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REACTIONS OF HYDROGEN AND OXYGEN ON PLATINUM WIRES AT LOW TEMPERATURES AND PRESSURES

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Introduction

In an attempt to make a study of a well-defined surface for a simple catalytic reaction, pure platinum wire was chosen as the catalyst, and for the reaction, the combination of hydrogen and oxygen to form water vapor. Wire drawn through a series of agate dies is cryptocrystalline. If annealed at dull red heat, strain is removed, but the crystals are still very small. By heating to a temperature near the melting point crystals readily visible to the unaided eye are formed in the wire. A pure platinum wire 0.1 mm. in diameter and 2 meters long was heated by direct current in the air to dazzling white heat for ten minutes. Many single crystals, extending clear across the wire, were about one millimeter long. However, because of the variability in catalytic behavior of every specimen of wire used, it was not possible to establish any relationship between the activity of cryptocrystalline and macrocrystalline wires. Both kinds of wire behaved much alike. In studying these wires some unexpected observations were made and are here presented.

Apparatus

The apparatus was designed to work at a few microns' pressure and is sketched in Fig. 1. It was constructed of 15-mm. Pyrex tubing, except that in some experiments

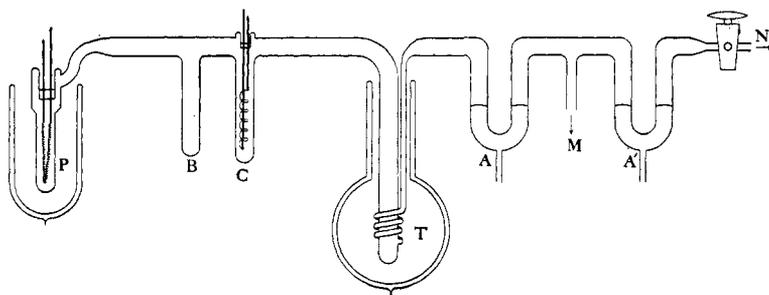


Fig. 1.—Apparatus: M, to McLeod gage; N, to pump and gas reservoirs.

tube C was made of transparent silica attached to the train by a graded seal. The catalyst wire was mounted in tube C and supported by heavy tungsten wires sealed through the glass. These supports were glass-coated except at the tips, where the platinum was spot-welded to the tungsten. The platinum wire, 58 cm. long by 0.10 mm. in diameter (area 1.8 sq. cm.), was used either in the form of a spiral, or of hairpin loops similar in arrangement to the filament in a vacuum Mazda lamp. The distance from the

wire to the wall of C was 3 to 4 mm., which is less than the mean free path of the molecules of the common gases at 10 microns' pressure.

The special form of Pirani gage¹ at P was capable of detecting the disappearance of 0.001 cu. mm. of gas, N. T. P., a quantity considerably less than that calculated to form a monomolecular layer of hydrogen on a surface area of one square centimeter. The trap at T was cooled with liquid air or solid carbon dioxide in methanol as occasion required. Mercury cut-offs, A-A', were used instead of stopcocks, and between them was attached a McLeod gage, range 0.01 to 100 microns. The total volume A to P, was about 75 cc.

Prior to a series of experiments and sometimes prior to each experiment, the apparatus was thoroughly baked out by flaming until a vacuum was obtained so low as to be unreadable on the McLeod gage. A small Tesla discharge brushed over the glass parts was found to be very effective in hastening the release of gases from the walls.²

The catalyst wire in C was heated electrically by making it one arm of a Wheatstone bridge, and its temperature was calculated from its resistance. The Pirani gage was calibrated against the McLeod gage with pure oxygen, pure hydrogen and electrolytic gas (2H₂:O₂). All gases used were carefully purified and stored in glass bulbs sealed to the line beyond the stopcock shown in Fig. 1. The electrolytic gas was generated from potassium-barium hydroxide solution with nickel electrodes. No gas was collected until the generator was evolving a gas mixture in equilibrium with electrodes and solution. The sample collected, 20 cc. N. T. P., furnished all the aliquots used in several hundred experiments.

