

# Gravimetric Interdiffusion Studies of the $\text{NaNO}_3$ – $\text{AgNO}_3$ and $\text{NaNO}_3$ – $\text{RbNO}_3$ Fused Salt Mixtures

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The interdiffusion coefficient has been measured over the whole range of compositions in the  $\text{NaNO}_3$ – $\text{AgNO}_3$  and  $\text{NaNO}_3$ – $\text{RbNO}_3$  molten salt mixtures, using an improved version of the gravimetric interdiffusion technique. At 340 °C the interdiffusion coefficient is about  $2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in mixtures with a high  $\text{NaNO}_3$  content. It increases slightly with increasing  $\text{AgNO}_3$  content and decreases with increasing  $\text{RbNO}_3$  content. Good agreement is found with data obtained with other methods. There is evidence that the interdiffusion coefficient is inversely proportional to the cation radii in the melt. Interionic friction coefficients are calculated. Only three ionic species are present in dilute solutions of  $\text{AgNO}_3$  and  $\text{RbNO}_3$  in  $\text{NaNO}_3$  but there is evidence of “complex ion formation” in dilute solutions of  $\text{NaNO}_3$  in  $\text{AgNO}_3$  and in  $\text{RbNO}_3$ .

The present investigation is a systematic study of the volume-fixed interdiffusion coefficient  $D_{12}^V$  (“the ordinary diffusion coefficient”), covering the whole concentration interval in the molten mixtures  $\text{NaNO}_3$ – $\text{AgNO}_3$  and  $\text{NaNO}_3$ – $\text{RbNO}_3$ . An improved version of the gravimetric technique<sup>1–3</sup> was chosen. In its original form it has been tested in molten salts with limited success<sup>3</sup> but the present modification (quartz glass frits instead of Pyrex frits, visual control of frit and its suspension during experiments) offers a very promising approach, its simplicity being an additional attractive feature. In “dilute solutions” of each component into the other the present gravimetric data can be checked against results obtained with other methods such as an optical technique<sup>4, 5</sup>, a constant mass diffusion cell<sup>6</sup>, chronopotentiometric techniques<sup>7, 8</sup>, the porous-frit technique<sup>9</sup>, and paper strip techniques<sup>10, 11</sup>. Since no independent data concerning  $D_{\text{Na}}$  in molten  $\text{AgNO}_3$  and  $\text{RbNO}_3$  and  $R_{\text{Rb}}$  in molten  $\text{NaNO}_3$  were available they were measured at tracer concentra-

tions in the present work with the porous-frit technique also. The agreement between the gravimetrically obtained interdiffusion coefficients and all these other results is quite good despite the widely different experimental methods.

In “dilute solutions” the observed ordinary diffusion coefficient  $D_{12}^V$  approaches the thermodynamic interdiffusion coefficient  $D_{12}'^{12, 13}$  as related to the gradient of activities, and information about the interionic friction coefficients may be obtained. Systematic variations with composition in  $D_{12}^V$  and the effective activation energy  $Q$  can be used to discuss the existence of aggregates of ions moving past each other<sup>9</sup>.

Moreover, the hole theory of liquids<sup>14, 15</sup> predicts a linear relationship between  $Q$  and the melting temperature  $T_m$ ; thus systems where  $T_m$  changes appreciably with composition can be used to check this aspect of the model (which at least in this respect has turned out to be unsuccessful in most pure molten salts<sup>16</sup>).

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## Experimental

Reagent grade  $\text{AgNO}_3$  and  $\text{NaNO}_3$  were obtained from Riedel de Haen A.G., Seelze-Hannover, and E. Merck A.G., Darmstadt, Germany, respectively. Purum grade  $\text{RbNO}_3$  (purity better than 98%) was obtained from E. Merck A.G. Prior to use the salts were dried in a drying oven at  $120^\circ\text{C}$  for more than 50 hours.

