Oxid	p(CO)	ΔE in eV
EuO Messung ×	1 at	0,68
EuO Messung ○	1 at	0,68
EuO Messung △	100 Torr	0,65
EuO Messung □	5 Torr	0,43
EuO — 3% Eu_2O_3	1 at	0,89

Tab. 3. Aktivierungsenergie ΔE in eV, gemessen an EuO im Temperaturbereich 300 °C bis 200 °C. Vergleiche hierzu die Abbildungen 1 und 2.

grenzen gedacht werden. An der Reinphase des EuO sowie an dem mit 3% Eu_2O_3 vermischten Monoxid wurde die Aktivierungsenergie im Bereich 300 °C bis 200 °C bestimmt und in Tab. 3 zusammengestellt.

Man erkennt hieraus, daß die durch Chemisorption der Donatoren $CO^{\cdot}$ hervorgerufene Verarmung der Randschicht an Ladungsträgern mit einer Zunahme der Aktivierungsenergie verbunden ist. Deshalb muß angenommen werden, daß die Werte der Aktivierungsenergie — besonders bei hohen CO-Drukken — vorwiegend die energetischen Verhältnisse in der Randschicht der Kristallite des EuO widerspiegeln. Der Wert, der dem homogenen Kristallinneren am nächsten kommt, dürfte bei der Messung unter $p(CO) = 5$ Torr gefunden werden.

Isotope Effects of Electromigration in Molten Lithium-Potassium Sulfate Mixtures

ARNOLD LUNDÉN and VLADISLAV LJUBIMOV *

Department of Physics, Chalmers Institute of Technology, Gothenburg, Sweden

(Z. Naturforsch. **23a**, 1558—1562 [1968]; received 25 June 1968)

The difference in mobility of the isotopes of lithium and potassium has been studied in molten sulfate mixtures over the concentration range 41 to 90 equiv. % Li_2SO_4. For the eutectic composition (80% Li_2SO_4) the temperature range 625 to 835 °C was covered. The mass effect, μ, (relative difference in mobility divided by relative difference in mass) was calculated. The accuracy, which is much lower for potassium than for lithium, was not sufficient to provide information on the temperature dependence of the mass effects, but it was evident that the ratio between the mass effects of the two cations depends upon concentration. Thus, while the mass effect for lithium is -0.13 ± 0.02 over the whole range, for potassium it is of the order of -0.16 for the eutectic concentration and -0.07 for the mixture with 41% Li_2So_4. The observed increase of the mass effect at low concentrations is in agreement with results for other systems and can be expected from simple models of the transport mechanism. For lithium the mass effect is the same in the molten sulfate mixtures as in pure fcc lithium sulfate.

We have recently described some electromigration experiments with solid and molten mixtures of lithium sulfate with silver sulfate or potassium sulfate[1]. Relative mobilities and transport numbers of the two cations were reported in this paper, called I, and we shall now discuss the isotope effects that were measured in the molten Li_2SO_4-K_2SO_4 mixtures. The heavy isotope of both cations was enriched on the anode side of the cell, see Fig. I:4 and I:5, which is in agreement with the isotope effects found in a large number of molten and solid salts.

The same symbols will be used as in I, i.e.
N = equivalents of salt, Q = total transported charge, Faradays, t = transport number, b = ion mobility.

The subscripts to the right 1, 2 and 3 denote Li, K and SO_4 ions, the superscript 0 marks the initial composition, and, in addition, the subscripts 1 and 2 to the left will indicate the light and heavy isotope of an element. We thus have, e.g. for the relative mobility of the two lithium isotopes[2]

$$\frac{\Delta b_1}{b_1} = \left(\frac{{}_1N_1}{{}_1N_1^0} - \frac{{}_2N_1}{{}_2N_1^0}\right) \cdot \frac{N_1}{t_1 Q} = \mu_1 \Delta m_1 / m_1 \qquad (1)$$

where $\Delta b_1 = {}_1b_1 - {}_2b_1$;

$$\Delta m_1 = {}_1m_1 - {}_2m_1 ; \quad m_1 = \tfrac{1}{2} ({}_1m_1 + {}_2m_1)$$

m = ion mass, μ = mass effect.

The salt samples to be analysed with our mass spectrometer were converted from sulfate to nitrate. As reported in paper I, the difference between the

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* Present address: Institute of Inorganic Chemistry, The Siberian Section of the Academy of Sciences, Novosibirsk, USSR.

[1] V. LJUBIMOV and A. LUNDÉN, Z. Naturforsch. **21a**, 1592 [1966].

