

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## THE RELATIVE HEAT CONTENTS OF THE CONSTITUENTS OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

BY T. F. YOUNG AND O. G. VOGEL

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The complete evaluation of activity coefficients from freezing point measurements is dependent upon the determination of relative partial molal heat contents. The data available for their evaluation are neither as extensive nor as accurate as desirable. In this paper are presented an examination of previously published data for aqueous sodium chloride solutions at 25°, a few new experimental determinations, a convenient method for utilizing a combination of heat of solution and heat of dilution data, and finally the results of new calculations.

The data first employed for the evaluation of relative partial molal heat contents of sodium chloride were those of Randall and Bisson.<sup>1</sup> They measured a series of heats of dilution from about 6.1 *m* to 0.41 *m* and the heat of solution of sodium chloride in sufficient water to produce compositions between 0.13 *m* and 0.54 *m*. Later Wüst and Lange<sup>2</sup> measured heats of solution between 0.43 *m* and 5.6 *m* and with a few heats of dilution extended their data to about 6.1 *m*. More recently Lipsett, Johnson and Maass<sup>3</sup> determined many heats of solution at both 20 and 25°. They made one dilution between 0.173 *m* and 0.0284 *m*.

Because the work of Randall and Bisson and that of Wüst and Lange were not extended to sufficiently dilute solutions, a change in sign of the heat of dilution was not revealed. Later Lipsett, Johnson and Maass, and Lange and Messner,<sup>4</sup> observed that heat was evolved by the dilution of a very dilute solution of sodium chloride at 25°. Several years earlier Pratt<sup>5</sup> had observed similar behavior of several electrolytes. His curves for sodium chloride exhibit evidence of the reversal phenomenon.

**Examination and Treatment of Previous Data.**—For comparison, the three series of heat of solution data were represented by separate plots. The *experimental* values reported in the first paper of Lipsett, Johnson

<sup>1</sup> Randall and Bisson, *THIS JOURNAL*, **42**, 347 (1920).

<sup>2</sup> Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

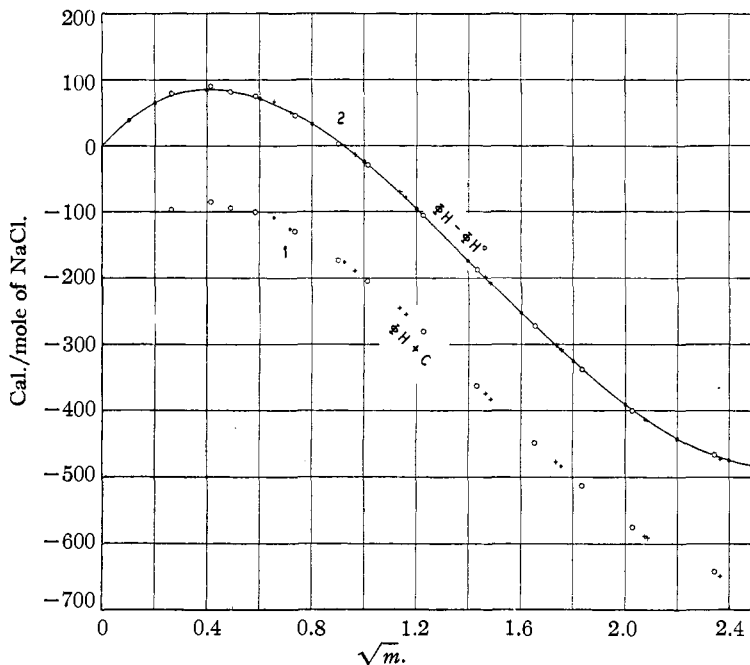
<sup>3</sup> (a) Lipsett, Johnson and Maass, *THIS JOURNAL*, **49**, 925 (1927); (b) **49**, 1940 (1927).

<sup>4</sup> (a) Lange and Messner, *Naturwissenschaften*, **15**, 521 (1927); (b) *Z. Elektrochem.*, **33**, 431 (1927).

