Thermoelectric Power of the Molten Systems (Cu, Me)Cl and (Cu, Me)Br (Me = Na, K, Rb, Cs)

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The initial thermoelectric power of the molten systems (Cu, Me) Cl and (Cu, Me) Br (Me=Na, K, Rb, Cs) was determined using copper electrodes. The results are compared with previous results obtained from the systems (Cu, Me) I and (Ag, Me) X (X=Cl, Br, I).

The investigation about the initial thermoelectric power of the molten systems (Ag, Me) X and (Cu, Me) I (Me = Na, K, Rb, Cs; X = Cl, Br, I), reported in previous papers[1], is now extended to the binaries (Cu, Me) Cl and (Cu, Me) Br.

Measurements are carried out in thermocells with copper electrodes and experimental data are worked out by means of the function $\psi \equiv F(\varepsilon - {}^0\varepsilon) - R \ln x_{\mathrm{CuX}}$, where ε and ${}^0\varepsilon$ are the thermoelectric powers of the mixture and of the pure CuX, respectively, F is the Faraday constant, and $R \ln x_{\mathrm{CuX}}$ is the ideal partial configurational entropy[2].

Experimental

The measurements were carried out under Argon atmosphere using a previously described apparatus[1]. ROC/RIC CuCl and CuBr, and Merck p. a. alkali chlorides and bromides were employed. The copper salts were dried by keeping them several days under vacuum in the cell. Usual precautions were taken for the alkali halides.

Results and Discussion

The pure CuCl and CuBr experimental data agree with those by Kvist et al.[3] and by Nichols and Langford[4] and are fitted by the following linear relations:

$$\text{CuCl:} \quad -{}^0\varepsilon(\mu\mathrm{V/deg}) = 451 - 0.016\, t\,(^\circ\mathrm{C})\,, \tag{1}$$

$$\text{CuBr:} \quad -{}^0\varepsilon(\mu\mathrm{V/deg}) = 452 + 0.056\, t\,(^\circ\mathrm{C})\,. \tag{2}$$

As for the mixtures, Tables 1 and 2 report the experimental ε and the calculated ψ values at the melting temperature of the pertinent sodium halide (801 °C for the chloride containing and 750 °C for the bromide containing mixtures). The ε values are reproducible within 1 – 2% and slightly depend on temperature. For 1000 K they are plotted in Figs. 1 and 2.

A picture of the ψ functions is given in Figure 3.

According to our usual procedure, ψ^0 (limiting value of ψ obtained by graphical extrapolation for $x_{\mathrm{CuX}} \to 0$) is related to the cationic heats of transport in the pure molten salts, ${}^0Q^*_{\mathrm{Cu^+}}$ and ${}^0Q^*_{\mathrm{Me^+}}$, through the expression:

$$\psi^0 = ({}^0Q^*_{\mathrm{Cu^+}} - {}^0Q^*_{\mathrm{Me^+}})/T - (S^e_{\mathrm{Cu^+}})_0 \tag{3}$$

	CuCl + NaCl		CuCl + KCl		CuCl + RbCl		CuCl + CsCl	
x_{CuCl}	$-\varepsilon$	ψ	$-\varepsilon$	ψ	$-\varepsilon$	ψ	$-\varepsilon$	ψ
1.00	440	—	440	—	440	—	440	—
0.80	410	1.14	357	2.36	370	2.06	365	2.18
0.60	405	1.83	350	3.09	352	3.05	346	3.19
0.40	410	2.51	360	3.67	342	4.08	340	4.08
0.20	415	3.77	378	4.63	350	5.27	345	5.39
0.10	440	4.57	403	5.43	373	6.12	355	6.10
0.05	460	5.49	430	6.10	410	6.60	400	6.80

