THE RELEVANCE OF JÄNTTI'S METHOD FOR THE FAST MEASUREMENT OF SORPTION OF WATER VAPOUR

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Abstract

The time necessary for the measurement of gas adsorption on a solid can be substantially reduced by using Jäntti's directions for data interpretation. This procedure already delivers results after measuring only a few values of the adsorbed mass. In earlier papers we introduced a second order adaptation to Jäntti's method to broaden its applicability. In the present paper we apply this second order treatment to the adsorption of water vapour from moistened air. Specially we pay attention to the diffusion delay caused by the boundary layer around the sample.

Keywords: *adsorption, diffusion, fast measurement, kinetics, sorption*

Jäntti's method

In 1970 Jäntti [1, 2] published a method for the calculation of the asymptotic value of the adsorbed mass immediately after the beginning of the adsorption measurements. He restricted himself to adsorptions expected to follow the first order differential equation:

$$\frac{dm}{dt} = f - \frac{m}{\tau}$$
(1)

With a step function in the gas pressure, the solution reads:

$$m(t) = m_i(1 - e^{t/\tau})$$
(2)

Jäntti used three equidistant measured points: m_1, m_2, m_3 at $t-\Delta t$, t, $t+\Delta t$ and used

$$J = \frac{m_2^2 - m_1 m_3}{2m_2 - m_1 - m_3}$$
(3)

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We shall use the limit J^* of J for Δt approaching zero.

$$J^* = m - \frac{(\mathrm{d}m/\mathrm{d}t)^2}{\mathrm{d}^2 m/\mathrm{d}t^2} \qquad (4)$$

Jäntti used his method for adsorptions satisfying Eq. (2) where the J function – calculated from the measured values of m – is independent of t and equal to m_i, what leads to a knowledge of this value very soon after the beginning of the measurements.

Water vapour sorption

We shall apply the above to the adsorption measurements of water vapour when these measurements are performed in accordance with the Dynamic Vapour Sorption approach [3]. This means that the sample on the microbalance is exposed to a continuous flow of air with a predetermined and constant relative humidity. As the humid air passes over the sample a zone of constant moisture concentration is established, so the sorption of the water vapour on the sample can be observed.
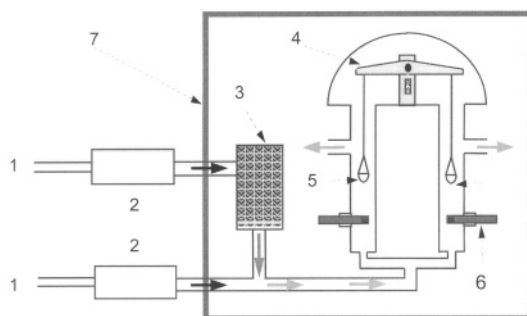
Fig. 1 Dynamic Vapour Sorption (DVS) apparatus of Surface Measurement Systems Ltd. 1 – regulated dry gas inlet, 2 – mass flow controller, 3 – vapour humidifier, 4 – microbalance, 5 – sample pan, 6 – temperature and humidity probes, 7 – temperature controlled incubator

In this paper we shall consider the situation where the partial vapour pressure of the water is varied stepwise. Due to the step, the buoyancy force will change due to the variation of the composition of the surrounding gas. When the total load has a volume of a few cm^3 and the variation of the partial vapour pressure amounts to some 10%, the buoyancy effect will be of the order of a few µg. The time necessary for the buoyancy effect to reach such a new constant value depends also on the velocity of the gas flow.

At the surface of all the parts of the balance there will be a boundary layer of air which, when such a balance is moving, will move with the same velocity as its surface. In principle the mass of this boundary layer will contribute to the measured mass but because of an equal contribution to the buoyancy, the total effect will be zero when sur-

rounding gas and boundary layer have equal composition. In the case of the step in the partial vapour pressure passing the different parts of the balance, there will however be a temporary difference between these compositions. This effect will be eliminated by the diffusion of the water vapour. In the case that no adsorption should occur, the time t_{del} necessary for this elimination can be estimated by the equation:

$$t_{del} = \frac{d^2}{D} \qquad (5)$$

where d stands for the thickness of the boundary layer and D for the diffusion coefficient of water vapour in air. Estimating this effect we use: $d = 5 \cdot 10^{-3}$ mm and $D = 2 \cdot 10^{-5}$ m^2 s^{-1} resulting in: $t_{del} = 1$ s.

