Thermoelectric Properties in Silver Bromide-Alkali Bromide Fused Mixtures *

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Using a silver electrode thermocell, the initial thermoelectric power of the molten salt mixtures (Ag+Me)Br (Me=Li, Na, K, Rb, Cs) has been measured around 700 °C.

These data enable to obtain relative values of the heats of transport for the alkali cations in pure bromides and also to discuss the behaviour of the mixtures in respect to the heat and electricity transport. Finally a comparison is made with the correspondent values obtained for the alkali chlorides.

Previous works [1] have reported measurements of initial thermoelectric power for the molten systems (Ag + Me)Cl (Me = alkali cation). In order to obtain a useful comparison, the present paper reports similar data for the family of the molten systems (Ag + Me)Br. Measurements have been carried out at various temperatures around 700 °C for different concentrations, using the same experimental features already described [1].

Results and Discussion

Figure 1 reports the values of the thermoelectric power (ε) of pure fused AgBr. These data can be expressed by the relation:

$$\varepsilon_{AgBr} = (-365 - 0.100\,t\,^{\circ}C)\ \mu V \cdot deg^{-1}. \quad (1)$$

Compared to the AgCl it is interesting to observe the increase in the absolute value of ε_{AgBr} as the temperature increases.

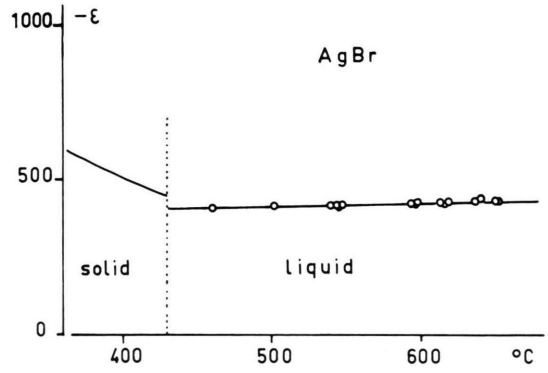

Fig. 1. Values of the thermoelectric power for pure fused AgBr as a function of temperature.

Table 1 reports the final results for the five binary mixtures examined. These data were obtained

x_{AgBr}	System (Ag + Li)Br		System (Ag + Na)Br		System (Ag + K)Br		System (Ag + Rb)Br		System (Ag + Cs)Br	
	$-\varepsilon$	Ψ	$-\varepsilon$	Ψ	$-\varepsilon$	Ψ	$-\varepsilon$	Ψ	$-\varepsilon$	Ψ
1.00	434	0.00	434	0.00	434	0.00	434	0.00	434	0.00
0.90	406	0.86	393	1.15	390	1.22	389	1.22	378	1.50
0.80	381	1.67	366	2.01	366	2.01	365	2.01	362	2.10
0.70	365	2.30	356	2.51	352	2.60	352	2.60	347	2.71
0.60	362	2.67	348	3.00	342	3.14	345	3.07	318	3.69
0.50	362	3.04	354	3.22	336	3.64	337	3.61	309	4.26
0.40	360	3.53	357	3.60	340	3.99	330	4.22	306	4.77
0.30	337	4.63	368	3.91	338	4.60	334	4.70	322	4.97
0.20	335	5.48	400	3.98	346	5.23	369	4.70	343	5.29
0.10	370	6.05	460	3.97	401	5.33	—	—	389	5.61
0.05	—	—	—	—	—	—	477	4.96	444	5.72
Ψ_0 (e.u.)		6.0		4.0		5.1		5.0		6.0
ΔQ (Kcal mole^{-1})		5.8		3.9		5.0		4.9		5.8

Table 1. Interpolated values of the thermoelectric power ε (μV deg^{-1}) and of the Ψ function (cal deg^{-1} mole^{-1}) for the systems (Ag+Me)Br at 700 °C. At the bottom there are also the Ψ_0 values (obtained by extrapolation of Ψ for $x_{AgBr} \to 0$) and the relative values ΔQ of the cationic heats of transport.

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[1] C. SINISTRI and E. PEZZATI, Z. Naturforsch. **25 a**, 893 [1970]; **22 a**, 590 [1967].

measuring the ε values at various temperatures around 700 °C and then interpolating them: in the case of the mixtures it was generally observed that the absolute values of ε decrease as the temperature increases.

Thermoelectric power measurements at zero time for the fused mixture (Ag + K) Br have been recently reported by CONNAN et al.[2]. Unfortunately these data are only in graphical form, thus a direct comparison is difficult; nevertheless the agreement seems good.

