1. Introduction

Regarding the problems of the storage of solar energy, different semiconductor materials are used as photoelectrodes for potential assisted photocellysis of water using visible and infrared light. In case of SO\textsuperscript{2−} containing water, the Ag-Ag\textsubscript{2}SO\textsubscript{4} electrode is often used as a reference in studies of current/voltage curves. The efficiency of the photoelectrolysis of water seems to depend notably on temperature at elevated temperatures. The knowledge of the potential of the Ag-Ag\textsubscript{2}SO\textsubscript{4} electrode in its dependence on the temperature and the SO\textsuperscript{2−} activity is essential for such studies.

A considerable restriction of the usefulness of the Ag-Ag\textsubscript{2}SO\textsubscript{4} electrode results from the solubility of Ag\textsubscript{2}SO\textsubscript{4} in acid media. Lietzke and Stoughton [1] have determined this solubility in 0.1, 0.5 and 1.0 m H\textsubscript{2}SO\textsubscript{4} to above 523 K. The observed solubilities were (0.029 m)\textsubscript{0.1 m H\textsubscript{2}SO\textsubscript{4}}, (0.033 m)\textsubscript{0.5 m H\textsubscript{2}SO\textsubscript{4}} and (0.035 m)\textsubscript{1.0 m H\textsubscript{2}SO\textsubscript{4}}, at 298 K, and (0.118 m)\textsubscript{0.1 m H\textsubscript{2}SO\textsubscript{4}}, (0.258 m)\textsubscript{0.5 m H\textsubscript{2}SO\textsubscript{4}}, and (0.511 m)\textsubscript{1.0 m H\textsubscript{2}SO\textsubscript{4}} at 473 K. From these results, Lietzke and Stoughton concluded that the electrode may perform satisfactorily in acid media at low temperatures or in very dilute acid media at higher temperatures.

In a previous work, Lietzke and Stoughton [2] have measured the potential (E) obtained by combination of saturated Ag-Ag\textsubscript{2}SO\textsubscript{4} and Hg-Hg\textsubscript{2}SO\textsubscript{4} electrodes in 0.5 m, 0.2 m and 0.05 m H\textsubscript{2}SO\textsubscript{4} from 298 to 523 K. In all three cases they reported a linear dependence of E on T up to about 373 K, with a slope of almost exactly the theoretical value at 298 K. The plot for 0.5 m H\textsubscript{2}SO\textsubscript{4} was found to remain linear up to 423 K, while those obtained for 0.2 and 0.05 m H\textsubscript{2}SO\textsubscript{4} became flatter between 373 and 423 K and then became linear again at higher temperatures. The authors related this deviation to the hydrolysis of Hg\textsubscript{2}SO\textsubscript{4} at elevated temperatures and low H\textsubscript{2}SO\textsubscript{4} concentration. They checked a possible hydrolysis of the Ag\textsubscript{2}SO\textsubscript{4}, which was sealed in a silica tube and heated to 523 K. Visual observation revealed no change in the appearance of the Ag\textsubscript{2}SO\textsubscript{4} crystals, and their composition remained stoichiometric after cooling.

The results of [1] and [2] seem to be partially in disagreement. Because of the drastic increase of the solubility of Ag\textsubscript{2}SO\textsubscript{4} (and probably of Hg\textsubscript{2}SO\textsubscript{4}) in 0.5 m H\textsubscript{2}SO\textsubscript{4} with increasing temperature, a linear plot giving a constant ΔS of the cell reaction seems to be impossible. Serious liquid junction potentials may be expected due to the increasing concentration of Ag\textsuperscript{+} (and probably Hg\textsuperscript{+}) in the electrode compartments.

In this paper we determined the standard potential of the Ag-Ag\textsubscript{2}SO\textsubscript{4} electrode up to 473 K by means of measurement of the emf of the cell

\[ \text{Pt–Hg} / \text{H}_2\text{SO}_4(m)/\text{Ag}_2\text{SO}_4/\text{Ag} \]  \hspace{1cm} (1)

The potential of the electrode in aqueous Na\textsubscript{2}SO\textsubscript{4} solutions of molalities up to 1 m has been calculated for temperatures up to 473 K using the corresponding activity coefficients determined previously by Rogers and Pitzer [3].