	CuBr + NaBr		CuBr + KBr		CuBr + RbBr		CuBr + CsBr	
x_{CuBr}	$-\varepsilon$	ψ	$-\varepsilon$	ψ	$-\varepsilon$	ψ	$-\varepsilon$	ψ
1.00	494	—	494	—	494	—	494	—
0.80	405	2.50	400	2.62	390	2.85	388	2.89
0.60	377	3.72	350	4.34	350	4.34	340	4.57
0.40	380	4.45	353	5.07	335	5.80	329	5.63
0.20	430	4.67	390	6.00	402	6.50	360	6.29
0.10	485	4.78	450	5.59	470	6.00	420	6.28
0.05	520	5.36	510	5.59	510	5.60	480	6.28

Tab. 1 and 2. Values of $\varepsilon(\mu\mathrm{V/deg})$ and ψ (entropic units) for various compositions of the systems (Cu,Me) Cl and (Cu, Me) Br, taken at T=801 °C and T=750 °C, respectively.

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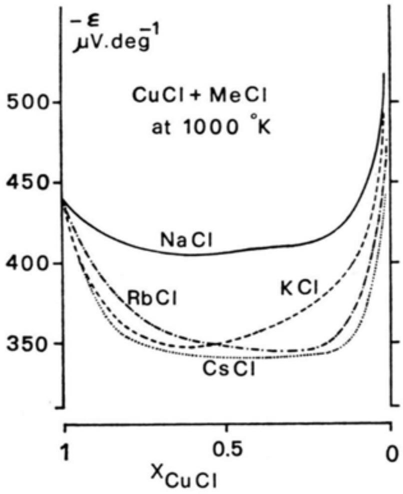

Fig. 1. $\varepsilon_{801\,°C}$ vs x_{CuCl}.

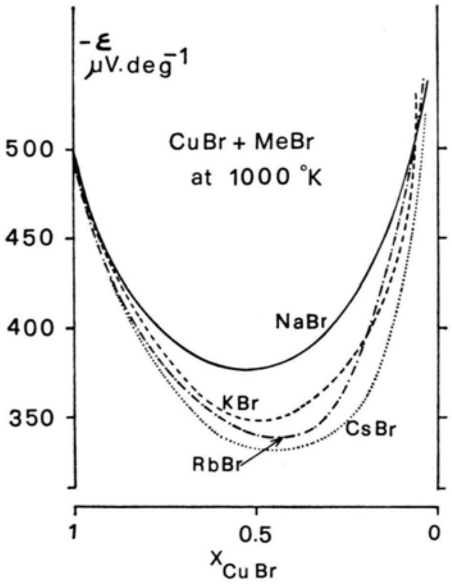

Fig. 2. $\varepsilon_{750\,°C}$ vs x_{CuBr}.

where $(S^e_{Cu^+})_0$ is the partial excess entropy at $x_{CuX} = 0$. The obtained ψ^0 values increase in the order Na, K, Rb, Cs, independently of the anion, and are reported in Table 3.

Tab. 3. ψ° values (entropic units) obtained by means of graphical extrapolations of ψ vs x_{CuX} plots.

Me	ψ° (Cu, Me) Cl	ψ° (Cu, Me) Br	ψ° (Cu, Me) I
Na	5.8	5.6	6.0
K	6.5	6.3	7.1
Rb	6.8	6.4	7.4
Cs	7.2	6.6	7.5

