

conclusions: first, the increments to TDF from this additional complexity of the model would be small (of the order of 0.004); second, the increments would, however, be more strongly dependent on halogen atom mass than the three genuine vibrations considered above; third, in aggregate, the additional complexities would not account for the degree of sensitivity to halogen atom mass indicated experimentally for either TIF or TDF.

For a consistent reaction coordinate motion, then, the obvious models fail to reproduce the experimental results. What of the possibility that each of the reactions actually involves a somewhat different reaction coordinate motion? If one insists upon linear or nearly linear transition states, one's freedom in calculation is limited mostly to the juggling of force constants and bond distances, differences in reaction coordinate motion being described essentially as differences in applicable values of a parameter such as the ρ of the Bigeleisen-

Wolfsberg treatment. Comparison of Table IV and the first column of Table III leads us to conclude that one might by this means bring the calculations for the methyl chloride and methyl bromide reactions into reasonable consonance, but TIF for the cyanization of methyl iodide is just too large to fit into such a picture. Departures from linearity in the configurations of the activated complexes result in lowering the calculated values of TIF; but, the shifts are moderate even for CN^- attack at 90° , and no better correspondence between calculated and apparent experimental values of TIF can be achieved by the assumption of halogen dependence of the single ABC. The rather large scatter in the data furnishes no refuge from these conclusions.

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The Thermodynamic Properties of High Temperature Aqueous Solutions. I. Standard Partial Molal Heat Capacities of Sodium Chloride and Barium Chloride from 0 to 100° ¹

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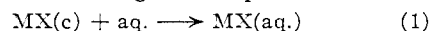
A sensitive submarine type solution calorimeter using electronic amplification and automatic recording has been constructed to measure heats of solution up to 100° . Nearly 300 integral heats of solution of sodium chloride and barium chloride have been determined at various concentrations from near 0 to 95° . From the extrapolated values of the heats at infinite dilution, values of $\bar{C}_{p_2}^0$ as a function of temperature have been calculated for these salts. The observed heat capacities show maxima between 50 and 70° and then decrease as the temperature is further increased.

Introduction

Within the past several years there has been an increasing interest in the thermodynamic properties of aqueous solutions at higher temperatures, both from a practical and theoretical point of view. One of the best methods of obtaining these properties at higher temperatures is to extend the known thermodynamic functions at 25° by use of partial molal heat capacities over the desired temperature range. Usually, it is the standard state functions (*i.e.*, at infinite dilution) that are desired; therefore, it is the partial molal heat capacity at infinite dilution and a function of temperature which is of real interest. Unfortunately, only a few reliable values have been reported at temperatures much above 25° .³⁻⁶ Furthermore, what values are available were obtained from extrapolations derived from specific heat measurements of concentrated solutions. The reliability of extrapolations from such concentrations to infinite dilution is subject to question. Indeed, even the

theoretical limiting slope for Φ_{C_p} at 25° is uncertain by 25% for a 1:1 electrolyte.⁷ Gucker⁸ has suggested that more reliable values of $\Phi_{C_p}^0$ can be obtained by combining the temperature coefficients of the relative apparent molal heat contents, Φ_L , with apparent molal heat capacities of more concentrated solutions. Harned and Owen⁹ have suggested that the use of the temperature coefficient of the relative heat content can lead to better values for $\bar{C}_{p_2}^0$. Gulbransen and Robinson¹⁰ in still another method have combined the heats of dilution, $-\Phi_L$, at two temperatures with the integral heats of solution at the same two temperatures to calculate $\bar{C}_{p_2}^0$ for $\text{NaCl}(\text{aq.})$ at 22.5° .

The approach used in this investigation is a slight variation on the latter method and will hereafter be referred to as the "integral heat method." It involves only heat-of-solution measurements. The amount of heat released when a solute is dissolved in water according to the equation



(1) Supported in part by a grant from the National Science Foundation.

(2) From the Ph.D. Thesis of Cecil M. Criss, Purdue University, 1961.

(3) M. Eigen and E. Wicke, *Z. Elektrochem.*, **55**, 354 (1951).

(4) E. Wicke, M. Eigen and Th. Ackermann, *Z. physik. Chem. NF*, **1**, 340 (1954).

(5) Th. Ackermann, *Disc. Faraday Soc.*, **24**, 180 (1957).

(6) Th. Ackermann, *Z. Elektrochem.*, **62**, 411 (1958).

(7) E. A. Guggenheim and J. E. Prue, *Trans. Faraday Soc.*, **50**, 710 (1954).

(8) F. T. Gucker, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 680 (1949).

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958, p. 352.

