

Salt-saturated salt solution as a standard system for sorption calorimetry

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Received 30 January 2004; received in revised form 24 March 2004; accepted 1 April 2004

Available online 28 May 2004

Abstract

The method of sorption calorimetry allows simultaneous monitoring of water activity and the partial molar enthalpy of mixing of water. The way of calibration of sorption calorimeter affects the accuracy of the data obtained in sorption experiments. In order to improve the accuracy of the method one can use physico-chemical calibration instead of electrical calibration. The system for use in the calibration should keep its properties constant during the sorption of water, therefore a heterogeneous system can be used. The particular system suitable for this purpose is magnesium nitrate hexahydrate in equilibrium with its saturated solution. The enthalpy of dissolution of the hexahydrate in its saturated solution needed for the calibration has been determined by isothermal titration calorimetry at 25 and 40 °C. The titration results are in agreement with the calculations based on van der Waals differential equation.

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Keywords: Sorption calorimetry; Isothermal titration calorimetry; Calibration; Partial molar enthalpy of mixing of water; Saturated solution; Magnesium nitrate; van der Waals differential equation

1. Introduction

Sorption calorimetry [1–3] is a relatively newly developed method successfully applied for studies of various materials—lipids [4], surfactants [5,6], DNA and other substances [7]. The method allows obtaining the data on the activity of water and the partial molar enthalpy of mixing of water in a solid or liquid substance in one experiment. The possibility of getting the data on the activity of water and the enthalpy of mixing means that the complete thermodynamic description of a studied system at a given temperature can be obtained. The method is universal from point of view of a studied system: any condensed phase system not containing volatile substances other than water can be studied. Non-aqueous systems can also be potentially examined [8]. The method requires relatively small amounts of samples (usually 10–50 mg), therefore it is suitable for studies of newly developed substances, which are usually very expensive. On the other hand the method has some disadvantages, one of which is lower accuracy comparing to the meth-

ods, which do not provide the complete thermodynamic description and require larger amounts of studied samples.

In the sorption calorimetric experiments two parameters—the water activity a_w and the partial molar enthalpy of mixing of water H_w^m —are measured as functions of water content. A way to improve the accuracy of the measurements of the water activity was proposed earlier [9]. Here a method to improve the accuracy of determination of the other measured parameter— H_w^m is proposed.

Sorption of water by a solid or liquid substance can be described in two ways: either by partial molar enthalpy of sorption of water by the substance H_w^{sorp} or by partial molar enthalpy of mixing of water with the substance H_w^m . Since the process of sorption of water vapour can be divided in two steps: condensation of the water vapour to the liquid water and then mixing of the liquid water with the substance, the values of H_w^m and H_w^{sorp} are related in the following way:

$$H_w^{\text{sorp}} = -H_w^{\text{vap}} + H_w^m \quad (1)$$

where H_w^{vap} is the enthalpy of vaporisation of pure water. Absolute value of H_w^{vap} is usually much higher than that of H_w^m , therefore, the main contribution to the enthalpy of sorption arises from H_w^{vap} , which is independent on the properties of the studied system. This fact means that the enthalpy

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of mixing is much more sensitive to the interactions between water and the studied material. Therefore the enthalpy of mixing rather than the enthalpy of sorption is normally used to describe results of sorption calorimetric experiments.

A sorption calorimetric cell consists of two chambers—sorption chamber and vaporisation chamber. In the sorption chamber the studied substance is placed, while in the vaporisation chamber water is injected. During experiment, the thermal powers from the two chambers P^{sorp} and P^{vap} are measured separately. These values are used to calculate the partial molar enthalpy of mixing of water:

$$H_w^m = H_w^{\text{vap}} + H_w^{\text{sorp}} = H_w^{\text{vap}} + P^{\text{sorp}} \frac{H_w^{\text{vap}}}{P^{\text{vap}}} \quad (2)$$

