

Palladium Alloy Diffusion Cells

COMMERCIAL UNITS FOR THE PRODUCTION OF ULTRA-PURE HYDROGEN

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An alloy of palladium for the diffusion of hydrogen that is dimensionally stable when thermally cycled through the alpha-beta phase transition temperature in the presence of hydrogen was discovered by the Atlantic Refining Company, Philadelphia, U.S.A. (1), and reported in this journal by J. B. Hunter (2). The principles on which the range of industrial-scale diffusion cells is based were worked out jointly by the Atlantic Refining Company and J. Bishop & Co., Malvern, Pennsylvania, an associated company of Johnson Matthey, who have world-wide rights to utilise the relevant patents (3). Since these diffusion cells were brought on to the American market just over two years ago a number of large-scale hydrogen purification plants incorporating them have been installed. Among such plants the 115,000 cubic feet per day unit operated by the National Cylinder Gas Division of the Chemetron Corporation has recently been described (4).

Construction of Diffusion Cells

While pure palladium has been known for many years to be selectively and very highly permeable to hydrogen, an alpha-beta phase transition which occurs at temperatures below 310°C makes the metal dimensionally unstable and liable to severe distortion and failure. The addition of silver to palladium, however, inhibits this phase transition and also increases its permeability without any loss of selectivity. An alloy having a composition of 23 per cent silver : 77 per cent palladium has been found in practice to give a maximum rate of diffusion of hydrogen under

Previous articles in this journal have described the development of palladium alloy diffusion cells for the purification of hydrogen. A range of commercial cells has now been made available by Johnson Matthey to make possible the large-scale production of ultra-pure hydrogen from hydrogen less pure, or from a range of industrial gases containing hydrogen. The construction, operation, performance and applications of these cells are described here.

a given set of operating conditions and is now employed as the basis of the construction of the diffusion cells described here.

In order to make the most economic use of the alloy while obtaining maximum diffusion area with a maximum of strength to withstand high differential pressures, it is employed in the form of small-diameter, thin-walled tubes. These tubes are of standard dimensions, and as the rate of diffusion of hydrogen under a given set of operating conditions is directly proportional to diffusing area the capacity of each cell is determined by the number of alloy tubes it contains.

Each alloy tube is closed at one end and has its open end extending into a manifold space. The impure hydrogen circulates over the outside surface of the tubes, but only hydrogen diffuses through their walls and is collected in the manifold space from which it passes out of the cell.

The bundle of diffusion tubes is contained

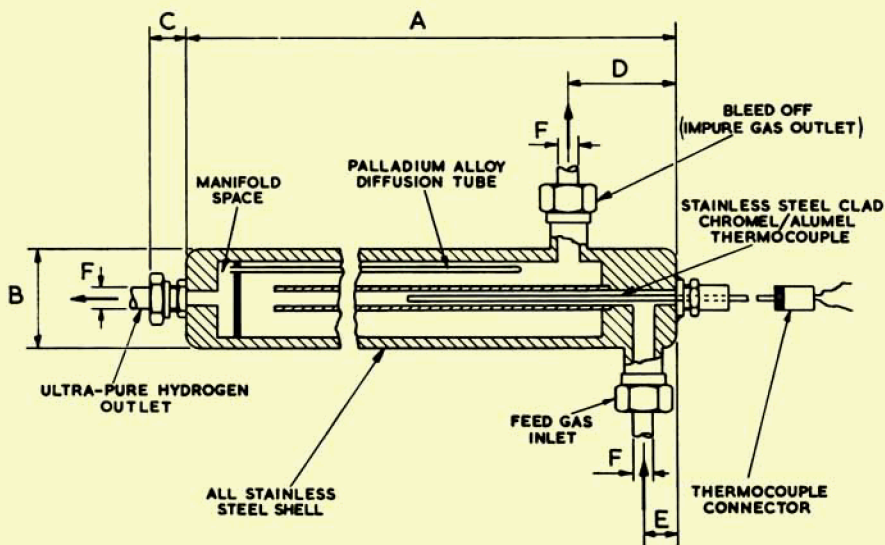


Fig. 1 General construction of a Johnson Matthey palladium alloy diffusion cell, showing connecting couplings and stainless steel clad thermocouple

within a stainless steel shell designed to withstand maximum internal pressures of up to 500 psig (34 atmospheres) at working temperatures up to 500°C. Connection to each cell is made by means of standard Ermeto stainless steel pressure couplings, the three couplings of each cell being the same size to ensure complete and easy interchangeability of each cell. The general construction

of a cell is shown in Figs. 1 and 2, while dimensions of the range of cells and their relative performance ratios are given in the table below.

