

The Separation of Hydrogen from Gas Mixtures

A PROCESS OF ABSORPTION AND DESORPTION BY PALLADIUM

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A pressure-cycling process has been developed by which hydrogen can be separated from gas mixtures using palladium sponge as an absorbent. At a temperature of 200°C, with pressure cycling between 1 and 35 bar, and a cycle time of 20 seconds, hydrogen of 99.5 per cent purity can be obtained from 75 per cent hydrogen-25 per cent nitrogen mixtures at a rate of 6 litres/hour per gram of palladium and a yield of 80 per cent.

The study of the palladium-hydrogen system spans more than one hundred years and many investigators have examined the relationships between hydrogen pressure, the concentration of hydrogen in palladium and temperature at equilibrium. Such relationships are generally expressed in the form of isothermal plots of gas pressure against gas concentration in the metal. A recent example of such a set of curves is shown in Fig. 1 (1, 2, 3, 4). Isotherms corresponding to temperatures below about 300°C indicate that the gas pressure initially rises steadily with increasing gas concentration until a critical pressure is reached, when the pressure remains constant over a range of concentration. Beyond this range the pressure continues to rise once again with increasing gas concentration in the metal. Isotherms corresponding to the absorption and desorption of hydrogen at a specific temperature show hysteresis. (Everett and Nordon) (5).

It is now generally accepted that when palladium absorbs hydrogen two non-stoichiometric phases are formed (6), an α -phase existing at gas pressures below the critical pressure, consisting of a solid solution of hydrogen in palladium with a face-centred cubic structure with a parameter of

about 3.89 Å, and a β -phase existing at pressures above the critical pressure, also with a face-centred cubic structure but with a parameter of about 4.02 Å. The compositions of these phases depend on temperature and pressure. At the critical pressure the two phases coexist, the compositions of the α and β phases corresponding with the lower and upper ends of the composition range respectively. Formation of both phases is exothermic and, correspondingly, decomposition is endothermic.

Much effort has been directed to studying the diffusion of hydrogen through palladium and this work has been summarised by Makrides and Jewett (7). The high diffusion rate has been exploited commercially in the diffusion process of hydrogen purification. However, the combined characteristics of high solubility in palladium and a high diffusion rate through the metal offer the possibility of another means of hydrogen purification. Palladium could be charged with hydrogen from a hydrogen-containing mixture under conditions of temperature and pressure which favour a high solubility of the gas in the metal, and subsequently the hydrogen could be recovered by altering the conditions to those which favour low solu-

