Thermoelectric Power of the Molten Systems (Cu, Ag) X (X = Cl, Br, I)

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Initial thermoelectric power determinations were carried out on the molten systems (Cu, Ag)X, (X=Cl, Br, I) at 1000 K. As for the employing of either cooper or silver electrodes thermocells, the choice was based on literature thermodynamic data.

Comparison between ideal and actual behaviour allowed to discover negative excess partial ionic entropies.

1. Introduction

Initial thermoelectric power determinations of the molten mixtures (Cu, alkali)X and (Ag, alkali)X (X = Cl, Br, I) have shown [1–4] that the heats of transport of Cu^+ and Ag^+ in the respective pure molten halides are very similar (see Tab. 1) and that the differences between the molar entropy of the metal and the partial molar entropy of its ion, viz. $({}^0S_{Cu} - {}^0S_{Cu^+})$ and $({}^0S_{Ag} - {}^0S_{Ag^+})$, have close values when the same halide is considered (see Table 1).

The comparison between experimental and ideal behaviour allowed to reach some qualitative evaluation about the excess ionic entropies.

2. Experimental

For details on both chemicals and the instrumental equipment cf. Reference [3]. After every cycle of determinations on a given thermocell the electrodes were freed from salt by leaving them for some days in aqueous ammonia and were then microscopically examined in order to check for possible deposition of the other metal. The surfaces were then scraped away and the obtained metallic powders were controlled by X rays diffraction. Local deposition (in traces) of either copper or silver was observed for thermocells containing melts of composition near to the predicted limits of use of a given kind of electrodes, as well as for cases where the temperature gradients imposed between the electrodes were too high ($\Delta T > 20$ K).

Halide	${}^0S_{Ag} - {}^0S_{Ag^+}$ (e. u.)	${}^0S_{Cu} - {}^0S_{Cu^+}$ (e. u.)	${}^0Q_{Ag}{}^*$ kcal/mole	${}^0Q_{Cu}{}^*$ kcal/mole
Cl	−6.79	−7.13	3.2	3.2
Br	−7.19	−7.58	3.7	3.6
I	−7.57	−8.22	3.5	3.3

Table 1. Metal-ion entropy differences and ionic heats of transport in the pure molten halides at 1000 K.

Nevertheless it is quite difficult to predict an ideal behaviour of the initial thermoelectric power of the molten mixtures (Cu, Ag)X especially because of the complex electrode-electrolyte equilibrium.

In the publications on thermocells containing molten (Cu, Ag)Cl mixtures [5, 6] no thermodynamic discussion is attempted on whether copper or silver electrodes are to be used for a given composition of the melt.

In the present work, which concerns the initial thermoelectric power of the three systems (Cu, Ag)X, either copper or silver electrodes were employed, taking into account that both the electrode standard potentials and the Ag/Cu phase diagram suggest the kind of reversible electrode which is to be employed for each melt composition.

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3. Results and Discussion

3.1. Thermodynamic considerations

According to the literature [7] the electrode standard potentials of copper and silver with respect to their molten halides are close to each other at 700 °C (see Tab. 2); therefore it may be predicted that at any intermediate composition of

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Table 2. Electrode standard potentials, $E_{Na}{}^0$ being taken as zero [7], standard free energy variation and corresponding equilibrium constants for reaction I at 700 C.

Halide	$E^0{}_{Cu/Cu+}$ (volt)	$E^0{}_{Ag/Ag+}$ (volt)	$-\Delta G^0$ kcal/mole	K
Cl	2.65	2.55	2.3	3.3
Br	2.29	2.25	0.9	1.6
I	1.98	1.74	5.5	17.2

the molten (Cu, Ag)X mixtures either copper or silver would undergo an exchange reaction taking place at the electrodes, viz.

$$Ag_{(s)} + CuX_{(l)} = Cu_{(s)} + AgX_{(l)} \,. \qquad \text{(I)}$$

In order to estimate the activity of the metal which is deposited onto the electrode surface, it may be tentatively assumed that the molten mixtures behave ideally and that the exchange reaction does not significantly affect the global composition of the melt *, so that one obtains

$$\frac{a_{Cu}}{a_{Ag}} = K \frac{1 - X_m}{X_m}$$

where K is the equilibrium constant calculated from the electrode standard potentials (see Tab. 2) and X_m is the molar fraction of AgX. The available thermodynamic data on the Cu-Ag system [8] finally allow to estimate the a_{Cu} and a_{Ag} values as well as the corresponding molar ratio in the whole composition range.

This calculation shows that copper electrodes are to be employed in the composition ranges

$$0 \leqq X_m < 0.96, \quad 0 \leqq X_m < 0.61,$$
$$0 \leqq X_m < 0.745$$

for the (Cu, Ag)I, (Cu, Ag)Br and (Cu, Ag)Cl systems, respectively **.

