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# Self-Diffusion of Lithium in Molten $\text{Li}_2\text{BeF}_4$ <sup>†</sup>

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## Abstract

The self-diffusion coefficients of lithium in molten  $\text{Li}_2\text{BeF}_4$  have been measured with the capillary reservoir technique using  $^6\text{Li}$  as a tracer. The concentration profiles of  $^6\text{Li}$  in a capillary were measured by an ion micro mass analyser and the self-diffusion coefficients were calculated. The result can be described with the Arrhenius equation:

$$D = 9.27 \times 10^{-8} \exp\left(\frac{-7770}{RT}\right)$$

where  $D$  is expressed in  $\text{cm}^2/\text{sec}$ ,  $R$  in  $\text{cal}/\text{mol-deg}$  and  $T$  in degree Kelvin. The activation energy for diffusion of lithium is much smaller than that of fluorine and slightly larger than that for electrical conductivity. This suggests that the movement of fluorine does not involve an electric current transfer and the mobility of lithium ions is much larger than that of fluoroberyllate ions.

## 1. Introduction

The correlation and interpretation of ionic transport properties in molten mixtures of beryllium fluoride with alkali fluorides are of interest because not only these systems may be considered as weakened analogous of alkaline earth-silicon oxide systems<sup>1)</sup> but as solvent for fessile and fertile components in molten salt thermal breeder reactors and the blanket medium of  $D-T$  nuclear fusion reactors.<sup>2)</sup> Especially  $\text{LiBeF}_3$  and  $\text{Li}_2\text{BeF}_4$  molten salts are considered to be most suitable for the both reactors.

The physical properties of molten alkali fluoroberyllate, such as viscosity<sup>3)</sup>, electrical conductance<sup>4)</sup>, density<sup>5)</sup>, thermal expansivity<sup>6)</sup> and so on, have been measured by Oak Ridge National Laboratory group. These results indicate the breakdown of the network structure of  $\text{BeF}_2$  with addition of alkaline fluoride, that is to say, the dissociation reaction  $\text{Li}_2\text{BeF}_4 \rightleftharpoons 2\text{Li}^+ + \text{BeF}_4^{2-}$ . However, the self-diffusion coefficient of each element of molten  $\text{LiF}-\text{BeF}_2$  (it seems that the value directly gives important informations to solve the structure of molten salt and is related to these characteristics) has been hardly obtained.

In previous paper<sup>7),8)</sup>, we discussed the self-diffusion of fluorine in molten  $\text{Li}_2\text{BeF}_4$  and  $\text{LiBeF}_3$ . The results showed significantly large self-diffusion coefficient in spite of the large activation energy. Moreover, the activation energies were much larger than those of

electrical conductance and viscosity. In order to explain qualitatively this phenomena, it seemed that possible mechanism involved the transport of fluorine resulting from the movement of fluoroberyllate anions, the exchange of fluorine between neighbouring anions, and ion-pair diffusion.

The present paper deals with lithium in molten  $\text{Li}_2\text{BeF}_4$  for which there are no data available in the literature except the calculation of molecular dynamics in  $\text{LiBeF}_3$  by Rahman et al<sup>9)</sup>. The diffusion coefficients of lithium ion were obtained with capillary reservoir technique using  $^6\text{Li}$  as a tracer. As  $^6\text{Li}$  is non-radioactive isotope, the distribution of  $^6\text{Li}$  in a capillary after a diffusion run was determined using an ion micro mass analyser.

## 2. Experimental Procedures

The procedures of the experiment were almost same way as described in the previous paper<sup>8)</sup>.

For the preparation of  $\text{Li}_2\text{BeF}_4$  in diffusion cell, a mixture of  $\text{LiF}$  and  $\text{BeF}_2$  was melted in a nickel container and treated with a  $\text{HF}-\text{H}_2$  mixture at  $600^\circ\text{C}$  and then sparged with  $\text{He}$ . The used chemicals were as follows:  $\text{LiF}$  prepared by Morita Kagaku Kogyo Co., analytical reagent grade;  $\text{BeF}_2$  prepared by Rare Metallic Co., known impurities (in ppm):  $\text{K}+\text{Na}$ , 600;  $\text{Ca}$  10;  $\text{Al}$ , 20;  $\text{Cr}$ , 30;  $\text{Fe}$ , 10;  $\text{Ni}$ , 10.

