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A new formula for accurate calculation of water activity in sorption calorimetric experiments

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Abstract

A sorption calorimetric method proposed by Wadsö and Markova allows determination of water activity. Calculation of water activity is based on Fick's first law. The correct form of the Fick's law takes into account not only vapour diffusion itself but also bulk flow of vapour. A new formula, which uses the correct form of the diffusion law for direct calculation of water activity, is proposed.

Keywords: Sorption calorimetry; Water activity; Diffusion; Corrections

1. Introduction

Method of sorption calorimetry [1,2] is used for study of sorption of water vapour on solid, liquid and liquid crystalline samples. In sorption calorimetric experiments three parameters are determined independently: water content in a studied sample, activity of water in the sample and partial molar enthalpy of mixing of water (sometimes referred as differential enthalpy of sorption of water). Therefore this method is a unique source of experimental data not only about process of sorption itself, but also about equilibrium thermodynamic properties of studied substances. Being universal from point of view of state of studied samples and obtained thermodynamic information, the method is sometimes less accurate than methods, which provide more specific data and applied to some particular classes of substances. For example, the method of titration calorimetry can provide more accurate data about enthalpy of mixing in liquid solutions, but it cannot be used for simultaneous determination of water activity; the sorption balance can give an accurate sorption isotherm (water activity–water content dependence), but cannot be used for direct determination of enthalpy of mixing.

In order to improve the accuracy of the method of sorption calorimetry, several procedures of corrections of calculated parameters are used [1]. One of the corrections which affects calculated value of water activity deals with the fact that the Fick's first law has different forms for the diffusive motion relative to the binary gas mixture or to stationary coordinates [3]. This correction, proposed by Wadsö and Markova [1] makes use of the correct form of Fick's law for practical calculations. Though it solves the problem, the proposed procedure is rather complicated and requires application of numerical methods. Below another approach is described, which allows direct calculation of water activity using an analytical formula.

2. A new formula

A sorption calorimetric cell consists of two chambers (sorption and vaporisation chambers) connected by a tube. Water vapour diffuses in the nitrogen atmosphere from the vaporisation chamber through the tube to the sorption chamber. For calculations of water activity in the sorption calorimetric experiments Fick's first law is used [3]:

$$N_\mathrm{w} = x_\mathrm{w}(N_\mathrm{w} + N_\mathrm{B}) - cD\nabla x_\mathrm{w} \tag{1}$$

where N_w and N_B are the molar fluxes of water vapour and nitrogen, respectively, c is the molar density of the gas mixture, D is a diffusion coefficient of the gas mixture and x_w is the molar fraction of water in the vapour. The first term of the right-hand side of Eq. (1) is the molar flux of water

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resulting from the bulk motion of the vapour and the second term is the molar flux of water resulting from the diffusion superimposed on the bulk flow. In practice the first term is often neglected for simplification. In that case for a steady state the flux of water vapour is proportional to the difference of water contents in vapour phases of sorption and vaporisation chambers, and therefore to the difference of water activities in the sorption chamber a_{w} and in vaporisation chamber $a_{\mathrm{w}}^{(\mathrm{v})}$:

$$N_{\mathrm{w}} \propto a_{\mathrm{w}}^{(\mathrm{v})} - a_{\mathrm{w}} = 1 - a_{\mathrm{w}} \tag{2}$$

When a drying agent, for example molecular sieves, is placed into the sorption chamber, $a_{\mathrm{w}} = 0$ and N_{w} reaches its maximum value $N_{\mathrm{w}}^{\max}$ (this experiment is the maximum flow calibration). Combining Eq. (2) for unknown activity a_{w} with the same equation for zero activity, one gets the expression for a_{w}:

$$a_{\mathrm{w}} = 1 - \frac{N_{\mathrm{w}}}{N_{\mathrm{w}}^{\max}} = 1 - \frac{P}{P^{\max}} \tag{3}$$

where P is the thermal power of vaporisation (proportional to N_{w}) and $P^{\max}$ is its maximum value. Formula (3) is often used for calculation of water activities in sorption calorimetric experiments (see for example [4]). Nevertheless, since in the experiments the water vapour moves from one chamber to another, for strict calculations of water activity the first term of the right-hand side of Eq. (1) should also be taken into account. In that case the rate of the water vapour transfer N_{w} at the liquid–vapour interface (rate of evaporation) is [3]:

$$N_{\mathrm{w}1} = \frac{cD}{z_2 - z_1} \ln\left(\frac{x_{\mathrm{B}2}}{x_{\mathrm{B}1}}\right) \tag{4}$$

where c is a constant, z_i is a coordinate and x_{B} is a concentration of B, which is air or nitrogen. Indexes 1 and 2 refer to positions corresponding to vaporisation of water and water sink, respectively.