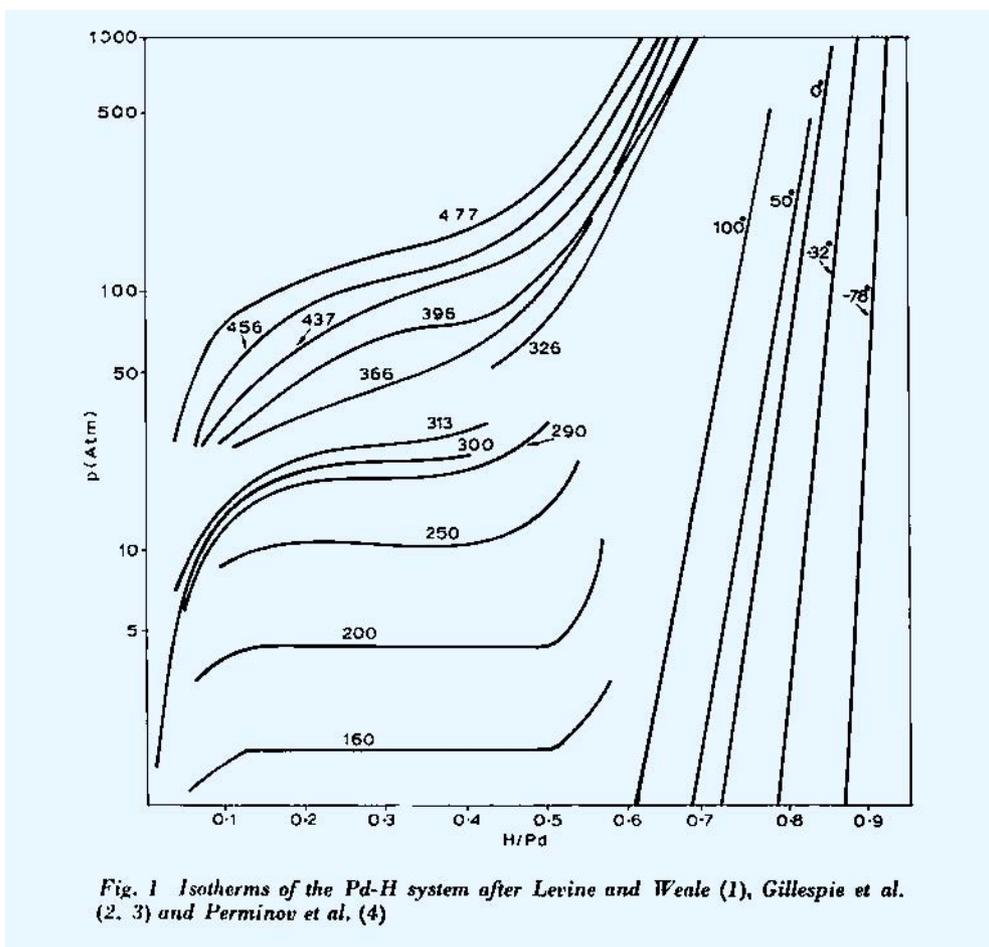


Fig. 1 Isotherms of the Pd-H system after Levine and Weale (1), Gillespie et al. (2, 3) and Perminov et al. (4)

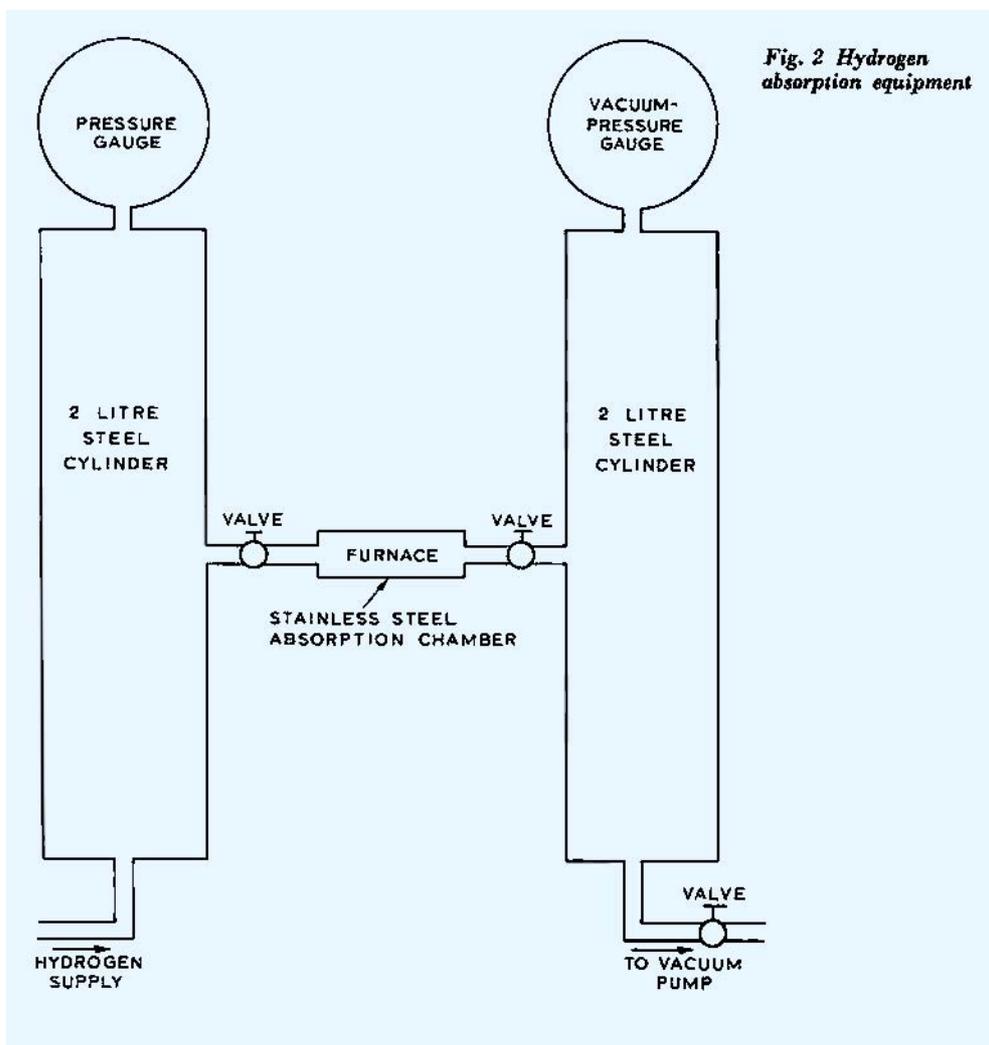
bility. Towards the end of the last century, Morley (8) used a simple method of this sort to separate hydrogen from nitrogen by absorbing hydrogen at low temperature and later expelling the gas by heating the metal. More recently Boice and Salmon (9) have described a method based on the same principle. Hydrogen was absorbed from the gas mixture by palladium at -78 to -100°C and was later recovered at 200 to 350°C . In this second process, while the rates of gas absorption and desorption were high at the temperatures used, the time taken to change the temperature of the palladium mass was long and, consequently, the process of separation as a whole was slow. As gas pressure is a factor that could be more readily changed

