[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Sodium Sulfate Solutions from Electromotive Force Measurements

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By precise measurements of the cells

$$Pb(Hg) \mid PbSO_4\,(s) \mid Na_2SO_4\,(m) \mid Na_xHg \mid Na_2SO_4\,(0.05) \mid PbSO_4\,(s) \mid Pb(Hg)$$

from 0 to 40°, the thermodynamic properties of sodium sulfate solutions from dilute to the saturated solutions have been studied. The only previous investigation of sodium sulfate solutions by electromotive force was made by Åkerlöf,[1] who employed mercury–mercurous sulfate electrodes in place of the two-phase lead amalgam–lead sulfate electrodes. Since his measurements were made at 25° only, the present results afford a much more comprehensive treatment of this system.

Materials, Experimental Procedures and Results

A high grade analyzed sodium sulfate was repeatedly crystallized from distilled water. The final product was dissolved in distilled water which formed a stock solution of approximately 1.3 *M*. This was diluted to give an approximately 0.05 *M* solution which was used as a reference solution. It was boiled under reduced pressure and kept under nitrogen. The solution which was used in the other half cell was boiled under reduced pressure. In this manner all solutions were air free. Analysis of the sulfate solutions was made by evaporating to dryness and weighing as Na_2SO_4.[2]

The lead sulfate was prepared as recommended by Bray.[3] It was precipitated from a 5% solution of carefully purified lead nitrate by adding an excess of a 10% sodium sulfate solution. The resulting solution with its precipitate was heated nearly to boiling for ten minutes in order to coarsen the precipitate. The latter was then washed by decantation and kept under distilled water.

The lead amalgam was prepared by electrolysis at a low current density of a 10% solution of lead nitrate. The platinum anode was in a 10% nitric acid solution contained in a porous cup which was suspended in the lead nitrate solution. The electrolysis was continued until the mercury cathode acquired six to ten per cent. of lead. Such an amalgam is two phase through the temperature range under consideration.[4] The effect of the concentration of lead on the electromotive force has been studied by several investigators.[5]

The sodium amalgam which was approximately 0.01% sodium by weight was made as described by Harned.[6] A detailed study of the lead–lead sulfate electrode has been made by Bray and the necessary conditions for its successful operation determined.[7]

The cell was similar to that employed in similar work of this kind,[6,8] but was modified to meet the demands of the present case. The amalgam electrode and the lead–lead sulfate electrode compartments were separable, the latter being removable. Between the two was placed a suitable three way stopcock which could be manipulated in such a way as to permit the preparation of the lead–lead sulfate electrode in the absence of air. Nitrogen was used to attain this end. Further, the solution from the amalgam electrode compartment could be withdrawn without affecting the lead–lead sulfate electrode. This feature was made use of in making measurements at the different temperatures which was accomplished in the manner described by us in our study of sodium hydroxide solutions. After the preparation of the cells, they were allowed to remain at the lowest temperature measured for four to six hours before the measurement was made. The solution was then withdrawn from the sodium amalgam compartment and then refilled with fresh solution. The amalgam reservoir was refilled and placed in position for the next measurement at a temperature 5° higher. This process was repeated until the 40° readings were taken. About two hours was allowed between measurements at the 5° temperature intervals in order that equilibrium be obtained.

The electromotive force of the cell after having made a very small correction in order to refer the results to the 0.05 *M* solution is related to the activity coefficients and concentrations according to

$$\log \frac{\gamma}{\gamma_{0.05}} = \frac{2E}{3k} - \log \frac{m}{0.05} \qquad (1)$$

where

$$k = 2.3026RT/F$$

The results which were carried out at sixteen concentrations were first smoothed to round concentrations by carefully plotting the right side of equation (1) against $m^{1/2}$. The results at constant composition were then expressed by the equation

$$E = E_{t'} + a(t - t') + b(t - t')^2 \qquad (2)$$

where $E_{t'}$ is the electromotive force at the lowest temperature measured, and *a* and *b* are constants. *a* and *b* were evaluated by the method of least squares. For purposes of brevity, we have

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[1] Åkerlöf, THIS JOURNAL, **48**, 1160 (1926).

