

Electronic Supplementary Information:

Second Ionization Constant of Sulfuric Acid in H₂O and D₂O from 150 to 300 °C at $p = 11.5$ MPa Using Flow AC Conductivity

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Table S1. Details of chemicals and solutions used in this work

Chemical	Brand	Product number	Lot number	Solvent	Stock solution concentration /mol·kg ⁻¹	Working solution concentration /mmol·kg ⁻¹
K ₂ SO ₄	Sigma-Aldrich	221325	MKBW3546V	H ₂ O	0.398593 ± 0.000001	9.9613 ± 0.0001
				D ₂ O	0.317773 ± 0.000001	9.5331 ± 0.0001
KHSO ₄	Aldrich	401544	MKCG9783	H ₂ O	0.026261 ± 0.000001	0.031879 ± 0.000002
				D ₂ O	0.033511 ± 0.000002	0.036741 ± 0.000002
KOH	Fisher Chemical	SP236	135219	H ₂ O	0.209391 ± 0.000022	0.199747 ± 0.000031 0.217558 ± 0.000031
KOD	Sigma-Aldrich	176761	MKCC3238	D ₂ O	0.170443 ± 0.000088	0.153859 ± 0.000081 0.149313 ± 0.000079
H ₂ SO ₄	Sigma-Aldrich	339741	SHBK1251	H ₂ O	0.41511 ± 0.00013	11.3257 ± 0.0036
				D ₂ O	0.370934 ± 0.000071	10.5123 ± 0.0020
HCl	Sigma-Aldrich	339253	SHBJ3824	H ₂ O	0.129939 ± 0.000097	0.26620 ± 0.00020
DCl	Aldrich	543047	MKCG2538	D ₂ O	0.092108 ± 0.000064	0.23893 ± 0.00017
KCl	Alfa Aesar	87626	L10Y036	H ₂ O	0.087129	0.268575
KCl	Alfa Aesar	87626	Z05D036	D ₂ O	0.145321	0.296134 ± 0.000011
NaCl	Alfa Aesar	87605	A18Z044	H ₂ O	0.10093	0.167566
KHP	Sigma-Aldrich	P1088	MKCG4802			
phenolphthalein	Sigma-Aldrich	319236	MKCG7813V			
CH ₃ COOD	Aldrich	151777	MKCF5554	D ₂ O		

Table S2a. Calculated molal concentrations of the aqueous species generated from a 0.009961 mol·kg⁻¹ solution of K₂SO₄ in H₂O at $p = 11.5$ MPa.

T	$m_{\text{SO}_4^{2-}}$	$m_{\text{HSO}_4^-}$	$m_{\text{KSO}_4^-}$	m_{K^+}	$m_{\text{K}_2\text{SO}_4}$	m_{OH^-}	m_{H^+}
°C	10 ⁶ mol·kg ⁻¹						
150.2	8653.47	10.95	1291.79	18620.6	5.09	11.33	0.38
200.1	7915.67	40.69	1979.47	17892.2	25.47	40.93	0.24
225.1	7352.48	66.28	2486.93	17324.5	55.60	66.47	0.19
250.1	6598.91	104.60	3137.17	16544.2	120.61	104.74	0.13
275.1	5595.97	169.47	3934.49	15465.4	261.36	169.55	0.08
300.3	4347.35	143.58	4890.00	13871.9	580.37	143.65	0.07

Table S2b. Calculated molal concentrations of the aqueous species generated from a 0.009533 mol·kg⁻¹ solution of K₂SO₄ in D₂O at $p = 11.5$ MPa.

T	$m_{\text{SO}_4^{2-}}$	$m_{\text{DSO}_4^-}$	$m_{\text{KSO}_4^-}$	m_{K^+}	$m_{\text{K}_2\text{SO}_4}$	m_{OD^-}	m_{D^+}
°C	10 ⁶ mol·kg ⁻¹						
150.2	7735.57	7.49	1779.10	17265.2	10.86	7.58	0.08
200.1	7043.14	25.60	2421.12	16558.6	43.17	25.67	0.06
225.1	6515.11	49.98	2882.88	16013.1	85.05	50.02	0.04
250.1	5821.03	86.44	3457.80	15272.7	167.75	86.46	0.03
275.1	4132.44	156.08	4132.44	14268.7	332.44	156.10	0.02
300.3	3789.84	180.77	4886.32	12827.5	676.10	180.78	0.01

Table S3a. Single Ion Limiting Molar Conductivities in H₂O from Erickson¹, Refit for This Work.

