Dissociation Degree of HSO_4^- and Mean Ionic Activity Coefficient of Aqueous Sulfuric Acid of Different Molalities up to 473 K and 975 bar

B. A. Bilal and E. Müller

Hahn-Meitner-Institut, Glienicker Str. 100, D-14109 Berlin

Z. Naturforsch. **49a**, 939–942 (1994); received August 12, 1994

The apparent formation constant and the dissociation degree of HSO_4^- in aqueous H_2SO_4 of the molalities 0.1, 0.5, and 1.0 m, as well as the real mean ionic coefficient have been calculated up to 473 K and 975 bar using the thermodynamic data reported by Holmes and Mesmer at saturation pressure and those given by the authors at higher pressure.

1. Introduction

Aqueous H_2SO_4 is used as conducting electrolyte in high temperature – high pressure studies of the electrolysis of water as well as in potential assisted photoelectrolysis using semiconductor electrodes. The knowledge of the thermodynamic properties of H_2SO_4 at high T and p is essential for such studies. In [1] we have reported on the thermodynamics of HSO_4^- formation up to 473 K and 975 bar in pure water and in aqueous NaCl at $I = 0.1$, 0.5 and 1.0 m. The thermodynamic formation constant K^0, the apparent formation constant Q and the partial molal data $\Delta\bar{V}$, $\Delta\bar{S}$, and $\Delta\bar{H}$ of the formation have been determined. Holmes and Mesmer [2] have determined the stoichiometric mean activity coefficient γ of H_2SO_4 (based on complete ionization), as well as the dissociation degree α of HSO_4^- as functions of H_2SO_4 molality up to 473 K along with the corresponding saturation pressure by means of isopiestic measurements. The results in [1] and [2] were here used to calculate α and the mean ionic activity coefficient $\gamma_\pm$ in pure aqueous H_2SO_4 having the initial molalities $m^0 = 0.1$, 0.5, and 1.0 m up to 473 K and 975 bar.

2. Calculation and Discussion

α and Q of HSO_4^-, the real ionic strength I_r and the mean ionic activity coefficient $\gamma_\pm$ of H_2SO_4 are related by the equations

$$Q(T, p, I_r) = [1-\alpha(T, p, I_r)]/m^0\alpha(T, p, I_r)[1+\alpha(T, p, I_r)], \quad (1)$$

$$I_r(T, p) = m^0[1 + 2\alpha(T, p)] \quad (2)$$

and

$$\gamma_\pm(T, p, I_r) = [4\gamma^3(T, p, I_r)/\alpha(T, p, I_r)\{1+\alpha(T, p, I_r)\}^2]^{1/3}, \quad (3)$$

where only the formation of HSO_4^- is considered, since according to Oscarson et al. [3] the formation of undissociated H_2SO_4 takes only place at $T \geq 573$ K.

We have found in [1] that the pressure dependence of $Q(I)$ at constant T obeys more or less the relation

$$-\ln\{[Q^p(I)]_T/[Q^{sat}(I)]_T\} = \{[\Delta\bar{V}^{sat}(I)]_T/RT\}\{p/(1+bp)\} \quad (4)$$

given by El'Yanov and Hamann [4], where $Q^{sat}(I)$ and $\Delta\bar{V}^{sat}(I)$ denote the apparent constant and the partial molal volume of HSO_4^- formation at saturation pressure, and for aqueous solution $b = 9.2 \times 10^{-5}$ bar^{-1}. The plots of $\log[Q^p(I)]_T$ vs. $p/(1+bp)$ give straight lines at $T \leq 373$ K up to 975 bar. At higher temperature there are deviations from linearity in the high pressure region. The linear parts of the curves were observed up to ≈ 650 bar at 398 K and up to ≈ 430 bar at 473 K.

To obtain $[Q^p(I_r)]_T$ of pure aqueous H_2SO_4, $\Delta\bar{V}^{sat}$ values corresponding to $[I_r^{sat}]_T$ are needed. $[I_r^{sat}]_T$ was first calculated according to (2) using $[\alpha^{sat}(m^0)]_T$ given in [2]. Table 1 slows $[I_r^{sat}]_T$ at different H_2SO_4 molali-

Reprint requests to Prof. Dr. B. A. Bilal.

