CXXXIX.—*Some Properties of Hydrogen Desorbed from Platinum and Palladium.*

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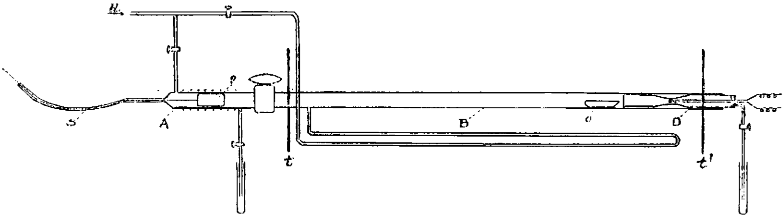
THE contact action of the platinum metals in catalysing hydrogenation reactions has been exhaustively studied since the time of Döbereiner. Of the abnormal activity of the hydrogen in the absorbed or " combined " state there can be no doubt. Is this activity completely and instantaneously lost on desorption, or does it have a finite period of decay? This question would appear to be of some theoretical and technical interest and an attempt has been made to investigate it.

EXPERIMENTAL.

A series of preliminary experiments was first carried out with the object of establishing a difference, if any existed, between the minimal reduction temperature of copper oxide as brought about on the one hand by ordinary pure hydrogen and on the other by hydrogen desorbed from an adjacent mass of platinised asbestos. An ordinary electric tube furnace was employed, the copper oxide and platinised asbestos being contained in small quartz combustion boats. The temperature of the furnace was raised very slowly through a rheostat, and the temperature at which reduction began in each case roughly determined by the condensation of moisture in the cold delivery tube. The results obtained with this apparatus were inconsistent but of sufficient promise to warrant the construction of a modified form of apparatus insuring exact temperature control, a highly purified hydrogen supply, and a delicate moisture detector.

FIG. 1.



For the sake of clearness in description, this apparatus may conveniently be divided into four integral parts : the hydrogen purification train, the chamber for preheating and purification of the catalytic mass from adsorbed foreign gases (*A*, Fig. 1), the reaction tube with its thermostat (*B*), and the moisture detector (*D*). The hydrogen purification apparatus presents no distinctive features and is not incorporated in the sketch. The hydrogen, obtained variously from a Kipp generator, an electrolytic barium hydroxide cell with nickel electrodes, and cylinders supplied by the British Oxygen Co., was purified first by passage through two Emmerling towers charged with solid potassium hydroxide, by which the carbon dioxide, halogens, and most of the moisture were removed. The gas was then passed through cocoa-nut charcoal cooled in liquid air for the removal of any traces of oxygen present, and finally through another tower of potassium hydroxide followed by a phosphoric oxide tube.

The chamber, *A*, and reaction tube, *B*, consisted of the arms of a large glass stopcock, which served to connect or isolate the sections at will. The bore of this stopcock was made equal to that of the arms—in this case 2 cm.—thus permitting the unobstructed movement of the glass capsule, *p*. This capsule contained the catalytic mass of platinised asbestos and was moved from without by means of an attached piano-wire passing out through the mercury seal, *S*. The preheating chamber was wound with resistance wire, by means of which its temperature could be gradually raised to about 300°. This section was also supplied with an inlet tube leading to the hydrogen supply and an outlet through a phosphoric acid trap.

The reaction tube, *B*, containing the copper oxide boat, *o*, in the position shown, was immersed in an electrically heated oil-bath thermostat subject to exact temperature control through an electric thermo-regulator. Thorough circulation of the bath was obtained in the usual manner by the use of a motor-driven agitator. The thermostat is diagrammatically indicated in the sketch by the heavy lines *tt'*. The purified hydrogen enters the reaction tube only after passing through a preheating worm immersed in the thermostat bath, insuring a uniform temperature throughout.

