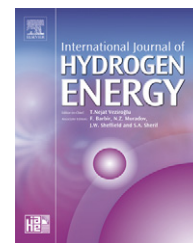


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Perturbed hydrogen permeation of a hydrogen mixture—New phenomena in hydrogen permeation by Pd membrane

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ABSTRACT

The newly developed constant concentration method was adopted to study the hydrogen permeation of a hydrogen mixture of $H_2 + Y$ through a palladium membrane tube. The hydrogen permeation of the hydrogen mixture differs from that of a single hydrogen feed. For the hydrogen mixture, the well-known Sieverts equation, $Q = J_H / [(P_R^H)^{1/2} - (P_P^H)^{1/2}]$, fails to yield the correct hydrogen flux or permeance even after the pressure terms are adjusted to the partial pressure of hydrogen. The hydrogen concentration in the mixture affects both the flux and the permeance.

Significant abnormal permeation of the non-hydrogen gas, Y, in the hydrogen permeates is detected during the hydrogen permeation of the mixture, $H_2 + Y$, even though Y-gas alone does not permeate through the defect-free palladium membrane. This Y-gas slippage in the presence of hydrogen in the mixture is tentatively attributed to the expansion of the palladium atomic lattice, enlarging inter-cluster openings. Y-gas permeates through the enlarged structure or grain boundary of the palladium atoms in the membrane.

The permselectivity of a palladium membrane cannot be measured simply from the ratio of two separate permeation fluxes of H_2 and Y. The permselectivity of a hydrogen mixture, $H_2 + Y$, measured by the constant concentration method in the retentate, is compared with that measured by the flowing-through method and with that determining from two separate measurements of H_2 and of Y. The three methods give different permselectivities of the same palladium membrane tube when the concentration ratio of H_2/Y is adjusted to 1.

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1. Introduction

The use of a palladium membrane to purify hydrogen from a hydrogen mixture, such as the reformat of the steam reforming reaction, which contains 75–78% of hydrogen, is important to supplying high-purity hydrogen for fuel cell applications [1–4]. We described earlier the abnormal diffusion of non-hydrogen gas, such as argon, nitrogen or

methane, through a defect-free palladium membrane in the presence of hydrogen, even though the same membrane rejects completely the non-hydrogen gas in the absence of hydrogen [5]. In the course of characterizing our palladium-membrane-assisted reformer to generate high-purity hydrogen from methanol, we determined that the hydrogen flux from the permeation of the crude hydrogen product mixture, about 75% of H_2 and 25% of CO_x , from 10 kgf/cm^2 in the

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Nomenclature			
F_0	flow rate of source stream in Pd membrane separator	P_P^H	hydrogen partial pressure in permeate side, kgf/cm ²
F_1	flow rate (stream) on retentate side	P_R^Y	Y-gas partial pressure in retentate side, kgf/cm ²
F_2	flow rate (stream) on permeate side	Q	hydrogen permeance, M ³ /M ² h (kgf/cm ²) ^{1/2}
F_3	flow rate (stream) from retentate side	$S_{H/Y}$	permselectivity of hydrogen mixture of H ₂ +Y-gas
J	hydrogen flux through Pd membrane, M ³ /M ² h	X_Y	molar fraction of Y-gas
		X_H	molar fraction of hydrogen

retentate side to atmospheric pressure in the permeate side, was always 47% to 49% of the hydrogen flux associated with single hydrogen permeation, rather than about 80%, which would be expected from Sieverts equation $[(10 * 0.75)^{1/2} - (1)^{1/2}] / [(10)^{1/2} - (1)^{1/2}] = 0.80$. Additionally, the permeation of the 50/50 mixture of H₂/CO₂ was only 24–25% of that of single hydrogen, rather than 57% as calculated.

The permeation of a hydrogen mixture differs from that of a single hydrogen feed in two important respects: the hydrogen partial pressure declines along the length of the membrane tube and the non-hydrogen component gas always contaminates the hydrogen permeate, even though this non-hydrogen gas alone does not permeate through the defect-free membrane. The hydrogen flux thus obtained corresponds to a particular average hydrogen concentration along the length of the tube—not to the concentration of the initial feed. Therefore, in applying Sieverts' equation, $Q = J_H / [(P_R^H)^n - (P_P^H)^n]$, or evaluating the “*n*” value to fit the equation for a hydrogen mixture, an inaccuracy arises because the obtained permeation flux does not correspond to the intended hydrogen concentration, the initial hydrogen concentration or the partial pressure in the mixture.

The second important difference in the diffusion of non-hydrogen gas through a defect-free palladium membrane in the presence of hydrogen in the mixture is that the measured magnitude of the permselectivity depends on the method of measurement [6]. The traditional method utilizes the ratio of fluxes, $S = J_H / J_Y$, obtained from two separate measurements of the two gases, H₂ and Y, and is very inaccurate, particularly for a defect-free membrane that has $J_Y \sim 0$ when a significant amount of Y-gas is present in the hydrogen permeate and measurements are made for an actual mixture of H₂ + Y.

Our earlier investigation also surprisingly showed that hydrogen flux decreased drastically as the hydrogen concentration in a hydrogen mixture decreased, even though the net hydrogen partial pressure was unchanged. The hydrogen flux of an H₂/Ar mixture (50/50) from 6 to 1 kgf/cm² was 4.76 M³/M²h, whereas that of a 75/25 mixture from 4 to 1 kgf/cm² was 7.84 M³/M²h, both mixtures had a hydrogen partial pressure of 3 kgf/cm² in the retentate side.

A better understanding of perturbed hydrogen permeation in a hydrogen mixture is important for future applications of membrane technology in hydrogen separation, especially as we enter the era of hydrogen energy. This investigation discusses in detail (1) the hydrogen permeation of hydrogen mixture, H₂ + Y with Y = Ar, CO₂, CH₄, N₂ at a constant concentration of hydrogen in the retentate side, to yield an accurate hydrogen flux and permeance at constant definite

hydrogen concentration; (2) evaluation of “*n*” in the Sieverts equation with accurate hydrogen flux at a constant hydrogen partial pressure; (3) the extent of permeation of non-hydrogen gases in the mixture and (4) a comparison of the permselectivity or separation factor for the palladium membrane as determined using different measurement.

