Palladium Alloy Diffusion Units

A NEW RANGE OF COMMERCIAL EQUIPMENT FOR THE PRODUCTION OF ULTRA-PURE HYDROGEN

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Hydrogen is capable of penetrating most metallic lattices, but pure palladium and certain palladium alloys are the only metals in which rapid diffusion of hydrogen occurs under conditions of moderate pressure and temperature.

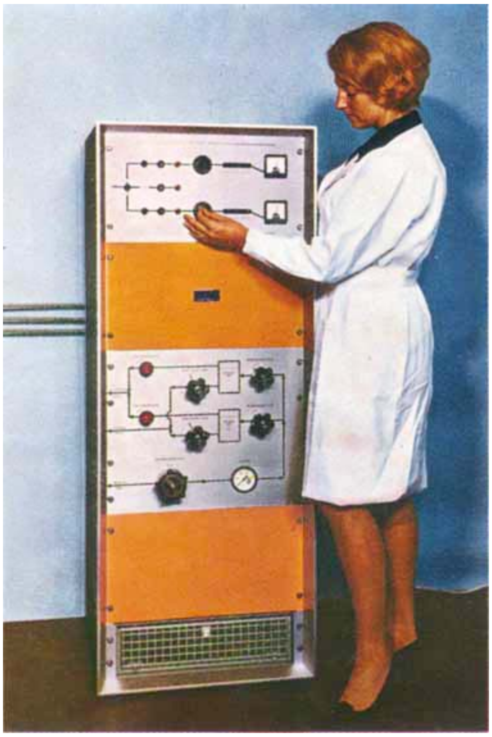
Pure palladium, however, is unsuitable for use as a diffusion membrane since at temperatures below 310°C an alpha-beta phase transition occurs which makes the metal dimensionally unstable and liable to severe distortion and, ultimately, to failure.

It was discovered by the Atlantic Refining Company, Philadelphia (1), and reported in this journal by J. B. Hunter (2), that this problem can be overcome by using an alloy having a composition of 23 per cent silver, 77 per cent palladium.

The new ranges of diffusion units now developed by Johnson Matthey, while still utilising the basic principles of hydrogen diffusion, incorporate in their design the results of several years' experience and development work in this field. They are compact, being constructed on the modular principle. Additionally, they are more reliable in service and have much higher output efficiencies in terms of the percentage of ultra-pure hydrogen recovered from the known hydrogen content of the impure feed gas than the models already described earlier in this journal (3).

Design Considerations

The design concept of the new ranges of hydrogen diffusion cells incorporated in the units has been arrived at after a complete reappraisal of the theoretical considerations of hydrogen diffusion through palladium alloy membranes, coupled with the results obtained from practical tests.



The new Johnson Matthey HK type diffusion units are based upon a modular cell type of construction and incorporate a much improved input gas heating system. The units recover as much as 90 per cent of the hydrogen present in the impure gas stream. This unit has an output of 14,000 litres per hour of ultra-pure hydrogen and is being used for the large-scale production of epitaxial crystals in the semi-conductor industry

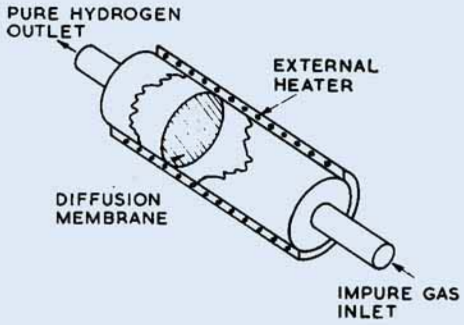


Fig. 1 A heated 23 per cent silver palladium membrane acting as a barrier. When impure hydrogen under pressure is applied to such a system pure hydrogen will diffuse through the membrane from one compartment to the other