[2] A. KLEMM, Molten Salt Chemistry (Ed. M. BLANDER), Interscience Publ. Inc., New York 1964, p. 535.

ionic mobilities of the two cations caused considerable changes in the chemical composition. This in turn meant that the samples analysed in the mass spectrometer differed very much in their melting points. For this reason it was for some samples difficult to measure the isotope abundances of both lithium and potassium. Of course, this difficulty could have been overcome by a chemical separation of the sample into a $LiNO_3$ and a KNO_3 fraction, which then could be analysed separately in the mass spectrometer. However, we desisted from this, partly because there is a risk that a slight isotope fractionation might occur during the chemical manipulations. For each experiment two or three independent series of mass analyses were performed, see Fig. I:4 and I:5, and the mass effect was evaluated separately for each series. The results are given in Table 1. The accuracy is much lower for K than for Li; this has to do both with the accuracy of the mass analyses and with the fact that the transport number t appears in the denominator of Eq. (1). Considering this latter contribution, it is obvious that errors in our transport number determination (paper I) are of greater importance for the mass effect of a diluted ion (K) than for an abundant ion (Li).

Due to the displacement of the two cations relative to each other, the concentration of K_2SO_4 increased in the upper part of the separation columns for exp. 51—60, cf. Table I:1 and Fig. I:4. Concentration changes of this kind can, in general, be expected to cause density changes, which, in turn, might give raise to convection. This ought not to be a serious problem in the present experiments, since the density at a given temperature is practically the same for all concentrations, e.g. at 750°C an estimation based on recent density measurements[3] gives a difference of 0.5% between the densities of mixtures with 80% and 50% Li_2SO_4. It might be worth mentioning that — in a cell-fixed coordinate system — the volume containing a constant amount (N_1 equivalents) of Li_2SO_4 increases, while that containing N_2 equivalents of K_2SO_4 decreases during an experiment (51—60 considered, the opposite occurs for 61). It is of interest in this connection to estimate the practical range of en-

Exp. no.	$100 \cdot c_1$ equiv. %	Temp. °C	$\frac{\Delta b}{b}$	Series of mass analyses		Range for calculated mass effects			Mass effect (best value)		Column length cm	Range of detected enrichment (cm)		
				Li	K	$-\mu_{Li}$	$-\mu_K$		$-\mu_{Li}$	$-\mu_K$		Li—K	$^6Li-^7Li$	$^{39}K-^{41}K$
51	89.6	685[a]	0.52	2	3	0.081—0.088	0.18 —0.25	(0.49)[e]	0.087	0.21	23	15	12	1.3
53	80.4	635[a]	0.56	2	2	0.073—0.081	—	(0.25)[e]	0.078	0.153	21	15	12	8.8
54	80.4	760[a]	0.80[b]	2	2	0.133—0.215	0.32 —0.75		0.169[b]	0.4[b]	21	—	—	—
55	81.0	625	0.69	2	2	0.106—0.124	0.115—0.153	(0.22)[e]	0.118	0.153	21	15	15	1.2
56	81.1	635	0.54	2	3	0.063—0.223	0.088—0.273		0.148	0.16	21	10	10	2.1
57	79.8	735	0.62	2	3	—	0.047—0.185		0.126	0.111	21	18	18	4.7
58	79.9	745	0.50[c]	2	3	—	—		0.075[c]	0.121[c]	20	14	10	6.3
59	79.9	835	0.59	2	2	0.141—0.168	0.230—0.315		0.155	0.272	20	19	18	12
60	59.8	735	0.15[d]	2	3	0.086—0.126	0.014—0.047		0.115[d]	0.031	21	21	21	5.4
61	40.8	745	— 0.20[c]	2	3	0.097—0.153	0.056—0.107		0.137[c, d]	0.074[c]	21	6	21	6.2

Table 1. Relative mobilities of the two cations ($\Delta b/b$), and mass effects for lithium (μ_{Li}) and potassium (μ_K) in molten sulfate mixtures.

[a] Large vertical temperature gradient,
[b] Pyrex in separation column,
[c] disturbance occurred during the experiment,
[d] Composition had changed in the whole column,
[e] calculated relative to a hump with enrichment of ^{39}K.

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[3] A. Kvist and K. Schroeder, Z. Naturforsch. **23a**, 676 [1968].