0932-0784 / 94 / 1000-0939 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

Table 1. The real ionic strength of H_2SO_4 at different molalities up to 473 K and saturation pressure.

T (K)	$I_r^{sat}(m)$		
	$m^0 = 0.1$ m	$m^0 = 0.5$ m	$m^0 = 1.0$ m
298	0.154	0.711	1.425
323	0.129	0.607	1.260
348	0.115	0.557	1.124
373	0.108	0.528	1.067
398	0.103	0.514	1.035
423	0.102	0.507	1.018
448	0.101	0.504	1.009
473	0.100	0.502	1.005

Table 2. The partial molal volume of the HSO_4^- formation at different H_2SO_4 molalities up to 473 K and saturation pressure.

T (K)	$\Delta\bar{V}^{sat}$ (cm^3 mol^{-1})		
	$m^0 = 0.1$ m	$m^0 = 0.5$ m	$m^0 = 1.0$ m
323	20.0 ± 0.6	18.5 ± 0.5	18.8 ± 0.6
348	23.0 ± 0.6	22.0 ± 0.6	22.2 ± 0.6
373	29.0 ± 0.7	27.2 ± 0.7	26.8 ± 0.7
398	37.0 ± 0.9	35.2 ± 0.8	35.8 ± 0.7
423	51.3 ± 1.0	48.4 ± 1.1	47.7 ± 1.0
448	70.2 ± 1.1	66.0 ± 1.1	63.6 ± 1.1
473	88.0 ± 1.1	84.0 ± 1.2	82.6 ± 1.1

ties and various temperatures. $\log [K^p]_T$ as well as $\log [Q^p(I)]_T$ given in [1] for different temperatures and ionic strengths were plotted vs. $p/(1+bp)$, and $[\Delta\bar{V}^{sat}(I)]_T$ (in NaCl medium) was determined from the slopes of the linear parts of the graphs. From the plots of the so obtained $[\Delta\bar{V}^{sat}(I)]_T$ vs. I, the $[\Delta\bar{V}^{sat}(I_r)]_T$ corresponding to $[I_r^{sat}]_T$ of pure aqueous H_2SO_4 was determined. These are shown in Table 2. The error due to the different media is negligible, particularly with increasing H_2SO_4 molality and temperature, where H_2SO_4 is increasingly considered as 1,1 electrolyte. $[Q^p(I_r)]_T$ and $[\alpha^p(I_r)]_T$ were then calculated by means of (4) and (1).

The pressure dependence of the mean ionic activity coefficient is given by

$$[\partial \ln \gamma_\pm(I_r)/\partial p]_T = [(\Delta\bar{V}(I_r, p) - \Delta\bar{V}^0(p)]_T/RT. \quad (5)$$

For integration of (5) from saturation pressure to p, the same function describing the pressure dependence of the partial molal volume given in [4] was used to obtain

$$\ln [\gamma_\pm^p(I_r)/\gamma_\pm^{sat}(I_r)]_T = \{[(\Delta\bar{V}^{sat}(I_r) - \Delta\bar{V}^{0\,sat})]_T/RT\}\{p/(p+bp)\}, \quad (6)$$

Table 3. The apparent formation constant of HSO_4^- at different H_2SO_4 molalities up to 473 K and 975 bar.