than temperature, it would seem that a more rapid process might be developed based on pressure change while keeping temperature sensibly constant. The feasibility of developing such a process is the subject of this study.

Basic Principles

A pressure-dependent absorption-desorption process could consist of three principal steps: absorption, purge and desorption.

Absorption: A hydrogen-containing gas mixture at high pressure would be fed continuously through the inlet valve of an absorption chamber containing a porous mass of palladium. Some hydrogen would be absorbed by the metal, and to maintain a hydrogen-rich atmosphere in the chamber,



hydrogen-depleted mixture would be released through an outlet valve. At the end of this step the palladium would be charged with hydrogen; some gas mixture would be trapped in the free space of the chamber.

Purge: During this step the inlet valve would be closed and the pressure reduced to a level at which some hydrogen would desorb from the metal flushing the impure gas out of the chamber and leaving a hydrogen atmosphere in the free space.

Desorption: The bulk of the hydrogen would be allowed to desorb from the metal at the reduced pressure.

By repeating these steps in sequence, intermittent outputs of hydrogen and hydrogen-depleted mixture would be produced. For such a process to work at an acceptable rate, a temperature level would have to be found at which both the absorption and desorption rates were fast at the respective pressures. It might be anticipated that the hydrogen absorption and desorption rates would be dependent on the nature of the palladium mass, its porosity, surface area, weight and geometry.

A feasibility study was planned to follow four stages:

- (1) Determination of absorption and desorption rates of hydrogen by palladium masses of differing porosity.
- (2) Separation of hydrogen from the mixture 75 per cent hydrogen–25 per cent nitrogen to test the principle of a fast separation process.
- (3) Separation of hydrogen from other gas mixtures containing those gases which are commonly associated with hydrogen in industrial gas streams.
- (4) Examination of the possibility of scaling-up the process to reach a minimum level of hydrogen output and purity thought to be of practical value, i.e. 1.5 m³/h and 99.5 per cent.

Experimental Procedure

Two types of palladium powder were used in the investigation. One type, of Fisher particle size 2.4 μm, had been prepared by firing palladosamine chloride in air at 450–500°C and then pulverising and sieving to less than 300 mesh, while the other of Fisher particle size 11.6 μm, had been prepared by firing the salt at 900°C and then pulverising and sieving to less than 16 mesh. Test specimens were prepared by hydrostatically pressing these powders into cylindrical compacts of density 2.5 to 8 kg/dm³. The specimens fitted snugly into the absorption chambers used leaving a minimum volume of free space.

The gases used in the study were hydrogen and hydrogen mixtures containing 10 per cent of either methane, ethylene, carbon monoxide, or carbon dioxide, 25 per cent nitrogen and up to 1 per cent hydrogen sulphide. They were fed directly to the equipment from cylinders without pretreatment.

