Electromigration in Molten and Solid Binary Sulfate Mixtures: Relative Cation Mobilities and Transport Numbers

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The electrolytic displacement of the two cations relative to each other has been studied in solid (Li, Ag)SO₄ (93 eq. % Li) at 700 °C, solid (Li, K)₂SO₄ (91% Li) at 575 °C and molten (Li, K)₂SO₄ (41—90% Li). For melts containing more than about 52% Li the Li ions have a higher mobility (at about 740 °C) than the K ions, while the latter have the highest mobility in mixtures where K is the more abundant cation. The relative difference (Δb/b) between the mobilities of the two cations exceeds 15% already at concentrations some 8% off from the equimobility concentration. For the eutectic composition, 80% Li, Δb/b was about 60% independent of the temperature (590—835 °C). For mixtures containing 90% Li it was established that Δb/b changes its sign at the melting point. Thus, the mobility of the Li ion was of the order of half the mobility of the other ion in the solid systems, while it was about twice as large in the melt. The cation transport numbers (relative to the anion) were calculated for all experiments, and for the melts also the difference between the cation mobilities. An estimation is made of the obtainable accuracy of electromigration experiments.

The experiments with melts were analysed for isotope effects. The light isotopes were always enriched towards the cathode, independent of whether Li or K had the higher mobility. The magnitude of the isotope effects shows a concentration dependence, i.e. the mass effect (relative difference in mobility divided by relative difference in mass) tends to increase when an ion is dilute, as previously found for other systems. Thus for the melts with 80% Li, the mass effect is higher for K than for Li.

In recent years a number of electromigration experiments on binary mixtures of molten salts with a common anion (chloride, bromide or nitrate) have been reported 1. There is often a pronounced dependence of the ion mobilities on the composition of the mixtures. Thus, it has been found for several molten mixtures, that the cation having a high concentration is more mobile than the diluted one 3—6. On the other hand, according to Øye’s investigation of the high temperature modifications of the Li₂SO₄-Ag₂SO₄ system, transport number measurements show that the foreign ion has the greatest mobility in the χ-Li₂SO₄ as well as in the χ-Ag₂SO₄ structure 7. (The two cation mobilities are about the same in the intermediate bcc LiAgSO₄ structure.) We consider it of interest to study electromigration in both molten and solid sulfate mixtures as an extension of our experiments with pure solid lithium sulfate 8, 9. The following cells have been investigated:

+ Pt/(Li, Ag)₂SO₄/Li₂SO₄/Zn— (Iₕ)  
+ Pt/(Li, K)₂SO₄/Li₂SO₄/Zn— (IIₕ)  
+ Pt/(Li, K)₂SO₄/Zn— (IIIₕ) and (IIIₗ)

The subscripts s and l denote if the sulfate was solid or liquid.

Experimental

Analytical grade chemicals were used without further purification. The sulfate mixtures were prepared by melting the dried salts under a vacuum, whereupon the salt was solidified and stored as lumps. For the solid mixtures (runs 11—14) 18 the U-shaped Vycor glass apparatus and the electrode were essentially the same as used previously 8, 9. For cells Iₕ and IIₕ pure Li₂SO₄ was first melted in the bottom of the U-tube, and the

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1 A few binary mixtures with a common cation have also been studied. Nearly complete lists of references to older work have been published recently 8, 9.


