zene). The cooled reaction product was treated with petroleum ether to remove the excess ethyl benzoate, and extracted several times with 25 ml. of water to dissolve the soluble portion and finally allowed to stand in contact with water for twenty-four hours. The residue consisted of rare earth benzoates and contained no bromide. The insoluble and soluble portions were separately converted to the oxides.

Analyses of both the original mixture and products were made for neodymium with an absorption spectrophotometer (Cenco Spectrophotelometer). Measurements on solutions of the chlorides were made on the absorption band of neodymium at a wave length of 521 mμ and calibration was accomplished by use of standard solutions of neodymium chloride of concentrations varying from 0.1 to 0.001 *m*. As a check on these results, analyses for lanthanum were made with a 35-foot Wadsworth mounted spectrograph. For the calibration data mixtures of neodymium and lanthanum oxides were used containing percentages of lanthanum which varied from 10% lanthanum to 0.01%. The results of typical runs are given in Table II. The accuracy is considered to be within a range of ±5%.

TABLE II

SEPARATION OF NEODYMIUM FROM MIXTURES OF NEODYMIUM AND LANTHANUM

Mixed bromides used, g.	$NdBr_3$ in mixture ± 5%, %	Recovery: Water insol. portion, oxide, g.	% Nd ± 5%	Water sol. portion, oxide, g.	% Nd ± 5%
2.0	38.1	0.1034	99	0.6899	32
2.6	56	.1568	97	.6156	49
2.3	56	.0635	100	.7985	49
2.0	56	.4473	72	.3892	44

The rare earth bromides react with diethyl oxalate and form ethyl bromide and the oxalates of the rare earths. A study of the reaction between the rare earth chlorides and both esters is planned.

Summary

The anhydrous bromides of the rare earth elements react with ethyl benzoate at 154° and produce ethyl bromide and the rare earth benzoate. Since the rates differ for the different rare earths and the benzoates are insoluble in water, this reaction affords a means of separation. From nearly equimolal mixtures of neodymium and lanthanum bromides, 25% of the neodymium is obtained in a degree of purity of 95% in one operation since neodymium bromide reacts at a much faster rate than lanthanum bromide to produce the benzoate.

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[CONTRIBUTION NO. 419 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution, Relative Molal Heat Contents and Heat Capacities of Aqueous Sodium Sulfate Solutions[1]

BY W. E. WALLACE AND A. L. ROBINSON

In the past numerous investigations[2,3] of the thermal properties of very dilute solutions of electrolytes have been shown[4,5] to yield results which, for the low valence types (1–1, 1–2, 2–1), are in substantial agreement with theory.[6,7] Most of these studies involved measurements at a single temperature, 25°. For this reason reliable data for the temperature dependent properties of dilute solutions are available in comparatively few cases.[3,8] In this paper are presented measurements of the intermediate heats of dilution of aqueous sodium sulfate solutions from 0.4 to 0.0001 molal at 15 and 20° and from 0.4 to 0.1 molal at 25°. These results, when combined with the extremely precise data of Lange and Streeck[9] for the very low concentration range at 25°, permit the evaluation of the partial molal heat contents at the three temperatures and the (average) heat capacities (15 to 25°) from zero to approximately 0.4 molal.

Experimental.—The apparatus was essentially that used by Dunkelberger and Robinson[8] with a few minor changes.

The Julius suspension, previously used for the support of the galvanometer, was replaced by a supporting shelf similar to that used by Amdur and Pearlman.[10] The details of the construction are given elsewhere.[11] This type of support proved to be so satisfactory that the scale dis-

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(1) From a thesis submitted by Mr. W. E. Wallace in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pittsburgh, 1940.

(2) E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931).

(3) E. A. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934).

(4) T. F. Young and W. L. Gronier, *ibid.*, **58**, 187 (1936).

(5) T. F. Young and P. Seligmann, *ibid.*, **60**, 2379 (1938).

