The Electrical Cationic Mobilities of $(Na-Rb)NO_3$ and $(Tl-Rb)NO_3$ Molten Mixtures

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The cationic internal mobilities of the $(Na-Rb)NO_3$ (over a large temperature range) and $(Tl-Rb)NO_3$ (at 325 °C) molten systems, have been determined. The trends of the mobility isotherms of $(Na-Rb)NO_3$ do not change with temperature. The preexponential factors of the Arrhenius plots are nearly (within the experimental accuracy) independent of composition. The activation energy of the Na^+ mobility, passing from $NaNO_3$ to $RbNO_3$, increases by about 0.8 $kcal \cdot mole^{-1}$; the activation energy of Rb^+ passing from $RbNO_3$ to $NaNO_3$ decreases by about 0.4 $kcal \cdot mole^{-1}$. The Tl^+ and Rb^+ mobilities in the $(Tl-Rb)NO_3$ system vary linearly with composition and are equal within ∼ 5%. The mobility results in both systems confirm the validity of equations for the equivalent conductivity excesses previously described.

In a previous paper[1] a procedure has been proposed which allows to obtain information about the cationic mobility (henceforth the cationic mobilities are always expressed as internal quantities; frame of reference = the anion) isotherms of binary systems with a common anion $(M_a-M_b)R$, from the excess conductivity (defined as the difference between the experimental value of the equivalent conductivity and the other one calculated additively from the pure components) isotherms, by means of a linear plot of $\Delta\Lambda/\mathfrak{F}X_a X_b$ vs. X_a, where $\Delta\Lambda$ = excess conductivity and $X_{a,b}$ = molar fractions of the components. In a subsequent paper[2] it has been demonstrated that a relationship of the same analytical form may be obtained from a simple physical model dealing with the polarization of the anion.

Accordingly, the decrease of the mobility of the smaller cation in mixtures is due to an increase of the respective activation energy because of the polarization of the anion (and conversely for the greater cation), the preexponential factors being supposed to be constant in the whole composition range.

The cited relationship has been applied to the $(Na-Rb)NO_3$ and $(Tl-Rb)NO_3$ systems (mobility data of which were lacking) in order to predict the cationic mobilities[1]. This work presents the results of an experimental determination of these mobilities carried out in order to check the applicability of the cited relationship.

Experimental

Experimental set-up, procedures and characteristics of the method used for determining the electrical mobilities, were previously described[3-5]. Sodium nitrate and rubidium nitrate, reagent grade, were used without further purification. $TlNO_3$ was twice recrystallized from the melt before use. Radioisotopes Na-22, Rb-86 and Tl-204 which were employed as tracers in the mobility determination experiments, were supplied by the Amersham Radiochemical Center.

Results

Table 1 reports the cationic mobilities in the $(Na-Rb)NO_3$ system in the temperature range 200 °C ÷ 500 °C. Figure 1 presents the Na^+ and Rb^+ mobility isotherms at 325, 400, and 500 °C. Table 2 and Fig. 2 present the cationic mobilities in the $(Tl-Rb)NO_3$ system at 325 °C. The equivalent conductivity values necessary for calculating the mobilities from the experimental data were taken from ref.[1]. For $(Na-Rb)NO_3$, in the temperature range 400 °C ÷ 500 °C, extrapolated

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[1] V. WAGNER and S. FORCHERI, Z. Naturforsch. **23 a**, 926 [1968]. A sentence in this paper must be modified: after Eq. (12 a) it should read: "is not a sufficient one for having $\Delta\Lambda=0$ [as in $(Tl-Rb)NO_3$]. If the condition (12 a) is adopted, it is in addition necessary that"

[2] V. WAGNER, E. BERRA, and S. FORCHERI, Z. Naturforsch. **24 a**, 887 [1969].

[3] S. FORCHERI and V. WAGNER, Ann. Chim. Rome **56**, 213 [1966].

