MURDOCH RESEARCH REPOSITORY

http://researchrepository.murdoch.edu.au/

This is the author's final version of the work, as accepted for publication following peer review but without the publisher's layout or pagination.

Schrödle, S., Königsberger, E., May, P.M. and Hefter, G. (2010) *Heat capacities of aqueous sodium hydroxide/aluminate mixtures and prediction of the solubility constant of boehmite up to 300 °C.* Geochimica et Cosmochimica Acta, 74 (8). pp. 2368-2379.

http://researchrepository.murdoch.edu.au/1545/

Accepted Manuscript

Heat capacities of aqueous sodium hydroxide/aluminate mixtures and prediction of the solubility constant of boehmite up to 300 °C

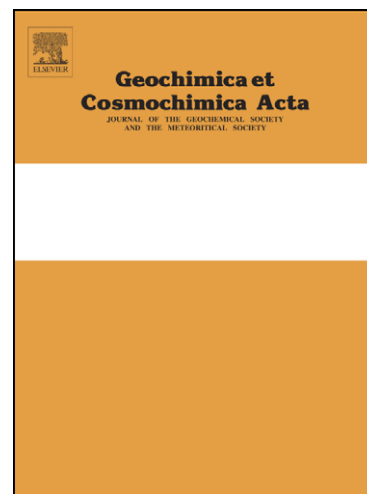Simon Schrödle, Erich Königsberger, Peter M. May, Glenn Hefter

Please cite this article as: Schrödle, S., Königsberger, E., May, P.M., Hefter, G., Heat capacities of aqueous sodium hydroxide/aluminate mixtures and prediction of the solubility constant of boehmite up to 300 °C, *Geochimica et Cosmochimica Acta* (2010), doi: [10.1016/j.gca.2010.01.002](10.1016/j.gca.2010.01.002)

Heat capacities of aqueous sodium hydroxide/aluminate mixtures and prediction of the solubility constant of boehmite up to 300 °C

Simon Schrödle[1], Erich Königsberger*, Peter M. May, and Glenn Hefter*

School of Chemical and Mathematical Sciences, Murdoch University,

Murdoch, WA 6150, Australia

[1]Current address: BASF SE, Catalysis Research,

D-67056 Ludwigshafen, Germany

Abstract

A modified commercial (Setaram C80) calorimeter has been used to measure the isobaric volumetric heat capacities of concentrated alkaline sodium aluminate solutions at ionic strengths from (1 to 6) mol kg^{-1}, with up

to 40 mol-% substitution of hydroxide by aluminate, at temperatures from (50 to 300) °C and a pressure of 10 MPa. Apparent molar heat capacities for the mixtures, $C_{p\phi}$, derived from these data were found to depend linearly on the aluminate substitution level, i.e., they followed Young's rule. These quantities were used to estimate the apparent molar heat capacities of pure, hypothetical sodium aluminate solutions, $C_{p\phi}$ ('NaAl(OH)$_4$'(aq)). Slopes of the Young's rule plots were invariant with ionic strength at a given temperature but depended linearly on temperature. The heat capacities of ternary aqueous sodium hydroxide/aluminate mixtures could therefore be modelled using only two parameters in addition to those needed for the correlation of $C_{p\phi}$ (NaOH(aq)) reported previously from these laboratories. An assessment of the standard thermodynamic quantities for boehmite, gibbsite and the aluminate ion yielded a set of recommended values that, together with the present heat capacity data, accurately predicts the solubility of gibbsite and boehmite at temperatures up to 300 °C.

* To whom correspondence should be addressed

(email: E.Koenigsberger@murdoch.edu.au, G.Hefter@murdoch.edu.au)

2

1. INTRODUCTION

Aluminium, the most abundant crustal metal, occurs in alkaline geothermal solutions predominantly as sodium aluminate, $NaAl(OH)_4(aq)$ (Tagirov and Schott, 2001). However, it is important to recognize that such solutions exist only in the presence of appreciable concentrations of $NaOH(aq)$ because pure binary $NaAl(OH)_4(aq)$ solutions are unstable with respect to the precipitation of aluminium (oxy-)hydroxides such as gibbsite and boehmite.

Accurate knowledge of the thermodynamic properties for $NaAl(OH)_4(aq)$ + $NaOH(aq)$ mixtures extending to high temperatures and pressures is useful for geochemical modelling purposes. The applications of such data include the quantitative description of the processes occurring during the formation or dissolution of aluminium-containing minerals, including gibbsite, boehmite, diaspore and other aluminium (oxy-) hydroxides (Wesolowski, 1992; Verdes et al., 1992; Bourcier et al., 1993; Castet et al., 1993; Diakonov et al., 1996; Bénézeth et al., 2001; Tagirov and Schott, 2001; Bénézeth et al., 2008), aluminosilicates (Wilkin and Barnes, 1998; Mashal et al., 2005), and the sodium aluminate-carbonate mineral, dawsonite, which has attracted recent interest in relation to the geochemical sequestration of the greenhouse gas CO_2 (Bénézeth et al., 2007; Marini, 2007).

Reliable thermodynamic data for alkaline sodium aluminate solutions, especially at high concentrations, are also important for the design and optimization of a number of major industrial processes. These include the recovery of purified alumina from bauxitic ores via the well-known Bayer process (Hudson, 1987) and the processing and storage of certain types of nuclear waste (Hummel, 2005; Mashal et al., 2005). Alkaline

3

sodium aluminate solutions are further used in paper production, for the preparation of certain construction materials, in water treatment, and as an intermediate in the production of synthetic silicate materials such as zeolites (Auerbach et al., 2003).

Recognizing its importance as a significant component of some geothermal solutions, Wesolowski (1992) proposed a Pitzer model for the thermodynamic properties of *hypothetical* pure binary aqueous solutions of sodium aluminate, hereafter abbreviated as 'NaAl(OH)$_4$'(aq), covering ionic strengths, I, up to 5 mol kg^{-1} and temperatures, ϑ, up to 100 °C. This model successfully described gibbsite (Al(OH)$_3$) solubilities in aqueous NaCl/NaOH mixtures over this range of conditions. Königsberger et al. (2006) presented a similar description for 'NaAl(OH)$_4$'(aq), but covering wider ranges of conditions ($I \leq 6$ mol kg^{-1}; $25 \leq \vartheta/°C \leq 250$), as part of their comprehensive Pitzer model for 10-component synthetic Bayer liquors (Königsberger et al., 2005). That model was able to reproduce the heat capacity data measured to high I by Picker flow calorimetry from (25 to 55) °C at atmospheric pressure (Magalhães et al., 2002; Hovey et al., 1988), and between (50 and 250) °C at near-saturation pressures (Caiani et al., 1989).

However, the database for heat capacities of NaOH/NaAl(OH)$_4$(aq) at high temperatures is rather limited. Apart from the data of Caiani et al. (1989), measured at $I \leq 1.2$ mol kg^{-1}, only the less precise measurements of Mal'tsev and Mashovets (1965) up to 90 °C at atmospheric pressure, and from 150 to 300 °C at variable (approximately saturation) pressure (Mashovets et al., 1969), are available. To address this deficiency, this paper presents a systematic study of the heat capacities of concentrated aqueous alkaline sodium aluminate solutions at $1 \leq I/\text{mol kg}^{-1} \leq 6$, over the temperature range $50 \leq \vartheta/°C \leq 300$ and at a pressure of 10 MPa.

4

2. EXPERIMENTAL

2.1. Calorimeter

Heat capacities were determined using a commercial Tian-Calvet type differential scanning microcalorimeter (Setaram, Lyon, France; Model C80, 5 µW sensitivity, 0.1 µW resolution). As described in detail by Schrödle et al. (2008), the pressure within the sample cell was kept constant by use of a large (~1 L) buffer volume of high-purity nitrogen. To prevent concentration changes by evaporation and the ingress of N_2 into the sample within the calorimeter, the sample cell and buffer volume were connected via an approximately 1 m long stainless steel capillaries of ca. 0.6 mm internal diameter joined to a Hastelloy expansion tube (~4 mm internal diameter, ~5 mL volume), which were kept at room temperature. The capillary and a small fraction of the expansion tube were filled with sample and then pressurised with N_2. Heat leakages from, and internal convection phenomena within, the cells were minimized by use of a pre-heater installed in the upper part of the calorimeter. The temperature of the pre-heater was kept slightly (~1 K) below that of the calorimeter block throughout each run.

Hastelloy C276 ('Ha') vessels obtained from Setaram were used for a set of experiments below 225 °C. At higher temperatures, because of the potential danger from stress-corrosion cracking of Ha in contact with highly alkaline solutions, special cells (of ~15 mL internal volume) were machined from nickel-201 material. Details of cell construction and the protocol for filling and emptying the sample cell are given by Schrödle et al. (2008).

