Summary

The oxidation potential of mixtures of thallic and thallous perchlorate in perchloric acid solution, and of thallic and thallous sulfate in sulfuric acid solution, were obtained by electromotive force measurements at 25° against a hydrogen electrode.

For the acid–thallic–thallous perchlorate mixtures, covering an acid concentration range 0.5 to 1.22 weight-formal $HClO_4$, the oxidation potential was found to be determined by the ionic strength μ of the solution, and by the concentration ratio $(\Sigma Tl^{+++})/(\Sigma Tl^{+})$ as shown by the two equations

$$E = E^0 + 0.02957 \log (\Sigma Tl^{+++})/(\Sigma Tl^{+}) \text{ and}$$
$$E^0 = 1.2466 + 0.0076\,\mu + 0.00482\,\mu^2$$

in which E^0 is the formal oxidation potential of the reaction $Tl^{+++} + 2E^- = Tl^+$.

For the acid–thallic–thallous sulfate mixtures, covering an acid concentration range 0.16 to 0.30 weight-formal H_2SO_4, the formal electrode potential computed by the first of the above equations was found to vary appreciably at the lower concentration ratios $(\Sigma Tl^{+++})/(\Sigma Tl^{+})$, but to remain nearly constant when the concentration ratio exceeded unity. This limiting value varied slightly with the acid concentration, from 1.205 volts in 0.16 formal to 1.207 volts in 0.30 formal sulfuric acid solution. The results of these measurements were shown to be in good agreement with those of Partington and Stonehill.[3]

The potential at the liquid junction

$$H_2SO_4(c_1),\ H_2SO_4(c_1) + Tl_2SO_4(c_3) + Tl_2(SO_4)_3(c_2)$$

which occurs in the type of cell investigated, was estimated by determining the change in the electromotive force produced by dissolving sufficient thallous sulfate in the sulfuric acid to give uniform concentration of this salt throughout the cell.

Incidentally the solubility at 25° of moist thallic hydroxide in solutions of perchloric acid and of sulfuric acid of varying concentration was determined. The solubility product of thallic hydroxide was estimated to be 1.5×10^{-44}.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Activity Coefficients of Some Bivalent Metal Sulfates in Aqueous Solution from Vapor Pressure Measurements

BY ROBERT A. ROBINSON AND RONALD S. JONES

Continuing our investigations on the activity coefficients of salts in aqueous solutions, measurements by the isopiestic vapor pressure method[1] have now been extended to solutions of some bivalent metals, *viz.*, copper, magnesium, zinc, cadmium, manganese and nickel. These salts were selected because it was felt desirable to obtain accurate data for salts other than those of the uni-univalent type and yet to retain that symmetry in the ion valences which renders theoretical treatment comparatively easy. The investigation proved more tedious than the previous work because a much larger number of determinations was necessary to cover the concentration range 0.1 *M* to the saturated solution. All measurements were made at 25° using pure recrystallized salts, except in the case of cadmium sulfate, which was prepared by the method of La Mer and Parks.[2]

Instead of tabulating the concentrations of isopiestic solutions of potassium chloride and metal sulfate, we shall record[3] values of the osmotic coefficient at round concentrations. These were obtained by first calculating the osmotic coefficient of potassium chloride, $\varphi' = (55.51/2m') \ln p_0/p$, from the molal vapor pressure lowerings of this salt previously recorded.[1a] Since p_0/p is the same for two isopiestic solutions, the osmotic coefficient of the sulfate, $\varphi = (55.51/2m) \ln p_0/p$, can be calculated from the concentration data. These values were plotted on a large-scale graph and no difficulty was experienced in drawing a smooth curve through the experimental points. The osmotic coefficients are recorded in Table I at sufficient concentrations to enable the curve of φ against $\sqrt{m}$ to be reproduced.

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(1) (a) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934); (b) Robinson, *ibid.*, **57**, 1161, 1165 (1935).

(2) La Mer and Parks, *ibid.*, **53**, 2040 (1931).

(3) Measurements on the sulfates of magnesium, zinc and cadmium were made by both observers; on magnesium sulfate 44 measurements were made by R. S. J. and 25 by R. A. R. In the case of cadmium sulfate the figures were 25 and 37, respectively, and in the case of zinc sulfate, 31 and 31. For the data on the sulfates of copper, manganese and nickel one of us (R. A. R.) must take full responsibility, the number of determinations being 30, 61 and 40, respectively.

