Self-diffusion of Na$^+$ and K$^+$ in their Molten Fluorides

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Self-diffusion coefficients of ^{22}Na$^+$ in molten NaF, and ^{42}K$^+$ in molten KF have been measured at various temperatures employing a capillary technique. The diffusion coefficients were found to obey the relations:

$$D_{Na^+} = (3.08 \pm 0.06) \times 10^{-3} \exp[(-8700 \pm 600)/RT]$$
$$D_{K^+} = (2.46 \pm 0.06) \times 10^{-3} \exp[(-7500 \pm 600)/RT]$$

As a result of information obtained in recent years concerning the structure and mechanism of motion in molten salts, interest in their transport properties (including self-diffusion data) has increased extensively. Developments in this field have been the subject of fairly recent review articles.[1,2]

The present paper deals with the cation self-diffusion coefficients of molten sodium and potassium fluoride, for which there are no data available in the literature.

The experimental methods applicable to the study of diffusion processes in molten salts do not differ in principle from the methods employed for aqueous solutions. However, special precautions have to be taken due to the corrosive nature of molten fluorides. A review of experimental techniques employed in molten salts has been given by Yang and Simnad.[3] The method best suited for the present purpose was found to be the "diffusion-into-the-capillaries" method employed by Bockris and Hooper[4] and others. The advantage of this method is that it avoids the necessity of filling the capillaries in a second vacuum furnace.

EXPERIMENTAL

Apparatus. A schematic diagram of the diffusion cell is shown in Fig. 1. The diffusion cell consisted of a fairly large platinum crucible (A), containing the molten salt, into which a platinum holder (B) with 4 platinum capillaries (C) (inner diameter 0.1 mm, length 30 mm) could be lowered. The capillary holder could be rotated around its vertical axis by a shaft (D) attached to a stirrer motor. The cell assembly was inserted into a ceramic radiation shield which was positioned into a Kanthal, resistance-heated, vertical tube furnace of standard design.[5] The furnace could be operated up to 1200°C. By means
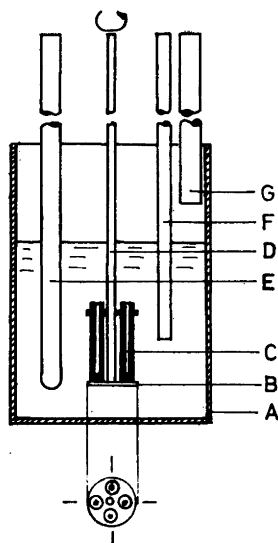
Fig. 1. A: Pt crucible. B: Pt capillary holder. C: Pt capillaries. D: Rotating shaft connected to stirrer motor. E: Platinum sheath for housing Pt/Pt10Rh thermocouple. F: Pt tube for bubbling argon. G: Sintered alumina tube for adding radioactive salt pellets.

of a sensitive, two-position potentiometric controller actuated by a Pt/Pt10Rh thermocouple, the temperature could be kept constant within $\pm$ 0.3°C. The temperature was measured with another Pt/Pt10Rh thermocouple enclosed in a platinum protection tube (E) which dipped into the molten salt. Purified argon was bubbled into the melt through a platinum bubbler tube (F). It was possible to move both the thermocouple and the Pt bubbler tube vertically during a run by means of precision bore teflon slipjoints located on top of the furnace. Thus the temperature distribution along the capillaries could be measured. It was possible to obtain a vacuum of 3 to 5 mm of Hg inside the furnace tube.

Chemicals. The sodium and potassium fluorides were procured from Merck AG (Darmstadt, Germany) and British Drug Houses Ltd. (Poole, England), respectively, and were analytical grade reagents (purity ≥ 99 %). They were pre-dried for 24 h at 150°C and then melted either under vacuum or in an argon atmosphere.

The radioactive isotopes ^{22}Na^{+} and ^{42}K^{+} which were used as tracers were obtained in the form of aqueous chloride solutions from the Norwegian Institute for Atomic Energy. These were converted to the solid fluoride pellets by a previously described method.[4,6]

Procedure. The capillaries were filled with non-active salt by submerging them in the liquid salt under vacuum, and then slowly increasing the pressure in the furnace by introducing argon.[4] After raising the capillaries approximately 10 cm above the melt surface, a known amount of radioactive pellets was added directly into the crucible through the tube (G) (see Fig. 1) by means of a spoon device located on the top of the furnace. The temperature then was raised 5°C and argon permitted to pass through the melt for 20 min to homogenize it. Then the capillaries were lowered again into the melt where they remained for 2−3 h. Since the salt in the bath had been heated 5°C above the temperature at which the capillaries had been filled, immersion of the capillaries into the warmer bath caused the escape of a small quantity of non-active salt from the top of the capillaries into the bath, thus minimizing the non-diffusive transfer of radioactivity into the capillaries at the start of the experiment.

