Transport Numbers of Molten (Cs, Ag) J and (Alk, Ag) Br Mixtures, Alk = Na, K, Rb, Cs

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The transport numbers of the molten systems (Cs, Ag) J, (Na, Ag) Br, (K, Ag) Br, (Rb, Ag) Br, and (Cs, Ag) Br have been determined by e.m.f. measurements on concentration cells with transference. We find again an inversion point (the mobility ratio reverses at a certain molar ratio) within experimental accuracy with the exception of (Na, Ag) Br and (K, Ag) Br, where the composition dependence is close to $t_{\mathrm{Alk}} = x_{\mathrm{AlkX}}$.

In previous papers [1, 2] we determined the transport numbers of the cation constituents of the systems (Li, Ag) Cl, (Na, Ag) Cl, (K, Ag) Cl, (Rb, Ag) Cl, and (Cs, Ag) Cl as well as (Na, Ag) J, (K, Ag) J, and (Rb, Ag) J by e.m.f. measurements on concentration cells with transference. Using the same method we now have measured the transport numbers of (Cs, Ag) J, (Na, Ag) Br, (K, Ag) Br, (Rb, Ag) Br, and (Cs, Ag) Br between 700 K and 1100 K.

The e.m.f. measurements are evaluated according to

$$t_\alpha = - x_{\mathrm{AlkX}} (\Phi'_{\mathrm{BB}} / \Phi'_{\mathrm{BC}}) , \qquad (1)$$

where t_α denotes the transport number of the alkali ion constituent, x_{AlkX} the mole fraction of the alkali halide. Φ_{BB} and Φ_{BC} are the e.m.f.'s of the concentration cell with silver electrodes and of the chemical cell, referred to the standard melt, respectively. The prime in (1) indicates the derivation with respect to x_{AgX}. The Φ_{BC}-values used for the calculation of the transport numbers were taken from the literature [3–7] and were linearly extrapolated to 1100 K. Unfortunately, Φ_{BC}-values are not available for all compositions and hence transport numbers can be calculated only for a restricted concentration range. The measured e.m.f. Φ_{BB} also shows a linear temperature dependence at constant composition:

$$\Phi_{\mathrm{BB}} = c + dT . \qquad (2)$$

The coefficients c and d for the five systems are gathered in Table 1 together with the maximum and mean errors of the Φ_{BB}-measurements. The composition and temperature dependence of the transport numbers may be represented by the polynomial

$$t_{\alpha,\mathrm{fit}} = x_{\mathrm{AlkX}} + x_{\mathrm{AlkX}} (1 - x_{\mathrm{AlkX}}) \cdot [(q_0 + q_1 \ln T) + (r_0 + r_1 \ln T)\, x_{\mathrm{AlkX}} + (s_0 + s_1 \ln T)\, x^2_{\mathrm{AlkX}}] . \qquad (3)$$

Equation (3) gives an excellent fit of the transport numbers for all five systems over the total temperature and composition ranges covered in this work. The constants $q_0, \ldots, s_1$ of (3) are given in Table 2. Table 3 lists the transport numbers t_α for all five systems at 960 K, calculated according to (1). The values for the maximum error, δt_α, and for the mean error, $\overline{\delta t_\alpha}$, given in Table 3 also include the experimental errors δt_α and $\overline{\delta t_\alpha}$ of the Φ_{BC}-measurements.

Figure 1 shows the transport numbers of the alkali iodide–silver iodide systems of the previous paper [2] supplemented with those of (Cs, Ag) J at 960 K, measured in this work. The dots in Fig. 1 represent the values obtained from (1), the full lines are from the polynomial fits according to (3). The dashed-dotted line is drawn through the experimental points, since (3) does not fit the data accurately in this range. Figure 2 shows the transport numbers of the alkali ion constituents in the molten mixtures (Na, Ag) Br, (K, Ag) Br, (Rb, Ag) Br, and (Cs, Ag) Br, measured in this work, as functions of composition at 960 K. The dashed line represents the extrapolation of the fit according to (3). This extrapolation yields reasonable results for (Rb, Ag) Br, but leads to t_{Cs}-values larger than unity for (Cs, Ag) Br as well as, though less pronounced, for

