



Standard partial molar heat capacities and enthalpies of formation of aqueous aluminate under hydrothermal conditions from integral heat of solution measurements



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ABSTRACT

Heats of solution of sodium aluminum oxide, $\text{NaAlO}_2(\text{s})$, were measured in aqueous sodium hydroxide solutions using a Tian–Calvet heat-flow calorimeter (Setaram, Model C80) with high pressure “batch cells” made of hastelloy C-276, at five temperatures from (373.15 to 523.15) K, steam saturation pressure, and concentrations from (0.02 to 0.09) $\text{mol} \cdot \text{kg}^{-1}$. Standard molar enthalpies of solution, $\Delta_{\text{soln}}H^\circ$, and relative standard molar enthalpies, $[H^\circ(T) - H^\circ(298.15 \text{ K})]$, of $\text{NaAl}(\text{OH})_4(\text{aq})$ were determined from the measured heats of solution. The results were fitted with the “density” model. The temperature dependence of $\Delta_{\text{soln}}H^\circ$ from the model yielded the standard molar heat capacities of reaction, $\Delta_{\text{soln}}C_p^\circ$, from which standard partial molar heat capacities for aqueous aluminate, $C_p^\circ[\text{Al}(\text{OH})_4^-(\text{aq})]$, were calculated. Standard partial molar enthalpies of formation, $\Delta_f H^\circ$, and entropies, S° , of $\text{Al}(\text{OH})_4^-(\text{aq})$ were also determined. The values for $C_p^\circ[\text{Al}(\text{OH})_4^-(\text{aq})]$ agree with literature data determined up to $T = 413 \text{ K}$ from enthalpy of solution and heat capacity measurements to within the combined experimental uncertainties. They are consistent with differential heat capacity measurements up to $T = 573 \text{ K}$ from Schrödle *et al.* (2010) [29] using the same calorimeter, but this method has the advantage that measurements could be made at much lower concentrations in the presence of an excess concentration of ligand. To our knowledge, these are the first standard partial molar heat capacities measured under hydrothermal conditions by the integral heat of solution method in a commercial calorimeter to be reported in the literature.

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1. Introduction

The thermodynamic properties of aqueous metal complexes under hydrothermal conditions are required to model mass transport and corrosion in a variety of areas, including geochemistry, hydrometallurgy, electric power cycle chemistry, and many industrial processes. Many of these applications rely on semi-empirical models, such as the on the HKF equations developed by Helgeson and co-workers [1], or other equations of state [2,3] to predict the standard-state properties of aqueous species up to $T = 623.15 \text{ K}$. These models are based on extrapolating or fitting expressions for the standard partial molar heat capacities of each

species, C_p° , from $T = 298.15 \text{ K}$ to the temperature of interest. Extensive databases for metal complexes with hydroxides, chlorides and other ligands, developed by Shock *et al.* [4], Sverjensky *et al.* [5], Beverskog and Puigdomenech [6,7] and others are now in widespread use. Some of the parameters in these databases are obtained by fitting formation and hydrolysis constants to high-temperature solubility and spectroscopic studies for the system of interest, however most are derived from heat-capacity correlations based on unrelated species, such as the oxyanions, and should be used with caution. This problem is particularly serious for the hydroxyl-complexes for which solubility data are notoriously difficult to measure [8] and almost no experimental values for standard partial molar heat capacities exist.

Calorimetric methods for measuring the apparent molar heat capacities of aqueous solutes, $C_{p,\phi}$, under hydrothermal conditions, from which values of C_p° are derived, were recently reviewed by Tremaine and Arcis [9]. Most of the values in the literature were

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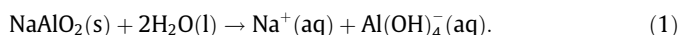
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measured using commercial Sodev Picker flow calorimeters [10,11], in the temperature range (283.15 to 328.15) K, and by sophisticated custom-made high-temperature Picker-type calorimeters designed by R.H. Wood and his co-workers at the University of Delaware [12–15] which operate at temperatures up to 718.15 K and 32 MPa, at molality $m \geq 0.015 \text{ mol} \cdot \text{kg}^{-1}$. More recently, accurate measurements of C_p° over the range $T = (278.15 \text{ to } 393.15) \text{ K}$ and at 0.35 MPa have also been reported by Woolley and his co-workers using commercial nano-differential scanning calorimeters [16,17]. These instruments measure the difference in the volumetric heat capacity of solutions relative to water, which yield values of the apparent molar heat capacities $C_{p,\phi}$ averaged over all the solutes in the solution on a mole fraction basis. As a result, they cannot be used to determine the properties of species that are only slightly soluble, or species that are only stable in solutions that contain a large excess of supporting electrolyte, ligand, acid or base, as is required for most metal complexes.

An alternative approach, developed by Criss and Cobble [18], the so-called “integral heat of solution method”, is based on determining standard molar heat capacities from the temperature dependence of the standard molar enthalpy of solution of a well-defined solid. The original method was used in pioneering studies to obtain values of simple electrolytes C_p° over the range $T = (273.15 \text{ to } 473.15) \text{ K}$ [19–21], before the Picker calorimeter was invented. Recently Djmalali and Cobble, have reported values of C_p° from integral heat of solution measurements obtained from a custom made isoperibol calorimeter [22] that operates at temperatures up to 598.15 K and to very low molality ($m \geq 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$) [23–26]. We are aware of no other reported studies that use this method at temperatures above 423.15 K, and the instrument constructed by Cobble and Djmalali [22], is no longer in use.

