Miscibility Gaps in Fused Salts

Note VII. Systems of LiF with Alkali Halides[1]

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Twelve systems formed with lithium fluoride and alkali halides were studied in order to put into evidence possible demixing phenomena. Liquid-liquid equilibra were found in the seven mixtures containing KBr, KI, RbBr, RbI, CsCl, CsBr, and CsI; however, the miscibility gaps could be fully detected only for LiF+CsCl, LiF+KBr and LiF+RbBr.

The tendency to demix in these systems, formed by typically ionic components, agrees with the reciprocal Coulomb effect rule.

On the basis of the solid-liquid and liquid-liquid equilibria, the LiF excess potentials were evaluated and compared with those calculated according to current theories.

The occurrence of demixing phenomena has systematically been investigated in fused systems type LiF + MeX (Me = Na, K, Rb, Cs; X = Cl, Br, I). Being formed with four simple ions, they constitute elementary cases of reciprocal ternaries. The corresponding binaries with a common ion were previously extensively studied and many of their properties were described in the literature[2]. Thus, it seems possible to test, by these systems, the degree of applicability of recent thermodynamic theories generally accepted for reciprocal salt mixtures.

The occurrence of a miscibility gap (MG) had already been observed in the system formed with LiF and CsCl[3, 4], KBr[5], CsBr[3]: moreover, the literature reports data for the solid-liquid (SL) equilibria in systems formed with LiF and NaCl[6], KCl[7]. However, it should be noted that the liquid-liquid (LL) equilibria were never specifically detected and no MG was fully reported.

Apparatus and Materials

Most of the SL and LL equilibria (up to ≅ 900 °C) were taken using the experimental equipment previously described[1]. To improve the latter and to enlarge the experimental temperature range (up to ≅ 1200 °C) a new and more compact oven was devised.

Briefly, this 70 × 130 mm oven contains six heating elements (about 200 cm of 0.2 mm Pt wire wound on a lava support) symmetrically plunged into a nickel block. A 1.5 × 10 mm vertical slot in the latter permits a direct observation of the sample, sealed into a 9 × 10 mm quartz vessel, whose temperature is measured by a Platinel thermocouple fitted at the bottom. The whole system is maintained under a slow N_2 stream and cooled by a water jacket.

The eutectic-points and a few SL equilibria were also confirmed by DTA (using the Du Pont de Nemours Mod. 900 apparatus).

Particular care was devoted to drying the compounds employed (Merck Suprapur): in fact, it was observed that if the salts were thoroughly dried the quartz vessel remained transparent.

The measured melting points of the employed halides were (°C):
LiF (848); NaCl (800); KCl (771); RbCl (717); CsCl (646); NaBr (747); KBr (736); RbBr (694); CsBr (637); NaI (664); KI (686); RbI (656); CsI (638).

Results

In Fig. 1 the SL and LL equilibria in the twelve pseudo-binary systems LiF(1) + alkali halide(2) are reported. They are the stable diagonals of the corresponding reciprocal ternary systems. In the same figure, demixing areas are shaded and the eutectic co-ordinates are indicated. In three cases complete investigation of the MG has been possible; for the other systems the detection of the upper part of the gap was difficult due to the relatively low boiling points of the concerned alkali halides (about 1300 °C).

As regards the systems containing chlorides, demixing occurs only with LiF + CsCl. In this system, the primary crystallization temperature (PCT) from one of the two liquid phases in equilibrium is at 830 °C while x_1 increases from 0.33_5 to 0.96. The