[2] Treadwell-Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, 1907.

[3] Bray, THIS JOURNAL, **49**, 2372 (1927).

[4] Puschin, *Z. anorg. Chem.*, **36**, 210 (1903).

[5] See Henderson and Stegmany, THIS JOURNAL, **40**, 84 (1918).

[6] Harned, *ibid.*, **47**, 677 (1925).

[7] Bray, *ibid.*, **49**, 2372 (1927); see also Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[8] Harned and Hecker, *ibid.*, **55**, 4838 (1933).

omitted the original observations and have simply given the constants of equation (2) in Table I. For the purpose of computing the relative partial molal specific heat, b was plotted against m and the smoothed values of b' given in the fifth column of the table were obtained from this plot. It is important to note that at 0.7 M and 0.8 M the solution is saturated at 0 and 5° so that E_t equals E_{10} at these concentrations and t' equals 10. At 0.9, 1, 1.2 and 1.3 M, $E_{t'}$ equals E_{20}, and t' equals 20. The reproducibility of these cells is estimated to be ±0.1 mv. The values calculated by equation (2) and the constants in Table I agree with the smoothed electromotive forces with an average deviation of less than ±0.05 mv.

TABLE I

CONSTANTS OF EQUATION (2)

m	$E_{t'}$	$a \times 10^6$	$-b \times 10^6$	$-b' \times 10^6$
0.075	0.00838 (1)	39	0.18	0.14
.1	.01823 (1)	82	.29	.25
.2	.03509 (1)	174	.47	.55
.3	.04418 (1)	249	.85	.81
.4	.05027 (1)	296	.95	1.01
.5	.05470 (1)	348	1.20	1.20
.7	.06533 (2)	367	1.35	1.54
.8	.06803 (2)	401	1.75	1.73
.9	.07446 (3)	391	1.83	1.92
1.0	.07670 (3)	425	2.44	2.14
1.2	.08053 (3)	470	2.73	2.54
1.3	.08212 (3)	489	2.74	2.74

(1) $E_{t'} = E_0$; (2) $E_{t'} = E_{10}$; (3) $E_{t'} = E_{20}$

(1) $t' = 0$; (2) $t' = 10$; (3) $t' = 20$

Activity Coefficients

The activity cofficient at 0.05 M was evaluated from the electromotive forces by employing the equation of the Debye and Hückel theory, namely

$$\log \gamma = -\frac{z_+ z_- u\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + B\Gamma - \log (1 + 0.018\,\nu m) \quad (3)$$

Since according to equation (1), the cell measures $\log \gamma/\gamma_{0.05}$, the constants A and B were evaluated from

$$\log \frac{\gamma}{\gamma_{0.05}} = z_+ z_-\ u \left[\frac{\sqrt{\Gamma_{0.05}}}{1 + A\sqrt{\Gamma_{0.05}}} - \frac{\sqrt{\Gamma_m}}{1 + A\sqrt{\Gamma_m}}\right] + B(\Gamma_m - \Gamma_{0.05}) - \log \frac{1.054m}{1.0027} \quad (4)$$

To do this, two equations were set up by employing the data at m equals 0.1 and 0.5 and were solved simultaneously for A and B. Since Γ is the ional concentration, or $\Sigma c_i z_i{}^2$, concentrations in moles per liter of solution were used. We did not employ the extended terms of the theory as given by La Mer, Gronwall and Greiff.[9] Since it is found that the observed activity coefficients agree with those computed by equation (3) quite closely and since our results can only be obtained at higher concentrations, we did not think that these additional calculations would be warranted. Our results at 25° agree closely with those determined by Åkerlöf,[1] who used mercury–mercurous sulfate electrodes.

