A practical method for determination of thermoelectric powers is developed. The method includes contributions from heat capacities and Thomson effects. We have applied the method to the cell $\text{Ag(T}_1)\mid\text{Ag}_2\text{SO}_4-\text{Li}_2\text{SO}_4\mid\text{Ag(T}_2)$, and calculated the transported entropy, $S_{\text{Ag}^+}$, and the heat of transfer $Q'$, from thermopotential measurements. Results show that the Thomson coefficient, $\tau_{\text{Ag}^+}$, is significant and that $S_{\text{Ag}^+}$ is relatively constant with structure and composition variations ($0.1 < x_{\text{AgSO}_4} < 0.175$). With electrolytes containing less than 10 mole% $\text{Ag}_2\text{SO}_4$, $S_{\text{Ag}^+}$ increases strongly with decreasing composition. For solid mixtures containing 10–17.5 mole% $\text{Ag}_2\text{SO}_4$, $Q'$ is negative and varies with composition. The negative sign indicates that $\text{Ag}_2\text{SO}_4$ is enriched at the hot side. For solid mixtures containing less than 10 mole% $\text{Ag}_2\text{SO}_4$, $Q'$ is approximately zero.

INTRODUCTION

Knowledge about transported entropies is important in calculating local heat effects in electrochemical cells, fuel cells and thermoelectric generators. Few values of transported entropies have been published, and there exist no good models. Data are mainly reported for single salts. The main purpose of this work is to contribute to the understanding of transported entropies and the phenomena causing heat transport in electrochemical systems. An additional purpose is to present results for salt mixtures. We shall present data of transported entropies and heats of transfer of the cell:

$$\text{Ag(T}_1)\mid\text{Ag}_2\text{SO}_4-\text{Li}_2\text{SO}_4\mid\text{Ag(T}_2)$$  \[a\]

There are three high temperature phases with different structures in mixtures of $\text{Ag}_2\text{SO}_4-\text{Li}_2\text{SO}_4$ (1). We shall consider the Li-rich phase in the solid state, and molten and solid $\text{Ag}_2\text{SO}_4$. Our theoretical derivations follow Førland et al. (2).
PRINCIPLES

The temperature difference across cell [a] causes an electromotive force (Seebeck effect), and a flux of matter (Soret effect). A current through the cell will cause Peltier effects. In the following derivation we denote Li$_2$SO$_4$ as component 1 and Ag$_2$SO$_4$ as component 2. The symbol $x_i$ is used for the molefraction, $s_i$ for the partial molar entropy, and $S_i$ for the molar entropy.

Five forces exist, $-\nabla \ln T$, $-\nabla \mu_{1, T}$, $-\nabla \mu_{2, T}$, $-\nabla \mu_{Ag, T}$ and $-\nabla \varphi$. Here $T$ is the temperature, $\mu_{i, T}$ is the chemical potential, and $\Delta \varphi$ is the electric potential. The fluxes are $J_q$ (heat flux), $J_1$, $J_2$, $J_{Ag}$ (mass fluxes), and $j$, electric current density. The dissipated energy per unit time, $T\Theta$, can be expressed by:

$$T\Theta = -J_q \nabla \ln T - J_1 \nabla \mu_{1, T} - J_2 \nabla \mu_{2, T} - J_{Ag} \nabla \mu_{Ag, T} - j \nabla \varphi$$  \[1\]

Since there is no pressure gradient in the system, $\nabla \mu_{Ag, T} = 0$. The sulfate ion is chosen as the frame of references, i.e.

$$J_{SO_4^2-} = 0 \quad \text{and} \quad t_{SO_4^2-} = 0$$  \[2\]

The condition of electro-neutrality must be fulfilled, hence :

$$J_{Li^+} + J_{Ag^+} - \frac{1}{2} (J_1 + J_2) = 0$$  \[3\]

The chemical potentials of Li$_2$SO$_4$ and Ag$_2$SO$_4$ are dependent through the Gibbs-Duhem equation, $x_i \nabla \mu_{1, T} + x_2 \nabla \mu_{2, T} = 0$. With the use of eq.[3] and Gibbs-Duhem eq., $J_1$ and $\nabla \mu_1$ can be eliminated from eq.[1]. Since the sum of the mole fractions is equal to unity, the term $(1 + x_2/x_1)$ can be reduced to $1/x_1$. This gives :

$$T\Theta = -J_q \nabla \ln T - J_2 \frac{\nabla \mu_{2, T}}{x_1} - j \nabla \varphi$$  \[4\]
Eq.[4] contains the three independent forces $-\nabla \ln T$, $-\nabla \mu_{\tau}$ and $\nabla \varphi$, with the conjugate fluxes $J_q$, $J_2$, and $j$. The flux equations are then:

\begin{align*}
J_q &= -L_{11} \nabla \ln T - L_{12} \frac{\nabla \mu_{\tau}}{x_1} - L_{13} \nabla \varphi \\
J_2 &= -L_{21} \nabla \ln T - L_{22} \frac{\nabla \mu_{\tau}}{x_1} - L_{23} \nabla \varphi \\
j &= -L_{31} \nabla \ln T - L_{32} \frac{\nabla \mu_{\tau}}{x_1} - L_{33} \nabla \varphi
\end{align*}

