# Heat Capacities of Concentrated Aqueous Solutions of Sodium Sulfate, Sodium Carbonate, and Sodium Hydroxide at 25 °C

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Heat capacities of aqueous solutions of $Na_2SO_4$ and $Na_2CO_3$ up to near saturation (1.9 and 2.5 mol·kg$^{-1}$, respectively) and of NaOH (to 7 mol·kg$^{-1}$) have been measured at 25 °C with a Picker flow calorimeter. The calorimeter performance was checked using concentrated NaCl(aq) solutions. On the basis of these measurements, an experimental protocol suitable for the reliable determination of the heat capacities of concentrated electrolyte solutions by Picker calorimetry was established. The heat capacities for $Na_2SO_4$(aq), $Na_2CO_3$(aq), and NaOH(aq) and literature data for the apparent molar volumes of NaOH(aq) at 25 °C were correlated using the Pitzer formalism. A number of inadequacies in previous models at high concentrations and for extrapolation to infinite dilution are discussed. In particular, it has been confirmed that the heat capacity data for $Na_2CO_3$(aq) at low concentrations must be corrected for the hydrolysis of the carbonate ion. Standard partial molar heat capacities for the three salts and the standard partial molar volume of NaOH(aq) have been derived at 25 °C.

## Introduction

In the industrial context, heat capacities of concentrated aqueous electrolyte solutions are of interest in almost any situation that involves significant temperature changes.[1] These include most hydrometallurgical processes, heat exchangers, boiler operations, and so on. Heat capacity data are also of environmental interest because natural waters often contain high concentrations of electrolytes, as can stratospheric aerosol particles.[2]

Sodium hydroxide and sodium carbonate are present at high concentrations in the solutions ("liquors") employed in the Bayer process for the extraction of alumina from bauxitic ores.[3] In some Bayer plants, sodium sulfate is also present at near-saturation levels. As Bayer liquors undergo significant temperature cycling during the extraction and precipitation process, there is particular interest in the heat capacities of the solutions of these three electrolytes up to high concentrations.

The heat capacities of $Na_2SO_4$(aq), $Na_2CO_3$(aq), and NaOH(aq) have been measured a number of times at 25 °C (Table 1).[4−12] Although the reported data are generally in reasonable agreement at moderate solute ionic strengths ($\leq \sim$1 mol·kg$^{-1}$), the values at higher concentrations are less well characterized. To provide a more comprehensive database and to resolve some of the discrepancies in the existing data, the present paper reports a detailed re-investigation of the heat capacities at 25 °C of the aqueous solutions of sodium sulfate and sodium carbonate (up to near-saturation) and of sodium hydroxide (up to 7 mol·kg$^{-1}$) using a Picker flow calorimeter.

Various models for correlating heat capacities of electrolyte solutions with concentration have been used. Most of the earlier work employed a Redlich−Rosenfeld−Meyer (RRM) type equation,[13,14] which for heat capacities may be written as follows[5,15]

**Table 1. Literature Data for the Heat Capacities of Aqueous Solutions of Sodium Sulfate, Sodium Carbonate, and Sodium Hydroxide at 25 °C**

| molality range/mol·kg$^{-1}$ | no. of points | ref |
|---|---|---|
| $Na_2SO_4$ | | |
| 0−1.5 | 12[a] | 4 |
| 0.022−0.33 | 7 | 5 |
| 0.038−0.29 | 15 | 6 |
| 0.019−0.50 | 7 | 7 |
| $Na_2CO_3$ | | |
| 0.19−2.07 | 9 | 8 |
| 0.009−0.98 | 9 | 5 |
| NaOH | | |
| 0−27.75 | 48[a] | 9 |
| 0.039−1.00 | 8 | 5 |
| 0.097−0.73 | 11 | 10 |
| 0.048−0.37 | 13 | 11 |
| 0.039−10.88 | 15[b] | 12 |

[a] Smoothed values. [b] Including eight data points recalculated from ref 5.

$$C_{p\phi} = C^{\circ}_{p2} + (\omega)^{3/2} A_C (\rho^{\circ}_1)^{1/2} (m)^{1/2} + B_C m \qquad (1)$$

where $C_{p\phi}$ is the apparent molar heat capacity of the solution (in J·K$^{-1}$·mol$^{-1}$), $C^{\circ}_{p2}$ ($= C^{\infty}_{p\phi}$) is the standard state (infinite dilution) partial molar heat capacity of the electrolyte in the solvent, $A_C$ is the molarity-based Debye−Hückel parameter for heat capacities, $\rho^{\circ}_1$ is the density of water, $B_C$ is an empirical parameter fitted from the data, $m$ is the molality of the electrolyte solution (amount of substance per unit mass; mol solute/kg solvent), and $\omega$ is a valence factor given by

$$\omega = {}^{1}/_{2} \sum \nu_i z_i^{\,2} \qquad (2)$$

where $\nu_i$ are the stoichiometric coefficients of the ions in

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the chemical formula of the electrolyte and $z_i$ are the formal charges of the ions.

The value of $A_C(\rho_1^\circ)^{1/2}$ in eq 1, at 25 °C in water, was reported as 28.95 $J{\cdot}mol^{-3/2}{\cdot}kg^{1/2}{\cdot}K^{-1}$ by Leduc et al.[16] and Perron et al.,[17] using the then accepted values of the dielectric constant and density of water as functions of temperature. This value has been widely used in studies of electrolytes employing Picker flow calorimeters. However, Hepler and Hovey[18] pointed out that it is about (12 to 23)% smaller than those used in later studies, based on more recent determinations of the temperature dependence of the dielectric constant of water. The value of 32.75 $J{\cdot}mol^{-3/2}{\cdot}kg^{1/2}{\cdot}K^{-1}$ proposed by Bradley and Pitzer,[19] which is in good agreement (within 3%) with the most recent evaluation by Fernández et al.,[20] has been adopted in this paper.

It is generally accepted that the RRM equation is adequate for correlating experimental $C_{p\phi}$ values only up to an ionic strength ($I$) of approximately 1 $mol{\cdot}kg^{-1}$. For more concentrated electrolyte solutions, the Pitzer formalism has been preferred. For heat capacities this takes the form[21]

$$C_{p\phi} = C_{p2}^\circ + v|z_M z_X| A_J (2b)^{-1} \ln(1 + bI^{1/2}) - 2v_M v_X R T^2 [m B_{MX}^J + m^2 v_M z_M C_{MX}^J] \quad (3)$$

$$B_{MX}^J = (\partial^2 B_{MX}/\partial T^2)_{P,m} + (2/T)(\partial B_{MX}/\partial T)_{P,m} \quad (4)$$

$$B_{MX} = \beta_{MX}^{(0)} + 2\beta_{MX}^{(1)}[1 - (1 + \alpha_1 I^{1/2}) \exp(-\alpha_1 I^{1/2})] (\alpha_1{}^2 I)^{-1} + 2\beta_{MX}^{(2)}[1 - (1 + \alpha_2 I^{1/2}) \exp(-\alpha_2 I^{1/2})](\alpha_2{}^2 I)^{-1} \quad (5)$$

$$\beta_{MX}^{(i)J} = (\partial^2 \beta_{MX}^{(i)}/\partial T^2)_P + (2/T)(\partial \beta_{MX}^{(i)}/\partial T)_P, \quad \text{for} \quad i = 0, 1, 2 \quad (6)$$

$$C_{MX}^J = (\partial^2 C_{MX}/\partial T^2)_P + (2/T)(\partial C_{MX}/\partial T)_P = [(\partial^2 C_{MX}^\phi/\partial T^2)_P + (2/T)(\partial C_{MX}^\phi/\partial T)_P](2|z_M z_X|^{1/2})^{-1} \quad (7)$$

