The Thermoelectric Power of the Molten System (Ag + K)Cl *

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In a silver electrodes thermocell the thermoelectric power ε_0 at zero time of the molten system (Ag+K)Cl at various temperatures has been measured.

The Ψ-function test, applied to this system at 800 °C, shows how its behaviour in connection with the transport phenomena is, on the whole, very near to the ideality.

It has been shown in a previous paper [1] how measurements of thermoelectric power at zero time on systems with variable compositions, enable to draw information about the behaviour of fused salt mixtures in connection with transport phenomena. Approximating values of the heat of transport for the single ions can be inferred.

In view of extending the application of these methods to mixtures of the type AgCl+MeCl, results on the fused system (Ag+K)Cl are reported in the present work. The measurements have been made on the thermocell:

$$\text{final stage} \;\Big|\; Ag_{(s)} \;\Big|_{T_1}\; (Ag+K)Cl_{(fused)} \;\Big|_{T_2}\; Ag_{(s)} \;\Big|\; \text{final stage} \qquad (1)$$

$(T_1 \neq T_2)$ at various temperatures and for nine different compositions of the binary mixture. The device we made use of permitted the measurement of the thermal emf at zero time. For this system, at the eutectic composition, MARKOV [2] has reported a thermoelectric power of $-0.383\ \mu V\ deg^{-1}$ at $t = 400-550$ °C.

Experimental

The "U" shaped cell, made of quartz, was placed in a nickel block divisible into three pieces. The whole was placed in a thermostat oven of great capacity. The differential heating of one of the two arms of the cell was obtained by means of thermocoax resistances (Philips).

The reversible behaviour of the silver electrodes has been tested for each mixture examined.

The silver chloride was freshly prepared; the KCl (C. Erba RP) was prefused and carefully dried before use. All the other experimental features were the same as those previously described [1, 3].

Results and Discussion

The results obtained are shown in Fig. 1. For each of the nine compositions examined the values ε_0 are reported as function of the mean temperature of the system. The dilution of the mixtures has never been carried on below $x_{AgCl} = 0.05$ to prevent the spontaneous reaction of silver with KCl [4].

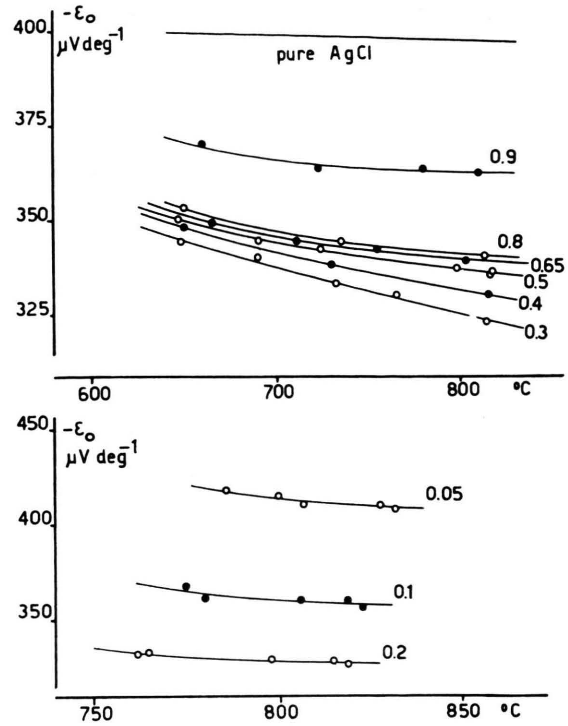

Fig. 1. Values of ε_0 as a function of the mean temperature of the thermocell (1). The composition of the system (in mole fractions of AgCl) is indicated at every curve.

As regards pure molten AgCl, the values of ε_{AgCl} are given by the relation [5]:

$$\varepsilon_{AgCl} = [-410 + 0.016\, t(°C)]\ \mu V\ deg^{-1}. \qquad (2)$$

From the data of Fig. 1 the values of ε_0 reported in Table 1 and in Fig. 2 have been drawn, by interpolation at 800 °C. In Table 1 also the values of the Ψ-function, previously defined as [1]:

$$\Psi \equiv F(\varepsilon_0 - \varepsilon_{AgCl}) - R \ln x_{Ag^+} \qquad (3)$$

are reported. The Ψ-function test for the system (Ag+K)Cl at 800 °C, is shown in Fig. 3.

By extrapolation for $x_{KCl} = 1$ it is possible to state a limiting value $\Psi_0 = 5.7$ cal mole^{-1} deg^{-1}. From this figure, the heat of transport ${}^0Q^*_{K^+}$ of the potassium ion in pure KCl, can be obtained by the approximated relation [1]:

$${}^0Q^*_{K^+} = -T\,\Psi_0 = -1073.2 \times 5.7 = -6.1\ \text{Kcal/mole}. \qquad (4)$$

In Eq. (4) the heat of transport ${}^0Q^*_{Ag^+}$ of the silver ion in pure AgCl, has been taken to be zero.