In order to derive an expression for water activity, one should use perfect gas laws and definition of water activity:

$$p_{\mathrm{t}} = p_{\mathrm{w}} + p_{\mathrm{B}} = a_{\mathrm{w}} p_{\mathrm{w}}^{0} + p_{\mathrm{t}} x_{\mathrm{B}} \tag{5}$$

$$x_{\mathrm{B}} = \frac{p_{\mathrm{t}} - a_{\mathrm{w}} p_{\mathrm{w}}^{0}}{p_{\mathrm{t}}} \tag{6}$$

where p_{t} is the total pressure, p_{w} and p_{B} are partial pressures of water and nitrogen, respectively, p_{w}^{0} is vapour pressure of the pure liquid water. Taking into account that at the point z_1 water activity is 1, one comes to the following expression:

$$a_{\mathrm{w}} p_{\mathrm{w}}^{0} = p_{\mathrm{t}} - (p_{\mathrm{t}} - p_{\mathrm{w}}^{0}) \exp\left(\frac{N_{\mathrm{w}}(z_2 - z_1)}{cD}\right) \tag{7}$$

Parameters z, c and D not change during experiment, therefore their combination $k = (z_2 - z_1)/cD$ is also a constant. In order to find this constant, a maximum flow calibration should be performed. Then

$$0 = p_{\mathrm{t}} - (p_{\mathrm{t}} - p_{\mathrm{w}}^{0}) \exp(N_{\mathrm{w}}^{\max} k) \tag{8}$$

and k is

$$k = \frac{1}{N_{\mathrm{w}}^{\max}} \ln \frac{p_{\mathrm{t}}}{p_{\mathrm{t}} - p_{\mathrm{w}}^{0}} \tag{9}$$

Substitution of this expression into Eq. (7) gives the following formula:

$$a_{\mathrm{w}} p_{\mathrm{w}}^{0} = p_{\mathrm{t}} - (p_{\mathrm{t}} - p_{\mathrm{w}}^{0}) \left(\frac{p_{\mathrm{t}}}{p_{\mathrm{t}} - p_{\mathrm{w}}^{0}}\right)^{(N_{\mathrm{w}}/N_{\mathrm{w}}^{\max})} \tag{10}$$

Since the rate of vapour transfer N_{w} is proportional to the thermal power P released in the evaporation cell, then the activity of water is:

$$a_{\mathrm{w}} = \frac{p_{\mathrm{t}} - (p_{\mathrm{t}} - p_{\mathrm{w}}^{0})(p_{\mathrm{t}}/(p_{\mathrm{t}} - p_{\mathrm{w}}^{0}))^{(P/P^{\max})}}{p_{\mathrm{w}}^{0}} \tag{11}$$

3. Discussion

In spite of the fact that Eqs. (3) and (11) have very different forms, in practice they give similar values of water activity. In order to compare the two formulas, water activities were calculated using values of thermal powers from 0 to $P^{\max}$, which in both cases gives values of water activity from 0 to 1. The difference of activities calculated using Eq. (11) (corrected activity) and Eq. (3) (not corrected activity) vs. not corrected activity is presented in Fig. 1. The calculations were performed for 25 and 60 °C. For the lower temperature the correction is small—about 0.3% in the middle range of activities, while at 60 °C it is higher than 2.5% in the same range. The correction is very small in the extreme values of activity—i.e. when activities are close to 0 or 1. In the latter case the vapour flow is very low, therefore the correction to the bulk flow is insignificant. In the former case the flow is high, but its highest value, reached when $a_{\mathrm{w}} = 0$ is determined in maximum flow calibration. Therefore the

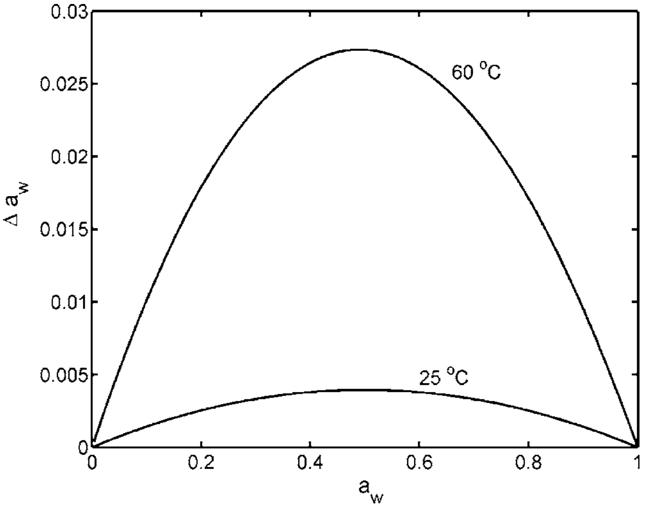

Fig. 1. Difference in values of corrected (Eq. (11)) and not corrected (Eq. (3)) activities of water vs. not corrected activity at 25 and 60 °C.

discussed correction is taken into account even in Eq. (3) but only when water activity in the sorption chamber is zero.

4. Conclusions

The bulk motion of water vapour contributes to value of water activity calculated in sorption experiments. The correction can add up to several percent to the value of water activity at higher temperatures. The correct value of water activity can be calculated using an analytical formula.

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