CCXCII.—*On Active Nitrogen. Part III. Active Nitrogen and the Metals.*

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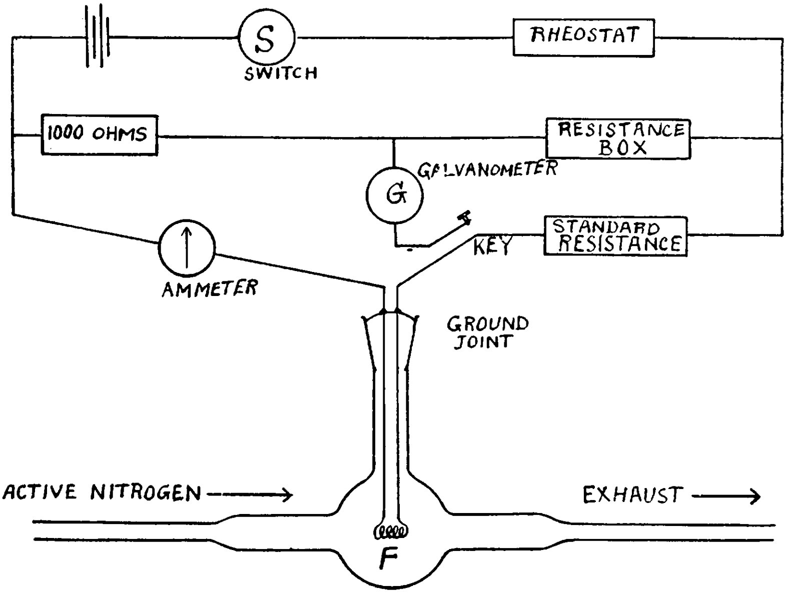
WHILST metallic vapours readily combine with active nitrogen to form nitrides (Rayleigh, *Proc. Roy. Soc.*, 1913, *A*, **88**, 539; Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 263), the clean, cold metals rarely exert any noticeable influence upon the afterglow. In ordinary circumstances, copper forms the only exception to this statement, but if mercury or low-melting alloys of lead be employed and the gas be bubbled through the liquid, this rapidly becomes foul and abundant nitride formation occurs, suggesting that the inactivity of the clean and cold metals is due to the formation of a skin of nitride, which, being inactive, protects the underlying portions of the metal against attack. In view of the fundamental importance of nitride formation in the catalysts employed in the synthesis of ammonia, it was decided to investigate in some detail the effect of active nitrogen on the metals; the results obtained support the foregoing theory, and, moreover, it has been found that in several cases the metals become active catalysts in the destruction of the afterglow at the temperature of decomposition of their nitrides. The experimental data also show that the energy of active nitrogen is *ca.* 45,000 cals./g.-mol., in excellent agreement with the value advanced in earlier communications (J., 1926, 1804; this vol., p. 669), and that the decay process is probably bimolecular with respect to the active nitrogen.

FIG. 1.



EXPERIMENTAL.

The apparatus employed is shown in Fig. 1. Active nitrogen, cooled to room temperature by passage down a thin-walled tube, flowed over the filament, F, which served both as a resistance thermometer and as a heating coil. The galvanometer and leads were enclosed in an earthed shield, and an auxiliary electrode, also earthed, was provided between F and the end of the discharge in order to afford protection from stray discharges; in this way, disturbance of the Wheatstone circuit was avoided. The filament was silver-soldered to heavy copper leads sealed through the ground joint as shown.

It was found that both with a bare platinum filament initially at room temperature and with filaments of other metals, as well as those obtained by electrodeposition of coatings so thin as not appreciably to alter the resistance of the original platinum, a very definite increase in temperature occurred when active nitrogen was drawn through the apparatus; this was least in the case of molybdenum and tungsten, and greatest with smooth-surface copper. No such increase in temperature was observed when the filament was replaced by a thermometer, thus showing that the heating effect is due to the decay of the endothermic active nitrogen at the surface of the metal.

With platinum, iron, silver, zinc, tungsten, and molybdenum, the relationship between the velocity of the gas stream (measured upon an arbitrary scale) and filament temperature was linear between the limits examined. The figures obtained for platinum are typical:

Flow speed	0·0	4·0	6·5	8·5	10·3	12·3
Resistance	1·302	1·313	1·320	1·325	1·330	1·335

(Owing to the limited capacity of the pump, it was not possible to work with flow speeds above 1·5 litres/hour, measured at atmospheric pressure.)

