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# EXPERIMENTS ON A CERAMIC ELECTROLYSIS CELL AND A PALLADIUM DIFFUSER AT THE TRITIUM SYSTEMS TEST ASSEMBLY

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## ABSTRACT

A ceramic electrolysis cell and a palladium diffuser are developed in Japan and is tested with tritium in Tritium Systems Test Assembly (TSTA) of the Los Alamos National Laboratory, in order to confirm the feasibility as possible upgrades for the fuel cleanup system (FCU). The ceramic electrolysis cell made of stabilized zirconia was operated at 630°C for an extended period with a mixture of 3% $T_2O$ in He carrier gas in the circulation system with oxidizing catalyst bed. The palladium diffuser was tested with circulated pure tritium gas at 280°C to verify the compatibility of the alloy with tritium, since the $^3He$ produced in the metal could cause a degradation. The isotopic effects were also measured for both devices.

## INTRODUCTION

This study was performed under a collaborative program between the U.S.Department of Energy and the Japan Atomic Energy Research Institute (JAERI) from March 1984. The ceramic electrolysis cell and the palladium diffuser were developed in JAERI as tritium processing components for a fusion fuel circulation system.

The ceramic electrolysis cell made of oxide solid electrolyte decomposes tritiated water in the vapor phase[1]. This method eliminates the problems of other techniques such as large tritium inventory in wet cells, radiation damage on SPE cells[2] and generation of solid waste in hot metal beds[3]. These features make it attractive for fusion fuel systems and a possible replacement for the hot metal beds in FCU of TSTA as shown in Fig.1. Electrolysis characteristics of the cell had already been studied in JAERI with normal[4] and heavy water[5] and high conversion ratios from water to hydrogen were obtained in the temperature range of 500-900°C.

The palladium diffuser continuously separates hydrogen isotopes from all impurities in the plasma exhaust. The advantages of this method are the purity of product and the ability of separation of helium ash. Figure 1 shows that it can be used in FCU in the place of the molecular sieve beds[6]. Feasibility studies without tritium have been performed in JAERI on the effects of impurities and thermal cycling[7],and the separation characteristics of the diffuser[8].

The object of the experiments at TSTA was to verify the performance, reliability and compatibility of these components with tritium.

## EXPERIMENTS

### Ceramic Electrolysis Cell

The small scale electrolysis cell, made of an yttria-stabilized zirconia (YSZ) tube with platinum electrodes, was sent to TSTA after the tests with normal water in JAERI. The structure of the cell is shown in Fig.2. At TSTA, tests were conducted in three phases: cold, low level, and high level tritiated water experiment. Figure 3(a) shows the schematic of the experimental setup for the phase 1. Water vapor from the bubbler is carried by an inert gas stream and is decomposed in the electrolysis cell. Humidity at the inlet and the outlet of the cell is measured with Panametrics hygrometers. Power for electrolysis is supplied by a potentiostat (Hokuto Denko HA-305), which is also used for the measurement of current and voltage.

The phase 1 was the test with normal water vapor to confirm the performance obtained in JAERI. The behavior of the third electrode, "reference" located at the downstream side of the cell was tested to measure the content of the product and/or to control the cell. Hydrogen carrier gas was also used.

The phase 2 and 3 were conducted in the INV glovebox using the apparatus shown in the Fig.3(b). In phase 2, low-level tritiated water (40 Ci/ml) was used and isotopic effect of tritium was measured in once-through flow. Glycol bubblers and a Packard liquid Scintillator were used to measure the conversion ratio of tritiated water.

The final test (Phase 3) was carried out with the circulation system with a metal bellows pump. Pure tritium gas (38Ci) was supplied from a bottle and mixed with He so that a mixture of 3% $T_2O$ is obtained by oxidation at a

bopcalite bed. The tritiated water is decomposed at the electrolysis cell, and generated $O_2$ and $T_2$ are mixed and recombined by bopcalite again.

### Palladium Diffuser

Experiments of the palladium diffuser is conducted in a gas circulation system composed of the palladium diffuser and a metal bellows pump as shown in the Fig.3(c). The pressures and flow rates of the gas in the system were measured with Baratron pressure transducers and Brooks mass-flow meters. Figure 4 shows the structure of the cell. A diffuser has 12 palladium alloy tubes. Each tube is 1.60mm and 1.44mm in outer and inner diameter, and 100mm long.

Permeability of the membrane for $H_2$ and $D_2$ were measured prior to the test with tritium in the temperature range of 300-450°C and the feed pressure range of 200-3300 torr. The pressure at the permeated side of the membrane was about one tenth of the feed pressure.

The hot test was performed with 1300Ci $T_2$ from a uranium bed. After the measurement of permeability at various temperature and pressure, the system was operated for a long period. The operation temperature was set at 280°C

In a related study of the material properties of the palladium alloy, small specimens were statically immersed in tritium at operating temperature for various periods up to 2 years. Progressive tests of tensile strength are performed on samples after they were cooled and subsequently withdrawn from the tritium atmosphere.

## RESULTS AND DISCUSSIONS

### Ceramic Electrolysis Cell

In phase 1, feed-back control of the cell and the use of hydrogen as a carrier, both of which are advantageous in actual operations, were tested, as well as the test of the basic performance obtained in JAERI. The electrolysis characteristics of the cell are studied in previous works[4,5]. The conversion ratio x from water vapor to hydrogen is expressed,

$$E\text{-}Ir = E_0 + \frac{RT}{2F} \ln\frac{x}{1-x}$$

where, E, I, r are the voltage, current and resistance of the cell, R is the gas constant, T is the temperature and F is the Faraday constant. Standard voltage for water decomposition $E_0$ is also a function of temperature and its value at 600°C is 1.041V. Little overpotential is observed in the reaction.

The value E-Ir is the open circuit voltage that can be measured at the reference electrode, where the electro-motive force (emf) is obtained corresponding to the content of the product gas at the cell. Therefore, the ratio of hydrogen and water concentrations, i.e. conversion ratio in the cell is continuously and simultaneously monitored. The cell voltage between the anode and the cathode can be changed automatically by a potentiostat so that the voltage at the reference is controlled to be a desired value. Figure 5 shows a typical characteristics of the cell obtained in the phase 1 experiment. The conversion ratios from water to hydrogen are plotted against the open circuit voltage measured as the reference potential. They agreed well with the theoretical values shown as a solid line in the figure. The result also proved that a feed-back control of the cell to obtain stable open circuit voltage,i.e. conversion ratio, is effective. It is advantageous in the operation of the cell in the PCU, where tritiated water DTO is supplied from the regenerating freezer and the vapor concentration in the carrier gas will not be stable.

