Sauerstoff-6-Ringe durch Kationen besetzt. Entsprechend wurde für LMS A 5 keine Verringerung der Absorptionskapazität für organische Moleküle gegenüber LMS A 4 beobachtet. Wenn die Ca-Ionen die Sauerstoff-8-Ringe zwischen den großen Hohlräumen besetzen würden, müßte die Absorptionskapazität beim Austausch der Na^+ gegen Ca^{3+} abnehmen. Man sollte daher annehmen, daß auch bei vollständigem Ersatz von Na durch Sr-Ionen die Sechsringe besetzt werden. In diesem Fall besteht der Aktivierungsschritt im Verlassen des Sechsringes. Für diese Annahme spricht auch die positive Aktivierungsentropie, die man nach folgender Abschätzung erhält.

Nach der von WERT, ZENER, EYRING und anderen entwickelten Diffusionstheorie kann die Aktivierungsentropie ΔS aus dem D_0-Wert nach folgender Gleichung berechnet werden:

$$D_0 = \tfrac{1}{6}\, p\, d^2\, \nu \cdot \exp(S/R). \qquad (2)$$

In Gl. (2) ist d der Abstand zwischen zwei Gleichgewichtspositionen, p das Produkt aus der Zahl der nächsten Nachbarplätze und der Wahrscheinlichkeit, daß einer dieser Plätze unbesetzt ist und ν die Schwingungsfrequenz der Kationen in einer Gleichgewichtsposition.

Nimmt man entsprechend den Schwingungsfrequenzen von Kationen in Ionenkristallen einen Wert von $\nu = 10^{13}\ \mathrm{sec}^{-1}$ an, so erhält man bei gegebenem p, d und ΔH aus D_0 entweder den richtigen oder einen zu kleinen Wert für ΔS, da die wirkliche Frequenz auf keinen Fall größer ist als $10^{13}\ \mathrm{sec}^{-1}$. Erhält man also einen positiven Wert für ΔS^+, ist das Ergebnis insoweit eindeutig. Mit $\nu = 10^{13}\ \mathrm{sec}^{-1}$, $d \approx 6$ Å und der Annahme $p/6 \approx 1$ ergibt sich aus (2)

$$\Delta S \approx 4{,}6\,(\lg D_0 + 2) \approx 13\ [\mathrm{cal/Mol\ Grad}]. \qquad (3)$$

Thermal Diffusion in Molten and Solid (bcc) Sulfate Mixtures, mainly Isotope Effects

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In molten eutectic $Li_2SO_4-K_2SO_4$ thermal diffusion causes an enrichment of the light cation (Li) as well as of the light isotope of both cations at the hot side. The temperature range was 599—853 °C. The heat of transport was found to be (273 ± 56) cal/equiv for the separation of Li from K, (36 ± 28) cal/equiv for the Li-isotopes and (43 ± 13) cal/equiv for the K-isotopes. The heat of transport for the lithium isotopes was found to be (161 ± 64) cal/equiv in solid (bcc) $LiNaSO_4$ (range 546—588 °C) and (316 ± 53) cal/equiv in solid (bcc) $LiAgSO_4$ (range 457—547 °C); the light isotope being enriched at the hot side. The quoted standard deviations correspond to statistical errors only, and in all cases the reported heats of transport might be too small due to systematical errors. There are indications of a correlation between the heat of transport and the activation energy of self diffusion.

We have recently reported on thermal diffusion of the cations in face-centered cubic and body-centered cubic sulfate systems [1]. For the latter systems we have now also measured the isotope effect for lithium, and for the molten eutectic lithium-potassium sulfate mixture (80 mol % Li_2SO_4) we have studied the separation of the two cations as well as the isotope effects for both of them.

Molten Eutectic $Li_2SO_4-K_2SO_4$

Four cells containing the molten salt mixtures were kept for 12 days in a furnace where the top and bottom plates were kept close to 853 °C and 599 °C, respectively. The distance between these plates was about 4 cm. After quenching, each cell was divided into 8 samples for each of which the chemical composition [2] as well as isotope abundance ratios were determined. For each of these entities the temperature coefficient was calculated by regression analysis [3, 4]. The obtained Soret-coefficients (σ) are quoted in Table 1.

Cell no	Li—K $\sigma \cdot 10^5$ degr.$^{-1}$	Separation of ^{6}Li—^{7}Li $\sigma \cdot 10^5$ degr.$^{-1}$	^{39}K—^{41}K $\sigma \cdot 10^5$ degr.$^{-1}$
1	22.5 ± 5.5	4.4 ± 3.9	0.2 ± 1.0
2	16.2 ± 3.3	2.2 ± 2.4	1.0 ± 2.0
3	12.3 ± 7.7	0.5 ± 0.8	2.5 ± 1.5
4	4.2 ± 5.6	0.2 ± 3.2	4.9 ± 1.2
Average	13.8 ± 2.8	1.8 ± 1.4	2.2 ± 0.6

Table 1. Soret coefficients for molten eutectic $Li_2SO_4-K_2SO_4$.