When adsorption measurements are performed with the Dynamic Vapour Sorption approach a sensitivity in the μg range might show spurious effects in the first few seconds after the introduction of the step in the partial vapour pressure.

Apart from the spurious effects dealt with in the above there may, after the passing of the step in the partial vapour pressure, remain a delay of the sorption on the sample due to the diffusion delay in the boundary layer. To estimate the influence of this delay we shall use a variant of the three phases model we reported about earlier [4, 5]. In those papers we considered the influence of a mass transport in series with the adsorption, caused by porosity of the part of the sample underneath the adsorbed layer. Where the original Jäntti description distinguished two phases, the gas phase and the adsorbed phase, we introduced a third phase, the porosity phase. This resulted in the second order differential equation:

$$\frac{d^2 m}{dt^2} + b \frac{dm}{dt} + cm = g \qquad (6)$$

with the general solution:

$$m = A\exp(x_1 t) + B\exp(x_2 t) + \frac{g}{c} \qquad (7)$$

where x_1 and x_2 are the solutions of the characteristic equation related to Eq. (6).

The possibility of the water vapour molecules to be in the boundary layer, we shall deal with by introducing the expression boundary phase. When we do not consider the existence of a porosity phase, we are again left with three phases for the adsorptive gas: the gas phase, the boundary phase, and the adsorbed phase. This allows us to use a procedure similar to that used in the earlier papers [6]. The number of molecules in the boundary and adsorbed phase we will refer to as m_b and m_a, respectively so $m = m_a + m_b$.

$f(t)$ we use for the number of vapour molecules entering the boundary phase from the gas phase per unit of time. At constant temperature and after a step of the gas pressure this function is constant and proportional to the vapour pressure after the step. We shall restrict ourselves to situations where, before the step was applied, the adsorption had reached its asymptotical value. τ_b, τ_{ba} and τ_{ab} are the time constants of the molecular model depicted in Fig. 2.
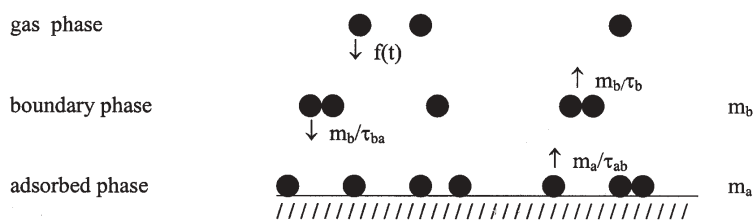
Fig. 2 Molecular sorption model. $\tau_b = \tau_{ba}$

For the parameters used in Eq. (6) it follows:

$$b = \frac{1}{\tau_b} + \frac{1}{\tau_{ba}} + \frac{1}{\tau_{ab}} \tag{8}$$

$$c = \frac{1}{\tau_b} + \frac{1}{\tau_{ab}} \tag{9}$$

$$g = \left(\frac{1}{\tau_{ba}} + \frac{1}{\tau_{ab}} \right) f \tag{10}$$

It implies that we can, for the asymptotic occupation of the boundary layer, use the value of J at the time $t=0$. In the above we explained that this value can be attributed to the buoyancy effect and will be difficult to account for with corrections. This value however will, as explained before, hardly exceed 1 μg. The J vs. t curve will be more useful at higher values of t. To illustrate this we consider Eq. (6) with the two solutions x_1 and x_2. These solutions are related to the two characteristic times τ_1 and τ_2 by:

$$\tau_1 = -1/x_1 \tag{11}$$

$$\tau_2 = -1/x_2 \tag{12}$$

When for establishing the asymptotical adsorption the m vs. t curve is used, one has to wait a time interval governed by the largest of the two τ values. When Jäntti`s method and so the J vs. t curve is used, much less time is necessary as the asymptotical behaviour of the J curve is governed by the smallest of the two τ values. The value of J at $t=0$ can be helpful by the estimation of the uncertainty caused by the buoyancy effect. The way how corrections for the buoyancy effect are to be made afterwards depend on the way how calibrations are carried out with extra measurements on dummy samples.

Conclusions

When fast adsorption of water vapour is to be measured with the Dynamic Vapour Sorption approach one has, apart from aerodynamic disturbances, to cope with buoyancy effects which during an interval of the order of 1 s can be of the order of 1 μg. When accepting this limitation, or making corrections using the results of calibration

measurements, Jäntti`s method can be used, leading to a determination of the asymptotical value of the adsorbed mass, much faster than the conventional method directly from the mass data.

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