The usual procedure for determining catalytic activity was to exhaust the apparatus thoroughly, introduce the gas, close A' and read the pressure on both the Pirani and McLeod gages. Then A was closed, the wire heated and the pressure change followed with the Pirani gage.

Experimental Results

Nature of the Reaction.—In the earlier experiments the platinum wires were never at any time heated above 500°. With electrolytic gas complete clean-up was seldom obtained, pure hydrogen being left when the reaction stopped. Figure 2 shows a typical rate curve with the wire at 90° and the tube wall at room temperature. In common with curves for many other experiments, there is an induction period at the start. This is followed by a section of curve which bends more and more pronouncedly in the opposite direction, not reaching zero pressure as demanded by theory if electrolytic gas reacted quantitatively to form water. The general shape of the curve shows that the catalytic formation of water on platinum is not a simple process.

When an equimolar mixture of hydrogen and oxygen was used, the clean-up was frequently as high as 90% instead of the 75% demanded by theory if water formation were the only reaction concerned. The gas left in this case was pure oxygen. The nature of the residue was easily ascertained by exhausting the McLeod gage, closing A', opening A and then comparing pressures read on the McLeod and Pirani gages. For example, if the actual pressure determined by the McLeod gage fell on the hydrogen calibration

¹ Tanner, *J. Phys. Chem.*, **34**, 1113 (1930).

² The Tesla coil was found much more effective when locating pinhole leaks if the apparatus contained a low pressure of hydrogen rather than air.

curve of the Pirani gage, introduction of oxygen always caused further reaction. A few typical results are given in Table I.

TABLE I
REACTION OF HYDROGEN-OXYGEN MIXTURES

Gas	Pressures, microns		Residue
	Initial	Final	
$2\text{H}_2 + \text{O}_2$	14.4	7.2	H_2
$2\text{H}_2 + \text{O}_2$	42.3	12.0	H_2
$2\text{H}_2 + \text{O}_2$	123.0	6.0	H_2
$\text{H}_2 + \text{O}_2$	19.7	2.2	O_2
$\text{H}_2 + \text{O}_2$	25.0	2.7	O_2

These results show that considerably more oxygen disappears than corresponds to water formation. This effect has been also noted by Langmuir,³ who attributed it first to oxidation of gases dissolved in the platinum, but later to evaporation of atoms from the surface and their subsequent combination with oxygen to form ozone, or with water vapor on the bulb walls to form hydrogen peroxide. The hypothesis of reaction with dissolved oxygen does not explain our results because the effect was observed after repeated heating and cooling in pure oxygen. If the atomic oxygen explanation is correct, there should have been a clean-up of oxygen after the reaction with hydrogen ceased, but this

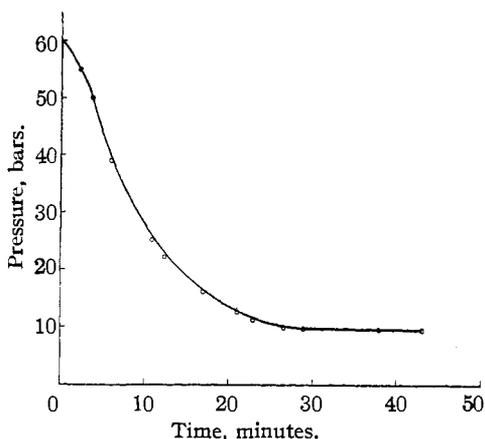


Fig. 2.—Rate of reaction of electrolytic gas on platinum.

was never observed at any temperature used for the catalysis experiments, *i. e.*, up to 380° . Hydrogen peroxide can be formed directly from its elements since its free energy of formation is half that of water,⁴ and it seems probable that it is formed directly on the catalyst surface.

The reaction at low pressures of hydrogen and oxygen on platinum has been widely quoted as a conspicuous example of a reaction retarded by one of the reactants.⁵ In one series of our experiments, the initial partial pressure of oxygen was kept constant and the hydrogen pressure varied fourfold. The results with the wire at 100° and the wall at liquid-air

³ Langmuir, *THIS JOURNAL*, 40, 1394 (1918); *Trans. Faraday Soc.*, 17, 621 (1922).