In eqs 3−7, $A_J = A_C(\rho_1^\circ)^{1/2}$ is the molality-based Debye−Hückel coefficient for heat capacities, $v = v_M + v_X$, where $v_M$ and $v_X$ are the stoichiometric coefficients of the cations and anions, respectively, in the salt $Mv_MXv_X$ and $I$ is the molality-based ionic strength ($I = {}^1/_2 \sum m_i z_i{}^2$), which will be used throughout this paper. The constant $b$ is 1.2 for all solutes, $\alpha_1 = 2$, and $\alpha_2 = 0$ (i.e., $\beta_{MX}^{(2)}$ is not required) unless both ions have a charge greater than or equal to 2.[21] It should be noted that $b$, $\alpha_1$, and $\alpha_2$ are assumed to be temperature independent. Thus, at fixed pressure and temperature, $C_{p\phi}$ is expressed in terms of up to five adjustable parameters per electrolyte: $C_{p2}^\circ$, $\beta_{MX}^{(0)J}$, $\beta_{MX}^{(1)J}$, $\beta_{MX}^{(2)J}$, and $C_{MX}^J$, which are generally determined by fitting the equations to experimental $C_{p\phi}$ data. Although lacking a fundamental theoretical justification, the Pitzer equations are able to correlate heat capacities to very high concentrations (up to saturation for many electrolytes).[21]

Another advantage of the Pitzer approach is that these heat capacity parameters can be combined with independently determined parameters for osmotic coefficients and relative apparent molar enthalpies to give a thermodynamically consistent description of the excess Gibbs energies of the solution as a function of temperature and concentration. Using these three types of Pitzer parameters, determined only at 25 °C, the excess Gibbs energy of electrolyte solutions can readily be extrapolated up to about 100 °C, providing the heat capacities are assumed to be temperature independent.[22] On the other hand, to model solubilities, the excess thermodynamic properties of an electrolyte solution must be known up to saturation; otherwise even a wrong temperature coefficient of solubility may be predicted.[22,23] Thus, a further motivation for the present work was to extend the heat capacity measurements to near-saturation concentrations, at least for $Na_2SO_4$(aq) and $Na_2CO_3$(aq).

## Experimental Section

Heat capacities per unit volume ($\sigma/J{\cdot}K^{-1}{\cdot}cm^{-3}$) of the various solutions were measured using a Picker flow calorimeter (Sodev, Sherbrooke, Canada) consisting of a specific heat unit, model CP-Cpr, a thermal detector, model DT-C, and a temperature control/program unit, model CT-L. The heat unit measures directly the difference in the volumetric heat capacity of two liquids ($\Delta\sigma$) flowing through reference and working cells, respectively.[24] Test solutions and the reference liquid (usually water) were introduced into the calorimeter using a four-way chromatography valve (Hamilton, USA, Model HVP). A flow rate of 0.6 $cm^3{\cdot}min^{-1}$ was maintained by a Gilson Minipulse 3 peristaltic pump. The output voltage from the detector was measured with an integrating voltmeter (Hewlett-Packard, model 34401A) for periods from (30 to 60) s. This quantity is directly proportional to the difference in the applied power $\Delta W_A$ necessary to maintain the "final" temperature of both liquids equal. When the test solution is in the working cell and the reference liquid is in the reference cell, the relative volumetric heat capacity difference between the two liquids is given by[25]

$$\Delta\sigma/\sigma^\circ = (\sigma - \sigma^\circ)/\sigma^\circ = \Delta W_A/W^\circ \quad (8)$$

where $\sigma^\circ$ is the heat capacity per unit volume of the reference liquid and $W^\circ$ is the baseline power applied to both cells to heat the flowing liquids.

On the other hand, when the test solution is in the reference cell and the reference solution in the working cell, the following relation applies[25]

$$\Delta\sigma/\sigma^\circ = -\Delta W_B/(W^\circ + \Delta W_B) \quad (9)$$

where $\Delta W_B$ is the extra power applied to maintain the reference liquid at the same "final" temperature as that of the test solution.

The values of $C_p$, the heat capacity per unit mass ($J{\cdot}K^{-1}{\cdot}g^{-1}$), of the solution were calculated from the volumetric heat capacities, using the expression[25]

$$C_p = C_p^\circ(1 + \Delta\sigma/\sigma^\circ)\rho^\circ/\rho \quad (10)$$

where $C_p^\circ$ and $\rho^\circ$ are the heat capacity and the density of the reference liquid, respectively. The solution densities ($\rho/g{\cdot}cm^{-3}$), needed for the calculation of $C_p$, are well established for the three electrolytes of interest in the present study and so were not remeasured. The required $\rho$ values were obtained using various literature models. The particular choices made for each electrolyte are discussed below.

The apparent molar heat capacities ($C_{p\phi}/J{\cdot}K^{-1}{\cdot}mol^{-1}$) of the solutions for binary systems were calculated from the expression

$$C_{p\phi} = MC_p + [1000(C_p - C_{p1}^\circ)/m] \quad (11)$$

where $C_{p1}^\circ$ is the heat capacity of water and $M$ is the molar mass of the electrolyte ($g{\cdot}mol^{-1}$).

**Table 2. Experimental Relative Volumetric Heat Capacities, $\Delta\sigma/\sigma°$, Densities, $\rho$, Heat Capacities, $C_p$, and Apparent Molar Heat Capacities, $C_{p\phi}$, of Aqueous Solutions of Sodium Chloride at 25 °C[a]**

| | | | $\rho^b$ | $C_p$ | $C_{p\phi}$ | $C_{p\phi}$ | |
|---|---|---|---|---|---|---|---|
| $m/m°$ | $n$ | $10^3\Delta\sigma/\sigma°$ | $g\cdot cm^{-3}$ | $J\cdot K^{-1}\cdot g^{-1}$ | $J\cdot K^{-1}\cdot mol^{-1}$ | $J\cdot K^{-1}\cdot mol^{-1}$ | |
| 0.4994 | 3 | −15.544(39) | 1.017 07 | 4.035 86(16) | −56.57(33) | $-55.88^c$ | $-55.92^d$ |
| 0.9856 | 2 | −27.296(2) | 1.035 68 | 3.916 00(1) | −40.92(1) | $-40.37^c$ | $-40.01^d$ |
| 1.9993 | 2 | −44.136(6) | 1.072 27 | 3.716 89(2) | −15.36(1) | $-15.14^c$ | $-15.16^d$ |
| 3.0002 | 3 | −54.062(33) | 1.105 84 | 3.566 66(13) | 3.38(5) | $3.33^c$ | $3.06^d$ |
| 3.9876 | 2 | −59.217(57) | 1.136 78 | 3.450 66(21) | 18.29(6) | $17.86^c$ | $17.43^d$ |
| 4.9941 | 3 | −61.006(45) | 1.166 42 | 3.356 58(16) | 30.91(4) | $30.45^c$ | $29.71^d$ |
| 5.9928 | 4 | −59.823(49) | 1.194 24 | 3.282 53(17) | 41.76(4) | $41.26^c$ | $40.32^d$ |

[a] $m° = 1$ mol·kg$^{-1}$; $n$ = number of independent measurements. Values in parentheses are standard deviations in the last significant figure. [b] Calculated from ref 36. [c] Interpolated values of Clarke and Glew.[35] [d] Calculated from ref 32.

