Table IV: Concentration ($\times 10^3$, equiv/l.) of $LaSO_4^+$ in Aqueous $La_2(SO_4)_3$ at 25°

P, atm		mequiv/l. of $La_2(SO_4)_3$					
	0.2	0.3	0.6	1.2	2.4	3.1	8.2
1 *a*	0.015	0.031	0.088	0.22	0.54	0.72	2.3
1 *b*	0.015	0.030	0.086	0.22	0.53	0.70	2.2
1 *c*	0.015	0.030	0.085	0.21	0.52	0.69	2.2
500	0.011	0.025	0.073	0.19	0.48	0.65	2.1
	0.011	0.024	0.070	0.18	0.47	0.63	2.1
	0.011	0.023	0.069	0.18	0.46	0.61	2.0
1000	0.009	0.020	0.061	0.17	0.43	0.59	2.0
	0.008	0.019	0.058	0.16	0.41	0.56	1.9
	0.008	0.018	0.057	0.15	0.40	0.54	1.8
1500	0.007	0.016	0.052	0.15	0.40	0.54	1.9
	0.007	0.015	0.049	0.14	0.37	0.50	1.7
	0.007	0.015	0.048	0.13	0.36	0.48	1.6
2000	0.006	0.014	0.045	0.13	0.36	0.49	1.8
	0.006	0.013	0.041	0.12	0.33	0.45	1.6
	0.006	0.012	0.040	0.12	0.32	0.43	1.5

[a] Data obtained using the Davies–Otter–Prue conductance equation with $\mathring{a}$ calculated from Bjerrum's equation, $\mathring{a} = |Z_1Z_2|e^2/2\epsilon KT$. [b] Data obtained using the Davies–Otter–Prue conductance equation, but with $\mathring{a}$ = 5 A for the 3–2 case and $\mathring{a}$ = 3.6 A for the 2–1 case. [c] Data obtained using the basic Onsager conductance equation.

Table V: Dissociation Constant K_m ($\times 10^4$) for Aqueous $La_2(SO_4)_3$ at 25°

P, atm		mequiv/l. of $La_2(SO_4)_3$					
	0.2	0.3	0.6	1.2	2.4	3.1	8.2
1 *a*	2.4	2.1	2.0	2.0	2.0	2.0	1.9
1 *b*	2.4	2.1	2.0	1.9	1.8	1.8	1.6
1 *c*	2.4	2.2	2.1	2.0	1.9	1.9	1.8
500	3.6	3.2	3.1	3.1	3.0	3.1	3.1
	3.7	3.2	3.1	3.0	2.8	2.8	2.6
	3.8	3.3	3.2	3.1	3.0	3.0	2.9
1000	5.2	4.6	4.4	4.3	4.3	4.5	4.6
	5.4	4.7	4.4	4.3	4.1	4.1	3.8
	5.6	4.8	4.6	4.5	4.3	4.5	4.5
1500	6.5	5.9	5.7	5.6	5.6	5.9	6.2
	6.9	6.1	5.8	5.6	5.4	5.5	5.2
	7.1	6.4	6.0	5.9	5.8	6.0	6.3
2000	8.0	7.6	7.3	7.2	7.2	7.5	8.0
	8.6	8.0	7.6	7.2	7.0	7.2	6.9
	8.9	8.4	8.0	7.7	7.6	8.0	8.4

[a] See footnote *a* of Table IV. [b] See footnote *b* of Table IV. [c] See footnote *c* of Table IV.

Table VI: $-\Delta V°$ (ml/mole) for Aqueous $La_2(SO_4)_3$ at 25°

P, atm				mequiv/l.			
	0.2	0.3	0.6	1.2	2.4	3.1	8.2
1 *a*	22.9	21.6	21.2	21.5	22.7	22.6	25.3
1 *b*	23.7	22.2	21.7	22.0	23.1	23.0	25.2
1 *c*	24.0	22.4	22.0	22.4	23.6	23.6	26.2
500	18.9	18.5	18.3	18.4	19.2	19.3	21.3
	19.6	19.2	18.9	19.0	19.7	19.8	21.5
	19.9	19.5	19.2	19.4	20.3	20.4	22.6
1000	14.9	15.5	15.4	15.3	15.7	16.0	17.3
	15.6	16.2	16.1	15.9	16.3	16.6	17.8
	15.8	16.5	16.5	16.4	16.9	17.3	19.0
1500	10.8	12.5	12.6	12.2	12.2	12.6	13.4
	11.5	13.2	13.3	12.9	12.9	13.4	14.1
	11.8	13.5	13.7	13.4	13.5	14.1	15.4
2000	6.8	9.4	9.7	9.1	8.7	9.3	9.4
	7.4	10.2	10.5	9.9	9.5	10.2	10.4
	7.7	10.5	10.9	10.4	10.1	10.9	11.8

[a] See footnote *a* of Table IV. [b] See footnote *b* of Table IV. [c] See footnote *c* of Table IV.