The coefficients $L_{ij}$ are the phenomenological coefficients. Positive direction of transport is from left to right, and one dimensional cases are considered. Eq.[5c] is solved with respect to $\nabla \varphi$, and introduced into eqs.[5a] and [5b]. This gives:

\begin{align*}
J_q &= -l_{11} \nabla \ln T - l_{12} \frac{\nabla \mu_{\tau}}{x_1} + \left( \frac{L_{13}}{L_{33}} \right) j \\
J_2 &= -l_{21} \nabla \ln T - l_{22} \frac{\nabla \mu_{\tau}}{x_1} + \left( \frac{L_{23}}{L_{33}} \right) j
\end{align*}

where $l_{ij} = \left( L_{ij} - L_{3j}/L_{33} \right)$.

From eqs.[5a] and [5c] the Peltier heat, $\pi$, can be expressed as:

\[\left( \frac{J_q}{j} \right)_{\Delta T=0, \Delta \mu_{\tau}=0} = \frac{L_{13}}{L_{33}} = \pi\]
There is only one independent transference coefficient. We choose $t_2$:

$$\left( \frac{J_2}{j} \right)_{\Delta T=0, \Delta \mu_2=0} = \frac{L_{12}}{L_{33}} - t_2$$ \[8\]

According to Onsager, the cross coefficients are related:

$$L_{ij} = L_{ji} \quad (i.e. \quad l_{12} = l_{21})$$ \[9\]

By introducing the relations given in eqs.[7], [8] and [9], into eqs.[6a] and [6b] we find:

$$J_q = -l_{11} \nabla \ln T - l_{12} \frac{\nabla \mu_2}{x_1} + \pi j$$ \[10a\]

$$J_2 = -l_{21} \nabla \ln T - l_{22} \frac{\nabla \mu_2}{x_1} + t_2 j$$ \[10b\]

Expressions for transported entropies, using well defined, measurable quantities, shall be derived. A reversible entropy balance and mass balances will be used. Consider first the local mass changes when one faraday of positive charges are transferred from left to right. The mass changes are listed in Table I. Table I shows that the transference coefficient of Ag$_2$SO$_4$, $t_2$, is equal to $-\frac{1}{2}t_{14v}$.

The Peltier heat is obtained from a reversible entropy balance at the electrode-electrolyte interface. We define the Peltier heat as positive if the left-hand side electrode-electrolyte interface receives heat. Each of the contributions to the heat balance are illustrated in Figure 1, and they are listed in Table II.

From Table II we have:

$$\frac{\pi}{T} + S_{Ag^+} + \frac{1}{2}t_{Li^+}S_{1^+} + S_{Ag^+}^* - t_{Li^+}S_{Li^+}^* + t_{Ag^+}S_{Ag^+}^* + \frac{1}{2}t_{Li^+}S_2$$ \[11\]
Table I. Local mass changes in the cell Ag(T₁) | Ag₂SO₄–Li₂SO₄ | Ag(T₂).
One faraday positive charges are transferred.

|                     | Left-hand side electrode (T₁) | Right-hand side electrode (T₂) |
|---------------------|-------------------------------|-------------------------------|
| Ag                  | −1 mole                       | 1 mole                        |
| Ag⁺                 | (1−tAg⁺) = tₙ₁⁺ mole          | (1−tAg⁺) = tₙ₁⁺ mole          |
| Li⁺                 | − tₙ₁⁺ mole                   | tₙ₁⁺ mole                     |
| Ag₂SO₄              | ½ tₙ₁⁺ mole                   | − ½ tₙ₁⁺ mole                 |
| Li₂SO₄              | − ½ tₙ₁⁺ mole                 | ½ tₙ₁⁺ mole                   |

Junction

|                     |                                |
|---------------------|--------------------------------|
| Ag₂SO₄              | ½ 1 ∫² dtₙ₁⁺ mole               |
| Li₂SO₄              | − ½ 1 ∫² dtₙ₁⁺ mole             |

Table II. Reversible entropy balance at the left-hand side electrode–electrolyte interface.
The entropy consumed and received is given for the transfer of one faraday of positive charges.

