Fused Salt Concentration Cells with Transference Transport Numbers of Molten Alkali Chloride and Silver Chloride Mixtures

R. Conradt, J. Richter, and H. Wettich
Institut für Physikalische Chemie der RWTH Aachen

Z. Naturforsch. **38 a,** 128–134 (1983); received October 22, 1982

Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

By emf measurements on concentration cells with silver electrodes the transport numbers of molten NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl have been determined over the whole concentration range at temperatures between 800 and 1075 K. All systems show an "inversion point" (equal cation mobilities), which shifts to higher silver chloride concentrations with higher temperatures. At high dilutions the diluted cation is always the less mobile one.

This paper reports on the transport numbers of the systems NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl over the whole concentration range and temperatures between 800 and 1075 K, as obtained from e.m.f.-measurements.

Experimental

The cells were of the type:

$$\begin{array}{c|cc|c||c|cc|c} \text{terminal} & \multicolumn{2}{c|}{\text{electrode}} & \text{melt I} & \text{melt II} & \multicolumn{2}{c|}{\text{electrode}} & \text{terminal} \\ \text{Ag} & \multicolumn{2}{c|}{\text{Ag}} & \text{MCl+AgCl} & \text{MCl+AgCl} & \multicolumn{2}{c|}{\text{Ag}} & \text{Ag} \\ & & & (x_{\text{I}}) & (x_{\text{II}}) & & & \\ \varphi_{\text{VII}} & \varphi_{\text{V}} & \varphi_{\text{III}} & \varphi_{\text{I}} & \varphi_{\text{II}} & \varphi_{\text{IV}} & \varphi_{\text{VI}} & \varphi_{\text{VIII}} \\ \multicolumn{8}{c}{T' \qquad\qquad T'' \qquad\qquad T'' \qquad\qquad T'' \qquad\qquad T'} \end{array} \qquad (1)$$

M stands for Na, K, Rb, and Cs. T' denotes the temperature of the equipment, T'' of the electrodes and the melts. The φ_i are electrical potentials, and x_{I} and x_{II} two different mole fractions of silver chloride. The double line indicates the liquid junction. The measurable e.m.f. $\Phi = \varphi_{\text{VIII}} - \varphi_{\text{VII}}$ depends on the composition and temperature and contains the liquid junction potential $\varphi_{\text{II}} - \varphi_{\text{I}}$.

The experimental setup ressembles that of our previous investigations on molten nitrates [1, 2]. However because of the higher melting temperatures a quartz cell had to be used (Figure 1). The temperature differences between corresponding points of the cell (I and II, III and IV, V and VI, VII and VIII) were within some tenth of a Kelvin and could be neglected. The half cells consist of quartz tubes with a length of 335 mm and an inner diameter of 20 mm. The electrodes are constructed from a 2 mm silver wire, forming a helix at the lower end around the quartz tube for the thermocouple (PtRh 90/10-Pt, Heräus).

The two half cells are joined by a capillary tube, 3 mm inner diameter, according to Figure 1. In the capillary tube the more dense melt is layered below the less dense melt at S'. The distance of the interface from the electrodes is long enough to ensure constancy of the concentrations near the electrodes within the time of measurement. Popescu [3] did show that concentration cells of that type are best adapted to carry out e.m.f. measurements on diffusion potentials.

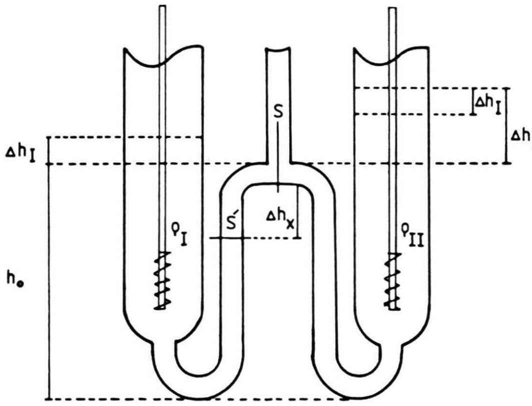

Fig. 1. Concentration cell with free liquid junction.

