Potential of the Aqueous $Ag-Ag_2SO_4$ Electrode in 1 m Na_2SO_4 in Contact with 1 m H_2SO_4 at up to 473 K and 975 bar

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The potential of the $Ag-Ag_2SO_4$ electrode in 1 m Na_2SO_4 solution in contact with 1 m H_2SO_4 solution has been determined up to 473 K and 975 bar. The potential of the electrode in aqueous 1 m Na_2SO_4 solution without accounting for any diffusion was calculated under the same p and T conditions taking the formation of $NaSO_4^-$ into account. Small differencies ($\leq 2\%$) have been found in comparison with the values given previously by the authors [1] assuming a complete dissociation of Na_2SO_4.

1. Introduction

The aqueous $Ag-Ag_2SO_4$ electrode is used as a reference in high temperature – high pressure cyclic voltammetric studies of current/voltage curves obtained during electrolysis, as well as potential assisted photoelectrolysis of aqueous sulfuric acid solution (up to 1 m) using semiconductor electrodes. At room temperature, $Hg-Hg_2Cl_2$, $Hg-HgSO_4$ and $Ag-AgCl$ reference electrodes have been used. At high temperatures, however, use of Cl^- containing electrodes is restricted due to the increasing diffusion of Cl^- into the outer solution and its possible anodic oxidation, which leads to various alterations of the surface of the semiconductor electrodes. The interpretation of the voltammograms becomes very difficult or even impossible. In addition, the use of Hg containing electrodes at high temperatures is obviously prohibited because of the evaporation of Hg.

In [1] we have studied the thermodynamics of the $Ag-Ag_2SO_4$ electrode up to 473 K and the corresponding saturation pressures. The standard potential of the electrode, as well as its potential in aqueous Na_2SO_4 solutions of different molalities were determined.

To prevent the liquid junction potential (ΔE_j), which can not be calculated due to lacking values of the ion mobilities at high temperatures and pressures, it should be advantageous to use sulfuric acid as inner solution of the $Ag-Ag_2SO_4$ electrode which has the same molality as the one electrolyzed. On the other hand, we have recently found [1] that no constant standard potential $E^0(T)$ of the electrode was obtained at H_2SO_4 molality > 0.0075 m due to the dissolution of the Ag_2SO_4 with increasing temperatures. This concentration is too low for a considerable electrolyte conductance. Higher H_2SO_4 concentrations of 0.5–1.0 m are usually needed.

The diffussion potential ΔE_j between sulfuric acid and aqueous Na_2SO_4 solution of the same concentration is mainly determined by the diffusion of H^+ and Na^+ ions. However, also diffusion of SO_4^{2-} arises with decreasing temperature due to the different formation degrees of $NaSO_4^-$ and HSO_4^-. We have, therefore, experimentally determined the potential of the $Ag-Ag_2SO_4$ electrode up to 473 K and 975 bar in the cell

$$Ag-Ag_2SO_4/1\,m\ Na_2SO_4//1\,m\ H_2SO_4/H_2(p)-Pt\,. \tag{1}$$

2. Experimental

The potentiometric measurements were carried out in the high temperature – high pressure cell described in [2]. The air in the autoclave was replaced by pure Hydrogen (99.999%) at 31.5 bar and 298 K. Further initial pressures at 298 K were obtained by pressurizing with Argon to 80, 130, 185, 236, 287, 336, 382, 485, and 590 bar. These pressures increased with the temperature to 60 and 146, 231, 326, 428, 528, 632, 732, 863, and 975 bar at 473 K. To obtain the hydrogen pressure $p_{H_2}(T)$, only Argon was pressurized at 298 K in the autoclave, containing the same solutions, to the above initial pressures minus 31.5 bar, and the temperature was increased to 473 K. $p_{H_2}(T)$ resulted by subtraction of the two corresponding pressures.

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Table 1. Molality, activity coefficient (mean ionic activity coefficient) and activity of H^+ in 1 m H_2SO_4 and the potentials E_1, E_2, E_3, and ΔE_j at different temperatures and pressures.