[4] A. Klemm, Z. Phys. **123**, 10 [1944].

richment, defined[4] as

$$x_{\max} = (\pi D_{\text{eff}} \tau)^{1/2}$$

where D_{eff} is the effective coefficient of diffusion, and τ is the duration. We have previously used this relation to estimate diffusion coefficients in i.a. molten lithium halides[5] and solid lithium sulfate[6] from a determination of the length of the separation column over which a change in composition can be detected. Of course this length depends on the accuracy of the analyses, and the concept of $x_{\max}$ thus is ambiguious, but we have estimated this entity for the separation of the two cations, as well as for the two isotope effects, see Table 1. With a couple of exceptions $x_{\max}$ (Li-K) is the same as $x_{\max}(6-7)$, while $x_{\max}(39-41)$ is much smaller. According to Eq. (2) the corresponding D_{eff} are of the order of 10^{-3} to 5×10^{-3} cm^2 s^{-1} for ^{6}Li—^{7}Li, which is much higher than what we found for the molten lithium halides: $(0.3-1.3) \times 10^{-3}$ cm^2 s^{-1}. This indicates that the efficiency of the separation columns was not as good in the present experiments with mixtures as in previous work with pure salts. In a few cases $x_{\max}$ approaches the column length, and we can then expect that the obtained values for $\Delta b/b$ and μ_{Li} are low. For ^{39}K — ^{41}K a calculation gives D_{eff} ranging from 10^{-5} to nearly 2×10^{-3}cm^{2}s^{-1}, but these results are to be considered as qualitative, only.

For at least three of the experiments (51, 53 and 55) an anomalous distribution of the K-isotopes was found. Thus after the first zone next to the anode with the expected enrichment of ^{41}K, there followed a zone where the light isotope ^{39}K was enriched, and then the rest of the column appeared to have the initial composition, cf. Fig. I : 4. As already stated above, the accuracy of the mass analysis is not as good as would be desired for the quantitative interpretation of the isotope effects for K, but the existence of an anomalous enrichment of ^{39}K is evident for three of the experiments, while it is not established for the experiments at temperatures above 700 °C. This anomaly in a mixture seems to be more difficult to interpret than the slight enrichment of the light isotope at the bottom of the separation column, which has been significantly established for pure $LiNO_3$ and KNO_3. This latter non-ideal behaviour of separation columns is discussed elsewhere[7]; concerning the anomaly reported now, we are currently investigating if it can be detected in other mixtures.

Run 54 differs from the other experiments in several aspects. While the other cells were made entirely of Supremax glass, this cell had its separation column packed with Pyrex glass. The temperature dependence of physical properties of glass is usually denoted by a number of temperatures, which are defined in a rather arbitrary way[8]. E. g. the annealing point, corresponding to a viscosity of $10^{13,0}$ poise, is 565 °C for Pyrex and 715 °C for Supremax[9]. Thus, for run 54 the Pyrex packing was used at about 200 °C above this temperature, while of the separation columns packed with Supremax glass, three (no 57, 58, 60) were run slightly above, and one (no 59) about 100° above the annealing point. The Pyrex powder used in run 54 was very strongly corroded, and the salt from the column, i.e. the water-soluble fraction[10], contained about 10% of oxide. In this run, and also in 51—53, the separation column was U-shaped, with the lowest point about 8 cm below the opening towards the large reservoir. (The columns used for 55—61 were designed as shown in Fig. I : 1). For run 54 strange distributions were obtained for the two cations as well as for the isotopes. Thus the highest concentration of K as well as enrichment of ^{7}Li were found at the bend of the column, instead of towards the anode. These strange distributions are probably due to the strong interaction between the Pyrex glass and the sulfate melt. Of importance is that the electrical conductivity of Pyrex is much higher (three orders of magnitude, or perhaps still more) than for Supremax at these high temperatures. This supports our view that ion migration through the Pyrex is by no means negligible in comparison with the transport in the melt. When migrating through the glass, the alkali ions are more "diluted" than when they are in the sulfate melt. It has been observed in different connections, see below and cit[11], that the isotope effect increases when an ion is diluted below a critical concentration. This fact might help to explain why the relative mobility of the two cations ($\Delta b/b$) as well as both isotope effects (the accuracy of the mass effect for potassium is, however, low) are higher for run 54 than for any of the other more normal experiments. The observations made for run 54 suggest that the packing of the column can have an influence on the separation effects, but a series of experiments would be required to establish under which conditions this might be the case.

As said above, two or three independent series of measurements of the isotope abundances were made for each run. Specially for K the calculation of the mass effect can be very sensitive to how the normal composition is evaluated. In order to study how the accuracy of the calculations is influenced by the

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[5] A. Lundén, S. Christofferson and A. Lodding, Chalmers Tekn. Högskol. Handl. No. 221, Göteborg 1959.

