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.

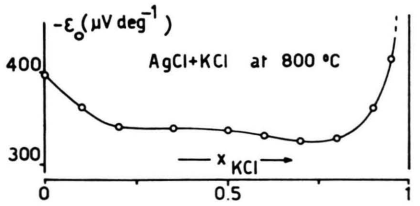

Fig. 2. Values ε_0 as a function of x_{KCl} at 800 °C.

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

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

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

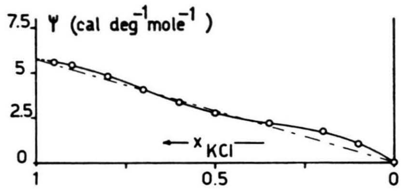

Fig. 3. Ψ-function test for the (Ag+K) Cl system at 800 °C. Dashed line represents the ideal behaviour.

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

Kerstin Wallin and Arnold Lundén

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

(Z. Naturforschg. **22 a**, 591—592 [1967]; received 20 February 1967)

The initial thermoelectric power of the cell

$$\mathrm{Ag}(T_1)\,/\,(\mathrm{Ag+Li})\,\mathrm{NO_3}/\mathrm{Ag}(T_2)$$

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].

Results and Discussion

Our experimental results are shown in Table 1, where they are compared with those of the two other investigations [3, 4]. Regarding the concentration dependence, Connan et al. who had chosen practically the same tempeature as we, start with a thermoelectric power that is about 5% lower than what we find for pure $AgNO_3$, and they have obtained both a maximum and a minimum (at about 60 and 35 mole % $AgNO_3$, respectively), while we get nearly the same increase of the thermoelectric power with increasing concentration of $LiNO_3$, as was obtained by Sinistri at about 340 °C. This is the case at least for the range 0 – 90% $LiNO_3$, while a comparison is more difficult for the remaining concentration range, where the concentration dependence becomes stronger, and the uncertainty in the determination of the concentration thus becomes more important. Our results are slightly (some 2 to 4%) lower than Sinistri's, corresponding to an increase of the thermoelectric power by about 0.05% per degree.

		Deviation (μV deg.$^{-1}$) from	
$AgNO_3$ mole %	$-\varepsilon_0$ μV deg.$^{-1}$	Connan et al [1]	Sinistri [2]
100	326	−16	4
100	322	−12	8
92.7	332	− 7	5
89.5	327	4	12
82.9	333	18	10
76.5	342	29	6
75.5	340	34	9
71.7	345	40	8
59.5	350	44	15
53.3	361	24	13
38.0	389	−39	13
28.6	410	−37	15
22.4	427	5	22
16.4	452	49	14
11.3	484	80	18
9.7	499	81	15
8.5	531		−11
4.8	573		− 7
2.9	589		17
2.8	586		25
2.6	591		25
1.9	638		− 1

Table 1. The thermoelectric power, ε_0, measured by us and compared with the results of previous investigations.

A temperature dependence of this order of magnitude is in agreement with two of the previous investigations of the thermoelectric power of pure molten silver nitrate. Thus Sinistri [5] found that it increased about 0.025% per degree, and another set of measurements [6] shows a "slight but distinct trend with temperature", while there is no significant trend in the third series considered [7].

Measurements of the thermoelectric power of pure molten silver nitrate at four different laboratories are summarized in Table 2. It is obvious that the reproducibility of the measurements within a laboratory is much better than between different laboratories. There are some differences between the different investigations regarding apparatus and experimental procedure. E. g. a type of "microelectrodes" were used in the last two French investigations, while wire electrodes were used in all other cases. Thermal decomposition of the salt might be suspected to influence some experiments [11]. Thus, e. g. while Connan et al. used fresh salt for each measurement, we often used the same salt filling several times, but when comparing the results of different series, we have not found any influence of the total time that the salt had been kept at an elevated temperature. Finally, it remains the possibility that the thermoelectric power might to some extent be influenced by impurities or other differences between the salt batches used in the different investigations, and at the present stage there is no obvious explanation of the deviations between the results of different investigations.

Laboratory	$-\varepsilon_0$ μV deg.$^{-1}$	Temperature range °C	Ref.
New York	330 – 352	240 – 308	6
New York	319	310	8
Strasbourg	301 – 315	222 – 281	7
Strasbourg	310	265	1
Strasbourg	320	310	9
Pavia	322 – 331 [a]	215 – 347	5
Pavia	330, 332	340, 360	2
Göteborg	322, 326	267	10

[a] A linear relationship between thermoelectric power and temperature established.

Table 2. The thermoelectric power of pure molten silver nitrate, as measured at different laboratories.

The interpretation of this type of experiments has been discussed by the other authors.

Acknowledgement

This investigation has been supported by "Helge Ax:son Johnssons Stiftelse".

---

[3] When making the comparison, the corresponding thermoelectric powers were obtained by numerical interpolations of the tabulated results of the other investigation. Since Connan et al. have plotted more results than they have tabulated, we also estimated thermoelectric powers from their graphical representation, but only the results obtained numerically are considered in our Table 1.

[4] The numerical value of the thermoelectric power will be considered in the following discussion.

[5] C. Sinistri, Z. Naturforschg. **20 a**, 1045 [1965].

[6] B. R. Sundheim and J. Rosenstreich, J. Phys. Chem. **63**, 419 [1959].

[7] J. Dupuy, C. R. Acad. Sci. Paris **258**, 158 [1964].

[8] R. Schneebaum and B. R. Sundheim, Discussions Faraday Soc. **32**, 197 [1961].

[9] J. Dupuy, Y. Nakamura, S. Brillant, and J. Brenet, J. Chim. Phys. (Paris) **63**, 886 [1966].

[10] This investigation.

[11] J. Dupuy, private communication.

Verantwortlich für den Inhalt: A. Klemm
Satz und Druck: Konrad Triltsch, Würzburg