2. Experimental

Materials: Palladium membrane tube, GHT110674, made of electroless plating of palladium membrane on porous stainless steel was supplied by Green Hydrotec Inc. of Tao-Yuan, Taiwan (<http://www.grnhydrotec.com>). The membrane tube had a palladium membrane thickness of about 15 μm estimated by weight and assuming a palladium density of 12. The membrane had a dimension of 9.5 mmOD × 114 mmL with a membrane area of 34.1 × 10⁻⁴ M². Prior to and after the measurement of hydrogen permeation, the membrane tube was tested for leakage with methane and helium gases under the pressure of 3, 4 and 6 kgf/cm² at 25 and 360 °C; the results are shown in Table 1. Generally the palladium membranes were kept under a temperature of 330–360 °C under inert gas when not in use for hydrogen permeation for a period of study of about 3 weeks. No cracking leading to leakage of these non-hydrogen gases (Y-gas) was detected. Hydrogen flux was also measured to characterize their performances; all these results were tabulated in Table 1.

All the argon, hydrogen and nitrogen gases were 99.995+% pure and were supplied by San Fu Gas Co of Taipei, Taiwan

Table 1 – Leak test of Palladium membrane with CH₄ and He gases at 360 °C^a

Operating pressure (atm)	Flow direction	CH ₄ leak amount (cc/min)	He leak amount (cc/min)
5	Inside out	Not detectable	0 ^b
10	Outside in	Not detectable	0 ^c

^a Leak test was routinely undertaken to make sure the membrane was in defect-free status before and after each series of permeation measurement of hydrogen.

^b Membrane tube was put in to water as He or CH₄ fed inside out. There was no bubble appeared during 5 min.

^c There was no He or CH₄ detected during 10 min.

(<http://www.sfgc.com.tw>) and gas mixtures of H₂ + CO₂ and H₂ + CH₄ were also supplied from the same source with CO₂ and CH₄ purity at 99% before mixing.

2.1. Measurement of hydrogen permeation of a hydrogen mixture with a constant concentration method

Hydrogen permeation of a hydrogen mixture, H₂ + Y, was measured with hydrogen partial pressure maintaining constant throughout the measurement in the chamber shown in Fig. 1. A fixed amount of Y-gas was first introduced into the

chamber to give a designated pressure of P_R^Y by opening the valve V1 and V5 and close the valves, V3, V4 and V6. Hydrogen was then introduced into the chamber until the total pressure, P_R = P_R^H + P_R^Y to attain the target hydrogen partial pressure of P_R^H, the molar fractions of the component gases are then X_H = P_R^H/P_R and X_Y = P_R^Y/P_R. Then V8 is opened to initiate the permeation of hydrogen through the palladium membrane; the hydrogen which permeates out of the membrane is made up by the fresh hydrogen from the hydrogen cylinder to keep its partial pressure constant at P_R^H. The rate of permeance, F₂, is the hydrogen flux under the

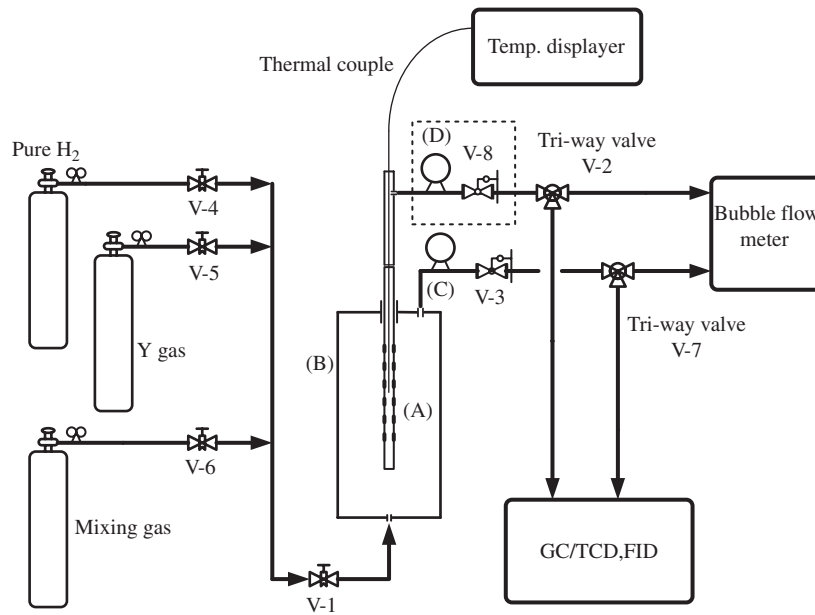


Fig. 1 – Schematic diagram of the new constant concentration method. (A) Pd membrane, 9.5 mmOD × 114 mmL, A = 34 cm²; (B) feed or retentate chamber: 30 mmID × 800 mmL; (C) pressure gauge of reactor; (D) pressure gauge of permeating stream; V-3, back pressure valve of vent gas; V-8, back pressure valve of hydrogen permeating stream in permeation side Y-gas could be Ar, N₂, He, CO₂, CH₄, etc.

Table 2 – Hydrogen fluxes from the permeation of H₂ + Y at 360 °C

P _R (kgf/cm ²)	Hydrogen fluxes through Pd membrane of H ₂ + Y in M ³ /M ² h								
	H ₂ /H ₂		H ₂ /Y(75/25)			H ₂ /Y(50/50)			
	Exp.	Cal. ^a	Exp.		Cal. ^a	Exp.		Cal. ^a	
			Y = Ar	Y = N ₂		Y = Ar	Y = N ₂		
2	3.81	5.22	2.68	1.89	2.83				
3	8.05	9.22	5.25	4.67	6.30	2.21	2.30	2.83	
4	11.73	12.60	7.84	7.34	9.22	3.18	3.48	5.22	
5	15.46	15.57	10.68	9.72	10.47	11.80	4.27	4.21	7.32
6	18.30	18.26	12.72	11.90	12.71	14.13	4.76	4.65	9.22
7	21.28	20.74	15.29	14.83	14.83	16.27	5.37	5.32	10.97
8	24.00	23.04	16.94	16.87	16.94	18.26	6.02	6.06	12.60

PS: the pressure of permeation side (P_p) was set in atmosphere.