<sup>5</sup> Pratt, *J. Franklin Inst.*, **185**, 663 (1918); *cf.* Thomsen, "Thermochemistry," Longmans, Green and Co., London, 1908, p. 178. Thomsen reported evolution of heat for the dilution of his 0.28 *m* solution, but the results of modern workers indicate that the opposite effect should have been observed.

and Maass were multiplied by 0.9995 to correct them in accordance with the second report of these authors and to convert them to 15° calories.

The experiments of Wüst and Lange and of Lipsett, Johnson and Maass were first compared. The difference between the two series was nearly constant. Since absolute values are not required for the determination of relative partial molal properties, one curve was superimposed upon the other and adjusted until the two appeared to be as nearly coincident as the data would permit. Appropriate constants, one of which was entirely arbitrary, were then added to the data in each series so that they could be represented on one plot. Curve 1 (indicated only) of Fig. 1 exhibits the satisfactory agreement of the relative values obtained from the two series.



+, Wüst and Lange; O, Lipsett, Johnson and Maass; ●,  $\int S dm^{1/2}$ .  
 Fig. 1.—Curve 1 (indicated) represents experimental determinations of the heat absorbed during the solution of one mole of sodium chloride, plus an arbitrary constant; the data are those of Lipsett, Johnson and Maass plus a convenient constant, -1100, and those of Wüst and Lange, -1108. Curve 2,  $\phi H - \phi H^\circ$  as determined by integration of the S curve, Fig. 2, plotted with the data of Lipsett, Johnson and Maass -924 and those of Wüst and Lange -932.

The heat of solution data calculated by Randall and Bisson were very different from the others, but that portion of their curve corresponding to the composition range in which they actually made solution experiments

is in good agreement with the measurements of Wüst and Lange. These data will be discussed after the significance and use of the curve has been considered.

The heat absorbed during the solution of one mole of sodium chloride,  $\Delta H$ , differs from the apparent molal heat content,  $\phi H$ , by the heat content of one mole of solid sodium chloride,  $H_2$

$$\phi H = \Delta H + H_2 \quad (1)$$

Curve 1, Fig. 1, therefore represents the apparent molal heat content plus a constant,  $C$ .

The  $\sqrt{m}$  was chosen as abscissa in Fig. 1, so that the slope of the curve would approach a finite value as  $m$  approaches zero. Investigations of the solubilities of salts in very dilute aqueous solutions of other salts have demonstrated that the activity coefficients,  $\gamma$ , of many strong electrolytes are nearly linear functions of  $\sqrt{m}$  in very dilute solutions, and that  $d\gamma/d\sqrt{m}$  approaches a finite limit as  $m$  approaches zero. For this to be true at more than one temperature  $d(\phi H)/d\sqrt{m}$  must approach either zero or a finite value. Randall and Rossini's<sup>6</sup> heat capacity measurements of sodium chloride solutions have established that this slope has a temperature coefficient and cannot in general be zero.

