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Solubility of hydrogen fluoride in the molten LiF–PbF$_2$

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Abstract

Measurements of the solubility of HF gas in LiF–PbF$_2$ binary molten mixture of its eutectic composition have been carried out over a temperature range between 923 and 1023 K by an elution method. In order to evaluate HF solubility and to obtain values of heat of solution and entropy, preliminary measurements of density of LiF–PbF$_2$ have also been performed. The solubility data were found to exhibit the characteristics of a chemical dissolution process.

1. Introduction

Besides the main requirement for the D–T fusion blanket to efficiently convert the fusion energy to the useful heat energy adequate tritium recovery is important. There are three blanket concepts in terms of their lithium-bearing type of breeder: the ceramic (solid) breeder concept, the liquid metal breeder concept, and the molten salt breeder concept. Although the last one has not been considered yet in a commercial design, molten salts still remain attractive because of the lower pumping load than that for liquid metals. Additionally, molten salts are advantageous because they do not suffer either from radiation damage or from phase transformations. For example, in [1] molten salt Flibe was chosen as a candidate material for the blanket design in helical-type reactor (FFHR). Among the advantages mentioned above, the authors also point out the fact that Flibe, as other fluorides, is quite stable, the reactivity with air and water is quite low, so that the potential hazard of fire is also very small. It is known that there are many requirements or issues in a selecting of materials for the blanket, such as tritium permeation, material compatibility, heat transfer, operation pressure, etc. Among them, tritium behavior in a blanket material is primarily important. Then, in order to evaluate tritium recovery or tritium inventory it is necessary to know values of gas solubility in molten salts and to study chemical and thermodynamic behavior of gases in this medium.

Thus, the purpose of our study is to measure the values of HF solubility in the LiF–PbF$_2$ system. The LiF–PbF$_2$ system with its eutectic composition ($x_{\mathrm{PbF_2}} = 60$ mol% [2]) is suggested herein just as a promising material. The reasons that system can be attractive are, at first, lead is a more plentiful resource than beryllium and, at the second, both of them have almost the same neutron multiplication factor [3].

Additionally, there are no data for the densities for the LiF–PbF$_2$ melt, therefore to evaluate HF solubility, preliminary measurements of densities were carried out.

The elution method was applied to study HF solubility in the LiF–PbF$_2$ melt. In order to calibrate the experimental apparatus beforehand, measurements of hydrogen chloride HCl solubility in the NaCl–KCl molten salt ($x_{\mathrm{KCl}} = 50$ mol%) were also performed.

2. Experimental

2.1. Density measurements

LiF and PbF$_2$ (Merck) used in this study were of 98% and 99.999% purity. The density was measured by the Archimedian method. The apparatus for the measurements is shown in Fig. 1. A platinum bob was connected with a thin platinum wire ($\phi = 0.025$ cm) and suspended from the balance pan. The density of the bob was calibrated by weighing in air and then in water at a known temperature to evaluate its volume V_0. The volume V_0 was calculated from the following equation

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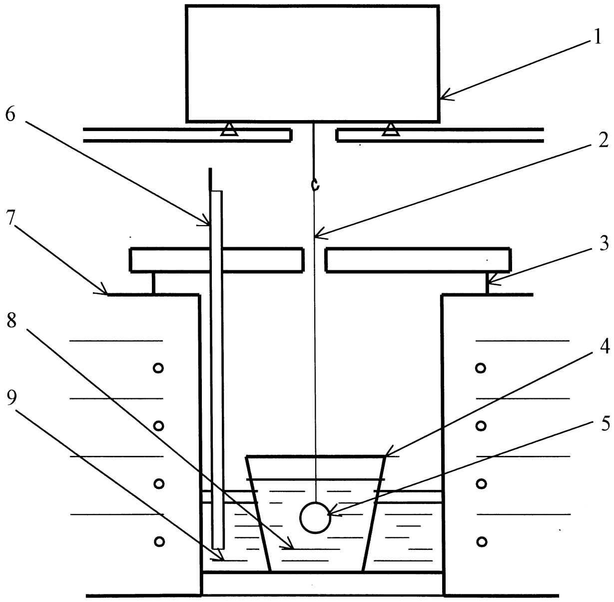

Fig. 1. Apparatus for density determinations by the Archimedian method. (1) Direct reading balance, (2) Pt wire, (3) cell, (4) Pt crucible, (5) Pt bob, (6) K thermocouple, (7) furnace, (8) LiF–PbF_2 melt, (9) graphite bath with NaCl–KCl melt.