6 E. P. Honig and J. A. A. KETELAAR, TRANS. Faraday Soc. 62, 190 [1966].


8 A. LUNDÉN, Z. Naturforschg. 17 a, 142 [1962].


10 In Table 1, the experiments with solid mixtures are numbered in sequence with the previous ten ones with pure Li₂SO₄ (l. c. 8, 9), while the experiments with melts start with no. 51.
temperature was decreased enough for the pure salt to solidify. Lumps of the mixture were then added and melted under a vacuum so that the narrow arm of the cell was filled to the desired height. The temperature was decreased below the solidification point of the mixture, and zinc metal was added to the wide tube. (The filling procedure was simpler in the experiment with the solid mixture in direct contact with the zinc: cell IIIa). The oven we used had a large vertical temperature gradient, which could be reduced considerably by placing the U-tube in a salt bath, see below. This was done for run 14. A common observation was that the anode moved much faster downwards than expected. While, when working with pure Li₂SO₄, this movement confirmed that the cation transport number was unity, the anode actually moved up to six times faster now, and it penetrated deep into the salt. Obviously, mixtures containing a few per cent of another cation are softer than the pure a-Li₂SO₄ (loc. cit. 11). Another similar observation was that the cathode zinc penetrated through the sulfate mixture of cell IIIa, while for pure Li₂SO₄, this does not happen until the temperature is at least 100 degrees higher than it was in run 13. After quenching, the salt column was divided into samples for chemical analysis. Ag was determined gravimetrically as AgCl and the alkali metals by flame spectrophotometry. Sulfate was precipitated as BaSO₄. Samples taken close to the zinc cathode were usually alcaline due to the formation of oxide at this electrode, and as an exception, a couple of samples from the anode side were slightly acid. The sums of the cations and of the anions were thus determined independently. They were in fair agreement with each other and with the total weight of the sample.

Since the anode had penetrated so deep into the salt that its upper tube of stainless steel had come into contact with the sulfate mixture, the salt sample that had been soaked off from the anode contained large amounts of iron and other corrosion products.

Another type of apparatus, made of Supremax glass, was used for the molten cell IIIa, see Fig. 1. Zinc metal and large lumps of the mixture were filled into the wide tube. The temperature was increased slowly until first the metal and then the salt melted. A reduced pressure was kept in the cell until gas bubbles ceased to evolve from the melt. The separation column, which is filled with Supremax powder of grain size DIN 24–30, was then lowered very slowly down into the melt. In order to fill the column completely with the melt, the whole apparatus was kept for a while under a vacuum. After atmospheric pressure had been restored, the platinum anode was inserted and the electrolysis could begin. A practical limit for the applied current was set by the fact that the sulfate melts showed a stronger tendency to foam at the anode than observed e.g. when nitrate melts are electrolysed. Just as for other melts, there was a tendency that the salt level sunk at the anode, and it was necessary to add more salt to the large volume during the run. A complication was that the melt became intransparent fairly soon, due both to corrosion of the glass and to the occurrence of cathode reaction products in the melt. After the end of the electrolysis the separation column was lifted up quickly from the wide tube, and after quenching, it was divided into samples for chemical analysis after the same lines as described above. In these samples also Mg was determined by an EDTA-titration. The concentration of this ion, up to about 10 eq. %, was correlated with the flow of the solid salt, A. LUNDÉN, B. JONSSON, and B. AUGUSTSSON, Z. Naturforsch. 21a, 593 [1966].

11 Work is in progress to study the rheological properties of sulfate mixtures. The addition of a few per cent of K₂SO₄ to Li₂SO₄ causes a strongly temperature dependent plastic
degree to which the Supremax glass had been corroded by the melt.

The temperature distribution along the separation column was studied by means of thermocouples. It was found that the temperature difference between the bottom and top of the column could be of the order of 50 degrees if the glass cell was in air or in an unstirred salt bath, but if the bath (mixture of 36 mole % KCl and 64% Na₂SO₄) was stirred properly, the temperature difference along the separation column could be reduced to about 10 degrees. The salt bath was not used in the first experiments, for which the temperature given in Table 1 is estimated for the height at which the transition between normal composition and enrichment was found, when the samples were analysed. It is in principle this temperature that is of importance for evaluating the experiments.

Besides the chemical analysis, the samples from the molten cells were also analysed with a mass spectrometer to determine the isotope abundances for lithium and potassium. No mass analysis was done for the solid cells, since the sample at the anode is so large that only a slight isotope enrichment can be expected, and the accuracy would be too low to allow for a comparison with the previous investigation of pure Li₂SO₄.

Results and Discussion

Experiments 11 and 12 were performed in a homogeneous phase isomorphus with α-Li₂SO₄ (for phase diagram see ref. [13]), while it is not quite clear whether experiments 13 and 14 were performed within a two-phase region. Thus, this should be the case according to NACKEN’s phase diagram [14], see Fig. 2 where, however, the dashed solidus curve is not determined by experiment. This curve is omitted in DOMBROWSKAJA’s phase diagram [15], which was consulted, when our experiments were planned. (More recent diagram gives only the liquidus curve [16].) Typical examples of the resulting concentration distributions are shown in Fig. 3 — 5, where the samples are numbered from the anode side. It was found for all the solid cells that lithium was enriched towards the anode, see Fig. 3. For those molten cells where lithium was the more abundant cation (experiments 51 — 60), the anode side was depleted of this ion (Fig. 4), while the opposite occurred for the one potassium-rich experiment (no 61, Fig. 5). Irrespective of the displacement of the two cations relative to each other, the isotope effects for both gave an enrichment of the heavy isotope (³⁷Li, ⁴¹K) towards the anode [17].