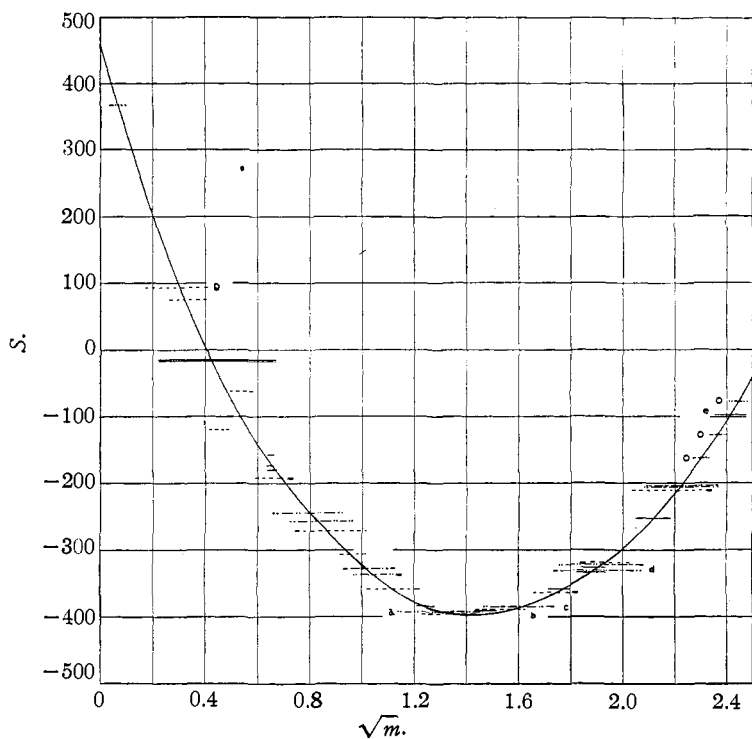
**The Derivative Curve.**—Customary graphical methods of differentiation are not convenient for the precise manipulation of both heat of solution and heat of dilution data. Figure 2 illustrates the method employed for determination of the slope,  $S \equiv d(\phi H)/d\sqrt{m}$ , of Curve 1, Fig. 1. Between any two values of  $\sqrt{m}$ , the average of the slope is  $\Delta(\phi H)/\Delta\sqrt{m}$ . The value of  $\Delta(\phi H)$  may be calculated directly from the heat of dilution of one mole of sodium chloride or from the difference in two heats of solution. The average values of the slope,  $S$ , are equal to the slopes of chords between corresponding points of Curve 1, Fig. 1.

Average values of  $S$  were determined from all of the data in the two series represented on Curve 1 and from one dilution experiment of Lange and Messner. These were plotted as lines drawn between corresponding values of  $\sqrt{m}$ . The true derivative curve should pass through each chord so that the two areas enclosed between the curve, the chord and imaginary vertical lines drawn through the ends of the chord, are equal.

Comparison of chords revealed the source of differences between the data reported by Randall and Bisson and by subsequent workers. The chords calculated from Randall and Bisson's measurements fell erratically on both sides of the curve, Fig. 2. The errors of several dilution experiments accumulated and affected the estimated form of their heat of solution curve. As a result, heat of solution data tabulated by those authors for large values of  $m$  are in error whereas actual solution measurements and

<sup>6</sup> Randall and Rossini, *THIS JOURNAL*, 51, 323 (1929).

the corresponding tabulations for dilute solutions agree well with the data of Wüst and Lange.



· · · · ·, Wüst and Lange; · · · · ·, Lange and Messner; - - - - -, Lipsett, Johnson and Maass; ———, Young and Vogel.

Fig. 2.—The curve represents  $S = d(\phi H)/d\sqrt{m}$ . Each horizontal line represents an experimental determination of  $\Delta(\phi H)/\Delta\sqrt{m}$  through the range indicated by the terminal abscissas of the line. The data of Lange and Messner and of Young and Vogel were obtained from dilution experiments. Most of the chords calculated from the work of Wüst and Lange and of Lipsett, Johnson and Maass represent differences in heats of solution. The few obtained from dilution measurements are distinguished by a symbol, D. Two chords of Wüst and Lange were omitted from the plot because they were nearly coincident with others designated, respectively, a and c. Similarly, chords of Young and Vogel were omitted because of proximity to those marked a, b, c and e. Two were omitted at d.

Since chords calculated from the early work of Randall and Bisson could not aid in locating the derivative curve, they were not added to the plot, Fig. 2. This somewhat arbitrary procedure required further justification. Furthermore in certain regions of the graph additional chords were desirable. Because heats of dilution yield directly the desired average slopes, they were determined experimentally.

### Experimental Procedure

The calorimeter is illustrated in Fig. 3. A silvered Dewar flask, D, of about one liter capacity was cemented with litharge and glycerin to a metal ring, R, to which was bolted the calorimeter cap, F. This cap was provided with five vertical tubes, one for each of the following: a stirrer, S; a heater, H; a thermel, T; a bulb, B; and a bulb crushing device, C. Each tube was equipped with a tight-fitting rubber tube, cotton packing moistened with oil, or with an oil seal. Corrosion was prevented by a coating of paraffin on various metal parts.