Reprint requests to Prof. Dr. J. Richter, Institut für Physikalische Chemie der RWTH Aachen, Templergraben 59, D-5100 Aachen, Germany.

0340-4811 / 83 / 0200-0128 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

Concentration differences $|x_{\mathrm{I}} - x_{\mathrm{II}}| \leqq 0.2$ where used. All measurements were summed up and referred to pure AgCl. The temperatures were chosen according to the phase diagram of the mixtures [4]. As highest temperatures, 1090 K was chosen for NaCl + AgCl and 1075 K for the three other systems. The lowest temperature was some 10 K higher than the melting point of the higher melting component, but at least at 775 K, which is above the melting point for the reference melt AgCl (730 K). Due to suggestions by Stern [5, 6] that at mole fractions $x_{\mathrm{AgCl}} \leqq 0.12$ the reaction

$$\mathrm{Ag} + \mathrm{AlkCl} \rightarrow \mathrm{AgCl} + \mathrm{Alk}$$

takes place, measurements below $x_{\mathrm{AgCl}} = 0.15$ were not evaluated though our own measurements did show that the e.m.f. data below this mole fraction are not affected by this reaction.

The filling amounts of the half cells resulted from the geometry of the cell and the demand that the phases have to meet at the junction level S'. The volumes of the half cells up to the height h_0 (Fig. 1) were evaluated to be 15.5 ml. First the phases are separated by a slight excess pressure of argon, put on the middle capillary tube. When the pressure is reduced, the phases meet at S. In order to shift the junction from S to S' ($\Delta h_x = 10$ mm), an additional volume $\Delta V_{\mathrm{II}} = A \cdot \Delta h_{\mathrm{II}}$ has to be added to phase II with the smaller density ϱ_{II} (A: sectional area of the wide tube). With that the filling amounts of the half cells result to be:

$$m_{\mathrm{I}} = 15.5\ \mathrm{ml}\ \varrho_{\mathrm{I}}\,;$$

$$m_{\mathrm{II}} = (15.5\ \mathrm{ml} + \Delta V_{\mathrm{II}})\, \varrho_{\mathrm{II}}\,.$$

The shift of the interface from S to S', causes a shift of the levels in the wide tubes by $\Delta h_{\mathrm{I}} = 2$ mm.

The densities ϱ_{I} and ϱ_{II} of the mixtures were calculated by linear interpolations from the densities of the pure components [7]. The shift of the junction level from S to S' causes a very narrow zone of mixing. The separation and contacting of the two phases by means of a combined pressure and protective gas apparatus is described in details by Conradt [8].

The cell is heated in a furnace "ASK 200" Fibrothal, Bulten and Kanthal, with three heating zones, each being separately regulated. The e.m.f. of the thermocouples and the electrodes are recorded by a digital multimeter 191, Keithley.

Theory and Results

From the sum of the equilibrium potential difference $(\varphi_{\mathrm{I}} - \varphi_{\mathrm{III}}) + (\varphi_{\mathrm{IV}} - \varphi_{\mathrm{II}})$ and the liquid junction potential $(\varphi_{\mathrm{II}} - \varphi_{\mathrm{I}})$, one gets [9] the measurable e.m.f. of the concentration cell with transference (1)

$$F\Phi = RT \int_{\mathrm{I}}^{\mathrm{II}} \frac{t_\alpha}{x_1}\, d\ln(x_2 f_2)\,. \qquad (2)$$

Therein it is assumed that the thermal diffusion potentials $(\varphi_{\mathrm{V}} - \varphi_{\mathrm{III}})$ and $(\varphi_{\mathrm{IV}} - \varphi_{\mathrm{VI}})$ of the electrodes and the contact potentials $(\varphi_{\mathrm{VII}} - \varphi_{\mathrm{V}})$ and $(\varphi_{\mathrm{VI}} - \varphi_{\mathrm{VIII}})$ compensates each other. This is the case in the experiment. F is the Faraday constant, R the gas constant, and T the temperature. t_α is the transport number of the constituent α, $\alpha =$ Na, K, Rb, and Cs. x_1 and x_2 are the mole fractions of component 1 and 2, respectively, and f_2 the activity coefficient of AgCl. In the following x_2 always stand for x_{AgCl}. It has to be stressed that (2) is only valid for melts of the type AC + BC [10]. The common anion constituent $\gamma = \mathrm{Cl}$ is the reference substance of the "Hittorf" frame of reference, where

$$t_\alpha + t_\beta = 1 \quad \text{and} \quad t_\gamma = 0$$

are always valid ($\beta = \mathrm{Ag}$).