The cells I₁ and II₁ had a sharp initial boundary between pure Li₂SO₄ and the mixture, and part of

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Table 1. Data of experiments, and results. Cells containing Ag₂SO₄ are marked I, those with K₂SO₄ II or III. Subscript: s = solid, l = liquid. c₁ = equivalent fraction of lithium; superscripts: o = initial composition; m = sample with lowest change.

<table>
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<tr>
<th>Exp.</th>
<th>Cell type</th>
<th>100·c₁⁰ equiv %₀</th>
<th>Temp. °C</th>
<th>Duration hours</th>
<th>Transp. charge Q mFaraday</th>
<th>Current density A/cm²</th>
<th>100·c₁ᵐ equiv. %₀</th>
<th>Δb/b</th>
<th>t₁</th>
<th>Δb·10⁴ cm²/Vs</th>
<th>ΔN/N</th>
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<td>27.4</td>
<td>0.55</td>
<td>98.1</td>
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<td>0.039</td>
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<td>680</td>
<td>11.00</td>
<td>137.9</td>
<td>0.90</td>
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<td>575</td>
<td>5.00</td>
<td>52.0</td>
<td>0.75</td>
<td>95.1</td>
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<td>575</td>
<td>4.00</td>
<td>59.4</td>
<td>1.03</td>
<td>94.4</td>
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<td>70.6</td>
<td>2.4</td>
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<td>735</td>
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<td>6.00</td>
<td>48.6</td>
<td>2.0</td>
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<tr>
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<td>76.4</td>
<td>1.8</td>
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<td>−0.20c</td>
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<td>−0.80</td>
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</table>

* Large vertical temperature gradient, b Pyrex in separation column, c disturbance occurred during the experiment, d composition had changed in the whole column.
Fig. 2. Experiments with (Li,K)$_2$SO$_4$ mixtures. A) Concentrations and temperatures of the experiments plotted on the phase diagram. The initial concentration is denoted by x below, and by • above the liquidus curve. (The symbol ○ is used for the run with Pyrex powder in the column.) For the experiments with melts the analysed samples showed compositions falling along the horizontal lines. (Since there was a temperature gradient along the separation columns, the use of a horizontal line is a simplification.) The phase diagram is according to NACKEN 14. (There are some deviations between this and other diagrams 15 - 16.) The phases are denoted as follows: I = solid solution in a-Li$_2$SO$_4$, II = solid solution in LiKSO$_4$, III = LiKSO$_4$, IV = a-K$_2$SO$_4$ and m = melt. B) Relative cation mobilities ($\Delta b/b$) versus initial concentration.

N.B. The abscissa is 100(1 - $c_1$).

Fig. 3. Distribution of components after electromigration in solid mixtures: run 11 (above) and run 14 (below). In both cases sample 1 consists of salt through which the anode had penetrated. The small sample 14:2 is collected from the platinum net at the edge of the anode. The lowest part of the U-bent Vycor cell was at the position marked U and the original boundary between the mixture and pure salt was at B. Sample 14:15 reached up to the zinc cathode. Dashed line: initial distribution. N.B. The amount of salt is counted from the anode side, i.e. it is on a scale that moves relative to the Vycor cell while U and B are at geometrically fixed positions.

The transport across this unstable boundary is of course due to diffusion. However, it is obvious that electromigration was the main mode of cation transport, also for these cells.

For the runs with melts the maximum change in chemical and isotopic composition usually was found in the second or third sample. The fact that the enrichment thus normally is less in the first sample is not surprising, since this sample contains salt that has condensed in the higher parts of the cell, or has foamed up round the anode. Such salt is obviously

not in rapid exchange with the molten salt in the separation column. Differences in vapour pressure of the two components might also be of importance for the composition of the first sample, cf. discussion of run 61 below.

