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A new method for determination of vapour sorption isotherms using a twin double microcalorimeter[1]

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Abstract

A new twin heat conduction microcalorimeter for the study of vapour sorption isotherms, sorption enthalpies and the kinetics of sorption has been developed. Each calorimeter has two calorimetric vessels which are connected by a steel tube. The upper vessel (a vaporization chamber) is charged with a vapour forming liquid and the lower vessel (a sorption chamber) contains the sorbent sample. An identical double calorimeter serves as a reference. During a measurement, the liquid in the upper vessel will vaporize and is allowed to diffuse to the sorption vessel. Thermal powers of vaporization and sorption are measured separately. The rate of vapour flow is obtained from a known value for the enthalpy of vaporization. Assuming equilibrium conditions and applying Fick's law of diffusion makes it possible to calculate the sorption isotherm. Results from test measurements of water vapour sorption on samples of crystalline NaCl and KCl in saturated aqueous solution and on cotton wool are presented.

Keywords: Vapour sorption isotherm; Microcalorimeter; Kinetics; Sorption enthalpy

1. Introduction

The ability to absorb vapours is an important property of many technical materials and products. This property is usually quantified as a sorption isotherm (equilibrium sorption curve).

The sorption of water vapour is of particular technological importance, e.g. for materials such as building materials, foodstuff, fibres and pharmaceuticals. Water vapour

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sorption isotherms are usually expressed in terms of equilibrium moisture content as a function of the relative humidity. Sorption isotherms are normally determined by weighing the samples after they have been equilibrated at different relative humidities. Accurate and stable relative humidities are usually obtained by the use of saturated salt solutions [1]. The moisture content (u) is calculated from

$$u = \frac{m - m_0}{m_0} \tag{1}$$

The method is simple but is time consuming as only one data point is obtained for each experiment. Sorption isotherms reported in the literature are therefore often derived from several experiments conducted in parallel on separate samples. By the method described here it is possible to derive sorption isotherms and sorption enthalpies from a continuous experiment conducted on one sample. Information about the kinetics of the process can also be obtained.

2. Method

Vapour is formed in one calorimetric vessel and is allowed to diffuse into a second calorimetric vessel serving as a sorption chamber. Thermal powers developed in the two vessels are measured independently. The rate of vapour sorption is derived from the thermal power measured for the vaporization vessel and the known value for the specific enthalpy of vaporization. This principle for determination of rates of vapour sorption was used earlier by Calvet [2–4]. The design of the present instrument and the method to derive sorption isotherms is, however, novel.

2.1. Instrument

The instrument can be characterized as a double heat conduction microcalorimeter in twin arrangement. Fig. 1 shows a simplified picture of a (partial) section through the aluminium heat sinks (d, j) enclosing the double calorimetric insertion vessel made from gold plated silver (e, q). The upper calorimetric vessel (e) is a vaporization chamber which is charged with the vapour forming substance, usually a liquid. The lower calorimetric vessel (q), is charged with the sorbent material. The two calorimetric vessels are connected by a thin-walled steel tube (h). Its upper end can be closed by an O-ring valve (o), shown in closed position.

The two calorimetric vessels fit into "vessel holders" (f, i) consisting of squared aluminium bolts with cylindrical holes. The vessel holders are fitted with electrical calibration heaters. The lower vessel holder (i) has a bottom on which the double vessel is resting. Semiconducting thermocouple plates (g) are positioned between the heat sinks and the flat surfaces of the vessel holders (including the bottom of the lower vessel holder). The two heat sinks are separated by a plastic disc (p). The heat sink assembly is surrounded by an air gap (k) and a steel container (l) which is inserted into the thermostated