After the time permitted for diffusion, the holder and capillaries were raised from the melt, up through a hole in the ceramic radiation shields, to the top of the furnace, where they were allowed to cool without opening the furnace chamber to the air. The long distance (about 35 cm) between the radioactive bath and the capillaries prevented the transport of radioactivity *via* the vapor phase while the furnace was cooling.

When cooled, the capillaries were moved from the furnace, and the salt on their outside was washed off. The salt inside the capillaries was analyzed for radioactivity by extracting with water, and the amount of ^{22}Na and ^{42}K, respectively, that had diffused into the capillaries was determined by analyzing the γ-radiation (in each capillary). A Frieseke and Hoepfner, type FH 90, scintillation counter and a scaler was employed for this purpose. Two samples of the reservoir salt were also weighed and analyzed.

RESULTS

From the total radioactivity of the diffusate, Q (in cpm), found by experiment, the diffusion coefficient, D (cm^2 sec^{-1}), may be calculated from the equation

$$Q = 2c_0 A \sqrt{Dt/\pi} \qquad (1)$$

where c_0 is the concentration of the radioactive species in the bulk of the salt (cpm cm^{-3}); A, the cross-sectional area of the capillary (cm^2); and t, the time of the experimental run (in seconds).

The results calculated from this equation must, however, be corrected for the so-called "Δl-effect". If the capillaries are stationary during the experimental run, the melt at the capillary mouth may be depleted of radioactive salt, which leads to an observed D smaller than the actual one. To avoid this, the capillaries are slowly rotated during the experiment. However, this rotation results in some of the liquid in the capillary being drown out by the liquid sweeping across its mouth and replaced by the surrounding liquid. This gives a positive error in the D values and is termed the "Δl-effect". A "Δl-effect" correction term has been given by Nanis, Richards and Bockris.[7]

$$Q = Ac_0[\Delta l + 2\sqrt{Dt/\pi}\,] \qquad (2)$$

Here

$$\frac{\Delta l}{d} = \left[\frac{N_{Re}}{20}\right]^{1/4} \qquad (3)$$

for N_{Re} (the Reynolds number) >20, N_{Re} being given by

$$N_{Re} = \frac{2\pi R \omega \varrho d}{60\,\eta} \qquad (4)$$

where d is the inner capillary diameter (cm); R, the radius of rotation of the capillaries (cm); ω, the rotation rate (rpm); ϱ, the density (g cm^{-3}); and η, the viscosity of the liquid (g cm^{-1} sec^{-1}). In these experiments the rate of stirring was maintained at 25 rpm.[7]

The results reported in this paper have also been corrected for the thermal expansion of the platinum capillaries.

In order to test the method and the apparatus, the diffusion of ^{22}Na$^+$ in molten NaNO$_3$ was studied prior to the measurements in the molten fluoride. The results are compared with values found by other workers using different methods [8-10] in Table 1. Table 2 gives values for the diffusion coefficients of

Table 1. Self-diffusion coefficient (D_+) of $^{22}Na^+$ in molten $NaNO_3$.

$T(°C)$	$D \times 10^5$ cm^2 sec^{-1}			
	This work	Dworkin et al.[8]	Angell et al.[9]	Spedding et al.[10]
328	1.96 1.89	2.00	1.97	
348	1.90 2.19 2.16	2.29	2.25	
368	2.20			2.62 2.64

Table 2. Self-diffusion coefficient (D_+) in molten fluorides.

D ($^{22}Na^+$) in NaF(liq.)		D ($^{42}K^+$) in KF(liq.)	
$T(°C)$	$D \times 10^4$ (cm^2 sec^{-1})	$T(°C)$	$D \times 10^4$ (cm^2 sec^{-1})
1022	1.03	870	0.93
1030	1.08	894	1.01
1045	1.10	902	1.02
1052	1.14	903	1.03
1069	1.19	928	1.11
1081	1.16	942	1.07
1102	1.24	962	1.15
1117	1.27	980	1.26
1120	1.28	994	1.29
1132	1.36	1017	1.37

$^{22}Na^+$ and $^{42}K^+$ in NaF and KF, respectively, as found in the present investigation. Each value reported is the mean value obtained from analysis of the four capillaries. A plot of log D *versus* the reciprocal absolute temperature (Fig. 2) appears to be fairly linear. Hence, the diffusion coefficients may be expressed by an equation of the form

$$D = D_0 \, \exp(-E_D/RT) \tag{5}$$

where D_0 is the pre-exponential factor and E_D the energy of activation expressed in cal/mole. These are temperature-independent constants. The numerical values of D_0 and E_D have been obtained from the experimental data by the method of least squares. The results are

$$D_{Na^+} = (3.08 \pm 0.06) \times 10^{-3} \exp[(-8700 \pm 600)/RT] \tag{6}$$

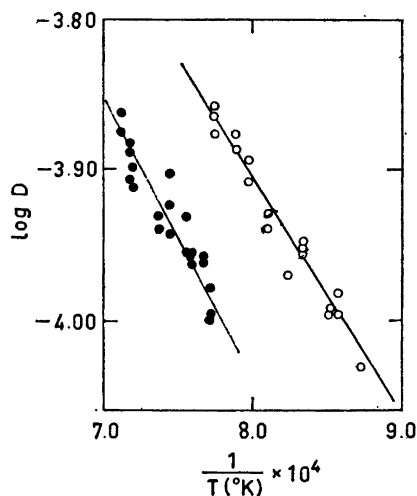$$D_{K^+} = (2.46 \pm 0.05) \times 10^{-3} \exp[(-7500 \pm 600)/RT] \tag{7}$$

Fig. 2. Log $D^{22}\text{Na}^+$ in molten NaF and log $D^{42}\text{K}^+$ in molten KF, versus reciprocal asbolute temperature, ● for Na^+, ○ for K^+.