For a quantitative interpretation of the experiments it is instructive to consider a binary salt mixture with a common anion 18. The two cations are present in the relative equivalent concentrations $c_1$ and $c_2$ ($c_1 + c_2 = 1$). The transport numbers of the cations relative to the anion ("internal transport numbers", cf. ref. 19) are $t_{1a}$ and $t_{2a}$. Consider the volume between an electrode that confines the cations at this side and an arbitrary boundary situated at a position where the concentrations remain the same ($c_1^0$ and $c_2^0$) during the whole experiment. A charge

18 The whole discussion refers to equivalents of salt and is thus valid independent of the valency of the ions.
of \( Q \) faradays is passed through the electrolyte, causing a change in the number of equivalents of cation 1 in the volume from \( N_1^0 \) to \( N_1 \), the position of the arbitrary boundary being adjusted in such a way that the total amount of equivalents \( N \) within the volume remains constant:

\[
N = N_1^0 + N_2^0 = N_1 + N_2.
\]

Then

\[
N_1 = N_1^0 + t_{1a} Q - c_1^0 Q
\]

and thus

\[
t_1 - c_1 = -(t_2 - c_2) = \Delta N/Q
\]

where

\[
\Delta N = N_1 - N_1^0.
\]

The subscript a and the superscript 0 are omitted in Eq. (3) and in the following (except that the superscript 0 is used in some parts of the discussion to avoid confusion).

It is in many cases preferable to calculate relative cation mobilities, \( \Delta b/b \), or mobility differences, \( \Delta b \) (loc. cit.\(^{19}\)), where

\[
\Delta b = b_{12} = b_{1a} - b_{2a}
\]

and \( b \) (often written \( b_{+a} \) or \( b_{ca} \)) is the mean internal mobility. By definition

\[
b = c_1 b_{1a} + c_2 b_{2a} = A/F
\]

where \( A \) is the equivalent conductivity and \( F \) the Faraday constant. It is easy to show that

\[
\frac{\Delta b}{b} = \frac{t_1 - c_1}{c_1 (1 - c_1)}.
\]

In the following we shall use the sign convention that $\Delta b$ is positive if the light component (subscript 1) moves faster than the heavy one (subscript 2).

When comparing results obtained by different investigators, it is worth noting that the chosen frame of reference depends on the type of experiment. Thus a number of electrophoresis experiments have been performed where the displacement along a strip of asbestos or glass fiber paper is measured. By dividing this distance with the time and the voltage gradient some authors calculate "ionic mobilities". However, these should be considered as apparent external mobilities, the true ones being larger by the square of the labyrinth factor (increase in average path length arising from the tortuous nature of the pores). Honig has found that this factor is only about 1.001 for his paper strips, which is surprisingly low. As a comparison, columns packed with glass powder or sintered glass discs often have labyrinth factors in the range 1.2 to 1.5 (loc. cit. 23, 24). In principle, all these external mobilities measured relative to a strip, are characteristic only of that specific supporting material (glass fiber, asbestos, etc.), although the obtained mobilities, as well as measured external transport numbers 19, 25, 26, seem to be, at least nearly, independent of the solid material used as reference. Since there is a difference in definition between the external mobilities and our internal mobilities of Eq. (6), precautions are to be taken, if relative ion mobilities measured by different methods are to be compared.

For our experiments subscript 1 refers to Li and 2 to either Ag or K. The results given in Table 1 are calculated with $N_1$ and $N_2$ according to the direct cation determination, i.e. flame spectrophotometry and AgCl percolation. Since we have determined also the anion content and the total weight of the samples, it would of course be possible to include either of these entities in the calculation of $N_1$ and $N_2$, which would alter the calculated transport numbers somewhat.

The accuracy of the calculated $t_1 - c_1$ depends on whether the produced change in composition is concentrated to a few samples, where a considerable change has taken place, or there is a slight change distributed over a large amount of salt. Evidently, in the last case a slight error in the chemical analysis will have a much larger influence on the result. If we assume as a first approximation that $c_1^i$ for the last sample (no i) with enrichment differs significantly from $c_1^0$, it is easy to show that an error of $p$ per cent in $c_1^0$ gives an error of $p\frac{c_1^0}{N}/AN$ per cent in $t_1 - c_1$. If $c_1^i - c_1^0$ is less than $p\frac{c_1^0}{100}$, $N$ is not the same for the two calculations, and the expression for the error in $t_1 - c_1$ becomes more complicated. However, we shall consider $AN/N$ as a "figure of merit" for the experiment, see Table 1.