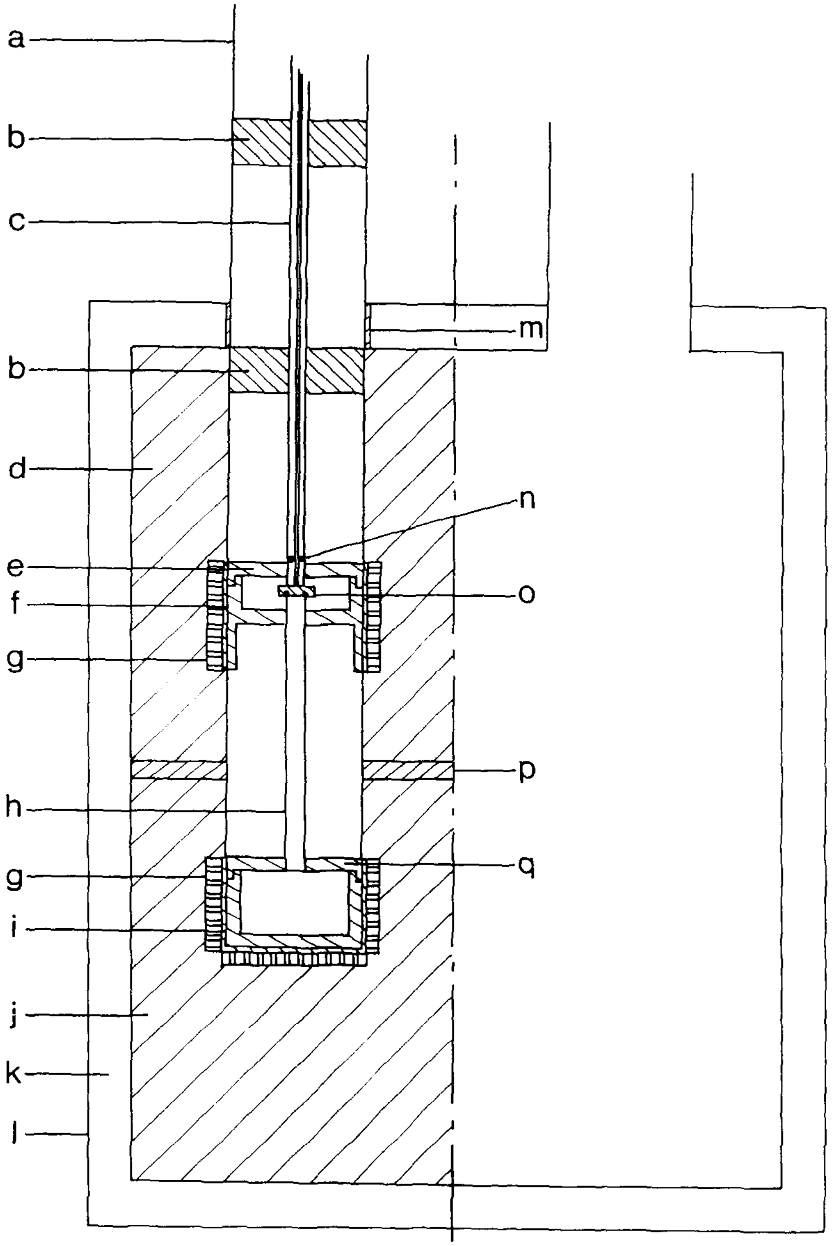

Fig. 1. Simplified schematic picture of the vaporization-sorption instrument. a, steel tube, inner diameter 20 mm, through which the double calorimetric vessel is introduced; b, brass bolt; c, steel tube; d, upper heat sink; e, vaporization vessel (vaporization chamber); f, ampoule holder; g, thermocouple plate; h, steel tube (diffusion tube); i, ampoule holder; j, lower heat sink; k, air gap; l, steel can; m, plastic tube; n, O-ring; o, valve; p, plastic disc; q, sorption vessel (sorption chamber).

water-bath of Thermometric's Thermal Activity Monitor (Järfälla, Sweden) The double insertion vessel is inserted into the steel tube (a) which is connected to the upper heat sink by means of plastic tubes (m).

The calorimeters were calibrated by use of electrical heaters inserted into the calorimetric vessels (e, q). The heaters are made from manganine wire. Current was applied to the heaters through copper wires, diameter 0.15 mm, introduced through the steel tube c.

2.2. Measurement principle

During the measurement vapour diffuses from the vaporization calorimeter (e) to the sorption calorimeter (q). The following equations describe this process and how sorption isotherms can be evaluated from the measurements (see list of symbols on p. 187):

$$F = K(p_{\mathrm{vap}} - p_{\mathrm{sorp}}) \tag{2}$$

$$K = D_{\mathrm{p}} \frac{\pi r^2 \kappa}{l} \tag{3}$$

$$F = \frac{P_{\mathrm{vap}}}{\Delta_{\mathrm{vap}} h} = \frac{P_{\mathrm{sorp}}}{\Delta_{\mathrm{sorp}} h} \tag{4}$$

$$\Delta_{\mathrm{sorp}} h = \Delta_{\mathrm{vap}} h \frac{P_{\mathrm{sorp}}}{P_{\mathrm{vap}}} \tag{5}$$

$$\phi_{\mathrm{sorp}} = \frac{p_{\mathrm{sorp}}}{p_{\mathrm{vap}}} = 1 - \frac{F}{K p_{\mathrm{vap}}} \tag{6}$$

$$u(t) = u(0) + \frac{1}{m_0} \int_0^t F(t)\,\mathrm{d}t \tag{7}$$

Eqs. (2) and (3) are expressions of Fick's law of diffusion through a tube of diameter r and length l. The factor κ is a correction for the vapour flow resistance of the vaporization and sorption chambers of the double calorimeter. In this work this correction factor is derived from results of computer simulations, but alternatively it may be obtained empirically from calibration experiments.