From the binary systems mentioned above, three types of isothermal-isobaric galvanic cells may be constructed:

Type BB: B | BC ‖ AC + BC | B
Type CC: C | BC ‖ AC + BC | C
Type BC: B | AC + BC | C.

Cells of the type BB and CC are concentration cells with transference, the e.m.f.'s Φ_{BB} and Φ_{CC} of which are referred to the standard melt. As usual the standard melt is the pure component with the ion species for which the electrodes are reversible ($x_2 = 1$). In Φ_{BB} the noncommon ion constituent determines the potential, in Φ_{CC} the common ion constituent. The cell of the type BC is a chemical cell, whose measurable e.m.f. Φ is referred to the e.m.f. $\Phi^{\bullet}$ of the standard melt: $\Phi_{\mathrm{BC}} = \Phi - \Phi^{\bullet}$.

The e.m.f. Φ_{BB} is given by (2). Cell (1) is an example for the type BB. The e.m.f. Φ_{CC}, according to Haase [9], is

$$F\Phi_{\mathrm{CC}} = RT \int_{\mathrm{I}}^{\mathrm{II}} \frac{t_\alpha - x_1}{x_1}\, d\ln(x_2 f_2) \qquad (4)$$

and the e.m.f. Φ_{BC} is

$$F\Phi_{BC} = -RT\ln(x_2 f_2)\,. \tag{5}$$

The combination of (2), (4), and (5) gives

$$\Phi_{BB} = -\int_{I}^{II} \frac{t_\alpha}{x_1}\left(\frac{\partial \Phi_{BC}}{\partial x_2}\right)_{T,P} \mathrm{d}x_2 \tag{6}$$

or

$$\Phi_{CC} = -\int_{I}^{II} \frac{t_\alpha - x_1}{x_1}\left(\frac{\partial \Phi_{BC}}{\partial x_2}\right)_{T,P} \mathrm{d}x_2\,, \tag{7}$$

respectively. Thus from (6) and (7) taking (5) into account we get

$$\Phi_{CC} = \Phi_{BB} + \Phi_{BC}\,. \tag{8}$$

This means that only two of the three e.m.f.'s of the cells considered above are independent of each other.

Table 1. The constants c and d of (12) for the evaluation of the e.m.f. Φ_{BB} of the system NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl. Mean deviation $\overline{\delta\Phi_{BB}}$ and maximum deviation $\delta\Phi_{BB}$.

System	Mole fraction x_{AgCl}	Constants c mV	$-d\cdot 10^3$ mV K^{-1}	Mean dev. $\overline{\delta\Phi_{BB}}$ mV	Max. dev. $\delta\Phi_{BB}$ mV
NaCl + AgCl	0.15	82.03	216.12	0.7	1.4
	0.2	68.10	181.21	0.6	1.3
	0.3	52.96	137.13	0.5	1.0
	0.4	40.62	105.02	0.4	0.9
	0.5	30.00	79.24	0.4	0.7
	0.6	21.77	58.58	0.3	0.6
	0.7	14.57	40.74	0.2	0.4
	0.8	9.43	26.08	0.2	0.3
	0.9	4.52	12.50	0.2	0.3
KCl + AgCl	0.15	10.65	229.22	0.9	1.7
	0.2	11.76	199.46	0.8	1.6
	0.3	14.28	154.63	0.7	1.3
	0.4	16.11	120.10	0.6	1.1
	0.5	15.08	90.01	0.5	0.9
	0.6	13.51	65.29	0.4	0.8
	0.7	10.81	44.06	0.3	0.6
	0.8	7.36	26.19	0.2	0.4
	0.9	5.00	13.11	0.3	0.5
RbCl + AgCl	0.1	−33.46	265.70	0.8	1.6
	0.2	−21.20	196.75	0.7	1.3
	0.3	− 9.61	153.81	0.5	1.1
	0.4	0.54	120.53	0.4	0.9
	0.5	6.69	91.23	0.4	0.7
	0.6	8.53	64.76	0.3	0.6
	0.7	8.23	42.90	0.2	0.5
	0.8	6.31	25.05	0.2	0.3
	0.9	4.00	11.39	0.2	0.3
CsCl + AgCl	0.1	−85.73	255.87	0.8	1.6
	0.2	−63.51	192.24	0.7	1.3
	0.3	−39.79	153.24	0.6	1.1
	0.4	−16.65	123.66	0.5	1.0
	0.5	− 1.44	95.32	0.4	0.8
	0.6	5.32	67.80	0.3	0.6
	0.7	6.75	43.82	0.2	0.5
	0.8	5.65	24.97	0.2	0.3
	0.9	3.52	11.03	0.2	0.3

