

ON THE APPLICABILITY OF JÄNTTI'S METHOD OF SHORTENING SORPTION MEASUREMENTS

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Jäntti published in 1970 a method to obtain equilibrium values at an early stage of gravimetric sorption measurements. In former papers the authors criticised and extended that method. In the present work we discuss problems of its applicability on practical measurements.

Keywords: adsorption, fast measurements, gravimetry, volumetry

Introduction

In 1970 Jäntti published a method to obtain equilibrium values at an early stage of gravimetric sorption measurements [1, 2]. He calculated the equilibrium value of the dynamic adsorption isotherm on the basis of a molecular model for the adsorption process by means of a computer [3]. He applied his method to a large number of series of gravimetric measurements, in particular of complete nitrogen sorption isotherms on activated carbons at 77 K and the determination of the specific surface area and the pore size distribution. He was able to reduce the measuring time by about 70%.

In earlier papers Poulis and co-workers criticized [4, 5] and extended that method by using different models for sorption processes [6–19] and introduced functions which could be used in the evaluation of sorption parameters [20–23].

Important technical applications of Jäntti's method are the measurement of uptake and release of vapours, the observation of drying processes and the determination of the dry mass. For such processes, the establishment of equilibrium may need days and even weeks. Often the measurements are truncated after a given period of time or when the variation of the signal is below a given value. Obviously slow mass changes, which may lead to another equilibrium value, can be overlooked. Therefore an early assessment of the equilibrium value in this way can only be applied in case the sorption behaviour of the material or of the material group is well known. If this is not the case, at certain pre-conditions, truncation of the measurement may nevertheless be done and then the asymptotical equilibrium value calculated by means of extrapolation. An appropriate procedure provides Jäntti's method.

Jäntti's method

If at constant temperature a solid sample is exposed to a sorptive vapour at a varied and then constant partial pressure, uptake or release can be described in many cases approximately by a simple exponential law:

$$m_a(t) = m_{as}(1 - e^{-t/\tau}) \quad (1)$$

where m_{as} = asymptotical equilibrium value of the mass adsorbed, m_a = adsorbed mass, t = time, τ = characteristic time. Here the initial value of mass is set as zero. This law fits in with a simple molecular sorption model [1, 2, 22].

Jäntti used three consecutive values m_{a1} , m_{a2} and m_{a3} at times, t_1 , t_2 and t_3 respectively and at equal time intervals, $\Delta t = t_2 - t_1 = t_3 - t_2$ and assessed the approximate equilibrium value m_{as} using:

$$m_{as} = \frac{m_{a2}^2 - m_{a1}m_{a3}}{2m_{a2} - m_{a1} - m_{a3}} \quad (2)$$

Poulis *et al.* proposed a differential form of Eq. (2) in order to evaluate continuously the measured mass curve and to observe whether Eq. (1) holds:

$$J(t) = m_a - \frac{(dm_a/dt)^2}{d^2m_a/dt^2} \quad (3)$$

By differentiating Eq. (1) and inserting in Eq. (3) it is easily shown that $J(t)$ has a constant value which equals the asymptotical equilibrium value m_{as} :

$$J(t) = \text{const.} = m_{as} \quad (4)$$

For the numerical calculation by using discrete measuring values Eq. (1) should be applied repeatedly to obtain:

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$$J(t) = \frac{m_{a2}^2 - m_{a1} m_{a3}}{2m_{a2} - m_{a1} - m_{a3}} \quad (5)$$

In principle, as expressed by Eq. (4) $J(t)$ should result in the equilibrium value m_{as} at a very early stage of the measurement. On account of disturbances which occur by the change of the gas pressure, the uncertainty of the signal may be great. Therefore the measurements should be repeated sequentially and recorded to give the Jäntti curve. Although Eq. (3) may not hold good in practice in a very early stage, the Jäntti curve approximates the asymptotical equilibrium value m_{as} much faster than the curve of the experimental mass values m_{ai} as is demonstrated in Fig. 1.