Body-centered cubic $LiNaSO_4$ and $LiAgSO_4$

The lithium isotope abundance ratio was measured for top and bottom samples of cells that had been used in the reported investigation [1], and the Soret coefficient was calculated, see Table 2.

Salt	Temperature top °C	Temperature bottom °C	Separation of ^{6}Li—^{7}Li 10^5 degr.$^{-1}$	Separation of cations 10^5 degr.$^{-1}$
$LiNaSO_4$	588	546	12 ± 4	-230 ± 456
$LiAgSO_4$	547	457	27 ± 4	65 ± 7

Table 2. Soret coefficients for body-centered cubic sulfates.

Regarding the investigated face-centered cubic systems [1], the concentration of the heavy component (K, Rb, Ag) was too small to allow measurements of the isotope abundance, and the isotope effect for lithium had already been determined in pure lithium sulfate [4].

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[2] Professor J. RYDBERG, Department of Nuclear Chemistry, has kindly placed an atomic absorption spectrophotometer at our disposal.

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Discussion

The errors quoted in Table 1 and 2 are standard deviations of the mean, and they account only for the uncertainty in the chemical and mass spectrometrical analysis. As shown previously there are for experiments with melts a number of disturbances that might occur, causing the measured Soret coefficients to become lower than the true ones [5]. The experiments with $LiNaSO_4$ and $LiAgSO_4$ were probably terminated before the steady state was reached [1, 5a], but we have not made any correction for this. Although the obtained results thus might be low due to systematic errors, it is possible to draw some conclusions. In Table 3 the heats of transport and activation energies of self-diffusion are summarized for all salts studied so far. For the molten mixture the isotope effects are of the same order as in the other molten salts, and they are significantly smaller than in the solid sulfates. It seems likely that the heat of transport is larger in the bcc systems than in fcc Li_2SO_4, and it is to be observed that also the activation energy for self-diffusion is higher in the bcc systems (and lower in melts than in solids). A correlation between the heat of transport and the activation energy is to be expected from theoretical considerations [14, 15]. The question whether the same mechanism governs different types of transport processes has been discussed by several authors, cf. e. g. LODDING [14]. In this connection it is to be noted that the isotope effect for electromigration is the same in molten eutectic $(Li, K)_2SO_4$ as in fcc Li_2SO_4, l. c. [16], while we have found a significant difference between these two systems regarding thermal diffusion.

Salt	Study of	Thermal diffusion Heat of transport cal/equiv	Temp. °C	Self-diffusion Activation energy cal/equiv	Ref.
	Li–K	273 ± 56	726		
$(Li, K)_2SO_4$, m	Li	36 ± 28	726		
	K	43 ± 13	726		
Li_2SO_4, fcc	Li	172 ± 8	750	7 850	4, 6
$LiNaSO_4$, bcc	Li	161 ± 64 *	567	14 460	7
$LiAgSO_4$, bcc	Li	316 ± 53 *	500	12 030	8
LiCl, m	Li	89 ± 14	800		9
$LiNO_3$, m	Li	25 ± 1	352	5 490	10, 11
	Li	33	370	5 490	12, 11
KNO_3, m	K	35	436	5 530	12, 11
$RbNO_3$, m	Rb	13	417	5 670	12, 13

Table 3. Heat of transport for molten (m) and solid (fcc, bcc) salts. Data marked by an asterisk are for experiments which were terminated before the steady state was reached.

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BERICHTIGUNG

Zu A. WÜLFING, „Zur Beschreibung der Coulombwechselwirkung in der Quantenelektrodynamik, Z. Naturforsch. **24 a**, 1151 [1969].

Folgende Berichtigungen sind notwendig:

3. Zeile vor (2,33) Positron statt Proton,

3. Zeile vor (3,13) $(\widetilde{S}_n - S_n)$ statt $(S_n - S_n)$,

(4,17) $\dot{g}_\perp(x_{b+1})$ statt $g_\perp(x_{b+1})$,

(5,11 a) $\widetilde{H}_G(t)$ statt $H_G(t)$,

(5,11 b) $H_\perp(t)$ statt $\widetilde{H}_\perp(t)$,

(5,16) $A_L^{m(+)}(x)$ statt $A_L^m(x)$.

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