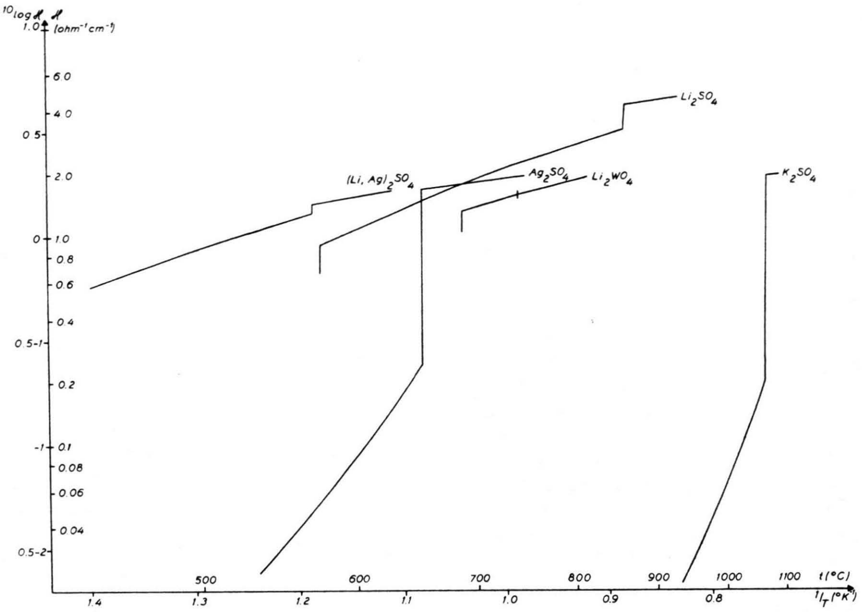

Fig. 2. The temperature dependence of the conductivity of some salts with high temperature modifications.

in a cooperative motion is 2.0 in the solid[2] and 2.7 in the melt[11] and the quotient between the electrical conductivity of the melt and the solid at the melting point is also about 1.3 (l. c.[1]). The radius of the sulphate ion (2.9 Å) is smaller than that of the tungstate ion (3.6 Å)[7] and it is probable that if the size of the anion is increased, the change in the mechanism of transport will be still smaller and also the jump in the conductivity.

The transition point 660 °C in Li_2WO_4 with 14.5% Li_2WO_4 seems to be in good agreement with the transition point found by us in the pure salt.

It is thus probable that lithium tungstate forms a cubic or pseudo-cubic high temperature modification from 684 to 738 °C.

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[11] A. Kvist, to be published.

The Isotope Effect for Electromigration of Rubidium Ions in Molten Rubidium Nitrate

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The relative difference between the electromigration mobilities of the two rubidium isotopes was found to be 0.0008 in molten rubidium nitrate at 350 °C, corresponding to a mass effect of 0.035. A comparison is made with new results for $LiNO_3$ and $RbNO_3$.

The isotope effect of cation electromigration in pure molten nitrates has been studied previously in lithium nitrate[1-3] and in potassium nitrate[4]. This investigation has now been extended to pure rubidium nitrate. The experimental arrangement is essentially the same as described before[4, 5], except that a U-shaped cell was used. With this cell the required amount of salt was about 15 g, instead of 100 g in the old type of cell[2, 4]. In the old cell the large cathode compartment formed a bath surrounding the separation tube, which was thus kept at the temperature of the cells, while in the new cell the separation tube becomes hotter than the two electrode compartments. The temperature of the sepa-

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[4] A. Lundén, C. Reuterswärd, and N. Sjöberg, Z. Naturforschg. **10 a**, 279 [1955]. In this paper the mass effect is reported as 0.036, since it was calculated with $M=39.1$ instead of the arithmetic mean 40.