[6] A. Lundén, Z. Naturforsch. **17a**, 142 [1962].

[7] A. Lundén, submitted to Z. Naturforsch.

[8] Cf. e.g. G. W. Morey, The Properties of Glass, 2nd Ed., Am. Chem. Soc. Monograph Series No. 124, Reinhold Publ. Corp., New York 1954.

[9] Physikalische und chemische Eigenschaften technischer Gläser, Jenaer Glaswerk Schott & Gen. Mainz, 1959.

[10] Cf. A. Lundén, Chalmers Tekn. Högskol. Handl. No. 289, Göteborg 1964.

[11] A. Klemm, J. Chim. Phys. **60**, 237 [1963].

precision of the mass analysis as well as by the estimation of the normal composition, for each series of analyses we made several choices of which samples that should be considered as having the normal composition. On an average μ_K was computed 11 times and μ_{Li} 8 times for each experiment. The ranges within which the mass effects were obtained under reasonable assumptions are quoted in Table 1 for most of the experiments. For each series of analyses the mass effect based on the most plausible assumption regarding the normal composition was chosen, and the average of these μ-values was taken as the best value for the mass effect, see Table 1.

For some of the experiments the calculation of μ_K is complicated by the enrichment of ^{39}K that was detected in a part of the separation column. In the beginning of such an experiment the isotope composition certainly was the normal one along the whole column. If by some obscure mechanism, see discussion above, an enrichment of ^{39}K is gradually built up in part of the column at the same time as ^{41}K is enriched at the anode side due to the ordinary isotope effect, sooner or later an initial zone with normal composition situated between the two zones with opposite enrichments will disappear. From then on, the enrichment of ^{41}K will proceed with a new reference composition, which probably will be time-dependent. For three experiments we made a calculation of μ_K also under the extreme assumption that the hump with a high ^{39}K concentration should be considered as the reference. These μ_K-values are in parentheses in Table 1; for all other calculations the possible existence of a hump in the separation column is neglected.

Although the values for both mass effects spread considerably from experiment to experiment, it is possible to draw some conclusions. Six runs (53, 55—59) with an initial concentration of about 80% Li_2SO_4 covered the temperature range 625—835 °C. For neither element is the accuracy sufficient to provide evidence on the existence of a temperature dependence of the isotope effect, although, if we assign different weights to the runs (no 58 for which a disturbance occurred during the experiment, gives low results for $\Delta b/b$ as well as for both mass effects; μ_{Li} for no 53 falls far below the other values), there might be an indication that the mass effect for potassium increases with increasing temperatures, while μ_{Li} does not show any pronounced temperature dependence. Previous investigations of temperature dependences show that the cation mass effects of molten KCl, KNO_3 and LiCl increase strongly when the temperature is raised[12–14], while the μ_{Li} of solid Li_2SO_4 and molten $LiNO_3$ hardly are affected by the temperature[6, 13].

The average value of μ_{Li} for runs 55, 56, 57 and 59 is -0.137, while -0.139 was obtained as the average for 9 experiments with solid Li_2SO_4 in the range 600—790 °C. This good agreement might of course be fortuitous, but the closely related isotope effect for the electrical conductivity (pure $^6Li_2SO_4$ versus $^7Li_2SO_4$) was also found to be the same for the solid and liquid states[15]; neither is there any temperature dependence over the range 575—930 °C. These observations indicate that the mechanism for cation transport is similar in the two states. On the other hand the relative mobility of cations of two different elements (e.g. Li and K) changes at the melting point, cf I and cit[16].

The experiments cover the concentration range 41 to 90 equiv. % Li, i.e. Li^+ is the abundant ion in all experiments but one. The mass effect for this ion does not change significantly with concentration, but a concentration dependence is evident for K^+. There is thus a significant difference regarding μ_K between the experiments 51—59 where this ion was diluted and the experiments 60 and 61 where the concentrations of both cations were about the same. It has been observed in several systems, that the mass effect of an ion increases when its concentration is reduced below a certain limit. The first systematical investigation of this concentration effect was made by KLEMM and MONSE who studied μ_{Li} in the $LiCl-PbCl_2$ system[17], covering the range 5—100 equiv.% Li. When comparing their results and ours, there appears to be a difference in one aspect, namely regarding the range in which the mass effect depends on the concentration. Thus while their μ_{Li} was nearly constant over the range 20—100% Li, our μ_K at 20% K is at least twice as great as at higher concentrations. This difference might be due to the fact that they studied the mass effect of the lighter

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[12] S. JORDAN and A. KLEMM, Z. Naturforsch. **21a**, 1584 [1966].

