

Enthalpies of Dilution of Aqueous Electrolytes: Sulfuric Acid, Hydrochloric Acid, and Lithium Chloride

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Calorimetric measurements at 25 °C of the enthalpies of dilution of aqueous H₂SO₄ (0.00090 to 6.4 mol·kg⁻¹), LiCl (0.026 to 6.7 mol·kg⁻¹), and HCl (0.018 to 1.6 mol·kg⁻¹) have been performed using two different isothermal calorimeters. The results of this work and that of three earlier calorimetric investigations and one Raman spectral investigation have been used to calculate values of the relative apparent molal enthalpies, and relative partial molal enthalpies for these electrolytes.

Key words: Calorimetry; electrolytes; enthalpy of dilution; heat; hydrochloric acid; lithium chloride; relative apparent molal enthalpy; relative partial molal enthalpy; sulfuric acid; thermochemistry.

1. Introduction

The relative apparent molal enthalpy (Φ_L)¹ or heat content of sulfuric acid is a complicated function of the molality. The determination of this quantity requires an extrapolation of enthalpies of dilution as measured down to extremely low molalities.

There have been numerous reports and discussions of the relative apparent molal enthalpy of sulfuric acid [1-4].² At the extreme dilutions attainable experimentally, sulfuric acid is known to have undissociated bisulfate ions [2]. This incomplete dissociation at the lowest dilutions complicates the extrapolation procedure, causes deviations from the Debye-Huckel limiting law (DHLL), and makes the final calculated values of the relative apparent molal enthalpy dependent on the method of data treatment.

Young and Blatz [2] performed an analysis of this problem in 1949. They took the degree of dissociation, and thence the enthalpy of dissociation, into consideration and

performed a semi-theoretical calculation of the relative apparent molal enthalpy of sulfuric acid. They also found a systematic difference of 460 calories (1 cal=4.184 J) between their values and those reported in the literature [5]. This discrepancy was also confirmed later by Harned and Owen [1]. Several years later, Giauque and his co-workers at the University of California began an analysis of the thermodynamics of sulfuric acid [6]. Thus, the work of Young and Blatz [2], the research of Giauque *et al.*, and the earlier measurements of Groenier and Young [7] indicated a need for additional experimental work on the dilution enthalpy of sulfuric acid which, in turn, led the junior author (YCW) to undertake this investigation, which also included measurements on aqueous HCl and LiCl, as a part of his Ph.D. dissertation. While some of the results obtained herein have been cited by Giauque *et al.* [6] and used both in the National Bureau of Standards Technical Note 270 Series [3], and in the review of Pitzer *et al.* [8], independent publication of the results was delayed by circumstances encountered by the senior author (TFY). Publication at this time serves both to better document the experimental results and the method of data treatment and to honor the memory of the late T. F. Young and his dedication to science.

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¹ The reader is referred to the treatise of Harned and Owen [1] for the definition of the terms used in this paper and to the glossary (sect. 6) for an explanation of the symbols which we have used.

² Figures in brackets indicate references at the end of this paper.

2. Experimental Procedure

Two calorimeters of different sensitivities were employed depending on the molality. A calorimeter with lower sensitivity, as described by Young and his co-workers [9, 10], was used for most of the measurements where the molality was greater than 0.01 mol kg^{-1} . For those measurements below 0.01 mol kg^{-1} , a more sensitive differential calorimeter was necessary. The latter instrument contained a thermel of 500 junctions on each side of a plastic plate which was held by petroleum "wax" in the center of a large Dewar flask having a volume of two liters. Its design was somewhat similar to that of the calorimeter used by Lange and his co-workers [11]. Details of the construction and operation have been described by Fagley [12] and Kasner [13].

All of the chemicals used in this study were purchased from Baker Chemical Company³ as "Chemically Pure Analyzed Reagents." Relatively concentrated stock solutions were prepared and were analyzed by standard methods. The two acids were analyzed by titration with sodium hydroxide which had been standardized with potassium acid phthalate using phenolphthalein as an end-point indicator. The hydrochloric acid and the lithium chloride were analyzed gravimetrically by precipitation as silver chloride. Sulfuric acid was also analyzed by measurement of its density and comparison with data given in the International Critical Tables [14]. Duplicate analyses and analyses with different methods agreed to within 0.1 percent (for all stock solutions). All stock solutions were further diluted by mass to the various molalities necessary for each experiment. Some of the solutions produced during the dilution experiments were subjected to additional tests of analytical accuracy.

