The Journal of the American Chemical Society

with which has been incorporated
The American Chemical Journal
(Founded by Ira Remsen)

VOL. 45 FEBRUARY, 1923 No. 2

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, MAHARAJAH'S COLLEGE]

THE PREPARATION OF ACTIVE HYDROGEN

BY Y. VENKATARAMAIAH

Received June 29, 1922

Following the activation of hydrogen by its explosion in a quantity of oxygen insufficient for complete combination,[1] four new methods of activation have now been developed, namely, the continuous burning of oxygen in hydrogen, surface combustion of hydrogen and oxygen on platinum, the high tension arc in hydrogen, and heating of hydrogen in arcs of various metals. In all cases the hydrogen was prepared by the electrolysis of barium hydroxide solution and purified as described in the previous papers. The test of activation was the action of the hydrogen on sulfur at room temperature to form hydrogen sulfide.

The apparatus for the continuous burning of oxygen in hydrogen is shown in Fig. 1.

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[1] *Proc. Sci. Assoc. Maharajah's Coll.*, Vizianagaram, July 10, 1921; *Nature*, 106, 46 (1920). Since the publication of these two papers, I came across the following significant line in the paper "On the Combined Volumes of Hydrogen and Oxygen," by F. P. Burt and E. C. Edgar, published in *Phil. Trans.*, 216A, 393 (1916). "In these four experiments a new phenomenon was observed. In each case, after the final explosion in which oxygen had been present in excess, brown stains were noticed on the walls of the explosion vessel. The stains were presumably oxide of mercury since they gradually disappeared when mixtures containing an excess of hydrogen were detonated in the vessel." It is clear from the above that hydrogen is activated when detonating gas is exploded with an excess of hydrogen. It is surprising to see how narrowly the above clever experimenters missed the discovery of "active hydrogen."

A bulb A, of nearly 2 liters' capacity, contains a platinum tube P of 14 mm. diameter, tapered at the mouth to 12 mm., which is fused through the glass wall. Two platinum electrodes TT are also sealed through the glass wall, their sparking tips being placed just beyond the mouth of the platinum tube. Oxygen entered through the tube P while hydrogen entered through the sealed-in glass tube H and left through the tube sealed into the opposite side of the bulb, passing through a plug of glass wool W over a thermometer B hung on a platinum hook in the side tube, thence over dry powdered sulfur S, and finally over a strip of filter paper moistened with lead acetate solution in C. S_1, S_2, S_3 and S_4 are mercury-sealed stopcocks.

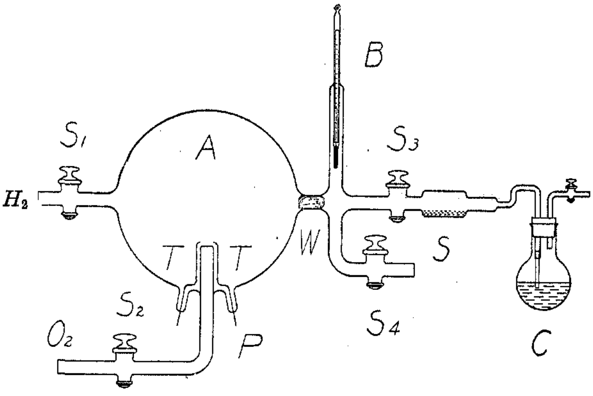

Fig. 1.

The bulb was first exhausted by means of a vacuum pump, and hydrogen was passed through it for 8 hours without causing a trace of discoloration on the lead acetate paper. Sparks were then passed between the platinum electrodes by means of a 5cm. induction coil, while oxygen was slowly admitted through the platinum tube. As soon as the oxygen took fire, the sparks were discontinued. The flame was nearly 6 cm. high, and after it had burned for half an hour the stopcock S_4 was closed and S_3 was opened. Within 3 minutes the paper became markedly blackened. The entire apparatus was cooled in water at 0° and the thermometer never recorded a temperature higher than 25°.

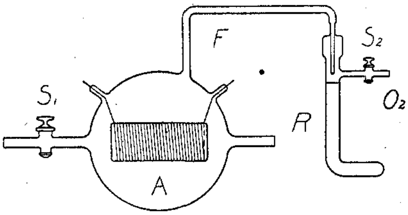

Fig. 2.

Fig. 2 represents the apparatus for the combustion of oxygen and hydrogen on the surface of platinum.

The bulb A contains a glass rod frame 12 cm. long and 10 cm. wide, upon which a platinum wire 0.4 mm. in diameter and 3 meters long is wound; the platinum leads were attached to this wire, being fused through the glass walls.