2. Experimental

The emf measurement was carried out in the high temperature–high pressure potentiometric cell de-
Table 1. The standard potential $E^\circ$ of the Ag–Ag$_2$SO$_4$ electrode and its potential $E$ in aqueous Na$_2$SO$_4$ solution of different molality at various temperatures.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$E^\circ$ (mV)</th>
<th>$E$ (mV) in solutions of $x$ mol Na$_2$SO$_4$/kg H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.05</td>
<td>x = 0.10</td>
<td>x = 0.25</td>
</tr>
<tr>
<td>298</td>
<td>653</td>
<td>699</td>
</tr>
<tr>
<td>303</td>
<td>646</td>
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<td>323</td>
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<td>463</td>
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<td>349</td>
</tr>
<tr>
<td>473</td>
<td>237</td>
<td>318</td>
</tr>
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Table 2. The values of $a$ and $b$ of (9) and the regions of their validity.

<table>
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<th>Temp.-region (K)</th>
<th>$a$ (mV K$^{-1}$)</th>
<th>$b$ (mV K$^{-2}$)</th>
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<tr>
<td>298 – 363</td>
<td>1.435</td>
<td>0.00480</td>
</tr>
<tr>
<td>373 – 473</td>
<td>1.425</td>
<td>0.00543</td>
</tr>
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Fig. 1. Standard potential $E^\circ$ of the Ag–Ag$_2$SO$_4$ electrode vs. $T$. 

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Fig. 2. $\Delta S^0$ of reaction (2) vs. $T$.

Fig. 3. $\Delta H^0$ of reaction (2) vs. $T$. 

B.A. Blain and E. Müller. Thermodynamics of the Ag-Ag$_2$SO$_4$ Electrode up to 473 K.
scribed by Becker and Bilal [4], where first no compartments were used to separate the Pt/H₂ and Ag/Ag₂SO₄ electrodes. In that arrangement no stable potential was obtained and the H₂SO₄ solution became milky. The turbidity, which was extractable in CS₂, seemed, to be sulphur. Probably the SO₄²⁻ was reduced in presence of Ag⁺ ions by the hydrogen dissociated in the Platin black to the atomic state. This interesting question is still a subject of our investigation.

The electrodes were, therefore, placed in compartments connected by sapphire-diaphragms with the H₂SO₄ solution acting as intermediate electrolyte. With this arrangement a stable potential was obtained and the H₂SO₄ solution remained clear.

Four sets of experiments were carried out using H₂SO₄ with the molalities 0.005 m, 0.0075 m, 0.01 m and 0.10 m. The experiments of every set were repeated three times.

3. Results and Discussion

The standard potential of the reaction

\[
\text{Ag}_2\text{SO}_4 + \text{H}_2 \rightleftharpoons 2\text{Ag} + \text{H}_2\text{SO}_4
\]  (2)

is given by

\[
E^0 = E + RT/2F \ln \left( \frac{a_{\text{H}_2\text{SO}_4}}{p_{\text{H}_2}} \right),
\]  (3)

where \(a = m_{\text{SO}_4^{2-}} (m_H^+)^2 (\gamma)^3\) denotes the activity of the H₂SO₄ solution and \(p_{\text{H}_2} = p_{\text{tot}} - p_{\text{vapour}}\) denotes the hydrogen pressure. The real mean activity coefficient \((\gamma)\) of the H₂SO₄ solution is related to the stoichiometric mean activity coefficient \(\gamma\) based on complete ionization by

\[
4m^3 \gamma^3 = [m_{\text{SO}_4^{2-}} (m_H^+)^2 (\gamma)^3],
\]  (4)

where \(m\) is the stoichiometric molality of H₂SO₄.

The activity of the sulfic acid was calculated using the \(\gamma\) values determined from the diagrams given by Holmes and Mesmer [5] and showing \(\ln \gamma\) as a function of \(m^{1/2}\) at different temperatures (these diagrams were completed by plotting the values reported in [5] for 323.15, 373.15, 423.15 and 473.15 K). The standard potential was calculated according to (3), where the \(E\) values were corrected to 1 atmosphere hydrogen pressure.

