

racy¹² of the values reported for these constants is of the same order of magnitude as the precision.

It is of interest to note that the slope $d \log K_1/$

(12) The accuracy of the determination of K_1 and Δ_0 , of course, depends on the function chosen for the final plot. This was discussed by Saxton and Darken² who pointed out that the plot of $\log K$ versus the concentration of undissociated acid seemed most suitable for extrapolation, where the activity coefficients included in K_1 are obtained from the formula $\log \gamma_1 = 0.5063 C_1^{1/2}$. The data on the acids considered in that paper seemed to indicate that the use of a denominator term in the above expression was undesirable. However, as oxalic acid is a stronger acid than any of those previously considered, it was thought that though the denominator term is negligibly small for the weaker acids it may not be so for oxalic. Hence the same method was applied using the expression $\log \gamma_1 = 0.5063 C_1^{1/2}/(1 + 0.200 C_1^{1/2})$. It was found that the omission of the denominator term from the Debye-Hückel expression results in no significant change in K_1 or Δ_0 but yields a limiting value of K_1 which is about 0.5% lower than if the denominator term is used. If $\log K_1$ be plotted against the total concentration instead of the concentration of undissociated acid, K_1 will be found about 1.5% higher (Δ_0 is found to be 0.5 conductance unit lower).

$d C_u = -0.45$ is in good agreement with the relationship found by Saxton and Darken² between the values of this slope and the molecular weights of monobasic acids. (The predicted value would be about -0.38 .)

Summary

The conductance method has been adapted to the determination of the ionization constants of oxalic acid. Application of this modified method to conductance data on oxalic acid and sodium oxalate in aqueous solution at 25° leads to the values $K_1 = 5.36_0 \times 10^{-2}$ and $K_2 = 5.3 \times 10^{-5}$. The limiting equivalent conductance of sodium oxalate was found to be 124.25 and that corresponding to the primary ionization of oxalic acid was found to be 390.0.

RECEIVED SEPTEMBER 17, 1940

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, AND THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE, NEW ZEALAND]

The Activity Coefficients of Lithium, Sodium and Potassium Sulfate and Sodium Thiosulfate at 25° from Isopiestic Vapor Pressure Measurements

BY R. A. ROBINSON,¹ JEAN M. WILSON AND R. H. STOKES

The activity coefficients of lithium, sodium and potassium sulfate have been determined at 25° by Åkerlöf² from measurements on cells with amalgam electrodes and in the case of sodium sulfate Harned and Hecker³ have extended the measurements over the temperature range 0 to 40°. We have now made measurements on these three alkali metal sulfates at 25° by the isopiestic vapor pressure method,⁴ extending the concentration range to 3 *M* for lithium sulfate and to 4 *M* for the sodium salt. In addition, we have made measurements on sodium thiosulfate up to 3.5 *M* which lead to the first determination of the activity coefficient of this salt.

The four salts were recrystallized several times from water and their purity checked by analysis. Solutions of each of the salts were brought into equilibrium with solutions of potassium chloride by the isopiestic method with the results given in Table I. Platinum dishes were used to contain the thiosulfate solutions.

(1) Sterling Fellow, Yale University, 1940.

(2) G. Åkerlöf, THIS JOURNAL, **48**, 1160 (1926); H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

(3) H. S. Harned and J. C. Hecker, THIS JOURNAL, **56**, 650 (1934).

(4) R. A. Robinson and D. A. Sinclair, *ibid.*, **56**, 1830 (1934).

TABLE I

MOLALITIES OF SOLUTIONS OF LITHIUM, SODIUM AND POTASSIUM SULFATE AND SODIUM THIOSULFATE, ISOPIESTIC WITH SOLUTIONS OF POTASSIUM CHLORIDE AT 25°

Lithium Sulfate					
<i>m</i> KCl	<i>m</i> Li ₂ SO ₄	<i>m</i> KCl	<i>m</i> Li ₂ SO ₄	<i>m</i> KCl	<i>m</i> Li ₂ SO ₄
0.09835	0.07310	1.114	0.8549	3.246	2.282
.1155	.08635	1.241	.9472	3.423	2.382
.1561	.1178	1.360	1.034	3.642	2.504
.1819	.1381	1.677	1.259	3.751	2.572
.3161	.2424	1.894	1.409	3.821	2.612
.3556	.2733	1.990	1.475	4.131	2.786
.5195	.4006	2.295	1.676	4.580	3.037
.5487	.4235	2.473	1.799	4.671	3.080
.7407	.5728	2.543	1.841	4.810	3.158
.8420	.6497	2.880	2.052	4.810	3.165
		3.107	2.194		
Sodium Sulfate					
	<i>m</i> Na ₂ SO ₄	<i>m</i> Na ₂ SO ₄	<i>m</i> Na ₂ SO ₄	<i>m</i> Na ₂ SO ₄	<i>m</i> Na ₂ SO ₄
0.1270	0.09830	1.031	0.9600	1.821	1.778
.1705	.1345	1.339	1.273	2.221	2.178
.1800	.1419	1.385	1.325	2.497	2.429
.3820	.3186	1.391	1.335	2.527	2.456
.5836	.5081	1.571	1.514	3.097	2.945
.6772	.5930	1.641	1.594	3.577	3.334
.8270	.7460	1.765	1.725	4.220	3.784
.9472	.8690			4.810	4.185