TABLE I

OSMOTIC COEFFICIENTS OF BIVALENT METAL SULFATES

m	$CuSO_4$	$MgSO_4$	$ZnSO_4$	$CdSO_4$	$MnSO_4$	$NiSO_4$
0.1	0.561	0.606	0.590	0.565	0.587	0.581
.2	.515	.562	.533	.513	.538	.533
.3	.494	.540	.506	.490	.516	.508
.4	.478	.529	.492	.476	.501	.488
.5	.469	.522	.483	.466	.490	.475
.7	.459	.518	.474	.453	.476	.459
1.0	.462	.526	.479	.453	.476	.460
1.2	.474	.543	.490	.462	.486	.473
1.4	.491	.567	.508	.476	.504	.492
1.6		.597	.533	.496	.527	.517
1.8		.630	.566	.522	.556	.551
2.0		.666	.602	.551	.588	.589
2.2		.707	.643	.583	.620	.632
2.4		.755	.690	.617	.657	.680
2.6		.807	.744	.650	.696	.736
2.8		.863	.803	.688	.738	
3.0		.924	.863	.728	.784	
3.2			.930	.769	.834	
3.4			.998	.812	.887	
3.6			1.073	.855	.940	
3.8					.995	
4.0					1.053	
4.2					1.112	

For the calculation of the activity coefficients the method of Randall and White[4] was found most convenient. The isopiestic method functions most satisfactorily with more concentrated solutions and in the case of uniunivalent salts no difficulty was experienced in the extrapolation of the data to zero concentrations but it is not possible to carry the data for these sulfates below 0.1 M. It was therefore necessary to assume some value for the activity coefficient at one concentration and for this purpose the values at 0.1 M given by Redlich and Rosenfeld[5] corrected to 25° from freezing point data have been utilized, except in the case of zinc sulfate for which the value from e. m. f. data given by Bray[6] was employed. Should any of these selected values be altered by more accurate determinations with very dilute solutions, our activity coefficients can be adjusted easily to the new standard. Such alteration in the reference value is most likely to occur in the case of the manganese salt, for which the freezing point data seem to be the least reliable. Except in the case of this salt, it was apparent that the values of φ obtained from vapor pressure data and from freezing point measurements, respectively, were practically coincident at concentrations of 0.1 M and in some cases this identity extended to more concentrated solutions. For this reason the freezing point data were of assistance in drawing the curve of $(1 - \varphi)/\sqrt{m}$ against $\sqrt{m}$ in order to obtain the curvature around 0.1 M.

The activity coefficients calculated in this way are recorded in Table II and compared with other determinations. Under R are given the present values. F. p. indicates data from freezing points[5] corrected to 25°. B refers to e. m. f. data[6] for zinc sulfate, L to similar data[2] for cadmium sulfate, and N to the e. m. f. data of Nielsen and Brown[7] for copper sulfate.

With regard to the accuracy of these results, the values of Bray exhibit very good agreement with our measurements, the average deviation being 1%. Only at the two highest concentrations is there appreciable discrepancy.[8] In the case of copper sulfate we agree with Nielsen and Brown within 0.4%. The comparison with the data of La Mer and Parks on cadmium sulfate is not so satisfactory. A deviation of 9% at 0.5 M becomes a deviation in the opposite direction of 22% at the highest concentration and the average deviation is 11%. We made measurements on this salt with particular care and as, in addition, we have obtained reasonable agreement with the freezing point data we are inclined to put considerable confidence in the present results.[9]

The accuracy of the activity coefficients corrected from freezing point data is not easy to assess. If we compare values for the two salts for which the data appear to be established, *viz.*, copper sulfate and zinc sulfate, we find that the average difference between the activity coefficients of copper sulfate derived from vapor pressure measurements and from freezing point data is 4% with a maximum difference of 5%. In the case of zinc sulfate the average difference is 6% but this figure is rendered high by the inclusion of values at high concentration. Similar figures are obtained if e. m. f. data are used in place of our vapor pressure measurements. It is probably safe, therefore, to rely on the freezing point measurements within 5% at not too high concentrations. By this criterion our measurements on cadmium

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(4) Randall and White, THIS JOURNAL, **48**, 2514 (1926).