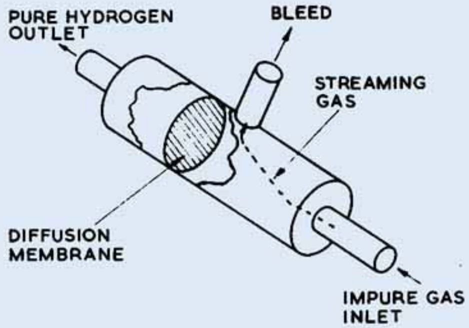


Fig. 2 The provision of a bleed-off tube prevents the formation of a layer of impure stagnant gas at the diffusion membrane surface between the two compartments

In an assembly of the type shown in Fig. 1, where a heated 23 per cent silver-palladium alloy membrane acts as a barrier between the two compartments, pure hydrogen will diffuse through the membrane from one compartment to the other.

In such a simple system the rate of diffusion falls off rapidly due to the build-up of a layer of impure, stagnant gas at the surface of the membrane on the input side of the assembly. The formation of the stagnant layer can be prevented by providing a bleed tube from the input compartment, as shown in Fig. 2.

Although this effectively overcomes the stagnation problem, in practice it is found that to maintain a steady diffusion rate a high bleed rate is necessary. A diffusion unit operating under such conditions has a very low efficiency in terms of the amount of ultra-pure hydrogen recovered from the impure gas source. This is because not only does it require a large volume of input gas to maintain the necessary flow across the diffusion membrane to sweep away the impurities, but a substantial proportion of the gas fed into the cell passes directly from the input to the bleed, and hence plays no part in the purging action.

It is therefore apparent that for high diffusion rate efficiency it is necessary that the geometric configuration of the diffusion membrane is such that it has the largest possible surface area compatible with an efficient purging action. It has been determined experimentally that these conditions

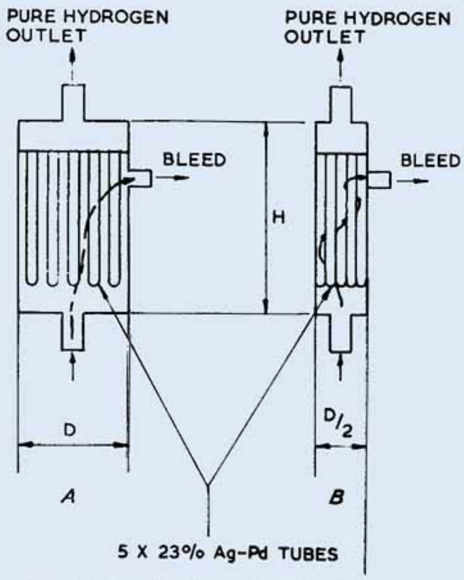


Fig. 3 The effective path of the impure gas stream over the surfaces of the diffusion membrane tubes under conditions of different packing density. The output from assembly B is much higher than that from assembly A due to the more effective purging action

are best satisfied by the use of small diameter thin-walled tubes. These not only provide a large surface area for diffusion but they can be economically produced by conventional tube drawing techniques.

The way in which the diffusion membrane tubes are presented to the incoming impure gas stream plays a very important part in the overall efficiency of the system. Figs. 3A and 3B show two chambers of equal length, containing equal numbers of diffusion membrane tubes, one chamber being only half the diameter of the other. When these two units are subjected to the same conditions of temperature and input hydrogen pressure, that having the smaller diameter produces approximately 40 per cent more ultra-pure hydrogen than the large diameter assembly.

This substantial increase in output is due to the much higher packing density of the silver-palladium alloy tubes in the small diameter cell. In this case, streaming of the impure gas from input to bleed is greatly reduced, since the gas, of necessity, follows a labyrinthine path through the assembly and a really efficient purging of the system is achieved.

One additional advantage that is gained by using a cell design incorporating high packing density of the diffusion membrane tubes is that fatigue failure of the brazed joints made between the membranes and the stainless steel manifold, a problem encountered with certain of the earlier models, has been virtually eliminated.

Methods of Heating

It can be shown experimentally that the rate of hydrogen diffusion depends upon the temperature of the membrane as well as the pressure of the feed gas applied to that membrane (3).

