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Co-permeation of deuterium and hydrogen through Pd

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Abstract

Experiments on permeation of deuterium through a palladium membrane, which was accompanied by co-permeation of hydrogen, were performed in the pressure range below 1 Pa. Permeation of deuterium exhibited features of surface limited regime (SLR) both with and without hydrogen co-existence. Release of D_2, HD, and H_2 molecules from the downstream side of the membrane was observed in presence of hydrogen. No visible blocking of deuterium permeation by hydrogen appeared. The net permeation rate of deuterons in D_2 and HD forms in the co-permeation experiments with hydrogen was found to be approximately the same as in the experiments without hydrogen, if the effective deuterium pressure $p(D_2) + p(HD)/2$ remained the same irrespective of the partial pressure of hydrogen $p(H_2)$. The experimental data were described by a steady-state permeation model, which took into account D_2, HD, and H_2 absorption and desorption. © 2001 Published by Elsevier Science B.V.

1. Introduction

Hydrogen permeation through solids is being widely investigated for various nuclear materials applications, and the isotopic effect is a hot topic of these researches. Isotopic effects have been discussed for interactions of mono-isotopes with solids. The case of co-existence of two or more isotopes in materials has not been understood well yet.

Several investigations were devoted both to experimental observation and numerical modeling of co- and counter-permeation of two isotopes [1–9]. Those researches were stimulated by ideas of using hydrogen permeation in hydrogen isotope separation columns, hydrogen vacuum pumps, helium–hydrogen separation windows, and in systems for tritium recovery from tritiated water. Besides, this effect is important for some other applications, for example, for estimation of tritium leakage from tritium breeding blanket and nuclear waste storage beds. It has been found that presence of one isotope influences the behavior of another.

Various approaches for modeling of the impact of one isotope on the another have been proposed and analyzed [2–6]. The purpose was to find an appropriate solution for D_2 and H_2 permeation rates in case they are mixed in the membrane. Though the modeling often gives a good agreement with the experiment, understanding of the physical nature of the effects observed has not been achieved yet. One may suggest that the effect of H–D recombination could be a reason for some experimental observations.

Formation of heterogeneous HD and HT molecules on the surface was observed in various experiments. For example, HD desorption was found in [10] in measurements of deuterium re-emission during ion bombardment and thermal desorption after implantation. Formation of HD molecules was also observed during heating of the sample in the mixture of H_2 and D_2 gases [11]. Thermal desorption spectroscopy (TDS) after co-adsorption from molecular beam also demonstrated

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desorption of HD molecules [12]. Many researches were devoted to abstraction of preliminary adsorbed atoms in HD form by hot gaseous atoms of another isotope [13–15]. Isotopic substitution and exchange on the surface with HD formation was observed also in low-temperature adsorption experiments [16]. Heterogeneous recombination also occurs on surfaces of liquid metals, for example, HT desorption during neutron irradiation of liquid Li17Pb83 alloy is accelerated by hydrogen added to the purge gas [17]. This effect was also important for ceramic breeder materials [18]. Permeation through solid metals in contact with liquid LiPb alloy is also accompanied by HT formation [19,20]. Heterogeneous HD desorption was discussed also in H and D co-permeation measurements through Pd as reported in the previous publications [2,3]. A similar effect of heterogeneous recombination between hydrogen and oxygen was also found in hydrogen permeation experiments in [21,22]. Admission of oxygen on the downstream side of Pd led to appearance of water, so at high counter-pressure of hydrogen, the net hydrogen permeation rate increased. Having these observations in mind, one may conclude that H–D recombination on the surface could really be an important factor in permeation, when two isotopes co-exist in the metal. For heterogeneous H–D, H–T and D–T molecular recombinations, the different interactions between different atoms could result in depression of the recombination of heavier mass molecules, known as a blocking effect, which is also the subject of the present work.

In this paper we first give a model description of the features connected with H–D recombination, which can be expected in co-permeation of hydrogen and deuterium; then we describe the experimental details, and compare the experimental observations with the model calculations.

2. Model

The main mechanism for thermal release of diatomic molecules from solids is the recombinative desorption from the chemisorption sites on the surface. To simplify modeling of the recombinative desorption, it is often supposed that a local equilibrium between on-the-surface chemisorption states and under-the-surface bulk absorption states establishes rather fast, and this was demonstrated in [23]. In this case, the rate of desorption is proportional to the square of the bulk concentration with a so-called recombination coefficient K as the proportionality parameter.

If two isotopes, protium H and deuterium D, co-exist in a metal, they may desorb from the metal as H_2, D_2, and HD molecules. If C_H and C_D are the numbers of H and D atoms per cm^3 in the near-surface layer, the total numbers of H–H and D–D pairs, which can be formed from these atoms are $C_H(C_H - 1)/2$ and $C_D(C_D - 1)/2$, respectively, while the number of HD pairs is $C_H C_D$. Therefore, the probabilities of formation of H_2, D_2, and HD molecules during desorption are proportional to these products. Since $C_H \gg 1$ and $C_D \gg 1$, the respective desorption rates expressed in molecules/cm^2/s are

$$J(H_2) = K_{HH} C_H^2/2, \tag{1h}$$

$$J(D_2) = K_{DD} C_D^2/2, \tag{1d}$$

$$J(HD) = K_{HD} C_H C_D, \tag{1hd}$$

where K_{HH}, K_{DD}, and K_{HD} are the coefficients of H–H, D–D, and H–D recombinations expressed in cm^4/s. One can easily see that

$$J(HD)^2 = 4J(H_2)J(D_2)[K_{HD}^2/K_{HH}K_{DD}]. \tag{2a}$$

If the efficiencies of H–H and D–D recombination are different, one may expect that the efficiency of H–D recombination has an intermediate value and therefore the ratio $K_{HD}^2/K_{HH}K_{DD}$ is approximately equal to 1. So, one can expect that

$$J(HD)^2 \cong 4J(H_2)J(D_2). \tag{2b}$$

In writing particle balance equations, it is easy to operate with fluxes expressed in units of H and D atoms leaving the surface. The rates of release of H atoms in H_2 molecules and HD molecules, as well as the net release rate of protium atoms, all in units of atoms/cm^2/s are

$$j_H(H_2) = 2J(H_2) = K_{HH} C_H^2,$$
$$j_H(HD) = J(HD) = K_{HD} C_H C_D,$$
$$j_H = j_H(H_2) + j_H(HD).$$

For deuterium, the respective rates are written similarly:

$$j_D(D_2) = 2J(D_2) = K_{DD} C_D^2,$$
$$j_D(HD) = J(HD) = K_{HD} C_H C_D,$$
$$j_D = j_D(D_2) + j_D(HD).$$

Due to HD desorption from the metal, HD molecules appear in the volume around the sample. Therefore, one can expect that not only H_2 and D_2 molecules, but also HD molecules in the gas contribute to adsorption of H and D atoms in the metal. The rates of absorption of H and D atoms due to dissociation of H_2, D_2, and HD molecules are

$$i_H(H_2) = 2\alpha_{HH} p(H_2),$$
$$i_D(D_2) = 2\alpha_{DD} p(D_2),$$
$$i_H(HD) = i_D(HD) = \alpha_{HD} p(HD).$$

Here $p(H_2)$, $p(D_2)$, and $p(HD)$ are the partial pressures of H_2, D_2, and HD molecules in gas, and α_{HH}, α_{DD}, and α_{HD}, are the respective coefficients of dissociative absorption. It is taken into account that dissociation of H_2 or D_2 molecule gives two H or D atoms respectively, while dissociation of HD molecule produces one H and one D atom.