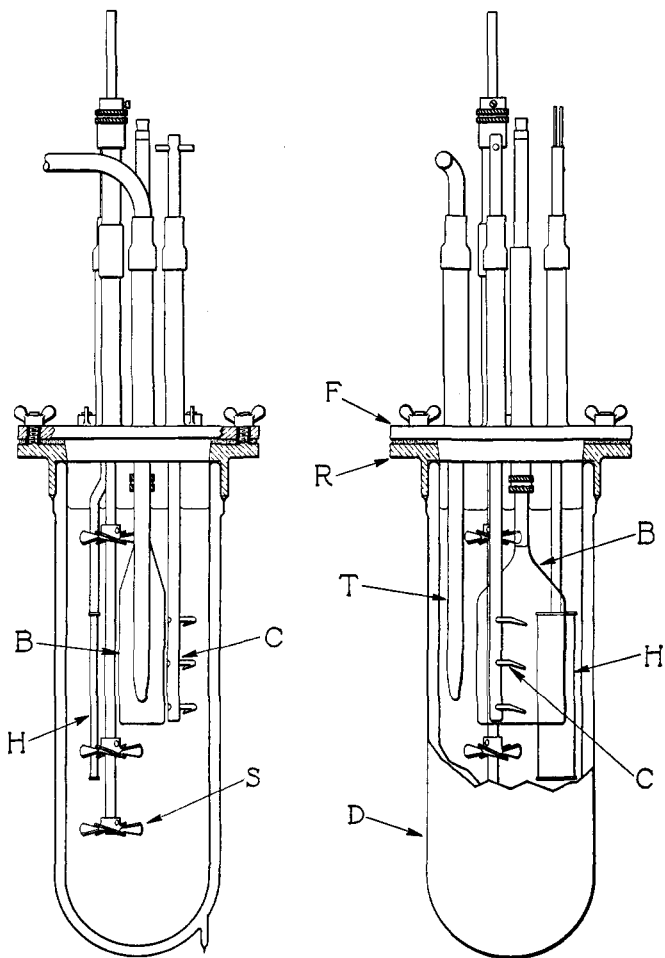


Fig. 3.—The calorimeter.

The bulbs were very thin-walled Pyrex glass vessels of 75–85 cc. capacity. During each dilution experiment, a bulb was broken by the manual rotation of the crushing device. The heat produced by the mixing process was measured several times. When there was water both inside and outside the bulb, about 0.07 calorie was produced. This corresponds to a temperature rise of about  $0.00009^{\circ}$ .

The stirrer was driven at about 500 revolutions per minute by a synchronous motor. Before each dilution the temperature of the liquid in the calorimeter was allowed to become practically constant. The equilibrium attained was about  $0.2^{\circ}$  above the surroundings.

The core of the calorimeter heater was a mica strip wound with constantan wire. It was enclosed in a tight-fitting metal sheath separated from the core by thin sheets of mica.

Current was supplied by a large storage battery. For several minutes before it was used, it was permitted to discharge through a coil, the resistance of which was nearly equal to that of the heater. During a customary three-minute heating interval the current, of about 0.04 ampere, varied but a few hundredths of one per cent.

Current was determined during each heating period from a measurement of the potential drop across a standard 0.1-ohm resistance. The length of the period was measured by a stop watch which had been compared with an accurate clock.

One or more heating periods (usually two) followed each mixing process. When a steady cooling rate had been established after the final period, current was again allowed to flow through the heater and was measured as before. With the potentiometer and standard 1 and 10,000 ohm resistances, the potential drop across the heater was also determined. These measurements revealed a variation, throughout the whole work, of only about 0.03% in the resistance of the heater.

