Thermodynamics of the $Ag-Ag_2SO_4$ Electrode up to 473 K

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$E^0(T)$, $\Delta S^0(T)$, and $\Delta H^0(T)$ of the reaction $Ag_2SO_4 + H_2 \Leftrightarrow 2Ag + H_2SO_4$ have been determined up to 473 K, using the cell $Pt-H_2(p)/H_2SO_4(m)/Ag_2SO_4-Ag$. Constant values of the standard potential $E^0(T)$ were obtained for $c_{H_2SO_4} \leq 0.0075$ m where the solubility of Ag_2SO_4 became negligible. The potential of the $Ag-Ag_2SO_4$ electrode (vs. SHE) in aqueous Na_2SO_4 solutions of different molalities has been calculated up to 1 m and 473 K.

1. Introduction

Regarding the problems of the storage of solar energy, different semiconductor materials are used as photoelectrodes for potential assisted photoelectrolysis of water using visible and infrared light. In case of SO_4^{2-} containing water, the $Ag-Ag_2SO_4$ 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 $Ag-Ag_2SO_4$ electrode in its dependence on the temperature and the SO_4^{2-} activity is essential for such studies.

A considerable restriction of the usefulness of the $Ag-Ag_2SO_4$ electrode results from the solubility of Ag_2SO_4 in acid media. Lietzke and Stoughton [1] have determined this solubility in 0.1, 0.5 and 1.0 m H_2SO_4 to above 523 K. The observed solubilities were $(0.029\text{ m})_{0.1\text{ m }H_2SO_4}$, $(0.033\text{ m})_{0.5\text{ m }H_2SO_4}$ and $(0.035\text{ m})_{1.0\text{ m }H_2SO_4}$ at 298 K, and $(0.118\text{ m})_{0.1\text{ m }H_2SO_4}$, $(0.258\text{ m})_{0.5\text{ m }H_2SO_4}$ and $(0.511\text{ m})_{1.0\text{ m }H_2SO_4}$ 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 $Ag-Ag_2SO_4$ and $Hg-Hg_2SO_4$ electrodes in 0.5 m, 0.2 m and 0.05 m H_2SO_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 plott for 0.5 m H_2SO_4 was found to remain linear up to 423 K, while those obtained for 0.2 and 0.05 m H_2SO_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_2SO_4 at elevated temperatures and low H_2SO_4 concentration. They checked a possible hydrolysis of the Ag_2SO_4, which was sealed in a silica tube and heated to 523 K. Visual observation revealed no change in the appearance of the Ag_2SO_4 crystals, and their composition remained stoichiometrie after cooling.

The results of [1] and [2] seem to be partially in disagreement. Because of the drastic increase of the solubility of Ag_2SO_4 (and probably of Hg_2SO_4) in 0.5 m H_2SO_4 with increasing temperature, a linear plott 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^+ (and probably Hg^+) in the electrode compartments.

In this paper we determined the standard potential of the $Ag-Ag_2SO_4$ electrode up to 473 K by means of measurement of the emf of the cell

$$Pt-H_2(p)/H_2SO_4(m)/Ag_2SO_4-Ag\,. \qquad (1)$$

The potential of the electrode in aqueous Na_2SO_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-

