

The Diffusion of Hydrogen through Palladium

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The high rate at which hydrogen can diffuse through heated palladium was first demonstrated by Thomas Graham. His experiments on gases in metals began in 1866, when he was Master of the Mint (1). Three years earlier, in 1863, Sainte-Claire Deville and Troost (2) had shown that hydrogen diffused rapidly through homogeneous plates of fused iron and platinum. Graham's original objective appears to have been to confirm the findings of these workers, to improve upon their experimental methods, and to study the effects of gases on other metals.

He showed that the only gas capable of diffusing through platinum was hydrogen. Appreciable quantities of this gas permeated through the walls of a platinum tube at a dull red heat. The solubility of hydrogen in platinum was considerable. In one instance a fused platinum rod heated at 230°C in hydrogen was found to absorb 1.45 times its own volume of the gas.

Graham's Experiments

These surprising results led to a similar series of experiments with palladium. Graham relates that the only specimen of this metal he was at first able to obtain was in foil form and weighed 1.58 gm. After first degassing *in vacuo* it was allowed to cool slowly in hydrogen from 245°C, and was found at room temperature to have dissolved 526 times its own volume of this gas. Further heating at 90–97°C in hydrogen increased the room temperature solubility to 643 relative volumes.

By this time a compact tube of palladium 1 mm in thickness had been made by George

Matthey. This tube had been rolled up and hammer welded from sheet made from powder and forged near the melting point of the metal. It was 115 mm in length and 12 mm in internal diameter. One end was closed by a thick plate of platinum which was soldered on. The other end was connected to a Sprengel pump by means of a platinum tube. The complete assembly was surrounded by a porcelain tube and a continuous current of hydrogen was passed through the annular gap. The palladium tube became permeable to hydrogen at 240°C and at a slightly higher temperature the rate of diffusion was several cc per minute. Only hydrogen was able to penetrate the tube, which was capable, however, of extracting this element preferentially from mixtures such as coal-gas.

Graham was greatly impressed by the extraordinary affinity of palladium for hydrogen. Because the amount of dissolved hydrogen varied over a wide range he concluded that the effects could not be explained by the formation of a definite compound, and that the "occluded" gas (a term specially invented by him to describe the effect) probably formed a true alloy with the palladium.

In order to account for the large increases of volume which resulted when palladium was heavily charged with hydrogen, tremendous mechanical forces would be required. Graham concluded that hydrogen could only exert such forces when present as a metal, which he called hydrogenium. The density of hydrogenium, calculated from that of fully charged palladium, appeared to be 1.708 gm per cc.

It was believed that the metallic hydrogen concept was supported by the results of experiments on meteoric irons which in some instances contained nearly three times their own volume of this gas. Ordinary wrought iron could not be induced to dissolve more than its own volume of hydrogen at atmospheric pressure. These facts, supported by spectroscopic evidence, led to the hypothesis of hydrogenium as an essential constituent of many types of star.

Other Early Researches

Troost and Hautefeuille (3) were led by the results of their researches in 1874 to conclude that hydrogen reacted with palladium to form a definite compound Pd_3H . This compound, once formed, was supposed to dissolve large volumes of hydrogen, thus explaining the wide composition range encountered. Hoitsema (4) in 1895 was able to show with the aid of some previously unpublished results of Roozeboom that the pressure solubility data could only be satisfactorily interpreted in terms of the formation of two non-miscible solid solutions. This is precisely the view now held. The more detailed X-ray and metallographic evidence now available confirms Hoitsema's original conception of the equilibrium diagram of the palladium hydrogen system.

Ramsay (5) suggested in 1894 that the hydrogen, during its passage through the walls of palladium membrane, was probably in atomic form. This hypothesis was confirmed by Winkelmann (6) in 1901, who showed that this dissociation of molecules into atoms on the surface of the palladium explained why the diffusion rate varied as the square root of the pressure difference across the membrane.