**ENTROPY RECEIVED**

| π/T                 | the interface receives entropy from the heat reservoir. |
|---------------------|--------------------------------------------------------|
| SAg                 | the disappearance of one mole Ag, liberates entropy.   |
| ½tₙ₁⁺S₁             | the disappearance of ½tₙ₁⁺ mole Li₂SO₄, liberates entropy. |
| SAg⁺                | entropy transported through the electrode to the interface. |

**ENTROPY CONSUMED**

| tₙ₁⁺S₁              | entropy transported through the electrolyte away from the interface. |
| Ag⁺S⁺               | entropy transported through the electrolyte away from the interface. |
| ½tₙ₁⁺S₂             | the formation of ½tₙ₁⁺ mole Ag₂SO₄, consumes entropy. |

We return to eq.[5c], solve the equation with respect to Vₚ, and introduce the relations.
given in eqs.[7], [8] and [9]. This yields:

\[ \nabla \varphi = -\left( \frac{\pi}{T} \right) \nabla T - t_2 \frac{\nabla \mu_{2,T}}{x_1} - \left( \frac{1}{L_{33}} \right) j \]  

We start with a mixture of uniform composition. The expression for the initial thermoelectric power, \( \varepsilon_0 \), is then, from eq.[12]:

\[ F \varepsilon_0 \left( \frac{\nabla \varphi}{\nabla T} \right)_{j=0,m=0} - \lim_{\Delta T \to 0} \left( \frac{\Delta \varphi}{\Delta T} \right)_{j=0,m=0} = - \frac{\pi}{T} \]  

where \( F \) is the Faraday's constant.

When eqs.[11] and [13] are combined, and remembering that \( t_{Ag^+} = (1-t_{Li^+}) \), the following expression for the initial thermoelectric power is obtained:

\[ F \varepsilon_0 - S_{Ag^+} - S_{Ag^+} - S_{Ag^+} - f_{Ag^+} \left[ (s_1 - s_2) - 2(S_{Li^+} - S_{Ag^+}) \right] \]  

At stationary state the flux \( J_2 \) is zero. Then the net entropy change in the electrolyte at the interface is the same as that caused by the transport of one mole of \( Ag^+ \) away from the interface. This gives (3):

\[ S_{Ag^+} = t_{Ag^+} S_{Ag^+} + t_{Li^+} S_{Li^+} + \frac{1}{2} t_{Li^+} s_1 + \frac{1}{2} t_{Li^+} s_2 + \frac{1}{2} t_{Li^+} \frac{Q^*}{T} \]  

Rearranging this equation and remembering that \( t_{Ag^+} = (1-t_{Li^+}) \) we obtain:

\[ \frac{Q^*}{T} = s_1 - s_2 - 2(S_{Li^+} - S_{Ag^+}) \]
All the terms in eq.[15b] are independent of forces, and the equation is valid whether we have stationary state or not. We can then combine eqs.[14] and [15b].

\[ F_{\varepsilon_0} - S_{Ag}^* - S_{Ag}^* - \frac{1}{2} t_{Li^*} \frac{Q^*}{T} \]  \[ \text{[16]} \]

There is only one observable heat of transfer in our system. This heat of transfer, \( Q^* \), is defined as:

\[ \left( \frac{J_3}{J_2/\Delta T-0} \right) = - \frac{l_{12}}{l_{22}} - Q^* \]  \[ \text{[17]} \]

Eq.[10b] is solved with respect to \( \nabla \mu_{2,T}/x_1 \) when \( t_2 = 0 \) (i.e. stationary state). This gives:

\[ \left( \frac{\nabla \mu_{2,T}}{x_1} \right)_{i=0} = \left( \frac{Q^*}{T} \right)_{i=0} + \left( \frac{t_2}{l_{22}} \right) j \]  \[ \text{[18]} \]

Remembering that \( t_2 = -\frac{1}{2} t_{Li^*} \), a combination of eqs.[12] and [18] yields:

\[ F_{\varepsilon_0} - \left( \frac{\nabla \varphi}{T} \right)_{i=0,0T-0} - \lim_{\Delta T-0} \left( \frac{\Delta \varphi}{\Delta T} \right)_{i=0,0T-0} \quad - \frac{\pi}{T} \frac{1}{2} t_{Li^*} \frac{Q^*}{T} \]  \[ \text{[19]} \]

By introducing eqs.[11] and [15b] into eq.[19] we obtain the transported entropy of Ag+, the ion to which the electrode is reversible:

\[ S_{Ag^+}^* = S_{Ag^+}^* + S_{Ag^+}^* - \frac{F_{\varepsilon}}{T} \]  \[ \text{[20]} \]
The expression for the heat of transfer is obtained from a combination of eqs. [13] and [19].

\[
\frac{Q^*}{T} = \frac{F(\varepsilon_0 - \varepsilon_\infty)}{\frac{1}{2} \mu_1^*} \quad [21]
\]