⁴ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 495.

⁵ Langmuir, *THIS JOURNAL*, 37, 1165 (1915); 38, 2291 (1916); *Phys. Rev.*, 8, 158 (1916); *Trans. Faraday Soc.*, 17, 654 (1922).

temperature are shown in Table II. Experiment 1 shows that oxygen in excess of electrolytic gas ratio has an accelerating effect on the reaction.

TABLE II

EFFECT OF VARIATION OF HYDROGEN CONCENTRATION				
Initial pressures, bars H ₂	O ₂	Ratio H ₂ : O ₂	Final pressure, bars	Minutes for re- action to stop
12.5	12.5	1:1	6.5	9
25	12.5	2:1	2.5	45
50	12.5	4:1	24.0	5

Experiment 3 shows that an excess of hydrogen over the amount present in electrolytic gas likewise accelerates the reaction. The composite nature of the reaction is still evident.

At much higher pressures Donnelly and Hinshelwood⁶ found the reaction rate to be independent of the hydrogen pressure.

After a wire had been seasoned by use for some time, the abnormal consumption of oxygen tended to disappear. Perhaps a fresh surface is composite, part of it promoting hydrogen peroxide formation and part water formation.

Wall-Temperature Effect.—When the tube containing the catalyst was surrounded by liquid air, the rate of the reaction was surprisingly accelerated.

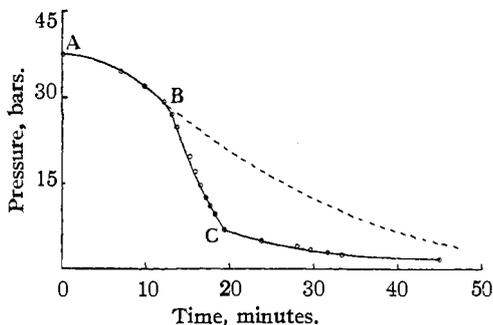


Fig. 3.—Effect of wall temperature on reaction rate of electrolytic gas.

Some acceleration would be anticipated because of the increased concentration of the reactants produced by cooling the tube. From Charles' Law, the increase in concentration by cooling from 298 to 90 Å., would be 3.3 to 1. At pressures where the mean free path is comparable with the diameter of the tube, the increase in concentration is the ratio of the square roots of the temperatures,⁷ in this case 1.8 to 1. This latter condition was approximately realized in the experiments, so that roughly the increase in concentration was 2 to 1 instead of 3 to 1. The increase in rate due to cooling the catalyst tube, although variable, was frequently as high as sixfold. The rate during the middle part of any one experiment with all temperatures constant changed comparatively little over small pressure differences. The effect is illustrated in Fig. 3. The curve from A to B shows the rate of reaction when the catalyst was at 200° and the wall at room temperature.

⁶ Donnelly and Hinshelwood, *J. Chem. Soc.*, 1727 (1929).

⁷ S. Dushman, *High Vacuum*, 135-36 (1922).

The steep slope of the curve from B to C shows the effect of placing liquid air around the catalyst tube, during which time the catalyst was maintained at 200°. Had no liquid air been used, the rate would have been more nearly described by the dashed line.

Unless the catalyst was specially activated (see below) no reaction occurred upon introducing electrolytic gas into the reaction tube when the catalyst and the tube wall were both at room temperature. If the wire only was heated, usually to 150°, a reaction started, increased in rate quite rapidly for the first few minutes, then settled down to nearly a straight line rate until the end was approached. If, however, the gas was introduced at room temperature and then both the wire and wall were heated simultaneously, no reaction occurred even by the time a temperature of 200° had been reached. If the wire was heated beyond this point and the wall held at 200°, reaction occurred when the wire attained a temperature of 300°.