[13] A. EKHED and A. LUNDÉN, unpublished.

[14] S. JORDAN, R. LENKE and A. KLEMM, Z. Naturforsch., in press.

[15] A. KVIST, Z. Naturforsch. **21a**, 487 [1966].

[16] Although there is reason to believe that there are significant differences between the mechanisms for electromigration and for diffusion, it might be of interest to note that it has been found also for thermal diffusion that the isotope effects have the same direction in all phases, while the relative displacement of two different cations might change its sign at the melting point, cf. A. LUNDÉN and J. E. OLSSON, Z. Naturforsch., in press.

[17] A. KLEMM and E. U. MONSE, Z. Naturforsch. **12a**, 319 [1957].

of the two cations in the mixture, while we are considering the heavy cation. The mass effect (in a good conductor, at least) is always less than the ideal value, $\mu = -0.5$, since ion motion in a condensed phase involves interaction between a number of particles. This is the common basis for the different models and theories which have been developed by KLEMM[11,12,17,18]. For our discussion it is sufficient to consider the simple model where the ions make two kinds of jumps in a quasilattice[18], viz. spontaneous and induced jumps. The number of the first type depends on the vibration frequency of the ion, i.e. on its mass, while the induced jumps are caused by processes in the surrounding of the ion, and their number is not depending on the mass of the isotope. We shall simplify the argument by considering only two-particle interaction. For a mixture of two cations (A^+, B^+) with a common anion (C^-) we can distinguish between three types of induced jumps for an A^+ ion, corresponding to A—A, A—B and A—C interaction. If n_s denotes the number of spontaneous, and n_i the number of induced jumps per unit time, the mass effect for ion A is thus proportional to $n_s/(n_s + n_i)$, where

$$n_i = n_{AA} + n_{AB} + n_{AC} \,. \tag{2}$$

E.g. the subscript AB corresponds to all interactions where a B^+ ion causes an A^+ ion to make a jump. Regarding the concentration dependence of the mass effect we can distinguish between several cases.

An extreme case is when cation-anion interaction dominates over cation-cation interaction, i.e. $n_i \simeq n_{AC}$. In this case both n_s and n_i are proportional to the concentration c_A, and the mass effect should thus be independent of c_A, loc. cit.[19]. If cation-anion interaction, and thus also n_{AC}, is negligible, the problem is reduced to an estimation of the relative importance of n_{AA} and n_{AB}. These terms depend not only on the concentration (being, at least as a first approximation, proportional to c_A^2 and $c_A c_B$, respectively) but also on other factors such as the masses m_A and m_B of the two ions. This latter fact is obvious if we consider a simple type of interaction, where a hole that has been created when a cation makes a spontaneous jump, is filled by a neighbouring cation which either is "dragged" or "pushed" into the hole. If the A^+ ions are diluted, the number of induced jumps due to A—A interaction is small, while the number of A—B interactions should depend on the ratio between the two masses m_A and m_B. If $m_A \ll m_B$ the probability of A—B induced A-jumps is likely to be relatively high, while it should be low if $m_A \gg m_B$. If we thus study the concentration dependence of both the cation mass effects (μ_A and μ_B) over the entire range it is probable that the mass effect of the light cation remains about the same over nearly the whole concentration range, while the heavy cation starts to show an increase in the mass effect already at a moderate dilution. Klemm and Monse measured the mass effect only for a very light cation, while we have done so for both cations. However, due to the high melting point of K_2SO_4-rich mixtures, we could not extend the present investigation to lower concentrations of Li than 40%. Due to their low melting points alkali nitrate systems seem to be the most suitable ones to check whether the concentration dependence of the mass effects is asymmetrical in the way we predict here.

This investigation is supported by "Statens naturvetenskapliga forskningsrad" and by "Statens rad för atomforskning". We are indebted to Mr. MANNE LÖVENBY for performing the analyses with the mass spectrometer. One of us (V. L.) acknowledges a scholarship from "Svenska institutet för kulturellt utbyte med utlandet".

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[18] A. KLEMM, E. LINDHOLM and A. LUNDÉN, Z. Naturforsch. **7a**, 560 [1952].

[19] The fact that we have a concentration dependence in the systems studied so far might thus be taken as evidence that cation-cation interaction always is of importance, in spite of the cations only being next-nearest neighbours. Since the anions often are of a much larger size than the cations, one could have expected a rather efficient screening. Further evidence of cation-cation interaction is given by the fact that the isotope effect for electrical conductivity is larger than for the electromigration studied in this investigation, cf. cit.[15].