# CCCLXXIV.—*On Active Nitrogen. Part VI. The Formation of Iron Nitride in the Iron–Nitrogen Arc.*

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In the course of an investigation upon the causes of brittleness in electric arc welds, it was found (Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 263) that when an arc is burned between poles of iron in an atmosphere of nitrogen the deposit forming on the walls of the vessel contains iron nitride to the extent of *ca.* 2%. Moreover, the electrodes absorbed nitrogen and retained it very tenaciously. It was suggested that this is due to the formation of iron nitride through the interaction of active nitrogen and iron vapour or the finely divided metal evaporated from the electrodes, and Dr. Rideal later pointed out to the author that this comparatively small nitride content

might be greatly increased if the vapours were quickly removed from the high-temperature zone and chilled to prevent a subsequent decomposition of the nitride, which is known to be somewhat unstable. Fowler (J., 1901, **79**, 285) found that $Fe_4N_2$ begins to decompose into its elements at about 600°, but Noyes and Smith (*J. Amer. Chem. Soc.*, 1921, **43**, 475) have shown that the equilibrium nitrogen pressure for the same substance is about 41,000 atmospheres at 460°, good agreement being obtained between the observed values and those calculated by an application of the Nernst heat theorem to the data of Fowler and Hartog (J., 1901, **79**, 299) upon the heat of formation of $Fe_4N_2$ (3040 cals./g.-mol.). Hägg, however (*Nature*, 1928, **121**, 826), has concluded from *X*-ray examinations that this "nitride" is not a definite compound but rather a solid solution of nitrogen in iron (compare Fry, *Krupp'sche Monatsh.*, 1923, **4**, 137; *Stahl u. Eisen*, 1923, **43**, 1271). The matter was therefore shortly investigated and Rideal's prediction verified.

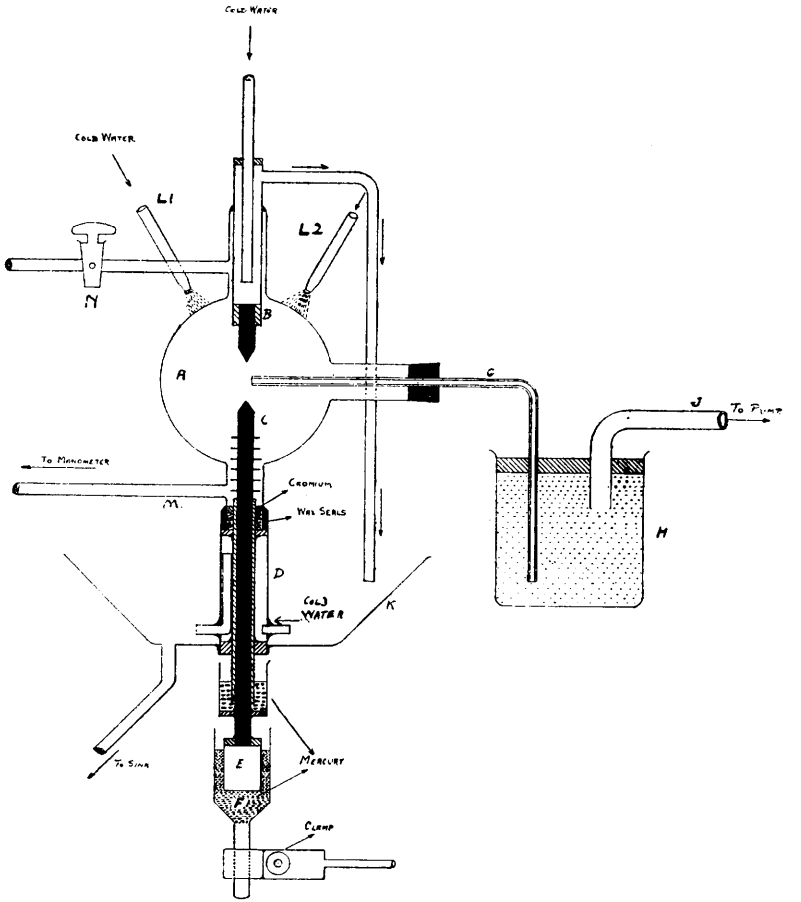
## Experimental.