(10) E. A. Gulbransen and A. L. Robinson, *J. Am. Chem. Soc.*, **56**, 2637 (1934).

can be expressed by

$$\Delta H_s = n_1 \bar{H}_1 + n_2 \bar{H}_2 - n_1 \bar{H}_1^0 - n_2 H_2 \quad (2)$$

where \bar{H}_1 and \bar{H}_2 are the partial molal heat contents of the water and solute, respectively, \bar{H}_1^0 is the heat content of pure water, H_2 is the heat content of the pure solute and n_1 and n_2 are the number of moles of water and solute, respectively. At infinite dilution

$$\Delta H_s^0 = n_2 \bar{H}_2^0 - n_2 H_2 \quad (3)$$

Over sufficiently small temperature intervals the temperature coefficient of this expression is

$$\Delta C_p^0 = n_2 \bar{C}_{p2}^0 - n_2 C_{p2} \quad (4)$$

where ΔC_p is the change in heat capacity of reaction 1 and C_{p2} is the heat capacity of the pure solute. Thus the problem is reduced to finding an accurate value for ΔH_s^0 at two temperatures.

Experimental

Apparatus.—The submarine calorimeter (hereafter referred to as laboratory calorimeter CS-1) was a 425 cc. glass dewar-type flask fitted with a standard taper joint and an evacuated stopper and contained a platinum resistance thermometer for temperature measurements. The glass stopper had three 23 cm. exit tubes, two of which were made from precision tubing from about two cm. above the top of the stopper.

One of these tubes contained the stirrer, the upper portion of which was made from a matching piece of precision bore tubing. The stirrer was hollow and contained a heating element in order to bring the calorimeter to the desired operating temperature. Two insulated metal slip rings were attached to the top of the stirrer and connected to the heating element so that the calorimeter could be simultaneously stirred and heated. The stirrer was driven by a synchronous motor at approximately 600 r.p.m.

The other precision bore tube contained the combined calibration heater and sample holder. The upper portion of this tube was also made from a matching precision bore tube. The sample bulbs were connected by rubber tubing to the lower end of the sample holder-heater. The bulbs could be broken by a vertical movement of the rod which caused the bulbs to be smashed on a small anvil which was fused to the bottom of the calorimeter.

The heating element of the calibration heater was made by winding about 80 inches of No. 36 manganin wire non-inductively around a six mm. Pyrex tube. This then was painted with "Glyptal" and baked for several hours. Four copper lead wires were attached: two No. 30 wires to carry the current and two No. 40 wires to measure the potential across the heater. The space inside the tubing was filled with silicone oil to conduct heat from the heating elements to the surroundings for both this heater and the rough heater previously mentioned.

The remaining tube in the stopper contained the platinum resistance thermometer which was adjusted so as not to touch the walls of the exit tube. The calorimeter was placed about 16 cm. below the surface of a bath thermostated to at least $\pm 0.002^\circ$. The modulus of the calorimeter under these conditions was about 1×10^{-3} cal. min.⁻¹ deg.⁻¹.

The resistance thermometer was connected to a standard Mueller bridge. This bridge was thermally and electrically shielded by specially constructed shielding and was internally calibrated. Corrections were applied to the resistances when necessary. In preliminary experiments, the output of the bridge was connected to a Leeds and Northrup, moving-coil, reflecting-type galvanometer which had an optical arrangement that gave a sensitivity of $1 \times 10^{-4}^\circ$. During the course of these measurements it was decided to use a d.c. linear breaker-type amplifier and recorder in place of the galvanometer. It was operated close to full gain and the output voltage attenuated by a voltage divider. A portion of this voltage was used to drive a four mv. recorder. The over-all gain was such that a 0.35 μ v. signal to the amplifier gave a full scale deflection of the recorder pen, resulting in a temperature sensitivity of $\sim 2 \times 10^{-6}^\circ$ C.

The power source for the calibration heater was a commercially available coulometric constant current source,

accurate to better than $\pm 0.1\%$. A mechanical timer built into the instrument provided time measurements to ± 0.1 second. The two No. 30 wires from the calibration heater were connected directly to the output of the current source and the two No. 40 wires from the heater were connected to a volt box so that periodic checks on the voltage drop across the heater could be made. All voltages were measured with a Leeds and Northrup type K-3 universal potentiometer. The current source was periodically calibrated by means of a 10,000 ohm standard resistor and potentiometer.

Corrections were made to the heat output of the heater caused in the slight difference in the resistance of the manganin wire at various calorimeter operating temperatures. Corrections were also applied for heat generated in the leads and the heat leak from the leads of the heater. The largest of these corrections was in the order of 0.2%.