Thermoelectric powers are usually determined from plot of $\Delta \varphi$ versus $\Delta T$. The entropy is generally a function of temperature. For large values of $\Delta T$, the variation with $T$ must be taken into account. We return to eq. [20], and assume that $S_{Ag}^* = 0$ (9). This gives:

\[
\Delta \varphi_{\text{Ag}} = \int_{T_1}^{T_2} (S_{Ag} - S_{Ag}^*) dT \quad [22]
\]

For constant $C_{p,j}$, the molar entropy, $S_i$ is:

\[
S_i(T) = S_i(T_1) + C_{p,j} \int_{T_1}^{T} \frac{dT}{T} - [S_i(T_1) - C_{p,l} \ln T_1] + C_{p,l} \ln T \quad [23a]
\]

We can then carry out the integration of $S_i dT$ from $T_1$ to $T_2$.

\[
\int_{T_1}^{T_2} S_i dT = S_i(T_1) \Delta T + C_{p,j} \left[ \ln \left( \frac{T_2}{T_1} \right) - 1 \right] \Delta T \quad [23b]
\]

In the same way, we can find $S_1^*$ as a function of the temperature, when the Thomson coefficient, $\tau_1$, is constant. We are now able to express $\Delta \varphi_{\text{Ag}}$ as a function of $\Delta T$ when $T_1$ is fixed. When all expressions are introduced into eq.[22], we get:
The term \([\ln(T_2/T_1)^{\Delta T/T_1} - 1]\) in eq.[24] has the limit value 0, when \(\Delta T \to 0\). Similar expressions can be derived for other thermocells like e.g. \(X_2 | AX | X_2\) and \(A | AX | A\) (3). If \(\Delta T/T_1 \ll 1\) we can introduce the approximation \(\ln(T_2/T_1) \approx \Delta T/T_1\). By introducing this approximation into eq.[24], we obtain:

\[
\Delta \varphi_{\text{em}} = - [S_{Ag}(T) - S_{Ag}^*(T_1)] \Delta T + \left[ C_{P,Ag} - \tau_{Ag} - \right] \ln \left( \frac{T_2}{T_1} \right) \frac{T_2}{\Delta T} - 1 \right] \Delta T \tag{24}
\]

This equation shall be used for evaluation of measurements.

**EXPERIMENTAL**

All experiments were performed in a "standard laboratory furnace". Details of its construction have been given by Motzfeldt (4). The cell inside the furnace is shown in Figure 2. An extra heating element (C in Figure 2), made from Kanthal wires embedded in aluminum cement, was used to produce temperature differences over the electrolyte. The furnace and the inner heating element were controlled separately by two temperature regulators. To reduce temperature variations, the thermocouples for control (D in Figure 2) of the extra heating element and the heating element were placed as close as possible to the Kanthal windings. The temperatures were measured with two Pt/Pt10Rh thermocouples. The silver electrodes were connected to a Hewlett Packard digital multimeter (HP 3457A). The emf was determined to an accuracy of ± 2·10⁻⁶ V. N₂(g) was used as a protection gas in all experiments.

The solid mixtures were made by melting dried Li₂SO₄ (Merck, Darmstadt, Germany) at about 900°C. A Ag₂SO₄ crystal was then dropped into the melt. The Ag₂SO₄ melted and dissolved quickly. After some stirring, the mixture was rapidly cooled by placing the cell into ice. The mixture was then ground to a fine powder, filled into a quartz cell and pressed together with a silver electrode at each end. For sintering, and to smooth out concentration gradients, the cell was placed in the furnace, at the actual temperature, for at least a day before starting the measurements.

To determine the initial thermoelectric power, the emf was measured at various
temperature differences in the range -10°C to 30°C. The length of the sample was about 7 cm. The temperatures at the top and the bottom of the sample were measured with two thermocouples, F in Figure 2, placed close to the electrodes. At the start of each measurement, the temperature difference, between the top and the bottom of the cell, was zero. The temperature on the top was increased. After about 15 minutes the temperatures became stable, and the emf and both temperatures were recorded. After each measurement the temperature difference was reset to zero, and maintained at zero for at least 30 minutes before changing the temperature again. This procedure was repeated for several temperature differences.