(6) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

(7) N. Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926).

(8) T. H. Dunkelberger and A. L. Robinson, THIS JOURNAL, **60**, 1301 (1938).

(9) E. Lange and H. Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

(10) I. Amdur and H. Pearlman, *Rev. Sci. Instruments*, **9**, 194 (1938).

(11) W. E. Wallace, Thesis, University of Pittsburgh, 1940.

tance could be increased from six to nine meters. With this scale distance the maximum sensitivity was about 0.00025 calorie per mm. deflection, corresponding to about 2×10^{-7}° per mm. deflection. For most of the measurements a sensitivity of one-fourth of this value was sufficient and was obtained by use of a parallel shunt of the proper resistance.

The above sensitivity was obtained using two 665 element (iron–constantan) thermels connected in parallel. Such an arrangement is superior to the customary series connection of the two thermels because of slightly increased sensitivity and considerably improved electrical stability.

The right and left pipets have volumes of 6.806 and 6.757 ±0.004 ml., respectively. The right and left halves of the calorimeter contain 1007 and 1000 ± 1 ml., respectively.

The water used throughout the investigation had a specific conductance of 3×10^{-6} mho or less.

The sodium sulfate was a Merck C. P. product which had been recrystallized four times from doubly distilled water and dehydrated at 800° in a muffle furnace. Sulfate analysis of the purified material gave the theoretical value within the limit of experimental error. Spectroscopic examination[12] indicated the absence of metallic impurities in amounts greater than a few thousandths of one per cent.

All solutions were made up on a volume basis at 25°. These were converted to the weight basis using the density data of Gibson.[13] The experimental procedure and the method for determining the value of the heat effect accompanying a dilution were the same as previously described.[3,14]

Experimental Results.—The first two columns of Table I give the initial and final concentrations of a dilution, respectively. The remainder of the table indicates the number of duplicate runs, the mean of the experimental heat effects and the average value of the intermediate heats of dilution. Since the volume of the two pipets was not identical, the number of moles involved in a dilution in one side of the calorimeter was not quite the same as in the other. The experimental heat effects listed in column 4 have been calculated on the basis of the number of moles being diluted in the left half of the calorimeter. The quantities in parentheses in column 5 are the smoothed probable errors of the intermediate heats of dilution, the significance and method of determination of which will be discussed in the next section. It is estimated that the systematic errors (errors in the measurement of concentration, time, potential, resistance, etc.) are less than 1%.