Materials.—All water used in the measurements was prepared from ion-exchange repurified distilled water. The specific resistance of the water varied from 2.7 to 18.0 megohm-cm.

The BaCl₂ used in all measurements was J. T. Baker analyzed reagent, dihydrate. The specifications indicated that the greatest impurity did not exceed 0.03%, making it unnecessary for further purification, except for the removal of water.

Samples of NaCl were also J. T. Baker analyzed reagent and were used without further purification. Specifications indicated that the greatest impurity was 0.004% (including potassium).

All salt samples were dried over 400°, weighed into sample bulbs and then returned to the 400° oven for at least 8 hr. They were then removed, cooled in a desiccator and sealed under vacuum immediately. The stock supply was kept in the furnace and was removed only when weighing samples.

A drop of phenolphthalein on the salts indicated no apparent hydrolysis for NaCl. However, a slight pink coloration was observed with the BaCl₂, indicating a slight amount of hydrolysis, but it has been shown by using synthetic samples containing Ba(OH)₂ to be less than 0.1%.

Experimental Procedure.—Very thin-walled sample bulbs having a diameter of about 8 mm. and a stem about 2.5 cm. long were made from 7 mm. Pyrex tubing. The stem had a narrow neck near the base of the bulb. These bulbs were filled as described above and sealed under vacuum by melting the glass around the neck of the bulb with a very thin flame, with due care to avoid excessive heating of the sample.

For determinations above 25°, water was placed in the calorimeter at room temperature and then heated to the desired operating temperature by the rough heater and permitted to come to a uniform temperature a few hundredths of a degree below the equilibrium temperature. For temperatures below 25°, water was placed in the calorimeter near 0° and heated to operating temperature. For the lowest temperature, 0.02°, the water in the calorimeter was cooled further by inserting a long "U" shaped tube in the opening for the sample holder-heater through which Dry Ice cooled acetone was passed. When the calorimeter water was very close to 0°, the tube was removed and the sample holder-heater inserted in its proper place. The system was then permitted to remain for several hours until a uniform temperature was established.

The bridge was kept as close to balance as the last decade would permit, using the recorder (or galvanometer) to interpolate between unit resistances of the last decade. When a linear time-temperature drift line was observed, it was assumed that a uniform temperature gradient had been established and a determination was started. An electrical calibration generally preceded and followed each determination, except at the lowest temperature. At this temperature the chemical determination was made first and was then followed by two electrical calibrations. When heat was introduced into the calorimeter (either electrical or chemical), the bridge was balanced again to keep the recorder pen from going off scale.

A "best" straight line was drawn through the linear portion of each of the time-temperature curves and extrapolated to the time at which either the sample bulb was broken or the calibration made. The differences between these lines were always determined at the six-tenths rise time¹¹ and compared with a standard deflection obtained

(11) H. C. Dickinson, U. S. Bur. Standards Bull., 11, 189 (1914).

by moving the last decade of the bridge one unit, *i.e.*, a value of 0.0001 ohm. This standard deflection was an average of several values obtained before, during and after each run.

The amount of heat released¹² when the sample bulb was broken was divided by the number of moles of the sample dissolved to determine the integral heat of solution per mole, ΔH_s , for that particular concentration. In general, two or more determinations were made for a particular concentration and the results were averaged.

Calculations and Results

A procedure for extrapolating heat of solution data to infinite dilution has been proposed.⁷ The relative apparent molal heat content, Φ_L , can be expressed by an extension of the Debye-Hückel expression

$$\Phi_L = \frac{\nu}{2} \delta_H |Z_+ Z_-| I^{1/2} \left[(1 + I^{1/2})^{-1} - \frac{\sigma(I^{1/2})}{3} \right] - 2.303RT^2 \frac{dB}{dT} m\nu_+ \nu_- \quad (5)$$

where δ_H is the theoretical limiting slope, $\nu = \nu_+ + \nu_-$, ν_+ and ν_- are the number of positive and negative ions produced by dissociation of one molecule of electrolyte, Z_+ and Z_- are the charges on these respective ions, I is the ionic strength, $\sigma(I^{1/2})$ is a special function¹³ defined by

$$\sigma(I^{1/2}) = \frac{3}{I^{1/4}} \left[1 + I^{1/2} - (1 + I^{1/2})^{-1} - 2 \ln(1 + I^{1/2}) \right] \quad (6)$$

and B is a constant for the specific electrolyte. If the first term on the right side of equation 5 is subtracted from both sides and the left side plotted against molality, a straight line with the slope $-2.303RT^2 (dB/dT)\nu_+\nu_-$ should be obtained. For the purpose of extrapolating heats of solution to infinite dilution, this equation can be written as

$$\rho = \Delta H_s^0 - 2.303RT^2 \frac{dB}{dT} \nu_+ \nu_- m \quad (7)$$

where ΔH_s^0 is the integral heat of solution at infinite dilution

$$\rho \equiv \Delta H_s - \frac{\nu}{2} |Z_+ Z_-| \delta_H I^{1/2} \alpha \quad (8)$$

and

$$\alpha \equiv \left[(1 + I^{1/2})^{-1} - \frac{\sigma(I^{1/2})}{3} \right] \quad (9)$$