For the systems studied in this paper, the equations

$$t_\alpha = -x_1\frac{\Phi'_{BB}}{\Phi'_{BC}} \tag{9}$$

and

$$t_\alpha = x_1 - x_1\frac{\Phi'_{CC}}{\Phi'_{BC}} \tag{10}$$

result from (6) and (7), where the prime indicates differentiation with respect to x_2, at constant T and P. At the concentration where the function $t_\alpha(x_1) - x_1$ changes sign (inversion point), one has

$$\Phi'_{CC} = 0\,. \tag{11}$$

The measured e.m.f. of cell (1) depends linearly on temperature at constant x_2:

$$\Phi_{BB} = c + \mathrm{d}T.$$

In Table 1 the coefficients c and d of the investigated systems are listed together with the maximum and mean error of the e.m.f.

The transport numbers are evaluated according to (9), where also the derivation of Φ_{BC} and with that the activity coefficient comes in. We have suggested a consistency test [11], to be able to choose reliable literature data for Φ_{BC}. According to it, for all four investigated systems, the Φ_{BC}'s of Pelton and Flengas [12] were taken for the evaluation of (9). The experimental transport numbers may be fitted by the following polynomial depending on the composition and the temperature of the melt:

$$t_{\alpha_{\mathrm{fit}}} = x_1 + x_1 x_2\,[(q_0 + q_1\ln T) + (r_0 + r_1\ln T)\,x_1 + (s_0 + s_1\ln T)\,x_1^2]\,. \tag{13}$$

Looking at the concentration dependence, (13) has the form of an extended Porter expression.

For all four systems the values of the constants $q_0, \ldots, s_1$ are summed up in Table 2. They are at least valid in the temperature range from 500 to 800 °C. Table 3 lists the transport numbers t_α of all four systems at 1075 K as calculated according to (9), the absolute maximum errors δt_α, the mean errors $\overline{\delta t_\alpha}$, the parameters of the polynomial (13), and the mobility ratios u_α/u_β. The errors listed in Table 3 result from the propagation of the mean and maximum errors of the e.m.f. values entering

Table 2. Values of the parameters $q_0, \ldots, s_1$ of (13).

	NaCl + AgCl	KCl + AgCl	RbCl + AgCl	CsCl + AgCl
q_0	-6.7573	-2.2653	-1.8900	-4.8507
q_1	0.9487	0.2762	0.2219	0.6562
r_0	28.1197	-14.4401	-15.1501	-10.3731
r_1	-3.9293	2.2774	2.3729	1.6496
s_0	-39.4882	15.0086	14.7740	21.8325
s_1	5.6093	-2.2479	-2.1969	-3.1666

Table 3. Transport numbers, t_α (α = Na, K, Rb, Cs), absolute maximum and mean errors, δt_α and $\overline{\delta t_\alpha}$, fits according to (13), $t_{\alpha \text{fit}}$, and mobility ratio, u_α/u_β, of the systems NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl at 1075 K.