Thermal powers of vaporisation and sorption usually have opposite signs and close absolute values. Therefore, on the right side of the Eq. (2) there is a difference of two large values, which gives a relatively small value of H_w^m . Consequently, the enthalpy of mixing calculated using Eq. (2) is very sensitive to the uncertainties of values of thermal powers. The thermal powers P are calculated from the calorimetric signals U and corresponding calibration coefficient ε :

$$P = U\varepsilon \quad (3)$$

The calibration coefficients are usually determined by electrical calibration. Conditions of the electrical calibration are very different from that of the real sorption experiments, therefore a significant error can be introduced. Another way of calibration of sorption calorimeter is to conduct a sorption experiment with a substance or a system with a well-known value of the partial molar enthalpy of mixing with water H_w^m . In that case not the values of the calibration coefficients but their ratio has to be determined:

$$H_w^m = H_w^{\text{vap}} + H_w^{\text{sorp}} \frac{\varepsilon^{\text{sorp}} U^{\text{sorp}}}{\varepsilon^{\text{vap}} U^{\text{vap}}} \quad (4)$$

A standard chemical system for the calibration should have the following properties:

- The value of H_w^m in this system should be well-known and/or can be determined independently by another method.
- H_w^m should not change during sorption of water.
- The substances of the system should not cause a corrosion of the sorption cell.
- The substances should be cheap and easily available.

The system, which meets these requirements, is a salt in equilibrium with its saturated solution. The particular salt chosen in this work is magnesium nitrate since this salt is already used for another application of sorption calorimetry—desorption experiments [10]. Isothermal titration calorimetry was used to determine the partial molar enthalpy of mixing of water in this system.

2. Materials and methods

Magnesium nitrate hexahydrate (purity >99%) was supplied by Merck; water passed through Millipore Q purification system was used.

Sorption calorimetric experiments were performed in a double-twin microcalorimeter with the inner diameter 20 mm [2,3]. The sorption calorimetric cell with the vaporisation chamber on the bottom and the sorption chamber on the top was used. The standard procedures of the method of sorption calorimetry [1,5,9] were used in sorption experiments. The calorimetric signal was converted into digital form using Pico ADC16 converter.

For isothermal titration calorimetric experiments 2277 TAM Thermal Activity Monitor System was used. The volume of the insertion vessel was 3 ml. Calibration of the calorimeter for titration experiments was performed by dissolution of propanol in water [11].

3. Enthalpy of dissolution of magnesium nitrate hexahydrate

3.1. Measurement of H_w^m using isothermal titration calorimetry

The partial molar enthalpy of mixing of water is by definition the enthalpy change upon an addition of a small amount of water at a constant temperature and pressure. Therefore this value can be directly measured in isothermal titration calorimetry when a small amount of water is injected into a studied solution or substance. For a system salt-saturated solution the partial molar enthalpy of mixing of water is equal to the enthalpy of dissolution of the salt in its saturated solution calculated per mole of water. This value remains constant in the whole interval of coexistence of salt and saturated solution. In order to measure this value using isothermal titration calorimetry, we tried to use the following procedure: the saturated solution of magnesium nitrate with a small amount of crystals of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was equilibrated in the titration vessel. A stirring was applied to this heterogeneous system and an injection of a small amount of water was made. After the injection the calorimetric signal did not return to a value close to the baseline even after several hours of experiment. Similar experiments were conducted several times but signals returned back to baselines in none of the experiments. This fact shows that the kinetics of dissolution does not allow to use this procedure to determine the heat of dissolution even when an effective stirring is applied. To solve the problem another procedure was proposed: the calorimetric vessel was filled with wet crystals of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and no stirring was used. The injection needle was inserted in the vessel in a way that provides a direct contact of the injection needle with the crystals. After injection of several milligrams of water the calorimetric signal returned to the baseline typically in 1 h. The values of

Table 1
Enthalpy of dissolution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in its saturated solution, kJ/mol H_2O

Temperature (°C)	Titration	Literature data	Calculation
25	4.13 ± 0.01	4.77 ^a 5.02 ^b 4.39 ^c 4.06 ^d	3.99 ^e
40	5.39 ± 0.07	–	–

Uncertainties are given as twice standard deviations of the mean (three measurements at 25 °C, 11 measurements at 40 °C).

