Interdiffusion in Dilute Solutions of Silver Nitrate in Alkali Nitrates

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(Z. Naturforsch. **23 a**, 1774—1779 [1968]; received 4 August 1968)

The ordinary diffusion coefficients in dilute solutions of $AgNO_3$ molten in $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, and $CsNO_3$ have been measured with a porous frit technique. The results can be summarized in Arrhenius equations:

Solvent:

$LiNO_3$ $D^V_{12} = 7.00 \times 10^{-3} \exp\{-7270/R\,T\}$ (272 – 399 °C)
$NaNO_3$ $D^V_{12} = 2.23 \times 10^{-3} \exp\{-5430/R\,T\}$ (310 – 382 °C)
KNO_3 $D^V_{12} = 0.354 \times 10^{-3} \exp\{-3530/R\,T\}$ (337 – 386 °C)
$RbNO_3$ $D^V_{12} = 4.00 \times 10^{-3} \exp\{-6670/R\,T\}$ (317 – 384 °C)
$CsNO_3$ $D^V_{12} = 2.88 \times 10^{-5}$ (428 °C)

where D^V_{12} is expressed in $cm^2\,s^{-1}$, R in cal $mole^{-1}$ $degree^{-1}$, and T in degrees Kelvin. The results are in good agreement with chronopotentiometric data on the $AgNO_3-NaNO_3$ and $AgNO_3-CsNO_3$ systems [1] and also with some recent data on the $AgNO_3-NaNO_3$, $AgNO_3-KNO_3$, and $AgNO_3-RbNO_3$ systems obtained with an optical method [2]. Interionic friction coefficients are calculated. Only three ionic species are present in the $AgNO_3-LiNO_3$, $AgNO_3-NaNO_3$, and $AgNO_3-KNO_3$ mixtures while there is evidence of "complex ions" in $AgNO_3-RbNO_3$ and $AgNO_3-CsNO_3$.

It is necessary to perform six independent transport experiments in order to completely characterize transport in a binary mixture of two salts (for instance $AgNO_3-LiNO_3$). These experiments are: one of equivalent conductivity, one of transference numbers (of the cations with reference to the common anion), three of self-diffusion, and finally one of interdiffusion [3]. The experimental methods for the first five experiments are reasonably well investigated now although the obtained experimental accuracies may leave somewhat to be desired. On the other hand there is no reliable and generally accepted technique for interdiffusion measurements in molten salts. Some different approaches have, however, been tried such as the constant mass diffusion cell [4, 5], the gravimetric technique [6], and very recently an optical technique [2]. In very dilute solutions of the diffusing ion it is possible to use the chronopotentiometric method [7] and also the ordinary capillary reservoir technique (with radioactive tracers) [8] which is often used for self-diffusion measurements. Most of these methods have shortcomings which make them less suitable for general application: The chronopotentiometric and capillary reservoir techniques can only be used in dilute solutions, the constant mass diffusion cell can only be used in systems where the two compartments form a concentration cell with a stable (and well known) EMF which is used to follow the concentration changes during the diffusion, and the optical method can be used for transparent liquids only (it has been used in dilute solutions so far but it should be applicable to more concentrated solutions as well). The only method which at least in principle does not have any limitations of this kind is the gravimetric technique which, however, gives somewhat low results in the only system ($AgNO_3-NaNO_3$) where a comparison with other methods is possible. The available data are still too meager and unsystematic for a decisive evaluation of the relative merits of the different techniques. A particular method might also be unsuitable for a certain system while it can be used to good advantage in other systems. Thus the chronopotentiometric method has been widely adopted as an analytic tool and also as a method for interdiffusion measurements. Nevertheless Angell and Tomlinson [8]

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[1] C. E. Thalmayer, S. Bruckenstein, and D. M. Gruen, J. Inorg. Nucl. Chem. **26**, 347 [1964].

[2] S. E. Gustafsson, L. E. Wallin, and T. E. G. Arvidsson, Z. Naturforsch. **23 a**, in press.

[3] R. W. Laity, Ann. N. Y. Acad. Sci. **79**, 997 [1960].

[4] R. W. Laity and M. P. Miller, J. Phys. Chem. **68**, 2145 [1964].

