Nach der früheren Berechnung war auch r_{++} von $PbCl_2$ negativ, aber es wird jetzt positiv, weil D^+ nach der neuen Messung kleiner als nach der alten ist. In allen drei Salzen sind Komplexionen auch bei nur zwei Komponenten möglich[62]. Dagegen sind solche Ionen in den Modellen mit quasikristallinem Gitter weniger wahrscheinlich, denn für das 3-Komponenten-Modell werden dann zu große Elektrolysierbarkeiten erhalten[63], während für vier Komponenten der Koeffizient der Reibung zwischen neutralen Komplexen und dem Gitter (r_{24}) negativ wird. Eine weitere Diskussion muß verschoben werden, bis mehr Selbstdiffusionsmessungen in zweiwertigen Halogeniden gemacht worden sind.

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[62] Für eine Reihe von zweiwertigen Halogeniden passen für ein Löcher-Modell die Ionen MX^+ und X^- am besten, vgl. Anm. [50].

[63] Zwar wird ζ_3 auch für Pb^{2+}-Ionen größer als eins, aber dies kann wahrscheinlich mittels des Meßfehlers der eingehenden Größen D^-, Λ und t^- erklärt werden.

Thermal Diffusion in the Fused Alkali Nitrates $LiNO_3$, KNO_3, and $RbNO_3$

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Thermal diffusion has been studied in pure fused $LiNO_3$, KNO_3, and $RbNO_3$. In all cases the light isotope was enriched on the hot side. The Soret coefficients were found to be $4.0 \cdot 10^{-5}$ degr.$^{-1}$, $3.5 \cdot 10^{-5}$ degr.$^{-1}$, and $5.0 \cdot 10^{-5}$ degr.$^{-1}$, respectively. Four mixtures of fused $RbNO_3$ and $LiNO_3$ were investigated regarding both isotope and chemical separation. Lithium nitrate as well as the light isotopes of lithium and rubidium migrated towards the hot department of the cell. The Soret coefficient of the chemical separation varied almost linearly from $33 \cdot 10^{-5}$ degr.$^{-1}$ at 31.8 mole % $RbNO_3$ to $79 \cdot 10^{-5}$ degr.$^{-1}$ at 64.4 mole % $RbNO_3$.

We have previously studied thermal diffusion in pure $LiNO_3$ and $RbNO_3$ and in mixtures of $LiNO_3$ and $AgNO_3$[1, 2, 3]. The pure salts were studied in cells with a vertical temperature gradient, i. e. no convection currents should occur in these cells. Due to the small separation factors it was essential to have as large a temperature difference between the top and the bottom of the cell as possible. An upper limit to the possible operation range for nitrates is set by their thermal decomposition. At 760 mm Hg the dissociation temperatures are 474 °C, 533 °C and 549 °C for $LiNO_3$, KNO_3, and $RbNO_3$, respectively[4, 5, 6]. The corresponding melting points are 252 °C, 334 °C, and 310 °C.

In this work the same furnace was used as in earlier experiments[1, 2]. The vertical cells inserted in the furnace were made of stainless steel tubing. The lower part, inner diameter 2.50 mm and outer diameter 3.00 mm, was 40 mm long and was kept in the temperature gradient. The upper part, about 10 mm in diameter, served as a large volume (about 1 cm^3).

In order to measure the temperature gradient, a thermocouple was welded to the top of the narrow tube, and another one to the bottom. The temperatures were kept constant within a few degrees with the help of two regulators, thus the average deviations of the temperature readings were ± 1.6 degrees at the top and ± 1.2 degrees at the bottom of the cell.

At the end of the experiment, the cells were taken out from the furnace and quenched, as described earlier. The salt in the large volume and in the lowest 5 mm of the cell were taken as samples and analysed with the mass spectrometer. In order to reduce influence from instrument drift the samples

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were analysed in close succession. The chemical analyses were performed with a Beckman DU flame spectrophotometer in the concentration ranges 4 – 16 ppm Li and 40 – 160 ppm Rb.

The time to reach equilibrium was estimated for $LiNO_3$ and KNO_3 from the theory given by Bardeen[7]. These two salts were considered as dilute solutions regarding the isotopes ^6Li and ^{41}K. Approximately the same running time was chosen for $RbNO_3$. The caracteristic time is $\Theta = 4\,a^2/\pi^2 D$, where a = cell height and D = self-diffusion coefficient. A running time of 120 hours corresponds to about $3\,\Theta$ for $LiNO_3$ and $2.6\,\Theta$ for KNO_3, if D is taken as corresponding to the mean of the top and the bottom temperatures.

Regarding the Soret coefficient, the definition used in this paper is slightly modified. If f is the ratio between the abundances of the light and the heavy isotope, the mole fraction n of the light isotope is $f/(f+1)$ and

$$D'/D = \frac{1}{n_T(1-n_T)} \cdot \frac{(n_T - n_B)}{(t_T - t_B)},$$

where n_T and n_B are the mole fractions at the top and at the bottom. Since the concentration difference between the upper and lower par of the cell was very small ($f_T \approx f_B$), we have

$$D'/D = \left(1 + \frac{1}{f_T}\right) \frac{f_T - f_B}{t_T - t_B}.$$

The isotope fractions $^6Li/^7Li$, $^{39}K/^{41}K$ and $^{85}Rb/^{87}Rb$ in this investigation were 0.0821, 0.0713 and 2.60 for samples of normal composition.