The gravimetric interdiffusion technique has been described in detail elsewhere<sup>2, 3, 17</sup>. Its general features are as follows: A fritted quartz glass disc<sup>18</sup> filled with a molten salt mixture is suspended from an analytical balance (Mettler H-18 GD). If the frit is immersed into a melt of different composition an interdiffusion will take place. During this process the buoyancy (and thus the reading on the balance) changes with time. It has been shown<sup>19, 20</sup> that in the final stage of the diffusion process a plot of the logarithm of the apparent frit weight versus time gives a straight line with a slope  $S$  proportional to the (volume-fixed) interdiffusion coefficient in the salt mixture *outside* the frit. After calibration of the frit with a 0.5 M KCl solution in the frit diffusing out into 0.075 M KCl solution (within this interval  $D_{12}^f$  is essentially constant) the proportionality constant to be used in the plot can be calculated from the formula

$$k = D_{\text{cal}}/S_{\text{cal}}$$

where  $D_{\text{cal}} = 1.853 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (the interdiffusion coefficient in 0.075 M KCl solution at  $25^\circ\text{C}$ <sup>21</sup>) and  $S_{\text{cal}}$  = The slope obtained in the plot over the calibration run.

The molten salt experiments were performed in an electrical furnace with a transparent lid made from Pyrex glass. Through this lid the frit suspension (a fine platinum wire) could be inspected for the absence of salt crystallization on the wire since this effect could cause erroneous balance readings.

The heating current was fed through a voltage stabilizer. In this way the temperature was kept constant to better than  $1^\circ\text{C}$  during a run (about 2 hours). The temperature was measured with a Platinum<sup>22</sup> thermocouple connected to a potentiometric bridge (Croydon type P 3). The experiments were performed at temperatures up to only  $70^\circ\text{C}$  above the melting points in order to reduce the thermal decomposition of the nitrates. These precautions were necessary since a whole series of runs (including cell filling) at only one set of melt compositions took over two weeks.

Tracer diffusion of sodium ions in pure molten  $\text{AgNO}_3$  and  $\text{RbNO}_3$  and of rubidium ions in molten  $\text{NaNO}_3$  was studied in the present work with the porous-frit technique<sup>23</sup>. Radioactive isotopes,  $\text{Na}^{22}$  and  $\text{Rb}^{86}$ , were obtained from N. E. N., Boston, Mass. USA.

In the previous tests of the gravimetric interdiffusion technique in molten salt work the porous discs were made of Pyrex instead of quartz glass. Later studies have shown<sup>9, 24</sup> that a rapid ion exchange takes place when a borosilicate glass is immersed into a melt containing alkali (particularly sodium) ions. Thus in addition to the "intended" interdiffusion between the two salt volumes there will be another diffusion across the glass-melt interface. Both effects are included into the weight change recorded by the balance<sup>25</sup>. The possibility of sodium and rubidium ions crossing Pyrex-melt and quartz-melt interfaces was investigated in connection with the present determinations of  $D_{\text{Na}}$  in  $\text{AgNO}_3$  and  $\text{RbNO}_3$  and of  $D_{\text{Rb}}$  in  $\text{NaNO}_3$  with the porous-frit technique. Diffusion of sodium ions into quartz and of rubidium ions into Pyrex glass was negligible (no traces of radioactive ions could be found inside the frit material) while on the other hand the diffusion of sodium into Pyrex glass was *greater* than the diffusion into the surrounding melt<sup>25</sup>. Using porous quartz glass discs constitutes an important improvement in the present version of the gravimetric interdiffusion technique.

The concentration difference between the two different salt mixtures in an interdiffusion run was 10 mole% in the  $\text{NaNO}_3$ – $\text{AgNO}_3$  series and 20 mole% in the  $\text{NaNO}_3$ – $\text{RbNO}_3$  series (cf. Tables 2 and 3). This choice may be made at will since the observed diffusion coefficient applies to the melt composition *outside* the frit<sup>20</sup>. The choice is made on the basis of experimental considerations differing from one salt system to another: Since recording of the weight changes of the frit during the diffusion process involves a slight vertical displacement it was found that a minimum initial weight difference was necessary in order to overcome some irregular pulling at the disc suspension wire due to the surface tension of the melt. While in  $\text{NaNO}_3$ – $\text{AgNO}_3$  a 10 mole% span was found quite adequate, a 20 mole% span was settled upon for  $\text{NaNO}_3$ – $\text{RbNO}_3$  after considerable testing. Runs with a greater span than 20 mole% showed evidence of a bulk flow of salt between the frit and the outside bath (the semi-logplot of weight versus time is curved). In mixtures with low  $\text{RbNO}_3$  concentration a 10 mole%

<sup>17</sup> C.-A. SJÖBLOM, Transport Properties in Molten Salts, Abstr. Goth. Diss. Sci. **8**, 8 [1968].

