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Thermoelectric Power of the Molten Systems (Ag+Me) I and (Cu+Me) I (Me=Na, K, Rb, Cs)

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The systems (Ag+Me)I and (Cu+Me)I were investigated by measuring their initial thermoelectric power; mixtures containing AgI show a behaviour much closer to the ideality than mixtures containing CuI. Interesting conclusions are suggested about the heats of transport of silver and copper ions in the pure molten iodides.

Introduction

Transport properties in molten binary mixtures were intensively investigated in the last years; particular consideration was devoted to mixtures of silver and alkali salts having a common anion: systematic investigations were carried out by means of initial thermoelectric power measurements [1, 2].

In the present paper we report the results of thermoelectric power measurements carried out both on pure silver and copper iodides and on the mixtures (Ag+Me)I, (Cu+Me)I, where Me=Na, K, Rb, Cs. Measurements were made by means of the following thermocells:

$$\mathrm{Ag}(\mathrm{T}_1) \mid (\mathrm{Ag}+\mathrm{Me})\mathrm{I} \mid \mathrm{Ag}(\mathrm{T}_2)\,, \qquad (1)$$

$$\mathrm{Cu}(\mathrm{T}_1) \mid (\mathrm{Cu}+\mathrm{Me})\mathrm{I} \mid \mathrm{Cu}(\mathrm{T}_2)\,. \qquad (2)$$

In the case, for instance, of (Ag+Me)I mixtures, thermodynamics of irreversible processes leads to the following expression for the initial thermoelectric power, ε [3]:

$$\varepsilon = \left(\frac{1}{F}\, S_{\mathrm{Ag}} - S_{\mathrm{Ag}^+} - t_{\mathrm{Ag}^+}\,\frac{Q^*_{\mathrm{Ag}^+}}{T} - t_{\mathrm{Me}^+}\,\frac{Q^*_{\mathrm{Me}^+}}{T}\right) \qquad (3)$$

where S_{Ag} = molar entropy of the metal; t_{Ag^+} and t_{Cu^+} = Hittorf ionic transport numbers, referred to the velocity of I^-; $Q^*_{\mathrm{Ag}^+}$ and $Q^*_{\mathrm{Me}^+}$ = heats of transport for the ions in the mixture; F = Faraday's constant. The partial molar entropy of the silver ion in the mixture,

$$S_{\mathrm{Ag}^+} = {}^{\circ}S_{\mathrm{Ag}^+} - R \ln X_{\mathrm{Ag}^+} + S^{\mathrm{e}}_{\mathrm{Ag}^+}\,,$$

is related to the same quantity in the pure salt, ${}^{\circ}S_{\mathrm{Ag}^+}$ †, through a configurational term, $-R \ln X_{\mathrm{Ag}^+}$, and the excess entropy, $S^{\mathrm{e}}_{\mathrm{Ag}^+}$.

As suggested in previous papers [1a], the above quantities may be worked out by means of a suitable function $\psi \equiv F(\varepsilon - {}^{\circ}\varepsilon) - R \ln X_{\mathrm{Ag}^+}$ such as

$$\psi = \frac{{}^{\circ}Q^*_{\mathrm{Ag}^+} - Q^*_{\mathrm{Ag}^+}}{T} + t_{\mathrm{Me}^+}\,\frac{Q^*_{\mathrm{Ag}^+} - Q^*_{\mathrm{Me}^+}}{T} - S^{\mathrm{e}}_{\mathrm{Ag}^+} \qquad (4)$$

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† In the following all the quantities noted with "°" are referred to pure salts.

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which allows to describe the general behaviour of the mixture with respect to the transport of heat and electricity. The quantity $({}^\circ Q^*_{\mathrm{Ag}^+} - {}^\circ Q^*_{\mathrm{Me}^+})$, that is the heat of transport for the alkali ion in the pure iodide (referred to the heat of transport of the silver ion in pure AgI), can be attained (aside from the excess entropy term) through extrapolation of the experimental ψ data, when $X_{\mathrm{Ag}^+} = 0$ is assumed.

Experimental

The cell was a U shaped quartz tube, where an Argon atmosphere was kept; the cell was settled in a three pieces assemblable steel block; a Philips thermocoax was wound around one of these part and enabled to set a temperature gradient between the two arms of the cell. Silver (99,99%) and copper (99,99%) bars of 8 mm outer diameter, bored to contain a Platinel thermocouple, were employed as electrodes. The whole apparatus was placed into a high capacity furnace driven by a thermoregulator. A Leeds & Northrup K-3 potentiometer was used for the e.m.f. measurements. The salts employed were: AgI, precipitated from $AgNO_3$ with KI, NaI, KI, RbI, CsI (Merck p.a.) and CuI (ROC/RIC); all of them were fully dried in a vacuum oven. The binary mixtures, of the desired composition, were previously ground to attain a good homogeneity and then melted in the cell.