[4] S. FORCHERI and A. BERLIN, J. Chromatogr. **26**, 239 [1967].

[5] S. FORCHERI and V. WAGNER, Z. Naturforsch. **22 a**, 1171 [1967].

Pure $NaNO_3$

T °C	325	346	400	420	460	500
$u_{Na} \cdot 10^4$*	4.91	5.09	6.74	7.28	8.23	9.36
$u_{Rb} \cdot 10^4$	4.22	4.20	5.43	6.40	7.01	7.95
	4.15	4.30	5.73	6.35		8.10
	4.09		5.76			
	4.11					
	4.09					

* $\Lambda_{NaNO_3}/\mathcal{F}$, from ref. [1].

$X_{Rb}=0.2$

T °C	325		400
$u_{Na} \cdot 10^4$	4.09	4.12	5.68
	4.05	4.06	
	4.03	4.05	
$u_{Rb} \cdot 10^4$	3.46	3.68	5.24
	3.73	3.60	
	3.72	3.58	

$X_{Rb}=0.6$

T °C	325	400	500
$u_{Na} \cdot 10^4$	3.18	4.59	6.80
	3.20	4.51	
	3.20		
$u_{Rb} \cdot 10^4$	3.03	4.45	6.36
	3.01	4.40	6.20

$X_{Rb}=0.4$

T °C	200	225	245	325	346	400	500
$u_{Na} \cdot 10^4$	1.29	1.84	2.12	3.58	4.04	5.05	7.08
	1.30	1.81	2.24	3.47	4.02	5.19	
		1.86	2.15	3.60	3.99		
$u_{Rb} \cdot 10^4$	1.16	1.41	1.90	3.31	3.57	4.60	6.83
		1.44	1.93	3.24	3.69	4.63	
		1.44		3.25	3.70		

$X_{Rb}=0.75$

T °C	325
$u_{Na} \cdot 10^4$	2.84
	2.90
$u_{Rb} \cdot 10^4$	2.92

$X_{Rb}=0.8$

T °C	325	400
$u_{Na} \cdot 10^4$	2.80	4.26
$u_{Rb} \cdot 10^4$	2.78	4.14
		4.24

$X_{Rb}=1.0$

T °C	325		400	460	500
$u_{Na} \cdot 10^4$	2.59	2.59	3.79	5.13	5.67
	2.71	2.52			5.59
	2.75	2.67			5.92
					5.60
$u_{Rb} \cdot 10^4$*	2.62		3.86	4.90	5.63

* $\Lambda_{RbNO_3}/\mathcal{F}$, from ref. [1].

Table 1. Cationic mobilities ($cm^2 \cdot sec^{-1}.Volt^{-1}$) in $(Na-Rb)NO_3$ at different concentrations.

values were used. The tendency of the $TlNO_3$ to decompose in transport cells exposed to the atmosphere[4] and even to dry N_2 prevents mobility determinations at temperatures >350 °C in $(Tl-Rb)NO_3$.