If $J(t)$ does not approximate to a constant value (Fig. 2) this will give a warning, that the adsorption process is more complicated. In some cases a

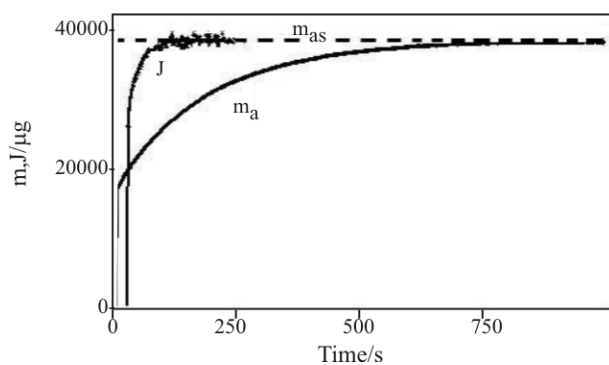


Fig. 1 Measured mass adsorbed Masse $m(t)$ after an increase step of adsorptive pressure $\blacklozenge\blacklozenge$ and curve calculated using Eq. (2): $\blacktriangle\blacktriangle\blacktriangle$ $J(t)$ with $\Delta t=22.5$ s, --- m_{as} . The adsorption process is well described by Eq. (1) and the Jäntti curve $J(t)$ approximates the asymptotical equilibrium value m_{as} much faster than the curve of the experimental mass values $m_a(t)$

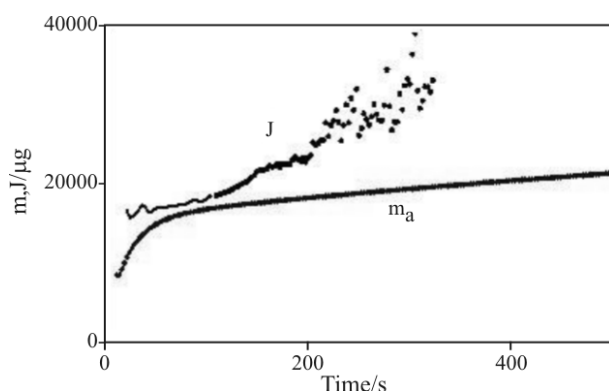


Fig. 2 Measured mass adsorbed Masse $m(t)$ after an increase step of adsorptive pressure $\blacklozenge\blacklozenge$ and curve calculated using Eq. (2): $\blacktriangle\blacktriangle\blacktriangle$ $J(t)$ with $\Delta t=22.5$ s. The adsorption process fits not a simple model as described by Eq. (1). Scattering of the Jäntti curve warns early that equilibrium may not be obtained in reasonable time

more complicated exponential function can be applied [10, 11, 19].

Gravimetric sorption measurements

In gravimetric measurements of gas adsorption isotherms the pressure of the adsorptive gas is varied stepwise. At each step, after introducing a certain amount of gas the gas pressure is held constant by means of a pressure controller until the dynamic isotherm curve has reached a constant value indicating adsorption equilibrium. The desorption isotherm is measured similarly by pumping out a certain amount of gas.

The Jäntti approach is applied to each dynamic isotherm. Because the Jäntti equation comprises a differentiation of the curve, disturbances are magnified. In some cases it may be necessary to smoothen the measured mass curve either mathematically or by damping of the signal. In the example in Fig. 3 it can be seen that actions of humidity control disturb the adsorption process. When applying the Jäntti method such disturbances should be avoided.

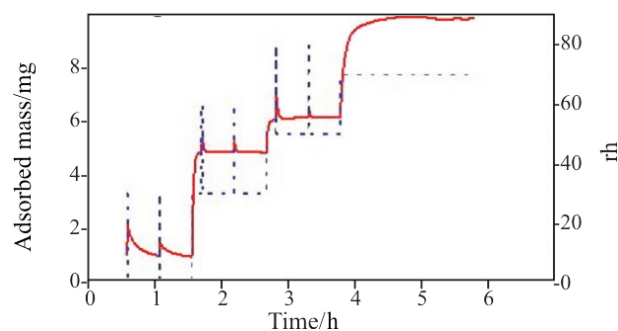


Fig. 3 Gravimetric isothermal measurement of water vapour adsorption. — mass, --- relative humidity of air

Volumetric sorption measurements

In volumetric determinations of adsorption isotherms measured proportions of the adsorptive gas are introduced into the calibrated sample vessel [7]. The adsorbed amount at isothermal conditions is calculated by the pressure decrease after closing the connection valve. A schematic pressure curve is depicted in Fig. 4. The Jäntti procedure can be applied to such pressure curves correspondingly [15, 16].