The laboratory's distilled water was further purified before use by redistillation with alkaline permanganate in a block-tin still [13]. The specific conductance of all water used was lower than $10^{-6} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

The temperature sensitivity of the differential calorimeter was about $2 \mu\text{K}$, which corresponds to an uncertainty in the heat measurement of 1.5 mcal. At a molality of $0.001 \text{ mol} \cdot \text{kg}^{-1}$, the heat liberated on dilution of sulfuric acid was about 50 mcal with a corresponding uncertainty of 3 percent. For lower molalities, the heat liberated would have decreased, thus magnifying the relative error. Therefore, the heat of dilution at $0.001 \text{ mol} \cdot \text{kg}^{-1}$ was about the limit that this could be measured using the then existing instrumentation.

The temperature sensitivity of the less sensitive calorimeter was about $20 \mu\text{K}$, which corresponded to a sensitivity in the heat measurement of 15 mcal. Thus, for the enthalpy of

dilution of HCl at about $0.02 \text{ mol} \cdot \text{kg}^{-1}$, where the heat liberated was about 60 mcal, the corresponding uncertainty is about 25 percent. However, the heat liberated for the enthalpy of dilution of sulfuric acid in the same molality range was about fifty times larger and the corresponding uncertainty was less than 1 percent.

3. Results and Calculation

The method of treating the data is essentially the same as described previously [10]. The molalities of the initial and final solutions are, respectively, m_1 and m_2 . The heat absorbed is Q , and Q divided by the number of moles contained in the solution is the enthalpy of dilution from m_1 to m_2 , $\Delta \Phi_L / \Delta m^{1/2}$. The derivative of Φ_L with respect to $m^{1/2}$ is S , which can be obtained from a "chord-area" plot [15, 16]. The experimental data are given in tables 1, 2 and 3 and in figures 1 and 2, where, for sulfuric acid, we also show the data of Groenier [7], of Lange *et al.* [5], and of Giauque *et al.* [6]. In order to calculate Φ_L at a given molality using the relationship

$$\Phi_L = \int_0^m \frac{d\Phi_L}{dm^{1/2}} dm^{1/2}, \quad (1)$$

it is necessary to provide some form of extrapolation to zero molality to aid in the integration of the chord-area plot. For HCl and LiCl, we have used the Debye-Huckel limiting law (DHLL) value of S° of $477 \text{ cal} \cdot \text{mol}^{-1/2} \cdot \text{kg}^{1/2}$ [16].

For H_2SO_4 the situation is more complex and warrants additional discussion. From Debye-Huckel theory, S° for a 2-1 electrolyte is $2480 \text{ cal} \cdot \text{mol}^{-3/2} \cdot \text{kg}^{1/2}$ [2]. In order to join this value with the experimental data in figure 1a, we consider one mole of H_2SO_4 to be a mixture of α moles of $\text{H} \cdot \text{H} \cdot \text{SO}_4$ and $(1-\alpha)$ moles of $\text{H} \cdot \text{HSO}_4$, where the dot between the symbols indicates the dissociation which has occurred. The relative apparent molal enthalpy of sulfuric acid will be

$$\Phi_L(\text{H}_2\text{SO}_4) = \alpha \Phi_L(\text{H} \cdot \text{H} \cdot \text{SO}_4) + (1-\alpha) \Phi_L(\text{H} \cdot \text{HSO}_4) + (1-\alpha) \Delta H_{\text{Diss}}^\circ + \Delta_m H \quad (2)$$

α has been evaluated by Young and Blatz [2] from Raman spectral data; we have taken the enthalpy of dissociation of bisulfate ion at infinite dilution ($\Delta H_{\text{Diss}}^\circ$) as $5200 \text{ cal} \cdot \text{mol}^{-1}$ [1]; we have estimated Φ_L for $(\text{H} \cdot \text{H} \cdot \text{SO}_4)$ from the Φ_L data for Li_2SO_4 [1]; we have used an average Φ_L for HCl and LiCl obtained in this investigation (see tables 6 and 7 and reference [17]) in estimating a value of Φ_L for $(\text{H} \cdot \text{HSO}_4)$; and we have taken the enthalpy of mixing of the ions ($\Delta_m H$) to be zero [10]. The results of our semi-theoretical calculations for Φ_L and S for H_2SO_4 are shown in table 4; the theoretical

³ Certain commercial materials are identified in this paper in order to adequately specify the experimental procedures. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.