[5] M. P. Miller, Application of the Diaphragm Cell Method to the Study of Diffusion in the $AgNO_3-NaNO_3$ Molten Salt System, Thesis, Princeton University N.J. USA 1962.

[6] C.-A. Sjöblom, Z. Naturforsch. **20 a**, 1572 [1965].

[7] B. R. Sundheim, Transport Properties of Liquid Electrolytes, a chapter in Fused Salts, ed. by. B. R. Sundheim, McGraw-Hill Book Co., New York 1964, p. 222 and 228.

[8] C. A. Angell and J. W. Tomlinson, Electrochemistry, Proc. 1st Austral. Conf., Pergamon Press, London 1964, p. 557.

have shown that the interdiffusion coefficient of cadmium in dilute solutions of cadmium chloride in the potassium chloride – lithium chloride eutetcic is 20 to 50% lower than the results previously obtained with chronopotentiometric and polarographic methods.

The present work is a systematic investigation of the interdiffusion coefficients in dilute solutions of silver nitrate in molten alkali nitrates, using a reliable and well-established experimental technique (the porous frit technique [9]). Thus these values can be used as a check on the different experimental techniques for interdiffusion studies of molten salt mixtures and since the necessary thermodynamic information is available they can also be used to provide more information about the interionic friction coefficients in these systems.

Experimental

Commercially available reagent grade salts were used after careful drying, first at 120 °C for 50 hours in a drying oven and then at 200 °C under a dry argon atmosphere. $AgNO_3$ and $LiNO_3$ were obtained from J. T. Baker Chemical Co., Philipsburg N. J., USA, $NaNO_3$, KNO_3, and $RbNO_3$ from E. Merck AG., Darmstadt, Germany, and $CsNO_3$ from Koch-Light Laboratories Ltd., Colnbrook, England.

The interdiffusion coefficients were determined with a porous-frit technique [9]. The experiments were performed in an argon-blanketed electrical furnace the temperature of which was kept constant to better than 1 °C with a temperature controller (West Gardsman JP). The temperature was measured with a calibrated Cr – Al thermocouple and recorded on a potentiometric recorder (Philips PR 2210/A21). A porous Pyrex glas frit [10] was filled inside the furnace with a melt consisting of 0.5 mole % silver nitrate dissolved in an alkali nitrate. After temperature equilibration the frit was immersed into a melt of the pure alkali nitrate for a suitable time (150 – 500 seconds). A radioactive tracer (Ag^{110m} obtained from N.E.N., Boston, Mass., USA) was used in order to determine the amount of silver in the melt inside the frit before and after the run. A flow of salt past the frit faces of 5 mm /sec was obtained by rotating the container with the pure alkali nitrate melt. The calibration of the frit and the radio-analysis procedure have been described in detail elsewhere [11] (the procedure for $PbBr^{82}$). Each frit was used only once since there was a diffusion of silver into the glass which had to be taken into account [12]. This immigration was determined after each run by measuring the radioactivity of the frit when the salt had been washed away with hot water and nitric acid. The scintillation counter was carefully corrected for drift between the different radioactivity measurements since the washing procedure took about 24 hours. New frits were inserted into the furnace through a port in the furnace lid. Thus up to 15 runs could be performed in rapid succession without allowing the furnace to cool down. A slight build-up of silver activity in the alkali nitrate melt occurs during such a series but it can be easily corrected for.

Results

The experimental results are shown in Figs. 1 – 4 and they can be summarized in Arrhenius equations obtained by least-squares fitting [13] of $\ln D$ versus $1/T$. It has been pointed out [2, 14] that this commonly used procedure might lead to incorrect values of the calculated constants due to improper weighting of the experimental points. This is an important effect if there exists a curvature in the $\ln D$ vs. $1/T$ plot [15] but in the present case the difference is negligible. The Arrhenius equations are:

$$AgNO_3 - LiNO_3: \quad D_{12}^V = 7.00 \times 10^{-3} \exp\left\{-\frac{7270 \pm 450}{RT}\right\} \quad (272 - 399\ °C)$$

$$AgNO_3 - NaNO_3: \quad D_{12}^V = 2.23 \times 10^{-3} \exp\left\{-\frac{5430 \pm 620}{RT}\right\} \quad (310 - 382\ °C)$$