5

2.2. Calorimetric measurements

Isobaric volumetric heat capacities of the solutions were measured in the calorimeter using discrete (step-by-step) increases of temperature interspersed with isothermal equilibration periods. Two different increments, of 5 and 20 K (10 K for the last two steps), measured at heating rates of 0.25 K/min and 1.0 K/min respectively, were used alternately throughout the investigated temperature range. This provided a check on whether the temperature increment (step height) or the scan rate affected the results. All calorimetric measurements were made isoplethically. Schrödle et al. (2008) give a full description of the experimental procedure employed for NaOH(aq), which was adhered to in this work with the following exception. To avoid precipitation of solid aluminium hydroxide, the alkaline sodium aluminate solutions were removed from the sample cell by thorough rinsing with ~3 M NaOH solution. The cell was then flushed with high purity water and dried with a stream of high purity N_2. Calorimetric data were processed as described by Schrödle et al. (2008) for NaOH(aq).

Nitrogen and water were used as calorimetric references as they are stable, readily available in high purity, and their heat capacities can be calculated accurately from internationally-accepted models (Span et al. 2000; Wagner and Pruss, 2002). The performance of the calorimeter was checked periodically using accurately prepared NaCl(aq) solutions. Heat capacities so obtained had a repeatability of ±0.1 % up to 200 °C and ±0.15 % at higher temperatures. For lower NaCl(aq) concentrations, they were in good agreement (±0.2 %) with the widely-employed extended Pitzer model of Archer (1992) over the whole temperature range (see the discussion by Schrödle et al., 2008).

6

Based on the calorimeter performance during test measurements with NaCl(aq), and including the small additional error arising from an uncertainty of the density measurements (assumed to be <0.1 %), Schrödle et al. (2008) estimated the overall accuracy of the c_p values for NaOH(aq) to be ~0.3 %, being somewhat better at lower concentrations (where $c_p \rightarrow c_p^w$) and lower temperatures but possibly slightly worse at higher concentrations or at temperatures in excess of 250 °C. This corresponds to uncertainties of (~15/m) J K^{-1} mol^{-1} in the apparent molar heat capacities, $C_{p\phi}$.

For the interpolation of the heat capacities with respect to temperature, Schrödle et al. (2008) proposed (their Eq. 7) an empirical quantity A, which was used to calculate (their Eqs. 9 and 10) the $C_{p\phi}$ values for NaOH(aq). As will be shown in Section 3.2, the latter expressions can also be conveniently included in equations to calculate the apparent molar heat capacities of NaOH/NaAl(OH)$_4$(aq) mixtures, including those for pure 'NaAl(OH)$_4$'(aq).

2.3. Densities of alkaline sodium aluminate solutions

The densities of the NaOH/NaAl(OH)$_4$(aq) solutions, ρ, required for conversion of the isobaric volumetric heat capacities to the more useful massic values ($c_p = \sigma \rho^{-1}$, with all quantities at the appropriate temperature, pressure and concentration) were those reported recently by Hnědkovský et al. (2009). These data were obtained using a purpose-built vibrating-tube densimeter at 10 MPa pressure on solutions prepared from the same stock solutions used for the present study and cover the same range of concentrations and temperatures.

7

Since the heat capacities and densities were measured at different temperatures the latter must be interpolated. This was done using the density differences $(\rho - \rho_{NaOH})$ between those of the ternary NaOH/NaAl(OH)$_4$(aq) solutions (ρ) and the binary sodium hydroxide solutions (ρ_{NaOH}) at the same temperature, ionic strength and pressure $(P = 10$ MPa) calculated by the empirical Eq. (1):

$$(\rho - \rho_{NaOH}) \, (\rho^{\circ} \, m/m^{\circ})^{-1} = (a + b\,\vartheta + c\,\vartheta^2 + d\,m_A/m^{\circ}) / (1 + e\,\vartheta + f\,\vartheta^2 + g\,m_A/m^{\circ}) \quad (1)$$

where m and m_A are the stoichiometric total and aluminate molalities of the solutions respectively, $m^{\circ} \equiv 1$ mol (kg H$_2$O)$^{-1}$, $\rho^{\circ} \equiv 1$ g cm^{-3}, $\vartheta = (T/T^{\circ}) - 273.15$, T is the thermodynamic temperature in Kelvin and $T^{\circ} \equiv 1$ K. The adjustable parameters a, b, … g are summarized in Table 1. An empirical expression for $(\rho_{NaOH} - \rho_w)$, the difference between the densities of the NaOH(aq) solutions and pure water (ρ_w), at $P = 10$ MPa was given by Schrödle et al. (2008) which, when combined with Eq. (1), enables calculation of ρ for the ternary solutions.

The present density model was able to reproduce the experimental density differences $\Delta\rho$ (= $\rho - \rho_w$) values to within ±0.3 %. This implies that the agreement in terms of densities varies from ca. ±0.03 % to ±0.1 %, depending on temperature and concentration. Note that Eq. (1) was employed in the present study rather than the more fundamental expressions (for apparent molar volumes) given by Hnědkovský et al. (2009) because it is simpler to use for the interpolation of densities. The minor differences in density calculated from these two expressions have a negligible effect on the calculated heat capacities reported in this work.

8

2.4. Materials

All solutions were prepared by weight from appropriate stock solutions. No buoyancy corrections were employed so the concentrations have an accuracy no better than ±0.1%. Sodium hydroxide solutions with carbonate impurities below 0.1 % of the total alkalinity were prepared as described by Schrödle et al. (2008). Stock solutions of aluminate were obtained by dissolving aluminium wire (BDH AnalaR, assay > 99.9 %) in ~8 mol kg^{-1} NaOH solution. A detailed procedure for the preparation of these stock solutions, which were the same as those used for the determination of the densities, is given by Hnědkovský et al. (2009). Briefly, the previous procedure (Sipos et al., 1998) was modified to ensure an inert atmosphere was maintained over the liquid during the preparation, to shorten the time required from 3 days to few hours and to enable better control of the reaction rate. This was achieved by adding aluminium chunks (ca. 1 cm × 0.5 cm, formed by twisting together a bundle of aluminium wires then cutting them to the desired length) through a 40 cm long condenser, held at 3 ℃ to minimize water loss and blanketed with N$_2$ gas, into NaOH solution maintained at about (60 to 70) ℃.

3. RESULTS AND DISCUSSION

3.1. Volumetric and massic heat capacities of NaOH/NaAl(OH)$_4$(aq)

9

Various sets of heat capacity data were acquired for NaOH/NaAl(OH)$_4$(aq) at temperatures ranging from 50 to 300 °C at a pressure of 10 MPa using Ni and Ha cells. These data are presented in an electronic annex (Tables EA-1 to EA-4). No significant differences were found between the data measured in the two types of cell, nor was any dependence observed on the size of the temperature increments or scan rates. The densities required for the calculation of massic heat capacities were obtained as described in Section 2.3 and for convenience are also listed in Tables EA-1 to EA-4. Figure 1 shows that the massic heat capacities of the NaOH/NaAl(OH)$_4$(aq) mixtures vary smoothly with ionic strength, aluminate substitution and temperature, and are broadly consistent with those of the corresponding NaOH(aq) solutions. The overall uncertainties in the c_p values are estimated to be ±0.5 %, which is slightly higher than those reported for NaOH(aq) by Schrödle et al. (2008), mainly because the increased compositional uncertainty.

3.2. Apparent molar heat capacities of NaOH/NaAl(OH)$_4$(aq)

Values of the 'mean' apparent molar heat capacity of the ternary NaOH/NaAl(OH)$_4$(aq) solutions

$$C_{p\phi} = M' c_p - 1000 \left(c_p^{\mathrm{w}} - c_p \right) / m \tag{2}$$

were derived from the present c_p data combined with the massic heat capacity of water, c_p^{w}, as given in the IAPWS-95 formulation (Wagner and Pruss, 2002). In Eq. (2), M' is the average molar mass (in g mol^{-1}) of the mixed solute, which is given by Eq. (3):

10

$$M' = (1 - \alpha) M_{\text{NaOH}} + \alpha M_{\text{NaAl(OH)}_4} \tag{3}$$

where M_i is the molar mass of solute i, $\alpha = m_A/m$ is the degree of substitution of hydroxide by aluminate and m_A and m (both in mol kg^{-1}) are the aluminate and total molalities respectively. Note that since both NaOH and NaAl(OH)$_4$ are 1:1 strong electrolytes, the stoichiometric molality-based ionic strength, I, is given by $I = m = m_A + m_{\text{NaOH}}$. These quantities are also listed in Tables EA-1 to EA-4.

As shown in Figure 2, the apparent molar heat capacities of NaOH/NaAl(OH)$_4$(aq) depend linearly on aluminate substitution for hydroxide, i.e., they conform closely to Young's rule (Wu, 1970). At any given temperature, the slope of this linear dependence is the same for all ionic strengths (Figure 2) but depends linearly on temperature (Figure 3). The intercepts of these linear functions correspond to $C_{p\phi}$(NaOH, T), the apparent molar heat capacities of NaOH(aq), which have been correlated by Schrödle et al. (2008). Therefore, the complete set of mean apparent molar heat capacities of the ternary alkaline aluminate solutions, $C_{p\phi}$ (NaOH + NaAl(OH)$_4$, T), at 10 MPa can be described by Eq. (4):

$$C_{p\phi}(\text{NaOH} + \text{NaAl(OH)}_4, T) = C_{p\phi}(\text{NaOH}, T) + \alpha (A + B T) \tag{4}$$

where A and B are empirical parameters, with $A = (264.94 \pm 2.54)$ J K^{-1} mol^{-1} and $B = (-0.13497 \pm 0.00550)$ J K^{-2} mol^{-1} (Figure 3) and α is defined above. It should be noted that Hnědkovský et al. (2009) have reported analogous Young's rule behaviour for the apparent molar volumes of NaOH/NaAl(OH)$_4$(aq) mixtures.