The same arrangement was used for determination of the thermoelectric power at stationary state. However, in this case the length of the sample was smaller. The distance between the electrodes was 1.5 cm. The procedure was as follows: First the temperature difference was set to a few degrees. The emf and temperatures were recorded after 3 days. Then the temperature difference was increased by a few degrees by increasing the temperature on the top, and the emf and temperatures were recorded after 2 days. This procedure was repeated for several temperature differences. Tyrrel (5) has derived the time dependency of the thermoelectric power:

\[ \varepsilon_t - \varepsilon_w = \frac{8(\varepsilon_w - \varepsilon_0)}{\pi^2} \exp(-t/\theta) \]  

\[ \theta = \frac{h^2}{D\pi^2} \]

Here \( \theta \) is the characteristic time and governs the rate at which the steady state equilibrium is established, \( h \) is distance between the electrodes, and \( D \) is the diffusion coefficient. If we assume that \( D \) is of the magnitude 1-10^{-5} \( \text{cm}^2 \text{s}^{-1} \), an electrode distance of 1.5 cm will correspond to \( \theta \approx 6.5 \) hrs. A running time of 48 hrs will be equal to 7.5\( \theta \).

RESULTS

Typical experimental observations for the emf, \( \Delta\varphi \) of the cell [a] as a function of \( \Delta T \) at stationary state, are shown in Figure 3. Eq.[25] contains a second order term in \( \Delta T \). Therefore "general regression significance tests" (6) were performed. In this case this means a check of the significance of adding a second order term to a linear model. For all compositions the adding of a second order term were found to be significant (95% confidence level). As a consequence, second order terms were included in the regression model for fitting the data (i.e. \( \Delta\varphi_a = A + B\Delta T + C\Delta T^2 \)). The thermoelectric powers at
stationary state, $\varepsilon_e$, are summarized in Table III.

| mole% Ag$_2$SO$_4$ | $\varepsilon_e$ (mV K$^{-1}$) | $T_1$ (°C) |
|-------------------|------------------------|---------|
| 5.0               | $-0.659 \pm 0.004$ (n=16) | 590     |
| 7.5               | $-0.558 \pm 0.004$ (n=70) | 590     |
| 10.0              | $-0.279 \pm 0.005$ (n=32) | 555     |
| 12.5              | $-0.326 \pm 0.011$ (n=29) | 543     |
| 15.0              | $-0.289 \pm 0.004$ (n=28) | 540     |
| 17.5              | $-0.355 \pm 0.002$ (n=33) | 540     |

In a similar way, as for the stationary state data, the significance of adding a second order term for the fitting of the initial state data was tested. For this case, however, the addition of a second order term was not found to be significant (95% confidence level). Hence the results were fitted to linear regression models. A typical plot of $\Delta \varphi$ versus $\Delta T$ for experimental observations at initial state are shown in Figure 4. The thermoelectric powers at initial state, $\varepsilon_0$, are given in Table IV.
From the plot of $\Delta \phi$ versus $\Delta T$ for the thermocell $\text{Ag} | \text{Ag}_2\text{SO}_4 | \text{Ag}$, the addition of a second order term was found to be significant in the solid state, but not in the molten state. The thermoelectric power in pure silver sulphate, $\varepsilon$, is given in Table V.

**Table V. Thermoelectric power, $\varepsilon$, in the cell $\text{Ag} | \text{Ag}_2\text{SO}_4 | \text{Ag}$.

The quoted errors are standard deviations. The number of experimental points, $n$, in the determination is given in parenthesis.

| SOLID $\text{Ag}_2\text{SO}_4$ | | |
|---|---|---|
| $T_1= 500^\circ\text{C}$ | $\varepsilon = -0.438 \pm 0.008$ (mV K$^{-1}$) | $(n=34)$ |
| $T_1= 680^\circ\text{C}$ | $\varepsilon = -0.316 \pm 0.003$ (mV K$^{-1}$) | $(n=7)$ |

**Table VI. Transported entropies of the silver ion, $S_{\text{Ag}^+}$, in the cell $\text{Ag} | \text{Ag}_2\text{SO}_4-\text{Li}_2\text{SO}_4 | \text{Ag}$.

The quoted errors are standard deviations. All values are for solids except the one with pure $\text{Ag}_2\text{SO}_4$ at $T=680^\circ\text{C}$.

| mole% $\text{Ag}_2\text{SO}_4$ | $S_{\text{Ag}^+}^*$ (J K$^{-1}$ faraday$^{-1}$) | $T$ (°C) |
|---|---|---|
| 5.0 | 134.5 ± 0.4 | 590 |
| 7.5 | 124.8 ± 0.4 | 590 |
| 10.0 | 96.6 ± 0.4 | 555 |
| 12.5 | 101 ± 1 | 543 |
| 15.0 | 97.1 ± 0.4 | 540 |
| 17.5 | 103.5 ± 0.2 | 540 |
| 100 | 110.1 ± 0.7 | 500 |
| 100 | 104.3 ± 0.3 (molten) | 680 |

Transported entropies of the silver ion, $S_{\text{Ag}^+}^*$, calculated from eq.[20] are listed in Table VI. The values of $S_{\text{Ag}^+}$ used in the calculations, were taken from Barin (7). The heat of transfer, $Q^*$, calculated from eq.[21] is listed in table VII. The transference number of silver ion, $t_{\text{Ag}^+}$, was taken from Øye (8).
Table VII. Heat of transfer, $Q^*$, in solid mixtures of Ag$_2$SO$_4$–Li$_2$SO$_4$.