TABLE 1. *Experimental dilution enthalpies for aqueous H₂SO₄ at 25 °C.*

$m_1^{1/2}$ mol ^{1/2} ·kg ^{-1/2}	$m_2^{1/2}$ mol ^{1/2} ·kg ^{-1/2}	ΔH_{Dil} cal·mol ⁻¹	$\frac{\Delta H_{Dil}}{\Delta m^{1/2}}$ cal·mol ^{-3/2} ·kg ^{1/2}
0.031705	0.030134	-52.85	33649
.033214	.031637 ^a	-50.71	32170
.040484	.038529	-66.61	34074
.041051	.039057	-65.49	32841
.056369	.053568	-83.86	29932
.056548	.053796	-78.62	28559
.095864	.091232	-93.33	20150
.100000	.095259	-93.38	19698
.21840	.20680	-83.67	7207.5
.25180 ^a	.23839	-77.97	5814.8
.25180	.23875	-73.08	5602.5
.37394	.35398	-61.78	3094.8
.37900	.35948	-58.88	3017.3
.37900	.35989	-57.97	3035.0
.38659	.36672	-57.35	2886.1
.42253	.40030	-53.42	2403.3
.42253	.40145	-50.40	2390.4
.47311	.44907	-48.02	1997.7
.47311	.44985	-45.78	1967.9
.50564	.48041	-44.78	1774.5
.62997	.59868	-35.60	1137.9
.71542	.68034	-31.73	904.7
1.0934	1.0328	-35.26	581.6
1.0934	1.0349	-34.04	581.8
2.5344	2.3640	-352.88	2071.6

^a Numbers followed by an (a) indicate corrections for typographical errors in the thesis [18].

TABLE 2. *Experimental dilution enthalpies for aqueous HCl at 25 °C.*

$m_1^{1/2}$ mol ^{1/2} ·kg ^{-1/2}	$m_2^{1/2}$ mol ^{1/2} ·kg ^{-1/2}	ΔH_{Dil} cal·mol ⁻¹	$\frac{\Delta H_{Dil}}{\Delta m^{1/2}}$ cal·mol ^{-3/2} ·kg ^{1/2}
0.14135	0.13470	-2.980	448.6
.14452	.13726	-2.840	390.8
.14686	.13960	-3.529	485.6
.20265	.19297	-4.000	412.9
.33828	.32164	-6.437	386.9
.39926	.37870	-8.089	393.4
.39926	.37920	-8.597	428.7 ^a
.49188	.46675	-9.347	371.9
.50776	.48089	-10.338	384.6
.55953	.53240	-10.242	377.4
.56746	.53842	-11.280	388.3
.82167	.77934	-17.686	417.8
.82167	.78062	-17.452	425.1
.88163	.83422	-20.258	427.2
1.2592	1.1978	-33.786	549.5
1.2592	1.1953	-34.469	539.3

^a This point was taken to be an outlier and was given zero weight in the construction of the chord area plot.

curve is the solid curve from zero to 0.30 mol^{1/2}·kg^{-1/2} shown in figure 1a. Since this semi-theoretical curve, based upon the above auxiliary information and assumptions, is seen to be in good agreement with the experimental data from 0.04 to 0.30 mol^{1/2}·kg^{-1/2}, we feel reasonably confident in relying upon it in the low molality region to perform the integration of the chord-area plot in obtaining Φ_L values for H₂SO₄.

TABLE 3. *Experimental dilution enthalpies for aqueous LiCl at 25 °C.*

$m_1^{1/2}$ mol ^{1/2} ·kg ^{-1/2}	$m_2^{1/2}$ mol ^{1/2} ·kg ^{-1/2}	ΔH_{Dil} cal·mol ⁻¹	$\frac{\Delta H_{Dil}}{\Delta m^{1/2}}$ cal·mol ^{-3/2} ·kg ^{1/2}
0.50658	0.16218 ^a	-112.95	327.96
.53508	.50658	-8.310	291.57
.80307	.75627	-12.764	272.75
1.0000	.94600	-15.745	291.57
1.2898	1.2165	-16.237	358.04
1.3381	1.2568	-28.573	351.62
1.4394	1.3475	-34.947	380.31
1.9716	1.8614	-64.330	583.81
2.5982	2.4359	-148.75	916.59 ^b