With earlier models, the impure hydrogen was fed to the diffusion cell via a separate pre-heater, the cell itself being provided with an external heating jacket, operating at 400°C, to minimise heat losses (Fig. 4). This heating system was found to produce large temperature gradients along the tubes, and as a result the output efficiency of the cell suffered.

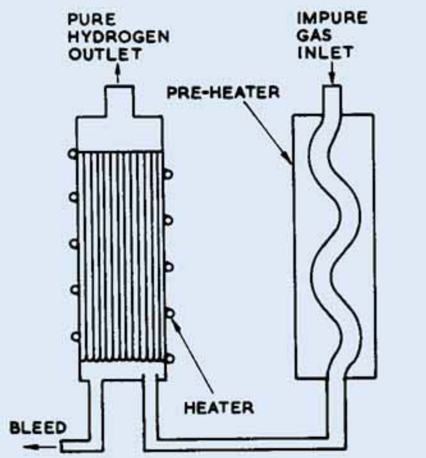


Fig. 4 The earlier method of heating the impure gas stream required an external pre-heater and an ancillary heating jacket around the cell. The system consumed approximately 3 kW

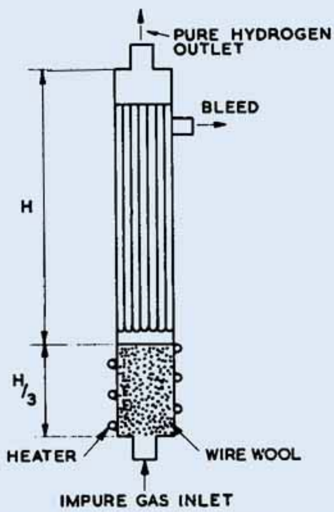


Fig. 5 The method of heating a single module now employs a small heat exchanger, integral with the diffusion cell. This system has a high efficiency with a power consumption of only 0.5 kW

Fig. 6 A typical Johnson Matthey H type diffusion unit. The models in this series are intended primarily for laboratory use in, for example, gas chromatography, and for pilot plant development runs in the production of semi-conductor devices

The occurrence of temperature gradients along the membranes can be prevented by passing the impure gas through an electrically heated, wire wool packed, stainless steel tube. This system (4), illustrated in Fig. 5, is used in the construction of both the H and HK ranges of diffusion units.

This method of heating the input gas has been found to be so efficient that additional external heating of the cells is now unnecessary.

The New Units

Unlike the earlier models, the new H and HK ranges are designed so that the entire length of the diffusion membranes operates at 300°C. The units are self-contained and can be connected directly to both electrical and impure gas supply.

The H range comprises four models, with outputs ranging from 1 ft^3/h (28 l/h) to 45 ft^3/h (1,260 l/h). Intended primarily for laboratory and small-scale production runs, for example, in the preparation of semiconductor materials, the heat treatment of metals, catalytic hydrogenation and the preparation of ultra-pure materials by the reduction of halides, all four models are housed in cases of the type shown in Fig. 6. The diffusion membrane tubes are arranged in the general form illustrated in Fig. 5, the only difference between the four models being the numbers of tubes used. The impure gas should be applied to the units via a pressure control valve which will limit the input pressure to 300 lbf/in^2 (21 kgf/cm^2).

The HK range also comprises four models, their outputs ranging from 250 ft^3/h (7,000 l/h) to 1,000 ft^3/h (28,000 l/h). The range utilises a series of diffusion membrane modules which are arranged in the ring form shown in Fig. 7. The heating column is centrally placed in the ring assembly. By