The quoted errors are standard deviations.

| mole% Ag$_2$SO$_4$ | $-Q^*$ (kJ mole$^{-1}$) | $T$ (°C) |
|-------------------|-------------------------|---------|
| 5.0               | -1 ± 1                  | 590     |
| 7.5               | -2 ± 1                  | 590     |
| 10.0              | 49 ± 2                  | 555     |
| 12.5              | 42 ± 3                  | 543     |
| 15.0              | 39 ± 2                  | 540     |
| 17.5              | 24 ± 1                  | 540     |

DISCUSSION

Thermoelectric power and Thomson coefficient of Ag$^+\cdot\tau_{Ag^+}$

The thermoelectric powers obtained in this work are all negative. This means that heat is transported from low to high temperature.

Our method for determination of thermoelectric power include a second order term, see eq.[25]. With pure Ag$_2$SO$_4$ as electrolyte, we find that the second order term is significant in the solid state, but not in the molten state (data not shown). This is in agreement with observations by Kvist and Randasalu (9). They found that the temperature dependency of the thermoelectric power, of the cell with solid Ag$_2$SO$_4$, could be described by a linear relation. With molten Ag$_2$SO$_4$ as electrolyte, no temperature dependency of $\varepsilon$ was observed. The temperature dependency reported by these authors cannot be directly compared with our result for the second order term, because they used a different calculation technique.

The second order term is significant for $\varepsilon$ of all mixtures at stationary state. The magnitude of the second order terms varies somewhat with composition, but it is mainly of the same magnitude as $C_{fAg}/T_1$. The standard deviation of the calculated second order terms were rather high, about 25% of the estimated value. The second order term was not significant for $\varepsilon_v$.

The experimental results for the thermoelectric power of a cell with pure Ag$_2$SO$_4$ can be compared with results reported in the literature (9,10). With molten Ag$_2$SO$_4$ as
electrolyte we obtain the thermoelectric power $-0.316 \pm 0.003 \text{ mV K}^{-1}$. This result agrees well with the values $-0.31 \text{ mV K}^{-1}$ (9) and $-0.33 \text{ mV K}^{-1}$ (10). With solid $\text{Ag}_2\text{SO}_4$ as electrolyte ($T = 500^\circ\text{C}$), we obtain $\varepsilon = -0.438 \pm 0.008 \text{ mV K}^{-1}$. This agrees reasonably well with the value $-0.45 \text{ mV K}^{-1}$ reported by Kvist and Randsalu (9). The result reported by Glagoleva and Markov (10), $-0.47 \text{ mV K}^{-1}$, is somewhat higher than our result. Glagoleva and Markov determine the thermoelectric power by fitting the plot of emf versus $\Delta T$ to a straight line, $\Delta T$ being in the range $-66^\circ\text{C}$ to $65^\circ\text{C}$. Thus, the difference between theirs and our result is due to different measuring and calculation techniques.

We conclude that entropy variations with temperature may be significant for thermoelectric powers. This has a bearing on the practical method used for its determination. We have developed a procedure which takes second order terms into account. The procedure should be applicable in other contexts. For solid mixtures of $\text{Ag}_2\text{SO}_4$–$\text{Li}_2\text{SO}_4$, and for $\text{Ag}_2\text{SO}_4(\text{s})$ we have confirmed by statistical methods that $\tau_{\text{Ag}^+}$ is smaller than $C_{\text{p,Ag}^+}$. For $\text{Ag}_2\text{SO}_4(\text{l})$ we conclude that $\tau_{\text{Ag}^+} = C_{\text{p,Ag}^+}(680^\circ\text{C}) = 30 \text{ J K}^{-1} \text{ faraday}^{-1}$.

The transported entropy of $\text{Ag}^+$

Values presented in Table VI for the transported entropy of the silver ion, $S'_{\text{Ag}^+}$, vary relatively little with composition, when $0.1 < x_{\text{Ag}_2\text{SO}_4} < 0.175$. The change from solid to molten state also has a small bearing on $S'_ {\text{Ag}^+}$ (Table VI).

The structure of the high temperature modification of pure $\text{Ag}_2\text{SO}_4$ is hexagonal, while the structure of $\text{Ag}_2\text{SO}_4$–$\text{Li}_2\text{SO}_4$ in the Li–rich phase is cubic face centered (1). The transported entropy does not seem to depend on these structure variations. A similar result for $S'_ {\text{Cr}^2+}$ was obtained by Tomii and Ratkje (11) for solid mixtures of $\text{ZrO}_2$ and $\text{Y}_2\text{O}_3$.