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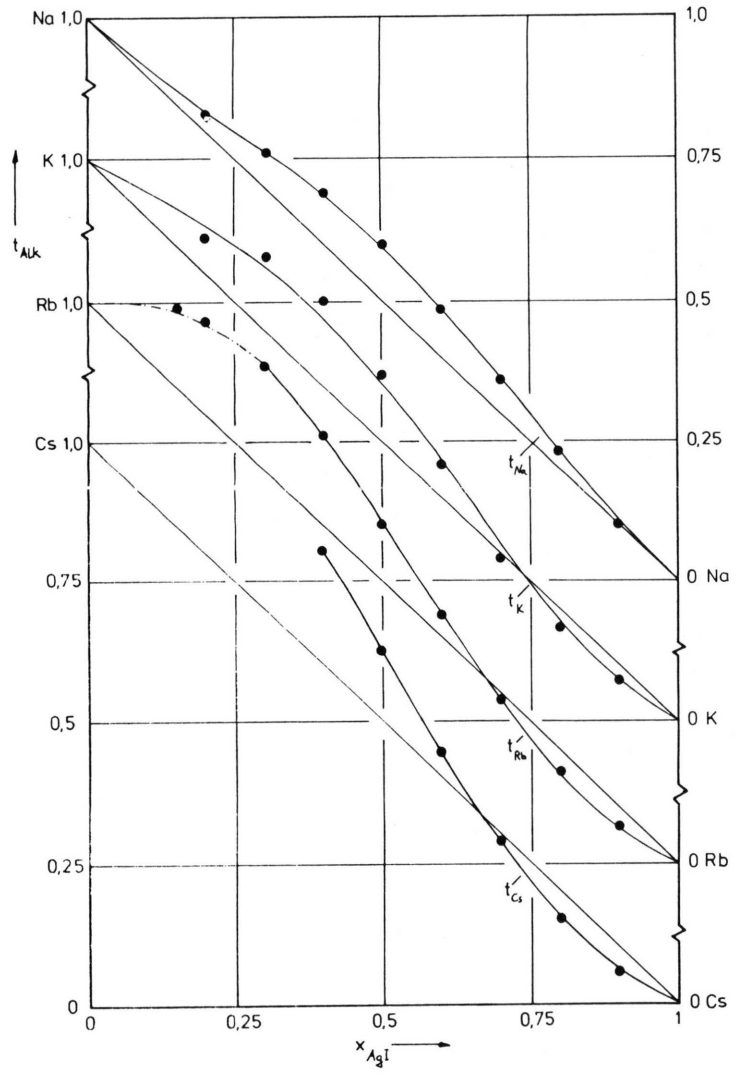

Fig. 1. Transport numbers of the alkali ion constituents in the systems (Na,Ag) J, (K,Ag) J, (Rb,Ag) J, and (Cs,Ag) J at 960 K as function of the mole fraction x_{AgJ}.