^a The calculation was calculated from equation as $J = Q[(P_H^R)^{1/12} - (P_H^P)^{1/2}]$, where Q was used as 12.6 M³/M² h (kgf/cm²)^{0.5}.

Table 3 – Hydrogen flux of single hydrogen under constant pressure differential at 360 °C

P_R (kgf/cm ²)	P_P (kgf/cm ²)	$P_R - P_P$ (kgf/cm ²)	$P_R^{1/2} - P_P^{1/2}$ (kgf/cm ²) ^{1/2}	J_{Exp}^a	J_1^b	$J_{1/2}^c$	$\frac{J_1}{J_{Exp}}$	$\frac{J_{1/2}}{J_{Exp}}$
3	1	2	0.732	8.05	7.20	9.22	0.894	1.145
4	2	2	0.586	6.07	7.20	7.38	1.186	1.216
5	3	2	0.504	5.31	7.20	6.35	1.356	1.196
6	4	2	0.449	4.71	7.20	5.66	1.529	1.202
7	5	2	0.410	3.95	7.20	5.17	1.823	1.309
8	6	2	0.379	3.57	7.20	4.77	2.017	1.336
4	1	3	1.000	11.73	10.80	12.60	0.921	1.074
5	2	3	0.822	9.67	10.80	10.36	1.117	1.071
6	3	3	0.717	8.51		9.03	1.269	1.061
7	4	3	0.646	7.48	10.80	8.14	1.444	1.088
8	5	3	0.592	6.61	10.80	7.46	1.634	1.128
5	1	4	1.236	15.46	14.40	15.57	0.931	1.007
6	2	4	1.035	12.96	14.40	13.04	1.135	1.027
7	3	4	0.914	10.75	14.40	11.52	1.339	1.072
8	4	4	0.828	9.87	14.40	10.43	1.459	1.057
6	1	5	1.449	18.30	18.00	18.26	0.984	0.999
7	2	5	1.232	15.07		15.52	1.194	1.030
8	3	5	1.096	12.78		13.81	1.408	1.080

^a J_{Exp} was the actual hydrogen flux from permeation experiment of pure hydrogen.

^b J_1 was calculated from $J_1 = Q_1[P_R - P_P]$ with $Q_1 = 3.60 M^3/M^2 - hr - P$ from Fig. 3.

^c $J_{1/2}$ was calculated from $J_{1/2} = Q_{1/2}[P_R^{1/2} - P_P^{1/2}]$ with $Q_{1/2} = 12.6 M^3/M^2 - hr - P^{1/2}$ from Fig. 4.

corresponding molar fraction of X_H . The results of hydrogen flux from three series of the hydrogen mixtures, $H_2 + Y$ with $Y = Ar, N_2, CH_4$ and CO_2 , are shown in Table 2.

2.2. Permeation with permeate pressure higher than ambient pressure

The permeation experiments were carried out in the same equipment described above except that a back pressure regulator was attached to the exit of permeate side. The pressure in the permeate stream, F_2 , was set by the back pressure regulator to the desired permeate pressure of P_P which differed from ambient pressure. The results are shown in Table 3.

2.3. Measurement of the minimum hydrogen partial pressure required for permeation of methane through Pd membrane

The hydrogen constant concentration method was used to obtain the minimum hydrogen flux permeating through palladium in hydrogen mixture with methane. Pure methane was first fed into the retentate chamber to a pressure of $P_R^{CH_4}$, and there was no methane leaking through palladium membrane to permeation side. Hydrogen was then fed into retentate chamber to a total pressure of $P_R = P_R^{CH_4} + P_R^{H_2}$; hydrogen was detected immediately in the permeate side containing some percentage of methane. If the pressure differential between the retentate and the permeate, $P_R^{H_2} - P_P^{H_2}$, was not high enough to diffuse out hydrogen permeate inside the membrane tube, the methane slippage

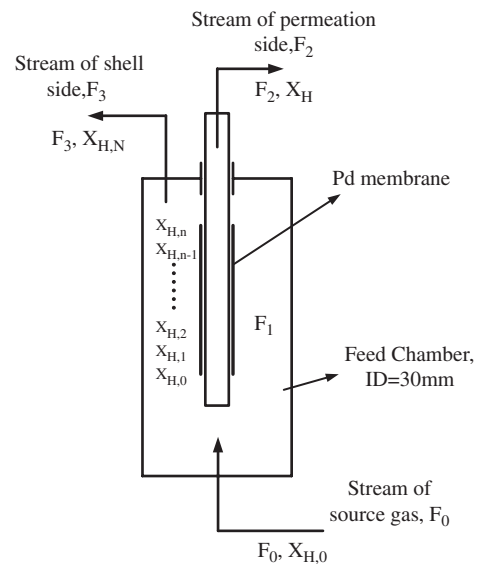


Fig. 2 – Flow diagram of the conventional flow stream method.

will stop as hydrogen partial pressure in the retentate and in the permeate became equal as in the case of Exps. 10 and 14. The minimum hydrogen partial pressure was measured when permeation had just started permeating and then stopped, and the pressure differential of hydrogen partial pressure decreased. As hydrogen permeation stopped, the concentration of methane was very high as shown in the case of Exps. 10 and 14. The leak test of the palladium membrane was conducted and showed no leakage with methane at

10 kgf/cm² after the whole series of experiment was completed (Fig. 2).

3. Results and discussion

Traditionally, hydrogen flux or permeance is measured using a flow-through of gas mixture along the length of the membrane of interest [7,8]; this procedure frequently causes variation in the hydrogen partial pressure along the membrane tube, unless special care is taken to maintain a small stage-cut, say 5%, to ensure a roughly constant concentration in the retentate side [9,10]. The hydrogen flux thus obtained in this way corresponds to a particular mean partial pressure of hydrogen between that at the inlet and that at the exit ends of the retentate. When this hydrogen flux is made to be correlated with the flux that corresponds to a pressure difference in Sieverts equation of $Q = J_H / [(P_R^H)^n - (P_P^H)^n]$, where J_H is the actual hydrogen flux when the pressure in the retentate is P_R and that in the permeate side is P_P , and Q is the permeance in units of $M^3/M^2 h (kgf/cm^2)^n$, the value of the exponent “ n ” is generally between 0.5 and 1.0. The value $n = 0.5$ is attributed to the fact that the rate determining step of permeation is the bulk diffusion of hydrogen atoms inside the membrane lattice while $n = 1.0$ corresponds to the rate determining step's being surface chemisorption [11–15]. Therefore, a value of “ n ” between these two values may result from experimental error or inconsistent hydrogen partial pressure along the membrane, since the preliminary results indicated that hydrogen permeance varies with the concentration of hydrogen in the mixture.