11

The values of $C_{p\phi}$ (NaOH, T) in Eq. (4) can be calculated using Eqs. (7 – 10) with the parameters from Tables 4 and 7 of Schrödle et al. (2008), which are valid for 1 ≤ I/mol kg^{-1} ≤ 8, 50 ≤ ϑ/°C ≤ 300 and P = 10 MPa. Equation (4) thus correlates $C_{p\phi}$ (NaOH + NaAl(OH)$_4$, T) over the complete range of experimental conditions covered in this work. The correlation agrees with measured $C_{p\phi}$ values to within (~20/m) J K^{-1} mol^{-1} in (Figure 4), which is in accord with the estimated uncertainty in the present c_p values (±0.5 %).

The linear dependence of $C_{p\phi}$ (NaOH + NaAl(OH)$_4$, T) on α, the fractional substitution of NaOH by NaAl(OH)$_4$, shown in Figure 2, implies that $C_{p\phi}$ of the mixtures can be extrapolated against α, using the two Young's rule parameters, to provide estimates for the pure, hypothetical 'NaAl(OH)$_4$'(aq) solutions at all ionic strengths investigated. The values of $C_{p\phi}$('NaAl(OH)$_4$', T) so obtained are plotted along with the data from previous studies in Figure 5. Since it is plausible that Eq. (4) is also valid for ionic strengths outside the range covered in this study, values of $C_{p\phi}$('NaAl(OH)$_4$', T) are listed in Table 2 at the concentrations (0 ≤ m_A/mol kg^{-1} ≤ 8) and temperatures for which values of $C_{p\phi}$ (NaOH, T) were reported by Schrödle et al. (2008). If the range of validity of Eq. (4) is assumed to extend to ionic strength zero (infinite dilution), the standard partial molar heat capacities, $C_{p\phi}^{\infty}$, of 'NaAl(OH)$_4$'(aq) can in principle be derived from the present data provided the corresponding quantities for NaOH(aq) are known. However, the last depend on the form of the extrapolation equation used (e.g., Redlich-Meyer or Pitzer) and on the Debye-Hückel parameters employed (see Schrödle et al., 2008). Table 2 therefore lists two sets of estimates of $C_{p\phi}^{\infty}$('NaAl(OH)$_4$', T) based on the values for $C_{p\phi}^{\infty}$(NaOH, T) obtained by using Debye-

12

Hückel parameters from Fernandez et al. (1997) and from Bradley and Pitzer (1979) respectively (Schrödle et al., 2008).
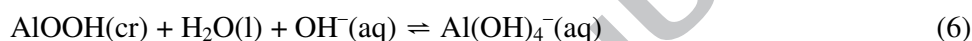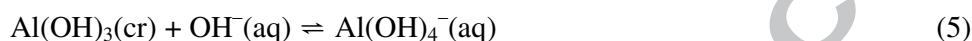
3.3. Literature comparisons

Comparison of the present heat capacities of NaOH/NaAl(OH)$_4$(aq) mixtures with literature data is not straightforward because the previous studies at higher temperatures were measured at varying pressures (Caiani et al., 1989) and/or were of comparatively low accuracy (Mal'tsev and Mashovets, 1965; Mashovets et al., 1969). On the other hand, Figure 5 shows that there is a broad consistency between the present data at 10 MPa and the earlier investigations at low temperatures and atmospheric pressure (Hovey et al., 1988; Magalhães et al., 2002), where the compressibility of aqueous electrolyte solutions is typically small.

4. SOLUBILITY CONSTANT OF BOEHMITE TO 300 ºC

Whilst there is a general agreement about the thermodynamic properties of gibbsite, Al(OH)$_3$(cr) (Hemingway and Robie, 1977; Hemingway et al., 1977; Verdes et al., 1992; Wesolowski, 1992; Königsberger et al., 2006), the corresponding values for boehmite, AlOOH(cr), and particularly for the aluminate ion, Al(OH)$_4^-$(aq), are considerably less certain. The present heat capacity measurements can be used to constrain the values for these quantities by comparison of predicted and experimental gibbsite and boehmite solubility constants.

13

4.1. Heat capacity changes of gibbsite and boehmite dissolution in caustic solution

The solubility equilibria of gibbsite and boehmite in alkaline solutions can be represented by reactions (5) and (6) respectively

$$Al(OH)_3(cr) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq) \qquad (5)$$

$$AlOOH(cr) + H_2O(l) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq) \qquad (6)$$

The standard equilibrium constants of reactions (5) and (6), $K^o_{s4}(T)$, using the common notation of Sillén and Martell (1964), can be calculated as a function of temperature if the corresponding standard enthalpy, $\Delta_r H^o_{298.15}$, entropy, $\Delta_r S^o_{298.15}$, and heat capacity, $\Delta_r C_p{}^o(T)$, changes of these reactions are known. Such thermodynamic information can be evaluated conveniently using the corresponding standard quantities of formation and the standard partial molar quantities of the aquated ions. The integration yielding $K^o_{s4}(T)$ can then be performed using standard thermodynamic relationships (McGlashan, 1979). Since experimental $\Delta_r C_p{}^o(T)$ functions for reactions (5) and (6) up to high temperatures were hitherto unavailable, $\Delta_r H^o_{298.15}$ and $\Delta_r S^o_{298.15}$ had to be determined by fitting measured solubility constants $K^o_{s4}(T)$ to various empirical temperature functions (e.g., Verdes et al., 1992; Wesolowski, 1992; Bénézeth et al., 2001; and references therein), including those derived from the revised Helgeson-Kirkham-Flowers equation (Tagirov and Schott, 2001). However, this procedure is unsatisfactory because the reliability of $\Delta_r C_p{}^o(T)$ obtained from these empirical $K^o_{s4}(T)$ functions (by appropriate differentiation

14

with respect to temperature) could not be assessed by comparison with directly-determined heat capacity data. In addition, there are no reliable boehmite solubility data at temperatures below 70 ºC. Consequently, the extrapolation of $K^o_{s4}(T)$ for boehmite to 298.15 K was not constrained by either experimental solubility or heat capacity data, which meant that the accuracy of the resulting thermodynamic quantities at 298.15 K could not be gauged. As an exception, Hovey et al. (1988) employed their heat capacity data for $Al(OH)_4^-(aq)$ (measured up to 55 ºC and extrapolated to higher temperatures using the Helgeson-Kirkham-Flowers equation) in fits of $K^o_{s4}(T)$ to boehmite solubility data and obtained a value of $S^o_{298.15}(Al(OH)_4^-(aq)) = 111.3$ J K^{-1} mol^{-1} which is very close to that of Königsberger et al. (2006). Wesolowski (1992), on the other hand, included the $C_p^o(Al(OH)_4^-(aq))$ data of Hovey et al. (1988) in a fit of gibbsite solubility data to an empirical $K^o_{s4}(T)$ function but concluded that the latter was not very sensitive to changes in $\Delta_r C_p^o$ in the rather small temperature interval covered.

The present $C_{p\phi}(NaOH + NaAl(OH)_4, T)$ data can be employed to predict $K^o_{s4}(T)$ functions up to 300 ºC without the need for empirical fitting parameters. The standard heat capacity functions for reactions (5) and (6), $\Delta_r C_p^o(5, T)$ and $\Delta_r C_p^o(6, T)$ respectively, are defined as:

$$\Delta_r C_p^o(5, T) = C_p^o(Al(OH)_4^-(aq), T) - C_p^o(OH^-(aq), T) - C_p^o(Al(OH)_3(cr), T) \quad (7)$$

and

$$\Delta_r C_p^o(6, T) = C_p^o(Al(OH)_4^-(aq), T) - C_p^o(OH^-(aq), T) - C_p^o(AlOOH(cr), T)$$
$$- C_p^o(H_2O(l), T) \quad (8)$$

15

Eqs. (7) and (8) involve the difference between the partial molar heat capacities of the aluminate and hydroxide ions, hereafter denoted $\Delta_{ion}C_p°$. This quantity can be obtained readily from the present data and rearrangement of Eq. (4) to give:

$$C_{p\phi}(\text{'NaAl(OH)}_4\text{'}, T) - C_{p\phi}(\text{NaOH}, T) = A + B\,T \qquad (9)$$

where the parameters A and B are those given in Section 3.2. Since Eqs. (4) and (9) also apply at infinite dilution, along with ionic additivity, this means

$$C_p°(\text{Al(OH)}_4^-(\text{aq}), T) - C_p°(\text{OH}^-(\text{aq}), T) = \Delta_{ion}C_p°(T) = A + B\,T \qquad (10)$$

The pressure dependence of $\Delta_{ion}C_p°$ was not determined in the present study. However, its value is given by the thermodynamic identity (McGlashan, 1979)

$$\left(\frac{\partial \Delta_{ion}C_p°}{\partial P}\right)_T = -T\left(\frac{\partial^2 \Delta_{ion}V°}{\partial T^2}\right)_P \qquad (11)$$

The density data of Hnědkovský et al. (2009) for NaOH/NaAl(OH)$_4$(aq) mixtures indicated that the difference between the partial molar volumes of the aluminate and hydroxide ions, $\Delta_{ion}V°(T) = V°(\text{Al(OH)}_4^-(\text{aq}), T) - V°(\text{OH}^-(\text{aq}), T)$, at $P = 10$ MPa is a linear function of temperature. This means that the r.h.s. of Eq. (11) is zero, and therefore that $\Delta_{ion}C_p°(T)$ is independent of pressure over the present experimental range.

