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Comparison of models for multi-component hydrogen isotope mixtures absorbing in or permeating through metals

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HIGHLIGHTS

- Four models to give relations between isotope separation factor and isotope effects are compared.
- Data of hydrogen isotope absorption in Pd and Li metals are correlated in terms of separation factor and isotope effect.
- Unresolved experimental results still remained in the hydrogen permeation through Pd.

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ABSTRACT

In the first place, dependences of isotope effects on temperature and compositions are discussed among hydrogen isotopes (H, D and T) absorbing in, diffusing or permeating through metals. Relation between the isotope effects and isotope separation factor is investigated when hydrogen isotope mixtures are absorbed in, diffuse or permeate through metals. Previous experimental results for the absorption of hydrogen isotopes in Pd or Li are correlated as a function of composition and temperature, and they are discussed based on several models proposed previously to explain the relation between the isotope effects and the isotope separation factor. It results in a fact that the ideal solution model with dissociation on metal surfaces can correlate most cases of absorption of hydrogen isotopes in Pd or Li. However, unresolved experimental results still remained that there is a quantitative difference in permeation rates when either $H_2 + D_2$ or $H_2 + D_2 + HD$ mixture is supplied to the high-pressure side of a gaseous phase.

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1. Introduction

Phenomena of hydrogen isotopes absorbing in or diffusing through metals appears in various situations in a D-T fuel cycle of a fusion reactor system [1]. When multi-component mixtures of hydrogen isotopes (H, D and T) contact with metals having higher affinity for hydrogen isotopes such as Pd or Li, they are smoothly absorbed in, diffuse inside and permeate through metals under their respective intrinsic capacities or rates. Since isotope effects among the hydrogen isotopes are present in each process of absorption, diffusion or permeation, their respective isotopes behave differently [2]. In the present study, several previous models to correlate the solubility of each isotope are compared when hydrogen isotopic mixtures contact with metals.

The model proposed by Hickman [3] was widely utilized for correlation of hydrogen isotopes absorption. The model predicts solubility of each component simply without any other information when any hydrogen isotope mixtures contact with metals. In addition, his model leads to a simplified relation that the isotope effect ratio between two solubilities is equal to the separation factor. Therefore, his model is widely accepted as the first approximation. However, since some experimental results were inconsistent with his model, it is necessary to develop another model that the isotope effect and isotope separation factor are a function of not only temperature but also compositions.

For examples, there are experimental facts that the separation factor on permeation at lower concentration is smaller than that at higher concentration [5]. Tanaka [4] or Nishikawa et al. [5] proposed independently each new model to predict the relation between the isotope separation factor and the isotope effect. Different from the above three models, another ideal solution model taking into account of dissociation process on metal surfaces [6,7] is at present accepted widely for analyzing absorption processes when isotopic

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mixtures are present in gaseous phase. However, there still remain unresolved issues. In the present study the relation between the isotope effect ratio of hydrogen solubility and isotope separation factor is investigated again based on wider experimental data ranging from the solid solution region to hydride phase. In special, previous experimental data of the Pd-H, D, T and Li-H, D, T systems are selected in details as specific examples.

2. Isotope effects in H absorption

It is found experimentally that there is an isotope effect when any single component among hydrogen isotopes of H, D and T is absorbed in metals or diffuses inside bulk metals. When any bimolecular gas of the hydrogen isotopes at lower pressure is absorbed in metals, it dissociates to each component atom on surfaces and the solubility obeys the Sieverts' law described as

$$x_i = K_{s,i_2}\sqrt{p_{i_2}}, \quad i = \mathrm{H},\ \mathrm{D\,or\,T}, \tag{1}$$

where x_i is a H-to-M atomic ratio for a hydrogen isotope component, i, in metals, p_{i2} is the pressure of bimolecular hydrogen and $K_{S,i2}$ is the Sieverts' constant which is a function of temperature. Then the isotope effect between two atomic hydrogen species of i and j, $\beta_{i/j}$, is defined as

$$\beta_{i/j} = K_{s,i_2}/K_{s,j_2} \quad i,j = \mathrm{H},\ \mathrm{D\,or\,T}. \tag{2}$$

The $\beta_{i/j}$ value is a function of temperature in the lower solubility region of $x_i < 0.1$ in Pd. Some metals show a $\beta_{i/j}$ value greater than unity and others show lower one than unity. With pressure increasing, hydrogen solubility starts deviating from the Sieverts' law. When a hydride phase starts forming in metals, a plateau region appears in the pressure-composition isotherm of the H_2-metal system [11]. A similar thing occurs in other D_2- or T_2-metal systems. The isotope effect in the whole region covering from the Sieverts' region to the hydride one is defined as follows:

$$\beta^*_{i/j} = \sqrt{p_{j_2}(x_j)/p_{i_2}(x_i)} \quad i,j = \mathrm{H},\ \mathrm{D\,or\,T}, \tag{3}$$

where $p_{i2}(x_i)$ is the equilibrium pressure at arbitral H, D or T to M atomic ratio, x_i. In all the pressure-composition-temperature (PCT) curves, the $\beta_{i/j}$ value is a function of temperature and H, D or T composition in metals, x_i.