TABLE I

EXPERIMENTAL INTERMEDIATE HEATS OF DILUTION OF AQUEOUS SODIUM SULFATE SOLUTIONS

m_1	m_2	Runs	q, cal.	ΔH cal./mole Na_2SO_4
		15°C.		
0.4014	0.002692	4	+1.480 ±0.010	+549.6 ±3.6(3.2)
.4014	.005366	4	+1.570 ± .000	+566.5 ±1.8(2.3)
.2006	.001351	4	+0.2556 ± .0016	+189.2 ±1.2(1.3)
.2006	.002692	4	+ .2887 ± .0026	+204.0 ±1.2(1.0)
.1005	.0006778	2	− .0065 ± .0006	− 9.6 ±0.9(0.5)
.1005	.001351	2	+ .0139 ± .0003	+ 5.5 ±0.5(0.4)
.05037	.0003401	4	− .0313 ± .0004	− 92.1 ±1.2(1.5)
.05037	.0006778	3	− .0256 ± .0003	− 83.6 ±1.2(1.1)
.02525	.0001705	6	− .0218 ± .0003	−127.9 ±1.7(2.3)
.02525	.0003401	6	− .0187 ± .0005	−118.6 ±2.5(1.7)
		20°C.		
0.4014	0.002692	2	+1.023 ±0.006	+380.2 ±2.2(2.2)
.4014	.005366	2	+1.177 ± .008	+408.8 ±1.8(1.8)
.2006	.001351	4	+0.0816 ± .0004	+ 60.4 ±0.3(0.6)
.2006	.002692	3	+ .1451 ± .0010	+ 84.0 ±0.4(0.6)
.1005	.0006778	4	− .0630 ± .0006	− 92.9 ±0.9(1.0)
.1005	.001351	4	− .0396 ± .0007	− 75.6 ±0.7(0.6)
.05037	.0003401	7	− .0513 ± .0006	−151.0 ±1.7(1.7)
.05037	.0006778	6	− .0413 ± .0006	−136.2 ±1.2(1.2)
.02525	.0001705	6	− .0283 ± .0003	−166.2 ±1.9(3.0)
.02525	.0003401	6	− .0243 ± .0006	−154.4 ±2.2(1.9)
.01267	.0000856	6	− .0122 ± .0002	−142.8 ±2.9(4.5)
.01267	.0001705	4	− .0113 ± .0004	−137.2 ±2.3(3.2)
		25°C.		
0.4014	0.002692	2	+0.5344 ±0.0038	+198.5 ±1.4
.4014	.005366	2	+ .7072 ± .0065	+230.7 ±1.4
.2006	.001351	2	− .0827 ± .0001	− 61.2 ±0.1
.2006	.002692	2	− .0095 ± .0024	− 34.2 ±0.9
.1005	.0006778	5	− .1171 ± .0012	−172.8 ±1.8
.1005	.001351	5	− .0894 ± .0018	−150.7 ±1.6

Treatment of Results

Apparent Relative Molal Heat Contents of Solute.[15]—The most satisfactory method for evaluating the ΦL_2's from the measured intermediate heats of dilution seems to be the method developed by Young,[4,5,16] the so-called chord-area method. Treatment of data using the chord-area method is most effective when the chords are short, *i. e.*, when the dilution range is small. In these measurements the chords are extremely long (148-fold dilution) and direct application of the chord-area method is quite tedious. To reduce the labor of the calculations a slightly modified version of the chord-area method was employed.

From Table I it is seen that there are two final concentrations given for each initial concentration. Hence, intermediate heats of dilution between the two final concentrations are readily

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(12) Thanks are due to Dr. Mary Warga and Mr. Lee L. Davenport for making this examination.

(13) R. E. Gibson, *J. Phys. Chem.*, **31**, 496 (1927).

(14) E. Lange and J. Monheim, *Z. physik. Chem.*, **149A**, 51 (1930).

(15) The following symbols will be used throughout the discussion: ΦH_2 = apparent molal heat content of solute. ΦH_2° = apparent molal heat content of solute in its reference state. $\Phi L_2 = \Phi H_2 - \Phi H_2^{\circ}$ = apparent relative molal heat content of solute. $\Phi C_{p_2} = d(\Phi H_2)/dT$ = apparent molal heat capacity of solute. $\Phi C_{p_2} - \Phi C_{p_2}^{\circ} = d(\Phi L_2)/dT$ = apparent relative molal heat capacity of solute. For all other quantities the terminology of Lewis and Randall has been employed.

(16) T. F. Young and O. G. Vogel, THIS JOURNAL, **54**, 3030 (1932).

obtained. These quantities, given in Table II, represent very short chords and are, therefore, just the type of data desired for the chord-area treatment; moreover, they are in the very dilute range where direct chords are difficult, if not impossible, to obtain experimentally.