16

To describe the standard heat capacity functions required for the calculation of $\Delta_r C_p°(T)$ using Eqs. 7 and 8, the following generic $C_p°(S, T)$ function for species S was used:

$$C_p°(S, T) = h_S + i_S T + j_S T^2 + k_S T^{-1} + m_S (T - T_a)^{-1} + n_S (T_b - T)^{-1} + p_S T^{-0.5} + q_S T^{-2}$$

(12)

where T_a = 227 K and T_b = 647 K. Heat capacity data for $H_2O(l)$ were generated from the IAPWS-95 formulation (Wagner and Pruss, 2002) at 10 K intervals and fitted to Eq. (12). Since solubilities are usually measured at saturation pressures, $C_p°(H_2O(l), T)$ was calculated for P_{sat} (which differed from $C_p°(H_2O(l), T)$ at P = 10 MPa by <1.75 %). The $C_p°(Al(OH)_3(cr), T)$ data of Hemingway et al. (1977) were also fitted to Eq. (12), while for AlOOH(cr), parameters were taken from the most recent temperature-dependent equation reported by Hemingway et al. (1991) and used directly in Eq. (12) (note that in the last term of Eq. (1) of Hemingway et al. (1991), the exponent of T should be –2). In the fit of $\Delta_{ion}C_p°(T)$ to Eq. (12), values measured at low temperatures and atmospheric pressure (Hovey et al., 1988; Magalhães et al., 2002) were combined with the present data given by Eq. (10). All resulting parameters for Eq. (12) are collected in Table 3.

Equations (7) and (8) can then be employed to calculate the parameters of the $\Delta_r C_p°(T)$ functions for reactions (5) and (6). Since these reactions are isocoulombic, their $\Delta_r C_p°(T)$ values are expected to be small. Indeed, both $\Delta_r C_p°(T)$ were found to be smooth functions of T, with values decreasing from (124.9 to 36.2) J K^{-1} mol^{-1} and from (89.8 to 2.5) J K^{-1} mol^{-1}, respectively, in the temperature range from (50 to 300) °C.

Since the present $\Delta_r C_p^\circ(T)$ functions for reactions (5) and (6) are based exclusively on accurate heat capacity data measured at temperatures up to 300 ºC, they can be employed to assess the reliability of $\Delta_r H^\circ_{298.15}$ and $\Delta_r S^\circ_{298.15}$ for these reactions. The latter two quantities were evaluated from the literature values given in Table 4 and used with $\Delta_r C_p^\circ(T)$ to calculate $K^\circ_{s4}(T)$ up to 300 ºC. These values were then compared with those derived from experimental solubility studies.

4.2. Evaluation of gibbsite and boehmite solubility constants

Using the present $\Delta_r C_p^\circ(T)$ function (Eq. 12) in conjunction with $\Delta_r H^\circ_{298.15}$ and $\Delta_r S^\circ_{298.15}$, the temperature dependence of $K^\circ_{s4}(T)$ can be obtained by analytical integration:

$$\log K^\circ_{s4}(T) = -\left[RT \ln(10)\right]^{-1} \left\{ \Delta_r H^\circ_{298.15} + \int_{298.15}^{T} \Delta_r C_p^\circ(T)\ \mathrm{d}T - \right.$$

$$\left. T \left[\Delta_r S^\circ_{298.15} + \int_{298.15}^{T} (\Delta_r C_p^\circ(T)/T)\ \mathrm{d}T\right] \right\} \qquad (13)$$

Inserting Eq. (12) into Eq. (13) results in

$$\log K^\circ_{s4}(T) = -\left[RT \ln(10)\right]^{-1} \left\{ \Delta_r H^\circ_{298.15} + \Delta_r h\ (T - T_r) + \frac{\Delta_r i}{2}\,(T^2 - T_r^2) + \frac{\Delta_r j}{2}\,(T^3 - T_r^3) \right.$$

$$+ \Delta_r k\ \ln\frac{T}{T_r} + \Delta_r m\ \ln\frac{(T - T_a)}{(T_r - T_a)} + \Delta_r n\frac{(T_b - T)}{(T_b - T_r)} + 2\,\Delta_r p\ (T^{0.5} - T_r^{0.5})$$

18

$$- \Delta_r q \ (T^{-1} - T_r^{-1}) - T \ [\Delta_r S^o_{298.15} + (\Delta_r h - \frac{\Delta_r m}{T_a} + \frac{\Delta_r n}{T_b}) \ln\frac{T}{T_r}$$

$$+ \Delta_r i \ (T - T_r) + \frac{\Delta_r j}{2} \ (T^2 - T_r^2) - \Delta_r k \ (T^{-1} - T_r^{-1}) + \frac{\Delta_r m}{T_a} \ \ln\frac{(T - T_a)}{(T_r - T_a)}$$

$$- \frac{\Delta_r n}{T_b} \ \frac{(T_b - T)}{(T_b - T_r)} - 2 \ \Delta_r p \ (T^{-0.5} - T_r^{-0.5}) - 0.5 \ \Delta_r q \ (T^{-2} - T_r^{-2})] \} \qquad (14)$$

where T_r = 298.15 K and $\Delta_r h$, $\Delta_r i$, … are calculated according to Eqs. (7) and (8) from the parameters for the individual species given in Table 3. The following discussion is based on the calculation of gibbsite and boehmite solubility constants using Eq.(14).

4.3. Thermodynamic properties of Al(OH)$_4^-$(aq)

In all of the present calculations, the standard (partial) molar enthalpies and entropies at 298.15 K for water and the hydroxide ion were the CODATA key values (Cox et al., 1989). The thermodynamic properties of gibbsite (Table 4) were the generally-accepted values of Hemingway and Robie (1977) and Hemingway et al. (1977). On the other hand, the corresponding values proposed by various authors for Al(OH)$_4^-$(aq), which for convenience are also listed in Table 4, differ widely. Although they have been discussed on a number of occasions (Verdes et al., 1992; Wesolowski, 1992; Bénézeth et al., 2001; Tagirov and Schott, 2001; Königsberger et al., 2006), no general agreement has been reached.

The present calculations show that the thermodynamic values for Al(OH)$_4^-$(aq) proposed by Hovey at al. (1988), Wesolowski (1992) and Königsberger et al. (2006) are

reliable. Thus, there is excellent agreement between the gibbsite solubility constants (Figure 6, upper solid line) calculated using these values in combination with the present $\Delta_r C_p°(5, T)$ derived above, and the constants obtained from experimental solubilities (Figure 6, solid symbols). These standard thermodynamic properties for $Al(OH)_4^-$(aq), given in **bold** in Table 4, are recommended for thermodynamic and solubility calculations involving this species. However, as indicated by the rather large uncertainties (Table 4) assigned by Bénézeth et al. (2001) to the thermodynamic data for $Al(OH)_4^-$(aq), these quantities are probably less certain than suggested by Zeng et al. (1994) on the basis of their calorimetric study.

4.4. Thermodynamic properties of AlOOH(cr)

Figure 6 also compares selected experimental boehmite solubility constants (corrected to infinite dilution where appropriate, using the Pitzer model of Königsberger et al., 2006) with the $K°_{s4}(T)$ values generated from the $\Delta_r C_p°(6, T)$ function derived above together with some of the thermodynamic property data for boehmite at 298.15 K listed in Table 4.

The experimental boehmite solubility constants appear to fall into two groups. The data of Russell et al. (1955), and the results of Verdes et al. (1992) obtained in NH₄OH/NH₄Cl buffers, especially in the lower temperature range, suggest considerably higher solubilities than the rest. It can be seen (Figure 6, dotted line) that the quantities for AlOOH(cr) and $Al(OH)_4^-$(aq) selected by Königsberger et al. (2006) result in predictions that are in good agreement with the group of higher experimental solubility constants for boehmite. This is not surprising since Königsberger et al. (2006) adjusted

the calorimetrically determined standard enthalpy of formation of AlOOH(cr), (–996.1 ± 1.3) kJ mol^{-1}, reported by Chen and Zeng (1996), by +0.6 kJ mol^{-1} so as to be consistent with the solubilities of Russell et al. (1955) in strongly alkaline solutions.