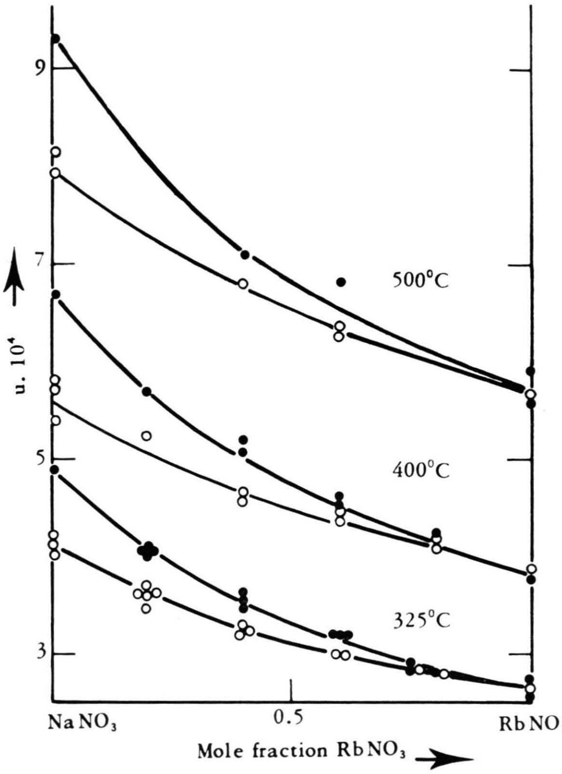

Fig. 1. Cationic mobility isotherms as obtained from experiments for the $(Na-Rb)NO_3$ system; ● $=Na^+$, ○ $=Rb^+$.

X_{Rb}	$u_{Tl} \cdot 10^4$	$u_{Rb} \cdot 10^4$
		3.60
0	3.81*	3.70
0.25	3.53	3.32
	3.68	3.40
0.28	3.52	3.20
		3.24
	3.30	3.08
0.50	3.30	3.14
	3.30	3.07
0.75	3.07	2.83
0.77	2.96	2.84
		2.74
	2.65	
1	2.57	2.62**
	2.50	

* $\Lambda_{TlNO_3}/\mathcal{F}$, from ref. [1]; ** $\Lambda_{RbNO_3}/\mathcal{F}$, from ref. [1].

Table 2. Cationic mobilities ($cm^2 \cdot sec^{-1} \cdot Volt^{-1}$) in $(Tl-Rb)NO_3$ at 325 °C.

Discussion

The isotherm for the equivalent conductivity excess in binary mixtures with a common anion

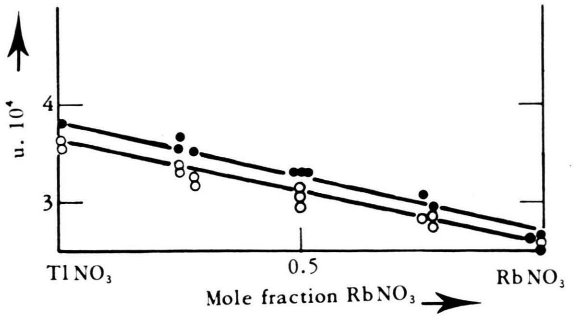

Fig. 2. Experimental cationic mobility isotherms at 325 °C for the (Tl—Rb) NO_3 system; ●=Tl, ○=Rb.

(when the mobility isotherm of the larger cation b is supposed, as a first approximation, to be linear) may be written in the form [1]

$$\Delta\Lambda/\mathcal{F}\, X_a X_b = u_{a,0} - u_{a,1} + u_{b,0} - u_{b,1} + 4\,\Delta u_a \cdot X_a \qquad (1)$$

where $\Delta\Lambda$ = excess conductivity and

$$\Delta u_a = u_{a\,(\text{exp.})} - u_{a\,(\text{linear})} = \text{excess mobility},$$

at $X_a = \frac{1}{2}$, of the smaller cation. The alphabetic subscript refers to the cationic species and the numerical one to the respective mole fraction (see for example Fig. 3 of ref. [1]). When the condition $u_{a,0} = u_{b,1}$ holds (this condition results to be roughly valid for systems, the components of which do not differ in their molar volumes by more than about 30%, as can be seen from mobility results of references [5–7], and as it has been pointed out in ref. [8]), then Eq. (1) reduces to

$$\Delta\Lambda/\mathcal{F}\, X_a X_b = u_{b,0} - u_{a,1} + 4\,\Delta u_a \cdot X_a\,. \qquad (2)$$

Under these conditions the values $u_{b,0} - u_{a,1}$ and Δu_a may be obtained graphically from a plot of $\Delta\Lambda/\mathcal{F}\, X_a X_b$ vs. $4\,X_a$. With the obtained parameters which for the two systems are reported in Table 3, both mobility isotherms may be drawn [1].