In the regeneration of the freezer in PCU, use of deuterium carrier is planned because pure hydrogen isotope mixture can be obtained as a product from the hot metal bed. Figure 6 is the relation between the open circuit voltage and the conversion ratio obtained in the experiment with $H_2$ carrier gas. The solid line shows the theoretical value. The result is quite different from that with inert carrier. Decomposition of water begins at about 1.2V and the conversion ratio reaches 99.9% at 1.47V. This result suggests that the use of hydrogen carrier is feasible with a little higher voltage on the cell.

In the test of phase 2, low-level tritiated water was decomposed and the conversion ratios for tritiated water and normal water were measured as a function of the open circuit voltage. The conversion ratio of tritiated water was estimated from the residual tritiated water vapor in the stream from the cell, trapped in a glycol bubbler. The isotopic effect of electrolysis reaction appears only in the constant term $E_0$ in the equation noted before. The difference between $H_2O$ and HTO was 0.04V in the experiment at 600°C.

In the test of phase 3, the electrolysis characteristics for $T_2O$ was measured at first. The open ciucuit voltage for decomposition of $T_2O$ was 0.08V higher than that for $H_2O$ and 1.38V was necessary for the conversion ratio fo 99.9% as shown in the Fig.7.

Continuous operation of the cell for an extended period has been performed from July, 1984. The processing rate of the tritium in the system is 20,000 Ci/day for decomposition and recombination of $T_2/T_2O$. The experimental condition of the test is summarized in Table 1.

### Palladium Diffuser

The basic permeation characteristics of the palladium alloy were studied in JAERI with $H_2$ and $D_2$ [6]. The permeation flow rate through the cell proved to be expressed by the square-root law around the operation pressure of 1 to 10atm.

Figure 8 summarizes the relations between the permeation flow rate and the difference of the square-root of pressures at the feed and the permeated side of the palladium membrane. Linear relationships are seen in the figure except for the data for large flow rates of $H_2$, where the deviation seemed to be caused by pressure drop in the tubing. The lines do not meet at the origin in the figure . It suggests that the square-root relationship is not held in the pressure region lower than 200torr.

The bleed rate, the ratio of bleed flow rate to feed, were changed from 0.01 to 0.5 and proved to affect little on permeability of the diffuser. In this experiment, bleed rate was kept to about 0.1. Operation pressure and the pressure ratio of the feed and permeated are limited by the capacity of the metal bellows pump.

The temperature variation of the permeability of H, D and T through the alloy are shown in the Fig.9. Permeation flow rate change little in the temperature range. The rate for the isotopes is, H:D:T = 1:1/1.8:1/2.3. This isotopic effect is a little larger than the reported value[9].

The system has been continuously operated from Aug. 1984 with pure $T_2$ of 1300 Ci. In order to reduce tritium permeation through the stainless steel outer shell into the glovebox, the operation temperature was set at 280°C. As seen in the Fig.10, that is measured with $H_2$ in JAERI, the permeability changes at the temperature lower than 200°C at the pressure around 1 atm. This result suggest that the palladium diffuser can be operated at as low as about 200°C without large reduction of the capacity. The conditions of the test is summarized in Table 2. The most important problem on the compatibility of the alloy with tritium is the production of helium-3 by disintegration of tritium in the metal. The "immersion-tensile test" will give informations on this problem. If there would be a change on the nature of the alloy, the permeability of the diffuser in the circulation system would change in the cource of the test.

## CONCLUSION

The new components for tritium processing, the ceramic electrolysis cell and the palladium diffuser, were tested with tritium at TSTA. They worked correctly with tritium and isotopic effects were measured with them.

The continuous operations of the components from the summer in 1984 will be completed in 1985 and their feasibility and reliability will be discussed based on the results.

The full scale components of the cell and the diffuser, that could be used as substitutes in FCU are planned.

## ACKNOWLEDGEMENT

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## REFERENCES

1. S. Konishi, H. Ohno, H. Yoshida and Y. Naruse, "Decomposition of tritiated water with solid oxide electrolysis cell", Nucl. Technol./Fusion, 1, 195(1983).

2. T. K. Mills, R. E. Ellis, and M. L. Rogers, "Recovery of tritium from aqueous waste using combined electrolysis catalitic exchange", Proc. ANS Topl. Mtg. Tritium Technology in Fission, Fusion and Isotopic Applications, Dayton, Ohio, 422(1981).

3. R. C. Kerr, J. R. Bartlit and R. H. Sherman, "Fuel Cleanup System for the Tritium Systems Test Assembly: design and experiments", Proc. ANS topl. Mtg. Tritium Technology in Fission, Fusion and Isotopic Applications, Dayton, Ohio 115(1981).

4. S. Konishi, H. Ohno, H.Yoshida and Y. Naruse, "Characteristics of Solic Oxide Electrolysis Cell for decomposition of tritiated water", JAERI-M 82-186, (1982).

5. S. Konishi, H. Ohno, H. Yoshida, H.Katata and Y. Naruse, "Solid Oxide Electrolysis Cell for decomposition of tritiated water", Hydrogen Energy Progress V, Proc. 5th World Hydrogen Energy Conference, Toronto, 537(1984).

6. H. Yoshida, S. Konishi and Y. Naruse, "Preliminaly design of a fusion reactor fuel cleanup system by the palladium alloy membrane method", Nucl. Technol./Fusion, 1, 471(1982).

7. H. Yoshida, S. Konishi and Y. Naruse, "Effect of impurities on hydrogen permeability through palladium alloy membranes at comparatively high pressure and temperatures", J. Less Common Met., 89, 429(1983)

8. S. Konishi, H. Yoshida and Y. Naruse, "A design study of a palladium diffuser for a D-T fusion reactor fuel cleanup system", J. Less Common Met., 89, 457(1983).

9. H. Fujita, S. Okada, K. Fujita, H. Sakamoto, K. Higashi and T. Hyodo, "Ratios of permeabilities of tritium to protium through palladium-alloy membrane", J. Nucl. Sci. Technol., 17, 40(1980).