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On the other hand,  $\text{Li}_2\text{BeF}_4$  labeled with  $^6\text{Li}$  was prepared as follows. At first time,  $^6\text{LiF}$  was produced from  $\text{Li}_2\text{CO}_3$  (ORNL) with a  $^6\text{Li}/^7\text{Li}$  abundance ratio of 19 which was treated with 48% hydrofluoric acid aqueous solution and dried heating. After  $\text{BeF}_2$  and  $\text{LiF}$  labeled with  $^6\text{Li}$  were weighed correctly and mixed sufficiently, the batch was melted in a platinum crucible.

$\text{Li}_2\text{BeF}_4$  melt labeled with  $^6\text{Li}$  was filled into Ni capillaries of which the length was 30 or 40 mm and the inner diameter was 1 mm. The capillaries were submerged in the reservoir melt to allow diffusion of  $^6\text{Li}$  from the capillaries for fifty minutes at each temperature. After the diffusion run, the capillaries were slowly lifted out of the melt and then removed from the cell.

The concentration profiles of  $^6\text{Li}$  in a capillary were measured by ion micro mass analyser (HITACHI IMA-SS) as follows. The capillary was cut by a saw at intervals of two millimeters. The  $\text{Ar}^+$  ions with an energy of 5KeV and a beam diameter of  $\sim 500 \mu\text{m}$  bombarded the each section of the capillary. In order to avoid the charging because of the insulated property of  $\text{Li}_2\text{BeF}_4$ , electrons from a tungsten filament were showered onto the specimen. As the double charged and molecular secondary ions were small quantities, mono-charged secondary ions of  $^6\text{Li}^+$  and  $^7\text{Li}^+$  were measured. It was assumed that the ratio of  $^6\text{Li}^+/(^6\text{Li}^++^7\text{Li}^+)$  gave the concentration profile of  $^6\text{Li}$  in a capillary. It seems to be reasonable because  $^6\text{Li}^+/(^6\text{Li}^++^7\text{Li}^+)$  was nearly 0.95 (this value accords to  $^6\text{Li}/^7\text{Li}=19$ ) within experimental error for the non-diffused capillary.

Moreover, the diffusion coefficient of impurity sodium in  $\text{Li}_2\text{BeF}_4$  melt was obtained. The experimental method was same way as that of lithium except that  $^{24}\text{Na}$  radio isotope was used as a tracer.  $^{24}\text{Na}$  was produced from  $\text{NaF}$  powder irradiated by thermal neutron for 1 minute in Japan Research Reactor-2.

### 3. Results

The typical concentration profiles of  $^6\text{Li}$  in capillaries are shown in Fig. 1. It is considered that errors may arise in the capillary reservoir technique due to disturbance at the capillary mouth on immersion and removal of the capillary into/from the molten salt bath. Therefore, the results which gave the abnormal concentration profile of  $^6\text{Li}$  were neglected in this study.

