

# Analysis of Simultaneous H and D Permeation through Lithium-Lead<sup>\*)</sup>

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Clarification of tritium transfer in blanket is an important issue for realizing fusion reactor. We perform an experiment of simultaneous H and D permeation through  $\text{Li}_{17}\text{Pb}_{83}$  by means of an unsteady permeation method in order to clarify the interactions and isotope effects between H and D atoms. The experiment is conducted under the condition where the Sieverts' law holds. As a result, it is found that (i) H and D atoms permeate independently regardless of the H/D component ratio in the upstream gas and (ii) diffusion process is the rate-determining step in the overall permeation process. The diffusivity of H is around 1.4 times larger than that of D. The solubility of H is close to that of D. We estimate two vibration modes at an absorption site and a saddle point of H in  $\text{Li}_{17}\text{Pb}_{83}$  based on the ratio of isotope effect. It is considered that the zero-point vibration energy of H at the absorption site in  $\text{Li}_{17}\text{Pb}_{83}$  is around 0.173 eV and that at the saddle point is around 0.235 eV. The ratio of isotope effect is almost in proportion to the square root of mass ratio of D to H. The diffusivity of T can be estimated as 1/1.7 times of H.

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## 1. Introduction

In order to operate a fusion reactor continuously, the establishment of tritium (T) fuel cycle and safety confinement is an important issue. A lithium-lead eutectic alloy ( $\text{Li}_{17}\text{Pb}_{83}$ ) is a promising liquid blanket material of an advanced fusion reactor because of its potential abilities for less radiation damage, high T breeding ratio, easy maintenance, and possible use as a coolant. Because of these outstanding features,  $\text{Li}_{17}\text{Pb}_{83}$  blanket concept is proposed for the ITER-TBM. Moreover, a  $\text{Li}_{17}\text{Pb}_{83}$  wet wall is adopted in a conceptual design of a laser fusion reactor, KOYO-Fast proposed by Osaka University in Japan [1].

When the output of a fusion reactor is 1 GW and authorized T leak to the environment is 1 g/year ( $\cong 10$  Ci/day), it is necessary that the ratio of recovery to production of T is more than 99% [2]. For realizing high T recovery from a  $\text{Li}_{17}\text{Pb}_{83}$  blanket loop and controlling to low T leak from a system, mass-transfer data of diffusivity and solubility of hydrogen isotopes in  $\text{Li}_{17}\text{Pb}_{83}$  are indispensable. These data have been reported by several authors [3–7]. However, there is some scattering among the solubility data determined by a constant volume method. We also have experimentally determined mass-transfer properties of single component of  $\text{H}_2$  or  $\text{D}_2$  in  $\text{Li}_{17}\text{Pb}_{83}$  by an unsteady permeation method [1, 2]. When recovering T from a blanket, isotopic exchange reaction is effective to

enhance T recovery rate. It is also considered that D atoms permeate through the D-T plasma chamber to the blanket. These phenomena mean that some hydrogen isotopes co-exist in the blanket. However, behavior of each hydrogen isotope in the multi-component system has never been clarified. In order to understand the interactions and isotope effects between H and D atoms in  $\text{Li}_{17}\text{Pb}_{83}$ , we performed an experiment in the H and D two-component system. The data of T can be estimated from isotope effects between H and D.

## 2. Experimental

A schematic diagram of the experimental apparatus was already shown in our previous paper [1]. The apparatus was composed of (a) a gas supply system; (b) an permeation system and (c) a measurement system. Gas supplied to (a) was purified with molecular sieve 5A adsorbent to remove  $\text{H}_2\text{O}$ . The following seven kinds of gas were prepared for the experiment;  $\text{H}_2 : \text{D}_2 = 0 : 100, 34 : 66, 44 : 56, 66 : 34, 80 : 20, 90 : 10, 100 : 0$ . Gas permeating through  $\text{Li}_{17}\text{Pb}_{83}$  was purged by Ar purified with a metal getter of Zr-V-Fe alloy (ST707, SAES Getters Japan Co., Ltd). An experimental system including a permeation pot in (b) was enclosed in a glove box of Ar atmosphere in order to avoid contact with impurities of  $\text{N}_2, \text{O}_2, \text{H}_2\text{O}$  and so on.  $\text{Li}_{17}\text{Pb}_{83}$  was put on an  $\alpha$ -Fe plate in the permeation pot, which sidewall was made of SUS304. The thicknesses of the  $\alpha$ -Fe plate, SUS304 sidewall and  $\text{Li}_{17}\text{Pb}_{83}$  were 1.0,

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1.7 and 10 mm, respectively. The pot was equipped with an electric furnace, and experiment was performed at constant temperature. A quadrupole mass spectrometer, QMS (Qulee BGM-102, ULVAC), and a gas chromatograph: GC (GC14B, SHIMADZU), in the measurement system of (c) were used to determine the H<sub>2</sub>, D<sub>2</sub> and HD concentrations in the Ar flow simultaneously.