Curve A of Fig. 1 (and for accurate reading Table 1) shows the standard potential of the Ag–Ag₂SO₄ electrode as a function of the temperature. The \(E^0\) values obtained for \(c_{\text{H}_2\text{SO}_4} = 0.005\) m and 0.0075 m were practically the same. The difference between the corresponding values was within the experimental error (≤ ± 1.5 mV). The calculation of \(E^0\) from the measurements of the set with \(c_{\text{H}_2\text{SO}_4} = 0.10\) m (curve C) yielded much higher values. The liquid junction potential, which has to be considered due to the increased solubility of Ag₂SO₄, was approximated as far as possible according to the Henderson equation. The difference between the two curves was about 7 mV at 298 K and increased to about 120 mV at 473 K. The deviation of the values in curve C was ≤ ± 3 mV below 373 K and ≤ ± 5 mV at higher temperatures. Curve B shows the values calculated from the measurements of the set with \(c_{\text{H}_2\text{SO}_4} = 0.01\) m. The error of these values was ≤ ± 2 mV up to 373 K and ≤ ± 3.5 mV at higher temperatures. The distance between curves A and B increased to be about 20 mV at 473 K.

These results indicate that the dissolution of Ag₂SO₄, which strongly takes place in 0.10 m H₂SO₄, is negligible at \(c_{\text{H}_2\text{SO}_4} ≤ 0.0075\). In 0.01 m H₂SO₄ it starts showing up.

The potential of the Ag–Ag₂SO₄ electrode is determined by the reaction of the half cell

\[
\text{Ag}_2\text{SO}_4 + 2e^- \rightleftharpoons 2\text{Ag} + \text{SO}_4^{2-}.
\]  (5)

Using aqueous Na₂SO₄ of the molality \(x\) m (\(x = 0.05, 0.1, 0.25, 0.5, 0.75\), and 1.0) as inner electrolyte, the potential values of reaction (5) (vs. SHE) were then calculated up to 473 K due to

\[
E = E^0 - RT/2F \ln [m_{\text{SO}_4^{2-}} (\gamma)_x \text{molar Na}_2\text{SO}_4],
\]  (6)

taking the values of the mean activity coefficient \(\gamma\) reported in [3] into account. The \(E\) values at different Na₂SO₄ molalities and various temperature are also listed in Table 1.

The standard potential of reaction (2) is by definition only a function of the temperature and is related to the standard molal free energy \(\Delta G^0\) and the standard molal entropy \(\Delta S^0\) of the reaction by

\[
E^0(T) = -\Delta G^0(T)/2F,
\]  (7)

\[
(\partial E^0(T)/\partial T)_{\text{p} = 1} = -[\partial (\Delta G^0(T)/\partial T)_{\text{p} = 1}]/2F
= \Delta S^0(T)/2F.
\]  (8)

\(\Delta S^0(T)\) was obtained from the slope of curve A in Figure 1. However, the temperature dependence of the standard potential was described to a good approxi-
mation by the empirical equation
\[
(E^0)^T = (E^0)^{T_r} - a(T - T_r) - b(T - T_r)^2,
\]
(9)
where \( T_r \) denotes the reference temperature 298 K. The coefficients \( a \) and \( b \) were determined graphically. Table 2 gives the values of \( a \) and \( b \) and the region in which they are valid. The differentiation of (9) with respect to the temperature yields \( \Delta S^0 \):
\[
\Delta S^0(T) = 2F(\frac{\partial E^0(T)}{\partial T})_{\rho=1} = 2F\{-a-2b(T-T_r)\}. \quad (10)
\]

\( \Delta H^0(T) \) of reaction (2) was then calculated from the fundamental equation
\[
\Delta H^0(T) = \Delta G^0(T) + T \Delta S^0(T) = 2F\{T\{-a-2b(T-T_r)\} - E^0(T)\}. \quad (11)
\]
\( \Delta H^0(T) \) was also determined graphically from the slope of the plot \( \Delta G^0(T)/T \) vs. \( 1/T \). Values of \( \Delta S^0(T) \) and \( \Delta H^0(T) \) are shown in Figs. 2 and 3.