In Table II we have assembled the results of these computations. The values of A, B and "a," the apparent ionic diameter, are given as well as the values of $\gamma_{0.05}$. The values of u and the universal constants employed are also given in the table. Normal concentrations, c, were computed from the densities.[10]

TABLE II

PARAMETERS OF EQUATION (3) AND ACTIVITY COEFFICIENT AT 0.05 M

	0	5°	10°	15°	20°
u	0.3445	0.3465	0.3495	0.3520	0.3550
A	.770	.813	.804	.802	.795
$-B$	.0266	.0273	.0210	.0183	.0150
a (Å.)	3.37	3.53	3.49	3.47	3.43
$\gamma_{0.05}$	0.532	0.535	0.534	0.531	0.529
	25°	30°	35°	40°	
u	0.3580	0.3615	0.3650	0.3690	
A	.809	.709	.805	.806	
$-B$	.0140	.0128	.0104	.0093	
a (Å.)	3.63	3.39	3.44	3.43	
$\gamma_{0.05}$	0.529	0.524	0.523	0.520	

Constants employed: $R = 1.9885$ cal.; 1 cal. $= 4.185$ joules; $F = 96{,}500$ coulombs; $t = T - 273.1$; $e = 4.774 \times 10^{-10}$; $N = 6.061 \times 10^{23}$; $k = 1.372 \times 10^{-16}$.

The values of "a" were computed from the equation $a = Ax$, by employing the values of x given in Table IV of our investigation of sodium hydroxide solutions. The constancy of the "a" parameter throughout the entire temperature range is very apparent. In this case, there is no definite trend in these values and the variation is within the limit of experimental error. We can say that from these computations "a" has a constant value of 3.5 Å. The B parameter is negative and increases rapidly with the temperature, a fact which indicates that the relative partial molal heat content at constant temperature will first increase, then pass through a maximum and finally decrease with increasing concentration.

The activity coefficient of sodium sulfate, γ', in aqueous solutions at the freezing point has been determined from freezing point data by

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[9] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

[10] "International Critical Tables," McGraw-Hill Book Co., New York, 1928, Vol. III.

Randall and Scott.[11] These results may be compared with the values obtained by us at 0°, but unfortunately only through a short concentration range, since our measurements could be successfully performed from 0.05 M to high concentrations and theirs were carried out up to 0.2 M only. At concentrations 0.05, 0.1 and 0.2 M they obtained 0.537, 0.449 and 0.374, respectively, while we obtained 0.532, 0.446 and 0.360. The major part of the discrepancy is probably due to the difficulty in extrapolating the electromotive force data. If we take γ equal to 0.537 at 0.05 M, we obtain 0.450 and 0.364 at 0.1 and 0.2 M, respectively, which compare favorably with the freezing point data, particularly since Randall and Scott's value at 0.2 M was not accurately evaluated.

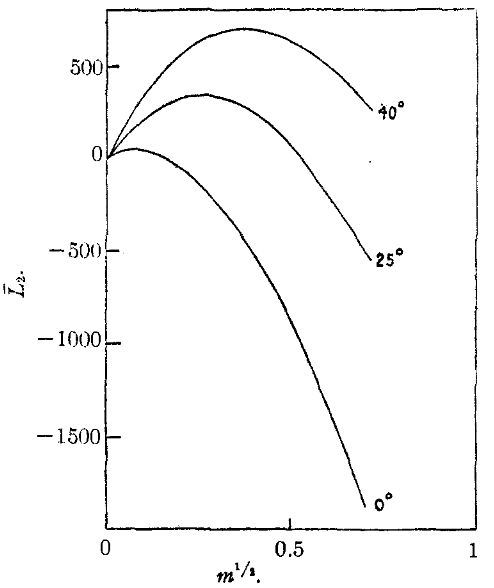

Fig. 1.—The relative partial molal heat content of sodium sulfate in aqueous solution.