Two copper-constantan thermels were constructed in accordance with many of the recommendations of White.<sup>7</sup> Because they were used principally for the determination of the ratio of successive temperature changes, great care in calibration and in several details of construction was not essential. Comparison with a mercury thermometer calibrated by the Bureau of Standards was sufficient for the determination of the temperature of the calorimeter contents. One of the thermels which contained twenty-four pairs of wires produced a galvanometer deflection somewhat greater than one centimeter per microvolt. The precision of reading was about 0.02 microvolt, corresponding to approximately  $0.00002^{\circ}$ . One end of the thermel dipped into the calorimeter, the other into a silvered Dewar bulb which was placed near the calorimeter in a thermostat.

The thermostat was controlled by a large mercury regulator. Its precision was investigated with a thermel, one end of which was immersed as usual in its Dewar bulb. The other end was exposed directly to the thermostat. No fluctuations greater than two thousandths of a degree were detected over periods of many minutes. Inside the calorimeter, fluctuations were very much smaller.

The e. m. f. produced by the thermel was determined each minute during the periods preceding the breaking of the bulb and before and after each heating interval. These values were plotted as functions of time and the appropriate linear portions of the plot were extrapolated to lines representing, respectively, the instant of breaking the bulb, and the center of each electrical heating period. From the plot, the e. m. f. change produced by each operation was ascertained. More elaborate methods for the estimation of thermal leakage were not justified.

The electrical energy required for an increase of one volt in the thermel e. m. f. was computed for each heating interval. There was no significant variation in successive values of this ratio. The heat of mixing was computed by multiplying this ratio, calories/volt, by the change in thermel e. m. f. produced by the mixing process.

**Materials.**—Concentrated solutions were prepared from fused sodium chloride and distilled water. They were analyzed gravimetrically, some by silver chloride precipitation, others by sodium chloride residue methods. In the latter determinations

<sup>7</sup> White, *THIS JOURNAL*, 36, 2292 (1914).

high temperatures were used in accordance with the observations of Richards and Hall.<sup>8</sup> Dilute solutions were prepared by the dilution of a stock solution about 5.5 molal.

### Experimental Results and Calculations

The small temperature changes produced precluded any attempt with available equipment to obtain a precision much better than one or two in a hundred. The dilution of solutions about 0.45 molal produced lowerings of only about 0.0002°. Nevertheless the average deviation from the mean of three such experiments represented an error in temperature measurement of only about 0.00002°. The precision of the experiments with concentrated solutions was limited by analytical methods. Because of the rapid variation of the slope,  $S$ , with concentration, an error of 0.1% in the analysis of a 6.1  $m$  solution of sodium chloride would correspond to an error of about 1% in the measured value of the chord.

The experimental results are in Table I. The first and second columns exhibit the initial and final values of the molality. The third column shows the temperature of the calorimeter contents before mixing and the fourth the approximate rise in temperature due to the mixing operation. The fifth contains  $\Delta(\phi H)$ , which is the heat (15° calorie) which would be absorbed per mole of sodium chloride in an isothermal dilution process at the temperature stated in the third column. In the sixth column is the value of  $\Delta(\phi H)$  calculated for 25°. The last column contains the chord for use in the determination of the  $S$  curve.