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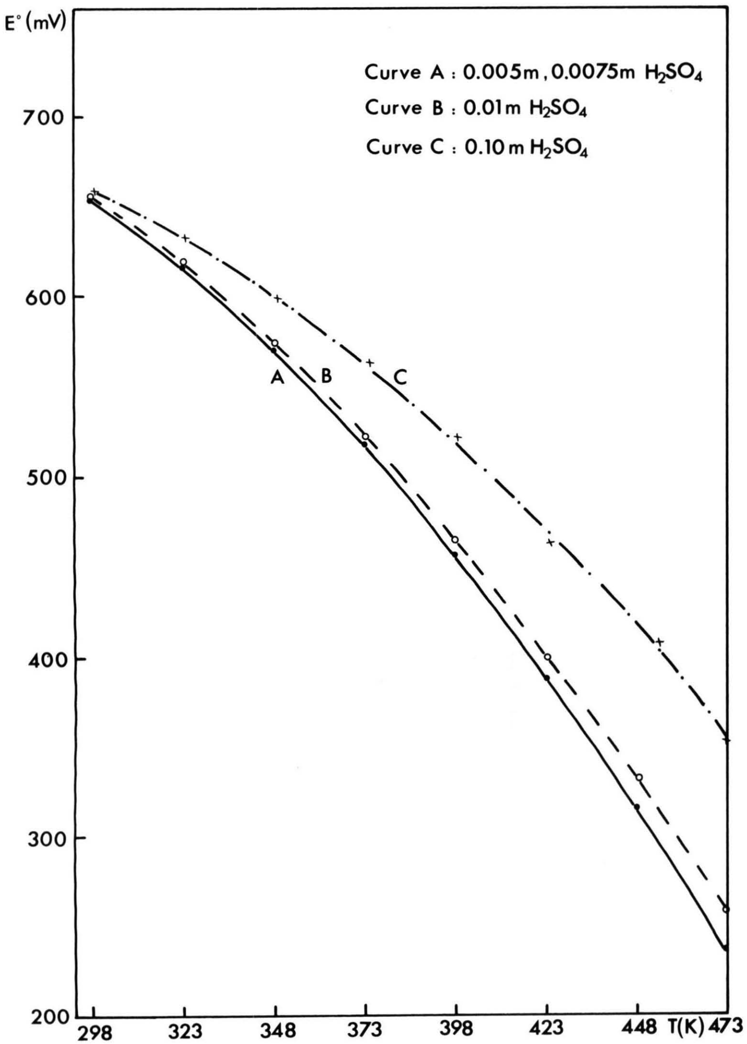

Fig. 1. Standard potential E^0 of the Ag–Ag_2SO_4 electrode vs. T.

Table 1. The standard potential E^0 of the Ag–Ag_2SO_4 electrode and its potential E in aqueous Na_2SO_4 solution of different molality at various temperatures.

T (K)	E^0 (mV)	E (mV) in solutions of x mol Na_2SO_4/kg H_2O					
		$x=0.05$	$x=0.10$	$x=0.25$	$x=0.50$	$x=0.75$	$x=1.00$
298	**653**	699	693	684	679	675	673
303	**646**	693	686	678	672	669	667
313	**630**	679	672	664	657	654	652
323	**614**	665	657	648	642	638	636
333	**597**	649	642	633	626	622	619
343	**579**	633	625	616	609	605	602
353	**560**	616	608	598	591	587	585
363	**539**	597	589	579	572	568	565
373	**516**	577	569	558	551	547	544
383	**493**	554	546	536	529	525	522
393	**469**	533	524	514	506	502	499
403	**444**	510	501	491	483	479	476
413	**417**	485	476	465	458	454	451
423	**389**	459	450	440	432	428	425
433	**362**	434	425	415	407	403	400
443	**332**	406	397	387	379	375	372
453	**302**	379	370	359	352	348	345
463	**270**	349	340	330	323	319	316
473	**237**	318	310	299	292	288	286

Table 2. The values of a and b of (9) and the regions of their validity.

Temp.-region (K)	a (mV K^{-1})	b (mV K^{-2})
298–363	1.435	0.00480
373–473	1.425	0.00543