$$AgNO_3 - KNO_3: \quad D_{12}^V = 0.354 \times 10^{-3} \exp\left\{-\frac{3530 \pm 1280}{RT}\right\} \quad (337 - 386\ °C)$$

$$AgNO_3 - RbNO_3: \quad D_{12}^V = 4.00 \times 10^{-3} \exp\left\{-\frac{6670 \pm 1270}{RT}\right\} \quad (317 - 384\ °C)$$

$$AgNO_3 - CsNO_3: \quad D_{12}^V = (2.88 \pm 0.13) \times 10^{-5} \quad (428\ °C)$$

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[9] C.-A. Sjöblom, Transport Properties in Molten Salts, Abstr. Goth. Diss. Sci. **8**, 6 [1968].

[10] Made by Sovirel SA, France. Diameter 20 mm, thickness 3 mm, porosity grade 4 (pore diameters 10–20 microns).

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

[12] C.-A. Sjöblom and J. Andersson, Z. Naturforsch. **21 a**, 274 [1966].

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

[14] A. G. Worthing and J. Geffner, Treatment of Experimental Data, John Wiley & Sons, New York 1943, p. 247.

[15] According to L. E. Wallin, Z. Naturforsch. **17 a**, 195 [1962] there exists a curvature in the plot of $\ln D$ vs. $1/T$ for molten $ZnBr_2$. Thus a conventional least-squares calculation according to Ref. [13] gives a value of 19 000 cal/mole for the activation energy while a properly weighted calculation according to Ref. [14] gives 15 600 cal/mole.

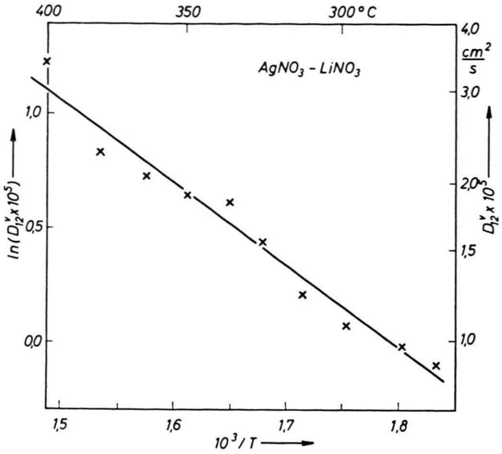

Fig. 1. The ordinary diffusion coefficient D_{12}^V in a solution of 0.5 mole % AgNO$_3$ in molten LiNO$_3$. The line corresponds to the quoted Arrhenius equation: $D_{12}^V = 7.00 \times 10^{-3} \exp(-7270/R\,T)$.

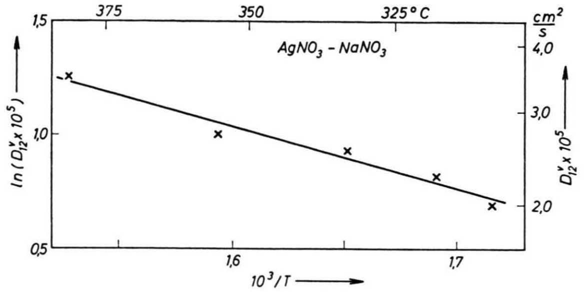

Fig. 2. The ordinary diffusion coefficient D_{12}^V in a solution of 0.5 mole % AgNO$_3$ in molten NaNO$_3$. The line corresponds to the quoted Arrhenius equation (the plotted points are means at each temperature): $D_{12}^V = 2.23 \times 10^{-3} \exp(-5430/R\,T)$.

D_{12}^V is expressed in cm^2 s^{-1}, R in cal mole^{-1} degree^{-1}, and T in degrees Kelvin. The stated errors are standard deviations. For D_{12}^V the standard deviation of the mean in the different solvents is: in LiNO$_3$ 2.2%, in NaNO$_3$ 1.7%, in KNO$_3$ 2.5%, in RbNO$_3$ 3.4%, and in CsNO$_3$ 4.5%. This increase in the standard deviations is due to an increase in the ion exchange between the silver and the glass frit.