TABLE I

$\sqrt{m_1}$	$\sqrt{m_2}$	$t, ^\circ\text{C.}$	$\Delta t, ^\circ\text{C.}$	$\Delta\phi H_t$	$\Delta\phi H_{25^\circ}$	$\Delta\phi H / \Delta\sqrt{m}$
0.670	0.215	24.93	-0.0003	7.7	7.2	-16
.670	.219	24.93	-.0003	8.2	7.8	-17
.6645	.6328	24.97	-.002	5.07	5.06	-160
.6641	.6307	24.93	-.002	5.81	5.78	-173
.6719	.6374	24.94	-.002	6.23	6.20	-180
1.2769	1.2071	24.96	-.04	26.77	26.73	-383
1.4791	1.4063	25.04	-.05	28.60	28.64	-393
1.5168	1.4282	25.06	-.07	34.52	34.59	-390
1.6254	1.5382	25.02	-.08	33.87	33.89	-389
1.6248	1.5364	25.02	-.08	34.00	34.02	-385
1.7991	1.7110	24.99	-.09	31.55	31.54	-358
1.9365	1.8199	25.21	-.12	38.51	38.85	-333
1.9365	1.8319	25.27	-.11	34.19	34.57	-331
1.9365	1.8338	25.16	-.11	33.73	33.96	-331
1.9365	1.8374	25.32	-.10	31.93	32.36	-326
2.1758	2.0432	25.07	-.13	33.36	33.46	-252
2.4789	2.3377	25.33	-.07	13.68	14.22	-100.7
2.4789	2.3488	25.31	-.06	12.27	12.76	-98.0
2.4789	2.3522	25.09	-.06	12.17	12.31	-97.1

<sup>8</sup> Richards and Hall, *THIS JOURNAL*, **51**, 709 (1929).

The value of  $\Delta(\phi H)$  at 25° (column 6) was calculated from the corresponding quantity at the temperature of observation by means of the apparent molal heat capacity,  $\phi C$ , which is the temperature coefficient of  $\phi H$ .

$$\phi C = d(\phi H)/dT \quad \Delta(\phi C) = d(\Delta(\phi H))/dT \quad (2)$$

For the purpose of the calculation,<sup>9</sup> a plot was prepared of  $\phi C$  versus  $\sqrt{m}$ . The data of Randall and Rossini were supplemented by  $\phi C$  data calculated from differences in the heats of solution determined by Lipsett, Johnson and Maass for 20 and 25°. Though these values of  $\phi C$  were merely averages for the five degree interval, they were sufficient for a satisfactory extension of the 25° curve.

**Final Construction of Differential Curve.**—After the new data had been added to the plot, a preliminary curve was carefully drawn in accordance with all of the chords. The curve was then tested and slightly readjusted as follows: the first derivative of the preliminary  $S$  curve was determined at numerous values of  $\sqrt{m}$ . For this purpose the tangentometer described by E. v. Harbou<sup>10</sup> was used. From a plot of  $S'$  the next higher derivative,  $S''$ , was estimated. When  $S''$  may be considered constant over the range covered by any chord, the following equation may be used for the calculation of the difference between  $P$ , a point on the curve directly above the center of any chord, and  $\bar{P}$ , the ordinate of the chord itself.

$$P - \bar{P} = -(S''/24)(\Delta\sqrt{m})^2 \quad (3)$$

Values of  $P$  were calculated for all of the chords and were plotted on a large graph. Since each chord was represented by a point, all of the data could be placed, without conflict, upon a single sheet of paper, and it was less difficult to draw the  $S$  curve with due regard to all of the data than on the original chord plot. The new diagram served as a convenient aid for testing and improving the fundamental chord plot.

Further confirmation of Fig. 2 in the region between  $\sqrt{m} = 0.4$  and 1.5 was obtained from the work of Richards and Rowe, who determined a few heats of dilution at approximately 15 and 20°. Chords for 25°, calculated from their 20° data by means of values of  $\phi C$ , read from a curve similar to that discussed above,<sup>11</sup> are in satisfactory agreement with the data represented in Fig. 2.

The position of the  $S$  curve in the neighborhood of  $\sqrt{m} = 0.05$  was largely determined by a measurement made by Lange and Messner. Except for the portion to the left of that chord, the curve seems to be sufficiently precise for application to thermodynamic problems.

<sup>9</sup> Cf. Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

<sup>10</sup> Harbou, *Z. angew. math. Mechanik*, **10**, No. 6 (1930).

<sup>11</sup> This curve, determined from the measurements of Lipsett, Johnson and Maass, represented average values of  $\phi C$  between 20 and 25°.