After Li<sub>17</sub>Pb<sub>83</sub> eutectic alloys was put in the pot and was melted with the ratio of Li : Pb = 17 : 83 at.% in a glove-box, its melting point of 508 K was checked. A gas mixture of H<sub>2</sub> and D<sub>2</sub> was supplied to the lower side of the pot. The gases of H<sub>2</sub>, D<sub>2</sub> and HD permeating through Li<sub>17</sub>Pb<sub>83</sub> were purged by Ar at the upper side of the pot. Their concentrations in Ar were measured by the QMS and GC. The flows rates of supply gas and purge one were 5.0 cc (NTP)/min and its total pressure was  $1.01 \times 10^5$  Pa. The experimental temperature ranged from 673 K to 973 K.

### 3. Model and Analysis

The overall permeation process of hydrogen and deuterium follows the following five fundamental steps:

- i) Adsorption and dissociation of H<sub>2</sub>, D<sub>2</sub> and HD molecules on the surface of an  $\alpha$ -Fe plate,
- ii) Dissolution and diffusion of H and D atoms in an  $\alpha$ -Fe plate,
- iii) Dissolution of H and D atoms from an  $\alpha$ -Fe plate to Li<sub>17</sub>Pb<sub>83</sub>,
- iv) Diffusion of H and D atoms in liquid Li<sub>17</sub>Pb<sub>83</sub>
- v) Recombination of H and D atoms into H<sub>2</sub>, D<sub>2</sub> and HD molecules and desorption from the surface of Li<sub>17</sub>Pb<sub>83</sub>.

Hydrogen and deuterium permeate in the atomic form through Li<sub>17</sub>Pb<sub>83</sub>, and the Sieverts' law applies to an interface between gas and liquid phases [8]. Because the rate of H or D permeation through the  $\alpha$ -Fe plate is around  $10^2$  times faster than that of Li<sub>17</sub>Pb<sub>83</sub>, the effect of the permeation resistance through the  $\alpha$ -Fe plate is estimated to be small. Moreover, it is found that the hydrogen leaks through the SUS304 sidewall are very small judging from estimation of the permeation rate in the one-dimensional or two-dimensional coordinate [9]. When diffusion of H and D in Li<sub>17</sub>Pb<sub>83</sub> is a rate-determining step among the overall permeation ones, permeability, diffusivity and solubility of hydrogen isotopes are determined by the following equation:

$$\frac{j_k l_{\text{LiPb}}}{c_{\text{LiPb}} D_{k,\text{LiPb}} K_{k,\text{LiPb}} \left( \sqrt{P_{k_2,\text{up}}} - \sqrt{P_{k_2,\text{down}}} \right)} = 2 \sqrt{\frac{l_{\text{LiPb}}^2}{\pi D_{k,\text{LiPb}} t}} \times \left( e^{-\frac{l_{\text{LiPb}}^2}{4D_{k,\text{LiPb}} t}} + e^{-\frac{9l_{\text{LiPb}}^2}{4D_{k,\text{LiPb}} t}} + e^{-\frac{25l_{\text{LiPb}}^2}{4D_{k,\text{LiPb}} t}} + \dots \right), \quad (1)$$

where the subscript k means H or D,  $j_k$  [mol/m<sup>2</sup>s] the per-

meation flux of hydrogen atom,  $t$  [s] time,  $l_{\text{LiPb}}$  [m] the thickness of Li<sub>17</sub>Pb<sub>83</sub>,  $c_{\text{LiPb}}$  [mol/m<sup>3</sup>] the molar density of Li<sub>17</sub>Pb<sub>83</sub>,  $D_{k,\text{LiPb}}$  [m<sup>2</sup>/s] the diffusion coefficient,  $K_{k,\text{LiPb}}$  [Pa<sup>-0.5</sup>] Sieverts' constant and  $P_{k_2}$  [Pa] the partial pressure of H<sub>2</sub> or D<sub>2</sub>. For the simultaneous H and D permeation, it is necessary to consider the contribution of HD. When HD is included, the values of  $y_{k,\text{up}}$  and  $y_{k,\text{down}}$  defined as molar fraction of H or D in the upstream or downstream side are described in terms of  $P_{k_2,\text{up}}$ ,  $P_{k_2,\text{down}}$  and  $P_{\text{Ar},i}$ :