Since the chords obtainable from Table II are not all of the same precision, it is necessary to assign to each a weight dependent on its relative uncertainty. If accurate values of the probable errors of the chords are known, the customary procedure of assigning weights (inversely proportional to the square of the probable error) may be used. However, in this case the number of measurements is so small that values for the probable errors as computed in the usual way are probably not too reliable. To increase their reliability the raw probable errors were smoothed in the following way: p_q, the probable error in q, was plotted as a function of q and a smooth curve drawn through the points. It seems reasonable to assume that p_q should vary in some regular fashion with q and that the deviations from the smooth curve are caused by the small number of experiments. The curve so obtained showed p_q to be almost independent of q for small heat effects (<0.05 cal.) and to increase with q for the larger heat effects. Such a curve conforms to expectation for the type of calorimeter used in this investigation. The finite sensitivity of the system places a lower limit on p_q, which limit is practically attained in cases involving small q's. For experiments in which the heat effects are relatively large other factors, namely, heat losses to the surroundings, control the magnitude of the error; hence the increase of p_q with q for large values of q.

From the smooth curve values of p_q were taken at the various q's and these quantities were used to compute the probable errors listed in parentheses in column 5, Table I. These latter values were used to calculate the probable errors listed in Table II.

Assigning weights to the chords inversely proportional to the square of the probable errors listed in Table II the following equations were obtained:

$$15\text{°C.}\quad \Phi L_2 = 1803m^{1/2} - 8042m \qquad (1)$$

$$20\text{°C.}\quad \Phi L_2 = 2193m^{1/2} - 7418m \qquad (2)$$

$$25\text{°C.}\quad \Phi L_2 = 2418m^{1/2} - 6701m \qquad (3)$$

TABLE II

DERIVED INTERMEDIATE HEATS OF DILUTION

m_1	m_2	ΔH cal./mole Na_2SO_4 15°C.	20°C.
0.005366	0.002692	−17.0±3.9	−28.6±2.8
.002692	.001351	−14.8±1.6	−23.6±0.8
.001351	.0006778	−15.1±0.6	−17.3±1.2
.0006778	.0003401	− 8.5±1.9	−14.8±2.1
.0003401	.0001705	− 9.3±2.9	−11.8±3.5
.0001705	.0000856	....	− 5.5±5.5
		25°C.	
0.005211	0.002640	−33.7±0.3[a]	
.002605	.001320	−27.0± .2[a]	
.001302	.0006600	−20.4± .3[a]	
.0006501	.0003300	−15.0± .3[a]	
.0003251	.0001650	−12.0± .3[a]	

[a] Calculated from the data of Lange and Streeck.[9]

The concentration range is so small that the parabolic equations are quite adequate. The effectiveness of this type of treatment is confirmed by comparison of the results of equation (3) with the equation derived from the same data by Young and Seligmann.[5] They obtained by using measurements up to 0.1 molar the following equation

$$25\text{°C.}\quad \Phi L_2 = 2432m^{1/2} - 7448m + 6511m^{3/2} \qquad (4)$$

The results of the two treatments are indistinguishable over the common concentration range.

Using equations (1) to (3) values for the ΦL_2's of column 4, Table III, have been calculated.

TABLE III

DATA USED IN THE EVALUATION OF THE APPARENT RELATIVE HEAT CONTENTS

m_1	m_2	ΔH $(m_1 \rightarrow m_2)$	ΦL_2 (m_2)	ΦL_2 (m_1)	Mean ΦL_2 (m_1)
		25°C.			
0.4014	0.002692	198.5	107.4	− 91.1	− 90.4
.4014	.005366	230.7	141.1	− 89.6	
.2006	.001351	− 61.2	79.9	141.1	141.3
.2006	.002692	− 34.2	107.4	141.6	
.1005	.0006778	−172.8	58.5	231.3	231.5
.1005	.001351	−150.7	79.9	231.6	
		20°C.			
0.4014	0.002692	380.2	93.8	−286.4	−287.2
.4014	.005366	408.8	120.8	−288.0	
.2006	.001351	60.4	70.6	10.2	10.0
.2006	.002692	84.0	93.8	9.8	
.1005	.0006778	− 92.9	52.1	145.0	145.6
.1005	.001351	− 75.6	70.6	146.2	
.05037	.0003401	−151.0	37.9	188.9	188.6
.05037	.0006778	−136.2	52.1	188.3	
.02525	.0001705	−166.2	27.4	193.6	193.0
.02525	.0003401	−154.4	37.9	192.3	
.01267	.0000856	−142.8	19.7	162.5	163.6
.01267	.0001705	−137.3	27.4	164.7	
		15°C.			
0.4014	0.002692	549.6	71.9	−477.6	−477.6
.4014	.005366	566.5	88.9	−477.6	
.2006	.001351	189.2	55.4	−133.8	−133.0
.2006	.002692	204.0	71.9	−132.1	
.1005	.0006778	− 9.6	41.5	51.1	50.5
.1005	.001351	5.5	55.4	49.9	
.05037	.0003401	− 92.1	30.5	122.6	123.9
.05037	.0006778	− 83.6	41.5	125.1	
.02525	.0001705	−127.9	22.2	150.1	149.6
.02525	.0003401	−118.6	30.5	149.1	