Determination of Rates of Absorption and Desorption

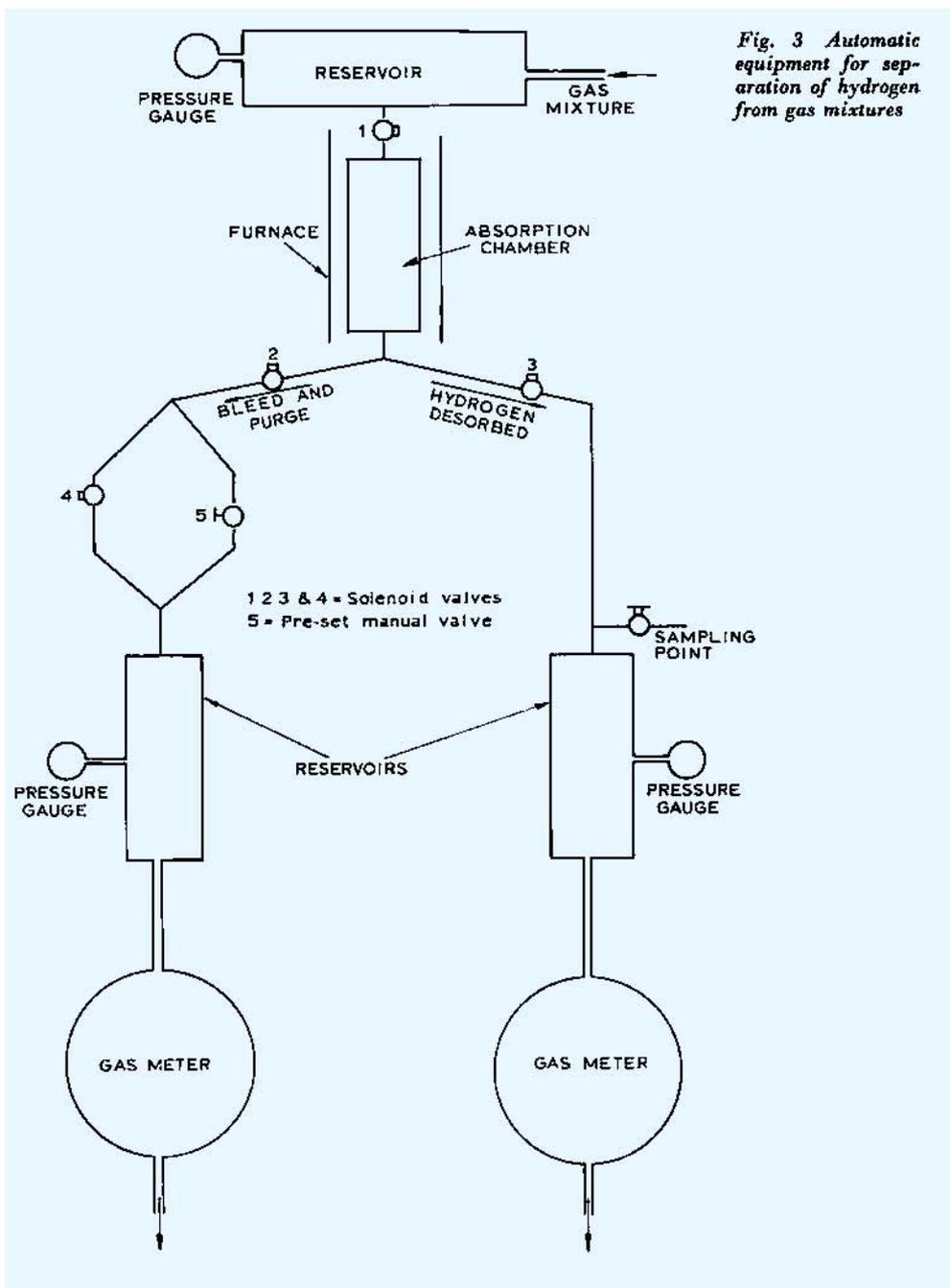
Palladium powder was pressed into cylindrical compacts 63.5 mm long, 12.7 mm diameter and of density 2.5 to 7.4 kg/dm³. The specimens were inserted into a snugly-fitting stainless steel absorption chamber which was heated to the desired temperature

within the range 150 to 240°C (Figure 2). Hydrogen at 3.1 to 14.6 bar was admitted into the chamber and held there for 5 seconds to 30 minutes. The absorbed gas was subsequently allowed to desorb for up to 30 minutes into a reservoir initially either evacuated or containing hydrogen at pressures up to 2 atmospheres. From the pressure changes that occurred in the reservoir, the quantities of hydrogen desorbed were calculated, an allowance being made for the quantity of gas trapped in the free space of the chamber and valves.

Separation of Hydrogen from Gas Mixtures

Figure 3 is a schematic diagram of the automatic equipment used to separate hydrogen from gas mixtures. The absorption chamber included in the equipment was the one that was used previously to establish the absorption and desorption rates, and the test specimen had the same dimensions, its density and weight being 6 kg/dm³ and 48 g respectively.