It is obvious that the experiments with solid cells are less accurate than those with melts. The reason for this is mainly the penetration of the anode into the salt, see above, which causes $AN/N$ to be low. The lower current density in these experiments has an effect in the same direction. For cell I, thermal decomposition of silver sulfate occurred. Thus, for run 11 five, and for run 12 fortyfour per cent of the silver detected in the chemical analysis consisted of decomposition products. The decomposition had advanced most for run 12, since (due to an accident with the anode) it was necessary to let this experiment stand for 46 hours at the high temperature before the electrolysis was started. We did not determine whether the decomposition products were silver oxide or metal. In the latter case electronic conduction might have taken place to some extent, which means that the calculated $t_1 - c_1$ (absolute value) is low at least for run 12. Although there thus might be some reason to consider the results obtained for run 11 as the more accurate of the two, both runs with cell II should be considered as qualitative only.

The conclusion that $t_1 - c_1$ changes its sign at the melting point for high Li-concentrations, is based on a comparison of runs 13 and 14 with 51. This interpretation seems obvious, although the analysis indicate that there might be a slight difference, about the order to the anion from measurements made relative to an asbestos paper. The labyrinth factor was neglected in this re-calculation. It has recently been pointed out, l. c. 6, that the temperatures reported in the original papers by CHEMLA and ARNIKAR are too low.

The total amount of silver found in the analysis was used for the calculation of $t_1 - c_1$.

The difference in sign between $\Delta b/b$ in melts and in cubic sulfate mixtures corresponds to a similar phenomenon in thermal diffusion. While the heavy cation is enriched at the cold side in the molten mixtures studied so far, it has been found that the heavy ion concentrates at the hot side in several Li$_2$SO$_4$ rich solid mixtures: A. LUNDE\ëS and J. E. OLSSON, unpublished.

Our result that $b_{Li} < b_K$ in the solid salt is in agreement with CHEMLA's observation that $D_{Na}<D_{K}<D_{Li}<D_{Cl}$ for tracer diffusion in single crystals of NaCl, cf. M. CHEMLA, Ann. Phys. Paris 13, 959 [1956].
of the experimental error, between the \( C_j^0 \) of the mixtures used in these experiments 29a- 29b. Eight runs (52 — 59) ... A. KVIST, Z. Naturforschg. 21 a. 1221 [1966].


... the average 

0.80 the average value \( \Delta b/b = 0.58 \) is obtained, and at least at this eutectic concentration the transport number seems to be independent of the temperature. The relative mobility \( \Delta b/b \) is about the same at the lithium concentrations \( (c_l) \) 0.9 and 0.8, but it is lower at 0.6, and at 0.4 it has the opposite sign.

It is obvious that there exists a concentration (here denoted \( C_j^{00} \)) for which \( t_1 \) equals \( c_1 \). A linear interpolation of \( \Delta b/b \) versus \( c \) (Fig. 2) in the region between experiments 60 and 61 gives \( C_j^{00} = 0.52 \), which result of course is approximate, since either or both (absolute) values of \( \Delta b/b \) might be low. There is, however, another way to estimate \( C_j^{00} \), since it should be expected that the final concentration at the anode and in the adjoining part of the separation column (steady state concentration) should become \( C_j^{00} \) irregardless of whether the initial concentration is greater or less than \( C_j^{00} \), loc. cit. 31, 32. The concentration \( C_j^{m} \) in the sample for which the largest change was found is given in Table 1. As seen in Fig. 2, \( C_j^{m} \) appears to fall below the liquidus curve for five of the experiments (51, 52, 53, 55, 56), but the temperature near the anode was always higher than the temperature given in Table 1, see discussion above, so Fig. 2 should only serve as an indication that at least partial solidification is likely to have occurred. An extreme value of \( C_j^{m} \) was obtained for run 53, but this was found for a single sample of small size, and the analysis of this sample showed some discrepancies, cf. Appendix 1. For run 61 \( C_j^{m} \) was found in the first sample (only experiment where this was the case), and since this was a sample consisting of foam and sublimed salt, the next sample should be used instead for the estimation of \( C_j^{00} \). Consequently, in Fig. 2 the “second samples” are taken as \( C_j^{m} \) for runs 53 and 61. A temperature dependence of \( C_j^{00} \) has been found for molten nitrates 33, and might well exist also in sulfates. If we limit our discussion to experiments at about 740 °C (runs 57, 58, 60, 61), we can estimate from runs 60 and 61 that \( C_j^{00} \) should be about 54%, which is in good agreement with the estimation from \( \Delta b/b \). Thus, it can be concluded that \( 0.48 < C_j^{00} < 0.56 \) at temperatures around 740 °C.