DISCUSSION

From the various theoretical models of the structures of molten salts it is possible to predict numerical values for the constants D_0 and E_D.

A discussion of this has been published by Bockris and coworkers.[4,6,11] Their self-diffusion results in molten alkali halides and in the group II salts, have been explained in terms of a Fürth hole theory.[12] According to Fürth, the energy of activation for diffusion is given by

$$E_D = 3.74 \; RT_m - \tfrac{1}{2} RT + RT^2 \left(\alpha + \frac{1}{\sigma} \frac{d\sigma}{dT} \right) \qquad (8)$$

where T_m is the melting point temperature (°K); α, the expansion coefficient (cm deg⁻¹); and σ, the surface tension of the molten salt (dyne cm⁻¹). It can be seen that the last two terms of eqn. (8) approximately compensate for one another, and the equation reduces to

$$E_D = 3.74 \; RT_m \qquad (9)$$

Table 3 shows that the values of E_D calculated for NaF and KF are in good agreement with the experimentally observed values.

Table 3. Activation energy of diffusion of cations in pure molten fluorides.

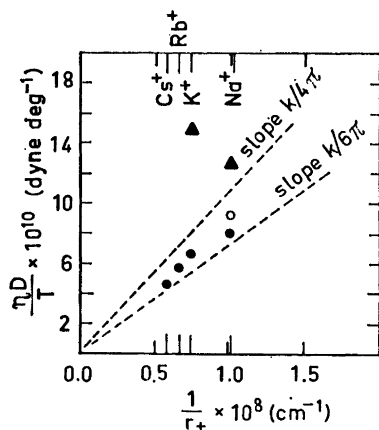| Salt	E_D (hole theory) kcal/mole	E_D (this work) kcal/mole
NaF	9.4	8.7 ± 0.6
KF	8.4	7.4 ± 0.6

Fig. 3. Applicability of Stokes-Einstein equation to the cations in molten alkali halides. Slope $k/4\pi$ corresponds to modified S.E. equation as given by Li and Change.[13]

● Na⁺, K⁺, Rb⁺, Cs⁺ in their molten chlorides.[4,11]
O Na⁺ in molten iodide.[4]
▲ Na⁺, K⁺ in their molten fluorides (our data).

The two classical equations treating transport processes, namely the Stokes-Einstein equation and the Nernst-Einstein equation, have been applied to molten salts by different authors.[2] The former equation is based on the assumption that the velocity of a diffusing ion is determined by the balance between the driving force for diffusion and the frictional resistance against the remaining ions. Assuming then that the frictional resistance can be described as viscous drag, the Stokes-Einstein equation is obtained

$$D = \frac{kT}{6\pi r\eta} \tag{10}$$

where r is the radius of the diffusing ion (cm), and η is the viscosity of the liquid (g cm⁻¹ sec⁻¹).

Fig. 3 shows $\eta D/T$ plotted against the reciprocal cation radii for several alkali halides at the temperature $\theta = T/T_m = 1.1$. The viscosity data for NaF of Vetyukov[14] and data published by Seiko[15] for molten KF, have been used. The data are compared with the regular form of the Stokes-Einstein equation (eqn. 10) and a modified S.E. equation given by Li and Chang,[13] which has a slope of $k/4\pi$. It can be seen from the figure that molten NaF and KF deviate more from the behavior predicted according to eqn. (10) than do the alkali chlorides and sodium iodide.

The Nernst-Einstein equation may be written in the form

$$\lambda = \frac{F^2}{RT}(D_+ + D_-) \tag{11}$$

where λ is the electric conductivity (cm² ohm⁻¹); D_+ and D_-, self-diffusion coefficients of the cation and the anion, respectively, and F, the Faraday constant. The applicability of this equation could not be tested in the present case, as we still lack anion self-diffusion coefficients for molten alkali fluorides. However, using data for the transport number of Na⁺ in molten NaF recently obtained in our laboratory,[16] the Nernst-Einstein parameter for cationic

transport, RTu_+/FD_+ (u_+ denoting the cationic mobility), has been calculated and found to be less than unity. This indicates that the Nernst-Einstein equation is not applicable in the present case. The general explanation of this is that not all ionic movement which contributes to mass transport also contributes to charge transport, and various mechanisms of conduction may be suggested. A detailed discussion will have to be deferred until anion self-diffusion coefficients have also been measured.

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