Adjusting Chen and Zeng's (1996) value for the standard enthalpy of formation of AlOOH(cr) by –0.5 kJ mol^{-1} results in very good agreement of the predicted log $K^{\circ}_{s4}(T)$ values (Figure 6, lower solid line) with the group of lower experimental solubility constants for boehmite, determined by Verdes et al. (1992, especially their data obtained in NaOH/NaCl solutions at higher temperatures), Bourcier et al. (1993), Castet et al. (1993), Palmer et al. (2001) and Bénézeth et al. (2008). The resulting, recommended value of $\Delta_f H^{\circ}(\text{AlOOH(cr)}) = –996.6$ kJ mol^{-1} is in excellent agreement with the value $\Delta_f H^{\circ}(\text{AlOOH(cr)}) = (–996.4 \pm 2.2)$ kJ mol^{-1} derived by Hemingway et al. (1991). The comparison between the lower solid and dotted lines in Figure 6 thus demonstrates the effect on the predicted log $K^{\circ}_{s4}(T)$ values of a change in $\Delta_f H^{\circ}(\text{AlOOH(cr)})$ by just 1.1 kJ mol^{-1} (which is less than the experimental uncertainty of $\pm$ 1.3 kJ mol^{-1} reported by Chen and Zeng, 1996).

Similar comparisons between predicted and experimental $K^{\circ}_{s4}(T)$ can be made by employing the thermodynamic data recommended by other groups to model boehmite solubilities. These are discussed in the following paragraphs.

When used together with the present $\Delta_r C_p^{\circ}(6, T)$ function, the properties selected for AlOOH(cr) and Al(OH)$_4^-$(aq) by Tagirov and Schott (2001), Table 4, underestimate all experimental data over the complete temperature range (by ~0.2 in log $K^{\circ}_{s4}(T)$ at 300 ºC). Tagirov and Schott's values for AlOOH(cr) and Al(OH)$_4^-$(aq) are obviously correlated (and should thus only be used) with parameters for the revised Helgeson-

21

Kirkham-Flowers equation that were determined by them simultaneously in fits to boehmite solubility constants.

The standard thermodynamic properties for AlOOH(cr) and $Al(OH)_4^-$(aq) at 298.15 K selected by Bénézeth et al. (2001) were derived from their own boehmite solubility data (Palmer et al., 2001; open squares). However, their $C_p°(Al(OH)_4^-$(aq)) value is considerably higher than those reported by other authors (Table 4). This difference in $C_p°(Al(OH)_4^-$(aq)) can be allowed for by adding a constant value to the present $\Delta_r C_p°(6, T)$ function. This results in the good fit shown in Figure 6 (dashed line) up to ~250 °C. Comparison between the lower solid and dashed lines demonstrates the effect of changing $C_p°(Al(OH)_4^-$(aq)) by ~60 J K^{-1} mol^{-1} on the curvature of the predicted log $K°_{s4}(T)$ function.

Verdes et al. (1992) did not specify a value for $C_p°(Al(OH)_4^-$(aq)) to be used in conjunction with their enthalpy and entropy values (Table 4). However, combining the latter two quantities with the present $\Delta_r C_p°(6, T)$ function predicts $logK°_{s4}(T)$ values that are higher than all experimental data (by ~0.45 in log $K°_{s4}(T)$ at 300 °C). It is noteworthy that both Bénézeth et al. (2001) and Verdes et al. (1992) employ the latter's value of $S°_{298.15} = 49.4$ J K^{-1} mol^{-1} for boehmite, which was obtained from fits to their solubility data. This value is considerably (~30 %) higher than the recommended, calorimetrically-determined value of $S°_{298.15} = 37.19$ J K^{-1} mol^{-1} (Hemingway et al., 1991; Table 4).

Overall, the above assessment of the thermodynamic properties for AlOOH(cr), $Al(OH)_3$(cr) and $Al(OH)_4^-$(aq) at 298.15 K provides recommended values (Table 4, **bold** numbers) that, combined with the present calorimetrically-determined $\Delta_r C_p°(T)$ functions, are fully consistent with the extensive solubility database for boehmite and

22

gibbsite (Figure 6). This set of thermodynamic quantities gives an accurate and consistent description of aqueous sodium hydroxide/aluminate solutions, including gibbsite and boehmite solubilities, at temperatures up to 300 ºC and at pressures up to 10 MPa.

5. CONCLUSIONS

The heat capacities of concentrated alkaline sodium aluminate solutions have been determined by differential calorimetry with an accuracy of better than ±0.5 % at ionic strengths $1 \leq I/(\text{mol kg}^{-1}) \leq 6$, temperatures up to 300 °C, and a pressure of 10 MPa. The apparent molar heat capacities of ternary aqueous solutions of NaOH + NaAl(OH)$_4$ show simple linear mixing (Young's rule) behaviour on the substitution of aluminate for hydroxide at all temperatures. These results are quantitatively consistent with measured gibbsite and boehmite solubility data up to 300 °C. The present data will therefore facilitate the comprehensive thermodynamic modelling of this geochemically- and industrially-important electrolyte system to high ionic strengths, temperatures and pressures.

REFERENCES

Archer D. G. (1992) Thermodynamic properties of the NaCl + H_2O system. II. Thermodynamic properties of NaCl(aq), $NaCl \cdot 2H_2O$(cr), and phase equilibria. *J. Phys. Chem. Ref. Data* **21**, 793-829.

Auerbach S. M., Carrado K. A. and Dutta P. K. (2003) *Handbook of Zeolite Science and Technology*, Marcel Dekker, New York, 928 pp.

Bénézeth P., Palmer D. A. and Wesolowski D. J. (2001) Aqueous high-temperature solubility studies. II. The solubility of boehmite at 0.03 m ionic strength as a function of temperature and pH as determined by in situ measurements. *Geochim. Cosmochim. Acta* **65**, 2097–2111.

Bénézeth P., Palmer D. A., Anovitz L. M and Horita J. (2007) Dawsonite synthesis and reevaluation of its thermodynamic properties from solubility measurements: Implications for mineral trapping of CO_2. *Geochim. Cosmochim. Acta* **71**, 4438–4455.

Bénézeth P., Palmer D. A. and Wesolowski D. J. (2008) Dissolution/precipitation kinetics of boehmite and gibbsite: Application of a pH-relaxation technique to study near-equilibrium rates. *Geochim. Cosmochim. Acta* 7**2**, 2429–2453.

Bourcier W. L., Knauss K. G. and Jackson K. J. (1993) Aluminum hydrolysis constants to 250 °C from boehmite solubility measurements. *Geochim. Cosmochim. Acta* 5**7**, 747–762.

Bradley D. J. and Pitzer K. S. (1979) Thermodynamics of electrolytes. 12. Dielectric properties of water and Debye-Hückel parameters to 350 °C and 1 kbar. *J. Phys. Chem.* **83**, 1599-1603.

Caiani P., Conti G., Gianni P. and Matteoli E. (1989) Apparent molar heat capacity and relative enthalpy of aqueous sodium hydroxoaluminate between 323 and 523 K. *J. Solution Chem.* **18**, 447–461.

Castet S., Dandurand J. L., Schott J. and Gout R. (1993) Boehmite solubility and aqueous aluminum speciation in hydrothermal solutions (90 – 350 °C): experimental study and modelling. *Geochim. Cosmochim. Acta* **57**, 4869–4884.

Chen Q. And Zeng W. (1996) Calorimetric determination of the standard enthalpies of formation of gibbsite, $Al(OH)_3(cr)$, and boehmite, $AlOOH(cr)$. *Geochim. Cosmochim. Acta* **60**, 1–5.

Cox J. D., Wagman D. D. and Medvedev V. A. (1989) *CODATA Key Values for Thermodynamics*. Hemisphere Publishing Corp., N.Y., U.S.A.

Diakonov I., Pokrovski G., Schott J., Castet S. and Gout R. (1996) An experimental and computational study of sodium–aluminum complexing in crustal fluids. *Geochim. Cosmochim. Acta* **60**, 197–211.

Fernandez D. P., Goodwin A. R. H., Lemmon E. W., Levelt Sengers J. M. H. and Williams R. C. (1997) A formulation for the static permittivity of water and steam at temperatures from 238 K to 873 K at pressures up to 1200 MPa, including derivatives and Debye-Hückel coefficients. *J. Phys. Chem. Ref. Data* **26**, 1125-1166.

Hemingway B. S. and Robie R. A. (1977) Enthalpies of formation of low albite (NaAlSi$_3$O$_8$), gibbsite (Al(OH)$_3$) and NaAlO$_2$; Revised values for $\triangle H^o_{f,298.15}$ and $\triangle G^o_{f,298.15}$ of some alumino-silicate minerals. *J. Res. U.S. Geol. Surv.* **5**, 413–429.

Hemingway B. S., Robie R. A., Fisher J. R. and Wilson W. H. (1977) Heat capacities of gibbsite, Al(OH)$_3$, between 13 and 480 K and magnesite, MgCO$_3$, between 13 and 380 K and their standard entropies at 298.15 K and the heat capacities of Calorimetry Conference benzoic acid between 12 and 316 K. *J. Res. U.S. Geol. Surv.* **5**, 797–806.

Hemingway B. S., Robie R. A. and Apps J. A. (1991) Revised values for the thermodynamic properties of boehmite, AlO(OH), and related species and phases in the system Al–H–O. *Am. Mineral.* **76**, 445–457.

Hnědkovský L., Königsberger E., Königsberger L.-C., Cibulka I., Schrödle S., May P. M. and Hefter G. (2009) Densities of concentrated alkaline aluminate solutions at

temperatures from (323 to 573) K and 10 MPa pressure. *J. Chem. Eng. Data,* in press, DOI:10.1021/je900584k.