The thermoelectric power measurements were carried out at different temperatures, properly chosen after having considered the phase diagrams and melt stability; generally, therefore, measurements were performed in a 150 degrees range in the region of 1000 °K.

Results and Discussion

Within the investigated range, the experimental data show that the values of ε are very slightly dependent on temperature.

E. g., the case of the mixture (Ag + Na) I with $X_{\mathrm{AgI}} = 0.7$, and the case of the mixture (Cu + Cs) I, with $X_{\mathrm{CuI}} = 0.6$, are shown in Figure 1.

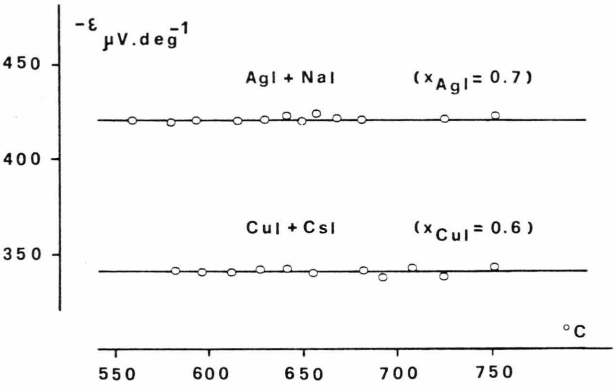

Fig. 1. ε vs T(°C) for the mixture (Ag+Na) I, $X_{\mathrm{AgI}}=0.7$; and (Cu+Cs) I, $X_{\mathrm{CuI}}=0.6$.

Table 1 and 2. Values of ε (μV/degree) and ψ function (entropic units) at $T=1000$ °K for various compositions of the systems (Ag+Me) I and (Cu+Me) I.

1) NaI+AgI			KI+AgI			RbI+AgI			CsI+AgI		
X_{AgI}	$\varepsilon-$	ψ	X_{AgI}	$\varepsilon-$	ψ	X_{AgI}	$\varepsilon-$	ψ	X_{AgI}	$\varepsilon-$	ψ
1.00	481	—	1.00	481	—	1.00	481	—	1.00	481	—
0.80	435	1.50	0.80	410	2.08	0.80	431	1.60	0.80	429	1.64
0.70	420	2.12	0.55	378	3.56	0.60	395	3.00	0.60	391	3.09
0.40	391	3.90	0.40	355	4.73	0.40	360	4.61	0.40	356	4.70
0.20	410	4.84	0.20	363	5.92	0.20	370	5.76	0.20	371	5.74
0.10	450	5.30	0.10	406	6.31	0.10	400	6.44	0.10	396	6.54
0.05	492	5.70	0.05	451	6.65	0.05	438	6.95	0.05	440	6.90

2) NaI+CuI			KI+CuI			RbI+CuI			CsI+CuI		
X_{CuI}	$-\varepsilon$	ψ	X_{CuI}	$-\varepsilon$	ψ	X_{CuI}	$-\varepsilon$	ψ	X_{CuI}	$-\varepsilon$	ψ
1.00	499	—	1.00	499	—	1.00	499	—	1.00	499	—
0.80	445	1.69	0.80	432	1.99	0.80	408	2.54	0.80	406	2.59
0.69	409	2.81	0.70	394	3.13	0.60	341	4.66	0.60	340	4.68
0.43	390	4.19	0.60	375	3.84	0.40	320	5.95	0.40	309	6.20
0.25	395	5.15	0.43	350	5.11	0.20	336	6.96	0.20	328	7.14
0.20	420	5.02	0.20	350	6.63	0.10	385	7.20	0.10	388	7.13
0.12	428	5.85	0.10	404	6.40	0.05	442	7.26	0.05	450	7.08
0.05	507	5.77	0.05	460	6.85	—	—	—	—	—	—

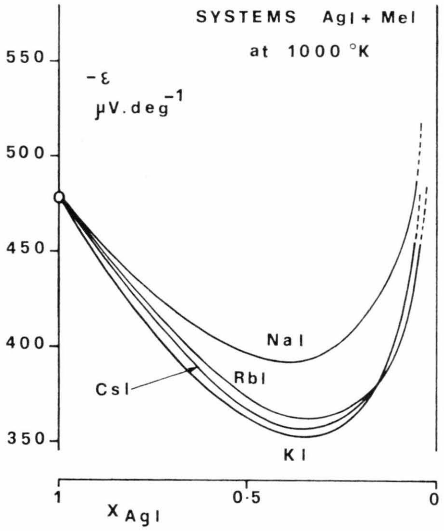

Fig. 2. $\varepsilon_{1000\,^\circ\mathrm{K}}$ vs X_{AgI}.