$\sum p$ (bar)	m_{H^+} (m)	$\gamma_\pm$	a_{H^+} (m)	E_1 (mV)	E_3 (mV)	E_2 (mV)	ΔE_j (mV)
			298 K				
100	1.218	0.298	0.363	772.0	−70.3	701.7	26.0
200	1.230	0.296	0.364	776.0	−70.2	705.8	30.1
300	1.247	0.295	0.368	779.5	−70.0	709.5	33.8
400	1.258	0.294	0.370	784.0	−69.8	714.2	38.5
500	1.270	0.292	0.371	789.0	−69.8	719.2	43.5
600	1.289	0.291	0.375	794.5	−69.5	725.0	49.3
700	1.300	0.290	0.377	801.0	−69.3	731.7	56.0
800	1.311	0.289	0.379	808.0	−69.2	738.8	63.1
900	1.326	0.288	0.382	817.1	−69.0	748.0	72.3
975	1.345	0.287	0.386	825.0	−69.9	756.1	80.4
			323 K				
100	1.137	0.265	0.301	755.0	−82.2	672.8	34.6
200	1.145	0.261	0.299	757.5	−82.5	675.0	36.8
300	1.152	0.259	0.298	761.5	−82.6	678.8	40.7
400	1.159	0.256	0.297	766.0	−82.7	683.3	45.1
500	1.167	0.253	0.296	771.0	−82.8	688.2	50.0
600	1.175	0.251	0.295	776.5	−82.9	693.6	55.4
700	1.183	0.249	0.294	783.0	−83.0	700.0	61.8
800	1.191	0.247	0.294	790.0	−83.0	707.0	68.8
900	1.200	0.244	0.293	798.0	−83.1	714.9	76.7
975	1.205	0.243	0.293	804.0	−83.1	720.9	82.7
			348 K				
100	1.067	0.260	0.277	732.0	−92.1	639.9	43.2
200	1.071	0.257	0.275	735.5	−92.3	643.2	46.5
300	1.075	0.254	0.273	739.0	−92.5	646.5	49.8
400	1.080	0.251	0.271	743.5	−92.7	650.8	54.1
500	1.085	0.248	0.269	747.5	−92.9	654.6	57.9
600	1.090	0.246	0.268	753.0	−93.3	659.7	63.0
700	1.095	0.243	0.266	759.0	−93.3	665.7	69.0
800	1.101	0.240	0.264	755.5	−93.5	671.9	75.2
900	1.106	0.238	0.263	773.0	−93.7	679.3	82.6
975	1.111	0.236	0.262	780.0	−93.8	686.2	89.5
			373 K				
100	1.036	0.240	0.249	710.0	−103.1	606.9	60.7
200	1.039	0.237	0.246	712.3	−103.5	608.8	62.6
300	1.042	0.234	0.244	715.3	−103.8	611.5	65.3
400	1.046	0.230	0.240	719.0	−104.3	614.7	68.5
500	1.049	0.228	0.239	723.3	−104.5	618.8	72.6
600	1.052	0.225	0.237	728.0	−104.8	623.2	77.0
700	1.056	0.222	0.234	734.0	−105.1	628.9	82.7
			398 K				
100	1.019	0.210	0.214	690.0	−115.7	574.3	82.0
200	1.021	0.207	0.211	693.0	−116.2	576.8	84.5
300	1.023	0.204	0.208	696.0	−116.6	579.4	87.1
400	1.026	0.200	0.205	699.7	−117.2	582.5	90.2
500	1.028	0.197	0.202	704.0	−117.7	586.5	94.2
600	1.030	0.194	0.200	709.0	−118.1	590.9	98.6
700	1.033	0.191	0.197	715.0	−118.6	596.4	104.1
			423 K				
100	1.010	0.190	0.192	681.0	−127.5	553.5	124.8
200	1.011	0.186	0.188	682.0	−128.1	553.9	125.2
300	1.013	0.182	0.184	685.0	−128.9	556.1	127.4
400	1.015	0.178	0.180	688.0	−129.7	558.3	129.6
500	1.017	0.174	0.177	692.5	−130.4	562.1	133.4
600	1.019	0.171	0.174	697.5	−130.9	566.5	137.8
			448 K				
100	1.006	0.162	0.163	668.0	−141.3	526.7	163.4
200	1.007	0.158	0.159	670.0	−142.3	527.7	164.4
300	1.008	0.154	0.155	672.0	−143.3	528.7	165.4
400	1.009	0.150	0.151	675.0	−144.4	530.6	167.3
500	1.011	0.146	0.148	678.0	−145.3	432.7	169.4
			473 K				
100	1.003	0.134	0.134	640.5	−156.7	483.8	192.0
200	1.004	0.12	0.130	642.1	−158.1	484.0	192.1
300	1.005	0.125	0.126	643.0	−158.5	484.6	192.8
400	1.006	0.121	0.122	644.1	−159.0	485.1	193.3

3. Results and Discussion

The potential E_1 of the cell (1) is due to the reaction

$$H_2 + Ag_2SO_4 \Leftrightarrow 2Ag + 2H^+ + SO_4^{2-}; \qquad (1)$$

$$E_1 = E_1^0 - RT/2F \ln[\{(a_{H^+})^2 \, a_{SO_4^{2-}}\}/p_{H_2}] + \Delta E_j, \qquad (1a)$$

and equals the potential difference $(E_2 - E_3)$ between the two half cells

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

$$E_2 = E_2^0 - RT/2F \ln a_{SO_4^{2-}} + \Delta E_j, \qquad (2a)$$

and

$$H_2 \Leftrightarrow 2H^+ + 2e^-, \qquad (3)$$

$$E_3 = RT/2F \ln[(a_{H^+})^2/p_{H_2}], \qquad (3a)$$

$$E_2 = E_1 + E_3, \qquad (4)$$

where a denotes the activity. To obtain $E_2(p, T)$, $a_{H^+}(p, T)$ was calculated according to