$$y_{k,i} = \frac{P_{k_2,i} + 1/2 P_{\text{HD},i}}{P_{t,i}}, \quad (2)$$

$$P_{t,i} = P_{\text{H}_2,i} + P_{\text{HD},i} + P_{\text{D}_2,i} + P_{\text{Ar},i}, \quad (3)$$

where the subscript k means either H or D, and i means either up or down. The isotopic equilibrium constants of H and D in the upstream or downstream sides,  $K_{\text{HD}}$  are defined as follows:

$$K_{\text{HD},i} = \frac{P_{\text{HD},i}^2}{P_{\text{H}_2,i} P_{\text{D}_2,i}} \quad i = \text{up or down}. \quad (4)$$

The values of diffusivity and solubility are determined by fitting Eq. (1) to experimental values of the H and D concentrations.

The isotope effects of diffusion and solubility between H and D are theoretically shown as follows [10, 11]:

$$\ln \left( \frac{K_{\text{H,LiPb}}}{K_{\text{D,LiPb}}} \right) = 3 \ln \left[ \frac{\sinh \left( \frac{h\nu_{\text{D},0}}{2k_{\text{B}}T} \right)}{\sinh \left( \frac{h\nu_{\text{H},0}}{2k_{\text{B}}T} \right)} \right] + \frac{G_{\text{H}_2,0} - G_{\text{D}_2,0}}{2RT}, \quad (5)$$

$$\ln \left( \frac{D_{\text{H,LiPb}}}{D_{\text{D,LiPb}}} \right) = 3 \ln \left[ \frac{\sinh \left( \frac{h\nu_{\text{H},0}}{2k_{\text{B}}T} \right)}{\sinh \left( \frac{h\nu_{\text{D},0}}{2k_{\text{B}}T} \right)} \right] - 2 \ln \left[ \frac{\sinh \left( \frac{h\nu_{\text{H},0}^*}{2k_{\text{B}}T} \right)}{\sinh \left( \frac{h\nu_{\text{D},0}^*}{2k_{\text{B}}T} \right)} \right], \quad (6)$$

where  $h$  [J/s] is the Planck's constant,  $k_{\text{B}}$  [J/K] is the Boltzmann constant,  $R$  [J/molK] is the molar gas constant,  $T$  [K] is temperature,  $\nu_{\text{H},0}$  or  $\nu_{\text{D},0}$  [s<sup>-1</sup>] are frequency of H or D at the absorption site,  $\nu_{\text{H},0}^*$  or  $\nu_{\text{D},0}^*$  are frequency of H or D at the saddle-point site and  $G_{\text{H}_2,0}$  or  $G_{\text{D}_2,0}$  [J] are the Gibbs free energy of H<sub>2</sub> or D<sub>2</sub> gas.  $G_{\text{H}_2,0}$  and  $G_{\text{D}_2,0}$  are theoretically shown as follows [12]:

$$G_{k_2,0} = -RT \ln \frac{L_{k_2} T^{3.5}}{1 - e^{-J_{k_2}/T}} - R \left( D_{k_2} + \frac{B_{k_2}}{3} \right), \quad (7)$$

where the subscript k means H or D. The value of each parameter is shown in Table 1.

### 4. Results and Discussion

Figure 1 shows the H concentration (molar fraction) curve in the downstream side under the conditions of temperature of 873 K-973 K,  $y_{\text{H},\text{up}} = 0.66$  and  $y_{\text{D},\text{up}} = 0.34$ . The

H or D concentration depends on temperature and reaches earlier to a steady-state value as temperature becomes high. The values of the parameters in Eq. (1) are adjusted so that the analytical equation fits well to experimental data. The diffusivity is determined from the transient concentration curve with time, the solubility is determined from the steady-state concentration.

Figures 2 and 3 show the diffusivity and solubility of hydrogen isotopes in  $\text{Li}_{17}\text{Pb}_{83}$ . The plots show the average value of diffusivity or solubility at each temperature. When temperature is lower than 523 K, the data are disregarded because the permeation concentration of H and D is very low so that the error becomes large. In this experiment, the values of diffusivity or solubility are not influenced by the H-D component ratio in the upstream gas. Permeation of H

and D atoms through  $\text{Li}_{17}\text{Pb}_{83}$  in the two-component system shows the same behavior as a single component system. Judging from this, it is considered that there is no interaction between H and D. When our experimental values on diffusivity are compared with other researchers' value, it is found that the activation energy of diffusivity obtained by this experiment is similar to literature ones. Moreover since its order is around  $10^{-9} \text{ m}^2/\text{s}$ , the diffusivity in this temperature range is considered to show high reliability. A different trend between experiment and literature value was observed on solubility. Although its order is in agreement among other solubility data, its temperature dependence shows different trend. The same trend was reported by the recent research [2]. There is possibility in that the conditions of  $\text{Li}_{17}\text{Pb}_{83}$  were different from run to run. For example, if free oxygen exists in  $\text{Li}_{17}\text{Pb}_{83}$ , it may cause permeation resistance when temperature becomes low. These things may be the reason for why temperature dependence of solubility is observed.