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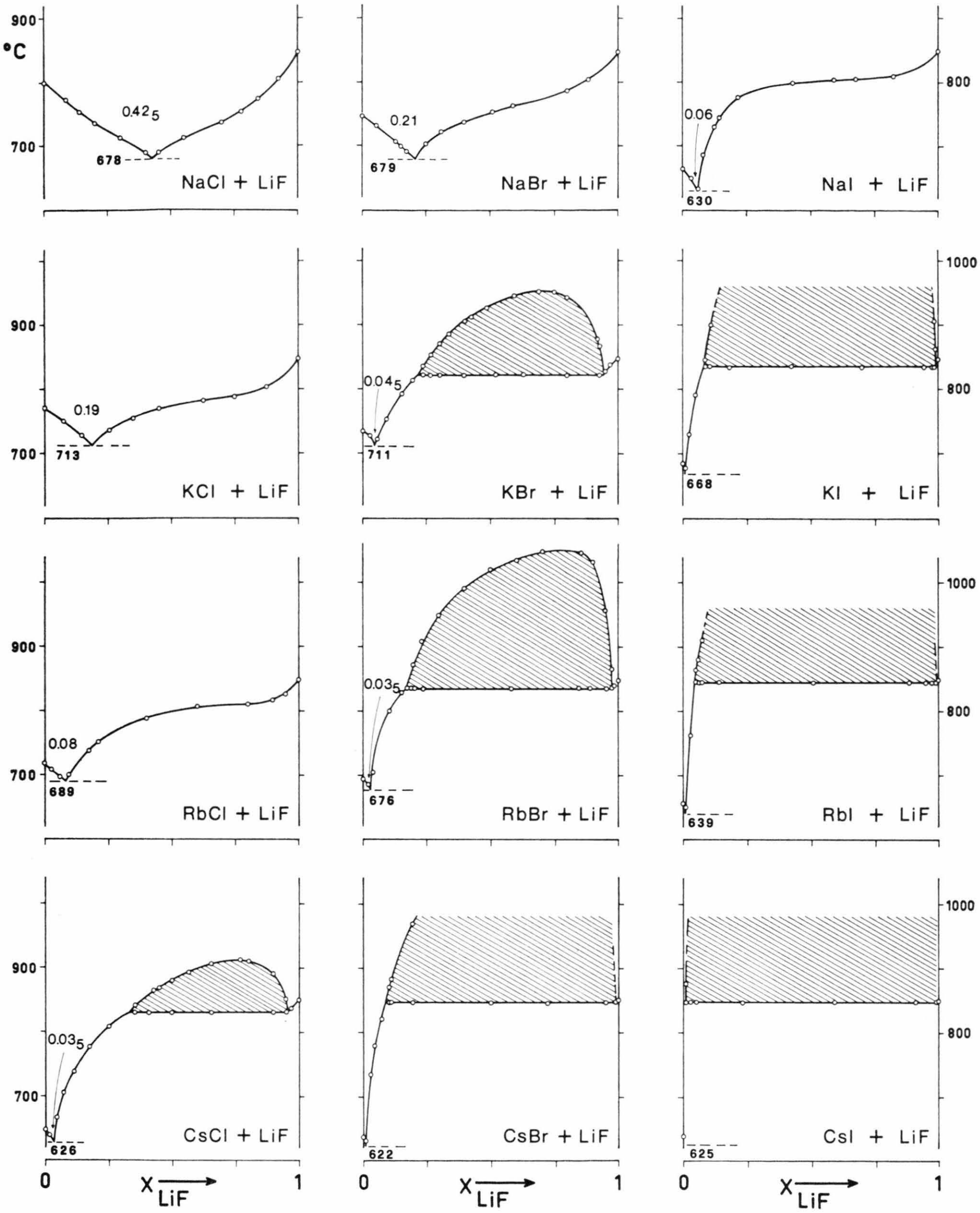

Fig. 1. SL and LL equilibria in the mixtures LiF+alkali halides. Demixing areas are shaded.

complete area of the MG has been measured: the co-ordinates of the point of maximum (PM) are: $x_1 = 0.76$; $t = 912$ °C. Bukhalova et al. report for the width of the MG in a first paper [3] a value of x_1 ranging from 0.30 to 0.90 at PCT = 820 °C, in a second one [4] a value of x_1 ranging from 0.33 to 0.94 at PCT = 824 °C. The eutectic has been found by the Russian authors at $x_1 = 0.04$ and $t = 619$ °C.