Before actual usage, the porous stainless supported palladium membrane tube underwent a leak test with helium and methane; the membrane was tested for leakage again after each series of permeation measurements to ensure the reliability of the data. The results in Table 1 show that the membranes were all defect-free without leakage at 25 °C up to a pressure of 10 kgf/cm² in the retentate side. However, less than 0.1 cc/min of helium, but not methane, may occasionally show leakage through the membrane when the pressure exceeded 10 kgf/cm² at 360 °C. Therefore, in the leak test of a palladium membrane, a higher testing temperature and pressure (> 10 kgf/cm²) are preferred.

Table 2 presents the results of the hydrogen permeation of various hydrogen mixtures, $H_2 + Y$, where Y is Ar, CH_4 or N_2 and $H_2/Y = 50/50$ and $75/25$ molar ratios. The hydrogen flux is strongly related to the variation of the hydrogen concentration at the same pressure differential. The sensitivity to concentration substantially exceeds that to the actual hydrogen partial pressure. Accordingly, while the hydrogen partial pressure in the retentate sides (P_R^H) was maintained at 3 kgf/cm², the fluxes of H_2/Ar and $H_2/N_2 = 50/50$ with $P_R = 6$ and $P_P = 1$ were 4.76 and 4.65 $M^3/M^2 h$, respectively, and were much smaller than those, 7.84 and 7.34 $M^3/M^2 h$ of H_2/Ar and $H_2/N_2 = 75/25$ at $P_R = 4$ and $P_P = 1$, respectively. Likewise, at a hydrogen partial pressure of 4 kgf/cm² (from $8 * 50/100$) in the retentate side, the 50/50 mixture has a hydrogen flux of about 6.02 or 6.06 $M^3/M^2 h$, which is lower than the value 9.72 or 10.68 $M^3/M^2 h$ for the 75/25 mixtures, even though the hydrogen partial pressure of the latter was lower, being only

3.75 kgf/cm² (from $5 * 75/100$). Except in the experiments in which the pressure differentials in the retentate and permeate sides are very small, the hydrogen flux was independent of the nature of the Y -gas, for the same pressure differential and the same hydrogen concentration; the hydrogen flux was almost the same regardless of whether $Y = Ar, CH_4$ or N_2 .

3.1. Evaluation of pressure sensitivity, “ n ” in equation, $J = Q[(P_R^H)^n - (P_P^H)^n]$

The permeance of hydrogen through a palladium membrane is typically given by an equation, $J = Q[(P_R^H)^n - (P_P^H)^n]$. The exponent, “ n ”, is a pressure sensitivity index and is related to the permeation mechanism, as mentioned above. In the permeation of single hydrogen, the pressure terms are straightforward. To find a suitable n -value, hydrogen permeance of single hydrogen feed was first evaluated by determining the relationship between the pressure differential, ΔP^n ,

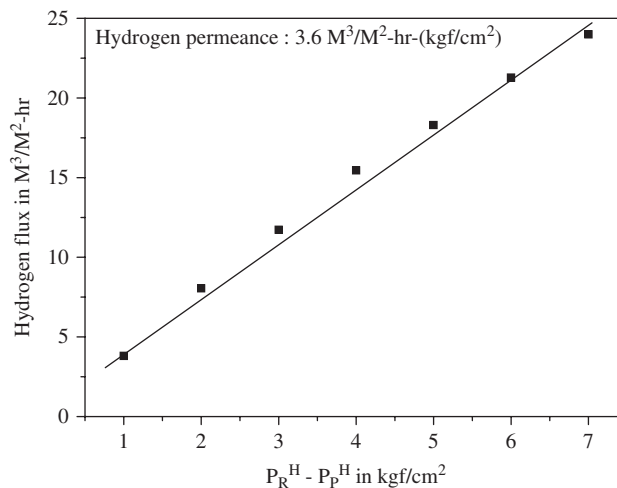


Fig. 3 – Correlation of hydrogen flux with $(P_R^H)^n - (P_P^H)^n$ for $n = 1.0$ using single hydrogen feed.

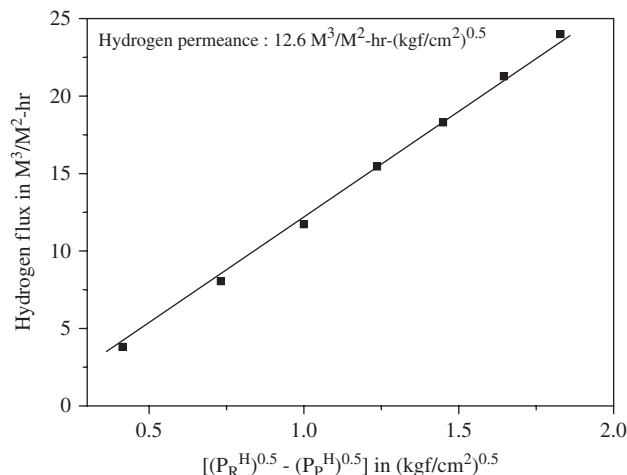


Fig. 4 – Correlation of hydrogen flux with $(P_R^H)^n - (P_P^H)^n$ for $n = 0.5$ using single hydrogen feed.

shown in Fig. 3, for $n = 1$ and that presented in Fig. 4 for $n = \frac{1}{2}$. The slopes in Figs. 3 and 4, respectively, were $Q_1 = 3.60 \text{ M}^3/\text{M}^2 \text{ h} (\text{kgf}/\text{cm}^2)$ with a correlation coefficient of $R^2 = 0.986$ and $Q_{1/2} = 12.6 \text{ M}^3/\text{M}^2 \text{ h} (\text{kgf}/\text{cm}^2)^{1/2}$ and $R^2 = 0.983$.