The purpose of the present research is to explore the use of a commercial Tian–Calvet calorimeter for determining standard partial molar heat capacities under hydrothermal conditions by the integral heat of solution method. The aqueous aluminate ion, $\text{Al}(\text{OH})_4^-(\text{aq})$ has been selected as a model system for this study. Experimental heat capacity studies on sodium aluminate were reviewed in 2002 by Magalhães *et al.* [27]. Values for the standard partial molar heat capacity, C_p° , have been determined from measurements of $C_{p,\phi}$ for dilute solutions from $T = (283.15 \text{ to } 328.15) \text{ K}$ by Hovey *et al.* [11], and from (323.13 to 523.15) K by Caiani *et al.* [28], using commercial and custom-made Picker flow calorimeters. Apparent molar heat capacities for concentrated mixtures $\text{NaAl}(\text{OH})_4(\text{aq})/\text{NaOH}(\text{aq})$, $m \geq 1 \text{ mol} \cdot \text{kg}^{-1}$, at temperatures up to 573.15 K have recently been reported by Schrödle *et al.* [29]. There has been one previous attempt to determine C_p° for $\text{NaAl}(\text{OH})_4(\text{aq})$ using the integral heat of solution method in a commercial Tian–Calvet calorimeter by Chen *et al.* [30]. That study used Gibbsite as the crystalline solid and was limited to temperatures below 423.15 K by the design of the commercial cell which contained Teflon and mercury.

This paper reports values for the standard partial molar heat capacity of $\text{Al}(\text{OH})_4^-(\text{aq})$ obtained by measuring the enthalpy of solution of sodium aluminate, $\text{NaAlO}_2(\text{s})$, in aqueous sodium hydroxide solutions at five temperatures from (373.15 to 523.15) K, using a Setaram C-80 Tian–Calvet calorimeter. The solution process corresponds to the reaction:



These measurements are challenging because corrections for heat effects associated with the release of the solid into the solution become large at elevated temperatures. The temperature dependence of the standard molar enthalpies of solution, $\Delta_{\text{soln}}H^\circ$, determined from experimental heats of solution, and the resulting values for the standard partial molar heat capacities for the aqueous

aluminate complex, C_p° are reported. To the best of our knowledge, this is the first such study to be reported in a commercial instrument above $T = 423.15 \text{ K}$.

2. Experimental

2.1. Chemicals and solution preparation

MilliQ nanopure water with an electrical resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$ was used for to prepare all solutions. Solid sodium chloride, $\text{NaCl}(\text{s})$ (Aldrich, ACS reagent), and sodium aluminate, $\text{NaAlO}_2(\text{s})$ (Alpha Aesar; CAS 1302-42-7, Lot No. K19T061), were dried in an oven overnight at $T = (523.15 \text{ and } 573.15) \text{ K}$ respectively, stored in a desiccator containing P_2O_5 , and re-dried before each loading of the calorimeter cells. Powder X-ray diffractograms (XRD) of the $\text{NaAlO}_2(\text{s})$ showed a major phase with the crystal structure of $\text{NaAlO}_2(\text{s})$ reported by Kaduk and Pei [31], *i.e.* a Pna21 unit cell with $a = 0.53871 \text{ nm}$, $b = 0.70320 \text{ nm}$ and $c = 0.52180 \text{ nm}$. Upon standing, diffractograms of unsealed samples showed the major reflections of the hydrate $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}(\text{s})$, which are attributed to its formation from atmospheric humidity. These results are consistent with Kaduk and Pei's finding that the dehydration of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}(\text{s})$ occurs at $T = 473 \text{ K}$. Broad weak reflections indicated a minor amount of nanocrystalline or amorphous material, which we could not identify, and there were no reflections corresponding to NaOH or Na_2O (detection limit $\sim 1\%$). In the calculations reported below, the dried sodium aluminate was assumed to be at the stoichiometric composition. NaOH solutions were prepared from Fisher (certified, ACS) carbonate-free 50% (w/w) NaOH solutions and standardized by titration against potassium hydrogen phthalate (Aldrich).

2.2. Experimental apparatus and procedure

A Setaram Model C-80 calorimeter was used for our calorimetric measurements. The calorimeter has been designed for operation at high pressures (up to 10 MPa) and high temperatures (up to 573.15 K). The C-80 calorimeter is based on Tian–Calvet heat flow principles that have been described in detail elsewhere [32,33]. The model used in this study included a reversal mechanism, so that it could be inverted back and forth with a rotational period of $\sim 10 \text{ s}$.

The Setaram C-80 heat flow calorimeter is made of two identical tubular wells, symmetrically located about the center line in an accurately thermostated aluminum block. Each well is surrounded by a thermopile (fluxmeter), which measures the heat flux between to or from the aluminum block. The two fluxmeters are designed identically and are connected in opposition to give a differential thermopile output. This differential arrangement is designed to compensate for the influence of the surroundings on the experiments. Two cells, identical in design, are made to fit snugly into the wells. One cell acts as a sample/measurement cell and the other as a reference cell. Hence, a caloric effect inside the cell results in a heat flow between the cell and the thermopile, thus leading to a time-dependent thermoelectric voltage signal proportional to the heat transferred between the cell and the thermocouple. The temperature of the calorimeter was calibrated by measuring the temperatures of fusion of indium (DSC Calibration Standard, NIST SRM 2232) and tin (mass fraction purity 0.99998, Aldrich) for scan rates of (0.05, 0.1, 0.15 and 0.2) $\text{K} \cdot \text{min}^{-1}$, in the same cells used for our experimental measurements. The transition temperatures of indium and tin specified by NIST are $T = (429.75 \text{ and } 505.09) \text{ K}$ respectively.

The high pressure “batch” cells, used in this study, were hastelloy C-276 cylinders with threaded top caps, supplied by Setaram.

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