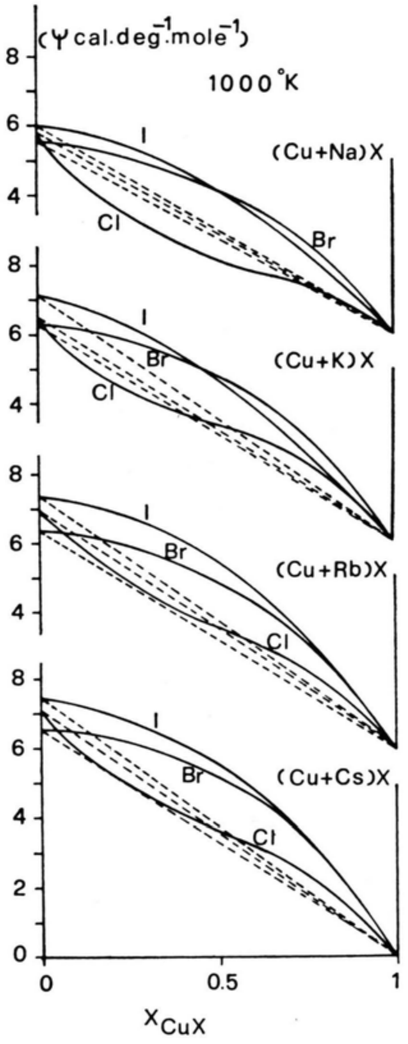

Fig. 3. ψ vs composition for the systems (Cu, Me) X.

The quantity ${}^0Q^*_{Cu^+}$ in (3) can be approximately obtained from the corresponding ${}^0\varepsilon$ value, when Pitzer's relation[5] for the partial ionic entropy is employed. The values obtained in the above way (3.2; 3.6; 3.3 kcal/mole for CuCl, CuBr and CuI respectively) allow to draw from (3) a value of -3 ± 1 kcal/mole for the quantities $[{}^0Q^*_{Me^+} + T(S^e_{Cu^+})_0]$.

Aside from experimental uncertainties, the differences between the above values and the ${}^0Q^*_{Me^+}$'s (obtained from ε measurements on pure molten alkali halides with halogen electrode thermocells[6, 7] and lying in the interval ± 1.5 kcal/mole) may be attributed either to the unknown excess entropy term or to the uncertainty affecting the evaluation of ${}^0Q^*_{Cu^+}$ and ${}^0Q^*_{Me^+}$ through Pitzer's relation[8].

It was already suggested in previous papers that, should ψ behave ideally (dashed straight lines in Fig. 3), the following conditions would be valid in the whole composition range:

$$S^{\mathrm{e}}_{\mathrm{Cu}^+} = 0; \quad {}^0Q_{\mathrm{i}}^* = Q_{\mathrm{i}}^*; \quad t_{\mathrm{i}} = x_{\mathrm{i}} \tag{4}$$

where Q_{i}^* and ${}^0Q_{\mathrm{i}}^*$ are the heats of transport in the mixture and in the pure halide, respectively, t_{i} represents the ionic Hittorf transport number (referred to the anion) and x_{i} is the ionic fraction of the i-th ionic species.

With respect to the ideal behaviour, the function exhibits: (a) small positive (for $x_{\mathrm{CuX}} > 0.5$) or small negative (for $x_{\mathrm{CuX}} < 0.5$) deviations in the case of mixtures containing chlorides, (b) larger positive deviations in the case of mixtures containing bromides or iodides.

Since a quite similar picture was already obtained for the systems (Ag, Me)X, it may be suggested as a general conclusion that in the mentioned series of molten mixtures silver can be substituted by copper without any significant variation of the transport properties.

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[1] a) C. Sinistri and E. Pezzati, Z. Naturforsch. **25 a**, 893 [1970]. b) E. Pezzati, Z. Naturforsch. **25 a**, 898 [1970]. c) E. Pezzati, A. Schiraldi, and A. Magistris, Z. Naturforsch. **28 a**, 1334 [1973].

[2] C. Sinistri, Z. Naturforsch. **21a**, 753 [1966].

[3] A. Kvist, A. Randsalu, and J. Svenson, Z. Naturforsch. **21 a**, 184 [1966].

[4] A. R. Nichols Jr. and C. T. Langford, J. Electrochem. Soc. **107**, 10, 842 [1960].

[5] K. S. Pitzer, J. Phys. Chem. **65**, 147 [1961].

[6] W. Fischer, Z. Naturforsch. **21 a**, 281 [1966].

[7] R. Connan, J. Dupuy, J. Leonardi, and G. Poillerat, J. Chim. Phys. Special issue, Oct. 1969, p. 64.

[8] C. Wagner, Progr. Solid State Chem. **7**, 1 [1972] (see pp. 28, 29).