For ternary systems (solvent plus two solutes), the mean apparent molar heat capacity of the solutions was calculated from the expression

$$C_{p\phi}(\text{mean}) = [C_p(1000 + m_2M_2 + m_3M_3) - 1000C°_{p1}]/(m_2 + m_3) \quad (12)$$

where the subscripts 2 and 3 denote the two solutes (1 is the solvent).

The density of pure water at 25 °C was taken as $\rho°_1 = 0.997\,047$ g·cm$^{-3}$, which is consistent with the IAPWS-IF97 value.[26] The latter formulation gives the maximum density $\rho°_{1max} = 0.999\,975$ g·cm$^{-3}$ at 4 °C, which is in excellent agreement with the currently recommended value.[27] The heat capacity of pure water ($C°_{p1} = 4.1819$ J·K$^{-1}$·g$^{-1}$) was also taken from IAPWS-IF97. This choice will be discussed later.

All reagents were of analytical grade quality. Sodium sulfate and sodium carbonate solutions were prepared by mass from commercial anhydrous solids (Univar, APS Chemicals Ltd., Australia, assay > 99 mol %) dried overnight at 110 °C and cooled under vacuum. Solutions were prepared using water that had been sequentially deionized, glass-distilled, and degassed. Buoyancy corrections were applied throughout.

Stock solutions of sodium hydroxide (~20 mol dm$^{-3}$) were prepared by dissolving solid sodium hydroxide (Univar, assay > 97 mol %) in carbonate-free water. The resultant solution was allowed to stand for about one month in a tightly sealed Pyrex glass container before being filtered (0.45 $\mu$m) under high-purity nitrogen to remove precipitated carbonate.[28] The hydroxide concentration of the filtered solution was then analyzed by the Gran method (to ±0.2% relative) by titration against hydrochloric acid (BDH concentrated volumetric standard), and its density was determined by vibrating tube densimetry (Anton Paar DMA 02D). More dilute solutions were prepared by weight using carbonate-free water. Carbonate was found by the Gran plots to be <0.1% of the total alkalinity in the diluted solutions. Although it was not specifically investigated here, it has been found that this procedure produces only slight silicate contamination of the concentrated hydroxide solution. Such contaminants do not exert a measurable effect on the physicochemical properties of diluted hydroxide solutions.[29]

After dissolution and homogenization, most solutions were filtered (0.45 $\mu$m) prior to introduction into the calorimeter. Separate tests showed that microfiltration had no measurable effect (<0.1% relative) on solution concentrations.

## Results and Discussion

***Calorimeter Performance.*** Flow calorimeters have revolutionized the measurement of heat capacities of fluids, because of their sensitivity, precision, and speed.[18] However, concerns have been raised about their accuracy because of possible heat losses. Various attempts have been made to quantify these losses (e.g., Desnoyers et al.[25]), but the results have been inconclusive, with the observable effects being similar to the likely uncertainties. Some authors have opted to "correct" their data (e.g., Hovey and Hepler,[30] Marriott et al.[31]) while others have not considered such corrections as meaningful (e.g., Allred and Woolley[11]). Archer[32] has made a detailed critique of such approaches.

The performance of the present calorimeter is well established at lower concentrations.[33,34] However, the measurement of the heat capacities of concentrated electrolyte solutions might involve extra uncertainty, because of the increased differences between the target solution properties and those of water (the usual reference liquid). It was therefore considered desirable to test the calorimeter performance by comparing the results of measurements on concentrated NaCl(aq) solutions to values obtained from various models.[32,35]

The heat capacity data obtained for concentrated NaCl(aq) solutions, uncorrected for any heat losses, are summarized in Table 2. Also listed in Table 2 are the relevant density data, calculated from the model of Rogers and Pitzer,[36] required for calculation of mass-based heat capacities from the experimental $\Delta\sigma/\sigma°$ values via eq 10. The densities of NaCl(aq) are very well established, with numerous literature models agreeing to better than ±100 $\mu$g·cm$^{-3}$, which corresponds to an uncertainty of less than ±0.5 J·K$^{-1}$·mol$^{-1}$ in the $C_{p\phi}$ of NaCl(aq) at $m \geq 1$ mol·kg$^{-1}$.

The value selected for the heat capacity of water, $C°_{p1} = 4.1819$ J·K$^{-1}$·g$^{-1}$ at 25 °C, needed for the calculation of $C_{p\phi}$ via eq 11, requires comment. This value, taken from the simplified "industrial formulation" IAPWS-IF97,[26] is almost identical to that given in the more comprehensive IAPWS-95 formulation ($C°_{p1} = 4.1813$ J·K$^{-1}$·g$^{-1}$)[37] but differs significantly from the value cited by Kell ($C°_{p1} = 4.1793$ J·K$^{-1}$·g$^{-1}$)[38] that has been widely used in heat capacity work. Calculations indicated that such a change in $C°_{p1}$ corresponded to a negligible variation (<0.1 J·K$^{-1}$·mol$^{-1}$) in $C_{p\phi}$ for NaCl(aq) over the whole concentration range.

Table 2 also includes values of $C_{p\phi}$ for NaCl(aq) from the critical reviews by Clarke and Glew[35] and by Archer.[32] Clarke and Glew[35] tabulated recommended values at rounded NaCl molalities, based on measurements from 16 studies, 10 of which utilized non-Picker (i.e., static) calorimeters. Their values were interpolated for the present purpose using a fourth-order polynomial. The maximum deviation between our results and their interpolated values is 0.7 J·K$^{-1}$·mol$^{-1}$ (average 0.4 J·K$^{-1}$·mol$^{-1}$). Archer[32] presented his assessment of the thermodynamic data for NaCl(aq) in the form of an extended Pitzer equation. The maximum deviation between our $C_{p\phi}$ results and those calculated by Archer's model is 1.4 J·K$^{-1}$·mol$^{-1}$ (average

0.8 J·K$^{-1}$·mol$^{-1}$). This is excellent agreement: better even than the minimum uncertainty of ±1 J·K$^{-1}$·mol$^{-1}$, estimated by Hepler and Hovey,[18] or ±2 J·K$^{-1}$·mol$^{-1}$, suggested recently by Marriott et al.[31] for such measurements. It implies that correction for possible heat losses is unnecessary, at least for the present calorimeter working at 25 °C with concentrated electrolyte solutions.

***Calorimeter Asymmetry.*** Measurements with Picker calorimeters typically employ a liquid flow sequence of reference−solution−reference, producing two measurements of $\Delta\sigma/\sigma°$.[24] For aqueous solutions, water is almost always the reference and thus the first measurement "leg" (eq 8) corresponds to the displacement of water in the calorimeter by solution. The second "leg" (eq 9) corresponds to the displacement of solution in the calorimeter by water. Early designs of the Picker calorimeter exhibited a small asymmetry in the results obtained from the two legs.[39] This was apparently rectified in later designs, and little mention of such effects has been made in recent times.

During the course of the present measurements, it was observed, consistent with our previous work[33,34] and that of others,[11,25] that the agreement between the two "legs" at low concentrations of NaCl ($m \leq 1$ mol·kg$^{-1}$) was quantitative (≤0.2 mJ·K$^{-1}$·g$^{-1}$). However, at higher concentrations, small but reproducible differences that increased with increasing concentration were observed. The question then arises as to which results are "best": the first or second leg or their average?