Again, starting with a fresh sample of gas, with wire and wall at room temperature no reaction occurred. Placing liquid air around the wall did not start the reaction, but when the wire was heated for a few seconds to 100°, the reaction started. Lowering the temperature of the wire to room temperature retarded the reaction but did not stop it until the wall was brought to room temperature by removing the liquid air. When wire and wall were again at room temperature, no reaction occurred. In a qualitative way these effects, with but occasional unexplainable exceptions, could be reproduced.

Other reactions than that between hydrogen and oxygen were investigated, *e. g.*, the hydrogenation of ethylene, the oxidation of carbon monoxide, and the decomposition of nitrous oxide. Changes in the slope of the rate curve upon cooling the catalyst tube were found, but these changes were comparatively small. The wall-temperature effect is masked if the rate of a reaction varies with pressure. Since the rates of the above-mentioned reactions change with pressure, the small accelerations observed when the catalyst tube was cooled are difficult to interpret. All that can be safely concluded is that the wall effect, if shown at all by these reactions, is comparatively small.

The wall-temperature effect shown by electrolytic gas reacting on platinum is independent of the geometrical position of the wire with respect to the wall. In many experiments the catalyst was wound in a short helix and located axially within the tube. In other experiments it was arranged in long hairpin loops.

No difference in the effect was observed with fused silica or Pyrex glass walls.

Gold was substituted for platinum. The higher temperature to which the gold had to be heated to cause electrolytic gas to react, and the added complication of the reaction rate changing rapidly with pressure masked

the wall effect. So far as these few experiments apply, the conclusion is reached that any wall effect which gold may show is so small as to be obscured by other complications.

Super-activity.—Along with the study of the wall-temperature effect, experiments were performed in the hope of finding the most potent causes of variability in the activity of the catalyst. The rate curves (for the electrolytic gas reaction) showed high variation from one experiment to the next, and they were not always consistent with each other as to form. Some of the curves were straight lines, others were hyperbolas, and others were S-shaped. The latter were the most frequent. At the start of a reaction the rate would become accelerated, reach a steady state and then decrease. Some of this curvature may be due to the reaction not proceeding to the formation of water only. The induction period portion of the curve may be due to variation in the composite nature of the catalyst surface.

In order to find out whether or not outgassing the wire and apparatus had any important influence on activity, the wire and walls were baked out at about 400° for several hours, during which time the pumps were running. No unusual variation in results was observed. A silica tube was substituted for the glass tube, and the wire catalyst was suspended on silica supports. This was baked out at 700° with pumps running for five hours, but no unusual results were obtained. Next, the catalyst was heated to 900° while the walls were gently heated by a flame for one-half hour during exhaustion. This procedure activated the catalyst so highly that a sample of electrolytic gas reacted while being introduced even though both catalyst and wall were at room temperature. The reaction was nearly complete in two minutes. The rate was so surprisingly rapid in spite of the fact that no temperature difference existed between the wire and wall that measurement of the rate could not be made. It was necessary to cool the wall and catalyst with liquid air before introducing the sample in order to control the reaction. Careful heating of the wire from -180 to -120° initiated a reaction which went from an initial pressure of 10.6 microns to completion in three hours and ten minutes. The pressure was followed to the gage limit of 0.01 micron. As far as we are aware, this is the lowest temperature at which a catalytic reaction has been observed.

Later it was found that this super-active state of the wire could be induced merely by heating the wire for a few seconds (*in vacuo*) to 900°. Another platinum wire catalyst surrounded by a Pyrex wall behaved similarly. This shows that the effect was not peculiar to a particular wire, and that the silica tube was of no consequence.

The super-active state was not permanent. Even when the catalyst tube was kept surrounded by liquid air so that no condensable gas could contaminate the wire, the super-activity had largely disappeared after five hours.