Values of ε vs. concentration at 700 °C for the five systems AgBr + MeBr are reported in Fig. 2. In

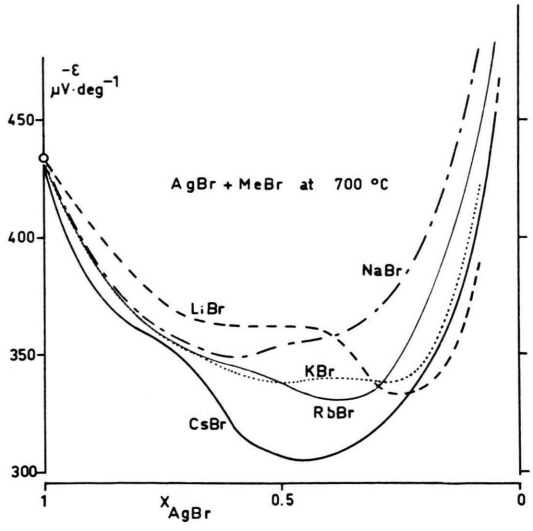

Fig. 2. Values of ε vs. composition for the systems (Ag+Me)Br (Me=alkali cation) at 700 °C.

comparison to the chloride family it is interesting to observe that the ε values show a more irregular behaviour: also in this case the function of the mixture containing Li intersects the ones of all the other systems at low concentration of AgBr.

Table 1 reports also values of the Ψ function, already defined in previous papers [1, 3]. The behaviour of the $\Psi(x_{AgBr})$ functions is shown in Fig. 3. Concerning the excess entropies of these systems the following information is reported in literature.

KLEPPA et al.[4] propose, on the basis of enthalpy measurements in connection with electrochemical data[5], the following values of excess entropies for equimolar mixtures (550 – 600 °C):

$$(Ag + Li)\,Br\ S^e_{0.5} = -0.12;$$
$$(Ag + Na)\,Br\ S^e_{0.5} = -0.06;$$
$$(Ag + K)\,Br\ S^e_{0.5} = -0.20;$$
$$(Ag + Rb)\,Br\ S^e_{0.5} = -0.33 \text{ e. u.}$$

Thus they conclude that "small negative excess entropies may be a common occurrence in this type of solution systems". The values reported by JANZ[6], on the basis of electrochemical measurements of the literature, show that $(s^e_{AgBr_2})_0$ is about zero for the mixtures

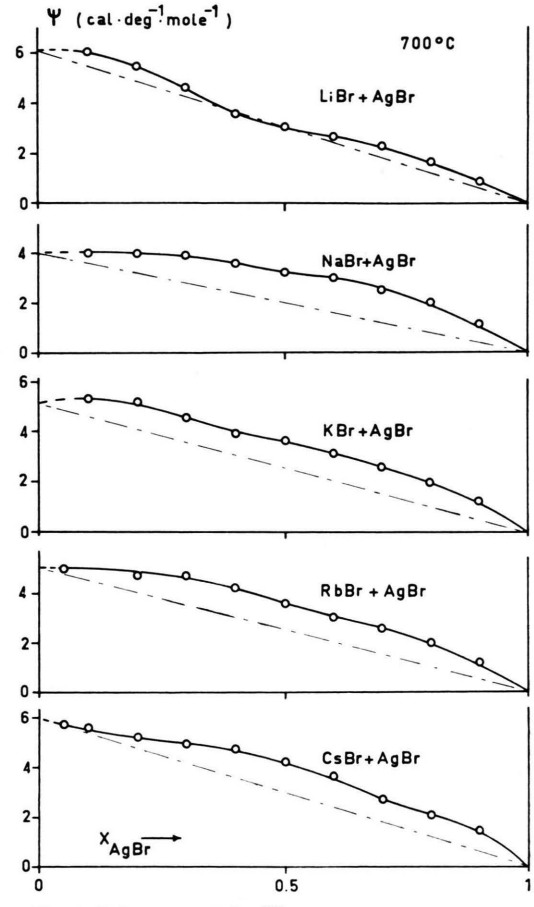

Fig. 3. Behaviour of the Ψ functions for the systems (Ag+Me) Br at 700 °C. Dashed lines represent the ideal behaviour.

[2] R. CONNAN, J. DUPUY, J. LEONARDI, and G. POILLERAT, J. Chim. Phys., Special issue, October 1969, p. 64.

[3] C. SINISTRI, Z. Naturforsch. **21 a**, 753 [1966]. — C. SINISTRI and C. MARGHERITIS, Z. Naturforsch. **23 a**, 1155 [1968].

[4] L. S. HERSH, A. NAVROTSKY, and O. J. KLEPPA, J. Chem. Phys. **42**, 3752 [1965].

[5] J. H. HILDEBRAND and E. J. SALSTROM, J. Amer. Chem. Soc. **54**, 4257 [1932].