All the data for both BaCl_2 and NaCl were extrapolated to infinite dilution by plotting ρ as a function of m .

It is believed that this method of extrapolation to infinite dilution is superior to the use of \sqrt{m} plots. This is largely true because the extrapolation using a linear m scale can be made from more concentrated solutions, and the distance over which the extrapolation must be made is smaller than with a \sqrt{m} scale.

The extrapolations of ρ to infinite dilution were also carried out such that both $d\rho/dm$ and the temperature coefficients of ΔH_s^0 were a smooth function of temperature. In some cases this did not represent the best line that could be drawn through the

centers of the experimental points, but in all cases the extrapolations were consistent with the average errors involved in the heats. It should be noted that the extrapolations are also in agreement with the known heats of dilution at some temperatures.^{10,14}

The average values of ΔH_s at various concentrations and temperatures are listed in Tables I and II. The first column gives the number of individual determinations that are involved in determining an average value for the listed heats. Columns two and three list the average molality and \sqrt{m} . Column five gives the theoretical values that are subtracted from the observed heats in column four to obtain ρ values which then are listed in column six. The extrapolated value of the integral heat of solution at infinite dilution, ΔH_s^0 , for each temperature is listed with the data for that temperature.

It is of interest to note that the present integral heats of solution of NaCl at infinite dilution are in agreement, within experimental error, with most of the previously reported values. The heats of dilution of NaCl at 20 and 25° reported by Gulbransen and Robinson¹⁰ combine with the heats of solution at 20 and 25° reported by Cohen and Kooy¹⁵ to give 1,080 and 915 cal./mole for the integral heat of solution at infinite dilution.¹⁶ A similar treatment of the data of Lipsett, Johnson and Maass¹⁷ gives 1,072 and 918 cal./mole for the same quantities at 20 and 25°. Likewise, a similar treatment of the data of Wüst and Lange¹⁹ yields 926 cal./mole at 25°.

The integral heat of solution at infinite dilution and at 25° for BaCl_2 was found to be more negative than the commonly accepted value²⁰ of 3,160 cal./mole. However, when a BaCl_2 sample was permitted to be in contact with the laboratory air for a few minutes, ΔH_s^0 changed to $3,150 \pm 10$ cal./mole, which suggests that the values reported in this research are perhaps to be preferred.

Tables III and IV summarize the values of $\bar{C}_{p,0}$ evaluated from equation 4. The heat capacities for the anhydrous salts, $C_{p,2}$, are those reported by Kelley.^{21,22}

Although the values of $\bar{C}_{p,0}$ obtained by the integral heat method as used in this research repre-

(14) See Harned and Owen, ref. 9, p. 707.

(15) E. Cohen and J. Kooy, *Z. physik. Chem. (Leipzig)*, **139A**, 273 (1928).

(16) These values are the same, within the experimental error, as those calculated by Gulbransen and Robinson¹⁰ from the same data.

(17) S. G. Lipsett, F. M. G. Johnson and O. Maass, *J. Am. Chem. Soc.*, **49**, 1940 (1927).

(18) The dilution data of Gulbransen and Robinson¹⁰ and those derived from the heat of solution data of Lipsett, Johnson and Maass¹⁷ do not agree. Therefore, the dilution data of Gulbransen and Robinson were applied to the heat of solution of the most concentrated solution for which the dilution data were valid (*i.e.*, at $\sqrt{m} = 0.844$).

(19) J. Wüst and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925).

(20) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

(21) K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy. XI. Entropies of Inorganic Substances. Revision (1948) of Data and Methods of Calculation," U. S. Bureau of Mines, Bulletin 477, 1950.

(22) K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat-Content, Heat Capacity, and Entropy Data for the Elements and Inorganic Compounds," U. S. Bureau of Mines, Bulletin 584, 1960.

(12) Except at the highest temperature, there was no noticeable heat of bulb breaking.

(13) Tables of this function are listed in Harned and Owen, ref. 9, p. 176.