p (bar)	$[Q^p]_T$ (m^{-1})		
	$m^0 = 0.1$ m	$m^0 = 0.5$ m	$m^0 = 1.0$ m
	323 K		
sat.	51.5 ± 0.70	15.1 ± 0.20	5.9 ± 0.25
100	47.8 ± 0.60	14.1 ± 0.20	5.5 ± 0.24
200	44.4 ± 0.50	13.1 ± 0.20	5.2 ± 0.22
300	41.3 ± 0.50	12.3 ± 0.18	4.8 ± 0.19
400	38.5 ± 0.50	11.5 ± 0.15	4.5 ± 0.19
500	35.9 ± 0.40	10.8 ± 0.14	4.3 ± 0.18
600	33.5 ± 0.40	10.1 ± 0.13	4.0 ± 0.17
700	31.3 ± 0.40	9.5 ± 0.12	3.8 ± 0.15
800	29.1 ± 0.39	9.0 ± 0.11	3.6 ± 0.14
900	27.5 ± 0.37	8.5 ± 0.11	3.3 ± 0.14
975	26.2 ± 0.34	8.1 ± 0.10	3.2 ± 0.13
	348 K		
sat.	113.5 ± 1.2	31.2 ± 0.40	14.3 ± 0.20
100	104.8 ± 1.1	28.9 ± 0.38	13.2 ± 0.20
200	96.9 ± 1.1	26.9 ± 0.35	12.3 ± 0.17
300	89.7 ± 1.0	24.9 ± 0.33	11.4 ± 0.14
400	83.2 ± 1.1	23.2 ± 0.33	10.6 ± 0.14
500	77.2 ± 1.0	21.6 ± 0.30	9.9 ± 0.12
600	71.8 ± 0.90	20.1 ± 0.27	9.3 ± 0.12
700	66.8 ± 0.90	18.8 ± 0.25	8.7 ± 0.11
800	62.3 ± 0.85	17.6 ± 0.23	8.1 ± 0.10
900	58.1 ± 0.80	16.5 ± 0.20	7.6 ± 0.10
975	55.5 ± 0.80	15.8 ± 0.20	7.3 ± 0.10
	373 K		
sat.	241.8 ± 2.1	67.5 ± 0.90	27.9 ± 0.36
100	220.2 ± 2.0	61.8 ± 0.90	25.6 ± 0.35
200	200.8 ± 2.0	56.7 ± 0.85	23.6 ± 0.32
300	183.4 ± 1.9	52.1 ± 0.85	21.7 ± 0.30
400	167.8 ± 1.8	47.9 ± 0.82	20.1 ± 0.28
500	153.7 ± 1.8	44.1 ± 0.80	18.5 ± 0.27
600	141.1 ± 1.9	40.7 ± 0.75	17.2 ± 0.24
700	129.7 ± 1.8	37.7 ± 0.75	15.8 ± 0.24
	398 K		
sat.	562.1 ± 3.5	134.9 ± 2.0	55.8 ± 0.90
100	502.2 ± 3.5	121.3 ± 1.9	50.3 ± 0.90
200	449.7 ± 3.3	109.2 ± 1.7	45.4 ± 0.80
300	403.2 ± 3.3	98.5 ± 1.5	41.1 ± 0.80
400	363.2 ± 3.0	89.1 ± 1.5	37.7 ± 0.75
500	326.8 ± 2.7	80.6 ± 1.3	33.7 ± 0.75
600		73.1 ± 1.1	30.6 ± 0.70
700			27.9 ± 0.70
	423 K		
sat.	1142.9 ± 5.5	262.7 ± 2.4	109.1 ± 1.2
100	987.2 ± 5.1	228.8 ± 2.2	95.4 ± 1.2
200	855.2 ± 4.9	199.8 ± 2.2	85.4 ± 1.0
300	752.2 ± 4.5	174.8 ± 1.9	73.4 ± 1.0
400	646.1 ± 4.1	153.4 ± 1.7	64.9 ± 0.9
500		134.9 ± 1.5	56.9 ± 0.9
600			50.4 ± 0.85
	448 K		
sat.	2505.3 ± 10.8	522.3 ± 3.7	208.1 ± 2.1
100	2073.2 ± 8.5	437.1 ± 3.5	175.5 ± 1.9
200	1722.2 ± 7.7	367.2 ± 3.3	148.5 ± 1.8
300	1434.3 ± 7.7	309.2 ± 3.0	125.9 ± 1.6
400	1198.8 ± 7.0	261.2 ± 2.6	107.2 ± 1.6
500			91.5 ± 1.6
	473 K		
sat.	6876.6 ± 18	1107.2 ± 5.5	398.5 ± 3.2
100	5492.3 ± 16	893.3 ± 4.8	322.6 ± 2.8
200	4492.6 ± 14	723.9 ± 4.4	262.6 ± 2.4
300	3546.2 ± 13	588.4 ± 4.1	214.4 ± 2.2
400			165.7 ± 1.9

Table 4. Dissociation degree of HSO_4^- and mean ionic activity coefficient of H_2SO_4 at different molalities, temperatures and pressures.