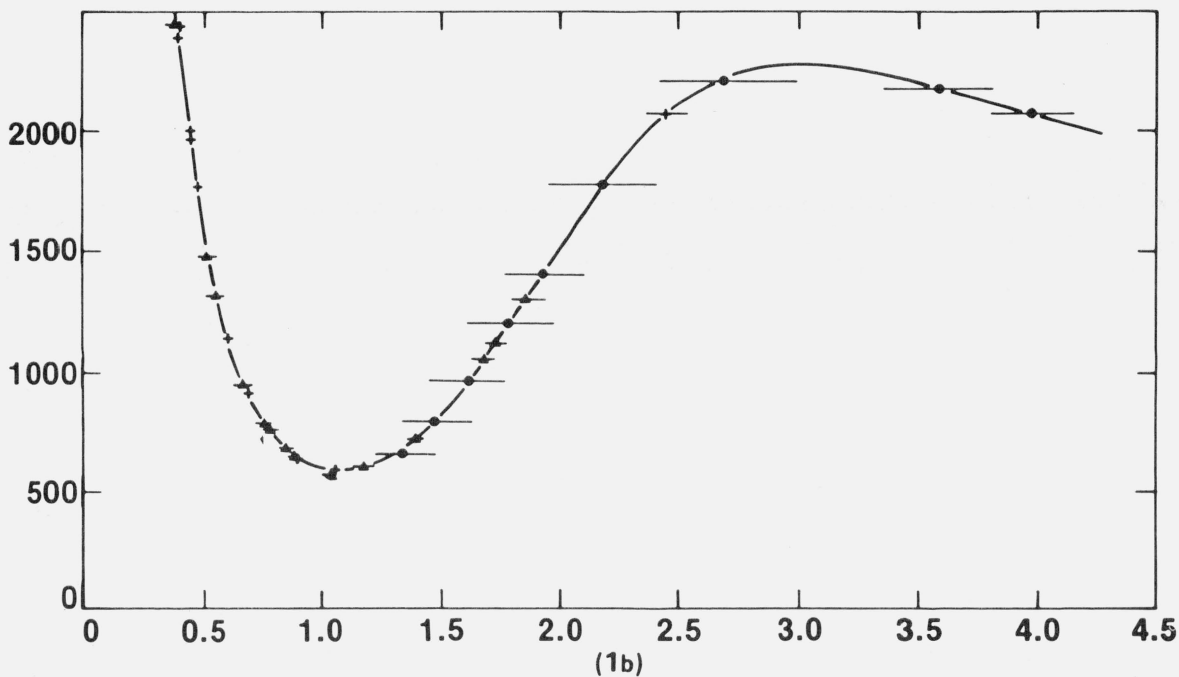
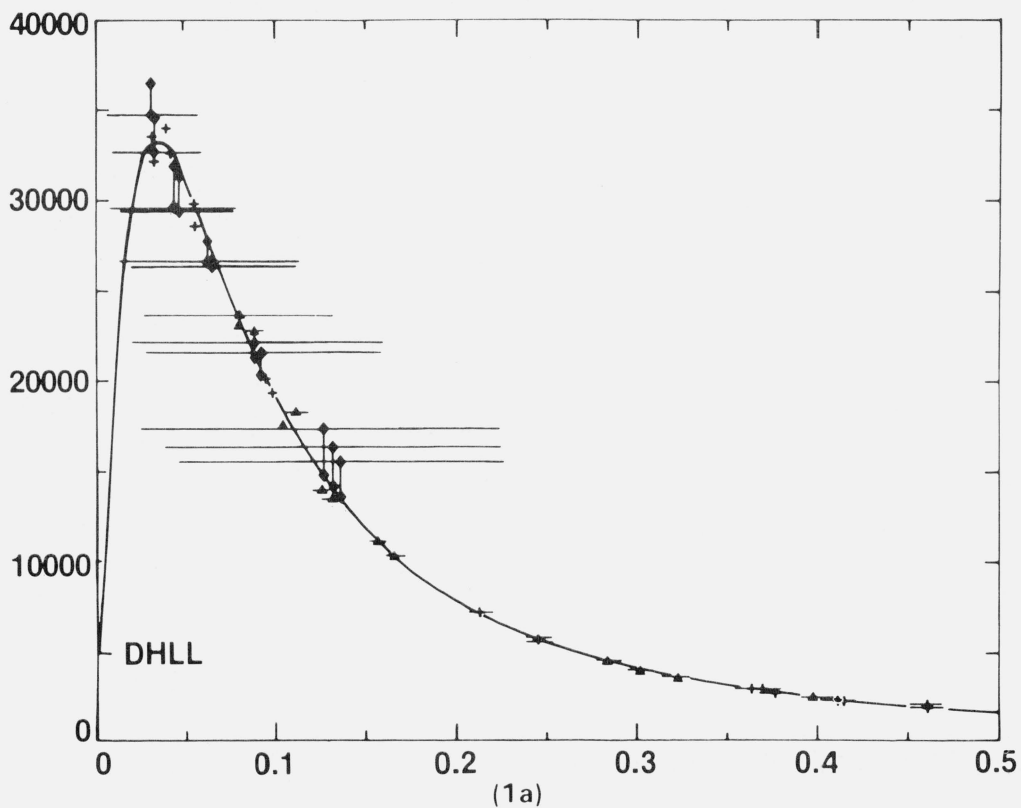
^a Typographical error in the thesis [18].