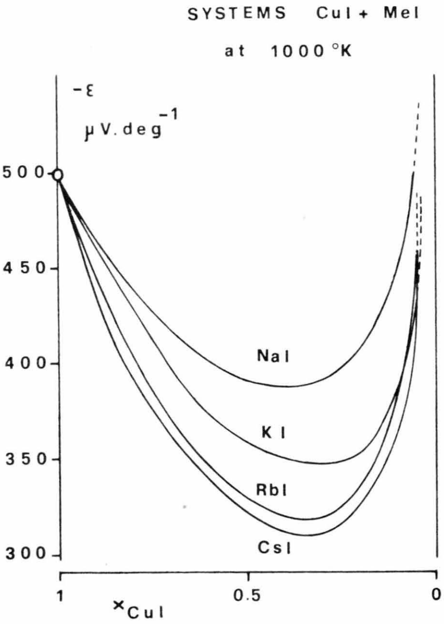

Fig. 3. $\varepsilon_{1000\,^\circ\mathrm{K}}$ vs X_{CuI}.

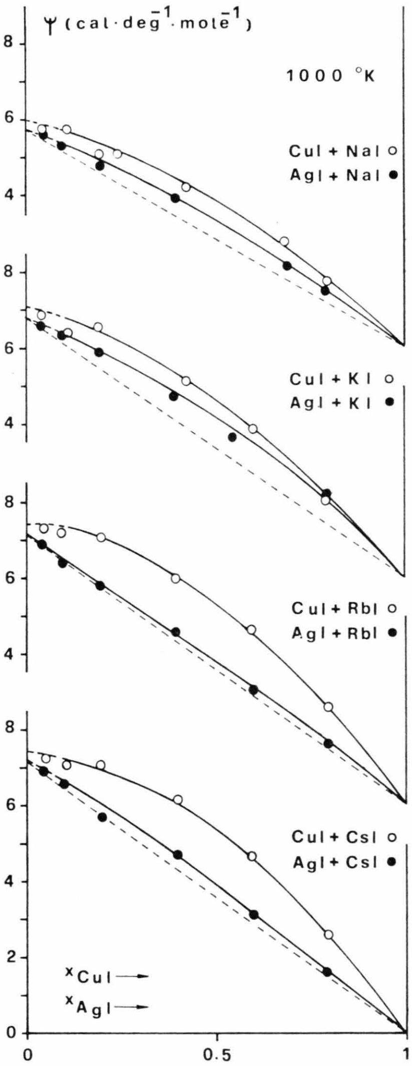

Fig. 4. ψ vs composition at 1000 °K; dashed lines represent the ideal behaviour.

Experimental data, at the interpolated temperature of 1000 °K, are reported in Tables 1 and 2, respectively for the mixtures (Ag + Me) I and (Cu + Me) I. The ε values, in the second column, are reproducible within $1-2\%$; the experimental results for the pure salts, AgI and CuI, are quite close to the values supplied by Kvist and coworkers [4].

Plots (ε vs X) are given in Fig. 2 and 3; Fig. 4 shows the behaviour of the ψ function for mixtures containing the same alkali iodide. In the latter figure the dashed straight lines represent the behaviour of the function ψ_{ideal}, which is supposed to have a linear dependence on composition, according to [1a]:

$$\psi_{\mathrm{id}} = \frac{{}^{\circ}Q^{*}_{\mathrm{Ag}^+} - {}^{\circ}Q^{*}_{\mathrm{Me}^+}}{T}\,(1 - X_{\mathrm{AgI}})\,. \qquad (5)$$

Small positive deviations from ideality are apparent in the case of (Ag + Me) I systems; quite wider deviations are observed for the systems (Cu + Me) I, particularly when Me = Rb, Cs.

