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Enthalpy Increment Measurements for NaCl(cr) and KBr(cr) from 4.5 K to 350 K. Thermodynamic Properties of the NaCl + H_2O System. 3[†]

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Enthalpy increments for sodium chloride and potassium bromide were measured from 4.5 K to 350 K with an adiabatic calorimeter. These measurements were combined with other selected values from the literature to generate models that represented the thermal properties of crystalline sodium chloride and potassium bromide to the melting points. The entropy, enthalpy relative to 0 K, and the heat capacity of sodium chloride and potassium bromide were calculated from these models. The new measurements and models were compared to previous measurements of the thermodynamic properties of crystalline sodium chloride and potassium bromide. Additionally, the equation for the thermodynamic properties of copper given by Martin (*Rev. Sci. Instrum.* **1987**, *58*, 639), which is useful for calibration of calorimeters for temperatures below 310 K, was adjusted for the difference of the International Temperature Scale of 1990 from the International Practical Temperature Scale of 1968.

Introduction

The entropy of crystalline sodium chloride is important not only for the thermodynamic model of brines and brine mixtures but also as one of the components of the sets of thermodynamic properties often referred to as “key thermodynamic values”. Aqueous sodium chloride is important in most of these “key” systems because it appears as a component in many chemical systems. However, aqueous sodium chloride should have an additional role in these key systems. That role is as a cornerstone of the system because the thermodynamic properties of aqueous sodium chloride have been more accurately determined than have been those for other aqueous electrolytes. In those key systems that attempt to present the thermodynamic properties of aqueous ions as formation properties (formation from the elements), the thermodynamic properties of the pure solid phases must also appear. This is because the thermodynamic properties for the solution process are the link between many of the aqueous ions and the thermodynamic processes that involve reactions of elements. As an example, the entropy of crystalline sodium chloride appears in combination with the entropies of the aqueous ions for the entropy of solution.

Difficulties in representing the thermodynamic properties of aqueous electrolyte systems when using thermodynamic properties of aqueous ions from the CODATA key values for thermodynamics (Cox et al., 1989) have been reported previously (Archer, 1992b; Rard and Archer, 1995). Improvement of the key values for thermodynamics in the future requires an understanding of what causes insufficiencies in the present values. Rard and Archer (1995) identified a deficiency in the determination of the CODATA key values due to the lack of consideration of entropies for the solution process for the aqueous electrolytes. Another potential source of inaccuracy in the CODATA key values is investigated in the present article. This is the assessment of the crystalline phase entropies for the electrolytes.

The entropy of crystalline sodium chloride in the key systems has been that calculated from heat capacity measurements from near 0 K to about 260 K. Part I of this series (Archer, 1992) showed that there were significant differences between the measured heat capacities from low temperatures to about 260 K given by Clusius et al. (1949) and by Morrison and Patterson (1956). It was also shown in part I that the measurements near 260 K from Clusius et al. agreed better with the higher temperature measurements reported by Leadbetter and Settatree (1969) than did the values given by Morrison and Patterson. The enthalpy increment measurements at high temperatures reported by several authors also generally agreed better with the Leadbetter and Settatree results than did the Morrison and Patterson results. It was stated in part I that the 298.15 K entropy of crystalline sodium chloride was uncertain by about 1% because of the systematic differences between the measurements from Clusius et al. and from Morrison and Patterson.

The situation just described for crystalline sodium chloride is common in the process of thermodynamic data evaluation. Often, evaluators are confronted with two or more sets of measurements that are simply discordant. Either set (in the case of two sets) might be erroneous or both might be erroneous. In such a situation, it has not been uncommon for a data evaluator to choose one set as superior to another entirely on the basis of the evaluator’s perception of the reputation of the author(s) of the chosen set. Indeed, the author has been forced on occasion to this last resort in some of his own data evaluations.

The author’s observation in part I that the Morrison and Patterson measurements near 260 K were in somewhat poorer agreement with the higher temperature measurements of others than were the Clusius et al. measurements and the author’s use of this observation in assignment of the relative weighting of the measurements elicited contrary comments from a reviewer. Those comments relied primarily on the “reputation” argument and made a claim

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[†] Certain commercial materials and suppliers are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by either the U.S. Government or the National Institute of Standards and Technology, nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.

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that Clusius's temperature scale was greatly in error for temperatures up to 80 K; an error which yielded a "similarity" of differences between Clusius's measurements and those of others below 80 K. (The reviewer's similarity of differences was shown in part I to not exist for the reviewer's choice of substances for 25 K < T < 100 K.)

Some of these factors may explain why the CODATA *Key Values for Thermodynamics* text (Cox et al., 1989) did not mention the differences between Morrison's measurements for sodium chloride and those of others and assigned an uncertainty of only ±0.28% to the entropy of crystalline sodium chloride, an uncertainty significantly smaller than the systematic differences between the different sets of heat capacity measurements.

The present paper provides new measurements of enthalpy increments for sodium chloride for temperatures from near the normal boiling point of helium to 350 K. The new measurements were made with an adiabatic calorimeter which had been shown previously to possess only small calorimetric biases that were independent of the identity of two different calibrating substances, namely, copper and aluminum oxide (synthetic sapphire). Enthalpy increment measurements are reported here also for crystalline potassium bromide.

Some changes to the electrical leads to the calorimeter were made. Consequently, copper was also measured for the present work to check the calorimeter's calibration. The demonstrated accuracy of the present calorimetric system and the present measurements should help close the debate regarding the relative merits of the previous calorimetric work on sodium chloride.

Experimental Section

The sodium chloride and potassium bromide used for the present measurements were taken from optical crystals obtained from Solon Technologies Inc. The optical crystals (<50 ppm impurities) were used without further purification. The filling of the calorimeter and all handling of the samples were performed in an argon-filled drybox. The optical crystals were broken into smaller pieces and the calorimeter was filled with pieces that had at least two dimensions greater than 1 mm. Approximately 8 kPa (300 K) of helium was sealed in the calorimeter with the sample. The masses of sodium chloride and potassium bromide used for the measurements were 5.0378 g and 7.4523 g, which corresponded to approximately 39% and 45% of the internal volume of the calorimeter, respectively. The calorimetric apparatus has been described previously (Archer, 1995). The densities and molecular masses of sodium chloride and potassium bromide were taken to be 2.16 $\mathrm{g \cdot cm^{-3}}$, 58.443 $\mathrm{g \cdot mol^{-1}}$ and 2.75 $\mathrm{g \cdot cm^{-3}}$, 119.002 $\mathrm{g \cdot mol^{-1}}$, respectively. The measured enthalpy increments of the filled calorimeter were converted into enthalpy increments for sodium chloride and potassium bromide by subtraction of the enthalpy increments for the empty calorimeter and for the small differences in amounts of helium and vacuum grease between determinations of the enthalpy increments for the empty and filled calorimeters. The enthalpy increments were corrected for the small systematic biases in the calorimetric system using the equations:

$$\epsilon\Delta H_{\mathrm{m}} = -[\{(T_2 + T_1)/2\} - 100\ \mathrm{K}]0.00001\ \mathrm{K}^{-1}\ \Delta H_{\mathrm{m}} \qquad (T_1 > 100\ \mathrm{K}) \quad (1)$$

$$\epsilon\Delta H_{\mathrm{m}} = -0.0025\Delta H_{\mathrm{m}} \qquad (T_2 < 13.8\ \mathrm{K}) \quad (2)$$

where T_2 and T_1 are the larger and the smaller of the two temperatures for the enthalpy increment, respectively, and $\epsilon\Delta H_{\mathrm{m}}$ is the correction added to the substance's enthalpy increment, ΔH_{m}. The origin of these corrections has been described previously (Archer, 1995). The present measurements on copper, described below, confirm the corrections.

Between the sodium chloride and potassium bromide measurements, a fatigued section of electrical leads leading from a tempering block on the bottom adiabatic shield was cut away and new copper leads were soldered in their place. This introduction of a soldered connection in each of the electrical leads resulted in a large reduction in the temperature-drift rate observed when the calorimeter was not being heated. (It also reduced the imprecision of the measurements for temperatures less than 20 K.) To check if this change, or any other changes made to the calorimetric system, changed the unaccounted heat transfers between the calorimeter and its surroundings, and thereby altered the calibration corrections given by eqs 1 and 2, the calorimeter was again calibrated with copper. The copper cylinder described previously (Archer, 1995) was heavily etched to a new mass of 44.0374 g, a removal of 6% of the cylinder's matter. The copper cylinder was sealed in the calorimeter with approximately 8 kPa (300 K) of helium.