Our experiments thus show that the dependence of the relative cation mobility upon the composition of the melt is so large that \( \Delta b/b \) changes its sign. A crossover of this type has been found for several other binary mixtures with univalent cations 4-6, 33, and a general observation is that in a melt the abundant cation is more mobile than the diluted one. Although there obviously is a concentration, \( C_j^{00} \), at which the two cations have the same mobility, \( \Delta b/b \), exceeds 15% fairly soon on both sides of \( C_j^{00} \), which is in contradiction to a suggestion that the mobilities of like-charged ions should be nearly equal at all concentrations of a molten mixture 2-4, 34, cf., however, cit. 21. For mixtures of ions of different valencies \( \Delta b/b \) is large at all concentrations investigated so far, and there is no indication of a crossover 35, 36, 21, 22.

The electrical conductivity of solid and molten \( \text{Li}_2\text{SO}_4 - \text{K}_2\text{SO}_4 \) mixtures has recently been measured by Kvist 37. The density of the molten eutectic mixture \( (c_l = 0.8) \) has been measured by James and Liu 38. For both this and other molten systems studied at the same time, they found that the deviations from volumetric additivity were small, and they concluded that reliable density data may be obtained over the whole concentration range by interpolation of molar volume/composition isotherms. It is thus possible to calculate the equivalent conductivity \( A \) for the mixtures studied by us. The
obtained mobilities of Li relative to K, \( \text{Ab} \), are given in Table 1.

Work is still in progress with the mass analyses, and a quantitative interpretation of the isotope effects regarding their dependence on the composition and the temperature of the melt must be postponed to a following paper. However, from the results available so far it is evident for the experiments at \( c_1 = 0.8 \) that the mass effect (i.e. relative difference in mobility divided by relative difference in mass) is greater for potassium than for lithium. A similar increase of the mass effect for a diluted element has been found by Klemm and Monse for LiCl – PbCl\(_2\) mixtures \(^{35}\). Our experiments also indicate that the mass effect for lithium (at high concentrations) is somewhat smaller in a sulfate melt than in pure solid Li\(_2\)SO\(_4\) (loc. cit. \(^9\)).

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Preliminary reports of this investigation were given at the 15th CITCE Meeting in London, September 1964, and at the Physics Conference in Uppsala, June 1965 \(^{39}\).

Note added in proof: The diffusion of Rb ions in NaCl, KCl and RbCl has been studied recently by G. Arabi and J. G. Mullen (Phys. Rev. 143, 663 [1966]). The diffusion coefficient of Rb in NaCl was found to be larger than that of Na. Although the magnitude of the pre-exponential term \( D_0 \) cannot be explained by Mullen’s theory (which gives good agreement for the activation energy of diffusion), a qualitative explanation is given: “a large ion like Rb in NaCl will be very tightly bound and could, thus, be expected to have a much higher frequency of vibration than an Na ion”. An argument of this kind might be applicable to cubic sulfate mixtures and would, thus, explain the high potassium mobility found by us as well as Kvisr’s recent results on the electrical conductivity of sulfate mixtures \(^{37}\). However, it must be remembered that the transport mechanism is not the same in the sulfate lattice with its highly mobile cations as in e.g. NaCl.

Appendix:

On the Accuracy of the Experiments \(^{40}\)

For most of the samples the following determinations have been made:

\(^{35}\) V. Ljubimov and A. Lundén, Arkiv Fysik 30, 571 [1965].

For simplicity, only the experiments with cell III\(_1\) will be discussed here. Similar treatments apply for the other cells.

Total sample weight: \( a \) mg. Flame spectrophotometry: \( L \) milliequiv. of lithium and \( K \) of potassium, which corresponds to \( l \) and \( k \) mg of the pure sulfates. EDTA-titration: \( M \) milliequiv. of magnesium, i.e. \( m \) mg of the sulfate. BaSO\(_4\)-precipitation: \( S \) milliequiv. of sulfate.