Both correlations for $n = 1.0$ or $\frac{1}{2}$ were linear, with $R^2 = 0.986$ for $n = 1$ vs. $R^2 = 0.983$ for $n = \frac{1}{2}$; the linear correlation alone therefore cannot distinguish case from the other. Hence, an additional test was performed by comparing hydrogen fluxes from the constant pressure differential ΔP^n from $P_p \geq 1$, for $n = 1.0$ and $\frac{1}{2}$. Table 3 compares the hydrogen fluxes of the actual permeation experiment with pure hydrogen, J_{Exp} , with the fluxes $J^{1.0}$ and $J^{1/2}$ that were calculated using the equation $J_n = Q_n[(P_R^H)^n - (P_P^H)^n]$ with $n = 1.0$ and $\frac{1}{2}$, respectively. First, the experimental J_{Exp} from a constant $\Delta P^1 = 2$ has no constant value ranging from 8.05 to $3.57 \text{ M}^3/\text{M}^2 \text{ h}$ when hydrogen fluxes from various pairs of P_R and P_P were used to obtain $\Delta P^1 = 2 = P_R - P_P = 3 - 1 = 4 - 2 = 5 - 3 = 6 - 4 = 7 - 5 = 8 - 6$. Similar results were obtained for J_{Exp} with $\Delta P^1 = 3, 4$ or 5 . On the $\Delta P^{1/2}$ side, exact equality was not attempted because of difficulty of fine-tuning the pressure gauge. However, when $\Delta P^{1/2}$ with a 10% deviation was used for the comparison, then the corresponding J_{Exp} values are all close enough within 10% variations. For example, when $\Delta P^1 = 3$, $J_{\text{Exp}} = 11.73 \text{ M}^3/\text{M}^2 \text{ h}$ from $P_R = 4$ and $P_P = 1$, $J_{\text{Exp}} = 8.51 \text{ M}^3/\text{M}^2 \text{ h}$ from $P_R = 6$ and $P_P = 3$ and $J_{\text{Exp}} = 6.61 \text{ M}^3/\text{M}^2 \text{ h}$ from $P_R = 8$ and $P_P = 5$. No such systematic decline was observed in J_{Exp} when $\Delta P^{1/2}$ was the basis of comparison. For instance, for $\Delta P^{1/2} = 0.822$ from $P_R = 5$ and $P_P = 2$ and 0.828 from $P_R = 8$ and $P_P = 4$; the corresponding J_{Exp} were 9.67 and $9.87 \text{ M}^3/\text{M}^2 \text{ h}$, respectively. When $\Delta P^{1/2} = 1.232$ from $P_R = 7$ and $P_P = 2$ and 1.236 from $P_R = 5$ and $P_P = 1$, the corresponding J_{Exp} values were 15.07 and 15.46, respectively. Likewise, for $\Delta P^{1/2} = 1.000, 1.035$ and 1.096 or for $\Delta P^{1/2} = 0.586$ and 0.592 , the corresponding J_{Exp} were within only 10% of each other.

When $J^{1.0}/J_{\text{Exp}}$ and $J^{1/2}/J_{\text{Exp}}$ were used to compare the deviations of the calculated flux of $J^{1.0}$ and $J^{1/2}$ with the experimental flux, J_{Exp} , $J^{1/2}/J_{\text{Exp}}$ always remained within 10% of each others except when pressure differential was small such as when $\Delta P^1 = 2$, whereas $J^{1.0}/J_{\text{Exp}}$ fluctuated substantially. When the pressure differential was small, experimental measurement of hydrogen flux became difficult and not reproducible, increasing the deviation of $J^{1/2}/J_{\text{Exp}}$ or $J^{1.0}/J_{\text{Exp}}$. In

conclusion, the Sieverts equation $J = Q[(P_R^H)^n - (P_P^H)^n]$ correlates better when $n = \frac{1}{2}$, indicating that lattice diffusion is the rate determining step inside the membrane bulk. However, in practical usage, when $P_p = 1 \text{ kgf}/\text{cm}^2$, the equation with $n = 1$ can also be used.

3.2. Dominant effect of hydrogen concentration on hydrogen permeance

As discussed in the preceding section, $n = \frac{1}{2}$ makes the Sieverts equation, $Q = J/[(P_R^H)^n - (P_P^H)^n]$ fits the results better. As presented in Table 2, the hydrogen flux is sensitive not only to the pressure differential but also to the hydrogen concentration or partial pressure in the retentate side. Therefore, if the hydrogen flux is not measured under a constant hydrogen partial pressure, it will not accurately reflect the flux of the corresponding concentration. In the traditional method, the feed mixture flows through a membrane tube and the hydrogen flux from the permeate side is measured with or without flashing gas or a vacuum in the permeate side. With such a setup, unless care is taken to ensure that the stage-cut is very small or near-zero by using a short membrane tube or by setting a very high feed flow rate, the hydrogen flux will be an average of the hydrogen concentrations at the inlet and the exit. As described below, hydrogen and Y-gas exhibit different sensitivities to pressure difference.

Table 4 presents the hydrogen permeance of pure hydrogen and hydrogen mixtures of $\text{H}_2 + \text{Y}$ with $\text{Y} = \text{Ar}, \text{N}_2$ and CH_4 . The partial pressure of hydrogen in the hydrogen mixture and $n = \frac{1}{2}$ are used to correlate J_{Exp} with $P_R^{1/2} - P_P^{1/2}$. The results in Table 4 indicate that the permeances of all three hydrogen mixtures are almost identical, as long as the hydrogen concentration in the feed is the same. However, the permeance decreases as the hydrogen concentration in the feed is reduced, even though the pressure term in the Sieverts equation has been adjusted according to the partial pressure associated with the concentration. Interestingly, the decrease in hydrogen flux from the single hydrogen feed to 75% or to 50% is much more severe than would be calculated using the partial pressure in the Sieverts equation. Thus, using a permeance of $12.6 \text{ M}^3/\text{M}^2 \text{ h } P^{1/2}$ at 360°C for single hydrogen

Table 4 – Hydrogen permeance of mixture, $\text{H}_2 + \text{Y}$ with $\text{Y} = \text{Ar}, \text{N}_2$ and CH_4 at 360°C