Much of the subsequent research work on palladium hydrogen dealt with more theoretical aspects of the system. Very exact determinations of the equilibrium solubilities and phase relationships have been made and much attention has been devoted to the pro-

nounced hysteresis effects observed when the two phases are present simultaneously.

Attempts to utilise the remarkable permeability of palladium to hydrogen for industrial purposes have not been energetically pursued until comparatively recently. Palladium thimbles were of course used for purposes such as the introduction of small quantities of pure hydrogen into gas analysis apparatus. In these instances the palladium septum was used only intermittently and the rate of diffusion was usually a secondary consideration. The metal, when cooled down, dissolved large volumes of pure hydrogen which could be discharged to the evacuated side of the system merely by gentle reheating. The palladium under these conditions acts merely as a pump.

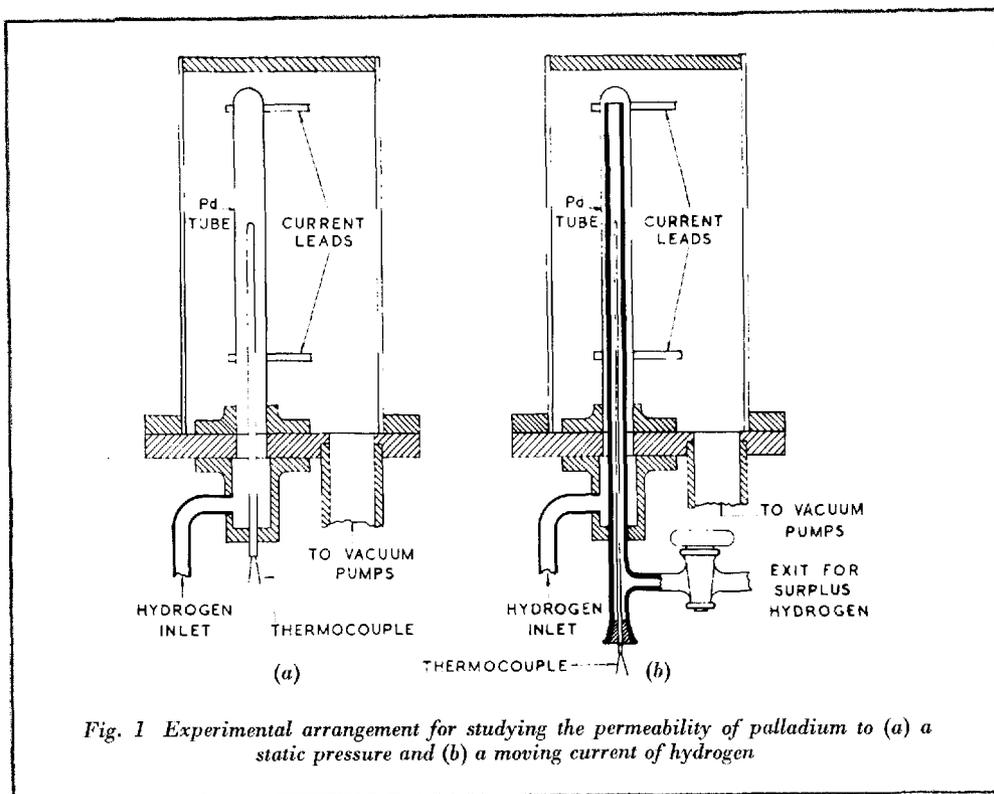
Under steady conditions, however, the rate of diffusion of hydrogen was very variable. Barrer reported in several of his papers that palladium, depending upon the treatment it had received, might be either permeable or impermeable to hydrogen, and Lombard (7) stated that the permeability could be reduced by more than a hundredfold merely by heating the metal.

This capricious behaviour made palladium unsuitable for industrial applications, since it meant that the performance of a diffusion unit would be unpredictable. The metal was expensive and potential industrial applications rather limited. These factors did not encourage extensive research on the variable permeability of palladium to hydrogen in the years before 1939.

