The surprising amount of energy which can be collected from gases after the electric discharge has passed

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It was found in earlier work (Rayleigh 1940 *b*) that a piece of gold sheet, say 1 cm. square, hung up in a stream of glowing active nitrogen became red hot, and collected an amount of energy which was very surprising. It was necessary to assume that every molecule of nitrogen in the stream imparted 10 eV to the gold plate.

In this form of experiment it was impossible to avoid large and undetermined losses of energy; thus the energy actually given up by each molecule was probably much larger still.

A new form of experiment is now described in which this loss is avoided. A platinum strip is kept hot by periodic discharges, and by making the experiment (1) with the platinum exposed to the gas and (2) with the platinum protected by a thin glass sheath it is possible to determine what part of the total energy is to be attributed to catalytic action of the discharge products. This amount of energy is found to be very great. Reckoning in electron-volts per molecule of gas present it increased rapidly as the gas pressure was lowered and at the lowest pressure used it rose as high as 223 eV/mol. Results of the same order were obtained with other gases, so it is not clear that the glow of active nitrogen is the essential condition. This great liberation of energy much exceeds what can be explained by dissociation of the molecules and single ionization of every atom which results, which would only afford 36 V.

In a former paper (Rayleigh 1940 *b*) I showed that metal plates, notably gold, silver, copper and platinum, hung up in a bulb containing glowing active nitrogen, but right away from the discharge which maintained the activity of the gas, would become red-hot, and that plates 1 cm. square of gold, silver and copper could even be made to melt, and run down.* This was made the basis of a minimum estimate of the energy contained in active gas. A stream of it was maintained by an air pump, so that the volume passed could be compared with the energy liberated on the metal. The work was of an exploratory nature, and the methods used were crude, but they indicated that the energy which was collected from the gas was so great that *every molecule in it* must be excited to the extent of at least 10 eV.

It was shown further that this energy was of the order of a thousand times the energy radiated under the most favourable conditions as visual nitrogen after-glow.

As regards the energy collected by the metal, the form of experiment then used has obvious weak points. The gas has to travel a considerable distance before it gets to the metal where its energy is given up, and in the course of doing so it is exposed to considerable areas of glass wall, with which its molecules may make repeated collisions. There is, moreover, a time lag while it travels considerable distances, and during this period decay of activity may occur. [If the reader is inclined to complain that the word activity is here used somewhat vaguely it may be defined simply as the capacity to impart energy to metals like gold and platinum initially cold.]

Another weak point was that the attempt to use the visual incandescence of the metal as an indicator of temperature was crude. It became obvious that a method of electrical resistance thermometry would be much better, and, indeed, this would

* *Note added in proof.* I have since melted a fine platinum wire in the same way.

have been used had it not been that the uncertainties of the time (1939–40) made it desirable to achieve what progress I could at once, without taking time to change the method.

In planning further experiments, it was desired to bring the metal catalyst as near as possible to the discharge where the gas was made active, so that it would have the minimum opportunity of losing its activity. At the same time it was necessary to make allowance for the direct-heating effect of the discharge on the catalytic metal, which cannot be altogether avoided without making the gas travel considerable distances—and this was inadmissible.

To produce the electrodeless discharges, the same oil condenser was used as in my previous work. It was charged by an induction coil with a slow mercury break. This break was generally of a design due to the late Sir James Mackenzie Davidson. An ebonite wheel with a conducting segment is mounted on an axle which is inclined at 45° to the horizontal. This wheel is immersed in mercury and makes and breaks contact once a revolution. The mercury is covered with a layer of alcohol.

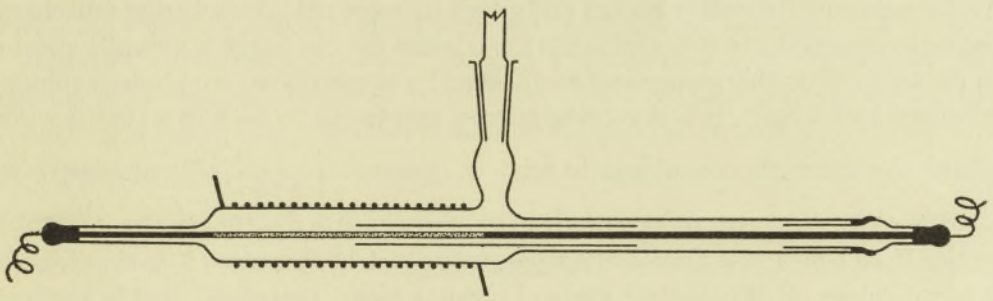

FIGURE 1. Reduction $\frac{2}{5}$.

The discharge vessel is as shown in figure 1. Along the axis there is stretched a platinum strip, over which a glass sheath can be slipped. The platinum can be heated by a current from a battery, and the tube is wound with a wire coil, which is used to excite the electrodeless discharge. When the discharge passes, the platinum strip gets heated, and its resistance increases. This is attributed partly to the direct-heating action of the discharge, and partly to the action of the platinum strip in catalyzing the discharge products (ions and dissociated atoms?).