The fluxes of molecules that dissociate with subsequent absorption are respectively

$$I(\mathrm{H_2}) = i_\mathrm{H}(\mathrm{H_2})/2 = \alpha_\mathrm{HH}p(\mathrm{H_2}),$$
$$I(\mathrm{D_2}) = i_\mathrm{D}(\mathrm{D_2})/2 = \alpha_\mathrm{DD}p(\mathrm{D_2}),$$
$$I(\mathrm{HD}) = i_\mathrm{H}(\mathrm{HD}) = i_\mathrm{D}(\mathrm{HD}) = \alpha_\mathrm{HD}p(\mathrm{HD}).$$

Having these definitions for the absorption and release fluxes, one can construct various schemes of interaction in the steady-state regime when the concentration of atoms in the metal does not change in time. Let us consider a membrane, which separates two volumes with gas either admitted in or evacuated out of them. In the case that the gas is admitted on two sides of the membrane, we meet a situation that can be described as the solubility experiment with the concentration of atoms being uniform along the depth. In the case of gas admitted on one side and evacuated from another, we meet the situation that can be described as the permeation experiment with a gradient of concentration along the membrane depth.

In previous researches [2,3] it was found that the permeation rate through Pd at low hydrogen gas pressure approximately linearly increases with the gas pressure. This pressure dependence is typical for the so-called surface limited regime (SLR) of permeation. Diffusion of hydrogen in the membrane is very fast in this regime, and the concentration gradient is very small. For simplicity of consideration, we assume the concentration profile to be absolutely flat, so the concentrations on the inlet and outlet sides coincide. Deviation from the pure SLR can be taken into account later when comparing the calculations with the experimental data. Let us consider the following modes of interaction.

2.1. Solubility of a mono-isotope gas.

In this case either H_2 or D_2 gas is admitted in both volumes, so the membrane is saturated from two sides and the gas release goes also from two sides. The balance of atomic fluxes for this case is

$$2i_\mathrm{H}(\mathrm{H_2}) = 2j_\mathrm{H}(\mathrm{H_2}),$$
$$2i_\mathrm{D}(\mathrm{D_2}) = 2j_\mathrm{D}(\mathrm{D_2}),$$

and the concentrations can be found to be

$$C_\mathrm{H}^2 = (C_\mathrm{H,S})^2 = (2\alpha_\mathrm{HH}/K_\mathrm{HH})p(\mathrm{H_2}) = S_\mathrm{H}^2 p(\mathrm{H_2}), \tag{3h}$$

$$C_\mathrm{D}^2 = (C_\mathrm{D,S})^2 = (2\alpha_\mathrm{DD}/K_\mathrm{DD})p(\mathrm{D_2}) = S_\mathrm{D}^2 p(\mathrm{D_2}). \tag{3d}$$

Index 'S' in $C_\mathrm{H,S}$ and $C_\mathrm{D,S}$ means 'solubility' or 'Sieverts' concentrations, which are proportional to the square root of the gas pressure, according to the classical Sieverts relationship $C = Sp^{1/2}$ with S known as the solubility or Sieverts constant. In our denotations

$$S_\mathrm{H} = (2\alpha_\mathrm{HH}/K_\mathrm{HH})^{1/2},$$
$$S_\mathrm{D} = (2\alpha_\mathrm{DD}/K_\mathrm{DD})^{1/2}.$$

2.2. Permeation from a mono-isotope gas

The difference of this case from the previous one is that the gas pressure is applied only from one side giving the incoming flux twice less than in the saturation mode, while the release goes from two sides of the membrane as it was in the saturation mode. The balance of atoms is written as

$$i_\mathrm{H}(\mathrm{H_2}) = 2j_\mathrm{H}(\mathrm{H_2}),$$
$$i_\mathrm{D}(\mathrm{D_2}) = 2j_\mathrm{D}(\mathrm{D_2}),$$

and the concentrations are $\sqrt{2}$ times less than those reached in the saturation experiment:

$$C_\mathrm{H}^2 = (\alpha_\mathrm{HH}/K_\mathrm{HH})p(\mathrm{H_2}) = (C_\mathrm{H,S})^2/2, \tag{4h}$$

$$C_\mathrm{D}^2 = (\alpha_\mathrm{DD}/K_\mathrm{DD})p(\mathrm{D_2}) = (C_\mathrm{D,S})^2/2. \tag{4d}$$

The molecular permeation rates can be expressed in one of the forms, convenient in different cases:

$$\begin{aligned} J(\mathrm{H_2}) &= K_\mathrm{HH}C_\mathrm{H}^2/2 = \alpha_\mathrm{HH}p(\mathrm{H_2})/2 = K_\mathrm{HH}C_\mathrm{H,S}^2/4 \\ &= K_\mathrm{HH}S_\mathrm{H}^2 p(\mathrm{H_2})/4 = I(\mathrm{H_2})/2, \end{aligned} \tag{5h}$$

$$\begin{aligned} J(\mathrm{D_2}) &= K_\mathrm{DD}C_\mathrm{D}^2/2 = \alpha_\mathrm{DD}p(\mathrm{D_2})/2 = K_\mathrm{DD}C_\mathrm{D,S}^2/4 \\ &= K_\mathrm{DD}S_\mathrm{D}^2 p(\mathrm{D_2})/4 = I(\mathrm{D_2})/2. \end{aligned} \tag{5d}$$

It is of much interest to note that one-half of the flux, which absorbs from the inlet side, $I(\mathrm{H_2})$ or $I(\mathrm{D_2})$, permeates through the membrane and desorbs from the outlet side. The permeation rates linearly rise with the pressures, as it should be in SLR. These are features of SLR.