Operation of Cells

In operation the impure hydrogen is led to the manifold-end of the diffusion tubes by means of a central inlet tube within the shell.

Principal Dimensions of Palladium Alloy Diffusion Cells and Relative Performance Ratios of the Four Cells in the Range							
Model	Relative performance ratio	Length "A"	Outside diameter "B"	Dimension "C"	Dimension "D"	Dimension "E"	Outside diameter "F"
A.11	1.0	30.13 in 76.52 cm	0.84 in 2.13 cm	1.09 in 2.78 cm	2.13 in 5.40 cm	0.50 in 1.27 cm	0.375 in 0.95 cm
A.31	4.3	30.13 in 76.52 cm	1.32 in 3.34 cm	1.09 in 2.78 cm	2.13 in 5.40 cm	0.50 in 1.27 cm	0.375 in 0.95 cm
A.51	9.3	30.75 in 78.1 cm	1.66 in 4.22 cm	1.16 in 2.94 cm	2.81 in 7.14 cm	0.69 in 1.75 cm	0.50 in 1.27 cm
A.71	16.0	30.75 in 78.1 cm	1.90 in 4.83 cm	1.16 in 2.94 cm	2.81 in 7.14 cm	0.69 in 1.75 cm	0.50 in 1.27 cm

From there it flows over the outside surface of the tubes to the "bleed-off" coupling, where undiffused hydrogen together with all impurities and "inert" gases leave the cell. It has been clearly demonstrated (5, 6) that in order to obtain high and reproducible rates of diffusion of hydrogen, the latter must be maintained in continuous movement over the alloy surface. This ensures that impurities and diluent ("inert") gases are continuously swept out of the cell. It also, however, reduces the proportion of the incoming hydrogen which is recovered in the ultra-pure form. For any given set of operating conditions (i.e. pressure differential across the walls of the diffusion tubes, temperature, volume-composition of the inlet gas), the rate of diffusion of hydrogen through the walls of the alloy tubes rises with increasing rate of "bleed-off" volume until it reaches a steady maximum value. This is illustrated very broadly in Fig. 3. The decrease of the percentage-recovery of the inlet hydrogen as the "bleed-off" rate increases is shown, also in broad principle, in Fig. 4.

It is thus apparent that an economic balance must be struck between a desirable high rate of diffusion and the accompanying undesirable loss of undiffused hydrogen. The manner in which such a balance is obtained depends on

- (a) The partial pressure of hydrogen in the feed-gas
- (b) The back-pressure of ultra-pure hydrogen
- (c) The operating temperature

Effect of Pressure

For a fixed set of other operating variables, the rate of diffusion of hydrogen depends on a concentration gradient, and is approximately proportional to the hydrogen partial pressure difference across the walls of the alloy tubes if this pressure difference is below about 200 psi (14 atmospheres). For partial pressure differences above 400 psi (27 atmospheres) the diffusion rate is proportional to the difference between the square roots of the



Fig. 2 A Johnson Matthey silver-palladium alloy diffusion cell, showing the ultra-pure hydrogen outlet uppermost

high and low pressures. At intermediate partial pressure differences the diffusion rate follows the difference between the high and low pressures, each raised to the power of 0.8.

A square root pressure dependence would be expected if surface reactions could be neglected and if the hydrogen concentrations within the membrane were well below the solubility limit. Such conditions do not apply industrially, and experience has shown that the form of the pressure dependence curve generally observed is explicable largely in terms of the pressure-solubility isotherms which determine the steepness of the hydrogen concentration gradients across the membrane.

Before hydrogen can dissolve in the metal it must dissociate into atoms. This dissocia-

tion takes place only at certain "active centres". Surface contamination limits the number of such active centres available. When an increase in hydrogen partial pressure has caused all such centres to be fully occupied a pressure rise does not contribute to the number of hydrogen atoms chemisorbed at the alloy surface. These surface reactions have a significant effect upon the shape of the pressure dependence curve when very thin membranes are being employed or when thicker membranes are significantly contaminated.

The rate of diffusion through reasonably clean membranes thicker than about 0.003 inch is, however, controlled largely by the ability of hydrogen atoms in the form of protons to permeate the metal lattice. Because of this the rate of diffusion of hydrogen is found to vary inversely as the thickness of the membrane within fairly close limits.