It is interesting to consider the ψ limiting values for $X_{\mathrm{AgI}} \to 0$ and $X_{\mathrm{CuI}} \to 0$, i. e. $\overset{\circ}{\psi}_{\mathrm{Ag,Me}}$ and $\overset{\circ}{\psi}_{\mathrm{Cu,Me}}$

respectively, which are related to the heats of transport in the pure molten salts through the following equations, derived from Eq. 4:

$$\overset{\circ}{\psi}_{\mathrm{Ag,Me}} = \frac{{}^{\circ}Q^*_{\mathrm{Ag^+}} - {}^{\circ}Q^*_{\mathrm{Me^+}}}{T} - (S^{\mathrm{e}}_{\mathrm{Ag^+}})_0 \,, \tag{6}$$

$$\overset{\circ}{\psi}_{\mathrm{Cu,Me}} = \frac{{}^{\circ}Q^*_{\mathrm{Cu^+}} - {}^{\circ}Q^*_{\mathrm{Me^+}}}{T} - (S^{\mathrm{e}}_{\mathrm{Cu^+}})_0 \tag{7}$$

where the excess entropies of silver and copper ions at infinite dilution of the mixture are included. The $\overset{\circ}{\psi}_{\mathrm{Ag,Me}}$ and $\overset{\circ}{\psi}_{\mathrm{Cu,Me}}$ values are listed in Table 3. It can be seen that these quantities, for mixtures containing the same alkali iodide, may be considered quite close to each other, particularly if extrapolation uncertainties are taken into account. Eqs. 6 and 7 show that the possibility of evaluating the heats of transport from the extrapolated ψ° values is limited by the knowledge of $(S^{\mathrm{e}}_{\mathrm{Ag^+}})_0$ and $(S^{\mathrm{e}}_{\mathrm{Cu^+}})_0$.

Me	$\overset{\circ}{\psi}_{\mathrm{Ag,Me}}$	$\overset{\circ}{\psi}_{\mathrm{Cu,Me}}$
Na	5.8	6.0
K	6.8	7.1
Rb	7.2	7.4
Cs	7.2	7.5

Table 3. ψ° values (entropic units) at 1000 °K.

As for the mixtures (Ag + Me) I, previous literature data concern some $S^{\mathrm{e}}_{\mathrm{Ag^+}}$ values, ranging between 0 and − 0.5 e. u., calculated by Sternberg and coworkers[5], for $T = 873$ °K and within the composition range $X_{\mathrm{AgI}} = 1$ and $X_{\mathrm{AgI}} = 0.2$.

According to these data it may be assumed that the quantity $(S^{\mathrm{e}}_{\mathrm{Ag^+}})_0$ at most attains about 10% of the $\overset{\circ}{\psi}_{\mathrm{Ag,Me}}$ value, even in the less favourable cases. Unfortunately no literature data are available for the mixtures (Cu + Me) I.

Table 4. $-F\,{}^{\circ}\varepsilon$ = Thermoelectric power (entropic units); ${}^{\circ}S_{\mathrm{M^+}}$ = ionic entropies according to Pitzer's equation; ${}^{\circ}Q^*_{\mathrm{M^+}}$ = heats of transport in the pure salts (Kcal/mole).

Salt	$-F\,{}^{\circ}\varepsilon$	S_{M}	${}^{\circ}S_{\mathrm{M^+}}$	${}^{\circ}Q_{\mathrm{M^+}}$
AgI	11.1	18.03	25.6	3.5
CuI	11.5	15.58	23.8	3.3

In spite of this uncertainty, a tentative interpretation of the data in Tab. 3 ought to involve the assumption that the quantiies ${}^{\circ}Q^*_{\mathrm{Ag^+}}$ and ${}^{\circ}Q^*_{\mathrm{Cu^+}}$ are equal or quite close to each other.

On the other hand the thermoelectric power measurements performed on pure silver and copper iodides can supply information about the heats of transport, when it is possible to evaluate the terms ${}^{\circ}S_{\mathrm{Ag^+}}$ and ${}^{\circ}S_{\mathrm{Cu^+}}$. This might be made by Pitzer's equation[6]:

$${}^{\circ}S_{\mathrm{M^+}} = \tfrac{1}{2}\,(S_{\mathrm{MX}} + \tfrac{3}{2}\,R \ln M_{\mathrm{M}}/M_{\mathrm{X}}) \tag{8}$$

where S_{MX} is the molar entropy of the salt MX; M_{M} M_{X} are the cationic and anionic equivalent weights. In this way we obtained the data listed in Table 4, which are referred to the temperature of 1000 °K.

The molecular entropies ${}^{\circ}S_{\mathrm{Ag^+}}$ and ${}^{\circ}S_{\mathrm{Cu^+}}$, reported in the second column, were calculated through eq. 8 and the calorimetric data supplied by the literature[7, 8].

Once more it seems likely to conclude that the heats of transport for these ions are quite close to each other, in agreement with the results obtained from the investigations of the mixture behaviour.

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