



Original Article

Behavior characteristics of hydrogen and its isotope in molten salt of LiF-NaF-KF (FLiNaK)



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ABSTRACT

Experimental studies to investigate the behaviors of hydrogen in molten FLiNaK (LiF-NaF-KF) have been conducted at 500–700 °C. On the basis of previous studies, the diffusivity and solubility of hydrogen in FLiNaK have been revised, and the expressions can be correlated to the following Arrhenius equations: $D_{H_2} = 1.62 \times 10^{-5} \exp(-48.20 \times 10^3 / Rg \cdot T)$ [m^2/s] and $S_{H_2} = 1.03 \times 10^{-4} \exp(-14.96 \times 10^3 / Rg \cdot T)$ [$mol-H_2/m^3/Pa$], respectively. The behavior characteristics of deuterium in FLiNaK were studied and compared with the hydrogen behaviors in FLiNaK. The results showed the behaviors of deuterium were consistency with the behaviors of hydrogen in FLiNaK. The difference between hydrogen and deuterium has not been observed upon the experimental research of the behavior characteristics of hydrogen and deuterium in FLiNaK, which suggested the results obtained here might apply equally to the behavior characteristics of tritium in FLiNaK.

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1. Introduction

The behaviors of hydrogen in molten salt of LiF-NaF-KF (FLiNaK) are studied because of the application of molten FLiNaK as a secondary heat-transfer fluid of an advanced high-temperature nuclear reactor of Generation IV [1,2], in which the radio-hazardous tritium may be produced at a very large ratio and causes a very serious issues of tritium control [3]. Understanding of tritium behaviors in FLiNaK can provide useful information for supporting the tritium control works in such high-temperature nuclear reactors. Unfortunately, there are very few studies have focus on the tritium behaviors in FLiNaK. In general, the stable isotopes of tritium, i.e., hydrogen and deuterium, are usually used to replace tritium on the study of tritium behaviors in molten salts. A few researchers have studied the hydrogen behaviors in FLiNaK [4–8], through which the behaviors of tritium in FLiNaK may be evaluated. However, there is still no research about the direct comparison between the behaviors of tritium and its stable isotopes in FLiNaK. It is therefore unsure that the hydrogen behavior characteristics are suitable for analogizing to tritium in FLiNaK.

In this paper, experiments were conducted on the permeation and diffusion behaviors of hydrogen in FLiNaK with a similar experimental installation that used by Fukada and Morisaki [4]. Primarily, we compared the results that obtained by Fukada and Morisaki with our experimental results to confirm the dependability of the experiment including the experimental method, the installation, and results. Secondary, experiments of deuterium behaviors in FLiNaK were also conducted. By comparing the behaviors of deuterium in FLiNaK with hydrogen, the aims were to assess the isotope effect on hydrogen behaviors in FLiNaK and prove its feasibility that hydrogen could be used to replace tritium in the experimental researches of tritium behaviors in FLiNaK.

2. Experiment

A testing system for determining the permeation and diffusion characteristics of hydrogen isotopes in molten salt was built in our laboratory [9]. The apparatus used in this system (seen in Fig. 1) was as same as that used in the research of Fukada and Morisaki [4]. The

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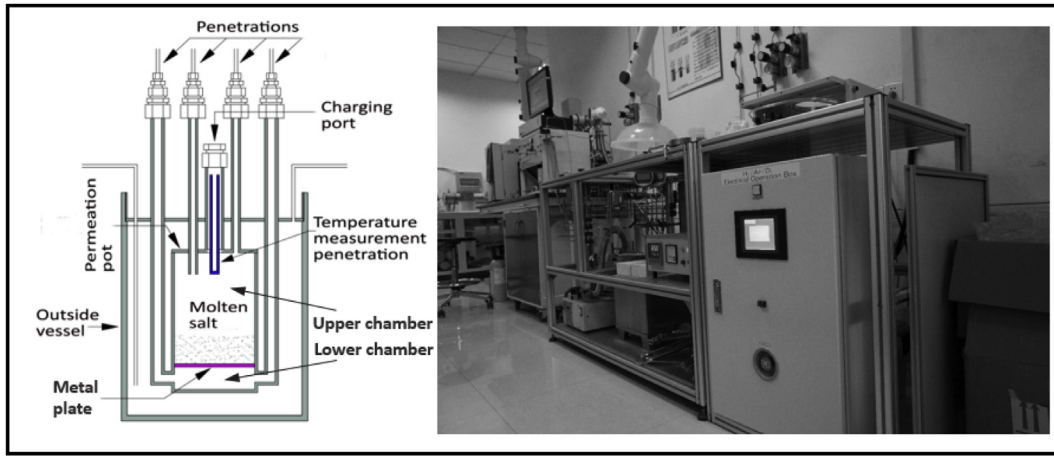