Effect of Temperature

The rate of diffusion is markedly dependent on the temperature of the alloy tubes. Virtually no diffusion takes place at room temperature, while increasingly rapid rates are obtained above 200°C. When all other variables are kept constant, a rise from 200 to 400°C in operating temperatures causes an increase of approximately 30 per cent in the rate of diffusion, as illustrated in Fig. 5.

An operating temperature of 350 to 400°C is recommended, and this is best obtained by pre-heating the feed-gas. A stainless steel clad chromel-alumel thermocouple is provided in each cell, and measures the temperature of the feed-gas immediately before access to the diffusion tubes is obtained. Pre-heating the feed gas is to be preferred to heating the cell by means of a tubular furnace, as the latter method is less efficient. Furnace heating requires higher element temperatures, while an unwelcome and wasteful temperature gradient would exist across the stainless steel shell of the cell. Furthermore, strong cooling effects are produced if cold feed-gas is led into a furnace-heated cell.

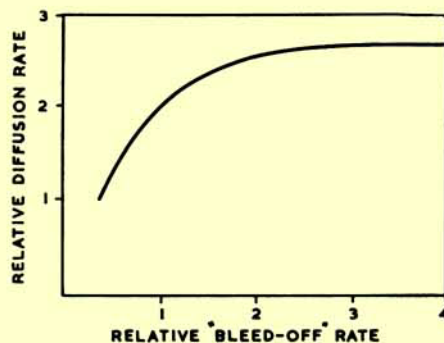


Fig. 3 Dependence of the rate of diffusion of hydrogen on the rate of "bleed-off"

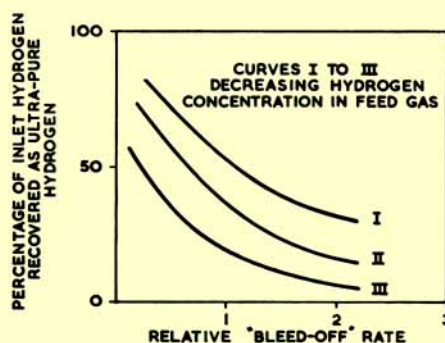


Fig. 4 Dependence of the percentage-volume of inlet hydrogen recovered in the ultra-pure form on the "bleed-off" rate

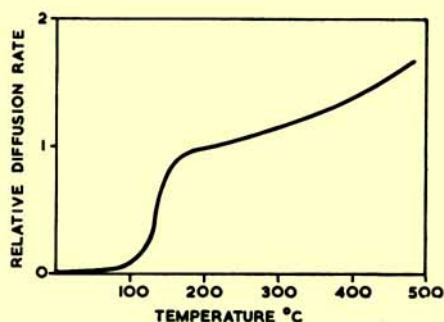


Fig. 5 Dependence of the diffusion rate on operating temperature. Data obtained with cylinder hydrogen and a constant pressure differential

A cell into which preheated gas is fed must be well insulated and an electric heating tape operating at 400°C may be wrapped around the cell in order to minimise heat losses.

Installation and Performance

Diffusion cells should be mounted vertically with the ultra-pure hydrogen outlet uppermost; this will enable the alloy tubes to hang freely downwards within the shell. Depending on the desired rates of diffusion and volumes of gas to be dealt with, two or more cells (of the same or different size) may be mounted and connected in parallel, enabling very large flow rates to be obtained.

As may be seen from the above, a number of variables affect the output of ultra-pure hydrogen of any one cell. It is not possible, therefore, to give specific outputs unless the operating conditions are also closely specified. As an example, however, it may be mentioned that one A71 cell (the largest of the range of four cells) will yield over 500 standard cubic feet (14,000 litres) per hour of ultra-pure hydrogen when using cylinder hydrogen as a feed-gas and operating at 350°C with a pressure-differential of 200 psi (13.6 atmospheres), the ultra-pure hydrogen being withdrawn at atmospheric pressure.

In order that the size, number and operating conditions of diffusion cells may be assessed for any given application, it is necessary to know the following:

- (a) The volume-composition of the feed-gas
- (b) The volume per hour of ultra-pure hydrogen required
- (c) The economic minimum percentage-recovery of the inlet hydrogen in the form of ultra-pure gas

Purity of "Ultra-Pure" Hydrogen

There is no evidence that any gas, other than hydrogen, is able to diffuse through silver-palladium under the conditions generally employed for the operation of diffusion cells. Oxygen, the only commonly-encountered gas which it might be thought could diffuse,

combines catalytically with hydrogen on the surface of the alloy and the resultant water vapour does not diffuse through the metal.