T	p	$\lambda^\circ(\text{Cl}^-)$	$\lambda^\circ(\text{K}^+)$	$\lambda^\circ(\text{H}_3\text{O}^+)$	$\lambda^\circ(\text{OH}^-)$
$^\circ\text{C}$	MPa	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$			
25.02	20.30	75.8	74.4	349.0	196.7
101.07	21.28	204.2	192.6	661.1	437.6
150.15	21.31	297.4	275.4	787.7	520.3
198.73	21.30	386.8	353.1	815.8	649.3
224.87	21.07	442.8	401.7	834.0	730.8
250.41	21.14	481.9	434.5	859.9	776.0
275.48	20.14	521.3	467.6	851.0	781.4
298.76	21.15	552.6	493.6	886.0	841.3

Table S3b. Single Ion Limiting Molar Conductivities in D₂O from Erickson¹, Refit for This Work.

T	p	$\lambda^\circ(\text{Cl}^-)$	$\lambda^\circ(\text{K}^+)$	$\lambda^\circ(\text{D}_3\text{O}^+)$	$\lambda^\circ(\text{OD}^-)$
$^\circ\text{C}$	MPa	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$			
25.02	20.30	62.2	61.0	246.6	112.6
101.07	21.28	177.3	167.3	464.6	231.9
150.15	21.31	258.3	239.3	563.4	212.4
198.73	21.30	336.6	307.4	629.7	460.5
224.87	21.07	380.9	345.5	668.6	570.0
250.41	21.14	420.4	379.1	687.7	611.2
275.48	20.14	462.5	415.0	674.1	628.9
298.76	21.15	502.7	449.1	681.6	675.4

Table S4. Quint-Viallard Conductivity Model Parameters (E , S , J_1 , and J_2) for the Conductivities of the Equivalent Electrolytes (Λ_1 , Λ_2 , Λ_3 , and Λ_4) under the Experimental Conditions in H₂O and D₂O.

T /°C	E		S		J_1		J_2	
	H ₂ O	D ₂ O	H ₂ O	D ₂ O	H ₂ O	D ₂ O	H ₂ O	D ₂ O
Λ_1								
150.2	78.8783	75.0388	477.099	419.025	1242.59	1119.51	1857.91	1677.07
200.1	175.731	166.435	708.693	633.929	2422.52	2220.50	4202.24	3864.33
225.1	258.699	245.229	845.556	763.467	3375.98	3123.53	6357.22	5909.25
250.1	383.219	363.978	1004.83	915.158	4772.77	4456.38	9842.18	9250.35
275.1	581.255	553.995	1200.04	1101.79	6964.25	6565.37	15943.5	15171.9
300.3	937.995	901.802	1465.25	1357.96	10898.3	10420.2	28419.4	27566.5
Λ_2								
150.2	851.585	647.567	1076.02	899.575	4660.27	3698.50	5113.55	4010.54
200.1	1481.32	1177.51	1549.81	1329.53	8636.31	7106.35	10621.3	8683.64
225.1	1973.11	1605.80	1827.63	1588.23	11844.1	9937.14	15591.3	13036.4
250.1	2680.45	2233.71	2150.97	1892.21	16575.0	14183.6	23588.3	20181.1
275.1	3772.80	3222.66	2549.07	2269.10	24092.6	21056.2	37598.1	32977.1
300.3	5704.79	5025.21	3095.26	2793.51	37861.9	34019.1	66444.4	60246.4
Λ_3								
150.2	283.876	266.053	871.149	763.239	2455.87	2215.98	2322.09	2125.98
200.1	683.578	639.572	1309.98	1169.73	5256.76	4823.80	5915.26	5488.08
225.1	1037.67	974.500	1573.84	1419.28	7692.42	7129.07	9470.39	8868.91
250.1	1582.20	1493.85	1885.30	1716.05	11451.2	10721.5	15513.9	14680.2
275.1	2471.65	2351.23	2273.49	2088.00	17677.6	16742.7	26641.4	25530.9
300.3	4125.87	3980.67	2812.08	2610.72	29551.9	28490.2	50675.5	49595.5
Λ_4								
150.2	282.767	210.856	623.213	515.939	2373.71	1874.15	3449.31	2741.73
200.1	461.828	357.062	879.826	747.219	4113.12	3349.41	6877.60	5658.50
225.1	593.923	468.246	1026.48	882.848	5425.81	4490.90	9831.41	8239.65
250.1	776.328	624.192	1193.85	1038.97	7267.40	6113.12	14415.3	12309.4
275.1	1045.99	858.318	1395.36	1227.95	10038.5	8586.81	22128.6	19227.9
300.3	1499.38	1261.70	1664.5	1483.22	14801.7	12936.7	37267.0	33350.4