^a Apelblat and Korin [24].

^b Calculated from the data cited by Treptow [22].

^c Extrapolated from [20].

^d Extrapolated from the data of the NBS tables [21].

^e Calculated using van der Waals differential equation.

enthalpies of dissolution obtained at 25 and 40 °C are given in Table 1. The value of enthalpy is higher at 40 °C than at 25 °C. This is caused by the fact that the composition range of coexistence of the phases is smaller at higher temperature, therefore an addition of the same amount of water at 40 °C causes the dissolution of larger amount of salt than at 25 °C. The main source of errors in these titration experiments probably arises from the absence of stirring. Usually the stirring is applied for two purposes: to mix the injected substance with the solvent in the calorimetric vessel and to evenly distribute the heat in the vessel. The former reason to use the stirring is not valid here: since the system is heterogeneous, the injected water does not need to be evenly distributed in the vessel. The distribution of heat in the vessel could still be a problem, but since the titration results were reasonably well reproducible, it apparently rather weakly affects the obtained data. In order to eliminate the problem and further increase the accuracy, it would be advisable to conduct this type of experiments in the calorimeters that have the calorimetric vessels covered by the thermocouple plates on all sides [12].

3.2. Calculation of H_w^m using van der Waals differential equation

Another way to determine H_w^m during a phase transition is to use van der Waals differential equation [5,13,14] (see also Appendix A):

$$\Delta V^{1 \rightarrow 2} dp = \Delta S^{1 \rightarrow 2} dT + (\partial^2 G / \partial x^2)_{T,P}^{(1)} \Delta x^{1 \rightarrow 2} dx^{(1)} \quad (5)$$

In the appendix it is shown that at a constant total pressure p the entropy term $S^{1 \rightarrow 2}$ is directly related to the integral \tilde{H} (Fig. 1) under the H_w^m curve:

$$T \Delta S^{1 \rightarrow 2} = \tilde{H} x_s^{(2)} \quad (6)$$

(here $x_s^{(2)}$ is the mole fraction of the salt in the second phase). From Fig. 1 one can see that the partial molar enthalpy of mixing during phase transition can be calculated in the following way:

$$H_w^m = H_w^{m(1)} + \frac{\tilde{H}}{\Delta r} \quad (7)$$

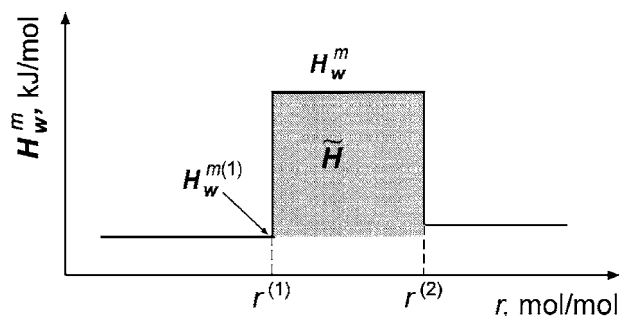


Fig. 1. Partial molar enthalpy of mixing of water H_w^m as a function of molar ratio r in a typical phase transition at a constant temperature. \tilde{H} is determined by Eq. (A.6).

In order to calculate the enthalpy term $H^{1 \rightarrow 2}$ using van der Waals differential equation:

$$T S^{1 \rightarrow 2} = H^{1 \rightarrow 2} = - \frac{RT^2 \left(\frac{d \ln a_w}{(1-x) dx} \right)_{T,P}^{(1)} \Delta x^{1 \rightarrow 2}}{(dT/dx)^{(1)}} \quad (8)$$