Extrapolation into the region of great dilution is, of course, uncertain.<sup>12</sup> However, an error as large as 200 in the estimated average value of  $S$  between  $\sqrt{m} = 0$  and  $0.05$  would introduce an error of only 10 cal./mole into calculations of  $\phi H$ .

Column 2 of Table II contains values of  $S$  read from the large plot. The curve between  $\sqrt{m} = 0$  and  $0.4$  is well represented by the following empirical equation<sup>13</sup>

$$S = 461.3 - 1427.6\sqrt{m} + 704.2m \quad (4)$$

$\sqrt{m}$	$S$	$\phi H - \phi H^\circ$	$\bar{L}_1$	$\bar{L}_2$
0.05	392	21	-0.0004	31
.1	325	39	-.0029	56
.15	263	54	-.008	74
.2	204	66	-.015	86
.3	96	81	-.023	95
.4	3	85	-.002	86
.5	-76	82	+.086	63
.6	-141	71	.27	29
.7	-196	54	.61	-14
.8	-244	32	1.13	-65
.9	-286	6	1.88	-123
1.0	-322	-25	2.90	-186
1.2	-377	-95	5.9	-321
1.4	-398	-173	9.8	-452
1.6	-386	-252	14.2	-561
1.8	-352	-326	18.5	-643
2.0	-297	-391	21.4	-688
2.1	-259	-419	21.6	-691
2.2	-215	-443	20.6	-679
2.4	-108	-475	13.5	-605
2.45	-76	-480	10.1	-573

In the third column of Table II are values of the differences between  $\phi H$ , the apparent molal heat content, and  $\phi H^\circ$ , the limit approached by

<sup>12</sup> For a summary of the important investigations of this problem by Lange and his co-workers, see Lange and Robinson, *Chemical Reviews*, 9, 89 (1931). See also Robinson, *THIS JOURNAL*, 54, 1311 (1932). At the time this paper was written the precise data of Robinson had not been published. Chords calculated from his measurements are in good agreement with Fig. 2 and contribute greatly to the reliability of extrapolation.

<sup>13</sup> According to the theory of Debye and Hückel  $dS/d\sqrt{m}$  is related to ionic size [see Bjerrum, *Trans. Faraday Soc.*, 23, 445 (1927), Equation 4]. From the second derivative, with respect to  $\sqrt{m}$ , of Bjerrum's equation 4, an expression was easily obtained for the limit of  $dS/d\sqrt{m}$  as  $\sqrt{m} \rightarrow 0$ . This was equated to a numerical value derived from equation (4). According to the resulting relation, the mean effective ionic diameter is  $4.7 \times 10^{-8}$  cm. This is the expected order of magnitude in spite of certain approximations in Bjerrum's equation. If theory can be used as a guide, our extrapolation is probably not far from correct.

$\phi H$  as  $\sqrt{m}$  approaches 0. These tabulated values of  $\phi H - \phi H^\circ$  were obtained from the equation

$$\phi H - \phi H^\circ = \int_0^{\sqrt{m}} S d\sqrt{m} \quad (5)$$

For  $\sqrt{m} < 0.4$  this becomes

$$\phi H - \phi H^\circ = 461.3 m^{1/2} - 713.8 m + 235 m^{3/2} \quad (6)$$

Mechanical integration was employed for the determination of values of  $\phi H - \phi H^\circ$  which were not calculated from equation 6.

**The Integral Curve.**—A plot of  $\phi H - \phi H^\circ$  was constructed and compared with the curve representing the heat of solution data of Lipsett, Johnson and Maass. The latter curve, according to Equation 1, represents  $\phi H - H_2$ . The difference in the ordinates of the two curves is therefore  $\phi H^\circ - H_2$ , which is the heat absorbed during the solution of one mole of sodium chloride in an infinite amount of water. One curve was placed over the other and shifted until the two were as nearly coincident as possible. From the amount of the shift,  $\phi H - H_2$  was determined as 924. In a similar manner Wüst and Lange's data yielded 932.