Consistent with the calorimeter performance at lower concentrations, it is unlikely that the present difference arises from the electronic operation of the calorimeter. Conceivably, this difference may be due to incomplete "flushing" of the (concentrated) solutions on the second leg due to the imperfect replacement of the concentrated solution by the reference liquid, especially toward the surface of the calorimeter tube. Alternatively, this effect may be due to the increasing differences between the properties of the two liquids. The most important of these would probably be a variation in thermal conductivity, which would lead to unequal heat losses in the two cells. Differences in surface tension, viscosity, and perhaps even $\sigma$ itself might also be significant. Unfortunately, it is difficult to devise a definitive test to distinguish among the various explanations.

Regardless of its origin, this effect of increasing concentration was observed for all of the electrolytes studied. By way of example, Figure 1 plots the difference in the heat capacities obtained from the first and second leg measurements for $Na_2SO_4$(aq). As for NaCl(aq), these differences were reproducible and increased monotonically with increasing solute concentration. To further investigate this effect, the heat capacities of $Na_2SO_4$(aq) were measured using 0.5 mol·kg$^{-1}$ $Na_2SO_4$(aq) as the reference instead of water. These data showed a much-reduced difference (Figure 1). This technique has been used by others,[10] but although it improves the apparent precision of the data, it does not improve their accuracy, since the uncertainties in the (new) reference and test solutions are cumulative.

Furthermore, substitution of water as the reference by a solution does not discriminate between the various possible explanations. Tests for incomplete chloride displacement in the second leg of the NaCl(aq) measurements, using silver nitrate, were negative. However, for the NaOH(aq) measurements, testing with pH paper clearly indicated incomplete displacement of the concentrated solution during the second leg measurement, as did the very slowly drifting baseline. This implies, but does not prove, that incomplete flushing and/or slow desorption of the electrolyte from the walls of the calorimeter tubing may be the source of this observed difference.

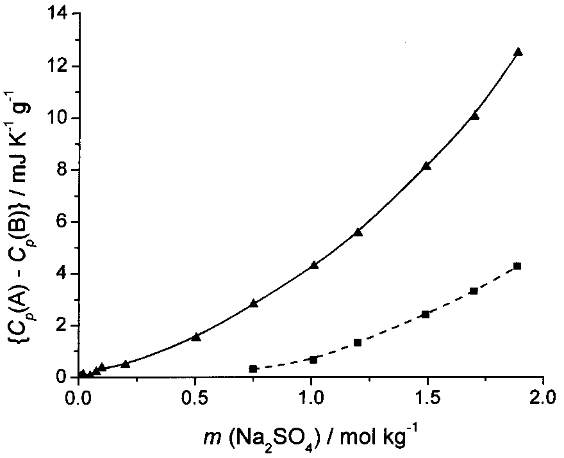

**Figure 1.** Difference between "first leg", $C_p$(A), and "second leg", $C_p$(B), heat capacities for $Na_2SO_4$(aq) as a function of the molality of the test solutions at 25 °C. The reference solutions were water (▲) and 0.5 mol·kg$^{-1}$ sodium sulfate (■), respectively.

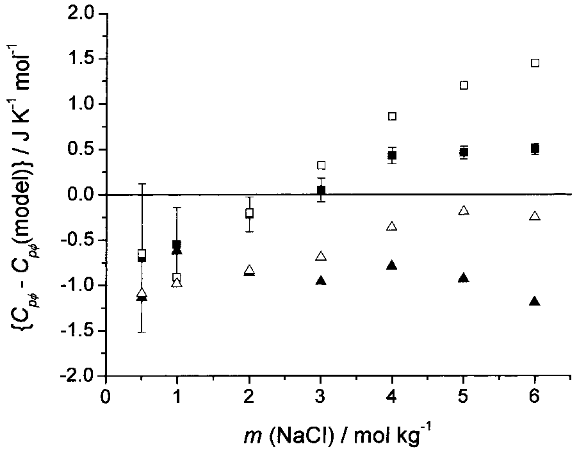

**Figure 2.** Difference between the present apparent molar heat capacities for NaCl(aq) at 25 °C (squares, "first leg"; triangles, "second leg") and calculated values obtained from the models of Clarke and Glew[35] (solid symbols) and Archer[32] (open symbols). The error bars show the effect on $C_{p\phi}$ of an uncertainty of ±100 $\mu$g·cm$^{-3}$ in the solution density.

Closer consideration of the present NaCl(aq) data sheds little further light on this matter. The differences between present heat capacity results (both legs) at high NaCl(aq) concentrations and the recommended values of Clarke and Glew[35] and those predicted by Archer's model[32] (both of which are not solely dependent on flow-calorimetric data) are plotted in Figure 2. Comparison with Clarke and Glew's values suggests that the first leg values may be more accurate while the same comparison with Archer's calculated values suggests the opposite! Apart from identifying systematic differences between Clarke and Glew's values and Archer's model, this is not of much use. Clearly this matter requires further detailed investigation.

The differences between the first and second leg values are somewhat greater for the other electrolytes than for NaCl(aq), but there are too few reliable static calorimetric data to make a meaningful comparison. However, taken collectively, the evidence presented above suggests that the results of the first leg measurements, in which the solution displaces water in the calorimeter, *may* be more reliable. Accordingly, while reiterating that the effects are small

**Table 3. Experimental Relative Volumetric Heat Capacities, $\Delta\sigma/\sigma°$, Densities, $\rho$, Heat Capacities, $C_p$, and Apparent Molar Heat Capacities, $C_{p\phi}$, of Aqueous Sodium Sulfate Solutions at 25 °C[a]**

| | | | $\rho^b$ | $C_p$ | $C_{p\phi}$ |
|---|---|---|---|---|---|
| $m/m°$ | $n$ | $10^3\Delta\sigma/\sigma°$ | $g \cdot cm^{-3}$ | $J \cdot K^{-1} \cdot g^{-1}$ | $J \cdot K^{-1} \cdot mol^{-1}$ |
| 0.01008 | 6 | −0.556(23) | 0.998 35 | 4.174 12(10) | −179.3(95) |
| 0.01998 | 3 | −1.070(26) | 0.999 62 | 4.166 67(11) | −170.3(55) |
| 0.04998 | 3 | −2.501(42) | 1.003 42 | 4.144 95(17) | −150.6(35) |
| 0.07496 | 3 | −3.568(53) | 1.006 55 | 4.127 64(22) | −137.6(30) |
| 0.09997 | 3 | −4.524(37) | 1.009 67 | 4.110 93(15) | −125.9(15) |
| 0.2019 | 3 | −7.881(24) | 1.022 17 | 4.046 97(10) | −93.48(49) |
| 0.5051 | 10 | −12.946(22) | 1.057 93 | 3.890 21(9) | −24.92(18) |
| 0.7505 | 2 | −13.353(47) | 1.085 56 | 3.789 63(18) | 15.61(26) |
| 1.0102 | 2 | −11.484(91) | 1.113 66 | 3.701 01(34) | 49.66(39) |
| 1.1991 | 2 | −9.053(21) | 1.133 41 | 3.645 46(8) | 70.43(8) |
| 1.4912 | 5 | −3.661(90) | 1.162 90 | 3.572 35(32) | 98.65(26) |
| 1.6999 | 4 | 0.776(41) | 1.183 23 | 3.526 61(14) | 115.43(11) |
| 1.8871 | 4 | 5.509(48) | 1.200 98 | 3.490 91(17) | 129.69(11) |

[a] $m° = 1$ mol·kg$^{-1}$; $n$ = number of independent measurements. Values in parentheses are standard deviations in the last significant figure. [b] Calculated from ref 41.