2.3. Solubility for a mixture of two isotopes

This case corresponds to equilibrium between H_2, D_2, and HD in gas on two sides of the membrane with H and D atoms in the membrane. The balances of atomic fluxes include now the influx from dissociation of HD molecules on the two sides:

$$2[i_\mathrm{H}(\mathrm{H_2}) + i_\mathrm{H}(\mathrm{HD})] = 2[j_\mathrm{H}(\mathrm{H_2}) + j_\mathrm{H}(\mathrm{HD})],$$
$$2[i_\mathrm{D}(\mathrm{D_2}) + i_\mathrm{D}(\mathrm{HD})] = 2[j_\mathrm{D}(\mathrm{D_2}) + j_\mathrm{D}(\mathrm{HD})].$$

The sum of the two equations divided by the factor of 2 gives

$$2\alpha_{HH}p(H_2) + 2\alpha_{HD}p(HD) + 2\alpha_{DD}p(D_2)$$
$$= K_{HH}C_H^2 + 2K_{HD}C_HC_D + K_{DD}C_D^2.$$

From this equation one can see that if the equilibrium establishes in the system of three gases H_2, HD, and D_2, the balance of incoming and outgoing fluxes takes place for every type of the molecules. Every molecule (H_2, HD, and D_2), which dissociates from gas with absorption of its atoms by the metal, is substituted by another molecule of the same type, which comes to the gas due to recombinative release of atoms from the membrane. This is the case of true thermodynamic equilibrium. The partial balances in this equilibrium are

$$2\alpha_{HH}p(H_2) = K_{HH}C_H^2,$$
$$2\alpha_{DD}p(D_2) = K_{DD}C_D^2,$$
$$2\alpha_{HD}p(HD) = 2K_{HD}C_HC_D.$$

The first and the second equations are identical to those written for H and D balance in Section 2.1. Therefore, one can say that the equilibrium concentrations of H and D atoms, which are established in metals in contact with an equilibrium mixture of two isotopes, are the same as in the case of mono-isotope solubility if the partial pressures of H_2 and D_2 molecules remain the same: the respective concentrations $C_H = C_{H,S}$ and $C_D = C_{D,S}$ are given by (3h,3d). Let us mention that at a given D_2 partial pressure, an additional absorption flux from dissociation of HD molecules does not lead to increase of H and D concentrations in metal. This is because this absorption flux is compensated by re-desorption of HD molecules. The third equation from the set above gives the equilibrium pressure of HD that establishes in the mixture in thermodynamic equilibrium with solid:

$$[p(HD)]^2 = 4(K_{HD}^2\alpha_{HH}\alpha_{DD})(\alpha_{HD}^2K_{HH}K_{DD})^{-1}p(H_2)p(D_2). \tag{6}$$

For practical purposes, one can simplify (6) suggesting that the coefficients for HD have some intermediate value between H_2 and D_2, so the square of the coefficients for HD approximately equals to the product of those for H_2 and D_2. In this case, (6) is reduced to the simple form

$$p(HD)^2 = 4p(H_2)p(D_2). \tag{7}$$

It is often convenient to operate not with the true partial pressures of molecules, $p(H_2)$, $p(HD)$, and $p(D_2)$, but with the 'effective' hydrogen and deuterium pressures, which correspond to the total number of atoms of the respective isotope in the gas mixture:

$$P_H = p(H_2) + p(HD)/2, \tag{8h}$$

$$P_D = p(D_2) + p(HD)/2. \tag{8d}$$

If a true equilibrium establishes in the system, one can find the partial pressures from (7,8h,8d)

$$p(H_2) = P_H^2/(P_H + P_D), \tag{9h}$$

$$p(D_2) = P_D^2/(P_H + P_D). \tag{9d}$$

Let us mention that the concentrations and the desorption fluxes are expressed in different ways as functions of partial and effective pressures.

2.4. Permeation from an equilibrium isotope mixture

Using the term equilibrium isotope mixture, we mean that all the three types of molecules in gas on the upstream side, H_2, HD, and D_2, are in equilibrium with solid. In this case, the partial fluxes entering the metal bulk and leaving the metal on the upstream gas–solid interface are equal. The difference of this case from the previous one is that the outlet side of the membrane is evacuated, so only one side of the membrane is open for the incoming fluxes while desorption occurs from both sides. The balances of fluxes in this case are

$$i_H(H_2) + i_H(HD) = 2[j_H(H_2) + j_H(HD)],$$
$$i_D(D_2) + i_D(HD) = 2[j_D(D_2) + j_D(HD)].$$

Following the procedure of the previous case, one can easily find that the concentrations of protium and deuterium are just the same as in the case 2.2 of permeation of mono-isotopes if the partial pressures of H_2 and D_2 molecules are the same in these two cases. Formulae (4h,4d) for H and D concentrations can be used in both cases. If so, the fluxes of H_2 and D_2 molecular desorption from the outlet side can be calculated from (5h,5d) as in the mono-isotope permeation mode. Desorption of HD follows Eqs. (2a,2b). It is important to note that the release rate of D_2 molecules from the downstream side does not depend on the H_2 partial pressure in co-permeation experiments if the D_2 partial pressure is kept constant. At the same time, desorption of HD with the rate given by (2a,2b) and (5h,5d) appears, and the net permeation of deuterons in D_2 and HD molecules increases. The net, or effective, permeation rates of protons and deuterons in units of molecules/cm^2/s are

$$J_H = J(H_2) + J(HD)/2,$$
$$J_D = J(D_2) + J(HD)/2.$$

The equilibrium partial pressure of HD molecules in gas on the upstream side, which establishes due to molecular exchange on the interface in the permeation mode, is the same as in the solubility mode, case 2.3, and is given by (6) and (7).

For our experimental purposes, one can write also the dependencies on the effective pressures (8h,8d):

$$J(\mathrm{H}_2) = [K_{\mathrm{HH}}S_{\mathrm{H}}^2P_{\mathrm{H}}/4][1 + P_{\mathrm{D}}/P_{\mathrm{H}}]^{-1}, \quad (10\mathrm{h})$$

$$J(\mathrm{D}_2) = [K_{\mathrm{DD}}S_{\mathrm{D}}^2P_{\mathrm{D}}/4][1 + P_{\mathrm{H}}/P_{\mathrm{D}}]^{-1}, \quad (10\mathrm{d})$$

$$J(\mathrm{HD}) = [K_{\mathrm{HH}}S_{\mathrm{H}}^2K_{\mathrm{DD}}S_{\mathrm{D}}^2/4]^{1/2}[P_{\mathrm{H}}P_{\mathrm{D}}/(P_{\mathrm{H}} + P_{\mathrm{D}})]. \quad (10\mathrm{hd})$$

The net permeation rates of hydrogen and deuterium in co-permeation experiments can be expressed from (10h,10d,10hd) as

$$J_{\mathrm{H}} = q_{\mathrm{H}}[K_{\mathrm{HH}}S_{\mathrm{H}}^2P_{\mathrm{H}}/4], \quad (11\mathrm{h})$$

$$J_{\mathrm{D}} = q_{\mathrm{D}}[K_{\mathrm{DD}}S_{\mathrm{D}}^2P_{\mathrm{D}}/4], \quad (11\mathrm{d})$$

where q_{H} and q_{D} are the correction factors, which are close to 1.

$$q_{\mathrm{H}} = [P_{\mathrm{H}} + P_{\mathrm{D}}(K_{\mathrm{DD}}S_{\mathrm{D}}^2/K_{\mathrm{HH}}S_{\mathrm{H}}^2)^{1/2}]/(P_{\mathrm{D}} + P_{\mathrm{H}}),$$
$$q_{\mathrm{D}} = [P_{\mathrm{D}} + P_{\mathrm{H}}(K_{\mathrm{HH}}S_{\mathrm{H}}^2/K_{\mathrm{DD}}S_{\mathrm{D}}^2)^{1/2}]/(P_{\mathrm{D}} + P_{\mathrm{H}}).$$

For the solubilities ratio of 1.23, which we discuss later, the upper limit is $q_{\mathrm{D}} = 1.23$ at $P_{\mathrm{D}} \ll P_{\mathrm{H}}$. The effective deuterium permeation rate as a function of the effective deuterium pressure is expected to be almost independent of the partial pressure of hydrogen as (11h) and (11d) say. This is because HD pressure has already been included in P_{D}.