The detection and quantitative estimation of impurities present in hydrogen to a concentration of less than 1 ppm present very considerable difficulties. It is believed that these impurities have, in fact, a concentration of about 0.1 ppm or less in the gas after diffusion, and that any such impurities detected result from leaks in the system or from out-gassing of its walls. Hydrogen purified by diffusion through palladium or silver-palladium is believed to be substantially purer than may be obtained by any other method.

Life of Diffusion Cells

There are no moving parts in a diffusion cell, which is designed to operate continuously at pressures and temperatures up to its rated maximum. Cell life, therefore, should be extremely long and only terminated by accidental mechanical failure.

In practice, however, the output from cells may progressively decline in time due to cumulative poisoning of the catalytically active surfaces of the alloy tubes. Two such forms of poisoning are recognised:

- (a) "Permanent", or irreversible poisoning resulting from contamination by compounds of sulphur, mercury, arsenic and certain other base metals. These poisons attack the alloy tubes in time and cause loss of diffusion rate. No quantitative estimate has been made to date of the degree of tolerance of the cells towards these poisons, but it is recommended that if known to be present their concentrations be kept down to a minimum.
- (b) "Temporary", or reversible poisoning, resulting from strong chemisorption of some unsaturated hydrocarbons, certain oxygen-containing compounds and higher hydrocarbons. This form of poisoning is easily rectified when a loss

of output is observed by purging the cell with nitrogen and blowing hot filtered air through it in place of the usual feed-gas while the cell is at operating temperature.

Applications

Diffusion cells have three potential fields of application:

- (1) As a means of purification to ultra-pure standards of hydrogen obtained from cylinders or other sources. In this instance the ultra-pure hydrogen is required for specialised applications, as for example in the heat-treatment of stainless steels or other metallurgical processes, or in the semiconductor or chemical industries.
- (2) As a means of obtaining pure hydrogen from a cheap but low-grade hydrogen-containing gas, for example cracked

ammonia, hydrocarbon reformer gas, petroleum reformat streams or other industrial process gases.

- (3) As a means of removing unwanted hydrogen from process gases.

In all these applications the diffusion process offers substantial advantages over some other possible systems, in that the cells are very compact and robust, require little attention and have a reclaim value on account of their palladium alloy content.

References

- 1 Atlantic Refining Company, U.S. Patent 2,773,561
- 2 J. B. Hunter, *Platinum Metals Rev.*, 1960, 4, 130
- 3 Atlantic Refining Company and J. Bishop & Co., U.S. Patent 2,961,062
- 4 *Platinum Metals Rev.*, 1962, 6, 47-48
- 5 A. S. Darling, *Platinum Metals Rev.*, 1958, 2, 16-22
- 6 Johnson, Matthey & Co., Limited, British Patent 825,973

Rhodium as a Polymerisation Catalyst

FURTHER STUDIES ON POLYBUTADIENE PREPARATION

The use of aqueous solutions of rhodium salts as stereo-specific catalysts in the polymerisation of 1, 4 butadiene has recently been reported by the research laboratories of the United States Rubber Company. This development may make possible the large-scale production of *cis*-polybutadiene by the commonly-used technique of emulsion-polymerisation.

Further aspects of this work have now been reported from the laboratories of the Shell Development Company, Emeryville, U.S.A., by A. J. Canale, W. A. Hewett, T. M. Shryne and E. A. Youngman (*Chem. & Ind.*, 1962, (24), 1054). These workers demonstrated that, in addition to *trans*-1, 4 polymerisation of butadiene possible with Rh^{3+} salts, a much broader steric control over such polymerisations is possible with other ions and complex compounds of the platinum group metals. Under the polymerisation conditions studied, for example, almost complete *trans*-1, 4 additions were obtained using rhodium trichloride, cyclo-octadiene rhodium chloride and iridium trichloride as catalysts. Palla-

dium, in the form of palladium chloride or ammonium chlorpalladate, gave high proportions of 1, 2 polymerisations but the polymers had low molecular weights. One of the highest proportions of *cis*-1, 4 additions obtained resulted from the use of ruthenium trichloride with triphenyl phosphine or tri-*n*-butyl phosphine. Cobalt catalysed polymerisations, however, yielded the highest proportion of *cis*-1, 4 polymers, and also gave the highest molecular weights.

The fact that certain compounds that normally inhibit the "classical" free radical polymerisations had no effect on the reaction studied indicates that a completely different mechanism is operative in these instances. While no specific mechanisms have been suggested to date, it is clear that the ligands, the nature of the transition metal ions and their valency states exert powerful influences on the steric course of the polymerisation, its rate and the molecular weight of the products. It is postulated that the transition metal hydride may play a part in the initiation of some polymerisations.