Fig. 1. Testing system for determining the permeation and diffusion characteristics of hydrogen isotope in molten salts.

analyze method was also illustrated in their research paper. Herein it could not take up much space on describing the research method and procedures of the experiments. In brief, hydrogen isotope was charged at one side of molten salt and permeated through molten salt to the other side, where the permeated hydrogen would be swept to the measure system. The hydrogen concentration was detected by a gas chromatography (Shimadzu model GC-2014 coupled with pulsed discharge helium ionization detector) with the H₂ sensitivity of 0.1 ppm. Then, the diffusivity and solubility of hydrogen isotope in molten salt would be determined by the analyze method which described in the research paper of Fukada and Morisaki.

There are two ways to charge hydrogen in the experiment: hydrogen charged from the upper chamber (H₂ charged at salt side) and hydrogen charged from the lower chamber (H₂ charged at metal side). When hydrogen is charged at salt side, it will permeate firstly through molten salt and then through metal (Nickel, 2 mm in thickness) plate. Otherwise, it could permeate firstly through metal plate before arriving at molten salt when hydrogen is charged at metal side. Because of the permeation orders of hydrogen through the molten salt and metal system, different experimental results may be derived [10]. In this paper, experiments at 500 °C, 550 °C, 600 °C, 650 °C and 700 °C with hydrogen charged at salt side and at metal side were carried out, respectively. Besides, deuterium (99.9%) was also used for experiments at 500 °C, 550 °C, 600 °C, 650 °C and 700 °C with deuterium charged at metal side. In these experiments, a mixture of 46.5 (LiF), 11.5 (NaF) and 42 (KF) in mole% was used, in which the thickness of the salt was 30 mm. The hydrogen (or deuterium) pressure in hydrogen-charging side (up-stream) was 1 atm for each experiment. In the swept side (down-stream), argon (Ar) was used and the flow rate was maintained at 20 cm³ (NTP)/min.

H₂ (D₂) diffusivities and solubilities in FLiNaK were derived from the transient and steady-state permeation processes of H₂ (D₂) through FLiNaK in the above experiments, which the detail analyze method can be found in the research of Fukada and Morisaki [4] and also in our previous study [9]. Based on the experiments and the analyze method, the results derived from the experiments of H₂ charged at salt and metal sides are compared, through which more reliable experimental results are expected to be obtained. By comparing the behavior characteristics of hydrogen and deuterium in FLiNaK, moreover, we look forward to investigate the isotope effect of hydrogen on hydrogen behaviors in FLiNaK, and provide supportive data for investigating tritium behaviors in FLiNaK.

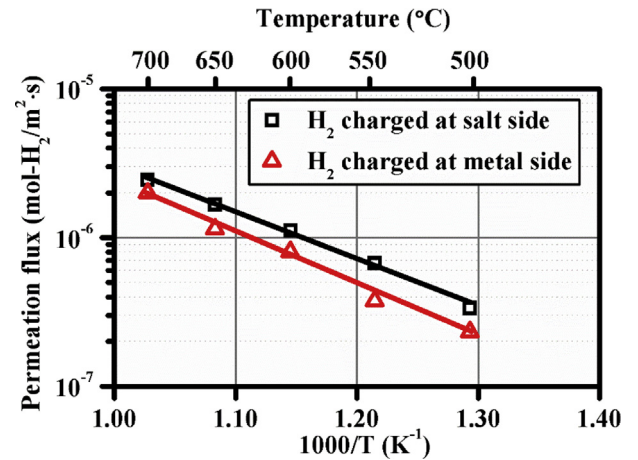


Fig. 2. The steady-state permeation fluxes of hydrogen permeated through FLiNaK and metal when hydrogen was charged at salt and metal sides, respectively.

3. Results and discussion

3.1. The effects of hydrogen charged at two sides of the apparatus

Fig. 2 shows the steady-state permeation fluxes of H₂ permeated through molten FLiNaK and Ni plate with H₂ charged at salt and metal sides, respectively. It was apparent that the steady-state permeation fluxes of H₂ charged at salt side was higher than that of H₂ charged at metal side. At the steady-state permeation process, the steady-state rate (j_{H_2}) of H₂ passing through molten FLiNaK and Ni plate can be simplified to the following equation:

$$\begin{aligned}
 (j_{H_2})_{steady-state} &= \frac{Pe_{(FLiNaK)} \cdot (P_{up} - P_{down})}{L_{FLiNaK}} \\
 &= \frac{Pe_{(Ni)} \cdot (\sqrt{P'_{up}} - \sqrt{P'_{down}})}{L_{Ni}}
 \end{aligned} \tag{1}$$

where $Pe_{(FLiNaK)}$ is the permeability of H₂ through FLiNaK, mol-H₂/m·s·Pa; $Pe_{(Ni)}$ is the permeability of H₂ through Ni plate, mol-H/m·s·Pa^{0.5}; P_{up} and P_{down} are the pressures of H₂ at the upstream and downstream sides of the molten salt, respectively; P'_{up} and P'_{down} are the pressures of H₂ at the upstream and downstream

sides of the Ni plate, respectively; L_{FLiNaK} and L_{Ni} are the thickness of molten salt and Ni plate.

In experiments of H_2 charged at metal side, H_2 permeates firstly through the metal plate and then through the molten FLiNaK. After permeating through the metal, the H_2 pressure will decrease because of the resistance of metal, which suggests the pressure decay of H_2 at the upstream side when H_2 permeating through molten FLiNaK. Accordingly, the steady-state rates of H_2 passing through molten FLiNaK decrease automatically, which are in accordance with the results obtained from Fig. 2.

As shown in the research of Fukada and Morisaki [4], the ratios of $Pe_{(FLiNaK)}/L_{FLiNaK}$ and $Pe_{(Ni)}/2L_{Ni}\sqrt{P_{up}}$ are calculated to be the standardized permeation rates of H_2 passing through molten FLiNaK and Ni plate, respectively. When the permeation rate of H_2 passing through FLiNaK is much smaller than that of Ni plate, it suggests that the process of H_2 passing through the Ni plate can be considered ignorable. Table 1 shows the standardized permeation rates of H_2 passing through FLiNaK and Ni plate when H_2 charged at salt and metal sides. Because the existence of the pressure item, it will result in the different permeation rates of H_2 passing through Ni plate when H_2 charged at salt and metal sides. As shown in Table 1, the permeation rates of H_2 passing through Ni plate are higher than those of H_2 passing through FLiNaK, no matter whether H_2 charged at salt or metal side. However, the permeation rates of H_2 passing through Ni plate when H_2 charged at salt side are higher than those when H_2 charged at metal side. Apparently, it is more appropriate to ignore the behaviors of H_2 permeating through Ni plate when H_2 charged at salt side, relative to that when H_2 charged at metal side. This suggests that the method of H_2 charged at salt side will be better for representing the behaviors characteristics of H_2 in FLiNaK.

3.2. Diffusivity and solubility of H_2 (D_2) in FLiNaK

Fig. 3 shows the permeabilities of H_2 (D_2) in FLiNaK as a function of the reciprocal of temperature. Among them, the permeabilities of H_2 (D_2) in FLiNaK derived from experiments of H_2 (D_2) charged at metal side were calculated with the revised pressures of H_2 (D_2) that calculated by Eq. (1). After the revisions, the permeabilities of H_2 in FLiNaK derived from experiments of H_2 charged at metal side were consistency with the results derived from experiments of H_2 charged at salt side, which suggested the experiments of H_2 charged at salt side could reflect the behavior characteristics of H_2 in FLiNaK while the corresponding revisions were needed for experiments of H_2 charged at metal side. Moreover, the difference has not been found between the permeability of H_2 and D_2 in FLiNaK, accordingly, the permeability can be expressed as the following equation:

$$Pe_{H_2, D_2} = 1.67 \times 10^{-9} \exp\left(-\frac{63.16 \times 10^3}{R_g \cdot T}\right) \left[\frac{\text{mol}}{\text{H}_2/\text{m/s/Pa}} \right] \quad (2)$$

where Pe_{H_2, D_2} is the permeability of H_2 and D_2 through FLiNaK,

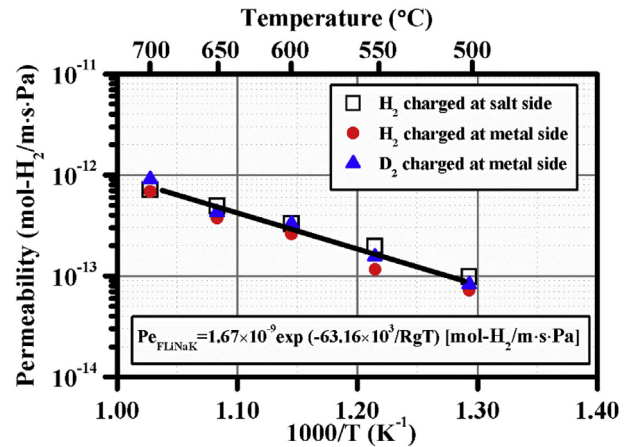


Fig. 3. The permeabilities of H_2 (D_2) through FLiNaK as a function of the reciprocal of temperature.

mol/m/s/Pa; R_g is the gas law constant, J/mol; T is the temperature of FLiNaK, K.