As regards the other systems of this family, no MG has been detected but only curves the "S" shape of which becomes more pronounced on going from NaCl to RbCl.

In the systems containing bromides demixing occurs with KBr, RbBr and CsBr.

LiF + KBr exhibits a constant PCT of 822 °C between $x_1 = 0.22$ and $x_1 = 0.94_5$. The complete area of the MG has been detected: the PM is at $x_1 = 0.70$ and $t = 953$ °C. The width of the gap found by Russian authors[5] is between $x_1 = 0.20$ and $x_1 = 0.97$ for a constant temperature of 804 °C.

Also for the mixture LiF + RbBr the complete MG could be detected: MG extends from $x_1 = 0.17$ to $x_1 = 0.97_5$ at the PCT of 834 °C and the PM is at $x_1 = 0.76$ and $t = 1050$ °C.

For the mixture LiF + CsBr, the MG extends from $x_1 = 0.09$ to $x_1 \cong 0.99$ at the constant temperature of 846 °C. Russian authors[3] give for the same system a gap extending from $x_1 = 0.09$ to $x_1 = 0.94$ at the constant temperature of 838 °C.

Also in the systems containing iodides demixing occurs when K^+, Rb^+ and Cs^+ are present.

For the mixture LiF + KI the PCT is constant at 836 °C from $x_1 = 0.08_5$ to $x_1 = 0.99$. For the mixture LiF + RbI the PCT is at 844 °C and the MG extends from $x_1 = 0.04_5$ to $x_1 \cong 0.99_5$. Finally, for the mixture LiF + CsI the PCT, once more constant, is at 847 °C and the MG extends from $x_1 = 0.01$ to almost pure LiF.

Figure 1 clearly shows that the tendency to demix in this family of salts

a) increases for mixtures containing the same halide (vertical series) as the radius of the alkali cation increases;

b) increases for mixtures containing the same cation (horizontal series) as the radius of the halide anion increases.

This agrees in general with the "reciprocal coulomb effect" according to which, in a reciprocal ternary system, the smallest cation and the smallest anion (Li^+ and F^-) on one hand, and the largest cation and the largest anion (Me^+ and X^-) on the other, tend to be the members of the stable pair.

It must be noted that this reciprocal coulomb effect is not the most important factor when other mixtures are considered. In fact, previously investigated families of systems containing one component stabilized by van der Waals interactions exhibit a tendency to demix increasing as the radius of the alkali cation decreases (or as the polarizing power of the alkali cation increases).

Discussion

The theory of the reciprocal ternary systems was discussed for the first time by Flood et al.[8], then developed by Blander[9] and Førland[10], and finally settled by Blander[11] who took also into account some applicative aspects[12]. A clear summary of these theories has been also given by Lumsden (see Ref.[2], p. 151).

Briefly, for the present case of mixtures type $LiF(x_1) + MeX(x_2)$, the excess potential of component 1 is written as

$$\mu_1^{E} = \mu_1^{E,R1} + \mu_1^{E,R2} + \mu_1^{E,NR}. \tag{1}$$

The term $\mu_1^{E,R1}$ in Eq. (1) is the contribution to the excess potential due to the cation-anion contacts (first co-ordination sphere) assuming that both the cations and the anions are randomly arranged on their sites. This term was evaluated[8, 11] as

$$\mu_1^{E,R1} = \Delta G^0 x_2^2 \tag{2}$$

where ΔG^0 is the standard molar Gibbs free energy change for the metathetical reaction:

$$\mathrm{LiF} + \mathrm{MeX} \rightleftharpoons \mathrm{MeF} + \mathrm{LiX}. \tag{3}$$

The term $\mu_1^{E,R2}$ is the contribution to μ_1^E due to the interactions between the nearest ions of the same sign (second co-ordination sphere) assuming random arrangement. This term was evaluated[10, 11] as

$$\mu_1^{E,R2} = x_2^2[k_{Me} + k_X + 2x_1(k_{Li} + k_F - k_{Me} - k_X)] \tag{4}$$

where k_i is the interaction parameter of the binary mixture containing the i-th ion as the common ion (for the meaning of this parameter see Ref.[2], pp. 34, 68).