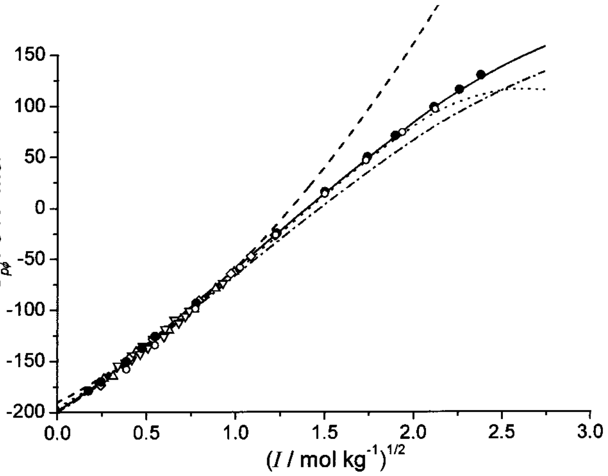

**Figure 3.** Apparent molar heat capacities of $Na_2SO_4$(aq) at 25 °C. Experimental data: ●, this work; ◇, Saluja et al.;[7] △, Perron et al.,[5] corrected for heat loss;[25] ▽, Olofsson et al.;[6] ○, Randall and Rossini.[4] Pitzer correlations: solid line, this work; dash−dot line, Holmes and Mesmer;[43] dotted line, Criss and Millero.[44] RRM equation: dashed line, Olofsson et al.;[6] a virtually identical line is obtained using the parameters of Desnoyers et al.[25]

(Figures 1 and 2), all the data reported in this paper were those obtained from first leg measurements.

***$Na_2SO_4$.*** The heat capacity data obtained for $Na_2SO_4$(aq) are summarized in Table 3. The densities of $Na_2SO_4$(aq), required for processing the data, have been investigated on numerous occasions and critically reviewed several times, most recently by Krumgalz et al.[40] For the present purpose, densities calculated from the Pitzer model of Monnin[41] were taken as representative of the available data. These values agree to better than ∼ ±100 $\mu$g·cm$^{-3}$ over the whole concentration range at 25 °C with the models of Krumgalz et al.[40] and Stanley et al.[42]

The present $C_{p\phi}$ values are plotted in Figure 3 along with the data of Randall and Rossini,[4] Perron et al.[5] (corrected for a heat loss in their early-model Picker calorimeter, as described by Desnoyers et al.[25]), Olofsson et al.,[6] and Saluja et al.[7] Also included in Figure 3 are representative lines calculated from an RRM model[6,25] and the Pitzer models of Holmes and Mesmer[43] and Criss and Millero.[44]

At moderate concentrations (∼ ≤0.3 mol·kg$^{-1}$), agreement among the present and literature $C_{p\phi}$ values is very good (±4 J·K$^{-1}$·mol$^{-1}$). The present results are in almost quantitative agreement (±1 J·K$^{-1}$·mol$^{-1}$) with the values of Saluja et al.[7] and, at higher concentrations, with Randall and Rossini's data[4] (to within 4 J·K$^{-1}$·mol$^{-1}$). However, as is often found for heat capacities measured in traditional static calorimeters, Randall and Rossini's data diverge increasingly from the flow-calorimeter values as the concentration decreases. The latter are probably more reliable, since the performance requirements placed on static calorimeters at low concentrations, where $C_p \rightarrow C_p^\circ$, become limiting.[32]

As expected, the RRM models do not reliably predict $C_{p\phi}$ values at $m >$ ∼0.5 mol·kg$^{-1}$. The Pitzer model of Holmes and Mesmer,[43] which was parametrized to correlate data up to 225 °C, also predicts $C_{p\phi}$ poorly above ∼0.5 mol·kg$^{-1}$. In contrast, the more recent Pitzer model of Criss and Millero,[44] which is restricted to 25 °C and which included the Randall and Rossini data,[4] correlates the present results very well up to ∼1.5 mol·kg$^{-1}$. Above this concentration, the Criss and Millero model shows a broad maximum that is *not* reflected in the present data. This emphasizes the dangers inherent in even short extrapolations of Pitzer models beyond their limits of parametrization. Thus, Pitzer heat capacity parameters, together with the standard partial molar heat capacity, were refitted to the present data using the ChemSage optimizer.[23] This new model represents the present experimental data within ±1 J·K$^{-1}$·mol$^{-1}$ over the entire concentration range (Table 4, Figure 3).

As would be anticipated from their slightly differing extrapolation functions (compare the first terms on the right-hand sides of eqs 1 and 3), the standard partial molar heat capacities of the solute, $C_{p2}^\circ$, obtained from the various models differ somewhat. The value of $C_{p2}^\circ$ derived from the Pitzer fit of the present data, (−198.3 ± 0.7) J·K$^{-1}$·mol$^{-1}$, agrees well with those of Criss and Millero (−195.6 J·K$^{-1}$·mol$^{-1}$),[44] Holmes and Mesmer (−199.5 J·K$^{-1}$·mol$^{-1}$),[43] Saluja et al. (−195.0 J·K$^{-1}$·mol$^{-1}$),[7] and Rogers and Pitzer (−196.5 J·K$^{-1}$·mol$^{-1}$).[46] In their critical review, Hepler and Hovey recommended a significantly different value ($C_{p2}^\circ = -190$ J·K$^{-1}$·mol$^{-1}$),[18] which is based on the older values reported by Desnoyers et al. (−191.7 J·K$^{-1}$·mol$^{-1}$)[25] and Olofsson et al. (−190.1 J·K$^{-1}$·mol$^{-1}$),[6] while the model of Pabalan and Pitzer yields an even less negative value (−187.5 J·K$^{-1}$·mol$^{-1}$).[47] In their recent review on the thermodynamic properties of $Na_2SO_4$(aq), Rard et al.[48] selected $C_{p2}^\circ = (-193.7 \pm 2.0)$ J·K$^{-1}$·mol$^{-1}$ as a reasonable compromise. Although not significantly different, the average of the more negative results, $C_{p2}^\circ = (-197.0 \pm 1.9)$ J·K$^{-1}$·mol$^{-1}$, would seem to be a better estimate.

***$Na_2CO_3$.*** The present heat capacity data for $Na_2CO_3$(aq) are summarized in Table 5. The densities of $Na_2CO_3$(aq) have been reviewed recently by Krumgalz et al.[40] Their Pitzer correlation gives values at 25 °C (Table 5) that are in good agreement (better than ±400 $\mu$g·cm$^{-3}$) with those calculated using a recently developed empirical model.[42]

Interpretation of the heat capacity data for $Na_2CO_3$(aq) is less straightforward than that for typical strong electrolytes because of the hydrolysis of the carbonate ion:

$$CO_3^{\;2-} + H_2O \leftrightarrow HCO_3^{\;-} + OH^- \qquad (13)$$

Figure 4 (filled circles) shows the present heat capacity data for $Na_2CO_3$(aq), as measured, that is, prior to correction for the effects of equilibrium 13. Note that the $C_{p\phi}$ values in Figure 4 are plotted against the square root of the stoichiometric ionic strength of $Na_2CO_3$ (3$m$/mol·

**Table 4. Pitzer Model Parameters for Heat Capacities (25 °C) Derived in This Work[a]**

| | $C^\circ_{p2}$ | | | |
|---|---|---|---|---|
| | $J \cdot K^{-1} \cdot mol^{-1}$ | $10^5 \beta^{(0)J}$ | $10^5 \beta^{(1)J}$ | $(2 \times 10^5)\lvert z_M z_X \rvert^{1/2} C^J$ |
| $Na_2SO_4$ | $-198.3 \pm 0.7$ | $-4.23 \pm 0.14$ | $-12.06 \pm 0.68$ | $1.022 \pm 0.084$ |
| $Na_2CO_3$ | $-228.5 \pm 0.7$[b] | $-3.019 \pm 0.040$[b] | $-15.42 \pm 0.03$[b] | 0.35[c] |
| NaOH | $-101.4 \pm 0.7$ | $-1.774 \pm 0.053$ | $-3.64 \pm 0.33$ | $0.234 \pm 0.012$ |

[a] Values in parentheses are standard deviations in the last significant figure. [b] Peiper and Pitzer.[45] [c] Estimated.