Relative Partial Molal Heat Content.—In our treatment of sodium hydroxide solutions,[8] a thorough discussion of methods of extrapolating heat data was given and the tables of data necessary for this purpose compiled. Consequently, the present calculations can be stated briefly if reference be constantly made to the former communication. The partial molal heat content relative to the 0.05 M solution was computed by the Gibbs–Helmholtz equation

$$\bar{H}_m - \bar{H}_{0.05} = NEF - NFT(\mathrm{d}E/\mathrm{d}T) \qquad (6)$$

The temperature coefficients of electromotive force were computed from equation (2) and the use of the constants a and b in Table I. $\bar{L}_2$ at 0.05 M, or $\bar{H}_{0.05} - \bar{H}_0$, was computed by the semi-empirical equation

$$\bar{L}_2 = \frac{\nu z_1 z_2 L \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + \frac{Kc}{(1 + A\sqrt{\Gamma})^2} + K'C \qquad (7)$$

which is equation (12) previously discussed by us. The values of K and K' are given in Table III. Values of L were taken from Table IV of our former paper. The final values of $\bar{L}_2$ when plotted differ from a smooth curve drawn through them with an average deviation of ±50 cal. and a maximum deviation of about ±100 cal. Although this is a large error, it corresponds to a very small error, estimated to be less than ±0.01 mv., in the determination of the temperature coefficient of electromotive force. For the purpose of brevity, we have expressed the values of $\bar{L}_2$ as a function of the temperature by

$$\bar{L}_2 = \bar{L}_{2(t')} + \alpha(t - t') \qquad (8)$$

the constants of which are given in Table III.

TABLE III

CONSTANTS OF EQUATIONS (7) AND (8)

m	$\bar{L}_2(t')$	α	t °C.	$(-K \times 10^{-3})$	$(-K' \times 10^{-3})$
0.05	+ 37 (1)	17.2	0	5.00	4.12
.075	− 50 (1)	21	5	1.62	4.32
.1	− 150 (1)	24	10	0.20	4.18
.2	− 565 (1)	30	15	− .36	4.04
.3	−1020 (1)	39.5	20	− 1.96	3.99
.4	−1430 (1)	46	25	− 3.80	3.95
.5	−1820 (1)	52	30	− 5.38	3.93
.7	−1850 (2)	62	35	− 7.18	3.88
.8	−2110 (2)	67	40	−10.28	3.99
0.9	−1650 (3)	74			
1.0	−1830 (3)	79			
1.2	−2160 (3)	89			
1.3	−2320 (3)	94			

(1) $t' = 0$; (2) $t' = 10$; (3) $t' = 20$

The characteristics of $\bar{L}_2$ as a function of m and T are shown in Fig. 1. As predicted from the temperature coefficients of the parameters of equation (3) they exhibit characteristic maxima. Lange and Streeck[12] have determined $\bar{L}_2$ at 25° by calorimetric measurements from very low concentrations to 0.1 M, which affords a comparison with our results in the limited concentration range from 0.05 to 0.1 M. They expressed $\bar{L}_2$ in terms of the hydrate, $Na_2SO_4 \cdot 10H_2O$. If we change their results to correspond to Na_2SO_4, we obtain 545, 545, 517 cal. at 0.05, 0.075 and 0.1 M, respectively, which differ by nearly a constant amount of 70 cal. from the values 467,

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[11] Randall and Scott, THIS JOURNAL, **49**, 647 (1927).

[12] Lange and Streeck, *Z. physik. Chem.*, **157**, 1 (1931).

475 and 450 obtained by us. This fact indicates the approximate nature of the extrapolation, but lends support to the validity of the measurements since good agreement for the partial molal heat content relative to 0.05 M is obtained and since the maximum value of $\bar{L}_2$ is at the same concentration.