With a copper-coated filament, however, the temperature increment was much greater than that obtained previously and the glow ceased abruptly at the metallic surface; moreover, the curve obtained (Fig. 2) is different in form, the temperature rapidly increasing to a value at which it remains constant over a certain range of flow rate, and then again increasing. The existence of this flat portion, AB, is explicable on the assumption that the maximum destruction of active nitrogen at the surface is reached with a gas-velocity corresponding to the ordinate of A, but that at B the gas-velocity is high enough to set up turbulent motion round the filament, causing increased circulation of the gas and a consequent increase in the number of molecules deactivated by the metal. Support for this view was obtained in two ways. It was noticed that so long as the gas-velocity was not too high, the coating of copper remained intact and the experiments could be repeated as often as desired. Above a gas-velocity corresponding closely with B, however, the point at which the afterglow ceased (initially about 2 m. downstream in such experiments) began to recede rapidly, until after about a minute no afterglow was visible except for localised patches round the electrodes. When the filament was dismounted, the copper coating was found to have vanished almost entirely, whilst the walls of the bulb had become reddish-brown in colour, just as if they had been " spattered " from a copper cathode. Prolonged treatment of the glass with nitric acid produced no change in its colour, and little or no copper could be detected in solution; but quantitative tests in which a long filament was first plated with copper and then cut in two, one half being used for a colorimetric determination of the copper and the other being subjected to the action of active nitrogen, showed that nearly the whole of the copper lost from the wire could be recovered from the bulb if this were powdered and fused with sodium carbonate. Even with the most rigorous protection against stray discharges, the result was the same, and hence it would appear that the disintegration is due to the evolution of heat at the copper surface owing to the decay of large amounts of active nitrogen thereat, whilst the scattered metal has so strong a catalytic effect as to " poison " the glass.

The nature of the copper surface has a great influence in this connexion. If the plating is spongy, the curve obtained shows only the merest trace of flattening, and the disintegration is rapid even at lower gas velocities than before. This " spattering " effect was still more pronounced when the coating had been prepared *in situ* by the reduction of copper oxide by means of active hydrogen in an auxiliary apparatus, whilst commercial copper wire which had been carefully cleaned did not show it at all. No other metal showed any disintegration.

It seems probable, therefore, that, in the case of other metals, the linear relation between gas-velocity and filament temperature corresponds with the portion of the curve to the left of A (Fig. 2), and that if a sufficiently high flow speed could have been attained, they would have given curves showing a similar flattening. It is possible, upon the basis of the data obtained here, to calculate (i) the relative order of catalytic efficiencies of these metals for the destruction of active nitrogen, and (ii), provided a certain assumption be made, the order of the decay process of active nitrogen.

(i) All other factors remaining constant, the increase in the temperature (ΔT) of a filament will be directly proportional to its area (A) and to the catalytic efficiency of the metal (E), and inversely proportional to its weight (W), *i.e.*, $\Delta T = kAE/W$. Now it was noticed that when a current of active nitrogen was drawn past a copper-coated filament, the glow appeared to be entirely extinguished provided that the flow speed was not too high, and hence we may assume that in these circumstances the whole of the active nitrogen reaching the surface of the filament was transformed to the inert variety. We may thus calculate the catalytic efficiencies of the various metals employed, relative to copper as unity, as shown in Table I. The measurements were all made with filaments immersed in nitrogen flowing at the rate of 1·5 litres/hr. (measured at *N.T.P.*), the gas being at a pressure of 10 mm. Hg and containing 1·5% of active nitrogen.

TABLE I.

Metal.	100 *W*.	ΔT.	$A \times 10^4$.	*E*.
Platinum	0·85	8·0	2·2	0·24
Silver	2·1	12·5	3·9	0·26
Zinc	2·1	12·5	3·9	0·26
Iron	2·0	13·0	3·7	0·27
Copper (smooth)	1·15	36·0	2·8	1·00
Copper (spongy)	1·84	15·0	3·6	0·33
Tungsten	2·3	0·0	—	0·0
Molybdenum	0·8	0·0	—	0·0

(ii) Let us make the very probable assumption that a constant fraction of the active nitrogen present at any instant is decomposed at the filament surface; then, from the linear relation between the flow speed and the temperature increment in the filament, we see that the number of active nitrogen molecules present at any instant varies directly with the flow speed of the gas and therefore inversely as the time (t) taken for a molecule to travel from the discharge to the filament, *i.e.*,

$$[N_2'] = k'/t, \text{ or } -d[N_2']/dt = k'/t^2.$$

Hence the decay process is, upon this assumption, bimolecular with respect to the active nitrogen.