Hovey J. K., Hepler L. G. and Tremaine P. R. (1988) Thermodynamics of aqueous aluminate ion: Standard partial molar heat capacities and volumes of $Al(OH)_4^-(aq)$ from 10 to 55 °C. *J. Phys. Chem*. **92**, 1323–1332.

Hudson L. K. (1987) Alumina Production. In *Production of Aluminium and Alumina*, Critical Reports on Applied Chemistry, Vol. 20, ed. A. R. Burkin, Wiley, New York, 11–46.

Hummel W. (2005) Solubility equilibria and geochemical modeling in the field of radioactive waste disposal. *Pure Appl. Chem.* **77**, 631–641.

Königsberger E., Eriksson G., May P. M. and Hefter G. (2005) Comprehensive model of synthetic Bayer liquors. Part 1. Overview. *Ind. Eng. Chem. Res*. **44**, 5805–5814.

Königsberger E., May P. M. and Hefter G. (2006) Comprehensive model of synthetic Bayer liquors. Part 3. Sodium aluminate solutions and the solubilities of gibbsite and boehmite. *Monatsh. Chem*. **137**, 1139–1149.

Magalhães M. C. F., Königsberger E., May P. M. and Hefter G. (2002) Heat capacities of concentrated aqueous alkaline aluminate solutions 25 °C. *J. Chem. Eng. Data* **47**, 960–963.

Mal'tsev G. Z. and Mashovets V. P. (1965) Specific heat of sodium aluminate solutions in the 25 – 90 ° temperature range. *J. Appl. Chem. (USSR)* **38**, 85–90.

Marini L. (2007) *Geological Sequestration of Carbon Dioxide*. Elsevier, Amsterdam, 453 pp.

Mashal K., Harsh J. B., Flury M. and Felmy A. R. (2005) Analysis of precipitates from reactions of hyperalkaline solutions with soluble silica. *Appl. Geochem.* **20**, 1357–1367.

Mashovets V. P., Puchkov L. V., Matveeva R. P. and Baranova, T. A. (1969) Heat capacity of solutions of the Na_2O–Al_2O_3–H_2O system at 150 – 300 °C. *Tsvet. Metall.* **42**, 60–63.

McGlashan M. L. (1979) *Chemical Thermodynamics*. Academic Press, London, 345 pp.

Palmer D. A., Bénézeth P. and Wesolowski D.J. (2001) Aqueous high-temperature solubility studies. I. The solubility of boehmite as functions of ionic strength (to 5 molal, NaCl), temperature (100 – 290 °C), and pH as determined by in situ measurements. *Geochim. Cosmochim. Acta* **65**, 2081–2095.

Russell A. S., Edwards J. D. and Taylor C. S. (1955) Solubility and density of hydrated aluminas in NaOH solution. *J. Metals* **7**, 1123–1128.

Schrödle S., Königsberger E., May P. M. and Hefter G. (2008) Heat capacities of aqueous solutions of sodium hydroxide and water ionization up to 300 °C at 10 MPa. *Geochim. Cosmochim. Acta* **72**, 3124–3138.

Sillén L. G. and Martell A. E. (1964) *Stability Constants of Metal-Ion Complexes*, 2nd ed., Spec. Publ. No. 17, The Chemical Society, London, 754 pp.

Sipos P., Hefter G. and May P. M. (1998) A hydrogen electrode study of concentrated alkaline aluminate solutions. *Aust. J. Chem.* **51**, 445–453.

Span R., Lemmon E. W., Jacobsen R. T., Wagner W. and Yokozeki A. (2000) A reference equation of state for the thermodynamic properties of nitrogen for temperatures from 63.151 to 1000 K and pressures to 2200 MPa. *J. Phys. Chem. Ref. Data* **29**, 1361–1433.

Tagirov B. and Schott J. (2001) Aluminum speciation in crustal fluids revisited. *Geochim. Cosmochim. Acta* **65**, 3965–3992.

Takahashi Y., Yamada K., Fukunaga T. and Mukaibo T. (1973) Heat capacity of hydrated and crystalline aluminas. *Denki Kagaku* **41**, 287–290.

Verdes G., Gout R. and Castet S. (1992) Thermodynamic properties of the aluminate ion and of bayerite, boehmite, diaspore and gibbsite. *Eur. J. Mineral.* **4**, 767–792.

Wagner W. and Pruss A. (2002) The IAPWS Formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **31**, 387–535.

Wesolowski D. J. (1992) Aluminum speciation and equilibria in aqueous solution: 1. The solubility of gibbsite in the system Na–K–Cl–OH–Al(OH)$_4$ from 0 – 100°C. *Geochim. Cosmochim. Acta* **56**, 1065–1091.

Wilkin R. T. and Barnes H. L. (1998) Solubility and stability of zeolites in aqueous solution: I. Analcime, Na-, and K-clinoptilolite. *Amer. Mineral.* **83**, 746–761.

Wu Y.-C. (1970) Young's mixture rule and its significance. *J. Phys. Chem.* **74**, 3781–3786.

Zeng W., Chen Q. and Chen X. (1994) Determination of the standard molar enthalpy of formation of the ion Al(OH)$_4$$^-$(aq). *J. Chem. Thermodyn.* **26**, 205–210.

Table 1. Parameters for Eq. (1), valid for $1 \le m/\text{mol kg}^{-1} \le 8$ and $50 \le \vartheta/°C \le 300$ at 10 MPa.

Parameter	
a	0.170153272
b	–0.00261681
c	$8.51408·10^{-6}$
d	21.77454133
e	0.000796463
f	$-8.5276·10^{-7}$
g	0.233283772

Table 2. Apparent molar heat capacities of pure, hypothetical 'NaAl(OH)$_4$'(aq) solutions at various concentrations and temperatures at 10 MPa pressure ($m° \equiv 1$ mol kg^{-1}), calculated from Eq. (4) using the $C_{p\phi}$(NaOH, T) and $C_{p\phi}^{\infty}$(NaOH, T) values given in Tables 6 and 10, respectively, of Schrödle et al. (2008).

ϑ/°C:	50	100	150	200	250	275	300
$m/m°$	$C_{p\phi}$('NaAl(OH)$_4$', T) / J K^{-1} mol^{-1}						
0 [a]	166.7	163.2	114.1	8.68	-245.9	-554.7	-1344
0 [b]	166.6	162.6	112.5	7.58	-242.2	-544.6	-1305
0.5	199.0	201.9	171.2	106.7	-35.9	-192.4	-552.6
1	214.4	217.9	191.9	137.5	22.5	-95.2	-337.5
2	235.9	237.0	216.2	174.3	88.2	2.3	-168.7
3	254.3	254.3	235.6	198.9	126.5	57.9	-69.5
4	268.3	266.3	248.7	216.2	153.8	95.9	-9.42
6	289.2	285.9	269.4	240.7	188.4	142.5	64.8
8	303.3	298.8	282.7	256.2	210.6	172.4	111.5

[a] Partial molar heat capacities at infinite dilution ($C_{p\phi}^{\infty}(I = 0) \equiv C_{p,2}^{o}$), calculated using Debye-Hückel parameters from Fernandez et al. (1997); cf. Schrödle et al. (2008).
[b] Partial molar heat capacities at infinite dilution ($C_{p\phi}^{\infty}(I = 0) \equiv C_{p,2}^{o}$), calculated using Debye-Hückel parameters from Bradley and Pitzer (1979); cf. Schrödle et al. (2008).

Table 3. Parameters of Eq. (12) for the various species in reactions (5) and (6).

S	$\Delta_{ion}C_p^{\circ}(T)$ [a]	$H_2O(l)$	AlOOH(cr)	Al(OH)$_3$(cr)
h_S	404.50261	85.187375	205.721	54.6974
i_S	-0.25602952	-0.087329256	-0.034921	0.1702721
j_S	–	9.60715E-05	–	–
k_S	-51413.841	–	–	–
m_S	5791.8356	–	–	–
n_S	–	2720.1163	–	–
p_S	–	–	-2635.27	–
q_S	–	–	1026660	-1221728

[a] cf. Eq. (10). Fit also includes values measured at low temperatures and atmospheric pressure (Hovey et al., 1988; Magalhães et al., 2002).

Table 4. Standard thermodynamic properties of boehmite, gibbsite and the aluminate ion at 298.15 K. Original data sources are given as footnotes. Various combinations of these values were incorporated into solubility models proposed by the authors listed in the last column (see also text). The values recommended for use with the present, calorimetrically-determined $\Delta_r C_p^{\circ}(T)$ functions (see text) are given in bold.