Table VII: Equivalent Conductivities at Infinite Dilution as a Function of Pressure

P, atm	$La_2(SO_4)_3$	La^{3+}	SO_4^{2-}	$LaSO_4^-$
1	149.5	69.5	80.0	23.2
250	150.4	69.8	80.6	23.3
500	150.6	69.4	81.2	23.1
750	150.6	69.2	81.4	23.1
1000	150.0	68.6	81.4	22.9
1250	149.6	68.2	81.4	22.7
1500	148.9	67.4	81.5	22.5
1750	147.5	66.3	81.2	22.1
2000	146.3	65.4	80.9	21.8

$\Lambda°_{LaSO_4^+}$ of 23.2 is used rather than the value of 40.0 proposed by Spedding and Jaffe[6] because this value yielded values of K_m which showed less concentration dependence. The pressure dependence of the $LaSO_4^+$ ion was taken to be the same as for $\Lambda_p°$ for $La_2(SO_4)_3$.

Results for pressure dependence of equivalent conductance at infinite dilution are shown in Table VII. The original data for $La_2(SO_4)_3$ solution are shown in Table VIII.

Discussion

It is seen from Table V that regardless which method is used, K_m at atmospheric pressure approaches values in the neighborhood of 2.4×10^{-4} at low concentration, in agreement with the results of Spedding and Jaffe.[6] The Davies–Otter–Prue equation used with the Bjerrum distances appears to give K values slightly less concentration dependent than for the other methods.

Table VIII: Copy of Original Conductivity Data for Aqueous Solutions of $La_2(SO_4)_3$ at 25°; Teflon Cell with Pyrex Bar between Electrodes: Cell Constant 0.457, Measured at 0.02 *M* KCl

P, atm	10^3 equiv/l. of $La_2(SO_4)_3$: 0.2046	0.3072	0.6144	1.206	2.412	3.072	8.190	H_2O
	Conductivity in μmhos							
1	53.88	76.31	131.2	217.1	361.2	433.4	880.7	2.31
250	56.73	80.81	140.3	233.9	391.6	470.8	960.0	2.70
500	59.16	84.69	148.4	248.9	419.5	505.1	1033.5	3.11
750	61.22	88.08	155.3	262.2	444.6	536.7	1103.8	3.59
1000	63.01	90.87	161.1	274.1	467.6	565.3	1171.0	4.09
1250	64.53	93.35	166.4	284.5	488.1	590.9	1229.8	4.64
1500	65.85	95.45	170.7	293.2	505.7	613.5	1284.5	5.26
1750	66.94	97.18	174.4	300.8	521.2	633.5	1332.3	5.88
2000	67.85	98.73	177.6	307.2	534.7	650.9	1376.8	6.52
1[a]	54.11	76.42	131.4	217.1	361.3	433.8	883.8	2.59

[a] Readings taken the day after the pressure run.

At atmospheric pressure there is at most only a 5% difference in the $\Delta V°$ values obtained by the three methods. At the highest pressures and highest concentration the largest difference in the $\Delta V°$ values occur.

The atmospheric pressure values of $\Delta V°$ are of the same order as observed for NH_4OH[11] and organic solutions[12] and very close to the value of -23.4 ml/mole calculated by Owen and Brinkley[2a] for water. It is not known if a possible multistate configuration[13,14] exists similar to that of $MgSO_4$ or $MnSO_4$ or if there exists only one form of the $(LaSO_4)^+$ ion pair. There is some indication that the rare earth sulfates show large ultrasonic absorption[15] but until detailed experimental results are available, it is not possible to make an interpretation incorporating acoustic data.

Based on values of partial molal volume assigned by Owen and Brinkley[2a] to La^{3+} of -38.3 ml/mole and SO_4^{2-} of $+14.5$, the partial molal volume of the $(LaSO_4)^+$ ion pair at atmospheric pressure and at the lowest concentration varies from -0.9 to $+0.2$ ml/mole depending upon the method used to calculate theoretical values of equivalent conductance.

(11) S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press, New York, N. Y., 1957, p 151.

(12) A. Disteche and S. Disteche, *J. Electrochem. Soc.*, **112**, 350 (1965).

(13) F. H. Fisher, *J. Phys. Chem.*, **69**, 695 (1965).

(14) G. Atkinson and S. K. Kor, *ibid.*, **69**, 128 (1965).

(15) G. Atkinson, private communication.