Eq. (4) gives the relation between the diffusive flow and the thermal powers of the two calorimeters. Eq. (5) is a rearrangement of Eq. (4) that gives the sorption enthalpy of the material.

Eq. (6) shows how Eq. (1) may be used to calculate the relative humidity (or corresponding property for non-aqueous vapours) in the sorption chamber. Eq. (7) shows that it is also possible to calculate the moisture content at any time by integrating the flow of vapour which is absorbed by the material. Together Eqs. (6) and (7) give the sorption isotherm.

From Eqs. (2)–(4) and (6), (7) it is seen that the sorption isotherm is evaluated from the thermal power of the vaporization calorimeter, whereas the thermal power of the sorption calorimeter (Eq. 5) is needed only for calculation of the enthalpy of sorption.

Eqs. (2) and (4) are valid only if the measurements are made under conditions close to equilibrium. In practice this means that two conditions must be fulfilled: (1) the sample should be small so that the rate of internal diffusion is not rate determining; (2) the material in the samples should not have time-dependent sorption properties ("non-Fickian behavior" [5,6]). From measurements conducted at different rates of change of the moisture content (by use of different sized tubes or samples of different mass) it is possible to check if these two conditions are fulfilled.

It should be noted that several of the parameters in the equations above are time dependent (F, P_{sorp}, P_{vap}) and that $\Delta_{\mathrm{sorp}}h$ is a function of the moisture content. Relative humidity in the sorption chamber and moisture content of the sample can thus be evaluated continuously as a function of time throughout the measurement. Provided that near equilibrium conditions prevail, these pairs of relative humidity and moisture content make up the sorption isotherm.

2.3. Measurement procedure

The two calorimetric vessels with the connecting steel tube form an insertion vessel which is taken out from its measurement position (shown in Fig. 1) for cleaning and charging. The lids of both vessels are then screwed off (threads and seals are not shown in the figure). The test experiments reported here involved water vapour sorption by saturated salt solutions and by small samples of cotton wool. All calorimetric measurements were conducted at 25°C.

After charging the vaporization chamber with water its lid was tightened and the valve (o) was closed. In the salt experiments the sorption chamber was charged with about 0.5 g of saturated salt solution, together with a similar quantity of salt. In the experiments with cotton wool the vaporization chamber was charged with material which was in equilibrium with the laboratory air (20–30% relative humidity).

After closing the lid of the sorption vessel the assembly was lowered step-wise into the measurement position of the calorimeters (cf. the procedure used with other calorimeters of the same series of instruments [7]) where it was left for equilibration during about 1 h after which the valve (o) was opened and the vaporisation-sorption process started.

Following the experiments with cotton wool the dry mass of the samples was determined by drying for about 1 h at 105°C. The samples were also weighed before the experiment.

In addition to the calorimetric experiments with cotton wool, its sorption isotherm at 25°C was also determined by a conventional technique involving determination of absorbed water by weighing [8].

3. Materials

Deionized (Millipore) water was used and salts were of analytical grade (Merck). The

Table 1

Water vapour sorption by mixtures of salt and saturated salt solution

Salt	$P_{sorp}/\mu W$	
	Exp.	Calc.
NaCl	79.7	80.4
KCl	48.4	48.3

Experimental P_{sorp} values are compared with values calculated by use of results of P_{vap} measurements and enthalpy of dissolution data for the salts.

cotton material was a non-chlorine bleached pure household cotton wool (Mölnlycke, Sweden).

4. Results and discussion

The value for the correction coefficient, $\kappa = 0.94$, was obtained from a computer simulation using an explicit forward difference program for cylindrical symmetrical simulations [9].

In the salt experiments water vapour was absorbed by the system saturated salt–salt crystals. It is thus assumed that the process in the sorption chamber consisted of condensation of water vapour accompanied by dissolution of the corresponding amount of salt. As expected both the vaporization vessel and the sorption vessel showed steady state thermal power values.