x_{AgCl}	t_α	δt_α	$\overline{\delta t_\alpha}$	$t_{\alpha \text{fit}}$	u_α/u_β
		NaCl + AgCl			
0.1	–	–	–	0.920	1.278
0.2	0.83_0	0.06_0	0.01_0	0.833	1.247
0.3	0.73_5	0.06_5	0.01_5	0.739	1.213
0.4	0.65_5	0.08_5	0.01_5	0.639	1.180
0.5	0.53_0	0.08_0	0.01_5	0.532	1.137
0.6	0.41_0	0.06_5	0.01_5	0.421	1.091
0.7	0.31_0	0.05_0	0.01_0	0.309	1.043
0.8	0.20_0	0.03_5	0.00_5	0.198	0.988
0.9	0.09_5	0.02_0	0.00_5	0.094	0.934
		KCl + AgCl			
0.1	–	–	–	0.938	1.681
0.2	$0{,}90_0$	0.04_5	0.01_0	0.863	1.575
0.3	0.76_5	0.05_5	0.01_0	0.773	1.459
0.4	0.68_0	0.05_5	0.01_0	0.670	1.354
0.5	0.55_5	0.05_5	0.01_0	0.555	1.247
0.6	0.43_0	0.05_0	0.01_0	0.433	1.146
0.7	0.30_5	0.03_5	0.01_0	0.308	1.039
0.8	0.18_5	0.02_0	0.00_5	0.188	0.926
0.9	0.08_5	0.01_5	0.00_5	0.082	0.804
		RbCl + AgCl			
0.1	–	–	–	0.943	1.838
0.2	0.87_0	0.02_5	0.00_5	0.869	1.658
0.3	0.78_0	0.03_0	0.01_0	0.778	1.502
0.4	0.66_5	0.03_5	0.00_5	0.673	1.372
0.5	0.54_5	0.03_5	0.00_5	0.556	1.252
0.6	0.44_5	0.03_0	0.00_5	0.432	1.141
0.7	0.31_5	0.03_0	0.00_5	0.307	1.034
0.8	0.18_5	0.02_0	0.00_5	0.187	0.920
0.9	0.08_0	0.01_0	0.00_0	0.082	0.804
		CsCl + AgCl			
0.1	–	–	–	0.948	2.026
0.2	0.86_5	0.04_5	0.01_0	0.875	1.750
0.3	0.79_5	0.05_0	0.01_0	0.783	1.546
0.4	0.69_0	0.05_0	0.01_0	0.676	1.391
0.5	0.55_0	0.04_5	0.01_0	0.558	1.262
0.6	0.42_5	0.04_0	0.01_0	0.434	1.150
0.7	0.31_0	0.03_5	0.01_0	0.310	1.048
0.8	0.19_5	0.02_5	0.00_5	0.192	0.950
0.9	0.08_5	0.02_0	0.00_5	0.086	0.847

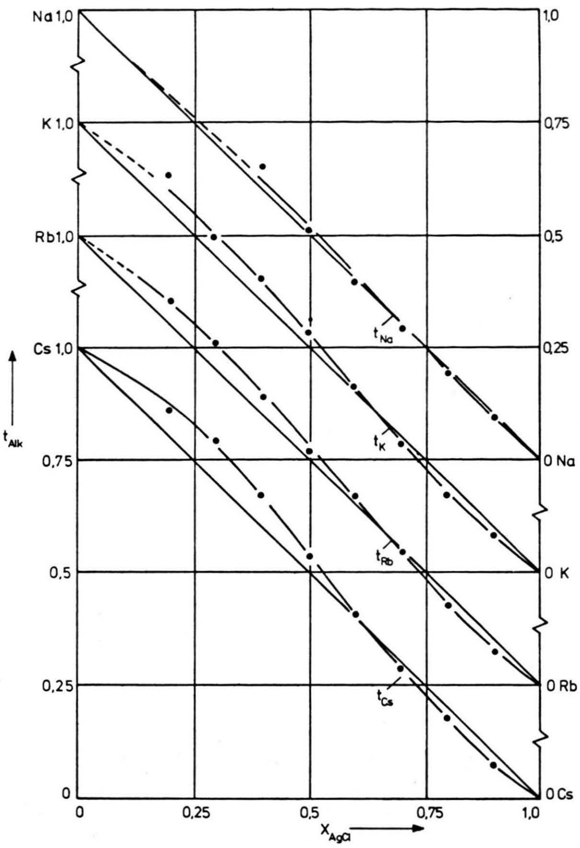

Fig. 2. Transport number of the alkali ion constituents in the systems NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl at 960 K as a function of the mole fraction x_{AgCl}.