Gas mixture at 14 to 35 bar was fed into the chamber and the palladium allowed to absorb hydrogen for 1 to 8 seconds while hydrogen-depleted mixture was bled away at a rate predetermined by a downstream manual valve. The inlet valve was then closed and the gas pressure was allowed to fall to near atmospheric pressure for about 0.1 second, so allowing the free-space gas to join the hydrogen-depleted stream. Finally, the bulk of the hydrogen was allowed to desorb from the palladium at atmospheric pressure for 1 to 8 seconds. This series of steps was repeated in sequence producing two intermittent gas streams of hydrogen and a hydrogen-depleted mixture. Volumes of gas were recorded by gas meters downstream of the absorption chamber. The rate of input of gas could not be controlled directly but was determined by adding the output rates of hydrogen and hydrogen-depleted mixture. The purity of the hydrogen desorbed in this manner was determined by gas chromatography.



Results

Figures 4A, B, C, D illustrate the effects of time, temperature and pressure on the absorption and desorption of hydrogen by palladium. Figures 5A and 5B illustrate

the effects of bulk density of the compacted palladium on the absorption and desorption characteristics. All of the gas volumes have been reduced to the standard conditions of pressure and temperature.

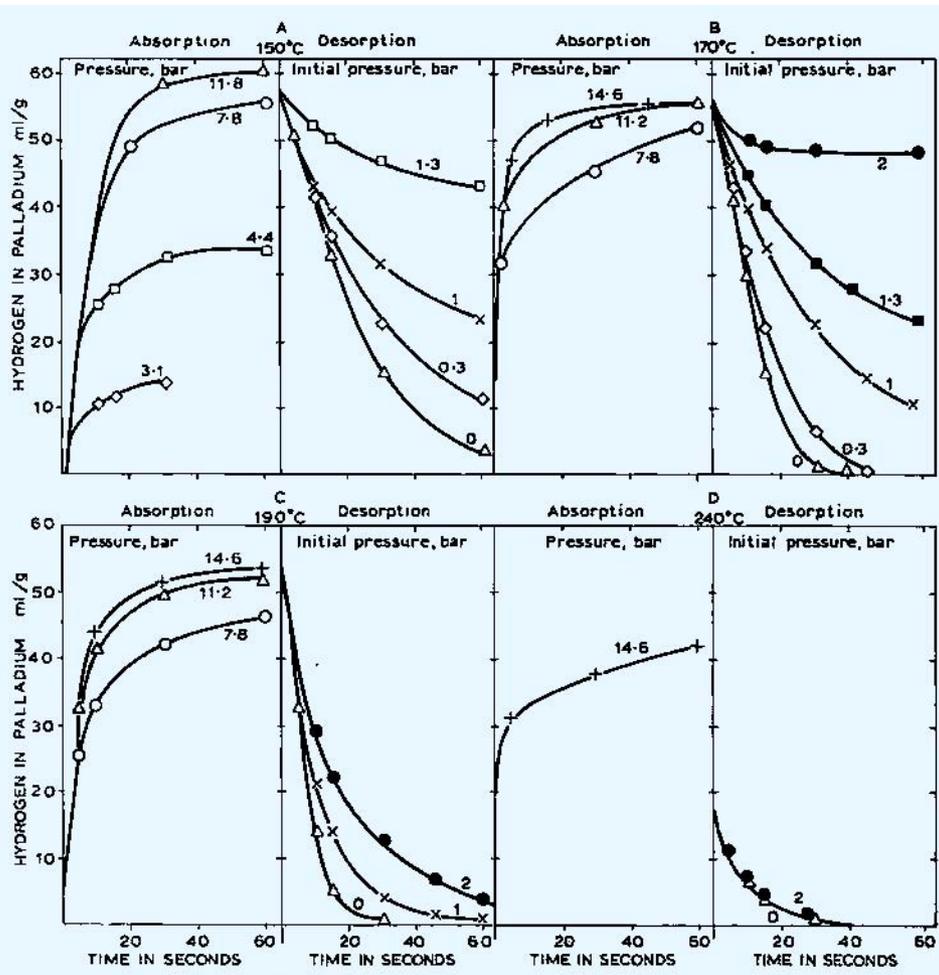


Fig. 4 The effects of time, temperature and pressure on the absorption and desorption of hydrogen by palladium. Bulk density of palladium 2.5 kg/dm³ and Fisher particle size 2.4 μm

Factors favourable to both the rate of hydrogen absorption and the amount absorbed are low temperature and high pressure. Factors favourable to the rate of desorption are high temperature and low pressure, though at 240°C (Fig. 4D) the rate of desorption was not altered between 0 and 2 bar.