TABLE I (Concluded)

Potassium Sulfate					
m_{KCl}	$m_{K_2SO_4}$	m_{KCl}	$m_{K_2SO_4}$	m_{KCl}	$m_{K_2SO_4}$
0.1215	0.09575	0.2899	0.2384	0.4801	0.4119
.1626	.1293	.2925	.2404	.4981	.4267
.1806	.1461	.3680	.3076	.5701	.4941
.2240	.1817	.3784	.3168	.5768	.4998
.2281	.1852	.4502	.3838	.6586	.5776
.2513	.2055	.4614	.3937	.7050	.6222
.2791	.2306	.4686	.3999	.7740	.6898

Sodium Thiosulfate					
$m_{Na_2S_2O_3}$	$m_{Na_2S_2O_3}$	$m_{Na_2S_2O_3}$	$m_{Na_2S_2O_3}$	$m_{Na_2S_2O_3}$	$m_{Na_2S_2O_3}$
0.1010	0.0771	1.308	1.109	2.597	2.136
.2037	.1579	1.314	1.112	2.937	2.382
.2998	.2365	1.697	1.436	3.116	2.501
.3370	.2668	1.783	1.507	3.200	2.564
.4482	.3610	1.980	1.659	3.246	2.585
.5676	.4613	2.019	1.688	3.511	2.766
.8800	.7345	2.318	1.932	4.003	3.073
1.092	.9198	2.501	2.066	4.362	3.285
1.260	1.065	2.549	2.102	4.810	3.541

From the data in Table I, osmotic and activity coefficients were calculated for the four salts. These coefficients are recorded in Table II

in the columns entitled V. P. The activity coefficients of sodium sulfate were referred to the value of $\gamma = 0.445$ at 0.1 M , the value which Harned and Hecker³ obtained by fitting an extended Debye-Hückel equation to their data at 0.05, 0.1 and 0.5 M . Their data up to 1 M are also given in Table II for purpose of comparison. The average difference between the two sets of activity coefficients is 0.4% with a maximum difference of 1% at 1 M .

In order to obtain a reference value for sodium thiosulfate at 0.1 M , a curve of the isopiestic ratio of sodium sulfate to sodium thiosulfate against the molality of the latter was constructed from the isopiestic data for each of these salts relative to potassium chloride. By using sodium sulfate as a subsidiary standard, a plot was obtained which could be extrapolated with reasonable assurance to an isopiestic ratio of unity at infinite dilution. This procedure gave $\gamma = 0.455$ at 0.1 M sodium thiosulfate. In the same way a value of $\gamma = 0.468$ was obtained at 0.1 M lithium

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF LITHIUM, SODIUM AND POTASSIUM SULFATE AND SODIUM THIOSULFATE AT 25°

m	Li_2SO_4			Na_2SO_4			$Na_2S_2O_3$	
	ϕ	γ	γ	ϕ	γ	γ	ϕ	γ
	V. P.	V. P.	(Åkerlöf)	V. P.	V. P.	(Harned and Hecker)	V. P.	V. P.
0.1	0.815	0.468	(0.468)	0.792	(0.445)	0.445	0.802	0.455
.2	.792	.399	.398	.754	.365	.365	.774	.382
.3	.782	.362726	.320	.322	.755	.340
.4	.777	.3385708	.2895	.290	.742	.313
.5	.775	.3215	.323	.693	.267	.268	.733	.292
.6	.776	.3085681	.249726	.276
.7	.778	.299671	.234	.234	.720	.263
.8	.781	.291661	.222	.223	.716	.252
.9	.786	.285653	.2115	.213	.713	.243
1.0	.791	.2805	.276	.646	.202	.204	.712	.236
1.5	.825	.2685	.272	.626	.171720	.212
2.0	.872	.269	.267	.624	.153744	.200
2.5	.926	.2775638	.143782	.197
3.0	.988	.293665	.138833	.201
3.5700	.136896	.209
4.0743	.137	...		