It was hoped to use the results of these experiments in conjunction with the Hertz–Knudsen equation (which provides a means of calculating the number of molecular impacts per unit area per second) to evaluate the energy of active nitrogen. Such attempts, however, did not lead to intelligible results. It was then thought that if the " blanketing " effect of the converted nitrogen round the filament could be eliminated by the use of a hot wire, data of more value might be obtained, for it is obvious that the conditions obtaining near the cold filaments are somewhat complicated. Furthermore, the metals should, *ex hypothesi*, become completely active at or about the temperatures of decomposition of their nitrides, and this view was tested in the next series of experiments.

The temperature of the wire was gradually raised by altering the adjustment of the rheostat, and its resistance was determined for each setting in a stream of inert nitrogen at 10 mm. pressure, a constant flow speed being maintained all the time; the usual parabolic relationship between current and resistance was obtained, as shown in Figs. 3 A, B, and C. The nitrogen was then activated and the procedure repeated, with the result that in the case of iron (Fig. 3 C), platinum, and silver (Fig. 3 A) marked "breaks" were found in the curves, at *ca.* 300°, 92°, and 30°, respectively. Moreover, at these temperatures the glow practically ceased as the

FIG. 2.

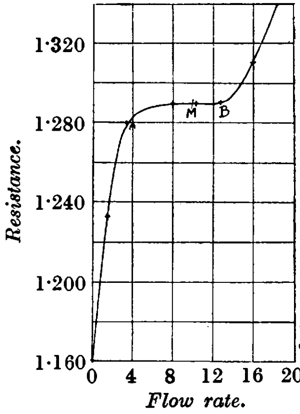


FIG. 3A.
Silver.

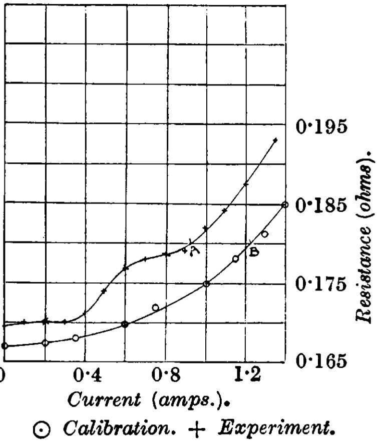


FIG. 3B.
Copper.

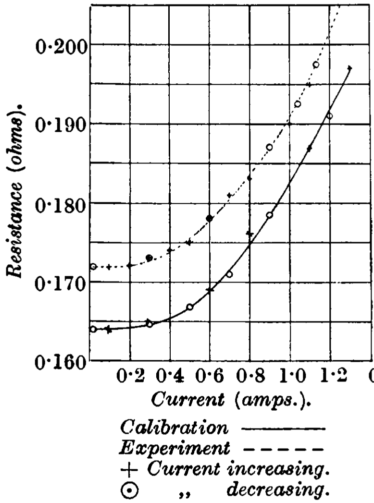
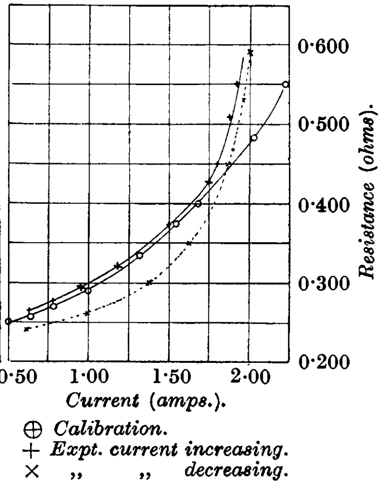


FIG. 3C.
Iron.



active nitrogen reached the filament, indicating that it was being destroyed by the hot wire. No departure from the calibration curve was noticed with tungsten and molybdenum filaments, but with copper (Fig. 3 B) the form of the curve shows that the section above the break has already been reached even at the ordinary temperature.