In table 1 the Soret coefficients from this work are compared with earlier measurements in a glass apparatus[1, 2]. The discrepancy between the results with the two types of cells is not significant, and it might be influenced by the temperature measurements. These were done in a more accurate way in the present work, where the thermocouples were welded to the walls of the cell. It was more difficult to estimate the temperatures in the earlier experiments.

The isotope as well as the chemical separation has been measured as a function of the concentration for four mixtures of $LiNO_3$ and $RbNO_3$.

	Metal Cells								Glass Cells			
Salt	$(D'/D) \cdot 10^5$ (degr.$^{-1}$)	$\alpha \cdot 10^2$	$-Q^*$ (cal/mole)	t_T (°C)	t_B (°C)	t_M (°C)	Time (hours)	Number of cells	$(D'/D) \cdot 10^5$ (degr.$^{-1}$)	t_M (°C)	Time (hours)	Number of cells
Ref.	—	—	—	—	—	—	—	—	1,2	1,2	1,2	1,2
$LiNO_3$	4.0 ± 0.3	2.6	33	452	287	370	119	15	3.6 ± 0.2*	350	140	15
KNO_3	3.5 ± 0.2	2.5	35	517	354	436	117	14	—	—	—	—
$RbNO_3$	5.0 ± 0.7	3.5	47	513	321	417	120	16	3.6 ± 0.7	409	120	16

*These values are not the same as those given in the reference, because the Soret coefficients are defined in a slightly different way.

Table 1. $\alpha = T_M\, D'/D$, thermal diffusion factor. $Q^* = -\alpha\, R\, T_M$, where Q^*=heat of transfer and R=gas constant. t_T and t_B are the temperatures at the top and at the bottom of the cell. t_M and T_M are mean temperatures. The probable errors are given in the tables.

Concentration mole % $RbNO_3$	Li $(D'/D)_{6,7} \cdot 10^5$ degr.$^{-1}$	Rb $(D'/D)_{85,87} \cdot 10^5$ degr.$^{-1}$	$(D'/D)_{Li,Rb} \cdot 10^5$ degr.$^{-1}$	t_T °C	t_B °C	t_M °C	Time hours	Number of cells
0	4.0 ± 0.3	—	—	452	287	370	119	15
31,8	1.6 ± 0.3	7.4 ± 1.4	33 ± 4	422	276	349	115	3
41,0	2.5 ± 0.2	11.8 ± 1.3	40 ± 8	423	279	351	115	4
50,1	3.5 ± 0.2	4.2 ± 1.3	59 ± 9	431	279	355	115	3
64.4	2.3 ± 0.4	5.0 ± 1.3	79 ± 7	431	274	352	115	4
100	—	5.0 ± 0.7	—	513	321	417	120	16

Table 2. $\left(\frac{D'}{D}\right)_{Li,Rb} = \frac{1}{C_0(1-C_0)} \cdot \frac{dC}{dT} \approx \frac{C_B - C_T}{C_T(1-C_T)\,(t_T - t_B)}$, where C_B and C_T are mole fractions of $RbNO_3$ at the bottom and at the top.

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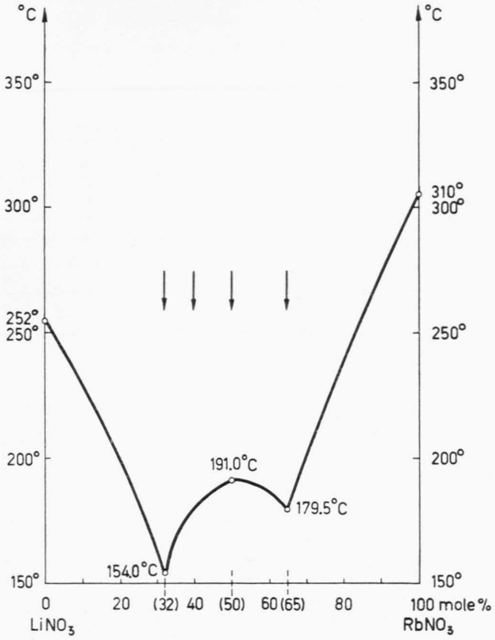

Fig. 1. Phase diagram of $LiNO_3-RbNO_3$ [8].

The mixtures were chosen by considering the existance of two eutectic concentrations and a maximum for $LiNO_3 \cdot RbNO_3$ in the phase diagram (Fig. 1). Regarding the chemical fractionation, the SORET coefficient seems to vary almost linearly between $33 \cdot 10^{-5}$ degr.$^{-1}$ at 31.8 mole % $RbNO_3$ and $79 \cdot 10^{-5}$ degr.$^{-1}$ at 64.4 mole % $RbNO_3$. It is difficult to make final conclusions about the isotope separation, since the errors originating from the determination of the isotope fractions are large. If the SORET coefficients from the mixtures are compared with those which are obtained in the pure salts, one can say that $(D'/D)_{6,7}$ is lower in the mixtures and $(D'/D)_{85,87}$ is higher at the low concentrations of $RbNO_3$. A more systematic study of both chemical and isotope fractionation in binary mixtures should give interesting information on the structure of fused salt mixtures.

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