System	T °C	Slope · 10^4 ($-\Delta u_a$)	Intercept · 10^4 ($u_{a,1} - u_{b,0}$)
(Tl—Rb) NO_3	325	0	0
(Na—Rb) NO_3	325	0.47	1.02
(Na—Rb) NO_3	400	0.67	1.40

Table 3. Slope and intercept of the straight line corresponding to Eq. (2) applied to (Tl—Rb) NO_3 at 325 °C and to (Na—Rb) NO_3 at 325 °C and 400 °C; values expressed in $cm^2 \cdot sec^{-1} \cdot Volt^{-1}$.

A comparison of the calculated mobilities with the experimental ones is shown in Fig. 3. In the case of the (Tl—Rb) NO_3 system, because Λ is linear with composition, one obtains directly $u_{Tl} = u_{Rb}$ (in the whole composition range) and a linear trend for both mobilities from $u_{Tl,1}$ to $u_{Rb,1}$ [1].

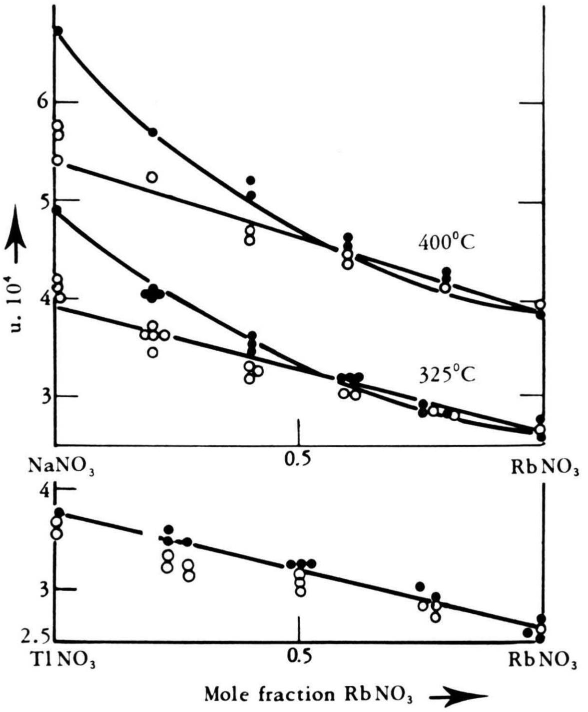

Fig. 3. Comparison between theoretical and experimental mobilities as a function of composition for the systems (Na—Rb) NO_3 (above, ●=Na^+, ○=Rb^+) and (Tl—Rb) NO_3 (below, ●=Na^+, ○=Tl^+). The continuous lines corresponding to the theoretical values have been calculated by means of the parameters of Table 3.

For both systems the agreement between the calculated and experimental mobilities is satisfactory (if the negative deviation from linearity, observed for the mobility of Rb^+ in (Na—Rb) NO_3 is neglected). Figure 4 presents the Arrhenius plot for the Na^+ and Rb^+ mobilities in the (Na—Rb) NO_3 system.

Table 4 and Fig. 5 report the preexponential factors and the activation energies (from the relationship $u = u' \cdot \exp(-\Delta E/R\,T)$ as a function of composition in the (Na—Rb) NO_3 system. The preexpo-

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[6] E. P. Honig and J. A. A. Ketelaar, Trans. Faraday Soc. **62**, 190 [1966].

[7] F. Lantelme and M. Chemla, Bull. Soc. Chim. France **1963**, 2200.

[8] S. Forcheri, Paper presented to the Euchem Conference on Molten Salts, Salice Terme (Italy) 5-10/5/1968.