From each of the two series of experimental data, values of  $\phi H - \phi H^\circ$  were calculated by subtraction of these respective constants. They were compared on Curve 2, Fig. 1, with the direct results of the integration of the  $S$  curve.

**The Relative Heat Contents.**—According to Lewis and Randall's convention<sup>14</sup> the difference between  $\bar{H}$ , the partial molal heat content of any constituent and  $\bar{H}^\circ$ , the partial molal heat content of that substance in its reference state, is termed the "Relative Heat Content."

When the infinitely dilute solution is chosen as the reference state of both constituents, the relative heat content of the solvent,  $\bar{L}_1$ , and of the solute,  $\bar{L}_2$ , may be calculated from the following equations, 7 and 8. These are easily obtained from formulas 4-D of each of the tables in the preceding paper.

$$\bar{L}_1 = \bar{H}_1 - \bar{H}^\circ_1 = -\frac{m^{1/2}S}{2(55.51)} \quad (7)$$

$$\bar{L}_2 = \bar{H}_2 - \bar{H}^\circ_2 = \phi H - \phi H^\circ + \frac{m^{1/2}S}{2} \quad (8)$$

Combinations of these with equations 4 and 6 give 9 and 10, valid for values of the  $\sqrt{m}$  less than 0.4.

$$\bar{L}_1 = -4.16 m^{3/2} + 12.86 m^2 - 6.34 m^{5/2} \quad (9)$$

$$\bar{L}_2 = 692 m^{1/2} - 1428 m + 587 m^{3/2} \quad (10)$$

The new determinations of  $\bar{L}_1$  and  $\bar{L}_2$  are exhibited in Table II.<sup>15</sup> Those corresponding to values of  $\sqrt{m} < 0.4$  were computed from equations 9

<sup>14</sup> Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York, 1923, pp. 351 and 354.

<sup>15</sup> For similar tables of properties of dilute solutions of sodium chloride at 18° see Rossini, *Bur. Standards J. Research*, 6, 791 (1931).

and 10. The others are the results of substitution in equations 7 and 8 of the data listed in Columns 2 and 3.

Lewis and Randall's<sup>16</sup> calculations of the activity coefficients of sodium chloride depended upon the classic  $\bar{L}_1$  data of Randall and Bisson. The data of Table II, together with the new heat capacity data of Randall and Rossini and of Lipsett, Johnson and Maass, were employed in a recalculation of activity coefficients. In spite of important differences between the above and the original values of  $\bar{L}_1$  the results of the new calculations differ so little from the original ones that we refrain from giving them.

It seems probable however that work now being performed at other temperatures will introduce more important corrections. Some preliminary measurements<sup>17</sup> indicate that the variation of  $\phi H - \phi H^\circ$  between 25 and 0° is much larger than is indicated by heat capacity data at 25°.

### Summary

Data applicable to the calculation of the relative heat contents of the constituents of aqueous sodium chloride solutions have been assembled. They have been critically examined by a method convenient for their inter-comparison and for differentiation. The collected information has been supplemented by new measurements.

From all of the available data, the relative partial molal heat contents have been calculated for 25°. Activity coefficients calculated with the aid of these values are not very different from those originally calculated by Lewis and Randall.

<sup>16</sup> Ref. 14, p. 351.

<sup>17</sup> J. F. Chittum, Dissertation, University of Chicago.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WESTERN RESERVE UNIVERSITY]

## THE SYSTEM CALCIUM CHLORIDE-MAGNESIUM CHLORIDE-WATER<sup>1</sup> AT 0, -15 AND -30°

BY C. F. PRUTTON AND O. F. TOWER

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### Introduction

Sodium, calcium and magnesium chlorides occur together in sea water, most salt brines and salt deposits, and provide a commercial source of the above chlorides. In connection with the separation of these chlorides, data on the quaternary system calcium chloride-magnesium chloride-sodium chloride-water are of importance.

<sup>1</sup> Presented by C. F. Prutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Western Reserve University, 1928.