$$a_{H^+} = m_{H^+}\,\gamma_{H^+} = (1 + \alpha)\, m^0\, \gamma_{H^+}, \qquad (5)$$

where m_{H^+} and γ_{H^+} denote the actual molality and the activity coefficient of the hydrogen ion, α = the dissociation degree of HSO_4^- and m^0 = the stoichiometric molality of H_2SO_4. Only the formation of HSO_4^- is considered in (5), since, according to Oscarson et al. [3], the formation of undissociated H_2SO_4 takes first place at $T \geq 573$ K. γ_{H^+} was taken as the mean ionic activity coefficient $\gamma_\pm$ of H_2SO_4. $\gamma_\pm$ and α have been calculated previously by the authors [4] up to 473 K and 975 bar using the data given by Holmes and Mesmer [5] up to 473 K along with the corresponding saturation pressure and the values of the apparent formation constant of HSO_4^- determined by the authors [6] up to 473 K and 975 bar. Table 1 shows the

Table 2. Q and α of $NaSO_4^-$, $\gamma_\pm$, sulfate activity $a_{SO_4^{2-}}$ and the potential of the Ag–Ag$_2$SO$_4$ electrode $E_{Ag-Ag_2SO_4}$ in aqueous 1 m Na$_2$SO$_4$ solution up to 473 K.

T (K)	Q (m^{-1})	α	$\gamma_\pm$	$a_{SO_4^{2-}}$ (m)	$E_{Ag-Ag_2SO_4}$ (mV)
298	0.351	0.635	0.270	0.171	675.7
323	0.366	0.627	0.280	0.175	638.2
348	0.382	0.618	0.272	0.168	596.7
373	0.413	0.602	0.254	0.153	546.2
398	0.441	0.588	0.230	0.135	492.3
423	0.551	0.541	0.209	0.113	428.7
448	0.742	0.477	0.191	0.091	363.3
473	1.171	0.382	0.178	0.068	291.8

molality, activity coefficient (mean ionic activity coefficient) and activity of H^+ in 1 m H_2SO_4 solution, as well as the potentials E_1, E_3, and E_2 and ΔE_j at different T, p.

The calculation of the potential of the Ag–Ag$_2$SO$_4$ half cell in aqueous Na$_2$SO$_4$ solutions of different molalities given in [1] (without accounting for any diffusion term), has been carried out using the stoichiometric activity coefficient γ of Na$_2$SO$_4$ given in [7, 8], which is based on complete dissociation. The formation of $NaSO_4^-$ was neglected, since Pabalan and Pitzer [9] found a good agreement between the experimental solubility data of Na$_2$SO$_4$ in water up to 300 °C and those calculated by them without an explicit accounting for $Na_2SO_4^-$ formation. However, the thermodynamic formation constants of $NaSO_4^-$ reported in [3] indicate that appreciable formation of $NaSO_4^-$ at least at high temperatures takes place. The potential of the Ag–Ag$_2$SO$_4$ electrode in 1 m Na$_2$SO$_4$ solution was therefore recalculated taking the dissociation degree α and the mean ionic activity coefficient $\gamma_\pm$ of Na$_2$SO$_4$ as function of T into account. According to the data given by Helgeson, Kirkham and Flowers [10] for aqueous Na$_2$SO$_4$, the pressure dependence of Q, α, and $\gamma_\pm$ is negligible up to 1 kbar at T up to 473 K. It remained, therefore unconsidered.

The apparent formation constants of $NaSO_4^-$ in 1 m Na$_2$SO$_4$ were calculated using the log K^0 values given in [3] and the Debye-Hückel-Term (DHT) due to

$$\log Q = \log K^0 - 4\,A\gamma I^{1/2}/(1 + B\gamma \mathring{a} I^{1/2}), \quad (6)$$

to obtain α according to

$$Q = (1-\alpha)/m^0\alpha(1+\alpha). \quad (7)$$

Since the real ionic strength I results from

$$I = m^0(1+2\alpha), \quad (8)$$

α has been iteratively determined by fitting (6), (7), and (8). The mean ionic activity coefficient $\gamma_\pm$ was then calculated according to

$$\gamma_\pm = [4\gamma^3/\alpha(1+\alpha)^2]^{1/3}. \quad (9)$$

Table 2 shows Q and α of $NaSO_4^-$, the mean ionic activity and sulfate activity of 1 m Na$_2$SO$_4$ solution, as well as the potential of the Ag–Ag$_2$SO$_4$ electrode in it up to 473 K.

The recalculated values are in the whole not very different from those given in [1] due to the weak interaction between Na^+ and SO_4^{2-}. They are higher by about 0.4% at 298 K to about 2% at 473 K. This is due to the increase of $\gamma_\pm$ with respect to γ on decreasing α.

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