Results

Copper and Performance of the Calorimeter. The equation for the thermodynamic properties of copper given by Martin (1987a) is adapted here for use in calorimetric comparisons, where the calorimeter to be calibrated uses a thermometer that has been calibrated in accord with the International Temperature Scale of 1990 (ITS-90). Martin (1987a) made his reference-standard-quality measurements on copper with an adiabatic calorimeter that could be used in a scanning mode. The American Society for Testing and Materials recently described their standard method for the calibration of scanning calorimeters (ASTM test method E1269-94). Their method, for ITS-90, involves calibrations to be accomplished through comparison of measured values of the heat capacity of synthetic sapphire with values calculated from the equation given for the heat capacity of synthetic sapphire, SRM-720 (Ditmars et al., 1982), and "upgrades" from the International Practical Temperature Scale of 1968 (IPTS-68) to the International Temperature Scale of 1990 obtained from an equation given in a Technical Report of the IUPAC Commission on Thermodynamics (Goldberg and Weir, 1992). ASTM stated that this "upgrade" changed values of heat capacity calculated from the reference equation for sapphire by "no more than 0.0004 J/g K" over the temperature range 150 K−1000 K (0.0004 J/(g K) corresponds to approximately 0.03%−0.04% of the heat capacity for temperatures above 400 K). The ASTM statements regarding the "upgrades" from IPTS-68 to ITS-90 are incorrect on three accounts. First, the equation given in the IUPAC report (Goldberg and Weir, 1992) is not appropriate for adjustment of least-squares generated equations, such as that of Ditmars et al. (1982) (Archer, 1993). Second, the change in heat capacity calculated from the IUPAC report is not "no more than 0.0004 J/g K"; in particular, the IUPAC Technical Report's calculational method gives changes in the heat capacity of synthetic sapphire up to *10 times* that value for some temperatures that fall within the range of ASTM's tabulated heat capacity values. Third, the "upgrades" introduce a discontinuity of approximately 0.3%−0.5% into the calculated heat capacity values for 903.75 K, a temperature within ASTM's calibration range and accessible to commercial calorimeters. This discontinuity would then be present in heat capacities subsequently measured with the "calibrated" calorimeter.

Copper is more important as a standard for calibration of calorimeters at low temperatures than is aluminum oxide because of the relatively high Debye temperature (approximately 1000 K) of aluminum oxide. Because of the above mentioned problems, the calculation given in the IUPAC report was not used as a means for changing Martin's (1987a) equation to become more compatible with the ITS-90. Martin (1987a) did not publish his experimental values, only his least-squares estimated representation of them. The equation given previously by Martin was adjusted from the IPTS-68 to the ITS-90 here by means of the method given by Archer (1993). To effect the change to ITS-90, a vector of change in *experimental* heat capacity against temperature was calculated for each integer Kelvin value in the interval of 14 K to 320 K. The change in experimental heat capacity (Archer, 1995) is

$$\delta C_{p,\mathrm{m}} = C_{p,\mathrm{m}} - C_{p,\mathrm{m}}{}' = -C_{p,\mathrm{m}}\{(T_2 - T_2{}') - (T_1 - T_1{}')\}/(T_2 - T_1) \quad (3)$$

$$\delta T_\mathrm{m} = T_\mathrm{m} - T_\mathrm{m}{}' = \{(T_2 - T_2{}') + (T_1 - T_1{}')\}/2 \quad (4)$$

where $\delta C_{p,\mathrm{m}}$ and δT_m are the changes in heat capacity and midpoint temperature, respectively, T_1 and T_2 are the initial and final temperatures for the finite-difference heat capacity, and the new and old scales are indicated with a prime and its absence, respectively. Martin stated "The temperature increments used were rather small ...". Other than this qualitative statement, the values of $(T_2 - T_1)$ for Martin's copper measurements are unknown. Because quantitative values of $(T_2 - T_1)$ are not known, the assumed change for Martin's *experimental* heat capacities was evaluated as the limit of eq 3 as $(T_2 - T_1)$ approached 0 K. If Martin's values of $(T_2 - T_1)$ were indeed small, use of this limit will not introduce a significant error into conclusions based on these calculations. The portion of the correction given by eq 4 was converted to an equivalent change in experimental heat capacity. The quantity $\mathrm{d}(T_{90} - T_{68})/\mathrm{d}T$ required for the limit of eq 3 was not taken from the table of this quantity given by Goldberg and Weir (1992). Cursory examination of their Table 2 showed their values of $\mathrm{d}(T_{90} - T_{68})/\mathrm{d}T$ sometimes did not agree with their tabulated values of $T_{90} - T_{68}$ against temperature. As an example, Goldberg and Weir gave in their Table 2 values of $T_{90} - T_{68}$ that changed from 0.003 K at 60 K to 0.005 K at 64 K and then to 0.007 K at 68 K. For all temperatures from 60 K to 68 K, they listed the first temperature derivative of $T_{90} - T_{68}$ as 0.0000, rather than the obvious ~0.0005. Thus, there appeared to be some problem in their calculation of temperature derivative.

The following procedure was used to approximate $\mathrm{d}(T_{90} - T_{68})/\mathrm{d}T$ for the temperature range of 14 K to 320 K. Values of $T_{90} - T_{68}$ from Preston-Thomas (1990) were fitted over the range of temperature 14 K to 21 K with a polynomial and from this polynomial was calculated the first derivative of $T_{90} - T_{68}$ with respect to temperature for 14 K through 17 K. Above 17 K, the upper and lower temperatures of the fitted range were increased by 1 K and the values of $T_{90} - T_{68}$ for this new range of temperature were fitted and the derivative calculated from this new polynomial near the middle of the fitted temperature range. This process was repeated throughout the range 18 K to 320 K. (Beyond 100 K, Preston-Thomas gave the differences of the two temperature scales at 10 K intervals rather than the 1 K intervals given below 100 K. As such, in the previously described method the fitted range was increased by 10 K increments for temperatures greater than 100 K.) The order of the fitted polynomial was adjusted appropriately to the fitted temperature differences. Some small artificial noise was introduced into this derivative by this method of estimation; this noise is eliminated in the next step of the procedure.

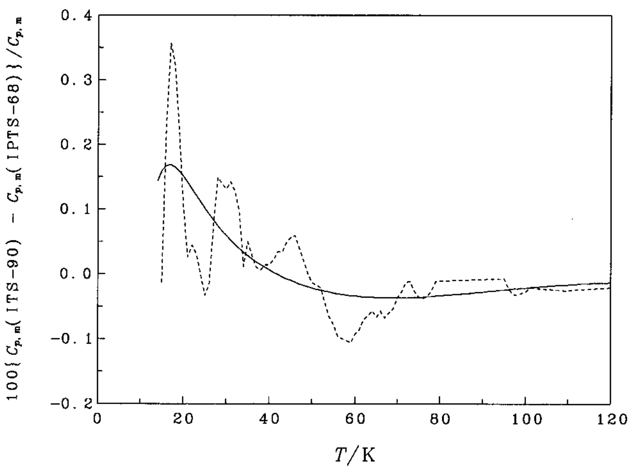

Figure 1. Values of the difference in calculated heat capacity of copper due to the difference of ITS-90 from IPTS-68 calculated by two different methods. The solid line is calculated from the method described by Archer (1993) and the present text. The dashed line is calculated from an equation described in the IUPAC Technical Report by Goldberg and Weir (1992), which is similar to the "upgrade" described in ASTM method E 1269-94, as described in the text.

Table 1. Revised Parameters for Equation 5

n	a_n	n	a_n
0	−0.8209550462989	9	$-0.1225710530439 \times 10^{-13}$
1	0.1877080114403	10	$0.6497060325945 \times 10^{-16}$
2	$-0.1572088570716 \times 10^{-1}$	11	$-0.2516789895111 \times 10^{-18}$
3	$0.5832484862761 \times 10^{-3}$	12	$0.7064523085264 \times 10^{-21}$
4	$-0.1452296533129 \times 10^{-5}$	13	$-0.1400131357648 \times 10^{-23}$
5	$-0.3457773461093 \times 10^{-6}$	14	$0.1858728557094 \times 10^{-26}$
6	$0.1029537684534 \times 10^{-7}$	15	$-0.1483505970215 \times 10^{-29}$
7	$-0.1620547240203 \times 10^{-9}$	16	$0.5382629833814 \times 10^{-33}$
8	$0.1677835991722 \times 10^{-11}$		

The Preston-Thomas (1990) values of $T_{90} - T_{68}$ and the just-described derivative with respect to temperature were then used to calculate the change in Martin's experimental heat capacity that would be expected due to a change in temperature scale from IPTS-68 to ITS-90. This vector was then used as ϵY_i in eqs 6−10 of Archer (1993). The ITS-90 adjusted parameters, a_n, for Martin's (1987a) polynomial

$$C^\circ_{p,\mathrm{m}}/C^\circ_p = \sum_{n=0}^{16} a_n (T/T^\circ)^n \quad (5)$$

are given in Table 1. In eq 5, $C^\circ_{p,\mathrm{m}}$ was the molar heat capacity, C°_p was 1 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and T° was 1 K. The difference in the heat capacity of copper calculated using Martin's original equation and eq 5, from 14 K to 120 K, is shown as the solid line in Figure 1. Also shown in Figure 1 are values calculated from an equation given in the IUPAC Commission on Thermodynamics Technical Report (Goldberg and Weir, 1992) using the above-described temperature derivative of $T_{90} - T_{68}$, not the table given by Goldberg and Weir.