These when combined with the experimental heats of dilution yield the ΦL_2's listed in columns 5 and 6 of Table III.

Equations have been derived to express the data of columns 4 and 6 of Table III. A third power equation proved to be sufficient to express $\Phi L_2 = f(m^{1/2})$ at 15 and 20° up to 0.4 molal. For the somewhat more accurate data at 25° a fourth power equation seemed desirable. Using the method of least squares the following were obtained

$$15\,°\text{C.}\quad \Phi L_2 = 1707m^{1/2} - 5691m + 2832m^{3/2} \tag{5}$$
$$20\,°\text{C.}\quad \Phi L_2 = 2067m^{1/2} - 6082m + 3336m^{3/2} \tag{6}$$
$$25\,°\text{C.}\quad \Phi L_2 = 2429m^{1/2} - 7734m + 8990m^{3/2} - 5036m^2 \tag{7}$$

The average deviation of the ΦL_2's calculated from equations (5) to (7) from those listed in columns 4 and 6 of Table III are 4.5, 3.0 and 1.0 cal./mole at 15, 20 and 25°, respectively. The corresponding deviations from the ΦL_2's taken from a smooth curve are 2.0, 2.0 and 1.0 cal./mole.

The effectiveness of the above equations in reproducing the data from which they were derived is illustrated in Figs. 1 and 2.

Limiting slopes calculated from equations (1) to (3) are preferable to those obtained from equations (5) to (7) since the chord-area method of treatment is one which is specifically designed for the evaluation of these slopes. However, even in the very dilute range equations (5) to (7) are quite satisfactory for computing values for the thermal properties of the solutions as earlier communications have shown.[16,17]

Partial Relative Molal Heat Contents.—The $\overline{L}_1$'s and $\overline{L}_2$'s are conveniently obtained from the ΦL_2's using the equations of Rossini:[18]

$$\overline{L}_1 = -\frac{m^{3/2}}{2(55.508)}\frac{\mathrm{d}\,(\Phi L_2)}{\mathrm{d}\,m^{1/2}} \tag{8}$$
$$\overline{L}_2 = \Phi L_2 + \frac{m^{1/2}}{2}\frac{\mathrm{d}\,(\Phi L_2)}{\mathrm{d}\,m^{1/2}} \tag{9}$$

Introducing into these relations equations (5) to (7) we obtain

15 °C.

$$\overline{L}_1 = -\,15.18m^{3/2} + 102.53m^2 - 76.53m^{5/2} \tag{10}$$
$$\overline{L}_2 = 2650m^{1/2} - 11382m + 7080m^{3/2} \tag{11}$$

20 °C.

$$\overline{L}_1 = -\,18.61m^{3/2} + 109.57m^2 - 90.15m^{5/2} \tag{12}$$
$$\overline{L}_2 = 3100m^{1/2} - 12164m + 8340m^{3/2} \tag{13}$$

25 °C.

