Da der Elektronenaustritt nicht scharf an der Ionisationsschwelle J_c einsetzt, wurde J_c hier durch Extrapolation des steilen Kurvenastes bis zur Abszissenachse gewonnen. Auf der Willkür dieser Bestimmungsmethode beruht hauptsächlich die Unsicherheit der J_c-Werte, die in der Tabelle 1 für eine Reihe der von uns untersuchten Substanzen zusammengefaßt sind. Die zum Vergleich angegebenen Literaturwerte, die mit der üblichen Methode erhalten wurden, zeigen recht gute Übereinstimmung mit unseren Werten. Dieses neue Verfahren hat aber den Vorzug wesentlich größerer Einfachheit und Bequemlichkeit.

Wir sind Herrn Prof. H. Straubel für seine freundliche Beratung beim Aufbau der Apparatur sehr zu Dank verpflichtet.

Stoff	Photo-Ionisationsschwelle [eV] Literaturwert [5]	hier gemessener Wert
Pyren	5,81	5,78 ± 0,07
Perylen	4,76 5,35	5,26 ± 0,07
1.2-Benzanthracen	5,68	5,63 ± 0,07
Rhodamin B	5,1	5,10 ± 0,07

Tab. 1. Mit der Lochblenden-Anordnung gemessene Photo-Ionisationsschwellen.

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Self-Diffusion in Molten Rubidium Nitrate

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The self-diffusion coefficient of the rubidium ion in molten rubidium nitrate has been measured with the porous-frit technique[1]. The result is well described with an Arrhenius equation

$$D_{\mathrm{Rb}} = 1.57 \times 10^{-3} \exp - \left(\frac{5670}{RT}\right) \qquad (318-499\,°\mathrm{C})$$

where D_{Rb} is expressed in $\mathrm{cm^2 s^{-1}}$, R in cal $\mathrm{mole^{-1} degree^{-1}}$, and T in degrees Kelvin. It is found that D_+ varies inversely with cation radius in all molten alkali nitrates. D_- has been calculated from the semi-empirical correlation equation between self-diffusion coefficients, equivalent conductivity, and external transport number in a pure molten salt developed by Laity[2]. D_- is within experimental accuracy equal to D_+ within the whole temperature interval.

The self-diffusion coefficient of the cation in molten rubidium nitrate has been measured with the porous-frit technique[1] in order to complete the picture of transport properties in molten alkali nitrates. With the exception of rubidium nitrate these liquids have been extensively studied and thus it has been possible to draw conclusions about the species present in these melts. The present investigation is also intended to test the applicability of a simple model which describes a melt as composed of three ionic species, one cation, one anion, and one tagged ion[3, 4].

Experimental

The experimental procedure has been described elsewhere in detail[5]. Its general features are as follows: A porous glass disc filled with a radioactive melt is suspended in a well-stirred inactive melt for a suitable time (of the order of 10 minutes). If a γ-active isotope is available the total radioactivity of the disc is measured with a scintillation counter before and after it has been immersed in the melt. The diffusion coefficient of the tagged ion can be calculated from these data, the immersion time, and the effective thickness of the disc (which has to be determined in a separate calibration experiment).

The experiments were not extended above 500 °C due to the onset of thermal decomposition of the melt. The experimental temperatures were measured with a calibrated thermocouple connected to a potentiometric bridge and they were kept constant within 1 °C with a temperature controller. The exchange of cations between the melt and the porous glass frit was investigated after each experiment but it was found to be insignificant below 500 °C.

Results and discussion

The results are given in Fig. 1 and they can be summarized in an Arrhenius equation obtained by least squares

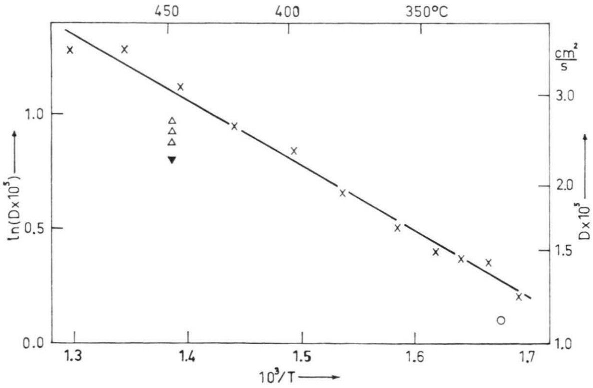

Fig. 1. D_{Rb} in molten $\mathrm{RbNO_3}$ according to the present investigation (×), Honig[7] (▼), Kwak[8] (△), and Forcheri et. al.[9] (○). The line corresponds to the equation $D_{\mathrm{Rb}} = 1.57 \times 10^{-3} \exp - (5670/RT)\ \mathrm{cm^2 s^{-1}}$.

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[1] C.-A. Sjöblom, Transport Studies in Molten Salts, Abstr. Goth. Diss. Sci. 8, 6 [1968].

[2] R. W. Laity, Disc. Faraday Soc. **32**, 172 [1962].

[3] A. Klemm, Z. Naturforsch. **15 a**, 173 [1960].

[4] R. W. Laity, J. Chem. Phys. **30**, 682 [1959].

[5] C.-A. Sjöblom and J. Andersson, Z. Naturforsch. **23 a**, 239 [1968].