Intuitively, the solid curve is the behavior one would expect from the change in *calculated* heat capacity due to the difference in IPTS-68 and ITS-90. This is because one expects the difference of the representation of the experimental heat capacities on IPTS-68 from the representation of the same measurements adjusted to ITS-90 to be a slowly

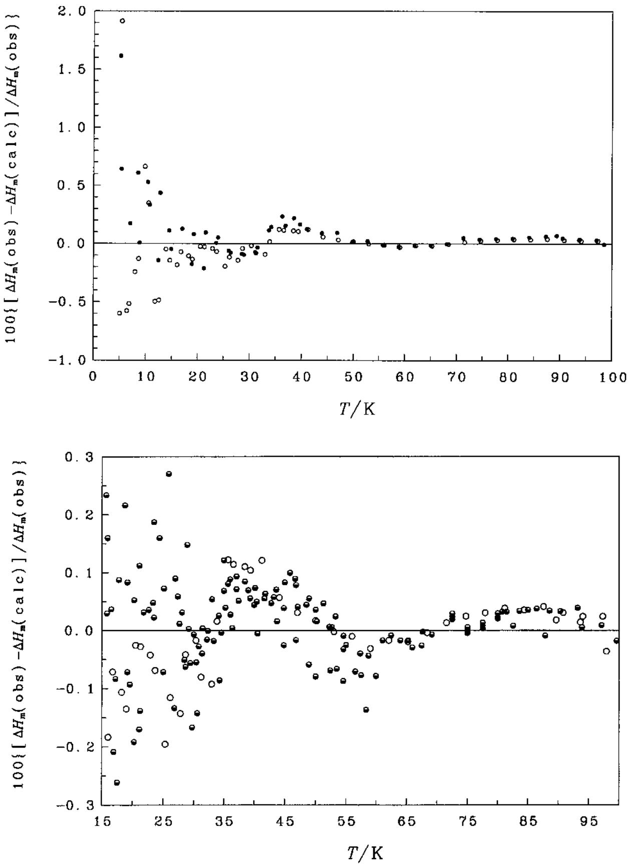

Figure 2. Comparison of enthalpy-increment measurements for copper with reference equations. The measured values are compared with the equation from Holste et al. (1972) for temperatures less than 15 K and are compared with eq 5, which is the ITS-90 modified representation of Martin's (1987a) measurements. (a) Symbols: (○) differences of presently measured values; (●) differences of previously measured values (Archer, 1995). (b) Symbols: (○) differences of presently measured values; (◒) differences of Martin's (1987a) measurements from his fitted equation, where the differences have been brought onto the same temperature basis as the present measurements.

changing function of temperature, because neither of these representations should be capable of the high-frequency fluctuations shown by the dashed line. Conversely, adding the ragged dashed line of Figure 1 to a least-squares representation of the heat capacity of copper (on IPTS-68) would result in a slightly ragged calculated heat capacity of copper on ITS-90, which is not the intuitively expected result. Applying the equation from the IUPAC Technical Report to values of heat capacity calculated from Martin's equation (Martin, 1987a), which is a procedure that would have been similar to the "upgrade" described in the ASTM method E1269-94, would have introduced into the calculated heat capacity values unnecessary errors of approximately −0.2% at 15 K, +0.2% at 17 K, +0.1% at 30 K, and ranging to −0.07% at 55 K.

Figure 2a shows the differences of the new measured enthalpy increments for copper for temperatures less than 100 K from the ITS-90 revision of Martin's reference equation, namely, eq 5. Also shown in Figure 2a are the differences of the earlier measured enthalpy increments of copper (Archer, 1995) from eq 5. The agreement of the older and present measurements was quite good for all temperatures. There is a small maximum, ~0.1%, near 35 K and a small negative bias ~(−0.1% to −0.15%) near 25 K. These effects, as well as a small positive bias, ~0.05%, from 40 K to 50 K and from 70 K to 95 K, probably resulted from an oscillation of Martin's high-order polynomial about his own measurements. The evidence supporting this assertion is twofold. First, the oscillatory model biases of high-order polynomials in the representation of a set of observations are well-known. Martin showed the differences of his fitted equation from his measurements in his Figure 6 (Martin, 1987b). Approximate values for his residuals were taken from his figures and after adjustment for temperature-scale differences were shown in Figure 2b. The differences of his measured values for copper from his equation show the same oscillation observed for the differences of the present measured values from his adjusted fitted equation. They showed an approximately 0.1% positive bias near 35 K, a −0.15% bias near 30 K, and a small positive bias from 40 K to 50 K (~0.05%). In fact, the only present measurements that fall outside of the spread of Martin's measurements about his equation are a few measurements from near 36 to 41 K. Thus, the agreement of the present measurements with Martin's *measurements*, after adjusting for different temperature scales, was well within 0.05% for temperatures from 30 K to 60 K and within 0.03% for temperatures from 60 K to 100 K. The second observation is that the biases shown for copper have not been observed with other substances measured with the present calorimeter. The probability that the two very different calorimeters (i.e. the present calorimeter and Martin's "tray" calorimeter) have very similar systematic biases as a function of temperature would seem to be very low. That possibility is essentially eliminated by the observation that these systematic biases have not occurred with other substances measured with the present calorimeter. Thus, it seemed most likely that the small systematic biases seen in Figure 2 resulted from typical high-order polynomial model biases, rather than any true systematic error. Indeed, oscillations in the pattern of residuals typical of high-order polynomial fitting were apparent also in residual plots for silver and gold in the temperature range of 100 K to 250 K given by Martin (1987b).

The agreement of the present measurements with those of Martin was quite satisfactory (within ~0.03%−~0.05% from 30 K to 100 K). The precision of the present measurements is somewhat better than that of Martin's measurements, even though the present measurements were performed on a sample about one-quarter the size of Martin's sample.

The present copper measurements, for temperatures below 15 K, were compared to the equation given by Holste et al. (1972) in Figure 2. Above 100 K, the new measurements agreed with the earlier copper measurements made with this calorimeter (Archer, 1995) with a root mean square (rms) difference of 0.03%, thus confirming eq 1.

Sodium Chloride and Potassium Bromide. The measured enthalpy increments for sodium chloride and potassium bromide are given in Tables 2 and 3, respectively. Above 30 K, the measurements for these two samples were expected to be uncertain by no more than ±0.1%, dependent upon the particular temperature. Below 30 K, the results must be considered less accurate, partly due to limits in accuracy of platinum resistance thermometer temperature scales below 30 K. These uncertainty values were based on the present and previous measurements of enthalpy increments for calorimetric reference materials (Archer, 1995), the present reproducibility, and the percentage of the total measured enthalpy increment that was due to either the sodium chloride or potassium bromide sample. These uncertainty estimates do not include contributions from low levels of impurities. The