TABLE 1 CONDITION OF LONG-TERM OPERATION OF THE ELECTROLYSIS CELL

| | | |
|---|---|---|
| LOCATION | : | INV BOX IN TSTA |
| DATE OF START | : | JULY 30, 1984 |
| INVENTORY | : | 38 Ci, FORM: $T_2O$ Vapor and $T_2$, MIXED WITH HELIUM |
| TEMPERATURE | : | 630°C CONTROLLED WITH VARIAC |
| GAS | : | MIXTURE OF 15 TORR $T_2/T_2O$ (3%) AND 485 TORR HE INSIDE OF CELL; 500 TORR PURE $D_2$ OUTSIDE OF THE CELL |
| FLOW RATE | : | 150 STD.CC/MIN TO THE INSIDE OF THE CELL |
| CONVERSION RATIO FROM $T_2$ to $T_2$ | : | 99.9% |
| PROCESSING RATE | : | ELECTROLYZED VAPOR - 20,000 Ci/DAY<br>...1/10 OF FCU IS TSTA |

TABLE 2 EXPERIMENTAL CONDITION OF LONG-TERM PALLADIUM-DIFFUSER OPERATION

| | | |
|---|---|---|
| LOCATION | : | SOLID WASTE DISPOSAL BOX IN TSTA |
| DATE OF START | : | AUGUST 15, 1984 |
| INVENTORY | : | 1400Ci, FORM: PURE $T_2$, 400 STD. CC |
| TEMPERATURE | : | 280°C, ON-OFF CONTROLLED |
| PRESSURE | : | FEED SIDE-1500 TORR, PERMEATED SIDE-150 TORR |
| FLOW RATE | : | FEED-210 SCCM, PERMEATION-190 SCCM, BLEED, 20 SCCM (SCCM = STD.CC/MIN) |
| PROCESSING RATE | : | PERMEATION FLOW RATE-680,000 Ci/DAY ...1/30 OF FCU IN TSTA |

FIGURE CAPTIONS

Fig.1. The diagram of the Fuel Cleanup System (FCU) of TSTA. The ceramic electrolysis cell and the palladium diffuser can be used as the replacements of the Hot Metal Beds and the Molecular Sieve Beds respectively as shown by the break lines.

Fig.2. The schematic of the ceramic electrolysis cell.

Fig.3. Experimental setups for the experiment of,
(a) the phase 1 of the electrolysis with normal water,
(b) the phase 2(break line) and 3(solid line) of the electrolysis with tritiated water, and
(c) the palladium diffuser.

Fig.4 The schematic of the palladium diffuser.

Fig.5. Relation between the open circuit voltage and the conversion ratio from water to hydrogen in the ceramic electrolysis cell at 600°C. The solid line shows the theoretical value.

Fig.6. The relation between the open circuit voltage and the conversion ratio in the electrolysis cell with inert and hydrogen carrier gas. The lines show the theoretical values.

Fig.7. The isotopic defference between $H_2O$ and $T_2O$ in the electrolysis at 600°C.

Fig.8 Permeation characteristics of the palladium diffuser for $H_2$, $D_2$ and $T_2$.

Fig.9. Temperature variation of permeation coefficients for H, D and T in the palladium diffuser.

Fig.10. Temperature variation of the permeation coefficient of the palladium diffuser for $H_2$.