We checked if, within experimental error:

\[ L + K + M = S \quad \text{and} \quad l + k + m = a. \] 

Sufficient agreement was usually obtained. Due to limited amounts of the samples, it was not always possible to repeat the analysis when remarkable deviations from (8), (9) or from other checks were obtained.

The concentration of impurity cations was always negligible for the initial salt, and impurities were neglected also when \( c_1 \) was calculated, since this latter entity is used to state the maximum displacement of the two cations relative to each other. In principle, \( c_1 \), can be calculated in two independent ways, either as

\[ c_1 = L/(L + K) \quad \text{(10)} \]

or

\[ c_1 = 2.7095 - 0.031099 a/S. \quad \text{(11)} \]

However, (10) is preferable even when it is reason to suspect that \( L \) and \( K \) are less accurately determined than \( S \) and \( a \), since the experimental inaccuracy of the latter two quantities causes a several times larger error in \( c_1 \) (or \( c_2 \)): e.g. an error of 1% in \( a/S \) corresponds to about 18% in \( c_2 \) for a mixture with \( c_2 \approx 0.1 \), and to about 4% if \( c_1 \approx c_2 \).

For the calculation of transport numbers, Eqs. (2) and (4), \( N_1 \) can be obtained in three ways, i.e. by summing \( L \), \( c_1(S - M) \) or \( c_1 a/E \) for the samples in question, where \( E \) is the mean equivalent weight for the mixture in a sample. In order to decide which way is preferable for estimating transport numbers, the reproducibility of the different analyses was studied for run 61. For this experiment the alkali determination was made twice, the results corresponding to the dashed and the solid line, respectively, in Fig. 5. (The two series will be denoted by the superscripts ' and '" in the following.)

The same solutions were used for measuring Li and K in the last series, while K was measured after an additional dilution in the first case. (This was done to obtain a more suitable K-concentration, according to the general recommendations for flame spectrophotometry.) There was a slight systematic shift between the two series, the results being somewhat lower in the last one, see below. In spite of the mentioned difference regarding dilution, the results were considered as double measurements of \( c_1 \), Eq. (10), and by calculating

\[ d = c_1' - c_1", \]

the standard deviation of \( c_1 \) was estimated with 95% confidence limits to be \(^{41}\)

\[ 0.01 < c_0 < 0.02. \]

For both series we calculated the ratios shown in Table 2, where \( R_1 \) corresponds to Eq. (8), \( R_2 \) to Eq. (9),

and $R_3$ essentially is a comparison of $S$ with $a$. A comparison of $\bar{R}_1 - 1$ ($\bar{R}_1$=average of the ratio) with the standard deviation $s_i$ supports our basic assumptions regarding the composition of the samples. However, samples 1–3 were excluded when calculating $\bar{R}_1$ and $\bar{R}_2$, since $R_2$ was significantly less than 1 for these samples, while $R_3$ was close to unity. From this we concluded that some cation impurity had been enriched at the anode. (This seemed to be the case also for other of our experiments.) This might be of some importance for attempts to estimate $c_i^{bm}$ from $c_i^{m}$, see above.

From the statistical tests we concluded it sufficient to base the calculation of transport numbers solely on $L$ and $K$ also when Eq. (8) or (9) was not valid for some incoming sample. Since normally 10 to 15 samples were included in the volume where the enrichment of a component had occurred, a suspected larger error in the results for an individual sample generally did not have much bearing for the error in the transport number, and for all experiments calculations of averages such as $R_i$ and $R_2$ gave confidence in the analysis. Among the samples that showed deviations from Eq. (9) was the one that gave the extreme concentration $c_i^{m} = 0.30$ for run 53. In Fig. 3 for run 11 the ratio $K/L$ (if we let $K$ stand for equivalents of Ag$_2$SO$_4$) is larger for sample 5 than for the initial salt, while this discrepancy disappears if we instead use $K$ and $a$ to calculate the ratio.