^b This point is not shown in figure 2.

TABLE 4. *Calculated values of Φ_L and S for H₂SO₄ at 25 °C.*

$I_m^{1/2}$ ^a mol ^{1/2} ·kg ^{-1/2}	$m^{1/2}$ mol ^{1/2} ·kg ^{-1/2}	Φ_L cal·mol ⁻¹	S cal·mol ^{-3/2} ·kg ^{1/2}
0.00	0.00000	0	2480
.01	.005785	46.68	12953
.02	.011639	150.48	21783
.04	.023754	481.42	31254
.06	.036638	903.65	33298
.08	.050421	1350.71	33183
.10	.065126	1782.05	27437
.12	.080702	2177.65	23425
.14	.097064	2529.63	19725
.16	.114108	2837.89	16561
.18	.131743	3105.71	13943
.20	.149845	3337.80	11781
.22	.168356	2539.05	10031
.24	.18720	3714.08	8604.8
.26	.20630	3866.97	7454.2
.28	.22563	4001.22	6484.0
.30	.24513	4119.73	5691.9
.32	.26478	4225.00	5038.8
.34	.28455	4319.00	4490.1
.36	.30441	4403.45	4028.6
.38	.32436	4479.47	3634.4
.40	.34437	4549.00	—

^a The values of the ionic strength given in column one were calculated using the relationship $I_m = \frac{1}{2} \sum m_i Z_i^2$, where the summation is over the ions H⁺, HSO₄⁻, and SO₄²⁻, i.e. cognizance is taken of the incomplete dissociation of the bisulfate ion. Thus, $I = (1 + 2\alpha)m$.



FIGURES 1a and 1b. Plots of S ($\text{cal} \cdot \text{mol}^{-3/2} \cdot \text{kg}^{1/2}$) as a function of $m^{1/2}$ ($\text{mol}^{1/2} \cdot \text{kg}^{-1/2}$) for aqueous H_2SO_4 at 25°C .

+ indicates the experimental data of this investigation, ▲ indicates the results of Groenier [7], ◆ indicates the results of Lange, Monheim, and Robinson [5] and ● indicates the results of Giaque *et al.* [6]. The solid curve from zero to $0.3 \text{ mol}^{1/2} \cdot \text{kg}^{-1/2}$ was calculated semi-theoretically using equation 2 and the rest of the curve was drawn in accordance with the chord-area principle [15, 16]. For each of the long-chords there are two points: one indicates the center of the chord and the other is corrected for curvature [16], i.e. the true derivative ($d\Phi_i/dm^{1/2}$ is not equal to $\Delta\Phi_i/\Delta m^{1/2}$) should pass through each chord such that the two areas enclosed between the curve, the chord, and vertical lines drawn through the ends of the chord are equal. Note that the ordinate scales for figure 1a and 1b differ by a factor of about 12; the contraction or expansion of those curves is apparent.