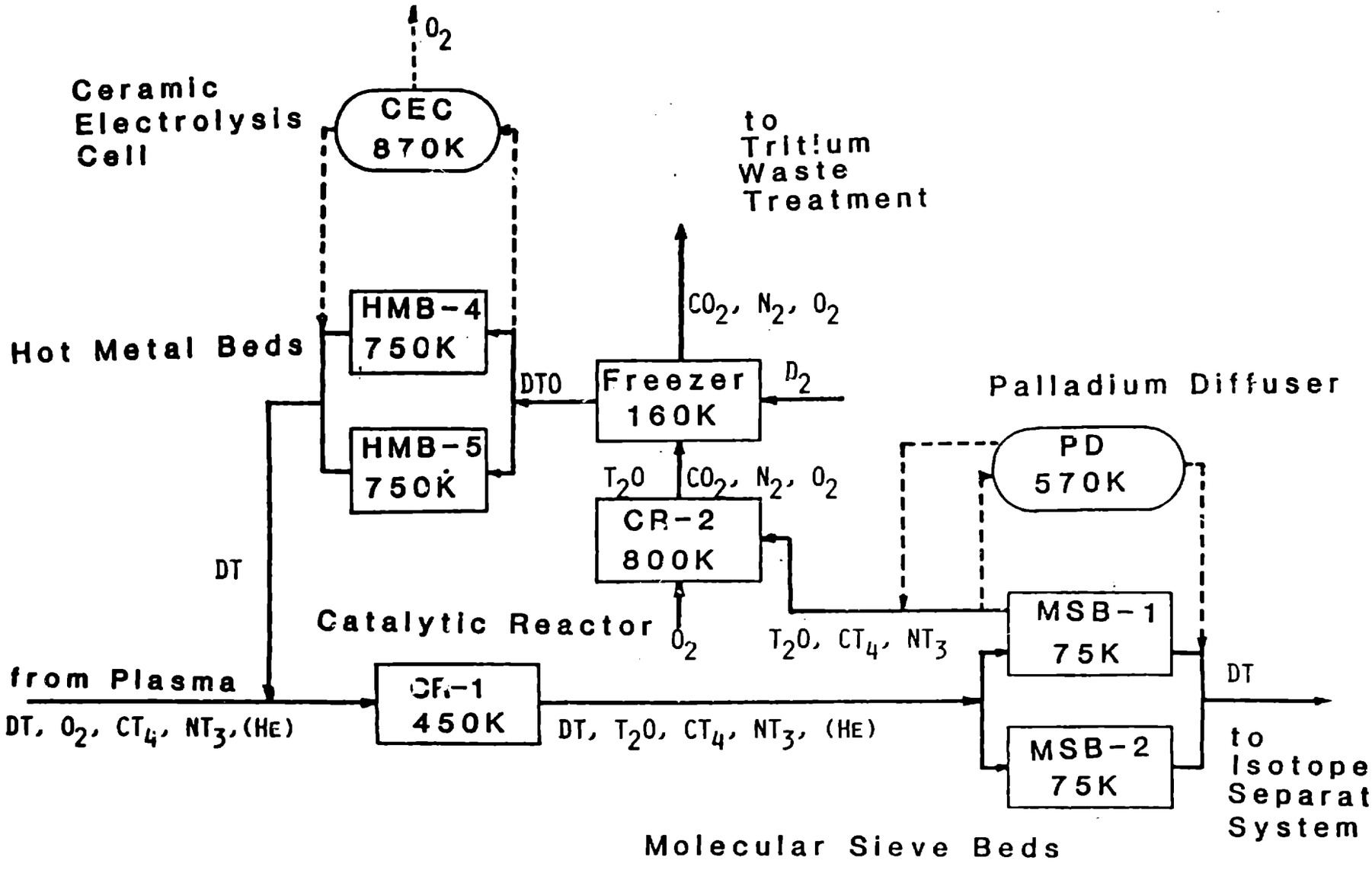

$O_2$
Ceramic Electrolysis Cell
CEC 870K
to Tritium Waste Treatment
$CO_2$, $N_2$, $O_2$
Hot Metal Beds
HMB-4 750K
HMB-5 750K
DTO
Freezer 160K
$D_2$
Palladium Diffuser
PD 570K
$T_2O$
$CO_2$, $N_2$, $O_2$
CR-2 800K
DT
Catalytic Reactor
$O_2$
$T_2O$, $CT_4$, $NT_3$
MSB-1 75K
from Plasma
DT, $O_2$, $CT_4$, $NT_3$, (HE)
CF-1 450K
DT, $T_2O$, $CT_4$, $NT_3$, (HE)
DT
MSB-2 75K
to Isotope Separat System
Molecular Sieve Beds

Fig. 1

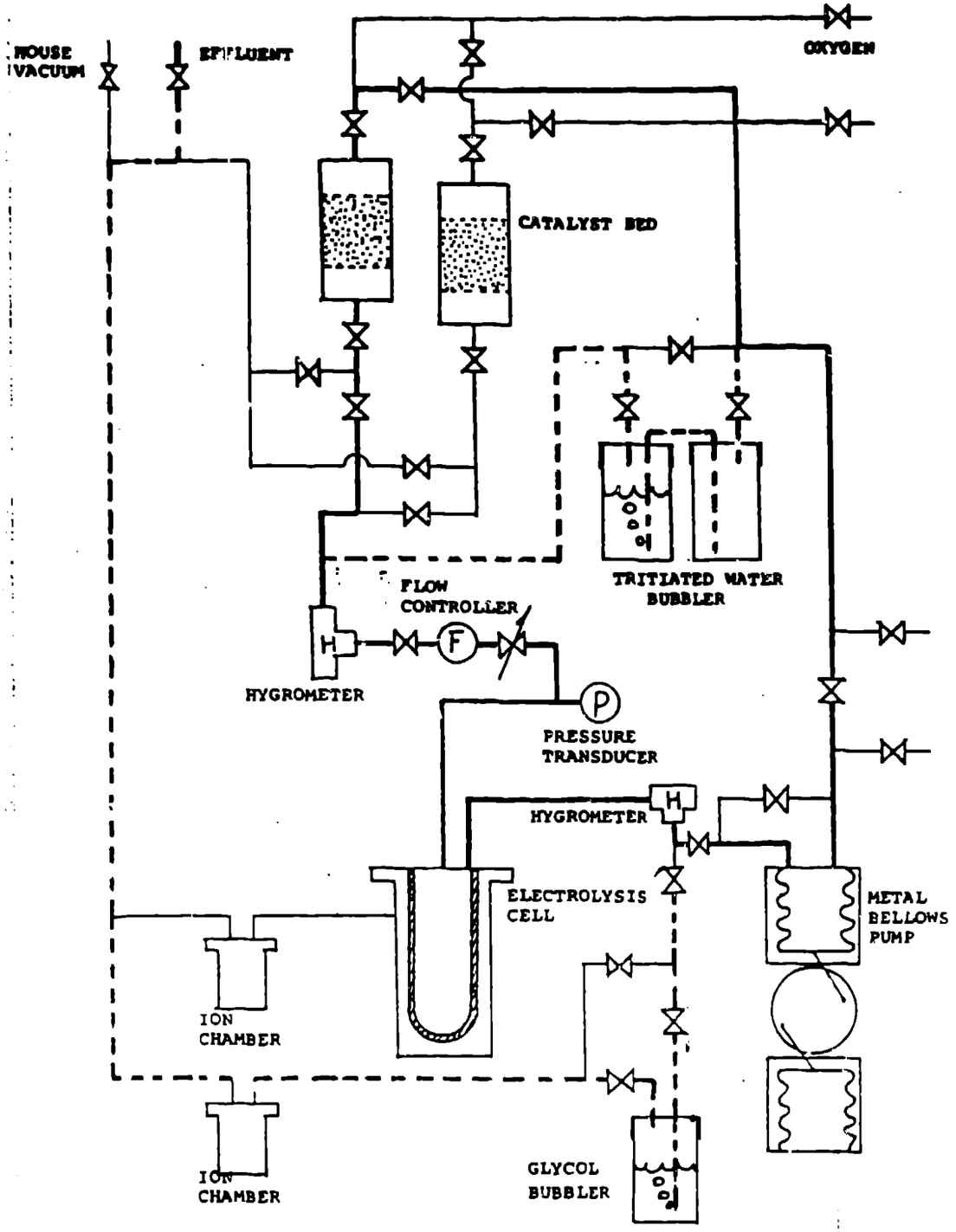

HOUSE VACUUM
EFFLUENT
OXYGEN
CATALYST BED
TRITIATED WATER BUBBLER
FLOW CONTROLLER
HYGROMETER
PRESSURE TRANSDUCER
HYGROMETER
ELECTROLYSIS CELL
METAL BELLOWS PUMP
ION CHAMBER
ION CHAMBER
GLYCOL BUBBLER

Fig. 3(b)