TABLE I

THE INTEGRAL HEATS OF SOLUTION AND ρ VALUES OF SODIUM CHLORIDE

No. of detns.	$m \times 10^3$ (moles/kg. H ₂ O) ^a	\sqrt{m}	ΔH_s (cal./mole)	$-\frac{\delta H_s}{T^{1/2}\alpha}$ (cal.)	ρ (cal./mole)
0.02°					
1	3.43	0.0586	1897	18	1879
3	9.24	.0961	1911 ± 21	28	1883 ± 21
1	13.27	.1152	1933	33	1900
3	19.16	.1384	1936 ± 14	39	1897 ± 14
$\Delta H_s^0 = 1905 \pm 8$ cal./mole					
5.00°					
4	3.43	0.0586	1705 ± 15	19	1686 ± 15
3	9.25	.0962	1665 ± 4	30	1635 ± 4
4	13.30	.1153	1689 ± 5	36	1653 ± 5
3	19.16	.1384	1674 ± 6	42	1632 ± 6
$\Delta H_s^0 = 1658 \pm 11$ cal./mole					
9.99°					
3	9.24	0.0961	1462 ± 10	33	1429 ± 10
2	19.14	.1383	1475 ± 2	46	1429 ± 2
$\Delta H_s^0 = 1440 \pm 5$ cal./mole					
15.00°					
1	9.24	0.0961	1280	35	1245
1	9.70	.0985	1282	36	1246
1	19.16	.1384	1288	49	1239
1	20.09	.1418	1281	51	1230
$\Delta H_s^0 = 1245 \pm 2$ cal./mole					
19.97°					
2	9.69	0.0984	1098 ± 9	39	1059 ± 9
2	20.06	.1416	1116 ± 11	55	1061 ± 11
$\Delta H_s^0 = 1071 \pm 8$ cal./mole					
25.00°					
3	1.45	0.0380	952 ± 33	17	935 ± 33
3	2.88	.0537	931 ± 18	24	907 ± 18
2	5.31	.0729	941 ± 15	32	909 ± 15
2	6.39	.0799	945 ± 47	37	908 ± 47
2	8.98	.0947	959 ± 2	41	918 ± 2
2	9.93	.0996	937 ± 6	43	894 ± 6
1	10.66	.1032	934	44	890
2	20.56	.1434	965 ± 5	59	906 ± 5
$\Delta H_s^0 = 914 \pm 5$ cal./mole					
34.96°					
1	0.899	0.0300	656	16	640
2	1.47	.0383	595 ± 13	20	575 ± 13
2	2.44	.0494	636 ± 27	26	610 ± 27
2	3.82	.0618	658 ± 9	32	626 ± 9
1	5.37	.0733	653	37	616
1	6.87	.0829	654	42	612
2	9.74	.0987	666 ± 3	49	617 ± 3
1	11.62	.1078	676	53	623
1	14.32	.1197	680	58	622
1	20.58	.1435	677	68	609
$\Delta H_s^0 = 615 \pm 6$ cal./mole					
45.00°					
2	3.68	0.0607	377 ± 7	36	341 ± 7
2	9.91	.0996	393 ± 2	57	336 ± 2
2	14.29	.1195	408 ± 2	67	341 ± 2
2	20.56	.1434	420 ± 2	80	340 ± 2
$\Delta H_s^0 = 340 \pm 2$ cal./mole					

TABLE I (continued)

No. of detns.	$m \times 10^3$ (moles/kg. H ₂ O) ^a	\sqrt{m}	ΔH_s (cal./mole)	$-\frac{\delta H_s}{T^{1/2}\alpha}$ (cal.)	ρ (cal./mole)
54.83°					
2	3.68	0.0607	124 ± 12	41	83 ± 12
2	9.95	.0998	146 ± 5	65	81 ± 5
2	14.25	.1194	154 ± 5	77	77 ± 5
2	20.62	.1436	167 ± 11	92	75 ± 11
$\Delta H_s^0 = 80 \pm 2$ cal./mole					
64.86°					
2	3.67	0.0606	-155 ± 5	47	-202 ± 5
2	9.90	.0995	-138 ± 5	74	-212 ± 5
2	14.04	.1185	-121 ± 4	88	-209 ± 4
1	20.49	.1431	-108	104	-212
$\Delta H_s^0 = -200 \pm 2$ cal./mole					
75.01°					
3	4.20	0.0648	-433 ± 15	57	-490 ± 15
2	9.91	.0996	-405 ± 2	85	-490 ± 2
2	14.41	.1200	-391 ± 2	101	-492 ± 2
3	20.30	.1425	-378 ± 23	119	-497 ± 23
$\Delta H_s^0 = -487 \pm 2$ cal./mole					
84.98°					
2	4.19	0.0648	-699 ± 13	65	-764 ± 13
2	9.93	.0996	-661 ± 2	97	-758 ± 2
2	14.39	.1200	-646 ± 6	115	-761 ± 6
2	20.33	.1425	-633 ± 3	135	-768 ± 3
$\Delta H_s^0 = -770 \pm 2$ cal./mole					
95.18°					
1	4.26	0.0652	-1039	74	-1113
2	9.94	.0997	-973 ± 2	110	-1083 ± 3
1	14.41	.1200	-957	131	-1088
2	20.35	.1427	-931 ± 3	154	-1085 ± 3
$\Delta H_s^0 = -1085 \pm 8$ cal./mole.					