From (11h) and (11d), one can find the isotope separation factor. Since the separation factor is defined as the ratio of the net fluxes of protons to deuterons from the downstream side divided by the ratio of pressures of hydrogen to deuterium on the upstream side, i.e. $s_{\mathrm{HD}} = [J_{\mathrm{H}}/J_{\mathrm{D}}]/[P_{\mathrm{H}}/P_{\mathrm{D}}]$, one can find $s_{\mathrm{HD}} = (K_{\mathrm{HH}}S_{\mathrm{H}}^2/K_{\mathrm{DD}}S_{\mathrm{D}}^2)^{1/2}$. This value is rather small. One can also determine the separation factor using the ratio of partial fluxes $J(\mathrm{H}_2)/J(\mathrm{D}_2)$ and partial pressures $p(\mathrm{H}_2)/p(\mathrm{D}_2)$. In this case $s_{\mathrm{HD}} = K_{\mathrm{HH}}S_{\mathrm{H}}^2/K_{\mathrm{DD}}S_{\mathrm{D}}^2$.

2.5. Permeation from a non-equilibrium mixture

A very low HD pressure on the inlet side characterizes this case. Therefore, the balances of fluxes do not contain the respective inlet fluxes $i_{\mathrm{H}}(\mathrm{HD})$ and $i_{\mathrm{D}}(\mathrm{HD})$ and are written as

$$i_{\mathrm{H}}(\mathrm{H}_2) = 2[j_{\mathrm{H}}(\mathrm{H}_2) + j_{\mathrm{H}}(\mathrm{HD})],$$
$$i_{\mathrm{D}}(\mathrm{D}_2) = 2[j_{\mathrm{D}}(\mathrm{D}_2) + j_{\mathrm{D}}(\mathrm{HD})].$$

Writing the expressions for all the fluxes and using Eqs. (3h,3d) to substitute the pressures in the left parts, we obtain

$$K_{\mathrm{HH}}(C_{\mathrm{H,S}})^2 = 2K_{\mathrm{HH}}C_{\mathrm{H}}^2 + 2K_{\mathrm{HD}}C_{\mathrm{H}}C_{\mathrm{D}},$$
$$K_{\mathrm{DD}}(C_{\mathrm{D,S}})^2 = 2K_{\mathrm{DD}}C_{\mathrm{D}}^2 + 2K_{\mathrm{HD}}C_{\mathrm{H}}C_{\mathrm{D}}.$$

These two equations are reduced to the following equations for the concentrations C_{H} and C_{D}:

$$4aC_{\mathrm{H}}^4 + 2b_{\mathrm{H}}C_{\mathrm{H}}^2 + (C_{\mathrm{H,S}})^2 = 0, \quad (12\mathrm{h})$$

$$4aC_{\mathrm{D}}^4 + 2b_{\mathrm{D}}C_{\mathrm{D}}^2 + (C_{\mathrm{D,S}})^2 = 0, \quad (12\mathrm{d})$$

where

$$a = 1 - (K_{\mathrm{HD}})^2/K_{\mathrm{HH}}K_{\mathrm{DD}},$$

$$b_{\mathrm{H}} = (C_{\mathrm{D,S}}K_{\mathrm{HD}})^2/K_{\mathrm{HH}}K_{\mathrm{DD}} - 2(C_{\mathrm{D,S}})^2 - (K_{\mathrm{HD}}C_{\mathrm{H,S}}/K_{\mathrm{DD}})^2,$$

$$b_{\mathrm{D}} = (C_{\mathrm{H,S}}K_{\mathrm{HD}})^2/K_{\mathrm{HH}}K_{\mathrm{DD}} - 2(C_{\mathrm{H,S}})^2 - (K_{\mathrm{HD}}C_{\mathrm{D,S}}/K_{\mathrm{HH}})^2.$$

Though the system of flux balances is simpler than in the previous case, its solution does not look so attractive. It can be well simplified suggesting all the recombination coefficients to be the same $K_{\mathrm{HD}} = K_{\mathrm{HH}} = K_{\mathrm{DD}} = K$:

$$C_{\mathrm{H}}^2 = [(C_{\mathrm{H,S}})^2/2][1 + (C_{\mathrm{D,S}}/C_{\mathrm{H,S}})^2]^{-1}, \quad (13\mathrm{h})$$

$$C_{\mathrm{D}}^2 = [(C_{\mathrm{D,S}})^2/2][1 + (C_{\mathrm{H,S}}/C_{\mathrm{D,S}})^2]^{-1}. \quad (13\mathrm{d})$$

One can see that the concentrations in the non-equilibrium case, given by (13h,13d), are less than those obtained for an equilibrium mixture, given by (4h,4d), at the same D_2 partial pressure. This is because the HD partial pressure is negligible in the no-equilibrium mixture. Therefore, HD does not give contribution to absorption, and HD recombination channel depletes deuterium concentration. Having these concentrations, one can easily calculate the rates of desorption of H_2, HD, and D_2 molecules on the downstream side from (1h,1d,1hd):

$$J(\mathrm{H}_2) = [K_{\mathrm{HH}}S_{\mathrm{H}}^2p_{\mathrm{H}}/4][1 + (S_{\mathrm{D}}^2p_{\mathrm{D}})/(S_{\mathrm{H}}^2p_{\mathrm{H}})]^{-1}, \quad (14\mathrm{h})$$

$$J(\mathrm{D}_2) = [K_{\mathrm{DD}}S_{\mathrm{D}}^2p_{\mathrm{D}}/4][1 + (S_{\mathrm{H}}^2p_{\mathrm{H}})/(S_{\mathrm{D}}^2p_{\mathrm{D}})]^{-1}, \quad (14\mathrm{d})$$

$$J(\mathrm{HD}) = [4J(\mathrm{H}_2)J(\mathrm{D}_2)]^{1/2}. \quad (14\mathrm{hd})$$

The net permeation rate of deuterons

$$J_{\mathrm{D}} = g(K_{\mathrm{DD}}S_{\mathrm{D,S}}^2, p_{\mathrm{D}}/4), \quad (15)$$

where g is a correction factor for the case of non-equilibrium on the upstream side, which is also close to 1.

$$g = [C_{\mathrm{D,S}}^2 + (K_{\mathrm{HH}}/K_{\mathrm{DD}})^{1/2}C_{\mathrm{H,S}}^2](C_{\mathrm{D,S}}^2 + C_{\mathrm{H,S}}^2)^{-1}.$$

It is interesting to compare the case of permeation from the non-equilibrium mixture (14h,14d,14hd,15), with a single isotope permeation (5h,5d). In both cases, the partial D_2 pressure equals the effective pressure of deuterium. One can find that the rate of D_2 permeation decreases in the mixture (14d,5h,5d), while the net permeation rate of deuterons (15,5h,5d) remains approximately the same.