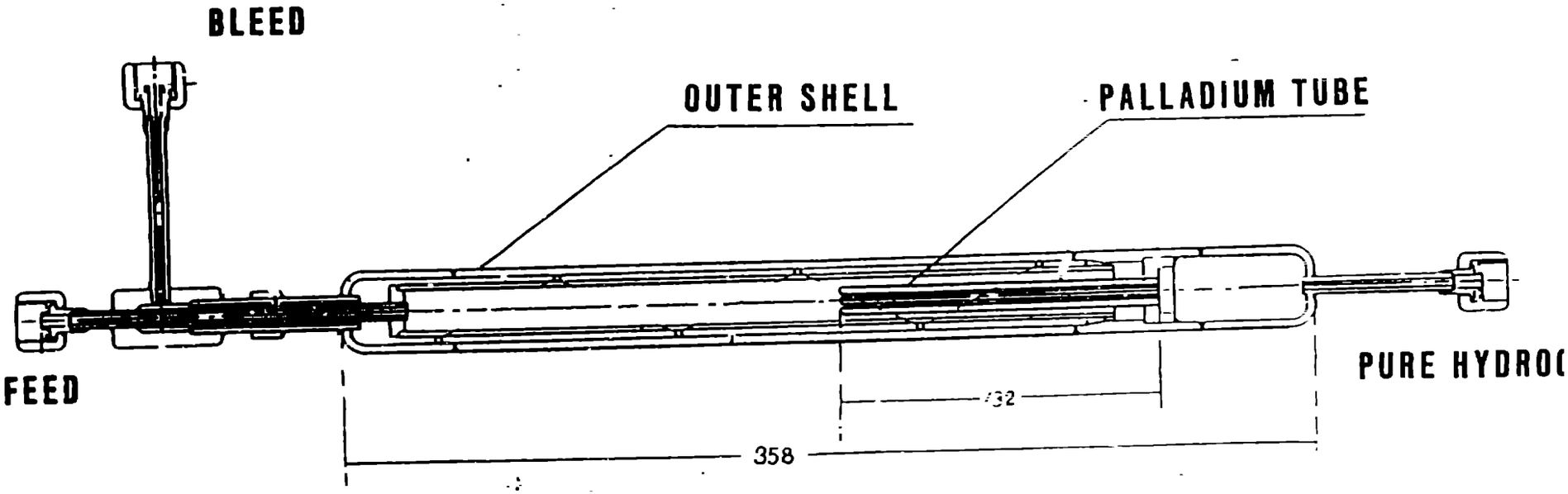
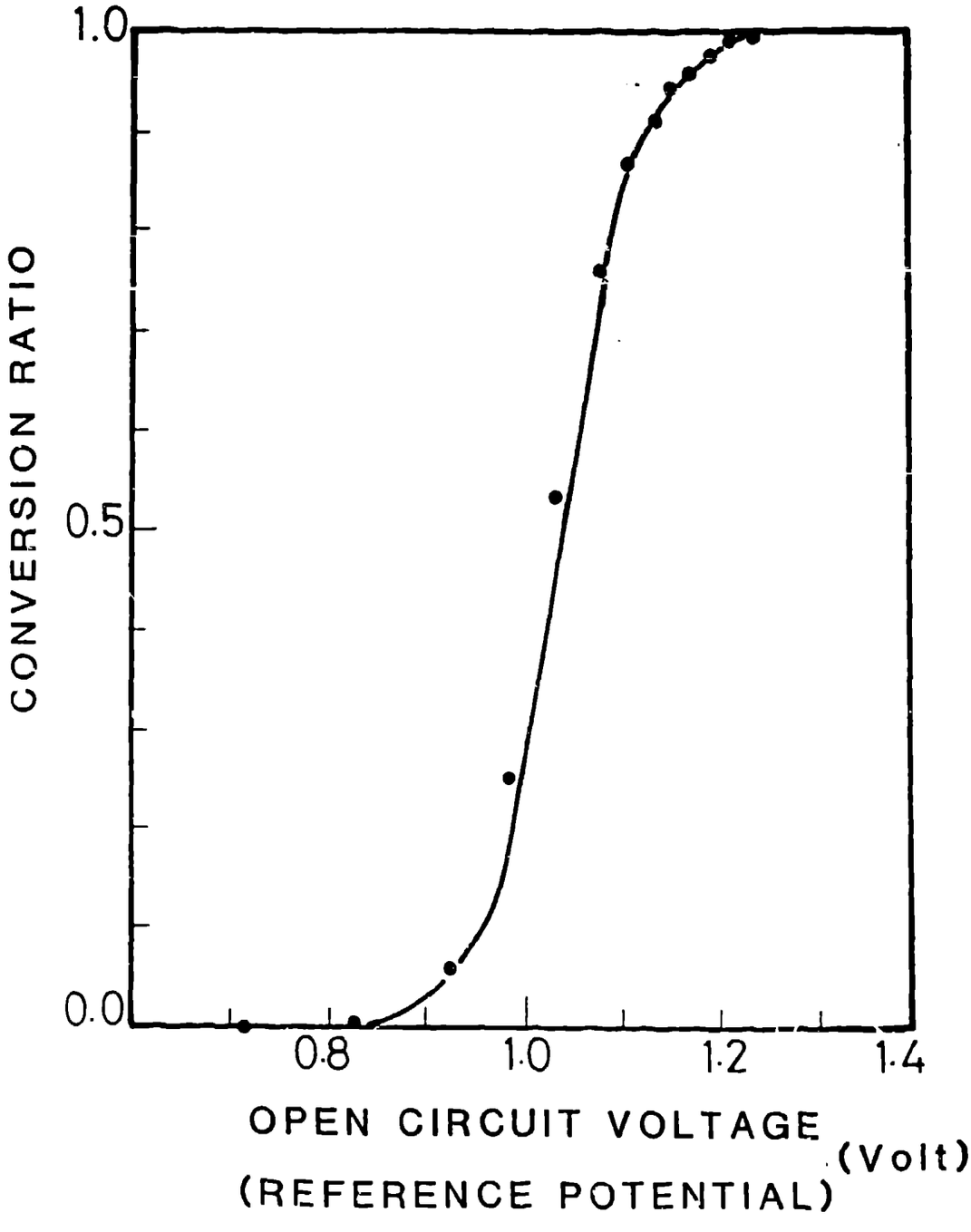



Fig. 4


1.0
0.5
0.0
CONVERSION RATIO
0.8
1.0
1.2
1.4
OPEN CIRCUIT VOLTAGE (Volt)
(REFERENCE POTENTIAL)