If long-range interactions are neglected, $\mu_1^{E,NR}$ is to be intended as a correction to account for the non random distribution of the ions. It is difficult to evaluate $\mu_1^{E,NR}$: this term, at least for the present systems, is mainly a correction on (2) since the correction on (4) is less important. Moreover, $\mu_1^{E,NR}$ becomes more significant as ΔG^0 increases. Blander[9] developed the quasi-chemical theory of Guggenheim[13] taking into account only the first co-ordination sphere. The results of this so called "symmetric approximation" are:

$$\mu_1^{E} = Z\,R\,T \ln[(1-Y)/x_1], \tag{5}$$

$$Y^2 x_1(1-\beta) + Y\beta - x_2\beta = 0, \quad [\beta = \exp\{-\Delta G^0/Z\,R\,T\}] \tag{6}$$

where Z = coordination number; Y = fraction of positions adjacent to the Li^+ ion occupied by X^- ions (for a random arrangement $\Delta G^0 = 0$, $Y = x_2$).

Thus

$$\mu_1^{E,NR} = Z\,R\,T\ [\ln(1-Y)/x_1] - \Delta G^0 x_2^2. \tag{7}$$

This equation has been simplified[11, 12] by a series expansion to give:

$$\mu_1^{\mathrm{E,NR}} = (\Delta G^0)^2 x_1 x_2^2 (3x_1 - 2)/12RT \quad (8)$$

having taken a value 6 for Z. The relatively high value of Z has been used to "partially compensate for the higher order terms" which have been neglected in the series[12].

On the basis of the experimental results, we have checked the degree of applicability of the symmetric approximation both in its original version (5) – (6) and in the simplified form (8).

First, the $(\mu_1^{\mathrm{E}})_{\mathrm{exp}}$ values were calculated starting from the SL and LL data. For the SL equilibria, assuming that no solid solution is formed, the equations already reported[14] were used with the proper[15] ΔH_{f} and ΔC_p values of lithium fluoride. As regards the LL equilibria, values of $(\mu_1^{\mathrm{E}})_{\mathrm{exp}}$ were calculated at fixed temperatures according to the general principles discussed in a previous paper[16].

From the $(\mu_1^{\mathrm{E}})_{\mathrm{exp}}$ values thus obtained, by subtracting the terms (2) and (4) calculated using the parameters reported by Lumsden (see Ref. [2], pp. 19, 69), it was possible to make a direct estimate of the quantity $\mu_1^{\mathrm{E,NR}}$.

In the case of the LiF + CsCl system, the results of the calculations are reported in detail in Figure 2. In particular Fig. 2 a reports the experimental values $(\mu_1^{\mathrm{E}})_{\mathrm{exp}}$ as a function of x_2^2. In order to have a picture of the weight of each term, in the same figure there are also reported the quantities $\mu_1^{\mathrm{E,R1}}$ and $\mu_1^{\mathrm{E,R2}}$ as calculated by Eqs. (2) and (4) along with the $\mu_1^{\mathrm{E,NR}}$ values which have been deduced by difference.

It should be noted that the functions in Fig. 2 are not isotherms: the temperatures, which are constant normally to the abscissa, are reported in the upper part of the figure. It should also be observed that as $x_2 \to 1$ each term tends to a finite value which is ΔG^0 for $\mu_1^{\mathrm{E,R1}}$, $(k_{\mathrm{Me}} + k_{\mathrm{X}})$ for $\mu_1^{\mathrm{E,R2}}$, zero for $\mu_1^{\mathrm{E,NR}}$ and $\Delta G^0 - (k_{\mathrm{Me}} + k_{\mathrm{X}})$ for μ_1^{E}.