Potential Industrial Applications

Developments of the immediate post-war period altered to some extent the basic problems of chemical engineering with the result that considerable interest is now being displayed in the behaviour of palladium as a semi-permeable membrane.

Obvious applications occur in the field of atomic energy where the separation of hydrogen isotopes is an essential process. The preferential diffusion of the lighter



isotope through palladium facilitates the separation process whether this is carried out directly from the gas phase at high pressure or at atmospheric pressure in electrolytic cells. The hydrogen deuterium separation factor is between four and five at room temperature and, by utilising the electrolytic migration of hydrogen through palladium membranes, the electrical requirements for electrolytic separation can be reduced considerably (8).

Potential large scale applications for palladium are also associated with the development of new refining methods in the petroleum industry. Efficient methods for the control and removal of hydrogen which builds up in cracking units and restrains the catalytic action are required, and the use of palladium has been suggested in this connection.

What is perhaps the most intriguing possibility is concerned with the direct production of power by electrochemical methods. The efficiency with which elec-

trical energy can be derived from fuel by mechanical methods is limited by restrictions imposed directly by Carnot's cycle and the Second Law of Thermodynamics, with the result that even the most modern power stations can utilise successfully only about one-third of the fuel with which they are supplied. Voltaic cells, which produce electrical energy by the oxidation of metal plates, can under certain conditions have a "thermal" efficiency approaching 100 per cent. Primary cells of this type have, of course, been used for many years but are generally considered to be unsuitable for the economic production of electricity on a large scale. This world shortage of fuel has, however, stimulated interest in the possibilities of "fuel cells" in which electrical energy is produced directly by the oxidation of coal, gas and oil under carefully controlled conditions (9, 10, 11).

All the various types of cell proposed depend upon the removal of electrons from

the fuel electrode and their transfer, via an external path, to the oxidising electrode by which they are consumed. An essential feature of the electrolyte employed is that it should prevent the molecular forms of the fuel and oxidant from mixing and transferring their electrons directly. In view of the semi-permeable character of palladium it is inevitable that it should have been considered as a material of great potential value for this type of work. It is doubtful whether any commercially successful cell will ever utilise pure hydrogen as a fuel. A semi-permeable membrane evolved for industrial use will have to deal with impure hydrogen and hydrocarbon vapours if it is to be successful.

Recent Experimental Work

Factors likely to have some bearing on the rather unpredictable permeability of palladium have been made the subject of a recent investigation in the Johnson Matthey Research Laboratories. Attention has been directed primarily toward determinations of the specific permeability to hydrogen after the establishment of conditions necessary for reproducible behaviour. Circumstances leading towards the severe distortion and cracking which frequently results in the destruction of palladium diffusion membranes have also been studied. Although the research has not yet been completed, it is felt that some of the results at present available are of sufficient interest to justify their inclusion in this article.

The first experiments were made using an apparatus similar to that shown in Fig. 1 (a). Hydrogen of commercial quality was fed at atmospheric pressure, via a flowmeter, to the interior of a palladium tube with a closed end. This tube was heated by the direct passage of a heavy current and temperatures were measured by the internal thermocouple shown. The space surrounding the palladium tube was evacuated. Measurements of the rate

of diffusion of hydrogen through the walls of the tube were obtained from the flow-meter and confirmed by the rate of rise of pressure on the evacuated side of the system when this was sealed off from the pumps.

The results obtained with this arrangement were rather surprising because it was found that very little hydrogen diffused through the tube. The permeability increased to a maximum at about 115°C after which it decreased rapidly. Whenever the temperature was held constant the permeability decreased until overnight annealing at 700°C reduced the amount of hydrogen diffusing through the tube walls to a negligible value. The tube was then vacuum annealed *in situ* at 800°C and retested. This annealing treatment reduced the rate of diffusion at lower temperatures still further.