<sup>18</sup> Made by Westdeutsche Quarz-Schmelze GmbH, Geesthacht, West Germany.

<sup>19</sup> F. GRÜN and C. BLATTER, J. Amer. Chem. Soc. **80**, 3838 [1958].

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<sup>22</sup> Obtained from Baker Platinum Division, Engelhard Industries Ltd., Sutton, England.

<sup>23</sup> C.-A. SJÖBLOM and J. ANDERSSON, Z. Naturforsch. **23 a**, 239 [1968].

<sup>24</sup> C.-A. SJÖBLOM and J. ANDERSSON, Z. Naturforsch. **21 a**, 274 [1966].

<sup>25</sup> The diffusion coefficient of a monovalent cation entering Pyrex glass at these temperatures is of the order of  $10^{-11} \text{ cm}^2 \text{ s}^{-1}$  but due to the large glass-melt interface a significant ion exchange would take place during the time of a gravimetric interdiffusion run. If porous discs made of quartz are used this ion exchange is insignificant.

difference can be successfully used but in mixtures with high  $\text{RbNO}_3$  content the scatter of the results becomes excessive.

Maintaining a constant concentration outside the disc during the diffusion process is an important experimental problem which is usually solved with some kind of stirring. In the previous version<sup>3</sup> the stirring was accomplished by oscillating the disc vertically causing a salt flow of about 1 mm/s past the disc faces. Although this flow is considered adequate, in the present work the flow was increased to 10 mm/s by application of a small radial temperature difference across the melt container<sup>26</sup>.

As mentioned above, in the porous-frit experiments with  $\text{Na}^{22}$  as tracer quartz glass frits had to be used. Quartz frits have a smaller structural strength than Pyrex frits thus repeated melting and solidification of a salt inside a quartz cell might affect the cell constant (the effective length). In the present case our tests showed changes up to 10% and data obtained with the porous-frit method show a greater spread when quartz is used instead of borosilicate glass as frit material. (This effect may vary with the kind of melt investigated.)

## Results

Calibration data for the quartz discs used in the interdiffusion experiments are given in Table 1. Great care is needed in order to obtain a reliable

Cell no.	$-S_{\text{cal}} \times 10^2$ ( $\text{min}^{-1}$ )	$k \times 10^3$ ( $\text{cm}^2 \text{min s}^{-1}$ )	Average deviation (%)
1	3.07	0.602	2
2	2.99	0.618	2
3	3.00	0.616	4
4	3.72	0.497	3
5	3.05	0.606	3
6	2.61	0.708	4
7	2.92	0.632	2

Table 1. Calibration results for the quartz glass discs used in the gravimetric interdiffusion experiments. Temperature of calibration 25.0 °C.

calibration since the weight changes when a cell is filled with 0.5 M KCl are very minute (the total change is about 5 mg, to be compared with the reproducibility of the balance 0.1 mg). This problem does not appear in the molten salt runs where the total weight change is of the order of 50 mg.

The observed (volume-fixed) interdiffusion coefficients obtained with the gravimetric technique

are given in Table 2 and Table 3 for the systems  $\text{NaNO}_3$ – $\text{AgNO}_3$  and  $\text{NaNO}_3$ – $\text{RbNO}_3$  respectively. The corresponding tracer diffusion coefficients ( $D_{\text{Na}}$  in  $\text{AgNO}_3$ ,  $D_{\text{Rb}}$  in  $\text{NaNO}_3$ , and  $D_{\text{Na}}$  in  $\text{RbNO}_3$ ) obtained in porous-frit measurements appear in Table 4. The data have been “least-squares” fitted<sup>27</sup> to Arrhenius equations and the constants are found in Table 5 together with their standard deviations. The standard deviations of (a single measurement of)  $D_{12}^V$  range from 2 to 8% and their value at a given concentration can be found in Figs. 1 and 2.