$\text{H}_2 + \text{Y}, \text{Y} =$	H_2 (% concentration)	Permeance ($\text{M}^3/\text{M}^2 \text{ h} (\text{kgf}/\text{cm}^2)^n$)		R^2 -correlation coefficient	
		$Q(1/2), n = 0.5$	$Q(1), n = 1.0$	$n = 0.5$	$n = 1.0$
H_2	99.995	12.6	3.60	0.983	0.986
Ar	75	11.5	3.6	0.995	0.978
	50	6.5	2.3	0.862	0.645
N_2	75	11.0	2.7	0.981	0.953
	50	6.5	2.3	0.794	0.532
CH_4	80	11.9	3.6	0.974	0.991
	75	11.4	3.5	0.995	0.952
	66	10.8	3.5	0.981	0.988

permeation would yield a calculated hydrogen flux of $23.04 \text{ M}^3/\text{M}^2 \text{ h}$ between $P_R = 8$ and $P_P = 1 \text{ kgf}/\text{cm}^2$ for the single hydrogen feed; 18.26 for both a single hydrogen feed with $P_R = P_R^H = 6$, $P_P = 1 \text{ kgf}/\text{cm}^2$ and for a 75/25 hydrogen mixture with $P_R = 8$ ($P_R^H = 6$) and $P_P = 1 \text{ kgf}/\text{cm}^2$; $12.60 \text{ M}^3/\text{M}^2 \text{ h}$ for a single hydrogen feed with $P_R = P_R^H = 4$ and $P_P = 1 \text{ kgf}/\text{cm}^2$ and for a 50/50 hydrogen mixture with $P_R = 8$ ($P_R^H = 4$) and $P_P = 1 \text{ kgf}/\text{cm}^2$, if the hydrogen pressure differential were the only driving force of hydrogen permeation. Experimentally, the corresponding hydrogen fluxes are 24.0 for the single hydrogen and 12.72 and $4.76 \text{ M}^3/\text{M}^2 \text{ h}$ (Table 2) for the 75/25 and 50/50 H_2/Ar mixtures, respectively. A similar deviation was observed for permeations between $P_R = 8, 5$ or 4 and $P_P = 1$. Reducing the concentration of hydrogen in the mixture appears to increase the deviation from the calculated flux. The cause of this deviation is intriguing and is speculated upon below.

The use of partial pressure as the pressure term in the equation is supposed to adjust for the difference from the actual hydrogen concentration to the 100% basis; the effect of the non-hydrogen component is thus assumed to be neutral or non-existent. Perhaps this assumption is incorrect and the decline in the permeance with the decline in the concentration of hydrogen in the mixture is attributable to the interference of the Y-gas in the retentate vapor space, which limits the mass transfer of the hydrogen gas, or/and to the increase in the interference of Y-gas with the permeation of hydrogen inside the membrane. If the external mass transfer in the vapor phase is limited in permeation, then the following results are expected; (1) $n = 1.0$ in the Sieverts equation; (2) the partial pressure proportionally affects hydrogen flux and permeance and (3) the effect of the Y-gas nature will have different effect on the flux or on the permeance because those Y-gases differ in molecular weight and have different abilities to be adsorbed onto the membrane surface to forming a thin film barrier to the transfer of hydrogen molecules to the membrane surface. These expectations were inconsistent with the experimental results that (1) $n = 0.5$ fits better in the Sieverts equation; (2) correcting the partial pressure fails to give a satisfactory result, and the deviation from the calculated flux obtained when the partial pressure of hydrogen is used increases with the amount of non-hydrogen gas; and that (3) the flux and permeance vary

with the concentration but not the nature of the Y-gas. Having ruled out external mass transfer limitation, we are forced to speculate about possible interference between Y-gas molecules and hydrogen atoms on the membrane surface or inside the membrane bulk. This interference may occur during the chemisorption of hydrogen on the membrane surface or during hydrogen diffusion inside the membrane bulk, the cause of which is unknown. These possibilities will be discussed in the following section on the variation of hydrogen purity in the permeate flux.

3.3. Perturbed hydrogen permeation of a hydrogen mixture

Table 5 compares the permselectivities of hydrogen and methane mixture at 350°C obtained using three methods. The conventional method of separately comparing individual flows of hydrogen and of non-hydrogen gas, $Y = \text{CH}_4$, yielded an almost infinitely large selectivity because the membrane was defect-free and no methane was detected using either a gas chromatograph (GC) or a soap-bubble flow meter. However, when a hydrogen mixture of $75\% \text{H}_2 + 25\% \text{CH}_4$ was used in the actual permeation test with the constant concentration method between $P_R = 10$ and $P_P = 1 \text{ kgf}/\text{cm}^2$, surprisingly, 154 ppm of methane was detected in the permeate side, corresponding to a permselectivity of $2164 [(1,000,000 - 154)/(154 \times (75/25))]$. Interestingly, when a flow-through method was utilized, the methane concentration increased to 280 ppm , resulting in a permselectivity of 1190 . Of the three values of permselectivity, 2164 is that obtained at a constant concentration of $75\% \text{H}_2 + 25\% \text{CH}_4$; the permselectivity of 1190 obtained using the flow-through method apparently corresponds to the hydrogen concentration between the inlet (75%) and the outlet (55%) under the flow conditions. The latter value is a realistic permselectivity that is obtained by performing an actual separation operation. Therefore, this flow-through method is recommended as a practical method of industrial hydrogen purification. However, the constant concentration method is recommended to characterize membranes (Fig. 5).

The higher methane concentration in the permeate side, 280 ppm , obtained using the flow-through method, was

Table 5 – Permselectivity of hydrogen mixtures, $\text{H}_2 + \text{CH}_4$, at 350 and 400°C

Y-gas	P_R (kgf/cm ²)	Method						
		Constant concen.		Flow-through		Indiv. flow (cc/min)		
		Y^a (ppm)	$S_{H/Y}^b$	Y^a (ppm)	$S_{H/Y}^b$	H_2	Y	$S_{H/Y}^b$
25% CH_4	8	99 [86 ^c]	3367 [3876 ^c]	252	1322			
	10	154 [124 ^c]	2164 [2688 ^c]	280	1190			
Pure CH_4	10					1193 [1569 ^c]	0	∞

^a GC analysis equipped with FID for CH_4 by a $1/8$ in $\text{OD} \times 2$ meter Poarapak Q column.