**Table 5. Experimental Relative Volumetric Heat Capacities, $\Delta\sigma/\sigma^\circ$, Densities, $\rho$, Heat Capacities, $C_p$, and Apparent Molar Heat Capacities, $C_{p\phi}$, of Aqueous Sodium Carbonate Solutions at 25 °C[a]**

| | | | $\rho$[b] | $C_p$ | $C_{p\phi}$ |
|---|---|---|---|---|---|
| $m/m^\circ$ | $n$ | $10^3\Delta\sigma/\sigma^\circ$ | $g \cdot cm^{-3}$ | $J \cdot K^{-1} \cdot g^{-1}$ | $J \cdot K^{-1} \cdot mol^{-1}$ |
| 0.009965 | 5 | −0.175(45) | 0.998 15 | 4.176 55(19) | −94(19) |
| 0.02012 | 4 | −0.431(22) | 0.999 27 | 4.170 80(9) | −109.7(47) |
| 0.04995 | 4 | −1.286(35) | 1.002 52 | 4.153 72(14) | −123.9(29) |
| 0.07434 | 4 | −1.959(25) | 1.005 15 | 4.140 06(11) | −124.0(14) |
| 0.09985 | 4 | −2.578(27) | 1.007 89 | 4.126 24(11) | −120.1(11) |
| 0.1998 | 4 | −4.528(26) | 1.018 46 | 4.075 44(10) | −100.87(54) |
| 0.4996 | 4 | −6.062(20) | 1.049 00 | 3.950 69(8) | −44.05(17) |
| 0.7498 | 4 | −3.810(38) | 1.073 38 | 3.869 70(15) | −6.22(21) |
| 1.0000 | 4 | 0.633(29) | 1.096 89 | 3.803 65(11) | 24.90(12) |
| 1.1996 | 3 | 5.390(17) | 1.115 06 | 3.759 46(7) | 46.32(6) |
| 1.4996 | 3 | 14.115(55) | 1.141 46 | 3.704 38(20) | 74.20(16) |
| 1.7492 | 3 | 22.567(30) | 1.162 66 | 3.667 15(11) | 94.40(7) |
| 1.9999 | 5 | 31.767(141) | 1.183 33 | 3.635 51(50) | 112.12(30) |
| 2.4986 | 4 | 52.355(88) | 1.222 84 | 3.588 24(30) | 142.72(15) |
| $Na_2CO_3 + 0.0503\ mol\ kg^{-1}$ NaOH with $0.0503\ mol\ kg^{-1}$ NaOH as the Reference Liquid[c] | | | | | |
| 0.01000 | 4 | −0.361(38) | 1.000 40 | 4.162 77(16) | −105.2(26) |
| 0.02002 | 3 | −0.704(18) | 1.001 49 | 4.156 80(8) | −112.6(11) |
| 0.05001 | 3 | −1.635(54) | 1.004 74 | 4.139 50(22) | −120.9(23) |
| 0.1000 | 3 | −2.966(12) | 1.010 10 | 4.112 07(5) | −119.5(3) |
| 0.2000 | 3 | −4.871(23) | 1.020 62 | 4.061 88(9) | −102.8(4) |
| $Na_2CO_3 + 0.0503\ mol\ kg^{-1}$ NaOH with Water as Reference | | | | | |
| 0.01000 | 4 | −1.228(29) | 1.000 40 | 4.162 76(12) | −105.4(20) |
| 0.05001 | 2 | −2.476(43) | 1.004 74 | 4.139 60(18) | −120.0(18) |
| 0.2000 | 2 | −5.725(39) | 1.020 62 | 4.061 91(16) | −102.7(7) |

[a] $m^\circ = 1\ mol \cdot kg^{-1}$; $n$ = number of independent measurements. Values in parentheses are standard deviations in the last significant figure. [b] Calculated from ref 40. [c] Heat capacities were calculated assuming a density of $0.999\ 29\ g \cdot cm^{-3}$ and a heat capacity of $4.1689\ J \cdot K^{-1} \cdot g^{-1}$ (obtained from the Pitzer models derived in this study) for the $0.0503\ mol \cdot kg^{-1}$ NaOH(aq) reference solution.

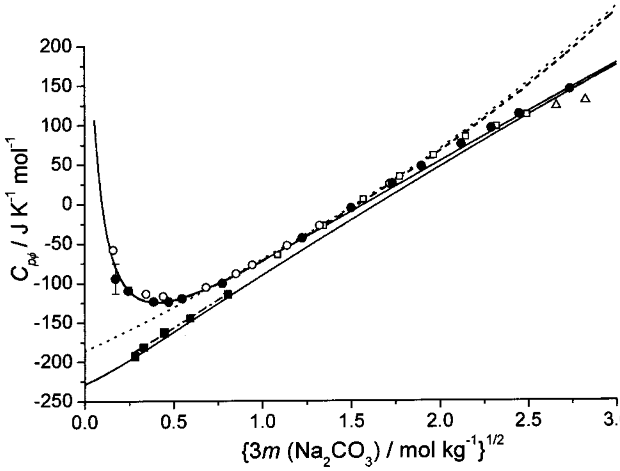

**Figure 4.** Apparent molar heat capacities of $Na_2CO_3$(aq) at 25 °C. Experimental data: ●, this work; ○, Perron et al.,[5] corrected for heat loss;[25] □, Chernen'kaya;[8] △, Aseyev;[49] ■, this work, in $0.0503\ mol \cdot kg^{-1}$ NaOH. Pitzer correlations: solid and dash−dot lines, this work (see text); dashed line, Peiper and Pitzer;[45] dotted line, Criss and Millero.[44]

$kg^{-1})^{1/2}$, rather than the total $I$, as some of the data refer to solutions with added NaOH; see below. The results are in very good agreement with those of Perron et al.[5] up to $0.3\ mol \cdot kg^{-1}$, the highest concentration studied by those authors. At higher concentrations, the present data also agree reasonably well with the values of Chernen'kaya,[8] although the curvature in the latter at $m > \sim 1.5\ mol \cdot kg^{-1}$ is less pronounced in our data. It is noteworthy that the two points attributed in Figure 4 to Aseyev[49] appear to be *extrapolations* from the data of Chernen'kaya and are almost certainly too low. The lines in Figure 4 are calculated from various Pitzer models. It can be seen that the two-parameter model ($C^J_{MX} = 0$ in eq 3) for $C_{p\phi}$ used by both Peiper and Pitzer[45] and by Criss and Millero[44] does not adequately describe the data at higher concentrations, for which a $C^J_{MX}$ term is required. This term was estimated from the present data (Table 4). Standard quantities of reaction 13 and Pitzer parameters for $NaHCO_3$(aq) were taken from ref 22.