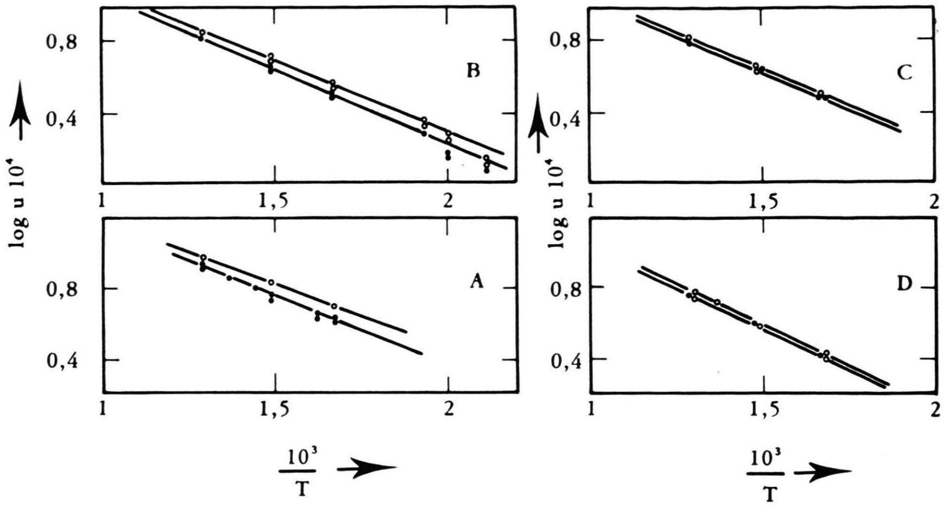

Fig. 4. Arrhenius plots of cationic mobilities for the system (Na—Rb)NO_3. A) $X_{Rb}=0$; B) $X_{Rb}=0.4$; C) $X_{Rb}=0.6$; D) $X_{Rb}=1$; ● $=Na^+$, ○ $=Rb^+$.

X_{Rb}	u'_{Na}	u'_{Rb}	ΔE(Na)	RMS	ΔE(Rb)	RMS
0	80*	85	3.30*	—	3.62	0.17
0.4	77	81	3.65	0.19	3.82	0.18
0.6	88	78	3.95	0.12	3.85	0.15
1	81	77*	4.06	0.18	4.01*	—

* Calculated from conductivity data of ref. [1].

Table 4. Preexponential factors (u', $cm^2 \cdot sec^{-1} \cdot V^{-1}$) and activation energies (ΔE, $kcal \cdot mole^{-1}$) for cationic mobilities in (Na—Rb)NO_3 mixtures. Temperature range 325 ÷ 500 °C.