The upper temperature limits of the measurements were chosen in order to avoid decomposition[16]. No attempt was made to determine the temperature dependence of D_{12}^V in AgNO$_3$ – CsNO$_3$ since a reasonable upper temperature limit for AgNO$_3$ is about 440 °C. (Cf. however Ref. [1] where nevertheless the measurements have been extended to 644 °C.)

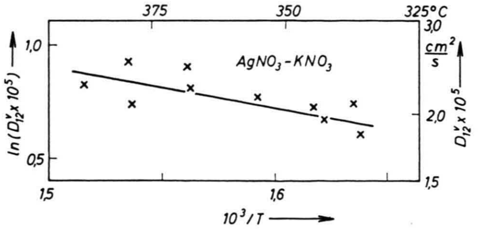

Fig. 3. The ordinary diffusion coefficient D_{12}^V in a solution of 0.5 mole % AgNO$_3$ in molten KNO$_3$. The line corresponds to the quoted Arrhenius equation: $D_{12}^V = 0.354 \times 10^{-3} \exp(-3530/R\,T)$.

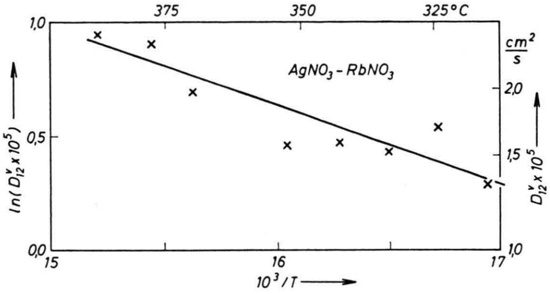

Fig. 4. The ordinary diffusion coefficient D_{12}^V in a solution of 0.5 mole % AgNO$_3$ in molten RbNO$_3$. The line corresponds to the quoted Arrhenius equation: $D_{12}^V = 4.00 \times 10^{-3} \exp(-6670/R\,T)$.

In the present investigation the experimentally obtained diffusion coefficient is the volume-fixed interdiffusion coefficient D_{12}^V which is often called the "ordinary" diffusion coefficient. Since the maximum concentration difference between the melts inside and outside the frit is 0.5 mole % the ordinary diffusion coefficient can be set equal to the thermodynamic mutual diffusion coefficient D'_{12} [17].

Discussion

The present results have been obtained with a method that has been shown to give reliable self-diffusion data [9]. Thus there is no reason to believe that the present results are affected by unknown systematic errors. A comparison with previous results is made in Table 1. For a meaningful comparison it is important to use the same reference frame for the interdiffusion coefficients. The diffusion coefficients

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[16] The temperature at which a molten salt decomposes is not well defined since it depends on thermodynamic equilibria between different (gaseous) reaction products. However, reasonable temperature limits are given in Handbook of Chemistry and Physics 46th ed., The Chemical Rubber Co., Cleveland, Ohio 1965, p. B-148 ff.

[17] R. W. LAITY, J. Phys. Chem. **63**, 80 [1959].

are concentration dependent and thus the comparison should be made as close to infinite dilution as possible in order to include the chronopotentiometric data. (LAITY and MCINTYRE[18] have shown that the chronopotentiometric diffusion coefficient is indeed equal to the ordinary diffusion coefficient at infinite dilution.) The error introduced by treating the data from the present investigation as infinite dilution values is negligible. The results by LAITY and MILLER[4,5] have been linearly extrapolated to zero $AgNO_3$ concentration. The reference frame used by GUSTAFSSON et al.[2] in their optical studies is not stated. This is a serious neglect in concentrated solutions but less so in dilute solutions (provided the variation in D with concentration is small) and the comparison in Table 1 shows also good agreement between their data and the rest.

Solvent	Temperature °C	$D^V_{12} \times 10^5$ $cm^2\,s^{-1}$	Reference
$NaNO_3$	310	2.05	19
	310	1.89	2
	310	1.93	1
	310	1.81	4
	321	1.30	6
KNO_3	360	2.13	19
	360	2.17	2
$RbNO_3$	360	1.98	19
	360	2.08	2
$CsNO_3$	428	2.88	19
	428	2.89	1

Table 1. A comparison between the ordinary diffusion coefficient D^V_{12} in dilute solutions of silver nitrate in alkali nitrates and previously published values.