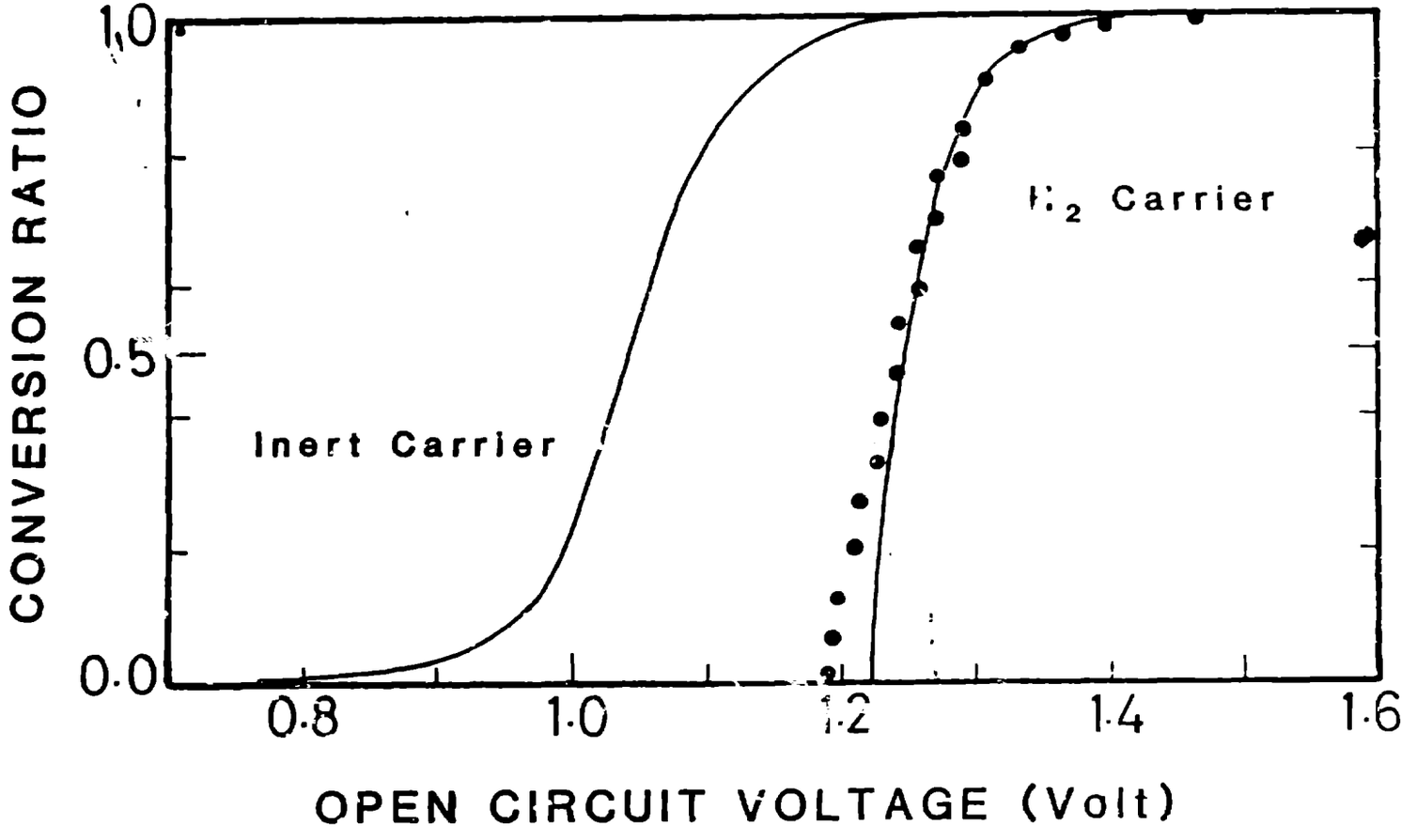

CONVERSION RATIO
1.0
0.5
0.0
0.8
1.0
1.2
1.4
1.6
Inert Carrier
H2 Carrier
OPEN CIRCUIT VOLTAGE (Volt)

Fig.6

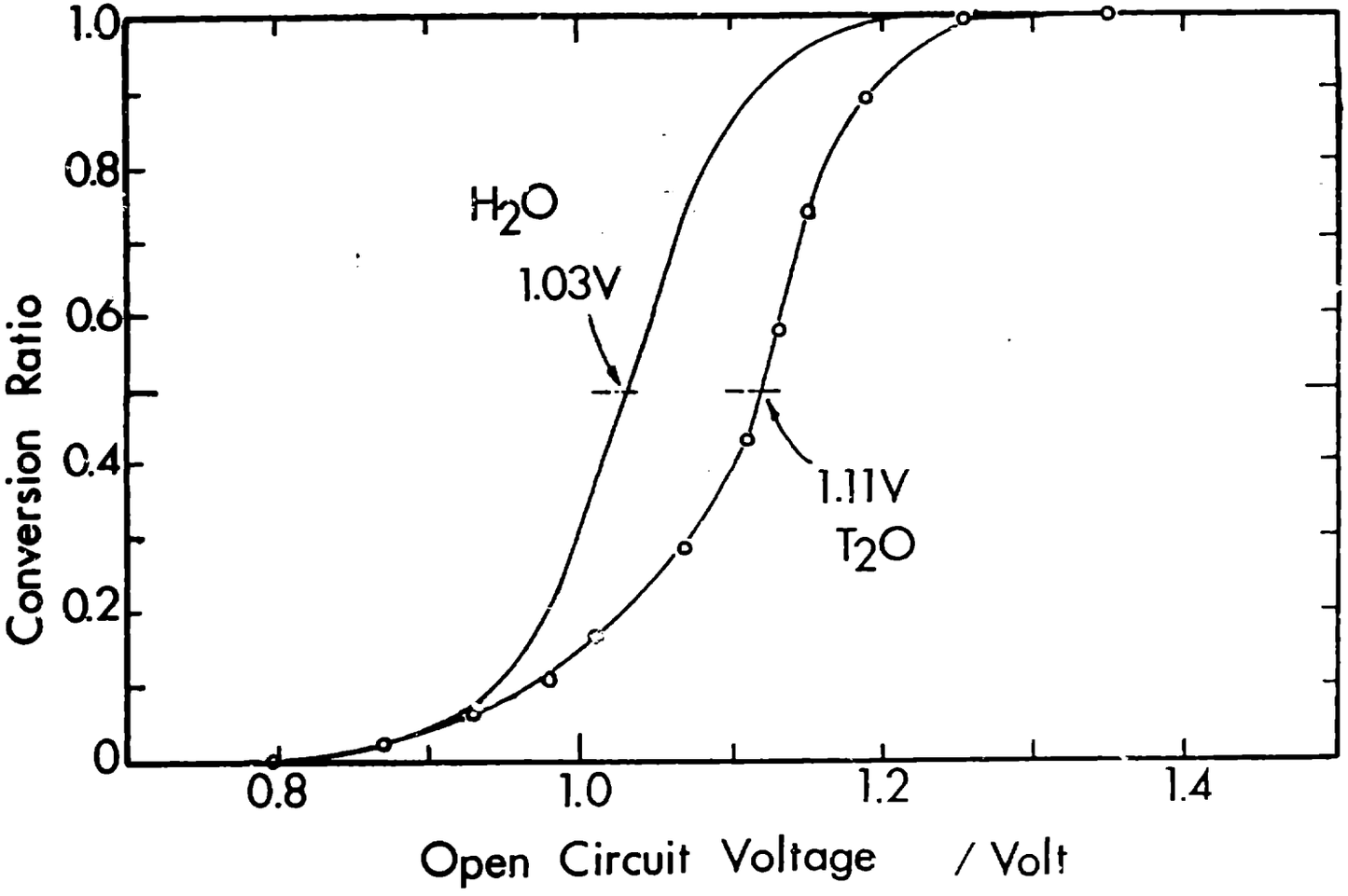

1.0
0.8
0.6
0.4
0.2
0
Conversion Ratio
H2O
1.03V
1.11V
T2O
0.8
1.0
1.2
1.4
Open Circuit Voltage / Volt