Nitrogen, purified and freed from oxygen by either hot copper or phosphorus, was led to the quartz globe, *A*, which was provided with three arms each with side tubes as shown. The upper electrode, *B*, was of Armco iron rod, about $\frac{1}{8}$" in diameter and screwed into the solid ends of the $\frac{1}{2}$" brass rod, which was bored out and fitted for water cooling as shown. The lower electrode, *C*, passed first through the water-cooled gland, *D* (made by accurate boring of another brass rod), provided with a mercury seal carried on the electrode as shown; access of mercury vapour to the bulb was prevented by a few carefully packed fragments of cadmium metal above the gland. Cooling fins on the electrode dissipated so much heat that the rod below *D* was rarely more than just warm, even when no water-cooling was employed on the gland. The steel float, *E*, rested on mercury in the column *F*, the height being adjustable by a levelling tube and reservoir. At *G* a quartz capillary, of 1·5 mm. bore, led to the stoppered litre beaker *H*, which was loosely packed with glass wool and fitted with an outlet tube, *J*, through which the nitrogen was drawn to a motor-driven oil pump of large capacity. The capillary was adjusted in trial runs so that it was in contact with the particular zone of the arc from which it was desired to draw the vapours. The electrodes and gland were fixed in position with Faraday wax, as was the tinned-iron funnel, *K*, to which the cooling water flowed; the bulb itself was also cooled by jets of water at *L*1 and *L*2. A manometer was also provided for the tube *M*.

Starting of the arc was effected by raising the reservoir *F*, until

the electrodes made contact; the level was then quickly dropped. It may be mentioned that, as found before, the arcs did not burn well after about an hour or so; this is clearly due to changes in the composition of the electrode tips owing to absorption of nitrogen, leading to a decrease in their ability to emit electrons and to give

FIG. 1.




iron vapour, which carries a large proportion of the current in the arc.

In the experiments, the tap, $N$, was closed, and the pump started to evacuate the system to 0·5 mm., the mercury reservoir being lowered, after which $N$ was opened, nitrogen admitted, and the flow adjusted until a rate of 10 litres per hour was obtained, the

pressure being about 730 mm. The arc was then struck and allowed to burn until a suitable quantity of the iron–iron nitride mixture had collected in *H*, after which the experiment was stopped.

The deposit was then separated from the glass wool by means of a magnet, or in some cases the mixed wool and deposit were weighed, and treated with dilute sulphuric acid, and the wool was separated by decantation, washed until no iron remained, dried thoroughly and reweighed, the amount of deposit being obtained by difference. The iron was determined by permanganate and the nitrogen by a Kjeldahl method, the ammonia in the distillate being either titrated back with *N*/50-alkali (methyl-red being used as indicator), or, if the samples were small, determined colorimetrically; the results were calculated to iron and iron nitride.

The amount of nitride present decreased from the metal-vapour zone outwards; at the edge of the brilliantly blue inner zone of the arc 12—15% of the iron was present as nitride, $Fe_4N_2$, whilst at the outer edge of the arc the proportion had fallen to 6—8%, and the sublimate obtained from the walls of the bulb when a gentle stream of gas (1—2 litres per hour) was maintained contained some 2—3%, as found in the previous experiments. Preliminary studies of the effect of power input on the yields showed that, whilst the distribution did not alter much, the actual quantities of nitride obtained from an arc of 1·5 cm. length varied roughly as the amperage; the currents employed were from 3—10 amps. at 35 volts and upwards.

*Discussion.*

The principal interest of these results lies in their bearing on the experiments in which evidence was obtained that nitrogen may be chemically active and yet show no luminosity (see Part IV, J., 1927, 2831). These have recently been largely confirmed by Kaplan and Cario's observation (*Nature*, 1928, **121**, 906) that the *D* lines in the sodium spectrum can be excited by the non-luminous active nitrogen, of which the existence had been inferred by the present author from the ability of the gas to react with nitric oxide and undergo its characteristic exothermic catalytic decay at copper oxide surfaces even when no glow is visible.

The arc in nitrogen is a brilliant bluish-white, with a reddish outer zone which may easily escape detection by reason of its comparative faintness. Examination of the arc light by means of a Hilger spectrometer showed that the bands (especially in the yellow) which are characteristic of the nitrogen afterglow spectrum could not be detected visually; they may have been masked by the iron lines which are abundantly developed, but as these are comparatively few in the yellow, the afterglow bands would have been

expected to appear. It may be that the reaction between the active nitrogen and the iron is so rapid that the quantity of the former present in the free state remains very low and hence cannot be seen, but the failure to obtain evidence of a glow would suggest either (1) that if the Rayleigh nitrogen be the active form it is here non-luminous, or (2) that, under the more intense mean-current and temperature conditions obtaining in the arc as compared with the condenser discharge, another and chemically more active modification of nitrogen such as Lowry's (J., 1912, **101**, 1152) is being produced.

The author's acknowledgments are due to Dr. Rideal for suggesting this investigation, to Mr. R. E. Stonebridge, who made the gland and float system, and to his assistant, Mr. R. Southward, for the accompanying diagram.

The experiments were carried out in the Laboratory of Physical Chemistry, Cambridge, early in 1925, and, although they had to be abandoned whilst still incomplete, it is hoped that they may lead to further investigations on reactions in the electric discharge—a subject which promises to be of much interest.

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