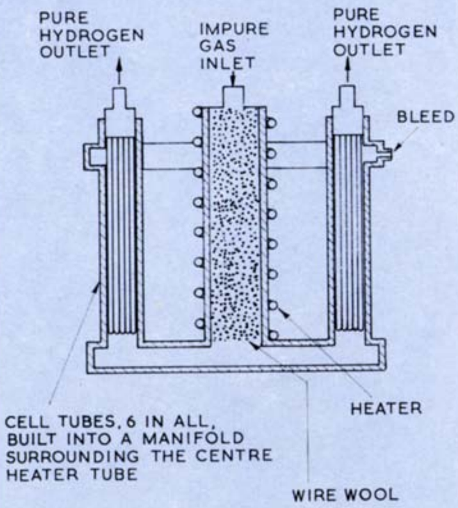


Fig. 7 This shows how the principle of heating a single module has been adapted for use with a multiple module arrangement. The system consumes approximately 1 kW

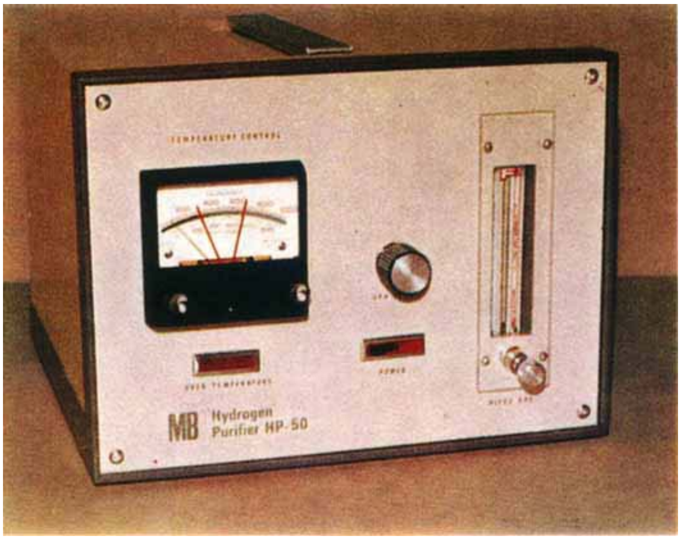


Fig. 8 This Matthey Bishop hydrogen purification unit has an output of 50 cubic feet per hour. Operating directly from 110 to 120 V, 50/60 Hz electrical supplies, the power consumption is 268 watts

adopting this configuration it has been found that the maximum temperature variation on any module, compared with the temperature of the gas as it leaves the heater, is only 5°C.

Unlike the H series, the HK range of diffusion units is designed for operation where the pressure of the impure gas fed to the units is only 150 lbf/in^2 (10.5 kgf/cm^2). The pressure control valve on the unit is pre-set to this value during manufacture so that this pressure cannot be inadvertently exceeded.

Models HK7 and HK14 are housed in cabinets of the type shown on page 141. The other models in this range can also be housed in cabinets of similar style, but since their outputs are so large, the user may wish to divorce the diffusion side of the apparatus from the electrical control circuits. Either of these requirements can be satisfied.

American Developments

It has already been shown in this article that for a hydrogen diffusion system to operate satisfactorily, efficient heating of the 23 per cent silver palladium alloy diffusion membrane tubes must be achieved. Additionally, it is necessary that the surfaces of the diffusion membranes are constantly subjected to the purging produced by the flow of impure input gas through the cell.

The methods of heating that can be employed to give the desired results are manifold. Efficient purging of the surfaces of the diffusion membranes is best achieved by utilising a high packing density. Here again there are several ways in which this ideal can be achieved.

Matthey Bishop in the United States have employed an alternative closely packed construction in their new range of portable hydrogen purification units. These compact units are intended for use in applications similar to those mentioned above for the Johnson Matthey H range of diffusion units and are designed to operate at temperatures between 700 and 750°F (370–400°C), with an applied input gas pressure to the diffusion membranes of 200 lbf/in^2 (14 kgf/cm^2).

The series comprises four models, one of which is shown in Fig. 8, with outputs ranging from 2 to 50 ft^3/h.

References

1 Atlantic Refining Company, *U.S. Patent* 2,773,561
2 J. B. Hunter, *Platinum Metals Rev.*, 1960, **4**, 130
3 H. Connor, *Platinum Metals Rev.*, 1962, **6**, 130
4 Johnson Matthey, Br. Pat. Appln 42821/69