The Relative Partial Molal Specific Heat

Mean values of $\bar{C}_p - \bar{C}_{p_0}$ may be obtained directly by differentiation of equation (8), and are equal to the values of α given in Table III. For general purposes, however, it is better to employ the equation

$$\bar{C}_p - \bar{C}_{p0.05} = -NFT2b \qquad (9)$$

and the values of b' given in Table I and then add 17.2 cal., the value found for $\bar{C}_{p0.05} - \bar{C}_{p_0}$ from the temperature slope of $\bar{L}_2$. Since it is a simple matter to compute this quantity by equation (9), we have not compiled a table but have plotted in Fig. 2 the results at 25° against $m^{1/2}$. The curve L. S. represents the limiting slope of the Debye and Hückel theory, and the curve denoted R., that computed by Randall and Rossini.[13] The agreement with the calorimetric data is by no means as good as that obtained by Harned and Ehlers for hydrochloric acid solutions or by us for sodium hydroxide solutions. The discrepancy is of the order of that found by Harned and Nims in the case of sodium chloride solutions.

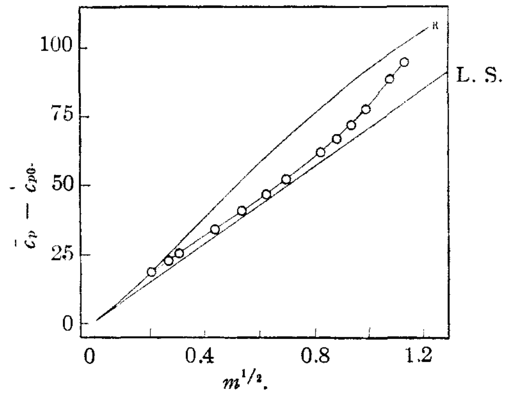

Fig. 2.—The relative partial molal specific heat of sodium sulfate in aqueous solution at 25°.

Summary

1. Measurements of the cells

$Pb(Hg) \mid PbSO_4\,(s) \mid Na_2SO_4\,(m) \mid Na_xHg \mid Na_2SO_4\,(0.05) \mid PbSO_4\,(s) \mid Pb(Hg)$

have been made from 0 to 40° at 5° temperature intervals.

2. From these calculations of the activity coefficient, the relative partial molal heat contents and specific heat of sodium sulfate in aqueous solution have been computed.

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[13] Randall and Rossini, This Journal, **51**, 323 (1929).

NOTE

The Electric Moment of Dioxane

By C. H. Schwingel and E. W. Greene

During recent years 1,4-dioxane has been used to a limited extent as non-polar solvent for the determination of the electric moments of polar molecules. However, both Williams and Smyth have made measurements in non-polar liquids at a single temperature and have reported electric moments $\mu = 0.4 \times 10^{-18}$ and $\mu = 0.45 \times 10^{-18}$ e. s. u. for this compound.[1] According to Williams, "this value is so small that it is indistinguishable from zero by the method used."

In order to determine whether or not dioxane possesses a finite moment, it was thought worth while to study the effect of temperature on its polarization in the vapor state. This method for the determination of electric moments is more precise than the single temperature-solution method.

The table gives dielectric constant and polarization values obtained in our investigation of dioxane vapor. These data clearly indicate that 1,4-dioxane has zero electric moment. This is shown by the fact that the total molar polarization does not change with temperature.

Dielectric Constant and Polarization Data for 1,4-Dioxane Vapor

Temp., °K.	Press., mm.	$(\epsilon - 1)10^6$	P, cc.
337.0	104.4	377.4	25.1
337.1	108.1	381.4	24.6
339.0	126.7	439.6	24.3
341.2	97.3	334.6	24.2
384.7	178.3	558.0	24.8
385.0	180.5	563.7	24.8
385.2	184.2	555.2	24.0
442.0	203.5	538.5	24.1
487.0	233.2	566.6	24.5
		Av.	24.5 cc.

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[1] Williams, This Journal, **52**, 1831–1838 (1930), and Smyth, *ibid.*, **53**, 2115–2122 (1931).