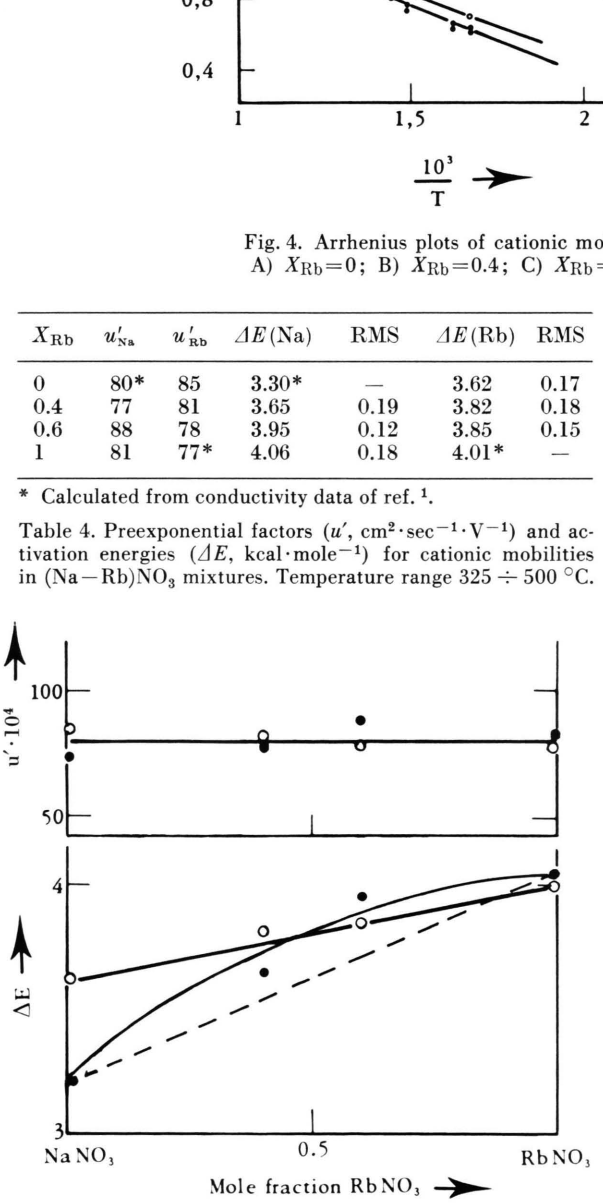

Fig. 5. Preexponential factors (above) and activation energies (below) for the mobility as a function of the composition for the system (Na—Rb)NO_3; ● $=Na^+$, ○ $=Rb^+$.

nential factors of the Arrhenius plots are roughly (within the experimental accuracy) independent of composition. The mobility variations can then be related to the sole variation of ΔE with composition, as previously foreseen [2] (note that the trend of the ΔE_{Na} isotherm is similar to that of the isotherm of the activation energy for the equivalent conductivity; compare Fig. 5 of this paper with Fig. 4 of ref. [9]). If the dependence of the mobility on concentration is considered due only to the variations of the cation-anion interaction because of the polarization of the common anion, the differences $\Delta W_a = \Delta E_{a,0} - \Delta E_{a,1}$, $\Delta W_b = \Delta E_{b,0} - \Delta E_{b,1}$, represent then the contribution of the polarization energy to the activation energy of the mobilities of the cations. These values are (see Table 4 and Fig. 5):

$$\Delta W_{Na} = \sim \quad 0.8 \text{ kcal} \cdot \text{mole}^{-1}, \tag{3}$$

$$\Delta W_{Rb} = \sim -0.4 \text{ kcal} \cdot \text{mole}^{-1}. \tag{4}$$

It results that the polarization plays a more important role for the smaller cation [5, 10]. Moreover, the fact that the two ΔW values have opposite sign indicates that the polarization effect plays an opposite role for the two cations.

From Fig. 5 one may also observe that the ΔE vs. X_b function for Na^+ seems to present a positive deviation from linearity (continuous line in Fig. 5).

[9] V. WAGNER and S. FORCHERI, Z. Naturforsch. **22 a**, 891 [1967].

[10] C. T. MOYNIHAN and R. W. LAITY, J. Phys. Chem. **68**, 3312 [1964].

In the previous paper [2] it has been supposed as a first approximation that ΔE varies linearly with composition [see Eq. (3) of ref. [2]] reaching the maximum value at $X_b = 1$. Nevertheless, the actual ΔE excesses (with respect to the linearity) are not very relevant in determining the trends of the mobility isotherms.

Fig. 6 shows the mobility values for (Na—Rb)NO_3 calculated by the relationships [2]

$$u_{a,x} = u_a' \cdot \exp[-(3.30 + 0.8 \cdot X_b)/RT], \quad (5)$$

$$u_{b,x} = u_b' \cdot \exp[-(4.01 - 0.4 \cdot X_a)/RT]. \quad (6)$$

One can see that in agreement with the above statements, the calculated and experimental values do not differ greatly. This confirms once more the mobility dependence of the activation energy variation.