Instead of the analysing the curve using the formula

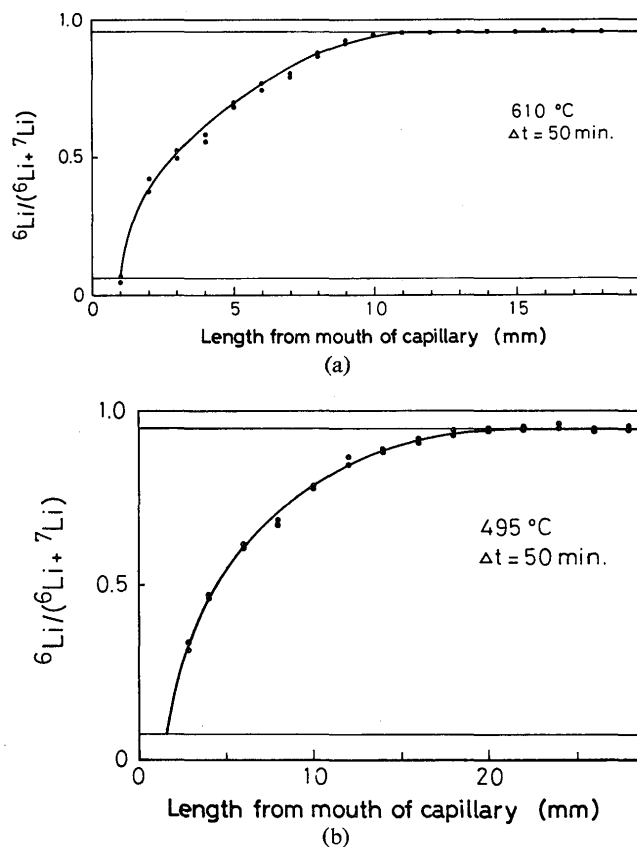


Fig. 1 Distribution of  $^6\text{Li}$  in a capillary after a diffusion run  
(a) temperature:  $610^\circ\text{C}$ , diffusion time: 50 min., capillary length: 40 mm  
(b) temperature:  $495^\circ\text{C}$ , diffusion time: 50 min., capillary length: 30 mm

$C_x = C_o \operatorname{erf}\left(\frac{X}{(Dt)^{1/2}}\right)$  where  $C_x$  is the concentration of  $^6\text{Li}$  at distance  $x$  from the boundary after time  $t$ , diffusion coefficient  $D$  was calculated from the well known solution of Fick's law for such boundary conditions that  $C=C_o$  for  $0 < x < L$  when  $t=0$ ,  $C=0$  for  $x=0$  for all values of  $t^{10}$ .

$$\frac{C_{av}}{8C_o} = \frac{1}{n(2n+1)^2} \exp(-(2n+1)^2\pi^2Dt/4L^2) \quad (1)$$

where  $C_o$  is the initial concentration of  $^6\text{Li}$ ,  $C_{av}$  its residual concentration,  $D$  the self-diffusion coefficient,  $L$  the length of the capillary, and  $t$  the duration time. The diffusion coefficient for values of  $C_{av}/C_o > 0.5$  was calculated by a similar expression<sup>11)</sup>

$$D = 0.785(1 - C_{av}/C_o)^2 L^2/t \quad (2)$$

The results of the experiments (solid circle) are given in Fig. 2 as the variation of  $\log D$  vs.  $1/T$ . The least-square line drawn through the experimental points can be represented by the Arrhenius-type equation.

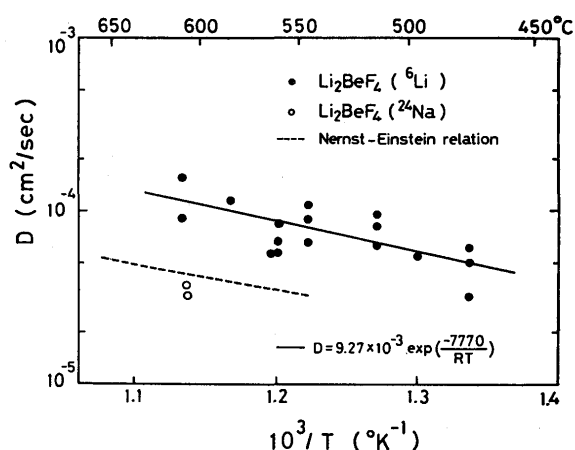


Fig. 2 Diffusion coefficients of lithium (solid line) and impurity sodium (open circle) in a  $\text{Li}_2\text{BeF}_4$  melt. Dashed line shows diffusion coefficient calculated from electrical conductivity.

$$D = D_0 \exp\left(\frac{-E_D(\text{Li})}{RT}\right) \quad (3)$$

where  $E_D(\text{Li})$  is the activation energy of lithium diffusion,  $R$  the gas constant, and  $T$  the absolute temperature.  $E_D(\text{Li})$  and  $D_0$  were calculated as follows:

$$E_D(\text{Li}) = 7.77 \text{ Kcal/mol}$$

$$\log D_0 = -2.03 \text{ cm}^2/\text{sec}$$

The open circles in Fig. 2 show the diffusion coefficients of Na impurity in molten  $\text{Li}_2\text{BeF}_4$  at  $607^\circ\text{C}$ . It was obtained by measuring the distribution of  $^{24}\text{Na}$  radio isotope in a capillary with a  $\gamma$ -ray spectrometer. The diffusion coefficients of sodium are smaller than those of lithium.

