measurement, which makes the correction factor rather uncertain.

The influence of end-effects (Δl-effects) on the results of the capillary method has recently been discussed by several authors. BOCKRIS et al.[7] claim that it is impossible to avoid Δl-errors even if the flow rate past the capillary mouth is carefully chosen. According to SPEDDING and MILLS[8], on the other hand, the Δl error will be negligible for certain flow rates. Since the investigation by DWORKIN et al. was performed before the importance of these end effects was fully appreciated, it is reasonable to suspect that end errors in their capillary method might have affected their results. However, since our values and their values of D_{Ag^+} in molten $AgNO_3$ are in good agreement, we find that DWORKIN et al. have succeeded in avoiding Δl errors (at least in their measurements of D_{Ag^+}).

The above results show, that the paper strip technique can be used for self-diffusion measurements in molten salts if a correction for the exchange of metal ions between the glass and the melt is applied when necessary. The glass-melt interface is very large, and this fact, in conjunction with the comparatively long diffusion times that are needed, enhances the exchange. (A somewhat similar situation is encountered in the porous frit technique[2, 3], but the corresponding problem is by no means so serious, since the diffusion times are of the order of 30 minutes only.) Due to the difficulty to determine the correction factor accurately, the paper strip method is not capable of the highest precision. It is, on the other hand, very simple to use, and it is able to give valuable independent checks of the results of other methods.

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Thermoelectric Power of Molten and Solid Silver Sulphate

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The thermocell $Ag(T_1)/Ag_2SO_4/Ag(T_2)$ has been studied over the temperature range 420 to 750 °C. The results can be described by the following linear relations[1]

$$-\varepsilon_l = (0.31 \pm 0.01)\ \mathrm{mV/^\circ C} \qquad (657-750\ ^\circ\mathrm{C})$$

$$-\varepsilon_s = [(0.687 \pm 0.011) - (0.472 \pm 0.019) \cdot 10^{-3} \cdot t_m]\ \mathrm{mV/^\circ C} \qquad (420-657\ ^\circ\mathrm{C})$$

ε_l and ε_s are the SEEBECK-coefficients of molten silver sulphate and the α-modification, respectively, and t_m is the mean temperature of the salt column in °C.

The standard deviation of ε_s was $4.3 \cdot 10^{-3}$ mV/°C.

The transported entropy of the silver ion and of the sulphate ion have been calculated. A discontinuous change of the emf and the transported entropies was found at the melting point.

A number of measurements of the thermoelectric power of solid and molten ionic salts has been reported[2, 3].

Between 412 and 657 °C silver sulphate forms a high temperature modification with a hexagonal structure[4]. This modification is characterised by a high cation mobility. The electrical conductivity increases strongly at the $\beta - \alpha$ transition and the conductivity of the α-modification is close to that of the melt. Similar high temperature modifications have been found in Li_2SO_4 and K_2SO_4.

We report here on the determination of the thermoelectric power of the system $Ag(T_1)/Ag_2SO_4/Ag(T_2)$ in the temperature range 420 to 750 °C.

Experimental

Reagent grade silver sulphate (Hopkin & Williams or May & Baker) has been used in all experiments without further purification. No detectable difference between the results from two lots could be found, and both lots were therefore considered to be of satisfactory purity.

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[1] All stated errors in this paper are standard deviations.

[2] A. KVIST and A. LUNDÉN, Z. Naturforschg. **19 a**, 1058 [1964] and references there.

[3] A. KVIST, Z. Naturforschg. **19 a**, 1159 [1964].

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All experiments were performed in air. According to HEGEDÜS and FUKKER[5] the decomposition of Ag_2SO_4 in air starts above 790°. This agrees with our observations.

Two series of measurements were performed.

In the first series of measurements (method A) only the emf of the α-modification was determined. Salt slabs, about 30 mm high and 12 mm in diameter, were pressed from dried salt and a slab was placed in a small furnace of Pyrophyllite (Fig. 1). The electrodes were silver discs, made of 0.5 mm silver foils. Thermocouples (Chromel-Alumel) were brought in contact with the electrodes. The silver electrodes were soldered to copper wires outside the furnace, and to prevent spurious thermopotentials, the silver – copper junctions were placed in a DEWAR flask filled with ice. The temperature gradients in the discs were found to be very small and were not taken into account.