p (bar)	$m^0 = 0.1$ m		$m^0 = 0.5$ m		$m^0 = 1.0$ m	
	α	$\gamma_\pm$	α	$\gamma_\pm$	α	$\gamma_\pm$
			323 K			
sat.	0.145 ± 0.0043	0.525 ± 0.0157	0.107 ± 0.0032	0.346 ± 0.0104	0.130 ± 0.0039	0.269 ± 0.0081
100	0.153 ± 0.0046	0.517 ± 0.0155	0.113 ± 0.0034	0.341 ± 0.0102	0.137 ± 0.0041	0.265 ± 0.0079
200	0.162 ± 0.0059	0.511 ± 0.0153	0.120 ± 0.0036	0.337 ± 0.0101	0.145 ± 0.0043	0.261 ± 0.0078
300	0.171 ± 0.0051	0.505 ± 0.0151	0.126 ± 0.0038	0.334 ± 0.0100	0.152 ± 0.0045	0.259 ± 0.0078
400	0.180 ± 0.0054	0.500 ± 0.0150	0.133 ± 0.0040	0.330 ± 0.0099	0.160 ± 0.0048	0.256 ± 0.0077
500	0.190 ± 0.0057	0.494 ± 0.0148	0.140 ± 0.0042	0.327 ± 0.0098	0.167 ± 0.0050	0.253 ± 0.0076
600	0.199 ± 0.0060	0.489 ± 0.0147	0.147 ± 0.0044	0.324 ± 0.0097	0.175 ± 0.0053	0.251 ± 0.0075
700	0.209 ± 0.0063	0.483 ± 0.0145	0.154 ± 0.0046	0.322 ± 0.0096	0.183 ± 0.0055	0.249 ± 0.0074
800	0.220 ± 0.0066	0.478 ± 0.0143	0.161 ± 0.0048	0.319 ± 0.0095	0.191 ± 0.0057	0.246 ± 0.0074
900	0.228 ± 0.0068	0.473 ± 0.0142	0.169 ± 0.0051	0.316 ± 0.0094	0.200 ± 0.0060	0.244 ± 0.0073
975	0.236 ± 0.0071	0.470 ± 0.0141	0.174 ± 0.0052	0.313 ± 0.0093	0.205 ± 0.0062	0.243 ± 0.0072
			348 K			
sat.	0.076 ± 0.0023	0.519 ± 0.0156	0.057 ± 0.0017	0.332 ± 0.0099	0.062 ± 0.0019	0.264 ± 0.0079
100	0.081 ± 0.0024	0.512 ± 0.0154	0.061 ± 0.0183	0.327 ± 0.0098	0.066 ± 0.0020	0.260 ± 0.0078
200	0.087 ± 0.0026	0.504 ± 0.0151	0.065 ± 0.0019	0.323 ± 0.0097	0.071 ± 0.0021	0.257 ± 0.0077
300	0.093 ± 0.0028	0.498 ± 0.0149	0.070 ± 0.0021	0.319 ± 0.0096	0.075 ± 0.0022	0.254 ± 0.0076
400	0.099 ± 0.0029	0.492 ± 0.0147	0.074 ± 0.0022	0.316 ± 0.0094	0.080 ± 0.0024	0.251 ± 0.0075
500	0.105 ± 0.0031	0.486 ± 0.0146	0.079 ± 0.0024	0.312 ± 0.0093	0.085 ± 0.0025	0.248 ± 0.0074
600	0.111 ± 0.0033	0.480 ± 0.0144	0.084 ± 0.0025	0.308 ± 0.0093	0.090 ± 0.0027	0.246 ± 0.0074
700	0.118 ± 0.0035	0.474 ± 0.0142	0.089 ± 0.0027	0.305 ± 0.0091	0.095 ± 0.0029	0.243 ± 0.0073
800	0.125 ± 0.0037	0.469 ± 0.0141	0.094 ± 0.0028	0.302 ± 0.0091	0.101 ± 0.0030	0.240 ± 0.0072
900	0.132 ± 0.0039	0.464 ± 0.0139	0.099 ± 0.0030	0.298 ± 0.0089	0.106 ± 0.0032	0.238 ± 0.0071
975	0.137 ± 0.0041	0.460 ± 0.0138	0.103 ± 0.0031	0.296 ± 0.0089	0.111 ± 0.0033	0.236 ± 0.0071
			373 K			
sat.	0.038 ± 0.0011	0.499 ± 0.0149	0.028 ± 0.0008	0.312 ± 0.0094	0.033 ± 0.0010	0.245 ± 0.0073
100	0.042 ± 0.0012	0.489 ± 0.0147	0.030 ± 0.0009	0.306 ± 0.0092	0.036 ± 0.0011	0.240 ± 0.0072
200	0.045 ± 0.0014	0.482 ± 0.0144	0.033 ± 0.0010	0.301 ± 0.0090	0.039 ± 0.0012	0.237 ± 0.0071
300	0.049 ± 0.0015	0.474 ± 0.0142	0.036 ± 0.0011	0.298 ± 0.0089	0.042 ± 0.0013	0.234 ± 0.0070