$D_{12}^V$  versus compositions is plotted in Figs. 1 and 2 for  $\text{NaNO}_3$ – $\text{AgNO}_3$  and  $\text{NaNO}_3$ – $\text{RbNO}_3$  respectively. For a comparison, independent data according to other investigators<sup>7–14</sup> and the tracer diffusion data from the present work are also shown. The scatter around 50 mole-%  $\text{AgNO}_3$  in Fig. 1 is ascribed to calibration differences. Figures 1 and 2

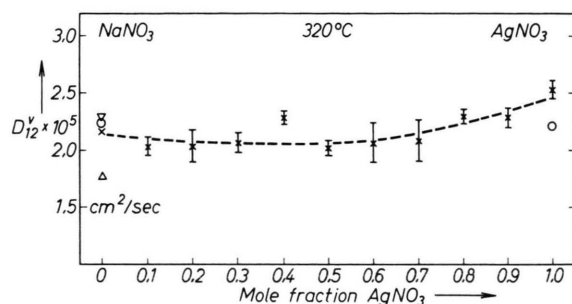


Fig. 1. The volume-fixed interdiffusion coefficient  $D_{12}^V$  at 320 °C in the  $\text{NaNO}_3$ – $\text{AgNO}_3$  mixture. The indicated errors are standard deviations.  $\times$ : present gravimetric results,  $\circ$ : present tracer results.  $\nabla$ : independent data by GUSTAFSSON et al.<sup>4</sup> ( $\nabla$ ) and by BOWCOTT and PLUNKETT<sup>8</sup> ( $\triangle$ ) are also given.

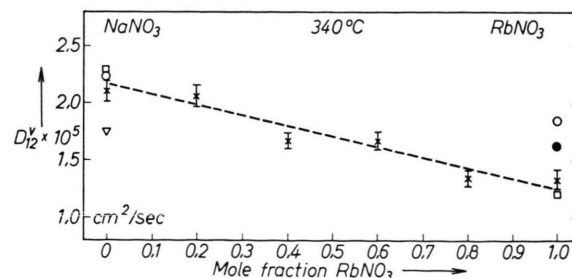


Fig. 2. The volume-fixed interdiffusion coefficient  $D_{12}^V$  at 340 °C in the  $\text{NaNO}_3$ – $\text{RbNO}_3$  mixture. The indicated errors are standard deviations.  $\times$ : present gravimetric results,  $\circ$ : present tracer results.  $\nabla$ : independent data by GUSTAFSSON et al.<sup>5</sup> ( $\nabla$ ), HONIG<sup>10</sup> ( $\square$ ) (extrapolated), and KWAK<sup>11</sup> ( $\bullet$ ).

<sup>26</sup> Temperature gradient 0.5 °C/cm.

<sup>27</sup> A. HALD, Statistical Theory with Engineering Applications, John Wiley & Sons, New York 1952, p. 522.

Mole% AgNO <sub>3</sub>		0	10		20		30				
Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )
1	318	1.99	1	317	2.00	1	312	1.98	1	312	2.04
1	318	2.11	1	318	1.93	1	314	1.88	1	314	1.99
1	333	2.21	1	333	2.02	1	331	2.16	1	331	2.12
1	333	2.26	1	333	2.12	1	332	2.13	1	332	2.09
1	333	2.31	1	350	2.26	1	350	2.24	1	351	2.57
1	353	2.48	1	352	2.14	1	350	2.72	1	352	2.47
1	353	2.65	1	353	1.99	1	352	2.34			
			1	353	2.11	1	352	2.43			
			1	353	2.20						

Mole% AgNO <sub>3</sub>		40	50		60		70				
Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )
2	283	2.00	2	283	1.64	3	271	1.82	3	271	1.67
2	283	2.01	2	284	1.68	3	271	1.95	3	272	1.70
2	301	2.07	2	300	1.83	3	272	1.83	3	296	2.20
2	301	2.20	2	300	1.88	3	296	1.83	3	297	2.23
2	301	2.23	2	333	2.17	3	296	2.06	4	298	2.20
2	335	2.34	2	334	2.11	3	297	2.01	3	329	2.17
2	335	2.48				4	298	2.01	3	329	2.25
1	353	2.49				3	329	1.81	2	330	1.96
1	353	2.55				2	329	2.53	2	330	2.00
						3	330	1.87	2	330	2.02
						2	330	1.96			
						2	330	2.25			
						2	330	2.26			
						2	331	2.18			