The temperature dependence of diffusivity in this experiment is given by the following Arrhenius equations:

$$D_{\text{H,LiPb}} = 4.68 \times 10^{-8} \exp(-17600/RT), \quad (8)$$

$$D_{\text{D,LiPb}} = 2.64 \times 10^{-8} \exp(-15600/RT), \quad (9)$$

and solubility is as follows:

$$K_{\text{H,LiPb}} = 1.49 \times 10^{-4} \exp(-57400/RT), \quad (10)$$

$$K_{\text{D,LiPb}} = 1.65 \times 10^{-4} \exp(-57600/RT). \quad (11)$$

Judging from the experiment results, the diffusivity of H was around 1.4 times larger than that of D and the solubility of H was close to that of D. The isotope effect for diffusivity is in proportion to the square root of the mass ratio of D to H. The diffusivity of T can be estimated as 1/1.7 times of H in the temperature range from 773 K to 973 K.

Figures 4 and 5 show the temperature dependence of isotope effect ratio of solubility and diffusivity between H

Table 1 Values of each parameter in Eq. (7).

	$L[\text{K}^{-7/2}]$	$J[\text{K}]$	$D[\text{K}]$	$B[\text{K}]$
H <sub>2</sub>	$4.293 \times 10^{-4}$	5986	51966.5	85.348
D <sub>2</sub>	$2.406 \times 10^{-3}$	4307	52837.9	43.027

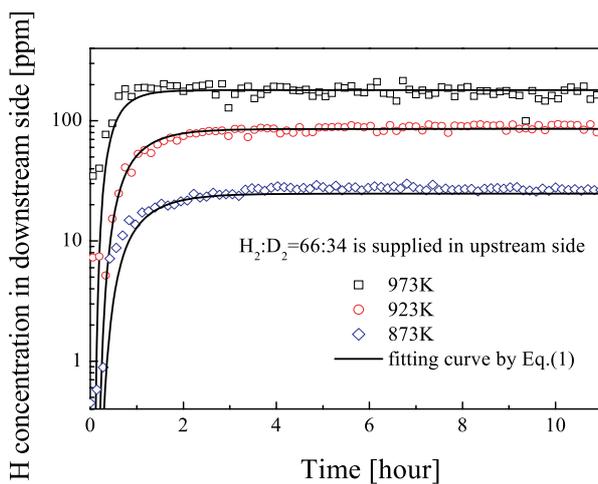


Fig. 1 Comparison between experiment and calculation.

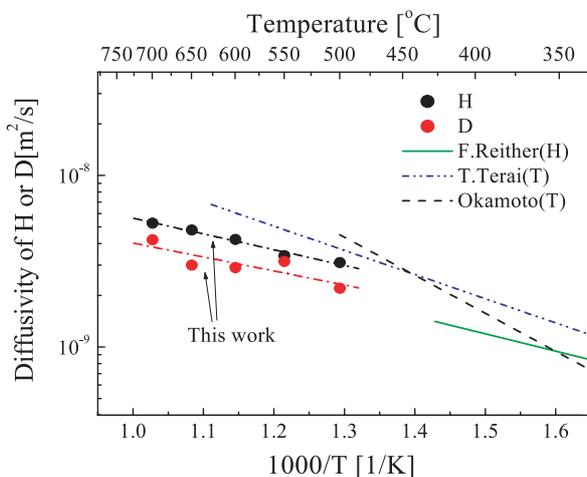


Fig. 2 Temperature dependence of diffusivity for H and D.

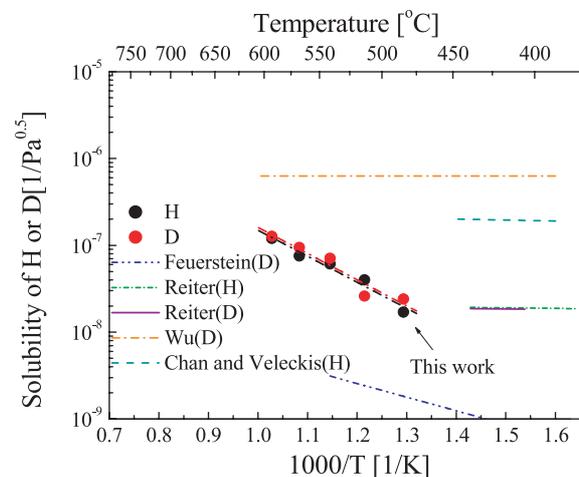


Fig. 3 Temperature dependence of solubility for H and D.