Table 2. Enthalpy Increment Measurements for Sodium Chloride

T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b	T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b
304.1041	309.2609	259.953	0.1	−0.05	64.2822	67.4453	73.515	0.1	−0.01
309.2428	314.4021	260.626	0.1	−0.08	67.4250	70.6078	78.419	0.1	−0.02
314.3731	319.5273	261.130	0.1	−0.01	70.5889	73.7838	82.950	0.1	−0.06
319.4934	324.6633	262.428	0.1	−0.04	73.7644	76.9846	87.693	0.1	−0.06
324.6211	329.7922	263.077	0.1	−0.04	76.9657	80.1990	92.035	0.1	0.04
329.7365	334.9184	264.205	0.1	−0.03	80.1800	83.4217	95.998	0.1	0.08
334.8599	339.9339	259.422	0.1	0.04	83.4029	86.6596	100.012	0.1	0.14
339.8681	344.9583	260.829	0.1	0.07	86.6407	89.9009	103.353	0.1	0.07
344.8832	349.9706	261.278	0.1	0.10	89.8825	93.1555	106.852	0.1	0.02
302.1373	307.3987	264.971	0.1	−0.06	93.1297	96.7077	120.167	0.1	0.00
307.3837	312.6411	265.428	0.1	−0.05	96.6979	100.2676	123.248	0.1	0.03
312.6172	317.8760	266.109	0.1	−0.06	100.2570	103.8323	126.480	0.1	−0.02
317.8433	323.1176	267.574	0.1	−0.03	103.8206	107.4101	129.916	0.1	−0.02
323.0728	328.3419	267.984	0.1	0.00	107.3965	110.9827	132.529	0.1	−0.03
328.2937	333.6769	274.495	0.1	0.04	110.9675	114.5590	135.319	0.1	0.00
333.6203	338.9995	274.758	0.1	−0.01	114.5441	118.1458	138.029	0.1	−0.06
338.9342	344.3090	275.203	0.1	0.02	118.1303	121.7323	140.296	0.1	−0.06
344.2352	349.7234	281.788	0.1	0.09	121.7161	125.3213	142.565	0.1	−0.03
4.6194	5.7522	0.0158	10.0	−14.4	125.3032	128.9122	144.734	0.1	−0.01
5.9368	7.2956	0.0461	6.0	−2.1	128.8919	132.5102	146.939	0.1	−0.03
7.3472	9.0505	0.1156	3.0	−0.4	132.4895	136.1097	148.708	0.1	−0.07
9.0407	11.0052	0.2529	3.0	−0.8	136.0868	139.7053	150.326	0.1	−0.05
10.9945	12.9935	0.4607	1.0	−1.38	139.6808	143.3000	152.007	0.1	0.02
12.9831	15.0913	0.8284	1.0	−0.63	143.2728	146.8959	153.718	0.1	0.07
15.0715	17.2376	1.3773	0.5	−0.36	146.8671	150.5014	155.558	0.1	0.04
17.2009	19.4937	2.255	0.5	−0.36	150.4692	154.1088	157.187	0.1	0.08
19.4679	21.8173	3.449	0.5	−0.09	154.0735	157.7100	158.298	0.1	0.06
21.7907	24.2357	5.116	0.2	−0.21	157.6465	162.0937	194.723	0.1	−0.19
24.2031	26.7274	7.265	0.2	−0.07	162.0541	166.4478	194.872	0.1	0.23
26.6981	29.2612	9.759	0.2	−0.22	166.4243	170.8087	195.399	0.1	−0.11
29.2316	31.8986	13.058	0.2	−0.19	170.7820	175.1582	196.814	0.1	0.04
31.8697	34.5926	16.729	0.1	−0.04	175.1309	179.5199	198.817	0.1	0.05
34.5618	37.3366	20.861	0.1	0.11	179.4912	183.8793	200.016	0.1	0.00
37.3101	40.1362	25.399	0.1	0.12	183.8497	188.2364	201.269	0.1	0.02
40.1117	42.9964	30.330	0.1	−0.12	188.2056	192.5909	202.511	0.1	0.07
4.3827	5.5790	0.0151	10.0	−12	192.5588	196.9436	203.498	0.1	0.00
5.5872	6.7910	0.0359	6.0	6.1	196.9096	201.2981	204.708	0.1	−0.02
6.7391	8.4382	0.0959	3.0	5.6	201.2682	205.6491	205.359	0.1	−0.04
8.4372	10.0117	0.1558	3.0	0.0	205.6183	210.0017	206.438	0.1	−0.05
9.9918	12.0252	0.3609	2.0	0.8	209.9699	214.3439	206.969	0.1	−0.04
12.0123	14.0712	0.6285	1.0	−1.10	214.3111	218.6943	208.151	0.1	−0.11
14.0491	16.2396	1.1250	0.5	0.33	218.6596	223.0324	208.654	0.1	−0.04
16.2136	18.4609	1.823	0.5	−0.23	222.9963	227.3781	209.908	0.1	−0.04
18.4276	20.7883	2.927	0.5	0.24	227.3369	231.7166	210.534	0.1	−0.07
20.7638	23.1722	4.349	0.2	0.10	231.6717	236.0574	211.615	0.1	−0.05
23.1422	25.6138	6.229	0.2	0.15	236.0093	240.3914	212.534	0.1	0.13
25.5833	28.1224	8.578	0.2	−0.06	240.3425	244.7189	212.908	0.1	0.10
28.0916	30.7445	11.677	0.2	−0.13	244.6690	249.0443	213.427	0.1	0.06
30.7114	33.3923	14.961	0.2	−0.06	248.9923	253.3631	213.802	0.1	0.04
33.3636	36.1390	19.155	0.1	0.05	253.2978	257.6836	215.069	0.1	−0.01
36.1112	38.9242	23.443	0.1	0.03	257.5145	262.0095	221.129	0.1	0.04
38.8972	41.7663	28.229	0.1	−0.13	261.9516	266.3361	216.262	0.1	0.03
41.7403	44.6605	33.368	0.1	−0.14	266.2749	270.6572	216.810	0.1	0.07
44.6329	47.5876	38.644	0.1	0.06	270.5930	274.9801	217.231	0.1	−0.10
47.5428	50.5755	44.668	0.1	0.12	274.9125	279.2946	217.729	0.1	0.00
50.5492	53.5909	49.801	0.1	0.10	279.2234	283.6099	218.442	0.1	−0.01
53.5660	56.6365	55.165	0.1	−0.01	283.5350	287.9198	218.956	0.1	0.04
56.6113	59.7158	60.648	0.1	−0.04	287.8407	292.2268	219.680	0.1	0.11
59.6918	62.8260	66.046	0.1	−0.01	292.1357	296.5368	220.684	0.1	0.01
62.8018	65.9578	71.207	0.1	0.01	296.4402	300.8465	221.528	0.1	0.06
65.9345	69.1068	76.085	0.1	−0.02	300.6661	305.1520	225.756	0.1	−0.04
69.0838	72.2824	81.083	0.1	−0.02	4.4025	5.5992	0.0177	10.0	1.2
72.2596	75.4817	85.852	0.1	−0.05	5.4755	7.3679	0.0660	6.0	9.1
75.4581	78.6904	90.145	0.1	−0.02	7.4270	9.1892	0.1229	3.0	−1.9
32.2369	34.6607	15.153	0.1	0.01	9.1872	10.9964	0.2402	3.0	0.24
34.6225	37.4493	21.384	0.1	0.14	10.9686	13.0371	0.4810	1.0	−0.69
37.4127	40.2538	25.671	0.1	−0.01	4.3853	5.5899	0.0175	10.0	0.2
40.2182	43.1057	30.712	U	0.47	5.5550	7.0848	0.0492	6.0	6.6
43.0800	46.0329	36.003	0.1	−0.08	7.0778	8.6322	0.0936	3.0	1.4
46.0086	49.0012	41.451	0.1	0.01	8.6170	10.5351	0.2161	3.0	0.6
48.9770	51.9961	46.772	0.1	−0.03	10.5132	12.5141	0.4077	1.0	−0.11
51.9729	55.0325	52.383	0.1	−0.02	12.5166	14.6232	0.7444	1.0	0.17
55.0100	58.1030	57.941	0.1	0.05	14.6205	16.7937	1.2657	0.5	0.47
58.0814	61.1952	63.107	0.1	−0.06	16.7760	19.0537	2.079	0.5	0.31
61.1741	64.3027	68.200	0.1	0.05	19.0303	21.3802	3.224	0.2	0.28

[a] σ is the percentage uncertainty assigned to the observation for the purposes of the least-squares calculation. A "U" indicates that observation was not included in the least-squares calculation. [b] δ is the percentage difference of the calculated enthalpy increment from that observed.