400	0.054 ± 0.0016	0.467 ± 0.0140	0.039 ± 0.0011	0.294 ± 0.0088	0.046 ± 0.0014	0.231 ± 0.0069
500	0.058 ± 0.0017	0.460 ± 0.0138	0.042 ± 0.0012	0.289 ± 0.0087	0.049 ± 0.0015	0.288 ± 0.0068
600	0.063 ± 0.0019	0.453 ± 0.0136	0.045 ± 0.0013	0.286 ± 0.0086	0.052 ± 0.0016	0.225 ± 0.0067
700	0.067 ± 0.0020	0.447 ± 0.0134	0.048 ± 0.0014	0.282 ± 0..0084	0.056 ± 0.0017	0.222 ± 0.0067
			398 K			
sat.	0.017 ± 0.0005	0.489 ± 0.0147	0.014 ± 0.0004	0.288 ± 0.0086	0.017 ± 0.0005	0.215 ± 0.0064
100	0.019 ± 0.0006	0.478 ± 0.0143	0.016 ± 0.0005	0.282 ± 0.0085	0.019 ± 0.0006	0.210 ± 0.0063
200	0.021 ± 0.0006	0.469 ± 0.0141	0.018 ± 0.0005	0.277 ± 0.0083	0.021 ± 0.0006	0.206 ± 0.0062
300	0.024 ± 0.0007	0.461 ± 0.0138	0.020 ± 0.0006	0.272 ± 0.0082	0.023 ± 0.0007	0.204 ± 0.0061
400	0.026 ± 0.0008	0.452 ± 0.0136	0.022 ± 0.0006	0.267 ± 0.0080	0.026 ± 0.0008	0.200 ± 0.0060
500	0.029 ± 0.0009	0.445 ± 0.0133	0.024 ± 0.0007	0.263 ± 0.0079	0.028 ± 0.0008	0.197 ± 0.0059
600			0.026 ± 0.0008	0.259 ± 0.0077	0.030 ± 0.0009	0.194 ± 0.0058
700					0.033 ± 0.0010	0.191 ± 0.0057
			423 K			
sat	0.008 ± 0.0002	0.455 ± 0.0136	0.007 ± 0.0002	0.259 ± 0.0078	0.009 ± 0.0003	0.195 ± 0.0058
100	0.010 ± 0.0003	0.440 ± 0.0132	0.009 ± 0.0003	0.251 ± 0.0075	0.010 ± 0.0003	0.190 ± 0.0057
200	0.011 ± 0.0003	0.430 ± 0.0129	0.010 ± 0.0003	0.245 ± 0.0074	0.011 ± 0.0003	0.186 ± 0.0056
300	0.013 ± 0.0004	0.419 ± 0.0126	0.011 ± 0.0003	0.240 ± 0.0072	0.013 ± 0.0004	0.182 ± 0.0054
400	0.015 ± 0.0005	0.409 ± 0.0123	0.013 ± 0.0004	0.235 ± 0.0071	0.015 ± 0.0005	0.178 ± 0.0053
500			0.014 ± 0.0004	0.230 ± 0.0069	0.017 ± 0.0005	0.174 ± 0.0052
600					0.019 ± 0.0006	0.171 ± 0.0051
			448 K			
sat.	0.004 ± 0.0001	0.428 ± 0.0128	0.004 ± 0.0001	0.232 ± 0.0069	0.005 ± 0.0001	0.168 ± 0.0050
100	0.005 ± 0.0001	0.411 ± 0.0123	0.004 ± 0.0001	0.224 ± 0.0067	0.006 ± 0.0002	0.162 ± 0.0049
200	0.006 ± 0.0002	0.400 ± 0.0120	0.005 ± 0.0002	0.217 ± 0.0065	0.007 ± 0.0002	0.158 ± 0.0047
300	0.007 ± 0.0002	0.388 ± 0.0116	0.006 ± 0.0002	0.211 ± 0.0063	0.008 ± 0.0003	0.154 ± 0.0046
400	0.008 ± 0.0003	0.378 ± 0.0113	0.007 ± 0.0002	0.205 ± 0.0061	0.009 ± 0.0003	0.150 ± 0.0045
500					0.011 ± 0.0003	0.146 ± 0.0044
			473 K			
sat.	0.0015 ± 0.00004	0.416 ± 0.0125	0.0018 ± 0.00005	0.203 ± 0.0061	0.0025 ± 0.00007	0.140 ± 0.0042
100	0.0018 ± 0.00005	0.397 ± 0.0119	0.0022 ± 0.00007	0.194 ± 0.0058	0.0031 ± 0.00009	0.134 ± 0.0040
200	0.0022 ± 0.00007	0.384 ± 0.0115	0.0027 ± 0.00008	0.187 ± 0.0056	0.0038 ± 0.00011	0.129 ± 0.0039
300	0.0028 ± 0.00008	0.369 ± 0.0111	0.0034 ± 0.00010	0.180 ± 0.0054	0.0046 ± 0.00014	0.125 ± 0.0037
400					0.0056 ± 0.00017	0.121 ± 0.0036