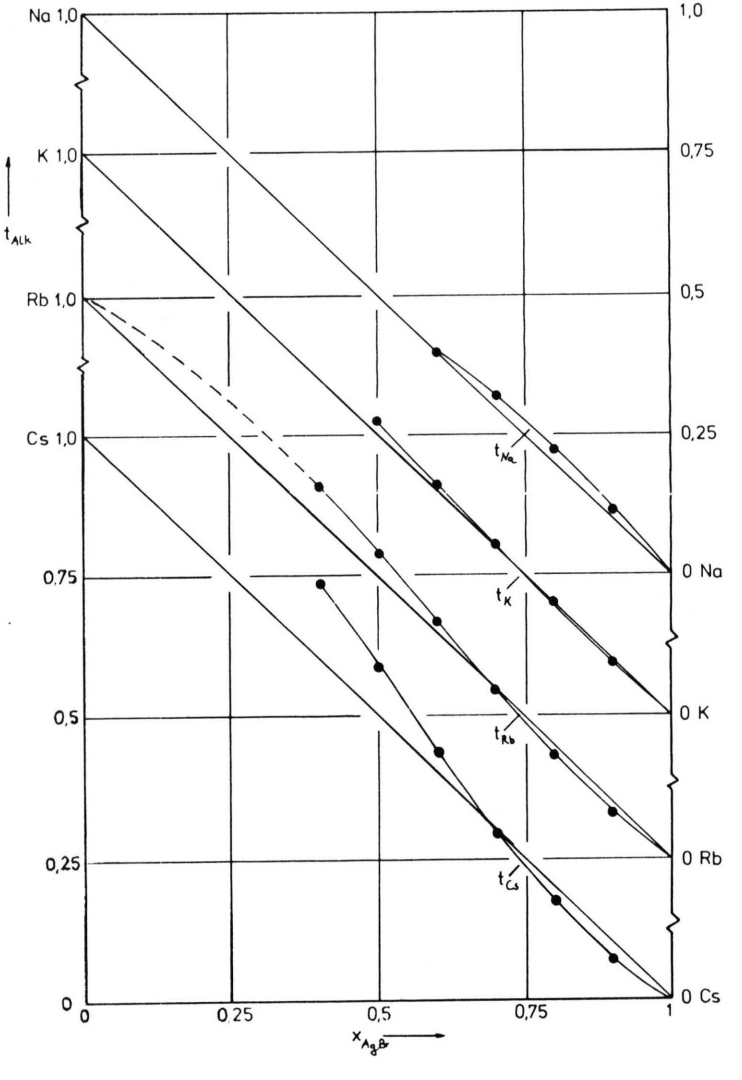

Fig. 2. Transport numbers of the alkali ion constituents in the systems (Na,Ag) Br, (K,Ag) Br, (Rb,Ag) Br, and (Cs,Ag) Br at 960 K as function of the mole fraction x_{AgBr}.

Table 1. The constants c and d of (2) for the evaluation of the e.m.f. Φ_{BB} of the systems (Cs, Ag) J, (Na, Ag) Br, (K, Ag) Br, (Rb, Ag) Br, and (Cs, Ag) Br. Mean deviation $\overline{\delta\Phi_{BB}}$ and maximum deviation $\delta\Phi_{BB}$.

System	Mole fraction x_{AgX}	Constants c / mV	Constants $-d \cdot 10^3$ / mV K^{-1}	Mean dev. $\overline{\Delta\Phi_{BB}}$ / mV	Max. dev. $\delta\Phi_{BB}$ / mV
CsJ + AgJ	0.1	−67.12	258.00	1.09	2.18
	0.2	−48.90	194.74	0.94	1.86
	0.3	−27.42	157.81	0.85	1.64
	0.4	−4.18	132.36	0.76	1.47
	0.5	12.82	108.11	0.68	1.29
	0.6	19.61	81.22	0.59	1.09
	0.7	17.88	53.86	0.49	0.88
	0.8	11.93	29.80	0.39	0.66
	0.9	5.86	12.25	0.27	0.43
NaBr + AgBr	0.1	80.03	260.19	1.05	2.10
	0.2	63.47	188.23	0.89	1.76
	0.3	50.88	144.51	0.78	1.57
	0.4	39.93	111.63	0.69	1.31
	0.5	30.81	85.65	0.61	1.13
	0.6	22.76	63.68	0.53	0.96
	0.7	16.26	45.24	0.45	0.79
	0.8	10.48	28.96	0.36	0.62
	0.9	5.51	14.74	0.25	0.41
KBr + AgBr	0.1	7.60	270.69	1.07	2.14
	0.2	13.14	203.44	0.91	1.81
	0.3	17.84	160.68	0.80	1.58
	0.4	19.95	125.89	0.71	1.37
	0.5	20.34	96.64	0.62	1.18
	0.6	18.17	70.50	0.54	0.99
	0.7	14.28	47.67	0.45	0.80
	0.8	10.22	28.96	0.36	0.62
	0.9	5.82	13.56	0.25	0.41
RbBr + AgBr	0.1	−29.97	264.12	1.06	2.12
	0.2	−15.58	200.02	0.91	1.80
	0.3	−2.07	160.23	0.80	1.58
	0.4	8.93	128.45	0.71	1.38
	0.5	15.52	100.18	0.63	1.19
	0.6	16.84	73.44	0.54	1.00
	0.7	14.44	49.25	0.46	0.81
	0.8	10.72	29.42	0.36	0.62
	0.9	6.74	14.43	0.25	0.41
CsBr + AgBr	0.1	−73.76	257.87	1.05	2.09
	0.2	−52.43	194.79	0.90	1.78
	0.3	−31.24	154.80	0.79	1.55
	0.4	−8.51	127.56	0.71	1.38
	0.5	6.98	101.45	0.63	1.20
	0.6	11.44	71.97	0.54	0.99
	0.7	10.57	46.02	0.45	0.80
	0.8	7.11	24.97	0.36	0.60
	0.9	3.83	10.47	0.25	0.40

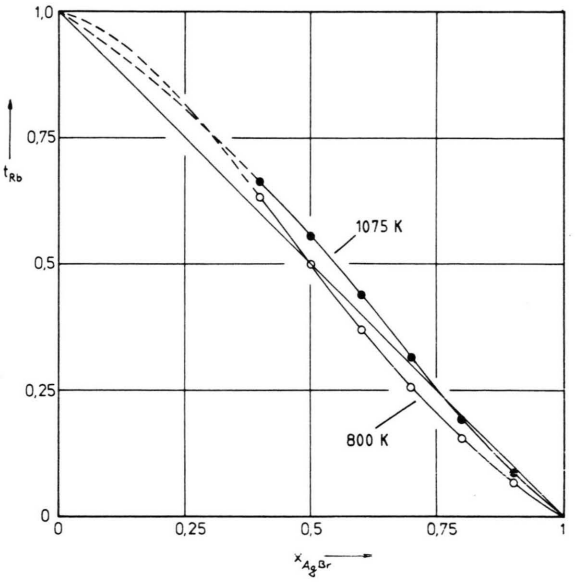

Fig. 3. Concentration dependence of the inversion point at 800 K and 1075 K of the system (Rb, Ag) Br.