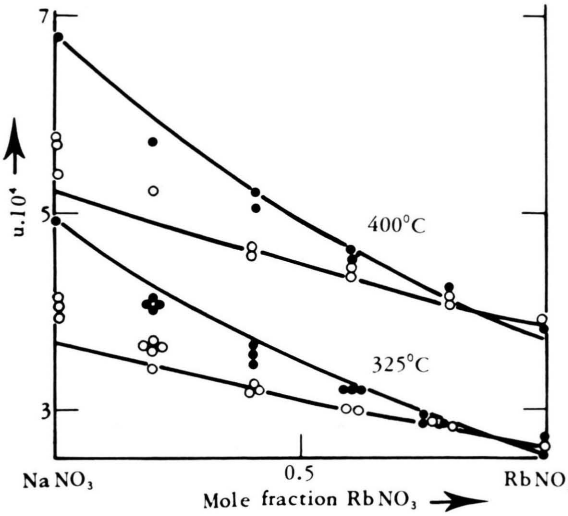

Fig. 6. Comparison between theoretical [continuous lines according to Eqs. (5) and (6)] and experimental mobility values; ● = Na^+, ○ = Rb^+.

The ΔW values are $< RT$, and this implies that the second exponential term of Eqs (5) and (6) may be developed in a power series and all but the quadratic terms neglected in extended composition ranges, without great errors. Accordingly, the linear form of relationships such as Eqs. (1) and (2) seems to be a particular case, valid when the polarization energy contributions are smaller than the thermal energy [2]. It is easy to demonstrate that the $\Delta\Lambda/\mathcal{F} X_a X_b$ vs. X_a plot for the system (Li—K)Cl (the ΔW_{Li} value of which is $> RT$)[10] shows in fact a pronounced curvature.

The (Tl—Rb)NO_3 system is one of the rare systems with mobility values of both cations *nearly equal* (within few percents) in the whole concentration range, and *varying linearly* with composition. The equivalent conductivity isotherm of such a system is also linear in analogy with that of the (Tl—Rb)$_2SO_4$ system [11].

Nearly equal (and constant) mobilities in the whole concentration range are also shown by the (Na—Ag)NO_3 system [12], for which, as in the case of the (Tl—Rb)NO_3 system, the polarization contribution seems to be negligible [1, 2]. It appears therefore that the linearity of the equivalent conductivity and mobility isotherms is a consequence of the negligible polarization contribution. Recently JOSEFSON and KVIST [13], as a conclusion of a series of investigations on the electrical conductivities in binary mixtures of molten monovalent sulphates observed that: "the conductivity excess in only caused by differences in the ionic radii between cations".

This means that the excess is zero when cationic radii are equal (i. e. when the "polarization factor is zero" [1, 2]). Nevertheless, if all excess contributions stem from polarization and if the polarization is negligible, the transport parameters should be independent of composition. Therefore in the case of (Tl—Rb)NO_3 other types of interactions, different from polarization, must be effective. This is probably due to the chemical character of Tl which is intermediate between that of the alkalis and that of silver. In fact, the equivalent conductivity of the pure alkali nitrates [14] (like alkali sulphates [11]) decreases when the crystal cationic radius increases, but the conductivity of $TlNO_3$ is considerably larger than that of $RbNO_3$ [1], despite the cationic radii are nearly equal. The contrary is observed for the corresponding activation energies. A strictly analogous behaviour is also shown by the Tl_2SO_4—Rb_2SO_4 couple [11]; also in this case, in fact, the equivalent

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[11] A. KVIST and K. SCHROEDER, Z. Naturforsch. **23 a**, 676 [1968].

[12] F. R. DUKE, R. W. LAITY, and B. OWENS, J. Electrochem. Soc. **104**, 299 [1957].

[13] A. M. JOSEFSON and A. KVIST, Z. Naturforsch. **24 a**, 466 [1969].

[14] G. J. JANZ, Molten Salts Handbook, Academic Press, New York—London 1967, p. 295.