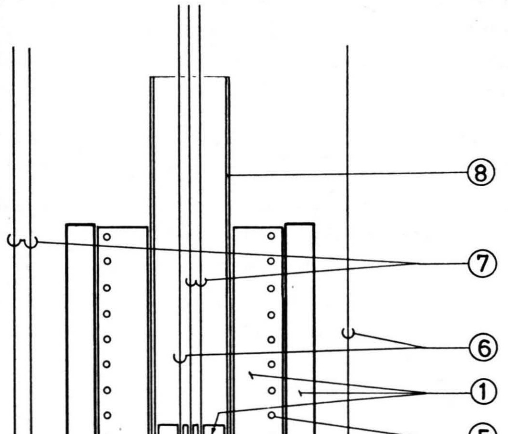

Fig. 1. Cell used for measuring the thermal emf of solid silver sulphate (method A). 1) pyrophyllite. 2) steel rings. 3) electrodes. 4) salt column. 5) auxiliary heating coils. 6) electrode wires. 7) thermocouple wires. 8) glass tube.

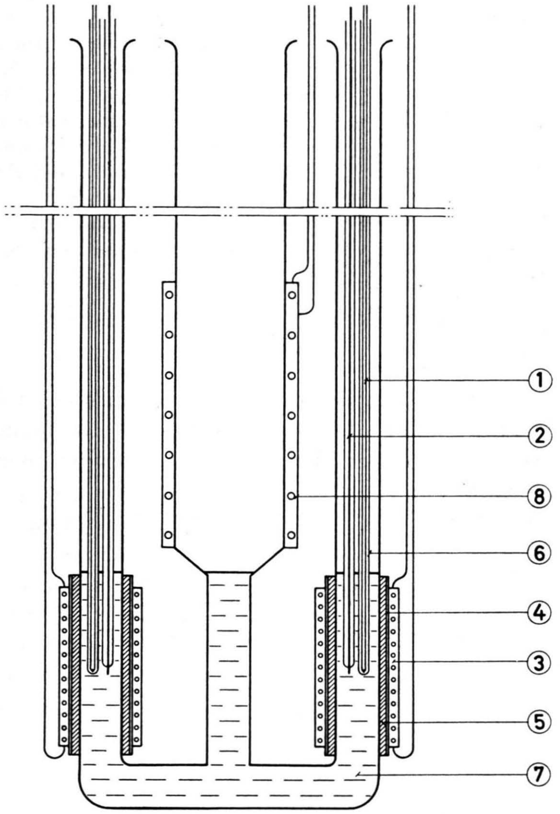

Fig. 2. Supremax cell used for measuring the thermal emf of molten and solid silver sulphate (method B). 1) Chromel-Alumel thermocouple. 2) electrode wire. 3) auxiliary heating coil. 4) thin layer of asbestos. 5) steel tube. 6) protecting glass tubes. 7) salt. 8) heating coil.

In method B the salt was first molten in a Supremax cell with three arms (Fig. 2). The electrodes and the thermocouples, which were surrounded by Supremax tubes, were then immersed into the salt. This arrangement, with small modifications, was used for several of the measurements. The temperature of the salt was, however, near the softening point of the Supremax glass when the electrodes were inserted, and it was therefore rather difficult to keep their sleves leak-free.

The thermocouples were connected to a compensation bridge (Norma Model 317) and the thermal emf was measured with a standard potentiometer method, using a microvoltmeter (Phillips GM 6020) as null detector and an adjustable standard voltage source (Knick model S 2).

We varied both the mean temperature t_m of the salt column and the temperature difference ΔT between the

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[5] A. J. HEGEDÜS and K. FUKKER, Z. Anorg. Allg. Chem. **284**, 20 [1965].

electrodes. The final measurements were performed with $\Delta T = 40$ °C. Some measurements were performed with interchanged temperatures of the electrodes. By comparison it was possible to check the reproducibility of the results. In the method B a small isothermal emf was found. This was caused by leaking electrodes and differences between the measured temperature and the temperature of the electrodes, cf however DUPUY[6].