$$V_0 = (W_a - W_w)/(d_w - d_a) + \pi\sigma_w a_0/g(d_w - d_a), \qquad (1)$$

where W_a, W_w, d_w, d_a, σ_w, g, a_0 are weights (in air and water) of the bob, densities (in air and water), surface tension of water, gravitational constant and a wire diameter, respectively. The expansion of the bob with increasing temperature is expressed by the following equation;

$$V_m = V_0(1 + \beta(t_m - t_a)), \qquad (2)$$

where β is the coefficient of cubical expansion of platinum, t_m and t_a are temperatures of the melt and air, respectively. The surface tension of the molten LiF–PbF_2 is not available, but its contribution to the value of volume, in this case, is very small ~(+0.001 ml), and it is neglected here. Therefore, the density of the melt can be expressed as follows;

$$d_m = (W_a + d_a V_0 - W_m)/V_m. \qquad (3)$$

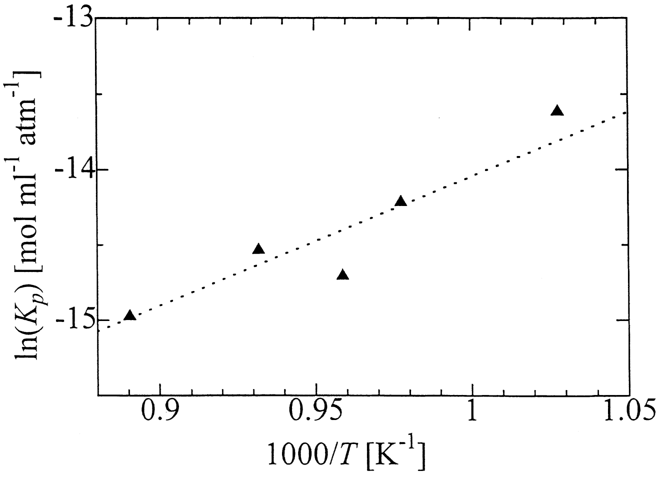

Fig. 2. Temperature dependence of HCl solubility in NaCl–KCl (x_{KCl} = 50 mol%) mixture. (Dotted line) – the results after Lukmanova and Vil'nyanskii [3], (▲) – this work.

2.2. Solubility measurements

As mentioned above, in order to examine the apparatus for the solubility measurement preliminary experiments to study HCl solubility in the NaCl–KCl melt were carried out. The experimental conditions were almost similar to those of Lukmanova and Vil'nyanskii [4]. Fig. 2 shows an agreement with the values of solubilities of our measurements and those of [4], and in both cases the solubility of HCl decreases with increasing temperature.

Anhydrous HF was obtained from a cylinder supplied by Hashimoto Chem. with purity of 99.9%, which was used without further purification. The saturator vessel was made from a stainless steel SUS 304. All rods of the saturator vessel in contact with the molten fluoride at high temperatures were of nickel (NILACO). Stopcocks, T-type cocks, gas transport pipes, and drexelers were of teflon and supplied by Flon Industry. Argon gas of 99.999% purity was used as a carrier gas. The fluoride eutectic mixture of LiF and PbF_2 ($x_{PbF_2} = 60$ mol%) was premelted inside a glove box at 1073 K under the Ar flow and then cooled and crumbled. The 70 g sample was in the alumina crucible during melting and solubility measurements.

The HF solubility apparatus is shown in Fig. 3. The melt was kept under the Ar flow throughout the experiment. HF saturation of the sample was carried out through the inlet pipe (3) with argon (15) as a carrier gas. After a settlement of 20 min the excess of HF was extruded when the stopcock of the inlet pipe was closed and one of the Ar lines was opened. The gas from the outlet in both procedures was caught by the protection line with two drexelers of the high concentration KOH and water (11 and 12, respectively). The dissolved HF was extruded from the melt by Ar gas for 20 min and caught by the drexeler (13) of the titration line. The attainment of an equilibrium was confirmed by changing the saturation time. At 923 K the following values of solubility were obtained; $(0.750 \pm 0.006) \times 10^{-6}$, $(1.03 \pm 0.01) \times 10^{-6}$, and $(0.86 \pm 0.04) \times 10^{-6}$ mol/ml after the saturation time of 30, 40, and 60 min, respectively. At 1023 K the values of solubility were $(0.034 \pm 0.001) \times 10^{-6}$, $(0.060 \pm 0.004) \times 10^{-6}$, and $(0.058 \pm 0.005) \times 10^{-6}$ mol/ml after the saturation time of 30, 40, and 60 min, respectively. The saturation time of 40 min was thus taken at the flow speed of HF gas about 0.1 l/min. The elution time of 20 min at the corresponded speed of Ar flow was enough to extrude all remaining of HF from the melt that was also controlled