^a In those cases where the concentrations of successive determinations were not exactly reproduced, the concentration listed is an average.

sent average quantities over a given temperature range, the temperature intervals were chosen so that there was no significant difference between $d\Delta H_s^0/dT$ and $\Delta(\Delta H_s^0)/\Delta T$.

Figure 1 shows the standard partial molal heat capacity as a function of temperature. The solid circles are those obtained in this investigation. The open circle for NaCl(aq.) is the value obtained by Guggenheim and Prue⁷ by the extrapolation of the direct specific heat measurements of concentrated solutions of Randall and Rossini.²³ The open triangle was obtained by combining the previously mentioned^{10,15,17} heat of dilution and heat of solution data at 20 and 25°. The quantity was calculated in the same manner as those of this investigation and is -19.8 cal. deg.⁻¹mole⁻¹.²⁴

(23) M. Randall and F. D. Rossini, *J. Am. Chem. Soc.*, **51**, 323 (1929).

(24) This same calculation has been performed by Gulbransen and Robinson¹⁰ with the data from the same two investigators, and they list a value of -21.9 cal. deg.⁻¹ for C_{p2}^0 . It has been impossible to reproduce their calculations. Furthermore, they compare this value, which is for 22.5°, to the values of Randall and Ramage²³ and Randall and Rossini,²² both of whom report C_{p2}^0 only at 25°. It can be seen from Fig. 1 that this is not a valid comparison since C_{p2}^0 is changing about one heat capacity unit for every 2.5 degree temperature change in this temperature region.

(25) M. Randall and W. D. Ramage, *J. Am. Chem. Soc.*, **49**, 93 (1927).

TABLE II

THE AVERAGE HEAT OF SOLUTION AND ρ VALUES OF BARIUM CHLORIDE

No. of detns.	$m \times 10^2$ (moles/kg.) ^a	\sqrt{m}	$-\Delta H_s$ (cal./mole)	$-3\delta_{HI}^{1/2}\alpha$ (cal.)	$-\rho$ (cal./mole)
0.02°					
3	1.40	0.0374	573 ± 46	57	630 ± 46
3	4.19	.0647	487 ± 14	96	583 ± 14
2	6.52	.0807	494 ± 5	118	612 ± 5
3	9.31	.0965	445 ± 7	138	583 ± 7
$\Delta H_s^0 = -590 \pm 13$ cal./mole					
5.00°					
3	1.40	0.0374	1143 ± 4	62	1205 ± 4
3	4.19	.0647	1103 ± 20	104	1207 ± 20
3	6.53	.0808	1066 ± 7	128	1194 ± 7
2	9.31	.0965	1052 ± 7	150	1202 ± 7
$\Delta H_s^0 = -1195 \pm 4$ cal./mole					
15.00°					
1	1.40	0.0375	2190	73	2263
1	4.40	.0663	2148	125	2273
1	6.53	.0808	2123	150	2273
1	9.78	.0988	2108	180	2288
$\Delta H_s^0 = -2265 \pm 2$ cal./mole					
25.00°					
5	1.84	0.0429	3109 ± 20	97	3206 ± 20
5	2.60	.0509	3077 ± 18	114	3191 ± 18
2	3.61	.0601	3125 ± 11	133	3258 ± 11
6	4.39	.0662	3068 ± 10	140	3208 ± 10
2	5.38	.0734	3067 ± 5	160	3227 ± 5
2	5.92	.0770	3085 ± 12	167	3252 ± 12
3	6.50	.0806	3064 ± 7	174	3238 ± 7
1	7.20	.0849	3070	184	3254
1	8.74	.0935	3027	199	3226
3	10.00	.1000	3037 ± 19	212	3249 ± 19
$\Delta H_s^0 = -3230 \pm 7$ cal./mole					
35.00°					
6	0.589	0.0243	4040 ± 55	66	4106 ± 55
2	1.36	.0368	4009 ± 57	98	4107 ± 57
4	2.33	.0483	3948 ± 30	126	4074 ± 30
1	3.92	.0626	3974	160	4134
5	4.52	.0672	3926 ± 24	171	4097 ± 24
1	6.99	.0836	3890	210	4100
2	10.00	.1000	3880 ± 15	246	4126 ± 15
$\Delta H_s^0 = -4090 \pm 7$ cal./mole					
45.01°					
6	0.575	0.0240	4900 ± 34	74	4974 ± 34
3	1.50	.0387	4813 ± 44	118	4931 ± 44
4	2.26	.0475	4740 ± 37	144	4884 ± 37
7	4.44	.0666	4703 ± 36	195	4898 ± 36
3	7.00	.0837	4697 ± 28	242	4939 ± 28
2	10.02	.1000	4701 ± 7	284	4985 ± 7
$\Delta H_s^0 = -4910 \pm 16$ cal./mole					
54.83°					
2	0.579	0.0241	5586 ± 60	83	5669 ± 60
2	1.50	.0387	5584 ± 9	135	5719 ± 9
4	4.46	.0668	5471 ± 13	224	5695 ± 13
2	7.01	.0837	5445 ± 39	276	5721 ± 39
1	8.10	.0900	5435	305	5740
2	10.01	.1000	5394 ± 41	325	5719 ± 41
$\Delta H_s^0 = -5705 \pm 9$ cal./mole					