These results were typical of many which were obtained using several different tubes and the experimental arrangement shown in Fig. 1 (a). Although confirming to some extent the findings of previous workers, the

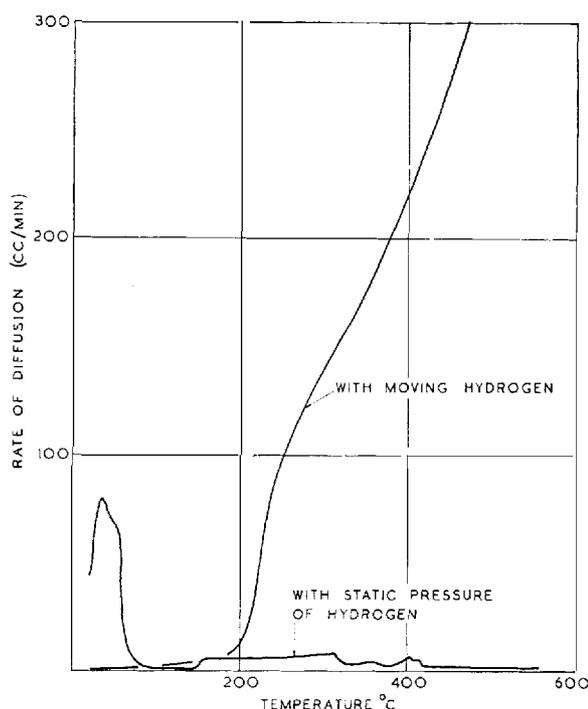


Fig. 2 Permeability of palladium tube with static pressure and moving current of hydrogen

results were difficult to understand because it was known that in many applications large volumes of hydrogen diffused continuously through palladium. It was felt that the palladium was becoming poisoned in some way. Oxidation followed by reduction, suggested by Lombard as a reactivation technique, was found to produce only small temporary improvements in permeability.

A paper by Davies (12) which became available at this stage suggested that hydrocarbon vapours were the chief factors causing poisoning of palladium. Experiments were therefore undertaken in which sources of organic vapours were eliminated from the apparatus by the use of mercury pumps and liquid air traps. In spite of these precautions it was not possible to maintain a high degree of permeability through a palladium tube at temperatures much above 150°C.

Experiments with a Moving Hydrogen Atmosphere

Palladium tubes in gas analysis apparatus are frequently heated under conditions which permit slight oxidation of the outer surface. This suggested a new approach to the problem and led to a number of *ad hoc* experiments in which evacuated palladium tubes were gently heated externally with an oxy-hydrogen flame. All the tubes tested in this manner allowed large volumes of hydrogen to diffuse through from the flame but

limitations of the apparatus prevented any determination of the quantities involved. The results were sufficient to show that high rates of diffusion were possible when oxygen was present in a hydrogen atmosphere which was in continuous movement over the surface of the tube.

Subsequent experiments showed that the presence of oxygen was not necessary and that high rates of diffusion were maintained so long as the hydrogen atmosphere surrounding the tube was in constant movement. In order to investigate the effect in greater detail the original apparatus was modified to provide the arrangement shown diagrammatically in Fig. 1 (b).

With this arrangement either a static pressure or a continuous flow of hydrogen could be maintained inside the diffusion tube. Fig. 2 illustrates some typical results obtained with and without an internal gas flow through the tube. The beneficial results of gas circulation are very evident from this illustration.

The rate of gas circulation required to maintain a high degree of permeability was surprisingly small and corresponded roughly to an excess flow rate of 25 cc per minute when hydrogen was diffusing through the walls of the palladium tube at a rate of 500 to 600 cc per minute. When this excess flow rate was completely stopped so that a static hydrogen pressure was main-