The most extensive comparison can be made in $AgNO_3-NaNO_3$ where five different investigations have been made[1,2,4,6,19]. The agreement between the data obtained with porous frit, optical, and chronopotentiometric methods is excellent. The result according to the constant mass diffusion cell (at infinite dilution) is somewhat lower and that according to the gravimetric method lower still. This fact might at least in part be due to the fact that only these latter methods give a value corresponding to zero silver concentration while the others give an average value of D over a concentration interval. (D^V_{12} decreases when the concentration decreases[4].)

The reproducibility of the present investigation is comparable to that of the optical method (which is the most accurate so far) for $AgNO_3$ dissolved in $LiNO_3$ and $NaNO_3$ but not quite as good in KNO_3 and $RbNO_3$ due to the higher ion exchange between the frit and the melt.

The agreement between the present data on $AgNO_3$ dissolved in $NaNO_3$ and in $CsNO_3$ and the values by THALMAYER et al.[1] is also very good. Thus the experimentally obtained chronopotentiometric diffusion coefficients and the "ordinary" diffusion coefficients agree in these systems. LAITY and MCINTYRE[18] have shown that the ordinary diffusion coefficient, the self-diffusion coefficient of the "dilute" cation, and the chronopotentiometric diffusion coefficient have the same limiting value at infinite dilution. This conclusion is rigorously derived from the thermodynamic flow equations and an experimental result showing the opposite would only mean that an experimental error had been made somewhere[8]. Table 2 shows on the other hand that there is no similar agreement with the tracer diffusion coefficient of the alkali cation in the mixture. However, both D_{tracer} and D^V_{12} vary inversely with cationic radius (except in the case of $AgNO_3-LiNO_3$ where the radius difference is greatest).

Solvent	$D^V_{12} \times 10^5$ $cm^2\,s^{-1}$	$D_{\text{tr}} \times 10^5$ $cm^2\,s^{-1}$	$r_+ \times 10^7$ cm	$D^V_{12}\,r_+ \times 10^{12}$ $cm^3\,s^{-1}$	$D_{\text{tr}}\,r_+ \times 10^{12}$ $cm^3\,s^{-1}$
$LiNO_3$	2.18	3.17	0.60	1.31	1.90
$NaNO_3$	2.94	2.48	0.95	2.80	2.36
KNO_3	2.13	1.63	1.33	2.84	2.17
$RbNO_3$	1.98	1.58	1.48	2.94	2.34
$CsNO_3$	1.94[a]	1.31[a]	1.69	3.24	2.21

Table 2. A comparison between the ordinary diffusion coefficient D^V_{12} and the tracer diffusion coefficient D_{tr} of the alkali ion in pure alkali nitrate[20, 20a] at 360 °C. r_+ is the Pauling radius of the alkali cation[22]. [a] = extrapolated.

The activation energies for interdiffusion in the dilute solutions of silver nitrate in alkali nitrates tend to be somewhat higher than the activation energies for self-diffusion in the pure molten salts[20, 21] despite the fact that the activation energy for self-

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[18] R. W. LAITY and J. D. E. MCINTYRE, J. Am. Chem. Soc. **87**, 3806 [1965].

[19] This work.

[20] A. S. DWORKIN, R. B. ESCUE, and E. R. VAN ARTSDALEN, J. Phys. Chem. **64**, 872 [1960].

[20a] C.-A. SJÖBLOM and A. BEHN, Z. Naturforsch., to be published.

[21] $AgNO_3-KNO_3$ is apparently an exception to this rule but due to the very narrow temperature interval the activation energy in this system is uncertain. In fact, according to Ref.[2] thus value is about 7 kcal/mole which is in better agreement with the general pattern.

diffusion in molten silver nitrate is considerably lower than any of the others. The difference is greatest in the $AgNO_3-LiNO_3$ system and thus the increase can be attributed to a change in the polarisation energy of the anions when cations of different sizes are mixed. The increase is, on the other hand, comparatively small which shows that the interdiffusion takes place in an environment very similar to the pure alkali nitrates.