^b $S_{H/Y}$ = separation factor of hydrogen = volume ratio of H_2/Y in the permeate/volume ratio of H_2/Y in the feed or (flow rate through Pd membrane)/(Y-gas flow rate through Pd membrane) in the case of individual flow measurement.

^c Operation temperature was 400°C .

attributed to the higher average concentration of methane in the retentate side, 25%, at the inlet and 50% at the outlet, when hydrogen permeated through the membrane along the 114 mm length of the membrane tube. The methane concentration in the permeate side would have increased with the methane concentration in the retentate, as was the case in Table 6. This phenomenon is tested using two mixtures, 95% H_2 + 5%Ar and 90% H_2 + 10%Ar. Since the permeation feeds at 10 kgf/cm² in the retentate side and at atmospheric pressure in the permeated side, 46.3 and 105 ppm of Ar were detected in the permeate, respectively, using a GC that was

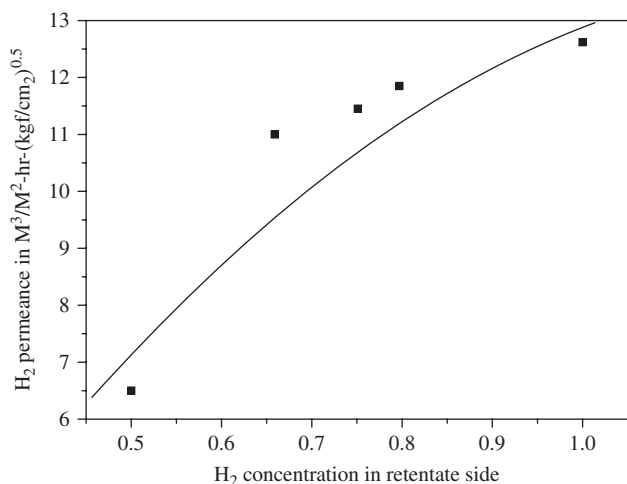


Fig. 5 – Relationship between permeance and hydrogen concentrations in hydrogen mixture.

equipped with DID detector. Argon has a larger kinetic diameter (35 Å) than CO₂ (3.3–3.9 Å) [16]. Unlike methane, argon is an inert gas that does not chemisorb on the membrane surface; therefore, diffusive leakage does not depend on prior chemisorption on the palladium membrane surface.

The results in Table 6 were obtained using a minimum hydrogen partial pressure differential that was sufficiently low to allow permeation and analysis of the permeate. Under this condition, the rate of methane leakage or permeation appeared to reach an approximately constant value at a concentration of as high as 5000 ppm when the hydrogen fraction was low, when the pressure differential of hydrogen between retentate and permeate sides was minimized. When the partial pressure of hydrogen in the retentate was low and only slightly higher than the atmospheric pressure in the permeate side, the low initial hydrogen permeate stopped when the hydrogen pressure in the permeate side reached atmospheric pressure, eliminating the pressure differential and thereby the driving force between the retentate and the permeate sides. As hydrogen ceases to permeate, methane leakage stops. Apparently, methane leakage can occur only when hydrogen permeates through the membrane; no methane leakage occurs when hydrogen is confined to the retentate side. This result seems to reveal that chemisorption of hydrogen on the palladium membrane surface alone does not allow the methane to leak through without actual hydrogen diffusion or dissolving through the palladium lattice under the influence of the pressure differential.

These findings raise an interesting question. Why does pure methane gas fail to permeate the palladium membrane while

Table 6 – Diffusion of methane through a palladium membrane with a feed of $H_2 + CH_4$ at 350 °C

Exp. #	P_R^a (kgf/cm ²)	$P_R^{CH_4}$ (kgf/cm ²)	H_2 permeate (scc/min)	CH_4 in permeate ^b (ppm)	J_{CH_4} permeate ^c (scc/min)	α^d
1	6	4	67	1584	0.106	1261
2	7	4	335	323	0.108	4127
3	8	4	418	248	0.104	4031
4	9	4	628	171	0.107	4678
5	10	4	744	154	0.114	4328
6	7	5	Nil.	–	–	–
7	8	5	85	2622	0.223	634
8	9	5	240	859	0.206	1454
9	10	5	363	550	0.200	1817
10	6.1	5	<10 → 0 ^e	4378	–	1034
11	8	6	Nil.	–	–	–
12	9	6	126	2513	0.316	794
13	10	6	286	1104	0.316	1357
14	9.5	8	<10 → 0 ^e	5070	–	1047

^a Total pressure in retentate composed of H_2 and CH_4 in a unit of absolute kgf/cm².

^b Concentration of methane was analyzed with GC equipped with FID.

^c The flux of CH_4 was calculated as $J_{CH_4} = (\text{total flux of } F_2) \times (\text{conc. of } CH_4)$.

^d The separation factor or permselectivity of H_2 over CH_4 is defined as = [molar ratio of H_2 over CH_4 in permeate]/[molar ratio of H_2 over CH_4 in retentate] = $[H_2/CH_4]_P/[H_2/CH_4]_R$.

^e The permeate flow quickly stopped as hydrogen in the permeate side fill up the inner tube to become $P_P^H = 1$ kgf/cm²; this made the hydrogen partial pressure differential diminished.

in a hydrogen mixture permeates? Similar phenomena were observed for CO₂ vs. H₂ + CO₂ and Ar vs. H₂ + Ar.

Since the membrane remains defect-free before and after the permeation measurements are made, the observed Y-gas slippage is not caused by pinhole diffusion. Additionally, this Y-gas slippage was observed only when hydrogen permeated the membrane.