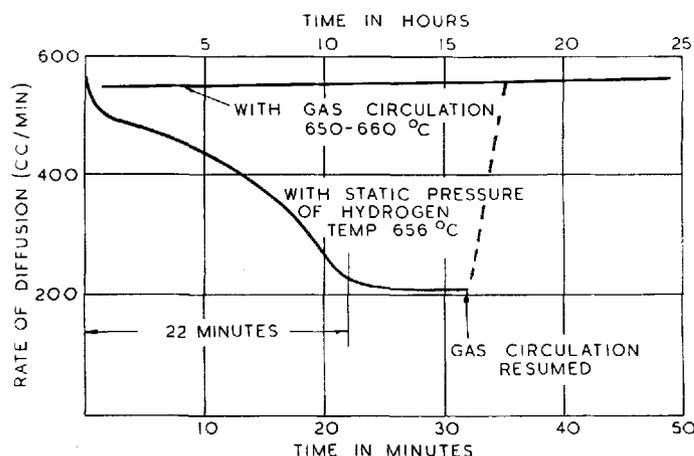


Fig. 3 Curves showing the rapid decrease of permeability which occurs without a continuous circulation of hydrogen

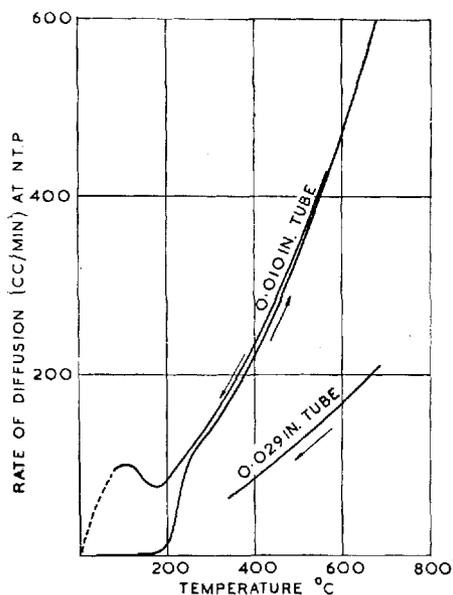


Fig. 4 Curves showing the rate of diffusion of hydrogen through palladium tubes at various temperatures

tained inside the tube, the rate of diffusion decreased rapidly as can be seen from Fig. 3. In this instance the rate of diffusion decreased from 546 to 210 cc per minute in a period of 32 minutes after the gas circulation had stopped, and regained its original value three minutes after the gas circulation was resumed. The upper curve on this figure shows that no decrease of permeability occurred over a 24-hour period when the gas circulation was maintained.

Results such as these suggest that the low permeability under static conditions is caused not by poisoning in the commonly accepted sense, but more probably by the formation, under stagnant conditions, of an inert layer of impurity gases either on, or near, the surface at which the hydrogen enters the palladium membrane. The impurities responsible for this effect have not yet been determined. A progressive decrease of permeability occurs under static conditions even when the hydrogen supplied to the tube has been freed from oxygen, nitrogen, and water vapour.

Consistent and reproducible results are,

however, obtained with a stream of gas, and Fig. 4 illustrates some typical experimental results. The rate of diffusion was found to vary inversely with the tube thickness and when this factor was allowed for, all the tubes tested had similar degrees of permeability. Fig. 5, in which the specific permeability, expressed in cc per minute per square cm per mm thickness for a pressure difference of 760 mm, is plotted against the temperature, summarises most of the results of this work.

The continuous circulation technique appears therefore at the present time to provide a satisfactory solution to the permeability problem under certain conditions, although its effectiveness under different types of industrial environment has yet to be assessed.