Expected values of P_{sorp} for the salt experiments can be calculated from the rate of vapour flow, derived from the determined value for P_{sorp}, the solubility of the salts [10],

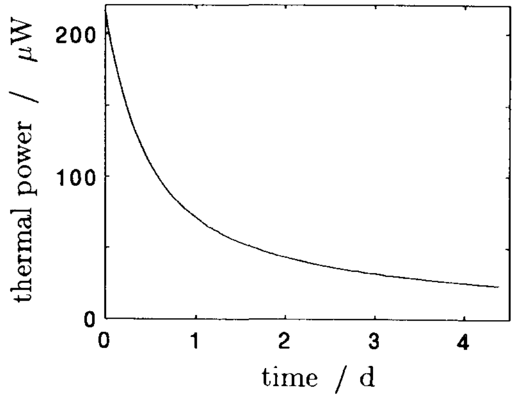

Fig. 2. Thermal power–time curve for vaporization calorimeter in experiment with water vapour sorption on 85 mg of cotton wool. Initial relative humidity was approx. 25%.

and the enthalpy values for dissolution of the salts at saturated conditions [11]. As shown in Table 1, experimental and calculated values for P_{sorp} are in good agreement.

Results from four sorption measurements on cotton wool (sample size 19, 30, 47 and 85 mg) are presented here. Fig. 2 shows P_{vap} for the 85 mg sample during the experimental period of 4 days. It is seen that the P_{vap} value decreases continuously as a result of an increased water vapour pressure in the sorption chamber. By use of Eqs. (6) and (7) sorption isotherms have been derived from the P_{vap} curves (Fig. 3). In the figure are also shown results from the conventional [8] measurement of the sorption isotherm conducted on duplicate samples (sample size 4 g). The four calorimetric isotherms are in excellent agreement and agree well with the "conventional" isotherm except at the highest value for the relative humidity.

The combination of results from the vaporization calorimeter and the sorption calorimeter will lead to values for the enthalpy of sorption of water vapour as a function of moisture content (Eq. 5). Derived curves are shown in Fig. 4 for moisture contents below 0.08. In the figure are also shown results from two studies reported in the literature [12,13]. These latter results were obtained from quite tedious calorimetric wetting experiments conducted on cotton wool in equilibrium with air at different relative humidi-

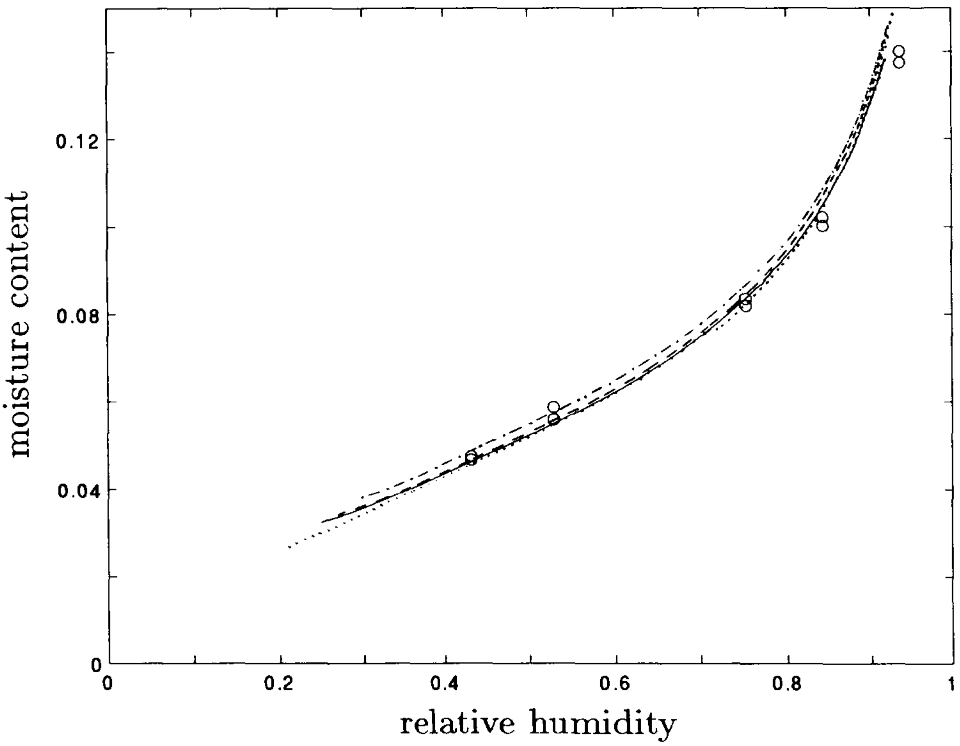

Fig. 3. Sorption isotherms for water vapour on cotton wool. Comparison between continuous curves derived from results of calorimetric measurements (85 mg cotton, ——; 47 mg cotton, - - - -; 30 mg cotton, – · – · –; 19 mg cotton, · · · · ·) and results from conventional weighing experiments conducted on duplicate samples (o).