The interval between two measurements was at least 45 minutes, which was the time required for the temperature to become constant.

Results

No temperature dependence of the SEEBECK coefficient of molten silver sulphate, ε_l, could be found in our measurements, because the temperature interval was too small.

The SEEBECK coefficient of solid silver sulphate measured in both cells was the same within the limits of errors. As a small isothermal emf, which was more marked in the α-modification than in the melt, was obtained with method B, only the results obtained with method A have been used for our calculations. Fig. 3 shows the emf as a function of the mean temperature T_m. It is clear that there is a discontinous change of ε at the melting point. The emf of molten Ag_2SO_4, ε_l, and that of solid Ag_2SO_4, ε_s, can be described by the following linear relations:

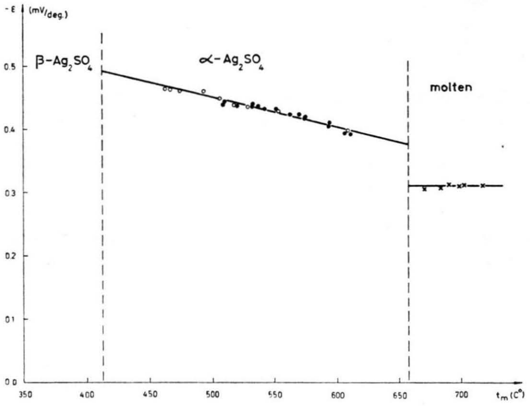

Fig. 3. Temperature dependence of the thermal emf of solid and molten silver sulphate.

$$-\varepsilon_l = (0.31 \pm 0.01) \text{ mV/degr.},$$
$$-\varepsilon_s = [(0.687 \pm 0.011) - (0.472 \pm 0.019) \cdot 10^{-3}\, t_m] \text{ mV/degr.}$$

t_m is the mean temperature of the salt column in °C. The standard deviation of ε_s was $4.3 \cdot 10^{-3}$ mV/degr.

According to these data the quotient of ε_s and ε_l at the melting point, 657 °C, is

$$\varepsilon_s / \varepsilon_l = 1.22 .$$

Discussion

The theory of thermocells has been discussed in several papers [7–13]. Following the terminology of AGAR[10], the emf of a thermocell with reversible silver electrodes is

$$\nu F \varepsilon = S_{Ag} - \overline{\overline{S}}_{Ag^+} - \overline{\overline{S}}_{e(M)} .$$

F is FARADAY's constant, ε the SEEBECK coefficient, S_{Ag} the molal entropy of the metal, $\overline{\overline{S}}_{Ag^+}$ the transported entropy of the silver ion in the silver salt and $\overline{\overline{S}}_{e(M)}$ the entropy of the electron in the metal.

$\overline{\overline{S}}_{e(M)}$ is very small according to TEMKIN and KHOROSHIN[14] and we have not found it necessary to take this term into account in our calculations.

The molal entropy of Ag_2SO_4 is the sum of the entropy of the silver ions and the sulphate ion[11]. This gives the relation

$$2\, \overline{\overline{S}}_{Ag^+} + \overline{\overline{S}}_{SO_4^{2-}} = S_{Ag_2SO_4}$$

The molal entropy of a substance $S(T)$ can be calculated from the molal heat capacity c_p and the state entropy S^0, i. e.

$$S(T) = S^0 + \int_{298.15}^{T} c_p \cdot \mathrm{d}T/T .$$

KELLY[15] has estimated the specific heat of silver sulphate from 298 to 930 °K. We have combined his equation with the standard entropy $S^0{}_{Ag_2SO_4}$ and the heat of fusion ΔH_F given by LANDOLT–BÖRNSTEIN[16].

$$S^0{}_{Ag_2SO_4} = 47.7 \text{ cal./mole, deg.}$$
$$c_p = (23.10 + 27.90 \cdot 10^{-3}\, T) \text{ cal./mole, deg.}$$
$$\Delta H_F = 4275 \text{ cal./mole} .$$