	$\Delta_f H^{\circ}$/kJ mol^{-1}	S°/J K^{-1} mol^{-1}	C_p°/J K^{-1} mol^{-1}	Recommended by
AlOOH(cr)	**-996.6**	**37.19**[a]	**54.24**[a]	This study
	-995.50	37.19[a]	54.24[a]	Königsberger et al. (2006)
	-996.4±2.2[a]	37.19[a]	54.24[a]	Tagirov and Schott (2001)
	-992.19[b]	49.4[b]	54.225[a]	Bénézeth et al. (2001)
	-992.19	49.4	65.63[c]	Verdes et al. (1992)
Al(OH)$_3$(cr)	**-1293.13**[d]	**68.44**[e]	**91.72**[e]	This study,
				Verdes et al. (1992),
				Wesolowski (1992),
				Tagirov and Schott (2001),
				Königsberger et al. (2006)
Al(OH)$_4^-$(aq)	**-1500.645**[f]	**111.24**[f, g]	**97.35**	This study,
				Königsberger et al. (2006)
	-1503.08	103.55	96.48[g]	Tagirov and Schott (2001)
	-1503.0±3.5	103.7±6.0	160±120	Bénézeth et al. (2001)
	-1491.48	141	–	Verdes et al. (1992)

[a] Hemingway et al. (1991)

[b] Verdes et al. (1992)

[c] Takahashi et al. (1973)

[d] Hemingway and Robie (1977)

[e] Hemingway et al. (1977)
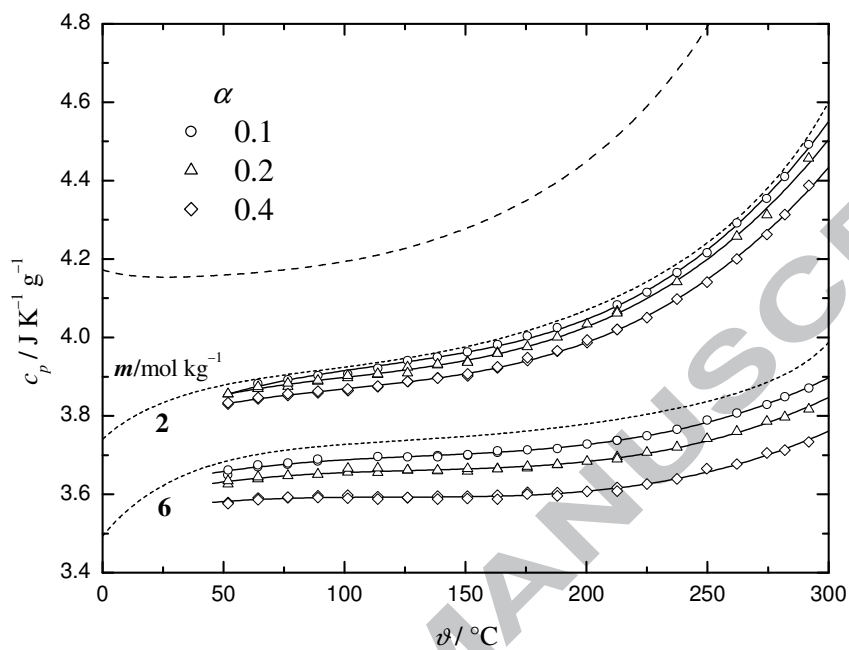
[f] Wesolowski (1992)

[g] Hovey et al. (1988)

Figure 1. Isobaric massic heat capacities (c_p) of ternary NaOH/NaAl(OH)$_4$(aq) mixtures at two ionic strengths ($I = m = (2$ or $6)$ mol kg^{-1}; experimental points and solid lines) compared with NaOH(aq) (dotted lines) and water (dashed line) at various levels of substitution of aluminate for hydroxide ($\alpha = m_A/m$).
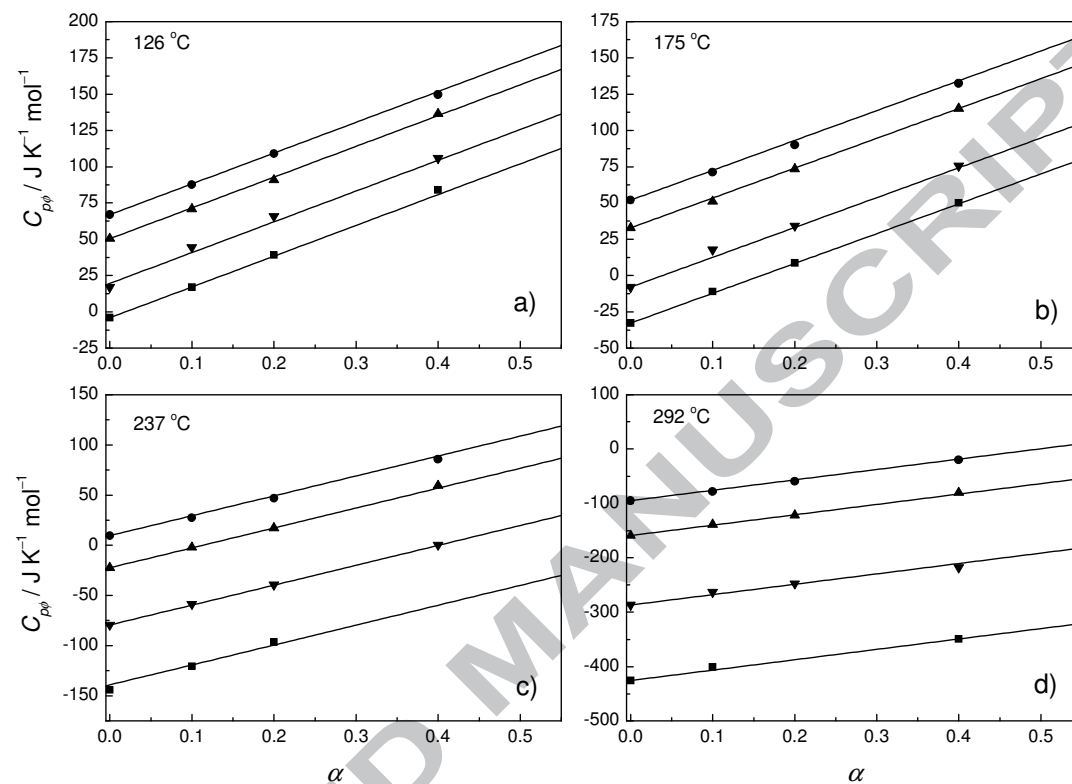
Figure 2. Isobaric apparent molar heat capacities, $C_{p\phi}$, of ternary NaOH/NaAl(OH)$_4$(aq) mixtures as a function of the level of substitution of aluminate for hydroxide (α) at various temperatures, P = 10 MPa and constant ionic strengths I/mol kg^{-1} of: 1 (■); 2 (▼); 4 (▲) and 6 (●); straight lines correspond to Young's rule behaviour.
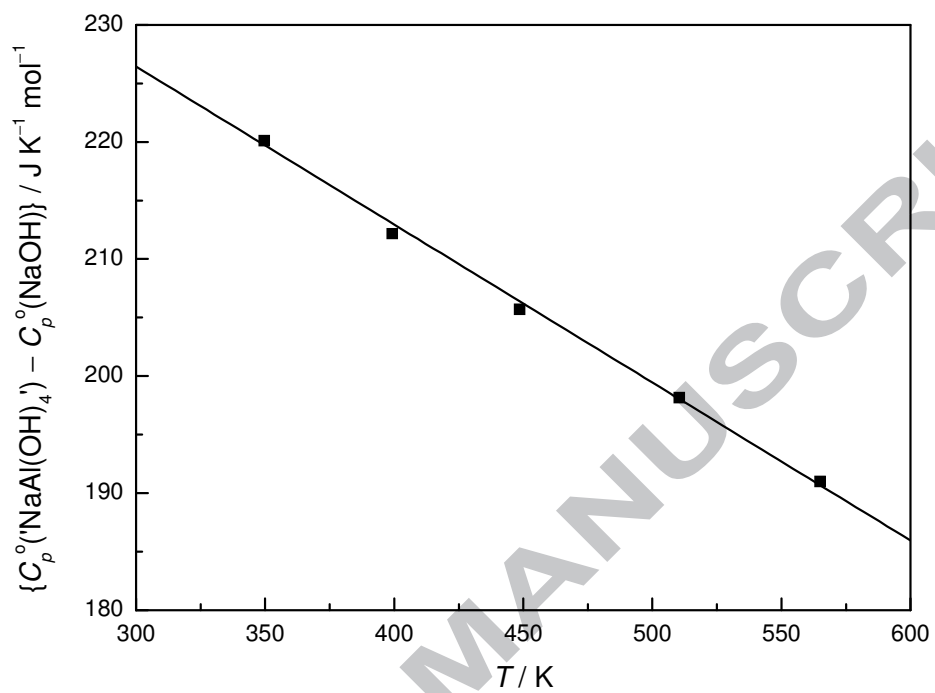
37

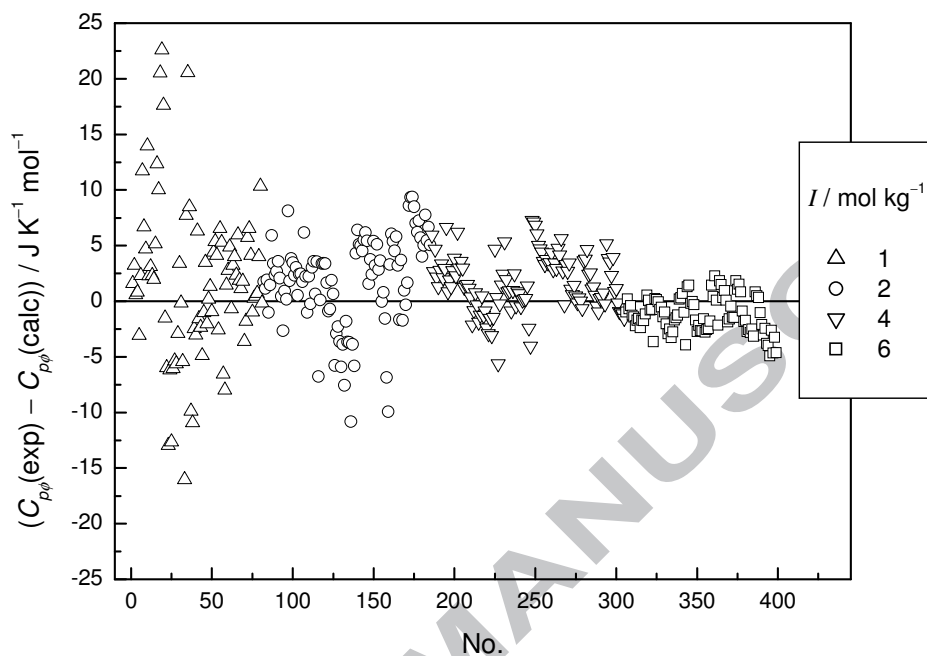Figure 3. Linear dependence of the slopes shown in Figure 2 on temperature at P = 10

MPa.