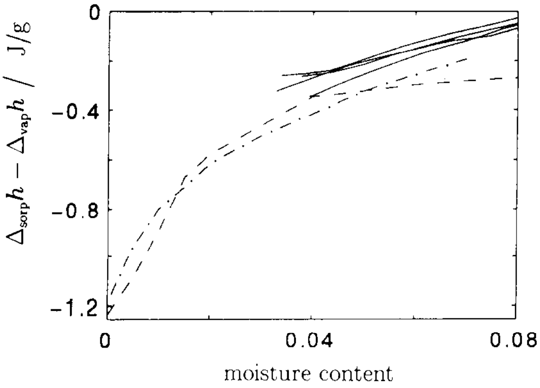

Fig. 4. Enthalpies of sorption of liquid water ($\Delta_{\mathrm{sorp}}h - \Delta_{\mathrm{vap}}h$) on cotton wool versus moisture content of the samples; a comparison between results derived from three investigations, cf. the text. This work ——, Rees [12] - - - -, Guthrie [13] – • – •–.

ties. Note that the results shown in Fig. 4 refer to the function $\Delta_{\mathrm{sorp}}h - \Delta_{\mathrm{vap}}h$, i.e. the enthalpy change for sorption of liquid water.

As seen from Fig. 4 the enthalpy curves determined in the three investigations (conducted with non-identical samples of cotton wool) are in fair agreement. However, at high values for the moisture content ($u > 0.08$) our results lead to values for $\Delta_{\mathrm{sorp}}h$ - $\Delta_{\mathrm{vap}}h$ which are positive instead of, as expected, gradually approaching zero. Our four experiments result in very similar enthalpy curves and we therefore suspect that some systematic error significantly interferes with the derived sorption enthalpies at high values of the moisture content. Even a very small systematic error in the P-measurements can have this effect.

The derived enthalpy function is proportional to $(1 - P_{\mathrm{sorp}}/P_{\mathrm{vap}})$ and at high values for the moisture content, the ratio $P_{\mathrm{sorp}}/P_{\mathrm{vap}}$ is close to unity making the derived enthalpy value very sensitive to disturbances. The nature of the suspected systematic error needs further investigations. In particular vapour sorption by the O-rings at n and o (Fig. 1) and by the walls of the sorption chamber might be critical. Determination of the dry mass and the mass at the start of the experiment is not a trivial task for small samples. However, our results do not suggest that these mass determinations should cause any systematic errors. Note that the determination of the sorption isotherm is not as sensitive to errors as is the sorption enthalpy.

It is also possible to investigate the kinetics of the sorption process by making measurements at different rates of relative humidity increase, i.e. by using different sized samples or diffusion tubes with different diameters. In the present experiments with cotton wool the four different sized samples show no systematic differences (Fig. 3) indicating that the vapour diffusion from the vaporization chamber to the sorption chamber (and not internal processes in the samples) were rate determining.

In conclusion, we have described an instrument by which it is possible to determine the sorption isotherm and corresponding enthalpy values from a single experiment on a very small sample. In cases where there is no need for determination of the sorption enthalpy (and sorption entropy) the sorption calorimeter can be inactive or the instrument can be significantly simplified.

We believe that the technique can be further improved. Such work, including investigations of possible systematic errors (in particular for experiments extended into the range of high moisture contents) are in progress at our laboratories.

List of symbols

D_{p}	diffusion coefficient in air with vapor pressure as potential, g (m Pa s)$^{-1}$
F	diffusive flow, g s^{-1}
$\Delta_{\mathrm{vap}}h$	enthalpy of vaporization, J g^{-1}
$\Delta_{\mathrm{sorp}}h$	enthalpy of sorption, J g^{-1}
K	inverse of the diffusion resistance of tube, g (Pa s)$^{-1}$
l	length of tube, m
m	weight of sample, g
m_{o}	dry weight of sample, g
p_{sorp}	vapor pressure in lower chamber, Pa
p_{vap}	vapor pressure in upper chamber, Pa
P_{sorp}	thermal power in lower calorimeter, W
P_{vap}	thermal power in upper calorimeter, W
r	radius of tube, m
u	moisture content, g g^{-1}
ϕ_{sorp}	relative humidity in lower chamber, Pa Pa^{-1}
κ	correction coefficient in Eq. (2), 1

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