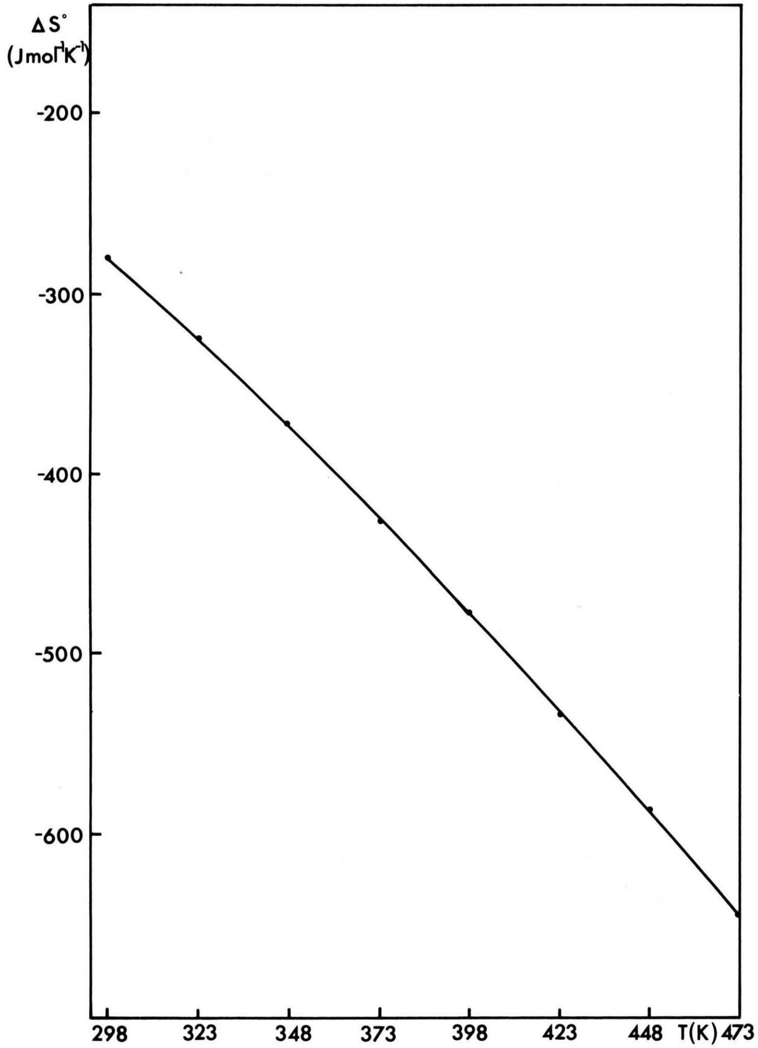

Fig. 2. ΔS^0 of reaction (2) vs. T.

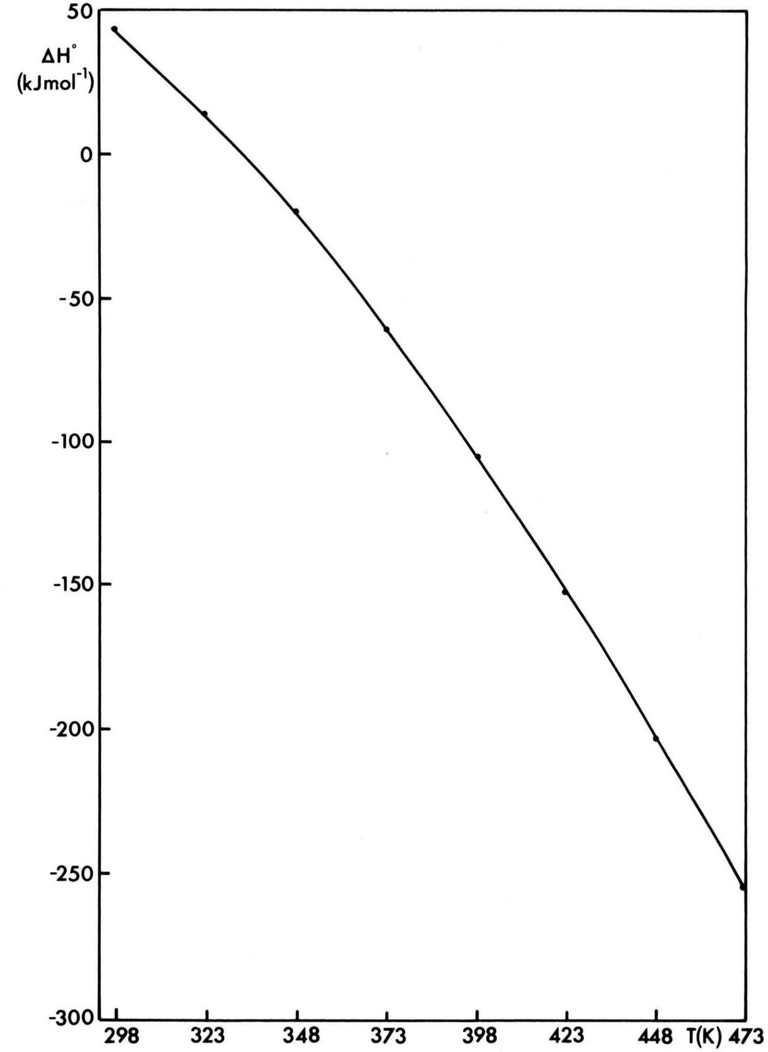

Fig. 3. ΔH^0 of reaction (2) vs. T.