Kvist (12) measured the specific conductance, $\kappa$, in $\text{Ag}_2\text{SO}_4$–$\text{Li}_2\text{SO}_4$ mixtures. The activation energy of conductivity, $E_a$, was calculated from a plot of $\ln(\kappa T)$ versus $1/T$. Results are $E_a=20 \text{ kJ mole}^{-1}$ for molten $\text{Ag}_2\text{SO}_4$, $E_a=117 \text{ kJ mole}^{-1}$ for solid $\text{Ag}_2\text{SO}_4$, and $E_a=42 \text{ kJ mole}^{-1}$ for solid $\text{Ag}_2\text{SO}_4$–$\text{Li}_2\text{SO}_4$ containing 17.5 mole % $\text{Ag}_2\text{SO}_4$. No correlation between $E_a$ and $\varepsilon$ or $S'_ {\text{Ag}^+}$ can be predicted from these results, as expected from a theory of Rice and Roth (13). Similar tendencies were observed by Tomii and Ratkje (11).

The transported entropy is calculated for the ion in the electrolyte which is reversible to the electrode. Results reported in the literature were used to analyze possible variations in $S'_{\text{Ag}^+}$ with the remaining ions in the electrolyte. Data are mostly available for pure salts. For the thermocell $\text{Cl}_2(\text{g}) | \text{MCI} | \text{Cl}_2(\text{g})$, with $\text{M} = \text{Li, Na, K, Rb, Cs}$; we find that $S'_{\text{Cl}^+}$ varies between 81 and 92 J K$^{-1}$ faraday$^{-1}$ (14,15). For the thermocell $\text{Ag} | \text{AgX} | \text{Ag}$, with $\text{X} = \text{Cl, Br, I}$; $S'_{\text{Ag}^+}$ varies between 104 and 119 J K$^{-1}$ faraday$^{-1}$ (16–18). Vreuls (19) has calculated $S'_{\text{Ag}^+}$ for the thermocell $\text{Ag} | \text{AgNO}_3$–$\text{MNO}_3(\text{l}) | \text{Ag}$, with $\text{M} = \text{Li, Na, K, Rb}$,
and Cs. For all compositions with more than 20 mole% AgNO₃ at \( T=633 \), except for \( M=Cs \), the results were between 88 and 110 J K\(^{-1}\) faraday\(^{-1}\). In mixtures containing less than 10 mole% Ag₂SO₄, the transported entropy increases strongly with decreasing composition. This tendency was also reported by Vreuls (19) for cells with AgNO₃–MNO₃, \( M=Li,Na,K,Rb \) and Cs. We may also note that the value of \( S^+_{Ag} \) is almost the same in sulphate and nitrate mixtures. Furthermore it is clear that the model of Ødegård et al. (21), using \( S^+_{M}=S^+_{M} \) in fluoride melts, is not valid. The molar entropy of Ag differs by 40–50 J K\(^{-1}\) mol\(^{-1}\) from \( S^+_{Ag} \). We conclude that the transported entropy is little affected by the presence of other ions in the electrolyte, provided there is a minimum amount of the ion reversible to the electrode. For mixtures containing small amounts (< 0.1) of the silver ion, the transported entropy seems to be strongly affected by concentration changes. We have no explanation for this at present.

The heat of transport in Ag₂SO₄–Li₂SO₄

The values obtained for the heat of transfer are all negative for mixtures containing 10 mole%–17.5 mole% Ag₂SO₄. The negative sign means that Ag₂SO₄ is enriched at the hot side, see eq.[18]. In this concentration range the absolute value of the heat of transfer increases with decreasing mole fraction of Ag₂SO₄, see also Table VII. In mixtures containing less than 10 mole% of Ag₂SO₄ the heat of transfer is approximately zero. This is in agreement with earlier observations by Lunden and Olsson (20). They have studied thermal diffusion in Ag₂SO₄–Li₂SO₄ containing 4–5 mole% Ag₂SO₄. Their reported Soret coefficient corresponds to \( Q^*= -2 \pm 2 \) kJ mole\(^{-1}\). Vreuls (19) also reports that the heat of transfer becomes zero in systems of the type AgNO₃–MeNO₃, \( Me=Li,Na,K,Rb \), and Cs, when the mole fraction of AgNO₃ becomes small (< less than 0.1). Since we found that the second order term is not significant for \( \epsilon_0 \), we expect that the "heat capacity" of \( Q^*/T \) in the solid mixtures, is of the same magnitude as \( -2C_{P,Ag}/t_{Li} \), see eq.[16].

Haase (22) and Kempers (23) have proposed that the heat of transfer is a function of the partial molar enthalpy of the components in the mixture. We shall show in a future work that this model is unlikely from a theoretical point of view.

