The Estimation of Standard Molar Enthalpies of Solution for VOSO$_4$·$n$H$_2$O(s) in Water and in Aqueous H$_2$SO$_4$

Ye Qin · Wei-Feng Xue · Jian-Guo Liu · Wei-Guo Xu · Chuan-Wei Yan · Jia-Zhen Yang

Received: 12 September 2009 / Accepted: 28 January 2010 / Published online: 11 June 2010
© Springer Science+Business Media, LLC 2010

Abstract The molar enthalpies of solution of VOSO$_4$·3.52H$_2$O(s) at various molalities in water and in aqueous sulfuric acid (0.1 mol·kg$^{-1}$), $\Delta_{\text{sol}}H_m$, were measured by a solution-reaction isoperibol calorimeter at 298.15 ± 0.01 K. An improved Archer’s method to estimate the standard molar enthalpy of solution, $\Delta_{\text{sol}}H^0_m$, was put forward. In terms of the improved method, the values of $\Delta_{\text{sol}}H^0_m = -24.12$ ± 0.03 kJ·mol$^{-1}$ of VOSO$_4$·3.52H$_2$O(s) in water and $\Delta_{\text{sol}}H^0_m = -15.38$ ± 0.06 kJ·mol$^{-1}$ in aqueous sulfuric acid were obtained, respectively. The data indicates that the energy state of VOSO$_4$ in aqueous H$_2$SO$_4$ is higher than that in pure water.

Keywords Vanadium redox flow battery · Enthalpies of solution · Vanadyl sulfate · Sulfuric acid

1 Introduction

The all vanadium redox flow battery (VRFB), an effective energy-storage system proposed by Skyllas–Kazacos et al. [1–3], has been investigated extensively. In the VRFB, the electrolyte is one of the most important components. It is not only the conductor of ions, but also the energy-storage medium. The VRFB employs the V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cell electrolytes, respectively, with sulfuric acid as the supporting electrolyte. The chemistry of vanadium has recently attracted considerable attention from industry and the academic community [4–6], because reliable thermodynamic data are needed both to help in providing an adequate description of interactions of various species in the VRFB solution and to provide clues to optimize the overall performance of the
VRFB. As a continuation of our earlier work [7], in the present paper the following results are reported: (1) the molar enthalpies ($\Delta_{\text{sol}}H_{m}$) of solution of VOSO$_4$·3.52H$_2$O(s) with various molalities in pure water and in aqueous sulfuric acid as measured by a solution-reaction isoperibol calorimeter at 298.15 ± 0.01 K; (2) considering association of aqueous VOSO$_4$ and second dissociation of aqueous H$_2$SO$_4$, an improved Archer’s method is put forward and the standard molar enthalpies of solution of VOSO$_4$·3.52H$_2$O(s), $\Delta_{\text{sol}}H_{m}^0$, in pure water and in aqueous sulfuric acid are estimated by this improved method; (3) the difference between Archer’s method [8] and the improved Archer’s method is discussed.

2 Experimental

2.1 Chemicals

The VOSO$_4$·$n$H$_2$O(s) used in the experiments, where $n = 3.52$ was determined by thermogravimetric analysis, was recrystallized twice from water and dried under reduced pressure at 353 K [9]. KCl, with a purity higher than 99.99%, was dried in a vacuum oven at 408 K for 6 h. THAM [tris-(hydroxymethyl) aminomethane], GR grade reagent, was dried in a vacuum oven. H$_2$SO$_4$ of GR grade reagent was used without further purification. Double-distilled water was used.

2.2 Determination of the Molar Enthalpies of Solution

On the basis of other calorimetric apparatus [10, 11], an on-line solution-reaction isoperibol calorimeter was constructed. It consisted of a water thermostat, a 200 cm$^3$ pyrex glass plated silver Dewar, a 4 cm$^3$ glass sample cell, a calibration heater, a glass-sheathed thermistor probe, an amplifier, a circuit used as an A/D converter and a personal computer for data acquisition and processing. 150 g solvent (water) was placed in the Dewar and 0.1 to 2 g solute [KCl, THAM or VOSO$_4$·3.52H$_2$O(s)] was placed in the sample cell. The inevitable heat transfer and heat generations owing to friction were compensated and the corrected temperature change (the adiabatic temperature change) $\Delta T^*$ was obtained according to the conventional method (the equal area method). The enthalpies of solution were calculated from the equation:

$$Q_s/\Delta T_s^* = Q_E/\Delta T_E^*$$

where $Q_s$ is the enthalpy of solution of the sample, $\Delta T_s^*$ is the adiabatic temperature change of the solution process, $Q_E$ is the electric energy used for calibration, and $\Delta T_E^*$ is the adiabatic temperature change of electric calibration.

The performance and accuracy of the calorimetric system was tested by measuring the molar enthalpy of solution of KCl in water (molar ratio: KCl/water = 1/1110) and THAM [Tris-(hydroxymethyl) aminomethane] solution in 0.1 mol·dm$^{-3}$ HCl(aq) [0.750 g of THAM dissolved in 0.150 dm$^3$ of 0.1 mol·dm$^{-3}$ HCl(aq)] at 298.15 K. The results are listed in Tables 1 and 2, respectively. As shown in these tables, the mean molar enthalpies of the solution, $\Delta_{\text{sol}}H_m = (17526 \pm 13)$ J·mol$^{-1}$ for KCl and $\Delta_{\text{sol}}H_m = (−29761 \pm 19)$ J·mol$^{-1}$ for THAM, which are in good agreement with the published data, (17536 ± 9) J·mol$^{-1}$ for KCl [12, 13] and (−29766 ± 31.5) J·mol$^{-1}$ for THAM [13], were obtained and these results verified the accuracy of the isoperibol calorimeter. Then the molar enthalpies of solution of VOSO$_4$·3.52H$_2$O(s) with different molalities in pure water and in 0.1 mol·kg$^{-1}$ aqueous sulfuric acid were measured using the tested isoperibol calorimeter.