The wire was heated to redness by a current from a 60-volt storage battery with a rheostat in the circuit. Oxygen was admitted to the bulb through the tube F and stopcock S_2 by means of a mercury regulator R. Careful regulation of the oxygen supply was necessary to avoid explosion, and the current through the wire was broken as soon as the oxygen had entered, the combustion of the oxygen being sufficient to maintain the wire in the glowing state. Blackening of the lead acetate paper was visible within 4 to 5 minutes. The apparatus was kept cooled so that its temperature never rose above 28.5°.

For the activation by the high tension arc the bulb was provided with silver electrodes 5 mm. in diameter and 1.5 cm. apart, the arc being maintained by a current of 20 amperes through the primary of an induction coil equipped with a Wehnelt interrupter. The apparatus was cooled as before. Blackening occurred in 3 to 4 minutes.

For the high temperature arc first gold, then platinum electrodes, 1 cm. in diameter, were sealed into the bulb, and an arc was established between them at 220 volts and 6 amperes. The hydrogen was led into the bulb through a platinum tube extending to within 5 mm. of the arc. Although the experiment was continued for some hours, no blackening of the test papers was observed with these electrodes. The gold electrodes gave out such volumes of gold smoke that it was necessary to reduce the current. When silver electrodes were used, however, decided blackening occurred within 30 minutes. The explanation of the failure of gold and platinum to give activation may lie in the adsorption of the active hydrogen in a thin film by these highly adsorptive metals,[2] or perhaps in catalytic decomposition of the active form, since Wendt and Landauer[3] have shown that finely divided platinum does have such a catalytic effect, while silver does not.

I have shown in one of the above experiments that hydrogen is activated combined with oxygen on platinum, but the work of Wendt and Landauer, which appeared since this work was completed, has shown that hydrogen can be activated over a hot platinum wire without the presence of oxygen as in the above experiment. Bone and Wheeler[4] explain the activation of gases in chemical reactions on surfaces as due to the surfaces themselves. They say that the function of the surface is to "activate" by dissociation (or ionization) the gases at the occlusion. In the case of the simple combustion of oxygen in hydrogen, however, the reaction itself activates the hydrogen. This is probably due to an ionization of the hydrogen by the electrons emitted by the reacting molecules. This suggestion agrees with the views of Wendt and Landauer, who used ionizing agents exclu-

[2] *Physik. Z.*, **8**, 659 (1907).

[3] Wendt and Landauer, THIS JOURNAL, **41**, 510 (1922).

[4] Bone and Wheeler, *Trans. Faraday Soc.*, No. **51**, 659 (1922).

sively and assumed that atomization accompanies or follows ionization, a triatomic molecule of hydrogen being formed from the combination of the free atoms with the neighboring H_2 molecules.

It is interesting to note that the active hydrogen is produced in all cases under circumstances analogous to those in which ozone is produced. The analogy is evident from the work of Burt and Edgar.[1] The analogy is still further shown in the work on the evolution of active hydrogen in the decomposition of metallic hydrides by water, which is almost finished by the author. Work on the production of active hydrogen in the process of evolution of hydrogen in an absorbed condition from palladium and platinum is being carried on.

It is a pleasure to thank Y. Narasimham, Professor of Chemistry, in the Maharajah's College, Vizianagaram, for the interest he has taken in this work.

I am greatly indebted to Dr. G. L. Wendt, formerly of the University of Chicago, for the great interest he has taken in me and my work.

VIZIANAGARAM, SOUTH INDIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE STRUCTURE OF BENZENE[1]

BY MAURICE L. HUGGINS[2]

Received July 11, 1922

The Structure and Dimensions of Graphite

The Disposition of Atomic Centers.—The structure of graphite has been studied by means of X-rays by Hull[3] and by Debye and Scherrer.[4] These investigators agree that the atomic centers are in layers of hexagons, as shown in Fig. 1. The relative intensities obtained by Hull from some of the "pyramid" planes indicate that each layer is "puckered" as in diamond, the nuclei being alternately in one or the other of two parallel planes (above and below the plane of the paper, in the figure). Debye and Scherrer give no evidence for or against such puckering, for they obtained no reflections from planes closer together than 0.815 Å., and it is only the reflections from such planes which can furnish evidence in regard to alternations of this type.

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[1] This paper is an abridgment of a thesis presented by the author in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Much of the subject matter was presented at a meeting of the California Section of the American Chemical Society held in conjunction with the annual meeting of the Pacific Division of the American Association for the Advancement of Science at Berkeley on August 5, 1921. A short note on the subject has appeared in *Science*, **55**, 679 (1922).

[2] Du Pont Fellow in Chemistry, 1921–1922.

[3] Hull, *Phys. Rev.*, [2] 10, 692 (1917).

[4] Debye and Scherrer, *Physik. Z.*, **18**, 294 (1917).