Mole% AgNO <sub>3</sub>		80	90		100			
Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )
5	269	1.99	4	258	1.96	4	259	1.92
5	270	2.07	4	259	1.95	4	259	2.02
5	302	2.14	5	269	1.94	4	289	2.23
5	304	2.11	5	272	1.87	4	289	2.28
5	330	2.26	4	288	2.11	4	323	2.50
5	331	2.38	4	289	2.28	4	323	2.61
			4	290	2.17			
			5	303	2.12			
			5	303	2.15			
			4	322	2.33			
			4	323	2.22			
			5	330	2.36			
			5	331	2.36			

Table 2. Volume-fixed interdiffusion coefficients  $D_{12}^V$  in the NaNO<sub>3</sub>–AgNO<sub>3</sub> mixtures obtained with the gravimetric technique. For frit calibration data see Table 1.

Table 2. Volume-fixed interdiffusion coefficients  $D_{12}^V$  in the NaNO<sub>3</sub>–AgNO<sub>3</sub> mixture obtained with the gravimetric technique. For frit calibration data see Table 1.

show good agreement between the results by different workers where a comparison is possible. However, since at intermediate compositions no data are available for a comparison it might be advisable to make a conservative estimate of the accuracy of the present data. Thus the error in  $D_{12}^V$  is estimated to be less than 10% in the NaNO<sub>3</sub>–AgNO<sub>3</sub> results and less than 15% in the NaNO<sub>3</sub>–RbNO<sub>3</sub> results (the reason for this difference will be discussed be-

low). The activation energy  $Q$  calculated from the NaNO<sub>3</sub>–AgNO<sub>3</sub> data is plotted versus composition in Fig. 3 together with the quantity  $3.74 RT_m$  originating from the hole theory<sup>14, 15</sup>.

### Discussion

Previously the gravimetric technique had shown a tendency to give low results<sup>4, 9</sup> but the present



Mole% RbNO <sub>3</sub>		0		20		40		$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )
Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	
6	322	1.92	6	322	1.90	6	323	1.44
6	323	1.95	6	323	1.95	6	328	1.57
6	338	1.94	6	338	2.03	6	338	1.60
6	341	2.04	6	341	2.08	6	340	1.73
6	359	2.35	7	358	2.32	6	357	1.76
7	360	2.47	6	360	2.24	7	360	1.79
6	362	2.19	7	360	2.41			
			6	362	2.15			

Mole% RbNO <sub>3</sub>		60		80		100		$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )
Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	$D_{12}^V \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	Cell no.	Temp. (°C)	
6	323	1.42	6	316	1.18	6	317	1.25
6	329	1.49	6	316	1.19	6	318	1.28
6	339	1.61	6	329	1.27	6	330	1.39
6	340	1.75	6	330	1.27	6	331	1.35
6	357	1.89	6	349	1.44	6	351	1.33
7	360	2.01	6	352	1.48	6	351	1.37

Table 3. Volume-fixed interdiffusion coefficients  $D_{12}^V$  in the NaNO<sub>3</sub>—AgNO<sub>3</sub> mixture obtained with the gravimetric technique. For frit calibration data see Table 1.

Na/AgNO <sub>3</sub>		Tracer/solvent Rb/NaNO <sub>3</sub>		Na/RbNO <sub>3</sub>		Mole%		AgNO <sub>3</sub>		RbNO <sub>3</sub>	
Temp.	$D_{tr} \times 10^5$	Temp.	$D_{tr} \times 10^5$	Temp.	$D_{tr} \times 10^1$			$D_0 \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	$Q \pm \Delta Q$ (cal equiv. <sup>-1</sup> )	$D_0 \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	$Q \pm \Delta Q$ (cal equiv. <sup>-1</sup> )
225	0.87	320	1.77	333	1.84	0 <sub>tr</sub>	223	5430 ± 620		68	4150 ± 1500
235	1.17	320	2.24	352	1.91	0	111	4710 ± 660		50	3860 ± 950
250	1.27	341	2.36	370	2.17	10	8.1	1640 ± 710			
267	1.49	345	2.28			20	81	4350 ± 1030		33.0	3370 ± 660
281	1.83	364	2.45			30	72	4190 ± 840			
305	1.92	364	2.64			40	15.3	2230 ± 240		39.2	3860 ± 820
326	2.29					50	34.6	3350 ± 270			
354	2.66					60	6.6	1370 ± 670		430	6770 ± 710
						70	8.7	1680 ± 860			
						80	7.4	1390 ± 310		52	4460 ± 210
						90	10.0	1740 ± 270			
						100	22.3	2560 ± 250		3.8	1270 ± 760
						100 <sub>tr</sub>	150	4970 ± 400		(27.5)	(3280)