(9). Figure 2 shows the concentration dependence of the transport numbers of the alkali ion constituents in the systems NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl, all at 960 K.

Discussion

The occurrence of inversion points, which has been discovered in 1960 by Périé and Chemla [13], is well settled for many systems but in some cases there exist controversary experimental results. Thus for the systems $AgNO_3 + KNO_3$ and $AgNO_3 + RbNO_3$ at 350 °C inversion points have been found at Aachen [2], [1] while they would not exist according to Duke and Owens [14] and to Okada and Kawamura [15], respectively. Therefore, in the following it shall be investigated if for the four systems of the present study the existence of inversion points withstands

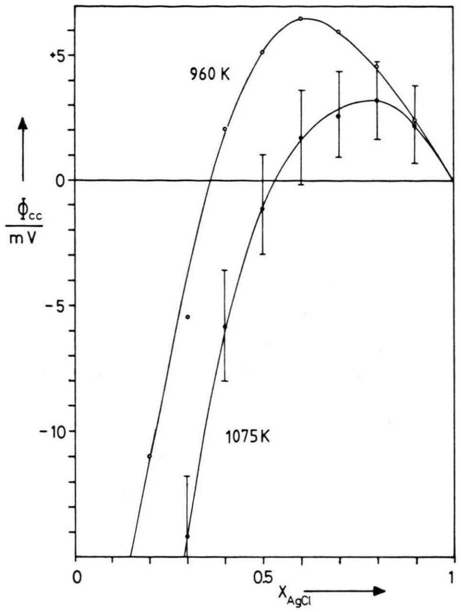

Fig. 3. E.m.f. Φ_{CC} of the system CsCl + AgCl at 1075 K and 960 K. The dashes represent the maximum errors of Φ_{CC}.

critical discussion. To do this with (8) we calculated by means of the Φ_{BC}-values of Pelton and Flengas [12] and our Φ_{BB}-values, the Φ_{CC}-values as well as the maximum error. In Figure 3 the concentration graph Φ_{CC} of the system CsCl + AgCl is plotted at 960 and 1075 K. According to (11) the inversion point is marked by $\Phi'_{CC} = 0$. The related maximum shows up very clearly, even when we consider the maximum error. With that, the existence of the inversion point in the system CsCl + AgCl (Figure 2) is unambigously proven. The same holds for KCl + AgCl, RbCl + AgCl and – though the absolute values of Φ_{CC} are very small – also for NaCl + AgCl, if only the mean errors are discussed. The temperature dependence of the inversion point is demonstrated in Figure 4 for the system CsCl + AgCl. Murgulescu and Popescu [16] give Φ_{CC}-values calculated from Φ_{BC} and Φ_{BB} for the melts here investigated which are in good accordance with our values, if NaCl + AgCl is excluded. But as in their experiments there was always $x_{\mathrm{I}} + x_{\mathrm{II}} = 1$ they were not suited to find inversion points.