Table 3. Enthalpy Increment Measurements for Potassium Bromide

T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b	T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b
308.1330	313.1718	261.452	0.1	−0.16	6.4860	8.2917	0.6546	2.0	−0.13
313.1600	318.2007	262.189	0.1	−0.08	8.2816	10.0213	1.2730	1.0	−0.34
318.1842	323.2213	262.590	0.1	−0.01	10.0279	11.9900	2.614	1.0	0.23
323.2006	328.2418	263.352	0.1	0.03	12.0097	14.0677	4.569	1.0	−0.07
328.2154	333.2557	263.448	0.1	−0.07	14.0811	16.2481	7.365	0.5	0.01
333.2234	338.8641	295.373	0.1	−0.05	16.2563	18.5711	11.230	0.5	0.08
338.8257	344.4669	295.978	0.1	−0.02	18.5735	20.9581	15.619	0.5	0.45
344.4203	350.0763	297.558	0.1	0.08	20.9613	23.4782	21.086	0.3	−0.24
304.3950	310.0388	292.825	0.1	−0.06	23.4775	26.0796	27.223	0.3	0.17
310.0332	315.6718	292.962	0.1	−0.10	26.0860	28.7402	33.436	0.3	0.10
315.6611	321.3005	293.578	0.1	−0.08	28.7494	31.4803	40.325	0.3	−0.02
321.2851	326.9190	293.795	0.1	−0.09	31.4868	34.2534	46.859	0.3	−0.08
326.8981	332.5477	295.166	0.1	−0.08	34.2586	37.0986	54.294	0.1	0.10
332.5207	338.1649	295.299	0.1	−0.11	37.1023	39.9870	61.168	0.1	0.09
338.0428	343.7719	300.478	0.1	−0.04	39.9897	42.9270	68.025	0.1	−0.14
79.3122	82.1270	111.156	0.1	−0.01	42.9264	45.8965	74.569	0.1	0.03
82.1288	85.3633	129.864	0.1	−0.03	4.3359	5.4954	0.1113	5.0	0.90
85.3647	88.6031	132.055	0.1	−0.11	5.5388	6.9272	0.2840	2.0	−0.29
88.6038	91.8477	134.470	0.1	0.05	6.9303	8.5851	0.7021	2.0	−0.25
91.8480	95.0882	136.076	0.1	0.00	8.5720	10.3943	1.510	1.0	0.40
95.0883	98.3307	137.862	0.1	−0.01	10.3801	12.3754	2.940	1.0	0.04
98.3305	101.5797	139.724	0.1	−0.02	12.4018	14.4660	4.993	1.0	−0.17
101.5790	104.8427	141.842	0.1	−0.01	14.4691	16.6388	7.873	0.5	−0.21
104.8415	108.1033	143.204	0.1	0.04	16.6395	18.9506	11.802	0.5	−0.04
108.1018	111.3683	144.700	0.1	0.04	18.9487	21.3900	16.677	0.5	0.14
111.3665	115.1739	170.122	0.1	0.02	21.3880	23.8869	21.822	0.3	0.06
115.1715	118.9720	171.283	0.1	0.00	23.9297	25.9143	20.968	0.3	0.05
118.9696	122.7737	172.745	0.1	−0.05	25.9193	28.6388	33.888	0.3	−0.12
122.7710	126.5841	174.427	0.1	−0.06	28.6427	31.3664	39.929	0.3	−0.14
126.5811	130.4057	176.076	0.1	−0.10	31.3691	34.1596	47.050	0.3	−0.05
130.4023	134.2220	177.072	0.1	−0.04	34.1616	36.9886	53.743	0.3	−0.05
134.2183	138.0365	178.055	0.1	−0.03	36.9902	39.8907	61.244	0.1	0.01
138.0327	141.8591	179.524	0.1	0.03	39.8919	42.8195	67.636	0.1	−0.09
141.8552	145.6864	180.612	0.1	−0.01	42.8214	45.8054	74.738	0.1	0.03
145.6823	149.5069	181.132	0.1	−0.03	45.8070	48.8176	80.807	0.1	−0.01
149.5017	153.3336	182.337	0.1	−0.01	48.8180	51.8660	86.882	0.1	−0.09
153.3286	157.1578	182.998	0.1	0.00	51.8665	54.9385	92.383	0.1	−0.09
157.1524	160.9809	183.732	0.1	0.01	54.9388	58.0501	98.214	0.1	0.03
160.9748	164.8047	184.509	0.1	0.01	58.0499	61.1928	103.303	0.1	−0.12
164.7982	168.6301	185.307	0.1	0.03	61.1922	64.3339	107.312	0.1	0.02
168.6233	172.4573	185.670	0.1	−0.18	64.3335	67.5108	112.159	0.1	0.01
172.4515	176.2711	185.972	0.1	0.03	67.5105	70.6929	115.682	0.1	0.00
176.2648	180.0908	186.694	0.1	−0.06	70.6924	73.8932	119.426	0.1	−0.01
180.0840	183.9158	187.827	0.1	0.09	30.1868	32.2045	31.529	0.1	−0.05
183.9080	187.7343	186.518	U	−0.75	32.2117	35.0739	50.221	0.1	−0.03
187.7271	191.5402	187.836	0.1	0.02	35.0790	37.9148	55.910	0.1	0.05
191.5332	195.3569	188.714	0.1	−0.05	37.9188	40.8287	63.360	0.1	0.02
195.3496	199.7085	215.770	0.1	−0.02	40.8315	43.7724	69.827	0.1	−0.03
199.7003	204.0526	216.004	0.1	−0.03	43.7744	46.7499	76.298	0.1	0.07
204.0440	208.3993	216.775	0.1	−0.01	46.7513	49.7838	83.086	0.1	0.03
208.3906	212.7431	217.040	0.1	−0.07	49.7848	52.8371	88.651	0.1	0.01
212.7339	217.0766	216.985	0.1	−0.11	52.8378	55.9206	94.296	0.1	0.04
217.0666	221.4207	218.127	0.1	−0.08	55.9211	59.0411	99.896	0.1	0.07
221.4096	225.7605	218.413	0.1	−0.10	59.0411	62.1773	104.475	0.1	0.01
225.7479	230.0913	218.660	0.1	−0.03	62.1770	65.3416	109.286	0.1	0.03
230.0780	234.4220	219.042	0.1	−0.07	65.3411	68.5244	113.476	0.1	0.02
234.4077	238.7443	219.224	0.1	−0.02	68.5238	71.7155	117.082	0.1	0.05
238.7284	243.0788	220.668	0.1	0.13	71.7147	74.9254	120.781	0.1	0.02
243.0633	247.4161	221.068	0.1	0.06	74.9242	78.1450	123.931	0.1	0.01
247.3994	251.7498	221.205	0.1	0.00	78.1435	81.3818	127.141	0.1	−0.02
251.7317	256.0655	220.711	0.1	−0.01	81.3802	84.6260	129.892	0.1	0.04
256.0462	260.3787	220.783	0.1	−0.12	84.6245	87.8724	131.966	0.1	−0.11
260.3581	264.6928	221.568	0.1	0.01	87.8693	91.1262	134.514	0.1	0.01
264.6709	269.0029	221.827	0.1	0.03	91.1225	94.3909	136.911	0.1	0.03
268.9791	273.3171	222.145	0.1	−0.13	94.3876	97.6707	139.232	0.1	−0.02
273.2917	277.6275	222.694	0.1	0.01	97.6678	100.9404	140.438	0.1	0.00
277.5997	281.9401	223.315	0.1	0.03	100.9375	104.2176	142.381	0.1	0.07
281.9106	286.2511	223.660	0.1	0.03	104.2146	107.4763	142.936	0.1	0.04
286.2189	290.5461	223.346	0.1	0.05	107.4748	111.0652	158.875	0.1	0.06
290.5111	294.8385	223.607	0.1	0.02	111.0634	114.6522	160.239	0.1	0.05
294.8012	299.1331	224.258	0.1	0.06	114.6499	118.2431	161.562	0.1	−0.10
299.0929	303.4268	224.528	0.1	−0.01	118.2410	121.7280	158.167	0.1	0.02
303.3835	307.7224	225.453	0.1	0.14	121.7250	125.2262	159.982	0.1	0.06
4.3362	5.3392	0.0911	5.0	0.86	125.2230	128.7235	160.852	0.1	−0.02
5.4007	6.5099	0.1956	2.0	0.38	128.7201	132.5460	177.005	0.1	0.03

Table 3 (Continued)

T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b	T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/J·mol^{-1}	σ^a	δ^b
132.5431	136.3675	177.987	0.1	0.02	216.9966	221.3508	218.253	0.1	−0.02
136.3636	140.1892	178.984	0.1	−0.02	221.3408	225.6899	218.496	0.1	−0.02
140.1851	144.0205	180.277	0.1	−0.08	225.6793	230.2380	229.585	0.1	0.01
144.0172	147.8433	181.068	0.1	0.10	230.2266	234.7823	229.820	0.1	−0.04
147.8400	151.8820	191.775	0.1	−0.11	234.7700	239.3371	231.086	0.1	0.05
151.8786	155.9102	192.901	0.1	0.27	239.3237	243.8855	231.318	0.1	0.06
155.9068	159.9498	193.909	0.1	0.07	243.8715	248.4296	231.389	0.1	−0.02
159.9459	163.9882	194.261	0.1	−0.14	248.4143	252.9714	231.864	0.1	0.02
163.9842	168.0225	195.548	0.1	0.23	252.9551	257.5064	232.084	0.1	0.06
168.0185	172.0609	195.783	0.1	−0.12	257.4878	262.0432	232.632	0.1	0.02
172.0565	176.0997	196.884	0.1	0.07	262.0225	266.5735	232.901	0.1	0.06
176.0949	180.1423	197.686	0.1	0.04	266.5512	271.1068	233.591	0.1	0.09
180.1374	184.1703	197.710	0.1	0.09	271.0829	275.6371	233.410	0.1	−0.13
184.1649	188.2038	198.524	0.1	0.05	275.6114	280.1628	234.126	0.1	0.08
188.1982	192.2249	198.534	0.1	0.07	280.1354	284.6886	234.488	0.1	0.03
192.2189	196.2557	199.469	0.1	0.02	284.6583	289.2156	235.168	0.1	0.08
196.2491	200.2819	199.675	0.1	−0.05	289.1831	293.7260	234.694	0.1	0.04
200.2752	204.2985	199.858	0.1	0.03	293.6905	298.2329	235.111	0.1	0.07
204.2911	208.3249	200.779	0.1	−0.01	298.1949	302.7373	235.484	0.1	0.08
208.3171	212.6694	217.216	0.1	0.02	302.6966	307.2453	236.194	0.1	0.10
212.6609	217.0058	217.130	0.1	−0.09	307.2014	311.7498	236.524	0.1	0.10

[a] σ is the percentage uncertainty assigned to the observation for the purposes of the least-squares calculation. A "U" indicates that observation was not included in the least-squares calculation. [b] δ is the percentage difference of the calculated enthalpy increment from that observed.

sodium chloride sample contributed 13%−14% of the total enthalpy increment for the lowest temperature measurement; the contribution for potassium bromide was 46%. For temperatures greater than 14 K, the contribution to the total enthalpy increment from sodium chloride was approximately 24%. For potassium bromide, the sample's contribution to the total measured enthalpy increment decreased from 60% near 20 K to approximately 22% near 300 K.

The present measurements do not span the whole temperature range of existence for the crystalline state of these two substances. To obtain thermodynamic properties for the full range of temperature, some previous measurements were selected and included in the least-squares representation. All of the selected enthalpy increments and heat capacities were fitted simultaneously by means of a cubic-spline method described previously (Archer, 1992a).