It is obvious from Eqs. (3) and (7) that the limits of error for the calculated transport numbers $t_i$ are smaller than for $t_1 - c_1$ or $\Delta b/b$. As a practical demonstration of this, Table 3 shows the results of some calculations made for run 61 with different values of the ingoing parameters. Since the range of enrichment seems to be less certain for the first than for the second series of analysis, and since the latter shows less straggling between the individual samples for the lower part of the separation column, the influence of the choice of $c_i$ for a given value of $N$ is demonstrated for the second analysis, while for the first series, different assumptions are instead made regarding the range of enrichment. Particulars regarding the choice of samples should be obvious from a comparison with Fig. 5. As mentioned above, the $S - M$ give a higher value for $N$ than the $L + K$ do, which in turn has a considerable influence on $\Delta b/b$. Since it has been shown above, that high values for $S - M$ likely are due to an enrichment of impurities at the anode, it is obvious that relative mobilities and transport numbers should be based on the determination of $L + K$.

In the same way as shown here for run 61, each run can be evaluated under different (more or less plausible) assumptions, of which one has been selected for the "final" calculation. Of course this method of over-determining the parameters might introduce a subjective factor when the final choice is made, but the advantage is that the additional analyses and calculations gives a good indication of the accuracy of the experiments. Obviously the accuracy of $\Delta b/b$ relative to that of $t_i$ is not the same over the whole composition range. However, while it is possible to determine $t_i$ within a few per cent, the calculated relative mobilities might better be considered as semi-quantitative information. It is regrettable that results on ion mobilities, transport numbers etc. often are reported without any serious attempt to estimate their accuracy. Such knowledge is essential for all discussions of transport properties.

#### Table 3. Demonstration how the relative mobility ($\Delta b/b$) and the transport number ($t_i$) are influenced by the choice of parameters. For symbols see text. Analysis no. 1 corresponds to the dashed, and no. 2 to the solid line in Fig.5.

<table>
<thead>
<tr>
<th>Analysis No.</th>
<th>$N$ includes samples</th>
<th>$c_1$ is average of samples</th>
<th>$c_1$</th>
<th>$S - M$ for $L + K$</th>
<th>$-\Delta b/b$ for $L + K$</th>
<th>$t_1$ for $S - M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1–6</td>
<td>7–14, 100</td>
<td>0.408a</td>
<td>1.155</td>
<td>0.203a</td>
<td>0.359a</td>
</tr>
<tr>
<td>2</td>
<td>1–6</td>
<td>7, 8</td>
<td>0.403</td>
<td>0.213</td>
<td>0.262</td>
<td>0.352</td>
</tr>
<tr>
<td>2</td>
<td>1–6</td>
<td>7–14</td>
<td>0.409</td>
<td>0.229</td>
<td>0.317</td>
<td>0.341</td>
</tr>
<tr>
<td>2</td>
<td>1–6</td>
<td>7–17, 100, 102</td>
<td>0.412</td>
<td>0.202</td>
<td>0.365</td>
<td>0.365</td>
</tr>
<tr>
<td>2</td>
<td>1–6</td>
<td>101</td>
<td>0.421b</td>
<td>0.196</td>
<td>0.578</td>
<td>0.357</td>
</tr>
<tr>
<td>1</td>
<td>1–5</td>
<td>100, 102</td>
<td>0.404</td>
<td>1.202</td>
<td>0.179</td>
<td>0.349</td>
</tr>
<tr>
<td>1</td>
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<td>100, 102</td>
<td>0.404</td>
<td>1.135</td>
<td>0.193</td>
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<tr>
<td>1</td>
<td>1–9</td>
<td>100, 102</td>
<td>0.404</td>
<td>1.107</td>
<td>0.201</td>
<td>0.355</td>
</tr>
</tbody>
</table>

*a Selected as final value for Table 1.  b Extreme choice for $c_1$.  

#### Table 2. Tests of accuracy of analysis for run 61.

<table>
<thead>
<tr>
<th>Ratios</th>
<th>Average value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$ = $(L + K + M)/S$</td>
<td>1.054 1.022</td>
<td>0.070 0.070</td>
</tr>
<tr>
<td>$R_2 = (\bar{R}_1 - 1)/a$</td>
<td>1.001 0.970</td>
<td>0.038 0.025</td>
</tr>
<tr>
<td>$R_3 = R_2/R_1$</td>
<td>0.969 0.968</td>
<td>0.063 0.064</td>
</tr>
</tbody>
</table>