Accordingly, for these composition ranges the heterogeneous contribution to the thermal emf is given by

$$S_{Cu} - S_{Cu^+} = ({}^0S_{Cu} + {}^0S_{Cu^+}) + R \ln \frac{1 - X_m}{1 - X_{el}} + (S^e_{Cu} - S^e_{Cu^+}) \qquad \text{(II)}$$

whereas for the remaining compositions where silver electrodes are more suitable one obtains the analogous expression

$$S_{Ag} - S_{Ag^+} = ({}^0S_{Ag} - {}^0S_{Ag^+}) + R \ln (X_m/X_{el}) + (S^e_{Ag} - S^e_{Ag^+}) \,. \qquad \text{(III)}$$

However, due to the narrow limits of intersolubility of Ag and Cu and to the negligible values of the respective excess partial entropy in the α (Ag richer) and β (Cu richer) alloys [8], respectively, the terms X_{el} (Ag mole ratio in the alloy), S^e_{Cu} and S^e_{Ag} may be dropped in Eqs. (II) and (III) for most melt compositions.

Finally, one may assume for the ideal heterogeneous thermal emf the following simple expressions:

$$S_{Cu} - S_{Cu^+} = {}^0S_{Cu} - {}^0S_{Cu^+} + R \ln (1 - X_m) \qquad \text{(IV)}$$

and

$$S_{Ag} - S_{Ag^+} = {}^0S_{Ag} - {}^0S_{Ag^+} + R \ln X_m \qquad \text{(V)}$$

where the ionic excess entropies too are neglected.

As for the transport terms, according to previous works [1—4], ideal values may be obtained from

$$\sum{}^* = \frac{X_m \, {}^0Q^*_{Ag} + (1 - X_m) \, {}^0Q^*_{Cu}}{T}$$

In this case at 1000 K for any of these systems the further simplication

$$\sum{}^* = \frac{{}^0Q^*_{Ag}}{T} = \frac{{}^0Q^*_{Cu}}{T} = 3.5 \text{ e.u.}$$

is justified by the small values of the differences $({}^0Q^*_{Ag} - {}^0Q^*_{Cu})$ (see Tab. 1) which range within the experimental errors.

3.2. *Experimental data and conclusion*

Fig. 1 reports both the ideal (dashed lines) and the experimental (full lines) behaviour of the initial thermal emf, F_ε, for the three systems.

The experimental data obtained for the (Cu, Ag)I and (Cu, Ag)Cl systems qualitatively reproduce the predicted ideal trend.

A worse agreement is found for the (Cu, Ag)Br system, where the limit between the composition

* A probably sharp decrease of the reaction rate should occur as soon as a thin layer of metallic product is formed on the electrode surface: diffusion toward the bulk of the electrode should then be the slow step which controls the rate of the whole process.

** On the other hand, if it is roughly assumed that the metal deposited onto the electrodes has unit activity one obtains that the composition ranges where copper electrodes are to be employed are $0 \leqq X_m < 0.94$, $0 \leqq X_m < 0.61$, $0 \leqq X_m < 0.76$, i.e. practically coincident with those calculated above.

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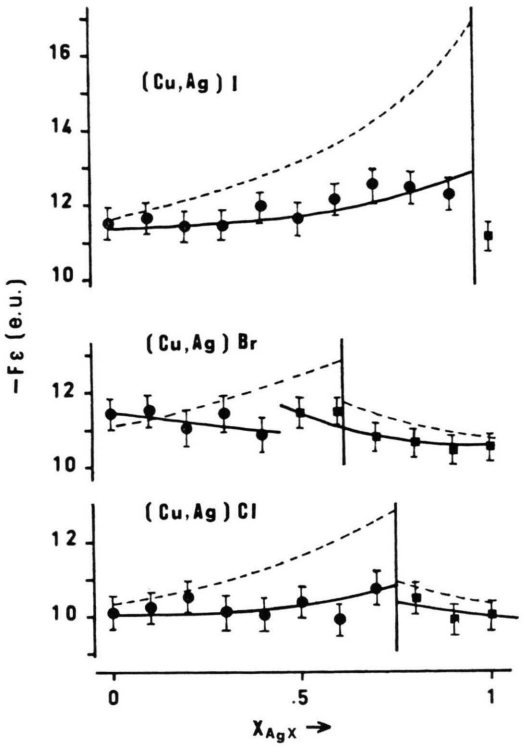

ranges for the use of silver or copper electrodes is shifted to a 10 mole% CuBr richer composition with respect to that quoted on the basis of literature thermodynamic data.

As a rule, the experimental F_ε's are lower (in absolute value) than the ideal ones, the largest differences being observed for the (Cu, Ag)I system. Such a behaviour is more likely due to the excess partial entropy of the ions, dropped out from Eqs. (IV) and (V), than to transport terms, as the heats of transfer are not significantly affected even when the halide ion itself is changed (see Tab. 1), so that, whichever is the role played by the transport numbers, the sum $\sum^*$ should actually remain almost constant throughout the composition range. Accordingly ionic entropies should contain a 4—5% and a 5—20% (according to the system and to the melt composition) negative excess contribution for Ag^+ and Cu^+, respectively.

Fig. 1. Initial thermoelectric power data. Circles and squares correspond to copper and silver electrodes thermocells, respectively; vertical lines separate the two composition ranges where the former and the latter should be used according to literatute thermodynamic data. The dashed lines represend the ideal behaviour.

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