one has to know the slope of the phase boundary in the first phase, activity of water and its derivative in the same phase and the length of the tie line $\Delta x^{1 \rightarrow 2}$. Since the thermodynamic data are better known for the solution than for the hydrate, the first phase is chosen to be the saturated salt solution while the second phase—the hexahydrate. There is a number of publications presenting the data about the solubility of magnesium nitrate (i.e. composition of the first phase), see for example [15–17]. Here we used the value 42.1 wt.% at 25 °C [17] which corresponds to $x_w^{(1)} = 0.9189$ and $r^{(1)} = 11.32$ and $\Delta x^{1 \rightarrow 2} = -0.0618$. For the calculation of the slope of the phase boundary the data of Sieverts and Petzold [17] and Sieverts and Muller [16] approximated by polynoms were used. The obtained value was $dT/dx = -2305$ K. The activity of water in the saturated solution of $\text{Mg}(\text{NO}_3)_2$ according to Greenspan [18] is 0.5289. The composition dependence of water activity near the saturation point was calculated from the data of El Guendouzi and Marouani [19]: $da_w/dx_w = 7.39$. The value $H^{1 \rightarrow 2}$ calculated using Eq. (8) is 3.41 kJ/mol, which corresponds to $\tilde{H} = 23.9$ kJ/mol. In order to find the value of H_w^m for the system salt-saturated solution one has to know this value for the solution which composition is close to that of the saturation— $H_w^{m(1)}$ (see Eq. (7)). Differentiation of the data of [20] gives the value $H_w^{m(1)} = -0.50$ kJ/mol. Finally, calculation using Eq. (7) produces the value of the partial molar enthalpy of mixing of water in the system magnesium nitrate hexahydrate-saturated solution as 3.99 kJ/mol.

3.3. Comparison to the literature data

In the literature the data about dissolution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are usually given in kilojoule per mole of salt: $\Delta_{\text{sol}} H(\text{salt})$. Therefore the values of the enthalpies were

recalculated per mole of water $\Delta_{\text{sol}}H(\text{H}_2\text{O})$ using the following formula:

$$\Delta_{\text{sol}}H(\text{H}_2\text{O}) = \frac{\Delta_{\text{sol}}H(\text{salt})}{r^{\text{sat}} - 6} \quad (9)$$

where r^{sat} is the number of moles of water per number of moles of salt in saturated solution. Values of enthalpy calculated using Eq. (9) are given in Table 1 (values marked a and b).

Data on enthalpies of dissolution of salts in their saturated solutions are rarely present in literature. More often the data are related to non-saturated solutions. In order to find the enthalpy of dissolution of magnesium nitrate in the saturated solution, the data on the enthalpy of dilution and the data on the enthalpy of formation of solution [21] were extrapolated to the saturation point (values marked c and d in Table 1).

The titration data presented here, the results of the calculation using van der Waals differential equation and the results obtained by extrapolation of the values from NBS tables [21] are in a good agreement. Other three values presented in Table 1 are higher but not in agreement to each other. There is no data about experimental technique employed in obtaining the highest value [22]. Therefore the data obtained by isothermal titration calorimetry are probably the most accurate. Since the accuracy of measurements of H_w^m in sorption experiments is not better than 0.5 kJ/mol, the present data can be recommended for use in the calibration of sorption calorimeter.

4. Calibration of the sorption calorimeter

The calibration of the sorption calorimeter was performed in the same way as a normal sorption experiment. The sample (wet crystals of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was placed into the sorption cell, and after the stabilisation of the baseline, water was injected into the vaporisation chamber. The dependences of the values of calorimetric signals with time are presented in Fig. 2. The signals kept constant values during the experiments both at 25 and 40 °C, which means that the selected system is suitable for calibration of the sorption calorimeter. The ratio of the calibration coefficients was calculated in the following way:

$$\frac{\varepsilon^{\text{sorp}}}{\varepsilon^{\text{vap}}} = \left(\frac{H_w^m}{H_w^{\text{vap}}} - 1 \right) \left(\frac{U^{\text{vap}}}{U^{\text{sorp}}} \right) \quad (10)$$

and the obtained value of the ratio was 1.354 both at 25 and 40 °C.