Figure 4. Deviations of experimental $C_{p\phi}$ values for NaOH(aq) + NaAl(OH)$_4$(aq) from the present model, Eq. (4), as a function of temperature, based on the model of Schrödle et al. (2008) for NaOH(aq) plus the two additional parameters for 'NaAl(OH)$_4$'(aq) derived in this study (see text), at various ionic strengths. Data are presented in the same order as in Tables EA-1 to EA-4.
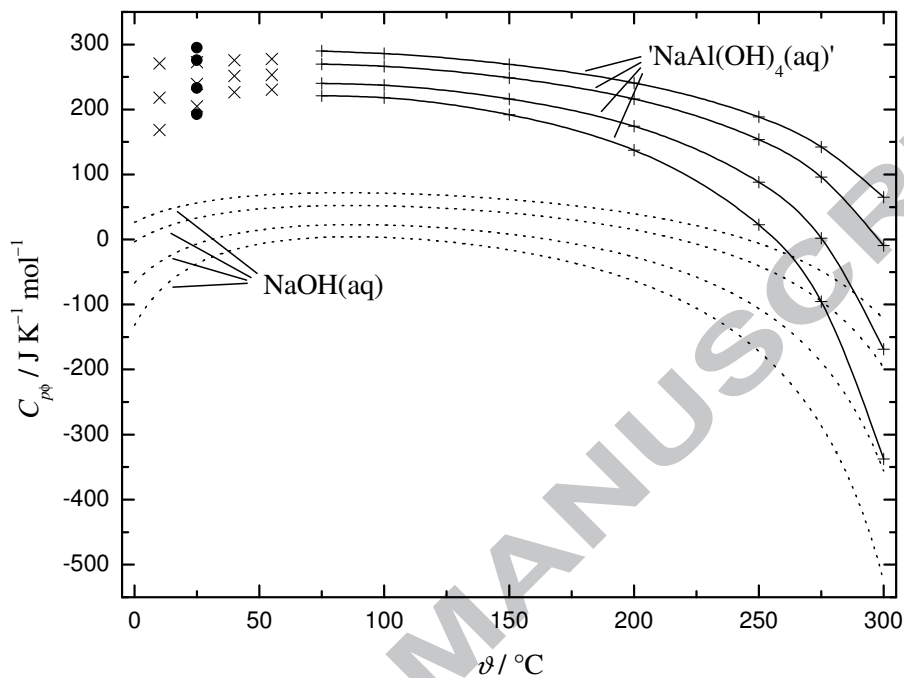
Figure 5. Apparent molar heat capacities, $C_{p\phi}$, of pure, hypothetical 'NaAl(OH)$_4$'(aq) at various ionic strengths (from bottom to top, I = (1, 2, 4 and 6) mol kg^{-1}): present data at P = 10 MPa (+, solid lines); literature data at P = 0.1 MPa ($\times$, I = (1, 2 and 4) mol kg^{-1}, Hovey et al., 1988; ●, Magalhães et al., 2002). Values for $C_{p\phi}$ (NaOH, T) included for comparison (dotted lines).

40
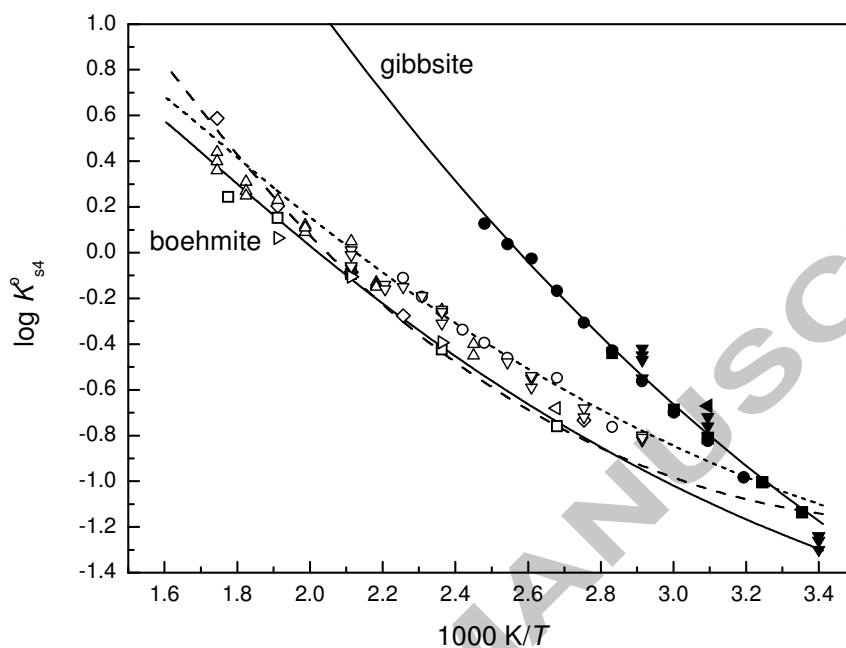
Figure 6. Standard solubility constants, log K^o_{s4}, of gibbsite and boehmite in sodium hydroxide solution obtained from solubility data (symbols) compared with those predicted (lines) using the present $\Delta_r C_p^o(T)$ values with thermodynamic property data at 298.15 K selected by various authors (Table 4, see text). **Gibbsite**: ●, Russell et al. (1955); ▼, Verdes et al. (1992); ■, Wesolowski (1992); ◄, Bénézeth et al. (2008). **Boehmite**: ○, Russell et al. (1955); ▽ (dissolution in NH_4OH/NH_4Cl), △ (dissolution in $NaOH/NaCl$), Verdes et al. (1992); ▷, Bourcier et al. (1993); ◇, Castet et al. (1993); □, Palmer et al. (2001); ◁, Bénézeth et al. (2008). Lines: dashed, Bénézeth et al. (2001); dotted, Königsberger et al. (2006); solid, this work (see text).

41

Electronic Annex Caption

Tables of heat capacities and densities of alkaline sodium aluminate solutions

Table EA-1. Isobaric volumetric (σ/J K^{-1} cm^{-3}), massic (c_p/J K^{-1} g^{-1}) and apparent molar ($C_{p\phi}$/J K^{-1} mol^{-1}) heat capacities and densities (ρ/kg m^{-3}) of alkaline sodium aluminate solutions at $I = m = 1$ mol kg^{-1}, degrees of substitution of hydroxide by aluminate, $\alpha = m_A/m$, where m_A is the aluminate molality, and 10.0 MPa ($m^\circ \equiv 1$ mol kg^{-1}).

Table EA-2. Isobaric volumetric (σ/J K^{-1} cm^{-3}), massic (c_p/J K^{-1} g^{-1}) and apparent molar ($C_{p\phi}$ /J K^{-1} mol^{-1}) heat capacities and densities (ρ/kg m^{-3}) of alkaline sodium aluminate solutions at $I = m = 2$ mol kg^{-1}, degrees of substitution of hydroxide by aluminate, $\alpha = m_A/m$, where m_A is the aluminate molality, and 10.0 MPa ($m^\circ \equiv 1$ mol kg^{-1}).

Table EA-3. Isobaric volumetric (σ/J K^{-1} cm^{-3}), massic (c_p/J K^{-1} g^{-1}) and apparent molar ($C_{p\phi}$ /J K^{-1} mol^{-1}) heat capacities and densities (ρ/kg m^{-3}) of alkaline sodium aluminate solutions at $I = m = 4$ mol kg^{-1}, degrees of substitution of hydroxide by aluminate, $\alpha = m_A/m$, where m_A is the aluminate molality, and 10.0 MPa ($m^\circ \equiv 1$ mol kg^{-1}).

Table EA-4. Isobaric volumetric (σ/J K^{-1} cm^{-3}), massic (c_p/J K^{-1} g^{-1}) and apparent molar ($C_{p\phi}$ /J K^{-1} mol^{-1}) heat capacities and densities (ρ/kg m^{-3}) of alkaline sodium aluminate solutions at $I = m = 6$ mol kg^{-1}, degrees of substitution of hydroxide by aluminate, $\alpha = m_A/m$, where m_A is the aluminate molality, and 10.0 MPa ($m^\circ \equiv 1$ mol kg^{-1}).