[15] A. J. DEKKER, Fisica dello Stato Solido, Casa Editrice Ambrosiana, Milano 1965, p. 124.

conductivity of the Tl salt is greater than that of the Rb one, whereas for the activation energy the contrary is observed. The tendency of $TlNO_3$ to decompose prevents the experimental determination of the mobility in $(Tl-Rb)NO_3$ in an extended temperature range. Nevertheless, the activation energies for the mobilities may be evaluated by supposing that the equivalent conductivity isotherms are linear also at $T > 325\ ^\circ C$ (this may be verified at $T = 350\ ^\circ C$ by means of the previously reported results[1]). By applying in fact the previous procedure[1] [see Eq. (2)] one deduces that the linearity and the coincidence of the cationic mobility isotherms is maintained (see Figs. 2, 3). Consequently the activation energy for the cationic mobilities should result to be nearly equal at each composition and to vary linearly with composition between

$$\Delta E(TlNO_3) \cong (3{,}2 \pm 0{,}1)\ \text{kcal}\cdot\text{mole}^{-1}\ {}^{9}$$

and $$\Delta E(RbNO_3) \cong (4{,}1 \pm 0{,}1)\ \text{kcal}\cdot\text{mole}^{-1}\ {}^{1,9}.$$

The activation energy for the equivalent conductivity in mixture should then coincide with the value common to the two cations, and therefore it should vary linearly with the composition. This point has been effectively verified in a previous work[9]. If one admits that the anion polarization is related to the difference between the cationic radii (or to the difference between the molar volumes of the components)[1] it is obvious that the variation with composition of the activation energy for the conductivity as well as the mobilities in the $(Tl-Rb)NO_3$ system cannot be caused by the anion polarization[16].

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[16] Recently the effect of the NO_3^- polarization on the electrical and diffusional mobilities, in alkali nitrate systems, has also been stressed by Jan C. TH. KWAK and J. A. A. KETELAAR (J. Phys. Chem. **73**, 94 [1969]).

X. Die Kinetik der Selbstdiffusion von Ba- und Sr-Ionen in synthetischem Zeolith

Isotopenaustausch-Untersuchungen an Silicat-Ionenaustauschern

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(Z. Naturforsch. **24 a**, 1784—1790 [1969]; eingegangen am 7. August 1969)

The isotopic exchange in Ba- and Sr-Zeolite X has been investigated over the entire range of the process. A special solution of the diffusion equation for the relevant case has been applied to evaluate self-diffusion measurements.

The diffusion process was found to be non-uniform. It has been shown that 80% of the exchangeable Ba-ions and 65% of the Sr-ions diffuse with a high diffusion coefficient and the remainder with a low one. They differ by four to five orders of magnitude at room temperature. In the temperature range 120° to 0 °C the activation enthalpy for the slow process is about twice as high as for the fast process.

This behaviour is explaned in terms of cation location in the zeolite X lattice. The cations are accommodated in two types of channel systems which are assumed to be separated from each other at least with respect to alkaline earth ions. The cation position within the channel systems are discussed.

Die in der III. Mitteilung[1] beschriebene Messung des Sr-Isotopenaustausches in Zeolith X bei 20 °C hatte ergeben, daß der Gesamtaustauschprozeß aus zwei Teilprozessen mit extrem unterschiedlichen Austauschgeschwindigkeiten besteht. Dabei ist der geschwindigkeitsbestimmende Schritt bei beiden Teilprozessen die Volumendiffusion. Etwa 70% der insgesamt vorhandenen Ionen werden schnell ausgetauscht. Ausgangspunkt der Untersuchungen war die Tatsache, daß im Zeolith X die Kationen auf drei strukturell ungleichwertigen Typen von Gitterplätzen untergebracht sein können, wobei der Besetzungsgrad der Positionen von der Art der Kationen abhängt. Wegen experimenteller Schwierigkeiten infolge der hohen Austauschgeschwindigkeit sind Selbstdiffusionsmessungen an diesen Zeolithen bis-

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[1] E. HOINKIS u. H. W. LEVI, Naturwiss. **53**, 500 [1966].