Fig. 7

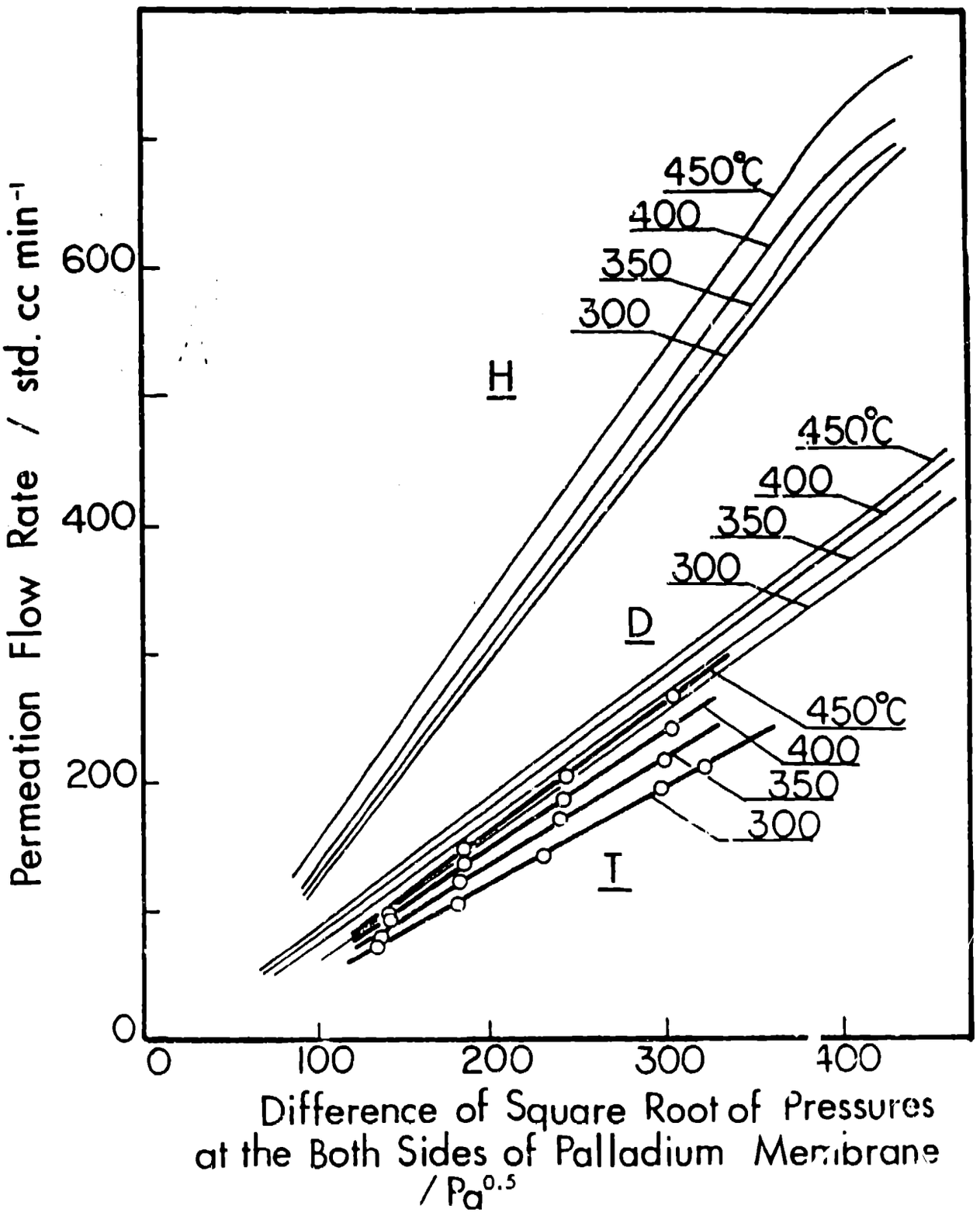

Permeation Flow Rate / std. cc min⁻¹
0
200
400
600
450°C
400
350
300
H
450°C
400
350
300
D
450°C
400
350
300
T
0
100
200
300
400
Difference of Square Root of Pressures
at the Both Sides of Palladium Membrane
/ Pa^0.5