3. Experimental

Permeation measurements were performed using the apparatus shown in Fig. 1. A sample palladium membrane separated two vacuum chambers. Two rotary pumps (RP) and two turbo-molecular pumps (TMP) evacuated both chambers. The base pressure of the system was maintained below 1×10^{-6} Pa and was measured by an ionization vacuum gauge (IG). The deuterium and hydrogen gas pressures supplied into the chambers were monitored by a capacitance manometer (CM), IG and a quadrupole mass spectrometer (QMS). The relative sensitivity factor of the ionization vacuum gauge for hydrogen was calibrated to be 0.4. Recent analysis [24] of sensitivities of various industrial ionization gauges to H_2 and D_2 gases has demonstrated that the ratio of sensitivities of H_2 to D_2 is in the range of 1.001–1.04. Therefore, for the purposes of our measurements we consider the isotopic effect of IG negligible. The pumping speed of the system was 1.0×10^{-1} m^3/s both for H_2 and D_2.

The membranes were made of Pd with the purity of 99.95%, which was supplied by Nilaco, Japan. Two membranes with thicknesses of 0.025 and 0.05 mm and surface area of 1.8×10^{-4} m^2 were used. The membrane was fixed on a stainless steel sample holders using Cu gaskets and the permeation cell was vacuum-leak tested. The membrane could be heated up to 1000 K by a molybdenum heater placed in the up-stream chamber. The temperature was measured by a K-type thermocouple. Measurements of permeation were performed at the temperatures of 820–870 K. The driving effective deuterium pressure P_D ranged from 7×10^{-4} to 3 Pa on the upstream side. The effective hydrogen pressure P_H was fixed at either 1.4×10^{-1} or 6.3×10^{-2} Pa on the same side. The values of the effective pressures of deuterium and hydrogen P_D and P_H are given by (8h,8d).

The experiments were performed in the dynamic regime with pumping the permeating gas out of the chamber. The effective flux of deuterium permeation through the membrane was determined from measurements of the increase in the effective deuterium pressure $\Delta P_D(t)$ at the downstream side $J_D(t) = \Delta P_D(t) S_{\text{eff}}/RTA$. Here S_{eff} is the effective pumping speed of the system, R, T, and A are the gas constant, the gas temperature, and the surface area of the membrane, respectively. The steady-state permeation was investigated.

The procedure of the co-permeation experiments was as follows. After introducing H_2 gas into the upstream chamber at a fixed pressure, a steady-state permeation of hydrogen to the downstream side was achieved. Then, without changing the H_2 leak flow rate (that is keeping the effective H_2 pressure constant), D_2 gas at low pressure was introduced into the same (upstream) chamber. This lead to a change of H_2, HD, and D_2 signals in the downstream chamber, which were measured by QMS until their steady-state levels had been achieved. With the H_2 leak rate kept constant in the upstream chamber (H_2 effective pressure constant), the D_2 leak into this chamber was raised stepwise, and the resulting partial pressures were monitored on the back side. In those experiments, we supposed that HD signal variation on the outlet side was mainly due to recombinative desorption of HD molecules from the membrane surface.

Admission of two isotopes in the inlet chamber also lead to isotope mixing, which produced three molecular species H_2, HD, and D_2 in the gas in the upstream chamber with the partial pressures $p(H_2)$, $p(HD)$, and

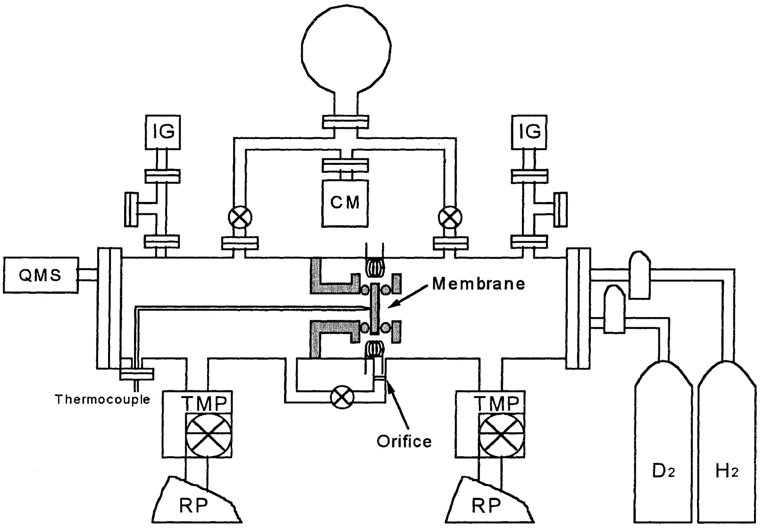

Fig. 1. Schematic diagram of the apparatus for co- and counter-permeation measurements.

$p(D_2)$, respectively. The total pressure P is the sum of the partial pressures

$$P = p(H_2) + p(HD) + p(D_2) = P_H + P_D.$$

This pressure was measured by a calibrated ionization gauge. The sensitivity of the IG was supposed to be equal for all the three species.

If only hydrogen is admitted to the upstream volume, the total pressure equals the effective pressure of hydrogen P_H. Admission of deuterium changes the partial pressures of H_2 and HD but does not change the effective P_H value, which remains constant during the series of experiments with different deuterium pressures. Therefore, the effective deuterium pressure P_D in co-permeation experiments can be easily calculated as the difference of the total pressures measured with and without deuterium in the upstream chamber.

It should be noted that the effective pressures of hydrogen and deuterium are taken from direct observations, and their values do not depend on the equilibrium conditions in the system. For getting their values, there is no need to make any suggestion about whether the equilibrium in the system is complete or not. The true partial pressures of the three molecules are unknown from measurements, and they can be calculated from the effective pressures only if additional knowledge about the system is available.

If there is no equilibrium at all, for example, the gas is purged fast through the upstream chamber, the true partial pressures and the effective pressures are just the same, and this is the case of part 2.5. If a true equilibrium establishes in the system, the case of part 2.4, the partial pressures can be calculated according to (7,9h,9d). In any intermediate cases, additional information is necessary for estimation of the true partial pressures. Therefore, in the present experiments, for simplicity, we did not use the true partial pressures and operated with the effective hydrogen and deuterium pressures (8h,8d). The effective pressures were also used in the previous publications [2,3] on counter-permeation.