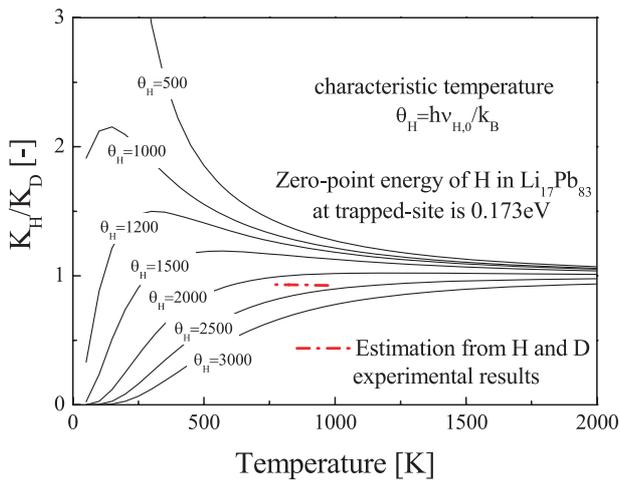


Fig. 4 Temperature dependence of isotope effect for solubility between H and D.

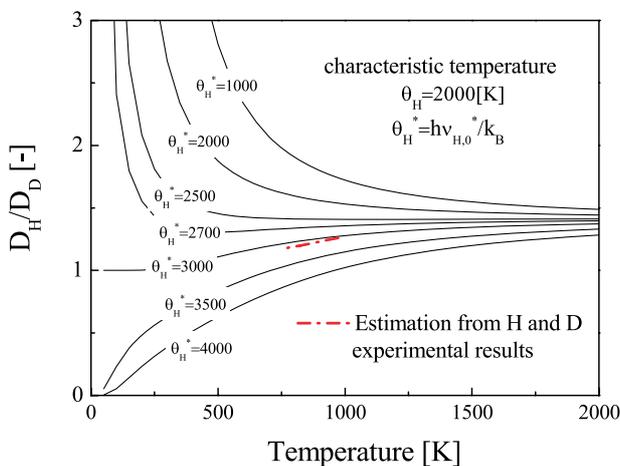


Fig. 5 Temperature dependence of isotope effect for diffusivity between H and D.

and D obtained by Eqs. (5)-(7). It is assumed there that a H atom is chemically combined with a Li atom and the absorption site is surrounded by Pb atoms. Therefore, its site is isotropic in the three-dimensional direction. In addition, isotopic difference between H and D is present only in vibration energy and the difference is correlated in terms of the zero-point energy. All those things lead to the harmonic oscillation model in the quantum mechanics, and the isotope effects can be correlated in terms of the characteristic

temperature of  $\theta_H (= h\nu_{H,0}/k_B)$ . The zero-point energy at the absorption site for solubility of H and D in  $\text{Li}_{17}\text{Pb}_{83}$  is determined as  $h\nu_{H,0} = 0.173 \text{ eV}$  from fitting.

The isotope effect ratio for diffusion of H and D is described by both the zero-point energy of the absorption site and that of the saddle-point site. In other words, the isotope effect of diffusivity is correlated in terms of another characteristic temperature of  $\theta_H^* (= h\nu_{H,0}^*/k_B)$  along with  $\theta_H$ . A hydrogen atom is absorbed in an absorption site, and it diffuses through the metastable saddle-point site that forms diffusion barrier of  $\text{Li}_{17}\text{Pb}_{83}$ . The zero-point energy at the saddle point is estimated  $h\nu_{H,0}^* = 0.235 \text{ eV}$  from fitting between experiment and calculation. The isotope effect in other temperature ranges can be estimated by using the two kinds of the zero-point energy.

## 5. Conclusion

Diffusivity and solubility in simultaneous H and D permeation through  $\text{Li}_{17}\text{Pb}_{83}$  are determined by means of the permeation method. As a result, it is found that (i) there is no interaction between H and D, (ii) diffusivity of H is around 1.4 times larger than that of D and (iii) solubility of H is close to that of D. The diffusivity of T can be estimated as 1/1.7 times of H in the temperature range from 773 K to 973 K based on the isotope effect determined. T behavior in  $\text{Li}_{17}\text{Pb}_{83}$  can be estimated by understanding the zero-point vibration energy.

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