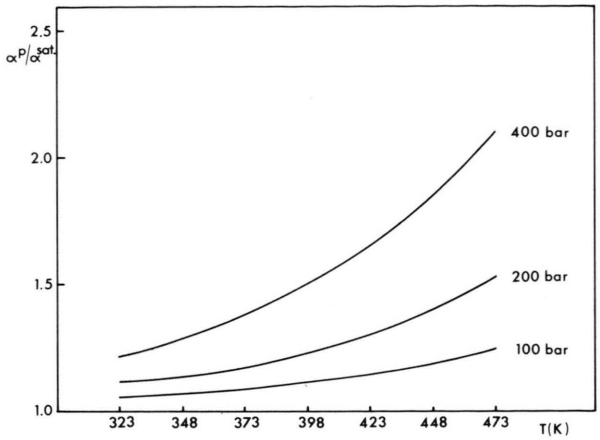

Fig. 1. The ratio α^p/α^{sat} as a function of T at $m^0 = 1.0$ m and $p = 100$, 200, and 400 bar.

where $\Delta\bar{V}^0$ denotes the standard partial molal volume of HSO_4^- formation. Its values are given in [1]. The Q values at different temperatures, pressures and various stoichiometric molalities of H_2SO_4 are shown in Table 3. Those of α and $\gamma_\pm$ are given in Table 4.

The dissociation degree decreases drastically with increasing temperature, but increases moderately with raising pressure. This expected variation is correlated with dependence of the dielectric constant of water on the parameters. It seems that the electrostatic interaction participates significantly in the H–O bond within the HSO_4^- which is anyhow strongly polarized. The break of the H–O bond is promoted by pressure increase, since the accompanying volume reduction is favoured if electrostriction in the system takes increasingly place due to more production of charged species.

Figure 1 shows the ratio α^p/α^{sat} as a function of T at $m^0 = 1.0$ m and $p = 100$, 200, and 400 bar. The difference between the curves at the three pressures becomes significantly larger with increasing temperature. This is probably due to the increasing destruction of the ordered water structure with raising temperature which allows a maximum orientation of the water dipoles around the hydrated ions, particularly H^+, resulting in a decreased entropy term and a higher free energy of the dissociation reaction.

[1] B. A. Bilal and E. Müller, Z. Naturforsch. **48a,** 1073 (1993).
[2] H. F. Holmes and R. E. Mesmer, J. Chem. Thermodyn. **24,** 317 (1992).
[3] J. I. Oscarson, R. M. Izatt, P. R. Brown, Z. Pawlak, S. E. Gillespie, and J. J. Christensen, J. Solution Chem. **17,** 841 (1988).
[4] El'Yanov and S. D. Hamann, Austr. J. Chem. **28,** 945 (1975).