K_2SO_4			
m	ϕ	γ	γ
	V. P.	V. P.	(F. Pt.)
0.1	0.779	(0.441)	...
.125416	(0.416)
.2	.745	.361	...
.25337	.331
.3	.721	.317	...
.4	.704	.287	...
.5	.690	.264	.265
.6	.680	.247	...
.625243	.243
.7	.671	.233	...

^a At 0.402 M .

sulfate. The values for the latter salt are compared with those of Åkerlöf in Table II, the same reference value being used at 0.1 *M*. The average difference between the two sets is 0.9% with a maximum difference of 1.6% at 1 *M* but there is no trend of the results away from one another.

A value of $\gamma = 0.441$ for 0.1 *M* potassium sulfate was taken from the computations of Redlich and Rosenfeld⁵ who corrected freezing point data to 25°. The comparison with freezing point data at two other concentrations is good. The agreement with the e. m. f. data of Åkerlöf is also good except at one concentration, the average difference between the two sets of activity coefficients being 0.7%.

The activity coefficient curves of these four salts lie below that of calcium nitrate⁶ and correspond to values of the closest distance of approach of the ions of approximately 3–4 Å. Thus considerable ionic association should occur and conductance data⁷ show that the extent of association

(5) Landolt-Börnstein, "Tabellen," Zweiter Ergänzungsband, 1931, p. 1122.

(6) R. A. Robinson, *THIS JOURNAL*, **62**, 3130 (1940).

(7) E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

increases with the atomic weight of the cation, this being the order in which the activity coefficients decrease. The curve for sodium thiosulfate lies above that for sodium sulfate but below that for lithium sulfate. This suggests that, although ionic association occurs with sodium thiosulfate, it is less in extent than in the case of sodium sulfate and the distance of closest approach of the ions is somewhat greater, *i. e.*, the thiosulfate ion is slightly larger in this respect than the sulfate ion.

We wish to thank Professor H. S. Harned for his interest in this work and the Chemical Society (London) for a grant from the Research Fund.

Summary

Isopiestic vapor pressure measurements have been made to determine the osmotic and activity coefficients of lithium, sodium and potassium sulfate and sodium thiosulfate. The activity coefficients obtained for the sulfates agree within approximately 0.7% with those derived from e. m. f. measurements.

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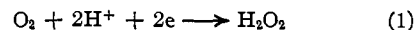
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

The Reduction of Oxygen at the Dropping Mercury Electrode

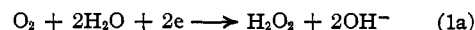
BY I. M. KOLTHOFF AND C. S. MILLER¹

Since the introduction of polarography by Heyrovsky it has been known that dissolved oxygen is reducible at the dropping mercury electrode.² In dilute electrolyte solutions the first reduction wave yields pronounced maxima, the suppression of which has been studied by Rasch,³ Varasova,⁴ Rayman⁵ and Hamamoto.⁶ Vitek⁷ applied the polarograph to the determination of oxygen in waste gases. In recent years this method has gained popularity in the determination of oxygen in biologically important materials.⁸ Vitek⁹ determined the "reduction po-

tentials" of oxygen by the 45° tangent method in various buffer and salt solutions. The first wave of oxygen corresponds to a reduction to hydrogen peroxide:



or



The second wave which is of equal height as the first one corresponds to the reduction of the peroxide to hydroxyl ions



or



This second wave coincides with that produced by an equinormal solution of peroxide in the same medium. The first wave has a much steeper slope than the second one. In the literature it is often stated that the first wave corresponds to a reversible reaction while the reaction on the second wave is irreversible. In the present

(1) From the experimental part of a thesis presented by C. S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the Ph.D. degree (1940).

(2) J. Heyrovsky, *Trans. Faraday Soc.*, **19**, 785 (1924).

(3) J. Rasch, *Collection Czechoslov. Chem. Commun.*, **1**, 560 (1929).

(4) E. Varasova, *ibid.*, **2**, 8 (1930).

(5) B. Rayman, *ibid.*, **3**, 314 (1931).

(6) E. Hamamoto, *ibid.*, **5**, 427 (1933).

(7) V. Vitek, *Chimie et Industrie*, **29**, 215 (1933).

(8) H. G. Petering and F. Daniels, *THIS JOURNAL*, **60**, 2796 (1938); K. S. Karsten, *Am. J. Botany*, **25**, 14 (1938).

(9) V. Vitek, *Collection Czechoslov. Chem. Commun.*, **7**, 537 (1935).