At this point we emphasize the difference between the two quantities. \( S^+_{Ag} \) is a property of the cell and the electrode–electrolyte interface, while \( Q^* \) is a property of the electrolyte only.

CONCLUSION

A new method for determination of thermoelectric powers is presented. We have applied the method to the cell \( Ag(T_1) | Ag_2SO_4-Li_2SO_4 | Ag(T_2) \), and calculated the transported entropy, \( S^+_{Ag} \), and the heat of transfer \( Q^* \).
The result extends and enhances information presented on thermocells by earlier investigators. The transported entropy of the ion reversible to the electrode is fairly independent of the other cation or anion present in the mixture, while the heat of transport show a larger relative variation at moderate concentrations. At low concentrations of Ag⁺ this picture changes. There are no good models for the heat of transport as well as for the transported entropy. More work must be done, to get a better understanding of these important effects.

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REFERENCES

1. H. A. Øye, Thermodynamic investigation of the system Li₂SO₄ – Ag₂SO₄, Thesis, Norwegian Institute of Technology, Trondheim (1963)
2. K. S. Førland, T. Førland and S. K. Ratkje, "Irreversible Thermodynamics, Theory and Applications", Wiley, Chichester (1988).
3. A. Grimstvedt, Thesis, The Norwegian Institute of Technology, Trondheim, Norway, To be published (1992).
4. K. Motzfeldt, "Physicochemical Measurements at High Temperatures", ed. by Bockris, White and Mackenzie. Butterworths Sci. Pubc. London (1960).
5. H. J. V. Tyrrell,"Diffusion and Heat Flow in Liquids", Butterworths, London (1961).
6. D. C. Montgomery,"Design and Analysis of experiments", sec. ed., Wiley, New York (1983).
7. I. Barin, "Thermochemical Data of Pure Substances", VCH Publ., New York (1989).
8. H. A. Øye, Acta Chem. Scand., 21, 111 (1967)
9. A. Kvist and A. Randsalu, Z. Naturforsch., 21a, 278 (1966).
10. N. A. Glagoleva and B. F. Markov, Soviet Electrochem., 19, 42 (1983)
11. Y. Tomii and S. K. Ratkje, manuscript in preparation.
12. A. Kvist, Z. Naturforsch., 22a, 208 (1967).
13. M. J. Rice, and W. L. Roth, J. Solid State Chem., 4, 294 (1972)
14. W. Fisher, Z. Naturforsch., 21a, 281 (1966).
15. R. Detig And D. Archer, J. Chem. Phys., 36, 661 (1963).
16. S. Senderoff and R. Bretz., J. Electrochem. Soc., 109, 56 (1962)
17. A. Kvist, A. Randsalu and I. Svensson, Z. Naturforsch., 21a, 184 (1966).
18. H. Meissner, D. White and G. Ullrich, Adv. Energy Conv., 5, 205 (1965).
19. W. Vreuls, "Zur Thermodynamik und Elektrochemie Nichtisothermer Binärer Salzschmelzen", Thesis, Aachen Germany (1978).
20. A. Lunden and J. E. Olsson, Z. Naturforsch., 23a, 2045 (1968).
21. R. Ødegård, S. Julsrud, A. Solheim, and K. Thovsen, Metall. Trans B (1991)
22. R. Haase, "Thermodynamics of Irreversible Processes", Addison-Wesley (1969)
23. L. J. T. M. Kempers, J. Chem. Phys. 90, 6541 (1989).
Figure 1. Schematic illustration of the thermocell Ag | Ag$_2$SO$_4$-Li$_2$SO$_4$ | Ag.

Figure 2. Cell and furnace, cross section.

A. Pythagoras furnace tube  
B. Heating element  
C. Inner heating element  
D. Controlling thermocouple  
E. Quartz glass cell  
F. Pt/Pt10Rh thermocouple  
G. Cell supporter  
H. Radiation shields
Figure 3. Plot of $\Delta \varphi_\infty$ versus $\Delta T$ for the cell
Ag($T_1$) | Ag$_2$SO$_4$-Li$_2$SO$_4$ | Ag($T_2$).
The plot is shown for an electrolyte containing 15 mole% Ag$_2$SO$_4$. $\Delta \varphi_\infty$ is the emf at stationary state. $T_1$ is held constant at 540°C.

Figure 4. Plot of $\Delta \varphi_0$ versus $\Delta T$ for the cell
Ag($T_1$) | Ag$_2$SO$_4$-Li$_2$SO$_4$ | Ag($T_2$).
The plot is shown for an electrolyte containing 5 mole% Ag$_2$SO$_4$. $\Delta \varphi_0$ is the emf at initial state. $T_1$ is held constant at 590°C.