TABLE II (continued)

No. of detns.	$m' \times 10^2$ (moles/kg.) ^a	\sqrt{m}	$-\Delta H_s$ (cal./mole)	$-3\delta_{HI}^{1/2}\alpha$ (cal.)	$-\rho$ (cal./mole)
64.88°					
2	1.50	0.0388	6351 ± 7	155	6506 ± 7
2	4.50	.0671	6233 ± 18	257	6490 ± 18
3	7.03	.0838	6195 ± 39	318	6513 ± 39
1	8.98	.0948	6165	353	6518
3	10.00	.1000	6125 ± 25	371	6496 ± 25
$\Delta H_s^0 = -6510 \pm 6$ cal./mole					
75.01°					
4	1.02	0.0319	7167 ± 33	147	7314 ± 33
1	2.50	.0500	7087	225	7312
3	4.01	.0633	7072 ± 16	278	7350 ± 16
1	7.01	.0838	6930	362	7292
3	8.50	.0922	6930 ± 25	394	7324 ± 25
$\Delta H_s^0 = -7330 \pm 11$ cal./mole					
84.99°					
2	1.01	0.0318	7976 ± 73	167	8143 ± 73
2	2.50	.0500	7896 ± 8	256	8152 ± 8
3	4.00	.0633	7844 ± 37	317	8161 ± 37
1	4.41	.0664	7780	331	8111
2	5.50	.0742	7744 ± 34	366	8110 ± 34
2	7.00	.0837	7744 ± 10	413	8157 ± 10
1	7.67	.0876	7660	429	8089
1	8.51	.0923	7637	448	8085
1	10.13	.1006	7586	483	8069
$\Delta H_s^0 = -8155 \pm 8$ cal./mole					
95.17°					
2	0.901	0.0300	8864 ± 35	179	9043 ± 35
3	1.35	.0368	8865 ± 6	217	9082 ± 6
2	1.83	.0427	8771 ± 33	250	9021 ± 33
2	2.93	.0541	8735 ± 35	312	9047 ± 35
2	4.82	.0694	8565 ± 5	393	8958 ± 5
1	6.52	.0808	8495	449	8944
1	12.53	.1119	8284	604	8888
$\Delta H_s^0 = -9045 \pm 12$ cal./mole					

^a In those cases where the concentrations of successive determinations were not exactly reproduced, the concentration listed is an average.

TABLE III

HEAT CAPACITY DATA FOR CRYSTALLINE AND AQUEOUS SODIUM CHLORIDE

$t_{av.}$	ΔC_p^0	C_{p2}	\bar{C}_{p1}^0
2.51	-50.4	12.1	-38.3
7.50	-43.7	12.1	-31.6
12.50	-38.9	12.1	-26.8
17.49	-35.0	12.1	-22.9
22.49	-31.2	12.1	-19.1
29.98	-30.0	12.2	-17.8
39.98	-27.4	12.2	-15.2
49.92	-26.5	12.3	-14.2
59.85	-27.9	12.3	-15.6
69.94	-28.3	12.3	-16.0
80.00	-28.4	12.4	-16.0
90.08	-30.9	12.4	-18.5

This is in excellent agreement with the smoothed value of -19.9 cal. deg.⁻¹ mole⁻¹ obtained from Fig. 1. The discrepancy in the smoothed value at 25° and that of Guggenheim and Prue⁷ probably is due to the extrapolation of the specific heats from concentrated solutions.