Sorption calorimeter requires three types of calibrations: calibration of vaporisation chamber, calibration of sorption chamber and the maximum vapour flow calibration. A new way of calibration of the sorption chamber is described here. The other two types of calibrations can also be done using the system salt-saturated salt solution as a standard. The calibration of the vaporisation chamber is usually done

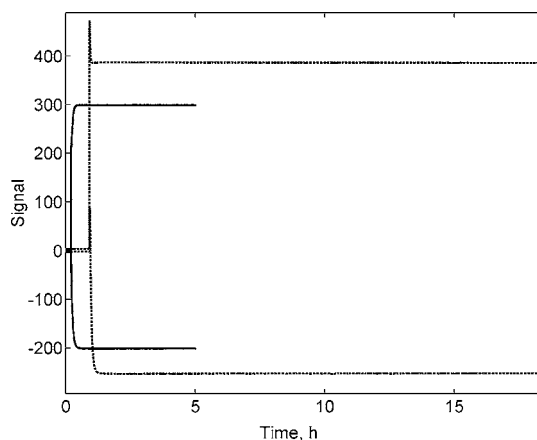


Fig. 2. Raw calorimetric signals U (see Eq. (3)) from the sorption calorimeter during calibration experiments at 25 °C (solid curves) and 40 °C (dashed curves). Negative values correspond to the signals from the sorption chamber; positive values from the vaporisation chamber.

electrically. An alternative way is to fill the sorption chamber with wet crystals of salt and perform a titration experiment in the chamber. Since the stirring is not used in the proposed type of the titration experiment, one can perform the titration in the sorption cell. Knowing the enthalpy of dissolution of the salt, one can calculate the calibration coefficient of the vaporisation chamber from this titration experiment.

The maximum vapour flow calibration is usually done in an experiment with molecular sieves. In that case the water activity in the sorption chamber is close to zero and the vapour flow between the chambers reaches the maximum value. In principle, one can get the information about the maximum vapour flow of the calorimetric cell in the experiment with saturated salt solution (Fig. 2) and therefore combine two calibrations in one experiment. Since the activity of water of the saturated solution of magnesium nitrate is well known, one can calculate the maximum value of the calorimetric signal from the signal registered in the experiment with the salt system. On the other hand it was noticed that the calorimetric signal from the vaporisation chamber was better reproducible in the experiments with molecular sieves than in the experiments with the salt system. The reason for this is probably the kinetics of sorption of water vapour on rather big crystals of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (the ratio of the signals from the two chambers is not affected by the kinetic problem). Therefore, in order to obtain more accurate results one can recommend to perform the maximum vapour flow calibration using the molecular sieves.

The calibration of the double-twin sorption calorimeter using the system salt-saturated salt solution as a standard allows one to simplify the procedure of the calibration and to increase the accuracy of measurement of enthalpy. The same standard can potentially be used for calibration of other types of sorption calorimeters.

Acknowledgements

Author thanks Gerd Olofsson for fruitful discussions.

Appendix A

In this section the heat effect observed in a phase transition is compared to the entropy term of van der Waals differential equation.

Van der Waals differential equation [5,13,14,23]:

$$\Delta V^{1 \rightarrow 2} dp = \Delta S^{1 \rightarrow 2} dT + \left(\frac{\partial^2 G}{\partial x^2} \right)_{T,P}^{(1)} \Delta x^{1 \rightarrow 2} dx^{(1)} \quad (\text{A.1})$$

can be used to calculate the slope of the phase boundary when the information about isothermal thermodynamic parameters is known [5]:

$$\frac{dT}{dx} = - \frac{RT \left(\frac{d \ln a_w}{(1-x)dx} \right)_{T,P}^{(1)} \Delta x^{1 \rightarrow 2}}{S^{m(2)} - S^{m(1)} - \Delta x^{1 \rightarrow 2} (\partial S^m / \partial x)_{T,P}^{(1)}} \quad (\text{A.2})$$

On the other hand, having the information about dT/dx one can calculate parameters related to isothermal conditions, for example the entropy term $\Delta S^{1 \rightarrow 2}$ (denominator on the right-hand side of the Eq. (A.2)). The entropy term is directly related to the enthalpy term $\Delta H^{1 \rightarrow 2}$:

$$\Delta S^{1 \rightarrow 2} = \frac{\Delta H^{1 \rightarrow 2}}{T} \quad (\text{A.3})$$

$$\Delta H^{1 \rightarrow 2} = H^{m(2)} - H^{m(1)} - \Delta x^{1 \rightarrow 2} \left(\frac{\partial H^m}{\partial x} \right)_{T,P}^{(1)} \quad (\text{A.4})$$

