THE COMBINATION OF HYDROGEN AND OXYGEN IN THE PRESENCE OF ACTIVATED MERCURY

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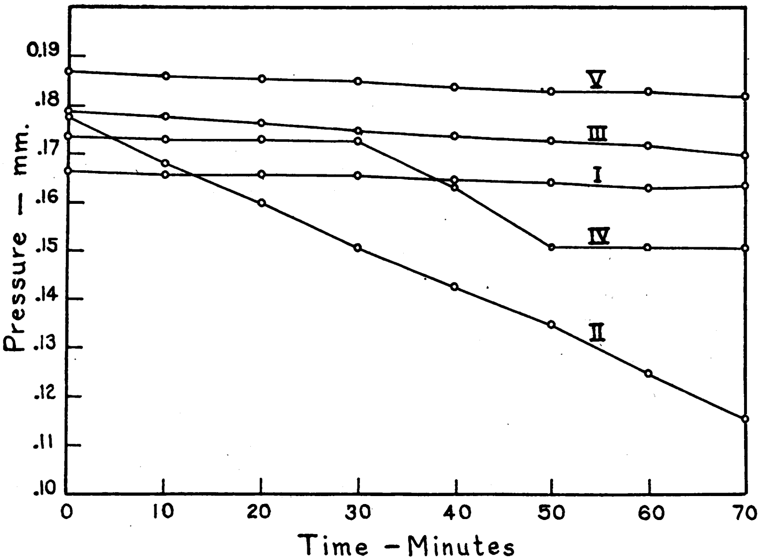
In order to demonstrate the ability of mercury atoms, excited by the absorption of the mercury line 2537 Å., to dissociate hydrogen by "collisions of the second kind," Cario and Franck[1] illuminated with a quartz mercury-arc lamp a mixture of hydrogen and mercury vapor in a quartz tube which also contained copper or tungsten oxide. The water formed in the reduction of the oxide by the activated hydrogen was removed by liquid air, and the consequent pressure decrease was followed with a MacLeod gauge. The writer has had occasion to make some similar experiments employing, however, gaseous oxygen instead of a metal oxide. In view of the importance of collisions of the second kind in other phenomena as well as in photo-chemical sensitization, the work will be briefly described.

Light from a quartz mercury-arc lamp was passed into a reaction tube contained in a cylindrical, electrically heated jacket whose end was closed by a quartz lens. The jacket was ordinarily kept at 45° as in the experiments of Cario and Franck; the reaction was, however, also found to go at room temperature. The quartz reaction tube, 2 cm. in diameter and 16 cm. long, had a clear quartz window fused to one end and a small quartz tube joined to the other. A sealing-wax joint on the latter connected the reaction tube with a narrow, glass U-tube immersed to a constant depth in liquid air. The total volume of the gas space was about 160 cc. A side bulb containing mercury which could be drawn out permitted the gas to to be expanded and recompressed facilitating the removal of condensible material by the liquid air. Through stopcocks the gas space could be placed in communication with either a mercury diffusion pump or a chamber containing a suitable gas reaction mixture. The hydrogen and oxygen used were produced by the electrolysis of a barium hydroxide solution. A strong blast of air on the mercury lamp was held fairly constant with the aid of a Pitot tube.

The experiments were made in the following manner: after pumping out the reaction tube system, a definite gas mixture was admitted and the pressure read. With a definite current passing through the lamp, the reaction tube was illuminated for a period (usually 10 minutes) timed with a stop watch. After the removal of any condensible material, the pressure was again read. This process was usually repeated a number of times.

The results of a typical series of experiments, numbered in the order made, are shown in the figure; the total pressure is plotted against the total time of illumination. One or two cc. of fresh mercury were placed in the reaction tube at the beginning of the series and remained through Experiment IV. In all experiments except parts of IV, the blast of air was maintained on the lamp. Experiment I was a blank made with pure hydrogen. In II, a mixture of 46 mol % hydrogen and 54 mol % oxygen was used. Experiment III was a blank made using pure oxygen. IV



differed from II only in having no air blast in the first 30 and last 20 minutes. V differed from II only in having no mercury present in the reaction tube. The rate of decrease of pressure in experiments like V seemed to depend greatly on the care used to remove all traces of mercury from the reaction tube; in some trials almost no decrease was observed.

In the above experiments a considerable rate of pressure decrease was obtained only when oxygen, hydrogen, and mercury were all present in the reaction tube and an air-blast was maintained on the lamp. In the absence of any one of the substances, or of a radiation capable of exciting gaseous mercury atoms (as when the air-blast was interrupted), the rate was comparatively small or zero. It seems clear, therefore, that excited mercury atoms can bring about the combination of hydrogen and oxygen when the latter is present in the elementary state. These results are in agreement with those of Cario and Franck on metal oxides.

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[1] G. Cario and J. Franck, *Zt. Physik,* **11,** 161, 1922.