Table 4. Tracer diffusion coefficients of Na<sup>22</sup> in pure AgNO<sub>3</sub> and RbNO<sub>3</sub> and of Rb<sup>86</sup> in pure NaNO<sub>3</sub> obtained with the porous-frit technique. The values in column 6 (Na/RbNO<sub>3</sub>) are averages obtained at each temperature.

Table 4. Tracer diffusion coefficients of Na<sup>22</sup> in pure AgNO<sub>3</sub> and RbNO<sub>3</sub> and of Rb<sup>86</sup> in pure NaNO<sub>3</sub> obtained with the porous-frit technique. The values in column 6 (Na/RbNO<sub>3</sub>) are averages obtained at each temperature.

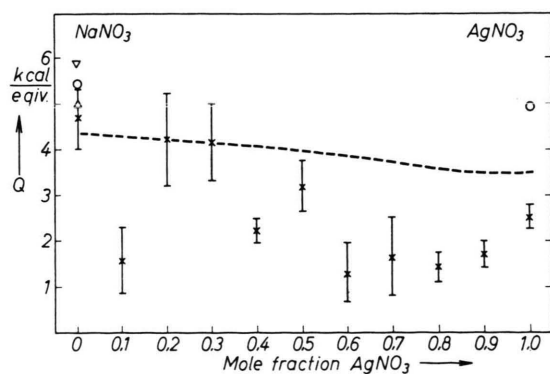


Table 5. Constants in the Arrhenius equations describing interdiffusion in the NaNO<sub>3</sub>—AgNO<sub>3</sub> and NaNO<sub>3</sub>—RbNO<sub>3</sub> molten salt mixtures. Subscript tr indicates that the data are obtained by tracer diffusion. The indicated errors are standard deviations calculated in the least squares fitting.

Fig. 3. The activation energy  $Q$  in the NaNO<sub>3</sub>—AgNO<sub>3</sub> mixture. The indicated errors are standard deviations.  $\times$ : present gravimetric results,  $\circ$ : present tracer results,  $\nabla$ : results by GUSTAFSSON et al.<sup>4</sup>,  $\triangle$ : by BOWCOTT and PUNKETT<sup>8</sup>. The dotted line is a plot of the relation  $Q = 3.74 R T_m$ .

data do not show any such trends and they are in good agreement with independent results by other workers<sup>4-11</sup> and also with the present tracer diffusion data. Figures 1 and 2 show smooth and indeed very reasonable changes in  $D_{12}^V$  with composition. Thus the present interdiffusion results can be considered accurate within the limits discussed above.

The interpretation of the experimentally obtained interdiffusion coefficients must be discussed in some detail. In the original paper by WALL et al.<sup>2</sup> the observed diffusion coefficient was regarded as an average value for the whole concentration interval between the original frit filling and the surrounding mixture. In a later paper WALL and WENDT<sup>20</sup> showed by numerical methods that for several different functional forms of the dependence  $D = D(c)$ ,  $c$  = concentration, the slope in the plot of weight versus time is in fact proportional to  $D_{12}^V$  in the mixture outside the frit. Their (mathematical) deduction reflects the (physical) fact that the average concentration inside the frit rapidly approaches the concentration on the outside. However, in mixtures where  $D$  varies strongly with  $c$  the part of the plot which (within experimental error) is considered linear might in effect correspond to an *average* of  $D$  taken over a part of the chosen concentration span. In the present investigation these spans were made as small as possible from an experimental viewpoint but the observed results must still be inspected for internal inconsistencies. Not even the 10 mole-% span used in the  $\text{NaNO}_3$ – $\text{AgNO}_3$  can be a priori considered "small" but Fig. 1 shows no indication that the values of  $D_{12}^V$  at the two ends of a span (for instance 90 and 100 mole-%  $\text{AgNO}_3$ ) would tend towards a common value. The picture for  $\text{NaNO}_3$ – $\text{RbNO}_3$  in Fig. 2 is different. The gravimetric inter-