The dashed line shown the diffusion coefficient obtained from the electrical conductance of molten  $\text{Li}_2\text{BeF}_4$  using Nernst-Einstein.<sup>12)</sup>

$$D = \frac{\sigma kT}{(Ze)^2 n} \quad (4)$$

where  $\sigma$  is electrical conductance,  $k$  Boltzmann constant,  $Z$  charge number of diffusion ion,  $e$  electron charge,  $n$  number of ions per unit volume,  $T$  absolute temperature. The values of  $\sigma$  was used after ORNL<sup>4)</sup>.

#### 4. Discussions

On ion microprobe self-diffusion measurements of lithium two kinds of stable isotopes  $^6\text{Li}$  and  $^7\text{Li}$  were analysed. The isotopic mass differences causes two different diffusion constants, respectively. J. Coles and J. Long<sup>13)</sup> calculated the isotope effect that the difference was 6.3%, in the self diffusion of lithium in single crystal lithium-fluoride assuming that the jump frequency is proportion to  $1/M^{1/2}$  ( $M$ ; mass number). In this study, it is considered that the isotope effect of

$^6\text{Li}$  and  $^7\text{Li}$  is probably negligible because of liquid state in this study.

Molten  $\text{BeF}_2$  is characterized as network liquids in which tetrahedral molecular units are bridged at corners. The addition of  $\text{LiF}$  to molten  $\text{BeF}_2$  indicates the breakdown of the network type structure of  $\text{BeF}_2$  and then it is considered that such complex anions as  $\text{BeF}_4^{2-}$ ,  $\text{Be}_2\text{F}_7^{3-}$  and so on are formed.<sup>8), 14)</sup> It seems that the peculiarity of diffusion coefficient of fluorine in molten  $\text{LiF-BeF}_2$  (significantly large self diffusion coefficient in spite of the large activation energy) depends on this phenomena.

On the other hand, both the self diffusion coefficient and the activation energy of lithium in molten  $\text{Li}_2\text{BeF}_4$  are found in Fig. 3 to have approximately the same values as those of alkaline cations in various molten salts having the typical ionic properties. (Figure 3 shows the comparison of self diffusion coefficients of lithium in molten  $\text{Li}_2\text{BeF}_4$  with those of cation in various molten salts and molten silicates.) J. Bockris and G. Hooper<sup>20)</sup> indicated from their self diffusion measurement in molten alkali halides that the diffusion

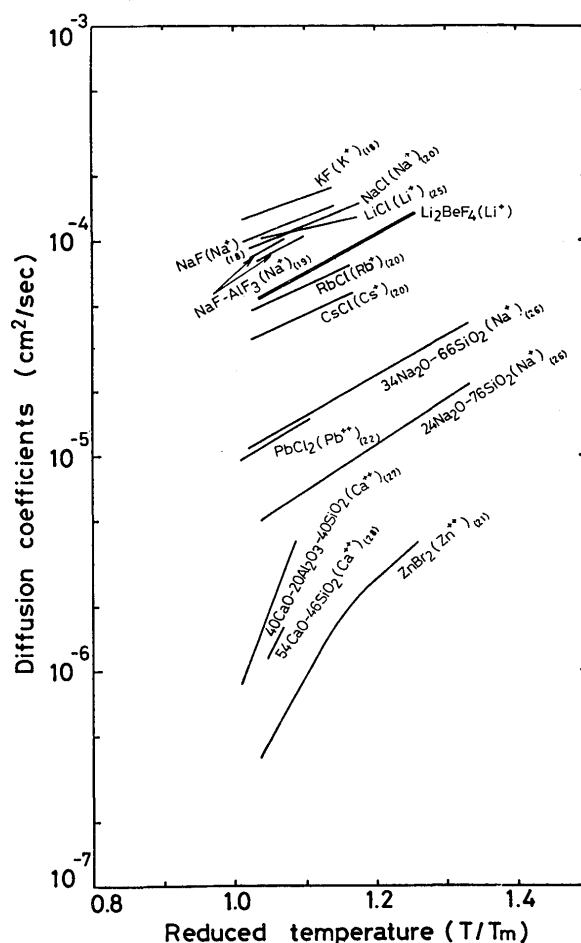


Fig. 3 Comparison of self-diffusion coefficients of various cations in molten salts and molten silicates.