Effects of Repeated Heating and Cooling in Hydrogen

Palladium diffusion tubes frequently crack and distort badly in service even when they have been kept continuously in hydrogen. Cracks originate at the grain boundaries although they may eventually spread to the interior of the grain. The evidence at present

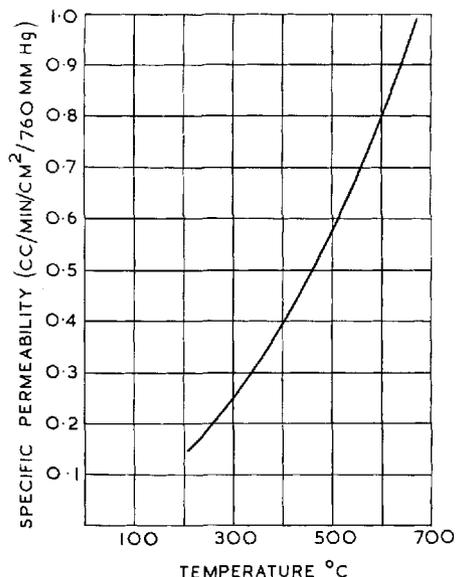


Fig. 5 Specific permeability of palladium to hydrogen

available suggests that the tendency towards cracking and distortion increases with the grain size of the material.

The dimensional changes which occur when palladium is heated and cooled in hydrogen have been almost completely ignored in the literature, although the general effects were discussed by Graham as early as 1866. Effects produced by the sudden expulsion of hydrogen from electrolytically charged foils and wires were studied by Loessner (13) in 1911 and by Krause and Kahlenberg (14) in 1935. D. P. Smith (15) seems to have been the first to associate these dimensional changes with the accompanying alpha-beta phase transformations. Experiments in these laboratories have shown that very spectacular effects can be produced by merely heating and cooling palladium in hydrogen at atmospheric pressure. Under these conditions the critical temperature range is between 100° and 250°C.

Thin sheet specimens were heated electrically in hydrogen at atmospheric pressure for 15 minutes at high and low temperatures alternately. Cycling between room temperature and 700°C resulted in considerable

distortion, blistering and thickening of the sheet. Similar results were obtained when the temperature was cycled between 20°C and 350°C. Temperature changes between 700°C and 350°C produced relatively little effect, however, and distortion of the specimen cycled between 700°C and 250°C occurred only at the ends which, being held in copper clamps, were probably well below the average specimen temperature.

Considerable distortion occurred when the specimen was allowed to cool to 100°C, and when the lower temperature was reduced to 75°C blistering, thickening and general change of shape were very pronounced.

The damage at atmospheric pressure appears therefore to be caused by phase transformations in the temperature range 100–250°C. The value of the critical temperature will depend upon the operating pressure. As the beta phase is unstable above 310°C even at the highest pressures, it appears reasonable to suggest that the effective life of industrial diffusion units could be considerably prolonged by maintaining them continuously above this temperature.

References

- 1 T. Graham Collected Chemical and Physical Researches, Ed. R. Angus Smith, Edinburgh, 1876
- 2 H. Sainte-Claire Deville and *Compt. rend.*, 1863, **56**, 977–983;
L. Troost 1863, **57**, 965–967
- 3 L. Troost and P. Hautefeuille *Compt. rend.*, 1874, **78**, 686–690
- 4 C. Hoitsema *Z. physikal. Chem.*, 1895, **17**, 1–42
- 5 W. Ramsay *Phil. Mag.*, 1894, **38**, 206–218
- 6 A. Winkelmann *Ann. Physik.*, 1901, **6**, 104–115
- 7 V. Lombard, C. Eichner and M. Albert *Bull. Soc. Chim. France*, 1936, **3**, 2203–2220
- 8 O. N. Salmon U.S. Atomic Energy Comm., Report KAPL-1272
- 9 R. G. H. Watson *Research*, 1954, **7**, 34–40
- 10 A. P. Paton *Elect. Rev.*, 1952, **151**, 888–890
- 11 Pittsburgh Consolidation Coal Co. British Patents 680, 982 (1951) and 690, 544 (1952)
- 12 W. D. Davies U.S. Atomic Energy Comm., Reports KAPL-1227
and KAPL-1375
- 13 F. Loessner Dissertn., Leipzig 1911
- 14 W. Krause and L. Kahlenberg *Trans. Electrochem. Soc.*, 1935, **68**, 449–469
- 15 D. P. Smith Hydrogen in Metals, University of Chicago Press,
1948