In Fig. 2 b, the term $\mu_1^{\mathrm{E,NR}}$ is reported as a function of x_2. To test the validity of the theories, on the same figure the values calculated by the "simplified" Eq. (8) (dotted curve) are shown together with those foreseen (dashed curves) according to the symmetric approximation [Eqs. (5) – (6)] for $Z = 6$ and $Z = 4$, these being extreme reasonable values for these systems. It must be underlined that most likely Z varies both with temperature and composition.

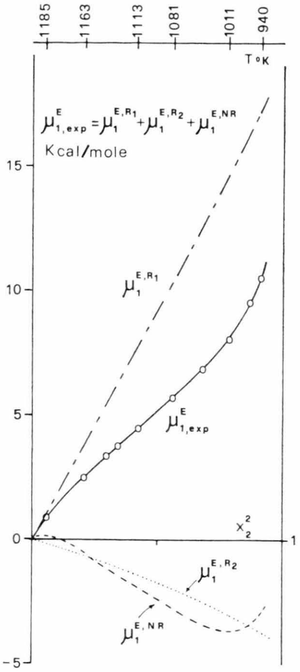

Fig. 2 a. Experimental values of μ_1^{E} as a function of x_2^2 for LiF+CsCl. The behavior of the single terms by which this quantity is made up [see Eq. (1)] is also shown.

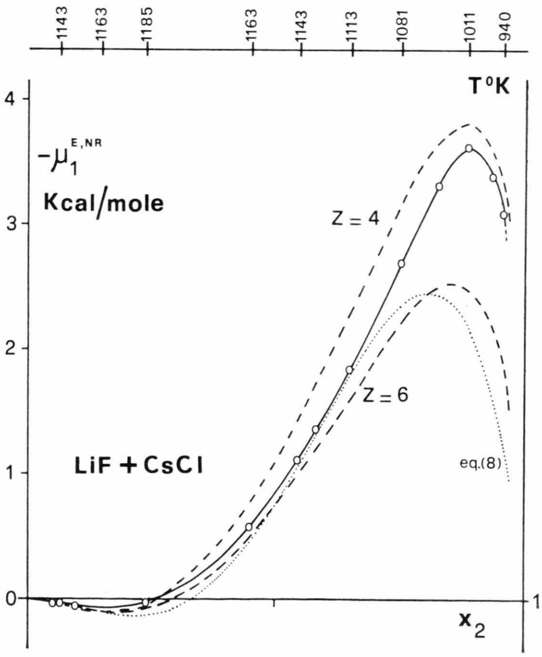

Fig. 2 b. Values of $\mu_1^{\mathrm{E,NR}}$ as a function of x_2 for the system LiF+CsCl. Values calculated according to Eq. (8) (dotted curve) and to Eqs. (5) – (6) (dashed curve) are also shown.