mechanism of the constituent ions was not explained by a quasi-random micro-jump model but by a hole model essentially developed by Furth. However, in molten  $\text{Li}_2\text{BeF}_4$  the difference between the activation energy of self diffusion of lithium and that of fluorine is extraordinarily large. Moreover the self diffusion coefficient of lithium in this study is larger than that calculated from molecular dynamics in molten  $\text{LiBeF}_3$  by Rahman et al.<sup>9)</sup> It seems, therefore, that lithium in molten  $\text{Li}_2\text{BeF}_4$  is bound feebly to complex anions such as  $\text{BeF}_4^{2-}$ ,  $\text{Be}_2\text{F}_7^{3-}$  and diffuses not only through holes but interstitial sites or as a result of redistribution of free volume. These assumption may be supported also from the fact that the self diffusion coefficient of impurity sodium in molten  $\text{Li}_2\text{BeF}_4$  is about one third smaller than that of lithium as shown in Fig. 2. This phenomenon may accord with the discussion of M. Cohen and D. Turnbull<sup>15)</sup> that, if the impurity molecule is larger than the solvent, the critical void for diffusion must be correspondingly larger; therefore the impurity should diffuse more slowly than the solvent.

The activation energies between diffusion and electrical conductance are shown in Fig. 4. The activation

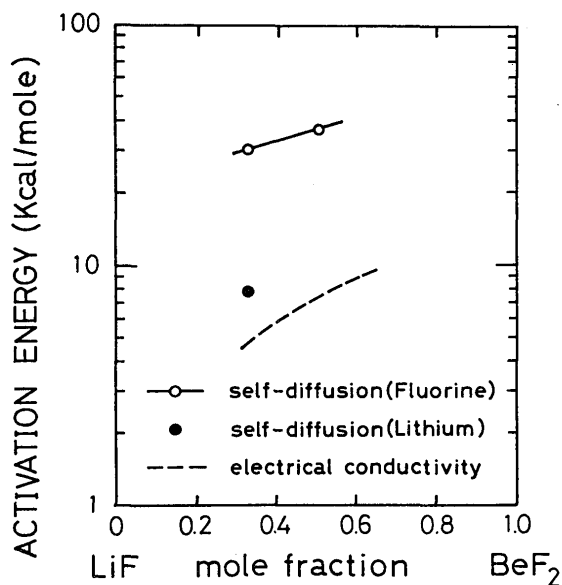


Fig. 4 Activation energy of self-diffusion coefficient of lithium and fluorine, and electrical conductivity of molten flibe.

energy for diffusion of lithium is much smaller than that of fluorine and slightly larger than that for electrical conductance. This suggests that the movement of fluorine does not involve an electric current transfer and the mobility of lithium ions is much larger than that of fluoroberyllate ions. In fact, according to K. Romberger and J. Braunstein<sup>17)</sup>, the transference

number of lithium ion in molten  $\text{LiF-BeF}_2$  is unity within the experimental error. It is, therefore, interesting to compare the diffusion of lithium with the electrical conductance in molten  $\text{Li}_2\text{BeF}_4$ . Figure 2 shows that the diffusion coefficient from the measurement is about three times larger than that obtained from electrical conductance according to Nernst-Einstein relation (equation (4)). Though the differences are much larger than that in usual molten salts such as  $\text{NaCl}^{20)$ ,  $\text{NaF}^{18)$ , and so on, it is considered to be caused considerably to paired-vacancy diffusion which does not accompany charge transfer. In order to clarify this phenomenon in experiment, it will be necessary to decrease the concentration of single anion vacancies by doping with a divalent cation impurity proposed by Hj. Matzke<sup>17)</sup>.