Fig. 1 summarizes the $\beta_{i/j}$ values for the Pd-H/D and Pd-H/T systems [5,8–10]. The reason why Pd is selected as an example is that the largest number of data has been reported so far. In a similar way to solid Pd, the liquid Li-H, −D and −T systems are correlated to Fig. 2 [12,13]. As seen in Figs. 1 and 2, there is less or no difference between $\beta_{i/j}$ at the Sieverts region and $\beta_{i/j}{}^*$ at the hydride region for the two metals. Nishikawa noticed that $\beta_{H/D}$ is different from $\alpha_{H/D}$ and the $\alpha_{H/D}$ chain line gives better fitting to the present data.

The Sieverts' solubility constant of K_{s,i_2} can be related with the thermodynamic values of the Gibbs free-energy for a metal, $G_{s,i}$, and that for gas, $G_{g,i2}$, as follows:

$$K_{s,i_2} = \exp\left[-\left(G_{s,i} - 0.5\,G_{g,i_2}{}^0\right)/RT\right] \quad i = \mathrm{H, D, T}. \tag{4}$$

Substituting Eq. (4) into Eq. (2), the difference between two isotopes leads to the following equation:

$$\beta_{i/j} = \exp\left[\frac{\left(G_{g,i_2}{}^0 - G_{g,j_2}{}^0\right)}{2RT} - \frac{\left(G_{s,i} - G_{s,j}\right)}{RT}\right] \quad i,j = \mathrm{H,\ D\,or\,T}. \tag{5}$$

Selecting i = H and j = D or T and substituting the standard Gibbs free-energy change of each gas, $G_{g,i2}{}^0$ and the Gibbs free-energy change for vibration of H isotope atoms in the fcc lattice of solid Pd [14], Eq. (5) predicts the thermodynamic-consistent $\beta_{i/j}$ value for the Pd-H/D system. Calculation results are shown in Fig. 3. Thus, it is found that the isotope effect is well understood by the traditional thermodynamic values of the Gibbs free-energy change of gas or atom in solid lattice.

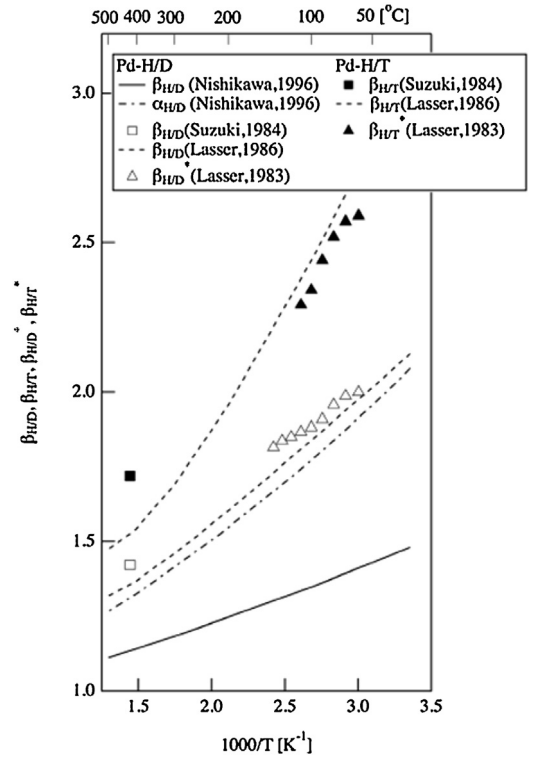

Fig 1. Isotope effect ratios among H, D and T absorption in Pd. Experimental data are quated from Ref. [5,8–10].

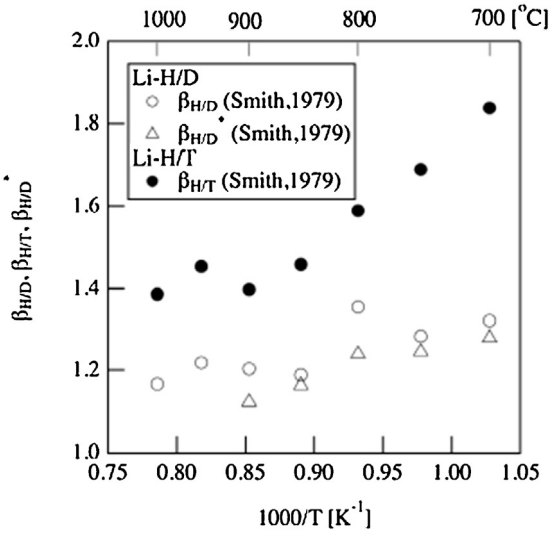

Fig. 2. Isotope effect ratios among H, D and T absorption in Li. Data are cited from Ref. [12].

Since, on the other hand, the $G_{s,i}$ value of H isotope i in a hydride phase is affected by surrounding metal atoms or H ones complicatedly, there is no theoretical estimation for $\beta_{i/j}{}^*$ of the hydride phase. Experimental data would be summarized as a function of not only temperature but also composition. However, the differences of the Gibbs free energy in the hydride phase among the three different isotopes are considered to be almost the same as that in the solid solution region. Consequently, it is empirically assumed that $\beta_{i/j}$ for

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