(5) Landolt-Börnstein, "Tabellen," fifth edition, zweiter Ergänzungsband, 1931, p. 1112.

(6) Bray, THIS JOURNAL, **49**, 2372 (1927).

(7) Nielsen and Brown, *ibid.*, **49**, 2423 (1927).

(8) Cowperthwaite and La Mer [*ibid.*, **53**, 4333 (1931)] have also made e. m. f. measurements on the same cell between 0.0005 and 0.05 M and the agreement with the results of Bray is excellent above 0.005 M.

(9) While this work was in progress Professor La Mer (private communication) has been engaged in a further study of the e. m. f. of cadmium salt cells and it seems probable that he will be able to decide between the two sets of data for the activity coefficient of cadmium sulfate in the near future.

TABLE II

ACTIVITY COEFFICIENT OF BIVALENT METAL SULFATES

	$ZnSO_4$			$CdSO_4$			$MnSO_4$	
m	R	B	F. p.	R	F. p.	L.	R	F. p.
0.1	(0.161)	0.161	(0.161)	(0.166)	0.166	(0.166)	(0.247)	0.247
.2	.113	.113	.116	.113	.114	....	.174	.176
.3	.0904	.0910	...	.0902	...	....	.140	...
.4	.0771	....	...	.0766	...	....	.120	...
.5	.0681	.0690	.072	.0674	.067	.0733	.106	.110
.7	.0566	....	...	.0554	...	....	.0877	...
1.0	.0472	.0477	.051	.0455	.045	.0507	.0727	.080
1.5	.0406	.0405	...	.0378	...	.0467	.0614	...
2.0	.0381	.0385	.043	.0352	...	.0377	.0579	.068
2.5	.0395	.0400	...	.0349	...	.0342	.0582	...
3.0	.0432	.0445	...	.0362	...	.0316	.0617	...
3.5	.0508	.0518	...	.0388	...	.0315	.0686	...
4.0	....	....	...	....	...	....	.0787	...
4.25	....	....	...	....	...	....	.0853	...

	$MgSO_4$		$CuSO_4$			$NiSO_4$	
m	R	F. p.	R	N	F. p.	R	F. p.
0.1	(0.195)	0.195	(0.164)	0.163	0.164	(0.180)	0.180
.2	.140	.142	.114	.114	.108	.126	.124
.3	.114	...	.0912	....	....	.101	...
.4	.0988	...	.0774	....	....	.0856	...
.5	.0882	.091	.0682	.0686	.0665	.0754	.078
.7	.0747	...	.0563	....	....	.0619	...
1.0	.0635	.067	.0465	....	.044	.0511	.056
1.5	.0559	...	.0403[a]	.0402	....	.0432	...
2.0	.0545	...	....	....	....	.0412	...
2.5	.0573	...	....	....	....	.0428	...
3.0	.0644	...	....	....	....	....	...

[a] At 1.38 *M*.

sulfate are reliable because they agree with the freezing point data within 1% up to 1 *M*, the higher concentration to which freezing point measurements have been extended.

In the case of magnesium, nickel and manganese sulfate, the freezing point data check our results within the range which is to be expected, *viz.*, 4%. We believe therefore that we are justified in claiming that the error in our data for the sulfates of zinc, cadmium and copper certainly does not exceed 1% and in the case of the other three sulfates the accuracy is probably of the same order.

If the activity coefficient is plotted against $\sqrt{m}$, the six curves so obtained are all similar in type, all except that of copper sulfate exhibiting a flat minimum at concentrations ranging from 1.77 to 2.40 *M*. The upward curvature is most marked in the case of magnesium sulfate; in the other five cases the differences in the activity coefficient must be determined largely by factors operative at concentrations less than 0.1 *M* for the curves exhibit little further divergence at higher concentrations, the greatest separation (in the ratio of 1.19) occurring between cadmium and manganese sulfate at 3.5 *M* concentration.

Summary

1. The osmotic coefficients and activity coefficients of the sulfates of copper, magnesium, zinc, cadmium, manganese and nickel in aqueous solution have been determined.

2. The activity coefficients of zinc and copper sulfate agree well with data derived from e. m. f. measurements. This agreement is not found with cadmium sulfate. The concordance with freezing point data is within the limits of the estimated experimental error.

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