$$\overline{L}_1 = -\,21.88m^{3/2} + 139.3m^2 - 242.9m^{5/2} + 181.5m^3 \tag{14}$$
$$\overline{L}_2 = 3644m^{1/2} - 15468m + 22475m^{3/2} - 15108m^2 \tag{15}$$

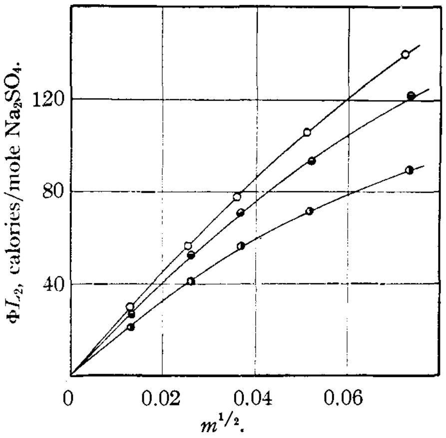

Fig. 1.—Apparent relative molal heat contents (ΦL_2) of sodium sulfate at low concentrations: O, 25°; ◒, 20°; ◑, 15°; curves from equations (1) to (3).

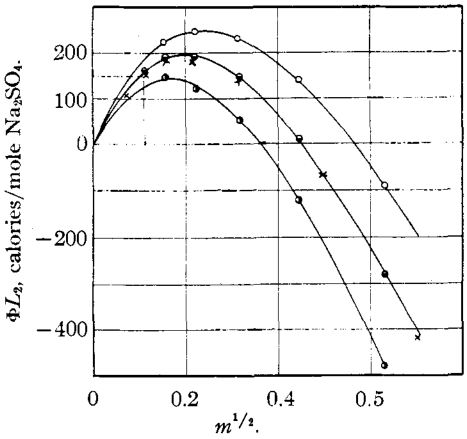

Fig. 2.—Apparent relative molal heat contents of sodium sulfate: O, 25°; ◒, 20°; ◑, 15°; × Plake; curves calculated from equations (5) to (7); see Fig. 1 for region within dashed lines.

Partial Relative Molal Heat Capacities.—These quantities have been evaluated from the $\overline{L}_2$'s in the customary way (*e. g.*, see ref. 8). The results of such calculations are summarized in the following equation

$$\overline{C}_{p_2} - \overline{C}^0_{p_2} = 84m^{1/2} \tag{16}$$

Using Randall and Rossini's[19] value for $\overline{C}^0_{p_2}$ as −50.0, equation (16) becomes

$$\overline{C}_{p_2} = 84m^{1/2} - 50.0 \tag{17}$$

The effectiveness of equation (17) in reproducing the data from which it was derived is demonstrated in Table IV and Fig. 3.

Apparent Relative Molal Heat Capacities.—The ΦC_{p_2}'s are derived from the ΦL_2's in the same way that the $\overline{C}_{p_2}$'s have been obtained from the

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[17] A. L. Robinson, THIS JOURNAL, **54**, 1311 (1932).

[18] F. D. Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

[19] M. Randall and F. D. Rossini, THIS JOURNAL, **51**, 323 (1929).

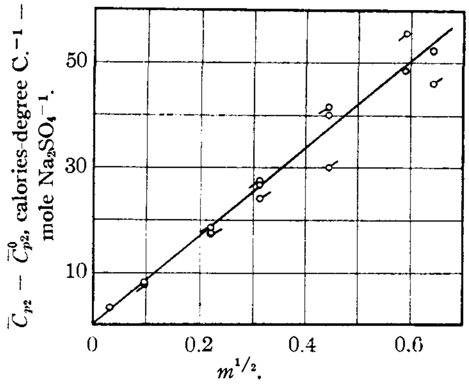

Fig. 3.—Relative partial molal heat capacities (average) of sodium sulfate: O, this research; ♂, Harned and Hecker; ♀, Randall and Rossini; straight line from equation (16).