The diffusion of metal ions into the glass frit takes place by exchange with sodium ions[12] (Pyrex glass contains 4.15% Na_2O). The two cations present in the melt compete in this process but it is only the diffusion of silver ions that is detected by the radio-analysis of the frit. A high amount of silver activity in the glass means that a small amount of the competing cation has been able to immigrate. The amount of silver in the glass after the experiment increases in the order (of different solvents) $NaNO_3 < LiNO_3 < KNO_3 < RbNO_3 < CsNO_3$ (highest). Since the process depends on exchange with sodium ions in the glass it is natural that sodium ions in the melt should compete most successfully with the silver ions but apart from this fact it is found that a cation with a smaller radius enters the glass more easily than a cation with a larger radius[22].

Due to the small initial concentration of silver nitrate the experimentally obtained ordinary diffusion coefficient D_{12}^{V} is within experimental error equal to the thermodynamic mutual interdiffusion coefficient D_{12}'. Thus the interionic (cation-cation) friction coefficient r_{12} can be calculated from the relation[4, 5]

$$D_{12}'/R\,T = 2/(r_{12} + X_2\, r_{13} + X_1\, r_{23}) \qquad (1)$$

where X_1 and X_2 are the equivalent fractions of the two salts and r_{13} and r_{23} the friction coefficients between cations 1 and 2 and the common anion 3 (in this case a mixture of two 1 : 1 salts with a common anion is considered). Duke et al.[23] have shown that $r_{13} = r_{23}$ in the $AgNO_3-NaNO_3$ mixture which leads to a particularly simple expression for these friction coefficients[5]

$$\Lambda/F^2 = 2/r_{13} \quad (= 2/r_{23}) \qquad (2)$$

where Λ is the equivalent conductivity of the mixture and F is the Faraday constant. An expression for the cation-cation friction coefficient can be derived from Eqs. (1) and (2):

$$r_{12} = 2\,R\,T/D_{12}' - 2\,F^2/\Lambda\,. \qquad (3)$$

In the plug-fixed reference frame Na^+-ions and Ag^+-ions in the pure molten nitrates have essentially the same mobilities. Duke and Owens[24] have shown, however, that to a good approximation $r_{13} = r_{23}$ in the $AgNO_3-KNO_3$ mixture also despite the fact that the difference between the cation mobilities in the pure salts is considerably greater. Thus Eq. (3) can be applied to this mixture as well.

No transport numbers of the cations relative to the anion have yet been determined in the $AgNO_3-LiNO_3$, $AgNO_3-RbNO_3$, and $AgNO_3-CsNO_3$ systems. External transport number studies[25] show, however, that there is reason to believe that the deviation from "ideality" is not greater in these systems. Thus cation-cation friction coefficients calculated from Eq. (3) are given in Table 3 for all mixtures investigated in the present work.

Table 3 shows that both r_{12} (the cation-cation friction coefficient in the mixture) and r_{++} (the cation-cation friction coefficient in the pure alkali nitrate melt[26]) decrease with temperature. Thus the interaction between the cations decreases when the thermal vibrations increase. Negative values of r_{12}

Solvent	Temperature °C	$r_{12}\times10^{-8}$ joule s cm^{-2} $mole^{-1}$	$r_{++}\times10^{-8}$ joule s cm^{-2} $mole^{-1}$
$LiNO_3$	280	4.79	0.48
	400	0.76	−0.10
$NaNO_3$	310	0.50	1.27
	380	0.08	0.74
KNO_3	340	−0.15	1.92
	380	0.21	1.42
$RbNO_3$	320	−0.43	—
	380	−0.56	—
$CsNO_4$	428	−0.72	0.69

Table 3. Cation-cation friction coefficients (r_{12} in dilute solutions of silver nitrate in alkali nitrates, and r_{++} in pure molten alkali nitrates) calculated according to Eq. (3) at the two temperature extremes. Self-diffusion data from Ref. [20] and equivalent conductivity data from Ref. [27].

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[22] The Pauling radii of the cations are: for Li^+ 0.60 Å, for Na^+ 0.95 Å, for K^+ 1.33 Å, for Rb 1.48 Å, for Cs^+ 1.69 Å and for Ag^+ 1.26 Å.

[23] F. R. Duke, R. W. Laity, and B. Owens, J. Electrochem. Soc. **104**, 299 [1957].