Increasing the bulk density of the palladium between the limits of 2.5 and 7.4 kg/dm³ had only a small effect in decreasing the rate of absorption or the amount of hydrogen absorbed (Figs. 5A and 5B), and though high bulk density decreased the desorption rate at

lower temperatures, the effect was not great at 210°C (Fig. 5B). Absorption and desorption rates at temperatures between 170 and 240°C were not significantly different for two grades of palladium of average particle diameters 2.4 and 11.6 μm, though it might be anticipated that if palladium of significantly greater particle size had been studied, the absorption and desorption rates would have been smaller as the surface area exposed to the gas would have been smaller.

Thermocouples sited in the wall of the absorption chamber and close to the pal-

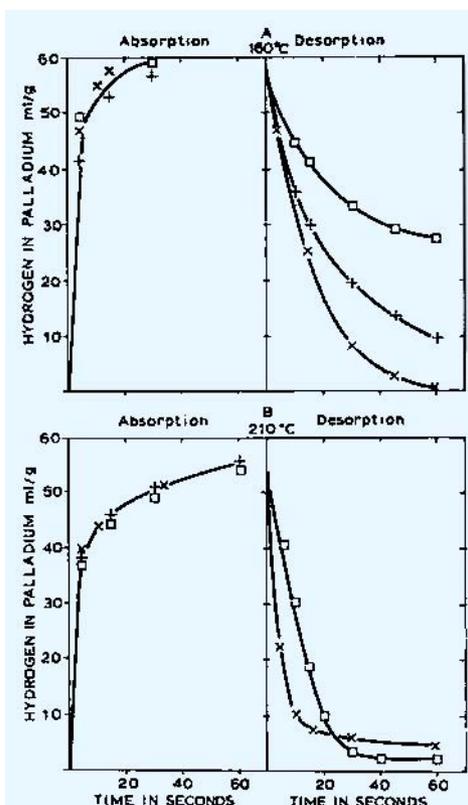


Fig. 5 Effects of the bulk density of the compacted palladium on the absorption and desorption characteristics. Absorption pressure 14.6 bar and desorption pressure initially 0 bar. Fisher particle size 2.4 μm . Bulk density of palladium:

- × 2.5 kg/dm^3
- + 5.1 kg/dm^3
- 7.4 kg/dm^3

ladium mass indicated increases in temperature of up to 10°C during absorption, and corresponding decreases in temperature during desorption. These changes were associated with the exothermic and endothermic natures of absorption and desorption, respectively. No measurements of temperature fluctuations in the palladium itself were made.

The rates of absorption and desorption of hydrogen, which were initially very rapid, fell appreciably as saturation or exhaustion was approached (Figs. 4 and 5). Maximum

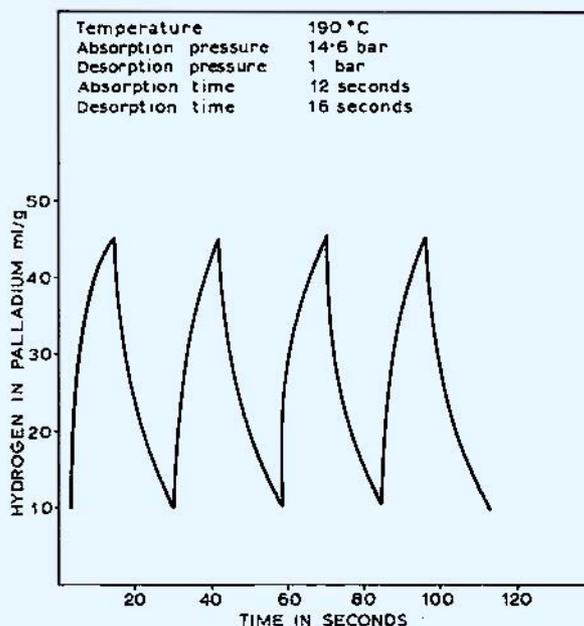
rates of hydrogen throughput would involve a time cycle confined to the steeper portions of these curves. For example, consider Fig. 6 based on the absorption-desorption data for 190°C (Figure 4C), which shows how under selected conditions, the hydrogen content of the metal could be changed rapidly from 10 to 45 ml/g for each cycle of 28 seconds. So if no hydrogen were lost in a purge step an estimated hourly output of hydrogen of 4.8 l/g might be maintained. The other data could be analysed in the same way.