To obtain the diffusivity of H_2 passing through the FLiNaK, the transient permeation fluxes with time were fitted by the analytical solution which was provided in Refs. [4,9]. As shown in Fig. 4, the fitting results agreed well with the experimental results when H_2 charged at salt side. H_2 diffusivities in the FLiNaK when H_2 charged at salt side were calculated by these simulations. However, H_2 diffusivities in the FLiNaK when H_2 charged at metal side would be skewed by this fitting method, in which the H_2 pressures at upstream side of the salt could be overestimated in the transient permeation processes because they were replaced by the pressures of H_2 that charged at metal side. The deviations caused the different results in calculating the diffusivity of H_2 in FLiNaK.

As shown in Fig. 5 (a), the black diamonds were the H_2 diffusivities in FLiNaK derived from experiments of H_2 charged at salt side, while the red circles were the H_2 diffusivities in FLiNaK derived from experiments of H_2 charged at metal side. The latter results came from the research of Fukada and Morisaki [4], which has been proved that the H_2 diffusivities obtained in their research were consistency with the results that derived from experiments of H_2 charged at metal salt in our previous study [8]. The diffusivities derived from experiments of H_2 charged at metal side were underestimated, relative to the results derived from experiments of H_2 charged at salt side. Because the difference between H_2 and D_2 might be ignorable in experimental research of the behavior characteristics of H_2 and D_2 in FLiNaK, thus the diffusivities of H_2 and D_2 in FLiNaK can be expressed as the following equation:

$$D_{H_2, D_2} = 1.62 \times 10^{-5} \exp\left(-\frac{48.20 \times 10^3}{R_g \cdot T}\right) \left[\frac{\text{m}^2}{\text{s}} \right] \quad (3)$$

where D_{H_2, D_2} is the diffusivity of H_2 and D_2 through FLiNaK, m^2/s ;

Table 1

The standardized permeation rates ($\text{mol-H}_2/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$) of H_2 passing through FLiNaK and Ni plate when H_2 charged at salt and metal sides.

Temperature °C	Permeation rate of FLiNaK	Permeation rate of Ni plate when H_2 charged at salt side ^a	Permeation rate of Ni plate when H_2 charged at metal side ^a
500	3.28E-12	7.84E-10	4.05E-11
550	6.57E-12	8.01E-10	5.58E-11
600	1.09E-11	8.93E-10	7.45E-11
650	1.64E-11	1.00E-09	9.60E-11
700	2.37E-11	1.09E-09	1.21E-10

^a H_2 permeability through Ni came from Ref. [11].

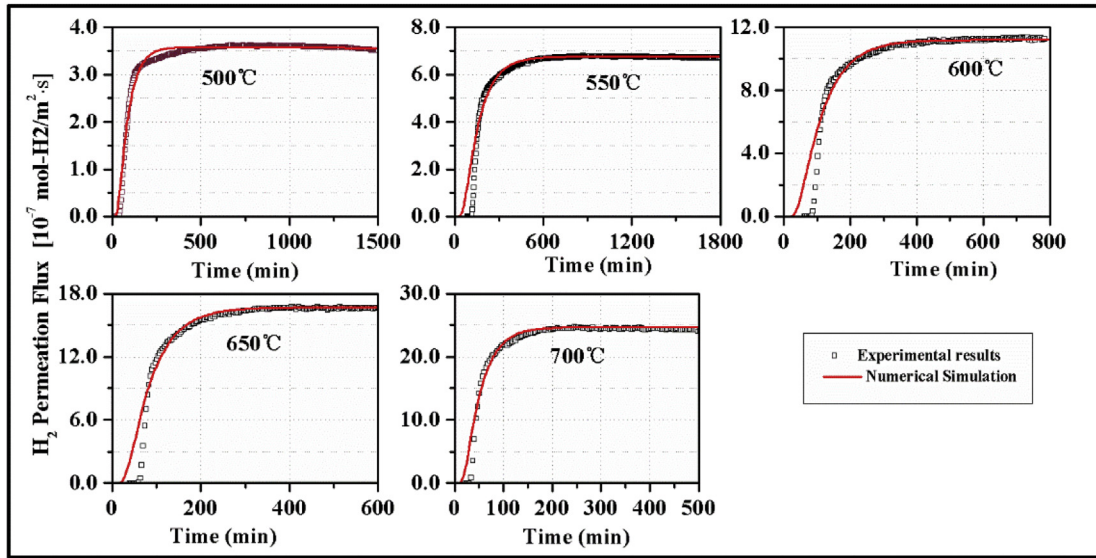


Fig. 4. H₂ transient permeation fluxes with time and the numerical simulations in experiments of H₂ charged at salt side at 500–700 °C.