Polya et al.[50] have recently measured enthalpies of dilution of $Na_2CO_3$(aq) from $m = 1.45\ mol \cdot kg^{-1}$ to $m = 0.008\ mol \cdot kg^{-1}$ at seven temperatures from 25 °C to 250 °C. They represented their data with a Pitzer ion-interaction treatment by taking the hydrolysis equilibrium (eq 13) into account. We have calculated $C_{p\phi}$ values at 25 °C from their model and found general agreement with our experimental data, although the calculated values deviate systematically by up to $-7.5\ J \cdot K^{-1} \cdot mol^{-1}$ and $+17\ J \cdot K^{-1} \cdot mol^{-1}$ below and above $m = 0.75\ mol \cdot kg^{-1}$, respectively. The present results for $C_{p\phi}$ should be more reliable, having been obtained more directly.

The most extraordinary feature of the data in Figure 4 is the upturn in the measured $C_{p\phi}$ values at $<0.05\ mol \cdot kg^{-1}$, originally reported by Perron et al.[5] and confirmed in the present study. This apparent contradiction of the Debye−Hückel theory arises from the shift in the hydrolysis equilibrium (eq 13) during the measurement of $\Delta\sigma/\sigma^\circ$ (the so-called "chemical relaxation" effect; see ref 18). This can be seen from the present and previous data[5] for solutions with low $Na_2CO_3$(aq) concentrations containing NaOH to suppress the hydrolysis (Figure 4). These $C_{p\phi}$ values, which were obtained from the raw measurements by subtracting the contribution from the NaOH(aq) using Young's rule (cf. ref 30), show the expected decrease with increasing dilution.

Also shown in Figure 4 are the hypothetical apparent molar heat capacities calculated for the fully dissociated, unhydrolyzed salt ($2Na^+ + CO_3^{2-}$). These values were obtained from the present Pitzer model (Table 4) by suppressing the chemical relaxation effect, that is, by ignoring $OH^-$ and $HCO_3^-$ in the calculation. The resulting solid line lies slightly (by $\sim 7\ J \cdot K^{-1} \cdot mol^{-1}$) below the present experimental (filled squares) and calculated (dash−dot line) results obtained in the presence of NaOH, because the latter have not been corrected for the chemical relaxation effect. The value of $C^\circ_{p2}$ ($-228.5\ J \cdot K^{-1} \cdot mol^{-1}$) was taken from Peiper and Pitzer's model[45] (which is identical to the present model at low concentrations) and is in reasonable

**Table 6. Experimental Relative Volumetric Heat Capacities, $\Delta\sigma/\sigma^\circ$, Densities, $\rho$, Heat Capacities, $C_p$, and Apparent Molar Heat Capacities, $C_{p\phi}$, of Aqueous Sodium Hydroxide Solutions at 25 °C[a]**

| | | | $\rho^b$ | $C_p$ | $C_{p\phi}$ |
|---|---|---|---|---|---|
| $m/m^\circ$ | $n$ | $10^3\Delta\sigma/\sigma^\circ$ | g cm$^{-3}$ | J K$^{-1}$ g$^{-1}$ | J K$^{-1}$ mol$^{-1}$ |
| 0.0221 | 5 | −0.388(29) | 0.998 04 | 4.176 13(12) | −94.2(55) |
| 0.0496 | 4 | −0.848(19) | 0.999 26 | 4.169 09(8) | −91.5(16) |
| 0.0503 | 5 | −0.856(25) | 0.999 29 | 4.168 93(11) | −91.1(21) |
| 0.0749 | 4 | −1.225(14) | 1.000 38 | 4.162 85(6) | −87.78(77) |
| 0.1002 | 5 | −1.609(19) | 1.001 50 | 4.156 62(8) | −86.01(80) |
| 0.2004 | 4 | −2.987(16) | 1.005 87 | 4.132 83(7) | −79.57(34) |
| 0.5009 | 4 | −5.786(12) | 1.018 70 | 4.069 33(5) | −61.98(10) |
| 0.7514 | 4 | −6.978(30) | 1.029 12 | 4.023 29(12) | −50.17(17) |
| 0.9993 | 4 | −7.276(15) | 1.039 23 | 3.982 98(6) | −39.75(6) |
| 1.0003 | 3 | −7.261(74) | 1.039 27 | 3.982 88(30) | −39.66(31) |
| 2.0017 | 4 | −2.289(24) | 1.078 19 | 3.858 32(9) | −7.33(5) |
| 2.0061 | 4 | −2.298(32) | 1.078 36 | 3.857 70(12) | −7.31(7) |
| 2.9966 | 4 | 8.762(11) | 1.114 15 | 3.775 16(4) | 15.26(2) |
| 2.9981 | 4 | 8.774(27) | 1.114 20 | 3.775 02(10) | 15.28(4) |
| 4.0013 | 4 | 23.257(29) | 1.147 96 | 3.716 62(11) | 32.37(3) |
| 4.0020 | 3 | 23.199(92) | 1.147 98 | 3.716 34(33) | 32.31(10) |
| 5.0005 | 4 | 39.258(33) | 1.179 31 | 3.674 38(12) | 45.47(3) |
| 5.0065 | 4 | 39.470(79) | 1.179 49 | 3.674 56(28) | 45.64(7) |
| 5.9989 | 4 | 56.133(39) | 1.208 62 | 3.643 48(14) | 55.98(3) |
| 6.0026 | 3 | 56.073(61) | 1.208 73 | 3.642 96(21) | 55.92(4) |
| 6.9938 | 4 | 72.743(29) | 1.236 10 | 3.618 53(10) | 64.18(2) |

[a] $m^\circ = 1$ mol·kg$^{-1}$; $n$ = number of independent measurements. Values in parentheses are standard deviations in the last significant figure. [b] Calculated from the Pitzer model derived in this study (Table 7).

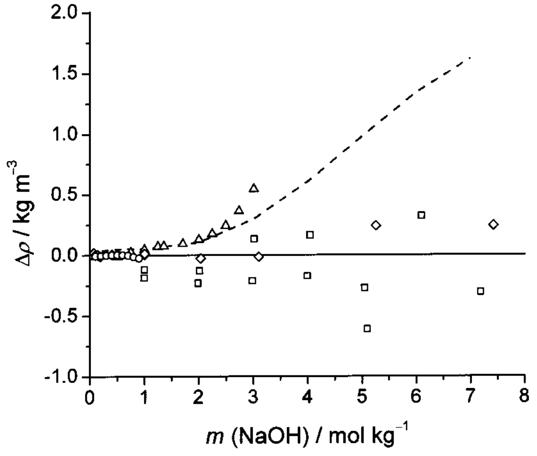

**Figure 5.** Difference between densities taken from the literature and the present Pitzer model for volumetric properties of NaOH(aq) at 25 °C. Experimental data: ◇, Roux et al.;[12] ○, Hershey et al.;[51] △, Herrington et al.;[52] □, Sipos et al.[53] Dashed line: Pitzer model of Simonson and Ryther.[54]

agreement with the −216 J·K$^{-1}$·mol$^{-1}$ proposed by Hepler and Hovey[18] in their critical review. The present, more negative value is more consistent with the experimental data. More importantly, both these values are very much more negative than that obtained by Criss and Millero ($C^\circ_{p2} = -186.0$ J·K$^{-1}$·mol$^{-1}$).[44] The latter is clearly in error, as a result of not allowing for the carbonate hydrolysis equilibrium (eq 13).