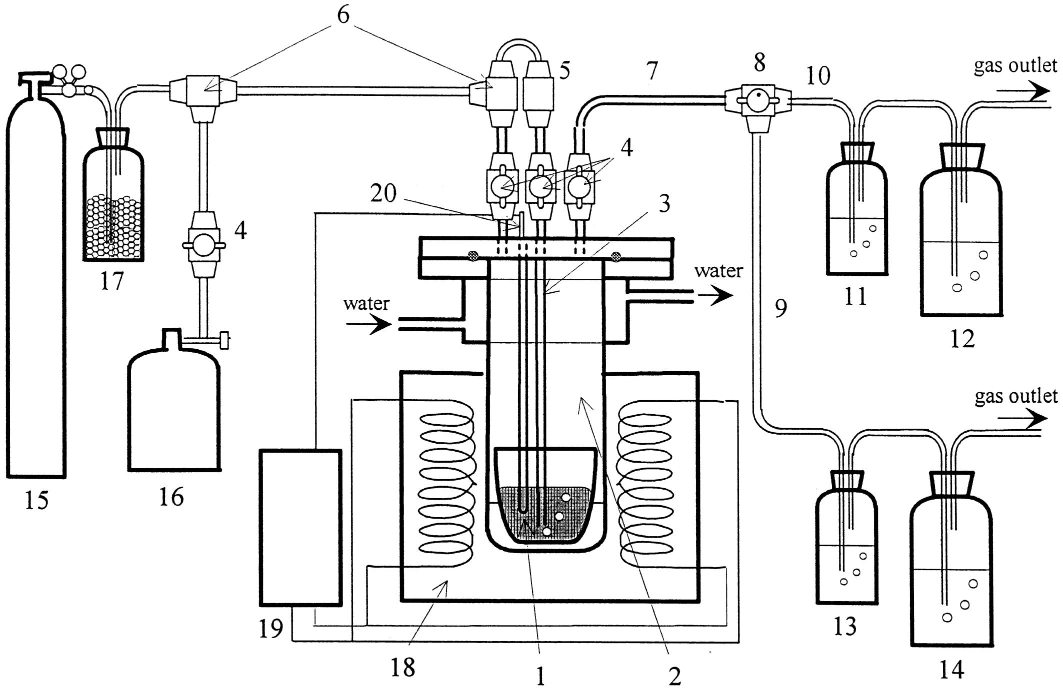

Fig. 3. HF solubility apparatus. (1) Crucible with melt, (2) saturator vessel, (3) inlet pipe, (4) stopcocks, (5) joint cock, (6) T-type cocks, (7) outlet pipe, (8) T-type stopcock, (9) titration line, (10) protection line, (11) protection drexeler with KOH, (12) outlet flask, (13) titration drexeler with KOH, (14) outlet flask, (15) Ar gas cylinder, (16) HF gas cylinder, (17) molecular sieve, (18) furnace, (19) temperature controller, (20) thermocouple.

Table 1
Densities of LiF–PbF_2 ($x_{PbF_2} = 60$ mol%) at various temperatures

Temperature (K)	Density (/10^3 kg m^{-3})
973	3.545 ± 0.011
993	3.528 ± 0.006
1013	3.509 ± 0.003
1033	3.491 ± 0.007
1053	3.473 ± 0.010
1063	3.458 ± 0.021
1073	3.449 ± 0.001
1093	3.432 ± 0.003
1113	3.410 ± 0.011
1123	3.405 ± 0.005

before. The solubility values were determined by a back titration by using the standard oxalic acid ($H_2C_2O_4{\cdot}2H_2O$).

3. Results and discussion

Table 1 indicates the values of measured densities and Fig. 4 shows the density changes for the LiF–PbF_2 system at varying temperatures. The experimental deviations are mainly due to the fluctuations of measured temperatures (±2°C) in a furnace. The temperature dependence of densities is expressed here by the following linear equation

$$d/10^3\ \mathrm{kg\,m^{-3}} = 4.48 - 9.61 \times 10^4 T. \quad (4)$$

The solubilities of HF in the molten LiF–PbF_2 were determined between 923 and 1023 K at the pressure of about 1 atm. Measured solubilities have units of (mole of HF)/(ml of melt).