[24] F. R. Duke and B. Owens, J. Electrochem. Soc. **105**, 476 [1958].

[25] A summary of external transport number data in pure molten salts is given in C.-A. Sjöblom and J. Andersson, Z. Naturforsch. **23 a**, 235 [1968].

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

[27] G. J. Janz, A. T. Ward, and R. D. Reeves, Molten salt data, U.S.—AFOSR No. 64-0039 [1964].

($AgNO_3$ dissolved in $RbNO_3$ and in $CsNO_3$) are generally interpreted as an indication of "complex ions" (which is another way of saying that a simple model with only three ionic species is inadequate). The small absolute value of r_{12} in the $AgNO_3-KNO_3$ mixture makes the experimental uncertainty more important. Thus the positive value at 380 °C indicates that also the value at 340 °C should be (small and) positive (since increased temperature should lead to increased "dissociation").

The present investigation shows that dissolving small amounts of silver nitrate in lithium, sodium, and potassium nitrates creates mixtures with a very simple structure (a melt consisting of only three ionic species) while there is evidence of "complex ions" when silver nitrate is dissolved in rubidium and cesium nitrates.

The authors are indebted to Dr. ARNOLD LUNDÉN for his kind interest in this work. It has been financially suported by Åke Wibergs Stiftelse.

The Temperature Dependence of the Isotope Effect for Electromigration of Potassium Ions in Molten Potassium Nitrate

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(Z. Naturforsch. **23 a**, 1779—1782 [1968]; received 8 August 1968)

The relative difference ($\Delta b/b$) between the electromigration mobilities of ^{39}K and ^{41}K in molten KNO_3 has been measured over the range 354° to 586 °C. The mass effect, $\mu=(\Delta b/b)/(\Delta m/m)$, becomes larger when the temperature is increased, following the relation

$$-\mu=0.0385+0.000124\ (t-337)$$

where t is the temperature in °C. Due to thermal decomposition, the nitrate is partly converted to nitrite, but it is proved by performing experiments with different initial concentrations of nitrite, that the isotope effect for potassium is not influenced noticeably by the concentration of the anions.

The experiment is designed to give an enrichment of the heavy isotope ^{41}K in a small anode compartment and in the upper part of the separation tube. However, it was possible to establish that a slight, but significant, enrichment of the light isotope ^{39}K was obtained in the lower part of the separation tube, i. e. just above the opening into the large cathode compartment. A separation factor of 1.003 was estimated for this enrichment effect, which is due to non-ideal conditions of the experiment.

13 years ago we reported that we had studied the isotope effect for electromigration of potassium ions in molten potassium nitrate[1], and similar measurements have been made recently by OKADA[2]. In recent years the temperature dependence of the isotope effect has achieved considerable interest[3], halides and sulfates being considered so far. As a first part of an investigation of the influence of temperature and concentration on isotope effects in molten nitrates, we can now report the results of experiments with pure KNO_3 as well as with mixtures of KNO_3 and KNO_2.

Experimental

The experimental arrangement is essentially the same as previously[1], i. e. a separation column (length 20 cm, inner diam. about 4 mm) separates a small compartment at the anode from a large compartment on the cathode side. To prevent liberation of alkali metal an excess of gas (either a mixture of NO_2 and O_2 or only NO_2, see discussion below) is bubbled through the aluminium cathode. The duration of the first experiments was 6 to 10 days, but due to increased accuracy of our mass spectrometer, it became possible to reduce the duration to 1 to 2 days. As usual, we worked with a very simple furnace made of two concentric glass tubes[4]. This arrangement allows us to observe the whole cell all the time, but a disadvantage is that considerable temperature differences are obtained in the furnace. For this reason we fitted three thermocouples onto the cell, sitting at the same height as the bottom, middle and top of the separation column.

In the chemical analysis of the samples we determined the total amount of anions, and the concentrations

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[1] A. LUNDÉN, C. REUTERSWÄRD, and N. SJÖBERG, Z. Naturforsch. **10 a**, 279 [1955].

[2] I. OKADA, Thesis, Tokyo 1966.

[3] A. KLEMM (Ed. W. SPINDEL), Advan. Chem. Ser. in press.

[4] A. LUNDÉN, Thesis, Göteborg 1956, p. 38.