diffusion coefficient are in good agreement with the independent data<sup>4, 5, 10, 11</sup> including the present tracer data. The gradual decrease in  $D_{12}^V$  with increasing  $\text{RbNO}_3$  content is quite reasonable and undoubtedly a physical reality. The experiments were performed across the concentration spans between 0 and 20, 40 and 60, 80 and 100 mole-%  $\text{RbNO}_3$  and there is a trend towards similar  $D$  values in each pair. Thus it is believed that the dotted line in Fig. 2 might better represent the actual change in  $D_{12}^V$  with  $c$ , and on these grounds the error in the  $\text{NaNO}_3$ – $\text{RbNO}_3$  data is estimated to (less than) 15% and in the  $\text{NaNO}_3$ – $\text{AgNO}_3$  data (less than) 10%.

Comparing Figs. 1 and 2 shows that  $D_{12}^V$  in "pure"  $\text{NaNO}_3$  is very similar in both systems but it increases with increasing  $\text{AgNO}_3$  content and decreases with increasing  $\text{RbNO}_3$  content. In Table 6 different pairs of solvent and solute salts are arranged in the order of increasing Pauling radius of the cation in the "solvent". SJÖBLOM and BEHN<sup>9</sup> have shown that in dilute solutions of  $\text{AgNO}_3$  in alkali nitrates  $D_{12}^V$  is inversely proportional to the cation radius of the solvent ( $\text{LiNO}_3$  as solvent forms an exception). Column 6 of Table 6 shows that the present results are consistent with their observation (the standard deviation of  $D_{12, \text{Ag}}^V$  is 15% but of  $D_{12, 1r_+}^V$  it is 11%). Moreover, column 7 shows that  $D_{12}^V$  varies inversely with the cation radius of the *solute* also: the standard deviation of  $D_{12}^V$  alone is 7.7%, it increases for  $D_{12, 1r_+}^V$  to 8.3% but it decreases for  $D_{12, 1r_+ 2r_+}^V$  to 5.6%.

The change in  $D_{12}^V$  with composition is slight in  $\text{NaNO}_3$ – $\text{AgNO}_3$  and somewhat more pronounced in  $\text{NaNO}_3$ – $\text{RbNO}_3$ . There are no sudden minima or maxima which might indicate a change in the nature of the diffusing species. On the other hand

Solvent	Solute	$D_{12}^V \times 10^5$ ( $\text{cm}^2 \text{s}^{-1}$ )	$1r_+$ (Å)	$2r_+$ (Å)	$D_{12, 1r_+}^V \times 10^{13}$ ( $\text{cm}^3 \text{s}^{-1}$ )	$D_{12, 1r_+ 2r_+}^V \times 10^{21}$ ( $\text{cm}^4 \text{s}^{-1}$ )
$\text{LiNO}_3$	$\text{AgNO}_3$	1.80	0.60	1.26	1.1	1.4
$\text{NaNO}_3$	$\text{AgNO}_3$	2.31	0.95	1.26	2.2	2.8
$\text{NaNO}_3$	$\text{RbNO}_3$	2.06	0.95	1.48	2.0	2.9
$\text{AgNO}_3$	$\text{NaNO}_3$	2.71	1.26	0.95	3.4	3.2
$\text{KNO}_3$	$\text{AgNO}_3$	1.95	1.33	1.26	2.6	3.3
$\text{RbNO}_3$	$\text{NaNO}_3$	1.61 <sup>a</sup>	1.48	0.95	2.4	2.3
$\text{RbNO}_3$	$\text{AgNO}_3$	1.72	1.48	1.26	2.5	3.2
$\text{CsNO}_3$	$\text{AgNO}_3$	1.70	1.69	1.26	2.9	3.6

Table 6. Test of the correlation between the ordinary diffusion coefficient  $D_{12}^V$  and the Pauling radii of the cations in the mixture. ( $\text{LiNO}_3$  data not included in the calculations of the standard deviations.)  $1r_+$  = the radius of the solvent cation,  $2r_+$  = the radius of the solute cation. <sup>a</sup> = a mean of the tracer and gravimetric value of  $D_{12}^V$ .