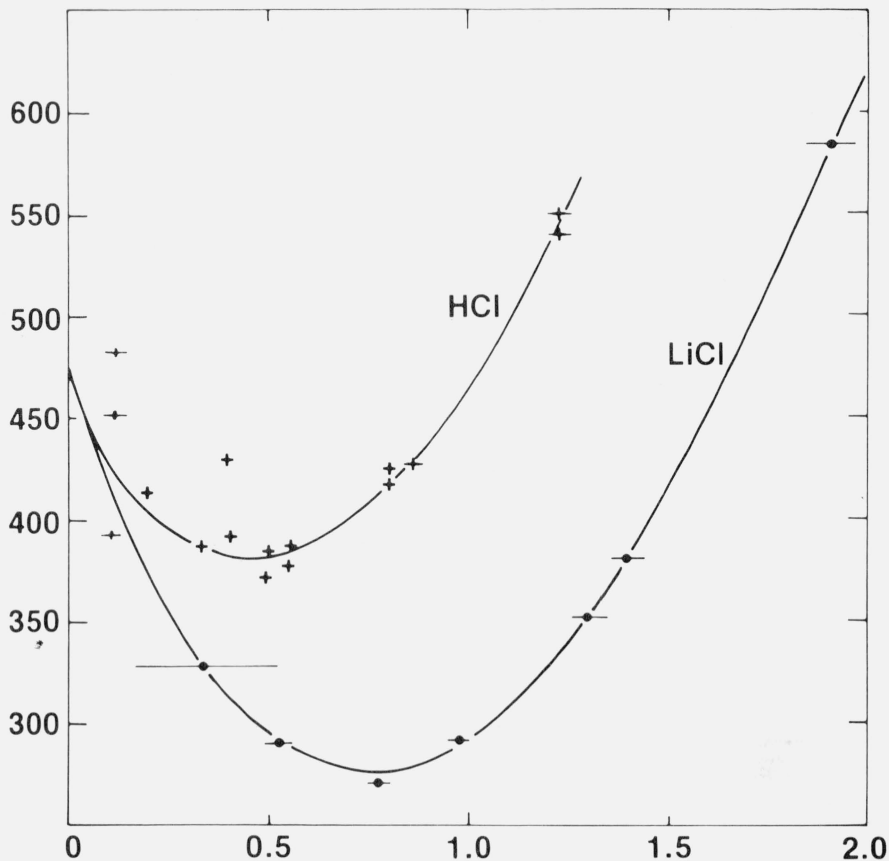


FIGURE 2. Plots of S ($\text{cal mol}^{-3/2} \cdot \text{kg}^{1/2}$) as a function of $m^{1/2}$ ($\text{mol}^{1/2} \cdot \text{kg}^{-1/2}$) for aqueous HCl and LiCl at 25 °C. The data for HCl are indicated by +, while that for LiCl are indicated by ●.

Tables 5, 6 and 7 give values of Φ_L for aqueous H_2SO_4 , LiCl , and HCl calculated using eq (1) and values of \bar{L}_1 and \bar{L}_2 calculated using the relationships:

$$\bar{L}_1 = -\frac{M_1 m^{3/2} S}{2000} \quad (3)$$

and

$$\bar{L}_2 = \Phi_L + 1/2 m^{1/2} S \quad (4)$$

It is interesting to note that our values of Φ_L for aqueous HCl compare very well with those "best values" compiled by Parker [17]. Our corresponding values for LiCl are somewhat higher than those given by Parker; the discrepancy has been discussed by Wu and Friedman [19].

4. Glossary

H = enthalpy or heat content

I_m = ionic strength on the molality scale: $I_m = \frac{1}{2} \sum m_i Z_i^2$

\bar{L}_i = relative partial molal enthalpy of i th component

m = molality

M_1 = molecular weight of the solvent ($18.015 \text{ g} \cdot \text{mol}^{-1}$)

Q = heat

$S = d\Phi_L/dm^{1/2}$

Z_i = charge of an ion i

α = degree of dissociation

Φ_L = relative apparent molal enthalpy

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TABLE 5. Values of Φ_L , \bar{L}_1 , and \bar{L}_2 for aqueous H_2SO_4 at 25°C