In the following we present a way to use calorimetric data to calculate the entropy term of van der Waals differential equation. In the sorption calorimetric experiments the partial molar enthalpy of mixing of water H_w^m can be measured. Integration of this parameter over the composition range $1 \rightarrow 2$ with respect to molar ratio $r = n_w/n_s$ gives the change of the intensive integral enthalpy of mixing H^m divided by respective content of the substance:

$$\begin{aligned} \int_{r^{(1)}}^{r^{(2)}} H_w^m dr &= \frac{1}{n_s} \int_{n^{(1)}}^{n^{(2)}} H_w^m dn_w = \frac{1}{n_s} (H^{m(2),\text{ext}} - H^{m(1),\text{ext}}) \\ &= \frac{H^{m(2)}}{x_s^{(2)}} - \frac{H^{m(1)}}{x_s^{(1)}} \end{aligned} \quad (\text{A.5})$$

where $H^{m(2),\text{ext}}$ is the extensive integral enthalpy of mixing at the composition number 2. If during a sorption experiment a phase transition occurs, it is observed on the enthalpy curve in a way presented in Fig. 1. The heat effect \tilde{H} corresponding to the transition can be determined as the area under the curve of H_w^m . If the baseline is taken as the value of the partial molar enthalpy of mixing of water before

transition, then:

$$\tilde{H} = \int_{r^{(1)}}^{r^{(2)}} (H_w^m - H_w^{m(1)}) dr = \frac{H^{m(2)}}{x_s^{(2)}} - \frac{H^{m(1)}}{x_s^{(1)}} - H_w^{m(1)} \Delta r \quad (\text{A.6})$$

In order to compare \tilde{H} and $\Delta H^{1 \rightarrow 2}$ one has to get rid of the derivative in Eq. (A.4):

$$\frac{\partial H^m}{\partial x_w} = H_w^m - H_s^m = H_w^m - \frac{H^m}{x_s} + H_w^m r \quad (\text{A.7})$$

Then:

$$\begin{aligned} \Delta H^{1 \rightarrow 2} &= H^{m(2)} - H^{m(1)} - \Delta x^{1 \rightarrow 2} \\ &\quad \times \left(H_w^{m(1)} - \frac{H^{m(1)}}{x_s^{(1)}} + H_w^{m(1)} r \right) \\ &= H^{m(2)} - H^{m(1)} \frac{x_s^{(2)}}{x_s^{(1)}} - \Delta x^{1 \rightarrow 2} H_w^{m(1)} (1 + r^{(1)}) \end{aligned} \quad (\text{A.8})$$

Dividing both sides of the Eq. (A.8) by the molar fraction of the component s, we obtain:

$$\begin{aligned} \frac{\Delta H^{1 \rightarrow 2}}{x_s^{(2)}} &= \frac{H^{m(2)}}{x_s^{(2)}} - \frac{H^{m(1)}}{x_s^{(1)}} - H_w^{m(1)} \frac{\Delta x^{1 \rightarrow 2} (1 + r^{(1)})}{x_s^{(2)}} \\ &= \frac{H^{m(2)}}{x_s^{(2)}} - \frac{H^{m(1)}}{x_s^{(1)}} - H_w^{m(1)} \Delta r \end{aligned} \quad (\text{A.9})$$

Comparing Eqs. (A.6) and (A.9) one can see that

$$\Delta H^{1 \rightarrow 2} = \tilde{H} x_s^{(2)} \quad (\text{A.10})$$

Eq. (A.10) means that the enthalpy term of van der Waals differential equation is equal to the area under the curve molar ratio–partial molar enthalpy of mixing of water multiplied by the molar fraction of the second component at the end of the phase transition if the baseline corresponds to the level of the partial molar enthalpy of mixing of water before the transition.

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