The moisture detector adopted after some experiment with various devices depended for its action on the change in the electrical resistance of anhydrous calcium chloride in the presence of slight traces of water vapour. The gas stream, after passing over the copper oxide, was concentrated by a constriction in a short glass tube fitting into the reaction tube as shown, and made to impinge on a globule of anhydrous calcium chloride bridging a 1 mm. gap between the ends of two parallel copper wires. A rubber stopper fitted to the outside end of the short tube served to support the wires together with the outlet tube. The $Cu–CaCl_2–Cu$ resistance element was connected as the "unknown resistance" in an ordinary Wheatstone bridge apparatus. The element was prepared for use by momentarily immersing the wire ends in molten calcium chloride and replacing the wires in the tube while still hot. Since the element was placed in position only while a stream of extremely dry hydrogen was flowing through the reaction tube and before the temperature had been raised near the reduction point of the copper oxide, the calcium chloride cooled in the anhydrous state and, on balancing, the bridge was found to have a resistance of the order of 30,000 ohms. At the first incipient reduction of the oxide, with the consequent formation of a minute quantity of water vapour, the resistance of the element suddenly dropped to the order of a few hundred ohms. This drop was always sharp and unmistakable, and formed the basis of the minimal reduction temperature observations.

The description of the apparatus is suggestive of the procedure of the determinations, which were made, in brief, as follows : The capsule containing the platinised asbestos remained in chamber *A* with the stopcock closed while a stream of purified hydrogen was passed both through *A*, which was heated at 250—300°, and through *B* at room temperature. After the sweeping-out process had continued for some time, the moisture detector was "loaded" as previously described and the temperature of the thermostat gradually raised until the drop in the resistance of the calcium chloride element indicated the initial reduction of the copper oxide. The thermostat was then allowed to cool to about 50° without interrupting the flow of gas. After the calcium chloride cell had recovered its high resistance, the capsule of platinised asbestos, which had by this time been thoroughly freed of all foreign gases and been allowed to cool to room temperature, was pushed into the reaction tube until some 3—5 mm. distant from the copper oxide boat. The stopcock was then closed after unhooking and withdrawing the wire. The temperature of the thermostat was then again raised and the reduction temperature determined as before.

The results of three typical determinations follow :

Exp.	Minimal Reduction Temp.	
	Control.	Pt. adjacent.
1	103·5°	81·0°
2	115·0	86·0
3	110·5	87·0

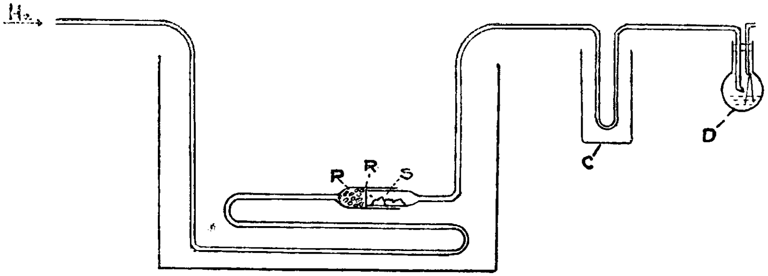
The copper oxide employed, it may be mentioned, was precipitated in asbestos fibre after a method recommended by Sir Robert Robertson for the preparation of a catalytically active oxide.

The results of the determinations never checked closely, a consequence of the variability in the activity of the copper oxide, but the differences observed between the "control" and "platinum adjacent" experiments were always marked and appear to indicate a certain increase in the activity of the desorbed hydrogen.

In order to determine the duration of the activity the thermostat was held constant at 90° and the capsule containing the platinised asbestos very gradually moved toward the copper oxide boat. Reduction was found to take place when the capsule had reached a distance of about 8 cm. from the copper oxide. The rate of flow of the hydrogen was held at 180 bubbles per minute during these tests.

With the object of obtaining further evidence by an independent method, a suggestion made by Professor E. C. C. Baly, of the University of Liverpool, was followed up and a series of determinations of the minimal reduction temperature of sulphur by normal and desorbed hydrogen made, using palladium-black as the activating agent. The hydrogen purification apparatus used in the previous experiments was again employed. A capillary grid or worm served to preheat the hydrogen to the temperature of the palladium-black contact mass (*P*, Fig. 2) and sulphur *s*. The short tube containing the sulphur was fitted closely into the tube containing the palladium and cemented in place. A perforated palladium diaphragm, *R*, served to prevent actual contact between the palladium and sulphur. The detector for hydrogen sulphide, *D*, consisted merely of a small strip of filter-paper dipping in lead acetate solution. The gas was directed in a fine jet against the impregnated filter-paper and the presence of a trace of hydrogen sulphide was immediately indicated by the appearance of a spot of the characteristic colour. A small condenser was introduced to prevent any vaporised sulphur passing over into the detector. A second apparatus identical with the foregoing except for the absence of the palladium activating agent was constructed and duplicate determinations made with both immersed in the same oil-bath thermostat, raising the temperature very slowly and keeping the rate of flow of the hydrogen in both the same. When the spot appeared on one detector, the temperature was noted and the heating continued until the second detector indicated that the minimal reduction temperature had been reached for the control observation. Some typical results follow:

FIG. 2.