Figure 3 shows a drastic change in  $Q$  with  $c$  in  $\text{NaNO}_3 - \text{AgNO}_3$ . Since the investigated temperature interval is small the errors in the calculated  $Q$ 's might in some cases be higher than the  $\Delta Q$  obtained by least-squares fitting (Table 5). Nevertheless the negative deviation from additivity in  $Q$  versus  $c$  is undoubtedly correct. In models where the diffusing species perform "jumps"<sup>14, 15</sup> the activation energy  $Q$  (the Arrhenius coefficient) is a measure of the energy needed by a species for much a jump. Thus Fig. 3 shows that the resistance to motion on a molecular scale should be smallest towards the middle of the composition range in  $\text{NaNO}_3 - \text{AgNO}_3$ . This picture of the molten salt mixture can be further checked using the friction coefficient model by KLEMM<sup>28, 6</sup>. In this model the interionic friction can be calculated. In order to perform these calculations for a binary salt mixture a detailed information about the thermodynamic properties is needed (in particular the single ion mobilities). This matter is further elaborated in Ref. 9. In Table 7 the

Solvent	Solute	Temp. (°C)	$r_{12} \times 10^{-8}$ (joule s cm <sup>-2</sup> equiv. <sup>-1</sup> )
$\text{NaNO}_3$	$\text{AgNO}_3$	300	1.1
		340	0.7
		320	2.5
$\text{NaNO}_3$	$\text{RbNO}_3$	360	2.2
		300	0.0
$\text{AgNO}_3$	$\text{NaNO}_3$	340	0.3
$\text{RbNO}_3$	$\text{NaNO}_3$	320	-0.5 <sup>a</sup>
		360	0.4 <sup>a</sup>

Table 7. Cation-cation friction coefficients  $r_{12}$  calculated according to the KLEMM model<sup>28, 6</sup>. Equivalent conductivity data from Ref. 29. <sup>a</sup> = a mean of the gravimetric and tracer  $D$  values has been used in this calculation.

cation-cation friction coefficient  $r_{12}$  is given for dilute solutions of  $\text{AgNO}_3$  and  $\text{RbNO}_3$  in  $\text{NaNO}_3$  and of  $\text{NaNO}_3$  in  $\text{AgNO}_3$  and  $\text{RbNO}_3$ . The behaviour of  $r_{12}$  is normal when  $\text{NaNO}_3$  is the solvent but it is abnormal when  $\text{NaNO}_3$  is the solute. Thus

it is found that a three component model is adequate for a description of  $\text{NaNO}_3 - \text{AgNO}_3$  and  $\text{NaNO}_3 - \text{RbNO}_3$  mixtures only when they have a high  $\text{NaNO}_3$  content. This result is consistent with the observations by SJÖBLOM and BEHN<sup>9</sup> of the interionic friction in dilute solutions of  $\text{AgNO}_3$  in alkali nitrates.

Fused salts with a high melting point  $T_m$  have in general a higher activation energy of diffusion than salts with a low melting point. On the basis of the "hole model" of liquids<sup>14</sup> BOCKRS et al. showed that a relation

$$Q = 3.74 R T_m \quad (2)$$

should hold within 10% for (self) diffusion in molten salts and they also produced several examples of this behaviour both in molten salts and other liquids. A later, more comprehensive investigation of molten salt self diffusion by SJÖBLOM<sup>16</sup> showed however that Eq. (2) is only qualitatively correct. A similar check can be made for the mixtures studied in the present paper. The dotted line in Fig. 3 is a plot of Eq. (2). Large deviations are found between the "predicted" and the observed values of  $Q$  in the case of  $\text{NaNO}_3 - \text{AgNO}_3$ . No graphical representation of Eq. (2) is shown for the  $\text{NaNO}_3 - \text{RbNO}_3$  mixtures since  $T_m$  is only known for the pure salts and the equimolar mixture. The agreement at these three compositions might, however, be considered acceptable but not good enough for any quantitative calculations.

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