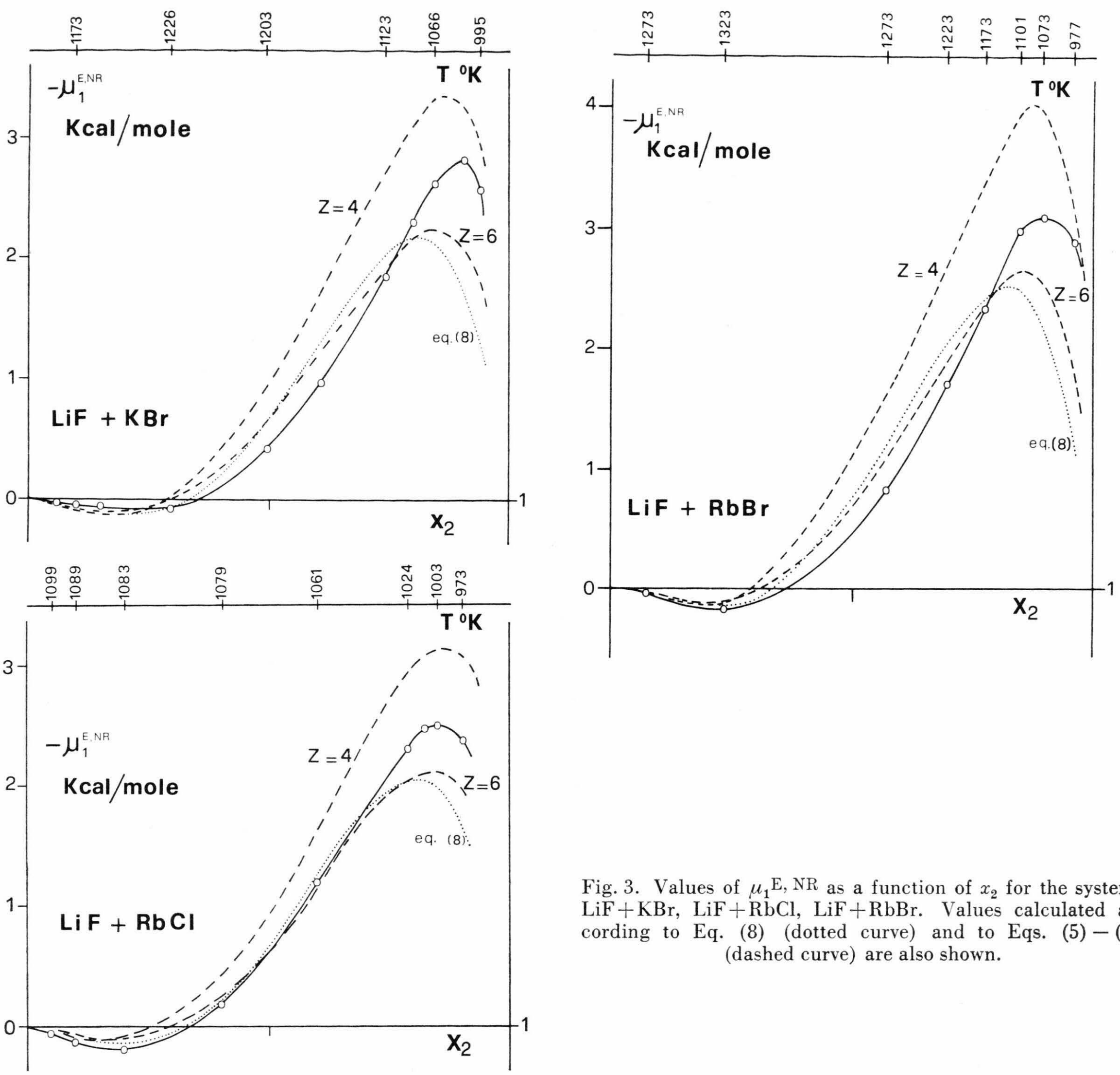

Fig. 3. Values of $\mu_1^{E,NR}$ as a function of x_2 for the systems LiF+KBr, LiF+RbCl, LiF+RbBr. Values calculated according to Eq. (8) (dotted curve) and to Eqs. (5) — (6) (dashed curve) are also shown.

Similar comparisons are also reported in Fig. 3 which presents the results obtained for the systems LiF + KBr, RbCl, RbBr, where it is possible to obtain significant data on the whole composition field.

To discuss the results presented in Figs. 2 – 3 it must be remembered that: a) in the calculated curves the correction for non-randomness on term (4) has been neglected; b) the values reported are obtained by difference between experimental quantities and the terms (2) and (4). Since these terms contain ΔG^0 and k_i, they might be slightly uncorrect.

Nevertheless the following general remarks can be made: a) qualitatively the theories reproduce the trend of the experimental data satisfactorily, both the minimum and the maximum being expected; b) in the original version of the symetric approximation [Eqs. (6) – (7)] the uncertainty on the value of Z gives rise to a large uncertainty in the calculated values particularly at $x_1 \cong 0.1 - 0.15$ where the function presents a maximum; c) as regards the simplified Eq. (8), it reproduces, only approximately, the original theory for $Z = 6$.

It can be concluded that, at least for the present systems, the theories seem to give a reasonable first approximation picture of the term $\mu_1^{E,NR}$ and thus a satisfactory general description of the thermodynamic behavior of the reciprocal ternary systems.

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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:

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

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

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]:

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

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

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

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