Our investigation shows that none of the systems satisfies the equation $t_\alpha = x_{\mathrm{I}}$ over the whole concentration range. Instead we find a clear deviation from linearity. This deviation is of the same kind for all systems. It is negative when the silver chloride concentration is high, and positive when it is low. The inversion point characterises the composition where the mobilities of the cations are equal, as is evident from the definition of the ion mobilities u_α and u_β:

$$u_\alpha = \frac{t_\alpha}{x_{\mathrm{I}}} \cdot \frac{\Lambda}{F}, \qquad u_b = \frac{t_\beta}{x_2} \cdot \frac{\Lambda}{F}, \tag{14}$$

where Λ is the equivalent conductance. With rising temperature the composition with equal cation mobilities shifts to melts with higher silver chloride

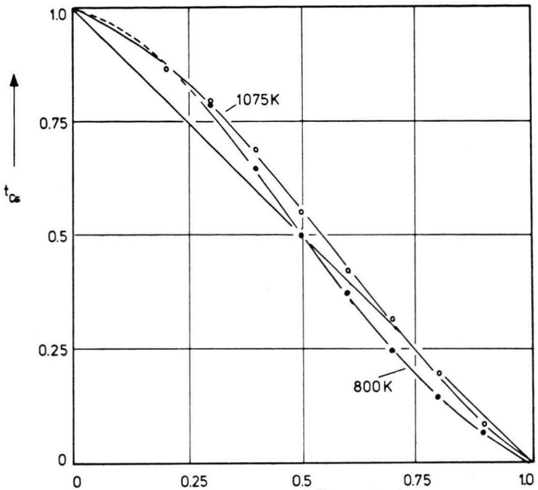

Fig. 4. The concentration dependence of the inversion point at different temperatures of the system CsCl + AgCl.

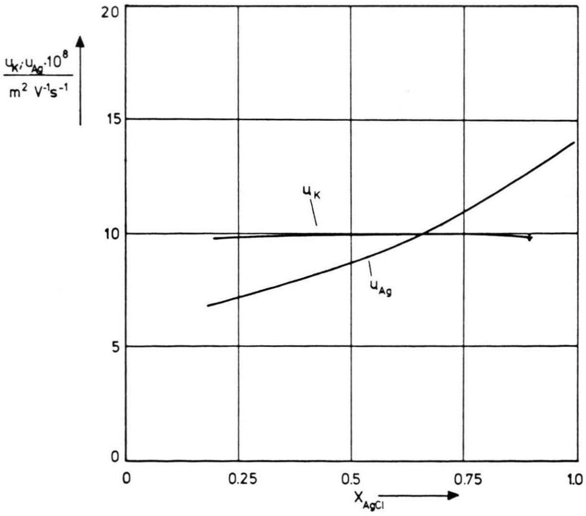

Fig. 5. Ion mobilities of the ion constituents K and Ag of the system KCl + AgCl at 960 K as a function of the mole fraction x_{AgCl}.

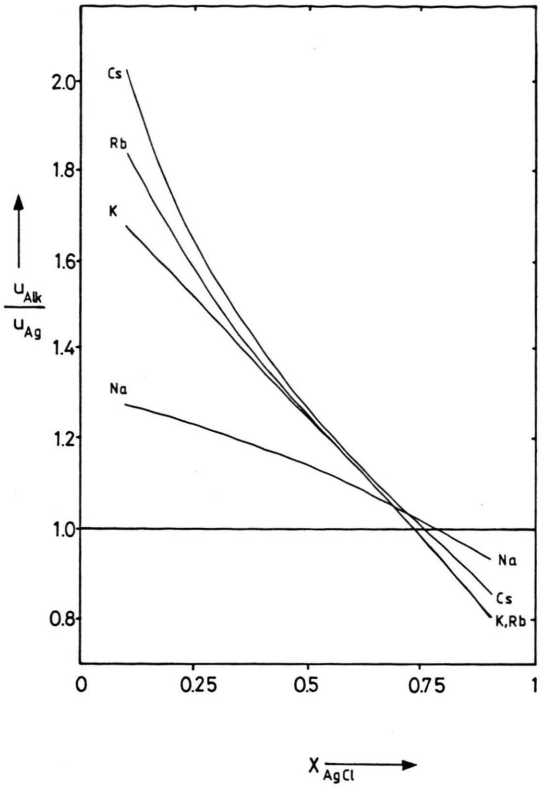

Fig. 6. Mobility ratios of NaCl + AgCl, KCl + AgCl, RbCl + AgCl, and CsCl + AgCl at 1075 K as a function of the mole fraction x_{AgCl}.

concentrations (Figure 4). Analogous shifts, in the sense that with rising temperature the less mobile ions become the more mobile ones in ever larger ranges of their concentration, have been observed for the systems LiBr + KBr [17], $AgNO_3 + RbNO_3$ [2], $LiNO_3 + TlNO_3$ [18], $LiNO_3 + KNO_3$ [19], $LiNO_3 + RbNO_3$ [20], $LiNO_3 + CsNO_3$ [20], $NaNO_3 + KNO_3$ [21] and $NaNO_3 + CsNO_3$ [22]. Examples for the opposite behaviour are not known.