Fig. 8

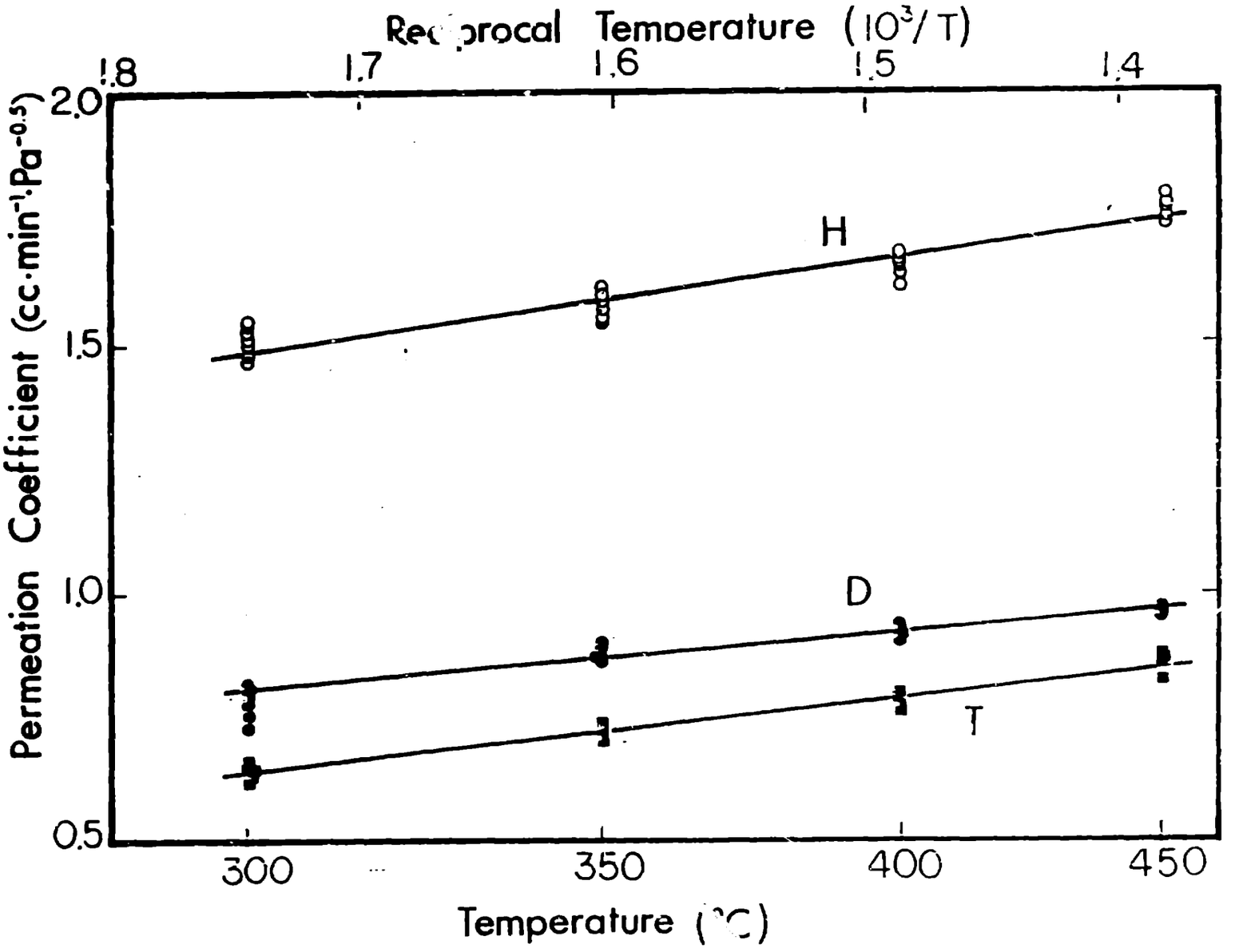

Reciprocal Temperature ($10^3$/T)
1.8
1.7
1.6
1.5
1.4
2.0
1.5
1.0
0.5
Permeation Coefficient (cc·min$^{-1}$·Pa$^{-0.5}$)
H
D
T
300
350
400
450
Temperature (°C)

Fig. 9

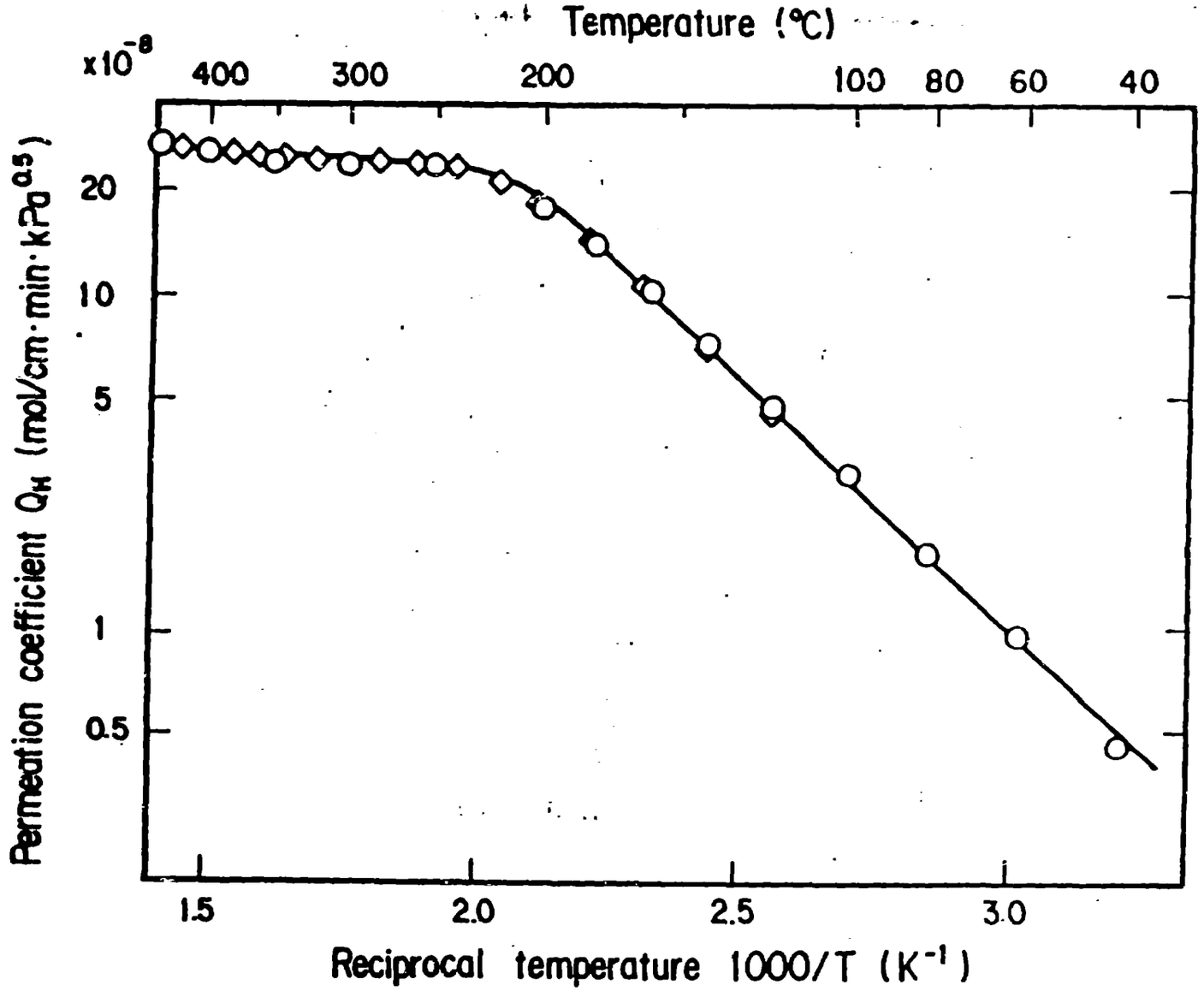

Temperature (°C)
x10⁻⁸
400
300
200
100
80
60
40
20
10
5
1
0.5
Permeation coefficient $Q_H$ (mol/cm·min·kPa$^{0.5}$)
1.5
2.0
2.5
3.0
Reciprocal temperature 1000/T (K$^{-1}$)

Fig. 10