scribed by Becker and Bilal [4], where first no compartments were used to separate the Pt/H_2 and Ag/Ag_2SO_4 electrodes. In that arrangement no stable potential was obtained and the H_2SO_4 solution became milky. The turbidity, which was extractable in CS_2, seemed, to be sulphur. Probably the SO_4^{2-} 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 H_2SO_4 solution acting as intermediate electrolyte. With this arrangement a stable potential was obtained and the H_2SO_4 solution remained clear.

Four sets of experiments were carried out using H_2SO_4 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

$$Ag_2SO_4 + H_2 \Leftrightarrow 2\,Ag + H_2SO_4 \qquad (2)$$

is given by

$$E^0 = E + RT/2F \ln (a_{H_2SO_4}/p_{H_2}), \qquad (3)$$

where $a = m_{SO_4^{2-}} \cdot (m_H^+)^2 (\gamma')^3$ denotes the activity of the H_2SO_4 solution and $p_{H_2} = p_{tot} - p_{vapour}$ denotes the hydrogen pressure. The real mean activity coefficient (γ') of the H_2SO_4 solution is related to the stoichiometric mean activity coefficient γ based on complete ionization by

$$4\,m^3\gamma^3 = [m_{SO_4^{2-}} \cdot (m_H^+)^2 (\gamma')^3, \qquad (4)$$

where m is the stoichiometric molality of H_2SO_4.

The activity of the sulfuric acid was calculated using the γ 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 $Ag-Ag_2SO_4$ electrode as a function of the temperature. The E^0 values obtained for $c_{H_2SO_4} = 0.005$ m and 0.0075 m were practically the same. The difference between the corresponding values was within the experimental error ($\leq \pm 1.5$ mV). The calculation of E^0 from the measurements of the set with $c_{H_2SO_4} = 0.10$ m (curve C) yielded much higher values. The liquid junction potential, which has to be considered due to the increased solubility of Ag_2SO_4, was approximated as far as possible according to the Handerson 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 $\leq \pm 3$ mV below 373 K and $\leq \pm 5$ mV at higher temperatures. Curve B shows the values calculated from the measurements of the set with $c_{H_2SO_4} = 0.01$ m. The error of these values was $\leq \pm 2$ mV up to 373 K and $\leq \pm 3.5$ 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 Ag_2SO_4, which strongly takes place in 0.10 m H_2SO_4, is negligible at $c_{H_2SO_4} \leq 0.0075$. In 0.01 m H_2SO_4 it starts showing up.

The potential of the $Ag-Ag_2SO_4$ electrode is determined by the reaction of the half cell

$$Ag_2SO_4 + 2\,e^- \Leftrightarrow 2\,Ag + SO_4^{2-}. \qquad (5)$$

Using aqueous Na_2SO_4 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

$$E = E^0 - RT/2F \ln [m_{SO_4^{2-}} \cdot (\gamma)_{x\,\text{molal}\,Na_2SO_4}], \qquad (6)$$

taking the values of the mean activity coefficient γ reported in [3] into account. The E values at different Na_2SO_4 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 ΔG^0 and the standard molal entropy ΔS^0 of the reaction by

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

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

$\Delta S^0(T)$ was obtained from the slope of curve A in Figure 1. However, the temperature dependence of the standard potential was described to a good approximation by the empirical equation

$$(E^0)^T = (E^0)^{T_r} - a(T - T_r) - b(T - T_r)^2, \quad (9)$$

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 ΔS^0:

$$\Delta S^0(T) = 2F(\partial E^0(T)/\partial T)_{p=1}$$
$$= 2F\{-a - 2b(T - T_r)\}. \quad (10)$$

$\Delta H^0(T)$ 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 plott $\Delta G^0(T)/T$ vs. $1/T$. Values of $\Delta S^0(T)$ and $\Delta H^0(T)$ are shown in Figs. 2 and 3.

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