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1 C. SINISTRI, Z. Naturforschg. **21 a**, 753 [1966].
2 B. F. MARKOV, Dokl. Akad. Nauk SSSR **108**, 115 [1956].
3 C. SINISTRI, Z. Naturforschg. **20 a**, 1045 [1965].
4 K. H. STERN, J. Phys. Chem. **60**, 679 [1956].
5 C. SINISTRI, unpublished results.

x_{AgCl}	$-\varepsilon_0$ μV deg^{-1}	Ψ cal deg^{-1} mole^{-1}
1.00	397	0.00
0.90	362	1.02
0.80	341	1.73
0.65	339	2.19
0.50	337	2.76
0.40	331	3.34
0.30	325	4.05
0.20	328	4.79
0.10	361	5.40
0.05	414	5.56

Table 1. Interpolated values of the thermoelectric power ε_0 and of the parameter Ψ for the system (Ag+K) Cl at 800 °C.

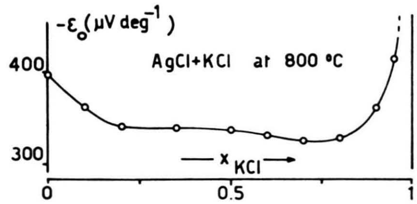

Fig. 2. Values ε_0 as a function of x_{KCl} at 800 °C.

It is also possible to draw the Ψ-function for the ideal transport behaviour of the system (Ag+K) Cl. This function is given by the relation

$$\Psi_{id.} = -\,({}^0Q^*_{K^+}/T)\,(1 - x_{AgCl}) \qquad (\text{for } {}^0Q^*_{Ag^+} = 0) \qquad (5)$$

which is represented by a dashed line in Fig. 3. For

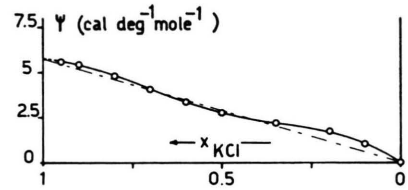

Fig. 3. Ψ-function test for the (Ag+K) Cl system at 800 °C. Dashed line represents the ideal behaviour.

many concentrations the system (Ag+K) Cl at 800 °C shows only small deviations from ideal behaviour. The deviations are more considerable for low values of x_{KCl}.

Now we point out that ideal behaviour regarding transport is obtained on the three conditions that (valid at constant temperature) [1]: a) the excess entropic terms are zero; b) the heats of transport of the single ions in the mixture are constant; c) the Hittorf transport numbers of the two cations are equal to the respective ionic fractions.

As for point a) it is interesting to observe that the comparison of state diagrams with heats of solution of solid KCl in molten AgCl led to the conclusion that for this system the mixture entropy is not too far from ideality [6]. As regards point b) no information is available. Finally, as regards point c) Murgulescu and Marchidan [7], on the basis of diffusion potential measurements in concentration cells, reach the conclusion that the transport numbers of the two cations are proportional to the mol fractions of the corresponding salts.

[6] J. Lumsden, Thermodynamics of Molten Salts Mixtures, Academic Press, New York 1966, p. 96.

[7] I. G. Murgulescu and D. I. Marchidan, J. Phys. Chem. 68, 3086 [1964].

The Thermoelectric Power of the Molten System Silver Nitrate–Lithium Nitrate

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The initial thermoelectric power of the cell

Ag (T$_1$) / (Ag+Li) NO$_3$/Ag (T$_2$)

has been studied in the range 250–286 °C. The obtained concentration dependence differs considerably from that found by Connan et al. [1] at 265 °C, but shows good agreement with Sinistri's [2] measurements at 340 °C. A comparison of these latter results with ours indicates that the (numerical value of the) thermoelectric power increases slightly, about 0.05% per degree, with increasing temperature.

Two investigations of the initial thermoelectric power of mixtures of silver nitrate with lithium nitrate have been reported recently [1, 2], which differ considerably regarding the concentration dependence. Thus, we consider it of interest to report on our measurements which were nearly completed when the other investigations came to our knowledge.

Experimental

The same U-shaped measuring cell, made of Supremax glass, was used for several measurements. The changes in composition were obtain by adding each time a weighed amount of salt. The salt was mixed thoroughly by pressing all of it up into one arm of the cell and letting argon gas bubble through the melt. Samples from both arms were analysed chemically, and the results were in agreement with the calculated composition. Pure silver wires were used as electrodes and high grade salts were used without further purification.

The cell was placed in a salt bath kept at about 250 °C, and one arm was heated with a separate coil. At each concentration the emf was measured for five temperature differences (about 0.5 to 40 degrees) and the thermoelectric power was obtained by a least squares fit.

[1] R. Connan, J. Dupuy, and J. Brenet, C. R. Acad. Sci. Paris **262**, 1120 [1966].

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