From the transport number, the electric conductance, and the density the ion mobilities may be calculated according to (14).

Only for the system KCl + AgCl could data of electric conductance and density be found in literature [9, 23], and also here interpolation is necessary. In Figure 5 the concentration dependence of the mobilities of the ion constituents K and Ag are plotted at 960 K. Beside the already discussed inversion point, it shows a pronounced concentration dependence for u_{Ag}, but only a minor one for u_K. The more or less concentration independent behaviour of K indicates a similar interaction between K and K as between K and Ag. The interactions between Ag and Ag seems to differ clearly from the former. A similar tendency – but not so distinctive – was also found with the systems $(K, Rb, Cs)NO_3 + AgNO_3$ [2]. In Fig. 6 the mobility ratios u_α/u_{Ag} at 1075 K are plotted for the four considered systems.

Acknowledgements

The authors express their thanks to the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, Düsseldorf, for financial support of this study.

[1] J. Richter and E. Amkreutz, Z. Naturforsch. **27a,** 280 (1972).
[2] J. Richter, U. Gasseling, and R. Conradt, Electrochim. Acta **23,** 1165 (1978).
[3] L. Popescu, Rev. Roum. Chim. **21,** 359 (1976).
[4] N. K. Voskresenskaya, Handbook of Solid-Liquid Equilibria in Systems of Anhydrous Inorganic Salts, Vol. 1, Israel Program for Scientific Translations, Jerusalem 1970.
[5] K. H. Stern, J. Phys. Chem. **60,** 679 (1956).
[6] K. H. Stern, J. Phys. Chem. **62,** 385 (1958).
[7] G. J. Janz, F. W. Dampier, G. R. Lakshminarayanan, P. K. Lorenz, and R. P. T. Tomkins, Molten Salts: Vol. 1, Nat. Stand. Ref. Data Sev. NBS (U.S.) **15,** (Oct. 1968).
[8] R. Conradt, Thesis, Aachen 1981.
[9] R. Haase, Electrochim. Acta **23,** 391 (1978).
[10] J. Richter, Ber. Bunsenges. Phys. Chem. **72,** 681 (1968).
[11] J. Richter, R. Conradt, and R. Becker, Z. Naturforsch. **36a,** 1100 (1981)
[12] A. D. Pelton and S. N. Flengas, J. Electrochem. Soc. **117,** 1130 (1970).
[13] J. Périé and M. Chemla, C. R. Acad. Sci. (France) **250,** 3986 (1960).
[14] F. R. Duke and B. Owens, J. Electrochem. Soc. **105,** 476 (1958).

[15] I. Okada and K. Kawamura, Electrochim. Acta **19,** 777 (1974).

[16] J. G. Murgulescu and L. Popescu, Rev. Roum. Chim. **18,** 737 (1973).

[17] O. P. Metho, F. Lantelme, and M. Chemla, Electrochim. Acta **14,** 505 (1969).

[18] K. Kawamura, I. Okada, and O. Odawara, Z. Naturforsch. **30 a,** 69 (1975).

[19] F. Lantelme and M. Chemla, Electrochim. Acta **10,** 663 (1965).

[20] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **34 a,** 498 (1979).

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

[22] C. Yang, R. Takagi, and I. Okada, Z. Naturforsch. **34 a,** 1186 (1980).

[23] G. J. Janz, R. P. T. Tomkins, C. B. Allen, J. R. Downey Jr., G. L. Gardner, N. Krebs, and S. K. Singer, J. Phys. Chem. Ref. Data **4,** 871 (1975).