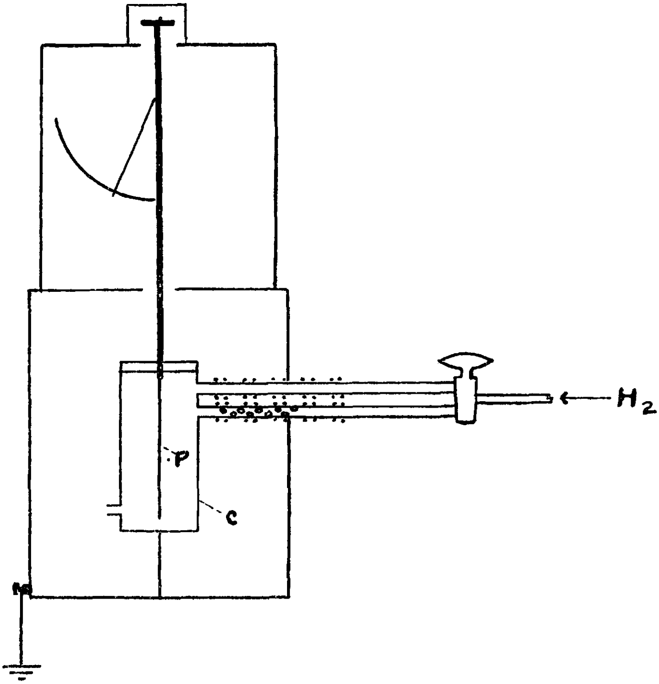


Exp.	Min. Red. Temp. of Sulphur.	
	Control.	Pd. adjacent.
1	112·0°	80·0°
2	118·0	80·5
3	119·5	83·0

These data lend strong support to the results obtained for copper oxide.

The study of the properties of the desorbed hydrogen was continued with a series of qualitative tests to determine whether or not the freshly desorbed gas was ionised to any degree. A gold-leaf electroscope of the type employed by Rutherford in his radioactive measurements was used. The horizontal plate of the instrument was replaced by a small vertical plate (*p*, Fig. 3), connected directly with the gold-leaf. Around the plate and insulated from it by a sulphur plug was fixed a cylindrical brass chamber, *C*, provided with two inlet and one outlet tubes. One of the inlet tubes contained a few grams of palladium-black, and both were equally and non-inductively wound with resistance wire designed to give the gas for " control " and " activated " tests approximately the same temperature. Both tubes were connected with a three-way stopcock leading to the pure hydrogen supply. The gold-leaf was charged and the rate of the collapse of the leaf observed through a telescope. The results obtained may be summarised in the following data :

Fig. 3.



	Angle of fall.	Time in minutes.
Natural leak	1°	78
Control	1	75
Activated	1	40
Check control..............	1	76

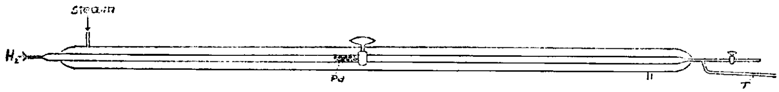
Some experimental work was carried out at this time by Dr. J. A. Christiansen, of the University of Copenhagen, collaborating with the author at University College, with the object of determining whether or not the desorbed hydrogen could be condensed by passage through a tube immersed in liquid air. A platinum–palladium "osmosis" tube, electrically heated to a temperature at which hydrogen readily diffused through the palladium section, was employed as the activating agent, and a McLeod gauge for the delicate measurements of pressure necessary. Consistently negative results were obtained. An experiment carried out later by the author indicated that hydrogen which had undergone slow diffusion through a palladium tube exhibited no abnormal activity, a result probably to be explained by the low desorption rate. The attempted condensation could accordingly have yielded only a negative result.

