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

Alberto Schiraldi and Elisabetta Pezzati
Centro di Studio per la termodinamica ed elettrochimica dei sistemi salini fusi e solidi del CNR
o/o Istituto di Chimica-Fisica e di Elettrochimica dell'Università di Pavia (Italy)

Z. Naturforsch. 33a, 42—44 (1978); received November 21, 1977

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. ($\delta S_{Cu}$ - $\delta S_{Cu^+}$) and ($\delta S_{Ag}$ - $\delta S_{Ag^+}$), have close
values when the same halide is considered (see Table 1).

<table>
<thead>
<tr>
<th>Halide</th>
<th>$\delta S_{Ag}$ (e. u.)</th>
<th>$\delta S_{Ag^+}$ (e. u.)</th>
<th>$\delta S_{Cu}$ - $\delta S_{Cu^+}$ kcal/mole</th>
<th>$\delta Q_{Ag^+}$ kcal/mole</th>
<th>$\delta Q_{Cu^+}$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>-6.79</td>
<td>-7.13</td>
<td>3.2</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>-7.19</td>
<td>-7.58</td>
<td>3.7</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>-7.57</td>
<td>-8.22</td>
<td>3.5</td>
<td>3.3</td>
<td></td>
</tr>
</tbody>
</table>

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 thermo-
dynamic 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.

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).

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

Reprint requests to Alberto Schiraldi, Istituto di Chimica-Fisica e di Elettrochimica dell'Università di Pavia, viale
Taramelli, I-27100 Pavia
Table 2. Electrode standard potentials, $E_{\text{Xa}}^0$ being taken as zero [7], standard free energy variation and corresponding equilibrium constants for reaction I at 700°C.

<table>
<thead>
<tr>
<th>Halide</th>
<th>$E_{\text{Cu}/\text{Cu}^+}^0$ (volt)</th>
<th>$E_{\text{Ag}/\text{Ag}^+}^0$ (volt)</th>
<th>$-\Delta G^0$ kcal/mole</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>2.65</td>
<td>2.55</td>
<td>2.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Br</td>
<td>2.29</td>
<td>2.25</td>
<td>0.9</td>
<td>1.6</td>
</tr>
<tr>
<td>I</td>
<td>1.98</td>
<td>1.74</td>
<td>5.5</td>
<td>17.2</td>
</tr>
</tbody>
</table>

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

$$\text{Ag} (s) + \text{CuX} (i) = \text{Cu} (s) + \text{AgX} (i). \text{ (I)}$$

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

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

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 $a_{\text{Cu}}$ and $a_{\text{Ag}}$ 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

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

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

$$S_{\text{Cu}} - S_{\text{Cu}^+} = (0S_{\text{Cu}} + 0S_{\text{Cu}^+})$$

$$+ R \ln \left(\frac{1 - X_m}{1 - X_{\text{el}}} + (S_{\text{Cu}}^0 - S_{\text{Cu}^+}^0)\right) \text{ (II)}$$

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

$$S_{\text{Ag}} - S_{\text{Ag}^+} = (0S_{\text{Ag}} - 0S_{\text{Ag}^+})$$

$$+ R \ln \left(X_m/X_{\text{el}} + (S_{\text{Ag}}^0 - S_{\text{Ag}^+}^0)\right). \text{ (III)}$$

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 z (Ag richer) and β (Cu richer) alloys [8], respectively, the terms $X_{\text{el}}$ (Ag molar ratio in the alloy), $S_{\text{Cu}}^0$ and $S_{\text{Ag}}^0$ 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:

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

and

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

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

$$\sum^* = \frac{X_m 0Q_{\text{Ag}}^* + (1 - X_m) 0Q_{\text{Cu}}^*}{T}$$

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

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

is justified by the small values of the differences $(0Q_{\text{Ag}}^* - 0Q_{\text{Cu}}^*)$ (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, $F_\varepsilon$, 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 $0 \leq X_m < 0.94, 0 \leq X_m < 0.61, 0 \leq X_m < 0.76$, i.e. practically coincident with those calculated above.
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 $F_e$'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 literature thermodynamic data. The dashed lines represent the ideal behaviour.