4. Results and discussion

4.1. Mono-isotope permeation measurements

Regime of hydrogen permeation through metals depends on the surface conditions and the gas pressure applied as was analyzed in [25]. In general, permeation is diffusion-limited at high pressures and surface-limited at low pressures. But for Pd, the square root dependence typical for DLR was usually observed even at as low pressures as 10^{-3} Pa, for example [26–28]. These experiments were performed with the purpose of the diffusion coefficient determination, and the surface was prepared to be clean. Linear dependence, which is typical for SLR, was found in [29] below 1 Pa.

Fig. 2 demonstrates our measurements of the permeation rate of deuterium as a function of the driving D_2 pressure on the upstream side. The experimental data for two membranes of different thicknesses (0.025 and 0.05 mm) and two temperatures (825 and 865 K) are shown. The lines represent p^1 and $p^{1/2}$ pressure dependencies.

One can see that at the lowest pressures, the experimental data are well proportional to the driving deuterium pressure, and this is the evidence that the permeation is in the pure SLR. At higher pressures, some deviations from the pure SLR dependencies are observed. The tendency of the curve is that it is going to approach to the square root pressure dependence at higher pressures. Nevertheless, the inclination of the curves in our pressure range is still far from that in DLR, and this is why one can say that mainly surface processes limit permeation in our pressure range. In this case, the depth profile may be approximated as a flat one, as we accepted for our modeling. The difference between 825 and 865 K is not large.

A rather unexpected observation comes from comparison of the permeation rates through the membranes of different thicknesses. Indeed, in SLR the permeation rate must be independent of the membrane thickness. Appearance of this dependence points to the diffusion-limited regime of permeation. But in these particular experiments, at least at the lowest pressures, we are very far from DLR conditions; therefore one must explain this observation by some surface effects. For example, it can be explained by difference in surface quality of the two samples. Also, a possible explanation is that the properties of the inlet and outlet surfaces are different for at least one of the two membranes. It is well known

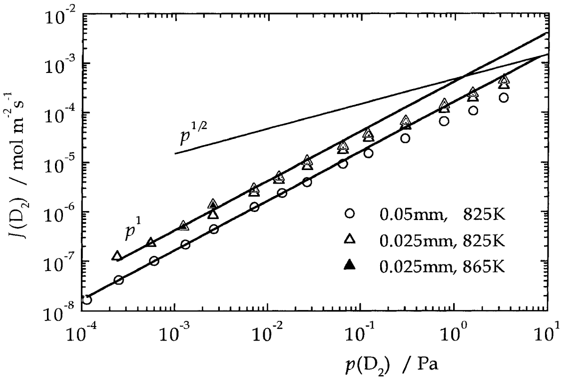

Fig. 2. Deuterium permeation flux as a function of the upstream deuterium pressure measured for two Pd samples of different thicknesses at two temperatures.

that the surface recombination rate efficiency is very sensitive to the surface conditions [30–35], and therefore one may expect that K values are different in contact with different environments on the two sides of the membranes. We performed several measurements one after another at the same pressure and temperature and found that the steady-state level of permeation increased gradually from experiment to experiment until some value, which did not change in further measurements, was reached. The effect of the quasi-steady state (permeation changes very slowly) was often observed in experiments. Often it is related either with surface oxygen removal or removal by long-term hydrogen exposure. In recent researches [21,22] on hydrogen permeation through a Pd membrane loaded with different H_2 pressures on both sides, oxygen was added either to the upstream or downstream chamber. In both cases, formation of water was observed in the respective volumes. If the oxygen was on the upstream side, water formation decreased the concentration of hydrogen on this side, and permeation decreased. If oxygen was on the outlet side, water formation promoted desorption of hydrogen, and the permeation of hydrogen increased. Even at a relatively high oxygen pressures and high coverage of Pd surface by oxygen on the downstream side, oxygen did not block hydrogen permeation. A gas, which blocks hydrogen permeation through Pd, is CO when it is admitted on one or both sides, and this has been directly demonstrated in [21,23,24]. Carbon monoxide was shown to block both dissociation of gas molecules and association of atoms on the surface. This gas is a well-known poison for catalysts. Influence of CO is very strong at low temperatures. Increase of the temperature above 523 K significantly reduces this effect even at 10–50% of oxygen in hydrogen, as found in [36].

Comparison of permeations of one-component hydrogen and deuterium is given in Fig. 3 for the membrane thickness of 0.025 mm and the temperature of 870 K. Permeation flux of hydrogen (open circle) was about 1.5 times larger than that of deuterium (closed circle). The permeation rate in SLR, according to (5h,5d), is proportional to the product of the recombination efficiency and the squared solubility, and this product is about 1.5 from Fig. 3. The solubility ratio for hydrogen and deuterium in Pd was derived in [27]. At 870 K, S_H/S_D is about 1.23. Therefore, from Eqs. (5h,5d), the phenomenological recombination rate constant of deuterium nearly equals to that of hydrogen. These ratios for the solubilities and recombination efficiencies we will use below in our analyses of co-permeation.

4.2. Co-permeation

The main feature of the experiments with the mixture of isotopes is formation of HD molecules on the surfaces. In the counter-permeation experiments [2,3], it was very difficult to follow HD signal. Co-permeation experiments gave this opportunity, and Fig. 4 shows the results obtained. The square of the HD permeation rate as a function of the product of desorption rates of H_2 and D_2 molecules perfectly follows the straight line predicted by the formulae (2a,2b). Increase either in H concentration or in D concentration gives rise to increase of H–D recombination on the surfaces of the membrane.

Fig. 5 shows comparison of the effective deuterium permeation rate as the function of the effective deuterium pressure for two cases: mono-isotope deuterium permeation experiment without hydrogen and co-permeation experiment with hydrogen. One can see that the difference between the two experiments is very small. This follows from the model consideration of part 2, where it was shown that the effective deuterium permeation rate as a function of the effective deuterium pres-

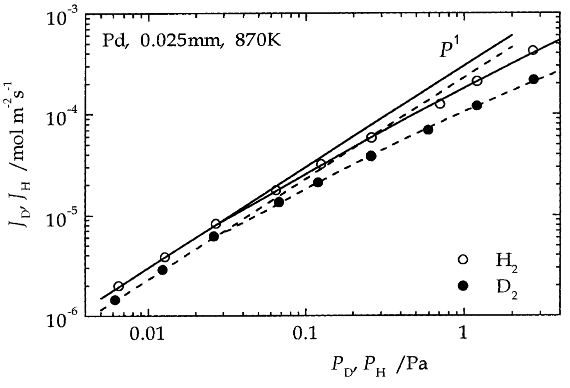

Fig. 3. Comparison of the permeation rates of protium and deuterium in the mono-isotope permeation experiments.