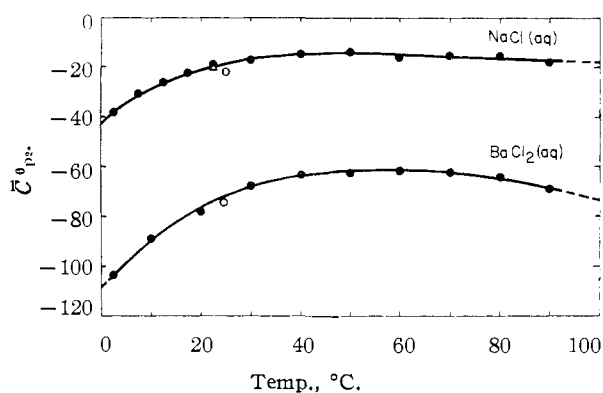


Fig. 1.—Standard partial molal heat capacities of NaCl(aq.) and BaCl₂(aq.) from 0 to 100°. The solid circles are the values obtained in this investigation. The open circle for NaCl is from Guggenheim and Prue⁷ and the triangle was calculated from heat of solution and dilution data.^{10,15,17} The open circle for BaCl₂ was obtained from White.²⁶

TABLE IV
HEAT CAPACITY DATA FOR CRYSTALLINE AND AQUEOUS BARIUM CHLORIDE

$t_{av.}$	ΔC_p^0	C_{v2}	\bar{C}_{p2}^0
2.51	-121.5	17.9	-103.6
10.00	-107.0	17.9	-89.1
20.00	-96.5	18.0	-78.5
30.00	-86.1	18.0	-68.1
40.00	-81.8	18.0	-63.8
49.92	-81.0	18.1	-62.9
59.86	-80.1	18.1	-62.0
69.95	-80.9	18.2	-62.7
80.01	-82.8	18.2	-64.6
90.09	-87.3	18.2	-69.1

Figure 1 also shows the corresponding curve for BaCl₂(aq.). The open circle is that from direct specific heat measurements of White.²⁶ Specific heats of BaCl₂ solutions also have been reported by Urban²⁷ at various temperatures, but the accuracy of this work is questionable for the purpose of obtaining \bar{C}_{p2}^0 . Smoothed values of \bar{C}_{p2}^0 at even temperatures are listed for both salts in Table V.

(26) C. M. White, *J. Am. Chem. Soc.*, **53**, 1615 (1936).

(27) F. Urban, *J. Phys. Chem.*, **36**, 1108 (1932).

TABLE V
SMOOTHED VALUES OF THE STANDARD PARTIAL MOLAL HEAT CAPACITIES OF SODIUM CHLORIDE AND BARIUM CHLORIDE

Temp., °C.	NaCl(aq.)	$-\bar{C}_{p2}^0$	BaCl ₂ (aq.)
0 ^a	40.5		110
10	29.0		90.0
20	20.9		77.5
25	18.9		72.6
30	17.2		68.9
40	15.3		64.0
50	14.6		62.1
60	15.2		61.7
70	15.8		62.7
80	16.5		65.2
90	17.2		68.5
100 ^a	18.0		72.5

^a Extrapolated values.

The partial molal specific heats of both of these salts reach a maximum between 50 and 70° and then decrease as the temperature is increased further. This is the same general trend that previous investigators³⁻⁶ have found for NaCl and other electrolytes in more concentrated solutions. Since the specific heats of the solid salts change very little over the temperature range involved, it can be seen that ΔC_p^0 varies with temperature in about the same way as \bar{C}_{p1}^0 . There has been considerable interest^{28,29} in the variation of ΔC_p^0 for various equilibrium processes. Unfortunately, equilibrium constants are not known well enough as a function of temperature to determine the exact temperature variation of ΔC_p^0 . This investigation shows that ΔC_p^0 for solubility equilibria is a complex function of the temperature.

It is apparent that the present data do not lend support to the proposed⁷ method of extrapolation of heat capacity data to infinite dilution. Accordingly, some readjustment of reported values of \bar{C}_{p2}^0 in the literature is indicated. This problem will be the subject of a future communication.

Acknowledgment.—The authors are indebted to Professor Leo Brewer for helpful discussions on the research.

(28) Harned and Owen, ref. 9, p. 643 and 661.

(29) T. F. Young, "Abstracts of Papers," American Chemical Society, 135th Meeting, Boston, Mass., April, 1959, p. 14-R.