.

In view of the limited range of pressures over which these experiments extend, it does not appear safe to attempt a further explanation of the results, but they are rather suggestive of a reaction having taken place on the surface as well as in the gas phase; it has repeatedly been noticed by the author that the life of the after-glow is dependent to a large extent upon the nature of the containing vessel, being as a rule much longer in Pyrex glass than in the soda glass used in these experiments, although the cleaning process was the same in both cases. Moreover, Herzberg (*Z. Physik*, 1928, **46**, 878) has shown that surface phenomena probably play a great part in the reactions which lead to the production of the after-glow.

The author is indebted to Dr. H. O. Kneser (private communication) for the information that his recent measurements tend to show that the decay of the after-glow is truly of the third order under his experimental conditions, and it is possible that the discrepancy between our results is to be found here.

Further emendations in the earlier paper are that paragraph (*a*), p. 1626, must be deleted, and (*e*), p. 1627, amended to the statement that, unless the impact of the neutral molecule upon the excited body first formed from the atoms occurs within the life of the latter, the energy of recombination may be lost by radiation, leading to an anticipation that the decay mechanism will alter at low pressures together with the chemical and physical attributes of the active nitrogen, as discussed. Equations (2) and (3) on p. 1627 must also be omitted.

It may finally be stated that references to $\sqrt{I}$ in the earlier paper should clearly be to $1\sqrt{I}$, since from equation (2) on p. 1625 we have

$$d\nu/dt = K\nu^2, \ \textit{i.e.}, \ -1/\nu = Kt + c,$$

hence

$$\sqrt{I} = \sqrt{\frac{K\nu^2}{k}} = -\frac{1}{Kt + c}\sqrt{\frac{K}{k}}$$

(where c is an integration constant), and hence $\sqrt{I}$ cannot possibly show a linear relation with time. The plot of $1/\sqrt{I}$ against time has, in fact, always been employed.

The author is much indebted to Mr. B. Topley for pointing out these errors.

Summary.

It is shown that, owing to an arithmetical error in an earlier communication (J., 1928, 1620), the conclusion that the decay process of the nitrogen after-glow is of the fifth order is incorrect, and that it is rather probably of the third order, but complicated by a surface reaction taking place at the same time as that in the bulk of the gas. The conclusions as to the chemically active nitrogen probably being formed during the degradation of energy from a high-level molecule initially formed from atoms through the medium of a ternary collision $2N + N_2 \longrightarrow 2N_2$ remain unaltered, as do other considerations upon the behaviour of active nitrogen.

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