[6] G. J. JANZ and C. G. M. DIJKHUIS, Section 1 of "Molten Salts: Volume 2", NSRDS-NBS 28, Washington D.C. 1969.

(Ag + Li) Br, (Ag + K) Br and (Ag + Rb) Br.

On the basis of this information only the Ψ function has been calculated disregarding the correction term $s^{e}_{AgB_2}$.

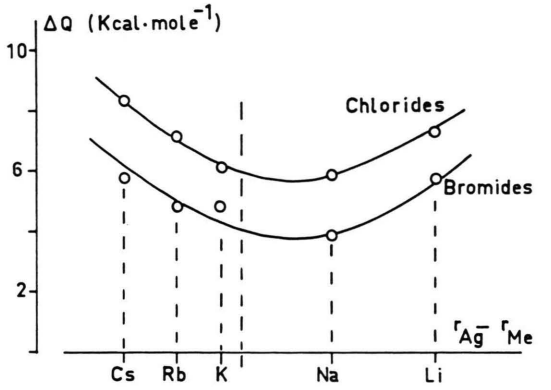

Fig. 4. Relative values of the cationic heats of transport ΔQ vs. relative values of cationic radii (in Å) for the two families (Ag + Me) Cl (at 800 °C) and (Ag + Me) Br (at 700 °C).

Compared to the chlorides, Fig. 3 shows that the bromide systems have large positive deviations from the ideal behaviour, with the only exception of the (Ag + Li) Br mixture.

At the bottom of Table 1 there are reported the extrapolated values (Ψ_0) of Ψ for $x_{AgBr} \to 0$: they range between 4 – 6 e. u. as compared to the 6 – 8 e. u. of the chlorides.

From these data it is easy to calculate the values $\Delta Q (= {}^0Q^*_{Ag^+} - {}^0Q^*_{Me^+})$ that are the differences between the heat of transport of Ag^+ in pure fused AgBr and the cationic heat of transport in pure fused bromides (see Table 1). Figure 4 reports the values ΔQ as a function of the differences $r_{Ag^+} - r_{Me^+}$ between the cationic radii. As it can be seen the two families (Ag + Me) Cl and (Ag + Me) Br show an analogous and characteristic behaviour. This could indicate that ${}^0Q^*_{Me^+}$ of a bromide differs from the one of a chloride by a constant quantity which is independent of the nature of Me^+. As particular case ${}^0Q^*_{Me^+}$ could be about the same either in a chloride and in a bromide.

Massenspektrometrische Untersuchung der Sauerstoffverluste an heißen Rheniumoberflächen im Druckbereich 10^{-8} bis 10^{-4} Torr

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The equivalent pumping speed of a heated rhenium surface for molecular oxygen has been measured. The surface was exposed to a constant oxygen gasflow and the oxygen pressure determined by means of a mass spectrometer. At a surface temperature of 2500 °K a pumping speed of $S_n = 7.6 \pm 1.5$ liters/sec cm² was obtained for O_2. Because filaments of mass spectrometers have typically 5 to 10 mm² heated surface this pumping speed may cause considerable errors during the calibration of the O_2-sensitivity of mass spectrometers using rhenium filaments.

Einleitung

Bei der Eichung der Empfindlichkeit von Massenspektrometern nach der Methode der druckbezogenen dynamischen Expansion kann man u. U. im Eichsystem einen im Vergleich zu anderen Gasen verkleinerten O_2-Partialdruck beobachten. Es liegt der Verdacht nahe, daß die Kathode in der Ionenquelle dieser Spektrometer molekularen Sauerstoff „pumpt" und so speziell den O_2-Partialdruck im Eichsystem verkleinert. Durch diesen Pumpeffekt wird die Genauigkeit der Sauerstoffeichung eingeschränkt. Es ist daher ein Ziel des hier beschriebenen Experiments, quantitative Meßergebnisse über die O_2-Saugleistung einer typischen *Rhenium*-Kathode zu bekommen.

Reaktionen des Sauerstoffs an heißen Wolframoberflächen wurden bereits in mehreren Arbeiten untersucht. So beobachteten SCHLIER [1] und BECKER et al. [2] die Bildung von CO, wobei der Kohlenstoff aus dem Wolframmetallgitter stammte. Massenspektrometrische Untersuchungen wurden von SCHISSEL

Sonderdruckanforderungen an J. GROSS, Physikalisches Institut der Universität Bonn, *D-5300 Bonn*, Nußallee 12.

[1] R. E. SCHLIER, J. Appl. Phys. **29**, 1162 [1958].
[2] J. A. BECKER, E. J. BECKER u. R. G. BRANDES, J. Appl. Phys. **32**, 411 [1961].