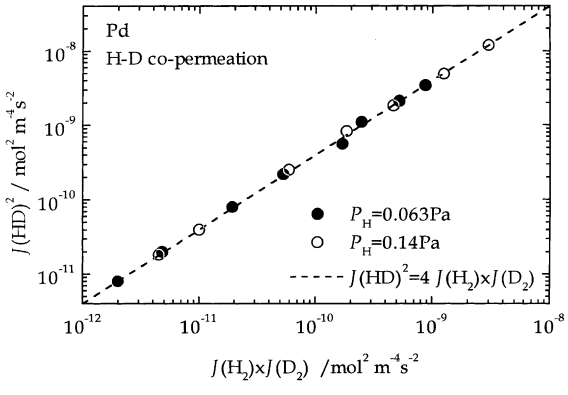

Fig. 4. The relation between the fluxes of HD, H_2, and D_2 molecules in co-permeation experiments.

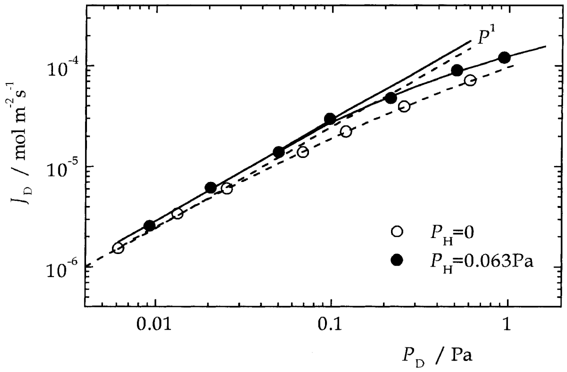

Fig. 5. The effective permeation rate of deuterium $J_D = J(D_2) + J(HD)/2$ as a function of the effective deuterium pressure $P_D = P(D_2) + P(HD)/2$ with and without H_2 co-permeation.

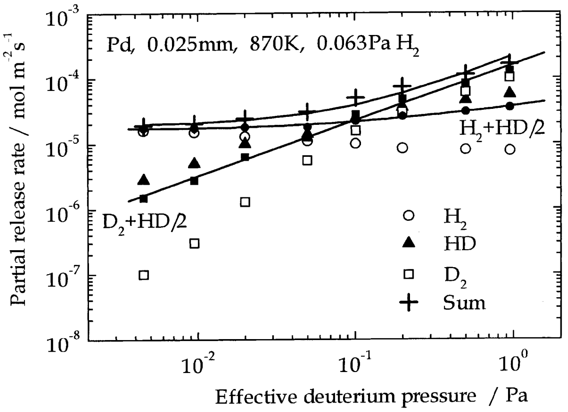

Fig. 6. Contribution of HD, H_2, and D_2 molecules in the net permeation flux of protons and deuterons $J_H = J(H_2) + J(HD)/2$ and $J_D = J(D_2) + J(HD)/2$ in co-permeation measurements as a function of the effective deuterium pressure $P_D = P(D_2) + P(HD)/2$ and at a fixed value of the effective H_2 pressure $P_H = P(H_2) + P(HD)/2 = 0.063$ Pa. Lines are a guide to the eye.

sure is a weak function of the pressure of hydrogen. It is important to mention that both permeation modes (with equilibrium and without equilibrium on the upstream side) lead to this result, as follows from (11h,11d,15). The fact that hydrogen gas on the upstream side does not influence the net permeation rate of deuterons can be interpreted as an evidence that hydrogen does not block adsorption of deuterium on the upstream side. Moreover, in the conditions of the present experiments, the concentration profiles of hydrogen and deuterium are very flat. Therefore, the concentrations of hydrogen and deuterium in the bulk of the membrane and on the downstream side are about the same as on the upstream side. This may be considered as a demonstration that there is no hydrogen-related blocking of deuterium diffusion in the bulk and no blocking of deuterium recombination on the downstream side.

Fig. 6 demonstrates the contribution of three recombination channels H_2, HD, and D_2 on the downstream side of the membrane as functions of the effective deuterium pressure. The net fluxes of deuterium and hydrogen are also shown. One can see that the rates of D–D and H–D recombination on the downstream side both increase with the effective deuterium pressure, while that of H–H recombination decreases. The net permeation of deuterons increases approximately linearly as it was without hydrogen, while the net permeation of protons remains approximately independent of the deuterium pressure. That is, the net fluxes of protons and deuterons seem to be separated being mutually independent as functions of the effective pressure.

Comparing Figs. 5 and 6 in more detail, one can mention the following tendency. The net permeation rate of deuterons slightly increased due to co-permeation of hydrogen in Fig. 5, and the net permeation rate of protons slightly increased due to co-permeation of deuterons in Fig. 6. Though the effect is within the experimental uncertainty, it was repeatedly observed.

Fig. 7 demonstrates comparison of experimental measurements and the model calculations of contributions of three recombination channels on the

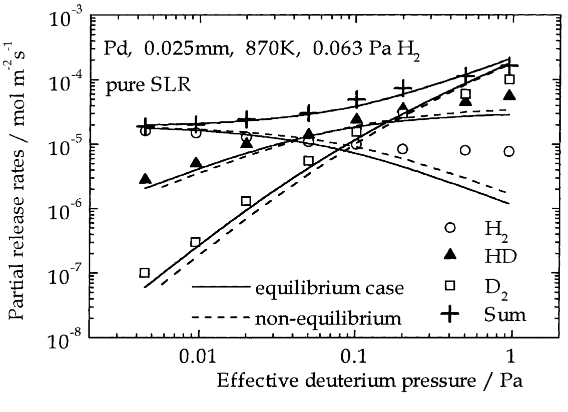

Fig. 7. Contribution of HD, H_2, and D_2 molecules in the net permeation flux in co-permeation measurements as a function of the effective deuterium pressure $P_D = P(D_2) + P(HD)/2$ and at a fixed value of the effective H_2 pressure $P_H = P(H_2) + P(HD)/2 = 0.063$ Pa. Lines give the results of model calculations. Solid lines are for equilibrium mixture of H_2, HD, and D_2 in gas on the upstream side (Eqs. (11h,11d) and (12h,12d)). Dashed lines are for non-equilibrium mixture of H_2 and D_2 (Eqs. (14h,14d,15) and (15)). Pure SLR of permeation is suggested.

downstream side. Both equilibrium and non-equilibrium situation on the upstream side is considered. It is important that the relationship of the respective rates strongly depends on the effective deuterium partial pressure on the inlet side. One can see that the model calculations agree with the experimental data rather well. The solubility ratio was taken as 1.23, and the only adjusting parameter was the product $K_{\mathrm{DD}}S_{\mathrm{D}}^2/4 = 2\times10^{-4}$ for equilibrium and 1.5×10^{-4} for non-equilibrium calculations. It follows from Fig. 7 that the condition of establishing equilibrium between the three types of gas species is not so important for explanations of the experimental observation. Both considerations gave equally good results.