It will be noticed that, in the case of the iron-coated filament, the curves obtained for increasing and decreasing values of the current do not coincide; it is possible that this is due to sintering, in view of the temperature to which the filament was raised, for when the original deposit was replaced by a fresh one the discontinuity occurred just as before. No formation of nitride was observed in any of these experiments, but the platinum filament became coated with a dense layer of platinum-black, as observed by Beilby and Henderson (J., 1901, **79**, 1253) when this metal was heated in a current of gaseous ammonia.

Since it seemed likely that the comparative inactivity of commercially drawn copper wire as a catalyst for the decay of active nitrogen is due to surface phenomena which might be minimised when a hot filament is in contact with active nitrogen, the ordinary material was used in this case, with the result, as will now be shown, that complete activity appeared when the hot metal was used. The significance of these breaks in the curves is clearly that at the temperature concerned the filament is becoming catalytically active in the destruction of active nitrogen; energy is therefore being liberated and the rise in temperature of the filament follows. From these data we may evaluate approximately the energy of active nitrogen, as follows.

Consider two points, A and B, on a line parallel to the abscissa (in Fig. 3 A) which is drawn to cut the two curves where they have become approximately parallel. Then the energy supplied by the active nitrogen (in cals./sec.) is

$$R_T(C^2{}_B - C^2{}_A)/4{\cdot}2 \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

where R_T is the ohmic resistance of the filament at the points A and B, and C_A and C_B are the currents (amps.) corresponding to A and B, respectively.

Since at this point the glow had almost entirely been lost in the gas below the filament, we may assume that all the active nitrogen passing was destroyed, and from a knowledge of the flow rate of the gas and its active-nitrogen content we can calculate n, the number of molecules undergoing conversion per second. Thus from (i) we have $R_T(C^2{}_B - C^2{}_A) = nq$, where q is the energy of a single molecule of active nitrogen. The energy of active nitrogen per g.-mol., Q, is then given by the expression :

$$Q = R_T(C^2{}_B - C^2{}_A) \times 6\cdot06 \times 10^{23}/4\cdot2n.$$

TABLE II.

Metal.	R_T.	C_A.	C_B.	Flow speed (c.c./hr. at *N.T.P.*)	$n \times 10^{-17}$.	Q.
Platinum ...	0·530	0·45	0·54	1500	1·7	40,200
Silver	0·180	0·92	1·24	3000	3·4	52,700
Copper	0·175	0·48	0·80	2000	2·2	47,000
					Mean	46,600

It will be noticed that if evaluations of Q are made from the two curves just after activity has set in, values much higher than 46,000 cals./g.-mol. are obtained. This is probably due to the "blanketing" effect mentioned on p. 2192, and it was therefore necessary to make calculations from points on the curves corresponding to a sufficiently high temperature to ensure an adequate circulation of the gas, *i.e.*, from points at which the curves are parallel.

It now remains to discuss the probable mode of action of the metals upon active nitrogen. The existence of definite points at which they became active (and in two cases, a definite action of the active nitrogen upon the metal surface) would point to the catalytic decay process being due to the alternate formation and decomposition of the nitride, and the temperatures in question lend a certain measure of support to this view. This is most apparent in the case of iron, since the activity sets in at about 300° and the nitride commences to decompose between 300° and 400° (Baur and Voerman, *Z. physikal. Chem.*, 1905, **52**, 467; White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1343; Noyes and Smith, *ibid.*, 1921, **43**, 475). The temperatures of decomposition of the corresponding substituted-ammonia compounds of silver, platinum, and copper do not appear to have been determined, although the data of Beilby and Henderson (*loc. cit.*) show that they are comparatively low, and in the absence of evidence to the contrary we may regard this tentative explanation as justified.

Summary.

The catalytic activity of certain metals in the form of fine filaments in accelerating the decay of active nitrogen has been studied both at the ordinary and at higher temperatures. From the data obtained an evaluation of the energy of active nitrogen has been made which agrees well with the value already found, and it appears

that the activity of the metals in this respect probably depends upon the stability of their nitrides; of the metals employed, copper appears to be by far the most active. It has also been shown that the decay process of active nitrogen in the gas phase is bimolecular with respect to the active nitrogen.

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