[6] A. Hald, Statistical Theory with Engineering Applications. John Wiley & Sons, New York 1952, p. 522.

fitting[6] (the stated error is a standard deviation):

$$D_{\mathrm{Rb}} = 1.57 \times 10^{-3} \exp\left(-\frac{5670 \pm 300}{RT}\right); \quad (318-499\,°\mathrm{C}). \tag{1}$$

D is expressed in $\mathrm{cm}^2\mathrm{s}^{-1}$, R in cal $\mathrm{mole}^{-1}\mathrm{degree}^{-1}$, and T in degrees Kelvin. The standard deviation of the mean in D is 1.4% (a very low figure in self-diffusion measurements).

Some scattered results by HONIG[7], KWAK[8], and FORCHERI et al.[9] obtained with the paper-strip technique are also included in Fig. 1. These data fall almost 15% below the "least squares" line. The present data are considered to be more reliable since the paper-strip technique is less suitable for measurements of absolute diffusion mobilities[10].

The activation energies Q for self-diffusion of the cations in the molten alkali nitrates are so close to each other that they might be considered equal (in $\mathrm{LiNO_3}$ 5.49 kcal/mole, in $\mathrm{NaNO_3}$ 4.97 kcal/mole, in $\mathrm{KNO_3}$ 5.53 kcal/mole, in $\mathrm{RbNO_3}$ 5.67 kcal/mole, and in $\mathrm{CsNO_3}$ 5.61 kcal/mole[11]). The melting points of these salts range, on the other hand, from 264 °C ($\mathrm{LiNO_3}$) to 414 °C ($\mathrm{CsNO_3}$). Thus it is obvious that the prediction by the hole model[12] $Q = 3.74\ RT_{\mathrm{m}}$ (T_{m} = the melting temperature in °K) is incorrect even for a relatively simple class of melts such as the molten alkali nitrates.

DWORKIN et al.[11] have pointed out that the product $D_+ r_+$ (where r_+ is the Pauling radius of the cation) is constant in the molten alkali nitrates investigated by them. The present investigation shows that molten $\mathrm{RbNO_3}$ follows this statement (see Ref. 15, Table 2).

In order to be able to test the simple three-component model by KLEMM[3] for both ions it is necessary to know D_- also. This quantity has not yet been determined for $\mathrm{RbNO_3}$.

Salt	Temperature °C	$r_{++} \times 10^{-8}$ joule s $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$	$r_{--} \times 10^{-8}$ joule s $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$
$\mathrm{LiNO_3}$	280	0.48	11
	400	− 0.10 [a]	3.7 [a]
$\mathrm{NaNO_3}$	310	1.3	4.5
	380	0.74	2.9
$\mathrm{KNO_3}$	340	1.9	2.9
	380	1.4	2.2
$\mathrm{RbNO_3}$	320	0.62	0.62
	380	0.18	0.18
$\mathrm{CsNO_3}$	430	1.1	1.2
	480	0.80	0.74

Table 1. Cation-cation (r_{++}) and anion-anion(r_{--}) friction coefficients in pure molten nitrates. Self-diffusion data from Refs. 11 and 17, equivalent conductivity data from Ref. 13. [a] = D-value extrapolated, r_{++} uncertain.

Fortunately a very good estimate of D_- in $\mathrm{RbNO_3}$ can be obtained from the semi-empirical correlation equation derived by LAITY[2]:

$$D_- = D_+ - \frac{RT\Lambda}{F^2}(2t_+ - 1) \tag{2}$$

where t_+ is the external transport number of the cation, Λ is the equivalent conductivity of the salt, and F is the Faraday constant. Both t_+ and Λ have been measured[13]. According to the most recent investigation[7] $t_+ = 0.494 \pm 0.011$ and since t_+ in nitrates has been found to be essentially temperature independent D_- is within experimental error equal to D_+ in the whole investigated temperature interval. Thus an equation for D_- will be

$$D_- = 1.6 \times 10^{-3} \exp - \frac{5700}{RT}. \tag{3}$$

The accuracy of Eq. (3) relies upon the assumption that Eq. (2) is strictly applicable to molten nitrates. A reasonable check can be made by comparing for the other alkali nitrates experimentally observed D_- values to values calculated from Eq. (2). It is found that the calculated values are on the average 20% too low. On the other hand, the quotient D_+/D_- is in the middle of each investigated temperature interval for $\mathrm{LiNO_3}$ 2.7, for $\mathrm{NaNO_3}$ 1.5, for $\mathrm{KNO_3}$ 1.1, and for $\mathrm{CsNO_3}$ 1.0[14]. Since $\mathrm{RbNO_3}$ can be expected to fall between $\mathrm{KNO_3}$ and $\mathrm{CsNO_3}$ the prediction $D_- = D_+$ should be quite accurate.

The three-component model (one cation, one anion, and one tagged ion which can be either a cation or an anion) leads to the following expression for the cation-cation friction coefficient in an 1 : 1 salt

$$r_{++} = 2\left(\frac{RT}{D_+} - \frac{F^2}{\Lambda}\right), \tag{4}$$

and a corresponding equation with + replaced by − for the anion-anion friction coefficient. Values calculated according to these equations are given in Table 1. Since $D_+ = D_-$ it follows that $r_{++} = r_{--}$ in $\mathrm{RbNO_3}$. The table shows that in all alkali nitrates the interionic friction coefficients are positive and that they decrease when the temperature increases (this is to be expected since increased thermal vibration of the ions should lead to decreased interaction. A negative friction coefficient, on the other hand, indicates a cooperative motion of some of the species in the model.) Thus the present data give evidence that a simple three-component model is adequate for pure alkali nitrates. It has been shown previously[15] that such a model is able to describe dilute mixtures of $\mathrm{AgNO_3}$ with $\mathrm{LiNO_3}$, $\mathrm{NaNO_3}$, and $\mathrm{KNO_3}$[16].

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[17] This paper.