Briefly, a function $f(T)$ was used, where

$$f(T) = [T(C^{\circ}_{p,\mathrm{m}}/C^{\circ}_{p})^{-1/3} - bT]/T^{\circ} \qquad (6)$$

and where b was a constant arbitrarily chosen to be 0.25 for the present case. The function $f(T)$ of eq 6 was fitted with a cubic spline using polynomials of the form

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i \qquad (7)$$

where the subscript i referred to the polynomial that contained the specified value of T and spanned the temperature range T_i to T_{i+1}. A particular (T_i, d_i) pair is referred to as a "knot". A "natural spline" end condition (*i.e.* second derivative equal to 0) was imposed at the highest temperature knot. The end condition imposed at the lowest temperature knot was a value of $-b$ (−0.25) for the first derivative. This was equivalent to assuming that the Debye temperature was independent of temperature near 0 K. (For the purpose of calculation: $T_{i+1} > T > T_i$.) The calculated heat capacity was thus

$$C^{\circ}_{p,\mathrm{m}}/C^{\circ}_{p} = \left(\frac{T}{T^{\circ}f(T) + bT}\right)^3 \qquad (8)$$

Equation 8 was integrated numerically to obtain the enthalpy. The model was fitted to the experimental values with a nonlinear least-squares program. The vector of residuals was calculated using eq 8 for the heat capacity or numerical integrations of eq 8 to obtain the enthalpy increments.

The estimated square root of the variance (srv) for the present measurements is required for the purpose of performing the least-squares procedure. Uncertainties for the measurements were calculated from twice the irreproducibility for a full calorimeter determination, the expected systematic biases determined from measurements of enthalpy increments of calorimetric reference materials, and the percentage of the observed enthalpy that was due to the measured sample. These values, given in Tables 2 and 3, were used as though they were the srv in the least-squares procedure; however, because the factor of 2 was used, those values actually corresponded to an approximate 95% confidence interval for the measurements.

Representation of the Thermodynamic Properties of Sodium Chloride. The heat capacity results from Leadbetter and Settatree (1969) were assigned an srv of 0.5% in the representation. Low-temperature heat capacity values were taken from Martin's (1955) figure of Debye temperatures, assigned an srv of 6%, and included in the representation. Enthalpy increments from Dawson et al. (1963), corrected for systematic calorimetric biases by means of the difference of their measurements for sapphire from the equation given by Archer (1993), were included in the least-squares representation. They were assigned an srv of 0.2%. The enthalpy increment measurements from Holm and Grønvold (1973), and from Magnus (1913) (with the exception of Magnus's 1037 K measurements) were assigned srv's of 1%. The enthalpy increments from Roth and Bertram (1992) and from Lyashenko (1935) were assigned srv's of 2%.

Representation of the experimental results over the full range of temperature required 14 variable values for the knot positions. The final knot positions are given in Table 4. The number of digits given in Table 4 should be sufficient for calculation of thermodynamic properties and was not meant to be representative of any statistical assessment. The Debye temperature calculated from the

Table 4. Least-Squares Estimated Knot Positions for Sodium Chloride and Potassium Bromide

sodium chloride		potassium bromide	
T_i/K	d_i	T_i/K	d_i
0	20.835 1	0	11.055 5
12	16.539 8	5	9.569 68
20	13.247 4	8	8.328 07
30	10.471 0	15	6.333 77
40	8.776 17	20	5.614 68
60	6.936 77	30	4.752 33
90	5.789 36	40	4.230 57
150	5.341 76	60	3.693 28
220	5.662 74	90	3.517 51
280	6.123 46	150	3.915 67
400	6.983 33	300	5.482 90
550	7.437 98	450	6.430 03
800	5.064 13	800	3.265 21
1100	−7.162 47	1100	−6.861 62

0 K knot was 327.6 K. The root-mean-square difference of the present measurements from the model was 0.06% for temperatures above 50 K. Agreement of other measurements with the model is discussed below. Calculated thermodynamic properties of sodium chloride are given in Table 5.

Representation of the Thermodynamic Properties of Potassium Bromide. The heat capacity results from Leadbetter and Settatree (1969) for KBr were corrected for a calorimetric bias as described below, and assigned an srv of 0.6% in the representation. Low-temperature heat capacity values were taken from Martin's (1964) figure of Debye temperatures, assigned an srv of 10%, and included in the representation. An enthalpy increment from Dworkin (1964) for the change from the melting temperature to 298.15 K was included in the least-squares representation and assigned an srv of 0.25%. The enthalpy increment measurements from Magnus (1913) were assigned srv's of 1%. The enthalpy increments from Cooper (1953) were assigned an srv of 1%.

Representation of the experimental results for potassium bromide over the full range of temperature required 14 variable values for the knot positions. The final knot positions are given in Table 4. The Debye temperature calculated from the 0 K knot was 173.8 K for potassium bromide. The root-mean-square difference of the present measurements from the model was 0.07% for temperatures above 50 K, excluding one unweighted measurement. Agreement of other measurements with the model is discussed below. Calculated thermodynamic properties of potassium bromide are given in Table 6.

It is not possible to give highly quantified values of the uncertainties of the calculated thermodynamic property values given in Tables 5 and 6 because the true uncertainties depend on measurements whose uncertainties are not well quantified. As an example, the difference between the measured temperature of the sample and the true thermodynamic temperature of the sample depends, in large part, on how well ITS-90 represents the true thermodynamic temperature, particularly for temperatures which are not ITS-90 "fixed point" temperatures, i.e., "interpolated temperatures". Because this uncertainty in measurement of thermodynamic temperature, and how it varies with temperature, is not well quantified, it cannot be included quantitatively in estimates of the uncertainty of calculated and measured thermodynamic properties that depend on temperature. If these unknown contributions to uncertainty are neglected, the uncertainty in calculated heat capacity values, for temperatures from 50 K to 300 K, is estimated to be no more than 0.05% and probably less than this value for entropy and enthalpy relative to 0 K, due to the integral nature of these functions. Above 350 K, the functions become somewhat less certain. The maximum uncertainty in enthalpy relative to 0 K and entropy for temperatures greater than 400 K can be estimated to range from 0.25% to 0.5% of the difference in the thermodynamic function between the considered temperature and 300 K (percentage increasing as the temperature increases from 350 K) summed to the uncertainty of the function at 300 K.

Table 5. Thermodynamic Properties of Sodium Chloride Calculated from Eqs 6 and 7

T/K	$C_{p,\mathrm{m}}$/ J·K^{-1}·mol^{-1}	$H_\mathrm{m}(T) - H_\mathrm{m}(0\ \mathrm{K})$/ kJ·mol^{-1}	S_m/ J·K^{-1}·mol^{-1}
5	0.0144	0.0000	0.0047
10	0.1273	0.0003	0.0403
15	0.492	0.0017	0.1490
20	1.317	0.0060	0.3902
25	2.715	0.016	0.824
30	4.652	0.034	1.482
35	7.020	0.063	2.373
40	9.668	0.105	3.481
50	15.231	0.229	6.236
60	20.46	0.408	9.48
80	28.97	0.907	16.60
100	34.89	1.549	23.74
120	38.99	2.291	30.49
140	41.82	3.100	36.72
160	43.88	3.958	42.45
180	45.47	4.853	47.71
200	46.71	5.775	52.57
220	47.70	6.719	57.07
240	48.51	7.681	61.26
260	49.18	8.659	65.17
280	49.76	9.648	68.83
298.15	50.23	10.556	71.97
300	50.28	10.649	72.28
320	50.74	11.659	75.54
340	51.16	12.678	78.63
360	51.55	13.705	81.57
380	51.92	14.740	84.37
400	52.27	15.782	87.04
420	52.61	16.830	89.60
440	52.94	17.886	92.05
460	53.26	18.948	94.41
480	53.58	20.016	96.68
500	53.9	21.091	98.88
520	54.2	22.172	101.00
540	54.5	23.258	103.05
560	54.8	24.351	105.04
580	55.1	25.450	106.96
600	55.4	26.555	108.84
620	55.7	27.666	110.66
640	56.0	28.783	112.43
660	56.4	29.907	114.16
680	56.7	31.038	115.85
700	57.1	32.176	117.50
720	57.5	33.322	119.11
740	57.9	34.476	120.69
760	58.4	35.639	122.24
780	58.9	36.811	123.77
800	59.4	37.993	125.26
820	59.9	39.186	126.74
840	60.5	40.390	128.19
860	61.1	41.607	129.62
880	61.8	42.836	131.03
900	62.4	44.077	132.42
920	63.1	45.332	133.80
940	63.8	46.601	135.17
960	64.5	47.883	136.52
980	65.2	49.179	137.85
1000	65.9	50.489	139.18
1020	66.6	51.813	140.49
1040	67.2	53.151	141.79
1060	67.9	54.503	143.08
1073.80	68.4	55.444	143.96

Table 6. Thermodynamic Properties of Potassium Bromide Calculated from Eqs 6 and 7