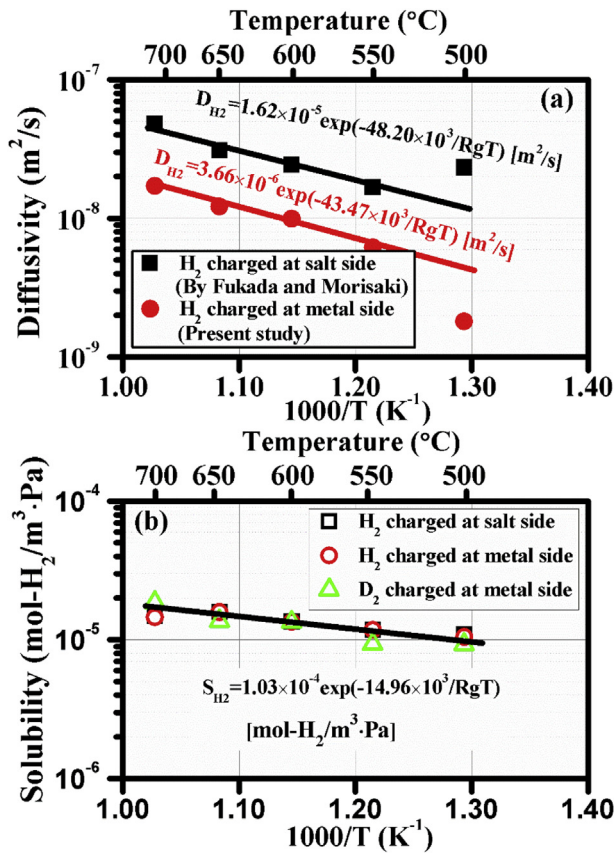


Fig. 5. Diffusivity (a) and solubility (b) of H₂ (D₂) in FLiNaK as functions of the reciprocal of temperature.

R_g is the gas law constant, J/mol; T is the temperature of FLiNaK, K.

Fig. 5 (b) shows the results of the solubility of H₂ and D₂ in FLiNaK derived from our present experiments, including H₂ solubility derived from the experiments of H₂ charged at salt side, H₂ solubility derived from the revised experiments of H₂ charged at metal side, and D₂ solubility derived from the revised experiments of D₂ charged at metal side. As seen in the figure, the three results

correspond with each other, which further suggested that the necessity and effectiveness of correcting experimental results of H₂ (D₂) charged at metal side, and no difference between H₂ and D₂ were found in experimental research of the behavior characteristics of H₂ and D₂ in FLiNaK. Thus, the solubility of H₂ and D₂ in FLiNaK can be expressed as the following equation:

$$S_{H_2, D_2} = 1.03 \times 10^{-4} \exp\left(-\frac{14.96 \times 10^3}{R_g \cdot T}\right) \left[\frac{\text{mol-H}_2}{\text{m}^3/\text{Pa}}\right] \quad (4)$$

where S_{H₂,D₂} is the solubility of H₂ and D₂ in FLiNaK, mol/m³/Pa; R_g is the gas law constant, J/mol; T is the temperature of FLiNaK, K.

4. Conclusions

The behavior characteristics of hydrogen and its isotope in molten salt of LiF-NaF-KF (FLiNaK) have been studied in this paper. Based on the previous studies, the diffusivity and solubility of H₂ in FLiNaK have been revised for improving the reliability of experimental results. The revised diffusivity and solubility of H₂ in FLiNaK can be expressed as: $D_{H_2} = 1.62 \times 10^{-5} \exp(-48.20 \times 10^3/R_g \cdot T)$ [m²/s] and $S_{H_2} = 1.03 \times 10^{-4} \exp(-14.96 \times 10^3/R_g \cdot T)$ [mol-H₂/m³/Pa], respectively. Besides, the behavior characteristics of deuterium in FLiNaK were studied and compared with the hydrogen behaviors in FLiNaK. The difference between H₂ and D₂ has been observed upon the experimental research of the behavior characteristics of H₂ and D₂ in FLiNaK, which suggested the results obtained here might apply equally to the behavior characteristics of tritium in FLiNaK.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.net.2018.10.008>.

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