In the 1997 paper by Bešter-Rogač *et al.*², Eqn. A6b in the Appendix should read:

$$Q_3 = -\frac{(|z_1| + |z_2|)\lambda_j^\circ Q_4}{\lambda_1^\circ + \lambda_2^\circ} - \left(|z_j| + \frac{2z_j|z_j|(z_1 + z_2)}{q|z_1||z_2|} \right) Q_5 + |z_j| Q_6 \quad \text{* MERGEFORMAT (18)}$$

Even when the same value for the distance of closest approach is used, the Quint-Viallard conductivity model from this work produces a different value of the J_1 term for the anion than was calculated by Bešter-Rogač *et al.*². This comparison can be seen at 298.15 K in Table S6.

Table S5. A comparison of the Quint-Viallard equation coefficients E , S , J_1 , and J_2 at 298.15 K for the tartrate anion and the proton from this work and that of Bešter-Rogač *et al.*² with the distance of closest approach, $a = 6.75 \text{ \AA}$.

	Bešter-Rogač <i>et al.</i> ²	This work
$S(\text{H}^+)$	153.77	153.77
$S(1/2 \text{ Tar}^{2-})$	81.92	81.96
$E(\text{H}^+)$	227.42	227.42
$E(1/2 \text{ Tar}^{2-})$	-46.81	-46.82
$J_1(\text{H}^+)$	1426.80	1426.76
$J_1(1/2 \text{ Tar}^{2-})$	279.07	17.27

In the 1999 paper by Tsurko *et al.*³, Eqn. 43 in the Appendix should read:

$$Q_1 = \frac{z_1^2 z_2^2 b^2 4(3 - 2q + 3\sqrt{q}) + |z_1||z_2|b(24 + 13q + 21\sqrt{q}) + 4(3 + 5q + 6\sqrt{q})}{12(1 + \sqrt{q})b^3} \quad \backslash * \text{MERGEFORMAT (19)}$$

Even when the same value for the distance of closest approach is used, the Quint-Viallard conductivity model from this work produces a different value of the J_1 term than was calculated by Tsurko *et al.*³. This comparison can be seen at 298.15 K in Table S7.

Table S6. A comparison of the Quint-Viallard equation coefficients E , S , J_1 , and J_2 at 298.15 K for the tartrate anion and the proton from this work and that of Tsurko *et al.*³ with the distance of closest approach, $a = 4.0 \text{ \AA}$.

	Na ⁺ + OH ⁻		Na ⁺ + HPO ₄ ²⁻		Na ⁺ + H ₂ PO ₄ ⁻	
	Tsurko <i>et al.</i>	This work	Tsurko <i>et al.</i>	This work	Tsurko <i>et al.</i>	This work
S_1	41.83	41.83	51.66	51.66	41.83	41.83
S_2	75.87	75.87	84.97	84.97	37.66	37.66
E_1	5.3153	5.3151	40.44	40.44	1.6722	1.6720
E_2	34.19	34.19	-52.50	-52.50	-0.5463	-0.5465
J_{11}	83.58	84.55	197.23	198.49	71.46	72.43
J_{12}	267.26	254.96	191.15	-40.16	62.80	55.94
J_{21}	108.17	108.16	255.12	255.10	90.58	90.58
J_{22}	319.88	319.86	-165.00	-165.00	71.01	71.00

REFERENCES

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