T/K	$C_{p,\mathrm{m}}$/ J·K^{-1}·mol^{-1}	$H_\mathrm{m}(T) - H_\mathrm{m}(0\ \mathrm{K})$/ kJ·mol^{-1}	S_m/ J·K^{-1}·mol^{-1}
5	0.099	0.0001	0.032
10	0.970	0.0023	0.296
15	3.292	0.012	1.080
20	6.689	0.037	2.475
25	10.622	0.080	4.384
30	14.679	0.143	6.680
35	18.592	0.227	9.239
40	22.208	0.329	11.962
50	28.353	0.583	17.605
60	33.07	0.891	23.21
80	39.33	1.621	33.67
100	43.02	2.447	42.87
120	45.35	3.333	50.94
140	46.91	4.256	58.05
160	48.03	5.206	64.39
180	48.90	6.176	70.10
200	49.59	7.161	75.29
220	50.16	8.159	80.04
240	50.64	9.167	84.43
260	51.06	10.184	88.50
280	51.44	11.209	92.30
298.15	51.76	12.145	95.54
300	51.79	12.241	95.86
320	52.13	13.280	99.21
340	52.45	14.326	102.38
360	52.77	15.378	105.39
380	53.08	16.437	108.25
400	53.4	17.502	110.98
420	53.7	18.573	113.59
440	54.0	19.650	116.10
460	54.3	20.733	118.51
480	54.6	21.82	120.83
500	55.0	22.92	123.06
520	55.3	24.02	125.22
540	55.6	25.13	127.32
560	56.0	26.25	129.35
580	56.3	27.37	131.32
600	56.7	28.50	133.23
620	57.1	29.64	135.10
640	57.4	30.78	136.92
660	57.8	31.93	138.69
680	58.2	33.10	140.42
700	58.7	34.26	142.11
720	59.1	35.44	143.77
740	59.5	36.63	145.40
760	60.0	37.82	146.99
780	60.5	39.03	148.56
800	61.0	40.24	150.09
820	61.5	41.47	151.60
840	62.0	42.70	153.09
860	62.5	43.95	154.56
880	63.1	45.20	156.00
900	63.6	46.47	157.42
920	64.2	47.75	158.83
940	64.7	49.04	160.22
960	65.3	50.34	161.58
980	65.8	51.65	162.94
1000	66.4	52.97	164.27
1008	66.6	53.50	164.80

Discussion

For sodium chloride, the present measured values and other values from the literature are compared to the least-squares estimated model in Figures 3 through 5. Figure 3 shows that at their respective lowest measured temperatures, the measurements from Morrison and Patterson (1956) and from Clusius et al. (1949) both diverged from the model, from the present measurements, and from the measured values from Martin (1955). Also of interest, is that Morrison and Patteron's results below 7 K diverged from the calorimetrically-determined Debye temperatures shown in their Figure 3 of an earlier paper (Morrison et al., 1955). The difference of Morrison and Patterson's measurements from values from the same laboratory, published only one year earlier, went unremarked by Morrison and Patterson. Also, the values Barron et al. (1964) gave in their table of "smoothed" heat capacities at rounded temperatures, for temperatures less than 10 K, did not agree with the measured values they listed in their Appendix B. For example, the heat capacity value they gave for 5 K was 5.6% smaller than what one would interpolate from their measured values. This discrepancy also was not mentioned.

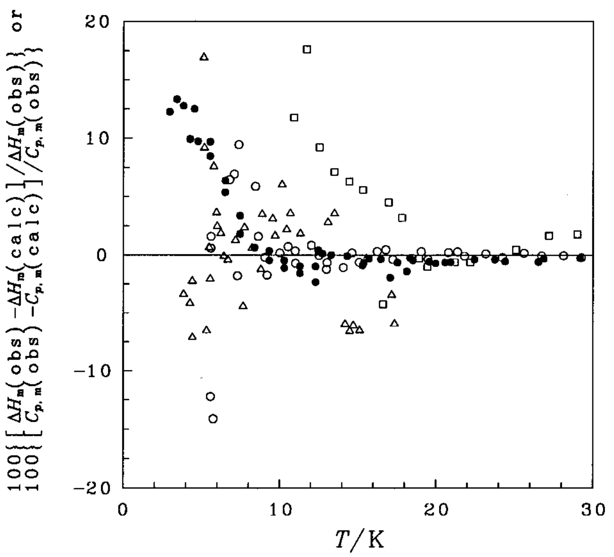

Figure 3. Comparison of measurements for sodium chloride to fitted equation for temperatures less than 30 K: (○) present results; (●) Morrison and Patterson (1956); (□) Clusius et al. (1949); (△) Martin (1955).

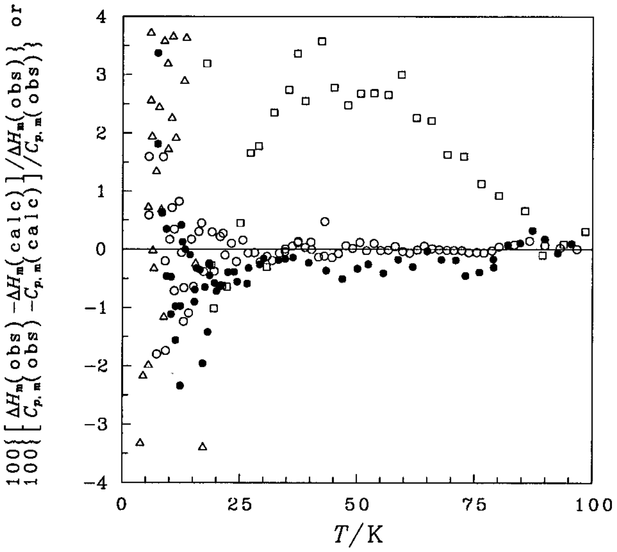

Figure 4. Comparison of measurements for sodium chloride to fitted equation for temperatures to 100 K: (○) present results; (●) Morrison and Patterson (1956); (□) Clusius et al., (1949); (△) Martin (1955).

In the temperature region from 20 K to 80 K (Figure 4), Morrison and Patterson's (1956) measurements were approximately 0.25% to 0.4% smaller than the present measurements. Clusius et al.'s (1949) measured values showed a systematic difference with a maximum about 2%−3% from the present measurements. Figure 5 shows that, from 80 K to 260 K, the measurements from Morrison and Patterson and from Clusius et al. both diverged significantly from the present measurements. Indeed, for temperatures greater than 80 K, one would be hard pressed

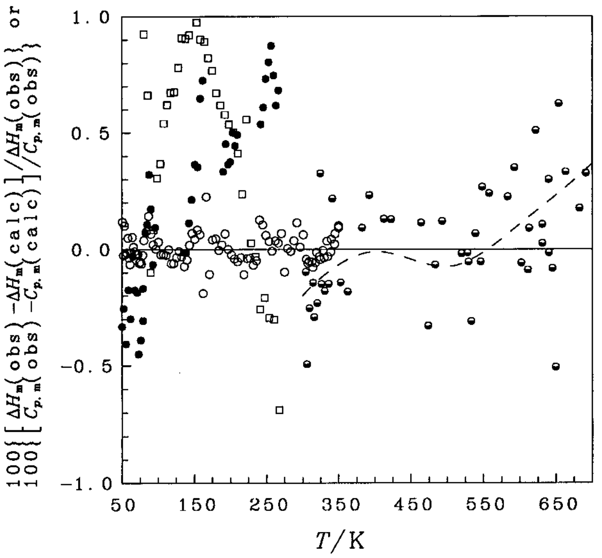

Figure 5. Comparison of measurements for sodium chloride to fitted equation for temperatures from 50 K to 700 K: (○) present results; (●) Morrison and Patterson (1956); (□) Clusius et al. (1949); (◒) Leadbetter and Settatree (1969). The dashed line is the difference of Leadbetter and Settatree's measurements for sapphire from the model given by Archer (1993).

to say that either of those two sets of measurements was more accurate than the other. However, as the experimental temperature neared the triple point of water, the measurements from Clusius et al. were in better agreement with the present results than were the measurements from Morrison and Patterson.

The differences of the high temperature heat capacity measurements from Leadbetter and Settatree (1969) are also shown in Figure 5. The dashed line shown in the figure represents the differences of their values for sapphire from the equation given by Archer (1993). Clearly, the small systematic biases from the fitted model for sodium chloride were similar to those observed for sapphire. This indicated that the systematic biases in their calorimetry were probably independent of the nature of the substance. If Leadbetter and Settatree's sodium chloride measurements were adjusted by the differences of their results for sapphire (in essence, this would be equivalent to using sapphire to calibrate their calorimeter), there would have been no systematic bias, only random differences, of their measurements from the fitted equation and also from the present measurements where the two sets overlapped. This correction was applied to Leadbetter and Settatree's measured values for potassium bromide.

Differences of the present model from the high-temperature enthalpy increment measurements from Magnus (1913), Roth and Bertram (1929), Lyashenko (1935), and Holm and Grønvold (1973) were similar to those observed in part I of this series and so were not shown here.

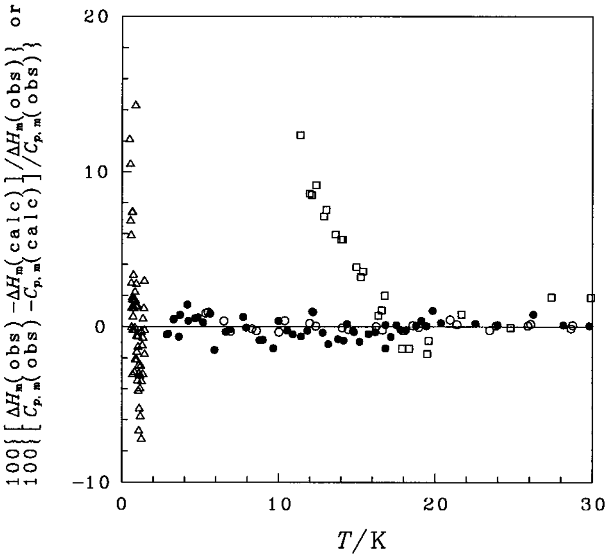

Figure 6. Comparison of measurements for potassium bromide to fitted equation for temperatures less than 30 K: (○) present results; (●) Berg and Morrison (1957); (□) Clusius et al. (1949); (△) Martin (1964).