This new observation was tentatively attributed to the lattice expansion of the palladium membrane when hydrogen was chemisorbed and dissolved into the bulk phase [17]. De Ribaupierre and Manchester demonstrated that the lattice constant of the atomic structure of the palladium lattice increased from 3.894 Å in the α_{\max} -phase ($n = \text{H}/\text{Pd} = 0.008$) to 4.025 Å in the β_{\min} ($n = 0.6$) and increased with the amount of hydrogen dissolved, for $n \geq 0.6$ using the empirical equation $\Delta v/\Omega = 0.198 \pm 0.01$, as the lattice volume further expands [18]. Here, $\Delta v/\Omega$ is the ratio of the change in volume caused by the dissolution of hydrogen to the mean atomic volume of the Pd-metal atom. This equation reveals increase in the lattice parameter from 3.894 to 4.13 Å when hydrogen permeates under a high pressure differential at a temperature of over 300 °C; under this condition, $n = \text{H}/\text{Pd}$ may increase to 0.9 or more. Conceivably, this lattice expansion increases the enlargement of the lattice structure itself by a factor of $(4.13/3.89)^3 = 1.197$, and increases the inter-grain distance as the cluster grains are enlarged. The non-hydrogen gas may then slip through the expanded channel while hydrogen chemisorbs and dissolves into the palladium lattice. We believe that this phenomenon always occurs, unless the Y-gas is too bulky to diffuse through such an expanded opening. In an earlier investigation, we observed a higher purity of hydrogen permeate >99.999% when 25% of cyclohexanol was used as the Y-gas in the hydrogen mixture H₂ + Y between $P_R = 5$ and $P_P = 1$ kgf/cm²; a purity of only 99.98% was observed when 25% of Y was CO₂ or CH₄ in that particular palladium membrane [19].

A higher concentration of Y-gas corresponds to greater slippage of Y-gas into the permeate, independently of the hydrogen partial pressure in the mixture. In Table 6, under the same hydrogen partial pressure differential, say 2, 3 or 4 kgf/cm², the hydrogen permeate decreases as the methane

partial pressure increases, as is also presented in Table 3. The observed decline in hydrogen flux as the partial pressure of Y-gas is increased may be attributed to the increased hindrance by the Y-gas of the hydride in the palladium lattice as they migrate inside the lattice structure. Therefore, as the concentration of hydrogen decreases or the concentration of Y-gas increases, the hydrogen flux declines, even for the same partial pressure of hydrogen. The hydrogen pressure differential between the retentate and the permeate alone is not the sole driver of the permeation of hydrogen; an additional interaction of Y-gas inhibits this permeation inside the membrane structure. This fact explains why the Sieverts equation derived from a single hydrogen stream fails for a hydrogen mixture, because the interference of the Y-gas in the mixture is not considered. When some molecular Y-gas permeates through the palladium membrane, the approach can be extended to the possibility of the permeation of molecular hydrogen along with the atomic hydrogen through the membrane. However, the permeation of molecular hydrogen from that of atomic hydrogen cannot be distinguished by only gas analysis of the hydrogen permeate. The use of deuterium to measure the isotopic effect and swapping deuterium for hydrogen may offer some insights into the permeation of molecular hydrogen through the membrane. The kinetic diameters of helium (2.55 Å) and hydrogen (2.89 Å) are very close to each other [16]; therefore, the permeation flux of helium may offer a rough estimate of permeation by molecular hydrogen; however, this estimate will be a lower limit because molecular hydrogen exhibits lattice expansion by atomic permeation, opening up the pathway. Therefore, the permeation of helium by a H₂ + He mixture may yield a better estimate if the fraction of helium in the hydrogen permeate can be measured. The extent of such molecular hydrogen permeation may increase with the pressure differential and the slope of hydrogen flux against $(P_R)^n - (P_P)^n$ may have a higher “n” value than $n = 0.5$ in the high-pressure region; this result is the focus of further study as an increase in the slope was observed when (P_R) was in the range of 20–36 kgf/cm².

This finding also explains the observed decrease in hydrogen purity in the permeate as the concentration of Y-gas

Table 7 – Hydrogen purity through Pd membrane in different component of source stream

Component of source stream	Permeated hydrogen purity %	Component of impurity
Industrial 99.99% H ₂ containing 88 ppmN ₂ and 1.15 ppmAr 5%Ar in industrial 99.99% H ₂	99.99994 ^a	0.625 ppmN ₂
	99.99532 ^a	46.3 ppmAr
10% Ar in industrial 99.99% H ₂	99.98937 ^a	0.484 ppmN ₂
		105 ppmAr
75% industrial H ₂ +25%CO ₂	99.98610 ^b	1.34 ppmN ₂
		16 ppmCO
		30 ppmCO ₂
Crude product of methanol steam reforming at 330 °C	99.9788 ^b	93 ppmCH ₄
		212 ppmCH ₄

^a Analyzed by GC with DID detector.

^b Analyzed by a GC with PolarPackQ column connected to a methanizer converter and FID.

increases in the mixed feed, even when the defect-free palladium membrane allows no leakage of Y-gas at a pressure differential of between 1 and 10 kgf/cm². With the industrial 99.99% hydrogen feed, the hydrogen purity in the permeate is 99.999998% (0.19 ppm of N₂); with the 95%, 90% and 75% hydrogen feeds, the purity becomes 99.995%, 99.99% and 99.98%, respectively, as presented in Table 7. This effect of the concentration of Y-gas is of interest in the field of the industrial purification of hydrogen from a mixed feed.

4. Conclusion

This study demonstrates that hydrogen permeation through a palladium membrane by a hydrogen mixture differs from that by a single hydrogen feed in the following respects:

- (1) With a single hydrogen feed, the Sieverts equation, $J = Q \cdot [(P_R^H)^n - (P_P^H)^n]$ fits better with $n = 0.5$ than with $n = 1$.
- (2) With a hydrogen mixture as the feed, the use of the partial pressure in the Sieverts equation does not suffice to yield an accurate result. The hydrogen concentration in the feed strongly affects the hydrogen flux, J , and the permeance, Q , such that Q is affected not only by the temperature but also by the hydrogen concentration in the retentate side. Therefore, the feed concentration must be specified when permeance is used to characterize a palladium membrane with a hydrogen mixture.
- (3) The magnitude of permselectivity is related to the choice of the measuring method. The conventional method, which takes two separate measurements of the two component gases, yields an unrealistically large permselectivity. The flow-through method provides the actual permselectivity in an industrial separation process, while the constant concentration method is recommended for formal characterization of the membrane.
- (4) Although a defect-free palladium membrane can prevent the leakage of non-hydrogen gas when the gas is tested alone, the membrane allows leakage of the non-hydrogen gas that is mixed with hydrogen as the feed for permeation. A higher fraction of non-hydrogen gas in the mixture corresponds to greater leakage of the non-hydrogen gas perhaps because of the lattice expansion of the atomic structure of the palladium membrane. This non-hydrogen leakage is observed only when hydrogen permeates the membrane.

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