[5] In the previous experiments washbottles containing an oil were used to indicate the gas flow. We now used nitric acid instead which is preferable.

ration column was raised about 30° when some 150 mA passed through the cell. Five experiments were made of which two were analysed completely. A source of trouble was that "dry spots" could be seen in the separation column, which might be due to partial decomposition of the salts. When these spots appeared, the cell resistance increased, and the electrolysis could be interrupted for some time. After the experiments a chemical analysis was made, and this showed that, in addition to the nitrate, also nitrite and oxide could be detected in some of the experiments. The amounts of sodium and potassium were negligible, i. e. ion exchange with the glass should not have occured. The main running conditions of those two experiments, for which also a mass analysis was made, are given in Table 1. The reliability of the mass analysis is essential for the interpretation of an enrichment. For this reason two separate series of mass analyses were made for both experiments, and for each series independent calculations of the relative difference in cation mobility were made. By dividing this difference with the relative difference in mass (2/86), the so called mass effect (μ) is obtained. Since the amount of salt in the cathode compartment is so much smaller in the present cell than in the old type, detectable changes in isotope composition had occured at both electrodes, although the change was small in the relatively large cathode volume (approx. 75% of the total amount of salt). In an intermediate part of the separation column (about half the column length) the isotope composition had remained at its initial value, and it was thus possible to calculate the mass effect for both the anode and the cathode side. Since the change in composition was small for most samples, the calculation of the mass effect is strongly influenced by the choice of the "normal" abundance ratio, R_0. Slightly different values for R_0 were obtained depending on how many samples from the intermediate part of the column that were considered as normal. Since we thus had more than one choice of R_0 within each separate series of mass analyses, a total of some twelve calculations of the mass effect were made for each experiment. The range within which the mass effects fell for the anode side is shown in Table 1. Due to the very slight enrichment at the cathode, the mass effects calculated for that side spread over a much wider range and they were not considered for the final evaluation. Since the precision of experiment A is better than for B, it is reason to conclude that the mass effect (μ) is about 0.035 for rubidium nitrate at 350 °C.

Experiment		A	B
Temperature	°C	354	346
Duration	hours	120.7	38.0
Transported charge	Ah	13.00	5.16
Current density	A/cm²	1.5	2.2
Sep. column, length	cm	22	23
Separation factor		1.06	1.03
Range for mass effect	($-\mu$)	0.034 – 0.035	0.028 – 0.041

Table 1. Conditions and results of experiments. The separation factor is the quotient between the abundance ratio of a normal sample and that of the most enriched sample (on the anode side).

The obtained mass effect for $RbNO_3$ should be compared with that previously found for other nitrates. For $LiNO_3$ $-\mu=0.50\pm0.013$ was reported by LUNDÉN et al.[2], while VALLET et al. obtained $-\mu=0.057$ for two of their four experiments[3]. However, in the first investigation[2] the abundance ratios were measured by means of a neutron activation method, which had a lower accuracy than a modern mass spectrometer has, and the duration of the experiments by VALLET et al. was longer than might seem safe for a determination of the mass effect. It is thus not surprising that some unpublished experiments have given higher values for the mass effect of $LiNO_3$, e. g. $-\mu=0.089$ at 292 °C (l. c. [6]). For KNO_3 the reported[4] mass effect $-\mu=0.037$ at 360 °C has been confirmed by other experiments at the same temperature[6], while $-\mu=0.057$ was obtained in experiments at 480 °C where both KNO_2 and KNO_3 were present in the cells[7]. (An investigation of the dependence of the mass effect of KNO_3 on temperature and ion anion composition is in progress.) The mass effect of $RbNO_3$ has been determined earlier for a mixture of $LiNO_3$ and $RbNO_3$ for which $-\mu=0.05$ was obtained[8], but since there is a general tendency that larger mass effects are obtained in mixtures than in pure salts, there need not be any discrepancy between the previous and the present results for $RbNO_3$. For the pure nitrates the observed decrease in mass effect with increasing cation mass is in agreement with the regularities found for molten halides[9].

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