(Cs, Ag) J. Φ_{BB}-data exist in the literature [8] for molten (Na, Ag) Br and (K, Ag) Br in composition ranges smaller than covered in this work, but they have not been used to calculate transport numbers. These Φ_{BB}-values agree with our data within the error limits. Laity and Tenney [10] found an inversion point ("crossover point") in the ionic conductances of K^+ and Ag^+ in (K, Ag) Br for $x_{AgBr} = 0.8$ at 823 K by direct current transference experiments combined with equivalent conductance data. This fits quite well with our result on (K, Ag) Br. Poillerat [9] gives transport numbers at five concentrations of the system (Cs, Ag) Br and finds an inversion point at nearly aequimolar mixture. Thus the concentration dependence of his transport numbers differs from ours. In Fig. 3 the concentration dependence of the inversion points at different temperatures is plotted for molten (Rb, Ag) Br. With increasing temperature the inversion point shifts towards mixtures rich in silver bromide. The same trend was observed in the previous investigations [1, 2]. In the systems (Na, Ag) Br and (K, Ag) Br, similar to the systems (Na, Ag) Cl and (Na, Ag) J previously studied, there is only a slight deviation from the relation $t_{Alk} = x_{Alk\,Br}$. The experimental accuracy was not sufficient to prove the existence of an inversion point in these systems.

Table 2. Values of the parameters $q_0, \ldots, s_1$ of Equation (3).

	CsJ+AgJ	NaBr+AgBr	KBr+AgBr	RbBr+AgBr	CsBr+AgBr
q_0	−4.4074	11.6844	−0.0820	−2.5770	−4.2307
q_1	0.5510	−1.6917	−0.0145	0.3271	0.5592
r_0	−26.6566	−140.1591	−37.6998	−25.4197	−21.4254
r_1	4.0501	20.5077	5.6001	3.8540	3.2477
s_0	60.8775	321.4717	62.7063	40.7879	47.7312
s_1	−8.5528	−47.1315	−9.2057	−5.9709	−6.7738

Table 3. Measured transport number t_α (α = Na, K, Rb, Cs), absolute maximum and mean errors, δt_α and $\overline{\delta t_\alpha}$, and fits according to Eq. (3), $t_{\alpha,\mathrm{fit}}$, of the systems (Cs, Ag) J, (Na, Ag) Br, (K, Ag) Br, (Rb, Ag) Br, and (Cs, Ag) Br at 960 K.

x_{AgX}	t_α	δt_α	$\overline{\delta t_\alpha}$	$t_{\alpha,\mathrm{fit}}$
		CsJ+AgJ		
0.4	0.802	0.088	0.022	0.802
0.5	0.622	0.071	0.018	0.623
0.6	0.444	0.053	0.014	0.444
0.7	0.282	0.035	0.010	0.282
0.8	0.150	0.020	0.006	0.151
0.9	0.056	0.008	0.003	0.056
		NaBr+AgBr		
0.6	0.392	0.062	0.017	0.397
0.7	0.315	0.054	0.015	0.315
0.8	0.219	0.038	0.010	0.218
0.9	0.110	0.016	0.005	0.110
		KBr+AgBr		
0.5	0.520	0.084	0.023	0.517
0.6	0.405	0.075	0.021	0.409
0.7	0.299	0.065	0.019	0.300
0.8	0.196	0.051	0.016	0.192
0.9	0.089	0.026	0.009	0.090
		RbBr+AgBr		
0.4	0.653	0.048	0.013	0.653
0.5	0.534	0.043	0.011	0.535
0.6	0.413	0.036	0.009	0.413
0.7	0.293	0.027	0.007	0.292
0.8	0.178	0.018	0.005	0.179
0.9	0.080	0.009	0.002	0.079
		CsBr+AgBr		
0.4	0.738	0.101	0.028	0.737
0.5	0.588	0.089	0.025	0.588
0.6	0.436	0.074	0.022	0.437
0.7	0.294	0.058	0.018	0.296
0.8	0.176	0.044	0.014	0.173
0.9	0.073	0.023	0.008	0.074

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