Bone and Wheeler⁸ found that platinum was made more active if heated to 165° in pure hydrogen prior to the addition of electrolytic gas. They found that many other catalysts, metallic and otherwise, behaved similarly. Some of these catalysts were given a preliminary heating in oxygen. One sample of porcelain used as catalyst had its activity increased whether heated in hydrogen or oxygen. Another sample was activated only by hydrogen. Oxygen reduced the activity of silver, which fact has been confirmed by Chapman and Hall.⁹

Since platinum could be made super-active by heating *in vacuo* to 900°, in view of the Bone and Wheeler experiments one might expect an even greater degree of activation if platinum was heated to this temperature in hydrogen. The temperature at which reaction began was taken as the criterion for estimating super-activity. No substantial difference was found in this temperature whether the wire was heated *in vacuo*, or in hydrogen at 0.1 mm. pressure, or in oxygen at this pressure. The super-active state could be produced in a cryptocrystalline wire as well as in a macrocrystalline wire. The temperatures at which the reaction of electrolytic gas was initiated varied even in check experiments from -75 to -120°.

In one experiment the wire had to be heated to +60° to start the reaction which would have gone to completion in several minutes had the temperature not been reduced to -35°. During this same experiment if the walls and catalyst were made 0° the reaction stopped. With walls at 0° the catalyst had to be heated to 110° to cause a reaction which stopped if the catalyst was allowed to cool to the same temperature as the wall. If the catalyst was heated to 60°, the reaction would start when the walls were cooled with liquid air. Removal of the liquid air stopped the reaction.

This experiment shows that the wall effect persists when the wire is intermediate between ordinary and superactivity, and indicates that the effect is not dependent primarily upon the degree of activity. At the highest degree of activation the wall-temperature effect has not yet been investigated.

A possible explanation of the temporarily increased activity of the wire by high temperature treatment is the evaporation of surface contaminations caused by diffusion of gases from the interior of the wire. It is well known that nearly all metals contain dissolved gases, principally carbon monoxide and hydrogen, which are difficultly eliminated by any treatment short of melting the metal *in vacuo*. Experiments with platinum completely outgassed by melting are projected.

In any case, the effect of high temperature treatment observed here is

⁸ Bone and Wheeler, *Phil. Trans. Roy. Soc.*, 206A, 1 (1906).

⁹ Chapman and Hall, *Proc. Roy. Soc. (London)*, 124A, 478 (1929).

quite the opposite of that which would be expected from current theories of sintering active metal areas by heat treatment. In the case of finely divided catalysts sintering must effect a reduction of surface and hence lessened activity. In the case of wires, the macrocrystalline one, whose sintered surface was obvious, was quite equal in activity to a cryptocrystalline one. This fact taken in conjunction with the remarkable activity at -120° of the heat-treated wire shows that sintering is of no consequence, at least in the case of platinum wires.

Summary

1. A study of the hydrogen-oxygen reaction at low pressures on platinum wires has been made.
2. The reaction is not as simple as is commonly supposed. An excess of oxygen may react. This fact is here attributed to hydrogen peroxide formation from the elements.
3. The activity of platinum is variable even under carefully controlled conditions.
4. The rate of this reaction varies with the temperature difference between the wire and the wall of the containing vessel.
5. Flashing the wire at 900° in vacuum, hydrogen or oxygen induces super-activation which decays after some hours. A wire in the super-active condition causes an easily measurable rate of reaction at as low a temperature as -120° .

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ELECTRIC MOMENT AND MOLECULAR STRUCTURE. III. DOUBLE AND TRIPLE BONDS AND POLARITY IN AROMATIC HYDROCARBONS

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The electric moments of simple molecules containing double and triple bonds have been investigated with the object of determining the polarities of these bonds and their relations to structure¹ and these results, together with those of Errera for acetylene dihalides,² have been examined in the light of electronic theories of valence.³ The need of further accurate measurements upon molecules in which ethylene and acetylene hydrogens are replaced by hydrocarbon groups has been evident for some time. An unusual opportunity for such measurements arose through the kindness of Professor Donald H. Andrews of the Johns Hopkins University, who

¹ Smyth and Zahn, *THIS JOURNAL*, **47**, 2501 (1925).

² Errera, *Physik. Z.*, **27**, 764 (1926).

³ Smyth, *THIS JOURNAL*, **51**, 2380 (1929); *Chem. Rev.*, **6**, 549 (1929).