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THE FORMATION OF ACTIVE HYDROGEN IN THE CREEPAGE CORONA DISCHARGE

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Wendt and Landauer[1] and Y. Venkataramaiah[2] have described an active modification of hydrogen formed in the corona discharge. The purpose of the present article is to describe a study of the creepage corona discharge in hydrogen. This discharge, especially with glass wool filling much of the discharge space, has been found comparatively effective in promoting the oxidation of nitrogen in air[3] and it was hoped that it might prove equally effective in increasing the activation of hydrogen in the corona discharge.

The electric circuits and the discharge tubes used were the same as those previously described.[3] Hydrogen, obtained by the electrolysis of 20% sodium hydroxide solution, was purified by sufficient contact with heated platinized asbestos, concd. sulfuric acid, lumps of fused potassium hydroxide, and distilled phosphorus pentoxide. A flow rate of 40 cc. per minute of hydrogen was maintained constant in all these experiments. For estimating the degree of activation of the hydrogen, the formation of hydrogen sulfide and the reduction of permanganate, while giving positive results when glass wool was used, were less satisfactory for quantitative measurements than the combination with nitrogen to form ammonia which could be adsorbed in water and nesslerized. The nitrogen obtained by the Van Brunt method[4] was freed from ammonia and moisture. After leaving the discharge tube the hydrogen passed through 5 cm. of tube, 1 cm. in diameter, and 50 cm. of 5mm. tube before coming in contact

[1] Wendt and Landauer, This Journal, **42**, 930 (1920); **44**, 510 (1922).

[2] Venkataramaiah, *Nature*, **106**, 46 (1920); *Chem. News*, **124**, 323 (1922).

[3] Anderegg, *Trans. Am. Electrochem. Soc.*, **44**, 203 (1923).

[4] Van Brunt, This Journal, **36**, 1448 (1914).

with nitrogen. Each step of the experimentation was controlled by carefully made blank runs.

In addition to a tube packed with glass wool, two tubes, one filled with fragments of earthenware and another with fragments of flint were made up; all three contained central electrodes of B. and S. No. 16 aluminum wire. A fourth tube was fitted with a B. and S. No. 29 platinum wire in a manner similar to that described by Wendt and Landauer.[1] Of these four tubes, the only one that gave an appreciable yield of activated hydrogen was the glass-wool tube. In the tube containing the platinum wire the linear flow rate was 50 cm. per minute. In the tubes containing the fragments it was approximately twice as great, while in the glass-wool tube it was about 65 cm. per minute.

In experimenting with the glass-wool tube, marked fatigue effects were observed. After a run of two or three hours, the yield had fallen to a very small value in spite of the flow of a very rapid stream of water through the outer jacket of the Liebig condenser. On standing, the tubes recovered from the fatigue according to the length of time of rest. Very long periods of inaction seemed to restore them completely and even improve the yield.

The replacement of a small part of the hydrogen in the tube by air followed by thorough sweeping out with hydrogen improved the yield markedly. This suggested that a trace of oxygen or nitrogen, adsorbed on the surface of the glass wool, might be functioning as an activating agent; but the introduction of traces of nitrogen or oxygen (1 part in 10,000) into the hydrogen had almost no effect on the yield.

The discharge was carried out at 9,000, 12,000 and 13,500 volts. The fatigue effects, however, were sufficient to obscure any variation caused by voltage changes.

Previously, when working in air the fatigue effects encountered could be removed by passing the discharge through a mixture of hydrogen and nitrogen. In a similar manner, passing the discharge through nitrogen for one hour after sweeping out all hydrogen was effective, since the discharge in pure hydrogen was then found to give a better yield. By

Table I

Results

Volts	Mg. of NH_3 per hour	Parts of H_3 per million	Volts	Mg. of NH_3 per hour	Parts of H_3 per million
9000	0.100	80	12,000	0.29	229
9000	.125	100	12,000	.31	245
9000	.200	160	12,000	.28	222
9000	.225	178	13,500	.42	332
9000	.230	182	13,500	.33	260[a]
9000	.240	190	13,500	.43	340

[a] In this run, the primary voltage as well as the secondary wattage was slightly lower than in the other two runs at the same secondary voltage.

successively discharging in nitrogen and in hydrogen, the formation of the active modification was steadily increased. Moreover, the higher the voltage the greater the yield under this treatment.

The two possibilities which must be considered in looking for an explanation of our results are the catalytic decomposition of activated hydrogen at the solid surfaces and a change in the nature of the discharge brought about by adsorption of some form of activated hydrogen. We might say that platinum, flint or earthenware promotes decomposition of active forms even more than glass, which has been reported by R. W. Wood[3] as bringing about recombination of hydrogen atoms Discharge in nitrogen or admitting a trace of air might be said to cover the surface and poison its activity. Prolonged standing might be regarded as allowing inert hydrogen to become tightly held on the surfaces, decreasing their catalytic action.

The second explanation has in its favor numerous observations made in air.[3] Although no variations in the appearance of the discharge or in the meter readings were observed in this work, marked changes in chemical results have been found to occur in certain cases almost without warning. This explanation is supported by observations made during a run, typical of many others. In one hour of discharge through hydrogen 0.12 mg. of ammonia was obtained. When the apparatus was swept out, the first five minutes produced 0.015 mg., the next 15 gave 0.010 mg. and the last ten minutes a trace (perhaps 0.002 mg.). Probably both possibilities will be needed to give a complete explanation of all the phenomena.

Summary

Glass wool in the discharge space tends to increase the yield of active hydrogen formed in the corona discharge.

The tube exhibits fatigue effects which may be removed by discharging in nitrogen. A trace of air admitted and then swept out produced a similar result, but traces of oxygen or nitrogen admitted with the hydrogen were without effect.

Disuse of the tube tends to allow it to recover very slowly from fatigue.

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