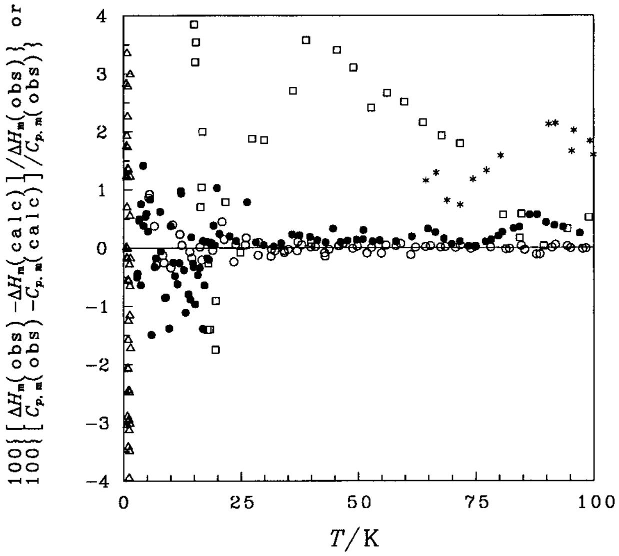

Figure 7. Comparison of measurements for potassium bromide to fitted equation for temperatures to 100 K: (○) present results; (●) Berg and Morrison (1957); (□) Clusius et al. (1949); (△) Martin (1964); (*) Telea et al. (1972).

Figure 6 shows the agreement of the model for potassium bromide with the lowest temperature results. The present enthalpy increments and the heat capacities from Martin (1964) were in good agreement with each other and with the model. Heat capacity values from Berg and Morrison (1957) were found in a JANAF folder at NIST. This document was titled "Appendix A. Experimental values of the heat capacity at constant pressure ..." and contained values for each of the substances reported by Berg and Morrison (1957). The differences of these values from the model, as well as those from Clusius et al. (1949) are also shown in the figure. The pattern of differences of the Clusius et al. results from the present results was quantitatively the same for both sodium chloride and potassium bromide.

The differences of the Berg and Morrison (1957) heat capacities from the present values to 100 K are shown in Figure 7. A negative bias of the results from Morrison and coauthors from the present measured values for both sodium chloride and potassium bromide was apparent near 15 K. However, the differences of Morrison et al.'s heat capacities from those calculated from the present model were of opposite sign for sodium chloride and potassium bromide over the temperature range 25 K to near 75 K. For this temperature range, the average differences were −0.28% and +0.14% for sodium chloride and potassium bromide, respectively.

In Figure 8 it is seen that the heat capacity values for potassium bromide from Berg and Morrison (1957) are systematically larger than the present values and the values given by Leadbetter and Settatree (1969). The Berg and Morrison measurements for potassium bromide were

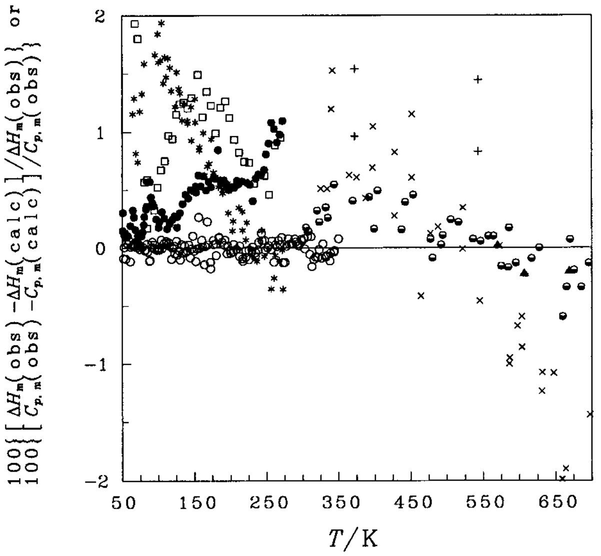

Figure 8. Comparison of measurements for potassium bromide to fitted equation for temperatures from 50 K to 700 K: (○) present results; (●) Berg and Morrison (1957); (□) Clusius et al. (1949); (◒) Leadbetter and Settatree (1969); (*) Telea et al (1972); (▲) Cooper (1953); (+) Magnus, (1911); (×) Mustajoki (1951).

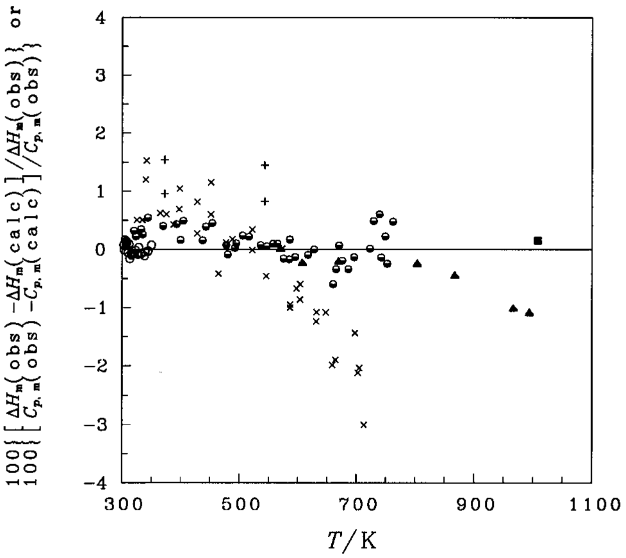

Figure 9. Comparison of measurements for potassium bromide to fitted equation for temperatures from 300 K to 1100 K: (○) present results; (◒) Leadbetter and Settatree (1969); (▲) Cooper (1953); (+) Magnus, (1911); (×) Mustajoki (1951); (■) Dworkin, (1964).

about 1% larger than the present values near 270 K. This was similar to the effect seen for sodium chloride, where the Morrison and Patterson (1956) values were 0.75% larger than the present values near 270 K. The rms difference of Leadbetter and Settatree's adjusted measurements from the fitted equation was 0.28%. The more recent values from Telea et al. (1972) were not in good agreement below 200 K, where differences as large as 2% were seen.

The high-temperature measurements from Cooper (1953) were in good agreement (average difference of −0.2%) with the model, and thus also with Leadbetter and Settatree's values of the heat capacity, for temperatures below 900 K. The two highest temperature measurements from Cooper were about 1% smaller than values calculated from the representation. The one enthalpy increment from Dworkin (1964) was 0.15% larger than the representation. The high-temperature heat capacity values from Mustajoki (1951) did not agree well with the representation. All of these differences are shown in Figure 9.

As discussed previously, the assigned standard entropies of aqueous ions are intimately related to the entropies of the crystal phases. In this regard, several of the crystal phase entropies used in the CODATA Key Values for Thermodynamics of Cox et al. (1989) were those taken from Morrison's laboratory. We now see these heat-capacity values to be not as accurate as previously thought. Because of the similarities of the biases observed for sodium chloride and potassium bromide, it might appear that the measurements from Morrison and coauthors could be corrected. However, this is not so. Morrison and Patterson's measurements for sapphire for 240.7 K to 249.3 K showed a rms difference of 0.23% and an average difference of +0.1% from the reference equation (Archer, 1993). Thus their measurements for sapphire did not show the systematic effects seen for sodium chloride and potassium bromide. Because Morrison et al.'s measurements for sapphire are in agreement with the accurate measurements of others and those for sodium chloride and potassium bromide are not, the bias seen for sodium chloride and potassium bromide for temperatures greater than 100 K was not a reproducible effect influencing all other calorimetric measurements. Because the bias was not reproducible for different substances, it cannot be corrected.

We now consider the possible import of the above observations on the CODATA Key Values for Thermodynamics. The 298.15 K entropy for crystalline potassium bromide obtained here, (95.54 ± 0.05) $J \cdot K^{-1} \cdot mol^{-1}$, was different from the value used by Cox et al. (1989), (95.90 ± 0.2) $J \cdot K^{-1} \cdot mol^{-1}$, by approximately twice the uncertainty assigned to it. The value obtained here for crystalline sodium chloride, (71.97 ± 0.04) $J \cdot K^{-1} \cdot mol^{-1}$, can be compared to that used for the Key Values, (72.13 ± 0.2) $J \cdot K^{-1} \cdot mol^{-1}$. The difference in crystal phase entropy for potassium bromide is the same magnitude as the differences in the entropy of ions that caused the difficulties in representation of the thermodynamic properties, described by Archer (1992) and by Rard and Archer (1995). The differences they found for entropies of aqueous ions from the CODATA Key Values were 0.33 $J \cdot K^{-1} \cdot mol^{-1}$ and 0.80 $J \cdot K^{-1} \cdot mol^{-1}$ for NaCl(aq) and NaBr(aq), respectively. Thus, the inability of the CODATA Key Values for Thermodynamics aqueous ion properties to represent the thermodynamic properties for aqueous electrolyte solutions may arise from a combination of neglect of incorporating the entropies of solution into their fitted database and of having uncertainties that were too small for some of the crystal-phase entropy values.

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