Table 2
Solubility of HF in molten LiF–PbF_2 ($x_{PbF_2} = 60$ mol%)

Saturating temperature (K)	HF solubility, average value (mol/ml×10^6)
923	1.02 ± 0.14
943	0.57 ± 0.02
973	0.26 ± 0.10
993	0.25 ± 0.05
1023	0.06 ± 0.01

The solubility values are presented in Table 2. It shows that HF solubilities decrease with increasing temperature. The small values of solubilities suggest this dependence to be linear or to obey Henry's Law. Fig. 5 shows the dependence of HF solubility in the LiF–PbF_2 melt on inverse temperature. The heat of solution, which is independent of temperature is estimated here by a least-square fitting from the van't Hoff relation

$$\Delta H^s = -R\,\mathrm{d}(\ln K_p)/\mathrm{d}(1/T). \quad (5)$$

In our case the heat of HF solution in the LiF–PbF_2 melt is

$$\Delta H^s = -0.205 \pm 0.002\ \mathrm{kJ\,mol^{-1}},$$

where uncertainties are taken as one standard deviation obtained here from the least-square fitting.

The entropy of solution is expressed by the following equation;

$$\Delta S^s = \frac{\Delta H^s}{T} + R\ \ln K_p R' T, \quad (6)$$

where R' is the gas constant in appropriate units of K_p, i.e. 82.05 ml atm/K mol.

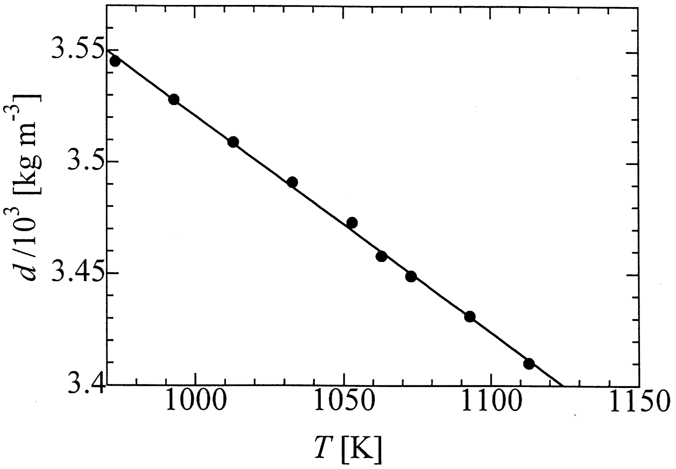

Fig. 4. Density versus temperature for LiF–PbF_2 (x_{PbF_2} 60 mol%) mixture.

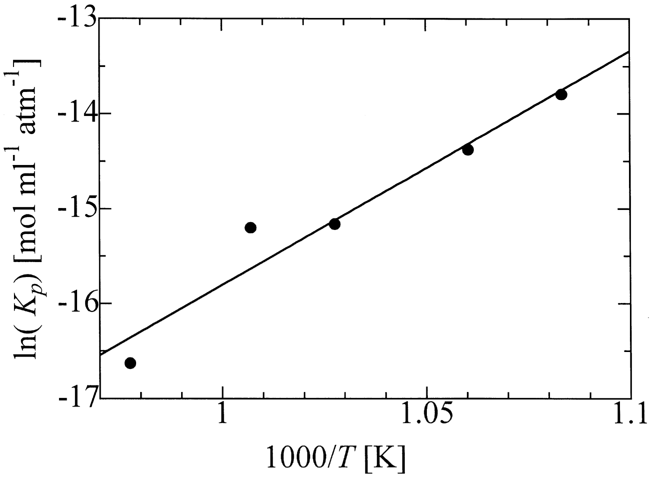

Fig. 5. Temperature dependence of HF solubility in LiF–PbF$_2$ (x_{PbF_2} 60 mol%) mixture.

Thus the entropy of solution at 1000 K is

$$\Delta S^s = -37.11 \pm 0.78\ \mathrm{J\ K^{-1}\ mol^{-1}}.$$

A decrease in HF solubility with increasing temperature and the value of heat of solution suggest that a dissolution is an exothermic chemical process. A mechanism of HF dissolution might assume that HF is present as monomers, whereas it is associated into complexes of the type F–H $\cdots$ F^-_{melt} in the molten fluorides. The same mechanism was suggested for the alkali-metal chlorides in [5].

4. Conclusions

The study of hydrogen fluoride solubility in the molten LiF–PbF$_2$ has been carried out in the present work. An evaluation of tritium recovery or tritium inventory in a D–T blanket is, of course, complex and is primarily limited by a poor data base. This new data for LiF–PbF$_2$ densities and the values of HF solubility contributes to a clearer understanding of gas behavior in this medium.

The elution apparatus described here performed satisfactorily and the data obtained is in agreements with that reported in [4].

The process of HF dissolution in LiF–PbF$_2$ melt, which is a slightly exothermic reaction, proceeds in a chemical way. The solubility of HF in the LiF–PbF$_2$ system is relatively low, and lower nearly by one order than that in Flibe [6], which means that the inventory rate of tritium is also low.

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