If a sub-atmospheric pressure were chosen for desorption an evacuating pump would be a necessary part of the separation equipment. Also there would be the risk that air might leak into the system during the desorption step and form an explosive mixture with hydrogen. Consequently it was decided to choose conditions under which the gas would desorb at a little above atmospheric pressure. By stipulating a minimum desorption pressure a limit was then set on the temperature, for at 170°C and below, desorption was slow. A temperature of about 240°C seemed a suitable upper limit to temperature, for higher temperatures would mean higher absorption pressures and consequently greater quantities of gas mixture trapped in the free-space. Therefore at higher temperatures it might be more difficult to purge the system of impure gas.

Separation of Hydrogen from Gas Mixtures

In the separation of hydrogen from 75 per cent hydrogen–25 per cent nitrogen, the mean output rate increased with greater hydrogen input, higher absorption pressure, and shorter cycle time. Factors favourable to increased mean output rate were also associated with lower extraction of hydrogen from the gas feed; for example, when the hourly output was 6 l/g the extraction level was 80 per cent, but when the output was raised to 8 l/g palladium by increasing the bleed, the extraction level fell to 50 per cent. The purity of the hydrogen produced was about 98 per cent for all tests.

Fig. 6 Rapid changes in the hydrogen content of palladium induced by changes in gas pressure, each cycle lasting 28 seconds



In a continuous 50 hour test, hydrogen was extracted from 75 per cent hydrogen–25 per cent nitrogen at the average hourly rate of 6.2 l/g at 98.3 per cent purity and an extraction level of 74 per cent. The operating conditions used were: absorption time 3 seconds, desorption time 1.9 seconds, purge time 0.1 second, absorption pressure 31 bar, desorption pressure a little above atmospheric,

and temperature 220°C. No gas was bled from the system during absorption as the free space in the chamber and valves was adequate to allow the entry of sufficient gas feed during each cycle.

As may be seen in the Table, no marked progressive reduction in hydrogen output due to the presence of other gases occurred in test periods of 8 to 12 hours when hydrogen

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Temperature 210°C; Absorption Pressure 21 bar; Desorption Pressure 1 bar; Purge Time 1.0 s;
Weight of Palladium 48 g

Gas mixture	Absorption time, seconds	Desorption time, seconds	Cycles per hour	Duration of test hours	Hydrogen Output litres/gram hour	Extraction per cent
H ₂ -10% CO	5	4.9	360	12	5.9	76
H ₂ -10% CO ₂	5	4.9	360	11	6.8	77
H ₂ -10% CH ₄	5	4.9	360	11	6.1	72
H ₂ -10% C ₂ H ₄	5	4.9	360	11	5.0	57
H ₂ -10% C ₂ H ₆	2	2.9	720	8	6.3	54

containing 10 per cent methane, ethylene, carbon dioxide, or carbon monoxide was passed through the equipment. The lower yield from the ethylene mixture was due probably to the reaction of hydrogen and ethylene to form ethane. Exposure of palladium to hydrogen containing 50 p.p.m. hydrogen sulphide caused no detectable deterioration in the ability of the metal to absorb and desorb hydrogen during a period of 13 hours, the hydrogen output being 6 l/gh. However when the concentration of hydrogen sulphide was raised to 100 p.p.m., the output of hydrogen fell sharply within 30 minutes to 0.5 l/gh. It was found, however, that palladium contaminated with hydrogen sulphide could be regenerated by treatment with sulphur-free hydrogen. For example, palladium which had been exposed to hydrogen containing 1 per cent hydrogen sulphide and contaminated so that the mean output fell to 0.5 l/gh was subsequently treated by allowing a stream of unadulterated hydrogen to flow over the metal at 210°C. The metal then absorbed and desorbed hydrogen giving a mean output of 6 l/gh.

Scaling up the Separation Process

The possibility of raising the hydrogen output fivefold by increasing the weight of palladium in the same proportion was examined. For this new absorption chambers were made from copper cylinders drilled with fourteen narrow-bore holes parallel to the long axes of the cylinders. With 250 g of palladium packed into these holes it was hoped to keep the temperature of the palladium more stable than if the metal had been concentrated in one large compact. To cope with the increased volume of free-space gas, hydrogen-depleted mixture was purged from both ends of the absorption chamber.