During an experiment, the platinum strip is kept at an arbitrary but constant resistance of R ohms. For this purpose it is made one arm of a Wheatstone's bridge, and the current adjusted to heat the strip until the given resistance is attained. The current (C_1 amp.) is measured. Then the glass sheath is slipped into position, so as to screen the wire from dissociation products. A larger current (C_2 amp.) must now be passed to restore the resistance to its standard value of R ohms. The energy given up to the platinum wire by the dissociation products is

$$(C_2^2 - C_1^2)\, Rt \text{ W-sec.},$$

when t is the time interval in seconds from one discharge to the next.

This energy is derived from, and therefore is contained in, the gas volume v at pressure p cm. of mercury.

Thus the energy per unit volume reckoned as at atmospheric pressure is

$$\frac{(C_2^2 - C_1^2)\, Rt \times 76}{vp} \text{ W-sec./c.c.}$$

In a typical experiment, when the conditions were adjusted to get the best effect at the chosen pressure, $C_1 = 0{\cdot}78$ amp., $C_2 = 1{\cdot}73$ amp., $R = 0{\cdot}470$ ohm., $t = 0{\cdot}25$ sec., $v = 19$ c.c., $p = 2{\cdot}6 \times 10^{-3}$ cm. of mercury. In this case the energy is 432 W-sec./c.c. as at N.T.P., or 98·5 eV/mol. of nitrogen present.

All the molecules in the vessel play their part, and must travel from the point in the discharge vessel where they receive energy to a point in the central strip where they give it up. They will not in general take the shortest path, that is, the path along the radius of the vessel. It is not worth while to enter upon elaborate calculations of the most probable length of path. I shall take it as 1 cm., about the same as the radius of the vessel.

If the molecule is to receive energy and give it up more than once during a discharge, it would in general have to travel some 2 cm. while the discharge is actually passing. The duration of discharge (several oscillations) was estimated by photographing a slit backed by its light, in a revolving mirror, and found to be $3{\cdot}76 \times 10^{-6}$ sec. This requires the molecule considered to have a velocity of $\frac{2}{3{\cdot}76} \times 10^6$ cm./sec. or say 5×10^5 cm./sec. Now the molecular velocity of nitrogen is 5×10^4 cm./sec. at 273° K. To raise it 10 times, the absolute temperature must be increased 100 times, i.e. to the temperature of the hottest stars. It seems clear, therefore, that a molecule could not travel fast enough to give up energy to the platinum strip more than once during the short duration of a discharge. If not, it must carry 98·5 eV at one time, and it is not easy to see how according to current ideas it could do this. The energy of dissociation of nitrogen is 7·4 (?) V, and this, together with the ionization of both the atoms, would only afford $7{\cdot}4 + 2 \times 14{\cdot}5$ V or 36 V. Considering that the discharge gives a band spectrum and not a line spectrum, the idea of complete dissociation and ionization is somewhat fantastic; but even if we make this assumption the difficulty remains.

There appears to be no advantage in increasing the number of turns to the maximum, and close winding was inconvenient, because the coil showed a tendency to spark over. A coil having 26·5 turns was used in further experiments, as being about the useful maximum.

The pressure was then varied, leaving the other conditions unaltered:

pressure (cm.)	W-sec./c.c.	eV/mol. present
26×10^{-3}	5·32	2·16
$12{\cdot}4 \times 10^{-3}$	19·1	4·37
$5{\cdot}2 \times 10^{-3}$	92·3	21·1
$2{\cdot}6 \times 10^{-3}$	309	70·6
$1{\cdot}5 \times 10^{-3}$	643	147
$1{\cdot}1 \times 10^{-3}$	1020	233

It appears, therefore, that the energy per molecule increases very greatly as the pressure is diminished.

It was of interest to see whether these very large values of the energy per molecule are peculiar to nitrogen, or whether they would be found in other gases also. A few results only are available at present:

gas	F, pressure (cm.)	W-sec./c.c.	eV/mol.
oxygen	$2{\cdot}6 \times 10^{-3}$	432	98·5
hydrogen	$4{\cdot}3 \times 10^{-3}$	470	107
nitrogen	$2{\cdot}6 \times 10^{-3}$	309	70·6

These are of the same order of magnitude as the results for nitrogen, one of which is repeated for convenience of reference.

Conclusion

If a platinum surface is exposed to nitrogen through which a discharge has passed, the energy which it collects from the gas is greatly in excess of what would be expected if the nitrogen were completely dissociated into atoms, and every resulting atom was singly ionized. It is difficult to see how the result can be explained by current conceptions. Similar results have been obtained with oxygen and hydrogen.

References

Rayleigh, 1940*a* *Proc. Roy. Soc.* A, **176**, 1.
Rayleigh, 1940*b* *Proc. Roy. Soc.* A, **176**, 16.