The most serious disagreement is observed at high pressures. One of the suggestions was that this effect could be possible due to deviations of permeation from the pure SLR as the slope of the permeation curves as the function of pressure decreases. We recalculated the rates of H_2, HD, and D_2 desorption with correction to possible deviation from pure SLR. For this purpose we suggested that the ratio of real concentrations to the concentrations given by the SLR is the same as the square root of the ratio of the experimental permeation fluxes to those predicted by the straight line of the SLR in Fig. 2. The results are given in Fig. 8. One can see that the agreement has not become much better. The adjusting parameter $K_{\mathrm{DD}}S_{\mathrm{D}}^2/4 = 3\times10^{-4}$ in those calculations.

In the co-permeation experiments, hydrogen permeates through the membrane along with deuterium. Fig. 9 demonstrates the ratio of how much deuterium permeates with respect to the sum of hydrogen and deuterium permeation:

$$j_r = [J(\mathrm{D_2}) + J(\mathrm{HD})/2]/[J(\mathrm{D_2}) + J(\mathrm{HD}) + J(\mathrm{H_2})].$$

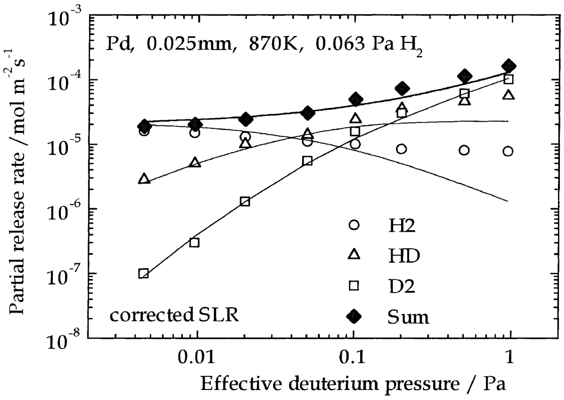

Fig. 8. The same as Fig. 7, for equilibrium case, but the calculations are corrected to take into account not exactly pure SLR of permeation.

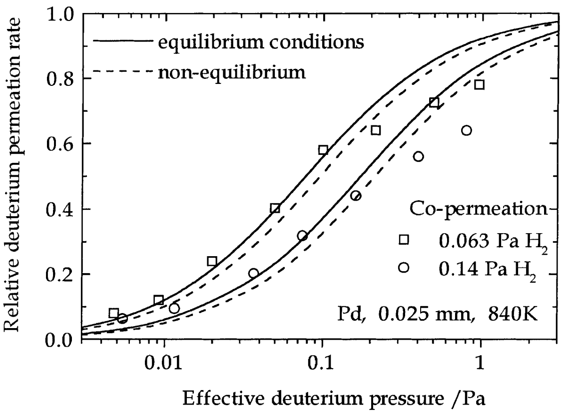

Fig. 9. The relative deuterium permeation rate $J_r = J_{\mathrm{D}}/(J_{\mathrm{D}} + J_{\mathrm{H}})$ in co-permeation experiments as a function of the effective deuterium pressure $P_{\mathrm{D}} = P(\mathrm{D_2}) + P(\mathrm{HD})/2$ measured at two effective hydrogen pressures. Pure SLR. Solid lines – equilibrium calculations, dashed lines – non-equilibrium case.

One can see that contribution of deuterium in the net permeation rate of two isotopes increases with increase of the effective deuterium pressure. The formulae for the relative contribution of deuterium to the total permeation can be written in the form which is valid both for the equilibrium and non-equilibrium in gas on the upstream side. If the recombination efficiencies of isotopes differ not too much, one can obtain

$$j_r = C_{\mathrm{D}}/(C_{\mathrm{D}} + C_{\mathrm{H}}).$$

Taking the values of concentrations for the two cases, one can find that the pressure dependencies are different:

$$j_r = [1 + (S_{\mathrm{H}}/S_{\mathrm{D}})(p(\mathrm{H_2})/p(\mathrm{D_2}))^{1/2}]^{-1}$$
$$= [1 + (S_{\mathrm{H}}P_{\mathrm{H}}/S_{\mathrm{D}}P_{\mathrm{D}})]^{-1} \qquad \text{for equilibrium,}$$

$$j_r = [1 + (S_{\mathrm{H}}/S_{\mathrm{D}})^2(p(\mathrm{H_2})/p(\mathrm{D_2}))^1]^{-1}$$
$$= [1 + (S_{\mathrm{H}}^2P_{\mathrm{H}}/S_{\mathrm{D}}^2P_{\mathrm{D}})]^{-1} \qquad \text{for non-equilibrium.}$$

Let us mention that for the non-equilibrium case $P_{\mathrm{D}} = p(\mathrm{D_2})$. The j_r plots for these two cases are shown in Fig. 9. The agreement between the experiment and model is seen to be rather good for both suggestions about equilibrium.

Modeling shown in Figs. 7 and 9 can be considered as evidence that the features of the co-permeation do not depend on the question whether the equilibrium on the upstream side is established or not.

There is a repetitive disagreement between modeling and experiment at the highest pressures. Experimental measurements demonstrated a sudden increase at the end of the pressure range, which was observed regularly both in experiments on co- and counter-permeation. It cannot be explained easily. Possibly, the surface conditions or bulk processes were in some ways different at higher pressures.

5. Conclusion

Permeation of deuterium through Pd in conditions of hydrogen co-permeation was investigated at H_2 and D_2 gas pressures below 3 Pa. It was observed that H_2, HD, and D_2 molecules desorb from the downstream side of the membrane. The total permeation rate of deuterons $J_D = J(D_2) + J(HD)/2$ in HD and D_2 molecules had distinct features of the SLR of permeation, though some deviations from the pure SLR were visible. SLR was also observed for the single-isotope permeation of hydrogen and deuterium.

It was found that the rate of the net deuterium permeation J_D approximately linearly rose with the effective pressure of deuterium $P_D = p(D_2) + p(HD)/2$. In presence of hydrogen, the net permeation rate of deuterons J_D was approximately the same as without hydrogen if the effective pressure P_D was kept constant. It was observed that the permeation rate of deuterons was even slightly enhanced by co-permeation of hydrogen, and the same effect was observed for hydrogen permeation with co-permeation of deuterium, but both effects were within the experimental uncertainty.

It was concluded that there are no visible effects of hydrogen-related blocking of deuterium adsorption on the upstream side, deuterium diffusion in the bulk, and deuterium desorption on the downstream side in conditions of these experiments. On the contrary, a small enhancement of the net permeation rate of deuterons J_D and protons J_H at a fixed effective pressure of an isotope was observed by adding another one.

The relationship between the desorption fluxes of the three molecules also depended on P_D. Increase in the ratio of D/H in the upstream gas promoted H–D recombination, retarded increase of D–D recombination, and diminished the H–H recombination.

The experimental data were well explained by a model, which takes into account both hydrogen and deuterium absorption and recombination. An analysis was performed for two different suggestions about the state of gas on the upstream side: either an equilibrium mixture of H_2, HD, and D_2 molecules or a non-equilibrium mixture of H_2 and D_2 molecules. The model calculations gave equally good quantitative agreement with the experiment in both cases. So, independent of whether the equilibrium in gas on the upstream side is achieved or not, the features of the co-permeation effects are similar.

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