With holes in the copper cylinder of diameter 4.65 mm it was possible to obtain a hydrogen purity of 99.5 per cent and an output of 1.5 m³/h with an extraction level of 80 per cent from the hydrogen-25 per cent nitrogen mixture. The optimum operating

conditions were as follows: absorption time 6 seconds, purge 0.5 seconds, desorption time 13.5 seconds, inlet gas pressure 35 bar, desorption pressure a little above atmospheric pressure, temperature 200°C.

With the copper absorption chambers, observed temperature fluctuations were limited to about 10°C from the mean. However, copper would not be a suitable material of construction if the gas feed were cracked ammonia containing traces of residual ammonia, as stress corrosion might occur. Other materials with lower thermal diffusivity such as mild steel or even stainless steel, as used in the small scale equipment, could probably be substituted with only a small loss in thermal efficiency.

Discussion

It has been demonstrated that hydrogen may be extracted from mixtures containing nitrogen, methane, ethylene, carbon monoxide, and carbon dioxide by a pressure-cycling process (10). Industrial gas streams containing one or more of these gases could be the feed of a commercial process. In particular a viable process of producing moderate outputs of hydrogen, say up to 20 m³/h, could be developed using a feed of cracked ammonia. Comparable with a process of this type is the hydrogen diffusion process which also may be fed with cracked ammonia. The outputs of hydrogen for equal weights of palladium would be about the same for the two processes. Although a single stage absorption process would not produce hydrogen of the high purity obtainable with the diffusion process, it would be capable of producing hydrogen of acceptable commercial purity. Higher purity could be obtained by coupling two or more absorption systems in series, though this modification would result in lower extraction.

A particular advantage of the pressure-cycling process is that, should poisoning by impurities in the gases occur, the palladium sponge may be self-purifying, as shown for sulphur, or the metal can readily be replaced.

Hydrogen may also be produced in moderate quantities by the electrolysis of water, but to compete economically this process depends on the availability of a cheap source of electricity. Other methods of producing hydrogen, such as by steam reforming, the cryogenic process and as a by-product of chlorine production, are essentially applicable only to the large scale production of the gas, and are therefore not comparable with the absorption technique.

Acknowledgement

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Deposition of Platinum Films by Radio-Frequency Sputtering

The successful use of radio-frequency sputtering for producing mechanically stable, closely adherent, and essentially non-contaminated and highly conductive platinum films on gallium arsenide crystals has recently been described by S. P. Murarka of the Bell Telephone Laboratories, Murray Hill, New Jersey (*Thin Solid Films*, 1974, **23**, 323-326). In developing the technique, a primary object was to establish such conditions that the films should be of well-controlled thickness and also stress-free so as to ensure that they remained in perfect contact with the semiconductor. These requirements have been found of the greatest importance in developing the new generation of high power microwave devices known as Infinite Multiplication Avalanche Transit Time Oscillating Diodes—or IMPATTS.

The equipment made use of an unusually large target, 8 inches in diameter and (to support the parts to be coated) an equally large substrate table, both made of pure platinum. To remove unwanted residual gases, the system was pumped down to 5.10^{-9} torr, using a titanium sublimation pump in the later stages. During sputtering, tank nitrogen was leaked into the chamber to maintain pressure at 5.10^{-3} torr \pm 4 per cent.

For sputtering, 100-500 watts of radio-frequency power was supplied at a frequency

of 13.56 MHz. The rate of deposition was remarkably high—470 Å per minute with 450 watts at room temperature. The effects of varying such controllable factors as argon pressure and deposition temperatures were found to follow a predictable pattern. The rate of sputtering increased with increase in argon pressure from 1 to 4.10^{-3} torr, but the rate of increase fell off at higher pressures owing to the greater probability of collisions between the ions. Again, the rate of sputtering decreased as the temperature was raised (up to 260°C) at the higher temperatures the probability of the bombarding ions sticking to the surface became less.

The electrical resistivity of the platinum films is influenced by chemisorption and trapping of gaseous impurity, by damage to the surface from back scatter, by the grain size, and by chemical reaction with the substrate.

In the best conditions, films 2000 Å thick were obtained with a resistivity of 15 microhm cm, about 60 per cent higher only than the value for bulk platinum. Adhesion as tested by adhesive tape peel was excellent, and internal stress could be varied from 5.10^9 dyn/cm² compressive to the same value tensile mainly by control of the substrate temperature.

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