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T_m °K	t_m °C	$-\varepsilon_s$ mv/deg	$-F \cdot \varepsilon_s$ cal/mole · deg	S_{Ag} cal/mole · deg	$\overline{\overline{S}}_{Ag^+}$ cal/mole · deg	$S_{Ag_2SO_4}$ cal/mole · deg	$\overline{\overline{S}}_{SO_4^{2-}}$ cal/mole · deg
700	426.8	0.486	11.20	15.55	21.15	78.63	36.33
750	476.8	0.462	10.65	16.00	21.33	81.62	38.96
800	526.8	0.438	10.09	16.43	21.48	84.50	41.54
850	576.8	0.415	9.56	16.84	21.62	87.30	44.06
900	626.8	0.391	9.01	17.23	21.74	90.01	46.53
930 (s)	656.8 (s)	0.377	8.69	17.48	21.83	91.61	47.95
930 (l)	656.8 (l)	0.31	7.14	17.48	21.05	96.21	54.11

Table 1. Results. (s) = solid, (l) = liquid.

We have calculated the transported entropies S_{Ag^+} and $\overline{\overline{S}}_{SO_4^{2-}}$ of solid and molten Ag_2SO_4 in the temperature range 427 to 657 °C (Table 1).

Pitzer [13] has evaluated $\overline{\overline{S}}_{Ag^+}$ of some pure silver salts from published data. $\overline{\overline{S}}_{Ag^+}$ can be written as the sum of the partial molal entropy S_{Ag^+} and the entropy of transfer of the ion Ag^+.

$$\overline{\overline{S}}_{Ag^+} = S_{Ag^+} + S^*{}_{Ag}{}^{+} .$$

It is not possible to measure S_{Ag^+} and $S^*_{Ag}{}^{+}$ directly, but S_{Ag^+} can be estimated from the specific entropy of the salt. However, the internal entropy of rotation and vibration of a free polyatomic ion is reduced when the ion is brought into a crystal. We have not found it possible to calculate this reduction of the sulphate ion in silver sulphate.

We wish to thank Dr. A. Lundén for his continuous interest during this work and we are very much indebted to Mr. R. Eliasson for the glass-blowing work. This work was supported by Swedish Technical Research Council.

Die Thermokraft einiger Zellen des Typs $Cl_2 \,|_{T}$ geschmolzenes Clorid $|_{T+\Delta T}\, Cl_2$

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The thermoelectric power of cells of the type $Cl_2 \,|_T\, MCl_\nu \,|_{T+\Delta T}\, Cl_2$ has been measured, using the molten salts LiCl, NaCl, KCl, RbCl, CsCl, AgCl and $PbCl_2$. The entropies of transfer and the heats of transfer for the ions in the melt are calculated. It is shown, that the part containing the heats of transfer is small compared to the heterogeneous part of the thermopotential and that this result is in accordance with a "quasi lattice" model describing transport processes in ion conductors proposed by Wirtz (1943).

Theoretical relations between the thermoemectric power of such cells and cells of the type $M \,|_T\, MCl_\nu \,|_{T+\Delta T}\, M$ ($MCl_\nu = AgCl, PbCl_2$) are experimentally verified.

Bringt man ein ionenleitendes, geschmolzenes Salz MX_ν in Kontakt mit zwei in bezug auf das Metallion $M^{\nu+}$ oder das Halogenion X^- reversiblen Elektroden, von denen die eine auf der Temperatur T, die andere auf der Temperatur $T + \Delta T$ gehalten wird, so entsteht zwischen den beiden Elektroden eine Potentialdifferenz $\Delta\varphi$. Der Quotient $\Delta\varphi / \Delta T$ ist die Thermokraft dieses Systems. Theoretische Überlegungen zeigen [1–6], daß die Thermokraft im wesentlichen abhängt von dem Entropiewert der Elektrodensubstanz und von der Größe der Überführungsentropie der Ionen im Elektrolyten. Aus EMK-Messungen an Thermozellen können daher Überführungsentropien berechnet werden.

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