An attempt was then made to discover the cause of the activity of the desorbed hydrogen. It was considered improbable that the slight ionisation indicated by the data quoted above would account for this increased activity. The possibility of the presence of monatomic hydrogen at the temperature and pressure of the experiments was dismissed on theoretical grounds and also disproved experimentally by the interposition of a short plug of glass wool between the platinised asbestos and copper oxide in the first experiment. The reduction temperature remained unchanged, although Langmuir has shown that monatomic hydrogen is destroyed on passage through glass wool.

May the activity be explained by the presence of triatomic hydrogen? Usher (T., 1910, **97**, 400) and Lind (*J. Amer. Chem. Soc.*, 1919, **41**, 545), among others, have shown that H_3 is produced on the bombardment of hydrogen by α-rays, whilst Collie and Patterson (P., 1913, **29**, 22, 217) and Chattock and Tyndall (*Phil. Mag.*, 1908, [vi], **16**, 24) give further evidence for its formation on sparking molecular hydrogen. The positive-ray evidence of Thomson, at one time disputed, now appears to be substantiated. Wendt (*J. Amer. Chem. Soc.*, 1920, **42**, 930) furthermore attributes the activation of hydrogen by α-rays, electric discharge in a vacuum, and by the corona discharge, to the generation of triatomic hydrogen. In the absence of a positive-ray apparatus experiments were made to determine whether or not the activated hydrogen desorbed from platinum or palladium expanded on decay, as would be expected if a measurable amount of triatomic hydrogen were present: $2H_3 \longrightarrow 3H_2$. An apparatus similar to a Liebig condenser was employed, with a stopcock introduced to divide the tube into two sections as shown (Fig. 4). A rapid current of live steam was passed through the jacket, maintaining a constant temperature throughout. The entering hydrogen was preheated on passing through the left-hand section, activated on passing through the palladium-black, and decayed in the right-hand section, passing out through the capillary tube and stopcock. A small globule of mercury was introduced into the capillary side tube, *T*, and the apparatus adjusted at such an angle that the mercury globule was just on the point of moving down the tube under its own weight, that is, a very slight increase in the pressure within the tube would cause it to move perceptibly. A cross-hair telescope was focused on the globule and after a steady stream of hydrogen had passed for a time both stopcocks were simultaneously closed. No movement of the mercury was detected in any one of the trials, though a light oil globule was later substituted for the mercury.

The refractive index of hydrogen containing some H_3 is necessarily different from that of pure diatomic hydrogen at the same temperature and pressure. The Rayleigh gas interferometer furnishes an excellent means of detecting very slight differences in the refractive indices of gases, and through the kindness of Messrs. Adam Hilger and Co. of London we were able to subject the activated hydrogen to this test. Interference bands were first obtained for the control setting while passing normal hydrogen through both comparator tubes of the instrument. Hydrogen activated by passage over platinum or palladium was then substituted in one of the tubes without breaking the gas flow and the position of the upper and lower bands noted. In no case was a displacement of the bands observed. The temperature and pressure of the hydrogen streams were of course kept constant. The evidence supplied by the interferometer thus reinforces that of the previous experiment in indicating the absence of a measurable amount of the triatomic modification in the desorbed hydrogen. The point can scarcely be considered as settled without a positive-ray test.

FIG. 4.



Another possible explanation of the activity of the desorbed hydrogen—an explanation to which we incline—is furnished by the concept of an increase in the internal energy of the hydrogen molecules themselves. If the Langmuir theory of adsorption on the surface of a crystal space-lattice through the bonds of residual valence is accepted, we may think of these bonds as "closing up" not instantaneously, but during a finite period corresponding with the duration of the abnormal activity. Or what is the same thing, expressed in terms of the quantum theory, the hydrogen molecule may be considered as having taken up a quantum or more of energy during adsorption and reaching internal equilibrium only after a given period succeeding its desorption.

In conclusion, it is a pleasure for the author to record his obligation and thanks to Professor F. G. Donnan, F.R.S., at whose suggestion and under whose direction this work has been carried out.

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NOTE.—The experiments described in this paper were undertaken at the suggestion of Dr. J. A. Harker, F.R.S., this suggestion being based on some preliminary (unpublished) work carried out by Dr. Judd Lewis on behalf of Mr. Colin Campbell.—F. G. DONNAN.