$m^{1/2}$	Φ_L	I_2	\bar{L}_2
$\text{mol}^{1/2} \cdot \text{kg}^{-1/2}$	$\text{cal} \cdot \text{mol}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$
0.005	40	69.5	-0.00001
.01	120	215.5	-0.0017
.02	370	663.0	-0.0021
.03	680	1173.5	-0.0080
.04	1015	1676.0	-0.0190
.05	1340	2120.0	-0.0351
.06	1640	2498	-0.0557
.07	1910	2822	-0.0805
.08	2160	3104	-0.1088
.09	2380	3336	-0.1395
.10	2585	3540	-0.1721
.12	2935	3874	-0.2436
.14	3220	4120	-0.3176
.16	3450	4310	-0.3966
.18	3650	4469	-0.4781
.20	3820	4605	-0.5657
.22	3965	4708	-0.6475
.24	4090	4800	-0.7366
.26	4200	4879	-0.8265
.28	4300	4850	-0.9180
.30	4370	4990	-1.0004
.35	4550	5100	-1.214
.40	4690	5184	-1.424
.45	4801	5250	-1.535
.50	4892	5303	-1.852
.55	4969	5345	-2.060
.60	5031	5382	-2.276
.65	5086	5415	-2.499
.70	5133	5446	-2.766
.75	5175	5475	-3.040
.80	5214	5506	-3.367
.85	5249	5547	-3.756
.90	5282	5566	-4.149
.95	5312	5598	-4.650
1.00	5342	5634	-5.262
1.10	5400	5719	-6.954
1.20	5460	5822	-9.401
1.30	5522	5942	-12.79
1.40	5589	6086	-17.55
1.50	5665	6273	-24.63
1.60	5752	6500	-34.50
1.70	5852	6762	-47.36
1.80	5967	7056	-63.56
1.90	6095	7377	-83.41
2.00	6237	7737	-108.1
2.20	6567	8536	-171.7
2.40	6958	9366	-250.9
2.60	7368	10196	-344.4
3.00	8267	11695	-555.6

TABLE 6. Values of Φ_L , \bar{L}_1 , and \bar{L}_2 for aqueous HCl at 25°C.

$m^{1/2}$	Φ_L	\bar{L}_1	\bar{L}_2
$\text{mol}^{1/2} \cdot \text{kg}^{-1/2}$	$\text{cal} \cdot \text{mol}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$
0.1	45.53	67.01	-0.0039
.2	87.30	127.9	-.0292
.3	127.1	185.6	-.0949
.4	165.7	242.2	-.2201
.5	203.8	299.1	-.4290
.6	242.3	353.6	-.7545
.7	281.7	422.0	-1.238
.8	322.6	489.6	-1.925
.9	365.4	562.6	-2.877
1.0	410.6	643.0	-4.187
1.1	458.6	732.1	-5.961
1.2	510.3	831.5	-8.334

TABLE 7. Values of Φ_L , \bar{L}_1 , and \bar{L}_2 for aqueous $LiCl$ at 25°C.

$m^{1/2a}$	Φ_L	\bar{L}_1	\bar{L}_2
$\text{mol}^{1/2} \cdot \text{kg}^{-1/2}$	$\text{cal} \cdot \text{mol}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$
0.1	44.80	65.75	-0.00377
.2	84.37	121.6	-.02684
.3	119.9	162.6	-.08216
.4	152.4	214.9	-.1801
.5	182.7	256.4	-.3317
.6	211.6	296.5	-.5506
.7	239.6	336.4	-.8546
.8	267.2	377.4	-1.2710
.9	295.0	421.5	-1.845
1.0	323.7	469.7	-2.630
1.1	353.6	522.5	-3.681
1.2	385.3	581.5	-5.090
1.3	419.3	648.4	-6.974
1.4	456.1	723.9	-9.457
1.5	496.0	808.8	-12.667
1.6	539.7	904.3	-16.817
1.7	587.3	1009.8	-21.995
1.8	639.1	1123.5	-28.274
1.9	695.0	1246.6	-35.872
2.0	755.2	1378.6	-44.924

^a We note that while the experimental data extend to 2.6 $\text{mol}^{1/2} \cdot \text{kg}^{-1/2}$, we have chosen to terminate this table at 2.0 $\text{mol}^{1/2} \cdot \text{kg}^{-1/2}$ rather than rely on only one measurement at 2.6 $\text{mol}^{1/2} \cdot \text{kg}^{-1/2}$.

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