$\bar{L}_2$'s. The results of such a treatment are summarized in Fig. 4. The plot shows that above approximately 0.01 molal ΦC_{p_2} is *not* a linear function of $m^{1/2}$. The curvature at the higher concentrations is similar in nature to that revealed in Young and Machin's[20] summary of the heat capacity data for sodium chloride.

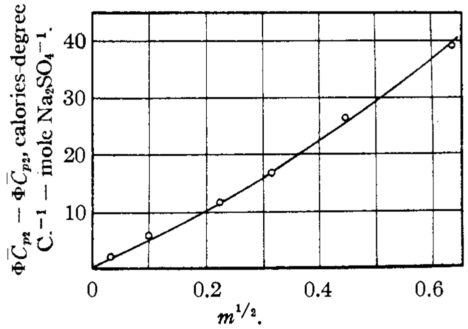

Fig. 4.—Apparent relative molal heat capacities of sodium sulfate.

TABLE IV

COMPARISON OF $\bar{C}_{p_2}$ VALUES

m	$\bar{C}_{p_2}$ cal./mole °C. This research From $\bar{L}_2$	This research Calcd. Eq. 17	Harned and Hecker	Randall and Rossini
0.00	-50.0^a	-50.0^a	-50.0^a	-50.0^a
.01	-41.9	-41.6	....	-42.2
.05	-32.8	-31.1	-32.8	-31.6
.10	-23.1	-23.5	-26.0	-22.6
.20	-10.0	-12.5	-20	-8.5
.35	-1.3	-0.3	....	5.8
.40	2.3	4.0	-4	....

[a] Taken from the results of Randall and Rossini.[19]

Discussion of Results

Comparison of the Measured Heats of Dilution with Other Calorimetric Work.

—Several measurements were made at 25° in the same concentration range as that covered by Lange and Streeck.[9] Agreement between these independent measurements was quite satisfactory as shown in Table V.

TABLE V

m_1	m_2	ΔH cal./mole Na$_2$SO$_4$ This research	Calcd. from smooth data of Lange and Streeck
0.1005	0.0006778	-172.8 ± 1.8	-172
.1005	.001351	-150.7 ± 1.6	-150
.02525	.0001705	-196.6 ± 2.2	-191
.02525	.0003401	-181.5 ± 2.5	-179.5

The only additional data which are of any appreciable value for comparison are the results of Plake.[21] Plake measured values for the intermediate heats of dilution of sodium sulfate in the concentration range between 0.5 and 0.0005 molal in the neighborhood of 20°. Unfortunately, his measurements were not made at a constant temperature and, in general, the experimental conditions were less carefully controlled than in this research. His results have been corrected to 20° and are included in Fig. 2. A "point-to-point" plot of his data was made and this plot was made coincident at the very low concentrations with the measurements of this research so that discrepancies arising from different methods of extrapolation would be eliminated. Figure 2 shows that the results of Plake are slightly more negative (average of 6 cal./mole) than those of this investigation. However, the agreement is reasonably good considering the wide scattering of Plake's data.

Comparison of Calorimetric and Electrometric $\bar{L}_2$'s.—Data for the heat contents of sodium sulfate solutions have been obtained by Harned and Hecker[22] by measurements on the temperature coefficients of appropriate cells. Results of the two series of determinations are given in Table VI. The results of the two methods are made coincident at a concentration of 0.1 m, so as to eliminate

TABLE VI

COMPARISON OF $\bar{L}_2$ VALUES

m	25°C. This research	25°C. Harned and Hecker	20°C. This research	20°C. Harned and Hecker	15°C. This research	15°C. Harned and Hecker
0.05	255	182	178	79	83	-19
.10	165	(165)	28	(28)	-104	(-104)
.20	-59	-100	-300	-267	-490	-429
.40	-614	-565	-795	-812	-1143	-1054

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[20] T. F. Young and J. S. Machin, THIS JOURNAL, **58**, 2254 (1936).