It should be recognised that in this adsorption process also a slight desorption takes place because of the decreasing pressure after disconnecting. For isotherms showing a hysteresis between the adsorption and the desorption branch this may lead to measuring errors. Therefore some commercial volumetric apparatus adjust the pressure (Fig. 5) as in the gravimetric method

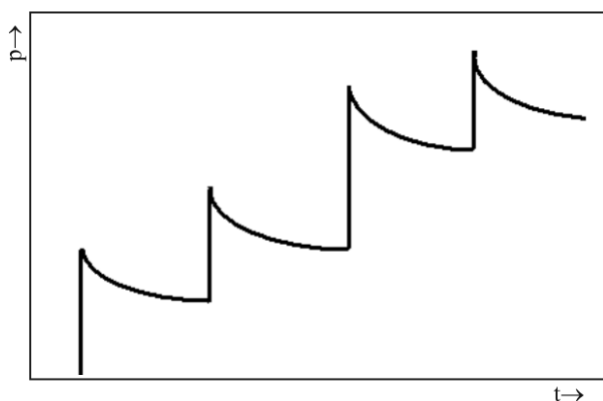


Fig. 4 Schematic record of the volumetric measurement of a gas adsorption isotherm. p pressure of the adsorptive gas, t time

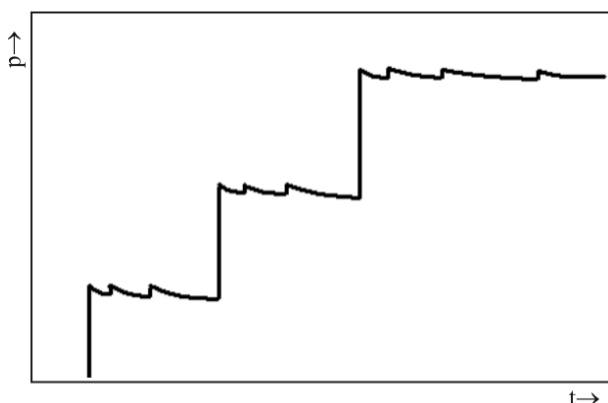


Fig. 5 Schematic record of the volumetric measurement of a gas adsorption isotherm with pressure control. p pressure of the adsorptive gas, t time

(Fig. 3). In this case the output signal is controlled and the Jäntti procedure cannot be applied.

Dynamic measurements

Dynamic adsorption measurements at continuously increasing pressure of the adsorptive gas are made for the fast determination of complete adsorption isotherms. We have shown that the Jäntti method can also be applied for such procedures [8]. Likewise quasi-isothermal thermogravimetric measurements may be shortened in this way.

Conclusions

Jäntti's method of shortening sorption measurements is a valuable tool for time consuming measurements of uptake and release of vapours, the observation of drying processes and the determination of the dry mass. Serial measurements of specific surface area and pore size distribution can be shortened remark-

ably. As discussed in cited papers the method allows, in addition, the determination of sorption parameters. Limits of the method as discussed in the paper should be carefully noted. The method has been recommended for the measurement of drying and adsorption of vapour in a German standard [24].

Dedication

We dedicate this paper in memory of Hannes Poulis who died recently. Since 1963 he was an active participant of the Vacuum Microbalance Techniques Conferences and in 1968 he organised the seventh conference at Eindhoven together with Carel Massen. For several years he was concerned with Jäntti's method and he intended to present a summary now. Unfortunately we are not able to complete and present his thoughts. So we present a paper on some practical aspects of Jäntti's method.

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