***NaOH.*** The present values for the heat capacities and the relevant density data for NaOH(aq) are given in Table 6. The densities of NaOH(aq) are less well characterized than those of the other electrolytes in this study. Selected data are plotted in Figure 5. After careful consideration of the available literature, the densities chosen for a Pitzer correlation were those reported by Roux et al.,[12] Hershey et al.,[51] Herrington et al.,[52] and Sipos et al.[53] These data are in good agreement (better than ±300 $\mu$g·cm$^{-3}$) but differ significantly (by up to 1600 $\mu$g·cm$^{-3}$) at higher concentrations from the values reported by Simonson and Ryther,[54] which are encapsulated in their Pitzer model (Figure 5). Calculations assuming Young's rule indicate that Simonson and Ryther's values are consistent with a contamination level of ~1% $Na_2CO_3$ in their NaOH(aq) (corresponding to ~2% of the total alkalinity). This might account for this difference, as Simonson and Ryther do not appear to have analyzed their solutions; nor would their stated method of preparation preclude carbonate contamination.[28] The results of the Pitzer correlation of the selected data are shown in Table 7. The standard partial molar volume so derived [$V^\circ_2 = (-5.29 \pm 0.06)$ cm$^3$·mol$^{-1}$] agrees almost perfectly with the result of Roux et al. [$(-5.27 \pm 0.02)$ cm$^3$·mol$^{-1}$][12] and very well with those of Allred and Woolley [$(-5.37 \pm 0.02)$ cm$^3$·mol$^{-1}$][11] and Perron et al. ($-5.20$ cm$^3$·mol$^{-1}$).[5] The average of these values [$V^\circ_2 = (-5.28 \pm 0.06)$ cm$^3$·mol$^{-1}$] is considerably less negative than Simonson and Ryther's value of $-5.60$ cm$^3$·mol$^{-1}$.[54]

**Table 7. Pitzer Model Parameters for Apparent Molar Volumes[a] of Sodium Hydroxide (25 °C) Derived in This Work**

| $V^\circ_2$ | $10^3\beta^{(0)V}$ | $10^3\beta^{(1)V}$ | $(2 \times 10^3)C^V$ |
|---|---|---|---|
| cm·mol$^{-1}$ | kg·mol$^{-1}$·bar$^{-1}$ | kg·mol$^{-1}$·bar$^{-1}$ | kg$^2$·mol$^{-2}$·bar$^{-1}$ |
| $-5.29 \pm 0.06$ | $7.61 \pm 0.23$ | $11.9 \pm 2.0$ | $-0.524 \pm 0.042$ |

[a] $V_\phi = V^\circ_2 + v|z_M z_X|A_V(2b)^{-1}\ln(1 + bI^{1/2}) - 2v_M v_X RT[mB^V_{MX} + m^2 v_M z_M C^V_{MX}]$, where $B^V_{MX} = \beta^{(0)V}_{MX} + 2\beta^{(1)V}_{MX}[1 - (1 + \alpha_1 I^{1/2})\exp(-\alpha_1 I^{1/2})](\alpha_1{}^2 I)^{-1}$, $I$ is the ionic strength, $A_V = 1.875$ cm$^3$·kg$^{1/2}$·mol$^{-3/2}$ is the Debye−Hückel parameter for volume,[19] $b = 1.2$, and $\alpha_1 = 2$.

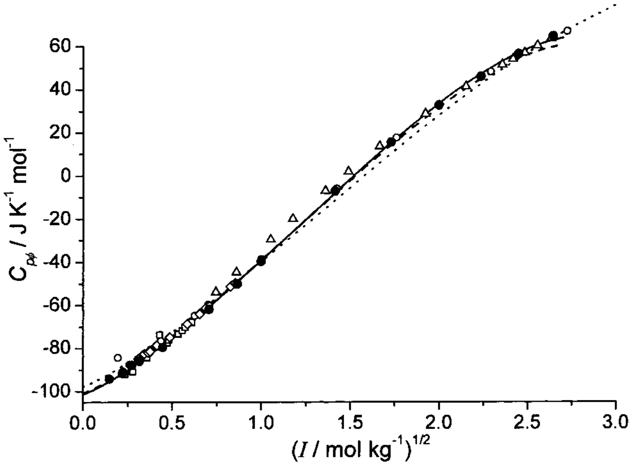

**Figure 6.** Apparent molar heat capacities of NaOH(aq) at 25 °C. Experimental data: ●, this work; △, Parker;[9] ◇, Singh et al.;[10] □, Allred and Woolley;[11] ○, Roux et al.[12] Pitzer correlations: solid line, this work; dashed line, Simonson et al.;[56] dotted line, Criss and Millero.[55]

For the heat capacities of NaOH(aq) (Figure 6), there is a very good agreement among the present and literature results obtained with Picker flow calorimeters (generally better than ±2 J·K$^{-1}$·mol$^{-1}$). The older data obtained by static calorimetry, as reviewed by Parker,[9] are higher by ~7 J·K$^{-1}$·mol$^{-1}$ at lower concentrations ($m <$ ~1.8 mol·kg$^{-1}$) but in excellent agreement, ±(1 to 2) J·K$^{-1}$·mol$^{-1}$, at higher concentrations.

The Pitzer model of Criss and Millero,[55] which is valid up to 12.33 mol·kg$^{-1}$, provides a worse fit to the data than that of Simonson et al. for $m < 6$ mol·kg$^{-1}$.[56] The latter, however, increasingly deviates from the available experimental data at higher concentrations (Figure 6). Accordingly, a new Pitzer model was fitted to the present results (Table 4). This represents the experimental data very well up to 7 mol·kg$^{-1}$ but shows a similar curvature to that of the model of Simonson et al.[56] at higher molalities. Obviously, it is not possible to describe the NaOH(aq) heat capacity data entirely satisfactorily to higher molalities using a three-parameter Pitzer model.

As for $Na_2SO_4$(aq), different correlation functions lead to somewhat different values for $C^{\circ}_{p2}$. Extrapolations using the RRM equation[10,25] and also Criss and Millero's Pitzer model[55] result in an average of $C^{\circ}_{p2} = (-96.5 \pm 1.4)$ J·K$^{-1}$·mol$^{-1}$, which is almost identical with the $-97$ J·K$^{-1}$·mol$^{-1}$ recommended by Hepler and Hovey.[18] On the other hand, combination of the present result (Table 4) with the values of Simonson et al.[56] and Allred and Woolley[11] values gives $C^{\circ}_{p2} = (-100.9 \pm 0.5)$ J·K$^{-1}$·mol$^{-1}$. Although this value is possibly more accurate, the difference probably lies within the limits of experimental uncertainty.[18]

## Conclusions

Accurate measurements of the heat capacities of concentrated aqueous electrolyte solutions can be made by flow calorimetry, providing the calorimeter “asymmetry”, which is probably related to inadequate flushing, is taken into consideration.

All heat capacity data were precisely correlated over the entire concentration range investigated using Pitzer models, but as is well established, if not always followed, great caution must be exercised in extrapolation of the values beyond the parametrization range.

Careful consideration of the present and literature data suggests that the present values of the standard partial molar heat capacities ($C^{\circ}_{p2}$) of $Na_2SO_4$(aq), $Na_2CO_3$(aq), and NaOH(aq) (Table 4) and the standard partial molar volume ($V^{\circ}_2$) of NaOH(aq) (Table 7) are probably more reliable than some previous estimates.

## Acknowledgment

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