[21] E. Plake, *Z. physik. Chem.*, **162A**, 257 (1932).

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

discrepancies arising from the different methods of extrapolation.

Harned and Hecker give as the precision of their measurements approximately ±50 cal./mole. The inference which may be drawn from Table VI is that the results of Harned and Hecker at 0.05 *m*. are in error and that the cell in this concentration range does not function well. At the higher concentrations the agreement is as good as could be expected.

Comparison of Calorimetric and Electrometric C_{p_2}'s.—Making use of the second temperature derivative of their cell measurements, Harned and Hecker[22] computed the heat capacities of sodium sulfate solutions. Also, Randall and Rossini[19] have determined these heat capacities by direct calorimetric means. Results of these two investigations together with those of this research are given in Table IV.

Comparison of the ΦL_2 Results with Theory.—Equations (1) to (3) may be used to determine the limiting value of the slope ($d\,\Phi L_2/dm^{1/2}$) at the three temperatures. These quantities are compared with values calculated[23,24] from the Debye–Hückel theory[6,7] in Table VII. The dielectric constant data required for the calculation of the limiting slopes were taken from the results of Wyman.[25]

TABLE VII

COMPARISON OF EXPERIMENTAL AND THEORETICAL LIMITING SLOPES FOR HEAT CONTENTS

t, °C.	Experimental	Theoretical
25	2418	2473
20	2193	2255
15	1803	2020

Table VII shows about the type of agreement that has been noted in other cases involving 1–2 type salts.[5] The relatively large discrepancy at 15° is not surprising since the experimental difficulties are considerably greater at this temperature than at the higher temperatures. Furthermore, for a given concentration deviations from the limiting law increase as the temperature decreases so that effectively the measurements at 15° have not been extended to as great dilutions as have the measurements at 20 and 25°.

Comparison of the $\bar{C}_{p_2}$ Results with Theory.—The Debye–Hückel theory predicts a linear dependence of $\bar{C}_{p_2} - \bar{C}^0_{p_2}$ on $m^{1/2}$

$$\bar{C}_{p_2} - \bar{C}^0_{p_2} = Am^{1/2}$$

Here the slope, A, is a complex function of a number of universal constants, the dielectric constant and the first and second derivatives of the dielectric constant with temperature. Because of the necessity of using the second derivative of the dielectric constant, the theoretical slope, as colculated, is probably not very accurate. Table VIII shows the values of A which were obtained from several different types of measurements as compared with the calculated theoretical value. The theoretical limiting slope has been calculated using LaMer and Cowperthwaite's[26] correction of the equation originally given by Randall and Rossini.[19]

TABLE VIII

COMPARISON OF EXPERIMENTAL AND THEORETICAL SLOPES FOR HEAT CAPACITIES

Source	A (slope)
Theory ($D = f(T)$ by Wyman[25])	69
Harned and Hecker[22]	74
Randall and Rossini[19]	76
This research (Eq. 16)	84

The errors associated with the slopes of Table VIII are so large that the discrepancies are probably without significance. In general, the results for sodium sulfate appear to be in as good agreement with theory as was the earlier work on sodium chloride.[3]

Summary

Intermediate heats of dilution of aqueous sodium sulfate solutions have been measured over the concentration range from 0.4 to 0.0001 molal at 15 and 20° and from 0.4 to 0.1 molal at 25°. Using the chord-area method in the extremely dilute range the measurements have been extrapolated to obtain values for the apparent relative molal heat contents.

The relative partial molal heat contents and partial molal heat capacities have been calculated for the concentration and temperature ranges of the measurements.

Results of this investigation appear to be in reasonable agreement with existing data. The apparent relative molal heat contents and partial molal heat capacities have been shown to approach the behavior predicted by the Debye–Hückel theory at very low concentrations.

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