According to Eyring, the pre-exponential factor  $D_0$  of Arrhenius-type equation is shown as follows:

$$D_0 = \lambda^2 e \frac{h}{kT} \exp \frac{\Delta S}{R} \quad (5)$$

where  $\lambda$  is the average jump distance,  $h$  Plank constant,  $k$  Boltzmann constant,  $T$  absolute temperature  $R$  gas constant,  $\Delta S$  the change of entropy. Table 1 shows  $\Delta S$  of various ions in molten salts and silicates<sup>24)</sup>. The values of  $\Delta S$  in most molten salts (except  $\text{Li}_2\text{BeF}_4$ ) are minus. The absolute values are small except the molten  $\text{NaF-AlF}_3$  which forms the complex anions. However  $\Delta S$  in molten  $\text{Li}_2\text{BeF}_4$  seems to be rather analogous to those in molten silicates. In molten  $\text{Li}_2\text{BeF}_4$   $\Delta S_{\text{Li}}$  is nearly zero and  $\Delta S_{\text{F}}$  is positive large value. It seems that this fact corresponds to nearly zero  $\Delta S$  of alkaline cation and large  $\Delta S$  of oxygen ion in molten silicates.

In previous paper, it was reported that the behaviour of oxygen in molten silicates is qualitatively similar to our results of fluorine in molten fluoroberyllate. However, in order to discuss more precisely the relations between various constituent ions of molten fluoroberyllate and molten silicate, it will be necessary to obtain the self-diffusion coefficients of other ions.

Table 1 Comparison of entropy changes for various molten salts and molten silicates

| sample   | cation                               |                 |                 |                  |                  |                  |                  |                  | anion                      |                |                            |                 | reference      |
|--|--------------------------------------|-----------------|-----------------|------------------|------------------|------------------|------------------|------------------|----------------------------|----------------|----------------------------|-----------------|----------------|
|  | alkaline                             | Ag <sup>+</sup> | Tl <sup>+</sup> | Zn <sup>++</sup> | Pb <sup>++</sup> | Ca <sup>++</sup> | Al <sup>3+</sup> | Si <sup>4+</sup> | Cl <sup>-</sup>            | I <sup>-</sup> | F <sup>-</sup>             | O <sup>--</sup> |                |
| NaF<br>KF  | - 4.33<br>- 5.79                     |                 |                 |                  |                  |                  |                  |                  |                            |                |                            |                 | 18             |
| 0.865NaF-0.135AlF <sub>3</sub><br>0.750NaF-0.250AlF <sub>3</sub><br>0.625NaF-0.375AlF <sub>3</sub>   | - 3.89<br>-10.37<br>-11.22           |                 |                 |                  |                  |                  |                  |                  |                            |                | - 2.50<br>-11.64<br>-13.32 |                 | 19             |
| NaCl<br>RbCl<br>CsCl<br>NaI  | - 3.86<br>- 5.93<br>- 6.93<br>- 6.90 |                 |                 |                  |                  |                  |                  |                  | - 6.51<br>- 7.52<br>- 6.60 |                |                            | -10.8           | 20             |
| ZnBr <sub>2</sub>  |                                      |                 |                 | - 8.89           |                  |                  |                  |                  |                            |                |                            |                 | 21             |
| PbCl <sub>2</sub><br>TlCl  |                                      |                 | - 3.14          |                  | - 6.13           |                  |                  |                  | - 6.19<br>- 3.75           |                |                            |                 | 22             |
| NaNO <sub>3</sub><br>KNO <sub>3</sub><br>RbNO <sub>3</sub><br>CsNO <sub>3</sub><br>AgNO <sub>3</sub> | - 4.53<br>- 5.56<br>- 6.40<br>- 6.89 |                 |                 |                  |                  |                  |                  |                  |                            |                |                            | - 6.75          | 23             |
| Li <sub>2</sub> BeF <sub>4</sub><br>LiBeF <sub>3</sub>   | - 0.16                               |                 |                 |                  |                  |                  |                  |                  |                            |                | +24.5<br>+27.8             |                 | our<br>results |
| silicates  | 0                                    |                 |                 |                  |                  | +10              | +20              | +25              |                            |                |                            | +35             | 24             |

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